Polymer/Palmitic Acid Blends as Shape-Stabilized Phase Change Material for Latent Heat Thermal Energy Storage

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Two composite blends of poly(vinyl alcohol)-palmitic acid and poly(vinyl chloride)-palmitic acid were prepared. In these composites, palmitic acid acts as latent heat energy storage during its solid-liquid phase change when the polymer (poly(vinyl chloride) or poly(vinyl alcohol)) has the function of supporting material because of its structural strength. There is no leakage of palmitic acid even when it is in melt state. Therefore, these composite blends are called shape-stabilized phase change materials and they have utility advantage of without encapsulation in passive solar latent heat thermal energy storage application. The maximum percentage miscibility ratio of palmitic acid with both polymers was found as 50 as the blends have the shape-stabilized property. The dispersion of palmitic acid into the network of polymer matrix was investigated using a dissection microscope. The miscibilities of palmitic acid with poly(vinyl alcohol) and poly(vinyl chloride) were proved by Fourier transfer infrared spectroscopy and differential scanning calorimetry methods. Furthermore, the melting temperatures and latent heats of both the shape-stabilized composite blends were determined as 56.2 and 54.4°C and 121.6 and 120.3 J/g, respectively. The results obtained indicate that the shape-stabilized composite blends have great potential for passive solar space heating and solar building heating in terms of their satisfactory thermal properties and cost-effectivity.

Key Words: Shape-stabilized, Poly(vinyl chloride), Poly(vinyl alcohol), Palmitic acid, Blends.

INTRODUCTION

Thermal energy storage (TES) is assuming an ever increasing proportion in the energy debate as an efficient potential means of utilizing solar energy. TES materials are chosen on the basis of their ability to store heat in two ways. Firstly, by means of a temperature increase, and secondly, by undergoing solid-liquid phase change. The second way is also known as latent heat thermal energy storage (LHTES) method. A LHTES system is employing a phase change material (PCM) as latent heat storage material. A number of searches have been made for possible PCMs such as salt hydrates, paraffins, fatty acids and their mixtures for LHTES applications[1-3]. The practical use of salt hydrates is limited by their undesired properties like incongruent melting, super-cooling and phase separation and corrosion effect on the storage container. Moreover, the paraffins do not have a large utility area because of their low thermal conductivity. Among these groups, the fatty acids are the most promising PCMs because of melting and cooling at almost constant temperature, large latent heat of fusion, self-nucleating behaviour, ready

availability, non-toxicity, non-flammability, non-corrosiveness, no or less volume change during melt/freeze processes and good thermal and chemical stability after continual heat/cool cycling[4-6]. However, the fatty acids cost more than the other PCMs on a bulk basis, but are cheaper to package; so the final module costs are comparable.

On the other hand, in recent times, developing a shape-stabilized polymer-PCM blend as a novel composite PCM for solar LHTES systems has gained more and more attraction because of its three important advantages: (1) it retains its shape in the solid state even when the temperature of the blend is above the melting point of the PCM. Therefore, it can be called as shape-stabilized PCM; (2) there is no requirement of its capsulation and thus it is considered as a cost-effective material; (3) it can be easily prepared in desired dimensions. Some studies on such PCMs have been carried out. The high density poly(ethylene) (HDPE)/paraffin blends as shape-stabilized solid-liquid PCM were studied from the point of view of preparing their blends and determining their thermal characteristics[7-10]. It was reported that these materials could be used as energy storage material without container in LHTES systems, which were developed for passive solar space heating applications. A shape-stabilized composite PCM consisting of a thermo-plastic-elastomer poly(styrene-butadiene-styrene) and paraffin was prepared and its thermal performance was investigated[11]. In that study, it was reported that the shape-stabilized PCM shows the same phase transition behaviour as paraffin and it has the same latent heat of fusion as paraffin (80%)[12]. A matrix type phase change thermal storage tile module with no surface covering was tested. A differential scanning calorimetry (DSC) analysis was performed on poly(ethylene glycol) (PEG)/fatty acid blends to indicate the feasibility of binary polymer-fatty acid for the TES systems working over large temperature ranges in terms of their thermal properties[13].

