Photocrosslinked biobased phase change material for thermal energy storage

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ABSTRACT: A series of novel photocrosslinked biobased shape-stabilized phase change materials (PCMs) based on octadecanol, eicosanol and docosanol have been prepared by UV technique for the purpose of thermal energy storage applications. Epoxidized soybean oil was reacted with acrylic acid to form acrylated soybean oil (ASO). The structure and composition, cross-section morphology, thermal stability performances and phase change behaviors of ASO and UV-cured PCMs were examined by using Attenuated total reflection fourier transform infrared spectroscopy, thermogravimetric analysis system (TGA), scanning electron microscopy, and differential scanning calorimetry. The results indicate that the UV-cured biobased PCMs possess perfect phase change properties and a suitable working temperature range. The heating process phase change enthalpy is measured between 30 and 68 J/g, and the freezing process phase change enthalpy is found between 18 and 70 J/g. The decomposition of UV-cured PCMs started at 260 °C and reached a maximum of 430 °C. All the biobased UV-cured PCMs improved latent heat storage capacity in comparison with the pristine ASO sample. With the obtained results we conclude that, these materials promise a great potential in thermal energy storage applications. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43757.

INTRODUCTION

In many developing countries, with the rapid economic improvements, energy shortage, and environmental issues have become a serious problem. Therefore, it has become a very critical issue to improve energy usage efficiency and also protect the environment. Thermal energy storage system is an essential approach to match the thermal energy claim and supply.[1–3] Thermal energy can be stored by heating, cooling, or melting a material with the energy and then enhancing accessible when the procedure is reversed. The overall thermal energy storage techniques are sorted as; latent heat or sensible heat thermal energy storage technology segments. Among these methods, latent heat storage is the most effective method of collecting thermal energy. Latent heat thermal energy storage depend on the storage material, emitting or discharging heat as it undergoes a solid to liquid, solid to solid or liquid to gas phase change or vice versa.[4–6]

Phase change materials (PCMs) are promising materials for latent heat storage applications due to their capacities to accumulate high latent heat storage per unit volume by phase change at an almost constant temperature. PCMs are being utilized to absorb, collect, and discharge thermal energy during the cycle of melting and freezing, converting from one phase to another. When such a material refrigerates, it releases a great deal of energy in the form of latent heat of fusion, or energy of crystallization. In contrast, when the material is melted, an equal deal of energy is emitted from the instant environment as it changes from solid to liquid.[7–10]

PCMs can generally be arranged into three classes: organic materials, salt hydrates and eutectics. Many kinds of organic and inorganic PCMs and their blends have been examined as latent heat storage materials.[11–13] Organic PCMs are rather expensive and they have average latent heat storage per unit volume and also have low density. Most organic PCMs are combustible in nature and also have a wide range of melting point. Organic PCMs can be categorized into two major categories: nonparaffinic and paraffin materials. Paraffin materials have been extensively used, due to their high latent heat and right thermal characteristics, such as minimal super cooling, varying phase change temperature, low vapor pressure while melting, good chemical and thermal stability, and self-nucleating behavior.[14–16] Polyethylene glycol (PEG), fatty acids, and fatty alcohols are alternative organic compounds used as PCMs and their melting points and latent heat depend on their molecular weights.[17,18] Inorganic PCMs, such as metals, alloy, salts, and salt hydrates have good thermal conductivity and high heat of fusion, nonflammable properties, and they are affordable.

Scheme 1. Chemical structures of octadecanol, eicosanol, and docosanol.

However, their applications are restricted, because they are corrosive to most metals and undergo super cooling and phase decomposition.[19,20]

As we review the literature we see that fatty alcohols have a leakage problem. One of the many advantages of UV-cured PCMs is that they prevent the interior PCMs from leaking. Shape-stabilized PCM is prepared by blending the PCM with a supporting material, usually polymers. This problem is minimized by coating the fatty alcohols with a photo-crosslinked biobased polymeric system. Leakage is minimized because photo-crosslinked polymer acts a matrix. Ultraviolet (UV)-curing technology has been generally used because it has many advantages, such as low energy consumption, high speed, high chemical stability, room-temperature operation, low processing costs, and environmental friendly. In UV-curing technologies, epoxy, polyurethane, epoxy acrylate polyurethane acrylate derivatives have found many applications like structural adhesives, surface coatings, and advanced composite materials.[21–23]

