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Synthesis and Testing of Polymer Crosslinked Materials for Applications in Energy Storage and Li-S Batteries

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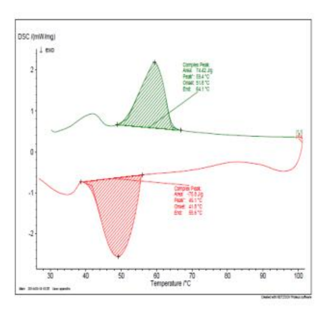
P. Tristão[1], H. Costa[1], P. Kadhirvel[1], R.C.S. Dias[1,], M.R.P.F.N. Costa[2]. (1) LSRE-Instituto Politécnico de Bragança, Quinta de Santa Apolónia, 5300, Bragança, Portugal; (2) LSRE-Faculdade de Engenharia da Universidade do Porto, Rua Roberto Frias s/n, 4200-465, Porto, Portugal; [*]rdias@ipb.pt.*



The feasibility of making polymer crosslinked materials with applications in improving energy efficiency is here demonstrated. The encapsulation of phase change materials (PCM), for thermal energy storage/release, and sulphur inverse-vulcanization (producing materials with useful electrochemical properties) are here used as case studies. Effective thermal properties of the produced encapsulated PCM materials were measured through TG/DSC analysis (see graphical abstract). Designing tools allowing the synthesis of materials with tailored thermal properties were exploited (e.g. use of controlled radical polymerization). Sulphur-rich networks are synthetized using different operation conditions (e.g. considering RAFT/NMRP). Testing of these materials in Li-S batteries to assess the impact of the synthesis conditions in their electrochemical properties is ongoing work.

Introduction

Energy efficiency is nowadays a central issue in human society. Many polymer materials play a key role in this context. Solar energy materials or windmill turbine blades are two well-known examples of such application areas.

In this work, we present our current research on the development of two different classes of polymeric materials with potential applications for improving energy efficiency: phase change materials (PCM) for thermal energy storage [1] and inverse-vulcanized sulphur materials for usage in Li-S batteries [2].

Materials and Methods

Methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) were used as monomer and crosslinker in the PCM encapsulation experiments. Paraffin wax (melting point in the range 50 to 60 °C) and n-octadecane (melting point in the range 26 to 29 °C) were selected as phase change materials. AIBN (2,2'-azobis(2-methylpropionitrile)) and BPO (benzoyl peroxide) were chosen as thermal initiators in this experimental program. This research also had an additional goal of assessing the use of controlled radical polymerization (namely RAFT polymerization) in the encapsulation process and the effect on the thermal properties of the resulting materials. Different commercially available RAFT agents are tried with this purpose, namely CPA (4-cyano-4-(phenylcarbonothioylthio) pentanoic acid) and CPT (2-cyano-2-propyl dodecyl trithiocarbonate). Polyvinyl alcohol (PVA) was chosen as the suspending agent in these encapsulation experiments. Elemental sulphur and 1,3-diisopropenylbenzene (DIB) were used in the inverse-vulcanization process here studied. Our aim was also the study of the effect of using controlled radical polymerization (CRP) on the properties of the sulphur/vinyl materials produced. Besides RAFT polymerization, Nitroxide-Mediated Radical Polymerization (NMRP) was also tried using TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) as chain controller agent.

