Macromolecular Symposia

www.ms-journal.de

Photo-Degradation of a Biopolyester Blend under UV-C Rays

Annamaria Visco, Cristina Scolaro,* Hossem Bellhamdi, and Antonio Grasso*

Biopolyesters, pure and mixed with a compatibilizer, are exposed to UV-C radiation in the interval 4–32 h. UV-C rays act as germicides and antibacterial on biomedical materials. The mechanical and physical characterization tests have shown how all the materials, pure and mixed, undergo UV-C photodegradation even if in a different way. The change in the structural order of the polymer, the embrittlement, and the change in the surface wettability of the water/blood is lower in the blend than in pure polymers. This is thanks to the cross-linked structure of the mixture, which is more thermally stable, mechanically resistant, and more hydrophobic than the individual components.

1. Introduction

Before their specific use, all the components for biomedical use, as well as the equipment for the use of biomedical devices, are necessarily subjected to sterilization processes mostly obtained with an exposure to physical (i.e., irradiations, dry heat, etc.) or chemical (i.e., ethylene oxide sterilization, etc.) methods to give a germicidal action.[1–3]

Among the possible methods of irradiation, the use of irradiation with natural or artificial ultraviolet (UV) light could be used as germicidal against the spread of viruses such as the Covid-19. The UV-C rays, which are in the wavelength range of 200–280 nm, are useful just for disinfection.[4,5] Anyway, at the same time, the UV-C irradiation is responsible for the decomposition and degradation of many organic compounds (such as polymers), as well as the loss of gloss and the loss in mechanical properties of the plastics.[6,7]

Many polymeric materials find application in the biomedical sector (such as orthopedic, dental, cardiovascular, gynecological, ophthalmic, gastroenterological, etc.). In particular, biopolyesters such as polycaprolactone (PCL) and polylactic acid (PLA) are used for making sutures or as scaffolds for cell growth.[8–11] These materials must be sterilized before use. One possible technique is exposure to UV-C germicidal. Knowing the mechanical and physical behavior of these polymers during the time of exposure to UV-C, we will be able to define their limits of use. It is important to consider that the mechanical and physical nature (inside and on the surface) of pure and blended biopolyesters should remain as unchanged as possible during their use for a correct application of these materials.

In this work, PLA and PCL were studied pure and mixed in a ratio of 50:50 by weight and chemically compatibilized with Ethyl Ester L-Lysine Triiso-cyanate to know their mechanical and physical performances both before and during exposure to UV-C. Very few literature data are present about this issue and the scientific community needs of more deepness, especially in this historical pandemic time.

2. Experimental Section

Poly(lactide) (i.e., PLA, purchased from FKUR company, code BioFlex-6510, M_n = 197 000 Da) and poly(ϵ-caprolactone) (i.e., PCL, purchased from Sigma–Aldrich, M_n = 80 000 Da) were both dried overnight at 50°C before processing. The PLA/PCL blend was obtained in a Brabender Plasticorder PL2000 (T = 180°C, 30 rpm, 15 min) to prevent PLA degradation.[12] The compatibilizer molecule of Ethyl Ester L-Lysine Triiso-cyanate (code: LTI purchased by Infine Chemicals Ltd., Shanghai, China) was added in 1 phr amount to the blend during the mixing after 5 min. The compatibilized blend (code BL50/50) was subsequently compressed in a stainless-steel mold measuring 12 cm × 12 cm, 1 mm thick, at 180°C, 100 bar for 10 min by means of a hot press (Campana-DGTS srl, Milano, Italia), with a Teflon release films (thickness 300 μm), and subsequently water cooled. Dog bone samples for the tensile test were obtained from a Ray-Ran cutter according to ASTM D-638 standard.

