

Abstracts from

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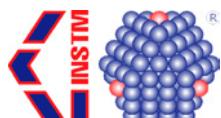
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CONGRESS ABSTRACTS

NATIONAL YOUNG RESEARCHERS' FORUM ON MATERIALS SCIENCE AND TECHNOLOGY JULY 11-13, 2016 | ISCHIA, ITALY

SELECTIVE LASER MELTING OF ALUMINIUM MATRIX NANOCOMPOSITES

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Introduction: Selective Laser Melting (SLM) is a powder based layer additive manufacturing process that can produce fully dense metal parts without the need of post processing steps. In the past years a wide range of materials such as steel, titanium, nickel and aluminum alloy were produced by this technology. This near net shape layer-by-layer process could be particularly suitable for the production of metal matrix composites (MMCs) because of the possibility to homogeneously disperse the second phase within the matrix. In this work an AlSi10Mg+Al₂O₃ composite samples were produced by SLM taking advantage of the reaction that arises between aluminum and silicon oxide.

Materials and methods: An EOS M270 Xtended system was used to build all the samples. This system works in argon atmosphere and uses an ytterbium fiber laser as energy source to selectively melt thin layers of metal powders. An AlSi10Mg spherical powder was used as a matrix and dry mixed with 0.5% wt SiO₂ nanoparticles in order to obtain an AlSi10Mg-Al₂O₃ composite. Cubic samples were built by varying the main building parameters in order to select the ones that allow the obtaining of fully dense samples. The Volumetric Energy Density (VED) parameter was used to understand the overall effect of the building parameters on the consolidation phenomena. The VED value is calculated by the following equation:

$$VED = \frac{P}{vhd} \quad [1]$$

where P is the laser power v the scan speed h the hatching distance and d the layer thickness. Samples for the mechanical test were built with the selected parameters and compared with the AlSi10Mg ones.

Results: The analyses of the porosity values revealed that the introduction of a small quantity of SiO₂ nanoparticles strongly influences the consolidation phenomena. The highest densities of the AlSi10Mg+Al₂O₃ samples were achieved by using low energy densities. On the contrary, in most of the cases, the higher the VED the lower the porosity. The mechanical tests revealed that the composites samples produced with the optimized parameters are characterized by lower yield strength.

Discussion: It is possible to produce fully dense aluminum based MMCs by SLM by using the optimized parameters. It was noticed that the nanoparticles alter the consolidation phenomena. The optical micrographs of the porous samples revealed that most of the pores have a spherical shape indicating that they are due to trap gas rather than to a consolidation issue. The mechanical tests revealed that the mechanical properties of the composites are strongly affected by the building parameters it is necessary to use.

MULTISCALE FABRICATION OF BIOMATERIALS AND BIODEGRADABLE SCAFFOLDS FOR REGENERATIVE MEDICINE

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Introduction: Regenerative medicine attempts to repair or improve the biological functions of tissues that have been damaged or have ceased to

perform their role through three main components: a biocompatible scaffold, cellular component and bioactive molecules. Nanotechnology, using advanced manufacturing techniques such as conventional and unconventional lithography, allows fabricating supports with geometries, sizes and displaying physical chemical properties tuneable over different length scales. In this work we report the fabrication of scaffolds made of fibrin gel and squid pen chitin, for the regeneration of tissues.

Materials and methods: Fibrin gel films are used to observe the growth of cells on random networks. Films of different thickness have been fabricated with special attention to the realization of a micro-frame that allows a simple manipulation of the structure. Such a standing fibrin scaffold prevents the artefacts arising from the interaction of the films with other surfaces. The fibrin gel clots have then been stretched to observe if the cells growth and migration is influenced by the orientation of the fibers. Fabricating a scaffold via bottom-up techniques to mimic tissues is not simple. We have chosen to adopt a top-down strategy using a scaffold manufactured by nature and composed of extremely ordered chitin fibers: squid pen. The squid's pen is a support consisting of chitin fibers transparent, biocompatible, low cost and displaying high mechanical resistance. We have changed the chemical and physical properties of the scaffold to promote cell adhesion. Both supports were functionalized with retinoic acid to obtain a support able to induce cell differentiation. We characterized the scaffolds by scanning electron microscopy and immunofluorescence technique.

Results: We have fabricated two types of scaffolds and we have observed cell growth on both scaffolds. We fabricated active scaffolds able to differentiate the stem cells into neuronal cells. The ultrastructure characterization of the scaffolds is crucial for evaluating their morphology, porosity and biological efficacy. Power spectrum analyses of the images have been performed to provide the characteristic lengths of the supports.

Discussion: An important goal of this work was the fabrication of 3D scaffolds with a well-defined morphology to be used as a starting point for the regeneration of portions of tissue. The realization of a fibrin scaffold, of different thickness and easy to handle fabricated under controlled spatial confinement has been demonstrated. Characterization of the fibrin network has helped us to understand how the morphology of fibrin network might affect the cell growth. We propose the squid pen as a scaffold because it is biocompatible, transparent, it withstands surgical sutures and, moreover, it is a waste material of the industrial chain. The purpose is to exploit as much as possible the original remarkable properties provided by the structure of squid pen chitin to obtain a scaffold transparent and able to support all the mechanical stress. Furthermore, in a period characterized by the necessity of producing goods by a sustainable chemistry and a green economy, finding the way for using an available natural biomass has become a must for all scientists and industrial manufacturers.

INFLUENCE OF CLIMATE CONDITIONS IN THE SETTING TIMES OF HYBRID MATRIX SYSTEMS USED FOR RECOVERY OF DAMAGED BUILDINGS

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Introduction: Nowadays, composite materials -fibers inside a polymeric resin- are successfully applied in the field of civil engineering. A promising variant of this technology involves the rehabilitation of damaged structures using hybrid matrices (inorganic component plus a polymeric resin). However, their use in construction yards with variable climate conditions influences the setting time (ST) of the mixture. This variability results in practical limitations that compromise the success of the application. In this research, a study of the influence of the climate conditions in the ST of three different hybrid matrices composed of gypsum and a polymeric resin was performed.

Materials and methods: Three commercial gypsums (A, B and C) and one aqueous polymeric resin were used. The composition of the gypsums was determined by XRD and DTA-TG. The measurements of the ST's were carried out inside a glove bag at controlled relative humidity (RH) and temperature (T). Their values were chosen based in their average maximum and minimum values in Europe: T = 5, 20 and 35°C and RH = 45, 67 and 90%. The tests were performed by combinations of each value of T and RH.

Results: XRD and TG analysis revealed that the gypsums are composed by $\text{CaSO}_4 \times 0.5\text{H}_2\text{O}$, CaSO_4 and $\text{CaMg}(\text{CO}_3)_2$ in different ratios. Here, ST's of the systems at the different T values will be presented in terms of RH at 45, 67 and 90%, respectively. When $T = 5^\circ\text{C}$, ST's of system A were 42, 39 and 66 min; ST's of system B were 110, 120 and 100 min and ST's >180 min at all the RH levels for system C. When $T = 20^\circ\text{C}$, system A shown ST's of 23, 22 and 109 min; system B shown ST's of 88, 92 and 158 min and system C shown ST's of 150, 141 and 161. Finally, when $T = 35^\circ\text{C}$, ST's of system C are 61, 53 and 81 min, while for systems A and B this measurement was not possible.

Discussion: The results obtained here revealed that temperature has the stronger effect in the ST's of gypsum. For all the systems, the predominant trend was a decrease in ST when temperature rises. This was correlated with the elimination of the residual water (that remains after gypsum hydration) from the system by evaporation. At 5°C , evaporation proceeds slow promoting longer ST's. On the other hand, evaporation becomes faster when increasing T. ST's at 35°C for systems A and B were correlated with the lost of water from the polymeric matrix before contact with the gypsum. Humidity has not a particular influence in the ST's in the range of 45–67%. At 90% RH, evaporation of residual water becomes slow and consequently, ST's are longer.

DESIGN AND SYNTHESIS OF NANOCOMPOSITE ELECTRODES FOR SOFCs

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Introduction: Solid Oxides Fuel Cells (SOFCs) are expected to become important devices for energy production. Their efficiency, superior to current power generation systems, would greatly help in reducing fuel consumption and pollutants' emissions. Materials optimization is crucial for the large scale application of the technology, as both the minimum working temperature and the device lifetime are linked to the chemical/physical properties of the layers. Single chamber fuel cells, following the elimination of the separation between the two gas compartments, have a very simple structure, and their operating costs is greatly reduced, as well as the hindrance of the whole device. On the other hand, they require an excellent catalytic selectivity of the electrodes, nowadays, not achieved by any known material. In this work, we try to synthesize a nanocomposite electrode, composed by two singularly un-active phases. Our aim is to develop new materials characterized by advanced functionality (catalytic activity and selectivity, mixed ionic/electronic conductivity) designed on the basis of the interaction between phases.

Materials and methods: LSGF ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.3}\text{Fe}_{0.7}\text{O}_3$) is a mixed ionic-electronic conducting (MIEC) perovskite. LSGF has an excellent thermal and chemical stability, even if compared to the other MIEC perovskites. It has a very good oxygen semi-permeation, although lower than state-of-the-art electrode perovskites. Despite its good conductivity and the high stability, LSGF is not good as electrode because of its poor catalytic activity. In the realization of our nanocomposites the catalytic activity is added through the deposition of nanoscale transition metal oxides (TMO). Simple oxides have not been previously considered as catalysts in SOFCs because of the too high operating temperature. Nowadays, prototypes of SOFCs works at temperatures gradually approaching 600°C , where simple oxides can be considered stable. This class of materials can offer interesting opportunities because of the low economic impact vs high and tunable catalytic activity. LSGF/TMO-based nanocomposites have been synthesized and characterized with TPR, BET, XPS, XRD, EDX and SEM. The synthesis of LSGF is carried out with a modified Pechini route, which was developed and optimized to investigate the influence of all the preparation parameters. The deposition of the nanodispersed TMO has been obtained by wet impregnation.

Results: The supporting LSGF was obtained as pure crystalline phase and its stability under reducing and oxidizing condition was studied. SEM and XPS confirmed the successful deposition of highly dispersed TMO nanoparticles. The deposition procedure was studied and optimized with the aim of tuning the oxidation state of the cations.

Discussion: The deposited TMO nanoparticles have been observed to be highly dispersed; the small size of the deposited particles is welcomed, because it can enhance catalytic properties of the material. The characterization results suggest that the perovskitic substrate has a stabilizing effect on the nanoparticles, preventing their coalescence and helping them in keeping

less usual oxidation states. In conclusion by means of our synthesis/deposition procedure we succeeded in developing nanocomposite perovskite/TMO materials in which the chemical and physical properties are strictly connected to the interface interaction.

INSTANT CONTROLLED PRESSURE DROP TECHNOLOGY APPLIED ON RICE HUSK ASH AS A PRE-TREATMENT, TO STABILIZE HEAVY METALS IN THE COSMOS-RICE PROCESS

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Introduction: Municipal solid waste incineration ash has is one of the major environmental concern in Europe. Fly ash generated by the air pollution control systems is a hazardous waste materials. Indeed, it contains leachable toxic metals, like Pb and Zn, thus they need to be stabilized, immobilizing the heavy metals. The inertization process employed in this work originates from a well-established process for treating heavy metals using a silica source (RHA) to obtain an inert material, by actuating a carbonation reaction that promotes metals stabilization. Sustainability is a key point in the process: no commercial chemicals are involved, since all the reagents are waste materials. In particular in this work an Instant Controlled Pressure Drop pretreatment (DIC technology) is performed on RHA to study its influence on the process.

Materials and methods: Rice husk was pretreated with the DIC technology. The best texturing process allows obtaining the final product at lower density and with less residual water content. For this aim, several DIC pre-treatments were tested, changing pressure steam, temperature in the chambers, maximum applied pressure, conditioning time and number of repetitions. To also obtain biochar from RHA, pyrolysis of rice husk was realized in O_2 -limiting conditions. Silica content in Rice Husk Ash was determined with a chemical extraction procedure, the solutions were filtered and analyzed by ICP-MS to determinate the silica content. Morphologic characteristics of rice husk ash sample were investigated by SEM and XRD. Stabilization of MSWI Fly Ash was performed adding water and other waste ash. The materials obtained were characterized by leaching tests when samples resulted completely dried. The leachate was analyzed with TXRF.

Results: Results from XRD analysis show that all the RHA are characterized by amorphous material, but the integrated area of the XRD patterns is different considering samples treated in O_2 -limiting conditions and not. TXRF results highlight that samples annealed in O_2 -limiting conditions exhibits higher Pb and Zn concentration in the leaching solutions. SEM analyses confirm the inner surface, instead, seems to be more structured for sample pretreated, in respect to not treated samples. This suggested that the pre-treatments do not produce any change in the crystalline phases in the final stabilized materials.

Discussion: Samples annealed in not O_2 -limiting conditions are mainly amorphous, whereas others have more biochar. Leaching solutions of samples pre-treated with DIC show lower Pb concentration than not pre-treated samples. Biochar in RHA, in respect to silica content, have a negative impact on the stabilization. DIC pre-treatment capability to increase RHA stabilization of heavy metals was observed especially in RHA samples containing biochar, characterized by high values of Zn and Pb in leaching solutions. DIC treatment produces structural changes on the organic part of the material, in fact structural swelling typical of DIC treatment on organic part are observed.

ANODISED TITANIUM AND LOCALISED CORROSION RESISTANCE

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Introduction: Titanium has an outstanding corrosion resistance due to the thin oxide protective layer that is formed spontaneously on its surface when exposed to aerated environment, which allow using titanium in severe working condition, such as offshore (up to 260°C), acid environment, high

temperature, chemical and food industry. Nevertheless pure titanium may suffer localized corrosion in hot salty water, generalized corrosion in acidic environment or hydrogen embrittlement. Anodic oxidation has been considered to tune TiO_2 layer in order to improve titanium corrosion resistance.

Materials and methods: Commercially pure titanium Gr. 2 (according to ASTM B861) was anodized in a 0.5 M H_2SO_4 solution, varying cell voltage (10 V-140 V) and anodic current density (5-80 mA/cm²). Oxide films crystal structure were investigated by means of X-ray diffraction. Corrosion resistance of anodized titanium was evaluated by anodic potentiodynamic polarization tests using a standard three-electrodes cell; potential was increased from 0 V up to 2 V SCE with a scan rate of 50 mV/min. Tests were performed in 35 g/L NaCl solution at increasing temperature and in NaF containing solution (1-35 g/L) at room temperature. Cathodic polarization curves were performed in 0.1 M HCl solution to study the effect on hydrogen evolution cathodic reaction. Titanium alloy Gr. 7 (Ti-Pd alloy) was tested in the same experimental condition for comparison purposes.

Results: In 35 g/L NaCl solution at room temperature, not anodized titanium had the same corrosion behavior of Gr. 7. After anodizing, a reduction of passive current density was measured. The maximum reduction (more than one order of magnitude) was obtained at the lowest anodizing voltages, 20 V. At higher anodizing voltages (higher than 80 V) the current density reduction was lower than one order of magnitude. Increasing solution temperature did not change the anodized titanium behavior. At the highest temperature (95°C) no pits were observed. Tests in fluoride containing solution confirmed that F⁻ promotes activation of titanium: the critical fluoride content is 3.5 g/L on not anodized titanium, and 10 g/L on anodized one. The maximum increase in corrosion resistance was obtained at the lowest anodizing voltages, 10 and 20 V. Cathodic curve in acidic solution pH 1 of titanium anodized at 20 V is in between the curves obtained with not anodized titanium and titanium Gr. 7.

Discussion: The corrosion behavior of anodized titanium is better than pure titanium not treated even if the high corrosion resistance of alloyed titanium was never reached. Anodizing at 20 V provided the lowest current density, and therefore the best improvement in corrosion resistance. The protectiveness of the anodic oxide was observed to decrease with increasing cell voltage applied during anodizing. Increasing the voltage oxide crystallization increases, as proved by XRD patterns. No peak appears at 20 V (amorphous oxide) while at 90 V and 140 V an increasing intensity of the anatase peak can be observed. Therefore, the protective character of the anodic oxide was related to its amorphous structure, and not to its thickness.

GLYCYDYL METHACRYLATE GRAFTING FROM CELLULOSE TO NANO CELLULOSE: PREPARATION AND PROPERTIES

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Introduction: The present work investigates the functionalization of cellulose and nano cellulose by GMA's grafting. Such modification, carried out by Fenton type reactions, did not modify the original crystallinity of cellulose, and led to a new material which is able, unlike native cellulose, to absorb organic molecules, like aromatic compounds, or active principles, like antibacterials and insecticides, by active interaction.

Materials and methods: Starting cellulosic materials can be: cotton yarn, cotton fabric, cotton gauzes, waste cotton, Posidonia algae, or bacterial nanocellulose. Chemical techniques for the surface functionalization of cellulose fibers by the grafting of vinyl monomers generally consist of a process in heterogeneous phase where the solid polymer fibers are dipped in a reacting mixture consisting by the functional monomer and other reagents suitable for the grafting process. The grafting reaction is essentially of radicalic type and it is initiated by the decomposition of chemical species like peroxides by means of redox or photo-redox reactions in order to produce free hydroxyl radical in the bulk solution. Such free radicals are able to activate the surface of the polymeric solid substrate allowing the attachment of the vinyl monomers. Absorption experiments were conducted in aqueous solutions of the tested compounds (amoxicillin trihydrate and beta-naphthol) at fixed concentrations.

Results: The substitution degree (DS = ratio between GMA and glucose units) of cellulose grafting can be modulated from very low DS (10^{-2}) to high values (1.4-1.6) by modifying reaction conditions. The absorption phenomenon of

active principles can be detected and followed by UV analysis. All the cellulosic materials were characterized by infrared spectroscopy and solid state NMR. SEM and TEM analysis were conducted to determine structure and dimension of oxidized and bacterial nano cellulosic fibrils. SEM analysis was also performed over cellulose fibers.

Discussion: GMA's grafting by Fenton reaction was possible in every tested case. Absorption phenomena were more effective for GMA-bacterial nanocellulose, but good results were also obtained with the other cellulosic derivatives.

EFFECT OF GLASS ADDITION OF FLASH SINTERING BEHAVIOR

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Introduction: In recent years, environmental-friendly sintering processes have been developed with the aim to reduce energy consumption and pollutants in industrial activities. Among them, Flash Sintering (FS) appears very promising, allowing to drastically reduce processing temperature and time. Flash Sintering has been applied to several crystalline ceramic materials although many practical compositions rely on the presence of a liquid/glassy phase in addition to the crystalline one. The aim of the present work is to extend this innovative sintering route to a very typical system constituted by alumina and magnesia-silicate glass.

Materials and methods: Magnesium nitrate and TEOS were dissolved in 2-propanol; then, 30% ammonium hydroxide water solution was added for promoting TEOS hydrolysis. The obtained powder was mixed with alumina powder (Almatis CT3000SG, 99.8 wt% pure, $d_{50} = 0.6 \mu\text{m}$) and ball milled in 2-propanol. The suspension was then dried and calcined at 750°C. In this way, Glass-Containing Alumina (GCA) powder with nominal composition (wt%) 90 Al_2O_3 – 8 SiO_2 – 2 MgO was obtained. The powder was shaped into dog-bone samples by uniaxial pressing. The specimens were sintered in a dilatometer (Linseis L75) using a constant heating rate of 20°C/min. Two platinum wires were forced within the holes produced on the opposite side of the green body and connected to a DC power supply (Glassman EW series) and to a multimeter (Keithley 2100). Current and field in the range 0.6-2.0 mA/mm² and 500-1500 V/cm, respectively, were used. Pure Alumina (A) was also tested for comparison. The density of the sintered bodies was measured by the Archimede's method and the microstructure was analyzed by SEM (Jeol-JSM5500).

Results: FS was observed in all samples treated with field in excess to 500V/cm. The glass-containing material shows much higher sintering rate if compared with pure alumina. The result is also confirmed by density measurements, which point out that the densification mechanisms are enhanced in GCA. SEM micrographs show features, which can be ascribed to solid state and liquid phase sintering for the A and GCA, respectively. The sample temperature, estimated from the power balance equations, is substantially always lower than the liquidus temperature of the ternary system Al_2O_3 – SiO_2 –MgO.

Discussion: The results show the applicability of FS to ceramic materials containing both crystalline and liquid/glassy phase and the beneficial effect obtained on FS behavior by the glass addition. This means also that it is possible to reduce the current needed for densification in GCA with respect to A. Microstructural features suggest an effective liquid phase sintering in GCA at temperatures not possible under conventional sintering procedures. In fact, if the temperature is lower than the liquidus, the glass would crystallize in a solid. Therefore, it is possible to suggest that the current flow upon FS accelerates more the densification mechanisms than the crystallization ones.

FLASH SINTERING OF ALUMINA

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Introduction: Pressureless field-assisted sintering processes, and above all Flash Sintering (FS), have acquired much attention in the last decade for allowing to drastically reduce processing temperature and time. FS has been applied to semiconductive and different conductive ceramics with outstanding results: some materials have been consolidated almost at room temperature in few seconds! Nevertheless, only few works have been carried out on insulators. The sintering event is also followed by an abrupt decrease in the resistivity

and by a strong photoemission, such events being not completely clarified yet. In order to explore the applicability of FS to resistive ceramics, field-assisted sintering of alumina was studied in the present work. The possible mechanisms controlling the overall densification process were analyzed reproducing the experiments on pre-sintered samples and recording light emission effects.

Materials and methods: Nearly pure α -alumina powder - Almatis CT3000SG (99.8 wt% pure, $d_{50} = 0.6 \mu\text{m}$) - was shaped to dog-bone samples using distilled water as binder. The specimens were connected to a DC power supply (Glassman EW series) and a multimeter (Keithley 2100). The experiments were carried out in a dilatometer (Linseis L75) using different combination of electrical field and current in the range 250–1500 V/cm and 2–7 mA/mm², respectively. The heating rate was fixed in 20°C/min. The density of the sintered samples was measured by the Archimede's method using an analytical balance (Gibertini); the microstructure was studied by SEM (Jeol, JSM5500). Samples pre-sintered at different temperatures (1250–1550°C) were subjected to flash sintering at constant temperature of 1200°C. The photoemission during these experiments was recorded using a spectrometer (USB4000).

Results: In the constant-heating rate experiments, the flash sintering event was observed using fields in excess to 500 V/cm. The sintering temperature is strongly related to the applied field and it can be reduced even down to 900°C. The current limit changes the densification properties and using 6 mA/mm² it was possible to obtain a nearly full dense material (relative density >97%) at temperature lower than 1000°C. The experiments on pre-sintered samples showed a consistent relation between the incubation time for flash sintering and the relative density of the tested specimens. In particular, it was proven that the runaway (abrupt resistivity decrease) for FS can be easily reproduced on porous samples, but not on dense ones. Finally, the analysis of the optical emission spectra did not show evidences of any luminescent effect during the process.

Discussion: The obtained results show the applicability of FS to insulating ceramics like alumina. On the basis of some previous findings, the presence of some impurities (0.2 wt%) appears to be beneficial for the activation of FS effect. Sintering temperature and applied field in the constant heating rate experiments are consistent with the model of thermal runaway for flash sintering. Light emission effect is coherent with the black body radiation induced by Joule heating.

The observed relationship between incubation time and pre-sintering temperature suggests the presence of surface mechanisms or the activation of different conduction route activated by field intensification around pores.

MATERIALS FOR PLASMON-FREE SURFACE ENHANCED RAMAN SCATTERING: DETECTION OF ENVIRONMENTAL CO₂ ON TiO₂ SURFACES

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Introduction: The ever-increasing anthropogenic production of carbon dioxide (CO₂) during the last century is causing serious issues related to global warming and deployment of fossil fuels reserves. Finding new strategies and tools for monitoring, capturing and recycling CO₂ is one of most urgent goals of current research in energy conversion and environmental remediation. The development of efficient materials for the photocatalytic reduction of CO₂ to produce chemical feedstock and fuels is mainly based on TiO₂. Thus, the spectroscopic characterization of the CO₂-TiO₂ system under real working conditions is crucial for monitoring reaction pathways and design better catalysts. Here we report the first example of high-sensitive Raman detection of CO₂ adsorbed on TiO₂ nanoshell photocatalyst under both environmental and real working conditions. This goal was pursued by tailoring SiO₂/TiO₂ core/shell beads (T-rex) in order to fully exploit light trapping and evanescent fields to enhance the Raman response and extend the CO₂ detection limit. As a result, Surface Enhanced Raman Scattering (SERS) is achieved without need of any interfering plasmonic particles, with a number of key advantages in terms of low invasiveness, reproducibility, versatility and recyclability. As the enhancement of the surface electromagnetic field is easily predicted from Mie-scattering theory, this approach could be extended to the detection of many other gaseous species, setting the basis for high-throughput platforms with exciting applications for environmental science and energy conversion.

Materials and methods: T-Rexbeads were obtained coating a conformal TiO₂ shell layer, from 5 nm to 100 nm, by atomic layer deposition on commercial

silica beads. A systematic investigation of environmental CO₂ was performed with a Raman μ -spectrometer. Numerical simulations of the optical properties of T-rex beads were run using a Mie-scattering based code.

Results: Environmental CO₂ (<400 ppm) was detected and real-time monitored for the first time in plasmon-free SERS experiments using T-Rex single beads and T-rex 3D colloidal crystals. The best-performing multilayered colloidal crystals show about 6 times more intense signals in comparison to their corresponding single bead counterpart. The optical losses of the individual bead under investigation are recovered by multiple scattering from neighboring spheres, with possible recycling of photons. 3D colloidal crystals have been tested also under dynamic conditions, like those met in chemical reactions or environmental monitoring of greenhouse gas emissions.

Discussion: The results here reported demonstrate that T-Rex can be designed, fabricated and assembled in the form of 3D colloidal crystals to obtain high-performance plasmon-free SERS substrates for detecting adsorbed CO₂ under real working conditions.

BIOACTIVE NANOCOMPOSITE FOR DENTAL APPLICATION OBTAINED BY REACTIVE SUSPENSION METHOD

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Introduction: The aim of this study is to realize an innovative nanocomposite material using PMMA powder, MMA and hydroxyethyl methacrylate (HEMA) as liquid phase, reinforced with *in situ* generated hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HA) nanoparticles. HA is an osteogenic and osteoconductive inorganic phase, similar to the bone mineral, and confers its bioactivity to polymer-based composites promoting bone regeneration.

Materials and methods: **HA Synthesis:** Hydroxyapatite was synthesized by reactive suspension method into hydroxyethyl methacrylate solution, using Ca(NO₃)₂·H₂O and (NH₄)₂HPO₄ as Calcium and Phosphorus precursors, the reaction was led for 4 hours keeping the pH ≈ 9 with the addition of NH₄OH drops, a silane coupling agent was also added during the reaction to stabilise the suspension, avoiding the precipitation of HA nanoparticles, and increasing the compatibility between the organic phase (HEMA) and the inorganic nanoparticles. **Nanocomposite preparation:** to prepare the nanocomposites MMA and PMMA powder were added to the HEMA/HA suspension under vigorous stirring, after the addition of 1 phr of BPO as radical initiator. The mixtures were then polymerized by thermal curing at 60°C for 1 h with a post-curing at 100°C for 1 h.

Results: The HA nanoparticles were found to increase the glass transition temperature in DSC analysis, an increase of storage modulus in DMTA analysis was observed also. Three-point bending test showed an increase of both strength and flexural modulus at the highest volume fraction of Hap. Simulated body fluid test showed that the hydroxyapatite confers bioactivity to the composite even at very low concentration (1phr).

Discussion: Poly(methyl methacrylate)/poly(hydroxyethyl methacrylate) polymer blends with hydroxyapatite as nanofiller were successfully prepared through the 'reactive suspension method'. Characterizations of the powders confirmed the formation of hydroxyapatite phase. The effect of the HA nanoparticles on the physicochemical and mechanical properties were investigated.

CVD CARBON NANO-COATING OF CARBON FIBER FOR SPACE MATERIALS PROTECTION AGAINST ATOMIC OXYGEN

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Introduction: The present work analyzes the possibilities to employ carbon nanostructures as basic material to prevent the effects of erosion by atomic oxygen suffered by the carbon fiber-reinforced polymeric materials

employed in low Earth orbit (LEO) space environment. The application of thin protective coatings to base materials is one of the most commonly used methods for preventing atomic oxygen degradation. Though these coatings are efficient in protecting polymer composites, their application imposes severe constraints, since their thermal expansion coefficients may differ markedly from those of composite substrates. The latter issues drive the aerospace research toward the development of lighter composite materials, as the polymeric carbon nanocomposites.

Materials and methods: The purpose is to integrate carbon nanostructures onto carbon fibers surface in order to develop the basic substrate of advanced nanocomposite for atomic oxygen protection. Final goal is the characterization of carbon nanostructures-reinforced carbon fiber in atomic oxygen-enriched environment, with the future objective to assess and optimize the process of carbon-multiscale advanced composites production. With such an aim, a wide investigation on the methane chemical vapor deposition (CVD) over catalyzed carbon fiber-based substrates has been carried out. The as grown nanostructures have been analyzed in terms of morphology, as well as regarding the main features of the resulting growth (yield, purity, homogeneity, coating uniformity, etc.) and relationship to the deposition route operating parameters (catalyst typology, gas flowing rate, growth time/temperature, etc.). Finally, atomic oxygen ground tests have been conducted, in order to evaluate the coating process effectiveness.

Results: An accurate definition of the main CVD parameters for the growth of carbon nanostructures onto carbon fiber surface has been developed: a high degree of reproducibility in terms of the relationship between the carbon deposit type/yield and the main process variables (catalyst and protocol) has been obtained. About the samples characterization in atomic oxygen environment, with respect to the performances of the reference carbon fiber (in terms of total mass loss and atomic oxygen rate of erosion), a worsening has been observed by the disordered carbon deposit, while an intriguing improvement was achieved by the high-yield carbon nanofilaments deposition. **Discussion:** A parametric analysis of the quantitative results has been carried out in order to obtain a functional relationship between the precursor flow rate and the growth yield in the several catalyst/protocol combinations, thus giving significant hints for further process optimization in terms of nanostructured deposit yield as well as of substrate coating homogeneity. An effective coating efficiency modeling has been introduced, in order to estimate the improvement provided by the coating with respect to the unavoidable deposition weight increase, which represents a factor which must be absolutely taken into account when a coating route is proposed for aerospace applications.

RELATIONSHIP BETWEEN MICROSTRUCTURE AND CORROSION RESISTANCE OF ALLUMINUM ALLOY PRODUCED BY SELECTIVE LASER MELTING

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Introduction: The term Additive Manufacturing refers to all the techniques for the production of almost finished products starting from a three-dimensional CAD model directly by building the material layer by layer. The component is made by using a bottom-up strategy – involving the deposition of material rather than its removal as in conventional machining. Initially, additive technologies were mainly applied to rapid prototyping. Recent development and research in this field made it possible to move to the direct production of final components. In comparison to traditional technologies, additive manufacturing surely offers several benefits, such as the savings in terms of time and costs of production and the realization of complex objects and geometries. This technique opens completely new ways to design and they can be considered one of the main keys-to-innovation and research for the next years. Materials made through this technology have unique macrostructure and microstructures, characterized by the presence of porosities, traces left by the laser source during the process and very rough surface finishing which can lead to different corrosion morphologies compared to alloys manufactured with traditional solidification processes.

Materials and methods: Microstructural and corrosion behavior have been studied on AlSi10Mg alloy produced by selective laser melting technique considering several operating parameters such as stress relieving tempera-

tures, heat treatments, and different surface finishing. Potentiodynamic, impedance spectroscopy and intergranular corrosion tests have been performed on cylindrical specimens in order to assess susceptibility to general, localized, and selective corrosion.

Results: The aluminum oxide film present on the alloy just after production and standard stress relieving at 300°C for two hours is less protective than that formed spontaneously in air. The corrosion behavior of the alloy can be improved by considering the mechanical removal of the film formed at high temperature, i.e. by polishing the surface with abrasive paper and alumina. A further improve of the corrosion resistance was obtained by means of a subsequent application of a conversion treatment with cerium. The morphology of the attack evidences a selective penetrating dissolution in correspondence of the border of the melt pools generated by laser scanning. It is strictly dependent upon the subsequent heat treatment, which causes a different distribution of second phase precipitates.

Discussion: The microstructure of the alloy changes from the center of the melt pools to borders. The microstructure in peripheral zone of the melt pools is mainly constituted by a matrix of aluminum with isolated silicon particles. A preferential dissolution occurs on aluminum matrix, favored by the silicon particles that act as cathodes. Heat treatments at temperatures above 400°C are suitable to obtain a more homogeneous structure, constituted by a matrix of aluminum and silicon coarse particles. The selective penetrating dissolution was not evidenced after high temperature heat treatment. The annealed specimens always showed generalized corrosion.

GELATIN/NANOCELLULOSE POLYMERIC BLENDS TO DEVELOP 3D SCAFFOLDS FOR TISSUE REGENERATION

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Introduction: The recent years are experiencing new regenerative approaches for the healing of diseased tissues and organs, with the aim to recover the original functionality and reduce the healthcare costs and the patient's pain. New trends are focusing on the unique characteristics and properties of natural structures to create biocompatible and biodegradable scaffolds with suitable pores size and interconnection to allow cell colonization and proliferation. To improve their characteristics, biopolymeric blends and hybrid composites are used to set up scaffolds for tissue regeneration. Biopolymeric blends allow to combine the best properties of two materials to obtain a scaffold with unique characteristics that are otherwise difficult to find: as an example, biopolymeric blend allows to shape a scaffold that has good mechanical properties without losing ductility and stability. In the present work, 3D, porous, safe and reliable scaffolds for tissue regeneration based on polymeric blend of gelatin and nanocellulose were designed and developed. Gelatin has been extensively studied as polymeric matrix due to easy production, low cost and high biocompatibility, but its effective use is limited due to its poor mechanical properties. In order to overcome the mechanically weak and easily degradable nature of gelatin biomaterial, biocompatible cellulose nano-fibers (CNF) have been proposed as a potential nano-reinforcement and were introduced to achieve composite scaffolds with improved properties. Effective and safe chemical cross-linker involving active groups of both gelatin and CNF were also studied to stabilize the polymeric network and control its degradation rate in simulated body conditions. Therefore, the following work has been set up to optimize nanocellulose-gelatin scaffolds in term of blend's concentration and ratio, cross-linking process and freeze-drying protocol.

Materials and methods: The polymeric blend is created by dissolving porcine gelatin in nanocellulose water suspension at 40°C with mechanical stirring. The blend was then treated with suitable amounts of cross-linker (genipin and HMDA), placed in Teflon moulds and freeze-dried. After the freeze-drying process the dehydrothermal treatment in oven was performed. Evaluation of morphological, chemic-physical and viscoelastic properties of the scaffolds in physiological conditions were carried out.

Results: CNF/gelatin ratio of 10 wt% and blend concentration of 6 wt% are optimized in order to obtain homogeneous blends and dried scaffold presenting good mechanical stability and well interconnected pores suitable for cell penetration. The best combination of crosslinkers was genipin with HMDA and DHT allowing to obtain a scaffold with a degradation percentage lower than 20 wt%.

Discussion: Different crosslinking agent and their synergic effect are evaluated and allow to reach a broad range of stability and microstructural homogeneity.

The SEM images show that freeze-drying is a suitable technique to obtain an interconnected porous structure with the suitable pores size distribution. Nevertheless the stability tests show that is necessary to combine different crosslinking agent to obtain a stable scaffold.

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THERMAL PROPERTIES OF FLY ASH BASED GEOPOLYMERS CONTAINING REFRACtORY POWDER

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Introduction: Geopolymers are a new class of material synthetized through the alkali activation of a low-calcium aluminosilicate precursor. Several studies highlighted their remarkable thermal stability. However, the majority of the research focus on metakaolin-based geopolymers and, in most of the cases, a thermal curing is performed. This study, instead, aims to investigate the thermal properties of fly ash-based geopolymers containing refractory powder, cured both at room and high (70°C) temperature.

Materials and methods: Fly ash was activated with sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 1.99$) and 8M sodium hydroxide solutions in order to achieve compositional ratios of Si:Al = 2.9, Na:Al = 0.9 and a water content of 16.5 wt%. Three different percentages of refractory powder (10, 20, 30 wt%), were added, obtained by milling wastes and scraps of commercial refractory roller production. After casting, each mixture was cured for 24h at room temperature and 70°C, then de-molded, and stored at room conditions until testing. Samples were labelled according to their content of refractory powder (expressed as wt%); samples cured at 70°C are indicated by the letter T. The thermal stability of geopolymers was investigated through heating microscope test (heating rates 5°C/min). In addition, samples were heated in a muffle furnace up to 800 and 1000°C with a constant heating rates of 5°C/min, then kept to each set temperature for 2 hours before being allow to cool naturally back to room temperature. Changes in bulk density, mass and dimensions were recorded.

Results: Heating microscope test showed that geopolymers without refractory powder are stable up to 1040°C when cured at room temperature, and to 1125°C when cured at 70°C, without suffering significant geometrical modifications. The addition of refractory particles leads to an increase of the thermal stability up to 1230°C and 1270°C, respectively for samples 30 and 30T. After the thermal treatment all samples, with the only exception of samples 20 and 30, showed external cracks; the damage extent decreasing for increasing content of refractory powder. For all samples cured at 70°C, the superficial damages appear more evident. Room and 70°C cured samples have shown similar mass loss when heated at 800°C and 1000°C. However, when increasing the amount of refractory particles, a slight decrease in mass loss mass is assessed (mass loss varying from 18% in samples 0 and 0T, to 15-13% in samples 30 and 30T). Finally, regarding the changes in density upon heating, the highest drop can be found at 100°C, corresponding to samples dehydration.

Discussion: According to the above listed results, it can be stated that all formulations tested exhibit remarkable thermal stability. The addition of refractory powder improves thermal stability of geopolymers. Regarding curing conditions, samples cured at 70°C can be exposed to higher temperatures, without suffering significant geometrical modifications, with respect to room temperature cured samples. On the other hand, thermal curing can produce a less permeable microstructure and a consequent greater capillary pressure during heating, which can explain the greater presence of cracks. Results are promising for promoting the use of fly ash based geopolymer in high temperature applications.

GOLD ALLOYS HARDENING: EFFECT OF COMPOSITION AND HEAT TREATMENT ON MECHANICAL PROPERTIES OF GOLD ALLOYS

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Introduction: The production of hollow and small thicknesses jewelry, obtained by plastic deformation processes and subsequent hardening by par-

ticular heat treatments, occupies a relevant place into the production of goldsmith companies. However, the used alloys have to maintain a good workability to guarantee the possibility of high reduction of section during the deformation process. In this work different hardening processes were tested with the aim to improve the hardness of the gold alloy used to make hollow chains. Different compositions of 18 Kt, 14 Kt, 10 Kt and 9 Kt yellow gold alloys were investigated. The influence of the hardening mechanisms, the compositions and process parameters on microstructure and mechanical properties was evaluated.

Materials and methods: All the different samples of gold alloys, coming from the production process, were considered in the annealed state. Hardening treatments were performed in a static furnace with an inert atmosphere. The samples were treated for different time (2h or 2h30') and temperatures, from 200°C to 300°C, in order to analyze the effect of these parameters on the mechanical properties and on the microstructure. Mechanical properties were evaluated with micro-hardness tests. The micro structural analysis was performed by optical microscope observation, SEM analysis and X-ray diffraction analysis.

Results: Regarding the 18 Kt gold yellow alloys, two different composition were tested. The alloy with the higher percentage of copper in mass presented the highest values of hardness. The X-ray diffraction showed a shift and broadening of the diffraction pattern, index of the re-ordering of the crystal structure. Time and temperature influence the ordering structure phenomena and, also, the precipitation of secondary phases. The hardness achieved depends on the chosen combination of these parameters. The micro-hardness tests performed on the 14 Kt gold samples showed, substantially, the same values from 250°C to 300°C. Regarding the two different 10 Kt gold alloys investigated, the hardness increased with the content of silver and not with the copper as previously. Considering the 9 Kt gold alloys the hardening mechanism that overcome is the precipitation hardening and not the re-ordering.

Discussion: It is possible to observe the influence of the percentage of copper and the disorder-to-order solid transformation as the major hardening mechanism for the 18 Kt gold alloys. The diffraction pattern shows that a partially ordered state has a stronger hardening effect if compared to a fully ordered state. With the lowest carat gold alloys (9 Kt, 10 Kt), instead, prevails the precipitation hardening phenomenon which increases with the percentage of silver and other elements (like grain refiners). A suitable control of the grain size and of the heat treatments allows to achieve the necessary properties to guarantee machinability and quality to the product.

IS THE PHASE TRANSITION OF TMB-TCNQ REALLY NEUTRAL-TO-IONIC?

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Introduction: Temperature-induced Neutral-to-Ionic phase transitions (TINIT) in mixed-stack charge-transfer (ms-CT) crystals have been discovered more than 30 years ago, and have been extensively studied in view of the many fascinating phenomena (nonlinear conductivity, dielectric anomaly, ferroelectricity on the ionic phase..) associated with them. Yet, only a handful of ms-CT crystals have been shown to undergo a TINIT. Among them, Tetramethylbenzidine-Tetracyanoquinodimethane (TMB-TCNQ) has been claimed to undergo TINIT at $T_c \sim 200$ K, but this finding is reported in just one old paper. We have then decided to re-investigate this system.

Materials and methods: TMB-TCNQ crystals have been prepared from the commercial components both by slow precipitation from solution and by sublimation in a closed ampoule. The phase transition has been characterized through single crystal polarized Raman and Infrared (IR) micro-spectroscopy.

Results: Vibrational spectroscopy is a well-established tool to ascertain the ionicity r of the CT crystals, i.e. the amount of charge transferred in the ground state from the electron donor D (TMB in the present case) to the acceptor A (TCNQ). To such aim, one has to identify the "charge sensitive" vibrations of D and A, i.e., the vibrational modes whose frequency is mostly affected by the charge residing in the molecule. Furthermore, the comparison between Raman and IR spectra allows one to ascertain if the DADAD... chain is regular (equal distances between the molecules) or dimerized (alternating distances, in such a case the crystal is potentially ferroelectric). The TMB-TCNQ phase transition is first order, with large hysteresis (~30 K), and often the crystal

breaks at the transition. As in many first order transitions with large hysteresis, T_c is still defined, depending on the sample history and thermal contact. The chain is regular in the high temperature (HT) phase, as shown also by X-ray diffraction, but becomes strongly dimerized in the low temperature (LT) phase. The ionicity r changes from ~0.3 to ~0.4, so that the transition can hardly be considered Neutral-to-Ionic, as the borderline between N and I ground states is conventionally posed at $r = 0.5$.

Discussion: From our measurements the driving force of the transition is not connected to the energy gain following the change in ionicity: some other mechanism/interaction triggers the transition *before* the N-I borderline is crossed. Since the crystal breaks, we do not have a structural characterization of the LT phase to shed light on this matter. One of the driving forces might be associated with a molecular deformation of TMB, which is planar in the HT phase. In any case, since the ionicity is intermediate and the stack is dimerized, the system is potentially ferroelectric. We are currently investigating other crystals of the same family, by changing the Acceptor, i.e. Chloranil and Bromanil in place of TCNO.

PEO COATING CONTAINING SILVER OR COPPER PARTICLES: ANTIFOULING PROPERTIES AND CORROSION RESISTANCE OF COATED AA7075

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Introduction: Plasma electrolytic oxidation (PEO) is a newly developed process that can produce an oxide ceramic coating on light alloys in order to improve the corrosion and tribological properties of the substrate. One of the main advantages of PEO process, if compared with traditional anodizing, is the possibility to form not only the predominant oxide of the substrate but also other compounds depending from the composition of the electrolyte. In particular, the addition of different type of particles in the electrolyte allows obtaining coatings that contain these particles. In literature this possibility was used to incorporate in the coatings hard particles to increase the wear resistance of the samples. In this work, copper and silver particles were added to the electrolyte in order to increase the anti-fouling properties of an aluminium alloy. In fact, even though the antifouling properties of these elements are well known in literature, the antifouling resistance of PEO coatings have not been studied yet.

Materials and methods: PEO coatings were produced on samples of 7075 aluminum alloy using a solution containing 5 g/l of NaOH and 25 g/l of Na₂SiO₃ and a current density of 0.3 A/cm² for 5 minutes. In the electrolyte were added different quantities of silver or copper powders. All the samples were characterized with SEM observation of the surface and of the cross section and with corrosion tests. Moreover, to evaluate the antifouling effect, all of them were immersed in the water of the river Piave and the fouling colonization was evaluated at regular intervals. After the antifouling tests the samples were characterized by optical observation and SEM analysis.

Results: The presence of silver and copper particles was revealed with SEM analysis both on the surface and inside of the pores that characterize PEO coatings. All the PEO coated samples exhibit an increase in the corrosion resistance and, in particular, even though the samples with copper or silver particles actually decrease the corrosion potential, the corrosion current density was lower than the untreated sample. In order to increase this resistance a sealing treatment was performed and resulted very efficacious, as can be observed from potentiodynamic polarization tests. From the preliminary antifouling tests is well evident the effect of copper particles whilst the effect of silver is not so great. Moreover there was a clear difference between the treated samples and the untreated AA7075 material. The colonies visible on the surface of the samples after two month of continuous immersion were mostly of diatoms.

Discussion: In conclusion, the PEO treatment resulted an easy and versatile way to improve corrosion resistance of aluminum alloy and it is possible to introduce in the coating silver and copper particles through their direct addition into the electrolyte. The particles are present on the surface and in the pores of the coating and can increase the antifouling effect, which is remarkably higher in comparison with untreated aluminum. The PEO treatment itself seems to increase the fouling resistance too, but more test are required to understand better this effect.

FLAME SYNTHESIZED CATALYSTS FOR HYDROGEN-ENRICHED SYNGAS PRODUCTION BY LOW TEMPERATURE STEAM REFORMING

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Introduction: The large scale production of nanostructured materials is a critical aspect for their progressive implementation in the commercial market. Flame Spray Pyrolysis (FSP) is a highly innovative and promising technique for this purpose, especially for the preparation of active catalysts. During the synthesis the particles are formed very rapidly within the flame and the aggregation mechanism could lead to different features of the catalysts in term of surface area, crystallinity, metal-support interactions, crystal size and active phase dispersion. In this work several Ni based catalysts (5-10 wt.%) with different supports (La₂O₃, TiO₂, ZrO₂) were prepared by FSP for the Steam Reforming of bio-ethanol producing H₂ from renewable sources.

Materials and methods: Catalysts were prepared by FSP by an optimized apparatus with a proper burner configuration. Titanium isopropoxide, lanthanum acetate, zirconium acetylacetone and nickel acetate were used as precursors. XRD, BET, TPR, TPO, Raman Spectroscopy, TEM and SEM were used for the characterization of fresh and used catalysts. Activity tests were performed by a micro pilot plant at atmospheric pressure and several temperatures (500-300°C). A space velocity of 2500 h⁻¹ was chosen with a stoichiometric water/ethanol ratio (W/E = 3).

Results: Characterization of the catalysts pointed out a good phase crystallinity, particle size distribution, and high-metal support interactions by thermal analysis. Activity tests showed complete ethanol conversion and high hydrogen productivity at the highest temperature (1.04 mol min⁻¹ kg_{cat}⁻¹) with only a 10% CH₄ selectivity for the ZrO₂ supported materials. A slightly lower hydrogen productivity and the presence of acetaldehyde was present using Ni/TiO₂. By contrast Ni-La₂O₃ catalysts didn't reach a satisfactory ethanol conversion at 500°C. Non negligible selectivity to acetaldehyde was also observed, together with incomplete methane reforming, overall depressing H₂ productivity. In order to study more challenging operative temperatures several tests at 400°C and 300°C were carried out with the best catalysts (zirconia supported materials). A productivity of 0.65 min⁻¹ kg_{cat}⁻¹ with a CO/CO₂ ratio equal to 1.2 was achieved at 400°C.

Discussion: The FSP synthesis proved very effective to impart good Ni dispersion and strong metal-support interaction, thus limiting the deactivation by coke. The intrinsic acidity of the support has also an important role to avoid ethanol dehydration to ethylene and its subsequent polymerization to form carbon deposits. Although a lower activity was detected for lanthana catalysts, the different acid-base character of the support and different ability to disperse and stabilize the active phase induced a remarkable difference in the coking resistance, being this catalyst the best in term of stability with time-on-stream. Decreasing the operating temperature is a key point for the process intensification. The uncommon results obtained by Ni/ZrO₂ materials revealed their beneficial role thanks to the higher steam adsorption ability, which promotes coke gasification, and strong interactions with Nickel.

NOVEL EXTENDED-RELEASED FORMULATION OF MONASCUS FERMENTED RICE EXTRACT (RYR)

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Introduction: Monascus fermented red rice (RYR) resulting from rice fermentation using *Monascus* sp. has been demonstrated to lower cholesterol in blood. Red yeast rice extract is sold over-the-counter as an alternative to cholesterol-lowering statin drugs, especially for those who stop taking the drugs due to side effects, like unbearable muscle pain. The goal of this work is to develop an extended-release formulation able to maintain the activity effect against the cholesterol, obtaining a constant release of water insoluble statins present in RYR throughout the staying of the tablets inside the intestine. This work is focused on the analysis different carriers for controlled release systems composed by polysaccharide-based matrices.

Materials and methods: RYR extract and polysaccharides were gently provided MediBase S.r.l. (Prato-Italy). Have been investigated two different formulations made by variable composition (from 10% to 90%) of:

- Carrageenan/Gellan gum (F1)
- Gelatin/Alginic acid (F2)

Tablet preparation: Polymers (thin powder forms) in the right percentage were dried and mixed by vortex agitator for 15 minutes. The resulting mixture was quantitatively transfer in a cylindrical steel sample holder ($\Phi 32$ mm) and submitted to 5 tons of pressure for 5 minutes. The results is a cylindrical tablets with surface area close to commercial ones. Then samples have been physico-chemical characterized by FTIR, DSC, TGA, Rheometer and TOF-SIMS. Water Uptake, water bond, water diffusion and mesoporosity have been also determined. The Monacolin K release has been monitored until 48 hours in simulated Intestinal fluid SIF. On the most promising samples, the HMG-CoA Reductase activity has been measured (ongoing experiment) to determine the formulation influence on statin activities against the lovastatin activity used as control.

Results: In F1, 2 candidates (S16 and S17) out of 10 analyzed and in F2, 4 candidates (S31, S32, S33 and S34) out of 10 analyzed samples have been selected for biological characterization. All the selected samples have warranted total release of statins in RYR but slowly and constant over the time. In all the formulations, the interactions between the polymers forming the carrier matrix seems higher than each polymer with RYR matrix in terms of water uptake, swelling and hydrogen bonds network formation. The influence of these interactions has been correlated to statin release behavior. The selected formulation enhances the statins release respect to the RYR matrix alone and, in addition, the preliminary biological results suggest that the activity of these samples is associated with the inhibition of HMG-CoA reductase.

Discussion: When a dry polysaccharide-based tablet is immersed in a physiological fluid, starts to uptake it. When a certain solvent concentration is reached, the polymeric chains unfold due to a glass-rubber transition, and a gel-like layer is formed. In the swollen region, the drug molecules can easily diffuse toward the outer dissolution medium, once they are dissolved. When the polymer network becomes extremely hydrated in contact with the outer biological fluid, processes like chain disentanglement take place, "eroding" the matrix and releasing the drugs. This research project was carried out thanks to the contribution Tuscany Region (Bando Nutraceutica d.d.650/2014).

SrF₂ BASED NANOPARTICLES: CORE@SHELL ARCHITECTURE, LANTHANIDE DOPING AND PERFORMANCE AS NANOTHERMOMETERS

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Introduction: The peculiar luminescent features of lanthanide ions make them suitable for materials with a wide range of applications in photonics, such as for laser crystals and glasses and for in LED for modern lighting. In the last years the interest of the scientific community has been focused on the possible use of lanthanide doped nanoparticles for biomedical applications, in particular for optical imaging. In this work, we analyzed the near-infrared emission of Yb³⁺ and Nd³⁺ ions to check their suitability as nanothermometers, useful for instance to monitor the local temperature during a photo-thermal therapy.

Materials and methods: Lanthanide doped SrF₂ core@shell nanoparticles (average size of 15 nm) are prepared following a simple hydrothermal method starting from water soluble metal and fluorine precursors, using citrate ions as capping agents. The core was activated with Yb³⁺, Nd³⁺ ions and also Tm³⁺, Er³⁺ or Dy³⁺ ions, while the shell was doped with Nd³⁺ ions. The relative amounts of dopant ions in the core were varied, keeping Nd³⁺ and Yb³⁺ ions concentration as fixed while varying the third lanthanide dopant concentration. The effect of the third dopant on the Yb³⁺ and Nd³⁺ near-infrared emissions was analyzed upon excitation with 808 nm laser radiation.

Results: Interesting variations of lanthanide relative emissions were found, suggesting that the third dopant significantly affects the energy transfer

between lanthanide ions and therefore modifying the emission features. A ratiometric approach, based on the relative changes of the emission intensities, is applied to investigate the thermometric performance of the nanostructured system.

Discussion: Remarkable changes in the sensitivity of the nanothermometers are found for the NPs doped with different lanthanides or, in the case of same third dopant ion, with different dopant concentrations, suggesting that the sensitivity of Nd³⁺-Yb³⁺ based nanothermometers can be tailored and increased optimizing the dopant combination.

FAST CALORIMETRY OF POLYSTYRENE AT DIFFERENT MOLECULAR WEIGHTS

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Introduction: Polymers in glassy state are not in thermodynamic equilibrium. Volume and enthalpy are subjected to continuous small changes and equilibrium is achieved by a thermic structural recovery or physical aging. These fluctuations are too slow to be measured in instrument response time by conventional differential scanning calorimetry (DSC) and thermal history and temperature gradient in the sample have to be consider too. Fast calorimetry allows to extend aging temperature and time scales for structural relaxation, providing a homogeneity of heat diffusion in sample of microscopic size. We can investigate structural recovery of polystyrene (PS) at two different molecular weights at high aging temperature and aging times as short as 0.01s, using high fixed cooling rates of 1000K/s.

Materials and methods: Two polystyrene from Sigma-Aldrich at $M_w = 2,000,000$ g/mol and $M_w = 212,400$ g/mol were analyzed. The DSC measurements were performed with a Mettler Toledo Flash DSC 1 with Huber Intercooler TP100 and nitrogen purge. The sample, cut under microscope to square shape, was placed directly on the centre of MultiSTAR UFS 1 MEMS chip sensor. Sensor chip was pre-heated before use with a standard annealing protocol in order to minimize the noise. Heating and cooling scans on sample were performed from 25 to 190°C at 1000K/s scanning rate after calibration of instrument with Indium. Flash DSC heating scans were observed after isothermal aging at $T_a = 80^\circ\text{C}$, $T_a = 90^\circ\text{C}$, $T_a = 101^\circ\text{C}$, $T_a = 104^\circ\text{C}$, $T_a = 107^\circ\text{C}$ and $T_a = 110^\circ\text{C}$ for aging time range from 0,012 to 18.000s.

Results: Structural recovery after isothermal aging of two PS with different molecular weights was investigated by fast differential scanning calorimetry, at cooling rate of 1000K/s. Flash DSC curves shows overshoot caused by aging below glass transition temperature (T_g is around 111°C), related to energy releases to relax. Peak shifts to higher temperature and its magnitude grows with aging time from 0,012s to 18000s. PS with $M_w = 212,400$ g/mol has been not achieved equilibrium yet at 80°C and 90°C after 18000 s of time aging. Whereas curves are unchanged over 600s of aging at 101°C, over 30s at 104°C, over 12s at 107°C and 3s at 110°C of aging temperature. Same recovery trend is in PS with $M_w = 2.000.000$ g/mol: equilibrium is achieved in 3s of aging time at 110°C and it is not reached up to 18000s at lower temperatures 80°C and 90°C.

Discussion: Flash DSC extends scanning rate range of thermodynamic phenomena between 0,1 K/s and 4000 K/s and decreases temperature gradients in the sample. The experimental data obtained in this work from Flash DSC at scan rate of 1000K/s confirms any dependence of configurational structure on molecular weight of sample over $M_w = 100.000$ g/mol, according to Fox-Flory theory. Same recovery time is in PS with $M_w = 2.000.000$ g/mol and PS with $M_w = 212,400$ g/mol at different aging temperature. Higher aging temperatures allow to have shorter relaxation times from over 300 minutes to 3s with increases of 20°C in aging temperature.

2,5D PATTERN REALIZATION FOR ION NANOLITHOGRAPHY USING FOCUSED ION BEAM NANOMACHINING TECHNICS

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Introduction: Nowadays various technologies are being used for surface micromachining for microelectronics industry and biological application. Most of the technology to achieve nano-scale features has several limitations due

to beam drift, diffraction and costs. The realization of 2.5D pattern needs lithographic techniques. Particularly, ion lithography enables to reduce typical electron and photolithography limitations as small depth, surface sample preparation (photoresist), use of a mask and costs. This work presents a possible solution based on a multiparametric scripting software developed to obtain complex 2.5D pattern producing a head-print to use as a master in the Indentation lithography (indL) or milling directly over large areas starting "simply" from its CAD. However, this technique have some drawbacks because it is time consuming, the patterned area is limited to few thousands of square microns and, after tens of minutes, the beam drift produces stitching mismatch. These limitations can be reduced, or even eliminated (on some materials), thanks to a proper milling strategy and beam control

Materials and methods: Recent FIBs, with Dual Beam system, allow to realize micro and sub-micropattern using script language (not attended modality) and to use stream file to design the milling pattern. The complete control of the ion beam needs to considerate most of the parameters involved in the process: Energy, Ion current, Ion beam diameter, Beam overlap, sample material (sputter rate) and strategy. As the milling process is time consuming (several hours), it is essential to consider a methodology to periodically control and correct the stage and beam drift. A sw interface has been developed to write a stream file (containing hundreds of thousands of rows) considering the above-mentioned parameters and to simulate the FIB operation with the advantage to reduce the instrument testing time). In some case, when large areas to pattern are required, it's more convenient to realize the negative of the pattern on an indentation diamond tip generally used in the nanoindentation applications. A patented method called Express Test allow to realize very fast indentations with nanometrical accuracy reducing the process time of several hours.

Results: A new method has been developed to realize 2,5D pattern with ion lithography exceeding the typical limitations. An interface allows in few seconds to prepare a stream file containing the beam coordinates and to simulate the process. For large patterned areas, a diamond tip has been patterned to use as a master in the fast indentation lithography.

Discussion: The difficulty to realize 2,5D patter with the lithography is known. Ion lithography, without masks and sample preparation, can produce very complex geometries but is critical to consider process parameters. For this purpose a new scan strategy and a dedicated software tool has been developed.

PLASMONIC EXOSOMES FOR ENHANCED MONITORING OF MONOCLONAL GAMMOPATHIES

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Introduction: Exosomes are vesicles with a size ranging from 30 to 150 nm secreted by most cells into the extracellular environment. These soft nano-objects carry rich molecular information of the parental cell and constitute an important route of intercellular communication. Exosomes participate in regulation of physiological as well as pathological processes, including the progression of different types of tumors. Recent studies suggest that exosomes carry determinant information about monoclonal gammopathies, like Monoclonal Gammopathy of Unpredicted Significance (MGUS) and Multiple Myeloma (MM). MGUS is a plasma cell disorder present in more than 3% of the population aged over 50 years, and often asymptomatic MGUS stages precede MM. New biomarkers are needed to better predict MGUS' progression to MM. MM exosomes' colloidal properties have not yet been investigated to this purpose. Results from this project will contribute to address this problem, strengthening the toolbox to elucidate MGUS-MM switching.

Materials and methods: We purified exosomes from serum of healthy donors, MGUS and MM patients. We then evaluated the purity and molar concentration of the exosome solutions by using a colorimetric nanoplasmonic assay we recently introduced. Relying on the discovery that cell surface's heparan sulfate proteoglycans (HSPGs) mediate exosome docking and processing by cells and that MM-derived exosomes experience a higher internalization rate compared to exosomes from MGUS and healthy individuals, we tested the ability of a Surface Plasmon Resonance (SPR) biosensor chip functionalized with heparin (a structural analogous of heparan sulfates), which constitute the side polysaccharide chains of HSPGs - to sort exosomes derived from healthy donors, MGUS and MM patients.

Results: The presence of typical exosomal markers in our sample indicates that we are actually dealing with exosomes. Over all, our analysis showed that MM patients produce more exosomes than MGUS and healthy individuals. In addition, we discovered that among the analyzed exosomes, only the MM-derived ones strongly bind heparin with an apparent dissociation constant equal to about 1 nM, indicating a high affinity binding.

Discussion: The analytical efforts and related biosensing strategies to study exosomes have been focused on their molecular profile, while colloidal properties, including size, molar concentration and cell membrane interactions, have been far less investigated. This work contributes to fill the gap combining colloidal gold nanoplasmonics and SPR biosensing. Our nanoplasmonic assay allowed to discover that serum from MM patients contain about four folds more exosomes than serum from MGUS and healthy individuals; SPR spectroscopy showed that among the analyzed exosomes, only the MM-derived ones have a significant binding affinity for heparin. Heparin, a structural analog of HSPGs, influences endocytosis through the interaction with several proteins. Findings lead us to think that antibody Free Light Chains (FLCs, produced and secreted via exosomes in both MM and MGUS) could play a major role in exosomes' internalization. SPR spectroscopy predicted that different exosomes, possibly with different FLC decorations, have different binding affinities for HSPGs. Since contradictory results are reported on the ability of FLCs to bind to HSPGs, further investigations are needed.

STUDY OF ADVANCED CEMENT-BASED COMPOSITES WITH ENHANCED FUNCTIONAL PROPERTIES

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Introduction: Cement-based composites are the most important and widely used building material at present. Progress in the field of nanomaterials is a great opportunity to further raise their performance and properties through the inclusion of nano-particles. Advanced Cement-based Composites (ACCs) can be obtained by using microsilica (MS), carbon-nano particles such as graphene, graphene oxide (GO), carbon nanotubes (CNTs), by enhancing not only ACC mechanical performance but also its thermal and electrical conductivity. In addition, the use of porous lightweight particles, especially those coming from recycling process of waste materials (such as wood waste (WW), recycled expanded glass (REG), pumice (P), lightweight expanded silica (LES) particles) can be significantly advantageous in terms of reduced thermal conductivity and improved lightness by promoting energy efficiency in building as well as sustainability.

Materials and methods: Careful attention has been dedicated to the mixing of nanomaterials such as MS and GO because their agglomeration is a common problem due to the strong van der Waal's attractive forces at the nanoscale (dispersion was obtained by means of sonication in the presence of proper admixture to avoid re-agglomeration). After suitable characterization (chemical-physical as well as by SEM observations) of the different particles (MS, GO, WW, REG, P, LES), several ACC mixtures were prepared by combining the various ingredients at suitable amount in order to obtained enhanced functional properties. Reference mixtures with quartz sand and conventional filler (limestone powder) were prepared, by adding several kinds of chemical admixtures such as water-reducing, shrinkage-reducing and antifoaming admixtures. Moreover, in certain cases (when the scope was to increase thermo-electrical conductivity as well as mechanical strength in bending) brass-coated metallic fibers were added. ACC mixtures were characterized in terms of fresh consistency (to check the influence of the various additions on the rheological properties), then at hardened state in terms of lightness in dry condition, from a mechanical point of view by means of compression and bending tests carried out up to 28 days of curing. Finally, ACCs were characterized in terms of thermal conductivity by means of guarded hot plate apparatus as well as in terms of electromagnetic shielding and propagation capacity by means of a nested reverberation chamber facility.

Results and discussion: As expected the MS addition in combination with water-reducing admixture allowed to refine the microstructure and to increase ACC mechanical performance. The use of GO nanosheets increased the water demand. This aspect has been taken into account for choosing the best GO dosage to take full advantage from the excellent intrinsic properties of GO nanosheet, which can strengthen the brittle cement matrix by promoting C-S-H nucleation and microstructure densification. The use of GO conductive

particles in ACCs, especially in combination with metallic fibers, proved to be a valid system for electromagnetic interference shield. On the other hand, the use of porous lightweight particles allowed to disclose application for ACCs as plasters for energy efficient building due to an excellent combination of lightness and thermal conductivity properties by maintaining satisfactory mechanical performance thanks to the addition of microsilica.

ASSESSMENT OF MAGNETIC PROPERTIES OF SILANE COATED NdFeB MAGNETS DURING AGING IN SYNTHETIC SALIVA

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Introduction: Magnets have been introduced in dentistry since the 1960s both for orthodontics and prosthodontics applications. The main problem limiting their long-term durability in the oral fluid is the poor corrosion resistance of permanent magnets and the consequent leaching of cytotoxic ions. In order to overcome the corrosion resistant lack of Nd-Fe-B magnets, new corrosion resistant materials or surface coatings become necessary also to preserve the magnetic properties. For this reason, silane-based coating has been taken into account. The interaction between hydrolysed silane solutions and metal substrates forms strong Si-O-Me covalent bonds, hence, guaranteeing a high degree of adhesion to the metal substrate.

Materials and methods: With regard to the average crown dimensions, neodymium iron boron rectangular nickel electroplated magnets having a length of 2.5 mm, width of 1.2 mm and height of 4.5 mm were chosen. The silane solution was obtained by mixing: 5.0 vol.% N-propyl-trimethoxy-silane monomer, 95.0 vol.% ethanol and 5 vol.% water. The solution obtained was pre-hydrolysed at 25°C, for 24 h. After immersion in the precursor for 30 s, each silane dipped film was cured at 60°C for 20 min. Samples at different silane layers were made (up to thirty layers).

The attractive force of NdFeB magnets was measured with a universal testing machine. A total of 5 measurements for each magnets batch were carried out before and after aging in synthetic Fusayama saliva solution at pH 5.5, to evaluate how corrosion affected the magnetic properties. ANOVA analysis was performed on obtained results. Corrosion behaviour was evaluated by means of DC polarization and electrochemical impedance spectroscopy (EIS) tests.

Results: The data showed a slight decrease in magnetic force at increasing silane layers. In particular, there was a reduction of the 9% for three layered samples and of the 13% for the thirty-layered samples. After that the magnetic force increases during immersion test. The peak values were found in the range between five and seven days. After fourteen days the degradation induced by corrosion phenomenon took place mainly on samples with low amount of silane layers, with a significant reduction of magnetic force. Only 30 layers silane samples evidenced good anticorrosion performances.

Discussion: The observed behaviour could be related to a reversible demagnetization phenomenon and subsequently progressive remagnetization on NdFeB magnets.

The data evidenced as a thermal treatment under Curie temperature could induce a progressive demagnetisation without phase changes, thus a spontaneous remagnetization could occur considering that the demagnetisation phenomenon is mainly a result of the bowing of pinned domain boundary walls or rotation of the domain magnetization vector. After 30 days of immersion in synthetic saliva only magnets coated with 30 silane layers exhibited effective anticorrosion properties preserving magnetic forces, indicating its potential application in orthodontics and prosthodontics fields.

DEVELOPMENT OF A SELF HEALING POLYMER FROM CYCLIC BUTYLENE-TEREPHTHALATE

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Introduction: This work is aimed to the development of a smart, self-healing material from cyclic butylene-terephthalate. Self-healing polymers have the

capability to recover their load transferring ability after damage. The material is composed of a mixture of catalyzed CBT (cyclic butylene terephthalate) and poly-butylenes terephthalate (PBT). The self-healing ability is based on the catalyzed ring opening polymerization (ROP) of molten CBT to PBT. Therefore the conversion of molten CBT to solid PBT represents the basic mechanism that welds the surfaces of the growing crack, thus restoring the mechanical properties of the material.

Materials and methods: CBT is a cyclic oligomer produced by Cyclops Corporation. Two catalysts were used:

- FASCAT 4101 (Butyltin chloride dihydroxide) by SIGMA-ALDRICH;
- FASCAT 4102 (butyltin tris-2-ethylhexanoate) by SIGMA-ALDRICH.

CBT, once melted, was mixed with the different catalysts, varying the amount and the mixing time. The first catalyst allows a faster reaction at a lower temperature than the second catalyst.

The evolution of the degree of conversion of CBT to PBT and the viscosity of the resultant mixture were analyzed by differential scanning calorimetry (DSC) and rheological analyses. Flexural tests were performed on partially reacted PBT samples; moreover, the surfaces of two partially reacted PBT samples were kept into contact at 190°C for 24 h. After this maintenance, the surfaces resulted welded because of the conversion of residual CBT into PBT. Adhesion tests were made to evaluate the strength of the welding.

Results: Although ROP of CBT is athermal, DSC was used to detect the existence of unreacted CBT after processing, by the presence of its melting peak, and to monitor the crystallinity of the PBT obtained by ROP. Rheological analyses were used to monitor the evolution of the degree of conversion of CBT to PBT, since ROP involves a significant increase of the viscosity of the material, associated to the increase of molecular weight. Flexural tests showed the brittleness of the material due to its high crystallinity. Also, an increase in the mixing time involved a higher uniformity of the properties. Finally, maximum shear strength was variable because of the roughness of the samples surfaces.

Discussion: The proposed approach has a series of advantages:

- no need to introduce fillers and/or fibers to heal the material;
- the material is thermoplastic;
- the healing reaction can be tailored by modifying the catalyst type and amount;
- the healing ability is preserved for very long times at room temperature;
- the shape stability is preserved, since the reaction occurs below melting of PBT, is completely athermal, and no gas is released.

Future tasks:

- addition of nanofillers and glass fibers;
- dispersion of catalysts in hollow glass fibers;
- addition of carbon nanoparticles, to improve the dielectric response of the material;
- addition of ferromagnetic fillers to make the material induction-heatable

EXPERIMENTAL STUDY OF RADIATION DAMAGE OF ELASTOMERIC MATERIALS USED IN ACCELERATORS FOR THE PRODUCTION OF RADIOACTIVE ION BEAMS

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Introduction: The SPES facility, under construction at Legnaro National Laboratories of INFN, is a second generation accelerator for the production of radioactive ion beams. The radioactive species are produced by nuclear fission induced by high-energy 40 MeV protons on a ²³⁸U target, at the foreseen rate of 10¹³ fissions/s. In this highly radioactive environment, the components of the Target & Ion Source (TIS) assembly experience severe radiation induced modifications due to intense neutron and photon fields. Vacuum O-rings made of elastomeric materials are the most critical components of the target unit. In this framework, a project aimed at performing extensive experimental campaigns of irradiation and testing of materials and products available on the market, that could be employed in the TIS system, was started. The main elements of innovation of this study, compared to the existing literature, are the use of mixed neutron and photon fields to perform the irradiations as well as the selection for the test of new products and materials,

recently developed by rubber companies. Indeed, radiation hardness tests of polymeric materials are routinely performed with photon fields only, therefore, the actual behavior of such materials submitted to intense neutron fields is generally uninvestigated.

Materials and methods: A protocol has been developed to assess the radiation-induced property modifications of elastomeric materials generally employed to produce vacuum O-rings. In the present work, 3 EPDM and 1 fluorinated (Viton) materials were selected. One of these materials is specifically designed for application in intense photon fields, while the others are conventional O-ring materials. Irradiations of the samples were performed in the neutron and photon mixed field of the TRIGA MARK II research nuclear reactor of the University of Pavia, at different values of absorbed dose. The mechanical and physical properties of irradiated and non-irradiated samples were measured at the Laboratory of Material Science and Technology of the University of Brescia.

Results: The evolution of the analyzed properties as a function of the absorbed dose was successfully measured, allowing the evaluation of the expected operational lifetime of the components in the TIS assembly of the SPES facility to be performed. As a result, the performance of materials chosen from different elastomeric families, including both specific and generic products, could be compared and the best candidate for the intended application identified. Moreover, some hypotheses on the correlations between the evolution of the measured physico-mechanical properties and radiation-induced modifications of the microscopic structure of the analyzed polymers were formulated.

