Poly(Ethylene Glycol)/Acrylic Polymer Blends for Latent Heat Thermal Energy Storage

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In the present study, polyethylene glycol (PEG) were blended with acrylic polymers like polymethyl methacrylate (PMMA), Eudragit S (Eud S), and Eudragit E (Eud E) as novel form stable phase change materials (PCMs) and characterized by optical microscopy, spectroscopy and viscosity techniques. Latent heat thermal energy storage (LHTES) properties of the blends were evaluated by using the differential scanning calorimetry (DSC) technique. In the form-stable blends, PEG acted like phase change-LHTES material when the acrylic polymers served as supporting material because of their adhesion property. The maximum percentage of PEG was found 80% w/w for any of the blend in which no leakage of PEG occurred for 100 heating/cooling cycles. The optical microscopy investigations revealed that the phase behavior of the blends was observed as self organized PEG distributed in the matrix of acrylic polymers rather than chain-like structures. The interactions between the blend components (PEG and one of the acrylic polymers) were analyzed by Fourier transform infrared (FT-IR) spectroscopy and the viscosimetry technique. The key LHTES properties (melting and freezing temperatures, and latent heats of melting and freezing of the blends) were evaluated by DSC. The DSC results indicated that PEG/PMMA, PEG/Eud S, and PEG/Eud E blends as form-stable PCMs were convenient materials for LHTES applications in terms of their satisfying thermal properties. Therefore, these form-stable PCMs could be incorporated into an LHTES system with the advantage of direct utility in order to store daytime solar energy for space heating. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3310–3314, 2006
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Introduction

Thermal energy storage for solar heating applications has gained scientific interest in modern technology due to the impending shortage and increasing cost of energy resources. Thermal energy can be stored in the form of sensible heat, latent heat, and thermo-chemical heat, or a combination of them. Among these forms, the most attractive one is LHTES using a PCM because of providing high-energy storage density and small temperature variation from storage to retrieval.[1,2] In that case, thermal energy is stored by PCM during the solid-liquid phase change process, and the stored energy is released when it changes from liquid to solid. A great variety of inorganic and organic compounds and their mixtures as PCM for LHTES systems have been investigated for a long time.[1-5]

The interest in developing the polymer-based PCMs as novel LHTES materials has been growing in recent years because of their following advantages[6-17]: (1) Such type PCMs can keep the similar shape in a solid state even when the temperature of the blend is over the melting point of the PCM. Therefore, they

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are called form-stable PCMs. (2) They contact with the heat transfer medium in actual LHTES systems; they do not need any extra capsulation. So they are cost-effective. (3) They can be easily prepared with desirable dimensions. These superior properties over traditional PCMs have directed researchers to develop novel form-stable polymer-based PCMs.

Poly(ethylene glycol) (PEG) is a white, free flowing powder or creamy white flakes, and is used as water-soluble lubricant for rubber molds, textile fibers, and metal forming operations.[8,9] It is also used in water paints, paper coatings, polishes, and in the ceramic industry, as well as for chromatographic stationary phases. Moreover, PEG has been considered as a promising PCM for solar LHTES applications because of its relatively high latent heat of fusion, congruent melting and freezing behavior, suitable melting temperature range, non-corrosiveness, non-toxicity, and non decomposition at its melting/freezing temperature range.[1,2,12,13]

PMMA and Eudragits belong to a group of commercially available acrylic resins.[18,19] Acrylic resins are thermoplastic polymers used to produce paints, synthetic rubbers, and light-weight plastics. They have high impact strength and chemical resistance in addition to optical clarity. These properties make them potential encapsulating materials for the PCM.

Based on literature survey, it can be noteworthy that polymeric encapsulants provide an opportunity to utilize PCMs within a unique composite structure. The aim of this study is to prepare novel form-stable PCMs—PEG/PMMA, PEG/Eud S, and PEG/Eud E blends—with maximum encapsulation ratio; to analyze morphology of the blend and secondary interactions in bulk and in solution by using optical microscopy, FT-IR spectroscopy, and viscosimetry, respectively; and to determine the thermal properties of the developed PCMs, such as melting and freezing temperatures, and the latent heat capacity of melting and freezing by the DSC technique.