The *simulation of the degradation* of the material took place in a black chamber at 25°C by a Stereo Glass lamp (model UVG54, P = 6 W, irradiation = 2200 mW cm^{-2}, wavelength = 254 nm of UV-C rays), with a distance sample/light source of 15 cm (**Figure 1**a). The UV-C exposure time has been indicated in each sample by adding the letter "U" after the code, with the number of the hours (4–8–16 and 32 h).

Sample's *surface roughness* (*Ra*) was calculated by Surftest roughness tester SJ-210- Series 178 (Mitutoyo S.r.l., Milan, Italy) considering that:

$$Ra = \frac{1}{N}\sum_{i=1}^{n} |Yi| \quad (1)$$

A. Visco, C. Scolaro, H. Bellhamdi, A. Grasso
Department of Engineering
University of Messina
C.da di Dio, Messina 98166, Italy
E-mail: annamaria.visco@unime.it; cristina.scolaro@unime.it
A. Visco, A. Grasso
Institute for Polymers, Composites and Biomaterials-CNR IPCB
Via Paolo Gaifami 18, Catania 95126, Italy

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/masy.202100330

DOI: 10.1002/masy.202100330

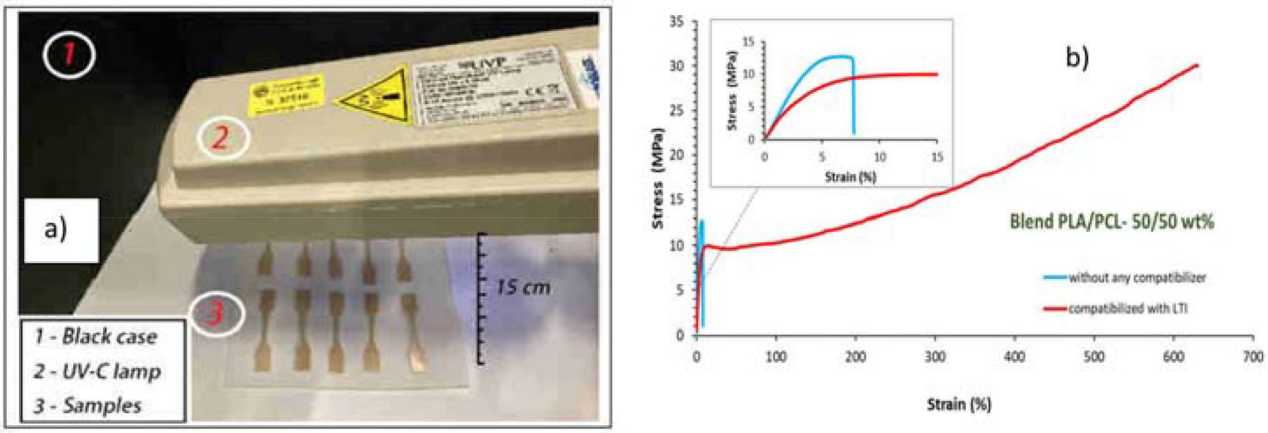

Figure 1. Image schematic system of UV-C test a); stress–strain curves of BL50/50 without and with the LTI compatibilizer b).

where *Ra* represents the arithmetic mean of the absolute values of the deviations of the evaluation profile (*Yi*) from the mean line.

Differential scanning calorimetry (DSC) was performed under nitrogen flow at a flow rate of 50 mL min^{-1}, from room temperature to 200°C, with a heating rate of 10°C min^{-1} and water cooling by a TAQ500 instrument (TA Instruments, New Castle, DE, USA).