Discussion: Using the developed protocol it will be possible to extend the experimental study to other families of elastomeric materials and to other specific products. In this connection, a couple of the major worldwide producers of radiation resistant rubbers have expressed their interest in this characterization, because it could represent an upgrade of their testing procedures, usually performed with gamma radiation only. As a further development of the study, other categories of critical polymeric components employed in the SPES project such as lubricants, power and signal cable insulators, optical fibres could be considered.

GOLD NANOPARTICLES FUNCTIONALIZED WITH BIFUNCTIONAL THIOLS: SYNTHESIS AND CHARACTERIZATION

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Introduction: Noble metal nanoparticles (MNPs) represent a new class of materials that can be employed in several field of application thanks to their unique properties (optical, electronic, chemical, and magnetic) that are conferred from their small size, from few units to hundreds of nm. In particular gold nanoparticles are mainly used in biomedicine, in catalysis and in opto-electronic devices. Silver nanoparticles found application as sensor materials and as substrates for SERS, optical labeling, and near-field optical probing. The use of bifunctional thiols as capping agents can allow the formation of interconnected systems of NPs with the consequent improvement of the optical and electronic properties of the whole system.

Materials and methods: Gold nanoparticles, AuNPs have been prepared following literature reports by using bifunctional thiols, i.e. 9,9-didodecyl-2,7-di(thioacetyl)fluorene (1) and the *trans*, *trans*-4,4' diethynyl (bistributylphosphine-Pt(II)thioacetyl) biphenyl(2). The ligand (1) has been obtained by a nucleophilic aromatic substitution between the dibromide precursor and the CH₃SNa in the presence of a polar solvent as the 1,3-Dimethyl-2-imidazolidinone; then the CH₃COCl has allowed the formation of the thioacetate product. Ligand (2) has been synthesized by starting from the 4,4'-diethynyl-biphenyl and the *cis*-[PtCl₂(PPh₃)₂] to obtain the bifunctional organometallic precursor in *trans* geometry and then the thioacetate derivative has been obtained with an exchange reaction by using the CH₃COSK.

Results: Gold nanoparticles, AuNPs-1 and AuNPs-2, have been prepared by using a double phase reduction in the presence of bifunctional thiols (1) and (2). The obtained AuNPs have been carefully characterized by means spectroscopic and microscopy techniques. In particular the Uv-Vis spectra, conductivity measurements and electron microscopies allowed to reveal the presence of AuNPs with size below 5 nm, with Plasmon resonance at about 525 nm.

Discussion: The obtained AuNPs showed a characteristic Plasmon resonance typical of small sized NPs, the conductivity measurement have shown an high improvement of the electrical conductivity of the organometallic ligand respect to the value show by the organic one. The presence of NPs of very

small size (<5 nm) with a good degree of monodispersity was assessed by electron microscopies studies that also evidenced the presence of dyads and 2D network formation.

BIODEGRADABLE AND THIOL FUNCTIONALIZED ALIPHATIC COPOLYESTERS

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Introduction: Biodegradable aliphatic poly(ester)s such as poly(lactide) (PLA), poly(ϵ -caprolactone) (PCL) and their copolymers (PCLA) are largely used in biomedical applications, such as porous scaffolds for tissue engineering. One drawback for their biomedical applications is the lack of suitable functional groups along the chains, which could e.g. allow the binding of biological motifs and enable the interaction with the cells. Therefore, the development of controlled synthetic approaches for the preparation of functional aliphatic polyesters is a deeply felt research topic.

Because of the ubiquity of thiol groups in the biological environment and the versatility of thiol chemistry, we designed a lactide-type monomer featuring a pendant cleavable thiol group. Such a monomer is an attractive "building block" for the synthesis of functionalized aliphatic poly(ester)s, which can provide biomaterials with enhanced biological response.

Materials and methods: Moisture and air-sensitive materials were manipulated under nitrogen using Schlenk techniques or a MBraun Labmaster glovebox. Reagents, monomers and solvents were purchased from Sigma-Aldrich. The monomers precursor and the catalyst have been reported in previous papers, as well as procedures for the polymerization tests.

Porous scaffolds were fabricated by salt-leaching method. The H-Arg-Gly-Asp-Cys-OH peptide (RGDC) was purchased from Bachem and used as received. The viability of human dermal fibroblasts cultured with the extraction medium was determined using an Alamar blue assay.

Results: The thiol-functionalized lactide-type monomer was synthesized in 3 steps, starting from L-lactide, in a good yield. The controlled ring-opening co-polymerization of the thiol-lactide with lactide and caprolactone, in the presence of an aluminium-based catalyst, afforded thiol-functionalized copoly(ester)s. By changing the comonomers feed ratio, different samples were prepared in high yield. The thiol-functionalized lactide was totally incorporated in the polymeric chains. The copolymers were fully characterized by NMR, SEC and DSC analysis.

Then, the pendant functional groups were modified into pyridyl disulphide and the modified sample was used to fabricate editable porous scaffold by salt leaching method, after blending with PCLA. By exploiting a disulphide-exchange reaction in aqueous solution, the pyridyl disulfide groups embedded in the porous scaffolds were replaced with the cysteine-terminated RGD peptide. The thermal and physical properties of the scaffolds were evaluated as well as cytotoxicity test, which revealed good cell viability.

Discussion: A lactide-type monomer with a thiol side group was designed and successfully synthesized. The monomer was used as building block for the synthesis of novel functional copoly(ester)s, achieving a good control over the chain growth. The functional polyesters, after modification of the pendant groups, were used for the fabrication of highly porous scaffolds. The thiol reactive pendant groups were easily modified with RGD oligopeptide sequences. This reaction is a proof of concept and demonstrates the great potential of these copolymers to be used as editable materials for biomedical applications, due to the pliability of the thiol functionality.

PREPARATION AND CHARACTERIZATION OF CARBON NANOTUBE REINFORCED ALUMINUM COMPOSITES

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Introduction: Aluminium is widely used in a lot of applications due to his versatile properties; it has the electrical conductivity ($37,7 \times 10^6$ S/m) and

thermal conductivity (237 W/m·K) of a metal with a relative low density (2.7 g/cm³) and a good resistance to oxidation. For this reason it has been used for decades in structural application (aeronautic industry) and for electronic application (high tension cable). Unfortunately the mechanical properties are not so promising. In order to improve the mechanical properties of this metal, "Carbon nanotube (CNT) Reinforced Aluminum" are studied even if the number of papers in the literature is decidedly lower by comparing with "Carbon Reinforced Polymers". This occurs because of the difficulty in the preparation of a composite with a good rate of dispersion of CNTs due, for example, to the low wettability between metal and carbon. Usually it is avoided the preparation of composites by melted metal because of the possibility of carbide formation with a consequent decreasing of several properties.

The most used way to prepare CNTs aluminium composites is the powder metallurgy that allows the possibility to mix nanoparticles with aluminium powder to obtain a good rate of dispersion. In this work the composites, with different CNTs content, were prepared by a controlled melting, in inert gas, and a fast casting of a mix powder of aluminium and CNTs. Tensile strength and Young modulus were evaluated and correlated with the% of CNTs in the matrix.

Materials and methods: MWCNTs were modified on the surface by autoclaving in alkaline aqueous solution of potassium peroxodisulfate according to the procedure reported in literature. After this treatment CNTs were mixed in a mortar and pressed into pellet with the aluminium powder. The pellets are, then, accommodated into the crucible of the furnace. After the heating the melted were fastly casted into a graphite mold attached to a centrifugal rotor. The specimens so obtained were tested with a tensile strength-testing machine (at different temperatures) and with a dynamic indenter. The microstructure was evaluated by SEM microographies before and after the tests and the exact content of CNTs were evaluated by TGA in different atmosphere.

Results: CNTs reinforced aluminium composites were prepared by melting aluminium with different concentrations of carbon. SEM microographies show the rate of dispersion of carbon nanotube in the matrix. The results of mechanical characterization have demonstrated that exist a threshold of doping after which the carbon nanotube decrease the properties of the matrix.

Discussion: The surface modification increases the repulsion between nanotubes and avoid their agglomeration. This involves a good dispersion in the matrix of aluminium. The mechanical properties have a trend with the carbon content: this proves that the change in terms of properties strongly depends on the rate of dispersion and on the preparation procedure.

MICRO AND NANOSTRUCTURATION OF FUNCTIONAL MATERIALS IN CONFINEMENT BY STAMP-ASSISTED TECHNIQUES

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Introduction: Controlled assembly and spatial distribution of functional materials on surfaces are key factors that determine both their properties and their technological applications. However, when materials from a solution are deposited on surfaces, often result in inhomogeneous thin deposits that compromise their use in many technological applications. For soluble functional materials, this issue can be overcome by using patterning techniques, which induce molecules to assemble into well-defined patterned structures by means of spatial confinement. Here we propose several examples, which encompass the most common cases for functional materials.

Materials and methods: Stamp-assisted techniques have been shown to be a versatile and technologically attractive route for the micro- and nanopatterning of a broad range of functional materials such as organic semiconductors, coordination compounds, magnetic precursors, proteins, DNA, cells, and colloids. These techniques are based on the use of micro- and nanostructured (rigid or soft) stamps that allow us to confine the assembly processes of a material into a spatially defined region between the stamp and the substrate. The overall result of the patterning is determined by (i) intrinsic self-organization properties of the material, (ii) interaction between solute and stamp/substrate; (iii) solvent nature, (iv) concentration of the solution, and (iv) size and shape of the stamp features. Among all stamp-assisted techniques, we

have use micromolding in capillaries (MIMIC) and lithographically controlled wetting (LCW). MIMIC and LCW are complementary techniques that allow the patterning of interconnected or isolated micro and nanostructures on both planar and curved surfaces.

Results: We have used stamp-assisted techniques for the micro and nanostructuration of organic semiconductors, and coordination polymers (CPs). In particular, LCW and MIMIC techniques have been employed to fabricate unipolar and ambipolar organic field effect transistors (OFETs) and logic-gate devices based on long-range ordered oligothiophene fibers, polymeric nanostripes and CP-based microelectrodes.

Discussion: The use of a stamp to control the deposition process of soluble materials on substrates is a useful strategy to exploit their organization properties in confinement, which in turn could improve their functional properties. Indeed, we have reported that using different stamp-assisted techniques the electrical performance of organic semiconductors can be improved and exploited to develop logic-gate devices, while the conducting properties of a platinum-based CP can be exploited for the fabrication of a new generation of microelectrodes.

WASTE MATERIALS IN THE PRODUCTION OF TRADITIONAL BUILDING CERAMICS: EFFECT OF GRP DUST WASTE ADDITION ON PROPERTIES OF FIRED BRICKS

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Introduction: The total amount of end-of-life and production waste generated by glass thermo-set composites market in Europe reaches 304,000 tonnes (2015) triggering interest in optimizing Glass Reinforced Plastic (GRP) waste recovery. Now, landfill as non hazardous waste remains the most popular solution to manage GRP waste for the difficulty of separating the different parts, its intrinsic thermo-set composite nature and the insufficient knowledge on recycling options. Recently, GRP dust (GRPD) waste in cementitious matrix has been investigated to improve performances. Effects of GRPD waste addition in the production of bricks can also be considered. The polymeric part in GRPD will burn during cooking: additional porosity can be left in the matrix improving final lightness; the glass fibers in GRPD waste can reinforce the ceramic matrix decreasing fragility and increasing the bricks bending strength.

Materials and methods: To manufacture bricks, clay was provided by a local company and GRPD from a shipyard (industrial by-product). GRPD volumetric composition is 20% of glass fibers and 80% of polyester resin. Density is 1.3 g/cm³. GRPD average diameter is 100 µm (LLS analysis). SEM-EDS analysis show polymeric granules surrounding low alkali glass with 0.02-20 mm lengths. Bricks are manufactured by mixing water with clay and specimens with GRPD replacing by volume the 5-10% of dry clay are prepared. At the dosage rate of 5%, GRPD previously sieved at d = 250 µm is also considered in order to increase the glass part (from 20% to 30% by volume) and consequently decrease the polymeric part. All mixes are cooked up to T = 850°C for 8 hours. Specimens are compared in terms of porosity, by mercury intrusion porosimetry, compressive (UNI EN 772-1) and flexural strengths, density and water absorption (UNI EN 771-21).

Results: The addition of GRPD waste in brick production decreases the compressive strength from 26 to 18 MPa (reduction 30%) and 14 MPa (reduction 46%) with 5% and 10% of GRPD respectively, regardless of previously sieved or not. This is not due to an increase in total porosity, constant at 42%, but to a shift of pore size distribution to larger sizes (median and modal pore diameters move from 0.49 and 0.57 µm and to 0.58 and 0.73 µm, respectively). This increases also water absorption from 21% with 0% GRPD to 27% with 10% GRPD, being more affected by bigger porosity. GRPD addition decreases only weakly the density of the final product from 1.5 to 1.4 gr/cm³. However, flexural strength increases from 5.1 to 5.9 and 6.7 MPa with of 5% and 10% GRPD specimens, respectively, with the corresponding deformations at the maximum load that increase for 25% and 90%. When a 5% of sieved GRPD is added, flexural strength is 6.2 MPa with a 150% higher deformation at maximum load with respect to 0% GRPD bricks.

Discussion: The inclusion of GRPD waste in brick production can lead to an improvement of the final performances of bricks, in terms of increased flexural strength and lower fragility, together with a viable technological solution for GRPD waste management.

PROBING MOLECULAR ORIENTATION IN CONJUGATED POLYMER FILMS VIA EPR SPECTROSCOPY

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Introduction: Organic photovoltaics is a promising technology aiming at replacing conventional inorganic photovoltaics based on Si or other inorganic semiconductors. The main advantages it offers are light-weight, flexibility and lower production costs thanks to *roll-to-roll* printing techniques. The photoactive layer of organic solar cells is a thin film blend of a conjugate polymer, acting as electron donor under light absorption, and a fullerene derivative, the electron-acceptor.

It was shown that morphology plays an important role in determining the photovoltaic performances of these materials. The formation of highly ordered polymer domains enhances hole-mobility, thus improving charge transport and reducing charge recombination. Moreover, the π -stacking direction was recognized as the preferred direction for hole-transport.

In this work we show that Electron Paramagnetic Resonance spectroscopy is a powerful tool to probe molecular orientation in photoactive materials. EPR spectroscopy was employed since it allows for detection of either intrinsic (radical defects) or photoinduced paramagnetic species, which can be used as probes for molecular orientation by exploiting the anisotropy of spin magnetic interactions.

Materials and methods: We used three different deposition techniques – spin-coating, drop-casting, gravure-printing – to produce films of the semi-conducting polymers such as polythiophene and other alternating copolymers (PSiFDBT and PBDT-BTD-BTA). P3HT samples were studied by means of steady-state EPR, a technique sensitive to long-lived paramagnetic species (ms time scale), like polarons induced by oxidation of the polymers. Films of other polymers were examined by means of time-resolved EPR (TR-EPR), which allows for detection of short-lived (μ s) photoinduced paramagnetic states, typically the polymers' triplet state populated by ISC upon photoexcitation. The orientational analysis was performed by fitting the EPR spectra obtained with different orientations of the films in the magnetic field. A uniaxial orientational distribution function was used and the order parameter was obtained from spectral fitting.

Results: EPR spectra of all P3HT films show the polymer polaron signal with high angular dependence, confirming the existence of ordered polymer domains. For polymers PSiFDBT and PBDT-BTD-BTA, TREPR highly oriented triplet spectra were detected upon photoexcitation with 532 nm laser light.

Discussion: Spin-coated P3HT films show an edge-on preferential orientation of the polymer chain, which is not influenced by the presence of the fullerene derivative PCBM. In the gravure printed films, the polymer backbone still lies parallel to the substrate with a higher disorder in the polymer crystallites orientation. The triplet state spectra of spin-coated films of polymers PSiFDBT and PBDT-BTD-BTA reveal the same kind of order seen for spin-coated P3HT: π -stacked ordered polymer domains form, with polymer chain lying parallel to the film, and having one main orientation of the aromatic plane with respect to the film substrate. The same kind of order is found for drop-casted PBDT-BTD-BTA, indicating that the deposition technique has little influence on morphology for this polymer.

TRANSPARENT CERAMICS FOR LASER APPLICATIONS

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Introduction: Transparent ceramics represent a state-of-the-art class of ceramic materials, with prerequisites of transparency being the absence of defects, secondary phases and pores. Since transparent ceramics are polycrystalline, they have good thermal and mechanical properties that make them valid substitutes to glasses and single crystals as solid state laser hosts. The crystalline structure and higher thermal conductivity of ceramics compared to glasses provide much better performance for high power pulsed lasers and more efficient cooling. On the other hand, the wide range of shaping methods represents a strong advantage of ceramic technology in comparison with that of single crystals, as it allows the production of near-net-shape components with a well-defined internal structure. Furthermore, in comparison with the ceramic production, common single crystal growth methods are time consuming and expensive processes. In the case of high-power lasers the performance may be negatively affected by the presence of temperature gradients inside the gain medium, and eventually

may lead to damage and destruction of the component. The presented work shows that it is possible to exploit the ceramic process for a better thermal management by the introduction of a non-uniform distribution of the laser-active ions within the medium. The system studied in the presented work is Yb-doped YAG (yttrium aluminium garnet, $Y_3Al_5O_{12}$) and structures with both uniform and variable dopant distribution were produced.

Materials and methods: Yb:YAG ceramics were prepared by solid state reaction sintering, where the cubic garnet phase is formed by reaction of oxide powders. The production process can be described as follows: mixing and homogenization of oxide powders and sintering additive – shaping – heat treatments in air and under vacuum (sintering) – annealing, polishing. Shaping was performed by two different methods: 1. pressing of granulated powders and 2. tape casting followed by thermal compression of stacked tapes. Structures with variable doping were obtained by combining of layers or tapes with different Yb concentration. Material quality was evaluated by SEM-EDX analysis of microstructure, measurements of optical transmittance, and characterization of laser efficiency. **Results:** Materials with good optical quality (transmittance higher than 80%, i.e. 95% of the theoretical transmittance) and laser performance (laser slope efficiency exceeding 50%) were prepared by both approaches. Structures with layered dopant distribution were produced, and both the pressing of powders as well as tape casting provided good results. The use of tape casting allowed a better control of dopant distribution and is more promising for the production of larger parts.

Discussion: Ceramic technology proved to be a convenient approach for the production of gain media for solid state lasers. A particular advantage lies in the possibility to produce in-situ not only a product of desired shape, but also with a controlled inner structure, the latter leading to improved laser efficiency under high thermal loading.

MULTIFUNCTIONAL LANTHANIDE ACTIVATED ALKALINE-EARTH FLUORIDE NANOPARTICLES FOR BIOMEDICINE

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Introduction: Lanthanide doped alkaline-earth fluoride nanoparticles have been investigated in the past years for their possible use in several technological applications, such as biomedical diagnostics. This contribution is focused on spectroscopic properties of water dispersible alkaline-earth fluoride (CaF_2 or SrF_2) nanoparticles activated with the lanthanide ions (such as Yb^{3+} , Nd^{3+} , Ho^{3+}), in particular for their possible use as multimodal luminescent markers for bioimaging in the biological windows.

Materials and methods: A facile hydrothermal synthesis at temperatures lower than 200°C has been used to prepare the activated nanoparticles, using water as the solvent. Citrate ions have been added as capping agents to guarantee colloidal stability in phosphate buffers (PBS) or saline solutions. DLS techniques have been used to investigate the hydrodynamic size and zeta potential.

Results: Emission spectra in the visible and near infrared (from 700 to 1000 nm, in the first biological window) optical regions upon excitation at 980 nm or 800 nm have been measured, also as a function of temperature in the 20–60°C range.

Discussion: The emission spectra have been analysed to investigate the performance of the nanoparticles as nanothermometers. Preliminary results indicate that the relative sensitivity is interesting and therefore it suggests a possible use of these NPs as both luminescent probes and nanothermometers in the biological windows.

STUDY OF INCONEL 625 ALLOY PRODUCED BY DIRECT METAL LASER SINTERING: CHARACTERIZATION AND HEAT TREATMENTS SET-UP

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Introduction: The aim of this work is to study the effect of different heat treatments on a nickel-based superalloy known as Inconel 625 (IN625), fabricated

by Direct Metal Laser Sintering (DMLS), the EOS tradename to indicate Selective Laser Melting (SLM) process. This technology is able to create full metal components, including components with very complex geometry, using computer-aided design (CAD) models. In this way, it is possible to eliminate the necessity to use molds and to reduce the subsequent machining operations, which is making it grow in popularity for its high flexibility with respect to the traditional processes, especially to build components with complex shapes.

Materials and methods: This alloy is generally used from cryogenic to high temperature up to 1000°C for applications in harsh environments, such as aeronautic, aerospace and marine industries, due to high strength, high weldability, high creep and oxidation resistance. However, the process develops unique microstructures with fine dendritic architectures, different with respect to the microstructures of the same alloy processed by casting or forging. Because of this, for high-temperature applications it can be a benefit to perform annealing or solution treatments to homogenize the microstructure and promote the grain growth, improving the creep resistance, as for turbine blades in aerospace industry. On the contrary, finer microstructures may increase mechanical properties and corrosion resistance for applications at room temperature, as in marine engineering field. For this purpose, different heat treatments, followed by water quenching to prevent the precipitation growth, were performed and the heat-treated samples were characterized by means of Optical Microscope (OM), Field Emission Scanning Electron Microscope (FESEM) equipped with an Energy Dispersive X-ray Spectroscopy (EDS) detector and hardness measurement.

Results: The as-fabricated samples exhibit melt pools created by the laser scan tracks and at higher magnifications dendritic structures with dimension less than 1.5 μm can be observed. In fact, during the SLM process the laser beam melts narrow areas in a very short time, resulting in high cooling rates, generally higher than 10³ K/s.

The heat-treated samples at a temperature over 900°C reveal a rapid grain growth, whilst heat treatments carried out below 900°C allow the formation of different precipitates, such as gamma double prime phase, delta phase and other nanometric-sized phases, that increase hardness.

Discussion: The results suggest that by changing the heat treatment conditions, as temperature and time, it is possible to create different microstructures that are desirable in different applications to meet the specific industrial demands. In the future, it will be performed mechanical test on the heat-treated samples, to compare them to IN625 produced by conventional technologies and the nanometric-sized precipitates will be studied to characterize their nature.

FUNCTIONALIZED CARBON BASED HYBRID MATERIALS FOR MgO/H₂O/Mg(OH)₂ CHEMICAL HEAT PUMP FOR THE RECOVERY OF MEDIUM TEMPERATURE WASTE HEAT

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Introduction: Medium temperature waste heat (200-400°C) can be recovered by MgO/H₂O/Mg(OH)₂ chemical heat pump, which is based on the following reversible chemical reaction:



The charge step takes place when thermal power is used to drive the endothermic Mg(OH)₂ dehydration reaction. In the discharge step, the exothermic MgO hydration reaction releases the stored heat when it is required. However, the potential storage capacity of this system is still not fully exploited. At this aim, it is here proposed the dispersion of Mg(OH)₂ over functionalized carbon materials: carbon nanotubes (CNTs) and exfoliated graphite (EG). The carbonaceous phase should improve the heat transfer properties of the storage medium.

Materials and methods: Carbonaceous materials (EG and CNTs) were functionalized through a nitric acid vapour phase treatment at 135°C for 2h. The functionalization degree is conventionally evaluated by Thermogravimetric Analysis as the weight loss under inert atmosphere up to 1000°C (heating rate 20°C/min). With respect to the more common liquid phase function-

alization treatment, the vapour phase should offers notable advantages, like the higher functionalization degree and the lower material loss. The DP synthesis reaction was optimized in order to obtain the highest Mg(OH)₂ yield, purity, crystallinity degree ad dispersion over the carbonaceous material by studying the influence of reaction temperature, pH, NH₄ feeding rate, Mg(OH)₂ load on the thermochemical behaviour of heat storage materials. The materials were characterized by means of Scanning Electron Microscopy and X-Ray Diffraction. Their thermochemical performances, in terms of heat storage and output capacities, were evaluated through an experimental simulation of a CHP that consists in a thermogravimetric unit and an evaporator for water vapour supply.

Results: At the same functionalization conditions, CNTs show higher functionalization degree than EG, respectively ≈21% and 11%. Regarding the DP on pristine and functionalized EG, it cannot be observed, by SEM images, a clear improvement of the overcoating in the sample with functionalized EG. Upon precipitation on functionalized CNTs it is, instead, evident a bettering of the homogeneity in comparison to that on pristine CNTs, in which, instead, the two components appear separated. The heat storage and output performances of both EG and CNTs (regardless for pristine or functionalized) heat storage materials are higher than that of pure Mg(OH)₂ (600 kJ/kg_{Mg(OH)2}). The functionalized and pristine EG based hybrid materials showed similar performances (900 kJ/kg_{Mg(OH)2}), while enhanced heat storage and output capacities are obtained in case of functionalized CNTs (1300 kJ/kg_{Mg(OH)2}) compared to the pristine CNTs (1000 kJ/kg_{Mg(OH)2}).

Discussion: The functionalization treatment was more efficient on CNTs rather than on EG. Due to the better Mg(OH)₂ dispersion on functionalized CNTs the potential storage capacity of pure Mg(OH)₂ has been fully exploited.

SIMPLE, VERSATILE, INEXPENSIVE: PROTON (TD)NMR FOR THE STUDY OF MATERIALS

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Introduction: Protons (H atoms) are present in water, many solvents and most organic molecules including polymers. Time domain nuclear magnetic resonance (TD-NMR) is a branch of nuclear magnetic resonance where the evolution of the proton magnetization vector is directly analyzed in the domain of time, without Fourier transform. This peculiarity makes the technique viable even on low-field benchtop instruments and not limited to soluble samples: solids can be investigated without special preparation and without magic angle spinning. Signal intensity can be linearly related to the protons in a sample, thus determining content of water in food, or the saturation in aviation fuel with precision and sensitivity sufficient even for forensics applications. An entire new level of versatility is provided by modern NMR pulse sequences that separate and quantify populations of H atoms according to their mobility: in turn, mobility at the microscopic level generally relates with macroscopic properties. Here we present several case studies, demonstrating how the ubiquity of protons combined with a toolbox of specialized NMR sequences can tackle several problems in the science of materials

Materials and methods: The presented case studies were developed using a Bruker mq20 Minispec. The NMR sequences used include standard CPMG, Hahn Echo, and the more advanced Magic Sandwich Echo and Baum-Pines sequences developed for the measurement of crosslink density in rubbers or the kinetics of gelation and crystallization. Core-Shell NPs were synthesized in microemulsion with a rubbery poly(butylacrylate) core, PBA, and a glassy shell of polystyrene, PS. Vulcanized natural rubber was prepared by curing commercially available natural rubber (NR), isoprene rubber (IR) and their blends for different times. Titanium oxide NPs were synthesized in organic environment, uncapped and dispersed in water.

Results: With TD-NMR we proved that the inner PBA core and the external PS shell of NPs evolve independently as two homopolymers: significant changes in the rigid fraction take place at PBA and PS characteristic Tg, demonstrating strong phase separation and the absence of significant interfaces. Additionally, a direct quantification of the amount of PBA and PS in the nanoparticles was possible. A second case study is vulcanized rubber for tyre industry. We could measure the density of crosslinks (CLD) with higher speed and precision than the traditional swelling methods and also investigate the CLD evolution during overcuring. Finally, even samples with negligible proton

content such as titania nanoparticles could be investigated by TD-NMR by dispersing them in water. The study of water protons relaxation provides indirect but precise information on their surface and morphology.

Discussion: The presented case studies describe the potential of TD-NMR for the characterization of polymers, porous systems and nanoparticles, including some examples of high relevance for the industry. The instrumental requirements are tiny in comparison of high field NMR, and many important properties of materials can be measured in easier, faster and cheaper way.

INFLUENCE OF CURING TEMPERATURE ON MECHANICAL PROPERTIES OF ALKALI ACTIVATED BINDERS FOR PRECAST CONCRETE APPLICATIONS

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Introduction: Climate change is posing several challenges for anthropic activities. Construction sector has determined a relevant environmental impact related to both natural resources depletion and greenhouse gases emissions (GHGE). In this scenario, the simultaneous increase of waste recovery and decrease of GHGE represent a strategic objective for sustainability. This paper deals with a recycling route for waste fly ash from coal-fired power plants. Part of the total fly ash is usually destined to blended cements after a quality assessment according to European standards. In this study, waste fly ash are recovered by means of alkaline activation technology for binders production in the construction sector. The focus is on curing temperature which is fundamental for precast applications and the development of mechanical performance.

Materials and methods: WFA was provided by the coal-fired power plant of Brindisi (Enel "Federico II"). The water content was equal to 15 wt% after drying in oven at 105°C until constant mass. For the mix design, the following parameters have been considered: (i) waste fly ash content (WFA); (ii) sodium silicate solution (Na_2SiO_3); (iii) sodium hydroxide solution (NaOH/10M). For the investigated system, considering the WFA content as reference (mass ratio = 1), Na_2SiO_3 and NaOH/10M have been added in amount equal to 0.33, respectively (0.66 as sum in terms of alkaline solution blend). The XRF analysis allowed to evaluate main oxides composition, particularly, the sum of contents of SiO_2 and Al_2O_3 was equal to 64.5%. Calcium oxide content was very low (0.5%). Paste samples were prepared by means of 5 minutes Hobart mixing after separate mixing procedure to pre-activate fly ash with NaOH solution. Physical and mechanical properties development and influence of curing temperature were evaluated by means of ultrasound pulse velocity (UPV) and unconfined compressive strength (UCS).

Results: Three different curing temperatures have been considered, namely 20°, 40° and 60°C. At 20°C, no early age strength development was detected, considering two curing periods of 2 and 6 days, respectively. After increasing the temperature at 40°C, satisfactory engineering results can be achieved (2.55 MPa and 9.67 MPa at 2 and 6 days, respectively) and the binder can be proposed for bricks production. By means of curing at higher temperature (60°C), structural performance is achieved, namely 20.11 MPa at 6 days. The evolution of stiffness follows similar trend but the relative gain due to increased curing time is reduced respect to UCS.

Discussion: The study shows effectively the sensitiveness of alkali activated systems respect to curing conditions. This sensitiveness is much higher than the case of traditional cementitious binders. Passing from 20°C to 40°C, it is possible to obtain a non-structural binder for bricks production, while, increasing the temperature up to 60°C, it is possible to obtain structural materials.

FUNCTIONALIZED MESOPOROUS SILICA NANOPARTICLES AS THERANOSTIC NANOPLATFORM FOR OPTICAL IMAGING AND PHOTODYNAMIC THERAPY

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Introduction: Nanomaterials that meet easy surface functionalization with high biocompatibility have emerged as good candidate for theranostic ap-

plications. In particular, the integration of multiple smart functions such as contrast agent (CA) and photosensitizer (PS) into a nanodevice platform can enhance diagnostic and therapeutic efficacies and is now a day a great scientific challenge. To obtain efficient nanodevices for coupling optical imaging together with photodynamic therapy (PDT), it is necessary to control the location of the contrast agent and/or of the photosensitizer and to optimize loadings and dispersion in order to avoid molecular aggregation that is detrimental both for imaging and photodynamic therapy. Among a variety of nanoparticles that can be used as nanovector, mesoporous silica nanoparticles (MSNs), have attracted great scientific attention due to the high specific surface area, high pore volume and uniform pore size that allow hosting, through simply synthetic procedures, different guests. In this contribution, Verteporfin (Ver), a PS belonging to the family of benzoporphyrin with high performances in singlet oxygen (${}^1\text{O}_2$) delivery upon red-light irradiation, and Rose-Bengal (RB), a halogen-xanthene dye which produces ${}^1\text{O}_2$ upon green-light excitation, have been covalently bound to MSNs. Furthermore, Rhodamine B (RhB) was chosen as CA and bifunctional nanosystems were prepared by immobilizing both RhB and PS on the same MSN. A multi-technique approach was used to characterize the nanosystems. ${}^1\text{O}_2$ generation efficiency was first evaluated by a chemical method, then the most promising samples were tested in vitro for their effect on cell proliferation in the presence of light activation in different cell lines, including the high malignancy melanoma cellular model (SK-MEL-28).

Materials and methods: PS and CA molecules were covalently attached to the amino groups of NH_2 -MSNs nanoparticles, obtained by one-pot synthesis. A detailed structural and morphological characterization was carried out by using XRD, HRTEM, volumetric and thermogravimetric analysis combined with spectroscopic characterization by using DR-UV-Vis, FTIR, SS-NMR and photoluminescence spectroscopies. The ${}^1\text{O}_2$ generation was evaluated by using uric acid, which reacts irreversibly with ${}^1\text{O}_2$.

Results: Loading rate, distribution and location of the PS molecules were carefully evaluated in order to optimize the singlet oxygen generation performances of the nanosystems. In addition, the location, the dispersion and the protection of RhB into MSNs have been carefully evaluated by using a high sensitive technique like photoluminescence coupled with lifetime measurements.

Discussion: The presented study has evidenced the advantages to covalent coupling PS into mesoporous silica nanoparticles for PDT applications given that the PS molecules are stably incorporated into the nanoparticles. The optimized nanodevices showed promising performances in reducing the viability of highly aggressive melanoma cell line SK-MEL-28, underlining their potential application as highly efficient PDT nanoplateform. In the case of the bifunctional system, the obtained results highlighted the importance of the protection of the fluorophore from photobleaching and that a careful control of the fluorophore loading is necessary to obtain nanodevices with optimal performances. The bifunctional nanodevice has evidenced high fluorescence performances and good efficiency in ${}^1\text{O}_2$ delivery, highlighting its potential applications in theranostic.

WHAT IF WE USE BIOMASS ASHES TO ACTIVATE ONE-PART GEOPOLYMERS?

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Introduction: Geopolymers are cement-like materials obtained by the chemical reaction between a powdered aluminosilicate precursor and an alkaline solution. Recently, researchers are studying alternative ways for geopolymer preparation in order to avoid the use of alkaline activators, which are difficult to handle in construction site works. These user-friendly materials are known as one-part geopolymers and appear as a cementitious powder that can polymerize only by water addition. This work deals with the use of potassium-rich biomass ashes for the activation of two types of one-part geopolymers.

Materials and methods: The first type of geopolymers (G1) was prepared with metakaolin obtained by the calcination at 700°C of kaolin from South England and biomass ash (BA) originated from a power plant located in Rodenhuize (Belgium) that uses wood for electricity generation. The second type of geopolymers (G2) was prepared with metakaolin obtained by the calcination at 700°C of Cameroonian kaolin (from the Mayouom kaolin deposit) and cotton shell ash (CSA) originating from a refinery in Maroua (Cameroon) that uses cotton seeds to produce cooking oil. River sand with maximum grain size of 2 mm was used for G1 and G2 mortars. Isothermal micro-calorimetric analysis was performed at 25°C on geopolymeric pastes with a constant water/solid ratio of 0.56 by varying the K/Al molar ratio of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 in order to investigate reaction kinetics. Geopolymeric mortars were prepared with sand/metakaolin ratio equal to 3 and by varying water/solid ratio, K/Al molar ratio and by using both unheated and heated ashes over 700°C in order to decompose carbonates with possible increase in reactivity. Mortars were cured for 24 h at 20°C and then oven heated at 70°C for another 24 h. Then, specimens were subjected to compression tests.

Results: The highest reaction enthalpy was obtained for G1 and G2 at K/Al = 2.5 and 2.0, respectively. Best compressive strengths were obtained for G1 mortars at K/Al = 2.5 (3.7 MPa), whereas for G2 mortars at K/Al = 2.0 (3.1 MPa), if prepared with unheated ashes. Compressive strength of G1 mortars prepared with heated BA ranged from 1.7 to 2.5 MPa. On the contrary, G2 mortars showed compressive strength over 6 MPa at K/Al = 2.0 if prepared with heated CSA.

Discussion: Isothermal micro-calorimetric analyses of G1 and G2 pastes showed that the heat flow increased with the K/Al molar ratio. However, integrating the heat flow evolution during time, the reaction enthalpy increased until a maximum. This value corresponds to the most reactive composition, in agreement with compression tests. Heating BA over 700°C deepened the compression behavior of G1 mortars. On the contrary, the elevated temperature increased the reactivity of CSA contributing to mechanical strengths the 50% higher for G2 one-part geopolymeric mortars with respect to G2 mortars prepared with unheated CSA.

LOW TEMPERATURE TITANIA COATINGS FOR CORROSION PROTECTION

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Introduction: Corrosion is one of the most serious problem affecting metallic materials. Several studies report that the costs of these phenomena amount to several points of Gross Domestic Product in developed countries. One of the most effective way to protect steel alloys is *via* chromate conversion coatings, but the proven toxicity of chromium VI, opens a new field in research activity. The present work is focused on preparing low temperature titania coatings, obtained *via* sol-gel dip-coating, on AISI 304 steel and characterizing them in terms of morphology, structure and anti-corrosive properties.

Material and Methods: The substrate chosen for the investigation was AISI304 stainless steel. Samples with a size of 10 × 20 mm² and 1 mm thickness were polished up to 3 µm diamonds suspension and then dipped in acetone in an ultrasonic bath. TiO₂ film preparation by sol gel route followed these steps:

1. solution preparation by dissolving 3 ml of titanium tetra-isopropoxide (Sigma-Aldrich, CAS n.546-68-9) under stirring at 200 rpm for 2 h in 50ml of ethanol in presence of 3 ml of acetic acid with both functions of acid catalyst and chelating agent;
2. immersion of the substrate in the solution for 30 s;
3. formation of a wet layer by extraction of the substrate at a speed of 4 cm/min;
4. gelation of the layer by solvent evaporation at room temperature for a night and subsequent destabilization of the sol.

To achieve a dense film, the samples were then dried in an oven at low temperature (80 or 100°C) with a slow heating rate (3°C/min) to ensure a further poly-condensation of the colloidal particles entrapped in the liquid phase of the gel. For some samples, the above procedure was repeated twice.

Samples were analyzed by XRD, XPS, EIS, and SEM/EDX before and after corrosion tests.

Results: XRD analysis performed on the samples revealed that the coatings showed no crystalline phase. The pattern showed only AISI 304 typical peaks. SEM analysis performed before corrosion tests showed that the coatings have

similar morphology, although some defects were observed on the surface. Electrochemical measurements were performed on the samples and on the bare alloy. Samples were dipped in 3%NaCl aqueous solution, for at least 7 days, recording a spectrum every 24 h. All samples showed a better corrosion resistance than the alloy. In particular samples Ti80-1D showed a slight increase of the corrosion performance, while the other samples (Ti80-2D, Ti100-1D, Ti100-2D) showed an increase of the resistance of at least 2 orders of magnitude for all immersion time. SEM and EDX performed after corrosion showed some corrosion attack. EDX showed presence of Ti on samples surfaces.

Discussion: In this work, titania coatings were deposited on AISI304 stainless steel via sol-gel dip-coating. Morphological and microstructural analysis showed that the obtained coatings were amorphous, compact and with good adhesion. Electrochemical analysis showed that the coatings (except Ti80-1D) showed resistance 2 orders of magnitude greater than the alloy.

MOLECULAR ROTORS IN POROUS MATERIALS

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Introduction: Molecular rotors in the solid state constitute an interesting area within the class of dynamic materials. They can be applied in several fields, including molecular machinery and tunable dielectric response for optical and electric devices. Rotary motion is usually hampered when the molecules are condensed in the crystalline state. However, by the exploitation of porous materials rotor dynamics at the incredible speed of 10⁸ Hz not only at room temperature but in some cases even below 200K can be achieved.

Materials and methods: We have prepared a series of micro- and mesoporous materials endowed with high surface areas up to 5000 m²/g that contain molecular rotors in their walls. In particular, porous molecular crystals held together by charge-assisted hydrogen bonds, hybrid mesoporous organosilicas (PMOs) and porous aromatic frameworks (PAFs) have been studied. The molecular rotors are constituted by p-phenylene moieties, typically pivoted on Csp₂-Csp and Csp₂-Si bonds. The key method to study the dynamics was ²H NMR spectroscopy, which is sensitive to the motional reorientation of the C-D bonds from 10³ to 10⁸ Hz. ²H NMR spectra were collected as function of temperature from 150 to 400 K and the energy barrier for rotation were determined by an Arrhenius plot. For this sake, porous materials containing deuterated p-phenylene moieties have been prepared.

Results: ²H NMR spectra of the porous materials change systematically as a function of temperature and their profiles were simulated by a two-site 180° flip reorientation mechanism. Extremely fast reorientational rates in the order of 10⁷-10⁸ Hz already at 200K were detected. The results suggest that such rotors are among the fastest ever described in the literature. At high temperatures large amplitude librations up to 36° have been observed, in addition to the 180° flip reorientation. Activation energies as low as 4-6 kcal/mol were determined.

When C-F dipoles are asymmetrically mounted on the p-phenylene units, rotor reorientation brings together a dipole reorientation, which is sensitive to an applied electric field.

The porosity of the materials offers a great advantage: guests diffusing in cavities can modulate at will the motional dynamics of the molecular rotors exposed in the channels. Actually, iodine molecules entered the pores and could regulate reversibly rotor dynamics.

Discussion: The present measurements demonstrate that the rotors decorating nanochannel walls gain a high degree of mobility when the channels are empty. When the materials are exposed to a vapor, even at a low pressure, molecular rotors extensively interact with the guest molecules and their dynamics is controlled.

SYNTHESIS AND CHARACTERIZATION OF ELECTROLESS Ni-P ALLOYS FOR ANTI-WEAR AND ANTI-FOULING COATINGS

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Introduction: Fouling is a typical problem in compressors used for processing of hydrocarbon gasses and it is caused by solids adsorption onto the internal surfaces of the machinery.

This phenomenon can influence the performance of the facility and, in some cases, it causes the stop or the failure of the system. Surface coating can be a suitable solution to this kind of problem.

Anti-fouling and anti-wear coatings can be obtained by electroless-nickel plating technique. It allows for depositing very uniform and dense Ni-P alloy coatings on irregular shaped surface and on different kind of substrate.

Materials and methods: Ni-P amorphous alloy was deposited on a steel substrate. The electroless plating bath is an acid solution and consists of a nickel source, a reducing agent (P compounds), stabilizing agents and a buffer. The temperature and the pH were continuously monitored during the deposition and kept constant. Plating parameters were optimized and several coatings were deposited. Nano-particles were added in order to improve the performance of the coating, in particular particles of polytetrafluoroethylene (PTFE) were chosen to improve anti-fouling behavior while nano-zirconia particles were added to improve wear resistance. In order to prevent agglomeration of nano-ZrO₂, nano-particles were previously surface modified with methacrylic acid. Ni-P coatings were characterized through SEM imaging and EDS analysis. Coating thickness and roughness were measured. Top view and cross section Vickers hardness was evaluated. The morphology of the samples was compared through a surface profilometry analysis. The wettability was evaluated considering the drop contact angle for different fluids.

Results: All deposited coatings (Ni-P, Ni-P with ZrO₂, Ni-P with PTFE, Ni-P with ZrO₂ and PTFE) are dense layers with a very good adhesion with the substrate. As expected the morphology of the coating follows the morphology of the substrate. SEM microographies show an optimal dispersion and distribution of nano-particles. Nano-zirconia addition allows for obtaining small values of roughness and high values of Vickers hardness. Nano-ZrO₂ and PTFE particles cause a reduction of drop contact angle for different fluid. In particular PTFE results to be more beneficial for a decrease of the wettability.

Discussion: Electroless Nickel Plating technique was well optimized resulting in dense coatings and good rate of deposition. The results show improvements of the desired coating properties in particular when PTFE and ZrO₂ are both added.

NANOSCALE CHARACTERIZATION OF EXTRACELLULAR VESICLE IS MANDATORY TO ASSESS THEIR BIOLOGICAL ACTIVITY AND BIOTECHNOLOGICAL EXPLOITATION

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Introduction: Cells release into the extracellular environment diverse types of nanosized extracellular vesicles (EVs) which serve in inter cellular communication by shuttling protein, lipids and small nucleic acids (miRNA). It is now becoming clear how they support both physiological or pathological mechanisms such as antigen presentation, immunostimulatory or inhibitory activities, disease progression. EV properties, including specific targeting, cargo protection, biocompatibility etc. open new exciting perspectives for their application in biotechnology as tools for drug delivery, therapeutic targets or source of new markers. EVs are separated from different biological fluids e.g. blood, cell culture medium, urine and depending on the applied protocol the resulting sample can be surrounded by different kind of exogenous nanostructured matrixes, which heavily influence in vitro and in vivo properties. Here we asses and apply nanodiagnostic techniques used in nanomaterial science to these new soft natural nanostructures and show that they add important information on their final biological activity.

Materials and methods: Exosomes from serum of Multiple Myeloma (MM) patients were purified following different purification protocols: sequential centrifugation steps (P3), discontinuous sugar gradients (sucrose and iodixanol) and a direct vesicle precipitation kit (ExoKit). Samples have been analyzed by Western Blot, colloidal nanoplasmonics, atomic force microscopy (AFM) and scanning helium ion microscopy (HIM). Resulting data allowed the determination of samples purity and their biological activity.

Results: Data obtained analyzing samples by Western blot indicate that all the isolation protocols allow obtaining comparable exosome population ex-

pressing characteristic markers (Hsp70, Tsg101, CD63, Annexin V). Colloidal properties and biophysical purity grade has been determined respectively with agarose gel runs and colorimetric nanoplasmonic assay. Results showed that gradients contain lower quantity of contaminants compared with ExoKit or P3. AFM and HIM imaging highlighted samples microstructure confirming that samples are composed of vesicle populations with typical exosome size (50-120 nm) and that residual matrix are absent in samples isolated by gradients whereas it's abundant in P3 and ExoKit samples. To demonstrate if the purity of each preparation can affect their biological effect, human endothelial cells have been exposed to MM exosome. It is known that EVs cellular internalization trigger NfkB nuclear translocation, this biological effect has been exploited to value if surrounding matrix influence samples biological activity. As expected, cells incubated with exosome obtained from gradients showed a strong NfkB nuclear translocation signal whereas P3 and ExoKit preparations showed no significant differences compared to those treated with the control buffer.

Discussion: These findings suggest that exosome preparation purity must be carefully assessed since it may interfere with exosome biological activity. Contaminants can be explored only by an integrated characterization approach aimed at both the molecular and the colloidal length scales.

CONFINED POLYMERIZATION IN POROUS MATERIALS

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Introduction: Porous materials with permanent porosity have recently emerged as an exciting research field with potential applications in gas storage, separation and catalysis. Porous aromatic frameworks and periodic mesoporous organosilicas showed high robustness and extraordinary chemical stability that made them ideal for supporting chemical reactions without framework destruction. Confined polymerization in nanopores allowed the synthesis of innovative nanostructured materials and nanocomposites with extended interfaces that couldn't be obtained otherwise.

Materials and methods: Porous aromatic framework (PAF-1) was synthesized through a Yamamoto-type Ullmann cross-coupling. *P*-phenylene silica (PSS) was prepared by a template synthesis. These porous frameworks were characterized with nitrogen adsorption measurement, IR spectroscopy, DSC, TGA and ss-NMR. The polymerizations were performed in the liquid phase: a solution of AIBN (azobisisobutyronitrile) in distilled acrylonitrile was diffused inside the pores of the matrixes and the samples were heated to activate the polymerizations. The nanocomposites were prepared either with stoichiometric amount of monomers or excess monomers. The nanocomposites were characterized with nitrogen adsorption measurement, thermogravimetric analysis and electron microscope techniques (SEM, HR-TEM). The interactions between the porous matrixes and the engendered polymer were investigated with fast magic-angle-spinning 2D ¹H-¹³C HETCOR NMR. The nanocomposites were heated at different temperatures (300-1000°C) under an inert atmosphere.

Results: The confined polymerization of acrylonitrile inside the pores of PAF-1 and PSS with stoichiometric amount of monomers led to the fabrication of nanocomposites with intimate relationship between host and guest. The matrixes and the polymer form extensively interdigitated nanophases through multiple interactions. By treating the PAF-1/PAN nanocomposite at 300°C the formation of a ladder polymer was observed, thanks to the cyclization of PAN. This process enhanced the electronic properties and permitted the fabrication of a 3D network of two rigid and nonmeltable materials that were not expected to be blended effectively otherwise. The thermal treatment at 300°C of the PSS/PAN nanocomposite similarly led to the formation of a ladder polymer inside the channel of the mesoporous silica. By treating the PSS/PAN at 1000°C structural changes were observed both in the polymer and in the matrix: the first formed a graphitic structure while the second showed the cleavage of C-Si bonds and the formation of siliceous species. This material contained a carbonaceous structure and a silica nanophase that were not easily blended otherwise.

Discussion: The present results show that it is possible to obtain linear polymers *in situ* within a 3D polymer architecture. In conclusion, confined polymerization is an interesting and unusual methodology that leads to the fabrication of novel nanomaterials with extended interfaces.

MAGNETIC NANOPARTICLES: FROM NANOPOWDERS TO FINAL PRODUCTS

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Introduction: In the recent years, the development of magnetic ceramic materials with improved physical properties for several technological applications has been focused on materials with size at the border between the micro and the nanoscale. Among the others, magnetic nanoparticles have gained increasing interest due to the improvement in their synthesis, allowing extraordinary fine control on their structure and morphology and then on the magnetic properties. However, despite of the promising properties, the applicability of nanosized magnetic materials still presents a major drawback, a suitable methodology to easily obtain the target products with high density, simultaneously preserving the properties characteristic of the nanoscale.

Materials and methods: Spinel ferrite magnetic nanoparticles were synthesized by two different approaches: coprecipitation and thermal decomposition. Posteriorly, these powders were compacted and sintered under different conditions. The compaction process was carried out with an uniaxial hydraulic system with different mold shape and was monitored with a pressure controller. Finally, different sintering approaches were investigated, performing standard heating treatments at various target temperature and using high pressure-field assisted sintering (HP-FAST) processes. Sintered products were characterized by magnetic and electronic measurements, in order to explore their use as free rare earth permanent magnets (hard nano-materials) and low power loss transformers (soft nano-materials).

Results: High crystalline spinel ferrite nanoparticles with average size below 20 nm were successfully obtained by the two different synthetic strategies. Both for the soft and hard magnetic materials final ceramic products with high density and nanometric structure were obtained. Micrometer samples were also produced, in order to compare their properties with the nanostructured ones. The magnetic properties (saturation magnetization (M_s), coercive field (H_c), blocking temperature (T_b) and Curie temperature (T_c)) and electronic properties (AC initial permeability and AC power losses) of all the synthesized materials allowed to identify the strategy to obtain materials with the best performances for the desired applications.

Discussion: This work was focused on the synthesis of magnetic ceramic nanoparticles, with both soft and hard properties, and on the development of suitable compaction and sintering strategies in order to obtain high density macroscopic materials. The two different synthetic strategies we explored, proved to be effective in providing nanopowders with spherical shape, narrow particle size distribution and a high degree of crystallinity. However, the nanostructured composites never displayed satisfying properties for the considered applications. This behaviour can be ascribed to the low density of the final products.

CORROSION RESISTANCE PROPERTIES OF PEO COATED AZ91 ALLOY AFTER SEALING WITH LANTHANUM-CONTAINING SOLUTIONS

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Introduction: Plasma electrolytic oxidation (PEO) is a newly developed but very promising process that can enhance the corrosion and wear resistance by producing a relatively thick and hard oxide coating on magnesium alloys. In order to increase the corrosion resistance of the coated samples a sealing post-treatment is often necessary and the use of cerium salts-containing solutions during this type of treatment was already reported in literature. Other rare earth salts, such as for example lanthanum salts, are reported to be used in solutions employed to produce conversion coatings on magnesium alloys. In this work lanthanum salts were used to prepare solutions used for a post treatment of sealing in order to increase the corrosion resistance of PEO coated AZ91 alloy.

Materials and methods: PEO coatings were produced on samples of AZ91 magnesium alloy using a solution containing 40 g/l of NaOH, 50 g/l of Na₂SiO₃ and 50 g/l of Na₅P₃O₁₀ working at 0.5 A/cm² for 2 minutes. The temperature of the electrolyte was maintained at 25°C. The sealing treatment was performed in a solution containing 12 g/l of La(NO₃)₃ at pH 4 at different temperatures and for different treatment times. The corrosion resistance was evaluated with potentiodynamic polarization and EIS tests and the results were correlated with the microstructure and chemical analysis of the coatings evaluated with SEM observation and XRD analysis.

Results: Potentiodynamic polarization test an EIS test shows that the sealing treatment with solution containing lanthanum nitrate cause an increase in the corrosion resistance. In fact a remarkable decrease in the corrosion current density and an increase in the polarization resistance, if compared with the sample obtained after the PEO treatment without sealing, could be recorded. From SEM observation the pores that characterize the surface appear to be mostly sealed after the treatment in the lanthanum containing solution. From the analysis of the cross section of the coating the presence of an external part of the coating, rich in lanthanum can be revealed. Considering the different treatment times 30 minutes of sealing treatment provide better results if compared with 10 minutes of treatment. An increase in the lanthanum content in the solution do not produce significant effect instead an increase in the temperature until 50°C seem to increase the formation of a uniform lanthanum-containing film.

Discussion: The improved corrosion properties of the samples after the sealing treatment can be explained in two different ways: on one hand the formation of the external layer rich in lanthanum produce an increase in the barrier effect of the coating increasing the corrosion resistance; on the other the presence of lanthanum compounds on the surface produce an increase in the corrosion properties due to the corrosion inhibition effect of the lanthanum ions. Treatment of ten minutes do not produce a complete sealing of the pores of the whole surface instead 30 minutes appear to be enough to obtain an uniform and sealed surface. Temperatures between 40°C and 50°C increase the rate of formation of the film permitting to obtain coatings with improved corrosion resistance.

GENERALISED FRACTAL MODEL FOR PREDICTING ABSORPTION PROPERTIES OF POROUS MATERIALS

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Introduction: Water capillary absorption is an important property, which influences the durability of building materials. Indeed, water movement into the microstructure is responsible for diverse decay phenomena as salt-crystallisation cycles, freeze-thaw cycles, dissolution, biological proliferation and reduction of mechanical properties. Owing to these reasons, determination of Sorptivity coefficient is a parameter, which provides useful information regarding service life of porous materials, especially installed on historical buildings. However, in Cultural Heritage, it is not possible to have the possibility to withdraw large quantity of materials to perform the laboratory tests. For this reason, the formalisation of indirect method capable of describing the kinetics of these phenomena is important. In this work, a fractal model has been proposed to predict Sorptivity coefficient. This approach is capable of reproducing porous microstructure experimentally acquired by MIP test, which needs small size samples (~1 cm³). Experimental data and fractal modelling calculations are in agreement better than predictions by other models from literature.

Materials and methods: The limestone analysed are from a quarry in Oristano area, which is widely used in the historical building, while the ceramic tiles are fabricated by Cotto-Possagno-SpA. The ceramic series consist of some clays, sand, carbonates and feldspars in different quantity. For this material, XRD tests and MIP analysis were carried out to define mineral composition and porous microstructure respectively. The capillary absorption tests were performed in accordance with the rules of the UNIEN15801:2010. In order to reproduce the porous microstructure similar to experimental ones, an IFU model is applied using different fractal base units intermingled together. Then, it is applied a fractal analytical procedure to calculate sorptivity coefficient. Solving IFU will be possible to obtain sorptivity and to compare it with the experimental data.

Results: The IFU analytical procedure aimed at predicting sorptivity coefficient has been applied and modelling calculations are compared with experimental data (IFU vs. exp): limestone A 22.43 vs. 24.49, B 24.25 vs. 26.52 and C 24.71 vs. 28.04 mg/(cm²s^{1/2}). Ceramics D 1.40 vs. 1.36, E 6.01 vs. 6.55, F 8.48 vs. 8.49 and G 10.40 vs. 10.13 mg/(cm²s^{1/2}).

Discussion: The IFU calculations are in agreement with experimental values, better than the results obtained by others models from literature. This provides the possibility to validate the proposed procedure as a generalised approach for porous building materials.

NOVEL REUSABLE CARBON-BASED SILICONE FOAMS FOR OIL RECOVERY

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Introduction: The sudden increase of exploitation, transport and use of oil have led to an increase of spills risk in the sea. The consequences are enormous contamination and sea pollution and a serious loss of energy resource. The common treatments of spilt oil include usages of oil dispersant, oil gelling agent, and oil sorbent. The use of sorbents is considered the most ideal solution because it can remove oil from the sea. Synthetic organic sorbents such as polymeric foams are the most commonly used commercial sorbents in oil spill cleanup. But they absorb not only oil but also water, decreasing the absorption efficiency. In this work a silicone foam comprising carbon nanotubes (CNTs) is synthesized. The foam is characterized by high absorption capacity, high selectivity, being oleophilic and hydrophobic, and excellent recyclability and reusability.

Materials and methods: CNTs were synthesized by chemical vapor deposition (CVD) of isobutane (C₄H₁₀) at 700°C on 17 wt.% Fe/Al₂O₃ catalyst. After reaction Al₂O₃ support and residual iron particles are removed by 1 M solutions of NaOH and HCl, respectively. Commercially silicon foam reactants (silane hydride, silanol and Sn catalyst) were supplied by Gelest. Carbon-based silicone foams synthesis process is described in the Italian patent pending n° 102015000088777. Absorption experiments were performed at room temperature by putting the sponge in contact with different oils (virgin nafta, kerosene, pump oil and crude oil) under stirring. The oil absorption capacity was evaluated as the percentage ratio between the final and the initial weight after full absorption. Absorption test in water was also performed to investigate hydrophobicity.

Results: The synthesized foam appears as a macroporous material with partially open cells. The macro-porosity is the cause of its light weight but anyway the foam is able to sustain high cyclic compression loads. Owing to its weight and hydrophobicity, the sponge easily floats on water surface identifying an effective application in oil recovery applications. In crude oil the absorption capacity reaches 213 wt.%, comparable with the one obtained in pump oil. While the optimal behavior is observed in kerosene and virgin nafta oils, where the absorption gets 900 wt.%. Once the sponge becomes saturated, the absorbed oil can easily be removed by squeezing mechanically. It is noteworthy to say that the same foam can be used for multiple cycles "adsorption-squeeze", without undergoing mechanical degradations and loss of absorption capacity.

Discussion: It is demonstrated that it is possible to obtain a CNTs-based silicone foam by using a simple synthesis process. Thanks to its oleophilic properties, CNTs-based foams can be an ideal candidate for use as an absorbent in oil recovery applications, furthermore, owing to the cheapness of the used materials, an easily scalability of the reported process is possible.

MICROSTRUCTURED POLYMERIC/SUGAR SYSTEMS FOR TOBRAMYCIN ADMINISTRATION IN CYSTIC FIBROSIS

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Introduction: The airways of cystic fibrosis (CF) patients are plugged with mucopurulent secretions containing abundant bacteria, like *P. aeruginosa*.

The efficacy of antibiotics, such as tobramycin, is limited by the ability to achieve sufficient levels of drugs at the site of infection, attributable to the poor mucus penetration and to the inactivation of the drug through binding interactions in this environment. In this field, aim of this work has been the development of microstructured polymeric/sugar systems for tobramycin administration able to give, thanks to their specific composition, a proper release of tobramycin into the whole thickness of CF mucus and to improve drug efficacy.

Materials and methods: The α,β -poly(N-2-hydroxyethyl)-D,L-aspartamide (PHEA) was covalently derivatized with ethylenediamine (EDA) and glucuronic acid (GlucA). Once prepared and characterized, the resultant PHEA-EDA-GlucA copolymer was used to prepare a ion pair complex with tobramycin by incubation of copolymer and drug solutions. Microparticles (MPs) were then obtained by spray drying a mannitol solution containing the ion pair complex, and then characterized in terms of morphology, size and drug content. Tobramycin release profile from MPs and their diffusion in mucus was tested by using a CF artificial mucus (CF-AM) model.

In vitro cytocompatibility of the copolymer, ion pair complex and MPs was tested towards human bronchial epithelial cells. Finally, the antipseudomonal activity of MPs was compared with free tobramycin determining minimum inhibitory concentration (MIC), minimum bactericidal concentration (MBC) values and the efficacy in inhibiting *P.aeruginosa* growth in CF-AM.

Results and discussion: In this work, a novel anionic derivative of PHEA, PHEA-EDA-GlucA, was synthesized, properly characterized and used to prepare a ion pair complex with tobramycin, that is able to slow the release of tobramycin, offering a sustained delivery. Mannitol MPs, loaded with the ion pair complex, were then prepared by spray-drying and showed suitable morphology and dimensions for a proper administration to the lungs and an optimal tobramycin entrapment efficacy. Further, obtained MPs are able to modify the rheological properties of CF-AM, facilitating the transport of the antibiotic through CF-AM, but at the same time, thanks to the participation of tobramycin in the ion pair complex with PHEA-EDA-GlucA, MPs are able to achieve a sustained tobramycin delivery. Finally, MPs showed better in vitro antipseudomonal activity compared with free tobramycin, in terms of MIC, MBC and efficacy in inhibiting *P.aeruginosa* growth in CF-AM, supporting the hypothesis that MPs could improve drug efficacy, because they give a decrease of MIC and MBC value. The unique performance of MPs in CF-AM is also attributable to mannitol ability to increase local water content and enhance drug penetration into it. Smart controlled delivery strategies could be a shorter-term approach to face the challenge of antibiotic-resistance and the lack of new antipseudomonal agents, being MPs potentially able to achieve a sustained tobramycin delivery at the site of disease, resulting in superior efficacy, lower required dose and side effects.

FUNCTIONALIZED GOLD NANOPARTICLES FOR QUALITY ASSESSMENT OF EXTRAVIRGIN OLIVE OIL

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Introduction: Phenolic compounds are presents in low concentration in extravirgin olive oil (EVOO), usually extracted with a methanolic solution. The purpose of this work is to develop a new extraction method using functionalized hydrophilic gold nanoparticles (AuNPs) in alternative to the traditional one.

Materials and methods: Chemicals involved were: deionized water by Milli-Q device, methanol and n-hexane by Sigma, hydrogen tetrachloroaurate (III) trihydrate, sodium borohydride and by Aldrich. Functionalized gold nanoparticles were prepared with a single phase Shiffin and Brust's reaction and characterized with FTIR, UV-Vis spectrometry and dynamic light scattering (DLS) to evaluate size and size distribution. The extraction of phenolic compounds was carried out using EVOO in the presence of AuNPs. After separation an extraction was executed on EVOO with methanol/water mixture. The quantification of phenolic compounds was carried out through Folin-Ciocalteu reagent, using a UV-Vis spectrophotometer.

Results: The hydrophilic AuNPs have been obtained with mean size 10-20 nm. The small dimensions of AuNPs, guaranteed an extended interaction area with phenolic compounds contained in EVOO and permitted the extraction of polar fraction. In order to optimize the extraction process, the combination of different experimental parameters on the extraction of phenolic compounds was

tested, such as quantity of AuNPs and contact time between AuNPs and EVOO. It was observed that optimal concentrations of polyphenols were extracted using the highest quantity of NPs tested, with longer time of contact. This method was validated in terms of precision and accuracy. Preliminary tests also showed promising results concerning the possible recovery of AuNPs: in fact the treatment with a basic solution allowed the release of phenolic compounds from AuNPs to the aqueous solution; this allow the re-use of the same AuNPs for others extractions.

Discussion: The extraction with AuNPs resulted comparable in terms of recovery with the traditional extraction (using methanol/water mixture). Synthesis of gold nanoparticles is quite expensive in terms of costs of reagents, time of reaction and purification. But the possibility of re-use for several consecutive extraction allows to save costs of production, volume of solvents used and chemical wastes.

PREPARATION AND CHARACTERIZATION OF NEW FLY ASH GEOPOLYMER-EPOXY COMPOSITES

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Introduction: Geopolymers are a family of inorganic materials obtained by reaction between an aqueous alkaline silicate solution and an aluminosilicate source. They are characterized by interesting mechanical properties, low shrinkage, thermal stability, freeze-thaw, chemical and fire resistance, long-term durability and recyclability. For these reasons they have the potential for utilisation as Ordinary Portland Cement (OPC) replacement in a wide range of applications, such as fireproof barriers, materials for high temperatures, matrices for hazardous waste stabilization, toolings and moldings. Very recently, we have developed an innovative, easy and cost-effective synthetic strategy to realize hybrid composite materials by using metakaolin-based geopolymers as inorganic component and different organic resins up to 25% in weight. These materials show significantly improved physical and mechanical properties and remarkably reduced brittleness with respect to the neat geopolymer, still preserving good thermal and fire resistance. This approach consists in the concurrent co-reticulation of both phases, that are mixed together when each polymerization reaction is already started but far to be completed, thus allowing to realize a chemical interaction between the organic component and the geopolymeric mixture based on the formation of a wide network of hydrogen bonding.

Materials and methods: Epoxy-geopolymer composites have been prepared starting from fly ash and metakaolin as raw materials and characterized regarding their chemical-physical and mechanical properties. After, these data have been compared to those ones of the neat geopolymers.

Results: The preparation and characterization of composite materials based on geopolymers obtained from fly ash and epoxy resins is reported for the first time, by using the synthetic method earlier described. In this way, innovative materials have been prepared, where it has been ensured high compatibility between the phases and a very good dispersion up to nanometric level of the organic phase into the inorganic one, without addition of external additives or compatibilizers.

It is worth pointing out that, despite the high concentration of organic resin (up to 20% by wt.), preliminary data show that these new materials are not flammable and do not produce smoke in significant amounts.

Discussion: This paper try to add new results in the field of sustainable building materials with reduced environmental footprint. In fact the following conclusions can be drawn:

- the mechanical properties of the composite materials are significantly better than that of the neat geopolymer, this means that it is possible to use smaller section for the same load condition, to reduce the number of cracks obtaining more durability and, thus, a longer service life;
- fly ash-based composite materials represent a valid alternative in place of more expensive raw materials, such as metakaolin, in particular for those applications for which it is important to save materials and limit the costs;
- the procedure is inexpensive and use easily available reagents.

Finally, having successfully replaced the metakaolin with fly ash, we can suggest that the novel composites may have all the conditions to be an Environmental Friendly Material. In order to confirm this hypothesis, a complete LCA study is in progress.

MODELING STRUCTURAL RECOVERY OF HIGH MOLECULAR WEIGHT POLYSTYRENE WITH FAST CALORIMETRY

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Introduction: When a glass is cooled from the melt state at a temperature below the T_g , its structure-sensitive properties, such as volume and enthalpy, deviate from the equilibrium and reach a non-stable thermodynamic state. Under isothermal condition, it's possible to observe a spontaneous and time dependent evolution of each property toward a stable thermodynamic state. This phenomenology is usually referred to as structural recovery or physical aging. In the present work, a modified version of the Tool-Narayanaswamy-Moynihan (TNM) model is used to describe the structural recovery of high molecular weight polystyrene. The material response was monitored using rapid scanning calorimetry, that allowed us to reach cooling rate up to 1000°C/s and aging times from 0.01s. Conventional differential scanning calorimetry (DSC) is unable to determine accurately enthalpy changes for aging times less than 1min, moreover, the maximum cooling rates are much slower. Our approach enables to overcome these limitations.

Materials and methods: The polystyrene sample under study have a molecular weight (M_w) of 200,000,000 g/mol. Experimental was performed with a commercial rapid-scanning calorimetry, the Mettler Toledo Flash DSC, purged with nitrogen. The temperature cycles used for aging experiments begin with a heating to 190°C for 6s to erase previous thermal history. The sample was then cooled at 1000°C/s to different aging temperatures T_a and aged for times ranging from 0.012s to 18000s. In addition to this, the effect of cooling rate on glass transition was investigated: after erasing thermal history, the sample was cooled to ambient temperature at different rates ($q = 0.1, 1, 10, 100, 1000^\circ\text{C}/\text{s}$). The evolution of structural changes was described with the fictive temperature T_f (Narayanaswamy, J.Am.Ceram.Soc.(1971)) in the environment of the TNM model.

The structural relaxation time of the original TNM model is known to be insufficient, here we used that proposed by Young et al. (2012). The model requires 5 parameters to be defined: C_1 , C_2 and T_R are the Williams-Landel-Ferry (WLF) equation parameters (Williams et al., J.Am.Chem.Soc.(1955)) that describe the dependence of temperature on the equilibrium relaxation time above T_g , b is a shape parameter and T_R is the relaxation time at reference temperature T_R .

Results: Quenching experiments showed that the T_g at $q = 1000^\circ\text{C}/\text{s}$ was more than 15°C greater than at $q = 0.1^\circ\text{C}/\text{s}$. Experimental data was used to fit the model and obtain the required parameters. In this work the T_R was set to the nominal T_R at $q = 10^\circ\text{C}/\text{s}$. The parameters to find reduced to just 4.

Discussion: Experimental data is coherent with that observed in conventional calorimetry. T_f evolve from the initial value (T_f equals T_g at zero aging) to a limiting value that coincide with the aging temperature. The modified TNM model seems to fit very well both kind of the performed experiments, but its accuracy need to be tested on more complicated thermal histories.

PROPERTIES OF 3rd GENERATION HVAF (High Velocity Air Fuel) SPRAYED Fe-BASED ALLOY, WC- AND Cr₃C₂-BASED HARDMETAL COATINGS

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Introduction: HVAF (High Velocity Air-Fuel) is a thermal spray technique for the deposition of thick coatings (100-800 µm) of metal alloys and hardmetals, used for protection against wear and corrosion of mechanical components. The first prototype was patented in the 80's, but HVAF started becoming widespread only recently thanks to a very recent breakthrough (2011 patent by Baranovsky). The peculiarity of this process, compared to the more widely known HVOF (High Velocity Oxygen-Fuel) is the use of air instead of oxygen as comburent for the flame combustion. This difference can lead to cost reductions, due to the replacement of pure oxygen with air and a signifi-

cant time reduction to coat large surfaces, as well as some interesting technical enhancements. The use of air, in fact, lowers the flame temperatures and is combined with an innovative torch design, which increases the particle speed up to 1000m/s during deposition, allowing the achievement of dense coatings with a lower chemical modification of the feedstock materials compared to HVOF. This work provides a general review of the most important feature of HVAF, through the study of the microstructure, the micromechanical properties the wear and the corrosion behavior of HVAF deposited metallic alloys and hardmetal coatings. The aim of this broad material selection is to assess the possible strengths and weaknesses of 3rd generation HVAF torches after controversial performances of the past generation equipment.

Materials and methods: Two iron-based gas atomized powders, two agglomerated and sintered WC-based and one Cr₃C₂-based powders were sprayed using an HVAF M3 Gun (Uniquecoat Technologies) onto steel substrates. The WC-based powders were also studied according to the increasing carbide grain size (CGS) (0.2-4.0 µm) and binder grain size (0.5-2.0 µm). All the coating materials were also HVOF sprayed as benchmarks for the coating properties. The microstructure and the micromechanical properties of the coatings were studied using electron microscopy and depth sensing indentation techniques. The wear resistances of the coatings were tested using dry sliding ball-on-disc test, dry sand rubber wheel test and block-on-ring test. The corrosion resistance was evaluated using accelerated tests and electrochemical polarization test.

Results and Discussion: The study of the microstructure and the micromechanical properties of the HVAF coatings allowed the understanding of the main features of the deposition technique. The assessment of wear and corrosion mechanisms of the coatings in the different test conditions, enabled to establish the correlation between feedstock powders features and coating properties. Moreover, the comparison of these results with the properties of the HVOF coatings, had helped to point out the advantages and drawbacks of this innovative deposition technique. A main conclusion of the various experiments is that HVAF coatings can achieve overall properties, which can be superior to standard HVOF protective layers, but the final performances, in particular as far as corrosion protection is concerned, are strongly dependent of the particle size distribution. While finer carbide powders are already available, fine metallic feedstock will be more challenging to produce at a reasonable cost.

