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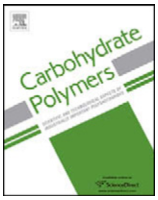

Biodegradable PEG/cellulose, PEG/agarose and PEG/chitosan blends as shape stabilized phase change materials for latent heat energy storage

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ABSTRACT

This study based on the preparation and characterization of PEG/cellulose, PEG/agarose, and PEG/chitosan blends as form/stable phase change materials (PCMs) for latent heat energy storage. 60/40% w/w PEG/cellulose, 70/30% w/w PEG/agarose, and 80/20% w/w PEG/chitosan blends were found to contain maximum PEG without leakage above melting point and are characterized using Fourier transform infrared (FT-IR) spectroscopy, polarized optic microscopy (POM), and differential scanning calorimetry (DSC) techniques. DSC analysis indicated that the form-stable PEG/cellulose, PEG/agarose, and PEG/chitosan blends melt at 58.51 °C, 57.73 °C, and 57.18 °C with 84.63 J/g, 110.87 J/g, and 152.16 J/g latent heats, respectively, as they crystallizes at 37.05 °C, 43.36 °C, and 44.76 °C with −78.92 J/g, −99.01 J/g, and −138.39 J/g, respectively. Accelerated thermal cycling tests were applied to present thermal reliability and chemical stability of the shape stabilized blends.

1. Introduction

Latent heat energy storage is one of the most attracting method of thermal energy storage due to allowing storage and release of energy in large quantities per unit weight of phase change material (PCM) at nearly constant temperature during the phase change (Abhat, 1983; Dinçer & Rosen, 2002). A great number of PCM materials have been investigated for heating and cooling applications (Alkan & Sari, 2008; Kenisarin & Mahkamov, 2007; Zalba, Marin, Cabeza, & Mehling, 2003). Among the studied PCMs, paraffins have been used as a latent heat energy storage material with the advantages of high enthalpy of phase change, small segregation of components, and small changes in structure during repeated phase transitions, negligible super cooling, low vapor pressure, self-nucleating behavior and low cost (Alkan, Sari, & Uzun, 2006; Hadjieva, Kanev, & Argirov, 1992; Himran, Suwono, & Mansoori, 1994).

Shape stabilized PCMs are prepared by encapsulation of PCM into a polymer matrix and have several advantages (Alkan et al., 2006; Ozonur, Mazman, Paksoy, & Evliya, 2006). No seepage is observed in shape stabilized PCMs during melting and an extra storage container is not needed. Also thermal resistance by capsule shell is eliminated and interactions between PCM and environment are prohibited. In addition, they are easily prepared with desired dimensions. Furthermore, they are feasible for some heating applications in buildings such as under floor space heating and reducing electricity peak load in heating in winter using wallboard and plasterboard prepared by absorption of a PCM. These beneficial properties directed the researchers to develop new kinds of shape stabilized PCMs by melt blending and use them in practical latent heat energy storage applications (Hong & Xin-shi, 2000; Inaba & Tu, 1997). On the other hand, considerably high values of PCM/polymer encapsulation ratios and thermal reliability have been reached using different matrix and PCM materials by solution blending method (Alkan & Sari, 2008; Sari, Alkan, Karaipekli, & Önal, 2008).

According to the literature survey, various synthetic polymers have been used as supporting material to produce shape stabilized PCM compounds while there is only a few number of natural polymers used as supporting material. In one of these rarely coincided studies, Pielichowska and Pielichowski studied gelatinized potato and cellulose derivatives as supporting materials in shape stabilized PCM blends (Pielichowska & Pielichowski, 2010a,b). Gelatinized potato starch and cellulose derivatives served as a biodegradable shape stabilized phase change materials with PEG inside. In those works, they found that enthalpy values of the blends were lower than theoretically calculated values, which was explained by strong intermolecular interactions (H-bonding interactions) between the hosting and the supporting polymers. In this work, some of the other natural polymers (cellulose, agarose, and chitosan) have been used in the preparation of shape stabilized phase change materials. PEG and of course natural polymers are