For many years PCMs have been used for heating and cooling industrial applications including textiles, refrigerators, construction, transportation packaging for temperature-sensitive products, a few solar energy-based systems, biomedical, and electronic materials.[24]

In this study, UV-curable, fatty alcohol containing biobased organic PCMs were obtained and characterized from acrylated soybean oil (ASO) which is acquired by reacting epoxidized soybean
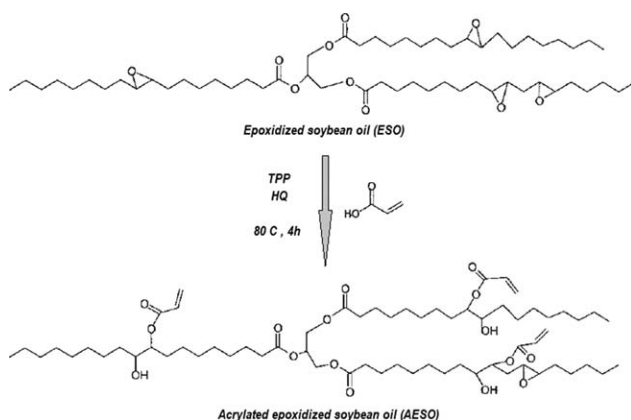
oil (ESO) with acrylic acid. The chemical structure of the acrylate modified soybean oil was confirmed by ATR–FTIR technique. The phase transition behaviors, thermal stability of the prepared UV-cured biobased PCMs were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The fractured surface morphology of the UV-cured biobased PCMs were monitored by scanning electron microscope (SEM).

EXPERIMENTAL

Materials

ESO (epoxide content 4.13 mol/kg) was received from İldeş Kimya (Kocaeli, Turkey). Triphenyl phosphine (TPP), and acrylic acid were obtained from Aldrich. Hydroquinone was obtained from Merck.1-Octadecanol (97%), 1-eicosanol (96%), and 1-docosanol were obtained from Alfa Aesar. Darocure-1173 photoinitiator was obtained from ESA Chemistry. Chemical structures of fatty alcohols are shown in Scheme 1.

Synthesis of ASO

ASO was synthesized as described in the literature [21] with minor modifications. Two hundred and fifty milliliter three-necked flask was equipped with a mechanical stirrer, a nitrogen inlet and a dropping funnel is added 30 g ESO, 0.3 g (0.001 mol) TPP, and 0.005 g (0.0015 mol) hydroquinone were added. Then, 10.67 g (0.124 mol) of acrylic acid was added dropwise into the flask from the dropping funnel for 1 h, while mixing the reaction at room temperature. The reaction was carried out at 80 °C and allowed to react for 4 h. The final product was clear and viscous. The reaction scheme is presented in Scheme 2.
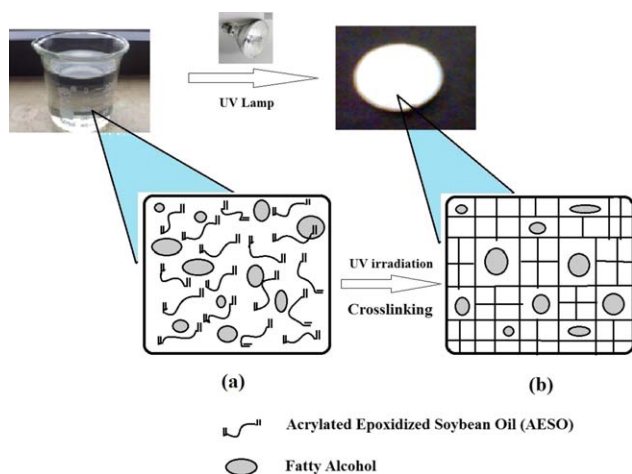
Preparation of Photocrosslinked Biobased PCMs

Biobased PCMs formulations were prepared by mixing ASO, 1-octadecanol, eicosanol, and 1-docosanol. Photoinitiator darocure 1173 (3 wt %) was added, and then the solid mixture was heated to 80 °C by stirring until the fatty alcohols were melted and dissolved homogeneously. The compositions of the PCMs are given in Table I. The PCMs were prepared by pouring the UV-cured biobased formulations into Teflon™ wells (10 mm × 5 mm × 1 mm). To keep the inhibiting effect of oxygen, the formulation in the well was protected with transparent thick polyester film before it was irradiated with UV-lamp (OSRAM, 300 W). After 180 s, irradiation under UV-lamp, UV-cured biobased PCMs were obtained. Preparation of the fatty alcohol-containing UV curable biobased PCMs are shown in Scheme 3.

