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Electrospinning of thermo-regulating ultrafine fibers based on polyethylene glycol/cellulose acetate composite

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Abstract

Ultrafine fibers of polyethylene glycol/cellulose acetate (PEG/CA) composite in which PEG acts as a model phase change material (PCM) and CA acts as a matrix, were successfully prepared as thermo-regulating fibers via electrospinning. The morphology observation from the electrospun PEG/CA composite fibers revealed that the fibers were cylindrical and had a smooth external surface. PEG was found to be both distributed on the surface and within the core of the fibers. Differential scanning calorimeter (DSC) was used to characterize the thermal properties of the composite fibers. The results indicated that the fibers imparted balanced thermal storage and release properties for their thermo-regulating function and the thermal properties were reproducible after 100 heating–cooling cycles.

Keywords: Electrospinning; Phase change material; Thermo-regulating fibers

1. Introduction

Phase change materials (PCMs) have been applied in many different areas because of their capability of storing or releasing large amounts of latent heat thermal energy as they change from one physical state to another. As renewable and clean energy storage materials, PCMs have been used in the preparation of thermo-regulating material fibers [1–3] and fabrics [4–6] for making smart textiles and garments. They work because the temperature of a PCM remains constant during the phase change and the textile will remain at a uniform temperature.

In the 1980s, Vigo and Frost [1,2] prepared several types of thermo-regulating fibers with various temperature ranges by immersing the hollow fibers into a PCM solution, such as an aqueous solution of hydrated inorganic salt and PEG solution (low molecular weight). Although the temperature-adaptable fabrics could impart desirable thermal storage and release properties, they exhibited unreliable and poor thermal behaviors on repeated thermal cycles. Thus, other approaches have been developed to improve the performance of the thermo-regulating fibers such as the microencapsulation technique of PCM [3]. In 1995, Pause managed to coat fibers with microencapsulated PCM (microPCM) and systematically studied the basic and dynamic thermal insulation of the fabrics using a range of different PCMs [4]. However, the surface coated fabrics became rougher and stiffer as the amount of microPCM increased, and thus the total hand value, which determines the tactile comfort perceived by humans, decreased [7]. Recently, Zhang et al. successfully prepared thermo-regulating composite fibers by embedding the microPCM into the fibers via both melt-spinning [8] and wet-spinning [9] techniques. Hu et al. [10] copolymerized PEG with poly(ethylene

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terephthalate) (PET), and melt-spun the copolymer into phase change fibers, which had solid–solid phase change characteristics at a certain temperature range without obvious liquid substance appearing. The phase change temperature range and the enthalpy of these spun thermo-regulating fibers could be adjusted by controlling the molecular weight and the corresponding proportion of PCMs added. However, the drawback of the conventional spinning method was that only a few types of thermo-regulating fibers could be made because of the poor processability for many polymers and PCMs. As a result, a new technology to prepare thermo-regulating fibers without the disadvantages mentioned above is essential for the realization of such smart materials. Here we discuss the use of electrospinning, which provides an extremely promising alternative.

Electrospinning [11,12] is a simple, convenient and versatile technique for generating ultrafine (sub-micron) fibers from a wide variety of polymers, polymer blends and nanoparticle- or drug-impregnated polymers [13]. Theoretically, almost any soluble polymer, including branched copolymers [14], with sufficiently high molecular weight can be electrospun. Electrospun fibers can be applied in a vast number of areas, such as healthcare [15], biotechnology and environmental engineering [14,16], defense and security [17] and energy storage and generation [18]. Recently, McCann et al. firstly prepared phase change nanofibers consisting of long-chain hydrocarbon cores and TiO_2-poly(vinyl pyrrolidone) (PVP) sheaths by melt coaxial electrospinning [19]. Here, ultrafine fibers of the polyethylene glycol/cellulose acetate (PEG/CA) composite, in which PEG acts as the PCM and CA acts as the matrix, have been successfully prepared via electrospinning and explored as thermo-regulating ultrafine fibers. The morphology and the thermal properties of the composite fibers were investigated using electron microscopes and differential scanning calorimeter (DSC).

