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Innovative solutions for thermal energy storage deployment

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Preface

It was a pleasure for Prof. Luisa F. Cabeza and the GREiA research group full team at the University of Lleida (Spain) to organize the ***Eurotherm Seminar #116 “Innovative solutions for thermal energy storage deployment”*** from May 24th to 26th, 2023, in Lleida (Spain).

This seminar did bring together researchers and practitioners from academia and industry, who are working in the rapidly expanding field of thermal energy storage (TES).

The most recent trends in such areas as novel storage materials, advanced storage concepts and configurations, TES for renewable energy systems, TES in buildings and industry, use of advanced techniques such as artificial intelligence in TES, and social, environmental, and educational aspects.

Theoretical, numerical, and experimental approaches will be presented for the entire range of applications, from material characterization to complete storage systems.

We want to thank all participants to the conference.





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***In-situ* Studies on Sulfonate Polyether Ether Ketone (SPEEK)-based Composite Coatings for Thermochemical Heat Storage**

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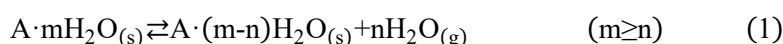
Abstract

Innovative Calcium Lactate/Sulfonate Polyether Ether Ketone (CaL/SPEEK) composite coatings were synthesized and characterized for investigating their structural and morphological modification during hydration/dehydration cycles through *in-situ* techniques. These studies can certainly provide an in-depth understanding of the reaction mechanism and materials changes during the charging/discharging operations, thus leading to valuable information for the advancement of TES materials. The SPEEK, being water vapor permeable, allowed the mass transfer during the CaL hydration and dehydration steps. What is more, the flexibility of the matrix allows the volume shrinkage/expansion of the salt caused by the cyclic dehydration/hydration reactions without significant damages. Such encouraging results support the idea of considering the coating technology for effective TCS applications.

Keywords: sulfonate polyether ether ketone (SPEEK), organic salt hydrates, calcium lactate, thermochemical heat storage, composite coatings, *in-situ* characterization

1. Introduction

Low-grade waste heat can be recovered through thermochemical heat storage (TCS) systems operating with salt hydrates through the following reversible reaction [1]:



Heat is transferred from a selected source to the salt hydrate, and the dehydration reaction takes place (storage step). The heat is stored for as long as the salt and kept in the dehydrated form. When heat is required, water is made accessible to the salt, the reversible hydration takes place, and heat is released (release step). Nevertheless, these materials suffer of severe issues caused by their tendency to undergo deliquescence, such as chemical instability, mass transfer hindering, and high-pressure drops that would lead eventually to the system failure, but also corrosion issues due to the dripping of the salt solution to other metal components of the systems [2,3]. Recently, a poorly soluble organic salt hydrated, calcium L-lactate pentahydrate (CaL), has been proposed as a novel TCS material in order to reduce and/or avoid deliquescence phenomena under operating conditions, albeit able to coordinate a high number of water molecules and stable under operation condition. Indeed, CaL can operate under conditions typical for low-temperature heat storage systems (20-120°C) with a heat storage capacity of ~1021 kJ/kg. In order to enhance the diffusion of vapour during the hydration process while increasing also the heat transfer efficiency with the heat exchanger, an innovative Calcium Lactate/Sulfonate Polyether Ether Ketone (CaL/SPEEK) composite coating was synthesized. We here investigated the structural and morphological modification during hydration/dehydration cycles of the coatings through *in-situ* studies. Specifically, a characterization protocol coupling temperature scanned X-ray diffraction (XRD), environmental scanning electron microscopy (ESEM) and thermogravimetric dynamic vapor sorption analysis was proposed. These studies can certainly provide an in-depth understanding of the reaction

mechanism and materials changes during the charging/discharging operations, thus leading to valuable information for the advancement of TES materials.

2. Materials and methods

CaCl was purchased from Sigma Aldrich, (purity >98%, $[\text{CH}_3\text{CH}(\text{OH})\text{COO}]_2\text{Ca} \cdot 5\text{H}_2\text{O}$) in form of fine powder. For the coating preparation SPEEK was solubilized in dimethylformamide (DMF), and then the organic hydrated salt is added, in different proportion (50-80% wt.). The coating deposition of the resulting solutions was performed, using drop casting technique, on aluminium strips. Morphological observation of CaL/SPEEK coatings while hydrating was carried out by an environmental scanning electron microscope (ESEM, FEI Quanta 450) operating with an accelerating voltage of 5 kV. Initially, the material was dehydrated in oven at 80 °C for 2h and then placed in the ESEM chamber for acquiring the micrographs under controlled water vapor atmosphere. The relative humidity (RH) has been varied between 0-90% by tuning the temperature and water vapor pressure in the ranges of 5-40 °C and 10-800 Pa. A full hydration/dehydration cycle in a controlled (temperature, relative humidity) and measurable (mass change) environment has been performed through a thermogravimetric dynamic vapor sorption system (DVS Vacuum Surface Measurement Systems). The coating structure was investigated by temperature scanned X-ray diffraction (XRD). Water vapor permeability was also investigated.

