Indian Journal of Fibre & Textile Research
Vol. 46, March 2021, pp. 34-40

Fabrication and characterizations of electrospun PAN/PEG1000/2000 composite fibres

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Received 27 March 2019; revised received and accepted 29 September 2020

Composite fibrous mats of polyacrylonitrile (PAN) and binary mixture of polyethylene glycol (PEG) 1000 plus PEG 2000 (1:1) have been fabricated using electrospinning. Phase change temperature range of PEG mixture is 24-33°C (cooling cycle) and 42-55°C (heating cycle), and corresponding enthalpy is 155J/g and 182J/g. The effects of PEG1000/2000 mass content on the morphology, thermal properties, structure of the produced composite fibres have been investigated thoroughly by scanning electron microscopy, differential scanning calorimetry, thermal gravimetric, fourier transform infrared spectroscopy and X-ray diffractometer. The experimental results show the preparation of three-dimensional nanofibrous mats. The fibre diameter varies with the PEG content. The latent heat enthalpy of the composite fibres increases with the increase in PEG blends content during cooling and heating cycles. Phase change temperature shows little difference between pure PEG and composite fibres. The obtained results also show that the super fine porous PAN mats can act as polymeric matrix of PEG1000/2000 and thus prevent the leakage of PEG1000/2000 during phase transition. PAN/PEG1000/2000 has potential to be a form-stable phase change material.

Keywords: Composite fibre, Electrospinning, Polyacrylonitrile, Polyethylene glycol, Phase change material

1 Introduction

As energy shortage is a global problem, thermal energy storage and exchange materials are attracting more and more attention. Phase change materials (PCMs) have high heat of fusion and can absorb heat to store energy at high temperature and release energy at low temperature. Phase change materials thus have been widely used in latent heat thermal-storage systems for thermal energy storage and exchange, heat transfer and temperature control applications[1-3]. A large number of organic (paraffin, fatty acids and polyethylene glycol), inorganic (salt hydrates), and eutectic PCMs have gained extensive attention[4-8]. Among them, polyethylene glycol (PEG), composed of linear dimethyl ether chains with hydroxyl end groups, is an excellent polymeric PCM. PEG as a polyether can be dissolved in many solvents including water, and has good biocompatibility as well as degradability. The physical shape of PEG with different molecular weight (MW) ranges from white viscous liquid (MW 200-700), to waxy translucent solid (MW 1000-2000), and then to hard waxy solid (MW more than 2000). PEG has been widely used as phase change materials due to its stable chemical and thermal properties, low thermal lagging effect, wide transition temperature intervals, high transition enthalpy, high crystallinity, intermolecular hydrogen bonding activity, safety and cost-effectiveness[9-13]. However, some limitations do exist in the PEG applications. One of the problems is the leakage of PCMs during their solid–liquid phase change. To prevent leakage, polymer-based shape stabilized PCMs have been developed. Nowadays, the form-stable PCMs fibres can be fabricated via several methods such as microencapsulation and sol-gel[14,15]. Since electro-spun fibres have super fine diameter, high specific surface area, continuous and complex porous structures, and polymer blending is convenient method for tailoring the properties of composite fibres for various applications, co-electrospinning method has also been widely used to produce three-dimensional microstructure to wrap PEGs. Chen *et al.*[16] fabricated ultrafine polyethylene glycol/cellulose acetate (CA) composites fibres through electrospinning of PEG and CA blended solutions; Tayebe[17] reported the electrospinning ability of PLA/PEG system at the melt state,

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discussed the effect of PEG(6000) concentration on the visco elasticity and spinnability of PLA/PEG system. Fortunato *et al.*[18] reported the electrostatic spinning of poly(vinylidene fluoride-co-hexafluoropropylene)-(PVDFhfp) and PEG (mixed with constant weight ratios but varying PEG MW) blended solutions. The results showed that polymer MW has a great impact on fibre structure and surface chemical composition. Wang *et al.*[19] fabricated a small diameter vascular graft from polyurethane (PU) and PEG solutions by blend electrospinning technology. Cai *et al.*[20] prepared PEG4000/PA6 composite phase change fibres using electrospinning.