2. Experimental part

An appropriate amount of cellulose acetate (CA, $\overline{M}_n = 29$ kg/mol, degree of substitution, DS = 2.45, Aldrich) was dissolved in *N*,*N*-dimethylacetamide (DMAc) and acetone mixture (DMAc/acetone = 1/2, w/w) at a concentration of 15 wt % [20]. PEG ($\overline{M}_n = 10$ kg/mol, Guangzhou Chemical Agent Company, China) was added to the CA solution (PEG/CA = 1/1, w/w) under constant stirring for 2 h. The viscosity, surface tension and conductivity of the solutions were measured using a viscometer (REOTEST II, Volkseignener, Germany), surface tension apparatus (BZY-1, Shanghai Apparatus Co., China) and a conductivity meter (DDA-11A, Shanghai Dapu Instrument Ltd., China), respectively. All measurements were carried out at 20 °C and an average value of each was obtained from at least three repeated measurements. Electrospinning was performed at 20 °C in air, using home-made apparatus similar to that used in the literature [21]. The as-prepared solution was placed in a 10 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 to a high voltage supply (BPS-20, Beijing Electrostatic Facility Ltd., China) with a fixed voltage at 14 kV, and a piece of aluminum foil was placed 15 cm below the tip of the needle to collect the fibers. The electrospun fibers were dried in a vacuum oven at room temperature for 24 h to remove the residual solvent. The composition of PEG and CA in the composite fibers was determined by immersing the fibers in deionized water to remove the PEG component for 24 h. Then, the wet fibers were dried at 40 °C under vacuum for 24 h. The content of PEG was calculated according to the weight loss of the composite fibers during immersion. The data showed that the mass of the washed fibers was approximately half of that of the original fibers (average of 50.8 wt%, calculated from three separate measurements), which is equal to the mixed ratio of PEG in the solution (PEG/CA = 1/1, w/w). PEG removal from the washed composite fibers was also confirmed by DSC (PE DSC-100, USA). The DSC curve of the washed composite fibers was similar to that of CA fibers (shown in Fig. S1 of the Supporting information), and no PEG melting peak was observed. The fibers were subsequently gold-coated and the morphology was observed by using a field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan) at an acceleration voltage of 20 kV under low vacuum. A transmission electron microscope (TEM, JEOL-100CX/II, NEC, Japan) was also used to observe the morphology of the electrospun fibers, operating at 100 kV. 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, as shown in Table 1.

Thermal treatment was conducted to determine the variations in the melting temperature (T_m), the crystallizing temperature (T_c), latent heat of fusion (ΔH_f) and latent heat of crystallization (ΔH_c) of electrospun PEG/CA composite fibers and PEG powder (reference sample) after 100 repeated heating–cooling cycles. The appropriate amount of PEG powder or composite fibers was placed into an unsealed empty aluminum pan, which was subsequently placed onto a hot stage (STC200, Instec, USA) for the thermal cycling treatment. A saw-tooth shaped thermal cycle consisted of heating the sample above PEG's melting temperature (up to 100 °C) and cooling the samples to room temperature (20 °C). The heating and cooling process times were maintained at approximately 20 and 30 min, respectively, until 100 complete thermal cycles had been undertaken. Thermal analysis was then performed (using 5.0 mg samples) on each of the cycled and uncycled PEG powder and electrospun PEG/CA fiber samples by DSC. The heating and cooling rates were 10 °C/min, ranging from −20 °C to 120 °C, in a nitrogen atmosphere. The

Table 1
Properties of the CA and the PEG/CA solutions and the average diameter of the electrospun fibers from the relative solutions

Solution	Viscosity (mPa s)	Surface tension (mN/m)	Conductivity (μS/cm)	Average fiber diameter (nm)
CA	160	40.0	8.46	721
PEG/CA	750	51.3	3.80	1579

surface morphology of the treated fibers was also monitored by SEM.

