Role of M_n of PEG in the Morphology and Properties of Electrospun PEG/CA Composite Fibers for Thermal Energy Storage

Changzhong Chen
Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China
Graduate School of Chinese Academy of Sciences, Beijing 100049, China

Linge Wang
Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China
Dept. of Chemistry, University of Sheffield, Sheffield, S3 7HF, U.K.

Yong Huang
Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China
State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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As an aim toward developing novel class of form-stable polymer-matrix phase change materials for thermal energy storage, ultrafine composite fibers based on cellulose acetate and polyethylene glycol (PEG) with five different molecular weight (M_n) grades were prepared by electrospinning. The effects of M_n of PEG on morphology, thermal properties and mechanical properties of the composite fibers were studied by field emission scanning electron microscopy, differential scanning calorimetry, and tensile testing, respectively. It was found that the composite fibers were smooth and cylindrical shape, with the average diameters ranging from about 1000 to 1750 nm which increased with M_n of PEG. Thermal analysis results showed that the composite fibers imparted balanced thermal storage and release properties in different temperature ranges with the variation of M_n of PEG. Thermal cycling test indicated that the prepared composites had excellent thermal stability and reliability even they were subjected to 100 heating-cooling thermal cycles. *AIChE J,* 55: 820–827, 2009
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Introduction

Thermal energy storage (TES) has gained extensive interest due to the impending shortage and increasing cost of energy resources nowadays.[1–5] Thermal energy can be stored in the form of sensible heat, latent heat, and chemical reaction heat, or a combination of them. Among these forms, the most attractive one is latent heat thermal energy storage (LHTES), which is commonly carried out using phase change materials (PCMs) because of their high-energy storage density and small temperature variation from storage to retrieval.[1–3,6] In that case, thermal energy is stored or released by PCMs during the phase change process. Various

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Correspondence concerning this article should be addressed to L. Wang at lg-wang@gic.ac.cn. or Y. Huang at yhuang@iccas.ac.cn.

inorganic and organic compounds and their mixtures have been examined for their potential as PCMs for LHTES systems for several decades.[1,3,7] Inorganic substances, like salt hydrates, were researched first as potential PCMs several decades ago, but supercooling and phase separation occurred during their applications often plague the thermal behavior of these materials and cause random variations or progressive drifting of the transition zone over repeated phase-change cycles.[3,5] Furthermore, corrosion is another shortcoming of those materials,[3] which results in their short service lives or high packing and maintenance costs. Later, organic PCMs, like paraffin waxes and fatty acids, are used extensively to many areas for their moderate thermal storage densities and a wide range of melting temperatures.[5,8] Meanwhile, they undergo negligible subcooling and are chemically inert and stable with no phase segregation. The problem is the necessity of the special storage devices or containers to encapsulate an organic PCM to store and to release the latent heat of the PCM. However, the container material not only increases the thermal resistance between PCM and heat transfer fluid but also augments the cost of the system.[3,7] Therefore, a novel class of polymer-matrix PCMs as LHTES 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.[6,9–17] These superior properties over traditional PCMs have directed researchers to focus on the development of new type form-stable or shape-stabilized 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.[18–20] 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.[21] Recently, a novel class of fibrous polymer matrix form-stable PCMs—ultrafine fibers of polymer/PCM composites have been developed via electrospinning technique.[22,23] McCann et al.[22] first prepared phase change nanofibers consisting of long-chain hydrocarbon cores and TiO_2-Polyvinylpyrrolidone (PVP) sheaths by melt coaxial electrospinning. In our previous work,[23] the ultrafine composite fibers based on cellulose acetate (CA) and polyethylene glycol (PEG) with the molecular weight of 10,000 have been prepared via electrospinning explored as thermo-regulating fibers. For the potential applications of the novel form-stable fibrous PCM in thermo-regulating material and TES, more systematic studies about the polymer/PCM composite fibers are needed to carry out, e.g., the effects of the polymer/PCM mixture ratio and the type of PCM on phase change temperature and latent heat of the composite fibers.

The molecular weight of an organic PCM is particularly relevant to its thermal and physical properties. Based on this idea, in this study, five different molecular weight grades of PEG were individually incorporated with the electrospun CA fiber for LHTES application. The effect of molecular weight of PEG on morphology, thermal properties, and tensile properties of the electrospun PEG/CA composite fibers were investigated by field emission scanning electron microscopy (FE-SEM), differential scanning calorimetry (DSC), WAXD, and tensile test, respectively. In addition, thermal properties and crystallization behaviors of the PEG/CA electrospun composite fibers and the corresponding cast film were compared.

Experimental Part

Materials

CA (M_n = 29,000 g/mol, DS = 2.45) was obtained from Aldrich. Five different molecular weight grades of PEG (M_n = 2000, 4000, 6000, 10,000, 20,000 g/mol, respectively) were purchased from Guangzhou Chemical Agent Company, China. Acetone and *N*,*N*-dimethylacetamid (DMAc) were purchased from Sinopharm Group Chemical Reagent Co., Ltd, China. All chemicals were used as received without further purification.