Encapsulation of PCM was performed using aqueous suspension crosslinking polymerization. Polymer particles were thus obtained (see Figure 1). A Parr 5100 pressurized glass reactor with 1 L maximum capacity was used to perform these aqueous suspension experiments. The reactor is equipped with a magnetic drive internal stirrer including double turbine type six-blade impellers at 45°. The reactor can work above atmosphere pressure (argon is used for this purpose). A total polymerization mass of 800 g was typically used in these experiments. Polymerizations were performed with a stirring speed of 600 rpm. In both crosslinking processes (PCM encapsulation and sulfur inverse-vulcanization), reaction samples collected at different polymerization times and final products were analyzed by SEC/RI/MALLS. The aim of these measurements was the searching for details concerning the molecular architecture of the products and the mechanisms involved in the crosslinking reactions. Samples were diluted in THF and filtered in order to inject the soluble fraction in the SEC/RI/MALLS system. The SEC/RI/MALLS apparatus is composed of a Polymer Laboratories PL-GPC-50 integrated SEC system with differential refractometer working at 950 ± 30 nm, attached to a Wyatt Technology DAWN8^{+} HELEOS 658 nm MALLS detector. The polymer samples were fractionated by molecular size using a train of 3 GPC columns PL gel (300 mm × 7.5 mm) with nominal particle size 10 μm and pore type MIXEDB-LS, maintained at constant temperature of 30 °C and using THF as the eluent at a flow rate of 1 ml/min. Thermal properties of the produced encapsulated PCM materials were measured using Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC). Netzsch instruments TG 209 F3 and DSC 204 F1 were used in these measurements.

Results and Discussion

Results showing the synthesis of encapsulated PCM materials with useful thermal properties are presented in Figures 1 to 5 and also in the graphical abstract. Formation of PCM particles and analysis of their thermal properties is illustrated in these figures using MMA/EGDMA/Paraffin as chemical system.

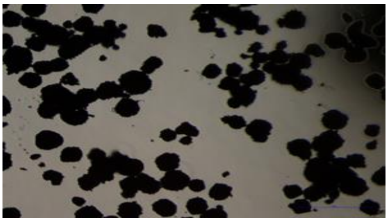


Figure 1. Microscopic images of encapsulated PCM particles produced using aqueous suspension polymerization of MMA/EGDMA (for shell formation) including paraffin wax. Polymerization at 85 °C.

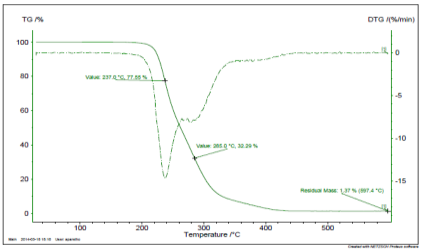


Figure 2. TG analysis for an encapsulated PCM (MMA/EGDMA/Paraffin) showing starting of thermal degradation above 200 °C, which confirms the effectiveness of the encapsulation process.

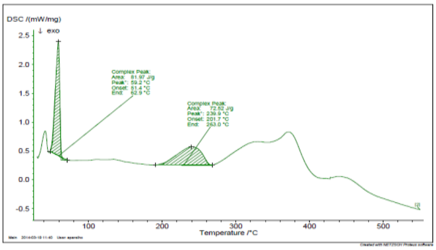


Figure 3. DSC analysis for an encapsulated PCM (MMA/EGDMA/Paraffin) showing the occurrence of a heat absorption peak in the region 51.4 to 62.9 °C during the heating process of the material. This observation confirms the usefulness of the synthetized PCM to store thermal energy. DSC analysis for the same material correspondent to the release process is presented in the graphical abstract of this work.

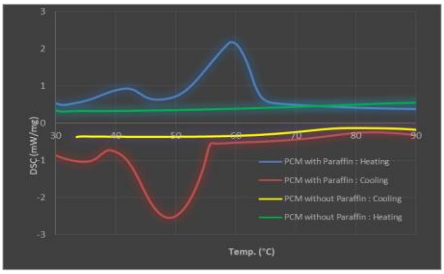


Figure 4. DSC analysis for an encapsulated PCM (MMA/EGDMA/Paraffin) and for just the encapsulation material (MMA/EGDMA without Paraffin), showing the effectiveness of the encapsulation process to generate materials with ability to store and release thermal energy. Heating and cooling processes are showed in both cases.