Measurements and Characterization

Fourier transform infrared (FTIR) spectra were recorded on Perkin-Elmer Spectrum 100 FT-IR spectrophotometer. The parameters of the device for the analysis had a resolution of 2 cm^{-1} and a frequency range of 400–4000 cm^{-1}.

Scheme 2. Synthesis of acrylated soybean oil (ASO).

Table I. Compositions of the UV-Cured Biobased PCMs

Samples	ASO (g)	1-Octadecanol (g)	1-Eicosanol (g)	1-Docosanol (g)	Darocure 1173 (g)
F1	1	—	—	—	0,03
F2	1	0,50	—	—	0,045
F3	1	—	0,50	—	0,045
F4	1	—	—	0,50	0,045

Scheme 3. Formation of photocrosslinked biobased phase change materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermogravimetric analyses (TGA) of the UV-cured biobased PCMs were determined by using Perkin-Elmer Thermogravimetric analyzer Pyris 1 TGA model. The PCMs were run from 30 to 750 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

Pyris Diamond DSC was used for the calorimeter analysis of the UV-cured biobased PCMs. The measurements were carried out under inert nitrogen atmosphere at 25 ml/min flow rate. All the DSC thermal analyses of PCMs were run from 0 to 100 °C at a heating and cooling rate of 10 °C/min for the determination of phase change enthalpy and temperature.

UV-cured biobased PCMs morphology was investigated with scanning electron microscope (Phillips XL 30 ESEM-FEG). The SEM analyses was operated at 20 kV accelerating voltage. The UV cured PCMs were prepared for SEM by freeze-fracturing in

liquid nitrogen and applying a gold coating of approximately 300 Å.

RESULTS AND DISCUSSION

The Synthesis of the ASO

The aim of this study was to obtain UV-curable biobased fatty alcohols containing PCMs with improved combination of phase change and thermal properties. For this purpose, the ESO was reacted with acrylic acid. ASO chemical structure was characterized with FTIR. In Figure 1, disappearance of the characteristic oxirane group at 825 cm^{-1}[21] in the FTIR spectrum and the appearance of stretching vibration band of —C=C— at 1635 cm^{-1}[22] double bond vibrations of acrylate groups can be seen.

Figure 2 shows the FT-IR spectrum of the 1-octadecanol, 1-eicosanol and 1-docosanol containing UV-cured biobased organic PCMs. The peaks at 3327, 2916, 2848, 1470, 1370, 1040 cm^{-1} are the characteristic fatty alcohol absorption bands.[25] As it can be seen from the FT-IR spectra, the characteristic absorption band at 3327 cm^{-1} can be assigned to OH group of fatty alcohol. When we examine the acrylated ASO spectra, we see that the characteristic —C=C— acrylate double bond vibration bands are present at 1635 cm^{-1} (Figure 1). Figure 2 shows the FT-IR spectrum of the biobased PCMs. We can see from Figure 2, after the UV-curing crosslinking process, the double-bond vibration band at 1635 cm^{-1} disappeared. This evidence proves that the photo crosslinking was achieved successfully.