Electrospinning

The PEG/CA composite fibers were electrospun by following the procedure described in our previous work.[23] Briefly, a 15 wt % CA solution in an acetone/DMAc mixture solvent (acetone/DMAc = 2/1, *w*/*w*) was prepared. After that, each of PEG samples with equal weight of CA was individually added into the CA solution under constant stirring for 2 h. Electrospinning was performed at 20°C in air and using homemade apparatus similar to that used in the literature.[24] During the electrospinning, each of as-prepared solutions 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 5 ml/h. The metallic needle (0.8 mm diameter) was connected a high voltage supply (BPS-20, Beijing Electrostatic Facility Ltd., China) with a fixed voltage at 14 kV. An aluminum flat sheet or wire drum (6 cm diameter and set at 2000 rpm to align the fibers) was grounded and used as the collector. The distance between the needle and the collector was fixed at 15 cm. The fibers were dried in vacuum at room temperature for 24 h to remove residual solvent. For comparison purposes, a PEG6000/CA composite film (PEG/CA = 1/1, *w*/*w*) was prepared by solvent-casting technique from the as-prepared PEG6000/CA solution onto a glass pan. The thickness of the dry film was about 100 μm.

Thermal cycles test

A test of 100 heating-cooling thermal cycles was performed to monitor the variations in melting temperature (T_m), crystallizing temperature (T_c), latent heat of fusion (ΔH_f) and latent heat of crystallization (ΔH_c) of the samples. The appropriate amounts of PEG/CA composite fibers and cast film were placed into the empty aluminium pan and then placed onto a hot stage (STC200, Instec). A typical thermal cycle is consisted of heating the samples above PEG's melting temperature and cooling the samples at room temperature (in the temperature interval 20–80°C). The heating and cooling process times were maintained at approximately 15 and 25 min, respectively. Thermal cycling test was continued until 100 consecutive melting and freezing process.

Measurement

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 using a DSC instrument (DSC-100, PEA). Thermograms were obtained at a heating and the cooling rate of 10°C/min at temperature range, 0–100°C and in nitrogen atmosphere. The crystalline behavior of the samples was investigated by WAXD (D/Max-1200, Rigaku, Japan), CuKα radiation (λ = 1.54 Å), Ni Filtration, scanning from 2θ = 5–40°.

The tensile properties of the electrospun composite fibers were determined by means of a fiber tensile tester (TM-2, Institute of Chemistry, Chinese Academy of Sciences, China) with an extension rate of 10 mm/min at room temperature. A bundle of aligned fibers was collected and kept in a fibril form during the measurement. The size of the samples was about 20 mm length, 1 mm diameter, and 30 mm distance between two clamps. Since there were many interspaces among the fibers in the testing fibril, the cross-section area of the fibril measured by a micrometer was not equal exactly to the real cross-section area of the fibers. Therefore, the collected data is semiquantitative to a certain extent.

Results and Discussion

Fiber morphology

Electrospinning is a very simple technique but involves a quite complicated process. The results from numerous researches showed that the morphology of the electrospun fibers is primarily influenced by the type of polymer, the solution properties[24–30] (e.g., concentration, viscosity, surface tension, conductivity and the polarity of solvent) and the process parameters[19,20,31] (e.g., applied voltage, flow rate, distance between needle and collector, and collecting method).

Because of the good quality of the electrospun fibers obtained from 15 wt % CA solution,[32] it was used as the original solution, and the five PEG samples were individually added into it with equal weight proportion of CA in this study, i.e., PEG/CA = 1/1 by weight in the all composite fibers. Since the electrospinning process parameters were fixed, the morphology of the electrospun PEG/CA composite fibers were dominated by the molecular weight of PEG and the PEG/CA solution properties. Figure 1a–f represented the typical SEM images of the electrospun fibers from CA solution and PEG/CA mixed solutions. All the electrospun CA fibers and PEG/CA fibers were cylindrical in shape with smooth surfaces, and there was no obvious phase separation occurred at the surface of all the PEG/CA composite fibers, which indicated that PEG (with various molecular weights) and CA were miscible in all the composite fibers. However, the fiber diameter and its distribution were different apparently for the six types of electrospun fibers. Figure 1g showed the AFD of the CA fibers and the PEG/CA composite fibers, respectively. It was clear that the CA fibers showed the smallest fiber diameter among them (around 720 nm), and the AFD of the PEG/CA composite fibers increased as

