

Preparation and Characterization of PEG/MDI/PVA Copolymer as Solid–Solid Phase Change Heat Storage Material

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ABSTRACT: In this article, a novel solid–solid phase change heat storage material was synthesized via a two-step condensation reaction of high molecular weight poly(ethylene glycol) (PEG4000) with poly(vinyl alcohol) (PVA) and 4,4'-diphenylmethane diisocyanate (MDI). To characterize the resulting product in comparison with pristine PEG4000, Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analyses, and polarization optical microscopy measurements were

employed to investigate functionality, thermal properties, and crystalline behavior. The results indicated that the crosslinking phase change material showed typical solid–solid phase transition properties, and its phase change enthalpy reached 72.8 kJ/kg. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2041–2045, 2009

Key words: heat storage materials; poly(ethylene glycol); phase change enthalpy

INTRODUCTION

Phase change materials (PCMs) are functional materials with energy storing and releasing properties. PCMs can impact the small environment around them by storing and releasing energy during phase change. Phase change heat of PCMs has two main characteristics: one is high enthalpy and capacity per unit volume and the other is that the temperature over the phase change process stays constant or changes slightly. PCMs are of great interest as they are one of the most important functional materials for storing thermal energy because of their high storage density and constant temperature during phase change.

The utilization of PCMs is extensive, such as in solar energy storage, waste heat recovery, smart air conditioning in buildings, temperature-adaptable greenhouses, electric appliances with thermostatic regulators, energy-storage kitchen utensils, insulative clothing, and so on.^{1–3} Especially today, as the energy crisis is becoming more and more serious, and PCMs have increasingly attracted attention.^{4,5} So far, a great number of organic, inorganic, polymeric, and eutectic compounds have been used as PCMs. Among them, solid–solid PCMs, which include polyhydric alcohol, crosslinked polyethyl-

ene, and some types of polymers and hydrated inorganic salts, are fairly recently developed functional PCMs which have been found to exhibit many desirable characteristics, (e.g., no liquid or gas generation, small volume change, no receptacles needed for sealing, easy shape processing, and being able to be used directly as a system material). They can obviously simplify fabrication procedures and cut down costs.^{6,7} However, there are several defects in most of the solid–solid PCMs reported in previous research, such as high transition temperature, low transition enthalpy, and unstable thermal properties. All these disadvantages greatly limit their application. In recent years, several attempts have been made to develop novel materials to overcome these defects, and composite polymeric solid–solid PCMs are in focus because of their excellent integrated performances.^{8,9} There are two approaches to prepare composite polymeric solid–solid PCMs. One approach is the physical approach in which the compound materials are obtained by dispersing PCMs into higher melting point polymeric materials which act as supporting materials; as long as the temperature is below the melting point of the supporting materials, the compound materials keep their solid shape, even when the PCM changes from solid to liquid. They are generally called shape-stabilized PCMs. The other approach is synthesis by chemical methods: chemical grafting, blocking, and crosslinking copolymerization are used to make good solid–liquid PCMs as the energy-storage working material components of solid–solid PCMs.¹⁰

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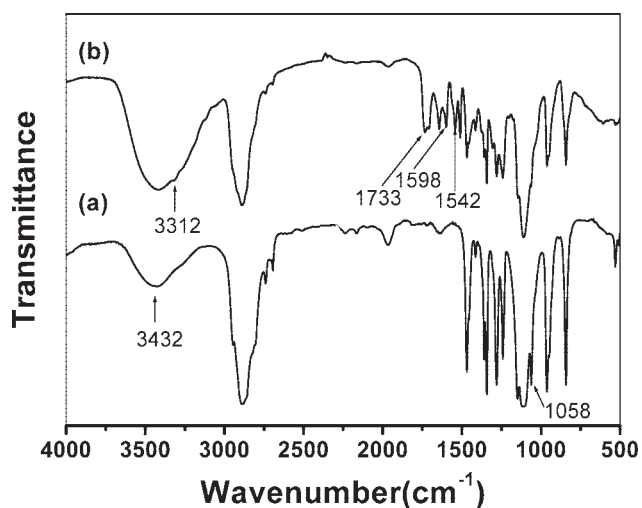


Figure 2 FTIR spectra of PEG4000 (a) and PEG/MDI/PVA copolymer (b).