Phase Transition Properties of the UV-Cured Biobased Organic PCMs

For the possible application in thermal energy storage, good thermal behaviors such as high latent heat capacity and sufficient phase transition temperatures are the most attractive
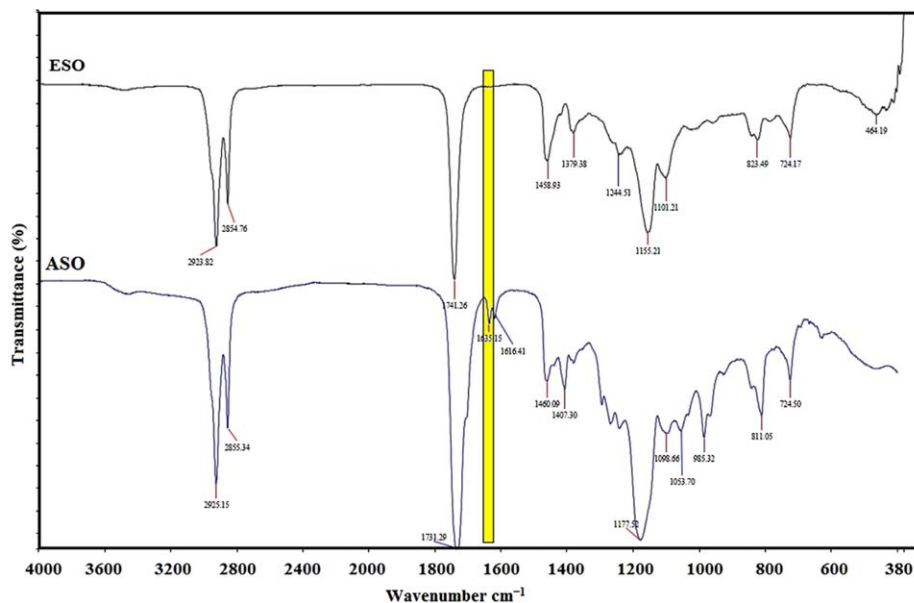

Figure 1. Attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) spectrum of epoxidized soybean oil (ESO) and ASO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
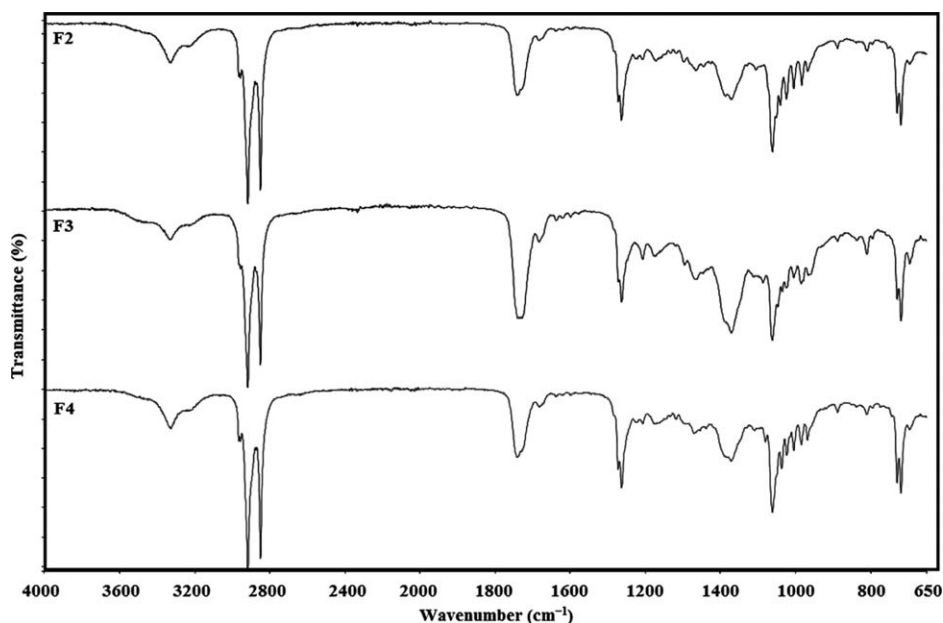
Figure 2. ATR-FTIR spectrum of F2, F3, and F4 biobased PCMs.

characteristics of PCMs.[26] DSC measurements were performed for testing phase change properties on all of the fatty alcohols and UV-cured PCMs. The melting and freezing temperature were taken as the peak point of the DSC curves. Figures 3 and 4 show the heating and freezing graphs of fatty alcohols and UV-cured biobased organic PCMs including melting and freezing temperature (T_m, the temperature of the endothermic peak T_f, the temperature of the exothermic peak), phase transition enthalpy of melting (ΔH_m), and phase transition enthalpy of freezing (ΔH_f). DSC results are given in Table II.