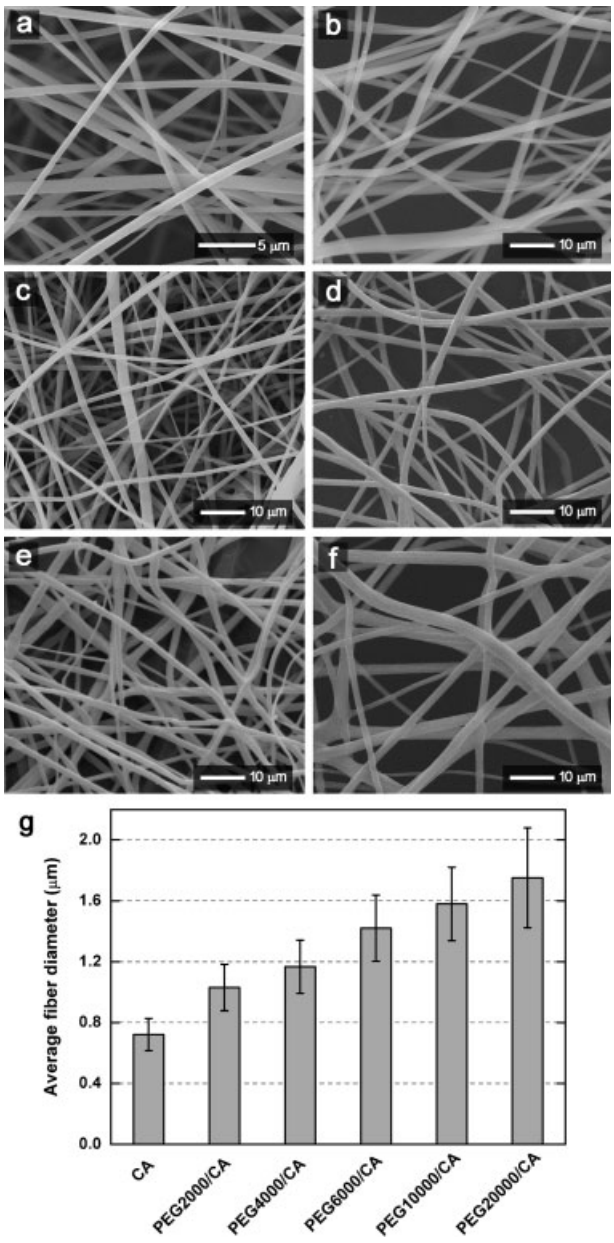

Figure 1. SEM images of electrospun fibers: (a) CA, (b) PEG2000/CA, (c) PEG4000/CA, (d) PEG6000/CA, (e) PEG10000/CA, (f) PEG20000/CA, and (g) the average fiber diameter of (a)–(f).

the molecular weight of PEG was increased, ranging between 1029 and 1752 nm. The increase of the fiber diameter after PEG adding into the original CA solution was attributed to the variations of the solutions such as a significant increase of viscosity and a decrease of conductivity of the PEG/CA mixed solution,[23] complimenting similar results reported in the literature.[25,27–30] Obviously, PEG with higher molecular weight has more effect on the increase of viscosity of the mixed solution and led to a large fiber diameter. In addition, the diameter distribution of the PEG/CA composite fibers became inhomogeneous and broad gradually with the increasing of the molecular weight of PEG (the diameter dis-

tributions of the electrospun fibers were shown in Supp. Info. Fig. 1).

Thermal properties

For TES applications, the high latent heat and good thermal stability and reliability are the most desirable thermal properties of PCMs. Figure 2 showed the DSC curves of the five types of electrospun PEG/CA composite fibers (the corresponding data of the thermal properties were summarized in Supp. Info. Table 1). Obviously, all the PEG/CA composite fibers had balanced thermal storage and released properties at heating and cooling process. It could be seen that the T_m (ranging from 51.14 to 62.27°C), ΔH_f (ranging from 53.23 to 86.03 J/g), T_c (ranging from 30.45 to 41.89°C), and ΔH_c (ranging from 47.93 to 73.48 J/g) of the PEG/CA composite fibers increased generally with the increase of the molecular weight of PEG in the composite fibers, which could be interpreted by the crystalline behaviors of the composite fibers. The crystalline behaviors of the CA fibers and the PEG/CA composite fibers were studied by their WAXD patterns from Figure 3. It was obvious that CA fibers showed a broad diffraction peak at about $2\theta = 21.3°$, which indicated that CA fibers were amorphous. Meanwhile, all the PEG/CA composite fibers had similar diffraction patterns and diffraction angles at about 19.5 and 24°, which were the same as the corresponding pure PEG powders. It was easily inferred that the diffraction peaks of the PEG/CA composite fibers were aroused by the component of PEG, and CA acted merely as a diluent in the composite fibers. The main difference between the WAXD curves of the five types of PEG/CA fibers was the diffraction peaks' shape, and the diffraction peaks became sharper with the increase of the molecular weight of PEG in the composite fibers, which meant that the degree of crystallization of the composite fibers increased, i.e., the larger the crystallization region and more regular the structure of the PEG molecular chains in the composite fibers. Consequently, the enthalpies for the phase change of the PEG/CA composite fibers in general increased (as shown in Figure 4).