The purpose of this study is to prepare the poly(vinyl alcohol)-palmitic acid (PVA/PA) and poly(vinyl chloride)-palmitic acid (PVC/PA) blends as shape-stabilized PCM, to prove the miscibility of PA with the polymers by microscopic investigation and FTIR spectroscopy, and to measure their thermal properties by DSC analysis method.

EXPERIMENTAL

Poly(vinyl alcohol) (PVA 72000; ash $\leq$ 2.5%) and poly(vinyl chloride) (PVC; M_r *ca.* 48000) were supplied by Fluka. Palmitic acid (PA; m.p. 61–64°C by manufacturer; purity 98 wt. %) was supplied by Aldrich.

The composite PCMs with amounts of 100 g were prepared by mixing PA and the polymer in molten state and cooling to room temperature. The composite PCMs consisting of different mass combinations of PA (20, 30, 40, 50%) were prepared to establish the maximum miscibility ratio of PA under which there is no leakage of PA from the composite mass at temperature between the melting point of the polymer and that of the PA.

Thermal properties of PVA/PA and PVC/PA that form stable PCMs, *e.g.*, glass transition temperatures, melting temperatures and latent heats of fusion were measured using a DSC (DuPont 2000) instrument. Indium was used as a reference for temperature calibration. The analyses were performed in the temperature range

20–80°C for pure PA and 20–275°C for the blends at the same heating rate (5°C/min) and under a constant stream of nitrogen at atmospheric pressure. The glass transition temperature (T_g) modification was determined by the method of base line deviation. The melting temperature of the PCM, T_m, corresponds to the onset temperature 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 fusion, H_{fus}, was calculated as the area under the peak by numerical integration. Infrared spectra were obtained on a KBr disk by a fourier transform infrared spectrophotometer (Jasco FTIR-430). The morphologic investigation on the PVA/SA and PVC/PA blends was carried out using a dissection microscope (Laica).

RESULTS AND DISCUSSION

In the prepared shape-stabilized composite PCMs, the polymers serve as supporting material for the PA, which melts and solidifies in their network structure. There is no leakage of PA even when it is in the molten state. Therefore, this property makes them possible for the solar LHTES systems without container. The mechanical strength and the highest enduring temperature of these composites decrease with increasing the mass percentage of PA. In our experiments, the maximum miscibility ratio of PA with PVA and PVC could go as high as 50 wt. % and under which no leakage of paraffin was observed over the melting temperature of PA for several heating cycles. It means that the mechanical strengths of these composites are weak when the amount of PA in the blends is over 50 wt. %.

In order to observe the dispersion of PA in PVA and PVC, morphologic investigations on the PVA/PA and PVC/PA blends were carried out using a dissection microscope and the obtained micrographs are given in Fig. 1. Both

(a)   (b)
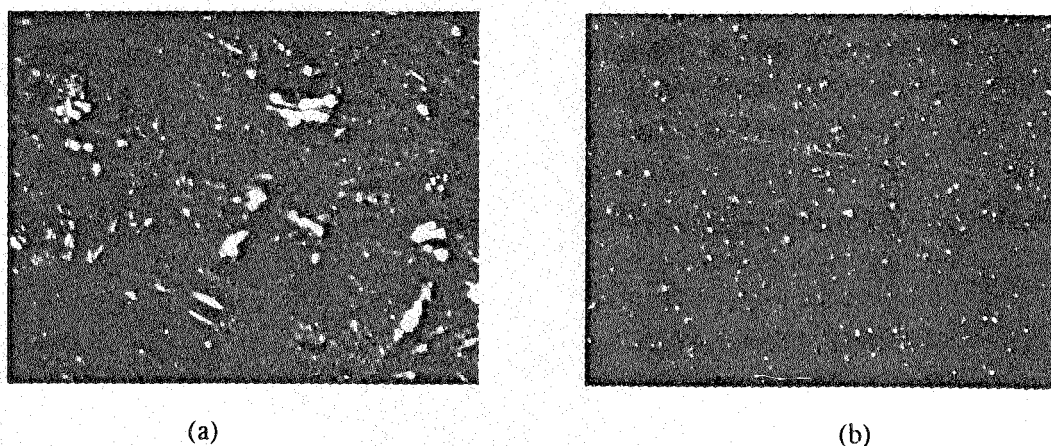
Fig. 1.   The micrographs of (a) shape-stabilized PVA/PA (b) shape-stabilized PVC/PA composite PCM

