

# Study on Phase Change Characteristics of PEG/PAM Coupling Blend

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**ABSTRACT:** A novel solid–solid phase change materials with polyethylene glycol (PEG) worked as phase change substance and polyacrylamide (PAM) as solid skeleton was synthesized by coupling blend. Their phase change behaviors and structure analysis was studied by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR), they had reversible solid–solid phase change properties. The result indicates that the PEG/PAM PCMs has great transition enthalpy and suitable phase transition temperature in the phase

transition process. It can be considered as promising PCMs. Otherwise, their crystallization behavior were analyzed by polarization optical microscopy (POM), the crystalline degrees of these phase change materials were affected due to the intermolecular interaction and chemical bond. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1591–1595, 2010

**Key words:** PEG; PAM; solid–solid phase change; coupling blend

## INTRODUCTION

Phase change materials (PCMs) are materials with heat storage and temperature-adjusting functions that change by giving off and absorbing latent heat during their phase change process. Phase change heat of PCMs has two main characters: one is high enthalpy and capacity of per unit volume and the other is that the temperature over phase change process keeps constant or changes slightly. Among them, solid–solid phase change materials (SSPCMs) are a major focus of attention. These SSPCMs can be applied in the fields of military and domestic affairs. The utilization of SSPCMs is extensive, such as solar energy storage, waste heat recovery, smart air conditioning buildings, temperature adaptable greenhouses, insulation clothing, and so on. Some chemical and physical methods have been used to prepare solid–solid phase change materials.<sup>1–5</sup> SSPCMs present reversible phase change procession. Their main advantage is little variation volume and no liquid lick when phase change happen, thus can decrease the requirement of vessel. SSPCMs even can be made structural materials directly and need no vessel. They have feasible phase change temperature, long using life, and steady properties, which is worthy of application in practice. SSPCMs are hot-spot in phase change materials research. Exploitation and application in SSPCMs overseas is more and more

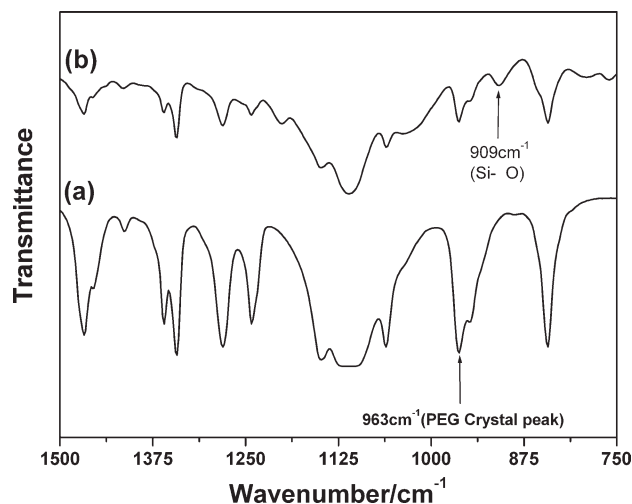
excellent in these years. As PCMS, polyethylene glycols (PEG) have enough latent heat and a proper phase change temperature region. The phase change characteristics depend on the molecular weight of PEG.<sup>6</sup> In our research, new kinds of polymeric SSPCMs (PEG/PAM) were prepared. In these materials, PAM worked as solid skeleton and PEG as working substance, which can be used as insulating padding directly or used as functional factor in spinning. In previous work, we adopted chemical crosslinking method to synthesis SSPCMs (PEG/MDI/PVA).<sup>7</sup> New kinds of polymeric SSPCMs (PEG/PAM) were prepared by means of coupling blend in this study. Their phase change behaviors was studied by differential scanning calorimetry (DSC) method, they had reversible solid–solid phase change properties. The melting point ( $T_m$ ) of blends and the peak crystalline point ( $T_c$ ) was related to the weight percentage of PEG.  $T_c$  was higher when the weight content of PEG/PAM was nearly 70/30 and  $T_c$  was lower when the weight content of PEG/PAM was 30/70. The enthalpy of blends was declined with the weight content of PEG decreased; We can intend to adjust phase change temperature by controlling molecular weight and enthalpy by controlling the weight content of PEG in blendings. The crystallization structure of SSPCMs (PEG/PAM) were analyzed by polarization optical microscopy (POM).