The reports on the production of PAN and PEG blends composite fibres by single nozzle co-electrospinning and their thermal properties and structure are limited. The main objective of this work is therefore to fabricate and characterize composite nanofibres electrospun from PAN and binary PEG system, and to provide important basis for selection of suitable phase change material system for climate garment. Phase change behavior of PEG1000 and PEG2000 (1:1) binary and the effect of PEG mass fraction on the structure and thermal properties of electrospun composite nanowebs have been studied in detail.

2 Materials and Methods

2.1 Materials

Polyethylene glycol (PEG, average molecular weight 1000 and 2000) and N, N-dimethylformamide (DMF) of analytical reagent were purchased from Shanghai Chemical Reagent Co. Inc., China. Polyacrylonitrile (PAN) powder (Mw=50000) was obtained from Shanghai Plastics Co.Ltd. (Shanghai, China).

2.2 Preparation of PEG1000/2000 Binary Mixture

PEG1000 and PEG2000 were blended with different mass ratio. The mixture was heated to transparent liquid in water bath and stirred uniformly. After that, the mixture was dried at about 100°C for 4h and the blended PEG1000/2000 was ground into powders by high speed disintegrator.

The phase transition mechanism of binary system of polyols is the same as that of monobasic system of polyols. The enthalpy of phase transition no longer corresponds to the average hydroxyl number in polyols in the binary system. The reason may be that the number of hydroxyl groups contained in polyols is different. When they form a co-melting binary system, some hydrogen bonds will bend and twist, thus in phase transition not all hydrogen bonds break and release hydrogen bond energy, which is related to the composition ratio of binary system.

According to the observation of blending uniformity and differential scanning calorimetry (DSC) testing results (Table 1), the optimum mass ratio of PEG1000/PEG2000 is selected as 1:1. This ratio was selected as the base concentration in following experiments.

2.3 Fabrication of PAN/PEG Composite Nanofibres

Twelve gram of PAN pellets was added to DMF, and the mixture was stirred magnetically until PAN was dissolved completely to obtain a 12%wt PAN solution. Various amounts of PEG1000/2000 binary mixture were added to the PAN solution with different mass ratio of PEG to PAN (0:10, 1:9, 2:8, 3:7 and 5:5). The mixture was stirred magnetically for another 4~5h to achieve a homogenous solution. The fibrous composite nanofibres were fabricated from the

Table 1 — Transition temperature and transition enthalpy of PEG1000/2000

PEG1000:PEG2000	Heating				Cooling			
	T_{on1}, °C	T_{end1}, °C	T_{p1}, °C	$\triangle H_1$, J/g	T_{on2}, °C	T_{end2}, °C	T_{p2}, °C	$\triangle H_2$, J/g
0:10	52.5	60.3	56.8	113.8	11.7	22.6	13.4	115.2
1:9	55.0	56.0	55.6	182.6	28.5	35.6	34.1	187.1
2:8	48.3	58.1	53.1	180.4	27.6	35.3	33.5	171.4
3:7	48.0	57.6	52.8	181.5	27.0	35.0	32.8	165
4:6	46.8	56	52	173.4	26.9	34.5	32.8	158.2
5:5	42.8	55.2	50.8	181.7	24.2	33.7	31.4	155.3
6:4	43.5	54.0	50.5	166.5	25.7	33.5	31.5	140.3
7:3	28.8	52.9	49.6	169.4	24.6	32.7	30.5	154.4
8:2	39.8	50.9	46.1	171	23.4	31.6	29	146.9
9:1	27.5	49.0	45.5	156.7	21.4	30.3	28.3	138.8
10:0	32.3	42.3	39.5	185.2	29.1	36.3	31.9	186.0

