Chemical Engineering Journal 150 (2009) 269–274

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Ultrafine electrospun fibers based on stearyl stearate/polyethylene terephthalate composite as form stable phase change materials

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ARTICLE INFO

Article history:
Received 28 October 2008
Received in revised form 1 January 2009
Accepted 3 March 2009

Keywords:
Electrospinning
Ultrafine fibers
Stearyl stearate
Form stable PCM
Thermal properties

ABSTRACT

As a novel solid–liquid phase change material (PCM), stearyl stearate (SS) was synthesized by esterification of stearyl alcohol and stearic acid, and the ultrafine composite fibers of SS/polyethylene terephthalate (PET) were prepared via electrospinning as form stable PCMs. The structure of SS, morphology and thermal properties of SS/PET composite fibers were characterized by FI-IR, FE-SEM and DSC, respectively. The average diameter of SS/PET composite fibers measured from the SEM images increased gradually with the increase of SS percentage, and the morphology of the composite fibers had no obvious variation after thermal treated, which confirmed the developed material had the feature of form stable phase change. The results from DSC showed that the enthalpy of the composite fibers increased with the increase of SS content, but the variation of SS percentage in the composite fibers had few influence on phase transition temperature of the fibers. In addition, the thermal performances of the fibers could well be maintained after 100 heating–cooling thermal cycles, which indicated that the composite fibers had good thermal stability and reliability.

1. Introduction

Thermal energy storage has gained extensive interest due to the impending shortage and increasing cost of energy resources nowadays [1–5]. Phase change material (PCM) is a significant and attractive material for latent heat storage because of its high-energy storage density and small temperature variation from storage to retrieval [1–3,6]. Thermal energy is stored or released by PCMs through the phase changing of PCMs from one state to another. Various inorganic, organic compounds and their mixtures have been examined for their potential as PCMs for latent heat storage systems for several decades [1,3,7], but there are some unavoidable shortcomings in the application of these PCMs [3,5,7]. Therefore, a novel class of polymer-matrix PCMs as latent heat storage materials has been developed in the last decade for their unique advantages such as direct use without additional encapsulation, cost-effective, shape-stable and easily prepared with desirable dimensions [6,8–10]. These superior properties over traditional PCMs have directed researchers to focus their attention on the so-called form stable PCMs. With the development of nano science and technology, some of new techniques are exploited and involved in the research of form stable PCMs.

Electrospinning is a simple, convenient, and versatile technique for generating ultrafine fibers with diameters on both the micro- and nanoscales [11,12]. With their ultrafine size and huge surface-to-volume ratio, electrospun fibers can be applied in numerous areas such as healthcare, biotechnology, environmental engineering, energy storage, etc. [13]. Recently, ultrafine fibers of PCM/polymer composites have been developed via electrospinning technique. McCann et al. firstly prepared phase change nanofibers consisting of long-chain hydrocarbon cores and TiO_2-polyvinylpyrrolidone (PVP) sheaths by melt coaxial electrospinning [14]. In our previous work [15–17], the ultrafine composite fibers of PEG/CA and fatty acid/PET have been fabricated via electrospinning and explored as thermo-regulating materials and thermal storage materials for their excellent thermal performances.

Stearyl stearate (SS) is a common fatty acid ester which is extensively used as raw material of emulsifiers or oiling agents for foods, spin finishes and textiles; lubricants for plastics; paint and ink additives; surfactants and base materials for perfumery. In this study, SS was synthesized by the esterification of stearyl alcohol and stearic acid and considered as a novel solid–liquid PCM for its high

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doi:10.1016/j.cej.2009.03.007

enthalpy, suitable phase change temperature and non-toxicity, and then stearyl stearate/polyethylene terephthalate (SS/PET) ultrafine composite fibers were prepared by electrospinning as form stable PCMs for thermal energy storage. The morphology and thermal properties of the electrospun SS/PET composite fibers were examined and investigated by field emission scanning electron microscopy (FE-SEM) and differential scanning calorimetry (DSC), respectively.