MULTI SENSITIVE INULIN GRAFT COPOLYMER COATED SPIONS FOR SELECTIVE TARGETING TO TUMOR CELLS

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Introduction: Superparamagnetic iron oxide nanoparticles (SPION) have been recently used for numerous in vivo applications such as drug delivery, hyperthermia and contrast enhancement for magnetic resonance imaging (MRI). Conjugating a tumor targeting ligand to the polymer coating SPIONs could be a promising strategy for enhancing the efficacy of drug delivery and cancer specificity. Among these ligands, folic acid (FA) represents a good targeting agent because folate receptors (FR) are selectively overexpressed on many human cancer cells. Therefore, the combination of the active targeting of the polymeric shell and the magnetic targeting induced by an external magnetic field could be an innovative approach to realize multi responsive drug delivery systems.

Materials and methods: Inulin (INU) was derivatized with lipoic acid (LA) and with PEG-FA to obtain an amphiphilic graft copolymer INU-LA-PEG-FA. This latter was used as biocompatible coating for SPIONs (IC-SPIONs) by mixing aqueous polymer dispersion with SPIONs (10 nm) and the anticancer Doxorubicin (DOXO). DOXO release profile was evaluated in different media simulating physiological environment. Moreover, the capability of IC-SPIONs to release payload with the trigger of redox potential was evaluated. Finally, in vitro cytotoxicity on three different cell lines was evaluated.

Results and discussion: Here, a stimuli sensitive graft copolymer INU-LA-PEG-FA was synthesized and properly characterized. LA was grafted to INU backbone to design reduction sensitive cross-linked nanoparticles, while

PEG-FA was introduced to induce active targeting to tumor. IC-SPIONs loaded with DOXO were prepared and showed spherical morphology and nanometric size. Magnetization vs magnetic field measurements confirmed the both nude SPIONs and IC-SPIONs are superparamagnetic at 300K. In addition, field dependence of residual magnetization (i.e. Henkel plot) was investigated at 5K, showing a clear improvement of magnetic properties after coating. Moreover, the magnetization study confirmed the presence of a homogeneous coating on the SPIONs. Release study showed as the amount of DOXO released increases when the system was incubated with the medium simulating intratumoral microenvironment, in which glutathione reductase was introduced to redox cleave the pendant disulfide linkages in the copolymer coated SPIONs. Finally, the selectivity of IC-SPIONs towards FRs-positive cancer cells was proved by the cytotoxicity assay using human breast and colon cancer cells and human fibroblast as non-cancer cell line. Data showed that tumor cells are more sensitive to DOXO loaded in IC-SPIONs if compared to normal cells. This can be explained with the ability of the folate-targeted system to be principally internalized by tumor cells, suggesting a folate mediated endocytosis mechanism. Our findings support the selectivity of IC-SPIONs towards cancer cells and suggest the possible selection of IC-SPIONs as a promising candidate for in vivo applications in treatment of tumors.

STRESS INDUCED CRYSTALLIZATION IN ETHYLENE-PROPYLENE-DIENE TERPOLYMERS

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Introduction: Many commercial rubbers are based on random terpolymers of ethylene, propene and a non conjugated diene (EPD), which introduces double bond in the lateral group to allow vulcanization of the rubber. EPD terpolymers with ethylene contents in the range 60-70 wt% appear amorphous in the undeformed state. However, crystallization of ethylene sequences may occur during deformation, resulting in increase of tensile strength of the rubber. In this communication we report a study of the stress-induced crystallization (SIC) in EPD terpolymers of different ethylene concentrations. The influence of ethylene content on the SIC and on the possible presence of crystallinity in the undeformed state is analyzed.

Materials and methods: EPD terpolymers with ethylene concentration in the range 44-78 wt% have been analyzed. The structural organization of bulk samples in the undeformed state has been studied by Wide (WAXS) and Small Angle (SAXS) X-ray Scattering and Differential Scanning Calorimetry (DSC). Occurrence of SIC has been analyzed by recording WAXS patterns during stretching and after relaxation of the specimens to verify whether crystals formed at high deformations melt during elastic recovery (reversible SIC).

Results: WAXS analysis has shown that EPD samples with high ethylene content of 78 wt% are crystalline in the undeformed state and crystallize from the melt in the pseudohexagonal form of PE. Samples with ethylene contents in the range 71-64 wt% show broad WAXS profiles typical of amorphous EP copolymers. However, the presence of endothermic peaks in the DSC heating curves reveals that a certain amount of crystals that are not visible by WAXS, is present in these samples. This result has been confirmed by SAXS patterns of these samples that have shown a well-defined correlation peak, typical of lamellar stacking, which disappear at 90°C. For samples with ethylene content lower than 64 wt%, WAXS profiles still show a broad halo. However, no correlation peaks are observed in the SAXS patterns and no endotherm peaks are present in DSC curves, indicating that these samples are really amorphous. WAXS patterns recorded during stretching reveal that further crystallization occurs during deformation of the samples even in the case of the apparently amorphous samples with ethylene content in the range 71-64 wt%. Crystals of pseudohexagonal form of PE develop upon stretching and the crystallinity increases up to ≈48% at high deformations with respect to the undeformed samples. The release of the tension produces loose of crystal orientation and partial melting of the PE crystals formed during deformation.

Discussion: In EPD terpolymers, even when the concentrations of propene units is high in the range 30-40 wt%, ethylene sequences are long enough to crystallize, due to partial inclusion of propene units in the crystals. The structural organization is surprisingly better demonstrated by SAXS than by WAXS data. Further crystallization occurs upon stretching. The crystallinity present in the undeformed state and its improvement during deformation are keys for understanding the remarkable mechanical performances of these rubbers.

MECHANICAL OPTIMIZATION OF HYBRID MATRICES IN FRP/FRCM COMPOSITE MATERIALS FOR APPLICATION IN STRUCTURAL RESTORATION OF HISTORICAL BUILDINGS

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Introduction: Since the early 90's, fiber-reinforced plastics (FRP) composites have been widely applied in the construction sector, particularly for restoration of buildings. These materials are composed of continuous fibers immersed into polymeric resins. In this study, polymeric resins were transformed into hybrid matrices by the addition of an inorganic component. This modification allowed the improvement of the ductility and the interfacial behavior between fibers and resin. The properties of these hybrid matrices made possible their use in the field of architectonic heritage restoration.

Materials and methods: The hybrid matrices investigated here were composed of polymeric resins (PA0, PD1, PR1 and PR2) and modified gypsums (S0, S1A and S1B). The single components were characterized in detail through various techniques. The efficiency of these materials was investigated in terms of mechanical, physical and thermodynamic properties using tensile tests of FRP specimens and mechanical tests of the matrices. SEM analyses were conducted to determine the quality of the impregnation of the fibers and the hybrid matrices.

Results: It was found that the most ductile matrices were those with modified acrylic (PR1) and styrene-acrylic (PR2) copolymers resins. These matrices presented the highest ultimate strain, while the PA0- and in particular the PD1-based matrices presented a higher ultimate strength but a pronounced brittle fracture. The mechanical tests and the SEM analysis revealed that the hybrid matrices containing the S1A and S1B gypsums present a higher ultimate strength and the best impregnation of the fibers. Nevertheless, the former characteristic leads to an intrinsic brittle nature of these matrices.

Discussion: The mechanical test revealed that the hybrid matrices investigated in this work have a practical desirable ductile nature and an acceptable capability in terms of strength. In particular, the matrices based in PR1 and PR2 resins offer a better elongation at collapse, while those based in PD1 resin present a very high ultimate strength, even if its brittle behavior is not suitable for matrices in structural composites; this behavior was correlated with its high glass transition temperature. Furthermore, the styrene-acrylic intrinsic hydrophobic nature of the resin PR2 suggests a possible application of these hybrid matrices in hydraulic infrastructures. It was found that the different analyzed gypsums have a great influence in the impregnation of the carbon and glass fiber yarns. This phenomenon was correlated with the fine granulometry of the gypsums. The FRP and FRCM technologies with some of the studied hybrid matrices has been successfully applied in the restoration of some historical building in the Emilia earthquake area.

EFFECTS OF FLASH-SINTERING ON GADOLINIUM DOPED-CERIA

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Introduction: Gadolinium-doped ceria (GDC) is an attractive electrolyte material for IT-SOFC applications, due to its relatively high abundance and its high ionic conductivity in the intermediate temperature range (600-900°C). One of the main drawbacks of ceria-based materials is the high sintering temperature required to obtain full densification. The present work was carried out with the aim to apply the innovative Flash Sintering technique for the densification of some GDC ceramics.

Materials and methods: Gadolinium-doped ceria powders with variable dopant concentration (ranging from 5 to 20%) and with different sintering aids (Li and Co) for a fixed dopant concentration (10%) were synthesized by co-precipitation with ammonia solution of Ce and Gd nitrates. The pro-

duced nano-powders were calcined at 600°C for 1 h. All samples crystallized in fluorite habit and no phase evolution occurred by thermal heating (up to 1300°C). Powders were then shaped into pellets by uniaxial pressing and sintered under the application of an electrical field (50 V/cm and 100 V/cm). The microstructure of the flash-sintered bodies was characterized by Scanning Electron Microscopy (SEM) while the electrical behavior was analyzed by EIS spectroscopy.

Results: The application of an external electric field upon heating allows to reduce significantly the sintering temperature of all considered materials. Sintering temperature is shown to decrease for more intense electrical field, even down to 400°C. The conduction behavior before upon Flash Sintering strongly depends on dopants amount. In particular, conductivity is enhanced by increasing Gd concentration or by adding lithium as sintering aid. Much lower effects on conductivity are observed by adding cobalt. In a similar way, the onset temperature for FS decreases with the powders conductivity. SEM analysis point out a nano-grained microstructure, although not all the obtained samples are fully densified. Impedance spectroscopy measurements show that the electrical properties of flash sintered bodies are perfectly comparable with values recorded on conventionally sintered GDC materials.

Conclusions: Flash sintering can be successfully applied to variously doped ceria based materials. The presence of different dopants with variable concentration influences both conductivity and the onset temperature for FS. This behavior is coherent with the model of thermal runaway for flash sintering. In spite of the very low sintering temperature (always below ca. 700°C), microstructural and impedance analysis results point out that the sintered bodies are suitable for possible application as solid electrolyte for IT-SOFC.

ANTIBACTERIAL FUNCTIONALIZATION OF PVC BY CHITOSAN ADDITION FOR AGRICULTURAL APPLICATION

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Introduction: During the last 5 years, there was an increasing interest in developing bio-based active materials, which are characterized by antimicrobial and antifungal activities, in order to reduce the environmental problems (underground water, lake eutrophication, public health issues) concerning the use of chemical pesticides. In fact, the ecological problems related to the excessive use of synthetic antibacterial materials have led to the search of alternative materials, such as biomaterials, which are both biodegradables and non-toxic. Natural polymer such as chitosan offers real potential for applications in the agricultural industry due to its particular physic-chemical properties, short time biodegradability, biocompatibility with human tissues, antimicrobial and antifungal activities, and non-toxicity. Among, the different possibilities, chitosan exhibits high antimicrobial activity against pathogenic and spoilage micro-organisms, including fungi, and both Gram-positive and Gram-negative bacteria. The present work highlights the potential of chitosan as ingredient for active bio-based polymeric materials with antimicrobial activity for agricultural application, by the formulation and mechanical/chemical testing of 0-40% chitosan-PVC composites.

Materials and methods: Composites of PVC and chitosan (0-40 wt%) were prepared to assess the effects of chitosan content on the mechanical, chemical, thermal, and morphological properties of the composites. The PVC pellets and chitosan powders were premixed and then were compression-molded at 150°C for 20 min in small hourglass specimens.

Results: The obtained blends have a reasonable extent of compatibility between their components up to the maximum chitosan addition (40 wt%). Fourier transform infrared spectra did not show any evidence of covalent bonding, but chitosan at the interface with PVC has reasonably formed dipole-dipole interaction between C-N bonds of chitosan and C-Cl bonds of PVC. The thermal analysis and the tensile tests showed that chitosan addition increases the thermal stability and significantly increased the flexural modulus and rigidity of pristine PVC. Instead, the elongation at break decreases as the chitosan is increased but it is acceptable up to 30 wt% of chitosan addition. SEM images of fracture surfaces showed good dispersion of chitosan domains indicating a strong interaction and good miscibility between chitosan and PVC. All the obtained blends present an interesting antibacterial activity.

Discussion: The composites studied in this work are promising candidates for a wide range of agricultural applications. In particular, an optimized formulation would allow reducing the environmental impact due to the use of synthetic polymers and the antibacterial properties should allow decreasing the use of pesticides. Future studies should focus on the technological application of the studied blends and on effect of the environmental conditions on the antimicrobial activity of chitosan compounds.

COMPATIBILIZATION OF TiO_2 NANOPARTICLES INTO ORGANIC MATERIALS THROUGH GRAFTING FROM AND GRAFTING TO SURFACE MODIFICATION

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Introduction: Surface ligand engineering is an effective tool used to enhance polymer nanocomposites materials performance because it plays on one of the most tricky issue related to this kind of materials: the incompatibility of the organic/inorganic phase. The introduction of a thin polymeric layer enables a good dispersion of the inorganic nanoparticles (NPs) in solvents and matrixes in which bare particles aggregate and precipitate. The surface modification is needed in order to tune the nanofiller morphology or introduce additional functionalities to the NPs giving new properties for a wide number of applications. In our contribution we explored the grafting of a wide range of polymers with different molecular weight onto rutile and anatase TiO_2 particles.

Materials and methods: The particles are synthesized with solvothermal, hydrothermal and colloidal methods, with or without capping agent. The polymers are synthesized with RAFT (Reversible Addition-Fragmentation chain Transfer) synthesis with two RAFT agents (chain transfer agent CTA). The NPs are characterized through scanning probe techniques, electron microscopy and spectroscopy and diffraction techniques. The polymers are investigated with Nuclear Magnetic Resonance NMR and vibrational spectroscopy. Thermogravimetric analysis (TGA), Elemental analysis and Small-Angle X-ray Scattering (SAXS) are used to quantify the amount of polymer grafted on the NPs. The behaviour of the nanocomposite material is analyzed with Dynamic Light Scattering (DLS).

Results: In this contribution two different RAFT agent ended with a carboxylic acid and a phosphoric acid group are used as initiators attached on the NPs surface and as grafting agent of macroCTA. Polymers of different chain length and type (poly(styrene) PS, poly(isoprene) PI, poly(acrylonitrile) PAN and poly(styrene)-block-poly(acrylonitrile) PS-b-AN) are grown or grafted on spherical anatase particles and rod-like rutile particles. In order to verify the real compatibility of the final materials with organic phases nanocomposite dispersions, in a wide range of polar and non-polar solvents, is studied with DLS.

Discussion: Is reported that in order to have a good covering of the NPs and enhance the compatibility of the nanocomposite material, high graft densities and long polymer chains are needed. We showed a connection between the graft density and the molecular weight of the polymers on the NPs surface with the grafting from approach, moreover we demonstrate how the polymer's mobility and the different end groups affect the grafting polymer conformation on the NPs surface. While is shown how the steric hindrance of the growing polymer limits the living polymerization in the grafting from approach.

NOBLE METAL NANOPARTICLES CAPPED BY CHARGED THIOL: ELECTRICAL CHARACTERIZATION OF THE INTERFACE IN WATER SOLUTIONS

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Introduction: In recent years many efforts are dedicated to investigate noble metal nanoparticles, due to their huge field of application, from catalysis to optoelectronics to sensors and biomedicine.

Materials and methods: Solvents: EtOH, CHCl_3 , and HCl are reagent grade (Aldrich). 2-diethylaminoethanethiol hydrochloride ($\text{HSCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2\text{HCl}$,

DEA) and sodium 3-mercaptopropanesulfonate ($\text{HS}(\text{CH}_2)_3\text{SO}_3\text{Na}$, 3MPS), tetrachloroauric(III) acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate (AgNO_3) and sodium borohydride (NaBH_4) have been used as received (Aldrich reagent grade). Synthesis of AuDEA and AgDEA nanoparticles: the synthetic procedure was in analogy with literature report, by using an M/ NaBH_4 molar ratio = 1/10 and M/S = 1/4 molar ratios. As example: 200 mg (5·10⁻⁴ mol) of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 20 ml of deionized water has been mixed with a solution of DEA in 20 ml of deionized water under vigorous stirring (320 mg). After stirring a solution of NaBH_4 in deionized water has been added and the reaction mixture has been allowed to react for 3 h. Yield: 75% Au-DEA and 35% AgDEA. Instruments: FTIR spectra have been recorded using a Bruker Verte $\times 70$ spectrophotometer. UV-vis spectra were run in H_2O solution by using quartz cells with a Varian Cary 100Scan UV-vis spectrophotometer. Size distribution of AuNPs in H_2O solution have been investigated by means of Dynamic Light Scattering (DLS) technique by using a Malvern Zetasizer instrument (Brookhaven, NY). FE-SEM images have been acquired with the Auriga Zeiss instrument on metallized film drop casted on a metallic sample holder.

Results: In this work, functional AuDEA and AgDEA nanoparticles were studied by means of dynamic light scattering (DLS) technique, and by ζ -potential measurements, allowing to describe the dielectric behavior for these charged colloidal particles in water solution: AuDEA nanoparticles show $\langle 2R_H \rangle$ below 13 ± 2 nm and ζ -potential below +33, and AgDEA nanoparticles show $\langle 2R_H \rangle$ below 5 ± 2 and ζ -potential below +30 mV.

Discussion: Noble metal nanoparticles show $\langle 2R_H \rangle$ below 13 ± 2 nm for AuDEA and 5 ± 2 nm for AgDEA, stable in water solution and suitable both for biological applications, where dimensions are required <100 nm. Moreover, studies were carried out in water at different pH (from 2 to 10) and temperature (25°C and 37°C) in order to verify the colloidal behaviour of nanomaterials: the environmental acid prevents aggregations phenomena while the temperature has a weak effect on $\langle 2R_H \rangle$.

USE OF INDUSTRIAL WASTE PAPER AS FILLER IN WOOD PLASTIC COMPOSITES (WPCS)

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Introduction: In recent years, paper consumption has increased, and, as a consequence, the problems related to its disposal grew. Only 50% of paper is used in recycling process, while the remaining is sent to incinerators or to waste dump. Despite recycling process provides economic advantages (as lowering raw materials' costs, storage costs and consumption of trees), it also produces relevant disadvantages; these are the possibility of reusing paper for a maximum of 5-6 times, the use of chlorinated compounds to bleach paper and the impossibility for inked or additivated paper to be subjected to recycling. The proposal is to use any type of cellulosic waste as a dispersed phase in existing Wood Plastic Composite. Potential application of these composites could be in nautical sector and green buildings.

Materials and methods: Eralene MP90, commercial name of high-density polyethylene from ENI (Versalis), has been chosen as matrix. A micronizing process that operates by friction, impact and turbulence allowed to obtain cellulosic recycled fibres with diameters of 15-20 micron and lengths of 200-250 micron. Wood flour of hardwood beech, which was provided by La.So.Le/Est/Srl-Italy, have diameters ranging between 500 and 250 μm . A new mixing process was used, turbomixing (3000 round/minute) since the introduction fillers in melted polymer resulted difficult. This process allowed to introduce higher fillers percentages and obtain their better dispersion. The melted charge was subjected to moulding under pressure, obtaining plates from which specimens were derived: samples were produced with only 30 wt% of wood, and 30 wt% of wood with 10 wt% cellulosic fibres. The main tests performed were the tensile test, SEM analysis and water absorption.

Results: The tensile test revealed an increase in breaking load and elastic modulus thanks to fibers introduction in WPC. SEM analysis showed a poor interface between wood particles and paper fibers with the matrix: to improve it we will both introduce maleic anhydride, and perform chemical

treatments on fibres. SEM has also shown a good dispersion of paper fibers and wood particles and the interaction between two different morphologies reinforcements: the simultaneous presence of fibres and particles allowed reducing the microporosity. The same result was confirmed from the water absorption. In fact, water absorption's test showed a higher mass variation for samples with 30 wt% of wood than 30 wt% of wood and 10 wt% of fibres: the fibres' presence improved the consistence of the composite during the mixing process, reducing microporosity.

Discussion: The results obtained support papers' introduction as filler in WPC. Nevertheless paper micronization treatment is needed: this step influence paper morphology before its introduction in the matrix. In future works particles will be tested to analyse soundproofing or damping. Turbomixing production wasn't the only option: an industrial widespread alternative is the twin-screw extruder, even if it results more expensive and complex to manage. In order to reduce the amount of polymer, a future improvement will be blending with starch derived polymers. Other tests will be performed to complete the composite characterization like impact tests, thermal analysis, and fire and UV resistance.

PAPER-BASED SMART INTERFACES: CONTROLLING INFORMATION STORAGE BY CHEMICALLY ACTIVATED OSCILLATIONS

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Introduction: Research on paper-based devices is currently blooming in a large variety of applications, in particular advanced diagnostics and flexible electronics. The capability to store information with controlled lifetime is expected to have major impact on cellulose-based materials, with interesting applications in security, anti-counterfeiting, device self-diagnostics, labeling, packaging and quality control. The idea of this work is to extend the advantages of adaptive and non-static materials to commercial cellulose, in order to store self-expiring graphical information on paper-based supports with precise temporal and spatial control. This goal is pursued by activating chemical oscillations from non-oscillating Belousov-Zhabotinsky (BZ) solutions loaded in cellulose supports.

Materials and methods: In the present work, we use the BZ reaction as a pacemaker to store information with spatial and temporal control in paper-based devices. In order to do this, we prepared the Belousov-Zhabotinsky reaction medium in an excitable nonoscillating state, by mixing the appropriate amount of KBrO₃, H₂SO₄, KBr, citric acid and Fe(phen)₃SO₄. Then, different amounts were dropped onto commercial cellulose filters. Writing/self-erasing was activated by means of iron tips or bullets. Analogous tests were carried out using small pieces of zinc, aluminum, magnesium, glass and polyethylene terephthalate. Further experiments of chemical activation were carried out by using aqueous solutions of different salts (FeCl₂, FeCl₃, KBr, KNO₃, NaCl, KCl and AgNO₃).

Results: When the BZ medium is absorbed onto the cellulose substrates, it acquires a blue color, typical of the reduced state of the catalyst present in the reaction medium. It has been noticed that when a contact between the BZ-functionalized cellulose and an external object is introduced, a change of color from blue to red, that is representative of a change of oxidation state of the catalyst, occurs. For example, small pieces of iron, like bullets, tips or wires, are able to activate the change of color and can be used as pens for writing graphical tracks on the paper substrate. Thanks to the oscillatory nature of the involved chemical reaction, the original color is restored over the time, as a consequence of a spontaneous self-erasing process. This offers the opportunity to program the storage of optical information within a specific temporal interval.

Discussion: Different experiments were carried out to gain more insight into the mechanism at the base of the writing process, demonstrated the chemical nature of activation. What is relevant is the capability of the material utilized as an "activator" to generate a local gradient of concentration of the species involved in the BZ reaction. The specific contribution of the main parameters affecting writing and self-erasing processes (temperature, reaction medium volume) was evaluated in a series of systematic experiments. This concept can be extended to other types of oscillating reactions, which offers a rich palette of applications for sensing, diagnostics, energy conversion and paper-based electronics.

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SHAPE MEMORY POLYCAPROLACTONE NON-WOVEN MAT BY COMBINING ELECTROSPINNING AND SOL-GEL REACTION

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Introduction: Shape memory polymers (SMPs) are a class of smart materials able to interconvert between a 'temporary' shape obtained after a programming step and a previously set 'permanent' shape, upon the application of an external stimulus. Electrospinning technology has been exploited to fabricate micro/nano fibrous matrices with shape memory (SM) properties that in some cases displayed an enhanced SM behavior than the corresponding bulk films. In order to obtain electrospun mats with good SM properties and to overcome the limitations of complex approaches, in this work we propose a novel approach by combining electrospinning process and sol-gel reaction that enabled to achieve high crosslinking degrees without using any template polymer.

Materials and methods: A partially crosslinked polycaprolactone (PCL), synthesized through sol-gel chemistry starting from a α,ω -triethoxysilane-terminated PCL was used to gain bead-free fibers. After electrospinning, the crosslinking degree has been subsequently increased and tuned by applying a controlled thermal treatment. Electrospun samples with different crosslinking degrees have been prepared and the effect of the different crosslinking extent was correlated to the SM property of the material by applying an ad hoc thermomechanical cycle. Furthermore, gel content, degree of swelling and morphology of the samples have been studied.

Results: Partially crosslinked α,ω -triethoxysilane-terminated PCL solutions were successfully electrospun, allowing to obtain bead-free fibrous non-woven mats. The viscosity of the electro-spinnable solution was optimized by controlling the hydrolysis/condensation reaction time activated by water and HCl, while the crosslinking degree of PCL fibers was controlled by varying the exposure time of non-woven mats to acidic vapors. The mechanical properties (storage modulus and tensile modulus) in the rubbery plateau region were consequently governed by the crosslinking degree of PCL.

Discussion: The evolution of fiber architecture within the non-woven mat with the applied strain was observed: the fibers underwent rotational/flexural motions, reorienting as the strain increases and, for strain values higher than 50% the fibers became highly stretched and aligned along the direction of strain. All the prepared electrospun non-woven mats exhibited very good one-way SM properties (high fixation and recovery capabilities), almost independently on the applied strain and the crosslinking degree of PCL fibers.

EFFECTS OF WAVINESS FACTOR ON DISTRIBUTION LENGTH AND IFSS OF NATURAL FIBERS COMPOSITES

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Introduction: During extrusion and injection moulding of composites, natural fibres suffer of entanglement phenomena in the polymeric matrix. Consequently the fibre waviness lead to lower mechanical properties of the composites than those expected on the basis of predictive models application. In fact the most widely used models for the estimation of the interfacial shear strength (IFSS) do not consider this phenomenon. This work introduces a method for IFSS calculation taking into account the waviness factor, which affects the weight distribution of the fibre length.

Materials and methods: Blends of polylactic acid (PLA) and polycarbonate (PC) (with and without catalyst) with addition of various percentages of cellulose fibres (5 wt%, 10 wt% and 15 wt%) were prepared and tested. All materials were dried in a drying oven at 60°C for, at least, 24 hours. The blends were processed on a Thermo Scientific MiniLab Haake twin-screw extruder; after extrusion the molten materials were transferred, through a preheated cylinder, to a Thermo Scientific Haake MiniJet II mini injection moulder.

The tensile tests have been carried out at room temperature on an Instron universal testing machine, at least five specimens were tested.

Scanning Electron Microscope (SEM) has been used to evaluate, post extrusion, the weight length distributions and the fibers waviness.

Results: The SEM analysis confirmed that natural fibers are subject to entanglements phenomena.

In order to consider the fibers waving, it has been proposed a corrective factor that corrects the real fibers length.

The hypothesis, from which the corrective factor has been obtained, comes from examining the fibers wave like a sinusoidal arc. In this manner the corrective factor depends on wavelength and amplitude. By using this approach the expected values and experimental values of mechanical properties resulted in agreement.

Discussion: The new length distributions, inserted in existing mathematical models, allow calculating with more accuracy the mechanical properties of biocomposites containing natural fibers, in particular the Interfacial Shear Stress and the Elastic Modulus.

CHITOSAN-BASED HYDROGEL FOR DYE REMOVAL PURPOSES: PREPARATION AND PRELIMINARY CHARACTERIZATION

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Introduction: Chitosan is a natural polymer with an excellent chelating capacity that make it a potential bio-sorbent for dye removal. Among the various forms in which chitosan can be produced for this purpose, chitosan hydrogels in the bulk form are particularly attractive as they can be easily handled limiting possible damages. This facilitates the recovery after use and regeneration for possible reuse. Despite the interest in this promising class of materials, low-cost chitosan-based adsorbents with high adsorption capacities are still under development to reduce the adsorbent dose and minimize disposal problems. In this work we propose a sustainable procedure for the production of mechanically resistant chitosan-based hydrogels for dye removal from aqueous solutions. The effect of different material-and process-related parameters on the mechanical properties and dye absorbent performance are investigated.

Materials and methods: Different concentrations of chitosan powder (CS, Sigma Aldrich) were dissolved in a mixture of bi-distilled water and acetic acid via magnetic stirring at room temperature for 72 h. Then, the polymer solution was poured into glass test tubes, and various amounts of gelling agent (GA) solutions were gently poured on top of the CS to allow for sample gelation at the CS-GA interface. The chitosan hydrogel was then cut into disk-shaped samples (diameter of 5 mm and thickness of about 5 mm) for the subsequent analyses. For the adsorption tests, the food dye Indigo Carmine (IC, Sigma Aldrich) was chosen as adsorbate. The chitosan-based samples were immersed into the pollutant solutions containing the dye and kept under constant agitation of 75 rpm and at 25°C. Aliquots of solutions were collected in preset time intervals and the dye concentration was determined by spectrophotometry analysis. For compressive tests, disk-shaped specimens were compressed without any confinement in quasi-static conditions.

Results and discussion: Despite their low specific surface, the adsorption capacity of our disk-shaped hydrogels is comparable to that reported in the literature for films and beads. In addition, the bulk samples can be easily separated from the liquid phase after the adsorption process, which is highly attractive from a practical point of view. Compression tests reveal that the gelled samples share the same overall behavior under compression: the stress-strain curve becomes non-linear at about 15% strain for both the gelling conditions, meaning that plastic deformation occurred for strains above this limit. Another interesting characteristic of the CS hydrogels is that even when they are compressed to more than 50% of their original length, no failure or cracking in the samples can be observed. Finally, it is worth not-

ing that the compressive behavior of the hydrogels has been reported to be correlated with the swelling properties. As the latter plays a crucial role in the dye adsorption kinetics, such a relationship is currently under investigation. To summarize, the obtained results suggest that the fine tuning of the process parameters allows the production of mechanical resistant and highly adsorbing chitosan-based hydrogels.

ANALYSIS OF TENSILE STRENGTHS OF FIBER REINFORCED COMPOSITE MATERIAL AFTER ACCELERATED AGING TESTS

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Introduction: Use of fiber reinforced composite in the production process and major applications could be much more rapid knowing the trend of their mechanical properties degradation due to aging caused by environmental conditions, even extreme. Accelerated-aging tests may be help to estimate potential long-term utilization of material systems under expected conditions of use. However, considering that the aging of a material and the alteration of its characteristics through time are a very complex phenomenon a mathematical modeling, even if approximate, may assist in the interpretation of the data collected by accelerated aging test and provide a sufficiently powerful and fast tool if necessary choose between different materials.

This experimental work describes activities carried out at Materials Technologies Laboratory of ENEA Trisaia Research Centre: the results of accelerated aging tests in climatic chambers to characterize carbon and glass fiber reinforced composites with reference to tensile strength variation and the development of a numerical model to simulate in a fast way the extent of degradation through a few parameters

Materials and Method: Three climatic zones have been considered for aging tests: temperate, tropical and polar one, each with different values of thermal excursion and relative humidity in order to simulate extreme conditions to which materials may be subjected in their life cycle. The length of aging cycles, related to the values of the thermal excursions inserted, has reproduced a real-life period of approximately twenty-five years. The tested samples were characterized by different matrix: polyamide (PA), polyphthalimide (PPA), PA66 nylon, and were reinforced with different percentage of glass fiber (long and short) and carbon fiber (long and short). All types of specimens were tested before the aging cycles to determine the tensile strength used as a reference (REF) for comparison with the results obtained on samples tested after accelerated aging cycles. Eight step for each type of aging were considered and in correspondence of each of them the tensile strength was evaluated. Tensile tests have been performed according to UNI EN ISO 527: 2012 and results have been analyzed to identify which FRP had the best performance according to the considered climates. Lastly, having a large number of experimental data resulting from aging test the results have been also analyzed using a statistical approach trying to identify a predictive model.

Results and discussion: Tests have shown a deterioration of the examined materials properties with reference to the tensile strength more accentuated for the polar cycle freeze - thaw than in the temperate one and tropical one with very high levels of humidity. A part of data collected by accelerated aging tests (from first to the third step) have been then processed with the Minitab software to obtain a forecasting model with an approach of non-linear regression analysis using the algorithm of Gauss-Newton. The model has been validated. Then starting from the fourth step the model has predicted the material behavior comparing the obtained results with the experimental measured ones providing very useful information to predict the extent of the material deterioration

CYCLIC POTENTIODYNAMIC POLARISATION TESTS FOR THE DEFINITION OF PEDEFERRI'S DIAGRAM OF STAINLESS STEELS

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Introduction: The Pedeferri's diagram, originally defined for carbon steel in concrete, aims to predict and to prevent chloride-induced corrosion, imperfect and perfect passivity conditions as a function of potential and chloride content. A first effort has been carried out to extend the use of Pedeferri's

diagram to stainless steel in chloride containing environment. The diagram is defined by kinetic parameters, i.e. the localized corrosion potential and the re-passivation potential, which are affected by factors related to the environment and the metal. Moreover, these parameters show a dependence on the electrochemical test adopted to measure it. In order to define a proper test protocol of Pedferri's diagram, different electrochemical tests can be considered, as cyclic potentiodynamic and potentiostatic polarization test. In the following, the first is described.

Materials and methods: Preliminary tests were carried out on austenitic AISI 304 L (17% Cr, 8% Ni) stainless steel specimens (surface 2 cm²) in solution containing 0.1-0.3-1.0-3.0 g·dm⁻³ chlorides in order to measure the immersion time before starting the potential scan. Cyclic potentiodynamic tests were carried out in aerated neutral solution containing 1 g·dm⁻³ chlorides (28·10⁻³ M). A MMO-Ti counter electrode and a Ag/AgCl_{KCl,sat.} reference electrode were used in order to supply the polarization current and to measure potential, respectively. Scan rate of 0.16 mV·s⁻¹ was applied from free corrosion potential up to the onset of localized corrosion, measured by a sharp increase of the polarization current density. Maximum current density before reverse scan is 3 A·m⁻². Tests were carried out at room temperature (20 ± 2°C) and fixed temperature (30 ± 0.1°C).

Results: In all conditions, free corrosion potential increases with time up to the achievement of a steady value after about 6 hours immersion. Free corrosion potential is in the range from -0.1 to about 0 V Ag/AgCl_{KCl,sat.}, indicating a stable passive condition. Potentiodynamic scan shows a passive behavior (passivity current density from 1 to 3 mA·m⁻²) up to onset of localized corrosion. Both pitting and crevice corrosion were observed on the surface. Localized corrosion potential at room temperature is between 0.41 and 0.52 V Ag/AgCl_{KCl,sat.}. The re-passivation potential (measured in the reverse scan) is in the range between 0 and +0.1 V Ag/AgCl_{KCl,sat.}, about 0.4 V lower than localized corrosion potential. Tests performed at room temperature (20 ± 2°C) and at fixed temperature (30 ± 0.1°C) do not show significant difference in localized corrosion and re-passivation potentials.

Discussion: Free corrosion potential monitoring shows that an immersion time greater than 6 hours is recommended in order to achieve a stable passive film formation in aerated solution. Potentiodynamic test shows good test repeatability at fixed test condition. Localized corrosion potential shows a deviation from the mean value of about ±60 mV in the tested condition. Further tests are mandatory to investigate the effect of environmental and metallurgical parameters. A comparison with potentiostatic anodic test is scheduled in order to define a proper test protocol.

TITANIUM POWDER IN ADDITIVE MANUFACTURING (DMLS) TECHNOLOGY: EFFECT OF RECYCLE ON THE FINAL PROPERTIES OF THE PRINTED COMPONENT

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Introduction: Direct Metal Laser Sintering (DMLS) is a powder bed fusion technology based on additive manufacturing process, which utilizes a laser beam as energy source to scan and melt selected areas of metallic powders in a layer-by-layer construction. In the wide scenario of materials commercialized for DMLS technology, Ti-6Al-4V alloy is widely used in aerospace, automotive and biomedical applications due to its unique characteristics such as high strength to weight ratio, corrosion resistance and wear performance, over excellent mechanical features. In every one of these sectors the evolution of mechanical properties, and then the material reliability in function of the powder reusing, is still representing a point of uncertainty for Quality Systems, since for every manufacture powder needs to be sieved and re-inserted inside the DMLS machine, being exposed to environment conditions. Furthermore, inherent in the technology is the impossibility to completely finish a powder batch, making economically convenient to mix already used powder with fresh one. Thus, the scope of the present activity was to investigate the evolution of mechanical properties of printed components in function of the powder reuses and mixings under storage conditions defined by OEB Quality Management.

Material and Methods: Different batches of Ti6Al4V powder (supplied by EOS GmbH) have been employed along this activity, for a total of five batches used at the beginning with a global weight of 40 kg, at which other six batches have been added in a quantity of 10 kg each one. The first mix of

five batches was used for forty Jobs; at that point other two were added and the composition was kept till the 57th Job, in which another one was employed. Successively, at the 64th, 71st and 79th Jobs, remaining batches were added respectively with that cadence. To better understand the aging effect, for every Job the powder weighted age was calculated, resulting that after each of the described additions, the weighted age of the used/new powder mix was respectively 257, 372, 363 and 505 hours. In every made Job two vertical – with – respect – to – the – platform cylinders with a diameter of 11 millimeters and a height of 110 millimeters, and a cube having an edge of 15 millimeters, were made grow up on the platform. Cylinders were machined getting tensile specimens, while cubes were polished to measure density and hardness. Then, tensile tests and hardness and density measurements were performed to monitor material features ongoing.

Results: Tensile strength proved to be between 1100 and 1200 MPa, and yield strength between 1050 and 1150 MPa. No evident detriment was observed proceeding with the powder aging. A slight decrease of elongation at break and of part density was obtained with prolonging powder reuse. Further analyses are ongoing aimed at appraising the statistical significance of such result.

Discussion: The powder global aging doesn't seem provoking negative effects on final mechanical properties of additive manufactured components. The only exceptions seem to be the elongation at break and density.

CHARACTERIZATION AND CORROSION RESISTANCE OF ZN-AL GALVANIZED WIRES IN CONTACT WITH CEMENT PASTE

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Introduction: The galvanized wires studied in this work are used to manufacture strand elements, which anchors the barriers employed for the protection against the rocks and avalanches falling. During the installation of the barriers, such elements are let down in wells to the ground where a cement paste is cast. In this work, galvanized wires were characterized by metallographic analysis and their corrosion behaviour in cement paste was studied.

Materials and methods: Two different galvanized wires were studied. One was obtained in a pure zinc bath (thickness 47.7 mm; 335 g/m²) and the other in a process where a Zn-5%Al coating is produced (thickness 31.8 mm; 180 g/m²). Both were embedded in several cement paste specimens having a cylindrical shape (f = 11.5 cm, h = 12.5 cm; cover = 1.5 cm). One half of the specimens were cured in laboratory dry conditions while the other half in wet conditions with tap water. Corrosion potentials and corrosion rate measurements were performed in the curing period for studying the interaction between galvanized wires and the cement paste in such exposure conditions. The cross sections of the galvanized wires were observed by means of optical microscope to characterize the corrosion attack and to determine the residual thickness of both zinc based coatings. Furthermore, an electrochemical characterization of the galvanized wires by means of Tafel plots was done in a saturated Ca(OH)₂ solution.

Results and discussion: Initially, pure Zn coating was more active giving a lower corrosion potential and higher corrosion rate compared with those of the alloy. In both cases, the potentials assumed suitable values for promoting hydrogen evolution, as confirmed at the end of the experimentation after breaking the specimens: in the interface between the wires and the paste, evidences of bubbles formation were clearly found. Going on with the exposure, when the passivation was occurred, the corrosion rate of pure Zn coating resulted lower than that of Zn-Al coating, showing in this way an inversion with respect to the initial stages of curing. Recoding Tafel plots in Ca(OH)₂ saturated solution, previous observations are confirmed: pure Zn wires showed a slight higher corrosion rate with respect to Zn-Al wires in initial active conditions, whereas a significant inversion was found after the wires were passive. The effect of this different corrosion behaviour produced a higher consumption of the Zn-Al coating (8-12 mm) with respect to Zn coating (7-9 mm), as obtained by the measurements of the residual thicknesses of their cross sections at the end of the experimentation. Of course, more consumption was found in wet exposure conditions. Furthermore, X-ray diffraction analysis of the coatings indicated that the passivation layer on Zn-Al is formed by calcium hydroxizincate (CHZ) and Ca₂Al(OH)₇·3H₂O, whereas on Zn coating only CHZ is present. The results of the present work indicate that the best protection is given by passivation film present on pure Zn coating with respect to that on Zn-Al coating, in agreement with literature data.

FOCUSED ION BEAM METHODS FOR MICRO-SCALE RESIDUAL STRESS ASSESSMENT IN THIN FILMS

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Introduction: Analysis and control of residual stresses in advanced engineering materials are important issues for reliability assessment at small scales, e.g. for micro-electromechanical systems (MEMS) and nano-crystalline and amorphous bulk and thin film materials. This presentation gives an overview of the recent advances in the field of sub-micron scale residual stress assessment by the use of focused ion beam (FIB)-controlled material removal techniques.

Materials and methods: The two step method consists of incremental FIB ring-core milling combined with high-resolution in-situ SEM/EG imaging of the relaxing surface and a full field strain analysis by digital image correlation (DIC). The through-thickness profile of the residual stress can be also obtained by comparison of the experimentally measured surface strain with finite element modelling using Schajer's integral method.

Results: In this presentation, we will review the most recent advances in the field of FIB-DIC methods for residual stress assessment at the micro and nano scales, with focus on recent efforts for development of automated procedures for local residual stress analysis of (i) thin films, (ii) microelectronics devices and (iii) polycrystalline and amorphous bulk materials.

Discussion: Practical applications of the method on several systems will be described and discussed. In particular, the issues of residual stress assessment on very thin films and micro-devices, stress depth profiling, stress measurement on amorphous materials and the effects of ion induced damage and elastic anisotropy on the relaxation strains will be reviewed.

AN INNOVATIVE SOLUTION FOR THE STRUCTURAL CONSOLIDATION OF RC MODERN ARCHITECTURE: INHIBITING-REPAIRING-STRENGTHENING (IRS) TECHNIQUE

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Introduction: In the study of cultural heritage conservation such as of its vulnerability and its protection from seismic risk, an important issue is the analysis of modern architecture which, in Italy, refers particularly to Fascism. There is a basic conceptual unity between restoration of ancient architectures and restoration of modern ones. The methodological approach to the design is similar but are implicated different building techniques and materials for the consolidation. In fact, the most of modern architectures are made of Reinforced Concrete (RC) and the use of composite materials for their consolidation is nowadays very widespread.

Materials and methods: In this work an innovative and alternative system for retrofitting of existing RC structures with deteriorated cover concrete and/or corroded bars, was conceived, designed and experimentally tested. It consists in the application of a new strengthening system (Steel Reinforced Geopolymeric Matrix, SRGM), composed by stainless steel strands embedded in an inorganic geopolymeric fireproof matrix. The latter is an eco-friendly material not only for its composition made of blast furnace slag, but also for the intrinsic characteristics of the geopolymers. These ones guarantee much more reduced emissions of carbon dioxide than a traditional Portland cement (from >1000 g/kg down to <250 g/kg) due to a production process with less energy consuming and a greater eco-compatibility. The geopolymers are also recyclable as aggregates and are good corrosion inhibitors, which means that it is not necessary to use additional special products to protect the bars, thus avoiding the use and consumption of polluting products.

The present paper, in addition to the use of an innovative material, analyzes also an advanced strengthening technique, different from the traditional Externally Bonded (EB), that includes three operations in one: Inhibiting-Repairing-Strengthening (IRS).

Specifically, the work aims to investigate, experimentally and theoretically, the structural performance of a consolidation innovative solution by comparing the structural behaviour of strengthened and un-strengthened RC beams. Two groups of large-scale RC beams with mechanical and geometrical properties that simulate existing structures, such as low concrete strength and corroded smooth/ribbed round bars, were strengthened with IRS-SRGM and EB-SRGM technique and were tested under four-point bending.

Results: Test results showed that the IRS-SRGM system provides greater load carrying capacity (from 16% for EB up to 30% for IRS) and, in general, a highest composite action and a good overall performance. Finally, a theoretical prediction of the structural behaviour showed that the model based on

deboning strain value, proposed for the Fiber Reinforced Polymer (FRP) system, is also usable for the RC beams strengthened with the EB-SRGM system, whereas, further research should be carried out in order to define a reliable analytical model for the IRS-SRGM system.

Discussion: In conclusion, the work highlights the structural effectiveness of a new composite material (SRGM) applied with a novel technique (IRS). The IRS-SRGM system is a durable and compatible solution that could be used for the restoration of modern cultural heritage with reduction of pollution, time and costs of intervention compared to other now used composite systems.

N-DOPED TiO₂ PHOTOACTIVE COATINGS FOR BUILDING MATERIALS

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Introduction: Self-cleaning property is an attractive feature for building materials, especially for exterior surfaces exposed at chemical agents and atmospheric pollutants. These agents cause high levels of sulphate and nitrate depositions, with development of black crusts that accelerate the decay and produce an aesthetically unacceptable staining of the stone surfaces. Therefore, to remove soiling material and slow down the deterioration processes, the development of photocatalytic products to transform pollutants, in both gaseous and liquid phases, into harmless species is worthy of attention also from an environmental sustainability perspective. Titanium dioxide is the photocatalyst most widely studied and the photoactive nanocrystalline titania obtained by sol-gel process is a promising de-soiling coating for building materials. However, the main deficiency for the practical applications of TiO₂ is due to its large band-gap (3.2 eV), meaning that effective processes require UV light irradiation. To enhance the absorption of visible light, different doping ions are investigated. Here, coatings based on TiO₂ nitrogen-doped nanoparticles, dispersed in an aqueous medium, are proposed for carbonatic stones.

Materials and methods: Two different N-doped TiO₂ sols (0.1M), henceforth called N-TiN and N-TiU, were obtained starting from titanium(IV) oxysulfate (TiOSO₄) and nitric acid as peptizer (N-TiN) and from titanium (IV) tetraisopropoxide (TTiP) and urea as peptizer (N-TiU), respectively. X-ray diffraction, Raman and X-ray photoelectron spectroscopies (XPS) were used to characterize the dried nanocrystalline powders. The penetration depth of the coatings was measured by SEM investigation. The compatibility of the coatings was examined according to the UNI-Normal protocols by measuring the water absorption by capillarity, the surface wettability and colorimetric parameters. The photocatalytic oxidation of methyl orange (MeO), Rhodamine B (RhB) and methylene blue (MB) under solar lamp irradiation was used as indicator of the activity of N-doped TiO₂ sols and TiO₂ coatings.

Results and discussion: XRD and Raman measurements confirm the crystalline nature of titania powders in anatase form with negligible brookite. The Raman peak positions and FWHM suggest anatase nanocrystals with 5-10 nm size, as confirmed by the XRD analysis. XPS measurements indicate that in the powder obtained by TiOSO₄ the doping by ammonia leads to the formation of Ti-N chemical interaction. The formation of Ti-N bonding by the introduction of nitrogen by urea is less evident. SEM-EDS results indicate a penetration depth of a few microns and surface distribution fairly homogeneous. The TiO₂-based treatment does not introduce colorimetric changes compared to the untreated limestone and does not alter the properties of the stone as determined by measurements of the water capillary absorption and wettability tests. A fast photocatalytic cleaning activity towards the dyes was measured for both TiO₂ sols and coatings.

EPOXY-BASED AMPHIPHILIC HYDROGELS: SWELLING BEHAVIOR AND MECHANICAL PROPERTIES

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Introduction: Polymeric hydrogels are soft materials with a network structure that retain large amounts of water and have found widespread application in different technological areas. Amphiphilic hydrogels contain both hydrophilic and hydrophobic segments and are presently investigated for instance as devices for controlled release of pharmacological substances or biomaterials in tissue engineering. The development of amphiphilic hydrogels for a specific

application requires the attainment of the most appropriate balance between hydrophobic and hydrophilic moieties, network cross-link density, and swelling degree. In the present work the versatility of epoxy resins chemistry was exploited to tune such parameters.

Materials and methods: Several epoxy networks were synthesized by changing the hydrophilicity/hydrophobicity of the monomers (epoxy resins and amines) and/or their ratio in the reaction mixture. For all hydrogels the room temperature equilibrium swelling ratio in 0.1 M NaCl was determined. For some materials swelling tests were carried out also at various temperatures to assess their thermosensitivity. The room temperature mechanical behavior of hydrogels equilibrated in 0.1 M NaCl was investigated by uniaxial tensile tests.

Results: The room temperature water content of the hydrogels investigated was in the 65–95 wt.% range. The water content decreased by about 45–55 wt.% as the temperature was increased from 6°C to 70°C. A more pronounced thermosensitivity was displayed by less cross-linked hydrogels. The tensile behavior of the hydrogels was dramatically influenced by the purification procedure: if the hydrogels were purified simply by soaking in 0.1 M NaCl, their tensile modulus and elongation at break were definitely lower than if the same systems were treated with organic solvents before equilibration in 0.1 M NaCl. In spite of these considerable mechanical property differences the room temperature water content of the two sets of materials was similar.

Discussion: The results obtained show that epoxy-based hydrogels with both chemical and physical cross-links can be successfully prepared. The extent of physical crosslinking, which is triggered by the association of hydrophobic groups, can be easily adjusted by a proper selection of the length and concentration of the latter. By changing the hydrophilic-hydrophobic balance and the chemical cross-link density it is possible to tune the swelling degree and the thermosensitivity (i.e. volume change as a function of temperature) of the hydrogels. The chemical cross-link density being the same, the mechanical behavior is considerably influenced by the extent of hydrophobic association, which in turn can be altered by absorption/desorption of molecules able to promote or inhibit hydrophobic interactions between the network segments.

DEPOSITION MECHANISMS IN COLD GAS SPRAYING OF METALLIC GLASS COATINGS: A FINITE ELEMENT ANALYSIS PARTICLES

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Introduction: There is a growing interest in the use of metallic glasses (MGs) as protective coatings, because of their unique combination of high hardness, high H/E ratio, and high corrosion resistance, imparted by the non-crystalline structure. Cold gas spraying (CGS), a coating deposition technique based on the projection of high-speed, solid-state particles towards a substrate, is well suited to process MGs, because of its ability to produce dense layers whilst limiting thermal alteration phenomena (such as oxidation and crystallization), which are particularly deleterious for such materials.

Whilst the deposition mechanisms of conventional, polycrystalline metal powders in CGS have been widely studied, those of MGs are not equally well understood. Proper knowledge of the deposition mechanisms is particularly important as it allows devising practical parameters to guide the optimization of the operating parameters.

Materials and methods: A fully coupled temperature-displacement finite element model of the impact of 30 µm-diameter MG particles onto an AISI4340 steel substrate was implemented using an explicit algorithm, suitable for high-rate, dynamic phenomena. The Vitreloy-1 MG composition was chosen, because detailed characterizations of its thermo-physical and mechanical properties as a function of temperature are available in the literature. Various impact temperature/impact velocity couples were analyzed, which correspond to realistically achievable deposition conditions with commercially available CGS systems.

The results were validated by comparing the simulated morphologies of impacted particles to those of actual MG particles deposited by CGS under analogous conditions.

Results: The deformation of MG particles is dependent on their Reynolds number at impact ($Re = \rho * V_{imp} * d / \mu$). For $Re < 0.01$, deformation is concentrated within shear bands, where the glass experiences shear-thinning and softening, due to the highly localized release of heat by viscoplastic deformation. As a result, the particle attains limited flattening, which experimentally results in porous coatings. At $Re \geq 0.01$, the particle deforms homogeneously and spreads out uniformly, which experimentally results in denser coatings.

Discussion: Based on the model outputs, the parameter $r = E_{elastic} / E_{viscoplastic}$ is defined as the ratio between the elastic recoil energy stored in the system at the end of the impact process and the overall viscoplastic energy dissipation. This parameter decreases rapidly at $Re \geq 0.01$, due to the much higher viscoplastic dissipation within the homogeneously deformed particle, whereas, at low Re values, strain localization within shear bands results in limited viscoplastic dissipation. An excessively large amount of the initial kinetic energy is thus stored elastically in the system; its subsequent release has high chances of causing the particle to rebound. Experimental deposition efficiencies accordingly jump from <50% up to ≥80% when Re becomes greater than 0.01. When Re is very low ($\approx 10^{-10}$), r is also low as the cold, hard particle penetrates deep into a plastically deformed substrate; however, this situation does not correspond to proper deposition.

It is concluded that Re is a controlling parameter to be employed for the optimization of the deposition conditions of MG coatings by CGS.

EFFECT OF POLYMER MODIFIED CEMENTITIOUS COATINGS ON CHLORIDE INDUCED CORROSION OF STEEL IN CONCRETE

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Introduction: Steel reinforcements in concrete are protected from corrosion by a thin oxide layer, promoted by the concrete alkalinity. Depassivation may occur because of concrete carbonation and by the presence of chlorides at the rebar surface in concentration higher than a critical level, which is generally in the range of 0.4-1% by cement weight for concrete structures exposed to atmosphere.

The paper deals with the study of the effect of polymer modified cementitious mortars on chloride-induced corrosion of steel reinforcement in concrete. Nowadays, many results obtained by standard and short-term tests are available in the literature. This paper reports more than 15 years exposure testing on two commercial coatings, with different polymer/cement ratio.

Materials and methods: Commercial cementitious coatings (mortars), modified with the addition of acrylic-based polymer and polymer-to-cement (p/c) ratio of 0.35 and 0.55 have been studied. Coating thickness was around 2 mm. Concrete was cast with cement type CEM II A/L 42,5R (EN 197/1) and crushed calcareous aggregates with 10 mm maximum size, w/c ratio 0.5. The effect of coatings on corrosion initiation and propagation has been studied by the monitoring of corrosion potential and corrosion rate of rebars in concrete subjected to chloride ponding; chloride profiles, coating adhesion, water content and corrosion morphology have been also analyzed at the end of exposure.

Results: Polymer modified cementitious mortars can delay corrosion initiation in concrete caused by chloride penetration. The protective effect is more pronounced as the polymer content (p/c) increases from 0.35 to 0.55. In concrete with 0.55 p/c ratio, reinforcements remained passive (negligible corrosion rate) even after 17 years testing.

Concrete specimens with 0.35 p/c coatings were broken at the end of the exposure (around 14 years): corrosion rate evaluated by mass loss was in agreement with electrochemical measurements. Adhesion of the coatings to concrete on the top surface was not significantly affected by the exposure, while macroscopic delamination of coatings has been observed at the edge of the specimens.

Discussion: Polymer modified cementitious coating can strongly delay chloride-induced corrosion initiation, and the protective effect is more pronounced as the polymer content (p/c) increases. The delay is mainly due to the ability of the coatings to reduce the chloride content in concrete, while the critical chloride content is not modified.

Owing to high resistivity of coated concrete, corrosion rate is reduced; this effect is less important due to the fact that for chloride induced rebar corrosion the time of propagation is much shorter than the time of initiation.

FUNCTIONAL BIOPOLYMER-BASED NANOCOMPOSITES INCORPORATING GRAPHENE NANOPLAQUELETS

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Introduction: The effectiveness of the antimicrobial activity over time is mainly determined by the release rate of the antimicrobial compounds. The

rate of release depends on different factors such as preparation method, environmental conditions, interactions between antimicrobial and matrix. In this regard, nanoparticles can potentially be used to control the release of antimicrobial agents. Moreover, it is well known that the incorporation of nano-sized fillers into a biopolymeric matrix is an effective way to improve its properties. Aim of this work was to prepare and characterize biopolymer-based nanocomposites with antimicrobial properties. In particular, graphene nanoplatelets (GnPs) as fillers and ciprofloxacin (CFX) as biocide were incorporated via melt-compounding in a biopolymeric matrix. The rheological, mechanical, and antimicrobial properties of the obtained nanocomposites were evaluated. Moreover, particular attention was paid to the influence of GnPs on the release kinetics of CFX.

Materials and methods: The biopolymeric matrix used in this work was a PLA based sample. Graphene nanoplatelets were supplied by XG Sciences Inc. Ciprofloxacin was supplied by Sigma Aldrich.

The incorporation of GnPs and/or CFX into the matrix was achieved via melt compounding by using a batch mixer. The specimens for the characterizations were obtained by compression molding using a laboratory press operating at the same temperature adopted for processing.

The morphology of all the materials was analyzed by scanning electron microscopy (SEM). The rheological characterization was performed using a plate-plate rotational rheometer. Tensile mechanical measurements were carried out on rectangular shaped specimens cut off from films prepared by compression molding. The antimicrobial activity of the materials was determined by the agar diffusion method evaluating the presence of inhibition zones. The release of CFX from the films was investigated for 6 weeks in distilled water at 37°C.

Results: The morphological analysis revealed that the GnPs were well dispersed in the biopolymeric matrix. The nanocomposites exhibited flow curves higher than that of the neat matrix, and the viscosity increased as the filler content was increased. The adding of GnPs improved the stiffness of the matrix. Large bacterial growth inhibition halos were observed around samples incorporating CFX although the presence of GnPs led to a reduction of the inhibition zone. The release of CFX was characterized by an initial burst phase followed by a second phase, which is characterized by a slower release rate. However, according to results of the agar diffusion test, the samples incorporating the GnPs released a lower amount of CFX during the entire six weeks of testing.

Discussion: The reduction of the inhibition zone can be explained considering that the antimicrobial properties of the films are dependent on the release of CFX from themselves and that the presence of the GnPs influenced the CFX release from the samples. Indeed, the different release kinetics can be attributed to the presence of GnPs into the polymer matrix that very likely were able to create a tortuous pathway, thus slowing down the diffusion of drug molecules through the polymeric matrix.

FUNDAMENTALS OF CORROSION BEHAVIOR OF STEEL IN CONCRETE

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Introduction: The work examines the fundamental aspects, which determine the protective behavior of steel rebars in concrete manufactured with traditional portland cements (OPC). The paper analyzes steel passivation in fresh condition, under erosion conditions, which promote passive film removal and re-formation, and in hardened concrete. The role of oxygen and hydroxyl diffusion process on passive film formation is addressed. The protective capacity of OPC and passivation kinetic is strictly dependent upon the pH of the pore solution (hydroxyls availability) and oxygen since early exposures.

Materials and methods: The smart properties of Portland cement related to rebar corrosion protection have been widely recognized in literature. Several tests have been carried out to prove the corrosion protection offered by OPC against carbonation, chloride and the self-healing properties offered by the presence of free lime, acting as alkalinity supply. EIS and cyclic voltammetry tests on OPC cement mixtures have been carried out in fresh and hardened conditions. The tests have been performed in concrete steel slabs and on stationary and rotating disk electrodes to evidence the influence of hydroxyl and oxygen diffusion on the passive film formation.

Results: The evolution of the corrosion potential of reinforcements in portland cement concrete during the setting and hardening shows characteristic changes in the early periods. The potential decreases just after immersion

and rapidly increases from negative values –when passive conditions are not yet well developed –to high levels, typical of passive conditions. Cyclic voltammograms show a decrease of the current at 0V vs SCE under moderate erosion conditions and a progressive increase at higher rotational speeds of the electrode. The behavior at early exposure confirms the active corrosion behavior of steel. EIS tests show a progressive shift to the left of the curves towards low frequencies - as the protective film is developed.

After more than 4 months, both EIS and cyclic voltammetry tests confirm the formation of well-established passive film.

Discussion: The initial decrease in the corrosion potential is ascribable to oxygen and hydroxyl depletion at the rebar/concrete interface before concrete setting. Setting retarders admixtures cause a prolongation of this phase – and the increase of the corrosion potential can be significantly delayed over time. The modification of the corrosion behavior of steel embedded in concrete can be well evidenced by the evolution of the electrochemical impedance spectra. The increase of the high-frequency module takes place due to the hydration of the cement, which progressively reduces the porosity and the amount of free water in the pores. The low frequency time constant moves from 1-10 Hz - typical of active corrosion behavior of steel - to lower values, thus denoting the development of the passive film. The passive film formation continues over times and stabilizes after fairly long time. Passive film forms since early exposures, but it requires a much longer time compared to bulk solutions at the same pH. Oxygen is initially consumed.

EFFECT OF CYCLIC LOADING ON HYDROGEN PERMEATION AND EMBRITTLEMENT OF HSLA STEELS UNDER CATHODIC PROTECTION

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Introduction: High Strength Low Alloy (HSLA) steels are commonly used in buried pipeline and off-shore applications under cathodic protection, applied to prevent general corrosion. Although the transport of gases and liquids through pipelines is an established and secure technology, a number of cases of Environmental Assisted Cracking (EAC) due to the effect of hydrogen uptake into steel have been reported worldwide. Hydrogen Induced Stress Cracking (HISC) can occur on susceptible steel under tensile stress if too high cathodic polarizations are achieved. Hydrogen permeation is influenced by the applied cathodic potential, material microstructure, applied load and dynamic straining.

Materials and methods: The experimental work aims to the evaluation of hydrogen diffusion coefficient under cyclic continuous straining. The tests were carried out on API 5L × 100 steel. Permeation tests were carried out using the Devanathan-Stachurski electrochemical methods described in ISO 17081:2014(E). The permeation cell was mounted on a tensile specimen, loaded by means of a hydraulic universal testing machine. The cathodic charging compartment was filled with a solution of boric acid/sodium borate at pH 9. The specimen was charged at 10 mA/cm² current density. In the anodic compartment, the specimen was polarised at +200 mV vs SCE in 0.1M sodium hydroxide solution. The permeation current was monitored during loading.

Results: The steel showed slight increase of the hydrogen permeation flux after loading in the elastic field. Under constant loading, the permeation current modifies as the specimens is strained in the plastic field, reaching the values oad after a short transient. In slow strain rate conditions, the hydrogen permeation flux decreases with the strain at high strain rate because trapping effect prevails. A constant value of the hydrogen permeation flux was observed at strain rate lower than 10⁻⁶ s⁻¹. Actually some tests are on going to evaluate the effect of frequency on the hydrogen permeation flux through the specimen during fatigue cycles. Preliminary results show little modification in the steady state.

Discussion: The tested steel is immune to HE in static loading conditions, but can show HE in slow strain rate or in corrosion fatigue tests in cathodic protection. The HE susceptibility increases with the applied cathodic potential and decreasing the strain rate. A clear positive correlation between the hydrogen diffusion coefficient and HE susceptibility in SSR tests at constant strain rate and potential was founded for hot rolled steels. Higher diffusivity was also found for older steel types that are characterized by high carbon and manganese sulfide inclusion content and by coarse ferrite/pearlite banded microstructure. Modern steels with very fine ferrite/pearlite microstructures showed lower hydrogen diffusion coefficients, and consequently lower HE susceptibility despite the higher tensile strength.

COMPOSTABLE POLYMERS AND NATURAL FILLERS BASED FILMS AS SUSTAINABLE SYSTEMS FOR FOOD PACKAGING APPLICATIONS

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Introduction: The growing use of non-biodegradable petrochemical-derived polymers in the food packaging sector has led to serious and dramatic environmental, ecological and pollution problems. Thus compostable polymers, including poly(lactide) (PLA), could be considered promising alternatives, even if their effective employment is prevented by their poor mechanical, thermal and barrier properties. Thus, the addition of inorganic fillers and 'oxygen scavengers' could provide mechanical reinforcement and oxygen barrier properties, respectively. It is well known that the mechanical properties of polymers can be improved by the well dispersed fillers addition and the barrier properties can be enhanced following two approaches, i.e. the dispersion of suitable particles in order to generate a tortuous path to the gases, or the use of specific molecules as oxygen scavengers. In this work, in order to improve the properties of solvent cast PLA films; these latter strategies have been combined by physi-/chemi-sorbing of specific biomolecules on the surface of natural particles. In this manner a double barrier effect, and the functionalized particles were able to exercise simultaneous functions, acting both as reinforcing fillers, and carrier of antioxidant and antimicrobial molecules, extending shelf life and food quality.

Materials and methods: In the case of composite systems, suitable antioxidant/antimicrobial molecules (e.g. ascorbic acid, tannic acid, sulfur compounds) were chemi/physi-sorbed on the surface of natural fillers (e.g. diatomite, sea/egg-shell derived calcium carbonate) and the obtained functionalized particles (1-10 wt%) were disagglomerated in chloroform or dichloromethane by sonication for 30-60 minutes. Then polylactide (PLA 3052D, *Nature Works*®, 5% wt/v) pellets were added to the prepared suspensions. All the obtained solutions/suspensions were magnetically stirred at room temperature, up to complete polymer dissolution, then cast on Petri dishes and maintained under fumehood until complete solvent evaporation. As a reference, neat PLA film was also prepared. The efficacy of the chemi/physi-sorption protocols was verified by scanning electron microscopy (SEM), X-ray diffraction and FT-IR spectroscopy. Morphology and filler dispersion were analysed at SEM, the thermal properties by differential scanning calorimetry (DSC), the phase analysis by XRD, the mechanical properties by uniaxial tensile tests. Finally, antimicrobial tests against *E. coli* BL21^{ampR} strain were carried out on selected systems.

Results: In this work multifunctional PLA based films were successfully prepared by solvent casting technique. The efficient immobilization of the selected antioxidant and antimicrobial agents on the particle surface was demonstrated by XRD measurements, observation at SEM and by the FT-IR analysis that evidenced the presence of the typical functional groups of the considered biomolecules in the acquired spectra. In the case of composite films, the addition of the inorganic fillers allowed to obtain a remarkable increment of the mechanical properties in terms of Young modulus and ultimate tensile stress. These results can be ascribed to a good dispersion of the used fillers within the polymeric matrix and to a good interface and wettability fillers/matrix, as corroborated by the SEM observation of the stress-strained fracture surfaces. Moreover, the effective antimicrobial action of the added agents was demonstrated by antimicrobial tests against ampicillin-resistant *E. coli* strain.

PRODUCTION OF WHITE SELF COMPACTING CONCRETE USING SYNTHETIC ZEOLITE

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Introduction: In recent years an increasing interest concerning the pozzolanic activity of natural zeolites and their incorporation in blended cements occurred. Natural zeolites show pozzolanic activity that depends on the presence of reactive SiO_2 and Al_2O_3 which react with the $\text{Ca}(\text{OH})_2$ released during the hydration of cement producing C-S-H (hydrated calcium silicates) gels and hydrated aluminates.

Natural zeolites are widely available, economically inexpensive thus being favourable for large-scale applications. However, there are the limitations in the extensive use of natural zeolites in the cement industry due to the variable chemical composition depending on their source and to the presence of variable amounts of impurities that make them unsuitable for architectural applications. Another disadvantage is that the natural zeolites before being used as additives in cementitious conglomerates must be finely crushed.

This limitation can be overcome by the use of synthetic zeolites that have particles with size of few microns distributed within a narrow range, controlled composition and white colour.

The aim of this research is to investigate the feasibility of using zeolite 5A in the manufacturing of white self-compacting concrete (SCC) and the microstructural interactions of the synthetic zeolite 5A with the cement matrix.

Materials and methods: The following materials have been used: calcium zeolites type A [LTA] (5A zeolite) supplied by UOP Italy; white CEM II B-L 32.5 R supplied by Italcementi; limestone, superpludificant and modifying viscosity additives and silica fumed supplied by MAPEI (Italy).

Interaction of the synthetic zeolite 5A in the cement matrix has been investigated through XRD, FT-IR, DSC-TGA, ^{29}Si -NMR, ^{27}Al -NMR. SCC properties have been evaluated following the specification of UNI 11040, UNI 11042 and UNI 11045.

Results: Diffractograms of pastes with 5A zeolite exhibit a lower increase of peak attributed at $\text{Ca}(\text{OH})_2$ content than those of pastes without zeolite. This occurrence can be associated with its consume in the pozzolanic reaction of the zeolites. The remarkable decrease of the $\text{Ca}(\text{OH})_2$ content is also confirmed by FT-IR spectrum of pastes samples hydrated for 28 days. All mixes showed values of slump flow test within the requirement of the current normative. The SCC mixes have compressive strengths exceeding 35 MPa at 28 days. Furthermore mix containing zeolite 5A showed higher mechanical properties at early ages.

Discussion: The overall performance of SCC mixes containing zeolite 5A is better with respect to limestone and comparable with respect to mix containing silica fume. This is due to the microstructural interaction between zeolite 5A and cement matrix. In fact, the zeolite exhibits an evident pozzolanic activity, is an ionic strength modulator and modifies the environment of cement hydration.

SUSTAINABLE MANAGEMENT AND VALORIZATION OF MINING WASTE ROCKS

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Introduction: Each year the international mining industry processes hundreds of millions of tons of rocks to extract industrial, construction and energy minerals. These intensive mining activities have produced a large amount of hazardous wastes throughout the world. In recent years, it was found out that one of the most effective treatments for industrial wastes, particularly suited to those containing heavy metals, is the solidification/stabilization (S/S). This process utilizes chemically reactive formulations to form stable solids minimizing the potential leaching of hazardous components, which results in easier waste handling and storage. During the last decade, geopolymserisation has emerged as a possible technique for the effective stabilization and immobilization of waste. In the framework of the activities of the European Commitment on raw materials (ROSE), which includes 35 partners coming from both the research world and the industry world, recently at the Federico II University of Napoli (Italy) a multidisciplinary research activity is going on to get an insight on the possible reuse of mining waste in manufacturing geopolymers. This paper aims to use fly ash based geopolymer as matrix to stabilize waste rocks deriving from mining activities.

Materials and methods: Fly ash was supplied by ENEL (Brindisi, Italy). The alkaline activator solution was prepared mixing a sodium silicate solution provided by Prochin Italia S.r.l. (Marcianise, Caserta, Italy) with 10 M sodium hydroxide solution prepared starting from NaOH in pellets (NaOH 98%) and bi-distilled water. The waste rocks came from a copper-zinc mine (Neves Corvo Mine, southern Portugal). A complete characterization of the waste rocks was carried-out in term of chemical, mineralogical and morphological composition as well as

physical and thermal properties (granulometry, density, water content). Different fly ash-based geopolymeric mortars were prepared adding various percentages of powdered mining wastes. All the samples were physically, morphologically and mechanically characterized, in order to evaluate the effectiveness of the proposed stabilization/immobilization technique.

Results and discussion: The proposed methodology represents a starting point for the investigation of possible beneficial uses of polluted waste in geo-polymer matrices. Preliminary results indicate that the way forward is to use the waste rock not as a reactive component in the formulation of the geopolymeric binder paste (for lack of reactivity), but as a substitute for part of the aggregates in combination with fly ash in the production of geopolymers-based building materials (e.g. geopolymers mortars).

ASSESSING THE SUITABILITY OF FLY ASH GEOPOLYMER FOR STRENGTHENING EXISTING REINFORCED CONCRETE STRUCTURE

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Introduction: Fiber-reinforced cementitious matrix (FRCM) composites have gained increasing interest as newly developed system for strengthening reinforced concrete structures. FRCM system provides for the embedding of high-strength fibers into an inorganic matrix. The possibility of using geopolymers instead of cementitious matrix is very attractive since this new class of inorganic material, synthesized through the alkali activation of an aluminosilicate precursor, showed competitive features when compared to cement based materials in both terms of performances and sustainability. However, research dealing with the use of geopolymers for strengthening and rehabilitation of reinforced concrete structures with externally-bonded composite materials are limited.

Materials and methods: Carbon fly ash (28.1 wt%) was mixed with sodium hydroxide (2.1 wt%) and sodium silicate (10.6 wt%) solutions. Three different mixtures were prepared by using different molar concentrations of NaOH solution (4, 6, 8 M). Finally, water (3.0 wt%) and siliceous sand (56.2 wt%, $d_{max} = 1$ mm) were added. Mixtures were cured at room temperature for 7 and 28 days and physical and mechanical characterizations were performed. In addition, Fiber Reinforced Geopolymer Matrix (FRGM) composites were obtained by applying onto a pre-treated surface of concrete prisms, high strength galvanized steel fibers embedded into two layers of geopolymers mortar. Single-lap direct-shear tests were performed on these specimens after at least 7 days of curing, in order to analyze the bond behavior of the FRGM-concrete joints. Samples were labelled according the type of precursor used (fly ash-FA) followed by the molar concentration of the NaOH solution.