## EXPERIMENTAL

### Materials

Polyethylene glycols (PEG), chemical pure reagent with  $M_w$  of 2000, 10,000, respectively, were obtained

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**Figure 1** The FTIR spectra of PEG10000 (a) and PEG10000/PAM coupling blend (b).

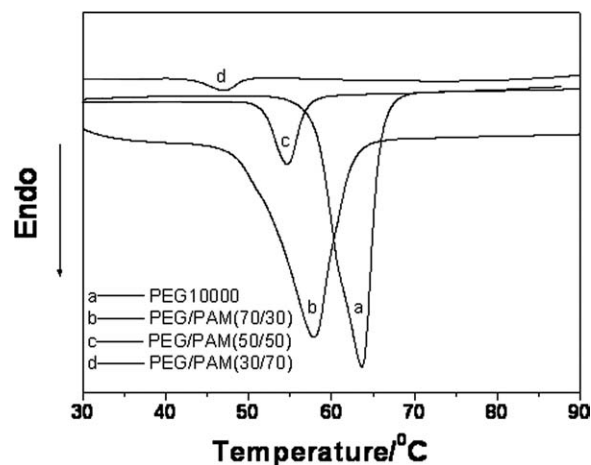
from Tianjin Chemical Reagent Co., China. Polyacrylamide (PAM) were obtained from Shanghai Chemical Reagent Co., China. Silane coupling agents (KH560) were obtained from Nanjing Shuguang Chemical Reagent Co.

#### Preparation of PEG/PAM coupling blend

The PEG was desiccated with a silica gel dryer, and PAM was dried in an oven at 80°C. A three-necked flask equipped with an agitator, a thermometer and a condenser charged with the calculated amount of PEG and PAM (mass ratio:  $M_{\text{PEG}}/M_{\text{PAM}} = 70/30, 50/50, 30/70$ ) was immersed in an oil bath at 80°C, and then the solution of coupling agents KH560 was added into the flask (solid content: 50%), and the reaction was continued for 24 h at 80°C. After the reaction was over, yellowish solid product was obtained by heating at 80°C in drying oven. The sample was washed with deionized water at 80°C repeatedly for 30 min, dried at 80°C in vacuum for several days, equilibrated to constant weight and then stored in a closed container at room temperature prior to measurements.

**TABLE I**  
DSC Thermal Properties of PEG and PEG/PAM Coupling Blends

Polymer	$T_m$ (°C)	$\Delta H_m$ (kJ/mol)	$T_c$ (°C)	$\Delta H_c$ (kJ/mol)
PEG2000	60.35	176.9	28.2	182.1
PEG/PAM(70/30)	57.9	129.6	24.6	124.3
PEG/PAM(50/50)	53.1	39.4	19.9	109.4
PEG/PAM(30/70)	35.3	19.8	12.8	25.2
PEG10000	63.9	225.9	61.2	202.6
PEG/PAM(70/30)	58.9	159.4	56.5	138.3
PEG/PAM(50/50)	54.2	44.1	52.1	118.9
PEG/PAM(30/70)	46.8	38.8	45.3	33.0