3. Results and discussion

Both CA and PEG dissolve very well in the DMAc/acetone mixture, but a pure PEG solution within a concentration range of 10–30 wt% cannot be electrospun. Due to the good quality of the obtained fibers electrospun from 15 wt% CA solution [20], it was used as the original solution and then PEG was added to it with equal weight proportion of CA. As shown in Fig. 1a and b, both the electrospun CA fibers and the electrospun PEG/CA composite fibers show smooth surfaces and are cylindrical in shape. From Table 1, it is clear to see that the addition of PEG into the CA solution affects the solution properties and the size of the resulting fibers considerably. For the PEG/CA composite solution, both the viscosity and the surface tension of the solution increased, whilst the corresponding conductivity decreased, compared with those of the CA solution. These variations in solution properties led to a dramatic increase in the fiber diameter and the AFD of the electrospun PEG/CA fibers was two times larger than that of the electrospun CA fibers, complementing similar results found in the literature [22–24].

Besides the fiber morphology, the distribution of PEG in the electrospun composite fibers is also of interest. Since PEG is a water-soluble polymer and CA is not, the morphology of the washed composite fibers provides information about the distribution of PEG. From the SEM observations (Fig. 1c), the water treated electrospun PEG/CA composite fibers still remain in a cylindrical form, but the AFD decreases slightly (from 1597 to 1524 nm). Meanwhile, a number of grooves are found on the washed fibers' surface (clearly seen when comparing the inset images of Fig. 1b and c, and Figs. S2 and S3 in Supporting information), demonstrating that there was PEG distributed on the surface of the electrospun fibers. This result is also confirmed by the morphological change of the composite fibers after thermal testing (Fig. 1d), which is discussed in more detail later. The longitudinal grooves on the surface of the washed fibers may also be attributed to the result of shrinkage caused by the removal of PEG from within the core of the fibers. As shown in the TEM images (Fig. 2 and Fig. S4 in the Supporting information), there are cavities within the washed fibers, which were not present in the original composite fibers. Therefore, the information from the SEM and TEM images indicates that PEG is not only distributed on the surface but also within the composite fibers themselves.