The increase of the chain length of the fatty alcohol, the melting and freezing temperature of UV-cured PCMs were increased evenly (Figure 3).[27,28] Figure 3 and Table II indicate that the phase change temperature for melting and freezing are 63.66 °C, 71.63 °C, 79.22 °C, 53.51 °C, 60.06 °C, and 66.19 °C for pure octadecanol, eicosanol and docosanol, respectively. Furthermore, the phase change temperature for melting and freezing are found to be 60.46 °C, 66.67 °C, 73.07 °C, 49.39 °C, 56.18 °C, and 60.82 °C for F2, F3, and F4, respectively. It can be concluded that the phase temperatures of UV-cured PCMs with those of

pure fatty alcohols (Table II) as follows: the change in melting point was −3.20, −4.96, and −6.15 °C and the change in freezing point was −4.12, −3.88, and 5.37 °C for UV-cured F2, F3, and F4 PCMs, respectively.

The heating and freezing phase change enthalpy is another important factor to determine the high performance PCMs that can be used as a measure of its thermal energy storage capacity.[29] The heating and freezing enthalpy curves obtained with DSC measurements of pure F2, F3 and F4 are given in Figures 5 and 6. In Table II, it can be seen that ASO sample does not exhibit phase change properties during heating and freezing run, while for the formulations containing fatty alcohols, endothermic and exothermic behaviors can be observed. The melting and freezing enthalpy of UV-cured PCMs containing fatty alcohols were increased from 0 J/g to 70 J/g with respect to UV-cured ASO (F1). Enthalpy for these materials was also increased when the length of fatty alcohols increased, from 253 to 268 J/g and from 18 to 70 J/g for fatty alcohols and UV-cured PCMs, respectively. The heating and freezing enthalpy values (both ΔH_m and ΔH_f) of all of UV-cured PCMs were insignificantly
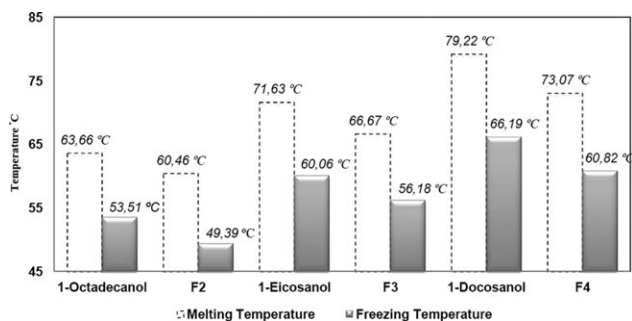

Figure 3. Changes in (a) melting and freezing temperatures of fatty alcohols and UV-cured biobased PCMs.
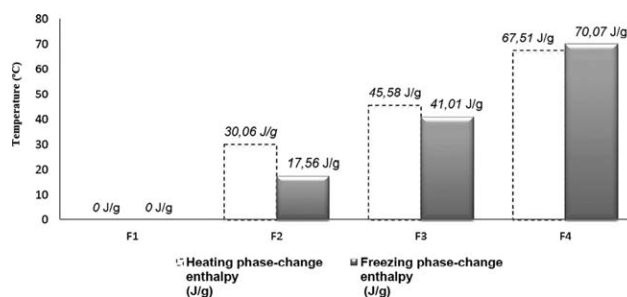

Figure 4. Changes in (a) melting and freezing phase change enthalpies of fatty alcohols and UV-cured biobased PCMs.

Table II. DSC Data of the Fatty Alcohols and UV-Cured Biobased PCMs

	Melting		Freezing		
Samples	Temperature (°C)	Latent heat (J/g)	Temperature (°C)		Latent heat (J/g)
1-Octadecanol	63,36	253,92	50,81	56,20	−244,79
1-Eicosanol	71,63	259,97	57,52	62,59	−249,31
1-Docosanol	79,22	268,36	64,41	67,97	−262,51
F1	—	—	—	—	—
F2	60,46	30,06	49,39		−17,56
F3	66,67	45,58	56,18		−41,01
F4	73,07	67,51	60,82		−70,07