Experimental

Materials

Poly(methyl methacrylate) (M_w 120,000 gmol^{-1}) was obtained from Aldrich and used without purification. Eudragit S (M_w: 135,000 gmol^{-1}), a 1:2 copolymer of methacrylic acid and methyl metacrylate, was a commercial product of Röhm Pharma (Darmstadt, Germany). Eudragit E (light yellow granules, M_w 150,000 gmol^{-1}), a 1:2:1 butyl metacrylate/(2-dimethyl amino ethyl) methacrylate/methyl methacrylate statistical copolymer, was also supplied by Röhm Pharma (Darmstadt, Germany). Chloroform was Merck grade and commercially available. The chemical formulas of the PEG, PMMA, Eud S, and Eud E are given in Figure 1.

Preparation of blends

The blends of PEG with PMMA, Eud S, and Eud E were prepared by the solution casting method. Solutions of PEG and acrylic polymers were dissolved in chloroform separately and PEG solution was added to each acrylic solution drop-wise. Then chloroform was casted at room temperature in 15 days. The blends were prepared at 50, 60, 70, 80, and 90% w/w PEG compositions to find the maximum encapsulation ratio without leakage of the PEG when the temperature was between the melting point of the PEG and that of the acrylic polymer in the blend (PMMA, Eud S, and Eud E).

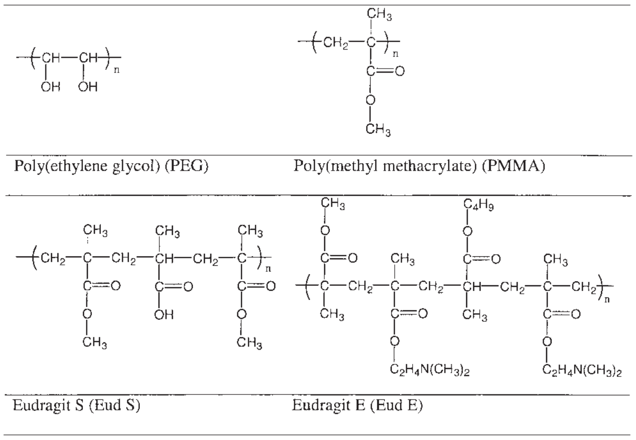

Figure 1. Chemical structures of poly(ethylene glycol) (PEG), poly(methylmethacrylate) (PMMA), eudragit S (Eud S), and eudragit E (Eud E).

Analysis of the blends

Thermal properties of PEG/acrylic polymers, such as melting and freezing points and latent heats, were measured by the DSC technique (SETERAM DSC 131). Indium was used as a reference for temperature calibration. The analyses were performed between the temperatures of 20°C and 100°C at 5°C/min heating rate under a constant stream of argon at flow rate of 60 mL/min. Heat flow repeatability was 0.2μW. A 5 to 10 mg sample was sealed in an aluminum pan. The melting and freezing points' onset temperatures were obtained by drawing a line at the point of maximum slope of the leading edge of the DSC peak and extrapolating the base line on the same side as the leading edge of the peak. The latent heat of PCM was determined by numerical integration of the area of the peak of thermal transition. Reproducibility was tested by three measurements. The mean deviation was ±0.19°C in phase change temperatures and ±1.78 J/g in latent heat capacity.

The morphology of the blends was investigated by a Laica optical microscope. FT-IR spectra of PMMA, Eud S, Eud E, and PEG, and form-stable PCMs (the blends) were taken on a KBr disk by using a Jasco 430 model FT-IR spectrophotometer.