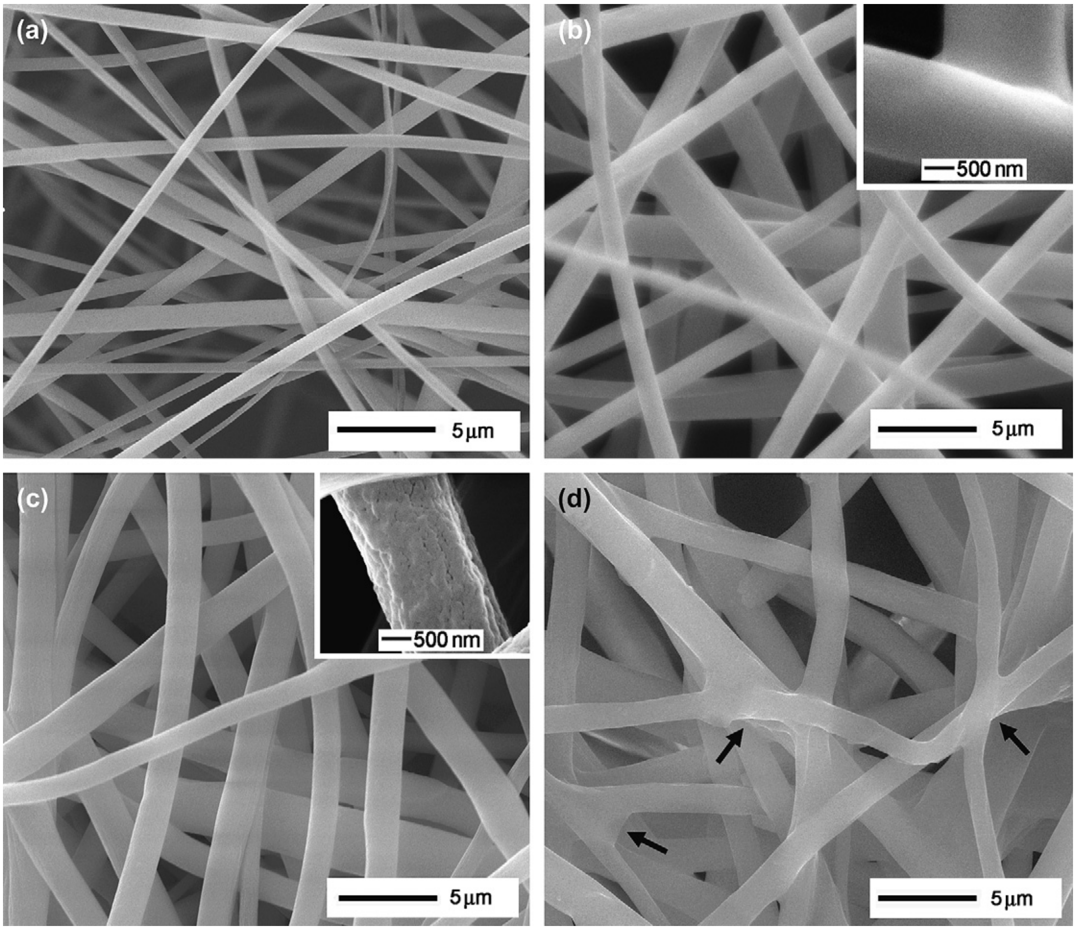

Fig. 1. SEM micrographs of (a) the electrospun CA fibers, (b) the electrospun PEG/CA composite fibers, (c) the washed electrospun PEG/CA composite fibers, and (d) the electrospun PEG/CA composite fibers after 100 heating–cooling cycles treated.

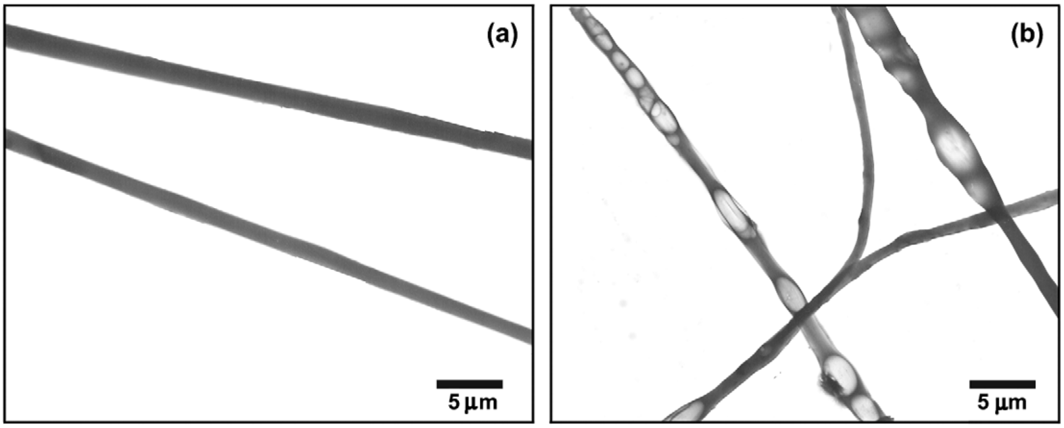

Fig. 2. TEM micrographs of (a) the original and (b) the washed electrospun PEG/CA composite fibers.