2. Experimental part

2.1. Materials

PET (M_n = 20,000 g/mol) were donated by Zhejiang Xiangsheng Group Co., Ltd., China. Dichloromethane (DCM), trifluoroacetic acid (TFA, purchased from Sinopharm Group Chemical Reagent Co., Ltd., China), sulphurous oxychloride ($SOCl_2$, purchased from Damao Chemical Regents Co., Tianjin, China), Stearyl alcohol, toluene, stearic acid and pyridine (purchased from Chemical Regents Co., Guangzhou, China) are analytic reagent grade. Except $SOCl_2$, all materials were used with further purification to remove trace water.

2.2. Synthesis of stearyl stearate

The synthesis procedure of SS is similar to that reported in the literature [18]. A four-necked flask equipped with an agitator, a thermometer and a condenser was charged with the calculated amount of stearic acid, sulphurous oxychloride, pyridine and toluene (molar ratio: stearic acid:sulphurous oxychloride = 1:1). The flask was first immersed in an oil bath at 50 °C for 2 h, and then toluene solution of stearyl alcohol (molar ratio: stearyl alcohol:stearic acid = 1:1) was dropped into the flask slowly and the reaction continued for another 10 h. Milky solid product was obtained after removing unreactive ingredients and solvent by heating in drying oven.

2.3. Electrospinning process

15 wt% PET solutions were prepared by adding PET in a 2:1 volume ratio of DCM/TFA mixture. And then, mixed solutions obtained by adding SS with different SS/PET mass ratios individually into the 15 wt% PET solution under constant stirring for 1 h, respectively. Electrospinning was performed at 25 °C in air and using a homemade apparatus similar to that used in the literature [19]. During the electrospinning, the solution was placed in a 5 ml syringe and was fed by a syringe pump (TS2-60, Baoding Changjing Pump Ltd., China) at a rate of 3 ml/h. The metallic needle (0.8 mm diameter) was connected to grounded counter electrode. A power supply (BPS-20, Beijing Electrostatic Facility Ltd., China) was connected to the aluminum collector. The applied voltage and distance between capillary tip and collector were 16 kV and 20 cm, respectively. The fibers were randomly deposited on the collector to form fibrous non-woven membranes. The fibers were dried in vacuum at room temperature for 24 h to remove residual solvent.

2.4. Thermal cycles test

A test of 100 heating–cooling thermal cycles was performed to monitor the variations in thermal properties of the samples. The sample was placed into the empty aluminium pan and then placed onto a hot stage (STC200, Instec, USA). A saw-tooth shaped thermal cycle consisted of heating process and the cooling process (in the temperature interval 20–80 °C). The heating and cooling process times were maintained at approximately 15 min and 25 min, respectively until 100 complete thermal cycles had been undertaken.

2.5. Characterization

FT-IR spectra of samples were taken in Infrared Spectrophotometer (NICOLET-760, Nicolet Co., USA). The fibers were gold-coated and the morphology was observed by FE-SEM (JSM-6700F, JEOL, Japan) at acceleration voltage of 20 kV under low vacuum. The average fiber diameter (AFD) of the electrospun fibers was obtained by using an UTHSCSA Image Tool Program to measure from at least five SEM images for each sample. Thermal analysis was performed (each used about 5.0 mg) by DSC (DSC-100, PE, USA). Both the heating rate and the cooling rate were 10 °C/min, ranging from 0 °C to 100 °C, in a nitrogen atmosphere. Thermogravimetric analyses were carried out using TA thermal analysis system (TGA2050, TA Instruments Co., USA). About 5 mg of samples were weighed into an alumina crucible and the profiles were recorded from 25 °C to 500 °C at a heating rate of 20 °C/min. The flow rate of N_2 was maintained at 80 ml/min.

3. Results and discussion

3.1. FT-IR study

SS was prepared as describe above, and its structure is confirmed by FT-IR shown in Fig. 1. The spectra of stearyl alcohol (Fig. 1a) and stearic acid (Fig. 1b) are references for comparison. From Fig. 1, the disappearance of the absorption peaks of –OH at 3382 cm^{-1} and 1050 cm^{-1} in Fig. 1c demonstrates that the hydroxyl group in stearyl alcohol had translated into ester bond after the esterification. It is clear that the peaks at 2848 cm^{-1} and 2924 cm^{-1} of Fig. 1c corresponding to the stretching vibration of C–H bond show no obvious migration, but the intensity of these peaks increases compared with that of Fig. 1a and b. The strong peak attributing to the vibration of the C═O group observed at 1703 cm^{-1} in the spectrum of stearic acid becomes broad and shifts to higher wavenumber around 1734 cm^{-1} due to the disappearance of polar internal hydrogen bonds and the formation of soft and unpolar ester bonds. The peak intensity of vibration characteristic absorption of methylene at 1464 cm^{-1} and 720 cm^{-1}, as well as the peaks at 2848 cm^{-1} and 2924 cm^{-1}, abruptly increases after esterification. The result coincides with the structure of aimed product.

