

# Poly(ethylene glycol)/poly(methyl methacrylate) Blends as Novel Form-Stable Phase-Change Materials for Thermal Energy Storage

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**ABSTRACT:** In this study, we focused on the preparation and characterization of poly(ethylene glycol) (PEG)/poly(methyl methacrylate) (PMMA) blends as novel form-stable phase-change materials (PCMs) for latent-heat thermal energy storage (LHTES) applications. In the blends, PEG acted as a PCM when PMMA was operated as supporting material. We subjected the prepared blends at different mass fractions of PEG (50, 60, 70, 80, and 90% w/w) to leakage tests by heating the blends over the melting temperature of the PCM to determine the maximum encapsulation ratio without leakage. The prepared 70/30 w/w % PEG/PMMA blend as a form-stable PCM was characterized with optical microscopy and Fourier transform infrared spectroscopy. The thermal properties of the form-stable PCM were meas-

ured with differential scanning calorimetry (DSC). DSC analysis indicated that the form-stable PEG/PMMA blend melted at 58.07°C and crystallized at 39.28°C and that it had latent heats of 121.24 and 108.36 J/g for melting and crystallization, respectively. These thermal properties give the PCMs potential LHTES purposes, such as for solar space heating and ventilating applications in buildings. Accelerated thermal cycling tests also showed that the form-stable PEG/PMMA blend as PCMs had good thermal reliability and chemical stability. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 929–933, 2010

**Key words:** blends; calorimetry; morphology; thermal properties

## INTRODUCTION

Latent-heat thermal energy storage (LHTES) is the most attractive method for thermal energy storage because it provides high-energy storage density and small temperature variation from storage to retrieval.<sup>1,2</sup> In this method, thermal energy is stored by a phase-change material (PCM) during the solid-liquid phase-change process, and the stored energy is released when it changes from a liquid to a solid. Recently, a great variety of inorganic and organic compounds and mixtures as PCMs for LHTES systems have been investigated.<sup>3,4</sup> The interest in developing polymer-based PCMs as novel LHTES materials has grown in recent years.<sup>5–10</sup> The shape of a material is stabilized in polymer-based PCMs because a solid-liquid PCM is encapsulated in the polymer matrix. Therefore, polymer-based materials are called *form-stable PCMs*. Form-stable PCMs have many advantages. For example, melted PCMs do

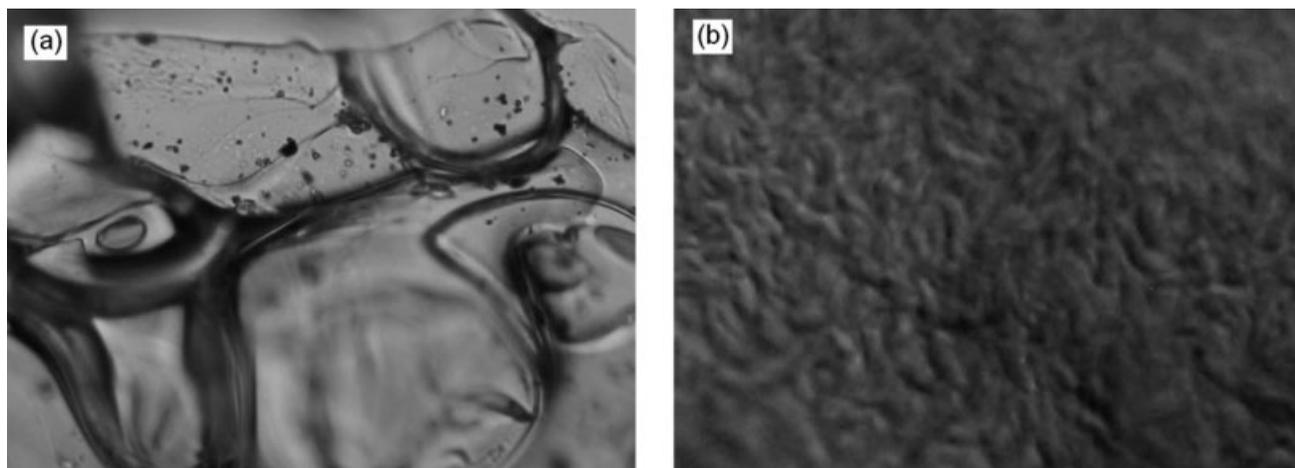
not ooze during heating, and the thermal resistance caused by the capsule shell is eliminated. In addition, polymer-based PCMs do not need an additional container, and therefore, they are cost effective. Also, they can be prepared easily in specific desired dimensions.