T_m, the temperature of the endothermic peak; T_f, the temperature of the exothermic peak; ΔH_m, phase transition enthalpy of melting; ΔH_f, phase transition enthalpy of freezing.
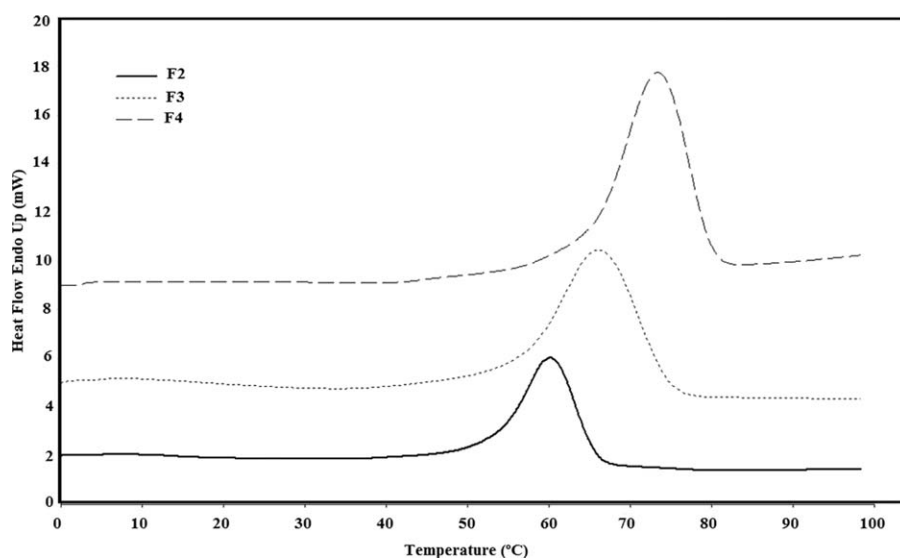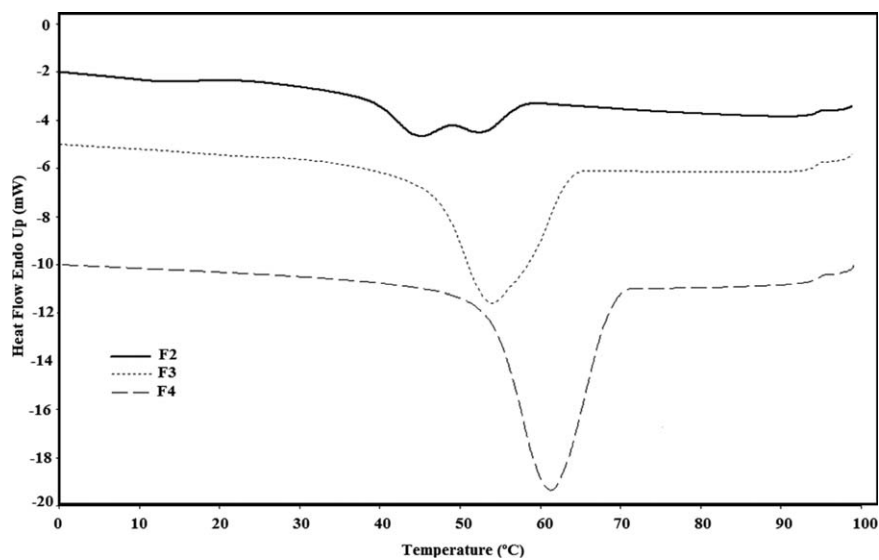

Figure 5. DSC curves of F2, F3, and F4 in the heating process.

Figure 6. DSC curves of F2, F3, and F4 in the freezing process.

Table III. Comparisons on Thermal Energy Storage Properties of Some Shape-Stable PCMs

Shape-stable PCMs	Melting		Freezing		Refs.
	Temperature (°C)	Latent heat (J/g)	Temperature (°C)	Latent heat (J/g)	
MMA/Octadecane (1:0)	30,02	46,00	13,00	−46,00	31
MMA/Octadecane (2:1)	26,50	93,00	14,40	−94,00	31
Urea-formaldehyde/Caprylic acid	18,85	93,95	3,00	−106,12	32
Melamine-formaldehyde/Caprylic acid	17,29	16,48	0,34	−8,56	32
Urea-melamine-formaldehyde/Caprylic acid	17,87	56,82	3,92	−52,63	32
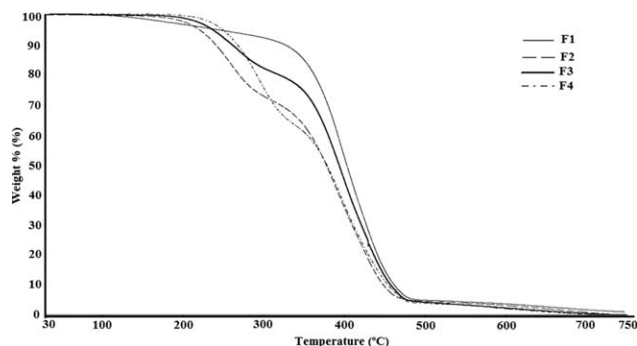
Figure 7. TGA spectra of UV-cured biobased PCMs with different fatty alcohols at nitrogen atmosphere.