Contact angle θ have been evaluated by the sessile drop method (Prototype, Engineering Department, Messina University, Italy) which measures the contact angle "theta" (θ) of 1 µL drop of liquids (deionized water, or human blood) of on the horizontal surface of the sample[13]:

$$\theta_w = 2\text{arctg}\left(\frac{2h}{d}\right) \quad (2)$$

$$\theta_Y = \arccos\left(\frac{\cos\theta_w}{r}\right) \quad (3)$$

where d is the diameter and h is the height (both in mm) of the drop, θ_w the Wenzel angle, r the surface roughness, and θ_Y is the Young contact angle of equilibrium on perfectly smooth surface. Human blood was extracted from a healthy adult volunteer in a clinical laboratory of biological analyses and immediately stored in the original sterile tube (BD Vacutainer K3E) with 5.4 mg ethylenediaminetetraacetic acid (EDTA) at a temperature between 2°C and 6°C. The EDTA solution inhibits the coagulation cascade, preserving the blood.[14]

3. Results

LTI chemically compatibilizes the two biopolyesters, usually immiscible, by means of a reactive mixing which forms crosslinks with isocyanic bridges.[11,15] This is demonstrated by the stress–strain curves that radically modify the mechanical behavior of the mixture from brittle to ductile after the addition of LTI (Figure 1b). The following results show the physical and mechanical behavior of the all the materials (pure and blended with LTI) tested under UV-C lamp. **Figure 2** shows the normalized static tensile test parameters as of the exposure times.

PLA is the stiffest and least deformable material of all, as expected.[16] In addition, PLA is also the one with the least resistance to photodegradation after 32 h of exposure. It becomes brittle because the modulus increases by 58% (Figure 2a), the stress at yield decreases of 26% (Figure 2b), strain at yield decreases by 82% (Figure 2c), and the work at break in decreases by 83% (Figure 2d).

PCL, on the other hand, is the most ductile polymer and it holds this feature better than PLA during UV-C exposure. In fact, after 32 h its stiffness improves by 11%, the stress at yield decreases of 46%, its strain at yield decreases of by 41%, and its breaking work decreases by 52%. The blend generally shows an intermediate behavior, demonstrating the good compatibility between the two materials. It has a fair stiffness (like PLA), ability to deform (like PCL), and resistance to photochemical degradation (like PCL). The yielding strength decreasing is reasonably due to the polymeric chain scission, molecular weight change, and Tg decreasing. Both PLA and PCL have a hydrophobic behavior toward distilled water (DW, see **Figure 3**a) and even more toward blood ($\theta > 90°$, see Figure 3b). The PLA and PCL's wet ability changes after 16 h of exposure to UV-C rays because it progressively decreases becoming hydrophilic ($\theta < 90°$). This result suggests that both biopolyesters are sensitive to UV-C rays. The blend has a greater contact angle than pure materials, with hydrophobic behavior both toward DW and toward blood ($\theta > 90°$). Therefore, the blend showed greater stability than the pure components for the whole period analyzed.

The DSC curves of pure PLA, PCL, and the BL50/50, before and after 32 h of UV-C exposure, are shown in **Figure 4**.

As already verified, PCL has a higher crystalline degree than PLA.[17] Both pure materials change their structural organization after UV-C exposure with a decrease in melting temperature (from 69.4°C to 65.9°C in PCL, and from 160.7°C to 159.2°C in PLA) and a growth in crystalline degree (of +80% in PCL and of +27% in PLA), according to the probable chemi-crystallization phenomena already observed in literature, under UVB rays and for longer exposure times (see Figure 4a,b).[18,19] The melting temperature of the single components in the mixture remains almost unchanged after 32 h of exposure to UV-C rays (~68°C in PCL, and ~157°C in PLA). The degree of crystallinity does not increase, as observed in the individual components since