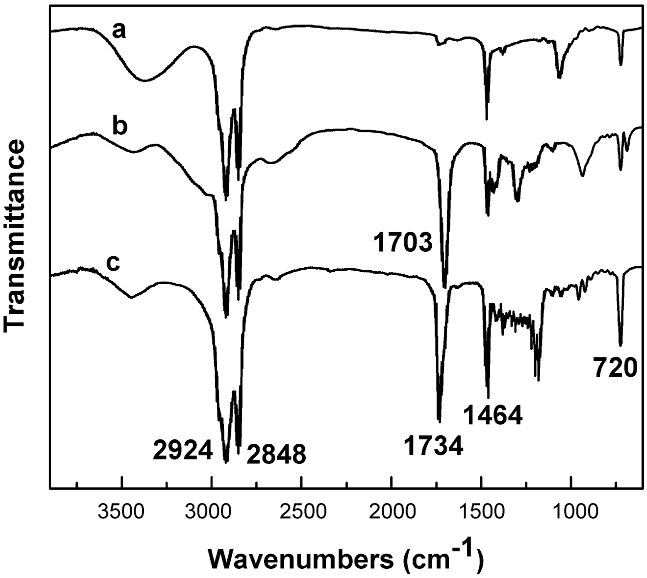

Fig. 1. FT-IR spectrum of stearyl alcohol (a), stearic acid (b) and stearyl stearate (c).

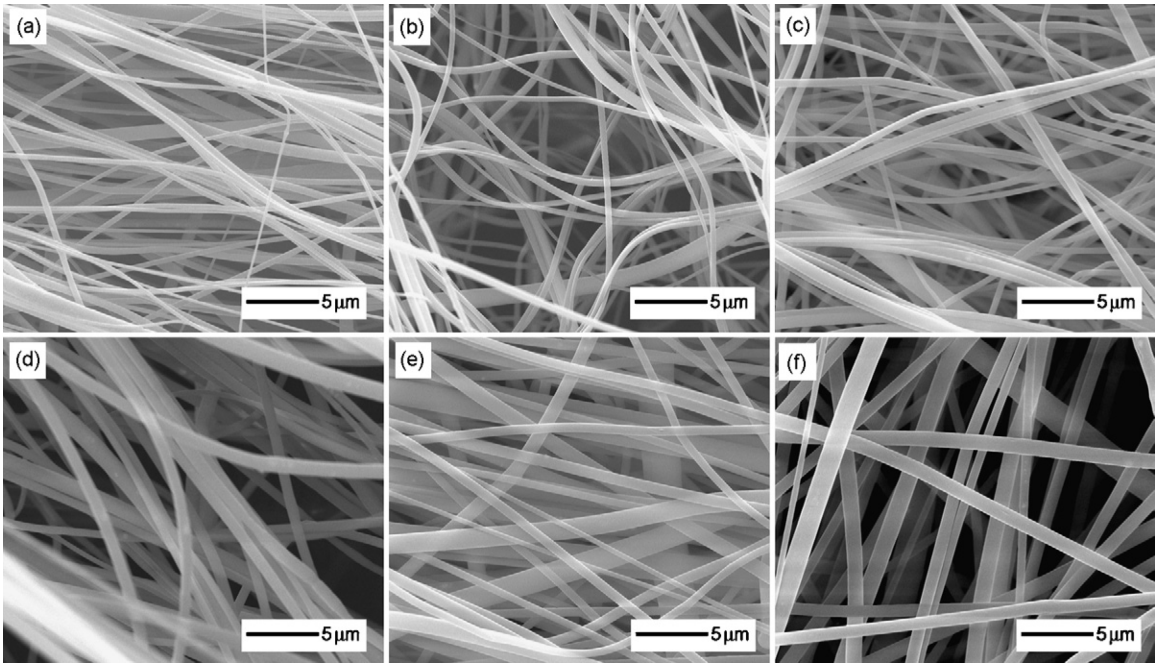

Fig. 2. SEM images of electrospun fibers: (a) PET; (b) SS/PET (10/100); (c) SS/PET (20/100); (d) SS/PET (30/100); (e) SS/PET (40/100); (f) SS/PET (50/100).

