

Studies on poly(vinyl chloride)/fatty acid blends as shape-stabilized phase change material for latent heat thermal energy storage

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The present study aims to prepare novel shape-stabilized phase change materials (PCMs) by using fatty acids [(lauric acid (LA), myristic acid (MA), palmitic acid (PA) and stearic acid (SA)] as PCM and poly(vinyl chloride) (PVC) as supporting material, and to determine their thermal properties such as melting temperature and the latent heat storage capacity. The maximum composition ratio of all fatty acids in the shape-stabilized PCMs has been found as 50 wt% in which no leakage of fatty acid is observed over their melting temperatures for several heating cycles. The miscibility of fatty acids with the PVC and the interaction between the blend components which is responsible for the miscibility has been proved by microscopic investigation and Infrared (IR) spectroscopy. The melting temperature and the latent heat of fusion of the shape-stabilized PCMs are measured by differential scanning calorimetry (DSC) analysis method. The melting temperatures and latent heats of the shape-stabilized PVC/LA, PVC/MA, PVC/PA and PVC/SA (50/50 wt%) PCMs are determined as 38.8, 49.2, 54.4 and 64.7°C and 97.8, 103.2, 120.3 and 129.3 J/g, respectively. The results indicate that the PVC/fatty acids blends as shape-stabilized PCMs have great potential for passive solar thermal energy applications in terms of their satisfactory thermal properties and advantages of easy preparation with desirable dimensions and direct utility in LHTES applications.

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Energy storage plays an important role in enhancing the applicability, performance and reliability of wide range of energy systems because the discrepancy between energy supply and demand can be eliminated by proper energy storage system. Thermal energy storage (TES) provides an energy reservoir to offset this discrepancy and to combat the fluctuations in energy needs. Latent heat thermal energy storage (LHTES) employing phase change material (PCM) is one of the most attractive TES methods because of the advantage of high energy storage density and isothermal characteristics of charging and discharging processes¹⁻³. So, the use of PCM as the latent heat storage medium in TES systems has gained considerable interest recently. A great variety of PCMs, such as salt hydrates, paraffins, non-paraffin organic compounds and their mixtures for HTES systems have been investigated¹⁻⁶. The fatty acids as non-paraffin organic compounds have superior properties over other PCM groups as follows: congruently melting and cooling, high latent heat of fusion, self-nucleating behaviour, easy availability, non-toxicity, non-flammability, non-corrosive, little

volume change during solid-liquid phase change, and good thermal and chemical stability after a large number of accelerated thermal (melt/freezing) cycles⁷⁻⁹. 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 years, there has been more and more increasing interest in polymer/PCM blends as novel PCMs for passive solar LHTES systems due to their some advantages: (i) such a type PCM is shape-stabilized because it can keep the similar shape in a solid state even when the temperature of the blend is heated over the melting point of the PCM; (ii) it does not require extra capsulation. Therefore, it is considered as cost-effective LHTES material; (iii) heat resistance caused by capsule shell is disappeared by using this kind of PCM. It can be used in case of direct contact with the heat transfer medium and thus, heat charging and discharging rate of the LHTES system significantly increases; (iv) it can be easily prepared in desired dimensions.

These superior properties over traditional PCMs above have directed the researchers to develop novel shape-stabilized PCMs. The high density