T_{on}–Initial temperature, T_{end}–Final temperature, T_p–Peak temperature, △H–Enthalpy, 1–Heating, 2–Cooling.

blended solution on the electrospinning set up, which consists of a high voltage power generator, an extrusion pump for delivering the spinning solution with constant flow, a syringe (10 mL) with a stainless-steel needle (0.5 mm inner diameter) on the tip, and an aluminum foil wrapped fibre collector at 80rpm. The solution was pumped at a speed of 0.8 mL/h with an applied voltage of 15 kV, and the distance between the tip of syringe and the collector was 15 cm. After spinning for 12h, the fibrous mats were collected and stored in dryer.

2.4 Characterization

Surface morphologies of the electrospun fibrous mats were examined using scanning electron microscope (SEM, JEOL, JSM-6510LV) with an acceleration voltage of 10 kV. All samples were attached on an aluminum stub using an adhesive conductive tape and sputter coated with gold under vacuum to prevent charging during imaging.

The enthalpy changes and transition temperatures of PEG1000/2000 and electrospun composite fibres were investigated by differential scanning calorimetry (DSC, NETZSCH DSC 204F1). Each sample (~ 5mg) was sealed in an aluminum pan (20mL capacity). DSC measurement was carried out from 10 °C to 70 °C at a heating and cooling rate of 10 °C/min under nitrogen protection. The flowing rate of nitrogen was 50 mL/min.

Thermal decomposition property of the composite fibrous mats was characterized by thermal gravimetric analysis (TG, NETZSCH STA409PC). The TG and DTG curves were recorded from 20 °C to 800 °C at a heating rate of 20 °C/min. The whole process was carried out under nitrogen with a flowing rate of 50mL/min.

Fourier transform infrared (FTIR) spectra of the PAN and PAN/PEG1000/2000 fibre composites were obtained on Avtar 360 (TENSOR 27X). FTIR spectrum of each sample was collected in the range of 400-4000 cm^{-1} by 32 scans with a resolution of 4 cm^{-1}.

The crystallinity and microstructure of the electrospun PAN and PAN/PEG1000/ 2000 were observed using an X-ray diffractometer (XRD, Dmax-RA) at 40 kV per 40 mA. XRD measurement was carried out with Bragg's angle 2θ from 10° to 90° at a rate of 10 °/min.

Tensile strength measurements were carried out by using a dynamometer (Instron 5566). The specimens in rectangular shape with a longitudinal length of 50 mm and a width of 20 mm were prepared. Five specimens were used for each sample and the average breaking stress and strain values were reported. The tests were performed with a fixed extension rate of 10 mm/min in air at room temperature (23 °C).

3 Results and Discussion

3.1 Morphological Characters of the Electrospun Fibrous Mats

SEM images of electrospun fibrous mats are presented in Fig. 1. As can be seen from the images, nanofibres are distributed randomly in a three-dimensional mat configuration. And it is seen that pure PAN fibres [Fig. 1 (a)] are cylindrical and long with a smooth surface and without beads in the webs. It is observed that the diameter of pure PAN fibres lies in the nanoscale and is centered at about 450 nm. The fibres produced from the blend solution with 10wt% PEG and 20wt% PEG are quite uniform and fine in diameters and keep membrane-like structure. The porous web structure of nanofibres may prevent the flow/leakage of molten PEG. The obvious change in fibres surface morphology occurs at the fibres produced from the mixture solution with the highest PEG concentration of 50 wt% [Fig.1 (e)]. This figure indicates that the nanoweb is thicker with beads and the obtained fibre diameter is smaller. These changes in fibrous morphology resulting from the addition of PEG might be explained by the changes in concentration and conductivity together with viscosity of the blended solution. Hydrogen bonds between polyacrylonitrile (C≡N) group in PAN and O-H bond in PEG might change the properties of blend solution and then the fibre structure[21].