lower than those of the corresponding fatty alcohols (as shown in Table II). Both the phase transition temperature and the heating and freezing enthalpy capacity have a tendency to increase with the increase of the alkyl chain of the fatty alcohols in the UV-curable formulation.[30] Table III summarizes the comparisons on thermal energy storage properties of the few examples of form-stable PCMs in the literature.[31,32]

Thermal Stability of the UV-Cured Biobased Organic PCMs
The thermal stability of UV cured biobased PCMs is considered the most important phenomenon in technological thermal energy storage applications. UV cured biobased PCMs should be stable at ambient temperatures.[2] The TGA thermograms are presented in Figure 7 and the TGA data is shown in Table IV.

In Figure 7, it can be seen that F1 showed 5 wt % weight loss temperature around 247 °C and maximum weight loss at temperature 385 °C where main chain was completely degraded. All

Table IV. Thermal Properties of the UV-Cured Biobased PCMs

Samples	$T_{\%5}$ (°C)	$T_{\%10}$ (°C)	Decomposition temperature		Char yield (%)
			T_{d1} (°C)	T_{d2} (°C)	
F1	247	327	385		1,02
F2	221	240	267	403	0,05
F3	238	261	272	429	0,07
F4	250	267	275	432	0,10

$T_{\%5 \text{ and } 10,}$ 5 and 10 wt % weight loss temperature; T_{d1} and T_{d2}. The first and second decomposition temperature.

UV-cured biobased PCMs (F2, F3, F4) were observed with two main weight loss stages. Octadecanol, eicosanol and docosanol-based UV-cured PCMs showed similar thermal behavior, with initial 5% weight loss of roughly at 230 °C. For UV-cured biobased PCMs, two weight loss stages were observed at 260–280 °C and 400–440 °C, respectively. The first weight loss at 260 to 280 °C is attributed to the decomposition of the fatty alcohol.[33] The second weight loss above 400–440 °C can be assigned to the thermal degradation of the main polymer chain. In Table IV, an increase in the alkyl chain length of fatty alcohol within the UV-cured PCMs increased the thermal weight loss temperature can be seen. The char yields of F1, F2, F3, and F4 are found as 1.02, 0.05, 0.07, and 0.10, respectively. The high latent heat storage capacity and thermal weight loss temperature results of the UV-cured biobased PCMs show potential thermal energy storage application of these materials.

Morphology of the UV-Cured Biobased Organic PCMs
The morphology of UV-cured ASO (F1) was monitored by scanning electron microscopy (SEM). Figure 8(a,b) show SEM images of the fractured surface morphology of (a) F1 (5000x) and (b) F1 (10,000x), respectively. We can see from the Figure 8(a,b) that F1 film has a smooth and homogeneous surface. Figure 8(c,d) shows SEM images of F2 and F3 prepared by using octadecanol and eicosanol, respectively. The morphologies of the F2 and F3 samples with octadecanol and eicosanol tended to be irregular, as shown in Figure 8(c,d). Moreover, much roughness can be found on the surface of the fatty alcohol containing samples (F2, F3) compared with the UV-cured polymer surface (F1).