Results: When the molar concentration of the NaOH solution was increased from 4 to 8 M, a linear increase in the compressive strength and a slight decrease in the total open porosity of the geopolymers mortars occurred. After 7 days of curing, the values of the compressive strength (R_c) were equal to 7.4 ± 0.2 MPa for FA4M, 8.7 ± 0.2 MPa for FA6M and 10 ± 0.1 MPa for FA8M. For all the samples R_c increased with curing up to 28 days, achieving the highest value of 33.6 ± 1.5 MPa for sample FA8M. Single-lap direct-shear tests indicate that in all cases, the de-bonding occurred at the matrix-fiber interface rather than at the matrix-concrete interface. The highest peak load was obtained for sample FA4M and was equal to 9.5 kN whereas sample FA8M and FA6M reached 7.8 and 7.0 kN respectively.

Discussion: When geopolymers are used as matrix for embedding high strength galvanized steel fibers, it has to be considered that the alkaline solutions required for the geopolymersation can chemically react with the zinc-coating of the fibers. This reaction produces hydrogen gas and, as a consequence, a diffused porosity between the fiber and the geopolymers thus hindering the adhesion process. Results showed that lowering the NaOH concentration seem to be effective in the enhancement of the bond between matrix and fibers without significantly affect the mechanical and physical properties of the geopolymers mortar. Extended studies are ongoing in order to prove the suitability of fly ash geopolymers for FRGM composites.

NOVEL ENGINEERING POLYMERS FOR ADDITIVE MANUFACTURING

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Introduction: Additive manufacturing (AM) is gaining increasing importance in industry not just as a technology for prototyping but also, and in most

cases for, the production of functional parts. The filament-based technique refers to the so-called Fused Deposition Modelling (FDM). The FDM method is recognized as the best AM technique when functional parts are required. FDM materials used are currently limited to a selected number of polymers. Consumer machines can operate with: PLA, ABS, PETG, Ny and, for some machines, PC. Professional machines (i.e. Fortus-Stratasys) can operate with: ABS, Ny, PC, PC-ABS, ASA, PEI, PPSF. The material choice for FDM printer, both consumer and professional, is still very limited. For example, to date, very few examples exist on the use of PEEK as a material for FDM despite the fact that PEEK is widely recognized as the polymer choice for SLS in demanding applications. The present paper is focused on bridging the gap by showing the potential of using high-end engineering polymers for FDM in a semi-professional machine.

Materials and methods: Commercial grades PEEK and PC were used as the reference materials for the development of novel FDM filaments in the present work. The formulations were compounded with a twin-screw extruder (Brabender KETSE 20/40). The compounds obtained were then processed into FDM filaments (1.75 mm diameter) using a single screw extruder (Collin, Teach Line E 20 TH) equipped with a pilot spinning line. All the filaments were then processed using an FDM machine (Roboze One +400) by Roboze equipped with a high temperature nozzle designed to process engineering polymers. Tensile and flexural specimens were printed accordingly to ASTM D639 and ASTM D790 respectively. Fractured surfaces were analyzed, after gold sputtering, with a SEM EVO from Zeiss.

Results: In a first attempt, PEEK polymers with different melt viscosity were processed with the single screw extruder using a die of 2 mm diameter. The extrusion trials revealed that proper screw design is a key factor to obtain uniform filaments. The filaments produced showed an average filament diameter of 1.71 mm with a standard deviation of 0.03 mm. The filaments produced were processed without any significant problem using a nozzle temperature of 350°C. Tensile specimens were tested revealing a tensile stress of 69 MPa and a tensile modulus of 3.4 GPa.

Discussion: The results presented here evidenced that PEEK filaments can be successfully produced and processed by FDM by carefully selecting the raw materials and the processing conditions. The performance analysis carried out comparing the mechanical properties of our filaments with commercial alternatives evidenced the possibility to offset technical polymers (i.e. PEI) printed with professional printers.

LIFE CYCLE ASSESSMENT OF ALKALI-ACTIVATED AND OPC CONCRETE PAVING BLOCKS MANUFACTURING PROCESSES

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Introduction: In the last thirty years, many researchers have studied and investigated new eco-sustainable building materials, such as alkali-activated ones. The primary area of application of these materials is currently in the development of reduced- CO_2 production process of binders as an alternative to Portland-based (calcium silicate) cements.

This work focuses on the production of sustainable concrete-bricks based on alkali-activated binders and recycled aggregates. The environmental evaluation of process has been determined by means of Life Cycle Assessment (LCA) methodology.

Materials and methods: Recycled clay soils from a local plant were used as solid precursors for binder and as fine aggregates for sustainable-bricks production. In addition, blast furnace slag and NaOH solution (5M) and sodium silicate as alkaline solutions were also used.

The proportions of raw materials to make conventional concrete mixtures are a typical mixture design used in the Italian paving blocks production facility. In all the cases, wastes coming from building demolition were used as coarse aggregates.

The evaluation of environmental impacts was carried out through the use of Life cycle assessment (LCA) methodology. LCA method includes the evaluation of the material and energy characteristics and efficiency of the system, identifying the input and output of a studied system, and, at the end, providing guidelines for next improvement.

The life cycle phases that are comparable for both materials may be excluded in a comparative LCA. The various life cycle stages of brick products have been modeled and assessed using SimaPro © LCA software. The Eco-indicator 99 and CML 2000 baseline in SimaPro were used to assess the

environmental impacts of the 1 m² of OPC and alkali-activated paving blocks manufacturing production.

Results: It is interesting to note that, in both environmental evaluation methodologies (Eco-indicator 99 and CML 2000), the case study reports negative values which show savings. In particular, these negative load indicate that the reuse and consequential processing of recycled clay soil as raw materials and minimizing the transport of raw materials have allowed savings in the production of virgin metals, electricity and heat by conventional routes so that impacts become negative and an environmental benefit is attained. These results stand that using recycled clay soil as solid precursors for alkali-activated concrete and as aggregates for conventional one affect and increase blocks industrial production sustainability. It should also be noted that additional transport and processing are needed for the recycling of clay soil, nonetheless, natural resources will be saved and waste disposal is avoided. **Discussion:** It is possible to note that alkali-activated building materials do not necessarily need to be products which compete on a global scale with the existing OPC industry infrastructure, but rather may be viewed as a technology which may be utilized by cement producers to offer a broader range of cementitious products to the market.

EFFECTS OF MELATONIN-ENRICHED EDIBLE COATING IN STRAWBERRY (FRAGARIA X ANANASSA) QUALITY TRAITS

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Introduction: Extending the shelf life of perishable food products represents a main goal in food technology: fruits and vegetables (including minimally processed products) deteriorate because of physiological ageing, biochemical changes and microbial spoilage that may result in degradation of food colour, texture and flavour. In this context, edible coatings have been successfully applied as selective barriers to control dehydration and O₂/CO₂ transport in fruits. Recently, active films have been developed by incorporating bioactive compounds or plant extracts into the edible coatings, in order to improve their antimicrobial and antioxidant properties as well as technological stability. This approach may also enrich foods with healthy nutraceuticals, thus meeting the consumer expectations and adding value to products. In this study, a new coating was developed from chitosan incorporating melatonin, as dietary supplement. The properties of active film were evaluated in terms of effectiveness in reducing fruit decay, weight loss, surface temperature, evapotranspiration-rate and fungal contamination.

Materials and methods: The coating was prepared with 1.5% chitosan (low molecular weight, 10-15 kD) dissolved in 1.5% acetic acid, 0.5% glycerol as plasticizer and 0.1% Tween 20 as surfactant. The same solution with 0.5 g L⁻¹ melatonin (Sigma) was prepared. Strawberries were dipped into the solution at constant speed (100 mm min⁻¹) and, then, stored at 24°C for 5 days. Microscope slides were also dipped to measure film surface profilometry and thickness. In strawberries, surface temperature as indicator of evapotranspiration-rate was determined by infrared thermography, weight loss by gravimetric analysis, fruit decay and pathogen infections by a visual arbitrary scale and imaging techniques.

Results: Both coatings increased the fruit surface temperature, reduced the weight loss and decreased post-harvest fungal colonization by *Botrytis cinerea* and *Rhizopus stolonifer*, pathogens typically associated with fruit decay. Not any significant difference was recorded between chitosan and chitosan plus melatonin coatings.

Discussion: These preliminary data confirmed that edible films are effective in extending fruit shelf life and preventing decay, thus encouraging further experiments in order to assess the potential of chitosan-based edible coatings, eventually loaded with bioactive compounds for dietary supplementation.

POLYETHYLENE/LAYERED-SILICATE NANOCOMPOSITE ORIENTED FIBERS: MORPHOLOGY AND MECHANICAL CHARACTERIZATION

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Introduction: Organo-modified montmorillonite clay layers are able to improve not only mechanical properties but also heat resistance, barrier prop-

erties and flammability of polymeric matrixes. To this extent, processing parameters are important for non-polar polymers, like polyolefin, and compatibilizers are necessary to obtain exfoliated/intercalated morphologies. Polyethylene fibers are widely used due to the good achievable mechanical properties after drawing which can be further increased by the use of properly exfoliated nanoclays. The aim of this work was to produce nanocomposite polyethylene fibers oriented at different draw ratios and to correlate this processing parameters to morphology and mechanical properties of fibers produced at various clay loading.

Materials and methods: A maleic anhydride modified metallocene linear low-density polyethylene (mLLDPE-g-MA) was used as matrix and an organo-modified layered silicate (Dellite 67G) as filler. Three different clay concentration were investigated: 3, 5 and 10 wt%, respectively. Nanocomposites were prepared using melt blending process in a twin-screw extruder. After compounding, strands were produced by a single screw extruder and fibers were drawn at room temperature by a universal testing machine at a crosshead speed of 4 mm/min. Five different draw ratios (7.25, 10.00, 13.50, 16.00 and 19.00) were investigated. Tensile properties of the as-spun and drawn fibers were measured and morphology was investigated by XRD, TEM and SEM analyses.

Results: XRD patterns of PE/clay compounds indicate the achievement of intercalated/exfoliated structure and clay layers exfoliation is confirmed by TEM investigation. Moreover, TEM micrographs of as-spun fibers show the orientation of silicate layers in the flow direction. Elastic modulus of undrawn fibers increases at increasing clay content. In particular, compared to neat PE fibers, an increase of 42, 56 and 115% (for 3, 5 and 10 wt% of clay content, respectively) was obtained. Increasing DR, the elastic modulus of all the investigated fibers increased almost linearly. The tensile strength of nanocomposites fibers with higher clay content (5 and 10 wt%, respectively) decreases at high DRs. On the contrary, tensile strength of nanocomposite fibers containing 3 wt% of clay layers, increases at increasing DRs. TEM micrographs of drawn nanocomposite fibers reported an increase of clay exfoliation but also a rotation of clay layers due to fibers drawing.

Discussion: Nanocomposites fibers exhibit always higher tensile strength than pure PE fibers. In particular, fibers containing 3 wt% of clays have the best performance. In the other cases, after a DR of 16 and 13.5, a reduction of the tensile strength occurs, for 5 and 10 wt% of nanoclay content, respectively. TEM micrographs of drawn fibers show that a partial orientation is still recognizable but at increasing draw ratios, a further re-arrangement of clay layers was observed. Moreover, at higher magnification an improved exfoliation of clay platelets was observed. At increasing draw ratio, clay layers tend to rotate and touch each other due to electrostatic attraction. Moreover, at increasing DR a modification of the surface texture was observed. In particular, while undrawn fiber surface was quite smooth, a roughness increase is recognizable at higher DRs.

SELF-HEALING WATERTIGHT CONCRETES MANUFACTURED WITH A CARBOXYLIC ACID WATERPROOFING ADMIXTURE

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Introduction: The present paper deals with an experimental research program carried out to evaluate performances of an innovative polycarboxylate acid based waterproofing admixture added in the mixer together concrete traditional ingredients in order to improve concrete watertightness. Reduction of water penetration under pressure in concrete can be ascribed to the precipitation of insoluble salt crystals capable both filling capillary pores and sealing cracks generated by shrinkage in the plastic phase.

Materials and methods: Rheological (in the fresh state) properties, compressive strength and water penetration under pressure (EN 12390-8) were measured on concretes manufactured with the carboxylic waterproofing admixture and a similar product already available on the market and compared to reference concretes produced by using only the traditional ingredients. Two reference concretes were manufactured with w/c ratio equal to 0.50 and 0.60. Dosage of waterproofing admixture was 1 and 2% by cement mass. The influence of wet curing period (1, 7 and 28 days) on concrete performances was also evaluated. In order to test the sealing ability of the waterproofing admixture, concrete slabs were exposed in a windy chamber (wind velocity 40 km/h and 30% R.H.) to favour crack formation due to plastic shrinkage. Self-healing ability was evaluated by means of water absorption test carried out with Karsten Tubes. Finally, observation with optical microscopy and Scanning Electron Microscope were carried out to assess the crack sealing ability of the waterproofing admixture.

Results: Addition of waterproofing products does not affect negatively rheological and mechanical performances of concrete. A significant reduction of water penetration under pressure was recorded for concretes produced with the waterproofing products with respect the reference mixture manufactured with the traditional ingredients only. Reduction of water penetration was detected independently of the wet curing period. In cracked slabs produced with the waterproofing admixtures reduction in water absorption was recorded as a consequence of the ability of the carboxylic-based products to seal cracks formed in the plastic stage. Observation with the optical and scanning electron microscope confirmed the presence of insoluble salts crystals precipitated in cracks responsible for the reduction of the water absorption. **Discussion:** Carboxylic acid waterproofing admixtures improve concrete water tightness. 1% by mass of the carboxylic polymer reduces the water penetration under pressure by 50% with respect the reference concrete with the same w/c provide that the wet curing time is 7 days. Lower reduction (about 20%) was recorded in concrete wet cured for 1 and 28 days. Waterproofing admixture is capable to fill cracks formed in the plastic stage. After seven days water absorption in the sound areas of a concrete slab is equal to that of areas where cracks are present.

THE USE OF WOOD BY-PRODUCTS WASTE FOR PRODUCING LIGHTWEIGHT AND THERMAL INSULATING CEMENT-BASED MATERIALS

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Introduction: Worldwide the wood industries generate a large amount of waste products. Sawdust is generated from cutting, milling, and drilling operations while preparing finished products. Wood dust consists of very fine particles generated during machining operations, and it is often collected in filter bags or dust collectors. Small amounts of paint, glue, fungicide, and insecticide were often present by preventing a safe reuse of this wood by-product as a fuel.

In general, the use of lightweight aggregates in concrete (such as wood chips) can be advantageous, by allowing reduced size of foundations and structural elements, as well as possibly due to the resulting improved thermal insulation. However, the most significant advantage of using lightweight aggregates in cement-based materials lies in its environmental value, in particular in this case by using wood processing by-products.

In addition the reduction of energy consumption in construction, and the production of thermally insulating materials are also relevant issues. As a consequence, the development of composite construction materials with low thermal conductivity by using wood by-products would be an interesting alternative that may help solve simultaneously energy and environmental concerns.

Materials and methods: In this study wood processing by-products were used for producing lightweight mortars by replacing natural sand at three different percentages: 2.5%, 5%, and 10% by volume. Wood by-products were pre-soaked in Ca(OH)₂ aqueous solution in order to obtain wood mineralization. Mortars containing wood by-products were characterized by means of compression and bending tests, free drying shrinkage, water vapour permeability, capillary absorption, as well as thermal conductivity measurements.

Results and discussion: The higher dosage of wood waste (10% instead of 5%) seems to dramatically worsen mortar mechanical performance (compressive strength never resulted higher than 5 MPa). A lower sand to cement ratio (1:2 instead of 1:3) allowed to reach 28-day compressive strength values of 20 MPa and 10 MPa, when adding 2.5% and 5% sawdust, respectively. WRA addition allowed to reduce the amount of water dosage by 20-25%, in this way values of 28-day compressive strength higher than 30 MPa (triple) were reached.

Wood by-products addition produced remarkably less evident detrimental effects on flexural strength than compressive strength, most likely due to the fibrous structure of the wood chips.

Mortar unit weights showed that lightweight mortar can be produced when at least 5% wood by-products is used. Therefore, only a mortar strength class of 10 MPa is achievable by adding wood by-products for producing lightweight mortars; nevertheless, the addition of WRA proved to be effective by allowing to reach a mortar strength class of 25 MPa.

In terms of drying shrinkage, significantly higher shrinkage was detected in the presence of wood waste and the reason probably lies in the very high water absorption of wood waste.

The addition of wood waste seems to show positive influence on lowering both resistance to water vapor permeability and thermal conductivity, which

resulted 25% lower by adding 5% waste material; on the other hand capillary water absorption resulted a little increased.

PREDICTING THE RESIDUAL STRENGTH OF OPEN-HOLE (OH) COMPOSITE SPECIMENS SUBJECTED TO CYCLIC LOADING

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Introduction: A procedure is reported that allows the prediction of the fatigue life and the residual strength of "open hole" composite specimens subjected to constant amplitude cyclic loadings.

Materials and methods: The approach reliability is checked in predicting the fatigue life and residual strength of AS4 carbon/epoxy 3k/E7K8 Plain Weave Fabric "open-hole" (OH) samples subjected to a very broad loading conditions from prevailing tension ($R = 0$ and $R = -0.2$) to compression ($R = 5$) to mixed tension/compression ($R = -1$) loadings

Results: The analysis allows us managing simultaneously the problematic of fatigue life and residual strength through a single, easy to obtain, set of parameters

Discussion: Along with the growth in composites usage the understanding of size effects and the mechanisms of notched failure are becoming increasingly important areas of research. A phenomenological two-parameter model, based on strength degradation, has been used to predict the residual strength and the fatigue life of "open hole" carbon/epoxy laminate subjected different loading conditions from pure tension to compression and mixed tension/compression. The procedure illustrated in this paper is the same used for un-notched samples and confirms the model reliability in terms of both fatigue life and residual strength predictions. It was argued that the same procedure can be applied when prevailing compression loadings are under concern, provided the pertinent set of model parameters is found. Depending on the mode of loading, the damage accumulation mechanisms show different kinetics and this will be reflected (even if not strictly correlated) to the strength degradation kinetics, and exclude the possibility for the parameters of the adopted model to be considered as truly material constants. However, the approach seems quite promising, yet it requires further verifications on different data sets and different materials.

DEVELOPMENT AND CHARACTERIZATION OF DEVICES FOR THE CONTROL OF THE AIR QUALITY IN INDOOR ENVIRONMENTS

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Introduction: Indoor air quality control is becoming increasingly important in relation to complex form of pollutants, i.e. solid particulates, bacteria, volatile organic compounds (VOCs). The filtration systems developed so far are able to block solid particulate and bacteria. However, they are not able to eliminate individual sources of pollution or to reduce their emissions due, for instance to the ability of bacteria to colonize the surfaces of such filters. Here we proposed a new class of TiO₂-treated activated carbon filters and studied both their filtration efficiency and photo activated surface-mediated antibacterial properties.

Materials and methods: We compared the performances of a traditional filter, a commercial antibacterial filter, and a TiO₂-treated activated carbon filter. The filters were inserted downstream of an air circulation fan and illuminated by means of UV LEDs, to induce activation of photo-catalysis. As a comparison an ionization device was also tested

Bacterial viability tests were carried out directly onto filter surfaces. Solid particulate and VOC were performed in a confined environment after contamination with suitable pollutant (cigarette smoke) up to 24 H.

Results: The ozonator did not induce any reduction of solid particulate, bacteria and VOCs while it was able to efficiently reduce odours. Untreated filters showed the ability to block solid particles and bacteria: however, bacteria remained viable.

Common filters treated with antimicrobials block solid particulate and bacteria, that are inactivated at least in the short term, but resulted in a negligible reduction of VOC.

Activated charcoal filters treated with TiO₂ and illuminated by UV LED system were able to efficiently filter solid particulate, VOCs and bacteria both allowing for their long-term inactivation. Their abatement capacity was closely

linked to the number of volume changes per hour, thus as a function of the fan system used.

Discussion: Experimental results showed that commercial filters are able to reduce indoor pollutants in a selective way, while the TiO_2 -treated activated carbon filters support both the reduction of all the contaminants and a significant reduction of secondary sources along the time. The tests carried out have in particular made it possible to optimize a device with 4 fans $92 \times 92 \times 25$ mm³, low noise, capable of a significant rapid reduction of smoking cigarette pollution and, by analogy, to traditional types of indoor environmental pollution (vehicular traffic, cooking food, etc.).

ASSESSMENT OF PHASE DIAGRAMS IN COMPLEX HYDRIDES

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Introduction: Complex hydrides are studied for various applications, including hydrogen storage, electrochemical energy storage, heat storage and, more recently, CO_2 capture/conversion. In all cases, thermodynamic properties and phase diagrams have to be known in details. The Calphad approach is a useful tool for the investigation of complex hydrides, being able to provide thermodynamic properties at different temperatures and pressures. However, the lack of reliable databases for hydrides is still a bottleneck toward a reliable use of this approach.

Materials and methods: Experimental data on temperature and enthalpy of phase transformation have been obtained for various complex hydrides by HPDSC under hydrogen pressure. Ab initio DFT calculations have been performed by the CRYSTAL program. In order to compute an enthalpy of reaction at $T = 298.15$ K and $P = 1$ atm, the computed electronic energy has been corrected for the zero point energy. Thermodynamic modeling has been carried out according to the Calphad approach.

Results and discussion: Assessed phase diagrams have been obtained for pure borohydrides, i.e. $NaBH_4$, $LiBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$. In several cases, it is observed that stable phases cannot be obtained experimentally during phase transformations, so that metastable phase diagrams have to be considered. From available database, the effect of anion and cation substitution in borohydrides has been considered and an estimation of interaction parameters has been obtained.

The description of thermodynamic properties of the liquid phase in borohydride systems remains a big challenge, because of lacking of experimental data. Examples of phase diagrams will be provided for eutectic mixtures (e.g. $LiBH_4$ - $NaBH_4$), often infiltrated into porous scaffolds to enhance hydrogen sorption properties.

The combination of different complex hydrides (e.g. $LiBH_4$ and $LiNH_2$) brings to the development of compounds with new crystal structures, characterized by open channels for fast Li-ion mobility. A description of thermodynamic properties has been obtained for $Li_4(NH_2)_3(BH_4)$ and $Li_2(NH_2)(BH_4)$ compounds, allowing the assessment of the $LiBH_4$ - $LiNH_2$ phase diagram.

SELF-CLEANING ABILITY AND COOLING EFFECT OF TiO_2 -CONTAINING MORTARS

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Introduction: The diffusion of TiO_2 -modified building materials has been constantly growing, especially in European countries, as attested by the number of publications, patents and international projects. This is correlated with the increase in the generation of pollution and depletion of natural resources caused by the intense and rapid industrial expansion, which pushes towards the development of sustainable materials, technologies and energy sources. The work here presented focuses on the characterization of a self-cleaning and photocatalytic system for building façades, aimed at improving urban surfaces and the surrounding air quality.

Materials and methods: Commercial mortars containing nanometric powders of anatase TiO_2 were considered; the addition of pigments to the mix proportion was also investigated by choosing different types of iron oxide pigments: Fe_2O_3 , Fe_3O_4 , $FeOOH$ or a mixture of the three, producing a red, gray, yellow or brown color, respectively. Mortars were characterized by photocatalysis tests, performed through the degradation of a model volatile organic compound, IPA (2-propanol), under UV irradiation. Exposure tests

in environmental conditions were then performed to evaluate the mortars self-cleaning attitude – depending not only on the material composition, but also on atmospheric conditions. Samples were exposed facing south, to maximize the amount of solar radiation that could reach the surfaces. Visible light reflectance spectra gave precious information on the surface soiling, and the consequent alteration of chromatic coordinates with environmental exposure (typically, a brightness decrease).

Results: Concerning photocatalytic activity tests, in all cases, white mortars caused 50% decomposition of IPA in 23 h on average, while colored ones exhibited a lower efficiency (30%), independently on the type of pigment, indicating that the iron-based pigments added to the mixture proportion inhibited the photocatalytic efficiency of TiO_2 of almost 40%.

Photocatalytic mortars were also exposed to the urban environment for 7 months, and soiling due to the adsorption of dust and polluting agents was monitored by spectrophotometry. Mortars containing TiO_2 underwent a smaller brightness variation compared to non-photoactive ones; they also experienced a yellow shift of surface color, owing to partial decomposition of organic contaminants adsorbed on the surface. This behavior proved the onset of the self-cleaning mechanism, activated by solar radiation from the 3rd month of exposure.

Discussion: The reduced photoactivity of colored mortars was ascribed to possible interactions of TiO_2 with iron oxides, and specifically to an enhanced recombination of photogenerated electron/ hole couples: this enhanced recombination effect is often observed in coupling TiO_2 with iron oxides in exceeding concentration, and is responsible for the reduction of photocatalytic activity.

INTERACTIONS BETWEEN FUNCTIONALIZED THERMOPLASTIC ELASTOMER AND LAYERED DOUBLE HYDROXIDES

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Introduction: The state of interface between matrices and nanofillers in polymer-based nanocomposites is a key factor to obtain advanced materials with enhanced properties. Particularly, the establishment of strong interactions between the two phases allows to obtain materials with engineered interface, suitable for several specific fields of application. In this work, nanocomposites based on maleic anhydride-grafted styrene-ethylene-butylene-styrene (SEBS-g-MA) copolymer and organo-modified layered double hydroxides (o-LDH) have been produced with the aim to understand the interactions at the interfacial zone. Specifically, the rheological behaviour of SEBS-g-MA/o-LDH has been deeply investigated and compared to that of pristine SEBS-based nanocomposites.

Materials and methods: Block copolymers SEBS-g-MA (Kraton® FG1901X) and SEBS (Kraton® G1633E); Organo-modified Layered Double Hydroxides (o-LDH) (Perkalite® F100S). Nanocomposites have been prepared in a Brabender mixer at 180°C, 50 rpm, 5 min, using 1, 2.5 and 5 wt.% of nanofillers. Rheological analyses (frequency sweep, time sweep and stress relaxation) have been carried out through an ARES-G2 at 180°C. Morphology of the systems has been evaluated through SEM and TEM observations. Interactions between matrices and nanofillers have been assessed through FTIR analysis.

Results: The addition of the o-LDH to pristine SEBS brings about a shift of the complex viscosity curves toward higher values with respect to the neat matrix, without substantially modifying the rheological behaviour. Differently, in SEBS-g-MA-based nanocomposites containing high amount of o-LDH significant alterations of the rheological behaviour can be noticed. Particularly, G' and G'' moduli tend to become almost independent from frequency and curves of tan δ vs ω show a well pronounced maximum. Stress relaxation analysis reveals that neat and functionalized SEBS experience degradation phenomena, involving crosslinking during test, recognizable in a upturn of G(t) curves at longer times. Concerning neat SEBS-based nanocomposites, the addition of 5 wt.% of o-LDH causes a significant increase of G(t) at long times, related to the interparticle attraction and flocculation phenomena, as probed by time sweep rheology measurements performed on the same sample. The SEBS-g-MA/o-LDH nanocomposites containing 2.5 and 5 wt.% of o-LDH show almost constant G(t) trends for the whole investigated time interval, while the nanocomposite with low o-LDH content exhibits a similar behaviour to neat matrix. Also, in this case, the time sweep analysis helps to understand the underlying phenomenon, suggesting that in nanocomposite the rise of G(t) is not attributable to

degradation but it could be due to reaction between SEBS functionalities and o-LDH in the course of test. Morphology analysis reveals that a good dispersion has been obtained using both matrices and a higher degree of exfoliation of o-LDH is achieved in SEBS-g-MA nanocomposites.

Discussion: Results coming from rheological analysis clearly suggest that in SEBS-g-MA-based nanocomposites, containing high amount of o-LDH, the formation of strong interactions between the dispersed nanoparticles and maleic functionalities of matrix occurs. A significant modification of the rheological behaviour can be noticed due to the formation of gel-like structures.

EFFECT OF GRAPHENE OXIDE ADDITION ON THE MECHANICAL AND THERMAL PROPERTIES OF CEMENT-BASED COMPOSITES

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Introduction: Nano-engineered concrete (NEC) can be obtained by using carbon-nano particles such as graphene, graphene oxide (GO), carbon nanotubes (CNTs). In particular, GO has a promising future in NEC because the 2D GO nanosheets provides an extra dimension to interact with cement-based matrix (planar structure of graphene sheets creates significant contact area). The excellent intrinsic properties of the 2D GO nanosheet can strengthen the brittle cement matrix. Furthermore, the GO oxygen-bearing functional groups are desirable for homogeneous dispersion in cement, nucleation of C-S-H and densify the microstructure.

Materials and methods: In this paper the effect of low content of GO (ranging from 0.02 to 0.05% by weight of cement) on rheology and mechanical performance of OPC paste was tested. Careful attention has been dedicated to the mixing of GO nanoparticles because their agglomeration is a common problem due to the strong van der Waal's attractive forces at the nanoscale (dispersion was obtained by means of sonication in the presence of proper admixture to avoid re-agglomeration). Then, GO suspension (ranging from 5% to 10% by weight of cement) was used to prepare several nano-engineered concretes (NECs), in which quartz sand was added, as well as several kinds of chemical admixtures such as water-reducing, shrinkage-reducing and antifoaming admixtures. Besides to GO other mineral additions were used: limestone powder, microsilica, and CaO-based expansive agent. Moreover, in certain cases also brass-coated metallic fibers were added at a dosage of 2% by weight of NEC. These mixtures were characterized in terms of fresh consistency, then from a mechanical point of view by compression and bending tests carried out after 1, 7 and 28 days of curing. Finally, these mixtures were also characterized in terms of thermal conductivity by means of guarded hot plate apparatus according to EN 12667.

Results: The addition of 0.05% GO on cement paste produced a 20% increased 28-day compressive strength, while fresh consistency and flexural strength remained practically unchanged.

The addition of either 5% or 10% GO on NECs required an extra dosage of water reducing admixture in order to compensate their high water demand. Both dosages produced a detrimental effect on compressive strength of about 15%, while in terms of flexural strength 10% addition left the value unchanged and 5% produced 15% increase. However, the addition of brass-coated metallic fibers resulted significantly more effective (fourfold bending strength).

In terms of thermal conductivity the addition of 5% and 10% GO reduced the value by 4% and 20%, respectively, while the addition of brass-coated metallic fibers increased the value by 23% (as already expected on the basis of data reported in the literature indeed).

Discussion: In general, results obtained by adding GO suspension were less significant than expected on the basis of some works reported in the scientific literature. In particular, the use of the less expensive brass-coated metallic fibers, even if used at a high dosage of 2% by volume of NEC, proved to be more effective than GO addition in enhancing both flexural strength and thermal conductivity.

ANTIMICROBIAL SILVER ZEOLITE BASE DI COATING FOR INTRA ORAL MAGNETS

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Introduction: Corrosion-inducing potential of intra-oral permanent magnets in the presence of a microflora can be amplified and the subsequent cyto-

toxic products release can be a cause for concern other than the lowering in magnetic properties. Metallic surfaces in saliva can permit the formation of a biofilm. Considering the high water uptake of the surrounded environment corrosion process can be generate. However, a system able to supply stability and biocompatibility to the whole magnetic assembly has not been taken into account until now. This study focused on avoiding the corrosion of neodymium-iron-boron magnets through the design of a functionalized coating able to prevent biofilm formation.

Materials and methods: Zeolite 4A, sodium-type zeolite was used as the host compound. Silver ions were loaded into the zeolite by the ion-exchange method. The suspension was stirred at room temperature in the dark for 24 h, then centrifuged, washed and air-dried at 90°C overnight. The silane solution consisted of 5.0 vol.% of N-propyl-trimethoxy-silane dissolved in 95/5 volume ratio ethanol/water mixed solvent. The precursor was pre-hydrolysed through magnetically stirring, at 25°C, for 24 h. Silver-zeolite (SZ) powder will be added to the silane solution to produce three different solutions with 20%, 50% and 70% in weight of silver-zeolite. All the samples have been immersed in the solution by dip-coating technique for 30 sec. The samples have then been dried at 70°C for 24 hours. Contact angles θ measurements were performed by Attension Theta equipment (Biolin Scientific). In addition, antimicrobial test have been carried out.

Results: The samples coated with thirty layers of silane showed an higher contact angle compared with bare nickel plated magnets, in particular the wettability angle increases from 74° to 97°. However, the achievement of hydrophobic films, with contact angles greater than 90°, can be observed for samples coated at increasing content of SZ filler. The antibacterial activity of SZ at different concentrations against *S.mutans* can be observed in all the agar plates. On the contrary, in the control group a greater bacterial growth can be described (1×10^6 CFU/g after 24 hours).

Discussion: The presence of SZ filler in the silane matrix increases the crosslinking density resulting in a reduction of the wettability on the surface, decreasing both the contact area and the interaction with the biological/electrolytic solution. The silane-SZ coating showed enhanced durability, good adhesion, high chemical resistance and high thermal properties. In addition, this coating guarantees both to reduce the number of adhesive streptococci as well as to increase the bacteria death and inactivation rate on the material surface. The SZ-based mixture acts as ion pump permitting the continuous and controlled release of small amounts of silver ions in the solution permitting to obtain a potential long-lasting antimicrobial material.

CALCINED WATER TREATMENT SLUDGE AND SEDIMENTS AS GEOPOLYMER PRECURSOR

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Introduction: Innovative management solutions are required for hydraulic reservoir since silting is an unavoidable issue. It is estimated that in Italy, the potential rate of silting in large reservoirs ranges from 0.1% up to 1%. Hence, the dredging activities can be expected to strongly increase in next decades, producing huge volumes of sediments. In this work, we study the calcination of dredged sediments and water treatment sludge for the production of geopolymer binders. These materials, at present, are considered as waste and must be disposed of in landfill or can be used for filling of disused quarries or for nourishment. The residues were previously characterized from the chemical point of view and, afterwards, a calcination process was carried out to produce solid precursors geopolymers binders.

Materials and methods: The chemical analysis was carried out by means of XRF and XRD. After the detection of main chemical parameters, both residues, calcined at a temperature of 750°C for 2 hours. In order to obtain insight into the influence of different Si/Al ratios, three mixtures were prepared using different sludge/sediment ratios, namely: 70/30 (M1), 50/50 (M2), 30/70 (M3). The curing conditions were: 24 h at room temperature and 24 h at 60°C; in both cases samples were then placed 6 days in a >95% RH environment. After 6 days of curing the compressive strength was measured.

Results: The results show that silica and alumina are the most abundant components (sediment sample: $\text{SiO}_2 = 50.95\%$, $\text{Al}_2\text{O}_3 = 16.86\%$; sludge: $\text{SiO}_2 = 34.64\%$, $\text{Al}_2\text{O}_3 = 28.07\%$) and, in particular, a molar Si/Al ratio very close to unity for sludge is observed. The XRD shows the presence of clays, quartz, calcite and feldspar as main mineral phases in sediment and quartz, gibbsite and clay in the sludge. M1/25°C and M1/60°C exhibited a compressive

strength equal to 21.88 and 11.24 MPa, respectively. This result indicates that the best curing condition (higher strength) is also the one which is more sustainable. M2/25°C and M2/60°C showed values equal to 19.60 and 19.14 MPa, confirming good results without the need of curing temperature increase. Finally, M3/25°C and M3/60°C reported values equal to 17.87 and 19.03 MPa, respectively. The general conclusion is that optimized geopolymers can be a high value added solution for the simultaneous recovery of water treatment sludge and clayey sediments after calcination.

DURABILITY BEHAVIOR OF BIO-EPOXY/JUTE-BASALT HYBRID COMPOSITES FOR CLADDING

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Introduction: The technology of dry assembly to produce multi-layer panels is an efficient alternative to traditional systems. Eco-sustainable systems are increasingly studied, particularly fiber reinforced composites for external cladding, based on natural fibers. However, the durability of these composites gives serious concern, in particular for their potential use in outdoor applications. To overcome this drawback, hybridization of natural fibers with mineral fibers as basalt ones appears promising. In this paper, the aging resistance of jute-reinforced laminate was compared with those of two hybrid laminates.

Materials and methods: A bio-based epoxy, named Super Sap 100/1000, was used as matrix. The laminates were manufactured through vacuum infusion and cured for 12 h at room temperature. All the laminates were manufactured by varying the number of layers to obtain similar volume fractions (i.e. ~30%) and thicknesses (i.e. ~5.50 mm). In particular, jute reinforced laminate was manufactured using eight layers of jute plain weave fabric (areal density of 290 g/m²). The hybridization of jute was performed using unidirectional basalt fabrics (areal density of 300 g/m²). Two hybrid laminates were manufactured. In the first one, layers were stacked as a sandwich sequence with six jute reinforced layers as core and two basalt layers as skins, for each side of the laminate. In the second hybrid laminate, jute layers were alternatively stacked with basalt ones. The laminates were exposed to accelerated aging in a climatic chamber developing aging cycles of hydrothermal stress and UV radiation, for a period of 56 days. Flexural tests, Charpy impact tests and dynamic mechanical tests (DMTA) were performed on specimens taken out from the climatic chamber at different exposition times (i.e. 0, 14, 28 and 56 days).

Results: The results showed that the flexural properties of the unaged hybrid laminates (i.e. both sandwich and intercalate configuration) are higher than those of the unaged jute laminates. In particular, the flexural strength and modulus of the sandwich laminate are 73% and 88% and the ones of the intercalated laminate are 112% and 110% higher than those of jute laminate, respectively. Moreover, the aging exposition leads to the slightest decrease of these properties for the sandwich laminates.

As concerns the impact properties, an improvement of the strength is found at the beginning of the aging exposition followed by a subsequent decrease, for each laminate. Even in this case, the sandwich configuration showed the best behavior. The DMTA showed that all the laminates, in the first phases of the aging, showed an increment of the Tg values and a decrease of the tan δ peaks. An inversion of both trends is found after 28 aging days.

Discussion: All the achieved results can be explained taking into account three competitive mechanisms (i.e. post-curing, plasticization and degradation phenomena). Anyway, these mechanisms affect the aging behavior of the laminates in a different way thanks to the protective role played by the external basalt layers. In particular, the sandwich configuration represents the best solution thanks to both thicker external basalt layers and lower number of basalt/jute interfaces.

NEW HEAT RESISTANT β -TI ALLOYS

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Introduction: Titanium alloys can be classified in three main groups, α , β and α - β according to their structure.

Among these, β -Ti alloys display good mechanical properties at medium-high temperature and are cold formable in most cases. However Ti alloys for aero-engines applications may undergo the so-called "titanium fire" under operating conditions. Burn resistant alloys are known in the ternary Ti-V-Cr system. The present work explores a few new compositions of this alloy family.

Materials and methods: Alloys with composition $Ti_{60}V_{20}Cr_{20}$, $Ti_{60}V_{20}Cr_{10}Zr_{10}$, $Ti_{60}V_{20}Cr_{18}Zr_1Ru_1$ and $Ti_{60}V_{20}Cr_{16}Zr_2Ru_2$ at.% were prepared by arc melting high purity elements.

Phase constitution was checked by microscopy and x-ray diffraction. The hardness has been tested by Vickers indentation and rolling deformation has been established at room temperature. Oxidation tests were performed by measuring mass gain.

Results and discussion: Three alloys ($Ti_{60}V_{20}Cr_{20}$, $Ti_{60}V_{20}Cr_{18}Zr_1Ru_1$ and $Ti_{60}V_{20}Cr_{16}Zr_2Ru_2$) were found to be fully b after arc melting. The alloy $Ti_{60}V_{20}Cr_{10}Zr_{10}$ is resulted $a+b$. The b microstructure is retained up to the highest temperature reached in this work (800°C) with minor precipitation of a Laves phase. The hardness spans a range between 370 HVN and 450 HVN both in the as-cast and annealed states.

The alloys can undergo deformation up to 4-5% before the development of cracks at room temperature.

The mass gain because of oxidation remains below 1 mg/cm² up to 600°C and increases to 9 mg/cm² when annealing for 15 h at 800°C.

HYDROGEN EMBRITTLEMENT OF A MARTENSITIC STAINLESS STEEL: INFLUENCE OF CATHODIC POTENTIAL

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Introduction: It is well known that in the presence of H₂S, metals, such as carbon and low alloy steels, may suffer hydrogen embrittlement (HE); prevention is carried out limiting the hardness of the material, according to ISO standard 15156. It is also well known that for high strength steels cathodic overprotection can favour hydrogen embrittlement (HE) even in absence of H₂S.

In the paper the effect of potential and residual stresses on the susceptibility to hydrogen embrittlement is studied.

Materials and methods: The studied material is a high strength martensitic stainless steel type AISI 420 (quenched and tempered), hardness 58 HRC, very susceptible to hydrogen embrittlement. Constant deformation tests (three point bending) according to NACE TM0177 method B have been carried out on Bent-Beam specimens cathodically polarised in acetic solution, pH 5.5 at room temperature, without addition of H₂S: specimens have been stressed at different level in the elastic range (from 20 to 90% of the yield strength).

Results: At potential higher or equal to -0.70 V vs E_{Ag} (Ag/AgCl/3 mol L⁻¹ Cl⁻) and for stresses lower than the yield strength (YS), the material AISI 420 C appears not susceptible to hydrogen embrittlement. At potential less noble than -0.70 V (vs E_{Ag}), the threshold stress is lowered, for example at E = -0.90 V (vs E_{Ag}) tends to values around 60% of YS.

The presence of defects, as residual stresses, worsens significantly the behaviour. Critical stress threshold is lowered to 20% of the yield strength and time to failure is reduced.

In case of absorption of hydrogen prior the testing, even without failure of the specimens and in conditions that promote the release of a large amount of hydrogen previously absorbed, the results are more critical: in correspondence with the threshold stress the time to failure is reduced and the number of failed specimens is increased even at more noble potentials.

Discussion: The experimental results showed that, even in the case of a material highly susceptible to HE, it is possible to find protection potential/applied stress fields where this type of damage is not probable. Assuming more severe and conservative conditions, like the presence of residual stresses due to mechanical damage, the threshold of these fields is modified significantly.

Nevertheless, in the case of tougher material and less susceptible to HE, these results suggest the possibility to prevent hydrogen embrittlement by means of proper application of cathodic protection. In any case, the operating parameters (protection potential) shall be assessed through suitable testing carried out in conservative and critical conditions.

HEMP REINFORCEMENT IN HYBRID CERAMIC FOAMS

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Introduction: Because of the strong impact of the building industry onto the environment, developing new materials with a reduced environmental impact has become a very important issue. Reducing the use of not renewable resources is a possible way to accomplish this goal. In the case of composite materials used for thermal insulation, the possible substitution of inorganic mineral fibers with natural ones from agricultural resources is one of the studied routes. Composites containing natural fibers from agricultural resources have been extensively studied, as natural fibers exhibit several positive characteristics: low thermal conductivity, low density, good specific tensile properties, obtained from renewable resources.

In this paper, novel hemp-based composite materials are presented and the results of a preliminary physical, thermal and mechanical characterization are reported and discussed. The composites were obtained by impregnating hemp fibers/grid with a new hybrid organic-inorganic foam.

Materials and methods: The Sodium Silicate (SS) (Na_2O 8.15%, SiO_2 27.40%) was provided by Prochit Italia Srl; the silico-aluminate powder, metakaolin (MK), has following composition: Al_2O_3 42 wt%; SiO_2 53 wt%; K_2O 0.60 wt%; Fe_2O_3 1.70 wt%; TiO_2 1.83 wt%; MgO 0.50 wt%; CaO 0.37 wt%. Si metal powder and Na_2SiF_6 catalyst were purchased by Merck and Sigma-Aldrich, respectively. Vegetable protein in water solution Isochem S/L (pH 7) was supplied by Isotech s.r.l.. As filler of the ceramic matrix hemp fibers and fabric was used.

Two composite were produced using chopped hemp fibers (CHC) or hemp grid (GHC), respectively. Composites have been subjected to physical, morphological and mechanical tests to provide their characteristics.

Results: The physical and morphological characterization showed a good stability of the composite to the thermic variation, in fact after heating cycle the composite showed a negligible variation of mass and volume.

The mechanical properties in a composite depend mostly on the fiber content and orientation, and also on the quality of the load transfer between the matrix and the reinforcement. This fact is closely related to the strength of the interface and consequently to the quality of bonding between the matrix and the fibers. Mechanical characterization showed an improved of resistance to flexural failure, from blank matrix (HCF) to GHC.

Discussion: Composite showed a good behavior at high temperature and despite the presence of fibers, density of the blank matrix is not very different than the one of the CHC or GHC. Moreover, composite showed an increase of mechanical behavior compared to the HCF. Particularly hemp fiber grid reinforcement can provide a significant improvement of the flexural behavior of the geopolymeric matrix; these composites could be consequently interesting in building applications.

UPGRADING OF POLYOLEFIN RECYCLED BLENDS BY ADDING POLYAMIDE NANOCOMPOSITES

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Introduction: In recent years, numerous researchers have reported that the addition of nanoscale fillers could affect the dynamic phase behavior and morphology of blends. The relative simplicity of this method, and the fact that it is applicable to a wide variety of blends, makes it an attractive alternative to current technologies in processing polymer wastes for which the composition can vary in an unpredictable manner and cost is a primary factor. The principal aim of this study was the upgrading of mixed polyolefin wastes through the addition of a sepiolite clay to obtain recycled products with improved properties. Moreover, a virgin polyamide and its nanocomposite with sepiolite, were also added to the recycled material in order to combine the advantages of the addition of a high performance plastic and the merits of polymer nanocomposites, also taking benefit of the function of nanofillers as potential blend compatibilizers.

Materials and methods: The recycled material, used as matrix, comes from flexible packaging wastes and it is mainly constituted of polyethylene and of

a small fraction of polypropylene. This recycled polyolefin blend was melt compounded with an organo-sepiolite having a needle-like shape (PM15, supplied by Tolsa) in a twin-screw extruder.

Nanocomposite systems at several contents (5,10 and 20 wt%) of sepiolite PM15 were also prepared by melt compounding, using as polymer matrix a copolyamide 6/66 (CS40LXW by Radici Group). Different amounts (2.5 and 5 wt%) of both the neat polyamide and its nanocomposite at 20% of PM15 were added to the recycled material in the twin screw extruder.

The dynamic viscoelastic properties of the materials were measured using a rotational rheometer; meanwhile, a capillary rheometer was used to investigate the processability.

Ribbons of the neat matrix and the corresponding nanocomposites were produced by means of a single screw extruder and were submitted to thermal (by DSC) and mechanical (according to ASTM D-638) characterization.

Results: The addition of both the neat polyamide and its nanocomposites to the recycled material determined interesting improvements in the mechanical properties of the post-consumer polyolefin blends. In particular, the recycled material with 2.5 wt% of copolyamide based nanocomposite at 20 wt% of sepiolite showed a very remarkable enhancement of ductility and, at the same time, a Young's modulus comparable to that of the recycled matrix.

Discussion: To effectively enhance the compatibility between different components of a polymer blend it is necessary to have a favorable interaction between the clay and at least one of the polymers in the mixture. To this purpose, a fine dispersion of the sepiolite nanoparticles was obtained in the copolyamide hybrid systems, due to the polarity of the matrix and the formation of strong interactions (H-bonds) between polymer and clay. Whereas, the addition in the recycled material of the sepiolite alone does not work so well either as nano-reinforcement either as compatibilizing agent, since it presents low affinity with both the main polymeric components of the recycled plastic.

IMPROVING INDOOR AIR QUALITY WITH PASSIVE SYSTEMS: A NEW PERSPECTIVE FOR SUSTAINABLE INDOOR BUILDING MATERIALS

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Introduction: In order to reduce energy consumption in buildings, more isolated and sealed structures are designed. The resulting poor air changing decreases indoor air quality in terms of not adequate levels of indoor humidity and high concentration of pollutants. Reactive building materials offer an opportunity to provide indoor air cleaning with minimal energy use. This research focuses on the development of innovative and multifunctional mortar for indoor panels with low environmental impact able to improve comfort and health of occupants. This material exploits the positive interaction between different constituents usually used separately (e.i. wool insulating panels or lime-zeolite mortars).

Materials and methods: Hydraulic lime is used as binder. Water/binder is 0.54 by weight. Aggregate/binder is 3.5 by volume. Standard mortar (STD) is manufactured with calcareous sand with maximum diameter (D_{max}) of 400 micron. From this recipe, 25% of aggregate volume is replaced with wool natural fibers due to their well-known thermal properties. Two mixes with different aggregates were prepared: one with sand (M1) and the other with zeolite (M2), D_{max} 250 micron. Workability and mechanical strength are tested according to the current standards. Morphology and microstructure of mortar are investigated with Scanning Electron Microscope (SEM). A simplified version of NORDTEST method is assessed for testing the moisture buffer performance. Depollution properties are evaluated monitoring the adsorption of a known quantity of Methylmethylethylketone (MEK) in a closed box.

Results: Workability results show that all mortars have the same stiff consistency when aggregates and fibers are pre-soaked for 24 hours and then added in the mix in saturated surface dry condition.

M2 is classified as lightweight mortar with the lowest density r equal to 1180 kg/m^3 , for STD mortar r is 1810 kg/m^3 and for M1 r is 1490 kg/m^3 .

Mechanical performances are influenced by the presence of wool fibers and the typology of aggregates with values of compressive (R_c) and flexural strength (R_f) ranging from $R_c = 5.6 \text{ MPa}$ $R_f = 1.2 \text{ MPa}$ for STD mortars to $R_c = 2.5 \text{ MPa}$ $R_f = 1.5 \text{ MPa}$ and to $R_c = 5.9 \text{ MPa}$ $R_f = 3.5 \text{ MPa}$ for M1 and M2 mortars, respectively.

The interaction with indoor environment is appraised with the evaluation of Moisture Buffering Value (MBV) and percentage of MEK adsorbed after 2 hours test. For the first, there is an enhancement of 40% and 150% in M1 and M2 mortars, respectively, in comparison with STD mortars. For the second, STD and M1 adsorb 80% whereas M2 adsorbs 40% of MEK after two hours test.

Discussion: Regardless lightness, zeolite with its pozzolanic activity helps to overcome the loss of compressive strength of mortars manufactured with fibers. However, flexural strength is increased up to 25% by fibers in M1 and up to 300% by zeolite in M2. Also in terms of depollution and moisture buffering ability, M1 and, especially, M2 mortars (zeolite and wool) show increased performances. In this prospective, also a 1:2 scale of real panel is successfully prepared with M2 mix.

EVALUATION OF DIFFERENT CLEANING METHODOLOGIES FOR THE CONSERVATION OF OUTDOOR BRONZES

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Introduction: Cleaning of cultural heritage surfaces is always a very important and delicate step. It is often a necessary procedure to both reduce degradation rate and guarantee a proper readability of works of art. However, it may lead to the loss of precious layers and to an initial temporary increase of the deterioration rate due to the reactivation of the surface. Before cleaning, it is therefore important to characterise the surfaces and their stratigraphy, in order to identify which are the layers to be removed and which are the ones that need to be preserved. Furthermore, there are many different methodologies that can be followed and it is important to identify the most suitable one depending on the conservation conditions of the surface. In this study, six different bronze statues have been characterised in terms of patina composition, colour, surface appearance and corrosion rate. Four different cleaning procedures have been tested and compared in order to choose the most suitable for each statue.

Materials and methods: The six different bronze statues are currently under restoration and are located at the *Cimitero Monumentale* of Milan. They have been selected according to their different conservation conditions. Surfaces and patinas have been characterised by the following techniques: VIS-spectrophotometry, digital portable microscopy, FTIR, XRD and SEM-EDX. Corrosion rate has been evaluated by LPR and EIS in-situ measurements.

Results: Results have shown that in some cases residues of previous organic treatments are still present over the surface. Patinas are mainly constituted by basic copper sulphates. The corrosion rate is strongly related to the presence of organic coatings, which, if still continuous, provide some protection to the statue. However, in other cases corrosion rate is quite high but can be significantly reduced by a proper cleaning procedure.

Discussion: The investigation further underlined the fundamental importance of a scientific diagnostic protocol in order to define the most proper cleaning procedure. It also allowed a deeper understanding of the impact that the different cleaning procedures may have on the corrosion rate of artefacts and to correlate it to the different initial conservation conditions.

EFFECT OF THE SHORT TIME CHAIN MODE ON THE STRUCTURAL RELAXATION OF AMOUPHOS POLYMERS

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Introduction: It is generally believed that the segmental model is the main relaxation mechanism that affects the structural relaxation in the vicinity of the glass transition. Recently data from C. Roth showed that ultra-thin polymer films have a double glass transition; this experimental evidence was explained by K. Ngai assuming that the upper glass transition was due to the Sub-Rouse mode of relaxation. Furthermore D. Cangialosi found out a double equilibrium plateau observing the enthalpic relaxation of ultra-thin polymer films. These two experimental evidence suggested that short time chain modes can have a role in the bulk relaxation mechanism of amorphous polymers.

Materials and methods: Shear and bulk rheology data of linear polystyrene, star polystyrene was examined in terms of shear and bulk retardation spectra. The shear spectra were fitted assuming that each mechanism responsible of

the softening dispersion can be described by a stretched exponential function and that the mechanisms are additive in strain. The effect of each mechanisms on the bulk relaxation was revealed by comparing the timescale window of each mechanism extracted from the shear response to the timescale range of the bulk response.

Results: The analysis shows that the timescale of the bulk compliance mainly covers those timescales of the segmental response but it is not confined to that extending up the faster timescales typical of the sub-Rouse modes. It is also found that the relaxed segmental compliance is only two times larger than the short time limit of it in contrast with the assumption of Ngai and Plazek that frequently reported a factor of 4.

Discussion: The contribution of the short time chain modes (also called sub-Rouse modes) to the structural relaxation is possible but it is not prevalent with respect to the segmental mode that rests to be the main one. These results are consistent with the finding of McKenna that the thermal expansion coefficient of linear polymers still evolves even if the number of backbone bonds overcomes 20. The results could also explain the double plateau observed by Cangialosi but it is not compatible with the double Tgs evidence observed by Roth and explained by Ngai: the contribution to the strength of the glass transition of the sub-Rouse is lower than that of the segmental and consequently the ultra thin polymer films upper Tg, that is the strongest one, cannot be related to the sub-Rouse mechanism.

PROPERTIES OF SELF-COMPACTING AND THIXOTROPIC MORTARS WITH RECYCLED SAND

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Introduction: Construction industry consumes around 40% of all extracted natural resources, produces large amount of waste from building demolition and it is highly energy consuming. Several approaches have been carried out to mitigate the environmental impact of construction practices, such as investigating on more sustainable binders and reusing demolition waste as recycled aggregates. Regarding the latter practice, an increased interest has been shown by the most recent European legislation, that strongly discourages extraction of aggregates from quarries or rivers, whereas promotes the reuse of large volumes of recycled materials. Aim of this experimental work is to produce cement mortars with high performance, uniform colour properties, minimizing or even eliminating efflorescence phenomena and environmentally friendly by replacing natural sand with recycled aggregates.

Materials and methods: Self-compacting and thixotropic mortars were prepared by using CEM II/A-L 42.5R as binder, a water/powders ratio equal to 0.15 and a sand/binder ratio equal to 2.28. Several additives were used during the experimental campaign, with their overall amount below or equal to 5% wt with respect to binder. Recycled sand has been obtained from the demolition of small concrete buildings and mainly contained lime and cement hydration products. The grinding was carried out in a specifically built equipment, with a low water consume, thus allowing an accurate moisture and particles size control. Recycled and natural sand with the same grading curve were used. Mortars obtained using natural sand have been used as reference.

Raw materials and products have been characterized by XRD, SEM and EDX analysis, while workability tests were performed according to UNI EN 1015-3. Compressive and flexural strengths have been determined on prismatic specimens with dimensions of 4 × 4 × 16 mm after 2, 7, 28 days of curing according to UNI-EN 196-1:2005. Drying shrinkage was measured according to UNI EN 12617-1. Durability test were carried out according to UNI 7928, UNI 8019, UNI 7087:2002.

Results: The use of recycled aggregate affects mechanical properties with a decrease of compression strength with respect to reference mortars, whilst shrinkage behaviour is only slightly dependent on the sand nature. Strength loss after freeze-thaw cycles is more pronounced in mortars using recycled sand, even if all the specimens have flexural compression strengths values higher than 3MPa and 15MPa respectively. Sulphate attack resulted in a loss up to 80% of the initial strength.

Discussion: The produced self-compacting and thixotropic mortars with recycled sand showed a satisfactory behaviour, with an overall limited decline with respect to the reference.

Nature and amount of additives used in the experimental campaign affected properties and durability of mortars.

SUSTAINABILITY OF REINFORCED CONCRETE SPECIMENS: A LIFE CYCLE ASSESSMENT STUDY

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Introduction: Since nowadays reinforced concrete is the material mostly used in the sector of civil construction, such as in buildings, bridges and roads, it seems necessary not only to make studies about its behaviour when using different types and quantities of materials, but also to investigate how these choices can affect its environmental impact. Here, the idea is to compare environmental performances by using different scenarios and LCA methodology has been adopted to this purpose. The different scenarios follow several criteria, as changing the plants where the cement is produced and also changing the type of cement used always guaranteeing the same resistance to compression, so their lifetime will be the same for all of them.

Materials and methods: The analysis follows the methodology defined by ISO 14040 and 14044 and it is performed using SimaPro 8.2 software adopting a cradle-to-gate perspective, i.e., from the materials production to the reinforced concrete specimens' production at laboratory scale. A large number of impact categories was investigated by assessing the impact with ReCiPe 2008 method. Both different cements and different materials production plants were compared.

Results: The more significant changes are reported for the categories of climate change, ozone depletion, terrestrial acidification, photochemical oxidant formation and metal depletion.

Among the considered cements, the most impacting is CEM I 42.5 R while the least one is a Pozzolanic cement (CEM IV/A 42.5 R).

When changing the plants and keeping constant the type of cement, the plant which has more transport impacts is Augusta, which is the one that requires more road transportation, nevertheless Siniscola needs transportation by ferry. On the other hand, the one that has less transport impacts is Vernasca, which is the closer to Milano, where the reinforced concrete specimens are produced.

Discussion: The materials production phase is the most critical among the overall impacts. The manufacture of Portland cement consumes a great deal of energy and results in high-embodied energy and carbon dioxide emissions from clinker calcination. This study shows evidences that concrete has become less energy intensive, by utilising higher levels of pozzolanic materials such as fly ash.

Furthermore, the transport impacts can play a significant role when distance is long and road transportation is used.

TENSILE CHARACTERIZATION OF PBO-FRCM COMPOSITES

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Introduction: Retrofitting of existing concrete and masonry structures with fibre-reinforced polymers (FRP) is a consolidated technology. Recently, Fabric Reinforced Cementitious Matrix (FRCM) has been proposed as effective sustainable and durable alternative to repair and strength structures. The latter systems consist of open fabric meshes embedded in a cementitious matrix that better perform at high temperature, show higher reversibility, removability, compatibility with the substrate and vapor permeability. Load transfer mechanisms at fiber-matrix interface and frictional bond among the internal fibers within the yarn, are complex and affect mechanical behavior under tensile loads. Furthermore, the evaluation of tensile response and identification of the constitutive behavior are essential in structural reinforcement design and verification. Despite their wide diffusion, standardized methodologies and test configurations are not currently available and procedures differ in specimens geometry and dimensions as well as in testing set-up and load application mode.

The aim of this work is to provide a further contribution in the tensile characterization of PBO-FRCM composite provided by Ruredil - San Donato Milanese (MI).

Materials and methods: The FRCM composite system consists of a PBO unbalanced mesh with longitudinal and transversal bundles spaced 10 mm and 20 mm respectively and a stabilized inorganic matrix. Tensile tests were car-

ried out on specimens of nominal dimensions equal to 500 mm × 50 mm × 10 mm obtained from a larger panel. One reinforcement layer of fabric was applied, pre-cut to panel size. Tests were performed by using clevis type grip, according to Acceptance Criteria AC434-2013. The influence of different load transfer lengths on the mechanical behavior was investigated, analyzing the failure modes. Furthermore, strains were evaluated and monitored by means of different measuring systems such as an clip-on extensometer, according to AC434, and four inductive displacement transducers used to investigate a more extended range and whole gauge length. At least five specimens for each configuration were tested.

Results: Failure mode was characterized by the slipping of the fabric within the matrix. Modulus of elasticity of the uncracked and cracked specimens, the tensile stress and strain corresponding to the transition point and the ultimate tensile strength and strain were evaluated. Results show that the average modulus of elasticity of cracked specimens for load transfer length of 100 mm and 150 mm are consistent. They showed multiple cracking behavior, developed perpendicular to the load direction and throughout the gauge length, until the ultimate stress was reached.

Discussion: Inductive displacement transducers applied on the whole gauge length resulted to provide the most reliable measurements. Load transfer length is a parameter that affects the response curve, with significant variations in terms of ultimate strength, strain and cracking configuration. Stress-strain diagrams are consistent with those obtained by other researchers.

LDPE AND ITS NANOCOMPOSITES: CREEP AND THERMOMECHANICAL BEHAVIOUR

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Introduction: Polymer nanocomposites are increasingly known for their potentialities and their unique features if compared to a neat polymer. The behaviour of polymer nanocomposites has been studied and reported in several papers in the Literature. These clearly suggest that the main properties of polymer nanocomposites strongly depend on several factors: the polymer matrix, the nanosized fillers used and their amount, the adopted processing parameters, the possible use of compatibilizers, etc. On the other hand, the Literature does not provide much information concerning the creep behaviour of polymer nanocomposites. In the present work, the creep behaviour of a low-density polyethylene (LDPE)/organomodified clay nanocomposite was investigated; in particular, the combined effects of different loads and different temperatures were assessed.

Materials and methods: The materials used were a film grade LDPE (MFR = 3.5 g/10 min at 190°C and 2.16 kg) commercialized by Versalis and an organo-modified clay (Cloisite 15A, Southern Clay, that is a ditallowdimethylammonium modified montmorillonite).

The nanocomposite systems were prepared in a Brabender PLE330 batch mixer at 180°C, mixing time 15 minutes, with a 5 wt% organoclay amount; the pristine polymer was processed in a similar way.

Creep tests were carried out by applying stresses from 1.5 to 3.5 MPa at different temperatures (60 and 80°C) in a specific equipment manufactured by I.De.A. Dynamic mechanical (DMA) and X-ray diffraction (XRD) analyses were also performed.

Results: The nanocomposites underwent lower creep deformations if compared to the pristine polymer matrix. XRD analysis reported an increase in the interplanar distance from 3.15 nm to 3.96 nm.

DMA tests highlighted higher moduli in the nanocomposites, over the whole temperature range. Increasing differences were found between the pristine polymer and the nanocomposites, on increasing the temperature and the applied stress.

Discussion: The reduced creep deformation is due to the increased rigidity of the nanocomposite and to the lower macromolecular mobility. This can be explained considering the presence of the nanoclay particles and their intercalation phenomena, as shown by the XRD analysis.

This was also confirmed by the results from dynamic-mechanical tests. Furthermore, the increasing importance of the viscous component of the elongation (in comparison to the elastic component) can be accounted for the increasing differences between the pristine polymer and the nanocomposite upon raising the temperature and the applied stress.

TI/TIO₂ PHOTOANODES FOR WATER SPLITTING CELLS: PREPARATION VIA BLADE COATING TECHNIQUE AND PERFORMANCE EVALUATION

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Introduction: The conversion of solar energy into hydrogen via water splitting process is one of the most attractive ways to obtain renewable and clean energy. Currently, TiO₂ is the most widely studied photocatalyst due to its activity, non-toxicity, low-cost and chemical stability. Several techniques have been reported for the deposition of TiO₂ thin layers over conducting substrate and the photocatalytic activities have been found to strongly depend on the preparing methods. Accordingly, the aim of this preliminary work has been the preparation, characterization and evaluation of the photocatalytic efficiency of TiO₂ films obtained via blade coating deposition of TiO₂ nanopowders. Different pre-treatments of the metallic substrate were also performed and evaluated from a morphological point of view.

Materials and methods: Ti foils (0.25 mm thick, 99.7% metal basis) were used as coating substrates and TiO₂ P25 (Degussa), a benchmark photocatalyst, as starting nanopowder. Ti foils were first pretreated by dipping in two different acidic solutions, i.e. 30% mol HNO₃ and 30% mol HCl, for different times and then dried at room temperature to enhance roughness and favor the oxide deposition. Acid-free formulations based on water, glycerol and polyvinyl alcohol (PVA) were developed to disperse and stabilize TiO₂ powders via steric-like interaction. PVA was used as rheology modulator to control viscosity and to enhance system stability. In a typical preparation route, PVA and glycerol were dissolved in distilled water under magnetic stirring at 85°C. TiO₂ powder was added to the obtained solution, then it was poured in a polyethylene jar and ball-milled (ZrO₂ grinding spheres) for different times. Coating deposition was carried out via the blade-coating technique with a linear velocity of 0.02 m/s corresponding to a shear rate of 200 s⁻¹. Coated samples were then flash dried for 5 minutes at 350°C and then thermal treated at 500°C for 1 h. Rheological properties of dispersions were assessed by means of a rotational rheometer and dynamic viscosities were investigated in the shear rates range 10⁻¹-10³ s⁻¹. Both centrifugation cyclic tests and gravity sedimentation tests were performed to evaluate stability of dispersions. The photoelectrochemical activity of the Ti/TiO₂ photoanodes was investigated under solar simulator illumination in a three-electrodes cell with SCE as reference electrode, a Pt wire as counter electrode and 0.1M KOH as electrolyte solution.

Results and discussion: Rheological flow curves and sedimentation tests showed a general stability of slurries. Only 4 hours of milling were sufficient to achieve a repeatable pseudo-plastic shear thinning behavior, which is suitable for blade coating technique. The (4 hours) HCl pre-treated substrate was found to be the best in terms of surface homogeneity and repeatability of deposited oxides. All the tested photoanodes were active towards water-splitting reaction even though low efficiencies were obtained, likely due to adhesion issues between active phase and substrate, which are going to be properly addressed in future works.

FUNCTIONAL MATERIALS SELECTION: FROM MATERIALS SCIENCE TO USER EXPERIENCE

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Introduction: When selecting materials for industrial products, systematic selection methods can be used to facilitate the process. Analytic methods like the one proposed by Ashby are well established and are efficient to individuate candidate materials that have appropriate physical and mechanical properties. Though, these methods usually exclude considerations on materials experience, i.e. the aesthetic and emotional aspects of materials. Nevertheless these aspects are crucial in designing desirable and valuable products. Also, existing frameworks focus on classical materials, such as materials that exhibit unusual properties, such as functional materials, are missing. Therefore, our objective is to propose a comprehensive framework that introduces both functional materials and aesthetic and emotional aspects into materials selection.

Materials and methods: The existing materials selection frameworks are not adapted for a direct inclusion of functional materials and aesthetic and emotional aspects. Functional materials have the particular ability to transform a given stimulus into a precise response. We call these behaviors "stimuli-responsive phenomena". They are at the core of functional materials selection, since they represent the main interest of these materials in product implementation. These specificities require an adaptation of the selection framework's structure and tools.

A first step for such an adaptation is to link together all aspects of functional materials from materials science to user experience. Then different tools are proposed to explore and characterize the different aspects of these materials. The tools are then connected together to build a coherent and comprehensive selection framework.

Results: Various tools have been proposed. A layered description of functional materials is used to link together Materials Science, Materials Engineering, Stimuli-Responsive Phenomena, Materials Experience and Product Experience. On the materials engineering side, a dedicated database is under development. It is based on the existing CES selector system but with a structure specially adapted to functional materials properties. On the experiential side, tools for the exploration and characterization of functional materials' behaviors and of product experience are being proposed.

Discussion: Some tools have been tested together in lessons and result efficient in a Design & Engineering teaching context. A further consolidation of the tools is required, and scenarios of use for materials exploration and selection are developed to reinforce the link between the various tools and to build a coherent framework. Tests in industrial context and for selection purpose will further indicate where the framework needs consolidation.

ON THE MICROSTRUCTURE AND PROTECTIVE PROPERTIES OF NICKEL MATRIX COMPOSITE ELECTRODEPOSITS CONTAINING EITHER MICRO- OR NANO- PARTICLES OF AL

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Introduction: Mechanical metal components working at high temperature in aggressive atmospheres could undergo a strong reduction of the service life. A possible solution to increase the oxidation resistance is to use coatings containing oxide-stabilizing elements. Composite coatings electroplating could be a valid and relatively low cost production method to codeposit either micro- or nano-particles of Al in Ni matrix. The microstructural modifications caused by the incorporation of the particles in the metal matrix and the intermetallic phases which are formed after thermal treatments modify the mechanical and protective properties of the composite coating when compared to the pure nickel deposits.

Materials and methods: The aim of this work is the production of Ni matrix composite deposits containing either micro (3-4 µm) nano (130 nm) particles of Al using parallel plate geometry composite plating and their characterization both prior and after heat treatments at different temperatures (400, 600 and 800°C) by means of microstructure, hardness and corrosion resistance. The obtained electrodeposits both before and after heat treatments at different temperatures have been observed by SEM at both top surface and cross section after metallographic etching and analysed by XRD in order to evaluate the formation of Ni/Al phases. The effect of the formation of different Ni/Al phases has been studied by means of microhardness measurements and potentiodynamic polarization tests in an aggressive environment. The corrosion mechanisms have been studied by AFM-SKFM prior and after immersion in the corrosive environment in order to identify the role of each phase to the overall corrosion behaviour.

Results and discussion: The pure Ni deposits present a columnar structure with the columns oriented along the direction of the electrical field. The recrystallization of Ni starts at 400°C and by increasing the heat treatment temperature, an increase of the grain size is noticed. The microhardness decreases by increasing the HT temperature, while the corrosion resistance is good at all temperatures. The codeposition of Al micro-particles leads to the interruption of the columnar growth. The diffusion of Al in the Ni matrix, starting at 600°C hinders the recrystallization of the Ni matrix and leads to the formation of Ni₃Al intermetallic phases. After HT at 800°C there is a solid solution of Al in the Ni matrix. The as plated Ni/µAl deposits exhibit a low corrosion resistance due to the galvanic coupling Ni-Al, which leads to the dissolution of Al in the Ni matrix. The pitting corrosion of the Al particles and favors the pitting corrosion of the matrix.

The HT at 600°C and 800°C lead to an increase of the corrosion resistance due to the formation of more noble phases. The incorporation of Al nano-particles causes a strong grain refinement. The fine-grained columnar structure is preserved after the HT at different temperatures due to the fast diffusion of the Al in the Ni matrix which lead to the formation of a solid solution of Al in the Ni. The nanocomposite deposits show a good corrosion resistance both prior and after HT. The microhardness of the deposits follows the microstructure modifications.

CORROSION BEHAVIOUR OF CORROSION RESISTANT STEELS IN CONCRETE MIXED WITH SEAWATER

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Introduction: The use of seawater and salt-contaminated aggregates is prohibited for reinforced concrete structures, since it can promote steel corrosion. However, environmental benefits, due to the save of natural resources, could be reached from their use for the production of concrete. Within the framework of ERA-NET Plus Infravation 2014, the SEACON project "Sustainable concrete using seawater, salt-contaminated aggregates, and non-corrosive reinforcement" was recently started. This project, that involves six academic and industrial partners, is aimed at demonstrating the safe utilization of seawater and salt-contaminated aggregates for a sustainable concrete production when combined with non-corrosive reinforcement (FRP and stainless steel bars). This paper focuses on the preliminary results of tests aimed at assessing the corrosion behaviour of stainless steels of different grade embedded in concretes made with fresh water and seawater.