3.2 FTIR Analysis

Typical FTIR spectrum of pure PAN nanoweb and PAN/PEG composite fibrous mats are presented in Fig. 2. It is observed that PAN spectrum has typical peaks at about 2240, 2942 and 1448 cm^{-1}, which are contributed to –C≡N bond (cyanogroups) stretching vibration, $–CH_2$ bond (methylene groups) asymmetric and symmetric bending vibrations[5], respectively. The wide peak at 3542cm^{-1} in spectrum of PAN/PEG composite fibre is due to the stretching vibration of –OH bond. The spectra of all PAN/PEG samples show characteristic peaks of PEG at 1244 cm^{-1}, 1110 cm^{-1} and 958 cm^{-1}, which are ascribed to –O– bond stretching vibration[22]. The bands belong to asymmetric bending vibration of $–CH_2$ bond, shifted towards wave number 2888 cm^{-1} in case of the spectra of the composite fibres[22]. All characteristic peaks of

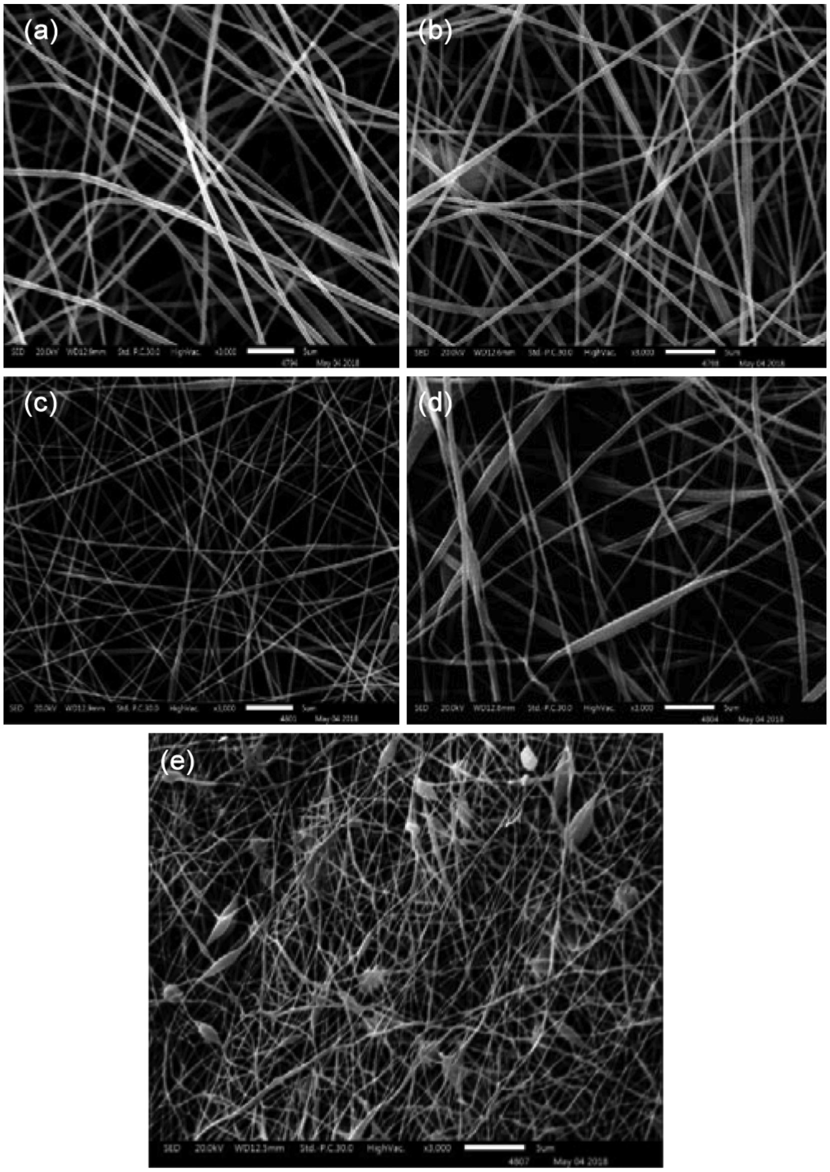

Fig. 1 — SEM images (×5 000) of nanofibres mats with mass ratio of PEG1000/2000 to PAN 0wt% (a), 10wt%(b), 20wt%(c), 30 wt% (d), and 50 wt%(e)