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poly(ethylene) (HDPE)/paraffin composites as shape-stabilized solid-liquid PCM were prepared and investigated in terms of thermal characteristics and thermo-physical properties¹⁰⁻¹³. In those studies, it was reported that the HDPE/paraffin blends as shape-stabilized composite PCM could be used as direct contact-heat exchangers in LHTES systems. A thermo-plastic-elastomer poly(styrene-butadiene-styrene) (SBS)/paraffin(P) as shape-stabilized composite PCM was developed and studied its thermal performance¹⁴. The shape-stabilized SBS/P PCM exhibits the same phase transition characteristics as paraffin and up to 80% of latent heat of paraffin. A stable heat storage tile module was investigated and it was concluded that the developed matrix type modules could be used as LHTES material with no outer container¹⁵. Encapsulated paraffin in bisphenol-A epoxy and styrene-ethylene-butylene-styrene (SEBS) polymers worked as shape-stabilized PCMs and showed that interaction between paraffin and epoxy resulted in a material with adequate thermal and mechanical performance¹⁶. In addition, some researches were made on encapsulation of fatty acids as PCMs in polymeric materials as supporting material. Thermal properties of poly(ethylene glycol)(PEG)/fatty acid blends, polyether/fatty acid and poly(ethylene oxide)/stearic acid blends were evaluated by DSC, thermal analysis, IR spectroscopy and optic microscopy methods. It was reported that prepared blends were suitable for TES systems working at large temperature ranges¹⁷⁻¹⁹.

In the present study, the blends of poly(vinyl chloride) (PVC) with fatty acids (lauric, myristic, palmitic and stearic acids) were prepared as novel shape-stabilized PCM and investigated the miscibility of PVC with fatty acids by optic microscope and IR spectroscopy method. In addition, DSC thermal analysis was performed to determine the melting temperature and the latent heat of fusion of shape-stabilized PCMs and thereby to indicate the feasibility of the blends for LHTES applications.

Materials and Methods

Poly(vinyl chloride) (PVC; $M_r \sim 48000$) were supplied from Fluka Company. Fatty acids (purity: >98%) used as PCMs in this work were lauric acid (LA; $C_{11}H_{23}COOH$), myristic acid ($C_{13}H_{27}COOH$), palmitic acid (PA; $C_{15}H_{31}COOH$) and stearic acid (SA; $C_{17}H_{35}COOH$). These acids were obtained from Aldrich company.

The blends with amounts of 100 g were prepared by mixing the fatty acids and the PVC in melted state and cooling to room temperature. In order to determine the maximum mass percentage for each fatty acid under which there is no leakage of the fatty acid from the PCM when the temperature is between the melting point of the PVC and that of the LA, MA, PA and SA, the fatty acids were blended with the PVC in the combinations of 20, 30, 40, 50, 55 and 60 % in weight.

Thermal properties of the PVC/fatty acid blends as shape-stabilized PCMs such as the melting temperatures and latent heats of fusion were measured by using a DSC (DuPont 2000) instrument. Indium was used as a reference for temperature calibration. The analyses were performed in the temperature range of 20-100°C for the pure acids 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 melting temperature, 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 base line on the same side as the leading edge of the peak. The latent heat of fusion, ΔH_{fus} , was calculated as the area under the peak by numerical integration. IR spectra were obtained on a KBr disk by an IR Spectrophotometer (Jasco 430). The blends were morphologically investigated by using a dissection optic microscope (Laica).

Results and Discussion

Miscibility of the fatty acids with the PVC

In the prepared shape-stabilized PCMs, the PVC serves as supporting material for the fatty acids, which melt and solidify in its network. So, it was not observed the fatty acid seepage even when the blend was heated over the melting temperature of the PCM. This property made them possible for the solar LHTES systems without outer container. On the other hand, it is naturally expected that the holding ability of the PVC over the melting point of the PCM gets weak with increasing the amount of the fatty acid in the blend. In our experiments, the mixture mass percentage of all fatty acids in the blends was determined as 50 under the condition of no leakage of acid after several heating cycles. This result means that the confining possibility of fatty acid by PVC is inversely proportional to the amount of fatty acid used in the blend and the leakage of the fatty acid initials when the ratio is over the 50wt%.