50 mL/min. The heating/cooling rate of $10^{\circ}\text{C}/\text{min}$ was applied as the best choice to ensure high resolution of the DSC curves. Prior to use, the calorimeter was carefully calibrated with an indium standard: an empty aluminum pan was used as a reference.

RESULTS AND DISCUSSION

In curve (b) of Figure 2, an obvious association peak appeared at 3312 cm^{-1} , which was attributed to N–H groups interacting with carbonyl groups of the hard segment and ether bonds of the soft segment

through hydrogen bond forces. The characteristic absorption of primary hydroxyl at 1058 cm^{-1} disappeared, which was due to the reaction between the hydroxyl and isocyanate groups to form urethane consumed hydroxyl end groups. Accordingly, characteristic absorption of isocyanate at 2265 cm^{-1} was not found in curve (b) of Figure 2. As marked in the curve (b), amide bond I (1733 cm^{-1}), amide bond II (1542 cm^{-1}), and a vibration peak of conjugated double bonds of benzene ring (1598 cm^{-1}) were distinctly found. Therefore, we could draw the conclusion that a high molecular weight crosslinking copolymer had been gained through the chemical reaction of PEG, PVA, and MDI.

Figure 3 shows the heating/cooling cycle curves of PEG4000 and PEG/MDI/PVA tercopolymer. All samples were preheated to 100°C and kept for 10 min to remove any thermal history. Their phase change temperature corresponded to the peak point temperature that could be obtained, and the latent heat of fusion was evaluated by the integration of the peak. As shown in Figure 3, like PEG4000, PEG/MDI/PVA tercopolymer was also a transition reversible latent storage material. Pristine PEG4000, consisting of ethyl–ether linkage segments with active hydroxyl end groups that easily formed intermolecular hydrogen bonds, crystallized easily and had a high transformation enthalpy of $168.4\text{ kJ}/\text{kg}$. Expectedly, the DSC curve of PEG/MDI/PVA tercopolymer was similar to that of pristine PEG because its structure contained PEG units. The phase change enthalpy of PEG/MDI/PVA tercopolymer reached $72.8\text{ kJ}/\text{kg}$, which means that its endothermic and

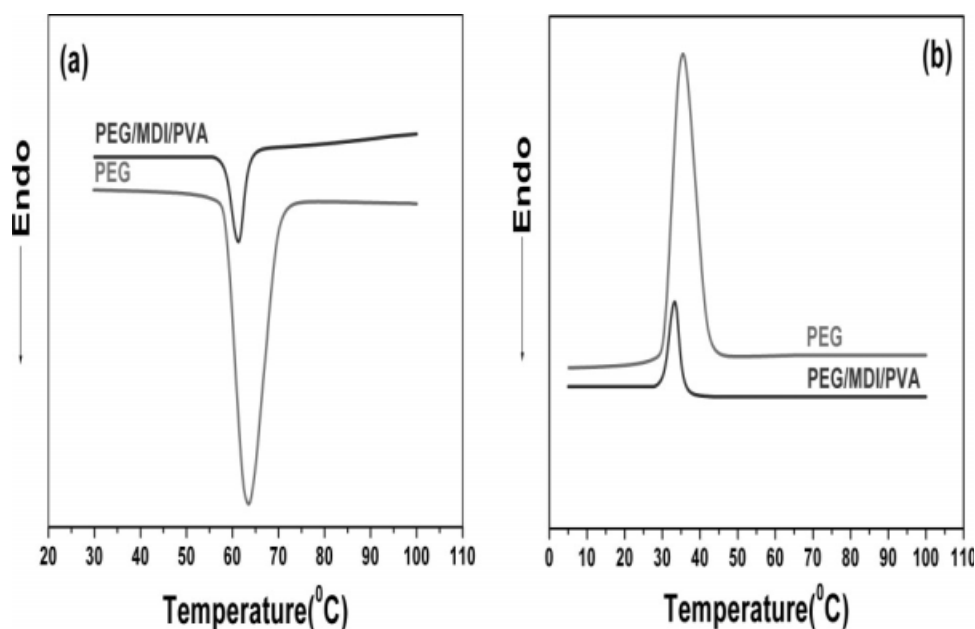


Figure 3 DSC heating (a) and cooling (b) curves of PEG4000 and PEG/MDI/PVA copolymer.