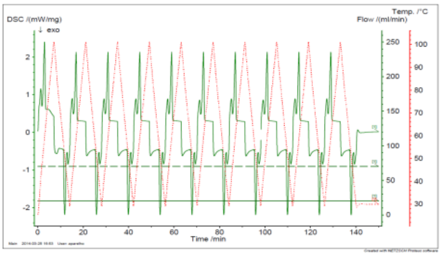


Figure 5. Cyclic DSC analysis (10 cycles of heating/cooling) for an encapsulated PCM (MMA/EGDMA/Paraffin) showing that the thermal properties of the material are not degraded in these cyclical thermal processes.

The inverse-vulcanization process of elemental sulphur with DIB is depicted in Figure 6. The different stages up to the formation of a processable material with useful electrochemical properties are illustrated in this picture. The experimental program performed includes the change of the initial composition (S/DIB amounts), feed policies (addition of DIB during the heating of sulphur) and use of CRP (NMRP and RAFT).

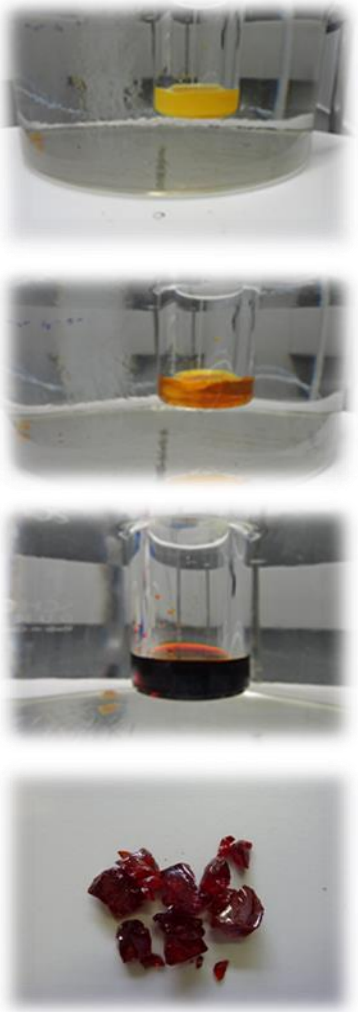


Figure 6. Different stages and final product of the sulphur inverse-vulcanization process with DIB (1 - sulphur melting at ~ 120 °C, 2 – S_8 ring opening at ~ 160 °C with radical formation, 3 – S/DIB copolymerization at 185 °C, 4 – final solid product).

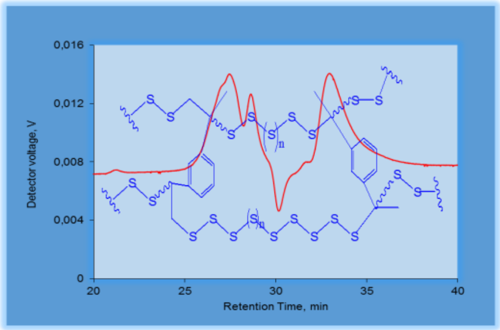


Figure 7. SEC/RI/MALLS chromatogram of the soluble fraction of a product resulting from the sulphur inverse-vulcanization process with DIB. With this analysis is possible to identify the formation of sulphur polymeric structures. These materials are processable copolymers that can be used as active materials in Li-S batteries [2].

In Figure 7 is presented a SEC/RI/MALLS chromatogram of a sample (soluble fraction) resulting from the sulphur inverse-vulcanization showing the formation of sulphur polymeric structures. Our goal is finding links between synthesis conditions, the molecular structure and the electrochemical properties of these materials.

Conclusion

The feasibility for generation of polymer crosslinked materials with applications in energetic efficiency is here demonstrated. Encapsulation of PCM (for thermal energy storage/release) and sulphur inverse-vulcanization were used as case studies. Effective thermal properties of the produced encapsulated PCM materials were shown through TG/DSC analysis. At the end of this research, hopefully, designing tools allowing the synthesis of materials with tailored thermal properties should be improved. The feasibility of the generation of sulphur-rich networks was also shown under different synthesis conditions. Ongoing studies should allow the assessment of the impact of crosslinking process in the electrochemical properties of the materials (e.g. through testing in Li-S batteries).

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