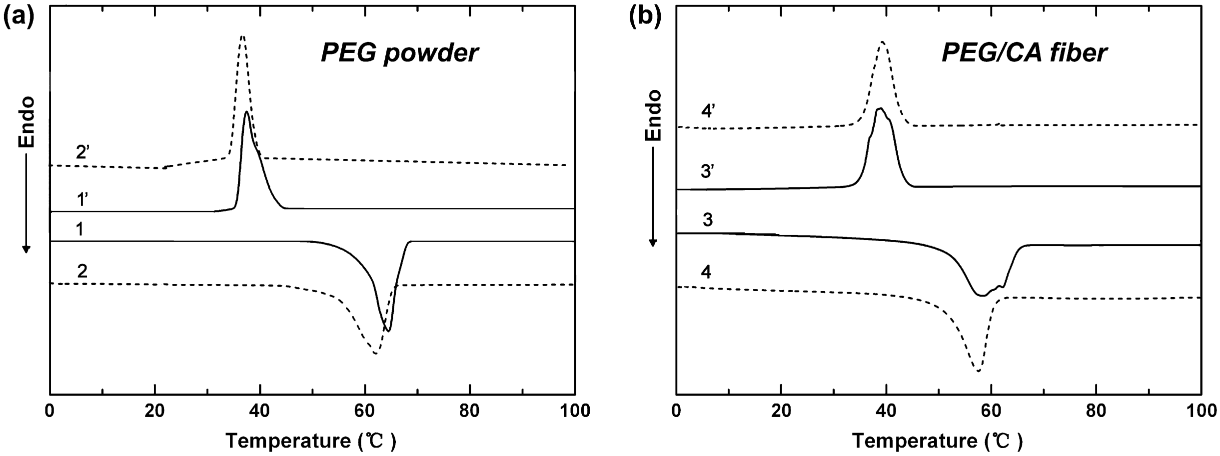

Fig. 3. DSC curves of (a) PEG powers and (b) the electrospun PEG/CA composite fibers before (solid line) and after (dashed) 100 heating–cooling cycles.

Fig. 3 shows the DSC thermograms for PEG powder and the PEG/CA composite fibers before and after 100 heating–cooling cycles. The corresponding thermal properties are summarized in Table 2. From the table, the T_m and T_c of the electrospun PEG/CA composite fibers are lower than those of PEG powder. Meanwhile, the corresponding ΔH_f and ΔH_c of the composite fibers are also lower than the theoretical values calculated by multiplying the latent heat of PEG and the mass percentage of PEG in the composite fibers, i.e., half of the ΔH_f and ΔH_c of PEG. The efficiency of enthalpy (the ratio of the experimental value to the theoretical value) is 97.0% and 77.7% for the ΔH_f and the ΔH_c of the composite fibers. The deviation of the thermal properties from their theoretical values can be accounted for the lower crystalline areas of PEG in the composite fibers, caused by hydrogen bonding between the OH group of PEG and the carbonyl group of CA [25,26], leading to entanglement between the molecular chains of PEG and CA. Similar results have also been reported in the literature on thermo-regulating fibers [7–9], but the efficiency of enthalpy of the electrospun PEG/CA composite fibers is much higher than that of other thermo-regulating fibers. It is suggested that the ultrafine diameter of electrospun fibers is probably one of the contributing factors to the better thermal permeability.

Table 2
Thermal properties of PEG powder and electrospun PEG/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)
PEG powder	64.18	177.38	37.52	167.75
Cycled PEG powder	62.14	158.90	36.96	155.38
PEG/CA fibers	58.47	86.03	38.96	65.15
Cycled PEG/CA fibers	57.59	85.91	38.23	64.95

T_m = Melting temperature, ΔH_f = Heat of fusion, T_c = Crystallizing temperature, ΔH_c = Heat of crystallization.