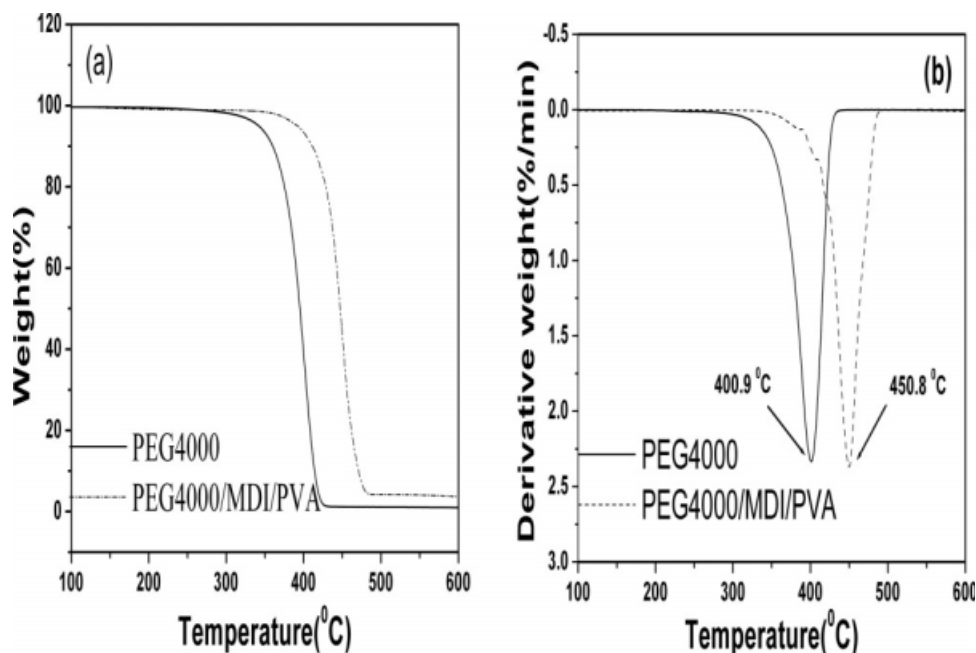


Figure 4 TGA (a) and DTG (b) curves of PEG4000 and PEG/MDI/PVA copolymer.

exothermic capacity had been weakened after cross-linking. Because of the presence of a crosslinked structure as well as rigid benzene rings in network, the number of segments available for the crystalline regions reduced, which consequentially led to the decline of enthalpy. The phase change point of PEG/MDI/PVA copolymer was slightly lower than that of pristine PEG, shifting from 63.4°C to 61.1°C. The segments near crosslinking sites were confined after active hydroxyl end groups of PEG reacted with isocyanate. Consequently the arrangement and orientation of PEG molecules were partially suppressed by the steric effect and the crystalline regions turned smaller, which caused the transition point to fall to a certain degree. The conclusion that crosslinking results in the decrease of phase change temperature and enthalpy agrees with the previous conclusion found by many researchers. The transition temperature of PEG/MDI/PVA tercopolymer was suitable for many applications such as solar energy storage, waste heat recovery, and temperature adaptable greenhouses. The novel solid–solid PCM with high phase change enthalpy will be a promising heat storage material and take the place of other similar energy-storage materials.