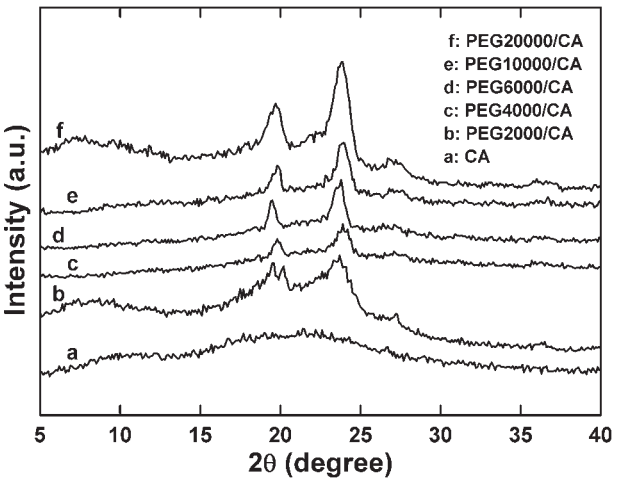

Figure 3. WAXD patterns of the CA fibers and the five types of electrospun PEG/CA composite fibers.

Theoretically, the enthalpy values of the PEG/CA composite fiber are obtained by multiplying the latent heats of pure PEG and its mass percentage in the composite fibers. As can bee seen from Figure 4, before and after 100 heating-cooling cycles the experimental values of melting enthalpy of the PEG/CA composite fibers were lower than the corresponding theoretical values. And the efficiency of enthalpy (the ratio between the experimental value and the theoretical value) before the thermal cycles for PEG2000/CA, PEG4000/CA, and PEG6000/CA electrospun fibers was only 65.68, 66.58, and 70.31%, respectively. However, it increased to 97.0 and 97.59% for PEG10000/CA and PEG20000/CA composite fibers, respectively. It was believed that the reduction of the

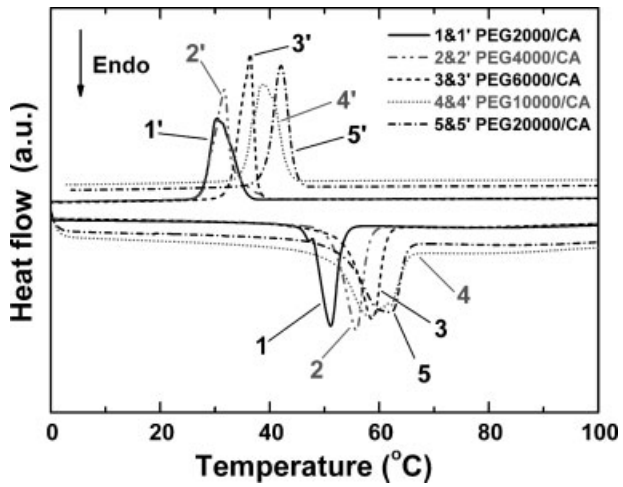

Figure 2. DSC curves of electrospun PEG/CA composite fibers in heating and cooling process: (1) and (1') PEG2000/CA, (2) and (2') PEG4000/CA, (3) and (3') PEG6000/CA, (4) and (4') PEG10000/CA, and (5) and (5') PEG20000/CA.

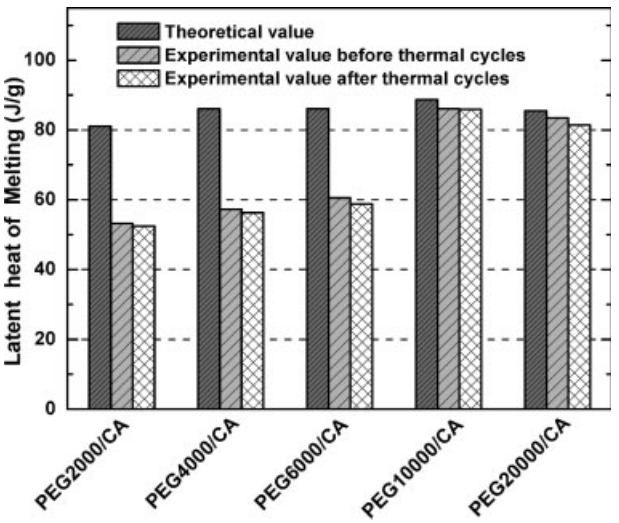

Figure 4. Theoretical and experimental values of melting enthalpy of the five types of electrospun PEG/CA composite fibers.

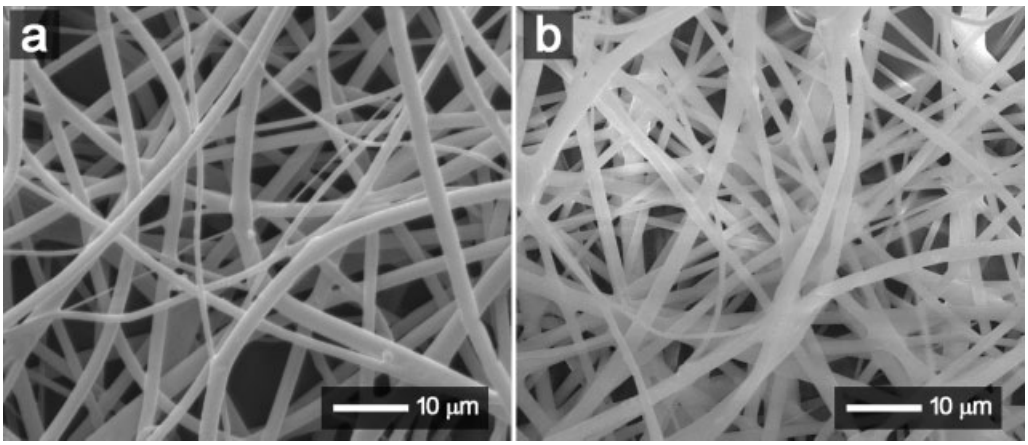

Figure 5. SEM images of the electrospun PEG10000/CA fibers before (a) and after (b) 100 heating-cooling cycles.