The morphologic investigations on the PVC/fatty acid blends were carried out to observe the dispersion of the fatty acid in the PVC by using a dissection microscope. The micrographs of PVC/PA and PVC/SA blend as shape-stabilized PCM are given as example in Fig. 1. Both micrographs are of similar

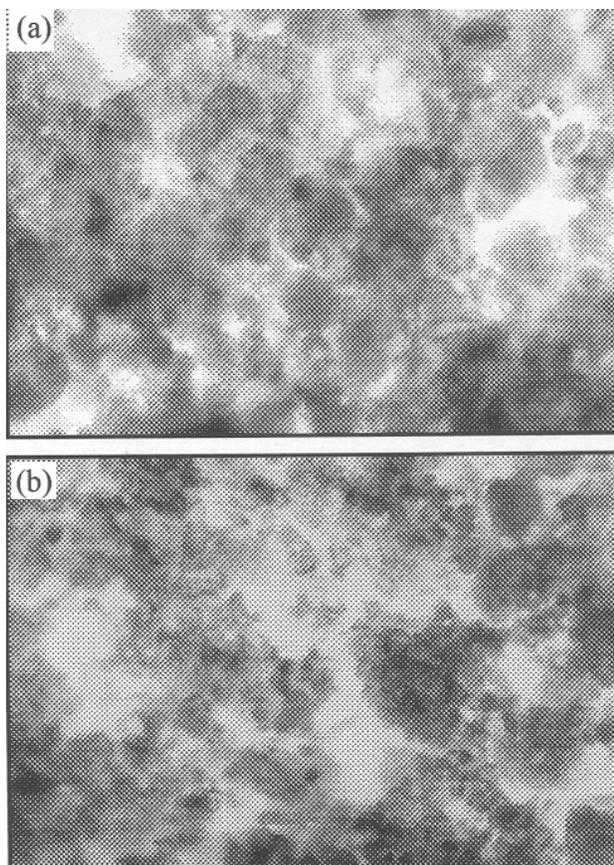


Fig. 1—The micrographs of shape-stabilized PCMs obtained by dissection microscope ($\times 100$) (a) PVC/PA and (b) PVC/SA.

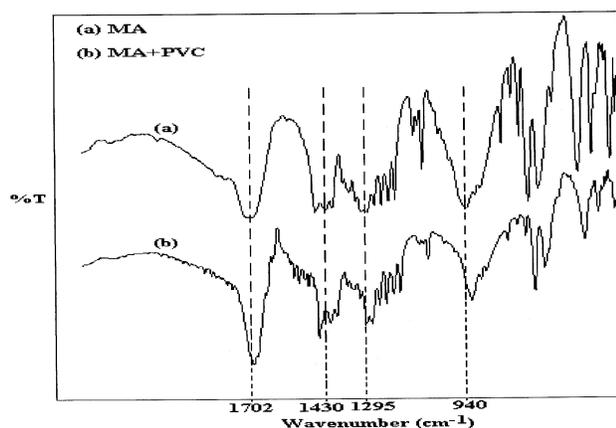
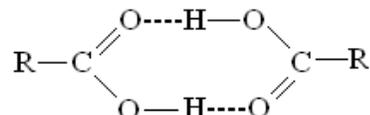


Fig. 2—Shifts in the main IR spectral peaks in MA and 50%PVC/50%MA(w/w) systems.

textures and indicate the dispersion of the fatty acid (black parts in micrograph) into the network of the solid polymer (white parts in micrograph). Moreover, the micrographs are also in agreement with the dispersion models¹⁰⁻¹⁴ and similar with the scanning electron microscope (SEM) photographs obtained for various shape-stabilized PCMs¹⁶⁻¹⁹.

On the other hand, the miscibility of fatty acid with PVC can be proved by IR Spectroscopy method. Fig. 2 may be considered as evidence of interactions between the fatty acid and the polymer. The shifts in the main IR spectral peaks of the C=O group in myristic acid (MA), and PVC/MA (50/50wt%) system. The C=O vibration of a pure fatty acid generally occurring at 1700-1725 cm^{-1} appears only when it has dimeric structure as below:



The absorption frequency of C=O group in dimeric structure of fatty acid slightly decreases from 1702 to 1698 cm^{-1} in PVC/MA system. This result could be interpreted as decrease of carboxyl association in fatty acid because of a new association between the fatty acid and the polymer. By adding PVC to MA, the absorption band at 1430 cm^{-1} due to a coupling of the deformation vibration of OH with carbonyl group vibration, the valence vibration band at 1295 cm^{-1} and OH deformation band at 940 cm^{-1} shift a lower frequency of 1428, 1293 and 936 cm^{-1} , respectively as seen in Fig. 2. The shifts in the IR spectra of other PVC/fatty acid blends were found as almost values. Based on the IR results, the probable reason for the miscibility of the fatty acid with PVC is that the both components in the blend have the polar groups and thus dipole-dipole interaction and the hydrogen bonding may be occurred between these groups.