The compatibility of blend components in solutions was determined by a viscometry technique. Viscosity measurements were obtained with an Ubbelohde viscometer in a constant temperature water bath at 25°C using chloroform as a solvent. A concentration of 0.5 g/dL was not exceeded in viscosity measurements. The obtained viscosity data were evaluated by the following equation expressing the specific viscosity (η_{sp}) of the polymer as a function of the concentration (C):

$$\eta_{sp}/C = [\eta] + K[\eta]^2 C \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, K is the Huggins coefficient, and $K[\eta]^2$ is the interaction term.

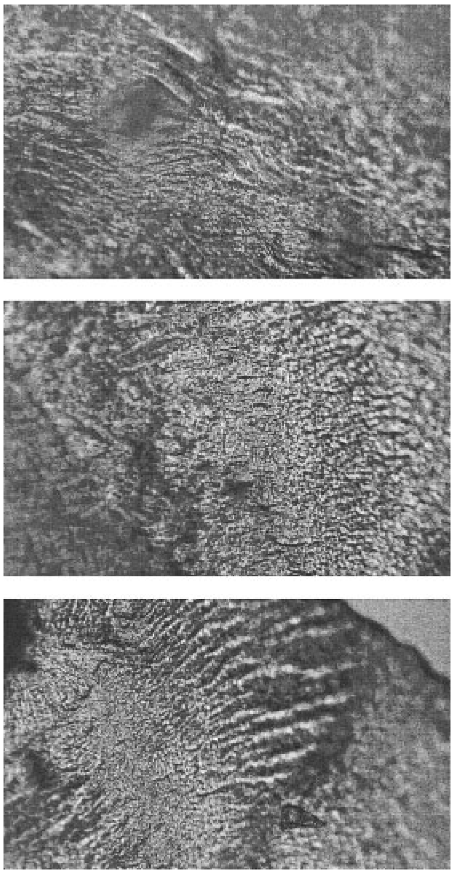

Figure 2. The micrographs of form-stable PCMs obtained by optical microscopy.

(a) 80%PEG/20%PMMA (w/w), (b) 80%PEG/20%Eud S (w/w), (c) 80%PEG/20%Eud E (w/w).

Results and Discussion

Characterization of PEG/acrylic polymer blends

PMMA, Eud S, and Eud E were supporting material for PEG in the blends melt and solidify in the matrix. The PCMs were stable,

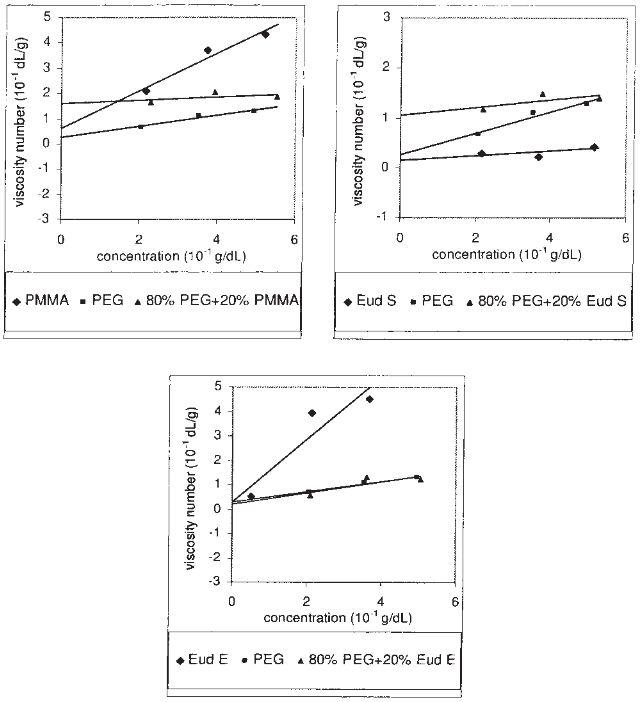

Figure 4. Viscosity number vs. concentration relationships of PEG/acrylic polymers in chloroform at 25°C.

that is, no seepage was observed when the blend was heated over the melting temperature of the PCM. Therefore, they were used for the solar LHTES systems without an outer container. The maximum mass percentage of PEG in all the blends was determined as 80% without leakage of PEG after 100 heating cycles.