Materials and methods: Concrete was made with water/cement ratio of 0.52, 335 kg/m³ of Portland-limestone cement, 30 kg/m³ of coal fly ash, 1824 kg/m³ of siliceous aggregate and 175 l/m³ of water, respectively deionized (*Ref*) and seawater (*Sea*). A superplasticizer was added to achieve a slump of 160-210 mm.

Compressive tests were carried out after 1, 7 and 28 days of curing. Electrochemical measurements of corrosion potential and corrosion rate were carried out on three replicate 250×50×100 mm prismatic specimens, with embedded bars of: carbon steel, two austenitic stainless steels (1.4307 and XM-28) and two duplex stainless steels (1.4362 and 1.4462). After 7 days of moist-curing they were exposed to unsheltered conditions in Milan for about two months.

Results and discussion: The compressive strength of the *Ref* concrete increased from about 14 to 50 MPa from 1 day to 28 days of moist curing. Slightly higher values were measured during the first week (e.g. around 16 MPa at 1 day) on the *Sea* concrete, showing a slight accelerating effect of seawater. After 28 days of curing strength of *Sea* concrete was comparable to the *Ref* concrete, suggesting that seawater is not harmful for concrete. Of course, the effect of chlorides present in the *Sea* concrete (about 1% vs mass of cement) was observed on the embedded steel. During the outside exposure, carbon steel bars embedded in the *Ref* concrete showed the expected passive behavior, whilst in the *Sea* concrete corrosion initiation was shown since the beginning by higher corrosion rates and lower corrosion potentials in comparison to those of the *Ref* concrete. As expected the results confirmed that carbon steel is unsuitable when seawater is used as mixing water. Conversely, all the stainless steel bars showed a similar corrosion behavior both when embedded in the *Ref* and *Sea* concretes. This indicated that during this initial exposure period of a few months and with mild temperatures (spring season, with outside temperature never exceeding 25°C), even the less alloyed stainless steels embedded in the *Sea* concrete maintained passive conditions and hence they could be suitable in *Sea* concrete. The effect of higher temperature as well as of the further chloride penetration is under study with specific ponding tests.

AGEING BEHAVIOUR OF ADHESIVE JOINTS

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Introduction: The exploitation of composite materials implies an increase in the use of adhesives in many industrial applications replacing existing traditional joining methods such as welding and soldering. Adhesive bonding is

in fact a suitable technology to bond dissimilar materials and it is often used to obtain a good uniform stress distribution in the joint area. Notwithstanding their high performances, structural adhesives are subjected to durability issues because of their polymeric composition, especially in harsh working conditions as high humidity levels. In this study the changes in static mechanical performances of a flexibilized and toughened epoxy adhesive was evaluated under different degradation conditions (relative humidity, applied load). **Materials and methods:** The adhesive used was a flexibilized and toughened epoxy adhesive (Scotch-welds DP490), selected on the basis of previous tests made on different structural adhesives. Steel and carbon fiber reinforced epoxy (CFRE) substrates, with a thickness of 3 mm, a width of 25.4 mm and a length of 101.6 mm (according to ASTM D1002) were employed. Lap shear joints were produced with a 10 mm bond overlap with a curing treatment at ambient temperature for 24 h and a post-curing procedure at 80°C for 1.5 h. Steel-to-steel and steel-to-CFRE lap shear joints were then aged at 50°C and different relative humidity levels (10, 50 and 90 RH%) for several times, evaluating their residual lap shear strength through tensile tests carried out with a cross-head speed of 1.3 mm/min. A home-made system able to maintain a constant force of 1800 N on each lap shear joint was employed to evaluate the combined effect of hydrothermal ageing and applied load.

Results: After four weeks, steel-to-steel lap shear joints aged at 50°C with a humidity level of 10 and 50 RH% did not present performance losses, whereas a relevant decrease in residual lap shear strength was recorded for samples aged in the harsher conditions. A similar behaviour was observed for steel-to-CFRE samples, even if a lower loss in lap shear strength was measured after ageing at 50°C and 90 RH% for 4 weeks. When the load was applied, shorter times were reached for 50 and 90 RH% aged samples, with the lap shear failures after 3 and 1.5 weeks, respectively. In these conditions, after ageing at 50°C and 50 RH% for 3 weeks very similar residual lap shear strength values were found for both types of samples.

Discussion: The changes in residual lap shear strength during ageing confirmed that at low humidity levels the temperature initially played a positive role by affecting the curing extent. At long ageing times and higher humidity levels, the water displaced the adhesive at the bond interface inducing adhesive failures and corrosion phenomena on the steel surface. These processes took place in shorter times when lap shear joints were under load, representing a relevant limit in industrial applications of adhesive joints. The results suggested the necessity to pre-treat the metallic surface in order to avoid corrosion phenomena.

ADDITIVE MANUFACTURING ACTIVITIES AT POLITECNICO DI TORINO

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Introduction: Additive manufacturing (AM), based on the building of a part layer by layer starting from a CAD model, offers many advantages in the production of components with very complicated geometries, optimized and integrated functional features and/or a high degree of product customization, often allowing a reduction in part weight without compromising its structural strength.

As concerns industrial applications, the unrivalled design freedom, the high flexibility due to the component being produced directly from a CAD model without the need for tooling and the ability to manufacture single or multiple components in a single-step process make additive manufacturing very interesting. In addition, it is impossible to neglect that, as near net shape processes, AM technologies imply the reduction of material waste and post processing operations, improving some relevant aspects in the industrial world such as the environmental impact and time and cost reductions.

Moreover, AM processes offer new possibilities to metals and alloys applications, thanks to the innovative component design feasible through these new technologies, but also in the choice of materials to be exploited. For example, the technology is particularly attractive for processing of advanced materials such as:

- titanium, where conventional processes can be prohibitively expensive;
- new alloys, having innovative compositions created during process or which can be only manufactured under high cooling rates typical of AM technologies;
- metal-matrix composites (MMC), in order to couple different mechanical and/or functional characteristics.

Materials and methods: Ni superalloys (Inconel 718 and Inconel 625), Al alloys (AlSi10Mg, A357, 7075) and Ti alloys (Ti6Al4V) powders were processed as received and/or mixed with ceramic fillers for MMC by using an EOS M270 Dual Mode system. It uses an Yb-fiber laser with a power up to 200 W to locally melt, in inert atmosphere, thin layers of metal powders deposited on a heatable platform. Compositional and microstructural features of produced samples were analyzed, also evaluating their effect on thermal and mechanical properties.

Results: Additive manufactured components present final microstructure and mechanical properties that strongly depend on the processing parameters (such as laser power, scan rates, hatching distance, bed-platform temperature, building direction) and the powders properties. The optimization of working conditions allows to reach very high final densities, with higher yielding and ultimate strengths and hardness values than the corresponding cast materials. In addition, it was also demonstrated that the optimization of post-process treatments are able to modify the final properties of AM parts according to the specific application.

Discussion: Generally AM materials are characterized by a very fine microstructure, because of the insufficient time for grain growth during cooling. In fact, the high energy-laser interactions implies a superfast heating and melting of the powder particles, with a rapid solidification during cooling limiting the grain coarsening. These microstructural peculiarities justify the high yielding and ultimate strengths and hardness values measured for the processed materials. In addition, post-processing heat treatments can induce further materials strengthening, such as precipitation of some constituents: for each material the proper combination of temperature and time must be selected.

THE USE OF PERLITE, PUMICE AND EXPANDED RECYCLED GLASS FOR LIGHTWEIGHT INSULATING PLASTERS

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Introduction: The reduction of energy consumption in construction, the production of thermally insulating materials, as well as the solution of environmental problems by recycling municipal waste are key challenges for the next future. For this reason, several plasters have been studied, in which virgin raw materials such as natural sand and limestone filler were replaced by lightweight expanded silica filler, pumice, recycled expanded glass.

Materials and methods: Lightweight expanded silica filler is a natural volcanic material also known as expanded perlite, characterized by bulk density of about 60 kg/m³, and particle size distribution in the range 0.1-0.3 mm. Pumice is also a natural volcanic material, characterized by bulk density of about 350 kg/m³, and particle size distribution in the range 0.3-1.5 mm. Recycled expanded glass is a material obtained from post-consumer recycled glass. The cullet is finely ground, mixed and formed to granules. After this, the raw grain is getting sintered and foamed (expanded) in the rotary kiln. This process creates lightweight spheres with a fine closed cellular pore structure, with particle size distribution in the range 2.0-4.0 mm and bulk density of about 190 kg/m³. Lightweight mortars were prepared by using these lightweight ingredients, by using as binder a mixture between cement (type CEM II/B-L 32.5R) and lime. As chemical admixture, a water-reducing admixture was used for increasing mechanical properties of such porous materials and an air-entraining admixture in order to lighten cement/lime paste. Moreover, a shrinkage-reducing admixture was added in order to avoid plaster cracking at early age together with polypropylene fibers at a dosage of 0.7% by volume. After optimization of mortar mixture proportions, nine selected mixtures were characterized at fresh state by means of fresh consistency evaluation as well as bulk density of fresh mortar measurements, then at the hardened state by means of compression and bending tests as well as thermal conductivity measurements by means of guarded hot plate apparatus according to EN 12667.

Results: Fresh consistency was always in the range 12.5-13.5% (target value for plasters), bulk density values of fresh mortars were in the range 500-1020 kg/m³, with the minimum value obtained by adding the maximum dosage of lightweight expanded silica. Concerning 28-day compressive strength the values achieved were in the range 0.3-5.0 MPa (in general the minimum accepted value for a plaster is at least 1.5-2.0 MPa). Concerning 28-day flexural strength the values achieved were in the range 0.1-1.65 MPa. Finally, thermal conductivity measurements showed extremely low values for a plaster ranging from 0.06 to 0.09 Wm⁻¹K⁻¹.

Discussion: On the basis of the results obtained the use of volcanic raw materials, such as lightweight expanded silica and pumice, as well as of expanded glass obtained by recycling municipal waste proved to be extremely promising in order to produce lightweight and thermal insulating plasters, suitable for energy efficiency improvement in building. Moreover, plaster satisfactory mechanical performance were obtained in most cases.

SYNTHESIS OF GRAPHENE OXIDE-SILICA-PERFLUOROCARBON NANOPLATFORMS FOR ENHANCING OXYGEN EXCHANGE

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Introduction: Graphene oxide (GO)-silica nanohybrids (GOS) are currently used in many fields, because of their electronic properties, chemical inertia and cytocompatibility. On the other side, perfluorocarbons (PFCs) are gaining an increasing interest in both biomedicine and electrochemistry, due to their ability to dissolve large amounts of oxygen, which is vital for cells differentiation and surviving, and for regulating redox reactions. Currently, the methods used for fluorinating GO involve drastic conditions, thus damaging its graphenic domains, and impart an uncontrollable wide variety of F-containing moieties. Furthermore, low functionalization degrees are usually achieved, since -COOH and epoxy often used for derivatization are scarcely present onto GO planes. An easy route to conjugate PFCs to GOS via aromatic nucleophilic substitution (SNA) operated by -OH abundantly present in GOS under mild conditions is herein explored, together with the possibility to gather the unique features of GO, silica and PFCs into a novel device.

Materials and methods: GOS, achieved via Fischer esterification in water, was conjugated with 3-pentadecafluoroheptyl-5-perfluorophenyl-1,2,4-oxadiazole molecules (PFCs) in DMF and K⁺(CH₃)₃CO⁻. The resulting ternary nanohybrid (GOSF) was characterized by FTIR, μ -Raman, NMR, XPS, SEM, EDX. Oxygen affinity tests were performed *in vivo* on saturated aqueous dispersions of GOS or GOSF.

Results: The SNA mechanism of this route was confirmed by FTIR and NMR, which detected the formation of aryl ethers to the detriment of F-C (aryl) bonds and the presence of the typical signals of PFCs, which surface concentration (30%) was assessed by XPS. SEM analysis evidenced that both GOS and GOSF show a hierarchical *lasagna*-like structure, constituted by lamellae intercalated by nanoparticles. EDX mapping remarked that PFCs were attached either on silica and GO. Raman results confirmed that the derivatization did not affect graphenic domains. Oxygen affinity tests highlighted that GOSF shows a faster O₂ uptake, a slower O₂ release during desaturation, higher saturation value and clearance constant, especially if compared to fluorinated polymers and PFCs surfactants, recently reported in the literature for biomedical applications.

Discussion: The novelty of this work consists of two main aspects: the synthetic route to anchor PFCs to GOS and the final properties of the resulting nanohybrids, particularly promising as O₂-reservoirs due to their exceptionally high oxygen affinity. Indeed, with respect to the other fluorination routes, this method allows achieving high yields without damaging the structure of either graphenic domains and PFCs and high selectivity, thus enabling to tailor the desired final properties. In this case, GOSF shows a remarkably high oxygen affinity, double-folded with respect to other fluorinated systems recently reported in literature for the same purposes, due to the synergistic effect of silica and PFCs. Moreover, the presence of GO leads to the achievement of free-standing, lightweight thin films, thus allowing to prepare devices that can be easily re-collected and recycled after being used. The success of the present preliminary study promises to use these novel nanohybrid thin films as oxygen reservoirs for a wide range of applications, concerning biomedical devices, water treatment membranes, fillers for functional nanocomposites.

NEW HEMP-BASED COMPOSITES FOR THE BUILDING INDUSTRY: PRELIMINARY STUDY ON THE CURING TIME PROCESS

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Introduction: Nowadays, sustainability represents a primary issue for construction industry. New material and low impact technological solutions are

widely proposed and investigated to meet sustainability requirements and natural fibers represent one of the most studied materials.

Among others, hemp (*Cannabis sativa*) has received a lot of attention because of its good thermal insulation properties, good mechanical properties, rapid growing, high dry biomass production (4 to 5 times higher than that produced by a forest of the same extension in one year) and high carbon storage potential. Several studies have investigated the insulating properties of hemp fibers and hemp hurds (i.e. the non-fibrous fraction), bonded by either organic or inorganic binders, and several hemp-based products, in the form of flexible mats and boards, have recently been introduced in the market.

In this work, new hemp-based composite materials for application in the building industry are investigated and the results of a preliminary study on the curing time process are reported and discussed.

Materials and methods: The composite materials were obtained by bonding hemp hurds with a new hybrid organic-inorganic binder, composed of a mineral oxide, which reacts when a proper aqueous salt solution is added, and a reactive vegetable fraction.

Physical (bulk density) and mechanical (flexural strength, according to EN 12089 Standard) behaviors of panels were studied as a function of the curing time passed from the panel production. Correlations between the investigated properties and curing time were made.

Results: Increasing the curing time till to 14 days, samples exhibit a decrease of density (i.e., -1.7% at 14 days of curing). This decrease is ascribed to a reduction of humidity in the composite materials. Flexural strength values of the samples increase with the curing time, reaching the maximum value at 7 days of curing, even if after just 3 days of curing, more than 95% of the final mechanical strength was obtained.

Discussion: It is fundamental to know the correct curing time: a good mix-design is not enough to reach the planned performances if panels are used, or just carved, before the composite material has reached a sufficient curing level. Results showed that the studied new composite material can be used after 3 days of curing. This time is adequate for the final industrial use of the material, because it requires a restrained storage of the material, also with high manufacturing capability of the plant.

EFFECT OF ZIRCONIUM CONCENTRATION FOR MODIFIED DIFFUSION ALUMINIDE COATING IN HOT CORROSION AND OXIDATION TESTS

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Introduction: Diffusion aluminide coatings are widely used in hot components of aero- and land-base gas turbines to protect from oxidation and hot corrosion. The effect of doping diffusion aluminide coating with reactive element (zirconium) was studied under different concentrations.

Materials and methods: Nickel-based super alloy were coated with diffusion aluminide by means of the Vapour Phase Aluminizing (VPA). Firstly the effects of different activators salts during the coating process was studied: for this reason several concentrations of two different fluorides activator salts (NH_4F and AlF_3) were investigated and the process parameters of the conventional (undoped) aluminide were optimized.

In a second step a Zr-doped coating was developed introducing ZrF_4 in the activator salts mix with the process parameters obtained from the first step of experimental procedure. The oxidation kinetics was evaluated by measuring the mass gain at different exposure times. The microstructural evolution induced by the high temperature treatments was investigated by SEM, EDS and XRD analysis. The zirconium concentrations were assessed by means of GDOES.

Results: The results of different activator salts in the VPA process are a thicker layer of $\beta\text{-NiAl}$ and a consequent interdiffusion zone (IDZ) for AlF_3 depositions. This increase can be explained by considering the different quantities of aluminum available on the super-alloy surface as diffusion occurs.

The effect of the reactive element addition, in terms of oxidation and hot corrosion resistance and microstructural evolution, was assessed by comparing the performance of the modified coatings with the standard diffusion aluminide systems.

Discussion: The results show that modified coatings exhibits an enhanced oxidation and hot corrosion resistance in comparison to standard diffusion

aluminide coatings. The improvement of oxidation resistance for the doped samples can be explained by EDS mapping results. After 100h of oxidation tests, Zr prevents the path of oxygen that penetrate through the Al_2O_3 scale blocking the degradation phenomena typical for the standard aluminide coating (spallation, depletion layer of aluminum with consequent change of concentration in $\beta\text{-NiAl}$). Furthermore the diffusivity of Zr can counteract against the porosity made by the different diffusivity of Al and Ni during oxidation (Kirkendall effect).

MESOPOROUS TITANIA PREPARED BY THERMAL TREATMENT OF AMORPHOUS PRECURSORS

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Introduction: The titania, TiO_2 , powders used in heterogeneous photo-catalysis reveal the trouble to separate them from the aqueous dispersion making the recycling difficult. This work describes the synthesis of mesoporous titania as recyclable aggregates either in the form of a single polymorphic form or in the form of binary or ternary mixtures of its different crystalline habits (anatase, rutile and brookite).

Materials and methods: Amorphous precursors of titania were prepared at room temperature by hydrolysis in ethanol of titanium tetra-ethoxide, $\text{Ti}(\text{OC}_2\text{H}_5)_4$ and catalyzed by NH_4OH with a less (0.07 M) or more (1.0 M) concentrated solution. The amorphous precipitates were peptized at 50°C for 1 or 3 h in the presence of HNO_3 0.02 M or 0.1 M, respectively. The solid of each suspension was separated by centrifugation, dried at 60°C and full crystallized by thermal treatment at 450°C for 2 hours with a heating rate of 2 or 30°C/min.

Results and discussion: The characteristics of amorphous precursors and their peptizing treatment both affect the crystallization of mesoporous titania resulting after the calcination treatment. The average mesopores size increases, in fact, with increasing crystals sizes of titania. Bigger crystals sizes result when the hydrolysis is performed in the presence of diluted ammonia, compared with crystals obtained in concentrated ammonia followed by a same peptizing and calcination treatment. With diluted ammonia, a lower water content is involved and, consequently, a lower hydrolysis rate must be expected. The limited aggregation process of colloidal particles, under stirring, favors the crystallinity of titania.

The presence of more concentrated solution of the peptizing agent and longer peptizing times favor the crystallization of TiO_2 with crystals bigger in size. In this circumstance a high de-agglomeration of the particulates and a consequent their high reactivity must be expected so promoting the crystallinity of titania and the anatase-rutile transformation. The formation of rutile as a single phase or in mixture with anatase can be also related to the doping effect of nitrogen.

The heating rate adopted in the treatment of calcination also affects the characteristics of crystallized titania. Adopting a heating rate of 30°C/min, more crystalline titania results compared to that crystallized at a heating rate of 2°C/min. At higher heating rate, in fact, a shorter time in the temperature range of nucleation results, so determining a reduced number of nuclei which in turns determines the formation of TiO_2 crystals bigger in size.

The characteristics of recyclable titania aggregates, including polymorph phases, mesoporosity, surface area, crystallinity can be controlled by numerous parameters of synthesis of the precursors such as the concentration of ammonia catalyst, the concentration and stirring time of the peptizing HNO_3 , and the heating rate adopted up to the temperature of calcination for the crystallization of titania.

A RAPID METHOD TO DETERMINE THE AGING TIME OF LIME PUTTY

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Introduction: Lime putty has been used in mortars for masonry construction for millennia reaching the maximum level of quality during the Roman empire. It is prepared by slaking quicklime under an excess of water.

An increasing use of hydrated lime as a binder occurring in recent years is connected with conservation of historic buildings being the lime mortars

characterized by appropriate compatibility with materials of ancient structures.

Lime putty aged for an extended period of time manifests improved quality of calcium hydroxide, $\text{Ca}(\text{OH})_2$, in lime mortar or plasters. High plasticity, easy workability, reduced shrinkage and increased speed of portlandite carbonation favor, in fact, better quality of corresponding mortar or plaster.

How old should lime putty be? As established by an ancient Roman law, an aging time longer than 36 months is necessary.

This communication concerns a rapid method for verifying the effective long aging of lime putty by using the thermo-gravimetric analysis.

Materials and methods: Starting from different quicklimes slaked under an excess of water, numerous lime putties aged for different times ranging from 3 to 66 months have been tested. Each sample was dehydrated by lyophilisation and submitted to thermo-gravimetric analysis (TGA). The weight loss below 250°C was attributed to the amount of adsorbed water, that one between 300° and 400°C to the decomposition of brucite, $\text{Mg}(\text{OH})_2$, the weight losses in the temperature ranges 400°–600°C and 600°–850°C were attributed to the decomposition of portlandite, $\text{Ca}(\text{OH})_2$, and calcite, CaCO_3 , respectively.

Results and discussion: From the weight losses resulting in TGA, the amounts of adsorbed water, brucite, portlandite and calcite were determined for each lime putty. Taking also into account the impurities present in the starting quicklime, the mineralogical composition of each lime putty aged for different time has been determined. It has been detected that the total mineralogical composition of lime putties aged for a time higher than 12 months was close to the expected value of 100%, while such value results lower than 100% for lime putties aged for lower times up to 12 months. To justify such result, an incomplete hydration of lime or magnesia of the quicklime putty precursor must be considered. The delayed hydration may be related to the presence of over burnt of some particles of lime present in the quicklime precursor.

An incomplete hydration results for lime putty aged up to 12 months, while above that time a complete hydration has been detected. This result suggests that the TGA may be a possible method for determining the effective long aging of lime putty, a feature which favors better quality of the corresponding lime mortar.

CHARACTERISATION OF QUATERNARY BRONZE ARTIFICIAL PATINAS FOR OUTDOOR CULTURAL HERITAGE APPLICATIONS

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Introduction: Effective corrosion protection for outdoor bronze monuments is nowadays requested as durable and non-hazardous solutions. The comprehension of the corroded substrates (patinas) on which the protective treatments are applied is a fundamental tool for optimizing bronze protection. So, the application of accelerating ageing tests simulating different exposure conditions of outdoor bronzes allows the production of artificial patinas similar to the real ones. In this study, patinas simulating very thin corrosion layer were characterized.

Materials and methods: The bronze is a quaternary alloy (base Cu, 6.9 ± 0.6 Sn, 3.1 ± 0.4 Zn, 2.0 ± 0.9 Pb also containing Al, P, Mn and Si in traces) with the typical dendritic structure due to sand casting. Patinated bronze surfaces were produced by the action of synthetic rain through Dropping and Wet&Dry test devices, in order to simulate unsheltered and sheltered exposure conditions of outdoor bronzes, respectively. In addition to the conventional microscopy observation, Focused Ion Beam (FIB) combined with SEM/EDS investigation was performed in order to analyse cross-sections at resolution scale of few nm.

Results: Corrosion surfaces produced by both the ageing tests show a similar general corrosion behaviour, in which central parts of dendrite are the most corroded (anodic areas), characterized by a marked Cu and Zn dissolution,

whereas dendrite borders and eutectoids are poorly attacked (cathodic areas). This trend is due to the tin content distribution related to Sn micro-segregation in the alloy: corrosion is more developed in low tin content areas. Corrosion layer by Dropping test is homogenous and nano-porous with a thickness of 2 μm. It is mainly composed by not well-crystallized Cu oxides and Sn-O compounds, due to the continuous leaching by Dropping test, as revealed by X-ray diffraction, Raman spectroscopy and XPS. However, Wet&Dry test produced a thinner corrosion layer (1 μm) characterized by an inner compact layer (<500 nm) and a more porous outer layer. In addition, nano-porosities in the bronze/corrosion interphase were observed in both the samples, confirming the strong Cu and Zn dissolution. Cu_2O and posnjakite, hydroxisulfate precursor of brochantite usually found in the case of longer exposure, were the main corrosion products detected on the surface.

Discussion: By comparison to previous results reported in literature, similar corrosion behavior was observed. Specific marked Cu and Zn dissolution, coupled with a relative Sn enrichment were detected. In this case, thinner porous corrosion layers were produced by both the ageing methods, due to higher tin content in the alloy.

Clear differences between the two ageing methods were observed: slight erosion was produced by Dropping test with the formation of not well crystallised oxides on the surface, whereas Cu compounds deposit was observed on Wet&Dry aged surface, composed of Cu oxides and hydroxisulfates. Chlorine element was detected in the inner part of the corrosion layer, present as anions linked to corrosion attack.

ELECTRICALLY CONDUCTIVE DSP CEMENT COMPOSITES

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Introduction: Electromagnetic shielding and propagation in concrete structures are getting more and more interest in radiation hazard problems and wireless communications. The protection of sensitive environment is nowadays carried out by appropriate shielding room made of metallic walls. Even if effective they are heavy structures not adequate for the installation over existing building walls. The using of concrete composites filled by conductive elements represents a valid alternative to metallic shielded room since they can be adopted to directly build up the building walls and/or to easily plaster existing walls.

Materials and methods: In this paper the densified with small particles (DSP) cement composites, containing different loading particles (rigid metallic fibers, flexible metallic fibers, micro-graphite powder and graphene oxide powder) have been investigated through the nested reverberation chamber (NRC) facility. EM shielding properties of DSP have been improved adding micro-graphite powder and stainless steel (rigid) fibers separately, as well as graphite plus flexible fibers (amorphous cast iron-based) and graphene oxide plus flexible fibers together. Taking advantage of an intensive mixer tool, different kinds of cement composites were manufactured varying the percentages of added graphite, graphene oxide and metallic fibers. In particular, seven samples have been created employing: DSP only, DSP plus 20% wt of rigid fibers (RF), DSP plus 10% wt of graphite (G), DSP plus 20% wt of graphite, DSP plus 10% wt of graphite plus 10% wt of flexible fibers (FF), DSP plus 10% wt of graphene oxide (GO) and DSP plus 10% wt of graphene oxide and 30% wt of flexible fibers. Particular effort has been spent in characterizing the SE behavior with the increasing drying and in improving the experimental practice to solve out previously faced measurement troubles.

Results: The addition of metallic fibers cement paste produced an increase in the shielding effectiveness (SE) of the samples. The choice of flexible fibers has been taken after noticing worse performance of rigid filaments in terms of SE. The samples containing graphite and graphene oxide powders together with flexible fibers better behave in terms of SE. In particular, considering the frequency behavior of SE for the samples containing 10 wt% G + 10 wt% FF and 10 wt% GO + 30 wt% FF, it sets approximately to 50 dB of shielding after 28 days and 45 dB after 70 days.

Discussion: In general, the results obtained by adding GO, G and FF show a high level of SE, with respect to the other samples, even if after 2 months the SE of the sample is reduced. This is probably due to the evaporation of the water contained in the mixtures. Better results are probably due to the fact that GO and G improve the adhesion between the cementitious matrix and the metallic fibers. Future developments will consider the possibility to reduce the evaporation of water using specific additives in the mixtures aimed

to reduce the shrinkage. In any case the obtained values of SE are considerably high given the fact that the materials available on the market show a SE between 15-30 dB.

RETROGRADE VITRIFICATION IN POLYSTYRENE-TOLUENE SYSTEM

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Introduction: Glass transition temperature (T_g) in polymers is affected by the presence of absorbed low molecular weight penetrants, generally promoting plasticization phenomena that bring about a decrease of T_g . In several polymer-penetrant systems a more complex phenomenology may occur, that is named 'retrograde vitrification'. In brief, if we start from a polymer that is at a rubbery state when in equilibrium with a vapour of penetrant at a fixed pressure and we decrease the temperature without changing the penetrant pressure, we observe that, at a certain temperature, a glass transition is observed due to reduction of macromolecular mobility promoted by temperature decrease. The increase of solubility with temperature decrease is not enough to counterbalance the effect of the temperature per se. However, further decreasing the temperature at the fixed pressure could promote such an increase in solubility that another glass transition could be observed bringing again the system into a rubbery state. We then observe, in sequence, as temperature is decreased at a fixed pressure of penetrant vapor, a rubbery, a glassy and again a rubbery system (retrograde vitrification). In this contribution we report on the retrograde vitrification phenomenon observed in the polystyrene-toluene system offering also a theoretical interpretation that provides an excellent qualitative and quantitative prediction of the experimental results of T_g vs. penetrant pressure.

Materials and methods: Sorption of toluene in polystyrene at equilibrium has been determined using an electronic CAHN D200 ultramicrobalance in which polystyrene thin sheets (between 450 and 800 nm thick) are exposed, at a fixed temperature, to a toluene vapor phase at a controlled pressure. By using an electronically controlled butterfly valve connected to vacuum to remove penetrant vapor and a solvent reservoir to feed penetrant vapor to the system, it is possible to control the pressure of the vapor and its rate of change.

Results: Using the experimental set up, we were able to monitor the amount of penetrant absorbed in polystyrene as a function of pressure that is decreased in a controlled manner. By this procedure, we started from a rubbery PS-Toluene system at a fixed temperature and, by decreasing the pressure, we were able to detect, at each temperature, the pressure at which a transition to glassy state occurs, thus determining the whole T_g vs pressure curve that was found to show the already mentioned retrograde vitrification features.

Discussion: Before analyzing the T_g vs pressure curve, we interpreted and fitted experimental toluene sorption isotherms in PS, in the rubbery state, by using a compressible nonrandom lattice fluid model rooted on statistical thermodynamics. After having determined the model parameters from fitting procedures, we were able to calculate the entropy of the PS-toluene mixture on the basis of the expression supplied by the model. Adopting the Gibbs-Di Marzio criterion, that suggests the glass transition as being determined by the condition of zero configurational entropy, we were able to construct the T_g vs pressure curve that is in excellent agreement with experimental data.

CHEMICAL SHRINKAGE OF ALKALI ACTIVATED BINDERS BASED ON VARIOUS SOLID PRECURSORS

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Introduction: Alkali activated binders can be synthesized starting from very different solid precursors, determining variable kinetics. Shrinkage of alkali activated binders needs to be investigated deeper, since – for instance – early age cracking may affect durability and prestress loss may hinder use in precast concrete industry, which is at the moment the most important application target for these materials. In this study, the basic mechanism of chemical

shrinkage is quantified for a wide and relevant set of alkali activated binders with reliable mechanical performance.

Materials and methods: The following raw materials (showing main oxides) were used for the preparation of the binders: coal fly ash ($\text{SiO}_2 = 44.3\%$, $\text{Al}_2\text{O}_3 = 20.2\%$, $\text{Fe}_2\text{O}_3 = 10.5\%$, $\text{K}_2\text{O} = 8.1\%$, $\text{LOI} = 11.30\%$); blast furnace slag ($\text{CaO} = 41.91\%$, $\text{SiO}_2 = 35.16\%$, $\text{Al}_2\text{O}_3 = 10.76\%$); commercial metakaolin ($\text{SiO}_2 = 51.20\%$, $\text{Al}_2\text{O}_3 = 43.98\%$); quartz filler (Sibelco® MILLISIL SA12); CEM II A-LL 42.5R; sodium hydroxide in pellets; sodium silicate solution R = 3.2; deionized water. Six alkali activated mixtures were considered and, furthermore, a cementitious paste ($w/c = 0.5$) was realized. The mixtures were tested after optimization in preliminary works where the materials demonstrated significant mechanical performance. Four mixtures (FAMK1, FAMK2, FABFS1, FABFS2) were designed with CFA as main solid precursor, with MK and BFS as secondary components at weight percentage equal to 10 (solution to precursor – S/P = 0.60 mass ratio) and 20% (S/P = 0.55). Two mixtures were realized considering alkali activated metakaolin, one in neat form (MK, S/P = 1.2) and the other containing quartz (50% respect to MK mass content) as shrinkage reducing component (MKF, S/P = 0.8). Chemical shrinkage of alkali activated binder pastes was evaluated according to ASTM Standard C 1608-07. The thickness of the paste was equal to 22 mm.

Results: Differences in rheology between FA-based blends and MK-based blends determine very different amounts of required alkaline solution (blend of sodium hydroxide and sodium silicate). Hence, a proper comparison for alkali activated binders of sufficient (up to good) mechanical performance needs to be carried out with the preliminary restraint of similar rheology and same efficiency in sample production (i.e. with a very similar content of air voids associated to paste viscosities). Blended systems based on fly ash exhibited chemical shrinkage values ranging from 5.0 and 11.6 mm^3/g . MK showed higher chemical shrinkage respect to FA-based blends (22.1 mm^3/g), which was significantly reduced in the system MKF containing quartz (12.2 mm^3/g). The cementitious reference showed a value equal to 41.3 mm^3/g , which is significantly higher than those exhibited by alkali activated materials.

MONITORING OF ELECTRICAL RESISTIVITY TO DETECT MOISTURE AND CARBONATION PROFILES IN CEMENTITIOUS MATERIALS

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Introduction: Electrical resistivity monitoring within the concrete cover of reinforced concrete structures have received much attention in recent years especially in relation to corrosion risk. They are usually carried out with embedded probes with electrodes either parallel or perpendicular to the outside concrete surface, which is exposed to the penetration of aggressive species. In this study, experimental tests and simulations were carried out, in order to evaluate which direction of measurement is more appropriate for monitoring the ingress of water as well as the advancement of carbonation through the concrete cover.

Materials and methods: The experimental study was conducted on a prismatic mortar specimen, made with ordinary Portland cement. Two electrodes lines of four stainless steel wires were embedded in the specimen for measuring electrical resistivity at different depths of concrete cover. The distance among the wires was 50 mm and 10 mm for perpendicular and parallel lines, respectively. After curing, the sample was dried and then was exposed to accelerated carbonation, followed by wet and dry cycles at temperature of 20°C. Experimental results were compared to those of numerical simulations aimed at modeling the changes in the concrete resistivity as a function of water uptake and sensors location. The model was based on Ohm's law ($\nabla\Phi = pJ$) in conjunction with the continuity equation ($\nabla J = 0$).

Results and discussion: During the carbonation period, the electrical resistivity of the mortar increased significantly. Nevertheless, no appreciable differences among measurements at different depths were noted, due to small variations of humidity in the specimen that significantly affected the resistivity. In the wet cycle, both experimental and numerical results indicated that the electrodes placed perpendicularly to the front of water ingress, are characterized initially by a gentle reduction, followed by a significant drop of the resistivity (about one order of magnitude). The latter significant occurred, when the waterfront reaches the same depth as the pair of electrodes. In addition, the numerical simulations showed that the resolution of water penetration depth increases, when the distance between the electrodes decreases. The pairs of electrodes, which were placed parallel to the water

penetration, showed a sharp decrease in the resistivity (higher than one order of magnitude), only when the waterfront reached the last electrode of the pair. Therefore, the electrical measurements carried out parallel and perpendicularly to the ingress of water should be combined to obtain complementary information. Combining the two types of resistivity measurements, the progressive advance of water can be observed with respect to both depth and time. These indications could be used to estimate the risk of corrosion at different depths in the concrete cover of the reinforced concrete structures or to evaluate the progress of carbonation. In fact, it's well known that the electrical resistivity of carbonated concrete is different from that of alkaline concrete in the same environmental conditions (i.e. temperature and humidity). Thus, comparing the electrical resistivity of two wet conditions at different times, when a change was observed, this could be attributed to the carbonation.

BIOCOMPATIBLE PHOSPHATE GLASSES AND FIBERS WITH OPTICAL FUNCTIONALITIES

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Introduction: In recent times, the growing interest toward multifunctional materials for biomedical applications has led to the investigation of phosphate glasses, since they can be properly designed to be at the same time biocompatible, resorbable and with optical properties. This intriguing combination of features paves the way towards the development of interesting solutions for drug delivery, neural growth and photodynamic therapy.

Materials and methods: A series of phosphate glasses with different compositions was fabricated, then thermally and optically characterized. Additional characterization concerning the dissolution tests in simulated physiological conditions (phosphate buffered saline solution, pH = 7.4 at 37°C) was performed following standard test protocols. The glasses were synthesized by melt-quenching technique and then, on selected compositions, core/cladding optical fibers were obtained by preform drawing.

Results: All glasses resulted to be homogeneous and crystal free. Their thermal stability was demonstrated by differential thermal analysis measurements and the prepared glasses showed an optical transmission window ranging from 200 to 2000 nm. The glasses demonstrated solubility in biological fluids and possibility to be processed into fibers. Different types of fiber configurations were successfully fabricated and tested: single glass fibers, holey fibers, and single-mode and multi-mode optical fibers. For the fabrication of optical fibers, the core glass was cast into a rod form, while the cladding glass, with lower refractive index, was shaped into a tube by casting the molten glass into a rotational casting mold. The optical loss of the fibers was measured by cut-back technique as 2 dB/m at the wavelength of 1300 nm, in line with typical phosphate glass optical fibers.

Discussion: The glasses developed for this study are suitable for fiber drawing and are soluble in simulated biological environment. The fabricated optical fibers demonstrated good transparency in the near infrared biological optical window and in the visible region, up to the near UV, thus opening possibilities for disinfection of tissues and excitation of new types of fluorophores. The attenuation of the fibers in the near infrared was the lowest among biocompatible optical waveguides, thus demonstrating that bioreversible optical devices are feasible.

ONE-PART GEOPOLYMERS ACTIVATED WITH POTASSIUM-RICH BIOMASS ASHES

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Introduction: Geopolymers are obtained by the chemical reaction between an aluminosilicate powder and an alkaline solution. Even if geopolymers do

not contain Portland cement, they are similar to cementitious materials. Recently, many authors have tried to prepare geopolymers without alkaline activators, since they are user-hostile. These new materials are called one-part geopolymers and appear as a cementitious powder that can polymerize with water.

The aim of this work is to investigate the possibility of using a potassium-rich biomass ash for the activation of one-part geopolymers.

Materials and methods: Metakaolin obtained by the calcination at 700°C of kaolin from South England and biomass ash originating from a power plant located in Belgium were used as powders for one-part geopolymers. River sand with maximum grain size of 2 mm was used to prepare mortars. The reaction kinetics of geopolymeric pastes with a constant water/solid (w/s) ratio equal to 0.56 but with different K/Al molar ratios equal to 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0, was investigated through isothermal micro-calorimetric analysis at 25°C.

Geopolymeric mortars were prepared by varying w/s and K/Al molar ratios at a constant sand/metakaolin ratio equal to 3. Mortars were prepared also with ash that has been thermally treated at 700°C in order to investigate if the decomposition of carbonates could increase the reactivity.

As a reference, a two-part geopolymeric mortar was prepared using metakaolin as aluminosilicate powder and a mixture of unheated ash, Aerosil (SiO₂ >95%) and KOH as alkaline solution.

Mortars were cured at 20°C for 24 h and then at 70°C for another 24 h. Finally, specimens were subjected to compression tests.

Results: The reaction enthalpy of pastes increased from -39 J/g at K/Al = 0.5 to -64 J/g at K/Al = 2.5.

While the compressive strength of the reference mortar was equal to 6.1 MPa, the compressive strength obtained by geopolymeric mortars prepared with unheated biomass ash at K/Al of 0.5, 1.0 and 1.5 were around 1.7 MPa, and when K/Al is 2.5 a compressive strength of 3.7 MPa was reached. If prepared with the heated ash, one-part geopolymeric mortars showed compressive strengths ranging from 1.7 to 2.5 MPa.

Discussion: The heat flow of pastes measured by isothermal micro-calorimetric analyses increased with the K/Al molar ratio. The reaction enthalpy increased until a maximum, which corresponds to the most reactive composition (K/Al = 2.5), in agreement with compression tests. However, best mechanical properties were still registered for the reference two-part geopolymeric mortar. The thermal treatment of biomass ash reduced the compressive strength of one-part geopolymeric mortars up to 32%.

SUPER ABSORBENT POLYMER AS AN INTERNAL CURING AGENT FOR REDUCING EARLY-SHRINKAGE

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Introduction: Cracking of concrete is a common problem that generally leads to several drawbacks experienced by concrete structures, mainly influencing and reducing durability and lifetime. This is of particular relevance in the case of slab-type structures. While long-term (drying) shrinkage has been the focus of various research, recent studies have shown that the loss of moisture from fresh concrete can produce large tensile stresses in concrete, leading to early-age shrinkage cracking. Cement materials with low water/cement (w/c) or low water/binder (w/b) ratios are vulnerable to early-age cracking also due to autogenous shrinkage. It was suggested and demonstrated that this problem can be solved by mixing superabsorbent polymers (SAP) into fresh concrete, thereby establishing small reservoirs of internal curing water. When a new component like SAP is introduced into the concrete matrix, it becomes important to investigate how this component influences concrete properties such as workability and mechanical properties.

Materials and methods: The actual work is related to concretes with a water-cement ratio of 0.4, the upper limit of HPC. The rate of SAP addition was 0.25% by weight of cement. In order to verify the effect of this admixture, a reference concrete and a concrete with SRA (Shrinkage Reducing Admixture) were also produced. Other researchers have hypothesized the amount of water absorbed by SAP during mixing and casting and they have added some extra water in the mixture. We preferred to produce concretes in both conditions: by adding some water to saturate SAP in one batch of specimens and without modifying the nominal composition in the second batch. The slump loss (very significant in the absence of extra water) was preserved by increasing the superplasticizer rate. Cube specimens to test compressive strength at several curing times and plate-type specimens held by anchors to evaluate

the cracking trend were manufactured. Plate-type specimens were tested in a short period of time (24 hours) in order to focus on the first cracking. The cracks pattern observed on the upper side was detected by digital camera and calculated using appropriate software. Overall length and area of the cracks were evaluated.

Results and discussion: The introduction of SAP (superabsorbent polymer) into HPC concrete appears to lead to a decrease in cracks nucleation and opening, only when no extra water to saturate SAP was added. In this case, the lower w/c overcame the penalization ascribed to SAP addition, and it allowed to preserve the compressive strength achieved by the reference concrete. The reduction in crack pattern, appears very similar to that obtained in the presence of the SRA (shrinkage reduction admixture). When the mixing water increased in order to obtain SAP saturation, the results are not so encouraging. May be it was expected a too high absorption.

INVESTIGATION OF RHEOLOGICAL AND DYNAMIC MECHANICAL PROPERTIES OF GRAPHENE- TGMDA NANOCOMPOSITES

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Introduction: In the last years the use of graphene and graphene-based polymer nanocomposites appears to meet relevant requirements in the area of nanoscience. The great interest in graphene is related to its exceptional properties. This work presents the rheological, dynamic mechanical and thermal behavior of a tetrafunctional epoxy resin filled with two types of graphene nanoparticles, namely partially exfoliated graphite (pEG) and carboxylated partially exfoliated graphite (CpEG).

Materials and methods: The pEG and CpEG nanoparticles are characterized by 56% and 60% of amorphous phase degree, respectively. Exfoliated graphite is prepared using traditional acid intercalation followed by a sudden treatment at high temperature (900°C).

The epoxy matrix is prepared by mixing TGMDA with an epoxy monomer 1-4 butanedioldiglycidyl-ether (BDE) that acts as a reactive diluent allowing to facilitate the dispersion step of nanofiller.

Epoxy blend and the curing agent DDS were mixed at 120°C, the graphene-based nanoparticles are added by a ultrasonication for 20 minutes (Hielscher UP200S-24KHz). All the mixtures are cured by two-stage curing cycles: a first isothermal stage at T = 125°C for 1 hour and a second isothermal stage at T = 200°C for 3 hours.

The rheological measurements in the liquid state, before curing, are carried out on a Physica-MCR301 (Anton-Paar) rotational rheometer equipped with a parallel plate geometry (50 mm diameter, 1 mm gap). Small amplitude oscillatory shear measurements, within the linear viscoelasticity regime, on the TGMDA, on the epoxy mixture and on the MWCNT-TBD dispersions with 0.1, 0.25, 0.5 and 0.70 wt% MWCNT content were performed at T = 75°C.

Dynamic mechanical properties of the cured samples were performed with a dynamic mechanical thermo-analyzer (Tritec2000 DMA-Triton Technology). Scanning electron microscope micrographs of the pEG and CpEG samples are obtained with SEM apparatus (JSM-6700F-JEOL).

Results: The rheological results show that the epoxy mixture is characterized by a Newtonian behavior. The inclusion of the pEG and CpEG produces a dramatic change in the viscosity trend, occurring at 3 wt% pEG and at 1 wt% CpEG content, with the viscosity curve showing a shear thinning behavior in the whole frequency range tested (0.01 to 100 rad/s). Moreover, at low frequency, the storage modulus G' of the uncured dispersions becomes nearly independent of frequency at 3 wt% pEG and at 0.75 wt% CpEG content in the liquid epoxy mixture.

TGA curves of the two nanofillers indicate an amount of carboxylated groups of about 10 wt% for the CpEG sample. The cured samples show a strong reinforcement in the modulus of the samples with CpEG embedded in the TGMDA. The SEM image of the CpEG shows a more fluffy morphology consistent with a higher percentage of exfoliated graphite.

Discussion: The presence of a storage plateau modulus at low frequencies can be interpreted in terms of an interconnected network of nanofiller in the epoxy liquid dispersion that provides an apparent yield stress, i.e. the rheological percolation threshold. As the carboxylated group content increases up to 10% in the CpEG sample, the rheological percolation threshold reduces from 3 wt% down to 0.75 wt%,

Self-assembly mechanisms, determined by attractive interactions between edge-carboxylated graphene particles, promote the rheological percolation and determine good mechanical performance of the cured nanocomposites.

VISCOELASTIC PROPERTIES AND MORPHOLOGY OF CARBON NANOTUBES FILLED EPOXY NANOCOMPOSITES

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Introduction: Epoxy resins with carbon nano-fillers offer tremendous potential to improve the properties of advanced composites and easy integration into current processing schemes. Multi-walled carbon nanotubes (MWCNTs) are widely used nano-fillers to enhance physical properties of epoxy matrix.

Materials and methods: The MWCNTs (3100 Grade) of ~20 nm diameter were obtained from Nanocyl-S.A. The carbon purity is >95% with a metal oxide impurity <5%.

The epoxy matrix is prepared by mixing TGMDA with an epoxy monomer 1-4 butanedioldiglycidyl-ether (BDE) that acts as a reactive diluent. Epoxy blend and DDS were mixed at 120°C (named TBD in the following). The MWCNTs were incorporated into the matrix by using a ultrasonication for 20 minutes (Hielscher model UP200S-24KHz). All the mixtures are cured by two-stage curing cycles: a first isothermal stage at T = 125°C for 1 hour and a second isothermal stage at T = 200°C for 3 hours.

The rheological measurements in the liquid state, before curing, were carried out on a Physica-MCR301 (Anton-Paar) rotational rheometer equipped with a parallel plate geometry (50 mm diameter, 1 mm gap). Small amplitude oscillatory shear measurements, within the linear viscoelasticity regime, on the TGMDA, on the epoxy mixture and on the MWCNT-TBD dispersions with 0.1, 0.25, 0.5 and 0.70 wt% MWCNT content were performed at T = 75°C.

Dynamic mechanical properties of the cured samples were performed with a dynamic mechanical thermo-analyzer (TA instrument DMA-2980). Thermogravimetric analysis (TGA) of the cured samples was carried out in air using a Mettler-Toledo TGA/SDTA 851 thermal analyzer.

TEM images were recorded on high-resolution transmission electron microscopy HRTEM JEM-2100 (JEOL-Japan).

Results: The complex viscosity of the TGMDA epoxy resin is constant in the whole frequency range tested. The inclusion of the BDE diluent significantly decreases the viscosity of the TGMDA, allowing to facilitate the dispersion step of the MWCNTs. The inclusion of the multi-walled carbon nanotubes, with a content between 0.25 and 0.70 wt%, in the formulated TBD epoxy mixture increases the complex viscosity of the uncured dispersions of about 2 orders of magnitude at low frequency. Moreover, the MWCNT-TBD dispersions show a strong shear thinning behavior in the range 0.01-10 rad/s, then the viscosity of all the dispersions become constant at higher frequencies. The storage modulus G' of the uncured dispersions at low frequency becomes nearly independent of frequency at 0.25 wt% MWCNT content.

The TGA analysis shows that the cured epoxy TBD mixture begins to degrade at 320°C. No changes in the thermogravimetric curves are shown when the MWCNTs are enclosed.

The dynamic mechanical analysis shows a slight increase of the storage modulus of the cured nanocomposites with a concentration up to 0.5 wt% of CNTs with respect to the unfilled epoxy matrix.

Discussion: The tendency to plateau in G' can be attributed to the formation of a percolation network in the nanocomposite. Large scale polymer relaxations in the nanocomposites are, in fact, restrained by the presence of the nanotubes. TEM investigation confirms that the MWCNTs are uniformly distributed into the epoxy matrix and they form a continuous network at MWCNTs higher ≥0.25 wt%.

PYROLYSIS OF AUTOMOBILE SHREDDER RESIDUE IN A BENCH SCALE ROTARY KILN

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Introduction: Automotive shredder residue or car fluff is one of the main end-of-life vehicles by-products. In order to minimize environmental impacts due to demolition processes, the reduction of flows to be landfilled is required by the EU 2009/1 Directive. Thus, recycling and energy recovery are strongly encouraged. Pyrolysis is a thermal conversion process able to recover energy from car fluff. Pyrolysis can be defined as a process in which a solid form of fuel is converted into a gas, an oil and a solid residue (char).

Additionally, the char has a high-energy recovery potential. In this context, the aim of the study was to investigate the pyrolysis of car fluff by means of a bench scale rotary kiln.

Materials and methods: The activities included the following steps: (i) Chemical-physical characterization of the inlet fluff; (ii) Bench scale experimentations; (iii) Chemical-physical characterizations of char, oil and syngas (pyrolysis outputs). Two type of car fluff were investigated. The first one, indicated as Car fluff A, represents the oversize fraction of a screening process based on a sieve of 3 cm. While, the second one, the under screen fraction. Car fluff A presented a moisture content of 0.62%, a volatile organic compounds content of 76.6%, a carbon content of 5.8%, an ash content of 16.8% and an high and lower heating values of 19 MJ/kg and 17.2 MJ/kg, respectively. Instead, car fluff B presented a moisture content of 1.64%, a volatile organic compounds content of 78.4%, a carbon content of 4.7%, an ash content of 15.2% and an high and lower heating values of 21.7 MJ/kg and 19.9 MJ/kg, respectively. Tests were carried out in a bench scale rotary kiln with a volume of 7.79 dm³. Furthermore, several parameters such as kiln rotation speed, temperature, car fluff and nitrogen flow rate had varied.

Results and discussion: Results related to the experiment tests in which temperature varied in the range 450-650°C, are as follows: (i) The yield of syngas increases with the pyrolysis temperature; (ii) The syngas had a lower heating value in the range 18-26 MJ/Nm³ as a function of the content of light hydrocarbons; (iii) The maximum production of oils (approximately 35%) takes place at a temperature of 550°C. The oil appear as a viscous liquid with a heating value in the range 12.5-14.5 MJ/kg and ash content negligible; (iv) The use of char as fuel requires standardization and an improvement in physical and chemical properties; (v) The char has a minimum of production at 550°C with a heating value of 12-18 MJ/kg and an ash content in the range of 48-58%. Finally, the SEM analysis showed that at higher temperature (650°C) the char structure becomes more porous.

NANOSTRUCTURED FUNCTIONAL MEMBRANES: OPTIMIZATION OF PROCESSING CONDITIONS

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Introduction: Nowadays, filtration technology is a widely used approach for making a healthier and cleaner environment, especially if "smart" materials, able to exhibit multiple functions are used. Polymeric membranes are mostly used for filtering applications due to their straightforward pore forming mechanism, higher flexibility, smaller footprints required for installation and relatively low costs if compared to inorganic membranes. However these membranes are mostly based on mechanical filtering. This mechanism of filtration produces an accumulation of the particles removed on the membrane itself resulting also in fouling effects limiting membrane's performances. For this reason, in some applications, it is needed to have an active filtration effect with chemical removal of toxic substances. In our previous work a standard process has been proposed in order to obtain hybrid organic/inorganic membranes with photocatalytic properties.

The aim of this paper is to optimize the conditions of the membrane production process.

Materials and methods: Polyethersulphone was selected as polymer for membrane production because of its widely accepted use in the membrane field. The polymer was dissolved in DMF:Toluene 1:1. The polymer solution was electrospun at 21 KV with a constant flux of 30 µl/min. The resulting membrane was free of defects and the average fiber diameter is 716 nm ± 365 nm. The ZnO nanowires were grown by an hydrothermal process. In a first step the electrospun fibers were immersed in a solution of Zn(Ac)/H₂O (0.5M) and stirred for 1h. Then they were annealed in a oven at 110°C overnight. The second step was a CBD (Chemical bath deposition) process by using Zn(Ac), H₂O and Etylenediammine (EDA). This process is very long due to the annealing step. For this reason many different solutions have been investigated. In particular, it is tried to reduce the annealing time increasing the temperature of the process.

Results: The morphology of the obtained fibers has been investigated by SEM analysis. It shows that massive and uniform ZnO nanoroads have grown on the fibers surface with an annealing temperature of 150°C and a time of 5 hours. Moreover XRD analysis has been performed in order to assess the crystallinity of the ZnO after the annealing process.

Discussion: The results presented here evidenced that it was possible to obtain a uniform growth of the ZnO nanoroads onto the fibers surface reducing by more than 50% the time of the annealing process, also if a little increase of the process temperature is necessary.

MSU-TYPE MESOPOROUS SILICA-BASED ALENDRONATE-LOADED MATERIALS FOR BONE-TARGETING PROMOTED BY ALENDRONATE

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Introduction: Bisphosphonates are a class of drugs used in the treatment of bone diseases or metastasis because they inhibit re-absorption of bone tissues. Bisphosphonates are able to bind very strongly hydroxyapatite, one of the main components of bones. For this reason, they can be also used as drug carriers because they are able to target bone tissues. Bisphosphonates can be employed in the design and development of bone-specific drug delivery of therapeutics such as radiodrugs, anti-inflammatory drugs, estrogens or proteins. Alendronate is a bisphosphonate employed in osteoporosis prevention and in the Paget Disease. Here is described the preparation and characterization of a mesoporous silica-based carrier for the targeting of hydroxyapatite in bone, aimed to the localized release of several kind of drugs.

Materials and methods: Tetraethylorthosilicate, Tryton X-100 and Alendronate have been provided by Sigma Aldrich. The obtained systems has been characterized using X-ray powder diffraction, Nitrogen adsorption, desorption, FT-IR spectroscopy, scanning electron microscopy. The amount of alendronate loaded was determined by UV-Vis spectrophotometry

Results: In this work MSU-type mesoporous silica, obtained through an interfacial synthesis procedure carried out at room temperature and without mineralizing agent, have been modified, by post-synthesis grafting, introducing a carboxyl group functionality able to bind alendronate through electrostatic interaction. Alendronate has been loaded in hybrid silica through a double loading procedure. Furthermore hydroxyapatite has been synthesized, characterized and pressed into pellets to be used as substrate to verify the targeting activity of the alendronate on the surface of the mesoporous silica-based system. The expected ability of the obtained hybrid MSU-alendronate system to bind hydroxyapatite has been evaluated at pH 7.4 in phosphate buffer. The structure of the obtained system has been confirmed using several techniques (see Materials and Methods section), the total drug amount resulted to be around 3% in weight.

It has been confirmed the migration of the hybrid MSU-alendronate on the surface of the hydroxyapatite pellets that mimics, *in vitro*, the bone-targeting activity

Discussion: Starting from a MSU-type mesoporous silica, an hybrid system in which alendronate electrostatically interacts with carboxylic groups on silica surface has been developed and characterized. The system is able to target hydroxyapatite and we believe that it is potentially interesting in bone-targeting of several kind of drugs.

EVALUATION BY CDF-TEST OF SURFACE OR BULK HYDROPHOBIC TREATMENTS TO INCREASE THE FREEZE THAW RESISTANCE OF CONCRETES

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Introduction: Deterioration of concrete from freeze-thaw actions may occur when concrete is critically saturated, which is when approximately 91% of its pores are filled with water. Distress to critically saturated concrete from freezing and thawing will commence with the first freeze-thaw cycle and will continue throughout successive winter seasons resulting in repeated loss of concrete surface. To protect from freeze/thaw damage, concrete should be air-entrained by adding a surface-active agent to the concrete mixture. This creates a large number of closely spaced, small air bubbles in the hardened concrete. About 4% air by volume is needed with a consequent reduction in compressive strength of about 20%.

In this work, the ability of a surface or bulk hydrophobic treatment to improve the concrete resistance to degradation due to freezing and thawing cycles was investigated and compared with a traditional air-entraining admixture. The CDF Test "Capillary suction, De-icing solution and Freeze thaw test" was used to check the resistance to freeze-thaw cycles with or without de-icing salts.

Materials and methods: Four different types of specimens were manufactured: one with a mixture according to EN 206 indications for concrete exposed to frost (class of exposure XF4); three with a mixture according to EN 206 indications for concrete not exposed to frost (class of exposure XC4): as it is, with an hydrophobic admixture, with a hydrophobic surface treatment. The CDF Test allows to measure the amount of scaling per unit surface area due to a number of well defined freezing and thawing cycles in the presence of deicing salt, and leads to an estimate of the freeze-thaw and deicing salt resistance of the concrete tested. In particular, according to RILEM 117-FDC and EN 12390 standards, after 28 freeze-thaw-cycles, the concrete mass loss Dm ($D_m \leq 500 \text{ g/m}^2$ to be frost resistant) and the concrete dynamic elastic modulus E ($E_{28} \text{ cycles} \geq 80\% E_0 \text{ cycles}$ to be frost resistant) were measured.

Results: The reference specimen XC4, as expected, did not satisfy the limits to be frost resistant. Also the specimen XC4 with the hydrophobic admixture did not satisfy the limits to be frost resistant, showing only a slight increase of degradation resistance in terms of elastic modulus and mass loss. The specimen XF4, guaranteed as frost resistant by EN 206, ensured an excellent resistance to degradation in terms of elastic modulus but not in terms of mass loss. Instead, the specimen XC4 with the hydrophobic surface treatment was the only one able to satisfy the limits in terms of both stiffness and mass loss, both in the presence and absence of de-icing salts.

GENERALISED FRACTAL MODEL FOR PREDICTING THERMAL CONDUCTIVITY OF POROUS MATERIALS

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Introduction: Thermal conductivity (k_{eff}) is one of the most important properties in the field of engineering and is a basic characteristic for classifying porous materials into different areas of application. Generally, k_{eff} is studied as a function of relative density and pore volume fraction of materials. Indeed, in literature, a large number of models, which depend on thermal conductivity of solid and fluid phase, are present. However, the comparison between experimental data and calculations by models are not always in agreement. For these reasons, it is necessary to describe porous microstructures using a phenomenological approach, which is able to take into account morphological features as pore size distribution. The aim of this work is to provide a general fractal modelling procedure (IFU), which is capable of reproducing every porous microstructure and consequently provides the possibility to obtain calculated values of thermal conductivity in agreement with experimental ones. Limestone, traditional and advanced ceramics are investigated. Moreover, a comparison between IFU and other models has been shown.

Materials and methods: The limestone analysed come from a quarry of Santa Caterina in Oristano. The traditional ceramics are obtained using two different pore forming agents: polypropylene and polymethyl-methacrylate. Moreover, YSZ and Al_2O_3 fabricated by freeze-casting and gel-casting technique respectively are studied.

Mercury intrusion porosimetry tests and thermal conductivity measurements have been considered in order to describe porous microstructures and heat transfer properties respectively.

An Intermingled Fractal Units' model (IFU) aimed at reproducing porous microstructures has been proposed. Model conversion into thermal patterns gives rise to an analytical procedure to calculate thermal conductivity (k_{eff}).

Results: IFU applications allow reproducing every pore size distributions of different porous materials studied in this work. Considering k_s for the specific solid phases and k_f for air, the calculations performed are compared with experimental data: limestone 1.22 vs. 1.27 W/(m·K), traditional ceramics 0.45 vs. 0.43 W/(m·K), YSZ 0.12 vs. 0.11 W/(m·K), Al_2O_3 0.37 vs. 0.32 W/(m·K). These results are compared with those obtained by other models from literature.

Discussion: The IFU's model calculations are in good agreement with experimental data, better than other models. In particular, IFU can be used as a generalised procedure aside from different peculiarities of porous microstructures.

INTEGRATION OF DURABILITY AND SENSORIAL PROPERTIES IN THE MATERIALS SELECTION FOR PROFESSIONAL APPLIANCES

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Introduction: Food service and laundry system appliances are characterized by an intense use in harsh environments; therefore, they need to communicate, through materials sensorial attributes, robustness and reliability. During their lifetime, professional appliances face specific chemical compatibility problems related to daily contact with food chemicals and detergent compounds compliance, and to misuse practices. For this reason, they are developed on one hand through a performance driven technical design process, and on the other through a sensorial-oriented materials selection, to improve the user experience with the product.

Materials and methods: The research focuses on the integration of durability and sensorial properties in the materials selection method applied to professional appliances.

As regards durability, the current quick preventive selection is based on nominal information, which is not strictly linked to time and degradation. Degradation may take place in professional food processing appliances through interaction among materials, detergents and food chemicals. The result is failure mechanisms that influence the component service life. Other external parameters, like temperature and pressure, can further change materials durability, and require "made-to-measure" life-testing solutions to simulate the real appliances use, based on DOE approach to optimize the experimental set up and correlate failures to the conditions from which they are generated.

The evaluation of expressive-sensorial properties of materials represents one of the most complex issues in materials selection. In order to communicate high quality, robustness, strength, reliability, and easy cleanability of professional products, material selection has been currently based on experience, taking as a reference material stainless steel. In order to evaluate different material alternatives by more concrete and comparable results, Sensory Evaluation Analysis techniques from food quality field, as the "Napping®" and "Sorting" tests, have been selected to translate sensorial properties of materials in a numerical system (numerical ranking, material sensory profile).

Results: The comparison between qualitative and quantitative properties of materials allows also evaluating the change in perception of aged materials after accelerated life-tests.

Discussion: The study set the basis for the development of a new method of materials selection, used both by designers and engineers, specifically designed for food service and laundry system appliances, able to couple qualitative and quantitative properties of materials.

MANUFACTURING AND CHARACTERIZATION OF NANO-COMPOSITE ABLATIVE MATERIALS

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Introduction: An efficient Thermal Protection System (TPS) is mandatory to protect re-entry space vehicles from the severe heating encountered during hypersonic flight through a planet or the Earth atmosphere. Ablative materials represent a traditional approach to thermal protection, used for over 50 years in a broad range of applications.

The Laboratory of Materials and Surface Engineering (LIMS) of Sapienza University of Rome has developed carbon-phenolic ablative materials with several densities and compositions. This work has the aim of improving the ablative materials performances by means of nano-fillers addition.

The addition of ZrO_2 nanoparticles can modify bulk properties, such as mechanical strength and thermal stability, with negligible consequence on density.

At the same time, nanoparticles are prone to agglomerate and this phenomenon can drastically reduce the desired beneficial effect: for this reason the ZrO_2 nanofillers were modified by several surface functionalization treatments to optimize the particles dispersion in the polymeric matrix.

Materials and methods: A resole phenolic resin was selected as matrix material because of the high oxidation resistance, high heat of ablation, high char yield (55-60%) at temperatures above 650°C in inert atmosphere and low viscosity (about 250 cP at T = 25°C). Two rigid graphitic felts (SGL Carbon SE), consisting of long carbon fibers connected together by a carbon binder, were selected as reinforcement materials. ZrO₂ nanoparticles (30-60 nm by IoLiTec GmbH) were selected as nano-fillers due to the high melting point (2680°C), low thermal conductivity (2.5 W/mK) and the possibility to be dispersible in many solvents after surface modification.

The ablative materials were characterized through SEM micrographs, four-point bending tests, compression tests on virgin and charred materials. Composite materials with different concentrations of nano-ZrO₂ were exposed in an oxyacetylene ablation testing facility in order to compare the ablation resistance and thermal protection capability of manufactured materials.

Results: FE-SEM micrographs highlight the good dispersion of ZrO₂ nanoparticles in the polymeric matrix; mechanical tests show that a nano-ZrO₂ content of 2 wt.% does not provide significant variation in the rupture stress values while a nanofiller content of 5wt.% drastically improves the mechanical performances, both of the virgin and charred material. The tests performed in the oxyacetylene ablation facility also confirm the enhanced properties of the manufactured nanocomposite materials in terms of weight loss and thermal stability.

Discussion: The addition of ceramic nanoparticles has the aim of improving the mechanical properties (rupture stress and elastic modulus) and the ablation performance (mechanical stabilization of char and reduction of recession rate) of the manufactured materials. The ZrO₂ nanoparticles provide an effective strengthening and stiffening effect only with a minimum content of 5 wt.%; in this case the charred material exhibits an evident enhancement of rupture stress, leading to a higher mechanical resistance of the surface exposed during the re-entry manoeuvre and, finally, to a lower recession rate of the thermal shield.

INKJET PRINTING TECHNOLOGY TO DECORATE HIGH RECYCLED CONTENT PORCELAIN STONEWARE TILES

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Introduction: Digital decoration has grown enormously since 2008 and nowadays it is a widely used way to decorate ceramic tiles due to its versatility, reliability and print quality. Several inks families have been developed especially for porcelain stoneware product that, among traditional tiles, is still at the top in terms of aesthetic and technical performances. Some research works have demonstrated that it is possible to obtain porcelain stoneware by using only secondary raw materials (industrial and urban scraps) instead of the natural ones with a firing process occurring at temperature significantly lower than 1250°C (mostly used temperature for porcelain stoneware tiles). However, the decoration of high-recycled content porcelain stoneware needs to be deepen studied to understand if the traditional inks are suitable or must be modified.

Materials and methods: An innovative mix for high recycled content porcelain stoneware tiles, made by 99% of secondary raw materials and able to sinter at 1060°C has been selected for this study. Two commercial additives (a rutile-based and a completely amorphous one) usually adopted to improve the colour rendering for traditional tile mixes, were added to the ceramic mix (0.5 and 5 wt%, respectively). Laboratory ceramic tiles (10 × 10 × 1 cm) were obtained by uniaxial pressing of the powdered mixes. Six traditional inks (black, red, yellow, beige, light blue and dark blue) were applied on the ceramic unfired tiles with and without additives by ink jet printing technology. For each tile the six selected colours were applied in form of squares of about 2 × 2 cm. Tiles were then sintered at three different temperatures (1040, 1060 and 1080°C).

The colour coordinates (the L*a*b* colour space also referred to as CIELAB) were determined by using a spectrophotometer. The colour ink penetration into the ceramic body was determined by optical microscopy of the cross section of the tiles and with the aid of an image analysis software.

Results: For each ink applied the colour coordinates change as function of the additives amount added (rutile-based and amorphous) and firing temperatures. The ink penetrating depth does not change significantly for all the investigated mixes (with and without additives) and at all the tested tem-

peratures. Red and black inks penetration depth is about 200 ± 11 mm. For yellow, beige, light and dark blue inks the penetration depth is about 150 ± 21 mm where the uncertainty of the measurement is bigger as the colour difference is more difficult to be detected.

Discussion: High recycled content porcelain stoneware tiles made by secondary raw materials can be decorated by using traditional inks for inkjet printing. The colour rendering improves with the increasing of the amorphous phase, thus by adding commercial additives and/or by increasing the firing temperature.

RECYCLABLE EPOXY PROCESSED BY RESIN INFUSION: LCA AND MECHANICAL PROPERTIES OF HYBRID LAMINATES

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Introduction: Epoxy resins are among the widest used thermoset resins in fiber reinforced composite. However, the increasing awareness of the environmental limits of non recyclable materials is raising growing concerns about the use of thermosets. The currently used recycling method for thermosets is based on burning them. This approach allows to recover the reinforcing fibers but destroy the matrix. Recently, novel chemical recycling approaches were presented in the literature which address these problems. Most chemical approaches are based on the use of strong acid solutions which, at medium to high temperatures (i.e. 200°C), break down the epoxy network allowing to recover clean reinforcing fibers and simple chemicals as byproduct of degraded matrix. The environmental friendliness of these approaches can be argued because of the use of strong acid solutions and high processing temperatures. To overcome all these limitations, Connora Technologies introduced on the market some novel amine systems with designed cleavable chemistry. These systems, named as Recycleamine™, can be mixed with standard epoxy and can be recycled in mild conditions (i.e. max 100°C) with a acetic acid solutions. The present paper discusses the use of this amine with a biobased epoxy resins using a hybrid natural fiber/carbon fiber laminate construction. Life cycle assessment (LCA) is carried out to establish the environmental benefits of the proposed approach.

Materials and methods: The cleavable amine named Recyclamine 301 was used in the present work with the addition of a proprietary inhibitor to allow room temperature curing.. The biobased SuperSap 300 epoxy resin was selected. For the reinforcements two fabrics were selected: a twill 200 gsm carbon fabric and a 400 gsm 2 × 2 twill flax fiber. Laminates were prepared with resin infusion techniques. Tensile and flexural were determined according to ASTM standards. LCA was performed with SimaPro 8.0 software.

Results: The hybridization was achieved combining flax fabric with carbon fabric. Two lay up were studied F/[C]_n/F and [C]_n/FF/[C]_n. The mechanical properties characterization, both tensile and flexural, showed that the full carbon lay up (i.e. [C]_n) is the best performing but the hybrid [C]_n/FF/[C]_n presented similar or even slightly better performances. Fully cured systems were also chemical recycled showing that fully reusable thermoplastic can be obtained out of the thermoset matrix. The chemical procedure was successfully applied on the natural reinforced systems too. The LCA evaluation performed on the hybrid systems outlined some advantages due to the use of biobased resin and flax fabrics in terms of CO₂ and Cumulative Energy reductions.

Discussion: The main advantages of the systems studied are that: the by-product of the chemical recycling is a reusable thermoplastic; the combination of natural fabrics and biobased resins allows to obtain truly green composites with lower environmental impact.

PHOTOCATALYTIC GEOPOLYMERS FOR NITRIC OXIDE DEGRADATION

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Introduction: The photocatalytic oxidation technology gained great attention recently thanks to possible applications in energy production and pollution control. Ambient applications involve typically the development of photocatalytic devices for air or water active treatment. Cement-based matrices are widely studied, but they represent however an environmental issue in terms of CO₂ emissions, accounting for 5-8% of global CO₂ production. In this

regard, alternative sustainable binders are represented by alkali activated materials (AAM) or, Geopolymers, which can be synthesized by means of alkaline activation of several environmentally friendly solid precursors such as fly ash, calcined clays, etc. Moreover, hybrid organic-inorganic geopolymers have been proposed in literature. These innovative functional materials are obtained by the *in situ* co-reticulation of metakaolin, a mixture of dialkylsiloxane oligomers and an alkaline solution, allowing the formation of a highly interpenetrated structures (on nanometric scale), based on the formation of a wide network of hydrogen bonding.

Materials and methods: In this study, geopolymer matrices obtained from different solid precursors (fly ash and metakaolin), composite systems (siloxane-hybrid, foamed hybrid) and curing temperatures (room temperature and 60°C), were investigated for the same photocatalyst content (i.e. 3% TiO₂ by weight of paste). The photocatalytic activity was evaluated as NO degradation in air and the results were compared with an ordinary Portland cement (OPC) reference. Furthermore, microstructural features and titania dispersion in the matrices were assessed by SEM and EDS analyses.