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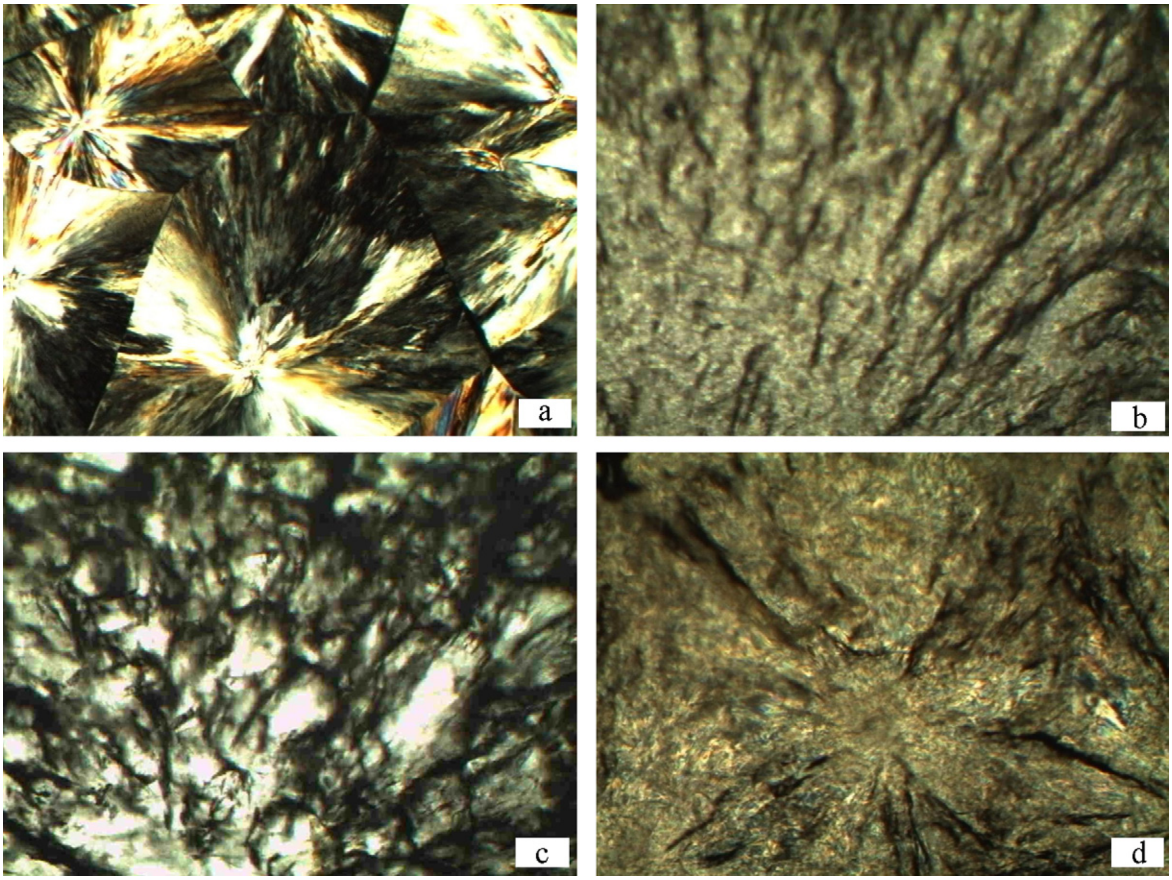

Fig. 1. Polarized optical microscopy images of PEG (a), 60/40% w/w PEG/cellulose (b), 70/30% w/w PEG/agarose (c), 80/20% w/w PEG/chitosan (d) shape stabilized blends.

considered as environmentally safe macromolecular materials that are not causing any danger to the users and the environment which is a prerequisite in design of advanced materials for energy storage applications.

2. Experimental

PEG (M_w 4000 g mol^{-1}, Merck), cellulose (Alfa Aesar), agarose (BIORON), and chitosan (MP Biomedicals) were used without further purification.

PEG/cellulose, PEG/agarose, and PEG/chitosan blends were prepared by solution casting method in water and tested for leakage according to the literature (Alkan & Sari, 2008). The maximum encapsulation ratio was found as 60/40 w/w for PEG/cellulose, 70/30 w/w for PEG/agarose, and 80/20 w/w for PEG/chitosan. The morphology of the form-stable blends was investigated using polarized optical microscope (Laica DM EP, 2010) as the spectroscopic analysis was performed on KBr disks by using a Jasco 430 model FT-IR.

Thermal properties of PEG/cellulose, PEG/agarose, and PEG/chitosan shape stabilized blends such as melting and crystallizing points and latent heats were measured by DSC technique (Perkin-Elmer JADE DSC, 2009). The analyses were carried out at 5 °C/min heating rate under a constant stream of argon at a flow rate of 60 mL/min. In order to determine thermal reliability of shape stabilized PCM blends, accelerated thermal cycling test (3000 melting/crystallizing processes) was conducted using BIDER-TC-25/H thermal cycling instrument according to the experimental procedure in literature (Alkan & Sari, 2008). The changes in thermal properties after thermal cycling were evaluated using DSC analysis. Moreover, the chemical stability of the PCM after thermal cycling test was also investigated by FT-IR analysis.