enthalpies was mainly caused by a retardation of the crystallization process of PEG in the composite fibers, which not only hindered by the quench process of electrospinning[30,33,34] but also influenced by the hydrogen bonding interactions between the PEG and CA chains.[6,23,35] Since the solvent removed from the polymer in subsecond time scales during the electrospinning process, the molecular chains of PEG have no time to form a well-defined, microscale equilibrium structure in the composite fibers. Meanwhile, PEG was found to be both distributed on the surface and within the core of the composite fibers,[23] the crystalline areas of PEG were very tiny within ultrafine fiber with a few microns, and surrounded by hydrogen bonding between the OH group of PEG and the carbonyl group of CA. Therefore, the short chain length of the lower molecular weight PEG, led to a lower crystalline areas of PEG in the composite fibers (reflected in the WAXD data in Figure 3) and a larger deviation of the enthalpies from the theoretical values.

It was worthy to notice that all the melting enthalpies of the composite fibers after 100 heating-cooling thermal cycles, namely the experimental values after thermal cycles, were almost identical to those of the corresponding experimental values before thermal cycles (the ratio of the enthalpies after thermal cycles to that before thermal cycles is 98.57, 98.32, 97.16, 99.86, and 97.54% for PEG2000/CA, PEG4000/CA, PEG6000/CA, PEG10000/CA, and PEG20000/CA, respectively, as shown in Figure 4), which showed good thermal stability and reliability of all the electrospun PEG/CA composite fibers. It had been found that less thermal oxidative degradation of PEG[36] occurred in the thermal cycling process of the composite fibers because the PEG distributed within the core of the fibers was protected by the surface shell of fiber.[23] On the other hand, the morphology of the composite fiber was also well retained after thermal treatment consisting of 100 heating-cooling cycles. Figure 5 showed the representative SEM images of the PEG10000/CA composite fibers before and after the thermal cycles. It was clear to see that the composite fibers had no obvious variations in the fibrous shape and the fiber diameter, i.e., the PEG/CA composite fibers were excellent form-stable PCMs, which also resulted from the polymer protection and supporting effect of CA matrix.

To investigate the difference in thermal properties between electrospun PEG/CA composite fibers and PEG/CA cast film, a comparative study of the electrospun composite fibers and the corresponding PEG6000/CA cast film was undertaken. Table 1 listed the thermal properties of the composite fibers and the film before and after thermal cycles. Before the thermal treatment, though the mass ratio of PEG in the cast film is the same as that in the electrospun composite fibers (at a content of 50%), the ΔH_f and ΔH_c were slightly higher than the latter. The WAXD data of them from Figure 6 gave an

Table 1. Thermal Properties of the Cast PEG6000/CA Film and the Electrospun PEG6000/CA Composite Fibers Before and After 100 Heating-Cooling cycles

Sample	T_m (°C)	ΔH_f (J/g)	T_c (°C)	ΔH_c (J/g)
Casting film	60.85	66.82	37.87	62.92
Cycled casting film	58.61	58.89	36.43	55.36
Electrospun fibers	58.24	60.54	36.46	54.92
Cycled electrospun fibers	56.85	58.82	35.79	53.53

T_m, melting temperature; ΔH_f, heat of fusion; T_c, crystallizing temperature; ΔH_c, heat of crystallization.

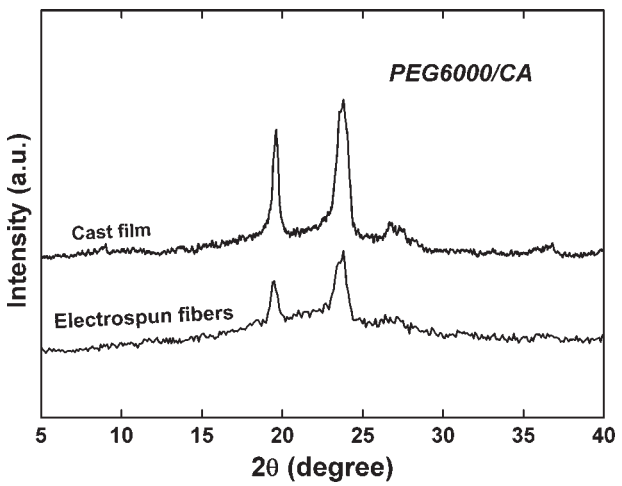

Figure 6. WAXD patterns of the cast PEG6000/CA film and the electrospun PEG6000/CA composite fibers.