micrographs indicate that the PA (black parts in micrograph) dispersed into the network of the solid polymer (white parts in micrograph). The blends gain a mechanical strength with dispersion of PA in the polymer and thus the PVA/PA and PVC/PA composite materials keep the same shape in solid state without seepage of molten PA even if PA melts during a heat storage process. The micrographs of PVA-PA and PVC-PA are similar to the scanning electron microscope (SEM) photographs obtained for the different composite types of paraffins/HDPEs

developed as shape-stabilized PCMs[7-10] and in agreement with the dispersion models[7, 11]

The miscibility of PA with PVA and PVC was proved by DSC analysis and FTIR spectroscopy method. Figs. 2 and 3 give evidence of the interactions between PA
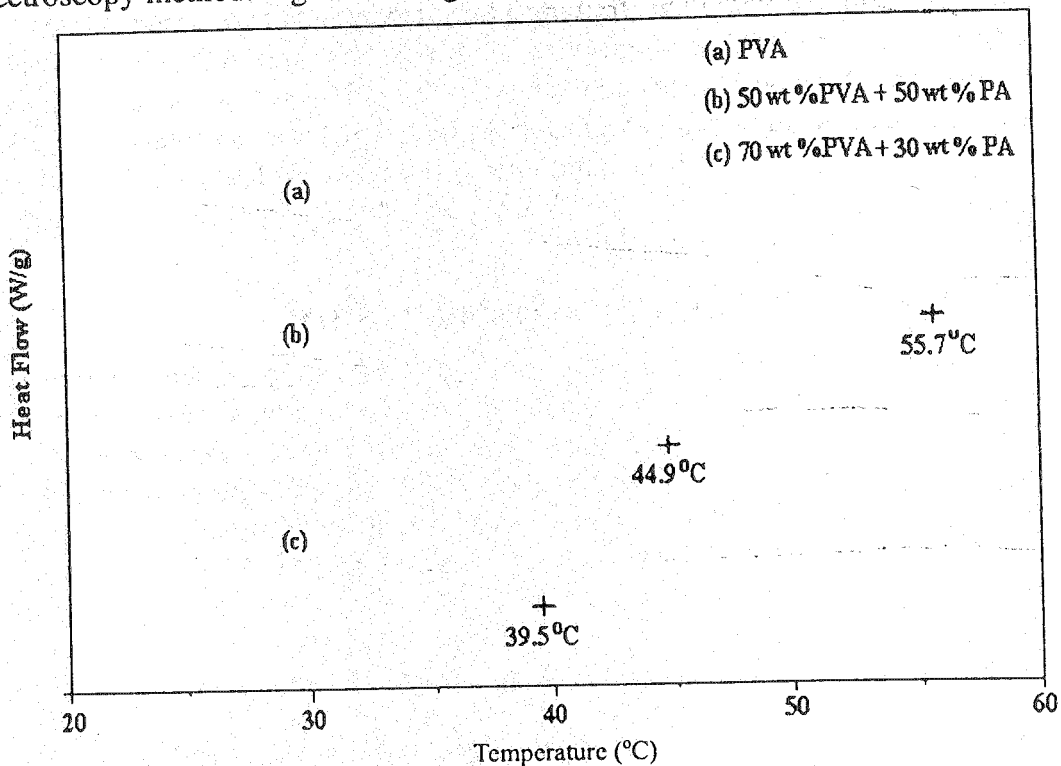