Morphology analysis

Figure 2 represents the single phase optical images of 80%PEG/20%PMMA, 80%PEG/20%Eud S, and 80%PEG/20%Eud E blends (w/w) with no leakage of PEG. The typical

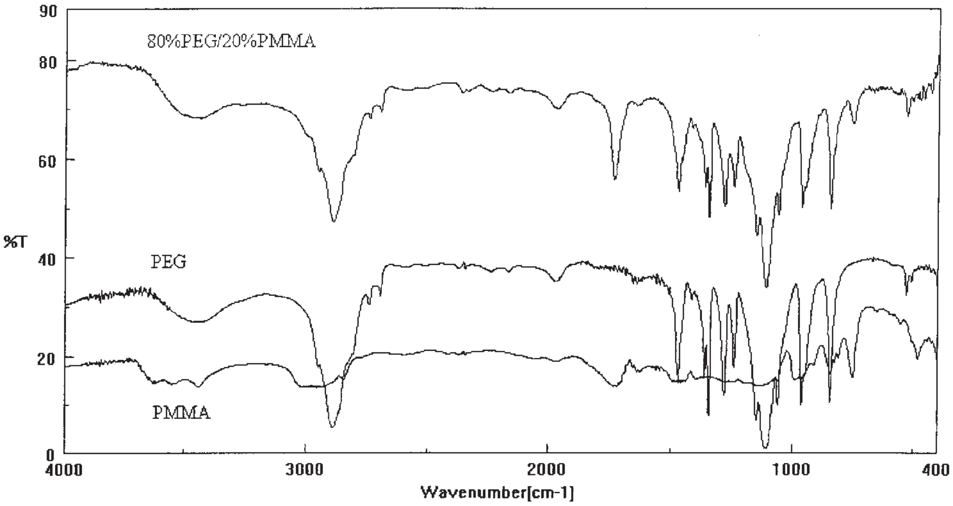

Figure 3. FT-IR spectra of PEG, PMMA, and 80%PEG/20% (w/w) PMMA blend.

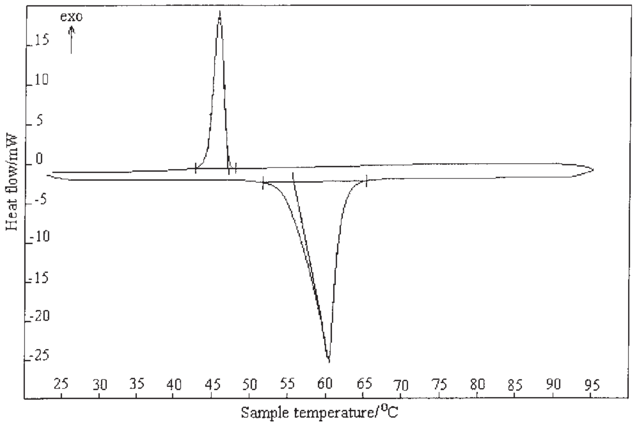

Figure 5. DSC curve of PEG.

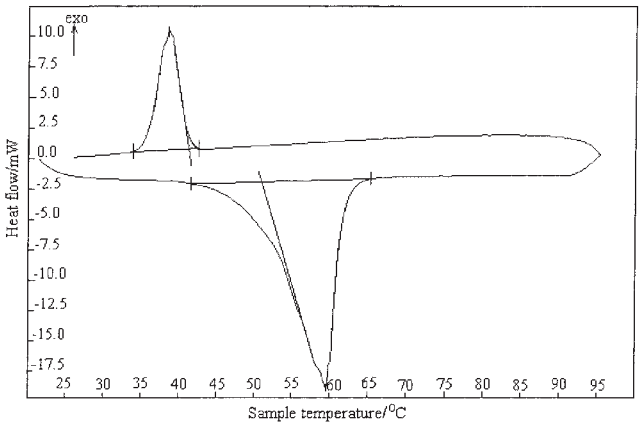

Figure 7. DSC curve of PEG/Eud S blend (80/20 wt%) as form-stable PCM.