Poly(ethylene glycol) (PEG) is a crystalline, thermoplastic, water-soluble polymer and exhibits miscibility or partial miscibility with many chemically different polymers.<sup>11,12</sup> It is a promising PCM for solar LHTES applications because of its relatively high latent heat of fusion, congruent melting and crystallization behavior, suitable melting temperature range, noncorrosiveness, nontoxicity, and high decomposition temperature range.<sup>13–16</sup> Its phase behavior should be considered in terms of both the conformation of individual molecules in the crystalline state and the arrangement of those molecules into microscopic and macroscopic structures.<sup>17</sup> Poly(methyl methacrylate) (PMMA) is a commercially available acrylic resin that is fully polymerized methyl methacrylate. It has a high impact strength and chemical resistance in addition to optical clarity. These properties make it a potential material for the encapsulation of PCMs.<sup>18,19</sup>

Our aim in this study was to prepare PEG/PMMA blends as novel form-stable PCMs using the solvent casting method. The blends were

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**Figure 1** OM images of (a) PMMA and (b) the form-stable PEG/PMMA blend.

characterized by optical microscopy (OM) and Fourier transform infrared (FTIR) spectroscopy. The thermal properties and thermal reliability of the form-stable PCM after thermal cycling were determined with differential scanning calorimetry (DSC).

## EXPERIMENTAL

### Materials

PEG (weight-average molecular weight = 20,000 g/mol) and PMMA (weight-average molecular weight = 120,000 g/mol) were obtained from Merck (Darmstadt, Germany) and Aldrich (St. Louis, MO), respectively. They were used without purification. Chloroform was reagent grade and commercially available.

### Methods

The PEG/PMMA blends were prepared by the solvent casting method. In our solvent casting method, solutions of PEG and PMMA in chloroform were prepared in separate beakers, and the PEG solution was added to the PMMA solution dropwise. Then, the solvent, chloroform, was evaporated at room temperature for 15 days. The blends were prepared in 50, 60, 70, 80, and 90% w/w PEG compositions to obtain the maximum encapsulation ratio without leakage of PEG when the temperature was over the melting point of PEG. The morphology of the form-stable blend was investigated with an optical microscope (Leica model, Wetzlar, Germany), and the spectroscopic analysis was performed on a KBr disk with a Jasco 430 model FTIR instrument (Tokyo, Japan).

The thermal properties of the form-stable PEG/PMMA blend, such as melting and crystallizing points and latent heats were measured by the DSC technique (SETARAM DSC 131, Caluire, France). The analyses were carried out at a 5°C/min heating rate under a constant stream of argon at a flow rate

of 60 mL/min. We tested the reproducibility by conducting three measurements, and the mean deviations were  $\pm 0.01^\circ\text{C}$  in the phase-change temperature and  $\pm 1.24$  J/g in the latent-heat capacity.

To determine the thermal reliability of the form-stable PCM, an accelerated thermal cycling test (3000 melting/crystallizing processes) was conducted with an experimental procedure from the literature.<sup>4</sup> The samples were subjected to a melting/freezing cycling process by a thermal cyler (Bio-Rad model, Hangzhou, China) in which they were heated from 20 to 100°C and cooled back to 20°C 1000, 2000, and 3000 times.

The chemical stability was checked according to the structural and thermal consistencies by FTIR and DSC techniques.

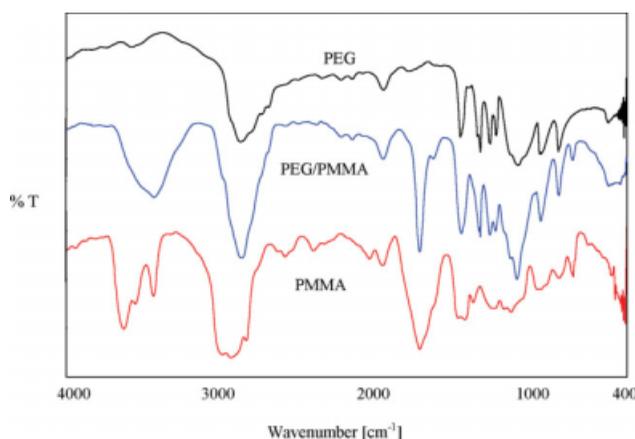
## RESULTS AND DISCUSSION

### Characterization of the PEG/PMMA blends

The maximum encapsulation ratio of PEG in the PEG/PMMA blends without leakage of PEG was determined as 70 wt %. Therefore, the 70/30 w/w % PEG/PMMA blend was identified as the form-stable PCM.

Polymer blends are commonly immiscible; this results in phase separation, which can be observed by microscopy. Figure 1(a,b) shows the OM images of the PMMA film and the form-stable PCM, respectively. Figure 1(a) shows the transparent PMMA film, and Figure 1(b) shows the nonuniform single-phase appearance. The single phase on the surface of the blend did not mean miscibility of PEG with PMMA on a microscopic scale. However, PEG was distributed in the PMMA matrix. Compared to the PMMA shown in Figure 1(a), the form-stable blend shown in Figure 1(b) was also not transparent.