**Figure 2** DSC heating curves of PEG10000/PAM coupling blends.

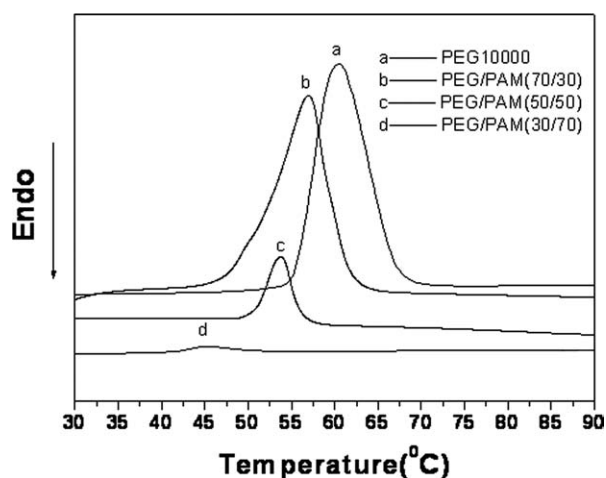
#### Characterization

The phase change temperature and enthalpy of PCMs were obtained by means of a differential scanning calorimeter (Mettler DSC-821e). Condition: 0–100°C–0–100°C (the first heating was to eliminate heat history); the heating and cooling rate was 10°C/min, protected by N<sub>2</sub>. FTIR spectra of pristine PEG and PEG/PAM Coupling blend were taken in VECTOR-22 (Bruker Co., Germany) infrared spectrophotometer. The KBr pressed disc technique (around 2 mg of sample and 200 mg of KBr) was used. An observation of polarization optical microscopy (POM) was performed on a OLYMPUS BX51 POL microscope equipped with a video camera. The sample was placed between a microscope glass and a cover slip and heated with a Leitz350 hot stage.

## RESULTS AND DISCUSSION

#### IR spectra analysis of PEG/PAM coupling blend

Figure 1 shows the IR spectrum of the PEG10000 and PEG/PAM coupling blend. The characteristic absorption bands of PEG appear at 3424 cm<sup>-1</sup> (stretching vibration of aliphatic O–H bond), 1125 cm<sup>-1</sup> and 1061 cm<sup>-1</sup> (stretching vibration of aliphatic C–O bond), 963 cm<sup>-1</sup> (PEG crystal peak). Accordingly, the characteristic absorption bands of PEG/PAM coupling blend appear at 909 cm<sup>-1</sup> (stretching vibration of Si–O bond), 1627 cm<sup>-1</sup> (stretching vibration of C=O bond). The IR spectrum indicates that the crystal peak strength of curve (b) decreased obviously compared with curve (a), and the stretching vibration peak (C=O) of curve (b) shifted 37 cm<sup>-1</sup> towards low wavenumber. Possible reasons, which were attributed to N–H groups of PAM interacting with O–H groups of PEG through intermolecular hydrogen bond forces and

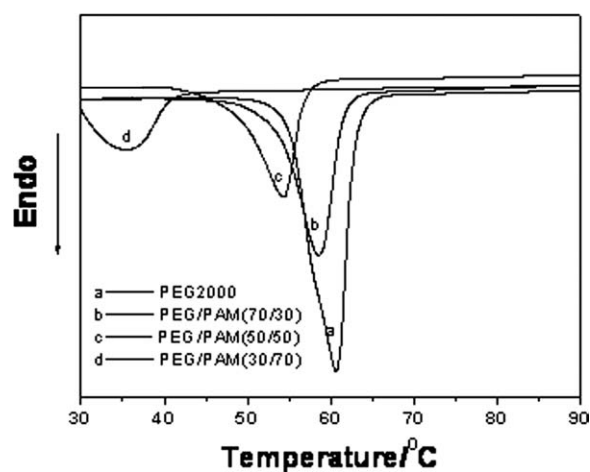


**Figure 3** DSC cooling curves of PEG10000/PAM coupling blends.

chemical bond forces of Coupling agents KH560. Therefore, we could draw a conclusion that PEG/PAM SSPCMs could be gained through coupling blend of PEG, PAM and KH560.