Figure 4 shows the TGA and DTG curves of PEG4000 and the PEG/MDI/PVA copolymer. It was observed that the PEG/MDI/PVA tercopolymer had better heat resistance, for its onset temperature and weight loss were 398.1°C and 2.6%, respectively, while those of pristine PEG4000 were 358.3°C and 3.8%. The absence of intermolecular hydrogen bond

interaction and the formation of soft ester bonds after condensation did not reduce the thermal resistance of PEG; on the contrary, thermal resistance of PEG/MDI/PVA tercopolymer increased to a certain extent because the introduction of rigid phenyl groups and the crosslinking network played a very important role in elevating the thermal resistance of PEG/MDI/PVA copolymer. The temperature at the maximum rate of weight loss increased by about 49.9°C for the PEG/MDI/PVA copolymer compared with pristine PEG4000 from DTG curves. Thus, the novel solid–solid PCM with good heat resistance will have application across a broad temperature range.

As shown in Figure 5(a,b), both pristine and copolymerized PEG had crystal spherulites at 25°C. Under the same test condition, the dimension of the spherulite of PEG/MDI/PVA tercopolymer was smaller than that of pristine PEG because of the restricted crystallization of PEG in the network. The presence of crosslinking did not alter the crystal form of PEG, but it limited degree of crystallization. Before the copolymer attained its transition temperature, with the increase in temperature, the spherulites showed no change; when the temperature approached transition point, the spherulites faded away and eventually disappeared. The POM micrograph of PEG/MDI/PVA copolymer at 100°C is shown in Figure 5(c): no spherulites appeared, which demonstrated that the crystal PEG had completely transformed to an amorphous state. The synthesized PCMs remained in the solid state during

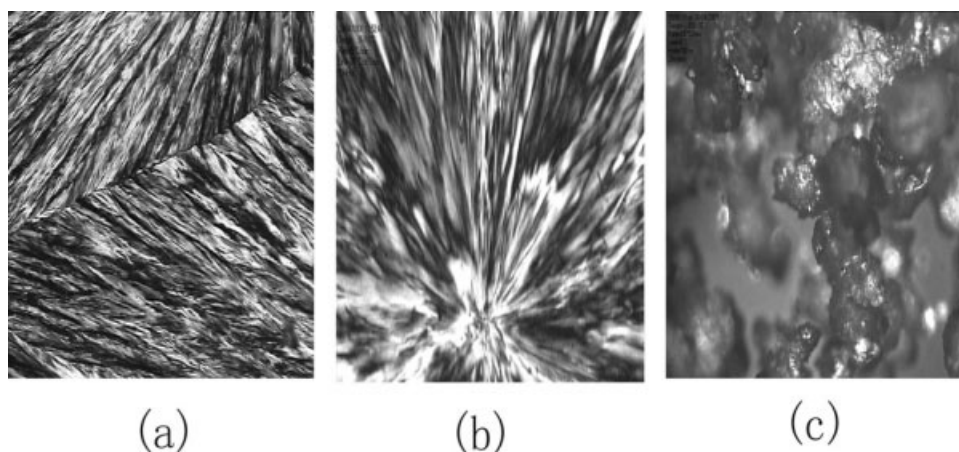


Figure 5 POM photos of pristine PEG4000 (a) at 25°C, PEG/MDI/PVA copolymer (b) at 25°C, and PEG/MDI/PVA copolymer (c) at 100°C.

transition temperatures because of the crosslinking structure which restricted free movement of the soft segment.

CONCLUSIONS

A novel solid–solid phase change heat storage material was prepared via a condensation reaction of PEG4000 with PVA and MDI. The results showed that the PEG/MDI/PVA crosslinking copolymer had typical solid–solid phase transition properties, high enthalpy reaching 72.8 kJ/kg, and a suitable transition point at 61.1°C. The thermal resistance of the PEG/MDI/PVA copolymer was improved by introduction of rigid phenyl rings and crosslinked structures. Initial decomposition temperature increased by about 39.8°C compared with pristine PEG4000; furthermore, the PCM retained its solid state when heated to 100°C, as the crosslinking structure

restricted the soft segment's free movement at high temperatures. The novel solid–solid PCM will be a promising heat storage material and have a very wide application.

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