Results and discussion: The experimental results suggest the following conclusions:

- The photocatalytic activity of AAM binders is strongly variable depending on the type of binder itself and the curing process.
- The highest photocatalytic activity is detected for fly ash-based AAM matrices cured at room temperature.
- Metakaolin-based AAM matrices exhibits also promising photocatalytic activity.
- EDS analysis of sample sections provides a clear picture of the photocatalyst distribution in the matrix surface layer.
- EDS data demonstrate segregation effects depending on AAM matrix and curing temperature, with clear depletion of the surface titania content for the samples cured at 60 C.
- Titania surface segregation measurements suggest a significant contribution to photocatalytic activity by transport phenomena of titania suspension during the curing process.

The described results demonstrate that AAM binders can be very interesting photocatalyst support matrices. The high variation of catalytic activity evidenced by the different samples suggest large possibilities in performance enhancement. Particularly, the described results suggest that the optimization of the photocatalyst dispersion by curing process tailoring and selection of the AAM aluminosilicate precursor/activating solution combination can play a fundamental role in the development of high performance AAM photocatalytic materials.

Moreover, in comparison to OPC matrices, AAM binders can also have distinctive advantages in photocatalytic materials development due to several features (e.g. fire resistance, surface carbonation and overall sustainability) that allows the synthesis of materials with optimized long-term properties. In this regard, future studies will be devoted to the exploration of AAM photocatalyst matrices concerning both the material performance and the aging effects in order to better understand the potential respect to traditional cementitious supports.

NOVEL GEL CASTING PROCESS FOR THE MANUFACTURING OF GLASS FOAMS

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Introduction: Glass foams (or cellular glasses) represent a fundamental class of glass-based building materials. As thermal insulators, glass foams contribute positively to energy saving and reduction of CO₂ emissions, but the same foaming reactions have a disputable environmental effect, since they generally occur well above 800°C.

The present paper presents a new approach to glass foams, based on alkali activation. Usual alkali-activated materials, generally known as "geopolymers", are produced through the reaction of an alumino-silicate typically with a concentrated aqueous solution of alkali hydroxide or silicate. The products of alkaline dissolution undergo condensation reactions, with water release and formation of chemically stable gels, at low temperature (below 100°C). When applied to glass powders, the alkali activation may lead to less stable gels, here considered only as precursors. Air may be trapped by vigorous mechanical stirring of mixtures at the first stages of gelification, with the support of a surfactant. A sintering treatment, at 700-800°C, is

finally applied to convert highly porous gels into glass foams, with the effect of limiting the leachability.

Materials and methods: Fine soda-lime glass powders (mean particle size of 75 µm) were inserted in an aqueous solution containing 2.5 M KOH, for a solid loading of loading of 65 wt%, and left for 3h, under magnetic stirring. Suspensions of partially dissolved glass powders were cast in closed polystyrene cylindrical moulds (60 mm diameter), and cured at 75°C. Gels obtained at different curing times were first added with 4 wt% Triton X-100 (a non-ionic surfactant) then foamed by vigorous mechanical mixing. Foamed gels were kept at 75°C for 3 days, in order to complete the hardening, before being demoulded. Finally, hardened foamed gels were fired at 700 and 800°C for 1h with a heating rate of 1-10°C/min.

Results and discussion: The pore architecture in the obtained sample was largely conditioned by curing conditions. After a longer gelation step, a stronger polymeric network impeded the coalescence of adjacent bubbles. As an example, the mean cell size in green samples, being 847 µm for 2 h curing time, decreased to 511 µm for 4 h. The total porosity, completely open, increased with the curing time from ≈65 to 75%. Firing treatments at 700°C determined a further increase of total porosity up to 90%, owing to the decomposition of the gels (hydrated compounds releasing water vapour), in a pyroplastic mass of softened glass. The viscous flow caused also the formation of membranes between adjacent pores, resulting in partially closed porosity. If applied at 800°C, the firing caused partial devitrification, resulting in a modified ratio between open and closed porosity in the foams. In selected conditions, the compressive strength of foams after firing exceeds 4 MPa, well above the data for commercial products.

SURFACE MODIFICATION OF Ti6Al4V SUBSTRATES BY YB FIBER LASER FOR STRUCTURAL ADHESIVE BONDING

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Introduction: Structural adhesive bonding is a widespread technique used for different engineering applications. It has many advantages compared to conventional joining methods, such as the ability to join different materials without generating geometric discontinuity and/or stress concentration offering also better resistance to corrosion.

However, the main problem that limits the massive use of adhesive bonding for structural applications is the occurrence of failure at the interface between adhesive and substrate. Among the various strategies of surface preparation, in order to limit the occurrence of interfacial failure, treatment with pulsed laser is very effective on a wide variety of materials.

This paper presents the results obtained by the application of a pulsed laser on titanium alloy substrates (Ti6Al4V). A wide experimental campaign was performed to assess the influence of laser process to obtain the desired surface characteristics. Surface conditions have been screened to draw quantitative information in terms of topography, chemistry and mechanical properties. The most suitable combination of laser processing parameters has been selected and adhesive bonded peel joints have been fabricated for subsequent mechanical testing and compared with the as received and chemically treated samples.

Materials and methods: The material used is Ti6Al4V titanium alloy. The surface modifications performed were based on chemical treatment and laser application. The last has been performed at varying scanning speed and pulse fluence. Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and surface roughness evaluation have been used to assess the evolution of surface topography and crystal structure after surface modifications. Contact angle measurements were also performed to obtain qualitative information on the effectiveness of the treated surface to be properly wet by the liquid adhesive. Finally, surface hardness has been assessed through nanoindentation tests, while the strength of Ti6Al4V / epoxy joints is analyzed using peel test coupon.

Results: Laser irradiation enabled different extents of morphological modifications. The pulse fluence, together with the laser scanning speed dictates the amount of energy delivered on the surface as well as the depth of the heat affected zone. At higher fluence and lowest speed, a fragile oxide is generated on the top surface that has a detrimental effect on the joint resistance. The mechanical highlight the beneficial effect of laser irradiation and the chemical treatments on the joint resistance that drastically increases in comparison with the as received samples.

Discussion: It is shown that the generation of surface structures modified by laser allows to customize the surface properties of the material by selecting a proper processing parameters window. The obtained Ti6Al4V/epoxy joints have mechanical characteristics and durability improved with respect to the as received material and comparable to those obtained with traditional methods, such as chemical treatments.

ELECTRODEPOSITION OF ZN-ALUMINA NANOCOMPOSITE COATINGS

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Introduction: Zinc-based coatings are widely used for sacrificial protection of steel, due to their low cost, high corrosion resistance and low environmental impact. In the last few years, the electrodeposition of several zinc and zinc alloy composites, containing ceramic micro or nanoparticles, has been object of several investigations because the incorporation of particles can lead to an improvement of mechanical, tribological and corrosion properties. Zn-Al₂O₃ coating electrodeposition has been studied by other authors from sulphate baths containing alumina microparticles.

The aim of the present work was to obtain by electrodeposition technique Zn-Al₂O₃ nanocomposite coatings on mild steel from a slightly acidic chloride bath used by galvanic industry for the barrel process.

Materials and methods: Pure zinc coatings were electrodeposited at 45°C on mild steel discs from a chloride bath, with the following composition: 70 g L⁻¹ ZnCl₂, 185 g L⁻¹ KCl, 26 g L⁻¹ H₃BO₃ and 2 g L⁻¹ gelatine (pH 5.7). Gelatine was added to the bath in order to enhance alumina incorporation. Zn-Al₂O₃ composite coatings were electrodeposited by adding to the deposition bath 10 or 20 g L⁻¹ Al₂O₃ particles (crystallite size: 1.3 nm). The tests were carried out galvanostatically with pulsed direct current using a cathodic square wave (peak current density 100–200 mA cm⁻², pulse frequency 1 Hz, duty cycle 50%). The obtained coatings were characterized by means of X-ray diffraction, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and Vickers microhardness measurement.

Results: Current efficiencies of pure zinc electrodeposition, calculated from the mass of the deposited zinc, were very high (>98%), due to the presence of gelatine in the bath. On increasing peak current density from 100 to 200 mA cm⁻², the deposition potential changes from -1.610 to -1.980. The addition of alumina nanoparticles to the bath does not significantly affect current efficiency and deposition potential. SEM observations showed that pure zinc deposits are homogeneous and compact, with low grain size; the incorporation of 1-2 wt% Al₂O₃ nanoparticles slightly modifies the coating morphology, leading to an increase in roughness. Pure zinc coatings are crystalline; according to previous results, the presence of gelatine in the deposition bath leads to a strong orientation of zinc deposit with the reflection from the (110) plane largely predominant. The incorporation of Al₂O₃ slightly changes zinc structure, leading to less orientated deposits, with an increase in the intensity of the peak related to the (100) planes. Vickers microhardness measurements indicate that the hardness of the nanocomposite coatings obtained in the present work is not significantly higher than that of zinc.

Discussion: The presence of Al₂O₃ nanoparticles in the used chloride bath does not affect zinc electrodeposition process; therefore Zn-Al₂O₃ composite coatings can be obtained with high current efficiency. However, the incorporation of alumina modifies zinc morphology and structure, leading to an increase in surface roughness and to less orientated deposits. These changes are probably responsible for the fact that the hardness of the Zn-Al₂O₃ nanocomposite coatings is not significantly higher than that of zinc.

GELESIS100, A NOVEL SUPERABSORBENT HYDROGEL, IS EFFECTIVE IN THE REDUCTION OF BODYWEIGHT IN OVERWEIGHT AND OBESE SUBJECTS

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Introduction: Overweight and obesity are becoming major health problems worldwide. The World Health Organization estimated that the worldwide prevalence of obesity has nearly doubled between 1980 and 2008. In 2008, approximately 500 million adults around the globe were obese and it is projected that by 2016, this number will reach 700 million. Overweight

and obesity are responsible for increased morbidity and mortality. Weight loss of at least 5 to 10% appears to lower the risk of many of the comorbidities. The therapeutic benefit of all currently available anti-obesity tools is limited by their marginal efficacy and variable tolerability and safety profiles. Gelesis100 is a novel, biocompatible hydrogel. Gelesis100 is administered in capsules, each containing thousands of tiny hydrogel particles that when hydrated expand in the stomach and mix with ingested foods. Gelesis100 increases the volume and elasticity of the stomach and small intestine contents, inducing satiety and reducing caloric intake.

Materials and methods: Gelesis100 is composed of two components, which are used as food ingredients, but when cross-linked, form a unique structure that increases in volume when hydrated. Gelesis100 does not create one big mass, rather thousands of small individual gel beads, which have similar elasticity (rigidity) as ingested foods, but without any caloric value. Gelesis100 partially degrades in the large intestine and loses its three-dimensional matrix structure and most of its absorption capacity. The water is absorbed from the hydrogel back in the colon and Gelesis100 is expelled in the feces. Subjects were randomized to two Gelesis100 arms (2.25 g twice daily, n = 43 and 3.75 g twice daily, n = 42) and a placebo/active comparator arm (n = 43). Treatment was administered in capsules with 500 mL of water before lunch and dinner, in a double-blind, parallel-group fashion, over 12 weeks, in subjects on hypocaloric diet (-600 kcal/day). The placebo/active comparator capsule contained microcrystalline cellulose, a ber which is used as a bulking agent.

Results: One hundred twenty-five subjects had at least one post-baseline body weight assessment. One hundred ten subjects completed the treatment. One hundred twenty-six subjects provided safety data (safety population). In the ITT population, the mean (\pm SD) body weight percent changes from baseline to the end of treatment were $-6.1 \pm 5.1\%$, $-4.5 \pm 4.5\%$, and $-4.1 \pm 4.4\%$, with Gelesis100 2.25 g, Gelesis100 3.75 g, and placebo, respectively. Weight loss was statistically significant with Gelesis100 2.25 g ($P = 0.026$). Lower tolerability leading to lower compliance may explain the observed efficacy result with Gelesis100 3.75 g. Subjects on Gelesis100 2.25 g had higher rate of weight loss $\geq 10\%$ and lower rate of weight gain.

Discussion: Chronic administration of Gelesis100 (2.25 g twice daily) to overweight and obese subjects significantly decreases the body weight. Weight loss is especially dramatic in subjects with impaired fasting glucose at baseline (prediabetic subjects). The treatment is safe and well tolerated.

NOVEL GELATIN-BASED HYDROGELS FOR TISSUE ENGINEERING APPLICATION

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Introduction: Biomaterials play pivotal roles in modern strategies of tissue engineering as designable biophysical and biochemical milieus that control cell fate and function. The key strategy relies on the optimum combination of cells with a suitable biodegradable matrix that could support the cell viability and remodelling of tissues. In tissue engineering, hydrogels, 3D network of hydrophilic polymers, have received much attention due to their biocompatibility, biodegradability, structural similarity to the extracellular matrix (ECM). Driven by enormous potential of hydrogels, we have developed a novel gelatin (G)-based hydrogel with tunable mechanical, degradation and biological properties. Chitosan (CH) and hydroxyethyl cellulose (HEC) were added to better match the native ECM composition and mechanical properties as well as to tailor the degradation resistance and available cell binding motifs. The effects of different material composition on physico-chemical properties, mechanical behaviour, cell adhesion and viability were evaluated.

Materials and methods: G-PEG hydrogel was prepared in aqueous solutions following a synthetic procedure which involves the reaction between gelatin amino-groups and the functional end groups of poly(ethylene glycol) (PEG). In order to obtain adducts with a number of reactive end groups able to produce crosslinking, an excess of PEG over protein amino-groups was employed. Moreover, in order to obtain insoluble materials with good mechanical properties, improved water resistance and controlled degradation rate, a specific crosslinking agent, i.e. ethylene diamine, able to react with unreacted epoxy groups, was added. G-PEG-HEC hydrogel and G-PEG-CH hydrogel were prepared adding the proper amount of HEC or CH solution to a G-PEG aqueous solution obtained starting from a 9% (w/v) solution of G.

Results: Hydrogels have been fully characterized by FTIR spectroscopy that confirmed the expected structure. Mechanical tensile tests were performed and swelling and weight loss were also monitored over a period of about 30 days. Interestingly, G-PEG hydrogel as well as G-PEG-HEC and G-PEG-CH, with a G/PEG ratio of about 3.6:1, display good stiffness, flexibility and extensibility. They show non-linear J-shaped stress-strain curves, similar to those found for ECM, with initial elastic modulus and strain at break over the range of 1.5-6.5 MPa and 30-70%, respectively. The swelling test revealed a wide range of equilibrium swelling rate (200-450%). Hydrogels showed no significant change in dimension and shape during degradation tests carried out at 37°C, and the resistance to hydrolytic degradation was longer than 30 days for all the formulations. All the hydrogels showed good cell viability during long term culture of a human fibroblast cell line.

Discussion: Functionalized PEG was chosen to verify the possibility of grafting on gelatin and chitosan to obtain hydrogel that could eventually undergo crosslinking in the presence of a suitable curing agent. The final purpose to obtain adequately stiff and strong biomaterials, which possessed at the same time limited solubility and degradation rate in comparison with pure gelatin or chitosan, was attained. This is in fact a perfect condition to obtain a suitable biodegradable/resorbable matrix promoting cell viability and remodeling of tissue.

PLA-BASED FOAMS AS SCAFFOLDS FOR TISSUE ENGINEERING APPLICATIONS

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Introduction: The need for alternative solutions to meet the demand for replacement organs and tissue parts continues to drive advances in tissue engineering because no material meets all the design parameters in all applications, but a wide range of materials finds uses in different tissue engineering applications. In this research work, starting from biocomposites based on crosslinked particles of poly(acrylic acid) (SAP) and poly-L-lactic acid (PLLA), new open-pore PLLA-based foams with good physico-mechanical properties are produced in absence of organic solvents and chemical foaming agents.

Materials and methods: Biocomposites based on a binary system containing crosslinked particles of (SAP), commonly used as superabsorbent polymer, and PLLA have been prepared by melt-blending in a discontinuous mixer. Components were melt-mixed in different ratios in the presence of plasticizers and fibers or blended with different biopolymers such as poly (ethylene glycol) (PEG), poly (ε-caprolactone) (PCL) and polyhydroxybutyrate (PHB). All samples were recovered from the mixing chamber and hot pressed using a laboratory compression molding machine to realize 0.2 mm thick sheets from which the specimens for mechanical tests were obtained.

Results: A fairly homogeneous dispersion of particles was obtained, as revealed by SEM micrographs, showed a biphasic system with a regular distribution of particles, with diameter ranging from 5 to 10 mm, within the PLLA polymeric matrix. This biphasic system also showed excellent swelling properties, demonstrating that cross-linked particles retain their superabsorbent ability even if distributed in a thermoplastic polymeric matrix. Furthermore, in aqueous environments the particles swell and are leached from PLLA matrix generating very high porosity with random and irregular open pore structure. Density and porosity were measured using liquid substitution method. As expected, reduced density and increased porosity were observed on the samples as a result of the increased amount of leached particles.

The biocompatibility of all samples and the influence of the surface on cell behavior were assessed in a preliminary investigation which evidenced optimal cell viability, adhesion and proliferation.

Discussion: These new open-pore PLLA-based foams, produced in absence of organic solvents and chemical foaming agents, with good physico-mechanical properties appear very promising for scaffold production technology. In fact, open porosity is a crucial point because scaffold must possess a highly porous structure with a fully interconnected geometry to provide cell ingrowth and survival and uniform cell distribution. This new methodology allows to obtain a polymeric scaffold, with a porosity that can be easily tuned by a proper choice of superabsorbent particles.

Another key point are surface properties, which include both chemical and topographical characteristics and can control and affect cellular adhesion and proliferation. The scaffold surface is the initial and primary site of inter-

action with surrounding cells and tissue. Surface properties can be selectively modified to enhance the performance of the biomaterials. For instance, by blending PLA matrix with PCL, PHB or PEG, optimal surface, chemical, and physical properties promoting cell viability were attained.

MELT DEVELOPMENT OF BIPHASIC FUNCTIONALLY GRADED SCAFFOLD

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Introduction: Interface tissue engineering requires scaffolds that temporary replace the mechanical function of transition regions between two adjacent tissues. The presence of multi-phasic bio-structures that gradually change are typical features of interface tissues such as ligament-to-bone, tendon-to-bone and cartilage-to-bone. In this work, bi-layered scaffolds (BLS) composed by PLA with pores in the range of 90-110 µm and PCL with pores ranging from 5 to 40 µm were prepared by combining melt mixing, compression molding and particulate leaching. The principal advantages of this method lay in the absence of organic solvent during the preparation and in the easy control and high predictability of porosity and pore size.

Materials and methods: In brief, PLA (or PCL), PEG and NaCl in the appropriate particle size, were fed to a batch mixer (Brabender PLE-330) and processed until a constant value of torque was achieved. After this step, the blend was fed out and rapidly cooled. The blends were then compression molded in a Carver laboratory press in appropriate cylindrical molds. The pre-compressed layers were eventually assembled to obtain the final devices.

Finally, the porogen parts of the blends (NaCl and PEG) were removed by selective leaching in demineralized water. The resulting structure was then let to dry for 12 hours at room temperature. BLS morphology was investigated with scanning electron microscopy (SEM) while the compressive mechanical behavior of the scaffolds was evaluated in air and under immersion in phosphate buffered saline (PBS) solution at 37°C, in order to simulate the physiological environment. Furthermore, tensile tests were also performed in order to investigate the interfacial adhesion strength between PCL and PLA layers.

Results: The PLA layer showed pore size distribution around 100 µm while the PCL in the range of 10-30 µm. The modulus of PLA was more than two times higher than that of PCL while the BLS elastic modulus (26.0 MPa) was almost in the middle. The tensile strength of BLS is comparable with that of the PLA layer and the fracture always occurred in the PLA region that is the more fragile of the entire device.

Discussion: The devices showed highly interconnected pore structure raising the predicted and high predictability of pore size of each layer by controlling the granulometry of NaCl during the melt mixing step, as confirmed by SEM and image processing analysis. Morphological analysis and tensile mechanical test showed that scaffold is characterized by a well joint interface region with an interface adhesion strength higher than the tensile strength of the device. Compressive mechanical tests showed the strong correlation between E value of the device and the elastic behavior of the PCL layer i.e. its weakest layer.

MEASUREMENT AND MODELLING OF THE TRANSPORT PROPERTIES OF OXYGEN SCAVENGING MULTILAYER PET FILMS

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Introduction: Polymer-based multilayer packaging systems are recognized as very effective solutions able to improve the shelf life and to keep the quality of packaged foods. In fact, by properly combining different materials with specific properties, it is possible to provide engineered barrier solutions against several environmental agents (e.g. oxygen, moisture, light, etc.). Further improvements of barrier properties can be obtained by incorporating in the multilayers structures some scavenging systems, which are able to decrease the level of specific undesired gases in the packaging, with beneficial effects on food preservation.

In such systems the overall features depend not only on the barrier properties of each layer, but also on the scavenging capacity of the active layer, its thickness and its position respect to other layers. Therefore, in order to design

the best film configuration, in terms of thicknesses of the different layers and positions, mathematical modeling can be recognized as an effective virtualization tool to limit the experimental trials before film production. In this work, a mathematical model was developed to predict the barrier properties and the scavenging performances of multilayer polyester films with oxygen scavenging activity. Model results were validated by experimental characterization with particular regard to oxygen permeability and transmission rate.

Materials and methods: "ABA" type symmetrical multilayer PET films and "B" type monolayer active PET films were considered for this study. The external "A" layers were pure PET, while the middle "B" reactive layer was PET loaded with 10 wt% of oxygen scavenger (Amosorb DFC 4020, by Colormatrix). Films with different layout were produced with a laboratory coextrusion cast film line (Collin Teach Line E2OT). Oxygen absorption measurements were performed putting the film in a vial and then measuring the decay of oxygen concentration in the vial itself.

The concentration profiles of oxygen in the film were calculated by making use of a mono-dimensional reaction-diffusion equation in both multilayer and monolayer systems. The equations were solved numerically using a finite element based multiphysics tool to predict the concentration profile.

Results: The scavenging capacity of the multilayer films increases linearly with the increase of the reactive layer thickness, and the oxygen absorption reaction at short times decreases proportionally with the thickness of the external PET layer. Both experimental and theoretical results also revealed that in multilayer PET films, at the exhaustion of the scavenging effect of the active layer, the steady transport properties are slightly different in comparison to pure PET. As a result, the oxygen transfer rates and permeability were also reduced.

Discussion: The oxygen scavenging kinetics depends on the layer thickness and the relative mass ratio of the constituents. At fixed active layer thickness and composition, the flux plateau of the oxygen diffused into the layer is lower in the multilayer films, having the reactive layer in the middle, than in the monolayer active film. As the thickness of the reactive layer increases, diffusion takes longer time and consequently contact time between oxygen and scavenger increases. This slows down the oxygen transport across the layers.

MICROMORPHOLOGY OF QUANTUM DOT SUPRAMOLECULAR SOLIDS

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Introduction: Semiconductor nanoparticles, known as quantum dots (QDs), are inspiring a growing number of applications, mainly due to their peculiar optical properties – such as the very strong and finely tunable absorption and photoluminescence in the visible range. Most of QD-based applications, however, exploit the properties of the individual QDs; however, quite an interesting and untapped potential lies in the collective properties (mainly optical and electrical) that emerge in arrays of interacting, rather than uncoupled, QDs. It is of great interest, therefore, to develop appropriate techniques to assemble QDs in a reliable and controllable way, ensuring on one hand a macroscopic shape appropriate to the selected application, and on the other hand the desired characteristics at the nanoscale – such as for example the degree of electric coupling, or the spatial distribution of the QDs. We have studied the conditions for QD assembly via a supramolecular approach, whereby assembly is mediated by metallic ion-induced bonding between opportunely selected capping molecules. Since the capping can be finely engineered – for example in terms of chemistry, positioning on the QD, electrical conductivity – the supramolecular assembly approach is expected to be a very powerful tool for controlling the morphology and therefore the properties of QD colloidal solids.

Materials and methods: Colloidal quantum dots made of II-VI compound semiconductors were prepared via standard hot injection synthesis in sizes varying between 2.5 and 4 nm, and the native oleic acid capping was then exchanged for selected terpyridines. The terpyridine-QD complexes were mixed with Co(II) ion solutions in concentrations such that the ratio QD/Co(II) would vary between 1:100 to 1:1; aliquots of the mixtures thus obtained were extracted at times varying between 10 minutes and 4 weeks, and examined after solvent evaporation via optical microscopy, scanning electron microscopy, and Raman spectroscopy.

Results: In most cases, a solid powder starts precipitating shortly after the QDs and the Co(II) are mixed; Raman spectroscopy confirms that the precipitate contains QDs. Optical microscopy and SEM show the formation of spher-

oidal particles of 1-5 µm, loosely aggregated. The general trend is that the diameter of the spheroidal particles grows as the QD/Co(II) ratio decreases.

Discussion: The formation of the precipitates can be explained by the formation of coordinative bonds, mediated by Co(II), between the terpyridine capping of different QDs, thus demonstrating the feasibility of a supramolecular approach for assembling QDs as colloidal solids.

ENHANCED PHOTOCATALYTIC ACTIVITY OF TITANIA NANOTUBES BY LIGAND-FREE AU NANOPARTICLE LOADING

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Introduction: In the last years titania nanotubes arrays (TNTAs) have attracted increasing attention in photocatalysis due to their unique properties, not least the possibility of a direct production of supported TNTAs by anodic oxidation of metallic titanium foils. Besides, loading of TiO₂-based photocatalysts with Au nanoparticles (NPs) has been extensively investigated so as to improve the photocatalytic efficiency. In order to combine the advantages of TNTAs with Au NPs decoration and to overcome the problems derived from current deposition methods this work proposes a simple and scalable synthetic protocol able to load size-controlled (<10 nm) and ligand-free Au NPs onto vertically aligned anatase TNTAs.

Materials and methods: Metal-supported TNTAs were produced by titanium foils anodization in a solution of 0.5 wt.% NaF/1M Na₂SO₄. The samples were then thermally annealed in air at 400°C for 2 h in order to achieve the crystallization of the obtained amorphous TiO₂. Ligand-free Au NPs were produced by the Metal Vapour Synthesis technique. Au vapours generated at 10⁻⁴ mBar by resistive heating of an alumina crucible filled with gold pellets were condensed at liquid nitrogen temperature (-196°C) with acetone. The Au NPs were loaded onto the TNTAs surface by simply dipping the samples into the resulting acetone NPs suspension. The photocatalytic activity was assessed by measuring the toluene degradation in air using a continuous-flow stirred photoreactor operated at constant toluene concentration.

Results: The obtained Au loadings were strictly related to the sample dipping time into the ligand-free Au NPs suspension. The morphological features of Au/TNTAs composites revealed a highly homogeneous Au NPs dispersion without the particle coalescence often reported using colloidal deposition methodologies. The photocatalytic activity of the pristine batch of bare TNTAs samples was quite homogeneous and a marked increase of activity after Au NPs deposition was observed for the 3.3 and 7.4 µg cm⁻² Au loading samples. At lower Au loading (<2 µg cm⁻²) the reaction rate was comparable to the untreated sample whereas at higher loading (>10 µg cm⁻²) a pronounced deactivation was observed.

Discussion: Using the described method the Au loading was finely tuned ranging from 1.5 to 11.6 µg cm⁻² by controlling the support/Au dipping time without significant change of Au NPs mean size. No further thermal or chemical post-treatments were necessary. The Au loadings strongly influenced the photocatalytic activities and the best performance results in a three times enhancement of the bare TNTAs activity obtained with a sample containing 3.3 µg cm⁻² of Au. The proposed protocol demonstrated a remarkable enhancement of the photocatalytic activity of metal-supported TNTAs at room temperature without any post-deposition process.

PHOTOCATALYTIC TOLUENE DEGRADATION IN AIR AT AMBIENT CONCENTRATION BY TITANIA NANOTUBE ARRAY: INFLUENCE OF SYNTHESIS PROCESS PARAMETERS

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Introduction: Titania nanotube arrays (TNTAs) are very interesting photocatalysts. Particularly, TNTAs obtained by anodic oxidation of metallic titanium foils allow the direct synthesis of high efficiency supported photocatalytic layers without the drawbacks related to the high temperature sintering of anatase nanopowders. The synthesis of TNTAs is however a critical process

with several parameters to be optimized in order to obtain high photocatalytic activities. This work investigates the optimization of titanium supported TNTAs for the photocatalytic degradation of toluene in air at ambient concentration.

Materials and methods: Metal-supported TNTAs were produced by titanium foils anodization using a solution of 0.5 wt.% NaF/1M Na₂SO₄. The anodization process (3-6 h) was performed at 20 V. The samples were then thermally annealed in air at different temperatures and duration times in order to achieve the crystallization of the obtained amorphous TiO₂. The photocatalytic activity was assessed by measuring the toluene degradation in air using a continuous-flow stirred photoreactor operated at constant toluene concentration (0.75 µmol m⁻³).

Results: The TNTAs photocatalytic activity demonstrates to be strictly dependent on several process parameters (e.g. the anodic oxidation solution, the oxidation time and the post-synthesis thermal annealing). The oxidation time was studied in the 3-6 h range demonstrating the best photocatalytic performance for the longest time. The post-synthesis annealing was studied in the 400-600 °C temperature range for 60 and 120 min duration. For both annealing duration times the highest activities were found at 600 °C process temperature, with >6.5 factor improvement from 400 to 600°C for 120 min process and >4 factor improvement from 500 to 600°C for 60 min process. At the highest temperature the curing time is however critical and the best activity was found for 60 min curing, with ≈30% activity decrease shown by the 120 min annealed sample.

Discussion: The results demonstrate the severe dependence of the TNTAs gas-phase photocatalytic activity on the synthesis process parameters. Particularly, the final TNTAs crystalline structure is critically dependent on post-synthesis annealing with a very pronounced dependence of the obtained photocatalytic activity on the process temperature and duration. The criticality of the annealing process is due both to the amorphous/crystalline and then the anatase/rutile phase transitions and to the morphological transformations triggered at high temperatures. TNTAs obtained by anodization of titanium foils can thus be very interesting natively supported photocatalysts after a fine tuning of the anodization and annealing process parameters.

ORIENTATION AND EXFOLIATION OF CLAY NANOPARTICLES IN THE SPINNING OF A NANOBIOCOPPOSITE SAMPLE

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Introduction: Polymer nanobiocomposites represent a new group of materials filled with inert nanosized particles that show very interesting properties with respect to the matrix and the same biodegradability of the matrix. In this work we have studied the effect of the elongational flow on the morphology and dynamic-mechanical properties of a new nanobiocomposite made by a matrix of biodegradable PLA and a filler of organomodified montmorillonite. **Materials and methods:** The polymer matrix is a biodegradable polymer blend (Bio-Flex® F2110 by FKUR) made of PLA and other biodegradable copolymers. The nanofiller, Dellite 72T, is modified with ditallow dimethylammonium. Bioflex with the silicate sample at a concentration of 5% wt/wt and neat Bioflex have been processed in a Brabender compounder at a die temperature of 170°C. The fibers were spun using a capillary viscometer (Rheologic 1000, CEAST, Italy) operating under a constant extrusion speed at 170°C. The filaments are extruded in air at room temperature. The take-up velocity was varied in order to obtain different draw ratio (DR), calculated as the ratio between the cross section of the die divided the cross section of the fiber. Dynamic-mechanical analyses were performed in duplicate by means of a 01 dB-METRAVIB DMA50N apparatus, choosing a heating rate of 5°C/min, strain of 0.05% and frequency of 1 Hz. TEM observations were performed at the Centro Grandi Apparecchiature-UninetLab, University of Palermo by a JEOL (Tokyo, Japan) JEM-2100 instrument under an accelerated voltage of 200 kV.

Results: The nanobiocomposite fibers at DR = 1 (isotropic sample) show an intercalated morphology without any presence of exfoliated layers. The presence of the organomodified nanoclay improves the thermo-mechanical properties of the biodegradable matrix and in particular the rigidity. Moreover, comparing the properties of the polymer fibers with the nanofilled fibers, the improvement of the properties with increasing DR is larger for the nanocomposites. Finally, a brittle-to-ductile transition is observed for the

anisotropic samples and this effect is again more evident for the nanocomposites.

Discussion: The rate of increase of the elastic modulus and tensile strength is larger for the nanocomposite samples with respect to the matrix. This behavior cannot be dependent only on the orientation of the macromolecules, that is the same for both materials, but also on the orientation of the nanoparticles along the drawing direction that strengthens the matrix. Moreover, some exfoliation of the organoclay nanoparticles is also observed as a result of the application of the elongational flow. Consequently, the exfoliated layers of the clay, oriented along the drawing direction, improve the rigidity of the nanocomposite fibers with respect to the fibers of the neat polymer. Of course, this phenomenon becomes more important with increasing the draw ratio.

SIMPLE AND SCALABLE SYNTHESIS OF EARTH-ALKALINE HYDROXIDES NANOPARTICLES IN AQUEOUS SUSPENSION

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Introduction: Ca-hydroxide nanoparticles are emerging as effective conservation materials for all carbonatic-based substrates and mortars of Cultural Heritage, guaranteeing compatibility, durability, reduced environmental impact and human risk. Parallelly, the development of nanoscale Mg-hydroxide, revealed considerable interest in the de-acidification of paper and wood, but also as antibacterial, flame retardant agent, and as MgO nanoparticles precursors. Ca- or Mg- hydroxide nanoparticles are obtained by several methods, generally characterized by some critical drawbacks: high temperature, processes are time and energy consuming, and low specific yield in the production, so determining a limit to their application to particular or restricted fields.

In this work we present a facile and scalable method, recently patented (RM2011A000370, WO2014020515A1), to synthesize Ca- and Mg- hydroxide nanoparticles in aqueous suspension. This eco-friendly and time-energy saving route is based on an ion exchange process, operates at room temperature, starts from cheap or renewable reactants, with no intermediate steps (washings/purifications), drastically reduces times of synthesis and has the ability to scale up the nanoparticles production. The produced nanoparticles are pure and crystalline, with dimension generally less than 80 nm.

Materials and methods: To synthesized Ca(OH)₂ (or Mg(OH)₂) nanoparticles, a CaCl₂·H₂O (MgCl₂) aqueous solution and an ion-exchange resin are mixed together, at room temperature and under moderated stirring. The substitution of hydroxyl groups on the resin substrate with the chlorides ions in solution leads, in supersaturation conditions, to the formation of a white precipitated phase inside the preparation, already after few minutes; maintaining the stirring, the preparation is rapidly separated from the resin by a sieving procedure. Resin can be regenerated to be reused for a scale-up production, according a cyclic procedure. The produced nanoparticles are characterized from structural and morphological point of view, by means of X-ray diffraction (XRD), infrared spectroscopy (FTIR), thermal analyses (TG-DTA), surface area measurements (BET) and transmission electron microscopy (TEM). Carbonatation efficiency of the produced Ca-hydroxides nanoparticles suspension is investigated too.

Results and discussion: From XRD measurements, only pure and crystalline Ca(OH)₂ (Mg(OH)₂) phases are produced after few minutes, as evidenced by the absence of peaks belonged to other substances in the experimental XRD pattern. The purity of the obtained phases is confirmed by FTIR and TG-DTA measurements. From BET measurements, we have obtained that the synthesized Mg(OH)₂ sample reaches values of surface area up to 155 m²/gr, generally higher than those reported in literature. TEM images referred to Ca(OH)₂ and Mg(OH)₂ samples, respectively, show nanoparticles characterized by a plate-like morphology, with dimensions generally ranging from 20 to 80 nm. Moreover, observations reveal that nanoparticles are formed by an oriented aggregation of Mg(OH)₂ primary hexagonal particles (singlets), crystalline, homodispersed, and with dimensions of about 3 nm.

The analysis of Ca(OH)₂ nanoparticles carbonatation process, investigated when the suspension is exposed to air (T = 20°C, RH = 70%), shows a complete transformation of Ca(OH)₂ into CaCO₃ (calcite), already after 3 h of air exposure time. This result is very interesting for the fast reactivity but also for the formation of pure calcite, that guarantees the perfect compatibility with all the carbonatic substrates.

NANOLIME MIXTURES WITH SILICA FUME OR NATURAL POZZOLAN.

PRELIMINARY INVESTIGATIONS

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Introduction: It is known that hydrated lime ($\text{Ca}(\text{OH})_2$) can be activated by reacting with siliceous materials, such as natural pozzolans (P) or silica fume (SF), in presence of water. During the interaction process, the active silica contained in siliceous materials reacts with hydrated lime to form calcium silicate hydrates (C-S-H), according to the pozzolanic reaction. Such reactions, however, could require enough time to complete mainly due to lime particles dimensions. Aim of the present work is to preliminarily study the interaction between commercial silica fume, or natural pozzolan, with nanostructured $\text{Ca}(\text{OH})_2$ particles, (nanolime), dispersed in aqueous suspension. The nanolime is synthesized in laboratory by our patented, simple, eco-friendly, time and energy saving and scalable route (RM2011A000370, WO2014020515A1). The interaction is carried out in water, at room temperature, considering a proper water/solid ratio, and different $\text{Ca}(\text{OH})_2/\text{SF}/\text{P}$ ratios in weight. The hydrates phases that forms are investigated at different hydration times by means of several techniques.

Materials and methods: Silica fume (Italcementi) and the natural pozzolan, coming to Sacrofano Italian site, are characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD) and BET surface area measurements. Nanolime is synthesized in laboratory by mixing, at room temperature and under moderated stirring, a $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ aqueous solution and an ion-exchange resin. After few minutes, a white precipitated is produced, which is analyzed in terms of structural and morphological features by means of XRD and transmission electron microscopy (TEM). The synthesized nanolime is mixed with SF, considering a weight ratio of about 1:1 and a water/solid ratio of about 8, (sample A); parallelly, mixtures of nanolime and P are prepared, by using a weight ratio of 1:1 and 1:2, (sample B and C, respectively). The hydrates phases that forms at different slurring times (1, 3, 7, 14, 28 and 45 days) are investigated by XRD, thermal analysis and scanning transmission microscopy (SEM).

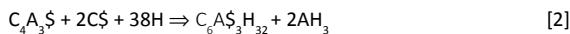
Results and discussion: Silica fume is mainly composed of 94.82% of amorphous SiO_2 , and characterized by a surface area of about $12.5 \text{ m}^2/\text{g}$. Natural pozzolan has a chemical composition of 69.17% SiO_2 , 1.16% TiO_2 , 0.80% Al_2O_3 , and minor amounts of SO_3 and K_2O ; a specific surface area of about $56.53 \text{ m}^2/\text{g}$ is measured. Nanolime suspension is constituted by pure and crystalline $\text{Ca}(\text{OH})_2$, with particles characterized by a lamellar morphology, generally agglomerated, with dimension $\leq 50 \text{ nm}$, as revealed by XRD and TEM measurements. In sample A, C-S-H can be observed at 7d of hydration and after 14 days all crystalline $\text{Ca}(\text{OH})_2$ is consumed; then, C-S-H formation proceeds and it appears more crystalline, mainly in the C-S-H(I) form, as In samples B and C, we have observed high reaction rate, with the C-S-H formation already at 3 and 1 days, respectively. The reaction proceeds, leading to a more crystalline C-S-H(I) phase with a consumption of crystalline $\text{Ca}(\text{OH})_2$ from 14 days of hydration process. SEM images of the phase formed after 45 days reveal highly wrinkled layers covering all particles, constituted by marked crumple and rough-edge surfaces.

A POROSIMETRIC INVESTIGATION ON HYDRATED CALCIUM SULPHOALUMINATE BINDERS

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Introduction: Calcium sulphoaluminate (CSA)-based binders can be used as (i) expansive cements and functional materials able to promote "shrinkage-compensating" and "self-stressing" effects or (ii) rapid-hardening cements and structural materials, also characterized by high durability and dimensional stability. Their technical properties are mainly controlled by $\text{C}_6\text{A}_3\text{S}_{32}$ (ettringite) formed during the hydration of $\text{C}_4\text{A}_3\text{S}$ (calcium sulfoaluminate, key-component), according to the following reactions:



Ettringite synthesized in the reaction (1) has expansive characteristics while the one formed in the reaction (2) is not expansive. Taking into account the equation (2), expansive CSA cements can be obtained in the absence of lime and by largely overstoichiometric addition of C\$.

In this paper, the hydration process of two CSA cements, consisting of the same industrial clinker plus 20 (A) or 60 (B) mass% added natural gypsum, able

to behave respectively as a dimensionally stable and an expansive binder, was explored through differential thermal-thermogravimetric (DTA-TG) and X-ray diffraction (XRD) analyses. Both cements were also submitted to shrinkage/expansion tests, together with a high strength and rapid-hardening commercial Portland cement (P), used as a reference term. Finally, the three hydrated cements were investigated by means of mercury intrusion porosimetry (MIP).

Materials and methods: The three cements were paste hydrated with a water/solid mass ratio equal to 0.6 for curing times comprised between 4 hours and 28 days. The paste samples were placed inside a thermostatic bath at 20°C. For the shrinkage-expansion measurements, cement pastes, shaped as small prisms, were cured for 24 hours (20°C), then demolded and kept in air conditioned (shrinkage) or under tap water (expansion).

Results and discussion: As far as the shrinkage/expansion behavior is concerned, B, due to its expansive nature, showed a quite high increase of length under water and the lowest shrinkage in air. Both expansion and shrinkage curves for A and P gave almost similar trends.

No effects were recorded by DTA-TG analysis above 300°C. From the early appearance of ettringite and aluminium hydroxide, it can be argued that the reaction (2) was very fast for both CSA cements. DTA-TG results were confirmed by those obtained with XRD analysis.

MIP outcomes showed that A and B are completely different from each other and from P too. In particular, at early curing ages, both A and B displayed prevailing regions of low porosity. These rapidly developed because the reaction rate for CSA cements was higher than that of P and, consequently, a larger amount of hydration products, able to reduce and isolate the interior space, was generated. Up to 1 day of curing, both CSA cements displayed a cumulative pore volume lower than that of P. However, at 7 and 28 days, the cumulative pore volume for B strongly increased due to the generation of expansive ettringite, while that for A had the same order of magnitude as the cumulative pore volume for P; furthermore, during the whole hydration period, compared to the other CSA cement, the expansive binder showed a higher threshold pore width, the curing time being the same.

UTILIZATION OF CHEMICAL GYPSUMS FOR THE SYNTHESIS OF CALCIUM SULPHOALUMINATE CLINKERS

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Introduction: Calcium sulphoaluminate (CSA) cements have aroused the interest of the international cement research community not only for their technical properties but also by virtue of the environmental sustainability of their manufacturing process which, compared to that of Portland cement, implies energy saving and reduced CO_2 emission. Another environmentally friendly feature associated with CSA cements production is represented by the possibility of using several industrial by-products as raw materials in place of limestone, bauxite and gypsum. To this end, industrial wastes such as coal fly ash, fluidized bed combustion residues, red mud, alumina powder, anodization mud and calcium looping spent sorbents were widely experienced in the past.

In this study different chemical gypsums (flue gas desulphurization gypsum, D, fluorogypsum, F, titanogypsum, T, and phosphogypsum, P) were separately employed as total calcium sulphate substitute for the synthesis of four laboratory-made CSA clinkers.

Materials and methods: The CSA clinker-generating raw mixes were heated in an electric oven for 2 hours at 1150°, 1200°, 1250° and 1300°C. Afterwards, the obtained clinkers were ground in a laboratory mill and submitted to X-ray diffraction (XRD) analysis in order to assess both conversion and selectivity of the reacting systems toward calcium sulfoaluminate, $\text{C}_4\text{A}_3\text{S}$ (key component). A reference mixture (RM), based only on limestone, bauxite and gypsum, underwent the same thermal treatments. CSA cements were prepared by grinding the CSA clinkers generated at their best synthesis temperatures with the amount of natural gypsum required by the reaction controlling the technical behavior of rapid-hardening and dimensionally stable CSA cements ($\text{C}_4\text{A}_3\text{S} + 2\text{C} + 38\text{H} \Rightarrow \text{C}_6\text{A}_3\text{H}_{32} + 2\text{AH}_3$). Cement pastes (water/solid mass ratio, 0.6) were hydrated for curing periods ranging from 2 hours to 28 days. XRD and differential thermal-thermogravimetric (DTA-TG) apparatuses were employed for the evaluation of hydration products; TG analysis was also utilized for the quantitative determination of ettringite ($\text{C}_6\text{A}_3\text{H}_{32}$), the main hydration products of CSA cements.

Results and discussion: The conversion of reactants was complete at all the investigated temperatures; in particular, the best selectivity towards $\text{C}_4\text{A}_3\text{S}$

were obtained at 1250°C for P-clinker-generating raw mix and MR, and at 1300°C for the other mixes. In all the synthetic clinkers, together with calcium sulphoaluminate, dicalcium silicate (C_2S), calcium sulfate (C_2S), calcium sulfofelsite (C_4S_2S) and gehlenite (C_2AS) were also detected. CSA cements, investigated by means of DTA-TG analysis, generally displayed a similar hydration behavior. As far as ettringite-generating ability was concerned, all by-products-based cements showed quite satisfactory performances; the best results were obtained with cements derived from P- and T-based raw mixtures whose ettringite concentration values after 28 days of curing (respectively equal to 68.7 and 67.1%) were higher than the one of the reference cement (59.6%).

In conclusion, it has been found that chemical gypsums can be successfully employed in place of natural gypsum as component of CSA clinker-generating raw mixtures. In terms of (i) selectivity of reactants toward C_4A_3S and (ii) ettringite-generating ability, raw mixtures based on phosphogypsum and titanogypsum, respectively heated at 1250° and 1300°C, exhibited the best performances.

USE OF BIOBASED POLYMERS IN RECYCLED PAPER-POLYETHYLENE COMPOSITES

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Introduction: In last decades, natural fibers have attracted great attention as filler in thermoplastic matrix composites. The various advantages of natural fibers over glass and carbon fibers are low cost, low density, renewability, recyclability and bio-degradability. The hydrophilic and hydrophobic nature of the filler for the matrix directly affected the properties of the resulting composites because of a weak fiber-matrix interface. The proposal is to introduce additives to improve the composites' performance, and to investigate on their effects on composites' properties. Moreover the addition of a bio-derived polymer is possible in order to reduce the amount of non-degradable charge keeping environmental resistance.

Materials and methods: Eraclene MP90 is the commercial name of high-density polyethylene from ENI (Versalis) that has been chosen as matrix. A micronizing process that operates by friction, impact and turbulence allowed to obtain cellulosic recycled fibres with diameters of 15-20 micron and lengths of 200-250 micron. Polybond 3029 has been chosen as additive to improve fiber-matrix interface: it is suitable for polyethylene matrix and cellulosic fillers. Polybond 3029 is a maleated polyethylene with MA content of 1.7 wt% (high). Bioplast 500 has been chosen as additive to introduce a bio-derived charge: it is a starch-derived polymer from Biotec. Bioplast 500 is a plasticizer-free, thermoplastic material that contains natural potato starch and other biologically sourced polymers. The share of biobased carbon exceeds 50% in the entire formulation. Turbomixing (3000 round/minute) was used to produce the composites, obtaining a good dispersion of the charge. The melted charge was subjected to moulding under pressure, obtaining plates from which specimens were derived. Samples with 10 wt% of fibres (10F) were produced and compared to the one with 1,3,5 wt% of Polybond (1P, 3P e 5P) and 15 and 40 wt% of Bioplast (15Bi e 40Bi). Tensile tests, DSC and SEM analysis were performed to investigate the influence of both additives' introductions in polyethylene composites.

Results: 1P samples showed higher ultimate strength and crystallinity compare to both other Polybond percentages and samples without additive: an improvement of 35% in ultimate strength was showed for 1P samples with respect to 10F. Crystallinity of 128% compared to 10F was recorded for 1P. SEM analysis showed a small improvement in both fiber-matrix interface and compactness of the matrix. Bioplast introduction in recycled paper composites reported similar results to samples with 1P. In fact ultimate strength was approximately maintained at 26MPa as shown by tensile tests although considering the high amount of biobased introduced. SEM analysis also showed an improvement in fiber-matrix interface and peculiar matrix morphology due to polymer blend.

Discussion: The influence of additives' introduction both in tensile tests, SEM and DSC analysis is evident. Actually SEM and DSC analysis validated tensile tests behavior: additives influenced matrix crystallinity and fiber-matrix interface and consequently composites performance. The positive results obtained from Bioplast introduction encourage studies in polymer blend with a biobased component: biodegradability tests will be necessary.

EFFECT OF CELLULOSE AND LIGNIN NANOPARTICLES ON DISINTEGRATION, ANTIMICROBIAL AND ANTIOXIDANT PROPERTIES OF PLA ACTIVE FILMS

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Introduction: This study reports the effects on antimicrobial, antioxidant, migration and disintegrability activities of ternary nanocomposite films based on poly(lactic acid) incorporating two biobased nanofillers (cellulose nanocrystals (CNC) and lignin nanoparticles (LNP)) in two different amounts (1 and 3% wt.).

Materials and methods: Lignin nanoparticles suspension was prepared by hydrochloric acidolysis. Microcrystalline cellulose (MCC, dimensions of 10-15 μ m) was used as precursor for cellulose nanocrystals extraction by acid hydrolysis procedure. PLA grafting with glycidyl methacrylate was performed in a twin-screw microextruder (DSM Explorer 5 & 15 CC Micro Compounder) in presence of dicumyl peroxide ad initiator. The materials, designed as PLA/3CNC and PLA-3LNP with direct incorporation of 3% wt. of CNC and LNP (mixing time 2 minutes) after 8 minutes of PLA heating, were produced as control, while the ternary PLA nanocomposite films having the code PLA-1LNP/1CNC, PLA-1LNP/3CNC, PLA-3LNP/1CNC and PLA-3LNP/3CNC were obtained by diluting different masterbatches. Biocidal activity of neat PLA film and PLA nanocomposites containing lignin nanoparticles and/or cellulose nanocrystals was evaluated against three different plant pathogenic bacteria, in addition DPPH radical scavenging activity for PLA films was also studied. Taking into account the possible application of the produced PLA nanocomposites for fresh food packaging, overall migration tests were performed in two different simulants. Finally, disintegrability of PLA and PLA nanocomposites films was evaluated by means of a disintegration test in composting conditions according to the ISO-20200 standard ones.

Results and Discussion: PLA systems containing cellulose nanocrystals and lignin nanoparticles revealed an innovative capacity to inhibit the bacterial growth along the time. LNP proved to be highly efficient in antioxidation activity based on the disappearance of the absorption band at 517 nm of the free radical, 2,2-diphenyl-1-picrylhydrazyl (DPPH) upon reduction by an antiradical compound, moreover the combination of LNP and CNC generates a synergistic positive effect in the antioxidation response of PLA ternary films. In the meanwhile, migrating substances for the films containing LNP also show high antioxidation activity. Based on these results, the LNP can be employed in both active packaging strategies generally including (1) the design of active compound releasing systems and (2) undesired compound scavenging systems, which seems to be reasonably attractive from the safety and marketing point of view, having lower cost and higher antioxidant ability. Results of disintegrability tests in composting conditions proved that PLA and PLA formulations loaded with 3% wt of LNP (binary and ternary films) have higher values of disintegration after 10 days of incubation in comparison to PLA/3CNC binary film and PLA-1LNP/1CNC or PLA-1LNP/3CNC ternary formulations, which may be ascribed to the lower crystallization ability for LNP.

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NEW BIOMIMETIC HYDROXYAPATITE NANOPHASES CO-SUBSTITUTED WITH ANTBACTERIAL IONS FOR ENHANCED BONE REGENERATION

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Introduction: The steady increase of disabling bone diseases requires effective and durable therapies for extensive regeneration. In this respect, bone regeneration requires the use of biomaterials with chemico-physical features enabling adequate signaling to cells to activate the regenerative cascade. However, the occurrence of post-surgical complications such as infections is a serious concern: bacterial contamination provokes the formation of biofilm at the bone-implant interface, leading to implant failure. Therefore the development of new smart solutions integrating a significant boosting of bone regeneration with adequate protection against bacteria is today highly desired.

In this respect, low crystalline, calcium-deficient hydroxyapatite (HA) with biocompetent ion substitution (Mg, CO_3) is considered as elective material for bone regeneration, as it closely resembles the bone mineral, possessing excellent biocompatibility and ability to establish tight interface with newly formed bone. Besides, recent studies suggest that the doping of the hydroxyapatite lattice with ions like Ga^{3+} and Zn^{2+} could provide antibacterial effect. In fact, zinc ions are commonly found in natural bones and can stimulate bone regeneration, while also showing antibacterial activity, especially against *Staphylococcus aureus*, a bacterial strain commonly found in post-surgical infections. Few studies have been performed so far on the antibacterial effect of gallium but systemic administration of gallium results effective against many bacterial strains. In the present work, new hydroxyapatite nanophases presenting multiple ion substitutions (i.e. Mg^{2+} , CO_3^{2-} , Ga^{3+} or Zn^{2+}) were synthesized to confer both enhanced osteogenic ability and antibacterial effect. The new materials were tested by means of inhibition of several bacterial strains, and evaluated in respect to the kinetics of ion release to associate the antibacterial activity to the presence or exposure of doping ions.

Methods: New biomimetic HA phases were synthesized by neutralization of a $Ca(OH)_2$ aqueous suspension containing Mg^{2+} , CO_3^{2-} , Ga^{3+} or Zn^{2+} ions (in the amount of 1-10 mol%) with H_3PO_4 solution. Then the product was left overnight for maturation and finally washed, dried and sieved into a fine powder. The as-synthesized materials were analyzed by means of composition, cytocompatibility, proliferation, osteogenic ability (ALP) and antibacterial effect.

Results: Single phase HA nanopowders with different extents of ion co-substitution were successfully synthesized. The presence of Zn^{2+} or Ga^{3+} , has been determined, also showing that a competition exists between Zn^{2+}/Ga^{3+} and Mg^{2+} ions for the occupation of Ca^{2+} sites in the HA lattice. MTT tests with Mouse Mesenchymal Stem Cells (MSCs) show excellent cytocompatibility and a statistically significant increase of cell proliferation. Antibacterial tests made with *Staphylococcus aureus* showed a marked antibacterial effect, in comparison with non-substituted HA.

Discussion: The present work shows the effectiveness of HA doping with multiple ions, thus enabling double functionality, i.e. enhanced osteogenic ability and antibacterial effect. The effects of the competition arising among the various ions supposed to populate the calcium site were studied, to determine adequate process parameters to achieve nanoapatites with the desired ion substitutions.

Therefore, these new biomaterials are very interesting and promising for the future development of new bio-devices, such as bone fillers, scaffolds or coatings with improved therapeutic performance.

BIOMINERALIZATION OF POLYURETHANE FOAM FOR BONE TISSUE ENGINEERING

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Introduction: In tissue engineering, the use of synthetic polymers, including polyurethanes (PU), for bone regeneration is extremely appealing due to their easy fabrication into 3D porous structures, appropriate cell adhesion, and controlled porosity. One of the essential requirements for a porous material to be used for the production of scaffolds for bone tissue engineering is its ability to stimulate the deposition of calcium phosphate (CaP) similar to bone hydroxyapatite (HA) on its inner and outer surface. In fact, the presence of an apatite-like layer can promote a positive biological response from the host tissues, as well as improve the mechanical properties of the obtained construct. In this perspective, the aim of this study was the preparation and characterization of biominerilized polyurethane foams for bone tissue reconstruction.

Materials and methods: PU foams were synthesized by a one-step bulk polymerization method previously set up, using as reagents MDI prepolymer (Bayer), an ad hoc polyether-polyol mixture, FeAA as catalyst and water (2% w/w_{polyol}) as expanding agent. To obtain the CaP deposition, PU foam specimens were immersed in $CaCl_2 \cdot 2H_2O$ solution for 3 days at 37°C and then soaked in $Na_2HPO_4 \cdot 12H_2O$ solution for 3 days at 37°C, and finally immersed in 1.5 Simulated Body Fluid (1.5SBF) for different time points ($t = 1, 2, 3, 4$ weeks, obtaining respectively PU-T1, PU-T2, PU-T3 and PU-T4 samples). The PU foam morphology was evaluated by micro-CT, and the PU foams after the nucleation treatment were characterized by SEM observation, density

analysis, XRD and FT-IR (on powders obtained from the treated PU at the different time points), and compressive mechanical tests in wet conditions.

Results: By micro-CT, the PU foam appeared to have round-shape pore morphology, with homogeneous size and distribution. As expected, the density of the treated PU foams increased with the incubation time in SBF, being significantly different ($p < 0.05$) for PU-T4 vs. PU and PU-T1. The powders obtained from the treated PU at the different time points were similar to native HA in bone, being monophase HA, with small particle size and low crystallinity. This result was confirmed also by FT-IR analysis. SEM observation assessed the presence of an entangled network of plate-like crystals (thickness ≈ 100 nm), with similar morphology for all the considered time points. The apatite crystal amount, plate width and size homogeneity increased with treatment time. By comparing the SEM images of PU foam and PU-T4, the induction of biominerilization was observed also into the bulk and cross-section of PU-T4 samples. Furthermore, the biominerilized PU foams, in particular PU-T4, possessed higher mechanical properties in respect to the untreated PU foam.

Discussion: The obtained results proved the efficacy of the proposed biominerilization method, as a deposit of HA similar to the one of the native bone can be obtained on the inner and outer surfaces of the PU foams, improving also the mechanical properties. Therefore, the biominerilized PU foams can be adequate as scaffolds for cancellous bone tissue regeneration, even if a deep material-cell interaction evaluation is necessary.

BIODEGRADABLE FE STENTS COATED BY ELECTROSPUN PCL

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Introduction: Fe and its alloys are promising metallic materials for biodegradable stents as they have no cytotoxic effects and adequate mechanical properties. From a structural point of view, iron-based alloys used as temporary biodegradable stents have several advantages over Mg-based alloys in terms of ductility and strength. Iron low degradation rate could be balanced using a thin iron wire instead of a laser cut iron tube to obtain stent struts. To have a major contact with the arteries endothelial layer, reducing the turbulent blood flow and alleviating restenosis and plaque progression, in this work, polycaprolactone (PCL) was electrospun on the whole home-made iron wire stent.

Materials and methods: Four coronary stent configurations ($\phi = 6$ mm) were manufactured, using a hard tempered iron wire ($\phi = 0.125$ mm, purity = 99.5%) coiled manually to obtain the stent grid. PCL (20% w/v in chloroform-dimethylformamide solution) was electrospun (ES) on the Fe cylindrical stent positioned over a rotating collector (rotation speed = 1000 rpm), using an AISI 316L or a Delrin mandrel. A morphological characterization was performed by SEM to observe and quantify (ImageJ software) ES-PCL fibers diameter and density, considering the collector (conductive vs non-conductive) effects. Ad hoc mechanical characterization was performed to evaluate radial stiffness and strength compared to commercial bare stents. The in vitro degradation, both under static and dynamic conditions, was carried out up to 30 days. Stents were also tested, analyzing their behavior after the expansion: post-expansion diameter and length variation and recoil were the considered parameters. In vitro cytotoxicity and cytocompatibility were evaluated using L929 fibroblast line cells, investigating viability and cell morphology up to 14 days.

Results: No morphological defects (e.g. beads) were observed. The presence of the iron wire caused a higher variability in fibres diameter, and the significant statistical difference between MMD and PPD confirmed that collector material induced important differences in fibres morphology. Recoil investigation demonstrated that there are no statistically significant differences of diameter recoil among the samples for 3 atm of inflation pressure, and at 5 atm, dissimilarities between the different kinds of stent were detected. Adhesion tests showed significant differences between the stent covered on M and on P, and no differences between the stent obtained on the same collector. In vitro cytotoxicity and cytocompatibility test demonstrated good cell viability and good cell adhesion onto the ES-PCL.

Discussion: The different investigated ES-PCL/Fe stents showed interesting results, in particular when the ES-PCL coating is on the inner and outer surfaces. Potentiostatic corrosion tests have to be performed together with a computational analysis to simulate their in vivo behaviour.

NEW NANOFIBERS AND HYDROGEL BIOACTIVE COMPOSITES: EXPLORING THEIR INTERACTION WITH HUMAN PLURIPOTENT STEM CELLS

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Introduction: biomaterials designed to interact with biological systems offer a unique and appealing strategy to advance Stem Cell research. They can overcome the issues associated with traditional human Pluripotent Stem Cell (hPSCs) protocols by mimicking stem-cell-like niches incorporating key niche elements to enable precise regulation of stem cell fate and function. In this work, new bioactive composite hydrogel scaffolds made of electrospun poly(lactic acid) (PLLA) nanofibers, carrying surface amine groups introduced by atmospheric pressure non-equilibrium plasma treatment, embedded in a hydrogel matrix of AGMA1 structure were investigated. AGMA1 is an amphoteric biocompatible and biodegradable polyamidoamine (PAA), whose repeating unit resembles the integrin-binding *arg-gly-asp* sequence responsible for cell adhesion. Their performance as substrates for expansion and self-renewal of hPSCs was evaluated in a short-term culture.

Materials and methods: composites from AGMA1 hydrogels with different crosslinking degrees were produced in five steps: preparing PLLA electrospun nanofiber mats; preparing α,ω -acrylamide-end-capped AGMA1 oligomers; surface-modifying the mats by exposing them to a non-equilibrium atmospheric pressure plasma generated by a micropulsed Dielectric Barrier Discharge (DBD) plasma source operated in nitrogen; embedding the treated mats with 30% aqueous solutions of the oligomers doped with a little amount of 4,4'-azobis(4-cyanovaleric) acid; curing by UV irradiation, which triggered the radical polymerization of the AGMA1 oligomers. Two hPSCs cell lines, namely human embryonic stem cells (hESCs) (H9 ESCs, WiCell, Research Institute, Madison, WI) and human induced pluripotent stem cells (hiPSCs) (piPSC line, SBI System BioSciences, Mountain View, CA) were seeded on each scaffold. Viability assay (MTT) was performed to assess cell growth on the scaffolds while the morphology of the cells was analyzed by immunofluorescence. After 7 days of culture, the expression of self-renewal related-factors (OCT-4, SOX-2 and NANOG) was investigated by qRT-PCR and immunofluorescence analysis.

Results: the resultant composites absorbed large amounts of water forming reinforced hydrogels that effectively combined the biomimetic properties and softness of the surface-exposed AGMA1 hydrogel with the strength of PLLA mats. In vitro preliminary experiments showed that the hydrogels composites effectively support the adhesion and proliferation of both hPSCs cell lines, which retaining their stemness features as demonstrated by qRT-PCR and immunofluorescence investigations of undifferentiated markers.

Discussion: the new composites seem to be endowed with many favorable properties: their components are known to be biocompatible and biodegradable and they exhibited good mechanical properties, also due to the presence of amine groups introduced by plasma treatment onto PLLA mats, which ensure that the fibrous and matrix components of the resultant composites remain indefinitely anchored to each other even when fully swollen in water. In addition, their bioactive features provide suitable binding sites for hPSCs adhesion and proliferation, maintaining their undifferentiated properties. Even though more detailed experiments are required, as long-term cultures, all these data point to PLLA/AGMA1 scaffolds as powerful new entry in the field of stem cell research.

HNT MODIFIED GELLAN-BASED SCAFFOLDS WITH TUNABLE MECHANICAL FEATURES

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Introduction: Gellan gum (GG) is a polysaccharide derived by microbial fermentation of the *Sphingomonas* microorganism. It can form ionically-crosslinked hydrogels with interesting thermosensitive properties. GG is able to jellify *in situ* closely to body temperature, therefore it could be used in applications that require injectable formulations. Moreover, GG has been recently proposed for cartilage regeneration, thanks to its high stability and nontoxic nature. However, similarly to most natural polymers GG presents relatively poor mechanical properties. In this respect, in order to improve its mechanical behaviour, different inorganic fillers have been proposed. In this study, for the first time, a new composite material based on GG and Halloysite nanotubes (HNT) is proposed to produce hybrid hydrogel scaffolds for biomedical applications. Fourier transforms infrared spectroscopy in attenuated total reflectance mode (FT-IR/ATR) and X-ray photoelectron spectroscopy (XPS) analyses are performed in order to obtain a preliminary analytical characterization of the novel hybrid biomaterial. Swelling and mechanical behaviour are also evaluated.

Materials and methods: GG (PhytageTM), HNT (Halloysite nanoclay), CaCl₂ (all supplied by Sigma-Aldrich) and glycerol (Baker Chemicals) are used without further purification. An aqueous solution of GG, glycerol (Glyc) and HNT is crosslinked with CaCl₂ using the external gelation method previously described. Gelled samples are successively conditioned in PBS and then freeze-dried. FT-IR/ATR analysis is performed on a Spectrum Two PE instrument using the Universal ATR accessory (Single Reflection Diamond) (PerkinElmer Inc, Waltham, MA) and XPS analysis is performed by a scanning microprobe PHI 5000 VersaProbe II (Physical Electronics, Chanhassen, MN). Mechanical tests are performed using a mechanical testing machine (Shimadzu, EZ-SX, Japan). The samples were tested at room temperature ($n = 5$). A 20N load cell was utilized to perform the analysis with a crosshead speed set at 1 mm·min⁻¹.

Results: No interactions between HNT and gellan matrix have been observed by XPS and FTIR-ATR analyses in the investigated scaffolds. The gellan-based dried polymeric scaffolds rapidly uptake water upon contact, reaching a maximum within few minutes independently of the presence of HNT. Compressive tests showed that, the content of glycerol and HNT dramatically influenced the mechanical properties. Particularly, the hydrogels with a GG:Glyc weight ratio of 1:3 presented 140% increment in Young modulus and 86% more fracture toughness, as compared to GG:Glyc weight ratio of 1:1. Moreover, by adding 25% HNTs, the compressive strength and modulus was significantly increased (48 kPa and 71 kPa) compared to pure GG hydrogels (37 kPa and 49 kPa).

Discussion: The HNT-modified scaffolds combine tunable mechanical behaviour with the swelling properties that characterize hydrogels. Moreover, the potential to easily obtain complex shapes makes this new composite material a promising candidate for many biomedical applications.

MULTILAYER NANOENCAPSULATION OF HUMAN ISLETS IN-VITRO AND IN-VIVO STUDIES

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Introduction: In an attempt to improve the outcome of pancreatic islet transplantation, we performed in-vitro and in-vivo experiments with isolated human islets coated by multi-layer nano-encapsulation.

Materials and methods: Human islets were isolated from 32 non-diabetic donors (age: 63 ± 17 years, BMI: 26.8 ± 3.5 kg/m², M/F: 17/15) by enzymatic digestion and gradient purification. Multi-layer nano-encapsulation was performed by electrostatic binding of differently charged polymers [chitosan and poly(sodium styrene sulfonate)], up to 9 layers. Morphological, ultrastructural, functional and transplantation studies where then accomplished with the nano-coated human islets.

Results: The procedure provided full coating of the human islets (thickness: 104.2 ± 4.2 nm), as assessed by fluorescence, confocal and electron microscopy (EM). Vital staining and EM showed 90% cell survival and well maintained beta and alpha cell ultrastructure, with unchanged morphology and morphometry

of intracellular organelles. Insulin secretion from nano-encapsulated islets was 44 ± 33 mU/ml (mean \pm SD) at 3.3 mM glucose and increased to 176 ± 120 mU/ml at 16.7 mM glucose ($p < 0.01$), with a stimulation index of 4.6 ± 2.7 . Perfusion studies showed maintained dynamics of insulin secretion. Toxicity by palmitate or cytokine exposure was significantly reduced in nano-coated islets. Transplantation of nano-encapsulated islets under the kidney capsule of C57Bl/6J mice with streptozotocin-induced diabetes allowed long term normal or near normal glycemia, with intra-peritoneal glucose tolerance test results similar to those of non-diabetic mice. Light and electron microscopy of nano-coated islet grafts was performed at one month post-transplantation, showing minimal mononuclear cell infiltration, preservation of islet cell ultrastructure and signs of revascularization.

Discussions: Isolated human islets were efficiently encapsulated by this multi-layer nano-coating approach, with preserved in-vitro and in-vivo function.

THE INFLUENCE OF GARLIC EXTRACTS ON THE THERMAL, MECHANICAL AND BIOLOGICAL PROPERTIES OF ELECTROSPUN POL(LACTIC ACID) FIBERS

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Introduction: The health features of garlic are associated to its organosulfur compounds (OSCs) able to supply antimicrobial, antioxidant, anti-inflammatory and chemo-sensitization properties and heart protection. The OSCs beneficial action is justified by their ability to release H₂S, one of three natural *gastransmitters*, able to favour specific enzymatic activities and prevent free radicals formation. Thus these compounds can be considered promising biomolecules to provide antimicrobial/antioxidant properties and improved biological responsiveness to scaffolding materials for tissue repair. Being chemically unstable and thermolabile, it is necessary to stabilize them and use processing techniques which do not require high temperatures, such as electrospinning. The electrospinning is a low-cost, user friendly, and versatile process that occurs at ambient conditions, and is very proper to entrap thermoable substances, ensuring their controlled release. Moreover, this technique allows to obtain fibrous structures which mimic the tissue extracellular matrix ones. In this context, both garlic oil-soluble allyl sulfur compounds (GaOs) and diallyl disulfide (DADS) loaded poly(lactic) acid (PLA) fibrous mats were prepared by electrospinning. The OSCs effect on the morphological, thermal, mechanical and biological properties of the produced fibers was investigated.

Materials and methods: OSCs loaded PLA fibers were prepared by electrospinning solutions obtained dissolving proper amounts of PLA pellets (3051D, *Nature Works*, 15% wt/v) and of OSCs (GaOs and DADS (*Sigma Aldrich*) (5% v/v) in a solvent mixture CHCl₃:DMF (67:33, in volume ratio), in the following conditions: applied voltage 12kV, flow rate 0.5 ml/h, needle-target distance 15 cm. Neat PLA fibers were also produced. The morphology of the electrospun membranes was observed at scanning electron microscope (FESEM, *Leo Supra 35*), the thermal properties investigated by differential scanning calorimetry (DSC, *TAIInstrument Q2000*), the mechanical properties analysed performing uniaxial tensile tests on dog-bone specimens (4.8 \times 22.25 mm²), at 1.2 mm/min to rupture (*Lloyd LRX*, load cell 50N), following ASTM D1708 and ASTM D882 standards. The H₂S release was estimated for PLA/GaOs and PLA/DADS by methylene blue assay and the cytotoxicity by analysis of the in vitro cell viability of human Lin⁺Sca1⁺ progenitor cardiac cells (hCPCs) up to 7 days, using MTT assay.

Results and discussion: The obtained mats were composed of defect-free randomly oriented fibers. For PLA/DADS bigger fibers ($d = 1.21 \pm 0.16$ μ m) were obtained with respect to the neat PLA ($d = 0.71 \pm 0.18$ μ m) and PLA/GaOs ($d = 0.65 \pm 0.10$ μ m). A significant increment of the mechanical properties was recorded in the case of OSCs loaded PLA fibers ($E = 28 \pm 1$ MPa/ σ_{max} = 1.1 ± 0.1 MPa for PLA; $E = 65 \pm 18$ MPa/ σ_{max} = 2.4 ± 0.2 MPa for PLA/DADS; $E = 52 \pm 6$ MPa/ σ_{max} = 2.7 ± 0.3 MPa for PLA/GaOs), suggesting an interaction between the sulfur compounds and the PLA chains, in agreement with DSC data that evidenced an increased crystallinity degree. The ability of the fibers to release H₂S was assessed, and thus these structures could be exploited as exogenous H₂S-donors for biomedical applications. Preliminary cytotoxicity tests with hCPCs were performed to investigate their potential application as platforms for tissue regeneration, demonstrating not cytotoxicity in all cases. Remarkably enhanced cell adhesion and viability were observed in the case

of the cells seeded on PLA/DADS systems. These data suggest a possible correlation between its H₂S-releasing ability and the improved stem cell viability for potential applications in regenerative medicine.