3.2. *Fiber morphology*

From the previous reports, morphology of the electrospun fibers are primarily influenced by the type of polymer, the solution properties [19–23] and the process parameters [11,24,25]. Since the electrospinning parameters and original solution concentration were fixed, the morphology of the electrospun fibers mainly depends on SS's percentage in SS/PET composite fibers. According to the experimental results, the SS mass percentage range (SS/PET) suitable for electrospinning is from 0/100 to 50/100 in SS/PET solution, namely, the mixed solution could not be electrospun to fibers when SS/PET mass ratio exceeded 50/100 because SS would be soluble incompletely with further increase in the mixed solution. Fig. 2a–f shows the typical SEM images of electrospun PET fibers and SS/PET composite fibers with different SS/PET mass ratios. Meanwhile, the average diameter of the six types of fibers in Fig. 2a–f is given in Fig. 3. Apparently, it could be observed that neat PET fibers show smooth surfaces and cylindrical shape, as shown in Fig. 2a, which means PET is easy to form fibers at the present condition, and the average diameter of PET fibers was about 375 nm. The surface morphology of the composite fibers electrospun from the SS/PET mixed solution has no obvious change at the concentration range suitable for electrospinning, as shown in Fig. 2b–f, and their appearances stay smooth. In addition, with the increase of SS's proportion in the composite fibers, the average diameter became larger gradually from Fig. 3, and the composite fibers with the SS/PET mass ratio of 50/100 have an average diameter of almost 1 μm. The improved diameter of the composite fibers is attributed to the variations of mixed solution properties such as higher viscosity and the lower conductivity which are caused by the introduction of SS into PET solution. Similar results of the effect of solution properties on the fiber diameter have also been reported in our previous researches [17,19,20].

In addition, to confirm the form stable characteristics of the electrospun SS/polymer composite fibers, the representative SEM images of SS/PET composite fibers with the mass ratio of 50/100 before and after 100 heating–cooling thermal cycles are illustrated in Fig. 4. It is clear to see that the composite fibers have no obvious variations in the fibrous shape and the fiber diameter after the thermal treatment (the fiber diameter is from 989 nm to 1021 nm), which results from the polymer protection and supporting effect of polymer (PET) matrix. Therefore, the SS/PET composite fibers were excellent form stable PCMs for further applications.

3.3. *Thermal properties*

For the applications of thermal energy storage or thermoregulation, thermal performances are significant factors to evaluate novel PCMs. Fig. 5 shows DTG curves of stearyl alcohol, stearic acid and stearyl stearate, respectively. Because sublimating behavior appears for stearyl alcohol and stearic acid before their decomposing point, Fig. 5a and b could not reflect their real weight loss actions, and it could be concluded that stearyl alcohol and stearic acid were unfitted for working materials at high temperature. How-

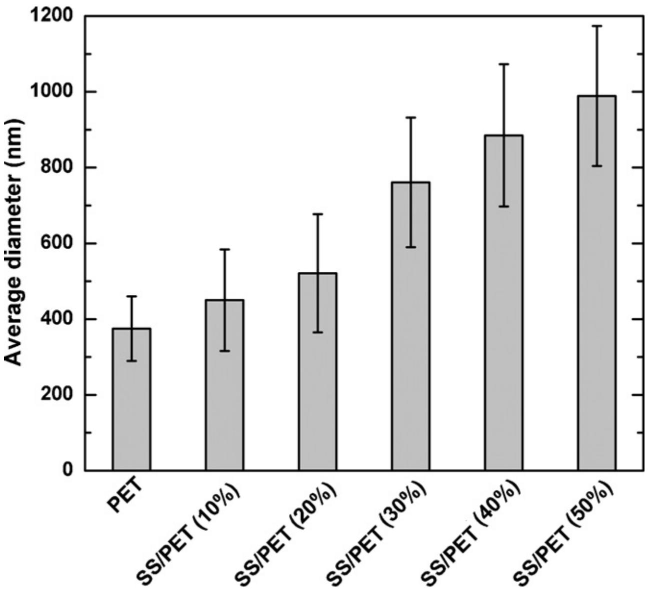

Fig. 3. The average diameter of electrospun fibers.