PCM appearances with lamellae structure were observed in the pictures. The phase behavior of the blends can be accounted for by the strong association of PEG encapsulated by acrylic polymers. This is in good agreement with the result of thermal cycling tests on form-stable PCMs in which no seepage of PEG from the matrices of the blends was observed. If there were no interactions between the blend components, leakage of PEG at higher temperatures than its melting points would be detected.

FT-IR spectroscopy analysis

FT-IR spectroscopy is a powerful technique to investigate specific interactions in polymer blends. Figure 3 shows the FT-IR absorption spectra for the pure components PEG and PMMA, and their corresponding blend, 80%PEG/20%PMMA (w/w), was given as an example.

The following remarks are based on the FT-IR spectroscopy analysis of the blends 80%PEG/20%PMMA, 80%PEG/20%Eud S, and 80%PEG/20%Eud E.

1. PEG concentration of the blends was considerably high, and peaks of supporting material (acrylic polymers) were absorbed by PEG peaks.
2. Blends constituted only the carbonyl peak of supporting acrylate materials in addition to PEG peaks. Carbonyl peaks shifted to 1731.76 cm^{-1} from 1734.84 cm^{-1} in 80%PEG/20%PMMA blend and to 1729.83 cm^{-1} from 1718.26 cm^{-1} in 80%PEG/20%Eud E blend. These changes were caused by interactions of the OH group in PEG and the carbonyl group in acrylic polymer.
3. Carbonyl peak in Eud S at 1731.76 cm^{-1} did not shift to another wavelength in 80%PEG/20%Eud S blend, since it was due to the interactions between OH and the carbonyl group of Eud S itself. On the other hand, another carbonyl peak at 1691.27 cm^{-1} caused by the interaction of the OH group of PEG and the carbonyl group of Eud S was observed.

Viscosity analysis

Because of simplicity, viscometry has become an attractive method for studying the compatibility of polymers in solution. The basis for using dilute solution viscometry as a method for compatibility determinations of polymer blends lies in the fact that the repulsive interactions between blend components may cause shrinkage of the polymer coils in solution. This causes a decrease in the solution viscosity of the blend compared to the specific viscosities of pure constituent components. A reverse behavior is expected for attractive interaction between components.[20]

Figure 4 shows the viscosity number versus concentration relationships for 80%PEG/20%PMMA, 80%PEG/20%Eud S,

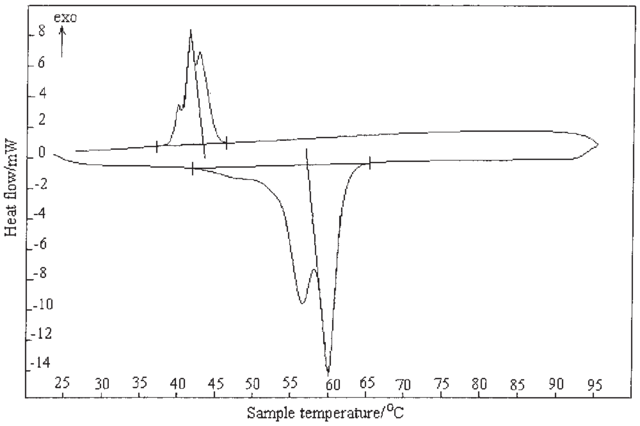

Figure 6. DSC curve of PEG/PMMA blend (80/20 wt%) as form-stable PCM.