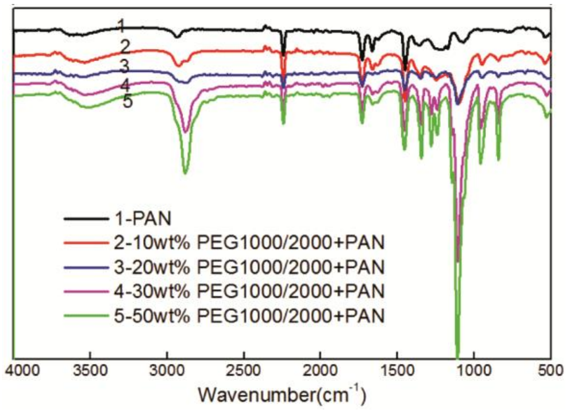

Fig. 2 — FTIR spectra of electrospun PAN and PAN/PEG1000/2000 composite fibres

PAN are also displayed in the spectrum of PAN/PEG fibrous mats. Spectrum results indicate that PAN and PEG structures are reserved in the composite fibre, and PAN and PEG1000/2000 have good adaptation[23], and PAN acts as a supporting matrix of PCMs PEG1000/2000.

3.3 Thermal properties

The phase change behavior of the PEG1000/2000 and the composite nanomats are conducted using DSC analysis. The DSC curves are shown in Fig. 3, and their thermal responses including transition temperature and enthalpy are summarized in Table 2.

As seen from Fig. 3 (a), pure PEG/1000/2000 has clear onset, peak and offset temperatures during heating and cooling cycles. The phase change enthalpy during cooling and heating cycle reaches the value of 155.3 J/g and 181.7J/g in the temperature intervals of 24.2–33.7 °C and 42.8–55.2 °C respectively. Figure 3 (b) shows that composite nanofibres have similar thermal transition characteristics as the pure PEG1000/2000. The enthalpies during cooling and heating process are close and the temperature decides the direction, which indicates that the structure and thermal properties of PEG PCMs are kept in the nano composite fibres and the composites can be taken as latent storage materials with reversible transition. The yields of the composite nanofibres in terms of their heat storage are increased obviously as PEG content increases from 20wt% to 50%wt, corresponding to 7%, 67% and 99% of pure PEG1000/2000 during cooling cycle, and 17%, 46%, 73% during heating cycle. Compared to pure PEG1000/2000, the endothermic and exothermic peaks of PAN/PEG composite fibres are much wider. These changes may be due to the fact that the integrity of the PEG crystallization is hindered by three-dimensional and multiporous structure of the nanofibrous composites[22]. However, three-dimensional nanofibrous PAN matrix will prevent the leakage of PEG1000/2000 during phase transition and thus form-stable phase change materials are fabricated successfully.