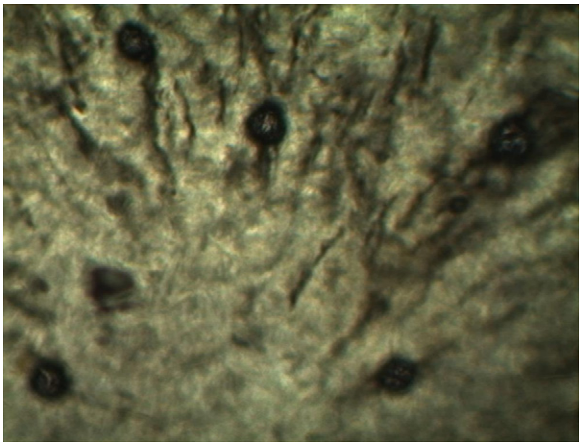

Fig. 2. Polarized microscopy image of 80/20% w/w PEG/agarose blend.

3. Results and discussion

PEG/cellulose, PEG/agarose, and PEG/chitosan shape stabilized blends were prepared starting with the minimum PEG encapsulation ratio and continuing up to the finding of the ratio with leakage of PEG. The maximum encapsulation ratio of PEG without leakage was 60/40 w/w for PEG/cellulose, 70/30 w/w for PEG/agarose, and 80/20 w/w for PEG/chitosan and therefore these blends were identified as shape stabilized PCMs.

Table 1
DSC data for 60/40 w/w PEG/cellulose, 70/30% w/w PEG/agarose, and 80/20% w/w PEG/chitosan blends.

Form stable PCM	Melting temperature (°C)	Latent heat of melting (J/g)	Freezing temperature (°C)	Latent heat of freezing (J/g)
PEG_{4000}	53.23	208.57	42.40	−204.97
				Beforethermalcycling
PEG/cellulose	58.51	84.63	37.05	−78.92
PEG/agarose	57.73	110.86	43.36	−99.01
PEG/chitosan	57.18	152.16	44.76	−138.39
				Afterthermalcycling
PEG/cellulose	53.18	91.80	37.38	−84.21
PEG/agarose	53.72	122.33	44.00	−109.64
PEG/chitosan	58.71	167.36	41.80	−166.18

Fig. 1a–d represents the cross-sections of PEG and PEG/cellulose, PEG/agarose, and PEG/chitosan shape stabilized blends, respectively. It can be found that the inner structures of the composite PCMs are more compact and uniform than that of the surface, which illustrates that PEG has been impregnated into natural polymers. The morphologies of the shape stabilized blends are slightly different as a result of the variation of natural polymer in the composites, but PEG is all enwrapped commendably by used polymers.

Fig. 2 shows a photograph of 80% w/w PEG/agarose blend at which PEG bleeds through the blend above its melting temperature and it leads to phase separation in the composite. The spherical particles in the picture show PEG domains after seepage.

FT-IR spectra of the blends were used to investigate possible interactions between PEG and cellulose, agarose or chitosan. Fig. 3 shows the FT-IR spectra for PEG/cellulose (a, b), PEG/agarose (c, d), and PEG/chitosan (e, f) shape stabilized blends before and after thermal cycling, respectively. Hydrogen bonding interactions are commonly observed in PEG and in all hosting polymers at the same time. CH_2 asymmetric and symmetric stretching peaks are also observed in both PEG and any of used polymers however the asymmetric stretching peak observed at 2900 cm^{-1} is broad in PEG.

It is also found from the blends spectra that the asymmetric stretching peak is broad in all, as the finger-print region resembles both PEG and any of the used natural polymers. In the blends, the hydrogen bonding peaks changes to split into two that can be explained with the number of different OH groups in the supporting polymers. There are at least two sources of hydroxyl group in the natural polymers used here and they distribute well due to the interactions between PEG and each of natural polymers. In case of the blends, the hydrogen bonding interactions are between oxygen atom in PEG and each of natural polymersǐ hydroxyl groups, or hydroxyl end groups in PEG chain and oxygen or nitrogen atom in the used matrix polymer.