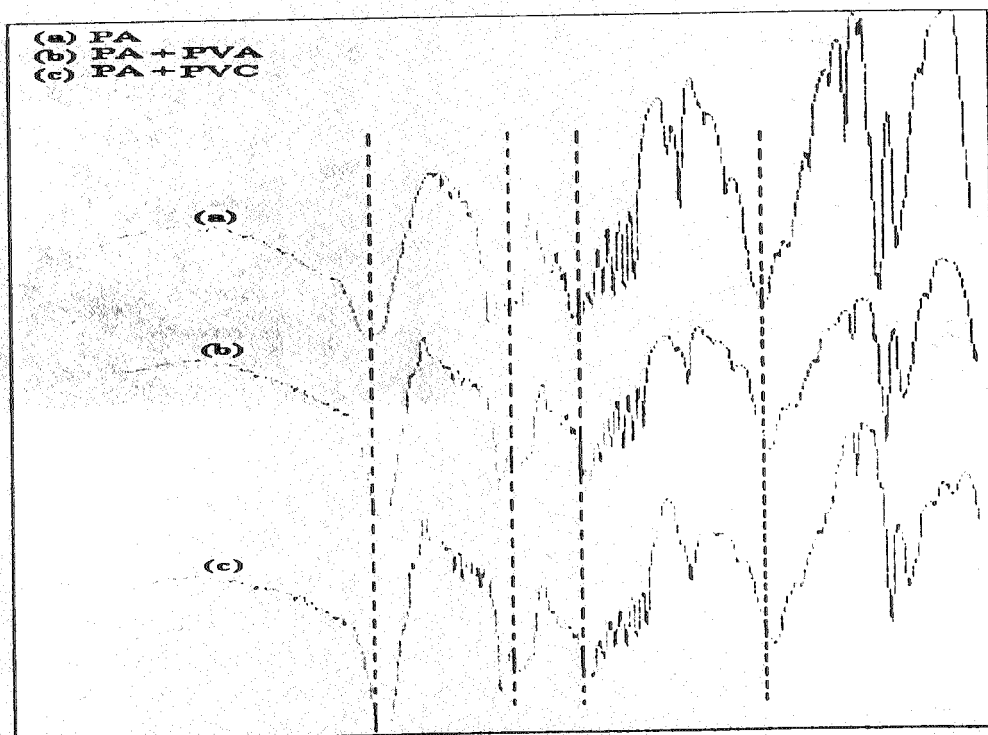Fig. 2.   The effect of the amount of PA on the glass transition temperature (Tg) of PVA

Fig. 3. Shift in the main FTIR spectral peaks of the C=O group in PA, PVA/PA

and the polymers. Fig. 2 is given as an example to observe the effect of the amount of PA in the blends on the glass transition temperature (T_g) of PVA. As seen from the DSC curves, the T_g value of PVA significantly decreases with increasing amount of PA. This is indirect evidence of polymer-fatty acid interaction. Moreover, Fig. 3 shows the shifts in the main FTIR spectral peaks of the $v(C{=}O)$ group in PA, PA/PVA (1/1 w/w) and PA/PVC (1/1 w/w) systems. The $v(C{=}O)$ vibration of pure PA generally occurring at 1725–1700 cm^{-1} appears only when dimers with two associated carbonyl groups are formed as below:

$$R—C \begin{matrix} O---H—O \\ \\ O—H---O \end{matrix} C—R$$

The frequency of $v(C{=}O)$ group in dimeric structure of PA slightly decreases from 1702 to 1698 cm^{-1} in the PVA/PA system and from 1702 to 1694 cm^{-1} in the PVC/PA system. These results could be interpreted as decrease of carboxyl association in PA because of a new association between PA and the polymers. By adding PVA to PA, the absorption band at 1430 cm^{-1} due to a coupling of the deformation vibration of OH with carbonyl group vibration, the valency vibration band at 1295 cm^{-1} and OH deformation band at 940 cm^{-1} shift a lower frequency of 1426, 1293 and 937 cm^{-1}, respectively, as seen in Fig. 3. These bands show similar shifts towards lower frequencies, which are 1423, 1291 and 934 cm^{-1}, respectively when PVC is added (Fig. 3). These results also may reflect a decrease in the association of carboxylic groups. The PA-PVA and PA-PVC interactions proved by FTIR and DSC methods can be considered as dipole-dipole type and as hydrogen bonding. The latter type interaction could be more likely responsible for miscibility of PA with the polymers12.

On the other hand, the DSC curves of PA, PVA and PVC compound are given in Figs. 4 and 5, respectively. These figures present reference data to evaluate the changes in thermal properties of the composite PCMs. The DSC curves of shape-stabilized PVA-PA and PVC-PA composite blends are also shown in Figs. 6 and 7,
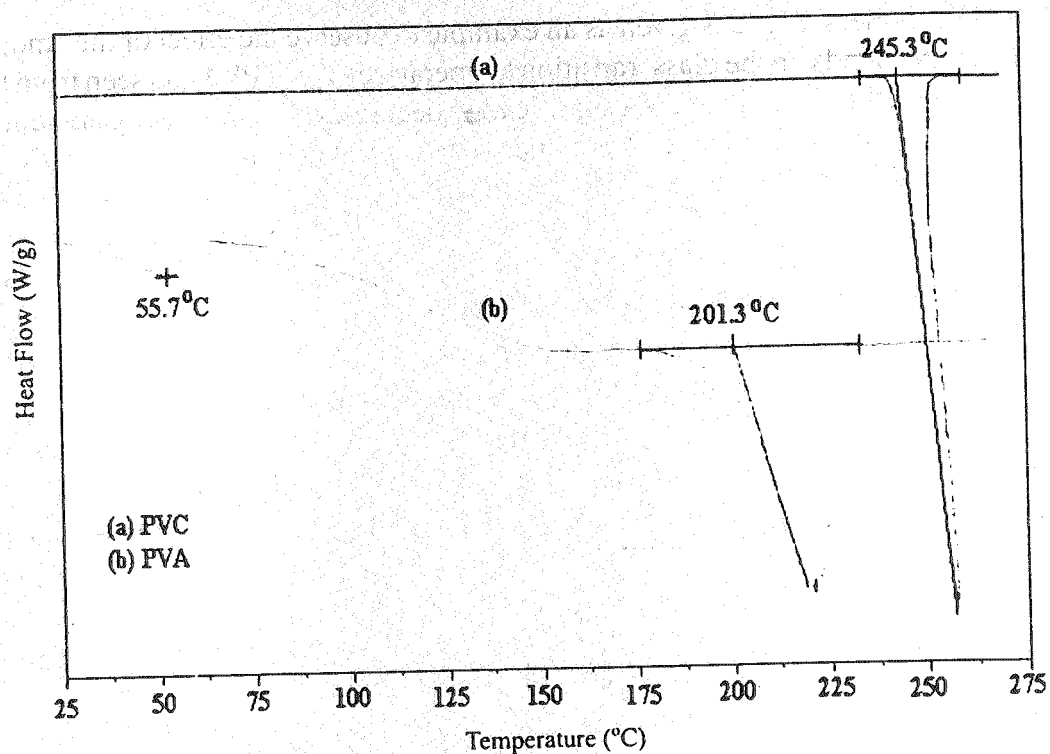

Fig. 4.   DSC curve of palmitic acid

Fig. 5. DSC curves of PVA and PVC.