GELATIN/NANOCELLULOSE POLYMERIC BLENDS TO DEVELOP 3D SCAFFOLDS FOR TISSUE REGENERATION

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Introduction: In recent years, new regenerative approaches for the healing of diseased tissues and organs have aimed to recover the original functionality and reduce healthcare costs and patient's pain. New trends are focusing on the unique characteristics and properties of natural structures to create biocompatible and biodegradable scaffolds with suitable pores size and interconnection to allow cell colonization and proliferation.

In the present work, blending processes are designed to combine the best properties of two bio-polymers and to obtain hybrid materials with improved mechanical performances without losing biocompatibility, chemical stability and flexibility. By means of cross-linking reaction and freeze-casting process, porous, stable and safe scaffolds for tissue regeneration based on gelatin and cellulose nano-fibers (CNF) were obtained. Gelatin has been selected as polymeric matrix due to its easy production, low cost and high biocompatibility, however, its effective use is restricted due to its poor mechanical properties and easy degradable nature. In order to overcome these limits, biocompatible CNF have been selected as a potential nano-reinforcement due to its exceptional mechanical properties, high crystallinity and surface area. Several blend compositions and effective and safe chemical cross-linkers involving active groups of both gelatin and CNF were studied to stabilize the polymeric network and to control its degradation rate in simulated body conditions. Preliminary in vitro and in vivo tests on the most performing scaffolds were performed.

Materials and methods: The polymeric blends were obtained by dissolving porcine gelatin in CNF water suspension at 40°C under mechanical stirring. The blends were then treated with optimized amounts of genipin and hexamethylenediamine (HMDA) and freeze-dried. After freeze-drying also a dehydrothermal cross-linking treatment (DHT) at 160°C in vacuum was performed. Evaluation of morphological and chemic-physical properties of the different specimens were carried out by SEM and FTIR analyses and degradation and swelling tests in PBS at 37°C. Moreover, viscoelasticity properties were evaluated by means of DMA. Preliminary in vitro tests with L929 cells and in vivo test on rats of the most performing scaffolds were performed.

Results: CNF/gelatin ratio of 10 wt%, blend concentration of 6 wt% and combination of different cross-linking treatments (1 wt% of genipin, 6 wt% of HMDA and DHT) allowed to obtain homogeneous blends and 3D polymeric scaffolds presenting well interconnected porous structure and suitable chemical stability in physiological conditions. DMTA analyses demonstrate an improving of mechanical performances respect to the pure gelatine due to the combination with CNF. In vitro and in vivo evaluations demonstrate the biocompatibility of the scaffold and its good interaction with cells.

Discussion: Different cross-linking agents and their synergic effect are evaluated and optimized to cross-link CNF/Gelatin blends to obtain 3D scaffolds suitable for tissue regeneration. SEM analysis, stability and viscoelasticity tests prove that by blending gelatine with suitable amounts of CNF and cross-linking with genipin, HMDA and DHT was possible to achieve well interconnected porous structures suitable for cell colonization with good performances in physiological conditions. Finally, in vitro and in vivo tests assess that the optimized cross-linking procedures don't affect the biocompatibility of CNF and gelatin biopolymers.

COATINGS OF TITANIUM SUBSTRATES WITH HYDROXYAPATITE PREPARED BY THE SOL-GEL METHOD FOR BIOMEDICAL APPLICATION

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Introduction: A material to be used as scaffold must meet requirements such as biocompatibility, surface topography and chemistry to promote cell adhesion, proliferation and differentiation, controlled biodegradability



and bioactivity. Due to the chemical similarity between Hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and mineralized bone of human tissue, HA synthesized via sol-gel technique exhibits strong affinity to host hard tissues because is able to form chemical bonds with the host tissue. However, sol-gel materials haven't mechanical properties suitable to be used as scaffolds for bone tissue engineering.

The aims of the present work have been to modify titanium grade 4 implants (Ti-4, commonly used in orthopedic and dental fields) in order to improve their biological properties. For this purpose on the implant surfaces a thin film of HA was applied by sol-gel dip coating technique and the biological properties of coated samples was evaluated.

Materials and methods: Hydroxyapatite sol was synthesized using phosphoric pentoxide (P_2O_5 , Sigma Aldrich) and calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Sigma Aldrich) as precursors. Both were dissolved in absolute ethanol (EtOH , 99.8% Sigma-Aldrich) and the pH adjusted to 11 using NH_4OH . The molar ratio of precursors Ca/P was 1.67 which is the desired ratio observed in hydroxyapatite. The sols obtained were used to coat Ti-4 implants by means of dip coating technique using a KSV LM dip coater. Withdrawal speed of the substrate was 15 cm/min. The coated substrates were heat-treated at 600°C and 1000°C for 2h and chemically characterized by ATR-FTIR spectroscopy.

In order to study coating bioactivity, the coated substrates were soaked in a simulated body fluid (SBF) with the temperature kept at 37°C. The ability to form an apatite layer was studied by SEM/EDS analysis. Coatings' biocompatibility was evaluated by WST-8 Assay seeding NIH 3T3 murine fibroblasts coated and un-coated substrates.

Results: FT-IR analysis of untreated and heat treated samples indicates that after 600°C the degradation of nitrates used in synthesis occurs. The treatment also leads to a carbonation of HA. SEM photos of the samples after SBF soaking show the formation of apatite layer and grains on the specimen, regardless of heating temperature, confirming the bioactivity of the prepared films. Moreover, the coated samples are more biocompatible than Ti-4 uncoated and there is no significant difference between the samples heated on 600°C and 1000°C.

Discussion: The HA coatings obtained via sol-gel dip coating could be proficiently used to modify the surface of implants to improve their biological properties and overall performance. The heat treatment allows the degradation of nitrate ions, which may adversely affect the biological response to the material. All samples were shown to be biocompatible and bioactive, a fundamental property necessary for their osseointegration after implantation.

INFLUENCE OF CA/P RATIO ON BIOLOGICAL PROPERTIES OF $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ COATINGS OBTAINED VIA SOL-GEL-DIP COATING

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Introduction: Ternary $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ systems have attracted considerable interest as bioactive materials able to form strong bonds to living bones. It is due to the release of soluble silica and calcium ions which are able to stimulate osteogenesis at the implant site, promoting bone tissue growth. It is known that the biological properties of these materials are influenced by both heat treatment and preparation method, because those two factors affect the structure of the obtained glasses. In the present work, bioactive and biocompatible coatings consisting of silica-reach $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ systems were obtained via sol-gel dip coating. This method was successfully used to synthesize glass and ceramic coatings at low temperature able to improve the biological properties of the coated substrates. Coatings with growing Ca/P ratio were obtained and characterized to study the effect of Ca/P ratio on the coating structure and, thus, their biological properties.

Materials and methods: $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ sols were synthesized by sol-gel technique using tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, Sigma Aldrich), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Sigma Aldrich) and triethyl phosphate ($\text{C}_6\text{H}_{15}\text{O}_4\text{P}$, Sigma Aldrich) as precursors of SiO_2 , CaO and P_2O_5 respectively. Four formulations were prepared which differ in the Ca/P atomic molar ratio. The sols obtained were used to coat glass coverslip by means of dip coating technique using a KSV LM dip coater. Withdrawal speed used was 10 cm/min. The coated substrates were heat-treated at 600°C for 1h to remove the synthesis by-products. The chemical structure of the coatings and their morphology were investigated by ATR-FTIR spectroscopy and SEM microscopy.

In order to study coating bioactivity, the coated substrates were soaked in a simulated body fluid (SBF) with the temperature kept at 37°C. The ability to form an apatite layer was studied by SEM/EDS analysis. The cellular response to coatings presence was evaluated by WST-8 Assay seeding osteoblast-like U2OS cells on coated and un-coated substrates. All results were expressed as a function of the Ca/P atomic molar ratio.

Results: FT-IR analysis shows that 600°C heating leads to a carbonation of the samples due to the atmospheric CO_2 as a consequence of high calcium content in glasses. SEM micrographs show that films porosity decreases with the Ca increase. Moreover, SEM of the samples after SBF soaking show the formation of apatite globules on the samples surface, regardless of Ca/P molar ratio. On the contrary, cell proliferation increase with the increasing of the Ca content.

Discussion: The excellent biological properties of $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ materials were transferred to the substrates. All samples were shown to be biocompatible and bioactive, a fundamental properties necessary for the use of a materials in biomedical field.

IN VITRO STUDY OF THE EFFECTS OF TITANIUM NANOSTRUCTURED SURFACES ON PROLIFERATION AND DIFFERENTIATION OF HUMAN BONE-MARROW STROMAL CELLS

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Introduction: Bone tissue engineering is a strategy to replace autologous or heterologous bone grafts with an artificial material (scaffold) that mimics the bone structure. The surface topography and chemistry take significant influences on the biological performance of biomedical scaffolds. In this context, titanium dioxide (TiO_2) represents a gold standard in bone tissue engineering. The nanotopography of TiO_2 raised several important properties that consent the use of this biomaterial to mimic the morphology and the hierarchical organization typical of the extracellular matrix (ECMs) in bone. TiO_2 nanostructured surface was obtained by the deposition of a supersonic beam of TiO_2 clusters. The typical features of this scaffold showed dimensions in a range between 1-100 nm. In this study, we evaluated the biocompatibility of TiO_2 nanostructured clusters deposited on a coverglass surface (Tethis® company), with respect to a microscopy coverglass (Glass). We performed a detailed investigation in terms of adhesion and differentiation towards bone phenotype of human multipotent stem cells (hBMSCs) seeded on nanostructured TiO_2 and Glass surface in the presence (osteogenic medium, OM) or absence (proliferative medium, PM) of osteogenic factors.

Materials and methods: Microscopy coverglass coated with a film of cluster-assembled TiO_2 were purchased from Tethis (<http://www.tethis-lab.com>). As a control surface, the same microscopy coverglass used for the coating deposition of the film of cluster-assembled TiO_2 was employed. We analyzed the microstructural surface of TiO_2 nanostructured surface with scanning electron microscopy (SEM). For adhesion and morphological analyses, hBMSC cells on Glass and TiO_2 were incubated with the primary antibody, vinculin clone (hVIN-1, Sigma-Aldrich) and antihuman pFAK (p397). We evaluated at 7 and 28 days gene expression by qRT-PCR of genes involved in osteogenic differentiation. In addition, at 28 days we evaluated the levels of the more important osteogenic proteins (collagen I, collagen III, osteocalcin, human decorin, osteopontin, alkaline phosphatase, osteonectin and bone sialoprotein), and we quantified calcium deposits by fluorescent calcein detection and calcium-cresolphthalein complexone methods.

Results: The surface of the nanostructured TiO_2 observed at SEM showed a uniform and particulate structure of the clusters, with diameter under 100 nm of dimension. TiO_2 surface showed an increment of about 5% in foci-positive area with respect to Glass. In addition, we did not note any visible morphological alterations between cells adherent to Glass and TiO_2 surface. Gene expression results showed that TiO_2 nanostructured surface enhanced

the expression of Osteocalcin, BMP-2 and Decorin genes at 28 days in PM and OM with respect to Glass. Moreover, there was a significant enhancement of protein deposition for ALP, type-I collagen, type-III collagen, OP, ON, OSC, FN and DCN at 28 days in OM for hBMSC cells seeded on TiO₂ nanostructured surface with respect to ECM deposition ratio on Glass.

Discussion: Based on molecular and protein results, we may assume that the main effect of TiO₂ nanostructured surface was to facilitate hBMSC cells adherence and, at the same time, to promote protein ECM deposition and cell differentiation. We demonstrated that the nanostructure of TiO₂ surface could be successfully employed for *in vitro* studies of biocompatibility.

COLLAGEN-BASED SCAFFOLDS WITH IMPROVED MECHANICAL PERFORMANCES USEFUL IN TENDON REGENERATION

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Introduction: The partial or full thickness tear of the supraspinatus tendon is a complex pathological process, which requires different therapeutic approaches, from conservative strengthening exercises to prompt surgical repair. When a repair cannot be accomplished, one of the surgical options consists in the tendon augmentation, i.e. the application of biological or artificial grafts to bridge otherwise irreparable tendon defects. This technique provides a rapid increase of the tendon thickness, therefore reducing stresses and deformations on the tendon itself, allowing cells migration and regeneration. Owing their biocompatibility, natural collagen scaffolds could be ideal candidates for this purpose: however, due to their high water uptake, swollen scaffolds show very weak mechanical properties and completely lose their tridimensional structure, often resulting in failure of surgery. The aim of this project was the preparation of novel collagen-based scaffolds for tendon regeneration, with improved mechanical properties, lower water uptake and higher resistance to enzymatic degradation, compared to natural collagen. To this purpose, collagen scaffolds were treated with different chemical and physical treatments, to obtain biomaterials with tunable properties, such as resistance to proteolytic enzymes, swelling and mechanical properties.

Materials and methods: A porous matrix of type I collagen sponge (Coll) was prepared by means of freeze-drying of a collagen solution. The different scaffolds were prepared with a treatment in heterogeneous phase to preserve, as much as possible, the porous matrix of the collagen sponge.

In one case (Coll-PLA), collagen was grafted with hydrophobic chains of PLA in NMP/DMSO; IIDQ, (1-isobutoxycarbonyl-2-isobutoxy-1,2-dihydroquinoline) was added for the activation of the terminal carboxyl groups of PLA. In another case, the collagen was treated according to the same procedure described above but without the addition of IIDQ, thus avoiding the reaction between PLA and collagen. This sample was considered a "blank treated" collagen (Coll-T). After purification, both samples were dried with two different techniques (freeze-drying or pressure-drying) to obtain scaffolds in form of sponges or films.

Results and discussion: Both the prepared sponges exhibited an overall behavior completely different in comparison with the starting material: (i) reduced water uptake ability, (ii) increased mechanical behavior; (iii) different resistance to enzymatic degradation. In addition, the grafted material showed higher resistance to large deformations and slower enzymatic degradation, in comparison with the "blank treated" collagen. The films exhibited a reduced porosity in comparison to the corresponding sponges, therefore, (i) lower water uptake, (ii) slower enzymatic degradation, (iii) a dramatic increase in Young modulus values and at the same time, lower resistance to large deformations. Preliminary cell viability test performed on the sponges with human primary dermal fibroblasts, demonstrated the biocompatibility of the samples. The materials showed a cell proliferation rate comparable to that of the untreated collagen. Furthermore, Coll-PLA showed a higher cell seeding efficiency, probably due to its higher mechanical properties and its ability to maintain its shape in the swollen state.

In conclusion, these scaffolds may be addressed as potential tool in tendon repair and regeneration. Further clinical evidence will be needed to confirm and validate this surgical regenerative approach.

3D SILK-FIBROIN HYDROGEL SCAFFOLDS FUNCTIONALIZED WITH PROTEIN-MICROSpheres FOR CARDIAC TISSUE REPAIR

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Introduction: The "cell delivery scaffolds" have a key role in tissue engineering, the cells are implanted or seeded into an artificial structure able to support three-dimensional (3D) tissue formation. Hydrogel-scaffolds can mimic physical, chemical, electrical and biological properties of most of the native tissues and can be cross-linked with other molecules to obtain composite hydrogels endowed with specialized characteristics. Recently, silk fibroin (SF) hydrogels have been produced by radical cross-linking formation induced by physical methods, such as sonication. Due to its unique mechanical and thermal properties, its high processability (into films, foams, or fibrous membrane), biocompatibility and biodegradability, SF represents an optimal scaffold material. In this study a new photopolymerizable PEGda-SF hydrogel (PSFHy) has been produced combining the SF biofunctionality with the structural versatility provided by the PEG molecules. Moreover, albumin microspheres (MSs) have been embedded into 3D-PSFHy as porogen agents, carriers of macromolecules and contrast agents for ultrasound imaging.

Materials and methods: SF was extracted and purified from *Bombyx mori* silkworm cocoon with an optimized protocol. 3D-PSFHy was achieved by free-radical polymerization of 8 mg/ml protein-PEGda solution adding 0.1% (w/v) of Irgacure®2959 after exposure for 5 min at long-wave UV light (365 nm, 4.5mW/cm²). MSs were produced using 5% BSA (w/v) and perfluorohexane (PHF) 10% (v/v); 20 kHz ultrasounds were applied for 60 sec at the air-water interface with an applied acoustic power of 180 Wcm⁻². Human Lin-Sca1⁺ cardiac progenitor cells (hCPC) were used for the *in vitro* studies. MITT assay was performed for analyzing the hCPC viability.

Results: A novel 3D hybrid hydrogel was synthesized by photopolymerization of SF/PEGda mixture and characterized using different techniques. The presence of SF improves the cell growth into 3D-PEGdaHy scaffolds and the cell viability of hCPC was comparable with that recorded in the case of PEG-fibrinogen hydrogel (PFHy). 3D-PSFHy biodegradability was assessed by proteolysis. Moreover, a functionalization of the 3D-PSFHy was performed using MSs. The stability of the embedded MSs into 3D-PSFHy was checked by fluorescence microscopy using FITC-MSs. This functionalization improved the cell viability compared to the growth into 3D-PSFHy of 41.8 ± 2.86% and 28.9 ± 5.04% after 7 and 14 days, respectively. An elongated cell morphology at 14th day into 3D-PSFHy was observed by immunofluorescence analysis. The integrity of the nuclei and the expression of a-smooth muscle actin were also assessed.

Discussion: The preliminary studies here presented highlight on the possibility to use this silk fibroin hydrogel as new injectable scaffold for tissue repair. Moreover, the increase of the hCPC viability into 3D-PSFHy functionalized with MSs will allow optimizing this 3D-system using MSs coated with growth factors and drugs.

REVERSE ENGINEERING AND ADDITIVE MANUFACTURING TO DEVELOP PHYSICAL MODELS

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Introduction: Reverse engineering and additive manufacturing have been suitably integrated to develop different kinds of devices. Many polymer-based materials have also been widely proposed for several applications, thus emerging as interesting alternatives to metals. Many objects, such as parts for devices or toys, can be fabricated by additive manufacturing. Starting from a computer-aided drawing, it is possible to manufacture an object or a functional part in a layer-by-layer fashion. Benefiting from user-friendly computer programs and from the availability of open source 3-D printers, many objects may become 3-D printable.

Materials and methods: As reported, in fetal ultrasound, 3D ultrasound basically allows visualizing some facial features and other parts such as toes and fingers and of the fetus, whereas 4D ultrasound represents 3D ultrasound in motion. Starting from a 3D/4D ultrasound images a fetal reconstruction was made using dedicated software.

3D models of human fetus were fabricated by fused deposition modeling (FDM) using a Zortrax M200 printer and a thermoplastic polymer (Acrylonitrile-Butadiene-Styrene, ABS).

Results: Different models of human fetus were developed starting from the optimization of the process and instrument parameters. The processability of the materials was assessed through functional and calorimetric analyses. Image capture and analysis techniques allowed obtaining the exact geometry, shape and size of the fetus.

Discussion: The obtained results demonstrated the possibility to develop customized models of a human fetus through the reverse engineering process and additive manufacturing (i.e., FDM).

SINGLE STEP PROCESS FOR THE CO-DEPOSITION OF NANOCOMPOSITE ANTIBACTERIAL COATINGS USING A NON-EQUILIBRIUM ATMOSPHERIC PRESSURE PLASMA JET

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Introduction: Cold atmospheric plasmas (CAPs), due to their low temperature, are able to support innovative processes for the modification of thermosensitive materials. While the use of cold low-pressure plasmas is well assessed, CAPs potentialities are still largely unexplored notwithstanding their advantages of cost and ease of use. In this contribution, a single-step plasma process performed by means of CAPs for synthesis and co-deposition of nanocomposite coatings containing silver nanoparticles (AgNPs) embedded in a pPAA matrix is presented.

Materials and methods: The process was performed using a non-equilibrium atmospheric pressure plasma jet enabling the separate and simultaneous introduction of acrylic acid (AA) and AgNPs dispersion in the plasma region. The plasma source was driven by a micropulsed generator producing high-voltage sinusoidal pulses with peak voltage (PV) up to 40 kV, frequency (f) 20–50 kHz, variable pulse duration and fixed pulsed repetition frequency (PRF) of 100 Hz. A thorough characterization of the morphology, by means of SEM analysis, and chemical characteristics of the nanocomposite coating through ATR-FTIR and XPS was carried out. Furthermore, the antibacterial efficacy of the deposited nanocomposite coatings was preliminary assessed against a test microorganism (*E. coli*) by means of agar disk diffusion tests.

Results: The thickness of the AgNPs/pPAA coatings co-deposited for 3 min was measured to be around 25 µm from SEM cross-sectional views of the samples. Despite enabling to estimate the coating thickness, SEM cross-sectional views of the samples did not reveal the presence or absence of AgNPs in the coating. On the other hand, SEM top views of the samples assessed the presence of AgNPs in the coatings. Regarding the investigation of the chemical characteristics of the co-deposited AgNPs/pPAA coating, the ATR-FTIR spectrum was found to coincide with the spectrum of pPAA coating without AgNPs embedded. In order to garner information on the presence of AgNPs in the co-deposited coating and on the retention of carboxylic groups in the pPAA matrix, XPS analysis was performed. The results highlighted a significant (21%) retention of carboxylic groups in the pPAA chemical structure, underlining that limited monomer fragmentation occurred during the process, and the presence in the coating of superficially oxidized AgNPs. Finally, the antibacterial efficacy of the co-deposited AgNPs/pPAA coatings was clearly demonstrated. In fact, while no growth inhibition area could be observed around the uncoated PE and pPAA coated PE samples, a clear zone with no bacterial growth was easily detected around the AgNPs/pPAA coated PE samples.

Discussion: The proposed approach turned out to be able to co-deposit coatings with antibacterial properties.

EVALUATION OF MAGNETIC GELS FOR APPLICATION IN DRUG DELIVERY

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Introduction: The ability to control the release over time of molecules and drugs, improving the biodistribution and minimizing the systemic effects of aggressive therapies, is still subject of study in the management of cancer treatments. In this regard, magnetic gels, also called ferrogels, represent one of the most attractive options in the field of drug delivery systems. Object of the present study was to test the biocompatibility *in vitro* of a carboxymethylcellulose hybrid hydrogel, containing Fe₃O₄ nanoparticles as cross-linkers (CMC-NP), designed for application in drug delivery under magnetic field stimulation.

Materials and methods: CMC-NP hydrogel was cultured with MG63 osteoblast-like cells up to 7 days. Assessment of cell viability and proliferation, cytotoxicity and osteoblasts activity was performed at different experimental times. In addition, a bone culture model with rabbit femoral condyles was set up; the material was tested, placed in a hole of about 2 mm created into the bone, to mimic the condition of bone implant *in vivo*. Bone segments were cultured up to 28 days and viability was assessed periodically (24 hours, 7, 14, 21, 28 days). At the end of experimental time, bone specimens were processed for both methacrylate and paraffin embedding.

Results: *In vitro* tests on MG63 cells showed that viability and proliferation were not affected by the presence of the CMC-NP hydrogel, with values comparable to controls. No alterations were found in cell morphology and the evaluation of LDH release revealed no cytotoxicity induced by the presence of the hydrogel; the expression of ALP and COLI seemed to be unaffected, suggesting a normal osteoblastic activity. As for bone cultures, the viability remained stable during the experimental times, without any differences between samples with hydrogel and controls. Histological assessment didn't note any alterations in the bone segments in culture with CMC-NP hydrogel.

Discussion: The advances in synthetic chemistry and innovative technologies allowed the development of more and more challenging therapeutic strategies, supported by both drug-releasing biomaterials and physical treatments. To evaluate the possible clinical application of these advanced therapies, the development of reliable *in vitro* and *in vivo* models, resembling at best physiological conditions, is required. The CMC-NP hydrogel investigated revealed a good biocompatibility, showing to be suitable for future applications in the treatments of bone tumors; furthermore, the possibility to test the material in a long term bone culture provided a more comprehensive picture, similar to *in vivo* conditions, thus offering a new model to evaluate and select the most appropriate and safe materials *in vitro*, in order to optimize and rationalize the subsequent animal testing.

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MICROFLUIDIC ENHANCED BIOPRINTING FOR MUSCLE REGENERATION

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Introduction: Skeletal muscle tissue engineering still poses several hurdles, mainly due to muscle tissue biological and structural complexity. Among currently available tissue engineering strategies, 3D bioprinting has the potential to produce 3D highly customizable and organized structures that, in theory, could be used for whole-muscle reconstruction. Here we present a 3D bioprinting method based on a coaxial microfluidic head that enables the deposition of multi-material and/or multi-cellular within a single scaffold by simultaneously extruding different bioinks or by rapidly switching between different bioink compositions. As muscular fibers have a highly aligned structural arrangement *in vivo*, the driving idea behind the presented work was that the simple geometrical confinement of muscle precursor cells into highly aligned 3D bioprinted hydrogel structures can lead to a better orientation of the arising myotubes, thus better mimicking the natural muscle morphology.

Materials and methods: A semi-synthetic bioink, composed of photocurable PEGylated fibrinogen and sodium alginate, compatible with our microfluidic co-axial printing head, was formulated and optimized for embedding high concentration (over 1×10^6 cells/mL) of C2C12 murine myoblasts. In a typical printing procedure, the formulated bioink was deposited in the form of Ca²⁺-ionically crosslinked hydrogel fibers to obtain a 3D multi-layered construct, showing parallel aligned cell-laden fibers with an avg. diameter below 250 µm. After printing, PEGylated fibrinogen was covalently crosslinked by exposure to cell-compatible UV radiation (365 nm).

Results: The process resulted in high cell viability (>90%), good bonding between fibers belonging to adjacent layers, and overall mechanical stability of the scaffolds. Within few days, we observed a good migration

and differentiation of C2C12 cells that started to spread and fuse, forming multinucleated myotubes within the 3D bioprinted fibers. Interestingly, we noticed that muscle precursor cells, before fusing with adjacent cells, elongates following the orientation of the fibers. This may find an explanation at the molecular level as polymeric chains, when extruded, tend to orientate according to the flow/extrusion direction and cells may then sense an oriented surrounding matrix. After 4 weeks in culture, the formed myotubes reached a good differentiation status, as confirmed by immunocytochemistry staining for laminin and myosin heavy chain and by gene expression levels of myogenic markers.

Discussion: The presented preliminary results show that the confinement of muscle cell precursors is beneficial for fabricating highly aligned networks of myotubes with a physiologically inspired structure. Moreover, as the presented method enables multiple bioinks to be dispensed with extremely small dead volumes, it represents an ideal candidate for creating more complex structures for muscle tissue engineering, e.g. including a vascular network and neuromuscular and myotendinous junctions.

A COMPREHENSIVE STUDY ON INORGANIC NANOPARTICLE - CELL INTERACTIONS

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Introduction: The use of nanotechnology in medicine has undergone a rapid development in the last few decades with significant impact on diagnosis and therapy of many diseases. Inorganic nanomaterials (INMs), such as gold nanoparticles (NPs), quantum dots, silica NPs, iron oxide NPs, carbon nanotubes and other inorganic NPs, have emerged as promising alternatives to organic systems for a wide range of biomedical applications.

The use of NPs in biology and medicine requires a molecular-level understanding of how NPs interact with cells in a physiological environment.

This study aimed to evaluate the biunivocal cell-INM interaction from morphological, physico-chemical and biological point of view using both standard methods and non conventional techniques.

Materials and methods: Silica and zinc oxide INMs and A549 cells were selected for the tests. The effect of INMs on the cell properties was evaluated in terms of cell viability (MTS assay), chemical modifications using FT-IR Chemical Imaging and dimensional change using Scepter cell counter. The effect of the cells on the INMs was evaluated by both dimensional analysis using DLS and chemical analysis using HPLC, FTIR and thermal analyses.

Results: Four independent MTS assays performed using different INM concentrations showed no cytotoxic effect in the case of silica oxide while for zinc oxide INMs at doses higher than 50 µg/ml a reduction of cell survival was detected. The morphological analysis pointed out a better dimensional homogeneity and stability for silica oxide than zinc oxide INMs in both aqueous and culture medium solutions. HPLC profile of INM aqueous solution after 24 h incubation showed an additional peak only in the case of zinc oxide particles. FT-IR Chemical imaging, carried out directly on the cells after 24 h incubation with the particles, showed a modification of spectra in correspondence of bands of phospholipids, nucleic acids and proteins if compared with no treated cells. Also cell volume resulted increased after 24 h incubation of cells with zinc oxide INMs.

Discussion: On the basis of cell viability results, a deeper investigation on the molecular interaction between the complex cell microenvironment and INMs was performed. The use of FTIR Chemical Imaging was an innovative tool to evaluate the effect of INMs on cell chemical composition. This effect resulted dependent on INM chemistry, dimension and or aggregation. This study allowed obtaining interesting molecular information about INM-cell interaction in view of a potential application of these INMs in the biomedical field.

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A NEW KERATIN-BASED SCAFFOLD WITH PROMISING FEATURES FOR BIOMEDICAL APPLICATION

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Introduction: Natural polymers exhibit several features that make them more biocompatible than the synthetic ones. One of the most studied natural polymers is the keratin, an abundant non-food protein found in hairs, wool and nails of mammals. It is highly hydrophilic and contains a high amount of cysteine, a sulphur-containing amino acid that gives rise to intra- and intermolecular disulphide cysteine bonds which largely influence its mechanical and chemical properties. Keratin can be extracted from natural sources using reducing or oxidizing agents, and successively regenerated in the forms of films, nanofibers, sponges and hydrogels. In this study, sheep's wool was used as a natural source to prepare keratin microfibril sponges for scaffolding, by disruption of the histological structure of the fibers through chemical-physical treatment. Subsequently, biocompatibility of wool sponges was evaluated using the osteoblast-like SAOS-2 cell line.

Materials and methods: Wool sponges were prepared using keratin extracted from sheep's wool throughout alkali treatment, followed by ultrasonication, casting and salt leaching. Morphological characterization was performed by analyzing sponge porosity and degree of crosslinking throughout SEM observations. Moreover sponge tensile and compression behaviors were studied using dynamometer according to the EN-ISO 5079 in dry and wet conditions. SAOS-2 cells were selected for biocompatibility-cell viability assay and represent an in vitro model for osteoblast studies. Cells were seeded on scaffolds and cultivated for 1, 3 and 7 days when MTT and FDA assays were performed to determine cell viability. Cell morphology was evaluated through SEM observations and actin and tubulin filaments were stained to study cell adhesion on keratin scaffolds.

Results: The wool sponges showed highly interconnected porosity (93%) and contain intrinsic sites of cellular recognition that mimic the extracellular matrix. Sponges were stable in water without structural changes and showed excellent resilience to repeated compression stresses. According to in vitro biocompatibility assays, wool fibril sponges showed a good cell adhesion and proliferation. In fact, consistent cell proliferation ($p < 0.05$) was reported for longer incubation times, showing a 2-fold and 4-fold increase related to the number of seeded cells after 3 and 7 days, respectively. After 24h, cells were widely spread on the wool fibril sponges as confirmed by SEM and confocal observations. At day 7, the wool fibril sponges were completely coated by cells and were even found in the pores.

Discussion: The unique structure of the cortical cell network made by wool keratin proteins with controlled-size macro-porosity make this scaffold suitable for cell guesting and nutrient feeding. Both the compression traces of the dry and wet sponges display a horizontal line most likely due to reversible crushing deformation of the macropore structure. However, the wet sponges are more resilient because the compression traces are almost overlapping each other and no permanent deformation was detected. In summary, the wool fibril sponges made of keratin contain cellular-binding motifs that mimic the sites of cell attachment found in the native extra-cellular matrix components which facilitate better growth via providing proliferation signals to the cells and minimize apoptotic cell death.

ADDITIVE MANUFACTURING AND FUNCTIONAL GRADIENTS TO DESIGN ADVANCED STRUCTURES FOR TISSUE ENGINEERING

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Introduction: Interfacial tissue engineering (ITE) purpose is to regenerate tissue by mimicking continuous biological and physico-chemical gradients. A surface-modified 3D scaffold with a biomolecule gradient could be a valuable candidate to reproduce some of the important tissue features. The main objective of this study was to optimize a two-step functionalization method in which: 1) a 3D morphologically-controlled poly(ϵ -caprolactone) (PCL) scaffold was aminolysed with a continuous gradient of amino-groups (NH_2) and 2) a collagen gradient was obtained via carbodiimide reaction.

Materials and methods: 3D scaffolds were produced by means of a rapid prototyping technique. PCL surfaces were modified by dipping the structures in a 1,6-hexanediamine/isopropanol solution. NH₂ density gradient was achieved along the length of the structure by controlling the time and the surface exposure to the reactive solution. Lyophilized collagen type I was covalently immobilized using a carbodiimide reaction. Ninhidrin and hydroxyproline assays, contact angle measurements, confocal laser scanning microscopy (CLSM), Fourier transform infrared spectroscopy (FTIR), collagen staining and biological analyses were performed to characterize the surfaces and gradients.

Results: The NH₂ concentration spans from 5×10^{-7} mol/cm² (15 min processing) to 15×10^{-7} mol/cm² (45 min processing). The PCL-NH₂ structures were treated with Rhodamine B Isothiocyanate to visualize the gradient by using CLSM. Results show an 8-fold increase of fluorescence intensity from the neat PCL to the region aminolysed for 45 min. Results from hydroxyproline assay reveal that the grafted collagen amount increases from 0.08 to 0.71 µg/cm², correlated with the ninhydrin assay. The introduction of collagen improves the hydrophilicity of the materials. Microscopy imaging shows the collagen distribution whilst FTIR confirms its grafting. Biological analyses highlight that MG63 labeled-cells are viable on all materials showing better proliferation on collagen-based materials.

Discussion: PCL has been widely employed for tissue engineering but it lacks of biological motifs for cell recognition. Furthermore, in the field of ITE, several efforts should be devoted to the production of 3D scaffolds with a continuous gradient in terms of their biochemical, mechanical and morphological features. The aminolysis represents a simple way to covalently graft NH₂ groups, free to interact with other biomolecules. Confocal and SEM analyses highlight the influence of aminolysis treatment on morphological performances of the materials. The improved hydrophilicity and the immobilized collagen have an effect on cell capability to interact with these surfaces. In conclusion, a method to obtain a collagen gradient on 3D PCL printed scaffolds was proposed. Future trends will be devoted to the production of scaffolds characterized by both chemical and morphological gradients. A promising route should be to produce scaffolds with suitable mechanical and mass transport features together with different material gradients, porosities and functionalities.

NOVEL MACROPOROUS BIOCERAMICS FOR BONE REGENERATION

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Introduction: Nowadays, despite the recent progress in the development of scaffolds for bone tissue engineering, versatile techniques able to tune the porosity, pore morphology and size distribution of bioceramic structures with different chemical compositions are still particularly demanded. In this respect, the direct foaming method allows the production of porous materials by incorporating air into a suspension, which is subsequently set in order to keep the structure of air bubbles created. In this work, β-tricalcium phosphate/titania (β-TCP/TiO₂) composites were firstly synthesized to obtain a bioactive/bioresorbable matrix reinforced with defined amounts of sub-micron sized titania particles. Then, scaffolds exhibiting high and interconnected macroporosity (>70 vol%) were prepared by direct foaming technique. Such forming process was also optimized with apatitic suspensions, leading to the shortening of the traditional process, while increasing the compressive strength of the final scaffolds.

Materials and methods: The starting materials for the synthesis of the composites were commercial hydroxyapatite (HA) and TiO₂ powders. The ceramic powders were wet mixed, freeze-dried and sieved, then slowly mixed in a jar mill to obtain homogeneous HA/TiO₂ mixtures with different titania content. The sintering process for sample consolidation was optimized by evaluation of unidirectional shrinkage upon heating at different temperatures. The foaming process was performed after calcining the mixtures to achieve a single-composition powder. Commercially available porous HA scaffolds (Engipore, Finceramica) were used as a reference material. Biological characterization was carried out for human MG-63 osteoblast-like cells proliferation, activity, attachment, and viability. A planetary ball mill was finally used to optimize the direct foaming process.

Results: Extensive chemico-physical and mechanical characterization was carried out on the composites, exhibiting values of flexural strength, fracture toughness and elastic modulus in the range or above the typical ranges of values manifested by human cortical bone. It was shown that titania particles provided a toughening effect to the calcium-phosphate matrix and a reinforcement in fracture strength, in comparison with sintered HA bodies.

The analysis of the macroporous scaffolds resulted in compression strength nearly three times higher than the reference scaffolds.

β-TCP/TiO₂ scaffolds showed high proliferation rate, viability, and good colonization rates. Moreover, an increased activity of the osteogenic marker alkaline phosphatase (ALP) was found.

The implementation of planetary ball milling led to the preparation of porous apatitic scaffolds exhibiting a reproducible control of the porosity and significantly improved compressive strength, compared to the traditional one.

Discussion: These results demonstrate that β-TCP/TiO₂ scaffolds have good potential as osteogenically active load-bearing scaffolds; moreover, given the high and interconnected macroporosity as well as the resorbability properties of β-TCP, these scaffolds may enhance *in vivo* osteointegration and promote the formation of new organized bone, thus resulting in very promising biomimetic scaffolds for long bone regeneration. A new method based on direct foaming was set up and optimized, towards the preparation of porous hydroxyapatite scaffolds with reproducible control of pore size distribution and improved mechanical performance.

ENCAPSULATION OF PROBIOTICS IN ALGINATE MICROBEADS

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Introduction: The oral administration of most probiotics results in a large loss of viability associated with passage through the stomach, which is attributed to the high acidic environment. The encapsulation of probiotic bacteria in cross-linked alginate beads is of major interest for improving the survivability against severe acid and bile conditions, and also from food matrices. Alginate micro beads containing a selected probiotic (*Lactobacillus Kefiri*) were produced by a novel technique based on dual aerosols of alginate based solution and CaCl₂ cross linking solution.

Materials and methods: Alginates are linear copolymer of 1, 4-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues extracted from various species of algae, and the bioadhesive properties of the polymer backbone facilitate the coating procedures. The mechanical properties, viscosity and permeability of alginate capsules, have been modified using a solution of alginate with another anionic polymer the Sodium salt of carboxy-methyl-cellulose (NaCMC), natural and biocompatible polymer. The resulting polymer solution, in which the *Lactobacillus Kefiri* has been dispersed, was stabilized by means of CaCl₂ solution vapour in a closed chamber. Briefly, bacterial cultures suspended in sterile 0.1% peptone and mixed with polymeric solutions solution: Alginate 2.5% w/w, Alginate 2.5% w/w + NaCMC 0.1% w/w, Alginate 2.5% w/w + NaCMC 0.5% w/w in 1:5 ratio.

An aerosol of sterile 1 M CaCl₂ solution was injected into the top of a closed chamber until complete saturation. A second aerosol with microbial suspension in alginate solution was injected from the bottom of the chamber. Alginate microbeads containing the probiotics were collected in a plate filled with CaCl₂ inside the chamber. The produced particles have been extensively characterized in terms of morphology, stability in different pH conditions and loading efficacy.

Results: The tested solutions demonstrated a good stability, and the particle size range is in a narrow window between 50 and 70 µm. The study on the effect of CaCl₂ crosslinking demonstrated that the NaCMC do not affect the stability of the capsules. The efficacy of the loading, as well as the stability in different pH solutions proved the efficacy of encapsulation compared to the control.

Discussion: The encapsulation of *Lactobacillus Kefiri* in alginate microbeads significantly increases the barrier effect against the deactivation produced by the lower pH conditions. The presence of NaCMC produced capsules with a better homogeneous morphology, but with lower stability. The proposed technique results to be effective in protecting *Lactobacillus Kefiri* during its transit in the gastrointestinal tract.

MODEL-PREDICTED EFFECT OF CELL PROLIFERATION AND DIFFERENTIATION ON THE DARCY PERMEABILITY AND PERFUSION PATTERN OF ANNULAR POROUS CONSTRUCTS CULTURED IN RPBBS FOR BONE TISSUE ENGINEERING

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Introduction: Radial medium perfusion of osteogenic cells cultured in annular porous constructs in radial packed-bed bioreactors (RPBs) has been

proposed to engineer in vitro bone tissue substitutes. Geometry and Darcy permeability of the annular porous scaffold influences the pattern in which nutrients and metabolic cues are supplied to cells, hence tissue maturation. As tissue matures, cell proliferation and differentiation locally changes pore size and geometry, and decreases construct Darcy permeability, thus affecting radial medium flux distribution and pericellular solute concentrations. In this work, a transient 3D transport model was developed to investigate how Darcy permeability changes as osteogenic cells proliferate and differentiate in annular porous constructs of varying geometry and initial permeability cultured in rPBBs with coaxial inlet and lateral outlet port, and how this affects the pericellular oxygen and glucose concentration profiles.

Materials and methods: Medium flow was described in terms of Navier-Stokes equations in the inner hollow cavity and peripheral annulus of the rPBB, and of Darcy-Brinkman equation in the construct. Dissolved oxygen and glucose transport was described in terms of the dispersion advection equations. Oxygen/glucose consumption and cell proliferation was described according to Michaelis-Menten and two-substrates Monod kinetics with a zero-th order death term, respectively. Kinetic parameters for osteoblasts were taken from literature. Cell proliferation was assumed to uniformly decrease the pore size, thus changing construct porosity and specific surface area during culture. Cell differentiation was assumed to affect only nutrients consumption rates. Construct average permeability at any time was assumed directly proportional to the cubed porosity and inversely proportional to the squared specific surface area, as stated by the Carman-Kozeny equation. Conservation equations were solved numerically with COMSOL Multiphysics® for high Darcy permeability and scaffold geometry and operation typical of bone tissue engineering.

Results: The model predicts that construct permeability significantly decreases during culture. At low medium feed flow rates, this equalizes possible initial axial non-uniform distribution of medium radial flux and solute concentrations although nutrients concentration may become low at construct periphery. With large construct radii, stagnation zones may form in bioreactor void zones in which oxygen and glucose concentrations are very low. High medium feed flow rates increasingly promote cell proliferation, which enhances the decrease of construct Darcy permeability in time. Increasingly higher medium feed flows are needed to obtain similar effects with constructs with high length-to-inner radius ratios, or thickness-to-inner radius ratio.

Discussion: Accounting for the variation of the construct Darcy permeability during culture is important to predict the actual time evolution of radial perfusion velocity and oxygen/glucose concentration profiles in rPBBs for bone TE, and to adjust bioreactor operation so as to maintain uniform cell perfusion, and physiological oxygen and glucose supply and pericellular concentrations, as tissue matures.

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CHARACTERIZATION OF CELL SCAFFOLDING PROPERTIES OF HOLLOW FIBER MEMBRANE BIOREACTORS (HFMBs) FOR BONE TISSUE ENGINEERING BY MICROCOMPUTED TOMOGRAPHY

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Introduction: Hollow fiber membrane bioreactors (HFMBs) in which cells are cultured outside and among hollow fiber membranes assembled in shell-and-tube configuration have been proposed to engineer bone tissue substitutes to repair large skeletal defects. In the development of HFMBs for tissue engineering, attention is generally paid only to their surface area, to deliver physiological oxygen supply to cells, their spacing, to permit cell migration, and their surface properties, to permit cell adhesion. However, a biomimetic approach to engineering bone tissue would require that membrane geometry and spatial arrangement in the HFMB be tuned to mimic bone ECM that hosts osteogenic cells *in vivo*. In this work, microcomputed tomography (mCT) was used for characterizing the extent to which shell-and-tube HFMBs with different membrane packing densities bear structural resemblance to bone tissue.

Materials and methods: Cell compartment of shell-and-tube HFMBs was characterized in either low membrane packing density (LD-HFMB) or high packing density (HD-HFMB) HFMBs. HFMBs consisted of a bundle of parallel capillary

polypropylene microporous hollow fibers (280 µm inner diameter, 380 µm outer diameter) glued at their ends to a cylindrical housing. A cylindrical region (10 mm diameter × 10 mm length) centered around the HFMB axis was selected as volume of interest (VOI). X-Ray microtomographic images of the selected VOIs were acquired at 10 µm³ voxel size either with a HECTOR µCT, at 120-140 kV, 71.5-83.4 µA, or a SkyScan 1174 mCT (Microphotonics Inc., Allentown, PA, USA), at 50 kV, 800 µA. 2D cross-sectional slices were acquired and segmented, and the VOI was reconstructed in 3D by means of the MIMICS® (Materialise, Leuven, Belgium) image-processing software. The following structural features were characterized: porosity, defined as the volume fraction of the VOI outside the fibers; interfiber distance, defined as the diameter of the spheres obtained through a "sphere-fitting" measurement made for all the voxels lying outside the fibers; degree of anisotropy, as a measure of the preferential alignment of fibers along particular directions. Such HFMB features were compared to those of natural equine trabecular bone harvested from horse femur (EFT).

Results: Porosity of the cell compartment of HD-HFMBs was significantly lower than the EFT. That of LD-HFMBs was closer to it, but more radially non-uniform. HD-HFMBs featured an interfiber distance in the range 0-660 µm close to the 10-980 µm range measured for the EFT. LD-HFMBs exhibited a much higher interfiber distance, not comparable to the EFT and making cell aggregation awkward. Interestingly, membrane spatial arrangement in both HFMB types was significantly anisotropic, similar to the natural EFT.

Discussion: Our analysis suggests that HFMBs in shell-and-tube configuration packed at high membrane density exhibit degree of anisotropy and interfiber distance resembling the natural trabecular bone. Poorly biomimetic HFMBs may still provide osteogenic cells with oxygen and good adhesion surface but are likely unfit for promoting 3D cell organization as in natural bone.

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MESOPOROUS GLASSES DOPED WITH THERAPEUTIC IONS AS SMART PLATFORM FOR FUTURE, HIGHLY TARGETED THERAPIES IN TISSUE REGENERATION

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Introduction: In the field of advanced bioceramics, mesoporous bioactive glasses (MBGs), which combine the textural parameters of ordered mesoporous matrices with the properties of conventional bioactive sol-gel glasses, have received increasing attention as bone-tissue regeneration systems. Very recently, the ambition is to impart other biological functions, including antibacterial activity, as well as stimulation of osteogenesis and angiogenesis, by incorporating therapeutic metallic elements and drugs. This fascinating concept is the underlying idea of MOZART project (funded in the frame of H2020-NMP6-2015), whose general objective is to develop a library of mesoporous glasses doped with selected ions, to be used as a new, smart platform technology for future, highly targeted therapies in pathological bone and skin.

Materials and methods: MTGs based on the SiO₂-CaO system and containing different doping ions (Cu²⁺, Sr²⁺, Ce³⁺...) have been synthesized both by an ultra-sound assisted sol-gel method and by an aerosol-based spray-drying process. The structural and morphological features of the obtained MBGs were investigated by several techniques (TEM and FE-SEM coupled to EDS, N₂ adsorption-desorption, XPS), as well as their ability to form hydroxyapatite (HA) *in vitro* by soaking the samples in a simulated body fluid (SBF) for different times. The release profiles of the therapeutic ions were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Results: FE-SEM observations of spray-dried mesoporous glasses based on SiO₂-CaO binary composition and doped with several ions, including Cu²⁺, Sr²⁺, Ce³⁺, showed micro-sized spherical particles mostly ranging between 500 nm and 5 µm. Doped MBGs prepared by high-frequency ultrasound assisted synthesis showed spheroidal shape and size between 100 and 200 nm, without large aggregates. The EDS quantitative analysis revealed element ratios very close to the theoretical ones. TEM observations of samples prepared by spray-drying and by ultra-sonication evidenced that particles contain mesopores throughout their inner structure, in the form of a worm-like system. Quantitative analysis using EDS mapping showed a homogeneous elements distribution.

High specific surface areas, about 200 m²/g for spray-dried MBGs and about 400 m²/g for MBGs prepared by ultrasonication-assisted method, and homogeneous pore size distribution were obtained by N₂ adsorption analyses. Excellent bioactivity, in terms of apatite-like forming ability in SBF, was found for doped MBGs samples, showing that the incorporation of doping ions does not affect the bioactive response. Cu and Sr-doped MBGs showed a sustained and almost quantitative release of ions after 14 days of soaking in SBF.

Discussion: Novel MBG matrices doped with controlled amount of therapeutic ions, characterized by high surface area, fully accessible nanopores, excellent bioactivity and sustained ion release properties, were prepared by different synthesis procedures. These nanomaterials can find various applications as multifunctional therapeutic agent for tissue regeneration.

DECCELLULARIZED MATRICES ENRICHED WITH ANTIBIOTICS: A PROMISING ENGINEERING APPROACH FOR TISSUE REGENERATION

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Introduction: During modern age, transplantation techniques changed reconstructive surgery scenario, making remarkable improvements concerning the functionality of transplanted organs or tissues. Transplantations show also several pitfalls, such as limited tissue availability and multiple surgeries needing. Moreover, one of the main causes of prosthetic transplants failure is the *in situ* infection of the surgical site, caused by bacterial colonization that can occur during the operating procedures. For these reasons, decellularization of native tissues has gained a significant attention especially for obtaining biological scaffolds that maintain the native tissues' ECM structure, thus preserving their biomechanical properties. In order to optimize the postsurgical rehabilitation process, the biological substitutes can be enriched with specific antibiotics and/or repopulated with different cell types.

Materials and methods: Our approach is based on antibiotic enrichment of decellularized bovine pericardium matrices, performed with sueGraft™ process. Antibiotic (4% gentamicin) has been covalently bound on the tissue surface in order to inhibit the colonization of *Staphylococcus aureus*, a dangerous nosocomial bacterial strain, until complete healing, and thus favour the postsurgical tissue regeneration. In order to evaluate decellularization and enrichment processes, DAPI nuclear staining and XPS analyses have been performed. The biomechanical properties of decellularized and enriched matrices have been characterized, with Young modulus analysis. Residual DNA has been also quantified. Matrix structure and protein content was evaluated with histochemical and immunohistochemical stainings. In order to verify cell viability on tissues, MTS assay on human umbilical vein endothelial cells (EA.hy926) have been performed. Sensitivity tests (inhibition halo, XTT assay) towards 4% gentamicin of *Staphylococcus aureus* were performed on enriched matrices subjected to continuous shear stress for 1, 3 and 7 days (dynamic conditions).

Results: DAPI staining confirmed the complete matrix decellularization. XPS analysis confirmed the efficiency of the enrichment method. Concerning the comparison between the mechanical properties of native and decellularized matrices, no significant differences have been found in Young moduli. Decellularized and enriched substrates maintain comparable structures with respect to native tissues, in terms of amount of collagen and laminin, while the matrix seems slightly looser than native tissue. MTS assay showed analogous cell viability values for gentamicin enriched samples and untreated controls, meaning that treated materials do not inhibit tissue regeneration. A significant difference, in terms of inhibition halo, between gentamicin (4%) coated and grafted decellularized scaffolds, has been observed: a large inhibition halo for the 4% gentamicin covalently enriched samples has been shown. XTT assay showed a decrease of bacterial viability for the 4% gentamicin covalently enriched samples towards other samples.

Discussion: Our tests confirm the efficiency of the "decellularized tissue" method and its ability to maintain adequate mechanical properties, as well as the ability of gentamicin enriched matrices to inhibit bacterial growth, while allowing cell adhesion and proliferation. Thus, the enriched biological substitutes could represent an innovative engineering approach for surgical application in regenerative medicine.

FUNCTIONALISATION AT THE NANOSCALE OF ELECTROSPUN MESHES FOR MIMICKING BONE HEALING AND REGENERATION

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Introduction: Bone tissue engineering is a complex and dynamic process that initiates with migration and recruitment of osteoprogenitor cells followed by their proliferation, differentiation and matrix formation along with remod-

eling of the bone. Particularly, biomimetic scaffolds have been achieved by incorporating bioactive molecules such as a native long chain of extracellular matrix (ECM) proteins as well as short peptide sequences by surface modification or by bulk incorporation. In this work, we proposed the Layer-by-layer (LbL) approach to modify the surface of osteoconductive electrospun membranes to impart nanoclusters by grafting bone peptide fragments into the discrete layers for mimicking the cascade of stimuli at the nanoscale in order to control the adhesion, proliferation, differentiation of mesenchymal stem cells and the formation of new bone matrix.

Materials and methods: Porous membranes were prepared by dissolving poly(D,L-lactide-co-glycolide) (PLGA, 75:25) (22% w/v) and nano-hydroxyapatite powder (20% w/w) in acetone prior to electrospinning. Then the membranes were surface functionalised by: (1) aminolysis treatment by immersion in 0.05 M ethylenediamine solution and allowed to react at 20°C to obtain a positive charge on the surface by -NH₂- grafting, and (2) LbL technique to generate functional polyelectrolyte (poly(styrene sulfonate)/poly(allyl amine) (PSS/PAH); Sigma) to obtain 14 nanolayers for the incorporation of specific bone peptide sequences (-KRSR-, -FHRRKA- and -NSPVN-SKPKACCPTELSAI; Biomatik) into the discrete layers. The functionalisation process was monitored by Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) and X-Ray Photoelectron Spectroscopy (XPS). The morphology of the porous matrices was evaluated by Scanning Electron Microscopy (SEM). In vitro biocompatibility was investigated using rat mesenchymal stromal cells and preliminary *in vivo* tests were carried out using a rat cranial model.

Results: ATR-FTIR showed that the typical absorption bands of PAH and PSS increased with layer number (i.e. SO³⁻ stretching vibrations at 1130 cm⁻¹ for PSS, and NH scissoring vibrations at 1580 cm⁻¹ for PAH). XPS spectra showed a N_{1s} peak at 399.5 eV and S_{2p} peak at 168 eV, indicating PAH and PSS have been successfully introduced. After LbL assembly, SEM analysis confirmed the porous morphology of the membranes, with a slight decrease of the porosity (~5-10%). Finally, the incorporation of bone peptides interfered positively with the processes of cells adhesion and proliferation within the functionalised membranes, showing a good cell viability and significant increase of Alkaline Phosphatase Activity. The functionalised membrane induced a favourable *in-vivo* response and showed evidence of osteoinduction.

Discussion: The advantages of the low temperature fabrication technology described here are evident, providing an opportunity to prepare structures with predictable physico-chemical and biological properties, ideally suited to Guided Bone Regeneration, in terms of its integrity, biodegradability, and biocompatibility including directed cell-membrane interaction.

SUB-POPULATIONS OF DERMAL FIBROBLASTS WITHIN THE SKIN SECRETE DISTINCT EXTRACELLULAR MATRIX AND DIFFERENTIALLY REGULATE KERATINOCYTE BEHAVIOR

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Introduction: Nowadays, there are several commercially available dermal scaffolds that promote wound healing, however, the achievement of complete skin regeneration still represents a major challenge. Three dimensional structures derived through the physiological cell secretion of extracellular matrix (ECM) may prove to be a valuable scaffold. On this basis, the present study was focused on the biological characterization of ECMs produced by three different subpopulation of fibroblasts found in human skin dermis; papillary fibroblasts (Pfi), reticular fibroblasts (Rfi), and dermal papilla fibroblasts (DP).

Materials and methods: Scalp skin biopsies from healthy donors were used for the isolation of epidermal keratinocytes, and dermal sub-populations. Specifically, Pfi and Rfi were obtained from the upper and lower regions of interfollicular dermal tissue, while DP were isolated from the base of hair follicles. Fibroblast sub-populations were cultured with ascorbic acid to promote matrix deposition. After 10 days, cells were removed from the dishes and the remaining matrices were characterized. Matrices were stained with

a panel of anti-ECM antibodies including Fibronectin, Collagens I and VI, Tenascin C and Thrombospondin, prior to being analysed by confocal microscopy. Fluorescence quantification, matrix and fiber morphology were evaluated. Moreover KCs, isolated from the epidermis were seeded on the top of the ECMs to generate epidermal only skin constructs. After 2 weeks of skin constructs culture, cells viability, histological and immunofluorescence analysis were performed.

Results: We found that the ECM produced by Pfi exhibited the largest and most randomly oriented fibers, associated with highest interfibrillar space. The immunofluorescence analysis showed that Fibronectin is highly abundant in Pfi, while Thrombospondin is mainly expressed in DP derived matrix. Moreover, epidermal only constructs grown on DP or Pfi matrices exhibited normal markers of differentiation and stratification. Comparatively, we were unable to find expression of ZO-1, a tight junction protein, in constructs supported by Rfi.

Discussion: The differences in matrix and fiber morphology observed in the different cell derived ECMs reflects differences that are physiologically present between the papillary, reticular, and hair follicle dermis within the skin. In addition, Rfi were unable to support growth of keratinocytes, reflecting their spatial location in the dermis. Inspiration should be taken from these physiologically different cell derived ECMs, to improve the design of reliable biomimetic materials with therapeutic potential for skin tissue engineering.

COLD ATMOSPHERIC PLASMA TREATMENT OF INFECTED SKIN TISSUE: STERILITY, VIABILITY AND INTEGRITY EVALUATION

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Introduction: Sterilization of equipment and tissues is a common clinical practice: there are different chemical, mechanical or electromagnetic aseptic techniques for inactivating microorganisms of all forms. In particular, Skin Tissue Banks are investigating innovative methods for microbial decontamination of skin tissues, preserving their functional and structural properties. Recently, Cold Atmospheric Plasmas (CAPs) have demonstrated bactericidal, virucidal and fungicidal properties, due to the generation of a blend of reactive species, charged particles and electromagnetic fields. For these reasons the aim of the present work is to demonstrate that the implementation of a dielectric barrier discharge (DBD) treatment in air can effectively decontaminate skin tissue from *Staphylococcus aureus*, retaining cell viability and skin integrity.

Materials and methods: Fresh skin samples were taken from the multi-organ and/or multi-tissue donors and cut under sterile conditions into 2 × 2 cm pieces. 100 µL of *S. aureus* (ATCC® 6538) (10²⁻⁴ CFU/cm²) were applied to the epidermal samples and were left for 15 minutes to permit bacterial attachment. Then contaminated samples were treated by means of DBD (dielectric: 1 mm thick alumina; air gap: 2 mm) driven by a micropulsed generator producing high voltage quasi-sinusoidal pulses at 20 kHz (AlmaPulse, designed by AlmaPlasma s.r.l.). In particular, both sides of the contaminated samples were treated for 2 minutes with a peak voltage of 7.3 kV. Alternatively, other contaminated samples (10²⁻⁴ CFU/cm²) were treated by 1% antibiotic in medium (RPMI) for 45 minutes. Untreated samples were used as positive control (CTR). Small uniform fragments (1 × 1 cm) of all the treated samples were incubated on Columbia Agar +5% sheep blood plates at 37°C for 24h for microbiological analysis. The maintenance of cell viability as well as structural properties of skin tissue were investigated respectively using MTT assay and Hematoxylin-Eosin staining (H&E).

Results: Our results show that CAP can sterilize skin tissue infected by *S. aureus* up to a bacterial load of 10³ CFU/cm², while only a drastic reduction of bacterial growth can be achieved for samples with higher load (10⁴ CFU/cm²). Moreover, plasma treatment is more effective than the antibiotic normally used at the Skin Bank for the decontamination of skin tissue. Finally, plasma treatment does not affect cell viability, compared to untreated controls, while the maintenance of skin structural properties is demonstrated through histological analysis.

Discussion: Thus, cold atmospheric plasma treatment can be considered as a novel method for decolonisation of human skin tissue.

ON-CHIP CELL CULTURE AND NON-VIRAL GENE DELIVERY

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Introduction: The use of nucleic acids for the treatment of genetic and acquired disorders that conventional medicine fails to cure is collectively known as gene therapy. The success of gene therapy depends on the development of safe and efficient gene delivery vectors. In the last few years, a great effort has been geared toward the development of microfluidic devices that proved to be leading tools for precise cell manipulation in a high-throughput manner. Herein, a novel microfluidic platform, fabricated in polydimethylsiloxane (PDMS) was specifically designed for the isolation of adherent cells into a well-defined spatial configuration, and for subsequent transfection studies.

Materials and methods: The proposed layout consists of a serial dilution generator (SDG) and a culture area of 165 chambers designed for cell trapping. The SDG allows the linear dilution (0%, 25%, 50%, 75% and 100%) of non-diffusive molecules such as DNA/polymer complexes (polyplexes). The culture area is composed of 5 units with 33 round chambers ($\phi = 500 \mu\text{m}$); each chamber is designed to accommodate approximatively 10-20 cells. Human glioblastoma-astrocytoma epithelial-like cells (U87-MG) were seeded at a density of 1.5×10^5 cells/mL in Dulbecco's Modified Eagle Medium (DMEM) supplemented with 50% Fetal Bovine Serum (FBS). Cell trapping efficiency and cell growth were assessed at t_0 and 24 hrs post-seeding, respectively. The efficiency of the SDG to generate a linear gradient of polyplexes was also tested using fluorescently labeled JetPEI®. The device allows to test a set of 5 different conditions at once: 5 polyplexes concentrations were generated independently, thus enabling the high-throughput screening of transfection outcomes.

Results: The cell trapping efficiency was first evaluated: the average number of trapped cells per chamber was 13 ± 0.25 ($n_{\text{chip}} = 11$). 24 hrs post-seeding the cell viability was around 80% with respect to the total number of trapped cells. Furthermore, the generation of 5 linear dilutions, ranging from 100% polyplexes to 0%, with decrements of 25% from line 1 to line 5 respectively, was also assessed.

Discussion: The proposed device allows the delivery of controlled concentrations and combinations of vectors that is a crucial issue to obtain fast and realistic results. Cells in each unit can be successfully treated with specific polyplexes doses, thus enabling the evaluation of the efficiency and the cytotoxicity of the polyplexes at once. In conclusion, this work shows a valid alternative to traditional gene delivery approaches since it allows the investigation of cell culture in a spatially defined configuration and the optimization of transfection protocols.

EFFECTS OF COMPLEXATION PROTOCOL, SIZE AND SEDIMENTATION ON TRANSFECTION EFFICIENCY OF PEI-BASED POLYPLEXES

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Introduction: Polyethylenimines (PEIs) are considered the gold standard polymeric gene delivery vectors. However, conflicting results on their performance are reported owing to the wide variability of experimental setups employed across laboratories. With this in mind, we investigated the influence of the complexation protocol and of the transfection medium on the properties and on the activity of PEI-based polyplexes.

Materials and methods: Polyplexes were prepared by combining plasmid DNA (pGL3 or pEGFP) and linear or branched PEI (IPEI, bPEI, respectively, MW 25 kDa) adding reagents dropwise (DROPPING) or by mixing by pipetting (MIXING). The final N/P was 30 and both 10 mM Hepes pH 7 and 150 mM NaCl were used as complexation medium. Hydrodynamic diameters (D_h) were measured by DLS before and after dilution in cell culture medium containing or not 10% FBS. For transfections, 2×10^4 HeLa cells/cm² were seeded and incubated for 24 hrs, then polyplexes were added. In some experiments cells were centrifuged at 1,000 g after polyplexes addition or transfected upside-down (seeded surface suspended and facing the bottom of the well).

24 hrs after transfection, cytotoxicity was evaluated by AlamarBlue and transfection efficiency by Luciferase Assay System.

Results: The method of addition of reagents strongly affected the dimensions of polyplexes for all the conditions tested, except for IPEI in NaCl. Particularly, adopting the MIXING method, polyplexes showed $D_h < 200$ nm with narrow size distributions ($PDI < 0.2$). Following the DROPPING protocol, D_h and PDI increased significantly, indicating the formation of bigger aggregates. Inversely, IPEI in NaCl always gave rise to bigger, polydispersed particles ($D_h > 1 \mu\text{m}$, $PDI \approx 1$). Upon addition of culture medium, a common trend was observed: polyplex dimensions were roughly stable in the presence of 10% FBS, while in absence of serum they increased up to values $> 1 \mu\text{m}$ within the first 2 hrs. Except for IPEI in NaCl, polyplex preparation by the DROPPING protocol induced a strong increase of transfection efficiency as compared to MIXING (≥ 2 times) when transfections were carried out in complete medium. Interestingly, differences in efficiency dropped or even disappeared when experiments were performed in the absence of FBS (i.e. in OptiMEM). In 10% FBS, where the D_h was stable, a direct relationship between D_h and transfection activity can be noticed: bigger polyplexes showed higher transfection levels; in serum-free medium, the growth of D_h led to big polyplexes which showed comparable gene delivery activity. Cytotoxicity was always lower than 20% except for bPEI polyplexes administered in serum-free medium for which it increased to values between 30 and 40%. Centrifugation of polyplexes over cells (to increase sedimentation) boosted transfection efficiency decreasing the difference in activity between DROPPING and MIXING protocols. Oppositely, in experiments with cells cultured upside-down (no sedimentation over cells), transfection strongly diminished, pointing out the importance of gravitational sedimentation of complexes.

Discussion: Herein we described how the complexation protocol influences the properties of PEI polyplexes, highlighting a relationship between D_h and transfection efficiency and identifying sedimentation over cells as a key driving force in their transfection process.

NON-EQUILIBRIUM ATMOSPHERIC PRESSURE PLASMA TECHNOLOGY FOR ANTI-CD 10 ANTIBODY IMMOBILIZATION ON PLLA NANOFIBRES

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Introduction: The conjugation of bioactive molecules onto polymeric surfaces has been investigated in the last decades for applications in different fields. Among polymeric biomaterials, poly(L-lactic acid) (PLLA) presents excellent biocompatibility jointly to interesting bulk properties. However, the absence of bio-recognition sites limits its use in the fields where cell-material interaction is required. Therefore, the surface conjugation with bio-molecules is needed and innovative techniques to carry out the process are demanded. The present work reports the comparison between a conventional wet-chemical method and a non-equilibrium atmospheric plasma process for the chemical conjugation of an antibody on PLLA fibers previously functionalized by introducing -COOH groups onto their surface. The aim of the work is to evaluate the possibility of substituting the widely employed chemical methods with the plasma technology for the environmentally friendly biomolecules immobilization onto polymeric substrates.

Materials and methods: The wet-chemical process was performed with NaOH hydrolysis, by incubating samples with NaOH solution at different concentrations and for different times. Plasma functionalization was carried out with a DBD operated in a controlled atmosphere of a He/air mixture and driven by a commercial nanosecond pulsed DC generator; treatments were performed for 5, 7.5 and 10 min.

Results: After functionalization, the physico-chemical and morphological properties of the fibers were thoroughly evaluated. The SEM analysis highlighted that the wet chemical and the 5 min plasma treatment did not induce any damage to the mats fibrous structure. The surface hydrophilicity of the functionalized PLLA mat was evaluated through water contact angle (WCA) measurements: while a constant WCA value of 120° was obtained for pristine PLLA mat, indicating a hydrophobic behavior of the material, an instantaneous penetration of water was achieved for chemically and plasma functionalized mats. The amount of -COOH groups created on the fiber surface was assessed with chemical derivatization technique. The functionalization

step was followed by the conjugation of an artificial antibody (anti-CD10) to chemically and plasma functionalized PLLA fibers by exploiting the carbodiimide chemistry. Although the derivatization analysis underlined that NaOH hydrolysis (solution concentration of 0.05 M, incubation time of 10 min) introduced a larger amount of -COOH onto the PLLA fibers than 5 min plasma treatment, the results of the anti-CD10 conjugation showed that the amount of antibody linked to chemically and plasma functionalized fibers was the same.

Discussion: The results highlighted that a high concentration of antibody was immobilized to chemically and plasma functionalized mats with respect to pristine PLLA and, even more interestingly, no great differences in terms of antibody conjugation efficiency was detected by comparing the two functionalization approaches. The performed study brought out the possibility to replace chemical methods with highly flexible and eco-compatible non-equilibrium atmospheric plasma processes for the effective immobilization of biomolecules.

SOLID-STATE CROSSLINKING OF POLYSACCHARIDE ELECTROSPUN FIBERS BY ATMOSPHERIC PRESSURE NON-EQUILIBRIUM PLASMA: A NOVEL STRAIGHTFORWARD APPROACH

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Introduction: Pullulan is a biodegradable polymer prepared by the culturing of *Aureobasidium pullulans* with starch or sugar. Pullulan is a water-soluble polysaccharide with low oxygen permeability, and it is used for food coating and drug processing. Although several chemical modifications of pullulan have been investigated for imparting thermoplastic properties and water resistance, nothing has been reported about the possibility of using non-thermal atmospheric plasma for pursuing the aforementioned objectives. In the present work, the effectiveness of atmospheric pressure non-thermal plasma to promote crosslinking of electrospun pullulan non-woven mats, in order to confer them water resistance properties, is investigated. The proposed approach is highly flexible, simple and cost-effective, without requiring toxic agents.

Materials and methods: The plasma source employed is an atmospheric pressure Dielectric Barrier Discharge (DBD) in static air and driven by a function generator producing high voltage signals with microsecond rise time connected to a HV Amplifier. In order to evaluate the effect of electrical parameters and treatment time on the crosslinking degree of pullulan fibers, plasma treatment was performed for a wide range of operating conditions. Initially, the peak voltage (PV) and the pulse repetition frequency (RR) were kept constant at 15 kV and 500 Hz, respectively, while the treatment time was varied. Then, fixed the treatment time at 15 min, PV and RR were changed independently.

Results: The characterization of the pullulan non-woven mats, aimed at evaluating the water resistance properties and identifying the most suitable operating condition to induce crosslinking, was performed. The obtained results highlighted a drastic increase of water stability of the non-woven electrospun mats after all the plasma treatments. The relevant enhancement of water resistance properties of pullulan mats was demonstrated by degradation and water adsorption experiments. Among the operating parameters taken into account and evaluated, the treatment time turned out the most relevant. In fact, the sample weight loss significantly decreased with the increase of the time of exposure to plasma; nonetheless, also the electrical parameters influenced substantially the properties conferred to the substrate. SEM analysis was performed with the aim to investigate both the morphological modification induced by the plasma treatment to the substrates and the morphology of the pullulan electrospun non-woven mats after dipping in water, in order to better understand if the mats nanofibrous structure was preserved after being soaked in water. The achieved results demonstrated that no relevant damage of the material morphology was induced by plasma treatment and that the substrates preserved their fibrous morphology after water dipping. Furthermore, ATR-FTIR analysis enabled to make hypothesis on the chemical modifications induced by plasma treatment in the substrate. **Discussion:** The method enables to crosslink water-soluble polymers directly in solid state.

DEPOSITION OF PLASMA-POLYMERIZED POLYACRYLIC ACID COATINGS BY A NON-EQUILIBRIUM ATMOSPHERIC PRESSURE PLASMA JET

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Introduction: Plasma-polymerized polyacrylic acid (ppAA) has raised great interest for the production of adhesion-promoting interlayers, e.g., in carbon fibre/epoxy composites, as well as for the development of biocompatible and anti-fouling coatings. Plasma polymerization of acrylic acid (AA) has been investigated in order to produce coatings with a high density of carboxylic acid (-COOH) groups, which make the substrate highly biocompatible to support cells adhesion and proliferation as well as immobilization of molecules. In the present work, results regarding AA plasma-polymerization by means of a non-equilibrium atmospheric pressure plasma jet, aimed at depositing pPAA coatings with high retention of carboxylic acid groups on substrates are presented.

Materials and methods: The process was carried out using a plasma jet developed by the authors and driven by commercial pulse generators. For the deposition of pPAA coatings, Ar with a flow rate of 3 slpm was introduced at first inside a bubbler, where the volume of the AA was kept constant, and then, carrying the monomer, to the plasma source. Different operating conditions were tested, by varying the electrical parameters for plasma generation, the flow rate of Ar carrying the precursor (from 2 to 3 slpm) and the treatment time (from 10 s to 10 min), to investigate their effect on the characteristics of the deposited coatings. The deposition was performed onto polyethylene, polyvinylchloride and silicon dioxide films.