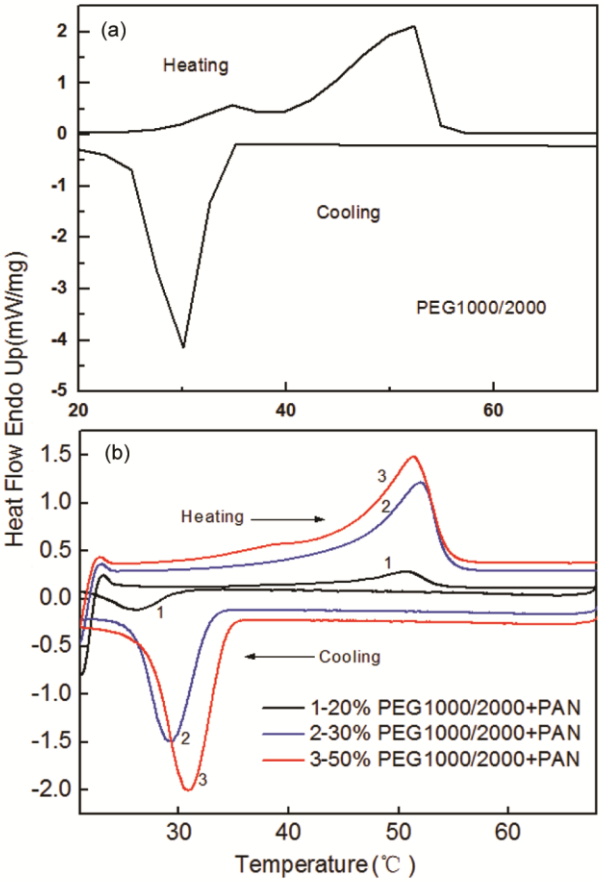

Fig. 3 — DSC curves of (a) PEG 1000/2000, and (b) electrospun PAN/PEG1000/2000 composite fibres

The TG and DTG thermograms of PAN and PAN/PEG1000/2000 nanofibres are displayed in Fig. 4. It is observed that with the increase in temperature mass loss happens to all samples. The thermal degradation of pure PAN and PAN/PEG composite fibres occurs mainly in two areas, the minor one starts at 280 °C and ends at 340 °C, and the major one is between 360 °C and 450 °C. The mass loss is related to the evolution of PEG oligomers and small molecules (NH_3 and HCN) and the cyclization of the nitrile groups[21]. The weight loss nearly stops at 500°C, which means that the decomposition is completed. The residues relating to non-volatile segment of polymer chains decrease as the PEG amount increases, confirming the presence of PEG (PCMs) in the composite fibres. It can be seen from DTG curves [Fig. 4 (b)], that the onset and end temperatures of thermal decomposition curves of composite fibres decrease gradually as the PEG1000/2000 content is increased from 10wt% to 50wt%, which means that the composite fibres exhibit less stability at high temperatures.

3.4 XRD Analysis

X-ray diffraction measurement is used to investigate the structure of the composite nanofibres. XRD patterns (Fig. 5) of the pure PAN and the

Table 2 — Transition temperature and transition enthalpy of fibrous mats with various PEG 1000/2000 content

PEG wt %	Heating				Cooling			
	T_{on1}, °C	T_{p1}, °C	T_{end}, 1°C	ΔH_1, J/g	T_{on2}, °C	T_{p2}, °C	T_{end2}, °C	ΔH_2, J/g
20	44.1	50.9	53.2	31.52	22.1	29.9	29.7	10.3
30	41.1	51.9	54.2	84.08	22.7	29.0	34.1	104
50	42.1	51.3	54.8	132.1	24.4	30.6	34.8	153.7
100	42.8	50.8	55.2	181.7	24.2	31.4	33.7	155.3

T_{on}–Initial temperature, T_{end}–Final temperature, T_p–Peak temperature, ΔH–Enthalpy, 1–Heating, and 2–Cooling.

composites nanofibres containing 10%wt and 20wt% of PEG1000/2000 are reported here for brevity (the behavior of all the other composite nanofibres is similar to those containing 20wt% of PEG1000/2000). PAN displays a board peak at 16°. PAN/10wt%PEG1000/2000 and PAN/20wt % PEG1000/2000 show same characteristic peaks at 2θ of 38°, 44°, 64° and 78°. The composite fibres with 20wt%PEG1000/2000 exhibit two narrow diffraction peaks at 2θ=14° and 16°, which are attributed to pure PEG1000/2000, indicating that the structure and crystallinity of PEG1000/2000 are well retained in the composite fibres. However, the composite fibres with 10wt%PEG1000/2000 show no sharp peaks in this range, maintaining the same pattern as that of pure PAN, which could be due to the relatively low contents of PEG1000/2000.