On the other hand, it is clear from the figure that the curves before and after thermal cycling are almost the same. They are slightly separated from each other thermal effect which enhances phase separation in the blends.

The results of DSC measurements of the shape stabilized PCMs are given in Table 1 and Fig. 4a–d. The DSC curves of pure PEG (a) display two distinguished peaks between 53 and 64 °C. This separation is not clear in solidifying process. The first peak is expected to be due to a solid–solid transition of one crystalline structure into another which is sometimes observed in the literature (Pielichowski & Flejtuch, 2002). The second peak is associated with the melting point of the crystallites. Since these two peaks are very close and overlapping in the solidifying process it is accepted as a single melting transition here.

Fig. 4 shows the DSC curves of PEG_{4000} (a) and its shape stabilized blends with cellulose (b), agarose (c), and chitosan (d) before thermal cycling. It is clear from the figure that PEG curves in the blends are similar to the curve of pristine PEG. However phase changes were observed in wide ranges and the peaks for solid–solid and solid–liquid phase transitions became more apparent due to strong H-bonding interactions. Table 1 shows the DSC data for the blends both before and after thermal cycling. It can be seen from the table that melting and crystallization temperatures of shape stabilized blends are higher than pure PEG before thermal cycling as the enthalpies are lower than calculated by

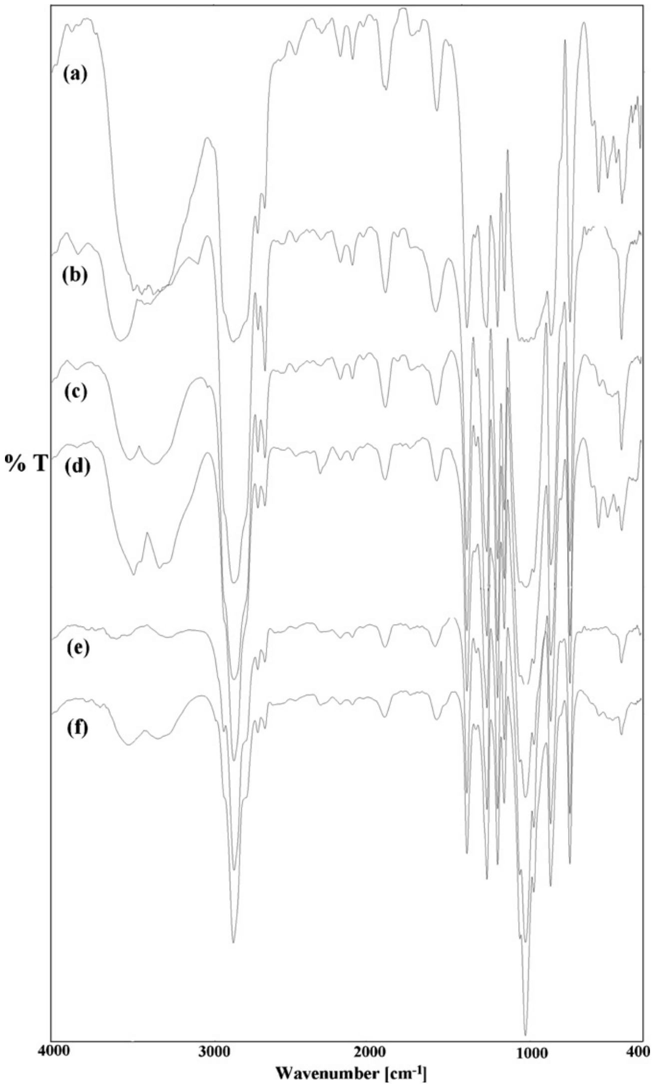

Fig. 3. FT-IR spectra of 60/40% w/w PEG/cellulose (a, b), 70/30% w/w PEG/agarose (c, d), 80/20% w/w PEG/chitosan (e, f) shape stabilized blends before and after thermal cycling, respectively.