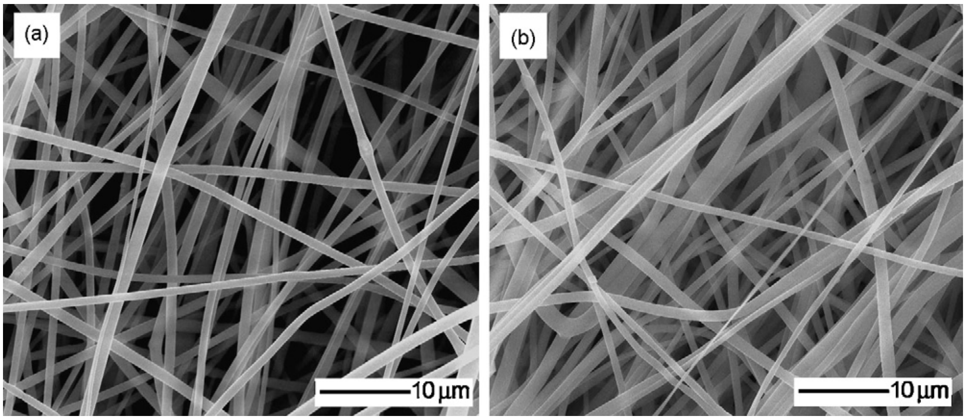

Fig. 4. SEM images of electrospun SS/PET (50/100) composite fibers before (a) and after (b) thermal treated.

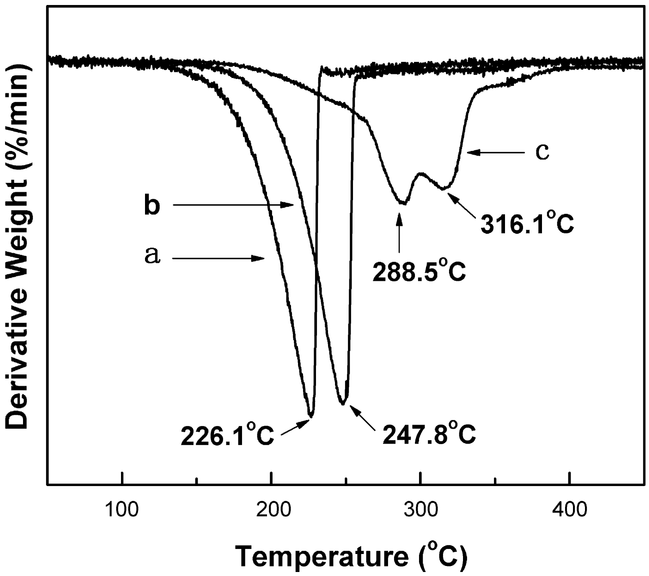

Fig. 5. DTG curves of stearyl alcohol (a), stearic acid (b) and stearyl stearate (c).

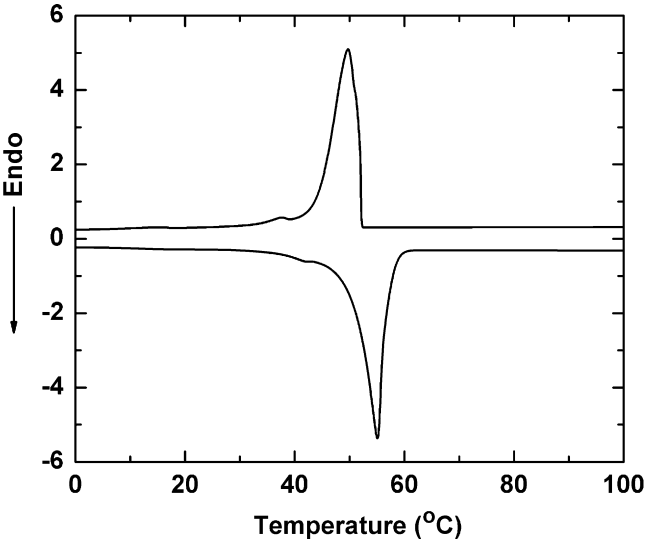

Fig. 6. DSC curves of stearyl stearate.