Thermal properties of the PVC/fatty acid blends as shape-stabilized PCM

The typical DSC curve for each fatty acid and PVC are given in Fig. 3 and Fig. 4, respectively. These curves present reference data to evaluate the changes in thermal properties of the shape-stabilized PCMs. The DSC curves of PVC/fatty acids blends as shape-stabilized PCM are also shown in Figs 5-8. The sharp peak and relatively minor peak in the DSC thermograms represent the solid-liquid phase change of the fatty acid and PVC, respectively. Thermal properties evaluated from Figs 5-8 are given in Tables

1 and 2. The melting temperatures (T_m) of the shape-stabilized PVC/LA, PVC/MA, PVC/PA and PVC/SA blends were measured as 38.8, 49.2, 54.4 and 64.7°C,

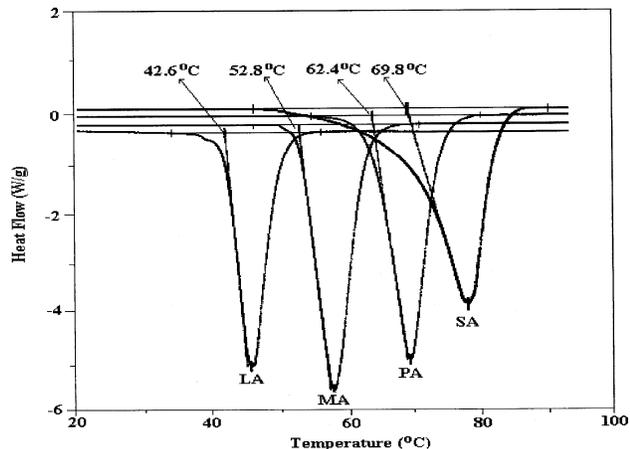


Fig. 3—DSC curves of fatty acids.

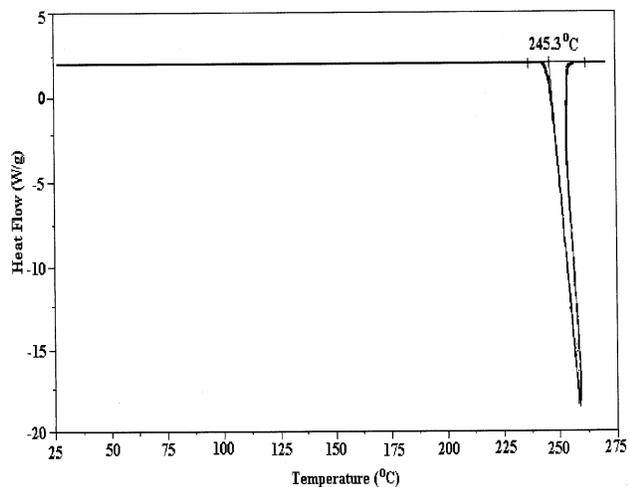


Fig. 4—DSC curve of poly(vinyl chloride) (PVC).

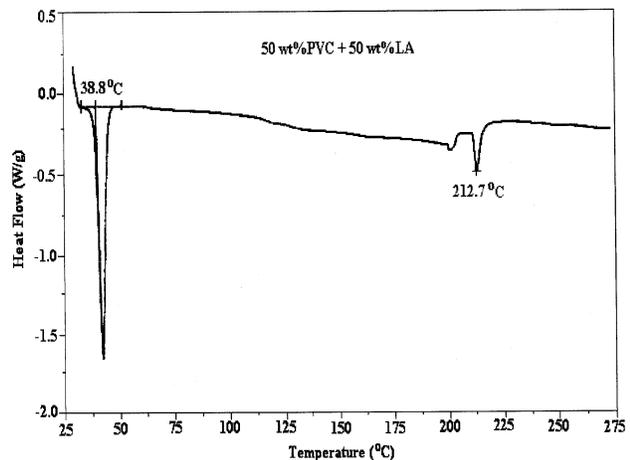


Fig. 5—DSC curve of 50%PVC/50%LA (w/w) blend as shape-stabilized PCM.