#### DSC analysis of PEG/PAM coupling blend

Since the phase change temperature region of PEG depends on its molecular weight, the phase change temperature of the PEG/PAM coupling blend should vary by adding PEG of different molecular weight in the blending process. The results of DSC analysis are listed in Table I. All these samples exhibited one melting peak and one crystallization peak in the heating and cooling process. The melting peak and crystallization peak of PEG2000 and PEG10000 appearing in the low temperature region (lower than 65°C), can be used for heat storage.<sup>7</sup> Figures 2–5 shows the heating/cooling cycle curves of PEG/PAM coupling blend with different PEG molecular weight. All samples were preheated to 100°C and kept for 10 min to remove 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 Figures 2–5, like PEG2000, PEG10000 and PEG/PAM coupling blends were also a transition reversible latent storage material. Pristine PEG2000 and PEG10000 consisting of ethyl–ether linkage segments with active hydroxyl end-groups that were easy to form intermolecular hydrogen bond crystallized easily and had high transformation enthalpy of 182.1 kJ/mol and 202.6 kJ/mol, respectively. Expectedly, the DSC curve of PEG/PAM coupling blend was similar to that of pristine PEG due to its structure containing PEG units. And, with an decreasing ratio of PEG/PAM, the phase change temperature and phase change en-

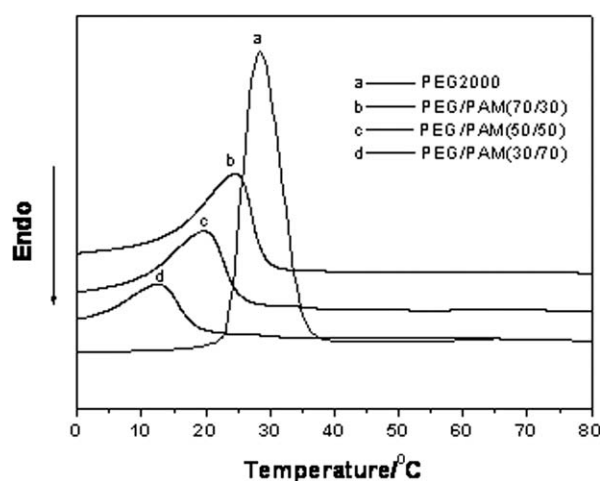


**Figure 4** DSC heating curves of PEG2000/PAM coupling blends.

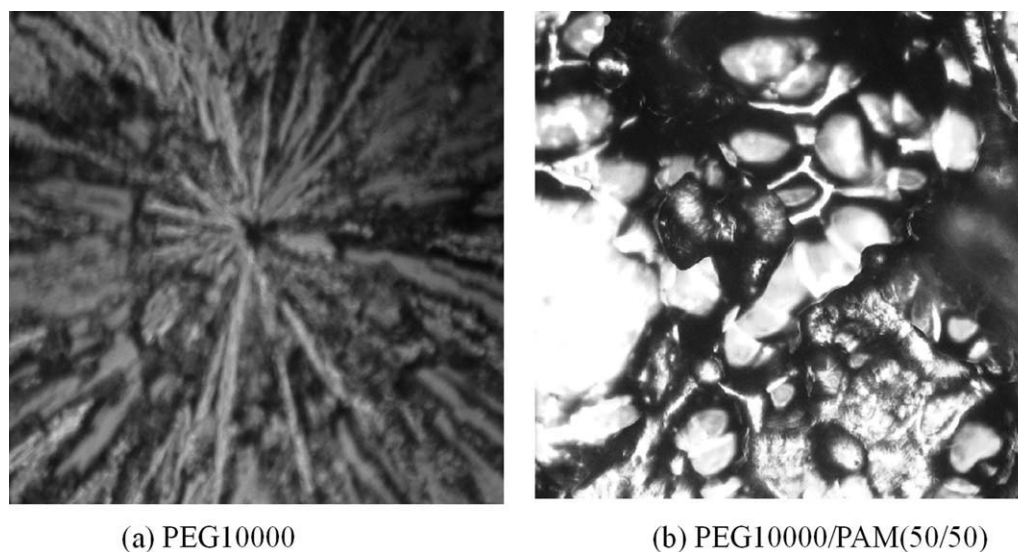
thalpy of PEG units decreased in coupling blend. The phase change enthalpy of PEG10000/PAM (30/70) coupling blend reached 38.8 kJ/mol and 33.0 kJ/mol, respectively, which meant that its endothermic and exothermic capacity had been weakened after coupling blend. The conclusion that intermolecular hydrogen bond forces and chemical bond forces between PEG and PAM result in the decrease of phase change temperature and enthalpy simultaneously agrees with the previous conclusion found by many researchers.<sup>8</sup>