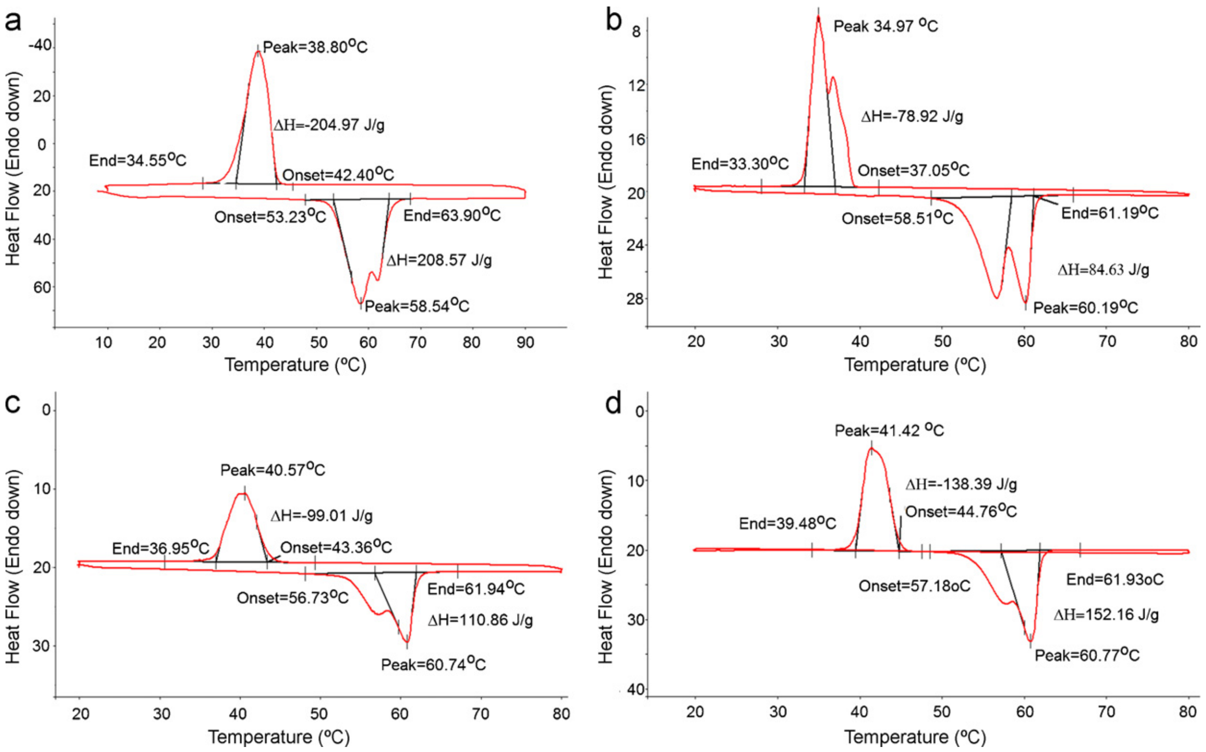

Fig. 4. DSC curves of PEG (a) 60/40% w/w PEG/cellulose (b), 70/30% w/w PEG/agarose (c), 80/20% w/w PEG/chitosan, (d) shape stabilized blends before thermal cycling.

the Eq. (1).

$$\text{PEG}\quad(\text{wt\%}) = \frac{\Delta H_{\text{formstablePCM}}}{\Delta H_{\text{PEG}}} \times 100 \tag{1}$$

where $\Delta H_{\text{formstablePCM}}$, and ΔH_{PEG} are measured enthalpies of shape stabilized PCM blend and pure PEG, respectively. It can be explained that PEG interacted with each of the used natural polymers positively and these interactions resulted in the increase of melting temperature of the shape stabilized PCMs. The enthalpies decreased because the interactions distorted the crystal structure of the PEG. After thermal cycling, the phase change temperatures of the shape stabilized blends decreased as the enthalpies increased. It is well known that polymers are generally immiscible to each other and thermal effect supports phase separation. Here, after 3000 thermal cycling, the component of the blends separated in the matrix of the blends and gave phase change temperatures close to the melting and crystallization temperatures of PEG and enthalpy values close to the expected values from the blends by Eq. (1).

4. Conclusions

Shape stabilized phase change materials, based on cellulose, agarose, and chitosan as matrix polymers and PEG as PCM were prepared in melt for latent heat energy storage applications. The shape stabilized PEG/cellulose, PEG/agarose, and PEG/chitosan blends kept their shapes even when the PCM undergoes phase change from solid to liquid. FT-IR analysis of the shape stabilized blends showed that PEG was hosted in each of the used natural polymers due to hydrogen bonding interactions between the blend components. The blends without leakage of PEG were in single phase morphology according to microscopy analysis as higher PEG constitution resulted in phase separation. The DSC analysis results indicated that the prepared shape stabilized PCM blends had suitable phase change temperatures, latent heats, good thermal reliability and chemical stability for latent heat energy storage in solar space heating and ventilating applications in buildings.

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