respectively. The melting temperatures of fatty acids in the shape-stabilized PCMs (50/50 wt%) were

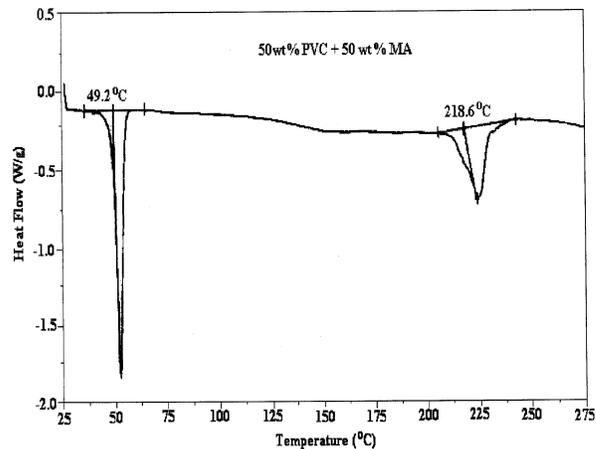


Fig. 6—DSC curve of 50%PVC/50%MA (w/w) blend as shape-stabilized PCM.

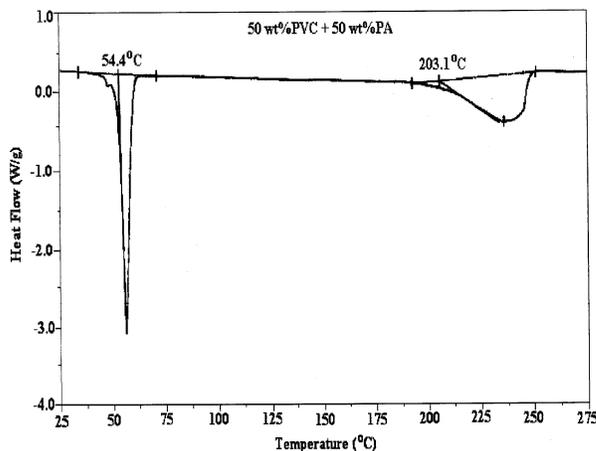


Fig. 7—DSC curve of 50%PVC/50%PA (w/w) blend as shape-stabilized PCM.

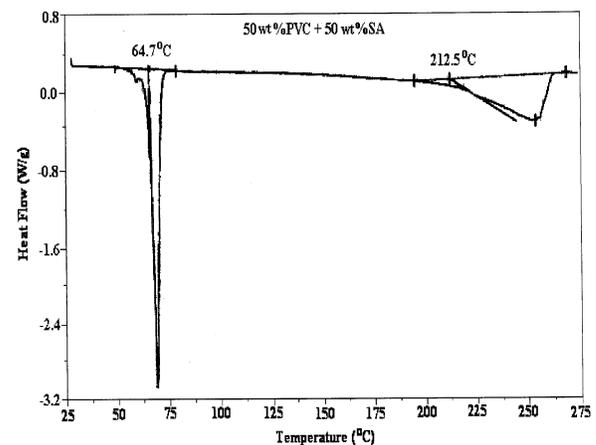


Fig. 8—DSC curve of 50%PVC/50%SA (w/w) blend as shape-stabilized PCM.

Table 1—Melting temperatures, T_m (°C) of shape-stabilized PCMs with different ratio of PVC and fatty acid.