respectively. The sharp peak in the curves represents the solid-liquid phase change (or melting) of the PA as the minor peak corresponds to melting of the polymer. The initial T_g of PVA (55.7°C) in the blend cannot be observed because it is masked by the melting peak of PA (Fig. 6). Thermal properties evaluated from the DSC curves
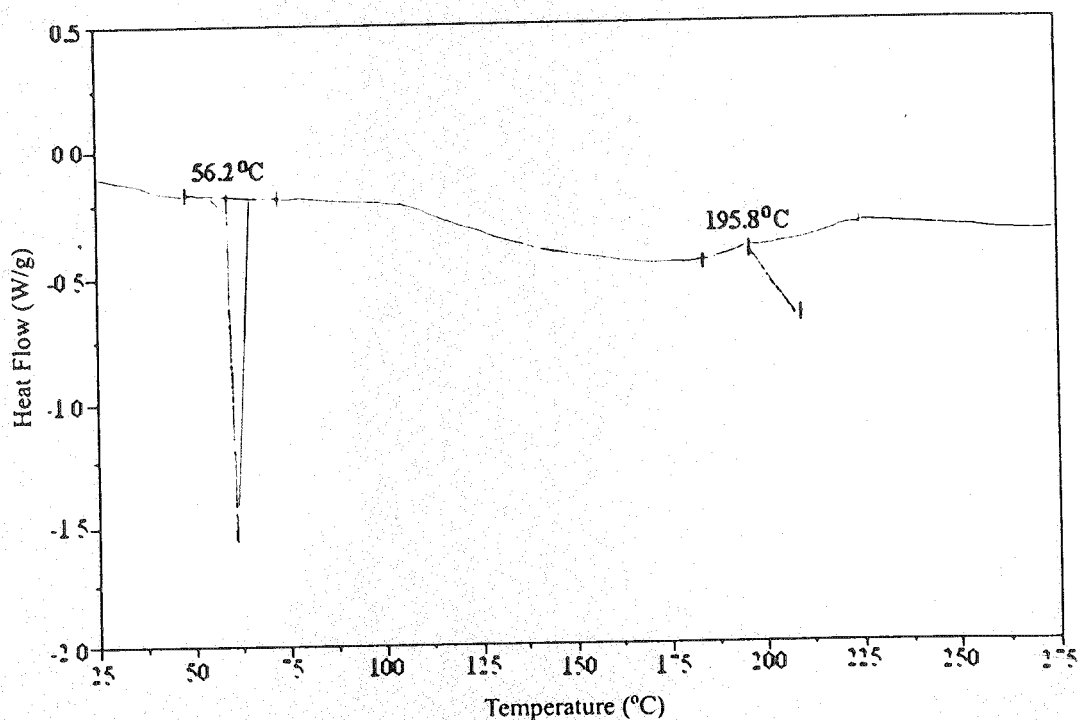

Fig. 6.   DSC curve of shape-stabilized PVA/PA composite PCM

are given in Table-1. The melting temperature and the latent heat of fusion of the PA decline by adding PVA and PVC. This change in trend not only depends on the chemical structure of polymers, but also on many internal and external factors, often located on the other microstructural levels[13]. However, these thermal properties of the composite PCMs approach those of PA with increasing amount of PA in the blends. The melting temperatures and the latent heats of fusion of PVA/PA and PVC/PA as shape-stabilized PCMs were found as 56.2 and 54.4°C, and 121.6 and

TABLE-1

MELTING TEMPERATURES T_m AND LATENT HEATS OF FUSION ΔH_{fus} OF SHAPE-STABILIZED COMPOSITE PCMS WITH DIFFERENT AMOUNTS OF PA

