Phenolic resin/PEO-PPO block copolymer composite materials as phase change materials (PCM) for latent heat thermal energy storage (LHTES)

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Felipe Rodríguez*, Betty L. López

Grupo Ciencia de los Materiales, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, Calle 70 #52-21, Medellín, Antioquía, Colombia

ABSTRACT

Many block copolymers can be used in the soft-template synthesis procedures of OMC (ordered mesoporous carbon). Some of the most common are block copolymers composed of PEO [poly (ethylene oxide)] and PPO [poly(propylene oxide)], like the triblock copolymer Pluronic F127 ($PEO_{106}PPO_{70}PEO_{106}$). DSC analysis of Pluronic F127 shows endothermic and exothermic peaks (at 54 and 30 °C) due to the melting and crystallization of the PEO blocks. This indicates that this commercially available block copolymer could be used as a phase change material (PCM).

Nanostructured polymer blends like the phenolic resin/PEO-PPO block copolymer composite materials prepared using some soft-template synthesis procedures of OMC could be useful as a solid-solid PCMs if the crystallization of the PEO blocks of the block copolymer is possible within the material.

DSC analysis of particles of a phenolic resin/F127 composite material (material P9) prepared using one soft-template synthesis procedure of OMC in solution in basic media (thermal treatment of an alkaline (pH around 9) aqueous solution of F127 and a phenol-formaldehyde resin, followed by centrifugation) shows no evidence of an endothermic or exothermic process. A reduction of the pH of the phenol-formaldehyde resin aqueous solution (from about 9 to 8.5) before the thermal treatment has an effect in the phase separation, that in this case leads to the formation of two layers; a polymer rich phase in the bottom of the reactor and above a layer composed mainly by water. Thermal treatment of the polymer rich phase at 100 °C for 24 h yields a solid composite material (material P8.5). DSC analysis shows an endothermic peak (35 °C) in every cycle, attributable to the fusion of PEO crystalline domains. This indicates that the crystallization of the PEO blocks is possible in this material; but there is not an obvious exothermic peak.

The material P8.5 has a higher F127 content (around 60%; estimated by TGA) than the material P9 (around 40%); this indicates that in these composite materials the final block copolymer content has an effect on the crystallization of the PEO blocks.

Other synthesis procedures of OMC like EISA (evaporation induced self-assembly) provide a better control of some characteristics, like the block copolymer content. Materials with a high F127 content (60% m/m) were prepared by EISA (controlled evaporation of the solvent of an ethanolic solution of F127 and a phenol-formaldehyde resin, followed by a thermopolymerization process at 100 °C for 24 h). The DSC analysis shows an endothermic peak (38 °C) and an exothermic peak at a low temperature (−20 °C).

These results indicate that the synthesis procedures of OMC using a phenolic resin and a PEO block copolymer could be a suitable alternative for the production of solid-solid PCMs.

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1. Introduction

Thermal energy can be stored as sensible or latent heat in a TES (Thermal energy storage) system. Latent heat thermal energy storage (LHTES) is an efficient way of storing this type of energy and there is an increasing interest in the use of some organic PCMs. These materials can provide a high energy storage density and a low temperature difference between storage and release during the solid-liquid phase transition. Many different organic compounds can be used as a solid-liquid PCMs. Some of the most common organic PCMs are paraffins, fatty acids and polymers like PEO. There are several detailed reviews about PCMs and their applications [1–4].

In many applications of these organic PCMs it is necessary to perform an encapsulation process to avoid the leakage of the liquid PCM or chemical reactions. There are several reports about the use of organic and inorganic materials like urea–formaldehyde resins, melamine–formaldehyde resins, polyurethanes or silica to create a shell around PCM particles with a small diameter (1–1000 μm) [1].

There is also interest in the synthesis of PCMs that can be able to remain solid during the phase transition in the LHTES process (solid-solid PCMs, also known as form stable or shape stabilized PCMs) [5–9].

Some inorganic-organic composites can be used as solid-solid PCMs. The SiO_2/PEO composite materials reported in Ref. [6] are solid at the phase transition temperature of the PCM if the silica content is higher than 15%. The use of an inorganic material like SiO_2 is also useful because it can increase the thermal conductivity of a solid-solid PCM. It has been reported that a PEO/SiO_2 composite with a 50% (w/w) of SiO_2 has a thermal conductivity that is 71.7% higher than the thermal conductivity of the PEO used in the synthesis [1]. Other materials that have a higher thermal conductivity than the organic PCM (like colloidal metallic particles or carbon nanotubes) can be used to increase the thermal conductivity of PCMs [1,10], like the Cu/SiO_2/PEO solid-solid PCM reported in Ref. [7].

Some organic-organic composite materials that can be used as solid-solid PCMs are synthesized by copolymerization of a polymeric PCM (usually PEO) and a suitable polymer with a higher melting point. This approach has been used in the synthesis of solid-solid PCMs, like some thermoplastic polyurethanes that can be processed into different shapes [8]. It is also possible to prepare organic solid-solid PCMs using PEO as a PCM, glucose as a molecular skeleton and 4,4-diphenylmethanediisocyanate as the crosslinking agent. Composites prepared using this type of polymeric PCMs and PEO can be used as high performance solid-solid PCMs that have a heat of fusion that is almost equal to that of the pure PEO [9]. Some polymer blends [composed by a polymeric PCM (usually PEO) and a polymeric supporting material (like PMMA or cellulose)] can also be used as solid-solid PCMs [11,12].