explanation of the deviation of their thermal properties. It was obvious that the diffraction peaks of the cast film were sharper than those of the electrospun fibers, which indicated that the former has higher crystallinity than the latter. Since the evaporation of the solvent from the film occurred in a much longer time interval and the crystallization regions of PEG in the film were larger than that in the submicron size fibers, the aggregation of the molecular chains of PEG in the cast film was more order and regular than those of the composite fibers, which caused a higher enthalpies for the cast film. However, the larger crystallization regions of PEG weakened the shielding effect of the CA matrix for PEG, and resulted in a worse protection of the thermal oxidative degradation of PEG. After the thermal cycle treatment, the T_m, ΔH_f, T_c, and ΔH_c of the PEG6000/CA film decreased by 2.24°C, 7.93 J/g, 1.44°C, and 7.56 J/g, respectively. In contrast, the thermal properties of the PEG6000/CA composite fibers were only slightly varied after the thermal treatment, and the T_m, ΔH_f, T_c, and ΔH_c of the cycled composite fibers only decreased by 1.39°C, 1.72 J/g, 0.67°C and 1.39 J/g, respectively, as shown in Table 1. Obviously, the thermal stability and reliability of the PEG6000/CA electrospun fibers was better than those of the corresponding cast film from the variations of the thermal performances after thermal treatment.

Tensile properties

Besides good thermal properties, high mechanical performance of the composite fibers is also an important factor for their various potential applications. The previous literature have reported that the tensile properties of the electrospun fibers could be affected by the fibers' alignment,[37] the testing direction,[38] the electrospinning solution concentration,[37,39] the fibers' component,[40] etc. In this work, the tensile properties of the electrospun PEG/CA composite fibers were measured by examining a fibril that consisted of hundreds of aligned fibers, and the data was compared with those of the electrospun CA fibers. As mentioned in the experiment section, the collected data is semiquantitative due to the approximate value the cross-sectional area of the fibers in the fibril.

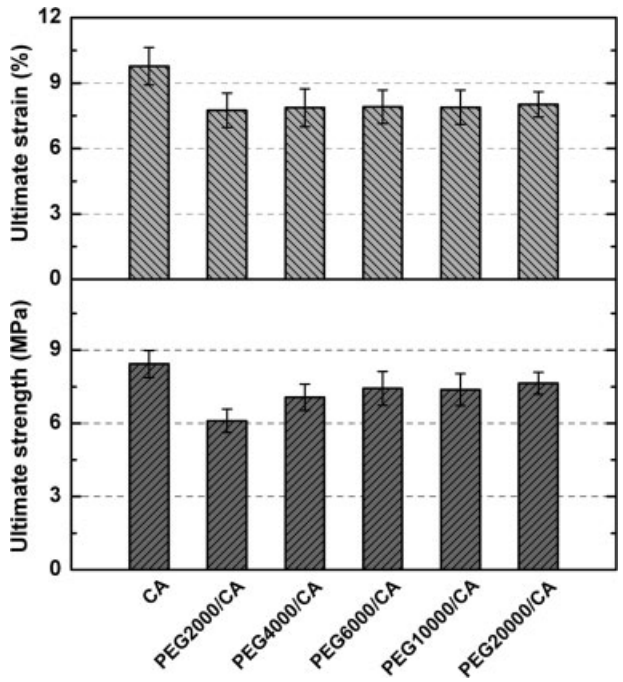

Figure 7. Tensile properties of the electrospun CA fibers and the five types of electrospun PEG/CA composite fibers.

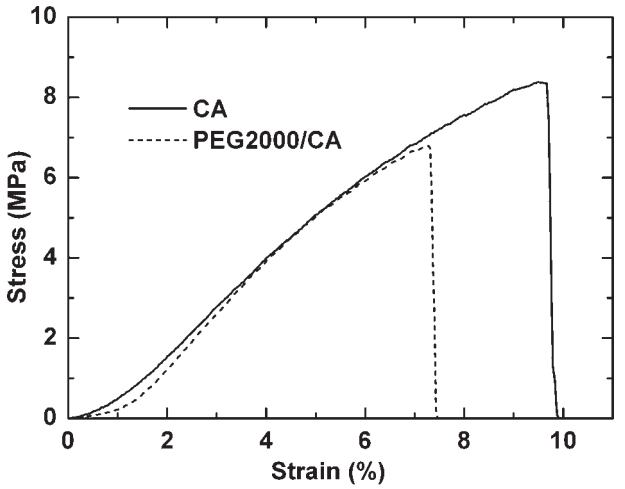

Figure 8. Typical strain-stress curves of the electrospun CA fibers and PEG2000/CA composite fibers.