Results: The investigation of the morphology of the coating, performed by means of SEM analysis and by using an optical profilometer, highlighted that the thickness of the deposited pPAA coatings drastically increases by varying the mass flow rate of the precursor introduced to the plasma region and, even more relevantly, by increasing the deposition time. Indeed, while sub-micrometric coatings were deposited after 10 s plasma-polymerization process, 10 min plasma-polymerization processes led to deposit coatings with thickness of some tens of micrometers, in relation to the employed AA mass flow rate. The chemical characterization of the coatings was performed by means of ATR-FTIR and XPS spectroscopy. The results underlined that the proposed method enabled the deposition of pPAA coatings with a high amount of -COOH groups, generally higher than 21%. Furthermore, with the increase of the plasma polymerization time, carbonyl moieties are detected and, operating at "strong" electrical parameters for plasma generation, the presence of C = O, O-C-O, and C-O functional groups, jointly to an increase of O/C ratio, that could be attributed to a crosslinked chemical structure, was observed, conferring stability upon water contact to the coatings.

Discussion: The proposed method enables to deposit pPAA coating presenting a high amount of -COOH groups.

DESIGN OF MULTIFUNCTION HYDROGELS TO DELIVER SPECIFIC BIOMOLECULES

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Introduction: Cardiovascular diseases represent a source of morbidity and mortality worldwide. This comprises ischemia, which is characterized by a suppression of blood supply to a tissue. New strategies such as the use of minimally invasive injectable therapeutic hydrogels to promote the neovascularization by delivering growth factors constitute a promising approach to enhance blood flow. The aim of the research was to propose a novel approach in developing a multilayer hydrogel based on collagen/collagen-gelatin nanoparticles (GNPs)/collagen-low molecular weight hyaluronic acid (LMWHA).

Materials and methods: Three-layer systems were developed integrating a conventional method and an electrospray-based technique. Each system consisted of a lower collagen layer, an upper collagen or collagen-LMWHA layer and a middle GNP-loaded collagen layer. A two-step desolvation method has been used for obtaining gelatin nanoparticles as a delivery vehicle

of a model protein drug, bovine serum albumin (BSA). The influence of BSA concentration on size, shape and release profile was also investigated.

Small amplitude oscillatory shear tests and steady state shear measurements were performed on all the proposed systems in order to assess their viscoelastic properties.

Finally, cell-particle interactions as well as different kinds of cell constructs were analyzed over culture time.

Results: The GNP preparation method allowed the production of uniform and spherical nanoparticles with a smooth surface. There were no differences on the morphology when BSA was added until a threshold BSA concentration. Nanoparticles with a mean size of 170 ± 36 nm were obtained. The BSA release profile showed a biphasic diffusion-controlled mechanism. All the proposed systems generally showed a gel-like and shear thinning behaviour, thus suggesting their injectability. A variation in cell morphology by varying BSA concentration over culture time has been observed. Furthermore, the number of viable cells adhering and proliferating increased over time for the different proposed system.

Discussion: A multilayer composite hydrogel with tunable mechanical properties and able to support cell adhesion and proliferation was developed. Desirable gelatin nanoparticles were obtained by an optimized two-step desolvation method. BSA was successfully encapsulated and a threshold concentration for BSA encapsulation was found. Controlled release of protein was observed, showing a biphasic modulation characterized by an initial rapid release phase followed by a slower and prolonged release phase. The effect of BSA concentration on cell adhesion and proliferation was evaluated.

ANALYSIS ON A MULTI-COMPONENT INTERBODY FUSION DEVICE

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Introduction: Spinal disorders as a consequence of pathology, trauma or normal aging compromises the quality of life. It is well known how the structure and function of the spine are very complex. With regard to the biomechanics of the spine, the intervertebral disc plays a crucial role in distributing loads and absorbing shock, however allowing the spine flexibility. In this context, a multi-component cage for spinal fusion surgery obtained by additive manufacturing was studied using Finite Element Analysis (FEA).

Materials and methods: A multi-component metal interbody fusion device obtained by additive manufacturing was modeled using SolidWorsk 2015 CAD software. The geometrical models were imported in the HyperWork® 13.0 (Altair Engineering Inc) environment and a 3D mesh was suitably created. Static numerical analyses were properly performed.

Results: The effect of the cage height on the stress and strain distributions was investigated, using different configurations. All the results also demonstrated that the cage was able to support the physiological loads.

Discussion: Numerical simulations provided interesting information on the stress peaks. Furthermore, the analysed cage was shaped according to the specific surgical approach and the finite element model was also employed to verify the design parameters.

A STANDARDISED PROTOCOL TO PRODUCE AND CHARACTERISE PLATELET-RICH-PLASMA FOR BONE HEALING

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Introduction: Platelet-rich-plasma (PRP) is defined as the plasma fraction of autologous blood, having a platelet concentration above baseline value, obtained after double centrifugation of anticoagulated whole blood. Upon activation, platelets release several factors (TGF-beta I/II, PDGF, VEGF, EGF, bFGF), which stimulate different steps of tissue repair including cell chemotaxis, proliferation, differentiation and angiogenesis. PRP has shown excellent results for wound and soft tissue healing, such as diabetic ulcers and skin lesions. However the literature regarding PRP effectiveness in bone healing in preclinical and clinical studies

is controversial and the PRP preparation procedure has been claimed among the main causes of such unpredictability. In fact, several methods exist, that may produce PRPs with different features. The aim of the present study was to survey the existing methods and their variability and, possibly, identify a method for PRP production allowing for a predictable platelet and growth factors content.

Materials and methods: MEDLINE and SCOPUS were searched using as search terms: platelet-rich-plasma; platelet concentrate; bone regeneration; bone healing; tissue healing; animal studies; clinical studies. Such terms were combined using boolean operators AND, OR. Only comparative studies in which the procedure was described and data regarding PRP content (platelet and/or growth factors concentration) were selected.

Results: More than 20 methods have been used in animal and clinical studies on bone healing to produce and characterize PRP. The majority of them have adopted two-step centrifugation procedure, with few studies considering only one centrifugation. Only few studies have measured GFs content: TGFbeta 1 and PDGF were the most measured, especially in animal studies. In almost all clinical studies, GFs were not measured. A high concentration of TGFbeta1 (>200 pg/ml) was obtained using a protocol with two low-speed centrifugations and presented an impaired bone healing. In contrast, protocol with two high-speed centrifugations (CURASAN kit) presented the highest concentration of PDGF-AB (>300 ng/ml) and did not lead to significant bone formation both in animal models and humans. A relatively high content of PDGF-AB and TGFbeta 1 obtained through a home-made protocol resulted in a minor bone density of patients treated with PRP in the early period.

Discussion: There is general consensus that regenerative effect of PRP depends on the platelet and GFs concentration, however in clinic the landmark consists in the fold increase of platelets in PRP compared to WB and the other parameters are not routinely measured. This determines a high variability of results obtained, because the differences of platelet and GFs content between patients are amplified by different methods used, instead of reduced. We developed a protocol consisting of a standardized platelets counts (1×10^6 platelets/microL) and a content of GFs, whose variability remained donor-dependent, but it was less than those reported in literature, leading to more predictable results on cell cultures.

In the future, PRP obtained with such procedure will be tested on bone and skin 3D models, which have been never reported regarding PRP use, before *in vivo* testing.

IMPROVED MECHANICAL AND BIOLOGICAL PERFORMANCES OF CELL-LADEN NATURALLY BASED HYDROGELS ENRICHED WITH GRAPHENE OXIDE

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Introduction: Graphene and its derivatives have recently emerged as promising materials for tissue engineering applications due to their unique mechanical, physical, chemical proprieties. Preliminary works suggest that both mechanical properties and bioactivity of polymeric 2D substrates may be enhanced when combined with graphene oxide (GO).

We here propose an innovative 3D nanomaterial, introducing GO nanosheets in alginate (Alg) based hydrogels, whose poor mechanical and structural features limit their wide use as implant for tissue engineering applications.

Materials and methods: GO nanosheets (Sigma Aldrich) aqueous suspension (1 mg/ml) was prepared by ultrasonic treatment. Alginate (Manugel GMB, FMC Biopolymer) was dissolved in physiologic solution; composite mixtures (0, 0.5, 2 wt% GO/Alg) were produced up to a final 2% w/v alginate concentration. Molds of agarose (1% w/v in CaCl 0.1M) were prepared to allocate GO/Alg solutions and to chemically cross-link gels via diffusion (2 h at 37°C). Go/Alg hydrogels were morphologically characterized through optical microscopy analysis.

Biocompatibility tests were performed embedding 3T3 fibroblasts (8 millions/ml) in the GO/Alg solutions to evaluate their viability (Dead/Alive) at different time points: 24 hours (T1), four, seven and fourteen days (T4, T7, T14 respectively). Mechanical proprieties were assessed via Dynamic Mechanical- Analysis (DMA) up to 28 days of culture (with and w/o cells) at different time points. All tests were performed in triplicate and statistical analysis carried out (Mann-Whitney *U* test, $n = 9$, $p < 0.005$).

Results: 3D GO/alginate hydrogels were successfully realized with 3 mm of height and 5 mm of diameter. Cell viability tests showed that the presence of GO does not decrease cell viability. For all time points cell viability was sta-

tistically higher in presence of GO, while there was no significant difference between 0.5 wt% and 2 wt% GO/Alg.

Hydrogels functionalized with GO exhibit an Elastic modulus about 3 fold higher than the Alg control (T0). After an initial decreasing of the Young Modulus for GO/Alg samples (T1), possibly due to a partial degradation of alginate based substrates, a drastic enhancement of the mechanical proprieties was observed up to 28 days of culture only for GO functionalized samples. Analysis of the storage and loss modulus in frequency showed an enhancement of the elastic behaviour after 28 days of culture for only GO functionalized hydrogels, possibly due to a GO nanosheets network formation, which is in agreement with the increase of Young Modulus, while Alginate hydrogels displayed a more viscoelastic behaviour. The mechanical features improvement was neither mediated nor triggered by cells activity.

Discussion: Cell viability tests confirmed the absence of toxicity of GO at least up to 2% wt and they also suggested a positive effect of graphene on biological activity *in vitro* in a 3D cell laden system. The delayed stabilization of GO/Alg mechanical proprieties may be due to GO nanosheets network formation processes over time (TEM analysis in run to investigate this hypothesis). Future developments will be carried out to investigate the topological role of GO on the results observed up to now.

COMPARATIVE STUDY OF THE MECHANICAL AND BIOLOGICAL FEATURES OF GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE COMPOSITE ELECTROSPUN MESHES

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Introduction: Electrospun scaffolds have been widely used in tissue engineering thanks to their ability to resemble the topological features of the native extracellular matrix. Polycaprolactone (PCL) has been greatly employed in its fibrous form thanks to its good spinnability; however its hydrophobicity and low mechanical proprieties limit its use in hard tissue engineering. Recently, different studies reported that the introduction of nano-sized materials could enhance both the stiffness and bioactivity of polymeric substrates. In particular, graphene-derived nanomaterials are emerging thanks to their unique mechanical, physical, chemical features.

In this work, electrospun graphene oxide (GO)/ and reduced graphene oxide (RGO)/PCL composite materials were fabricated and the effects of the two nanomaterials on the final morphology, mechanical proprieties and bioactivity of the fibrous meshes were evaluated.

Materials and methods: Fibrous meshes were realized via electrospinning. In brief, either GO (Sigma Aldrich) or RGO dispersions in ethanol (1 mg/ml) were added to PCL solution (in chloroform) to obtain 0.25 wt% GO-PCL and RGO-PCL composites mixtures. The RGO dispersion was previously prepared adding to GO solution L-Ascorbic acid (L-AA) (10/1 w/w AA/GO)(Zhang *et al.*, 2010). Not-electrospun films and pure PCL electrospun meshes were used as controls. The morphology was evaluated by scanning electron microscopy (SEM). Chemical composition was assessed with FTIR analysis. Zwick/Roell electro-mechanical machine was employed to perform tensile measurements. After sterilizing the samples by UV irradiation o.n., biocompatibility tests were performed cultivating fibroblasts ($40000/\text{cm}^2$) to evaluate their viability (DEAD/ALIVE kit) and spreading (toluidine blue staining, SEM) after 24 hours.

Results: Randomly oriented linear fibers were successfully realized. Morphological analysis revealed that their average diameters are not affected by nanosheets introduction ($n = 3$, t test, $p < 0.005$). FTIR analysis confirmed the GO reduction and the absence of superficial un-bound ascorbic acid in the RGO/PCL mesh.

Mechanical tests showed an enhancement of the Young Modulus and tensile strength by 18% and 32% in GO-PCL and by 28% and 14% in RGO-PCL if compared with pure PCL.

In vitro cell culture showed cell viability statistically higher with the nanomaterials introduction, more significantly in presence of RGO. Interestingly, also cell spreading was dramatically improved with the introduction of GO and much more with RGO both for electrospun or not samples.

Discussion: The fabrication process of nanofibrous GO- and RGO-PCL materials has been set up and optimized. In particular, the choice of ethanol allowed the complete miscibility of graphene-based solutions with PCL without surfactants addiction, besides improving the final solutions spinnability by decreasing

the surface tension. The functionalization of PCL fibrous meshes allowed to significantly increase the mechanical properties of the final material, as expected being well known the excellent properties of graphene, but also to enhance the cellular survival and cell-material interaction, possibly due to the higher roughness of the material, especially in RGO-PCL. Functional studies with adult stem cells are in run to evaluate the potential of graphene derived nanomaterials to induce osteogenic and chondrogenic differentiation.

PREPARATION OF NOVEL 3D POROUS GELATIN/PVA HYDROGELS USING ALGINATE MICRO-PARTICLES

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Introduction: Three-dimensional porous scaffolds and their fabrication technologies play an important role in tissue engineering; porosity favors the graft integration with the host tissue, besides offering the spatial volume where deposit newly generated matrix. Porogen leaching technique has been widely used to fabricate interconnected porous structures, because it allows controlling the pore size and total porosity of the whole scaffold. However, conventional porogens are water-soluble, making very difficult the adoption of this technique with a wide range of hydrophilic polymers. In this work we developed a protocol to realize micro-porous gelatin/polyvinyl alcohol (Gel/PVA) composite hydrogels using sodium alginate micro-particles as porogen.

Materials and methods: PVA powder (Mw = 85000-124000), gelatin powder from bovine skin type B, sodium alginate from brown algae and Calcium Chloride were purchased from Sigma-Aldrich.

Alginate micro-particles were produced using an aerodynamically-assisted jetting equipment (Nisco Encapsulation Unit VAR J30). Briefly, alginate solution 1% in water (w/v) was sprayed in a calcium chloride (0.1M) gelling bath. The encapsulator parameters were optimized to obtain spherical micro-particles with the required diameter. After preparation, the micro-particles were toughly washed in water before being used for experiments.

Gel/PVA solution (7% w/v PVA/water; 20/80 w/w Gel/PVA) was prepared in DI water at 90°C with constant stirring for 2 hours.

The composite solution was mixed with alginate micro-particles (1×10^6 /ml) for 15 min under constant stirring for homogenous mixing and then added into a mold. After centrifugation for 2 min, the mixture was physically cross-linked by a freeze-thawing method at -20°C for 20 hours and then thawing at room temperature for 4 hours. This freeze-thawing cycle was repeated 5 times.

The hydrogels were immersed into 0.1 M EDTA solution at 37°C for 2 days to leach out the alginate particles and then immersed into water to remove EDTA. Hydrogels were morphologically characterized through optical microscopy analysis of thin histological sections and morphological features such as porosity and pore size dimensions were derived. Mechanical proprieties were assessed via Dynamic Mechanical-Analysis. Chemical bonds were evaluated through FTIR analysis.

Results: Porous Gel/PVA hydrogels with 3 mm of height and 5 mm of diameter were successfully realized. Mean pore size dimension is 104.5 ± 15.9 μm and there are no significant differences along the z-axis (n = 6, t-test, p<0.005). Open porosity is about $74.5\% \pm 15.9$ (n = 6).

FTIR analysis revealed that there are chemical bonds between PVA and gelatin, probably due to the hydroxyl groups of the PVA. Elastic Modulus under dynamic compression at 1Hz of frequency (physiologic frequency) is about 348 ± 33.3 kPa.

Discussion: Alginate porogens allowed to obtain a 3D Gel/PVA hydrogel with an open porous structure, preserving the features of great elasticity, tribological proprieties and high water content, typical of PVA hydrogels. Moreover, gelatin addition could enhance the bioactivity and biodegradation propriety of the final scaffold. Therefore, in vitro cell cultures are in run to evaluate the potential of this composite scaffolds to support cell activity, especially for cartilage tissue engineering applications.

REVERSE ENGINEERING AND ADDITIVE MANUFACTURING TOWARDS THE DESIGN OF AN INNOVATIVE INSOLE FOR FOOTWEAR

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Introduction: The aim of the current study was to analyse the application of Reverse Engineering (RE) and Additive Manufacturing (AM) techniques to design an innovative low-cost insole recently produced by insole-makers. Taking into consideration all the modern developments in the shoe-manufacturing field, a polymer-based prototype of the insole was developed through the photogrammetric technique and a low-cost 3D Printer.

Materials and methods: Agisoft PhotoScan, Geomagic Studio, Rhinoceros and ZSuite softwares were used to obtain the model fabricated by fused deposition modeling (FDM) using a Zortrax M200 printer and a thermoplastic polymer (Acrylonitrile-Butadiene-Styrene, ABS).

Mechanical and thermal tests were carried out to optimize the process conditions. The pressure distribution under the feet were analysed in different conditions using F-Scan 7.0 Research and MATLAB R2015b softwares.

Results: Models of insole for footwear were developed taking into account the results obtained from calorimetric and mechanical analyses as well as those from pressure distribution. The instrument and process parameters were properly optimized. Shape and size were obtained by image capture and analysis techniques

Discussion: The results confirmed the possibility to use RE/AM techniques for the development of an innovative insole for footwear.

ADHESION, GROWTH AND CHARACTERIZATION OF HUMAN UMBILICAL CORD STEM CELLS ON DEMINERALIZED BONE MATRIX SCAFFOLDS

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Introduction: Cancellous bone has been reported to contain significantly lower levels of bone morphogenetic proteins although it is still osteoconductive. Demineralization of bone results in a spongy deformable scaffold that can be used as a bone void filler and as a matrix for cells. The impact of matrix mechanics of cell-free and demineralized scaffold, independent from microstructure, on the osteogenic differentiation of endogenous osteoprogenitor cells orchestrating bone repair and regeneration remains not to be fully understood.

Materials and methods: We obtained three-dimensional (3D) bone spongy scaffolds from bovine cancellous bone. Slices of about 2-3 millimeters of thickness were first washed with sodium hypochlorite and then demineralized using 2% (v/v) HCl solution in water. Bath solution was changed every day and decalcification was evaluated mixing one part of bath solution with two parts of 5% (v/v) NH₃ solution. If after 24 hours there was no precipitate, decalcification was stopped. Young's moduli of 3D bone scaffolds were evaluated using uniaxial testing machine Zwick/Roell mod. Z005. Human umbilical cord mesenchymal stem cells (hUC-MSCs) were cultured for 7 and 14 days on the demineralized 3D scaffolds to ascertain adhesion, proliferation and osteogenic differentiation.

Results: Histological and electron microscopy studies as well as qRT-PCR analysis revealed hUC-MSCs adhesion, division and maintenance during the 14 days of in vitro culture.

Discussion: According to the results, scaffolds prepared demineralizing bovine cancellous bone could be a suitable tool to study in vitro cell behaviors such as attachment, division and differentiation due to the inductive effects of extracellular matrix derived molecules. More investigations are still required to elucidate the exact effects of this scaffold and its interactions with mesenchymal stem cells.

SURFACE MODIFICATION OF TITANIUM BY MICRO ARC OXIDATION FOR CARDIOVASCULAR APPLICATIONS: A FEASIBILITY STUDY

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Introduction: Coronary artery disease is one of the leading causes of death worldwide. Coronary angioplasty with deployment of stent is the most popular non-surgical treatment of the cardiovascular disease which caused narrowing or occlusion (stenosis) of the affected vessel. Nevertheless, deployment of stents combined with the balloon expansion is a traumatic event which often results in inflammatory cell activation and vascular SMCs proliferation leading to the formation of a new neointimal tissue. In some cases, uncontrolled

growth of this tissue leads to neointimal hyperplasia and re-occlusion of the treated vessel (in-stent restenosis).

In this work we investigated the possibility to modify titanium surface to make it suitable for coronary stents. Micro Arc Oxidation (MAO) technique was considered to dope titanium oxide with elements such as Ca, P, Na and Si. The aim of this project was to demonstrate the possibility to modify the surface chemistry and morphology of titanium to make it suitable for next stent generations in titanium.

Materials and methods: An electropolishing treatment of titanium was optimized to homogeneously polish the surface of complex shaped devices, such as cardiovascular stents. MAO technique was used to modify the surface of titanium with an electrolytic solution, previously developed, containing Si, P, Ca and Na. For the coating process a wide range of final voltage was considered, ranging between 155V and 295V. The obtained treatments were analyzed and characterized by SEM, EDS, Laser Profilometry, Contact Angle, ICP-OES. Mechanical performance was assessed by severe bending test on coated metal sheets.

Results and discussion: SEM, EDS and ICP-OES showed that the MAO coating above 175 V can effectively enrich titanium with the solution elements. Laser Profilometry indicated a slight roughness increase after the electrochemical treatment, while Contact Angle measurement showed an increase of the wettability for all electrochemical treated samples. Three points bending test, providing high plastic deformation on samples (up to 12% in tensile strain), showed that no delamination occurred on the surface of coatings obtained in the low-voltage range. The 175 V treatment appeared to be the best combination in term of physio-chemical properties and mechanical properties.

This study demonstrated the possibility to safely dope the titanium surface using the Micro Arc Oxidation technique. Further in vitro investigations are now required for the assessment of the biological response on this titanium modification treatments.

PLASMA DEPOSITED NANOCOMPOSITE COATINGS WITH EMBEDDED RELEASABLE BIOMOLECULES: A NEW SURFACE FOR DRUG-RELEASE SYSTEMS

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Introduction: Non equilibrium (cold) plasmas, offer several established and newer tools for biomedical applications, from surface modification processes for biomaterials, to decontamination and sterilization methods, to experimental therapies for wound healing, cancer treatments, and dentistry. In this talk advances in the field of Surface Modification Plasma Processes will be highlighted, relative to a new kind of plasma deposited coatings produced by means of Atmospheric Pressure (AP) plasmas fed with gas/vapour compounds and with the aerosol of a solution/suspension of a compound or of nanoparticles (NPs) of biomedical interest. Coatings deposited with this recent approach in aerosol-assisted AP plasma deposition processes consist of an organic/inorganic matrix that embeds NPs or a biological compound (peptide, enzyme, protein, drug, etc.); ions from NPs or the biomolecule itself can be released in active form in a proper biological liquid/medium, or when in contact with a biological tissues. The term nano/bio-composite coatings can be used to describe this newer class of thin films.

Materials and methods: Nano/bio composite coatings are deposited in our lab in Dielectric Barrier Discharges (DBD) or AP Plasma Jets (APPJ) fed with an inert gas (usually He, but also Ar or N₂ can be used) to form the aerosol from a solution of a biomolecule (we are working with antibacterial molecules such as lysozyme and vancomycin and other compounds) or a suspension of NPs (e.g., antibacterial metals or oxides), and with a compound (we are using ethylene, but other gases/vapors can be used), whose fragments will form the matrix of the nano/bio-composite coating. XPS, FT-IR, SEM, Water Contact Angle (WCA) and other techniques are utilized to characterize the coating; HP-LC and other approaches are utilized to quantify the release of the biomolecules (or of metal ions) from the coatings, while biological tests (e.g., of the antibacterial activity) are performed to evaluate the efficacy of the coatings for selected biomedical applications.

Results and discussion: Nano/bio-composite coatings loaded with lysozyme (an enzyme with antibacterial activity) or with vancomycin (a common anti-

otic) have been successfully tested as drug release antibacterial systems. The structure and the bio-activity of the biomolecules could remain preserved in the coating due to the protection offered by nano-sized water droplets that act as a shield from the aggressive environment of the plasma. The release of the drug could be modulated by the plasma deposition of a nanometric outer barrier layer.

EXTRACELLULAR MATRIX SCAFFOLD AS A NEW STRATEGY FOR HUMAN PANCREAS BIOENGINEERING. INSIGHTS AND PERSPECTIVES OF REGENERATIVE MEDICINE FOR THE CURE OF DIABETES

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Introduction: Diabetes is a metabolic disorder that has reached pandemic levels worldwide. Type 1 diabetes mellitus is triggered by an autoimmune-mediated destruction of the insulin-producing β-cells in pancreatic islets whereas type 2 diabetes results in a progressive islets cells dysfunction with subsequent need for exogenous insulin treatment. Daily administration of exogenous insulin, often combined with correct diet and physical exercise, could maintain euglycemia state although, even with the most accurate therapeutic plan it's hard to keep the normal range. This trouble brings to several chronic and degenerative complications including retinopathy, neuropathy and atherosclerosis. Islet transplantation is recognized as the only curative treatment for diabetes. This technique is anyway strongly limited by the presence of a source of transplantable islets and secondly to the need of an immunosuppressive therapy after the transplant. Alternative strategies able to bypass these limitations are necessary. Regenerative medicine has shown a huge potential to address the limited number of transplantable organs and to allow immunosuppression-free transplantation. Cell-on-scaffold seeding technology seems to offer the quickest route to clinical application. This technology is based on the striking evidence that extracellular matrix (ECM) plays essential roles in the determination, differentiation, proliferation, survival, polarity, welfare, and migration of cells.

The aim of our study has been to produce acellular extracellular matrix scaffolds from the human pancreas (hpaECMs) as a cornerstone to the production of a new-generation, fully human-derived bioartificial endocrine pancreas. In this bioartificial endocrine pancreas, the hardware will be represented by hpaECMs, whereas the software will consist in the cellular compartment generated from patient's own cells. Extracellular matrix (ECM)-based scaffolds obtained through the decellularization of native organs have become the favoured platform in the field of complex organ bioengineering. This will be the first critical step towards the production of a new generation bio-artificial endocrine pancreas (ngBAEP), whereby insulin producing beta cells will be embedded within a supporting scaffolding biomaterial that recapitulates their native niche.

Materials and methods: To achieve our goal human pancreata (N° = 25) were decellularized with Triton-based solution and profoundly characterized. Primary endpoints were complete cell removal and DNA clearance, preservation of ECM components, growth factors and stiffness, ability to induce angiogenesis, conservation of the framework of the innate vasculature, and immunogenicity has been defined as primary end-points. As corollary we aimed to explore hpaECMs' ability to sustain growth and function of human islet and human primary pancreatic endothelial cells.

Results: Results show that hpaECMs can be successfully and consistently produced from human pancreata maintaining their characteristic molecular and spatial framework, their stiffness and vital growth factors. Importantly, hpaECMs inhibit human naïve CD4 β T-cell expansion in response to polyclonal stimuli by inducing their apoptosis and promoting their conversion into regulatory T cells. hpaECMs are cytocompatible and supportive of representative pancreatic cell types.

Discussion: Our research shows that human pancreas ECM-derived scaffold has the potential to become an ideal platform for investigations aiming at the manufacturing of a regenerative medicine-inspired bioartificial endocrine pancreas.

PLASMA TREATED PCL SCAFFOLDS COATED USING SURFACE ENGINEERED HYDROXYAPATITE NANOPARTICLES

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Introduction: Tissue Engineering combines biological sciences, chemistry and engineering to regenerate biological tissues. The key role is played by the scaffold, biodegradable and biocompatible 3D structure, that should be able to guide and promote the growth of new tissue and ultimately degrade gradually to promote new tissue formation. In the present paper, focused on the regeneration of bone tissue, scaffolds in polycaprolactone (PCL), specially designed to mimic trabecular bone microstructure, have been manufactured starting from a CAD model. Subsequently the scaffolds have been coated with hydroxyapatite (HA), through microplasma techniques working at atmospheric pressure. The HA, having a chemical composition similar to the mineral fraction of the bone tissue, promotes the osteointegration of the used material. Microplasma is a cold plasma technique that allows obtaining a good degree of coating, without any kind of damage to the scaffold structure. Moreover, the used plasma techniques are able to modify some surface properties of the material, allowing getting better results in terms of surface coating and biocompatibility.

Materials and methods: The scaffolds have been manufactured using Selective Laser Sintering of PCL powder. The interconnected porous structure exhibits a square section of 500 µm x/y, the entire specimen has a diameter of 15 mm and a height of 5 mm, so that the specimen could fit into a standard 24-well cell culture plate. Two different plasma techniques have been used to treat the scaffolds. A preliminary treatment has been performed on the scaffold surface using a radiofrequency (RF) atmospheric pressure plasma. At the same time a colloidal suspension, prepared using ethanol (EtOH) and HA nanoparticles, was subjected to a Plasma Induced Liquid Chemistry (PiLC) technique. After these preliminary treatments, the scaffolds have been immersed into the treated colloidal suspension and, treated again via the PiLC technique. Several analyses, such as SEM, TEM, Z-Potential, etc., have been carried out in order to characterize the materials and to assess the amount of particles on the surface of the scaffolds after the plasma treatments.

Results: The analyses revealed that the different surface properties of the materials have been changed by the PiLC treatment. The Z-Potential analysis showed that the surface charge of the HA particles was modified by the treatment. TEM scans showed less particle aggregation and the formation of small nanoparticles with a diameter of a few tens of nanometres. Moreover, the scaffolds showed an increased hydrophilicity, that is pivotal for a good osteointegration. SEM analysis of the surface of the coated scaffolds showed a uniform and well distributed layer of particles. Furthermore, the treatment did not cause any damage to the scaffolds.

Discussion: The proposed experimental procedure demonstrates to be able to produce good results in terms of scaffold coating and adhesion of the coating layer to the substrate. The ongoing *in vitro* tests on the treated scaffolds are carried out in order to evaluate and quantify the potential obtained improvements in terms of cell adhesion.

PLASMA DEPOSITION OF FREE-STANDING BIO-FUNCTIONAL NANOFILMS

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Introduction: Free-standing nanofilms (NFs) are polymer-based films with area of many cm², and tunable thickness of tens/hundreds nm. NFs are characterized by ultra-conformability and can be injected through a needle without losing integrity. They have been used as nanopatches for closing incisions in surgery, as platforms for tailored cell-substrate interaction and, when loaded with nanoparticles or drugs, as drug-release systems for therapeutic treatments. NFs can be fabricated by single step spin-assisted deposition in combination with a sacrificial layer. In this work we present the use of atmospheric (AP) and low pressure (LP) plasma assisted deposition (PE-CVD) processes for fabricating free-standing NFs with non fouling, antibacterial, and drug-release capabilities.

Materials and methods: A water-soluble 400-500 nm sacrificial layer of Poly-Vinyl Alcohol (PVA) was spin-coated on SiO₂ substrates, then baked. Different PE-CVD processes were performed to fabricate different NFs. A LP deposition/sputtering process fed with vapors of DiEthylene Glycol DiMethylEther (DEGDME) and Ar (Ar/DEGDME ratio 12.5), was performed directly on PVA-coated substrates to fabricate polyethylene-oxide (PEO)-like coatings with (Ag/PEO-like) or without silver nanoclusters embedded. For the second process, a layer of polylactic acid (PLA, 20 mg/ml) was deposited onto the PVA layer. PVA/PLA silica substrates were then coated with a nano/biocomposite PE-CVD coating composed of an hydrocarbon matrix embedding vancomycin molecules. A cold AP PE-CVD process performed in a Dielectric Barrier Discharge reactor fed with He, C₂H₄, and the aerosol of a 10 mg/ml water solution of vancomycin was used to deposit this bioactive layer.

Results and discussion: PEO-like, Ag/PEO-like and PLA/C₂H₄/vancomycin free-standing NFs with thickness in the range 50-400 nm could be easily obtained after dissolution of the PVA layer in water. FT-IR and profilometry show that no residual PVA was present after its dissolution in water. For the PLA/C₂H₄/vancomycin NFs the total release of the drug after 24 h was shown, leading to antibacterial activity. Antibacterial tests have shown also the antibacterial activity of Ag/PEO-like NFs, with no cytotoxicity against eukaryotic cells. This work is one of the few examples that demonstrate the possibility to deposit free-standing NFs by plasma assisted technology, with potential applications as antibacterial products. The matrix and the antibacterial agent or metal can be replaced by others to match different needs. This possibility opens the way to the use of NFs in many biomedical applications.

NOVEL POLYURETHANES MIMICKING ANTIMICROBIAL PEPTIDES

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Introduction: Most of the medical devices are susceptible to bacterial colonization and prone to formation of biofilms. Adverse implications of bacterial colonization include chronic infections, which often are life threatening for the patient and are also a major cause of rejection of implants. Polyurethanes (PURs) are a large group of polymers widely used in the biomedical and industrial field. Materials with varying chemical, mechanical, biological, and degradation properties can be achieved by proper selection of different reagents. Herein we report the synthesis and characterization of novel PURs mimicking the structure of antimicrobial peptides (AMPs). AMPs act as a first line of defense in the human body against bacterial infections. AMPs are built by short sequences of cationic and hydrophobic amino acids, which imparts amphiphilicity and undergoes self-assembly and self-organization. Hydrophobic domains and electrostatic interaction stemming from their amino acid composition, cationic charge and size, allow them to interact with the bacterial membrane forming pores and consequently disintegrates the structure. Moreover, AMPs are selective to bacterial cell membrane over mammalian one. The objective of this work is to synthesize PUR particles by mimicking the structure of AMPs so that it is possible to reach a balance between the compatibility and ability to target desired bacteria.

Materials and methods: Synthesis of PUR: PUR was synthesized by reacting polaxamer P407, HDI and N-Boc serinol using anhydrous 1,2-dichloroethane as solvent in the presence of Dibutyltin dilaurate.

Synthesis of polyurethane-g-poly(allyl mercaptan) (PU-SH): PUR was dissolved in water. Subsequently, the temperature was raised to 45°C. 5, then allyl mercaptan and ceric ammonium nitrate were added. The reaction was stopped after 16 hours and the product was purified by dialysis.

Thiol-ene polymerization of PU-SH and cationic/zwitterionic monomer: PU-SH was dispersed in water and the temperature was raised to 70°C. 5 ml of monomer of interest i.e. (2-Acryloyloxyethyl trimethylammonium chloride or 3-Acrylamidopropyl trimethylammonium chloride or 2-Methacryloyloxyethyl phosphorylcholine) was added with a syringe followed by addition of ammonium persulfate. The reaction was stopped after 16 hours. The obtained dispersion was dialysed with distilled to remove unreacted monomer and APS.

Polymer and particle size characterization: Attenuated total reflectance Fourier transform infrared (ATR FTIR) spectra were obtained in the spectral range from 4000 to 600 cm⁻¹. The particle size was determined at a temperatures range from 25°C to 60°C by Dynamic Light Scattering Measurement. In vitro cytotoxicity testing: NiH3T3 fibroblasts and HaCat keratinocytes were seeded at 10⁴ cells/well on the AMPU films. After 24, 48 and 72 h of incubation, MTT

(0.5 mg/mL) was added to each well and plates were incubated for an additional 3 h. Optical density (OD) was read at 660 and 570 nm in a microplate reader to evaluate cell viability.

Results and discussion: The successful synthesis of polyurethane was confirmed by FT-IR, Raman and NMR analysis. The Zeta potential of particles was also determined. The change in the hydrodynamic diameter of the particles with temperature was elucidated. The PUR biocompatibility evaluation using fibroblast and keratinocyte cell lines and MTT test is under development.

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MMP-9/GELATINASE B REGULATION IN RESPONSE TO BIO-MECHANICAL STIMULI IN ABDOMINAL AORTIC ANEURYSM (AAA)

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Introduction: Abdominal aortic aneurysm (AAA) is a multifactorial degenerative disease which involves a complex interaction between genetic and hemodynamics factors. AAA is typically asymptomatic and the rupture is associated with high mortality rate. Chronic inflammation and extracellular matrix degradation are the major pathological features of AAA. The process involved in AAA formation is associated with the upregulation of matrix metalloproteinases (MMPs) activity. MMPs belong to the family of proteolytic enzymes that degrade several components of ECM. However, the role of endothelium in the pathogenesis of these vascular disorder is relatively poorly understood. Monocyte activity during inflammation is modulated by a variety of mediators such as cytokines, chemokines, and growth factors that allow interaction with the endothelium of the vessel wall through the upregulation of adhesion molecules. During this process, pro-inflammatory cytokines such as TNF- α and IL-1 β promote the secretion of MMPs.

We sought to elucidate the role of endothelial matrix metalloproteinase-9 (MMP-9), in response to biochemical and mechanical stimuli.

Materials and methods: Endothelial cells (EA.hy926) have been seeded on collagen type I pre-coated silicone sheets and maintained under static conditions for 24h order to optimized the adhesion before applying mechanical stress. hrTNF- α has been added to stimulate an inflammatory condition. Cyclic uniaxial 10% substrate deformation was applied at a frequency of 1Hz for 3 days and compared with non-stressed controls. Cell viability and inflammatory markers, such as E-selectin, interleukin-6 (IL-6) and matrix metalloproteinase-9 (MMP-9) have been evaluated.

Results: Physiological mechanical stress controls inflammatory markers such as IL-6, MMP-9 and E-selectin when compared to static experimental conditions. Moreover, mechanical stress counteracts the pro-inflammatory effects of TNF- α on endothelial cells.

Discussion: In AAA, MMP-9 is secreted also by endothelial cells and it is regulated in response to bio-mechanical stimuli. Data on endothelial cells show the benefits of MMP-9 silencing in vitro to restore the function of vascular wall in terms of inflammatory response and extracellular matrix (ECM) remodeling.

INNOVATIVE PHOTOCROSSLINKABLE RESIN FOR APPLICATION IN STEREOLITHOGRAPHY

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Introduction: Stereolithography is a solid freeform technique (SFF) that was introduced nearly 25 years ago. Although many other techniques have been developed since then, stereolithography remains one of the most powerful and versatile of all SFF techniques. It allows 3D (micro)fabrication of solid structures from models created using computer-aided design (CAD) programs. The limited number of resins that are commercially available for processing by stereolithography has often been considered the main limitation of the technique. This work aims at developing photo-curable resins and applying it in stereolithography. Methacrylate end-functionalised poly(D,L-lactide) and divinyl fumarate Polycaprolactone (VPCLF) oligomers of varying molecular weight were synthesized and photo-crosslinked in the presence of non-reactive and reactive solvent. Suitable resin compositions were used in stereolithography to prepare porous

structures with mathematically defined architectures at high resolution. Cell attachment and proliferation on photo-crosslinked networks were assessed.

Materials and methods: *PDLLA dimethacrylate synthesis:* Linear hydroxyl-telechelic poly(D,L-lactide) oligomers were synthesised by ring opening polymerization of D,L-lactide for 40h at 130°C under an argon atmosphere, using 0.0015 wt% stannous octoate as a catalyst and hexanediol as bifunctional initiator. The oligomers were functionalized by reacting the terminal hydroxyl groups with methacrylic anhydride in dry dichloromethane under an argon atmosphere.

Divinyl fumarate Polycaprolactone (VPCLF): A Sn-free catalyst based on Al has been used in the polymerization of e-CL at room temperature. Hydroxyethyl Vinyl Ether (HEVE) as photocurable initiator has been used. The polymerization reaction was performed in a Schlenk tube under a nitrogen atmosphere, at room temperature overnight under magnetic stirring, then quenched by addition of methanol. After the synthesis of the vinyl-terminated PCL, the polymer was reacted with fumaryl chloride, resulting in a divinyl-fumarate polycaprolactone.

Network preparation and 3D porous structures: Networks were formed by UV irradiation (365 nm) using Lucirin TPO as a biocompatible initiator, Orasol Orange dye and different type of reactive and non-reactive solvent. Mathematically defined porous structures were prepared using the synthesized resin.

Results: The resulting polymers were characterized by their specific molecular weights, functional end groups and transition temperatures, using several techniques including: Nuclear Magnetic Resonance (NMR), Fourier Transformed Infrared Spectroscopy (FTIR), Differential Scanning PhotoCalorimetry (DPC) and Differential Scanning Calorimetry (DSC). Photo crosslinked disk-shaped specimens were seeded with human mesenchymal stem cells (hMSCs) to assess material's biocompatibility. Cell morphology and cell spreading pattern interaction onto crosslinked network specimens were evaluated by confocal laser scanning microscopy. SEM images and micro tomography (μ -CT) reconstruction show structures with an open pore architecture fully interconnected, allowing cell seeding and proliferation.

Discussion: A resin based on chemical modified biocompatible polymers (PDLLA and PCL) were developed and applied in stereolithography. Designed porous scaffolds with mathematically defined architectures were prepared and characterized. Results proved that it is possible to obtain refined porous scaffolds with a homogeneous micro architecture by stereolithography technique using non-commercial photocurable resin.

CALCIUM PHOSPHATE FILM ON TITANIUM OBTAINED BY CATHODIC POLARIZATION FOR IMPROVED OSTEOINTEGRATION PROPERTIES

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Introduction: Calcium phosphate coatings can improve the rate of bone growth to metallic implants, such as dental implants and joint prostheses. Long-term studies indicate that there is a statistically significant difference between both the amount of bone growth and the strength with which bone adheres to coated implants versus uncoated implants.

In our research a relatively simple, low temperature technique for reproducibly depositing calcium phosphates on metal surfaces was adopted.

The aim was to optimize the coating conditions necessary to electrolytically produce highly pure brushite $\text{Ca}(\text{H}_2\text{PO}_4)_2$ films on titanium substrates.

Materials and methods: Saturated solutions of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ were prepared by dissolving $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in water. The solutions were then stirred vigorously for approximately 30 min to assure saturation and then filtered through a medium-porosity glass frit to remove suspended monobasic calcium phosphate crystals. The resulting filtrate was used as the electrolyte solution for subsequent electrochemical depositions. An Amel 7060 potentiostat/galvanostat was used to control the current during the depositions. The device to be coated was used as the cathode, and a platinum sheet was used as the anode.

The sequence used to produce calcium phosphate coatings on metallic surfaces is a combination of electrochemical half reactions, acid-base reactions, and precipitation reactions. Hydroxide ions are produced at the cathode area, where they react with dihydrogen phosphate ion to form $(\text{HPO}_4)^{2-}$ that reacting with Ca^{2+} gives rise to precipitation of brushite $(\text{CaHPO}_4 \cdot 2\text{H}_2\text{O})$.

Twenty implants were inserted for *in vivo* studies 10 (test group) whose surface was covered by a Calcium Phosphate obtained according to the above mentioned procedure (Feeling film), and 10 implants with sandblasted and acid etched surface (SLA) (control group).

Results and discussion: Feeling implants exhibited a thin and homogenous layer, approximately one micron thick, of calcium phosphate nanocrystals,

mainly 90% Brushite and Hydroxylapatite as a balance. This new surface should be able to release in the tissues Calcium and Phosphate ions, accelerating the process of biomineralization that leads to the growth of newly formed bone tissue at the interface bone-implant. The Calcium Phosphate thin coating, with high adhesion over every kind of titanium surfaces, works as a protection for the surface from external contaminations and keeps the surfaces wettable in atmospheric environment for long time.

The Feeling surface tested by the present study, increased in a significant way the bone amount directly contacted to implant (expressed as %BIC) in respect with sandblasted and acid etched alone (SLA).

COLLAGEN-BASED SEMI-IPNS FOR THE TREATMENT OF ALZHEIMER'S AND PARKINSON'S DISEASES

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Introduction: Polymer-based gels have been widely studied in the field of tissue engineering and regeneration for their ability to deliver therapeutic agents directly into the central nervous system¹⁻³. Type I collagen represents an appealing candidate for neural tissue regeneration because of its self-assembly at physiological conditions and its ability to interact with cells⁴. Many efforts have been made to develop innovative strategies for improving drug permeability across the BBB, also including drug delivery via nanoparticles or liposomes⁴. An innovative injectable collagen-based semi-interpenetrating polymer network (semi-IPNs) for potential delivery of neuroprotective proteins (e.g. 70 kDa-heat shock proteins, Hsp70) has been proposed in this work in the treatment of Alzheimer's and Parkinson's diseases.

Materials and methods: Collagen/LMWHA and collagen/PEG semi-IPNs were obtained by inducing collagen fibrillogenesis in the presence of LMWHA or PEG, respectively. Furthermore, the effect of the inclusion of gelatin nanoparticles (GNPs), obtained via double step desolvation method, in the collagen-based gels has been also evaluated. Small amplitude oscillatory shear tests and steady state shear measurements were performed in order to assess viscoelastic properties for all the proposed semi-IPNs. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) have allowed to obtain informations related to hydrogel morphology. Hydrogel biological behavior was assessed both in vitro and in vitro. SH-SY5Y human neuroblastoma cell line were embedded within gels and their metabolic activity was quantified by MTS assay. Collagen-based semi-IPNs were injected in mouse striatum. The inflammatory response was evaluated by glial fibrillary acidic protein (GFPA) and CD11b staining on 30 µm-thick coronal sections, after 7 days.

Results: All the proposed semi-IPNs have shown a gel-like and a shear thinning behavior. Furthermore, a threshold concentration of gelatin nanoparticles has been founded. MTS assays have provided interesting information on cell metabolic activity over time, suggesting that SH-SY5Y cells may proliferate within gels.

Discussion: Results of this work suggested that collagen-based semi-IPNs are suitable for brain applications. Future studies will be addressed on the capacity of the proposed gels to appropriately deliver Hsp70.

ANTIRESORPTIVE PROPERTIES OF STRONTIUM SUBSTITUTED AND ALENDRONATE FUNCTIONALIZED HYDROXYAPATITE NANOCRYSTALS IN AN OVARIECTOMIZED RAT SPINAL ARTHRODESIS MODEL

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Introduction: Advanced age, osteoporosis and unhealthy life-style diminish bone formation and remodeling rate so fusion enhancement techniques could be beneficial for patients with osteoporosis who need to undergo spinal

arthrodesis. The purpose of this study was to comparatively investigate the posterolateral fusion rate in ovariectomized (OVX) rats using two new bone graft materials: strontium (Sr) substituted hydroxyapatite (HA) nanocrystals and alendronate (AL) functionalized HA nanocrystals. SrHA was synthesized in the presence of different Sr concentrations (SrHAS; SrHA10) and HA-AL nanocrystals at increasing bisphosphonate (BP) content (HA-AL7; HA-AL28).

Materials and methods: A posterolateral spinal fusion model in twenty-five Sham-Operated and in twenty-five OVX female rats was used and materials were bilaterally implanted between transverse processes of lumbar vertebrae. Sham and OVX animals were divided in five groups depending on the material: HA, SrHAS, SrHA10, HA-AL7 and HA-AL28. The assessment of bone fusion was carried out by µCT, histology and histomorphometry.

Results: Some gaps between the transverse processes were observed by µCT in OVX HA group, while they were not present in the other groups. These results were consistent with histological and histomorphometrical analyses showing that in OVX animals SrHA and HA-AL materials displayed significantly higher BV/TV and Tb.Th and significantly lower Tb.N and Tb.Sp in comparison with HA alone.

Discussion: Results of this study suggest that in spinal fusion the incorporation of bioactive ions or drugs as Sr and AL improves the biological performance of HA representing a promising strategy especially in osteoporosis patients with high risks of spinal fusion failure. Results also suggest the existence of a Sr and AL dose response effect and that HA containing the highest AL dose could be the candidate biomaterial for spinal fusion in osteoporotic subjects.

EFFECT OF DEXTRAN-GRAFTED MAGHEMITE NANOPARTICLE INCORPORATION ON CHITOSAN SCAFFOLD PROPERTIES

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Introduction: The current strategies for the treatment of large bone defects are still severely limited. Alternative successful approaches, able to face and ameliorate bone tissue regeneration dynamics, need to be pursued. Recently, magnetism has been reported to play a significant role in cell response, enhancing cell proliferation and osteogenic differentiation. In order to exploit magnetism with the specific aim of improving the regeneration process, magnetic biomaterials can be developed by integrating magnetic nanoparticles (MNPs) within synthetic or natural scaffolds. In the present work, chitosan scaffolds incorporating dextran-grafted maghemite (DM) nanoparticles were synthesised and characterized as a first step toward the wider and more ambitious purpose of designing a magnetic three-dimensional platform as a tunable tool for bone tissue regeneration.

Materials and methods: Chitosan scaffolds incorporating magnetic nanoparticles were developed by using a freeze-drying technique. Chitosan slurry (1,67% w/v) was mixed with colloidal suspensions of DM nanoparticles at different percentage (5-10-15% w/v with respect to the weight of chitosan used). Scaffolds properties were evaluated by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectrometry (EDX), unconfined uniaxial compression test in PBS and stability test in Tris-HCl at pH 7.4 and 37°C. Preliminary cytocompatibility of the synthesized scaffolds was assessed by standard MTT proliferation assays on the MG63 human-derived cell line as a suitable osteoblast-like model. Cells were seeded directly onto the surface of cylindrical scaffolds (5 mm diameter × 5 mm height, pre-hydrated by complete D-MEM cell culture medium) put into 96-well plates, and grown for 24, 48 and 72 hours before assaying viability.

Results: Scaffolds with open and interconnected pores were obtained. Increasing the DM content, the average pore diameter decreases from 180 µm to 150 µm. EDX analysis showed a uniform distribution of DM within the entire volume of the MNPs functionalized scaffold, evidencing also an increase in the iron elemental content, proportional to the DM content. The compression tests highlighted that the value of Young's modulus (calculated as the slope of the linear part of the stress-strain curve) increases as the DM percentage rises up to 10% (Cs = 1 ± 0,07 kPa; Cs/DM5 = 1,58 ± 0,24 kPa; Cs/DM10 = 1,62 ± 0,21 kPa) with the exception of Cs/DM15, where a significant reduction in the Young's modulus (0,92 ± 0,14 kPa) was recorded. By proliferation assays, a minor cytocompatibility of Cs/DM5 was revealed at each time-point (24, 48 and 72 h post-seeding); instead, Cs/DM10 and Cs/DM15 both showed a higher proliferation at 72 h post-seeding than at 24 h.

Discussion: DM MNPs were homogenously dispersed within chitosan scaffolds increasing their mechanical properties and at the same time enhancing the cytocompatibility and proliferative responses. Future tests have been planned to evaluate the effects of the scaffolds magnetic properties on a biological environment in order to investigate while the developed magnetic three-dimensional platform could represent a successful tool for guiding regeneration in critical bone defects.

ENGINEERING ISLETS-LIKE MICROTISSUES FOR TYPE I DIABETES

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Introduction: Type-1 diabetes mellitus is a disease characterized by an inability to maintain proper systemic glucose levels due to an autoimmune destruction of the insulin-producing β-cells in the pancreatic islets of Langerhans. In cases of patients with hypoglycaemia unawareness, current treatments of glucose monitoring and insulin infusion are not adequate, and pancreas or islet transplantation would be ideal. Islet transplantation is a minimally invasive 'micro-tissue' therapy aimed at eliminating severe hypoglycaemia, but high tissue demand, life-long immunosuppression and high associated costs may limit its widespread implementation as preferred treatment. This work aims to overcome these limitations and improve clinical outcomes by engineering functional islet-like microtissues by physically protecting islets from host environments, standardizing islet size using 3D bioprinting technology while promoting a vascular network formation. A novel 'bioink' hydrogel composed of Collagen type I, Alginate and Fibrin (CAF) has been developed for this aim, bioprocess β-cell into 3D islet-like microtissues.

Materials and methods: CAF hydrogels were produced in a 2:1:1 ratio at three collagen concentrations (0.5%, 1% and 2.5%). MIN6 β-cells were incorporated within the hydrogels and crosslinked with CaCl₂ and thrombin. Micro-tissues were manufactured using existing 3D bioprinting techniques. Physico-chemical and morphological properties were evaluated. Biocompatibility of CAF hydrogels containing MIN6 β-cells were also assessed following 7 days of culture.

Results: CAF hydrogels at different collagen concentrations presented pore sizes ranging between 40 and 200 μm. Rheological analysis demonstrated that CAF hydrogels had a G' modulus, similar to bulk human pancreatic tissue ~1000 Pa [3]. The presence of higher collagen content enhances hydrogel stability, obtaining stable CAF hydrogels for >15 days of biodegradation tests. High cell viability and β-cells re-organized into pseudo-islets were detected using Live/Dead assay for the three CAF hydrogel formulations (in comparison to controls) over 7 days of in vitro culture. In terms of printability, the extrusion of bioinks at higher collagen concentrations became more difficult and inaccurate.

Discussion: A novel collagen type I, alginate and fibrin hydrogel (CAF) has been successfully developed as a bioink for the manufacturing of islet-like microtissues. The CAF system offers some capacity to tailor mechanical properties to match the desired tissue as evidenced here with the pancreas. Hydrogel stability and porosity are enhanced with increasing collagen content. The three hydrogels recipes exhibited good nutrient diffusion within the first 2 hours of incubation and excellent biocompatibility over 7 days of culture. Further analyses on cellular functionality are currently in progress. This pilot-data demonstrates the CAF can offer a suitable material for the manufacture of microtissues; providing appropriate cell microenvironments to encourage successful engraftment by mimicking the native ECM.

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GENERATION OF A BIOENGINEERED 3D BONE-MUCOSAL ORAL MODEL FROM HUMAN DERIVED PRIMARY CELLS

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Introduction: Animal experimentation has been extensively and for long time applied in several research fields, but since 2011 it has been greatly limited by the Commission of the European Parliament to ensure people safety, animals welfare and reduce research costs.

To respond to these directives, many attempts, under the instruction of the Commission's International co-operation program on Alternative Test Methods (ICATM), have been focused on the development and validation of new in vitro methods.

Thanks to the improvement of cellular isolation protocols and cultural conditions, several in vitro three-dimensional (3D) systems have been developed and commercialized, bypassing the traditional bi-dimensional (2D) cell culture systems. To this regard, diverse approaches of tissue engineered bone and oral mucosa have been developed independently or in combination with animal or tumoral cells.

Despite the promising premises and the cutting-edge results, the actually used 3D in vitro bone-oral mucosal models still lack of primary human cells, therefore the proposed project aims to create implemented and customized 3D models, fully made with primary cells (keratinocytes, fibroblasts and osteoblasts all of human origin), able to mimic the natural structure of bone and oral mucosa. A direct future application will be the complex, multi-tissue periodontal regeneration, still a matter of debate, needing synchronized restoration of the gingival and bone compartments, besides cementum and periodontal ligament.

Materials and methods: For the in vitro reconstruction of the engineered 3D oral mucosa counterpart, the dermal compartment was enriched with a pool of primary human fibroblasts, freshly obtained from the normal gingiva of young healthy and informed consent donors, put into a culture insert and submerged into defined culture media. A pool of primary human keratinocytes was then plated upon the gel to build up the epithelial component. When keratinocytes reached confluence, they were grown at the air-liquid interface, starting to stratify in about 2 weeks. Reconstructed- and bioptic control-epithelial tissues were morphologically analyzed by hematoxylin/eosin (H&E) staining and examined for the expression of proliferation-, basement membrane-, citokeratin- and fibroblasts-expression markers.

Regarding the bone compartment, a multilayered chitosan (CH)-based porous scaffold (enriched with tricalcium phosphate and type I collagen) was synthesized, morphologically characterized by SEM and cut to obtain 6 mm diameter discs of about 3 mm thickness. Primary human osteoblasts (HTB-80) were integrated into the discs by using fibrin gel. Cells proliferation was directly and indirectly assessed by Alamar blue assay, while cells morphology was made by SEM observation.

Results: Preliminary results show that the in vitro H&E analysis of the in vitro reconstructed epithelial tissues stratify with a normal differentiation pathway resembling the typical histology of normal epithelia. 3D mucosa models characterization also confirms these data as shown by PCNA, BrdU, collagen IV, cytochrome 10/14 and vimentin immunofluorescent analysis. In vitro test of the bone compartment also showed excellent morphology and cytocompatibility.

Discussion: The preliminary results demonstrate that the proposed bone-oral mucosa model could open new in vitro frontiers for the accomplishment of the complex physiological processes at the basis of periodontal regeneration.

UNPAIRED RESPONSE OF NEONATAL HUMAN EPIDERMAL KERATINOCYTES (NHEKS) AND E6E7 HPV16 LENTIVIRAL INFECTED NHEKS TO COLD ATMOSPHERIC PLASMA (CAP)

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Introduction: Cold Atmospheric Plasma (CAP) has risen great interest as a promising tool for medical applications, thanks to the synergic effects of its physical and chemical components and to the possibility of tuning them for specific employ. Since a plethora of signalling pathways is involved and triggered by CAP, many attempts must be devoted to ensure the possibility of using CAP at a safe level in the dermatological area; so, the main purpose of the present work was to in vitro assess the most performing CAP treatment to selectively target cancer cells avoiding any toxic side effect to normal tissues. To achieve this goal, CAP was used to treat epithelial cells infected by High Risk Human papillomaviruses (HR-HPV), known to cause oral and ano-genital cancer.

Materials and methods: Normal- (NHEKs) and E6E7 HPV16 lentiviral infected- human epidermal keratinocytes (E6E7 HPV16-NHEKs) were seeded into 24 wells plates and allowed to adhere. CAP treatment, generated with 2 mm gap, 25 kV peak voltage, 20 kHz pulse repetition frequency, 7.5% duty cycle, was carried out for 30 and 60 seconds using a Dielectric Barrier Discharge (DBD), operated in open air and driven by a micro pulsed high-voltage generator. After 24 and 48 hours, cell viability was evaluated by the MTT assay, while the percentage of S phase cells and wound closure capability were assayed in a scratch test, after BrdU incorporation, by immunofluorescent staining. Moreover, plasma-generated reactive species (ROS and RNS) were evaluated. According to preliminary data, a different response to CAP treatment was highlighted between HPV-positive and-negative wounded monolayers; thus, as a further investigation, CAP influence towards epithelial formation capability of 3D organotypic epithelial raft cultures made with either normal and infected keratinocytes has been evaluated by means of haematoxylin/eosin (H/E) and BrdU staining.

Results: CAP treatment confirmed its toxic effect towards HPV infected NHEKs; in fact, viability was significantly decreased in comparison to untreated control cells ($p<0.05$). However, a toxic effect was observed for uninfected cells too. Moreover, ROS and RNS evaluation confirmed that their production is directly related to the duration of CAP treatment. BrdU staining and wound healing results further confirmed previously obtained data. Finally, the epithelial formation capability of both cells, at different time points after CAP irradiation, was evaluated by *in vitro* reconstruction of 3D epithelia, by means of H/E, BrdU, caspase-3 and annexin V assays.

Discussion: Considering the observed CAP ability to influence free radical species production, proliferation rate modulation, apoptosis and necrosis, it seems to be very important to finely regulate standard parameters in order to apply this innovative technology for medical purposes. Finally, our data suggest that further investigations are still strongly necessary to set-up effective standard conditions prior to apply CAP for epithelial tumours therapy.

CONSTITUTIVE MODELS OF HADM: PARAMETERIZATION THROUGH 3D FINITE ELEMENT MODELLING COUPLED TO UNIAXIAL EXPERIMENTAL TESTS

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Introduction: Human acellular dermal matrices (HADMs) are used in reconstructive surgery as scaffolds promoting autologous tissue regeneration. However, the dermis behavior is not well understood and predicting its deformation through constitutive models has always been challenging. The complexity of dermal tissue behavior subjected to *ex vivo* uniaxial stress is due to relevant geometric and material nonlinearities. In fact, during the test, the specimen undergoes very large deformations and engineering stress and strain definitions are not suitable to provide a good representation of material behavior. This work introduces a methodology to parameterize material behavior from experimental curves, and tries to assess which model complexity would be adopted to reach a good description.

Materials and methods: A set of experimental engineering stress-strain curves, obtained through uniaxial loading of HADMs specimens, was used for the validation of different finite elements models. As a first step, two linear elastic models under small deformations or large deformations hypothesis (Linear GNL) were implemented, considering the tissue as homogeneous, and the constitutive material as linear elastic. However, experimental tests have proved that the actual material behavior is not linear since the elastic modulus grows at higher strains. Therefore more complex mathematical formulations have been inquired, which take into account both mechanical and geometrical non-linearities through hyperelastic material models (Mooney-Rivlin and Ogden).

Finite element models replicated tensile test conditions: geometries were built according to experimental specimens sizes; all degrees of freedom of the lower surface were totally constrained, while a 10 N load was applied on the upper surface.

Results (specimen elongation, necking area and mean axial stress in the specimen mid- section) were compared to experimental true curves, calculated from force/displacement data, having acquired both the specimen width and thickness at the neck region during the whole tensile tests.

Results: Linear elastic models underestimate the mean stress value up to 29%, due to the small deformation hypothesis, which implies the use of the

undeformed cross-section for stress calculation. On the contrary, the linear GNL model always overestimated the peak stress since the material stiffening behavior was here neglected and estimated elongations were higher (leading to smaller necking areas) than experimental ones. Hyperelastic models produced similar stress mean values in correspondence of the necking area. However, according to Ogden model, a large specimen volume undergoes uniform axial stress (σ_y) values, while, according to the Mooney-Rivlin model, the peak stress is not reached at the middle of the specimen, but midway between this point and the specimen lateral surfaces.

Discussion: Hyperelastic models give a far more realistic representation of actual stress patterns: while GNL model provides the best estimation of two parameters out of three (necking area and mean σ_y), it leads to a very high overestimation of the elongation (94%), making this model not suitable to the description of the tensile tests on HADMs. Ogden incompressible model has given the best performance.

NANOTECHNOLOGY-BASED STRATEGIES TO TREAT CHRONIC WOUNDS

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Introduction: Skin lesions are a global healthcare problem since they can compromise the integrity and the functionality of significant skin areas. More than 40 million people suffer from chronic wound worldwide (8 million in Europe and 6.5 million in US in 2009), most commonly caused by poor blood supply to the lower limbs. Chronic wound is a frequent and very severe problem in patients with diabetes mellitus, a pathological condition involving more than 285 million people globally. In this work, different approaches to treat chronic wounds are presented based on antibacterial chitosan (CS) sponge and nanofibres or innovative polyurethane-based hydrogels.

Materials and methods: Silver nanoparticles (AgNPs) and gentamicin sulphate (GS) loaded sponges and nanofibres were obtained by freeze-drying and electrospinning, respectively. Thermosensitive amphiphilic polyurethanes (APU) were synthesized according to a patented procedure.

Results: The antibacterial properties of AgNPs and GS loaded sponges and nanofibres were tested against five pathogenic bacteria isolated from infected wounds (*Staphylococcus aureus*, *Escherichia coli*, *Enterococcus faecalis*, *Pseudomonas aeruginosa* and *Proteus mirabilis*) and high efficiency against tested strains was observed.

APU were successfully synthetized showing: (1) biocompatibility; (2) long-term stability in biological environment and degradation rate compatible with tissue regeneration rate; (3) solubility in aqueous media; (4) low viscosity at 20°C; (5) gelation at 37°C; (8) ability to encapsulate biomolecules and drugs to achieve a therapeutic effects (Boffito et al., 2016). Furthermore, this innovative polymers has been proposed to treat infected wounds within the MOZART project recently financed by H2020 program.

Discussion: The treatment of chronic wounds required a multifunctional approach based on nanotechnology to combine long-term antibacterial properties with tissue regeneration strategies. In this work, recent findings using CS based scaffolds are reported and novel concepts and future targets are presented exploiting the properties of smart polyurethane-based hydrogels.

PLASMA DBD GENERATED RONS IN BIOLOGICAL LIQUIDS FOR IN VITRO STUDIES ON EUKARYOTIC CELLS ON 2D AND 3D SUBSTRATES

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Introduction: Plasma Medicine is the area of medical applications where plasma sources operating in air at atmospheric pressure (AP) are investigated to treat cells or biological tissues for therapeutic applications. Although until today a complete understanding has still to emerge on the application of AP plasmas on eukaryotic cells, it is clear that among all plasma agents (UV-Vis light, electric field, charged particles, etc.) reactive oxygen and nitrogen species (RONS) play a key role in the cell response as they are involved in both oxidative stress and in signaling processes. There is evidence for selective, possibly growth stimulating, plasma-generated RONS effects on living cells

and tissue. It is also known that biological responses to air plasma exposure are mediated by the presence of liquids in both *in vivo* and *in vitro* applications. Indeed, *in vivo* targets generally include a thin layer of aqueous solution, (blood serum, intercellular fluid), while for *in vitro* studies few ml of culture medium or other liquids are exposed to plasma. For these reasons a deep characterization of the chemistry triggered by plasma treatment is needed. Possible applications of these investigations are the stimulation of cell proliferation and colonization on 3D porous polymeric biodegradable scaffolds for Tissue Engineering.

Materials and methods: We have exposed cell culture media to ambient air Dielectric Barrier Discharge. Two different eukaryotic cell types (immortal line vs primary cells), grown on Petri dishes, were incubated with the medium exposed to air plasma to evaluate the role mediated by RONS on their behavior. Differences in cell viability were addressable to the cell type and to the specific culture medium under study, attesting for a key role played by the liquid composition in this process. Particular attention was devoted to the superoxide radical anion (O_2^-), detected by the Cytochrome C reduction reaction.

Results and discussion: This study led us to hypothesize that the O_2^- generation is mainly due to side reactions triggered by plasma, involving thiyols or thiol-containing components of culture media (e.g., glutathione, and cysteine). Indeed, such molecules seem starting cyclic red-ox reactions. A further aspect of our interest was the evaluation of the proliferation of cells on 3D porous polymeric biodegradable scaffolds for Tissue Engineering. Cells seeded on native poly-caprolactone scaffolds were incubated with plasma-modified medium. Interestingly, differences in cell viability and morphology were observed, confirming the vector role played by the treated medium also for possible Tissue Engineering applications.

MICRO-PATTERNED PATCHES FOR CLOBETASOL TOPICAL DRUG DELIVERY

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Introduction: Clobetasol propionate is the most potent steroid currently available in the market, used only for dermatological application because of the very high lipophilicity. To date, the ideal clobetasol delivery system, to treat oral mucosa lesions, is still lacking and demanding. Here, we developed chitosan-based, muco-adhesive, micro-patterned patches, via electrochemical deposition, in presence of ethanol solvent for the topical delivery of clobetasol.

Materials and methods: Random and micro-patterned porous patches were obtained via Electrophoretic Deposition of medium molecular weight chitosan, by adapting the procedure to the ethanol-based electrolytic bath where clobetasol was dissolved together with chitosan. Patches were characterized in terms of surface morphology (Scansion Electron Microscopy), swelling properties and mechanical test. Clobetasol loading and release were verified by UV-vis spectrophotometric analysis.

Results: Ethanol-made patches showed a decrease in thickness as well as in random porosity, resulting in a lower swelling rate and in a plastic mechanical behavior. Clobetasol was successfully loaded on patches and a time-dependent release profile could be observed.

Discussion: Feasibility of micro-patterned patches for clobetasol topical drug delivery was confirmed. Electrophoretic Deposition of chitosan is a very promising technique for producing devices to be loaded with highly lipophilic agents, as clobetasol propionate.

CHONDROPROTECTIVE EFFECTS OF N-ACETYL PHENYLALANINE GLUCOSAMINE DERIVATIVE IN A MURINE MODEL OF OSTEOARTHRITIS

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Introduction: Osteoarthritis (OA), the most common chronic degenerative joint disease, is characterized by joint structure changes and inflammation,

both mediated by the I κ B kinase (IKK) signalosome complex. The ability of N-acetyl phenylalanine derivative (NAPA) to increase cartilage matrix components and to reduce inflammatory cytokines, inhibiting IKK α kinase activity, has been observed *in vitro*. The present study aims to further clarify the effect of NAPA in counteracting OA progression, in an *in vivo* mouse model after destabilization of the medial meniscus (DMM).

Materials and methods: Mice were divided into 3 groups:

- DMM group: DMM surgery without NAPA;
- DMM + NAPA group: DMM surgery with NAPA treatment;
- NO DMM group: no DMM surgery.

DMM surgery was performed in the right knee, while the left knee did not undergo any surgery. Four weeks after surgery (mild-to-moderate OA), some animals received one intra-articular injection of NAPA (2.5 mM) and after 2 weeks, the animals were pharmacologically euthanized. The animals were euthanized 4 weeks after treatment.

At the end of experimental times, both knee joints of the animals were analyzed through histology, histomorphometry, immunohistochemistry and subchondral bone microhardness.

Results: The injection of NAPA significantly improved cartilage structure, increased cartilage thickness ($p<0.0005$), reduced Chambers and Mankin scores ($p<0.005$), fibrillation index ($p<0.005$) and decreased MMP13 ($p<0.05$) and ADAMTS5, MMP10, and IKK α ($p<0.0005$) staining. The microhardness measurements did not show statistically significant differences between groups.

Discussion: This study demonstrated the chondroprotective activities exerted by NAPA *in vivo*. NAPA markedly improved the physical structure of articular cartilage and reduced the amount of catabolic enzymes, and therefore of extracellular matrix remodeling. The reduction in OA grading and catabolic enzymes paralleled the reduction of IKK α expression. This further hints at a pivotal role of IKK α in OA development by regulating MMP activity through the control of procollagenase (MMP10) expression. We believe that the preliminary preclinical data, here presented, contribute to improve the knowledge on the development of disease modifying drugs.

SMART SCAFFOLDS FOR OSTEOFOROSIS TREATMENT

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Introduction: Osteoporosis (OP) is a common, worldwide disease with a rapidly growing incidence as the population ages; it results in bone loss and deterioration and in a decreased bone strength, which involve an increase in the risk of fractures. The main clinical consequences of this condition are bone fractures, which are associated with significant morbidity and mortality. Antiresorptive agents such as bisphosphonates are mainstays of the therapy for OP and currently four of these agents have received FDA approval for clinical treatment. The perfect solution to treat OP is still not within grasp and recently attention was drawn to the negative outcome of some drugs clinically used to treat OP. In the frame of the ERC-consolidator grant BOOST, a scaffold purposely developed for osteoporosis treatment will be developed.

Materials and methods: In the present work, healthy and early osteoporotic bone geometries will be obtained from tomographic scans of human bone tissues discarded from surgery on healthy and early-stage osteoporotic patients. Smart scaffolds will be biofabricated combining different rapid prototyping techniques using collagen as a matrix and mesoporous bioactive glass as reinforcing and bioactive phases. The scaffolds will be tested in bioreactors using co-culture of osteoblasts and osteoclasts in order to codify the influence of both chemical and topographical stimuli on the osteoblast-osteoclast coupling.

Results: Ethical approval to retrieve human healthy and osteoporotic bone had been obtained at the *Istituto Ortopedico Rizzoli*. Protocols for the co-culture of osteoblast and osteoclast are currently under development. Mesoporous glasses based on the SiO₂-CaO system containing different doping ions (Cu²⁺, Sr²⁺) have been prepared both by an ultra-sound assisted base-catalyzed sol-gel method and by an aerosol-based spray-drying process, in order to control

both the particle size and their morphology. The structural and morphological features have been investigated by TEM and FE-SEM coupled to EDS, N₂ adsorption-desorption, XPS as well as their ability to form hydroxyapatite in vitro. The release profiles of the therapeutic ions have been measured by inductively coupled plasma-atomic emission spectrometry. FESEM image of spray-dried mesoporous glasses shows micro-sized spherical morphology, with a size ranging between 500 nm and 5 µm without the formation of aggregates. The parti-

cles prepared by ultra-sonication showed spheroidal nanoparticles with size of ca 100 nm, with a slight tendency to aggregate. The EDS quantitative analysis revealed element ratios very close to the theoretical ones.

Discussion: The proposed approach will allow to codify how biomaterial chemistry and topography at the macro-, micro- and nano-scale influence the multifaceted coupling process of bone resorption and formation, with special emphasis on the cell cross-talk between osteoclasts and osteoblasts.

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