CONCLUSIONS

In this study, ASO-based PCMs containing different fatty alcohols were prepared by UV-curing technique. Octadecanol, eicosanol, and docosanol were homogenously dispersed into crosslinked ASO matrix. There was no chemical reaction between fatty alcohols and ASO, which shows that they have good compatibility. Thermal performances of UV-cured PCMs were investigated by differential scanning calorimeter (DSC). ASO sample (F1) does not exhibit phase change properties during heating and freezing run, while for the formulations containing fatty alcohols, endothermic and exothermic behaviors can be observed. The results indicate that, fatty alcohols could enhance the thermal performance of PCMs. The melting and freezing temperature of UV-cured biobased PCMs is remarkably decreased compared to that of pristine fatty alcohols. The latent
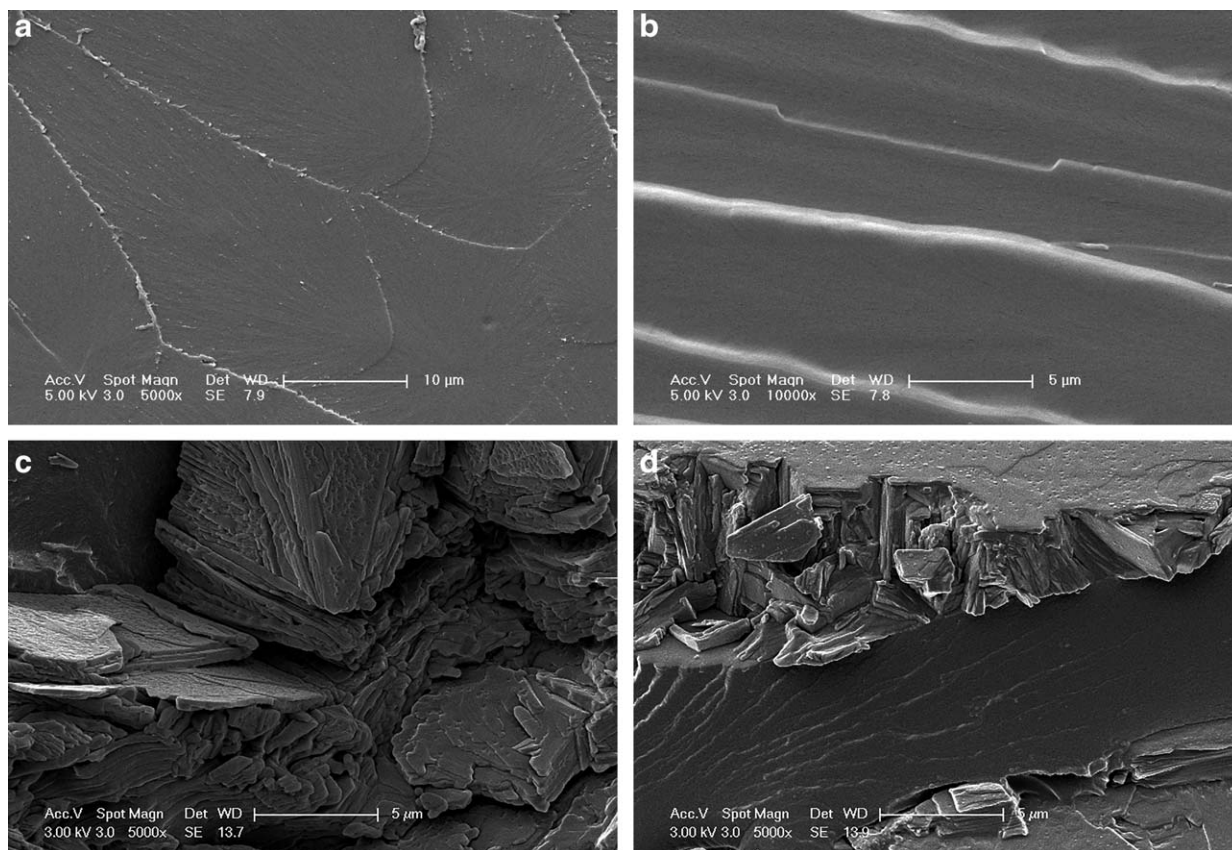
Figure 8. SEM micrographs of the ASO (F1): (a) F1 (5000×), (b) F1 (10000×) and ASO-Octadecanol (F2): (c) (5000×), ASO-Eicosanol (F3) (d) (5000×).

heat enthalpies of heating and freezing cycle varied from 30 to 68 J/g, and 18 to70 J/g, respectively. The results also showed that the phase change temperatures and the enthalpies of melting and freezing for particular fatty alcohols increased with the increase of the alkyl chain/size of fatty alcohols. Considering our findings, these PCMs can be promising anduseful in thermal energy storage applications.

ACKNOWLEDGMENTS

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(a)   (b)

Acrylated Epoxidized Soybean Oil (AESO)

Fatty Alcohol