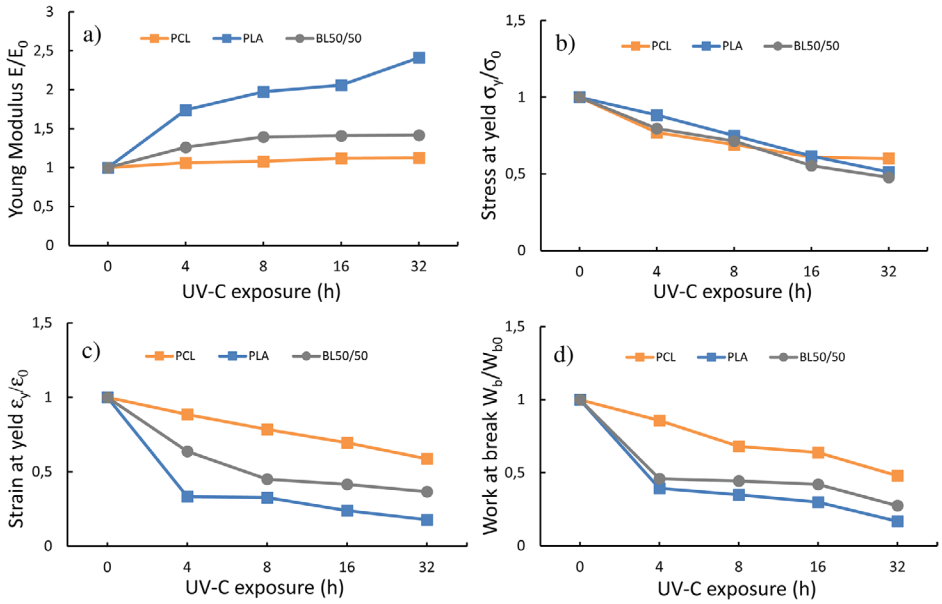

Figure 2. Normalized values of Young modulus a), stress at yield b), strain at yield c), and work at break d) versus the UV-C exposure time of PLA, PCL, and BL50/50. PCL, polycaprolactone; PLA, polylactic acid.

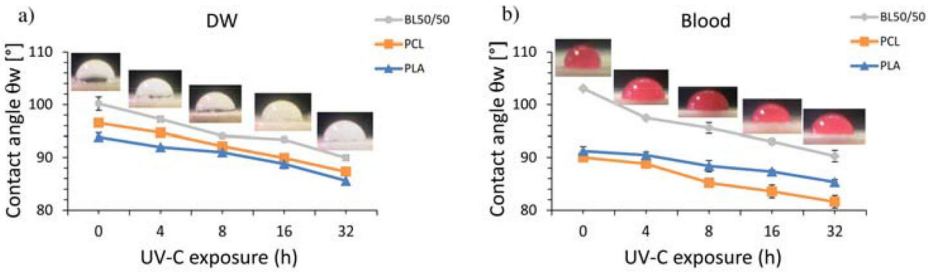

Figure 3. Distilled water (DW) a) and blood b) contact angle values of pure materials and the blend versus the UV-C exposure time.

the presence of cross-links inhibits the chemi-crystallization reaction. Rather, degree of crystallinity decreases of ~10%–20% in both pure components (see Figure 4c). This confirms the greater stability of the mixture to photodegradation compared to the individual components, due to its cross-linked structure.

4. Conclusions

In this research, PLA and PCL (pure and blended) were subjected to UV-C irradiation for 32 h at room temperature to simulate the sterilizing action that is applied to medical devices based on these biopolymers. UV-C rays, used for disinfection, act as germicides against the spread of viruses (such as the current Covid-19), and fall within the wavelength range between 200 and 280 nm, which is more powerful than that of rays UVB and UVA. The purpose of this study was to understand the variations in the mechanical and physical performance of biopolymers, as they are and blended, due to the photodegradable action during exposure to such radiations.

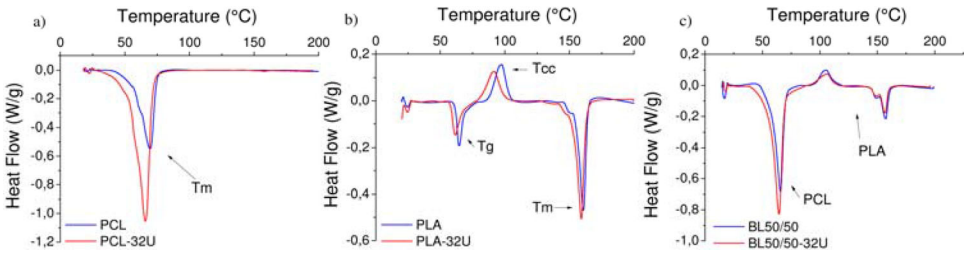

Figure 4. DSC curves of PCL a), PLA b), and BL50/50 c) before and after 32 h of UV-C ray exposure. DSC, differential scanning calorimetry; PCL, polycaprolactone; PLA, polylactic acid.