ever, SS exhibits better thermal stability for the disappearance of sublimation. Seen from Fig. 5c, there are two weight loss peaks. Since the bond energy of C–C bond (346.9 kJ/mol) is lower than that of C–O bond (359.1 kJ/mol), the left decomposing peak in low temperature range is attributed to long chains alkyl, while the right peak at high temperature belongs to ester groups. The peak point of decomposition increases by about 60 °C and 40 °C for stearyl stearate compared with stearic acid and stearyl alcohol, respectively. Fig. 6 presents the DSC thermogram of stearyl stearate, and it shows the existence of two peaks during heating and cooling process, which may be caused by two different crystal forms coexisted in the substrate. The lower temperature peak became weak and was nearly covered by the higher temperature peak. The thermal properties of stearyl alcohol before and after 100 heating–cooling thermal cycles are summarized in Table 1, respectively. Apparently, SS has balanced thermal properties in the process of melting and crystallization. After thermal treatment, the enthalpy and phase change temperature of melting and crystallization decreases in a certain extent, which indicates that the thermal reliability of SS is relatively weak for recycled use itself.

DSC curves of the composite fibers with different SS/PET mass ratio is shown in Fig. 7. Enthalpy of melting for the SS/PET composite fibers with 10/100–50/100 mass ratio increases gradually from 14.25 J/g to 53.77 J/g. Clearly, Enthalpy of SS/PET composite fibers with various mass ratios is much lower than that of SS (172.70 J/g) because PET in the composite fibers has no contribution to the latent heat at this temperature range. Theoretically, the enthalpy values of SS/PET composite fibers are obtained by multiplying the latent heats of pure SS and the mass percentage of SS in the composite fibers. Data summarized from DSC curves, Fig. 8 shows the theoretical values, original values and thermal treated values for latent heats of fusion of SS/PET composite fibers with different mass ratios, and the phase transition temperature of the SS/PET composite fibers at melting process before and after thermal cycles is illustrated in Fig. 9. The experimental values (both before and after 100 heating–cooling cycles) of melting enthalpy for the SS/PET composite fibers are lower than the corresponding theoret-

Table 1
The thermal properties of stearyl stearate before and after thermal cycles.

Sample	Enthalpy of melting (J/g)	Melting point (°C)	Enthalpy of crystallization (J/g)	Crystallizing point (°C)
Original	172.7	55.1	175.0	49.7
Thermal cycled	159.0	52.9	157.3	48.3

ical values. It is believed that the reduction of the enthalpies was mainly caused by a retardation of the crystallization process of SS in the composite fibers, which hindered not only by the quench process of electrospinning [19,26,27] but also by the diluent effect of PET in the composite fibers. It is worthy noting that all the melting enthalpies of the composite fibers after 100 heating–cooling thermal cycles, namely the experimental values after thermal cycles, decrease slightly compared with those of the corresponding experimental values before thermal cycles (the ratio of the enthalpies after thermal cycles to that before thermal cycles is 99.30%, 97.27%, 94.31%, 94.89% and 91.09% for SS/PET, respectively, as shown in Fig. 8). Meanwhile, T_m of all the electrospun SS/PET composite fibers is in the range of 50–51 °C, which indicates that the phase transition temperature of the composite fibers has mo obvious variations as the SS proportion changes. The phase change temperature of the composite fibers also has few decreases after thermal treatment, which is attributed to the shield supporting effect of PET. Compare with the obvious variations of thermal properties for SS in Table 1, SS/PET composite fibers show better thermal stability and reliability than SS, which indicates that the composite fibers have more valuable applications in thermal energy storage.