The tensile properties of the electrospun CA fibers and the five types of electrospun PEG/CA composite fibers was shown in Figure 7, and Figure 8 revealed the typical stress-strain curves of the CA fibers and the PEG2000/CA composite fibers. The ultimate strength and the ultimate strain of the CA fibers were about 9.5 MPa and 10%, respectively, and those of the composite fibers were all lower with the introduction of PEG. The ultimate strength of the composite fibers had a tendency of increasing from 6.0 to 7.8 MPa when the molecular weight of PEG in the composite fibers increased, but their ultimate strain almost remained the value of about 7.5%. Obviously, the reduction of the tensile strength of the PEG/CA composite fibers was attributing to the introduction of PEG, similar result was also found in poly(ε-caprolactone)/CA/PEG blends.[41] In the PEG/CA composite fibers (PEG/CA = 1/1, *w*/*w*), the PEG crystalline regions were dispersed in the CA matrix, the structure of the composite fibers exhibited a thin network-like continuous phase of the CA material.[23] Therefore, the dispersed phase, PEG, had a little contribution to the elongation of the composite fibers. In contrast, the hydrogen bonding interaction between PEG and CA chains was of advantage to the tensile strength of the composite fibers which was mainly sourced from the CA molecular chains entanglement. And with increasing the molecular weight, the molecular chains of PEG became longer, which led to more tight entanglement and stronger interaction between the PEG and CA molecular chains and resulted in the increase of ultimate strength. Moreover, the degree of crystallinity of the composite fibers increased with increasing the molecular weight of PEG,

which was also partly contributed to the increase of ultimate strength of the composite fibers.

Conclusion

The ultrafine composite fibers based on CA and PEG with five molecular weight grades were prepared as a novel class of form-stable PCMs for TES by electrospinning. The morphology observation revealed that the PEG/CA composite fibers are cylindrical shape with smooth surface, with the average diameters of ranging from about 1000–1750 nm. The PEG/CA composite fibers imparted balanced thermal storage and released properties, and the phase change temperature and the enthalpies of the composite fibers varied with the increase of the molecular weight of PEG, respectively. In general, the AFD and the enthalpies the composite fibers were increased with the increase of molecular weight of PEG. Because of the shielding and supporting effect of CA matrix on PEG dispersed crystalline regions, the electrospun composite fibers not only showed good form-stable morphology, but also reveled a better thermal properties (i.e., efficiency of enthalpy and thermal stability and reliability) compared with those of the corresponding cast film after repeated thermal cycles treatment. Moreover, with the increase of the molecular weight of PEG, the tensile properties of the PEG/CA composite fibers had a tendency of increase from 6.0 to 7.8 MPa, whereas their ultimate strain almost remained the value of about 7.5%. Therefore, it is indicated that such electrospun PEG/CA composite fibers are competent and suitable for the potential applications in TES.