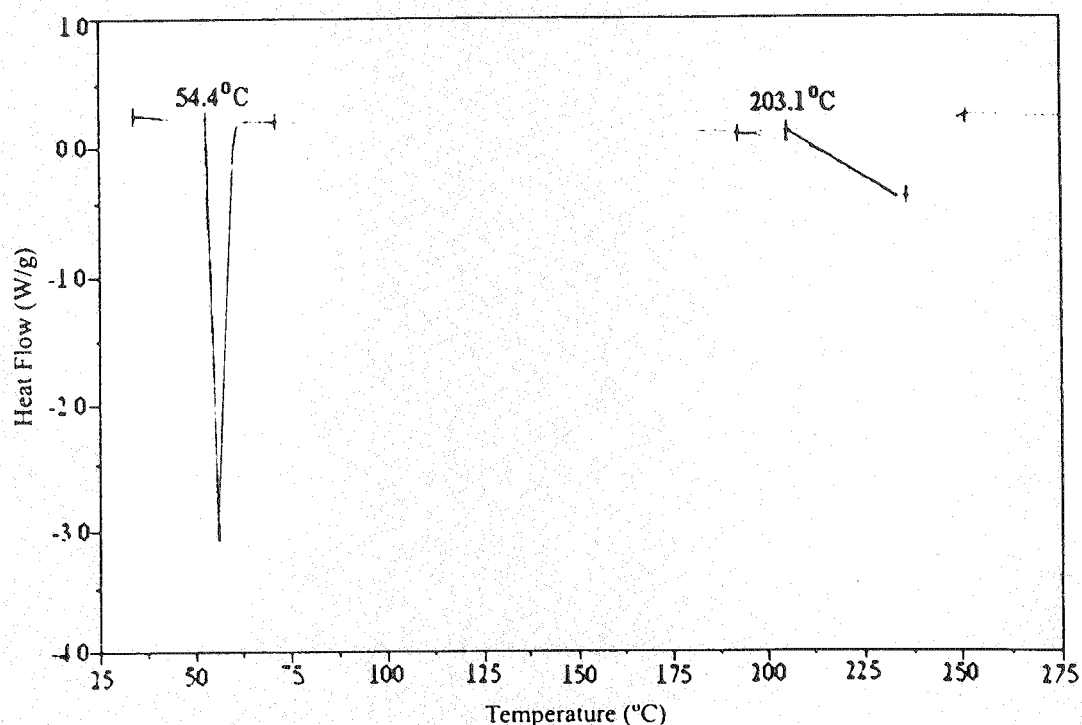|	T_m (°C)	ΔH_{fus} (J/g)
PVA : PA (wt. %):		
0.0 : 100.0	62.4	224.8
80.0 : 20.0	58.1	48.4
70.0 : 30.0	57.3	68.6
60.0 : 40.0	56.7	101.2
50.0 : 50.0	56.2	121.6
PVC : PA (wt.%):		
80.0 : 20.0	57.7	47.6
70.0 : 30.0	56.3	66.5
60.0 : 40.0	55.1	99.8
50.0 : 50.0	54.4	120.3

Fig. 7.   DSC curve of shape-stabilized PVC/PA composite PCM

120.3 J/g, respectively. It is also remarkably noted that that the melting temperatures of the composites are suitable for LHTES and their latent heats of fusion are as high as compared to some salt hydrates and paraffins[1-3]. Therefore, these shape-stabilized PCMs have direct use advantage in passive solar space heating and solar building heating applications since they do not require any capsulation.

Conclusions

It is possible to prepare shape-stabilized PVA/PA and PVC/PA blends as new latent heat storage material with outer container. In the blends, the PA compound is dispersed into the network of solid polymer and it serves as a latent heat storage material when the polymer acts as a supporting material. Therefore, the solid polymer prevents the leakage of molten PA because of its structural strength. The miscibility ratio of PA with PVA and PVC composites without any seepage of PA when it is in molten state were found as high as 50 wt. %. The melting temperatures and latent heats of the shape-stabilized PVA-PA and PVC-PA blends were determined as 56.2 and 54.4°C and 121.6 and 120.3 J/g, respectively by DSC analysis. These satisfactory thermal properties of the shape-stabilized blends make them possible for different TES applications. Furthermore, the shape-stabilized PVA/PA and PVC/PA composite PCMs can be considered cost-effective LHTES materials because they do not require any container in practical use.

ACKNOWLEDGEMENT

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