After the thermal cycle treatment, the T_m and ΔH_f of PEG decreased by 2.04 °C and 18.48 J/g, respectively, and the crystallizing process also shows similar changes (calculated from Table 2). Since the maximum heating temperature (100 °C) is much higher than the T_m of PEG and the samples are exposed to air during the thermal treatment, partial thermo-oxidative degradation of PEG [27,28] may occur during the thermal treatment, resulting in variations in the thermal properties of PEG. As shown by curve 3 in Fig. 3b, the untreated electrospun PEG/CA composite fibers show a wider melting peak at around 55–65 °C. In contrast, the thermally treated composite fibers show a strong, sharp melting peak at around 57 °C (curve 4 in Fig. 3b). This indicates that the crystalline microstructures of PEG in the fibers are more defined highly ordered after the thermal treatment because the PEG molecular chains inside the electrospun fibers have not had sufficient time to microphase separate during electrospinning. During electrospinning the solvent is removed from the polymer in sub-second time scales (like a quench process), causing a retardation of the crystallization process [22,29] and so the corresponding DSC curve of the original composite fibers shows a wider melting peak. However, after thermal treatment, the PEG in the fibers was able to form perfect crystalline microdomains as the composite was cooled down at a much slower rate (than the time taken to remove the solvent during electrospinning), producing a sharper melting peak (Fig. 3b). Table 2 demonstrates that the thermal properties of the composite fibers are only slightly varied following the thermal treatment. T_m, ΔH_f, T_c and ΔH_c of the treated composite fibers decreased by 0.88 °C, 0.12 J/g, 0.73 °C and 0.20 J/g, respectively. The efficiency of enthalpy is 96.9% and 77.4% of the theoretical values for the ΔH_f and ΔH_c of the thermally treated composite fibers, respectively, which are almost identical to those of the untreated composite fibers. This shows that the composite fibers have good thermal stability and reliability. Since the PEG distributed within the core of the fibers is protected by the surface shell of fiber, less thermal oxidative degradation of PEG occurs in the thermal cycling process of the composite fibers. The morphological change of the surface of the thermally treated fibers can be seen in Fig. 1d, where no obvious variations in the shape and size of the fibers were found, but some "*physical crosslinks*" or cohesion occurred between the fiber junctions (indicated by black arrows), which resulted from the flow of the melt PEG distributed on the fibers' surfaces. During the thermal treatment, PEG melts into a liquid phase when the fibers are heated up to the T_m of PEG, thus the PEG on the fiber surface is able to flow along the fibers. However, the movement of the PEG distributed within the core of the fiber is limited by the shielding effect of the CA matrix, and the PEG cannot leak out of the composite fibers. Furthermore, hydrogen bonding interactions between the PEG and CA chains [25,26] could also contribute to the restriction of the free movement of PEG on the surface and inside in the core of the fibers when the temperature is not excessively high (20–100 °C). Thus, only traces of PEG distributed on the fiber surface was able to participate in the aggregation of fibers at their junctions and the thermo-oxidative degradation of the PEG in the composite fibers is also hampered. This results in the formation of the so-called "*shape-stabilized*" PCM [30–32], which demonstrates more stable and reliable thermal properties of the composite fibers.

4. Conclusion

Ultrafine PEG/CA composite fibers have been successfully prepared as a thermo-regulating material by electrospinning. The composite fibers show cylindrical shape with a smooth surface and PEG is distributed not only on the surface but also within the core of the composite fibers themselves. Due to the ultrafine diameter, the electrospun composite fibers show high latent heats of fusion and crystallization and a maximum in the efficiency of enthalpy. ΔH_f, T_m, ΔH_c and T_c of the composite are 86.03 J/g, 58.47 °C, 65.15 J/g, 38.96 °C, respectively. The thermal properties and morphology of the composite fibers are well retained after thermal treatment consisting of 100 heating–cooling cycles. These results indicate that the fibers have good thermal stability and reliability. Therefore, the electrospun PEG/CA composite fibers with reliable thermal properties are suitable and promising in serving as thermo-regulating materials in many fields.

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Appendix. Supporting information

Supporting information associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2007.06.069.

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