Acknowledgments

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Literature Cited

1. Abhat A. Low temperature latent thermal energy storage system: heat storage materials. *Sol Energy*. 1983;30:313–332.
2. Kurklu A. Energy storage applications in greenhouses by means of phase change materials (PCMs): a review. *Renew Energ*. 1998;13:89–103.
3. Zalba B, Marin JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Appl Therm Eng*. 2003;23:251–283.
4. Sharma SD, Sagara K. Latent heat storage materials and systems: a review. *Inter J Green Energy*. 2005;2:1–56.
5. Kenisarin M, Mahkamov K. Solar energy storage using phase change materials. *Renew Sust Energ Rev*. 2007;11:1913–1965.
6. Alkan C, Sari A, Uzun O. Poly(ethylene glycol)/acrylic polymer blends for latent heat thermal energy storage. *AICHE J*. 2006;52:3310–3314.
7. Farid MM, Khudhair AM, Razack SA, Al-Hallaj S. A review on phase change energy storage: materials and applications. *Energ Convers Manage*. 2004;45:1597–1615.
8. Varun PV, Singal SK. Review of mathematical modeling on latent heat thermal energy storage systems using phase-change material. *Renew Sust Energ Rev*. 2007;12:999–1031.
9. Hong Y, Xin-Shi G. Preparation of polyethylene-paraffin compound as a form-stable solid-liquid phase change material. *Sol Energ Mat Sol C*. 2000;64:37–44.
10. Xiao M, Feng B, Gong KC. Preparation and performance of shape stabilized phase change thermal storage materials with high thermal conductivity. *Energ Convers Manage*. 2002;43:103–108.
11. Sari A. Form-stable paraffin/high density polyethylene composites as solid-liquid phase change material for thermal energy storage: preparation and thermal properties. *Energ Convers Manage*. 2004;45:2033–2042.
12. Lin K, Zhang Y, Xu X, Di H, Yang R, Qin P. Experimental study of under-floor electric heating system with shape-stabilized PCM plates. *Energ Build*. 2005;37:215–220.
13. Peng S, Fuchs A, Wirtz RA. Polymeric phase change composites for thermal energy storage. *J Appl Polym Sci*. 2004;93:1240–1251.
14. Sari A, Alkan C, Kolemen U, Uzun O. Eudragit S (methyl methacrylate methacrylic acid copolymer)/fatty acid blends as form-stable phase change material for latent heat thermal energy storage. *J Appl Polym Sci*. 2006;101:1402–1406.
15. Sari A, Alkan C, Karaipekli A, Onal A. Preparation, characterization and thermal properties of styrene maleic anhydride copolymer (SMA)/fatty acid composites as form stable phase change materials. *Energ Convers Manage*. 2008;49:373–380.
16. Pielichowski K, Flejtuch K. Differential scanning calorimetry study of blends of poly(ethyleneglycol) with selected fatty acids. *Macromol Mater Eng*. 2003;288:259–264.
17. Alkan C, Sari A. Fatty acid/poly(methyl methacrylate) (PMMA) blends as form-stable phase change materials for latent heat thermal energy storage. *Sol Energy*. 2008;82:118–124.
18. Reneker DH, Chun I. Nanometre diameter fibres of polymer, produced by electrospinning. *Nanotechnology*. 1996;7:216–223.
19. Huang ZM, Zhang YZ, Kotaki M, Ramakrishna S. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Compos Sci Technol*. 2003;63:2223–2253.
20. Li D, Xia YN. Electrospinning of nanofibers: reinventing the wheel? *Adv Mater*. 2004;16:1151–1170.
21. Ramakrishna S, Fujihara K, Teo WE, Yong T, Ma ZW, Ramaseshan R. Electrospun nanofibers: solving global issues. *Mater Today*. 2006;9:40–50.
22. McCann JT, Marquez M, Xia Y. Melt coaxial electrospinning: a versatile method for the encapsulation of solid materials and fabrication of phase change nanofibers. *Nano Lett*. 2006;6:2868–2872.
23. Chen CZ, Wang L, Huang Y. Electrospinning of thermo-regulating ultrafine fibers based-on polyethylene glycol/cellulose acetate composite. *Polymer*. 2007;48:5202–5207.
24. Wang L, Li CM, Ryan AJ, Armes SP. Synthesis and peptide-induced degradation of biocompatible fibers based on highly branched poly(2-hydroxyethyl methacrylate). *Adv Mater*. 2006;18:1566–1570.
25. Theron SA, Zussman E, Yarin AL. Experimental investigation of the governing parameters in the electrospinning of polymer solutions. *Polymer*. 2004;45:2017–2030.
26. Wu XH, Wang LG, Huang Y. Effect of solvent on morphology of electrospinning ethyl cellulose fibers. *J Appl Polym Sci*. 2005;97:1292–1297.
27. Taepaiboon P, Rungsardthong U, Supaphol P. Drug-loaded electrospun mats of poly(vinyl alcohol) fibres and their release characteristics of four model drugs. *Nanotechnology*. 2006;17:2317–2329.
28. Tungprapa S, Jangchud I, Supaphol P. Release characteristics of four model drugs from drug-loaded electrospun cellulose acetate fiber mats. *Polymer*. 2007;48:5030–5041.
29. Wang M, Wang L, Huang Y. Electrospun hydroxypropyl methyl cellulose phthalate (HPMCP)/erythromycin fibers for targeted release in intestine. *J Appl Polym Sci*. 2007;106:2177–2184.
30. Wang L, Topham PD, Mykhaylyk OO, Howse JR, Bras W, Jones RAL, Ryan AJ. Electrospinning pH-responsive block copolymer nanofibers. *Adv Mater*. 2007;19:3544–3548.
31. Teo WE, Ramakrishna S. A review on electrospinning design and nanofibre assemblies. *Nanotechnology*. 2006;17:R89–R106.
32. Liu HQ, Hsieh YL. Ultrafine fibrous cellulose membranes from electrospinning of cellulose acetate. *J Polym Sci Part B: Polym Phys*. 2002;40:2119–2129.
33. Deitzel JM, Kleinmeyer JD, Hirvonen JK, Tan NCB. Controlled deposition of electrospun poly(ethylene oxide) fibers. *Polymer*. 2001;42:8163–8170.
34. Zong X, Kim K, Fang D, Ran S, Hsiao B, Chu B. Structure and process relationship of electrospun bioabsorbable nanofiber membranes. *Polymer*. 2002;43:4403–4412.
35. Oyama HT, Hemker DJ, Frank CJ. Effect of the degree of ionization of poly(methacrylic acid) on the complex formed with pyrene end-labeled poly(ethylene glycol). *Macromolecules*. 1989;22:1255–1261.

36. Han S, Kim C, Kwon D. Thermal/oxidative degradation and stabilization of polyethylene glycol. *Polymer*. 1997;38:317–323.
37. Kim KW, Lee KH, Khil MS, Ho YS, Kim HY. The effect of molecular weight and the linear velocity of drum surface on the properties of electrospun poly(ethylene terephthalate) nonwovens. *Fiber Polym*. 2004;5:122–127.
38. Matthews JA, Wnek GE, Simpson DG, Bowlin GL. Electrospinning of collagen nanofibers. *Biomacromolecules*. 2002;3:232–238.
39. Li L, Bellan LM, Craighead HG, Frey MW. Formation and properties of nylon-6 and nylon-6/montmorillonite composite nanofibers. *Polymer*. 2006;47:6208–6217.
40. Ding B, Kimura E, Sato T, Fujita S, Shiratori S. Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-jet electrospinning. *Polymer*. 2004;45:1895–1902.
41. Rosa DS, Guedes CGF, Casarin F, Braganca FC. The effect of the M_w of PEG in PCL/CA blends. *Polym Test*. 2005;24:542–548.

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