These composite solid-solid PCMs have a solid structure that does not undergo a solid-liquid transition in the LHTES process and an organic PCM that does. The polymer network of a thermoset polymer (like a phenolic resin) in some nanostructured thermoset/block copolymer blends, like the materials prepared using some soft-template synthesis procedures of OMC [13–18], could make these materials useful as solid-solid PCMs. Many block copolymers can be used in soft-template synthesis procedures of OMC [17]. Some of the most common are block copolymers composed of PEO [poly (ethylene oxide)] and PPO [poly (propylene oxide)] blocks, like the triblock copolymer Pluronic F127 ($PEO_{106}PPO_{70}PEO_{106}$) [18]. If the crystallization of the PEO segments of the block copolymer is possible in this type of phenolic resin/PEO-PPO block copolymer nanostructured polymer blends, then these materials could be useful as solid-solid PCMs.

It has been reported that the crystallization of the poly(ethylene) blocks of a block copolymer is possible inside an organic-inorganic composite (PEO-poly(ethylene)/SiO_2) [19]. The crystallization of both blocks of a PEO-poly(ethylene) block copolymer is also possible inside a nanostructured thermoset/block copolymer blend [20].

However, to the best of our knowledge, the phenolic resin/PEO-PPO block copolymer composite materials prepared using some soft-template synthesis procedures of OMC have not been tested as solid-solid PCMs.

Some soft-template synthesis procedures of OMC, like EISA, are relatively simple and could be suitable for the production of PCMs. Also some modifications of these procedures [21–24] developed to change characteristics of the OMC (like the porosity), could be useful to change some properties of the materials (like the phase transition temperature) to make them more suitable as PCMs for specific applications.

This work shows that the DSC analysis of materials prepared with some soft-template synthesis procedures of OMC using a phenolic resin and a PEO block copolymer indicates that with some modifications these synthesis procedures could be a suitable alternative for the production of solid-solid PCMs.

2. Materials and methods

2.1. Materials

Pluronic F127 triblock copolymer ($PEO_{106}PPO_{70}PEO_{106}$), Phenol, aqueous formaldehyde (37%), ethanol (98%), aqueous HCl (37%) and Sodium hydroxide were purchased from Sigma-Aldrich.

2.2. Synthesis phenolic resin/F127 composite materials

2.2.1. Material P9
Synthesis was carried out using a slightly modified procedure for the preparation of micrometric particles of FDU-16 [13]. A low molecular weight phenolic resin (**resol A**) was synthesized by polymerization of phenol and formaldehyde at 70 °C during 30 min in the basic solution (pH around 9) having the following composition: 42/197/10/6000 mmoles of phenol/formaldehyde/NaOH/H_2O, respectively. Two solutions [resol A and aqueous solution of Pluronic F127 block copolymer (1/5555 mmoles of F127/H_2O, respectively)] were kept in an oil bath at 40 °C (the block copolymer solution under reflux in a reactor and the resol in a closed plastic container). After 15 min of stirring the resol was slowly added to the reactor. Then temperature was raised to 66 °C and the resulting solution was kept in the reactor under reflux for 4 days at this temperature. Next, temperature was raised again to 70 °C and the synthesis mixture was kept at this temperature for one day. The particles of the composite material (material P9) were separated from the continuous phase by centrifugation. These particles where redispersed in distilled water and then separated from the continuous phase twice. The concentrated dispersions of the composite materials were dried in a Petri dish in a vacuum oven at 30 °C.

2.2.2. Material P8.5
A reduction of the pH (from about 9 to 8.5) of a fraction of resol A was performed with a 7 M HCl aqueous solution before the synthesis. This fraction was labeled **resol B** and was used in the synthesis of the material P8.5 following the same procedure used in the synthesis of composite P9; however the stirring was stopped after 6 h and the thermal treatment after 16 h (since the phase separation in this case leads to the formation of two layers, a polymeric rich phase in the bottom of the reactor and a layer on top composed mainly by water). The polymer rich phase was extracted from the reactor and transferred to a Petri dish to perform a thermal treatment at 100 °C for 24 h in a vacuum oven.

2.2.3. Material PE
The synthesis was performed in acid media using a slightly modified synthesis by EISA similar to that reported in [21]. 0.8 g of F127 were dissolved in 4 g of ethanol and 0.5 g of a 0.2 M HCl aqueous solution. This solution was mixed with 2.5 g of resol C and 0.33 g of H_2O. After 2 h of stirring the solution was transferred to a petri dish to evaporate the solvent at 25 °C. After the solvent evaporation a thermal treatment at 100 °C for 24 h was performed. The final composite PE was scrapped off the petri dish to perform the analysis by DSC. The % (m/m) of F127 in this material is almost 60% due to the quantities of the precursors used in the synthesis.