3. Results and discussion

The as prepared coatings, regardless the CaL content, appear as a transparent layer on the aluminum lamina (Figure 1a) and, due to final drying after deposition, CaL is in its dehydrated form as can be inferred from XRD analysis (Figure 1b, black curve). The CaL is fully dissolved into the polymeric matrix. After hydration the material turns in its crystalline phase structure (Figure 1b, red curve).

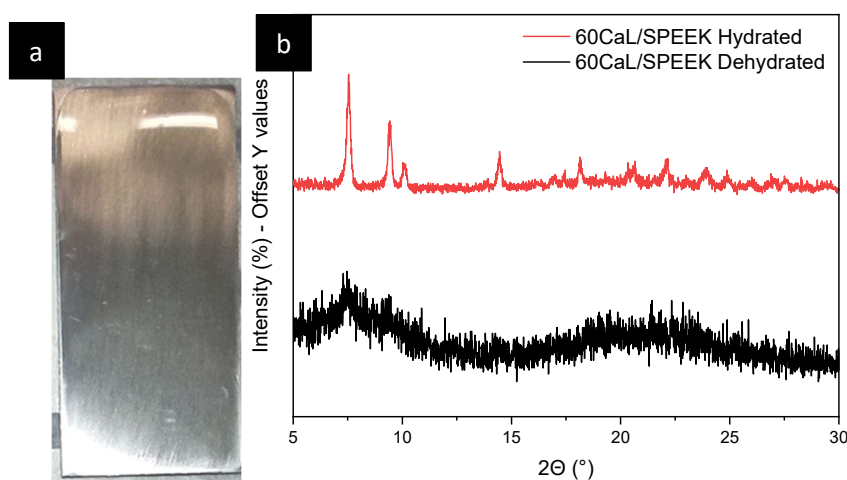


Figure 17. (a) CaL/SPEEK coating on aluminum lamina with 60% wt. of CaL (code: 60CaL/SPEEK). (b) XRD analysis on

The ESEM analysis conducted on the CaL/SPEEK coating simulated the hydration/dehydration reaction conditions. This approach allowed to visually evaluate the morphological modification while hydrating and dehydrating the CaL salt embedded in the water vapor permeable SPEEK. The dehydration and hydration conditions were obtained varying temperature and water vapor pressure in the ranges of 5-40 °C and 10-800 Pa, respectively, in order to vary the chamber RH at which the material is exposed. For brevity, *in-situ* ESEM micrographs of only 60%CaL/SPEEK are shown in Figure 2. The material in its initial state (Figure 2a) shows a smooth surface with the CaL finely dispersed in the polymeric matrix. After hydration for 2h at 95% RH a needle-like particles still embedded in the SPEEK appear on the analysed surface. The final step of the dehydration carried out for 2h at 60 °C and 0% RH brings to the formation of some cracks on the coating surface, albeit the structural integrity is still preserved.

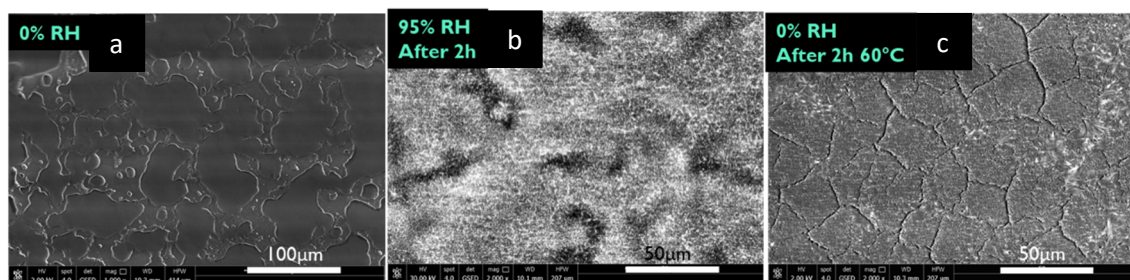


Figure 18. ESEM analysis simulating the hydration/dehydration cycle by varying the RH: (a) RH=0% initial state; (b) after 2h at 95% RH – hydration state; (c) after 2h at 60°C and 0% RH – dehydration state.

4. Conclusions

Innovative Calcium Lactate/Sulfonate Polyether Ether Ketone (CaL/SPEEK) composite coatings were synthesized and characterized for investigating their structural and morphological modification during hydration/dehydration cycles through *in-situ* techniques. The environmental SEM analysis simulated the hydration/dehydration reaction conditions, thus allowing the evaluation of the interaction between the salt and the water vapor environment in the SPEEK. The results show the complete dissolution of the salt into the polymeric matrix. SPEEK, being water vapor permeable, allowed the mass transfer during the CaL hydration and dehydration steps. Additionally, despite some cracks are visible on the coating surface after a hydration/dehydration cycle, the flexibility of the matrix allows the volume shrinkage/expansion of the salt caused by the cyclic dehydration/hydration reactions without significant damages. These encouraging results paved the way for breaking new ground on CaL/SPEEK composite coatings for TCS applications. The hydration/dehydration kinetics are still object of investigation and as well as their stability upon several hydration/dehydration cycles.

Acknowledgments

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