Experimental results suggested to us that pure materials both undergo photodegradation more than the compatibilized mixture. The better resistance of the blend is due to its cross-linked structure formed by isocyanic bridges during the chemical reaction with LTI, thus avoiding the excessive embrittlement typical of PLA. Therefore, the mixture maintains a ductile performance, a thermal stability, and a hydrophobic behavior both toward the DW and the blood during the 32 h of exposure to UV-C rays.

Future studies could consider adding inert fillers of inorganic nature to the mixture as suggested by the scientific literature to increase the resistance to photodegradation and therefore the duration over time of these materials for biomedical applications.[19]

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Received: August 31, 2021
Revised: November 1, 2021

[1] F. Arregui, F. Gavara, J. Soriano, L. Pastor-Jabaloyes, *Water* **2018**, *10*, 612.
[2] S. D. Flint, M. M. C. Stephan, *Ecology* **1984**, *65*, 3.
[3] N. P. Tipnis, D. J. Burgess, *Int. J. Pharm.* **2018**, *544*, 455.
[4] M. Elbay, T. Tanir, A. Kiziltay, V. Hasirci, N. Hasirci, *J. Biomater. Sci.-Polym. Ed.* **2018**, *29*, 863.
[5] E. Baran, H. Erbil, *Colloids Interfaces* **2019**, *3*, 43.
[6] P. Gijsman, G. Meijers, G. Vitarelli, *Polym. Degrad. Stab.* **1999**, *65*, 3.
[7] H. J. Haroosh, Y. Dong, G. D. Ingram, *J. Polym. Sci. Polym. Phys.* **2013**, *51*, 1607.
[8] H.-M. Chen, L. Wang, S. B. Zhou, *Chinese J. Polym.* **2018**, *36*, 905.
[9] M. Herrero-Herrero, *Eur. Polym. J.* **2018**, 11.
[10] M. Lopes, B. Cruz, P. Westerhoff, *Environ. Sci. Technol.* **2019**, *53*, 10880.
[11] A. Visco, D. Nocita, A. Giamp, S. Ronca, G. Forte, A. Pistone, C. Espro, *J. Mech. Behav. Biomed.* **2017**, *68*, 308.
[12] ASTM D7334-08, *Am. Soc. Test. Mater.* **2013**, 05.06, Reapproved, 1.
[13] A. Marmur, N. V. Brill, **2009**, pp. 1–18.
[14] R. M. Bertina, B. P. K, T. Koster, F. R. Rl, R. J. Dirven, H. de Ronde, P. A. V, P. H. Reitsma, *Nature* **1994**, *369*, 64.
[15] D. Nocita, G. Forte, S. Drakopoulos, A. Visco, A. Gianporcaro, S. Ronca, *Polymer* **2017**, *132*, 252.
[16] M. Catauro, C. Scolaro, F. Barrino, A. Visco, *Macromol. Symp.* **2020**, 389.
[17] A. Visco, C. Scolaro, A. Giamporcaro, S. De Caro, E. Tranquillo, M. Catauro, *Polymers* **2019**, *11*, 901.
[18] D. C. França, D. D. Morais, E. B. Bezerra, E. M. Araújo, R. M. R. Wellen, *Mater. Res.* **2018**, *21*, e20170837.
[19] E. Olewnik-Kruszkowska, *J. Therm. Anal. Calorim.* **2015**, *119*, 219.