PVC : Fatty acid	PVC/LA	PVC/MA	PVC/PA	PVC/SA
0.0 : 100.0	42.6	52.8	62.4	69.8
80.0 : 20.0	35.2	46.5	52.5	52.6
70.0 : 30.0	36.8	47.8	53.2	56.9
60.0 : 40.0	37.7	48.5	53.9	62.3
50.0 : 50.0	38.8	49.2	54.4	64.7

decreased as 3.8, 3.6, 8.0 and 5.1°C for the shape-stabilized PVC/LA, PVC/MA, PVC/PA and PVC/SA blend, respectively. As it can be seen from Table 2, the latent heats (ΔH_{fus}) of the shape-stabilized PVC/LA, PVC/MA, PVC/PA and PVC/SA blends were determined as 97.8, 103.2, 120.3 and 129.3 J/g, respectively. These values are little more than the data that would be calculated according to the following equation^{14,18};

$$\Delta H_{FA/B} = W_{FA} \% \Delta H_{FA} \quad \dots (1)$$

where $\Delta H_{FA/B}$, $W_{FA} \%$ and ΔH_{FA} are the calculated latent heat of fatty acid in shape-stabilized blend, mass percentage of the fatty acid in the blend, latent heat of pure fatty acid, respectively. It means that the shape-stabilized PCMs should also include the sensible heat of PVC until the phase change temperatures of the fatty acids. This idea was also reported for the HDPE/paraffin blend as shape-stabilized composite PCM¹¹. In addition, the reducing trend in T_m and ΔH_{fus} values only depends on the chemical structure of the polymer, but also on many internal and external factors, often located on the other microstructural levels¹⁷. By considering the melting points of the shape-stabilized PCMs, it is remarkably noted that they are suitable for various LHTES applications range of 38-65°C. Furthermore, the latent heats of fusion of shape stabilized PCMs are as high as compared to some salt hydrates and paraffins¹⁻⁶.

Conclusions

From the results of this study, the following conclusions are drawn: (i) It is possible to prepare PVC/fatty acid blends as novel shape-stabilized PCMs for LHTES systems. In the blends, the fatty acid compound is dispersed into network of the solid polymer and it serves a latent heat storage material when the polymer acts as a supporting material. Therefore, as long as the operating temperature is

Table 2—Measured and calculated latent heats of fusion, ΔH_{fus} (J/g) of shape-stabilized PCMs with different ratio of PVC and fatty acid.

PVC : Fatty acid	PVC/LA	PVC/MA	PVC/PA	PVC/SA
Measured ΔH_{fus} values (J/g)				
0.0 : 100.0	183.2	198.4	224.8	238.6
80.0 : 20.0	44.2	45.1	47.6	51.8
70.0 : 30.0	61.1	61.4	66.5	72.6
60.0 : 40.0	77.5	80.3	99.8	103.9
50.0 : 50.0	97.8	103.2	120.3	129.3
Calculated ΔH_{fus} values (J/g) according to Eq. (1)				
80.0 : 20.0	36.6	39.7	45.0	47.7
70.0 : 30.0	55.0	59.5	67.4	71.6
60.0 : 40.0	73.4	79.4	89.9	95.4
50.0 : 50.0	91.6	99.2	112.4	119.3

below the melting point of supporting material the blends can keep its shape even when the PCM undergoes phase change from solid to liquid. The maximum ratio of the fatty acids in the shape-stabilized blends was found as high as 50 wt%. (ii) The melting temperatures and latent heats of the shape-stabilized PVC/LA, PVC/MA, PVC/PA and PVC/SA (50/50 wt%) PCMs were determined as 38.8, 49.2, 54.4 and 64.7°C and 97.8, 103.2, 120.3 and 129.3 J/g, respectively. These satisfying thermal properties of the shape-stabilized blends make them possible for passive solar TES applications at the temperature range of 38-65°C. (iii) The prepared shape-stabilized PCMs are cost-effective materials because they don't need extra capsule shell. It directly contacts with the heat transfer medium of LHTES system. Therefore, heat loading and releasing rate of LHTES system employing with shape-stabilized PCM will be high. In addition, they can be easily prepared in desired dimensions. As a result, the PVC/fatty acids blends as shape-stabilized PCMs have great potential for passive solar TES applications.

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