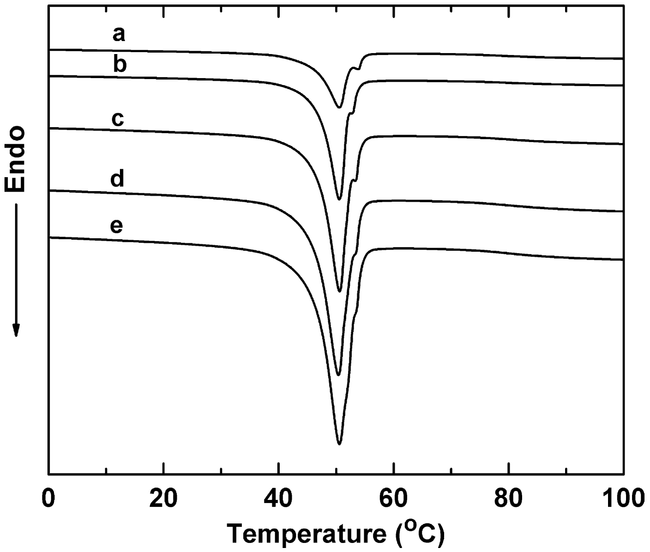

Fig. 7. DSC curves of electrospun SS/PET composite fibers with different mass ratios: (a) 10/100; (b) 20/100; (c) 30/100; (d) 40/100 and (e) 50/100.

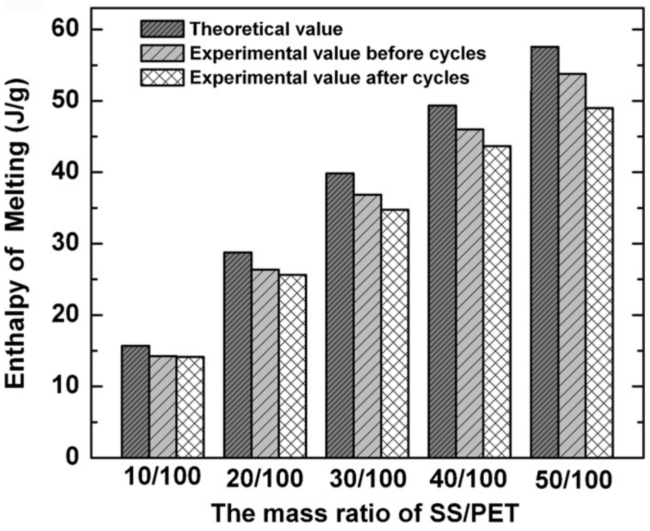

Fig. 8. Theoretical and experimental values of enthalpy of electrospun SS/PET composite fibers before and after thermal cycles.

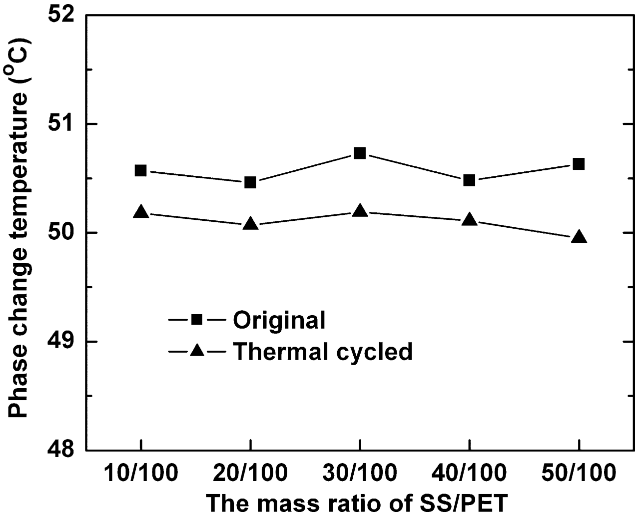

Fig. 9. Phase change temperature of SS/PET composite fibers before and after thermal cycles.

4. Conclusion

A novel solid–liquid phase change material stearyl stearate (SS) was synthesized and the composite ultrafine fibers of SS/PET were electrospun successfully for thermal energy storage. The morphology and the thermal properties of the composite fibers changed dramatically by adjusting the SS/PET mass ratio. The average fiber diameter increased generally with the content of SS in the composite fibers. Due to the shielding and supporting effect of polymer (PET) matrix, the electrospun SS/PET composite fibers revealed good thermal properties after repeated thermal cycles treatment. Therefore, the electrospun SS/PET composite fibers are promising in serving as form stable PCMs for thermal energy storage.

Acknowledgments

Financial support by the National Natural Science Foundation of China (Nos. 50521302 and 50473057) is greatly appreciated. The authors also thank Dr. Weidong Li for his valuable contribution and advice.

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