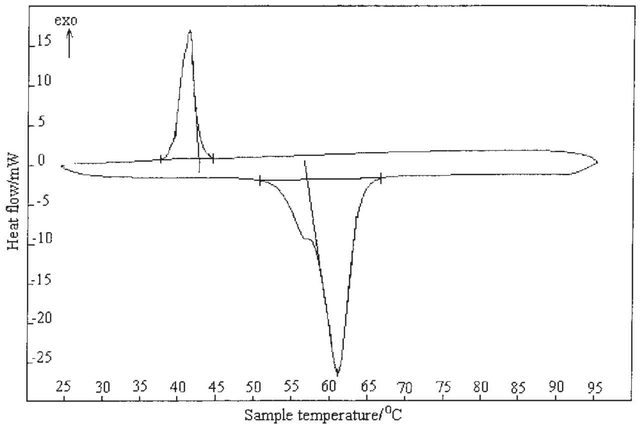

Figure 8. DSC curve of PEG/Eud E blend (80/20 wt%) as form-stable PCM.

Table 1. Thermal Properties of PEG, PEG/Eud-E, PEG/Eud-S, and PEG/PMMA Blends (80/20 wt%) as Form-Stable PCMs

	Melting Point (°C)	Latent Heat of Melting (J/g)	Freezing Point (°C)	Latent Heat of Freezing (J/g)
PEG	55.83 ± 0.12	176.10 ± 1.42	46.91 ± 0.23	162.05 ± 1.65
PEG/Eud E	56.94 ± 0.21	148.85 ± 1.81	42.73 ± 0.13	144.87 ± 1.72
PEG/Eud S	50.96 ± 0.24	144.23 ± 1.21	41.32 ± 0.16	141.53 ± 2.30
PEG/PMMA	56.90 ± 0.17	141.62 ± 2.03	43.15 ± 0.27	140.02 ± 2.10

and 80%PEG/20%Eud E blends. It is clearly seen from the figure that the intercepts of the plots correspond to intrinsic viscosities ($[\eta]$s) of the blends. Higher values of $[\eta]$s of blends than that of the blend components indicated attractive interactions between the acrylic polymers and PCM.

Thermal analysis

The DSC thermograms for PEG and PEG/acrylic polymers are given in Figures 5–8, respectively. Thermal properties obtained from DSC curves are also given in Table 1. As the changes in the melting temperature of PEG are in the range of 1.07-4.87°C, the changes in the freezing temperature are between 3.76 and 5.59°C in the blends. These changes are not significant for an LHTES application. Latent heat values of melting and heat of freezing values of the blends are slightly higher than the theoretical values calculated by multiplying the mass percentage of PEG in the blend, and latent heat of pure PEG, respectively. This is probably due to the attractive interactions between the PEG and acrylic chains. Results from FT-IR spectra of the blends are in good agreement with this conclusion.

The melting and freezing points of PEG in the form-stable PEG/acrylic polymer blends showed that they were suitable for passive solar space heating and solar building heating applications. Nevertheless, the heat of melting and freezing of form-stable PCMs were as high as some salt hydrates and paraffins used for low temperature LHTES systems.[1-5]

Conclusions

PEG/acrylic polymer blends were prepared as novel form-stable PCMs for LHTES systems. In the blends, PEG was dispersed into the matrix of acrylic polymers and served as an LHTES material. As long as the operating temperature was below the melting point of supporting material (acrylic polymers), the blends kept their shape even when the PCM underwent phase change from solid to liquid. The maximum mass percentage of the investigated PEG in the blends without leakage in the melted state was found as 80%. The extended encapsulation was achieved by using this kind of PCM, and heat resistance caused by a capsule shell was eliminated. PEG/acrylic polymer form-stable PCMs are cost-effective materials because of their direct usage advantage without outer containers in LHTES systems. Besides, PEG/acrylic polymer blends have an additional advantage of easy preparation with desirable dimensions. As a result, 80%PEG/20%PMMA, 80%PEG/20%Eud S, and 80%PEG/20%Eud E blends with satisfying thermal properties are suitable materials for day time solar energy storage for space heating.

Acknowledgments

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