#### POM analysis of PEG/PAM coupling blend

The crystallization structure and morphology of PEG/PAM SSPCMs were analyzed by polarization optical microscopy (POM). As shown in Figure 6(a,b) and 7(a,b), both pristine and PEG/PAM coupling blend had crystal spherulites at 25°C. Their



**Figure 5** DSC cooling curves of PEG2000/PAM coupling blends.

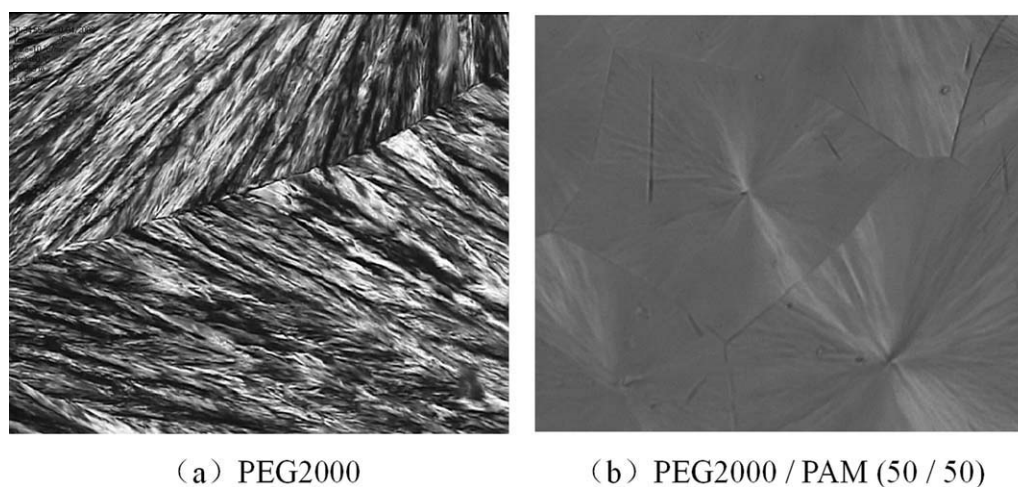


**Figure 6** POM photos of pristine PEG10000 (a) at 25°C, PEG10000/PAM (mass ratio: 50/50) coupling blend (b) at 25°C.

melting and crystalline procedure was affected due to the addition of PAM, but their crystalline structure had not been changed. The crystalline degree of coupling blends decreased gradually with the weight content of PEG decreased as the results of DSC analysis. Under the same test condition, the dimension of the spherulite of PEG/PAM coupling blend was smaller than that of pristine PEG due to the restricted crystallization of PEG in the coupling blend network. The presence of intermolecular hydrogen bond forces and chemical bond forces did not alter the crystal form of PEG, but it limited the degree of crystallization. Otherwise, the synthesized PEG/PAM PCMs kept solid state during the temperature range of transition due to the intermolecular hydrogen bond forces and chemical bond forces between PEG and PAM restricting free movement of the PEG segment.

## CONCLUSIONS

The PEG/PAM coupling blends were successfully prepared. To obtain the SSPCMs with desired phase change characteristics, PEG was added into the system. The PEG segments in PEG/PAM coupling blend could also show good phase change characteristics when the ratio of PEG/PAM was close to the 70/30 (mass ratio) for PEG2000 and PEG10000. The PEG/PAM coupling blends are a kind of solid–solid phase change material. There were intermolecular hydrogen bonds between PEG and PAM, so that the materials remained in the solid state even when the temperature higher than the melting point of PEG. The novel high performance solid–solid phase change heat storage material PEG/PAM coupling blend with high phase change enthalpy and suitable transition temperature, maybe, has extensive potential applications.



**Figure 7** POM photos of pristine PEG2000 (a) at 25°C, PEG2000/PAM (mass ratio: 50/50) coupling blend (b) at 25°C.

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