FTIR spectroscopy was used to investigate the possible interaction between PEG and PMMA in the



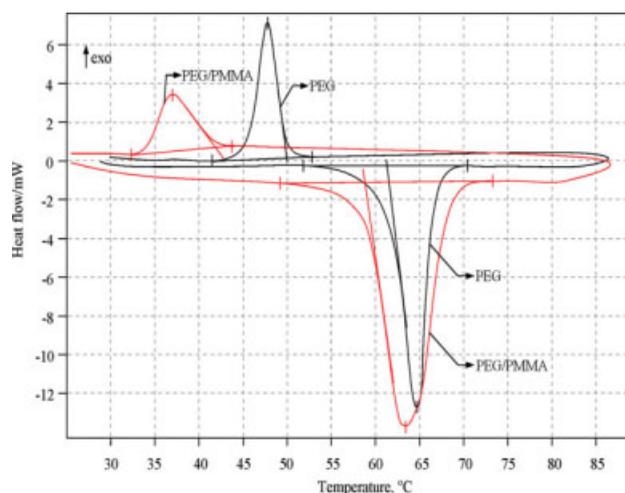
**Figure 2** FTIR spectra of PEG, PMMA, and the form-stable PEG/PMMA blend. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

blend. To investigate the interactions between PMMA and PEG, the spectra of all of the PEG, PMMA, and form-stable PEG/PMMA blends are given in Figure 2.

CH stretching peaks were observed at nearly the same wave numbers. The carbonyl peak position in the blend was almost the same as that in PMMA, but it had a narrow shape. The OH stretching peaks at about  $3450\text{ cm}^{-1}$  became broader in the blend, which may have been caused by the carbonyl-hydroxyl interaction. As a result, the FTIR analysis confirmed the constitution of both of the blend components and the possible interactions between the components. Similar results were reported for different polymer-based PCMs.<sup>10,19</sup> However, the course of phase transition depends not only on the basic chemical structure of a polymer but also on many internal and external factors.<sup>12</sup>

#### Thermal properties and thermal reliability of the form-stable PEG/PMMA blends

The DSC curves of the PEG and form-stable PCM are shown in Figure 3. The thermal properties evaluated from the curves indicated that the form-stable PCM blend melted at  $58.07^\circ\text{C}$  and crystallizes at  $39.28^\circ\text{C}$  when pure PEG had a melting point of



**Figure 3** DSC curves of the pure PEG and form-stable PEG/PMMA blend. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$61.21^\circ\text{C}$  and a crystallization point of  $49.35^\circ\text{C}$ . Pielichowski and Flejtuch<sup>20</sup> analyzed the phase transitions of PEG with different molecular weights under modulated-temperature conditions and revealed that PEG with a molecular weight of 10,000, among PEGs with molecular weights of 3400, 10,000, and 35,000, exhibited the highest degree of crystallinity with the smallest nonreversing signal.<sup>20</sup> This effect was attributed to the favorable structural features associated with the spatial alignment. The PEG with a molecular weight of 20,000 in this study was expected to have a high degree of crystallinity with no complications of very low and high molecular weights.

The form-stable PCM had a latent heat of  $121.24\text{ J/g}$  during the melting period and a latent heat of  $108.36\text{ J/g}$  during the crystallizing period, whereas the pure PEG had latent heats of  $176.24$  and  $154.18\text{ J/g}$  for melting and crystallization, respectively. The thermal properties of the PEG/PMMA blends prepared with different mass fractions of PEG are given in Table I. The depressions in the phase-change temperatures of the blends from that of pure PEG was accounted for by hydrogen-bonding interactions between the OH groups of PEG and the oxygen of

**TABLE I**  
Thermal Properties of the Pure PEG and PEG/PMMA Blends

	Melting temperature ( $^\circ\text{C}$ )	Crystallization temperature ( $^\circ\text{C}$ )	Latent heat of crystallization (J/g)	Latent heat of crystallization (J/g)
Pure PEG	61.21	49.35	176.24	154.18
50/50 wt % PEG/PMMA	57.73	38.86	86.28	76.41
60/40 wt % PEG/PMMA	57.81	38.97	102.71	89.16
65/35 wt % PEG/PMMA	57.93	39.10	112.54	97.21
70/30 wt % PEG/PMMA	58.07	39.28	121.24	108.36

PMMA, as the deviation of latent-heat values from the theoretically expected values were explained by the lower crystalline areas of PEG in the blend due to entanglements between the molecular chains of PEG and PMMA.<sup>21,22</sup> When we compared the measured latent-heat values of the form-stable PCMs (Table I) with the theoretical data, which was found with eq. (1), we could clearly see that the measured values were slightly lower than the theoretically expected values:

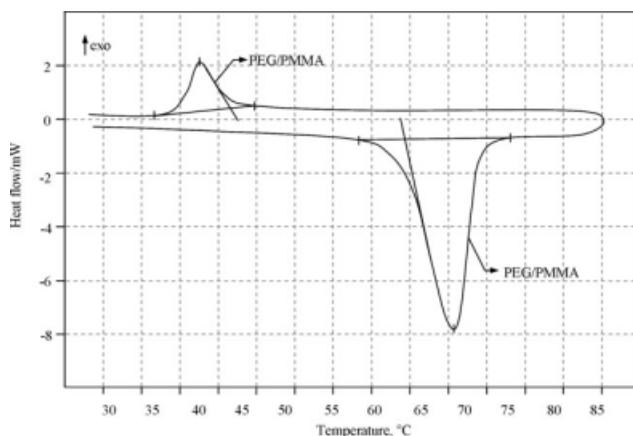
$$\Delta H_{\text{PEG/PMMA}} = W_{\text{PEG}} \times \Delta H_{\text{PEG}} \quad (1)$$

where  $\Delta H_{\text{PEG/PMMA}}$ ,  $W_{\text{PEG}}$ , and  $\Delta H_{\text{PEG}}$  are the calculated latent heat of the form-stable PEG/PMMA blend, mass percentage of PEG in the blend, and measured latent heat of the pure PEG (Table I), respectively.

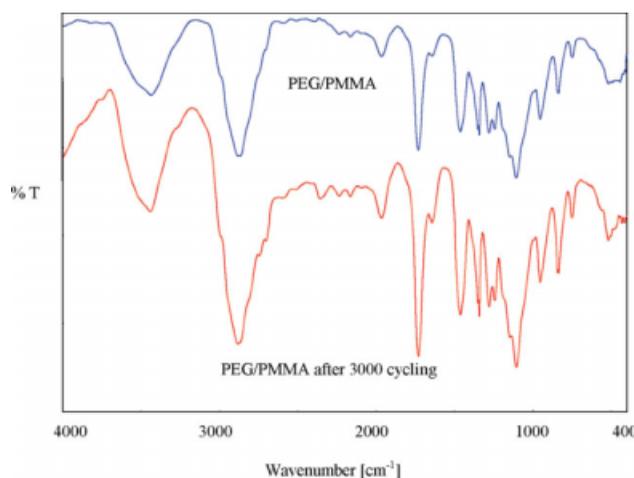
Figure 4 shows the DSC curves of the form-stable PCM after 3000 thermal cycles. Its melting point changed from 1.17 to  $-1.51$  to  $0.38^\circ\text{C}$  when its crystallizing point changed from  $-0.07$  to  $-0.58$  to  $1.12^\circ\text{C}$  after 1000, 2000, and 3000 thermal cycles, respectively. On the basis of these results, we concluded that the form-stable PCM had good thermal reliability in terms of the changes in its phase-change temperatures. On the other hand, the latent heat of melting of the PCM changed by  $-3$ ,  $-13.5$ , and  $-10\%$  and the latent heat of crystallization changed by  $-5.2$ ,  $-14.7$ , and  $-9.8\%$  after 1000, 2000, and 3000 repeated thermal cycles, respectively.

These results indicate that the decreases in the latent-heat values of the form-stable PCM were of insignificant magnitude for LHTES applications, although they were subjected to a large number of phase-change processes.

The chemical stability of the form-stable PCM after repeated thermal cycles was also investigated by FTIR analysis. As shown clearly in Figure 5, the



**Figure 4** DSC curves of the form-stable PEG/PMMA blend after 3000 thermal cycles.



**Figure 5** FTIR spectra of the form-stable PEG/PMMA blend before and after 3000 thermal cycles. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

FTIR spectra were identical before and after 3000 thermal cycles. This means that no chemical degradation of the PCM occurred during thermal cycling. The result also indicates that the prepared form-stable PCM had good thermal stability over a large number of melting/crystallizing processes.

## CONCLUSIONS

The PEG/PMMA blend was prepared as a novel form-stable PCM for LHTES applications. In the blend, PEG was dispersed into the polymer matrix and served as a latent-heat storage material. The form-stable 70/30 w/w % PEG/PMMA blend kept its shape even when the PCM underwent the phase change from a solid to a liquid. The blend was characterized by OM and FTIR techniques. The OM analysis showed that there were single-phase morphologies in both PMMA and the form-stable blend as FTIR confirmed the possible interactions between PEG by PMMA. The DSC analysis results indicate that the prepared form-stable PCM had suitable phase-change temperatures and latent heats and good thermal reliability and chemical stability for LHTES in solar space heating and ventilating applications in buildings.

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