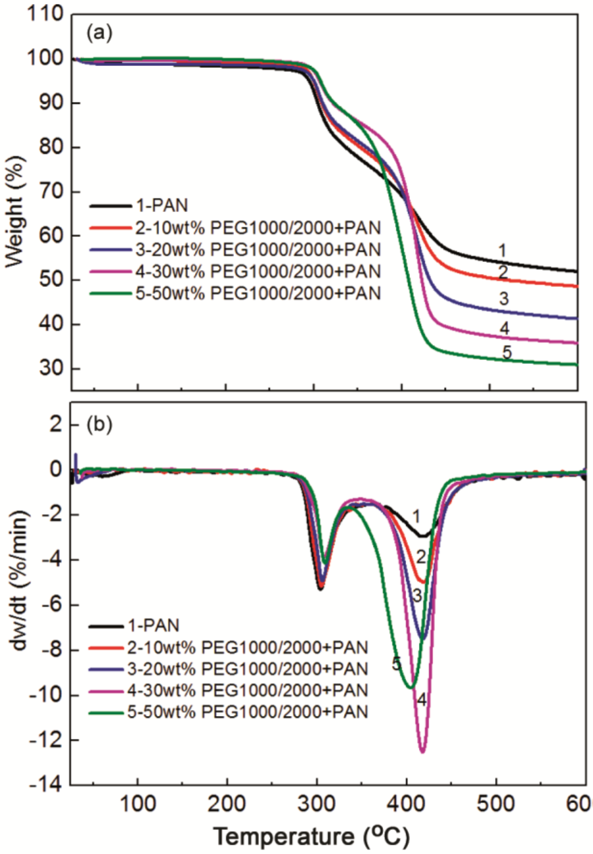

Fig. 4 — Thermograms of electrospun PAN and PAN/PEG 1000/2000 composite fibres (a) thermogravimetric analysis, and (b) derivative thermogravimetric (DTG) curves

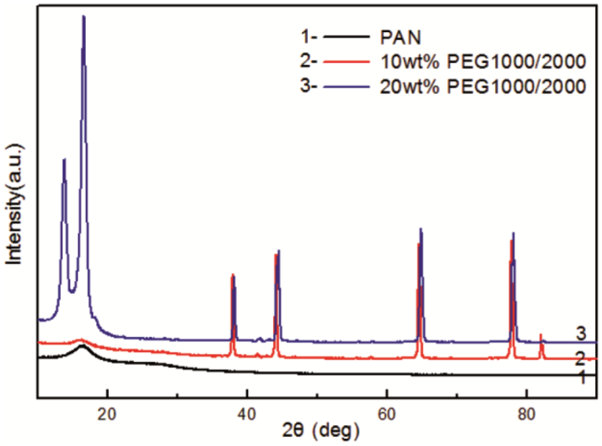

Fig. 5 — XRD patterns of electrospun PAN and PAN/PEG1000/2000 composite fibres

3.5 Tensile Properties

The mechanical properties of nanofibre mats are related to the morphology, orientation and crystallinity degree of the fibre. The mechanical properties of the nanofibre mats have been measured and the typical tensile stress-strain rate curves of the electrospun mats with various PEG1000/2000 contents are presented in Fig. 6, and the data are reported in Table 3. PAN and PAN/PEG1000/2000 nanofibre mats demonstrate typical behavior of thermoplastic materials. It can be clearly seen that the elastic modulus and maximum tensile stress of composite fibrous mats are enhanced as a function of PEG1000/2000 content. The improvement in tensile

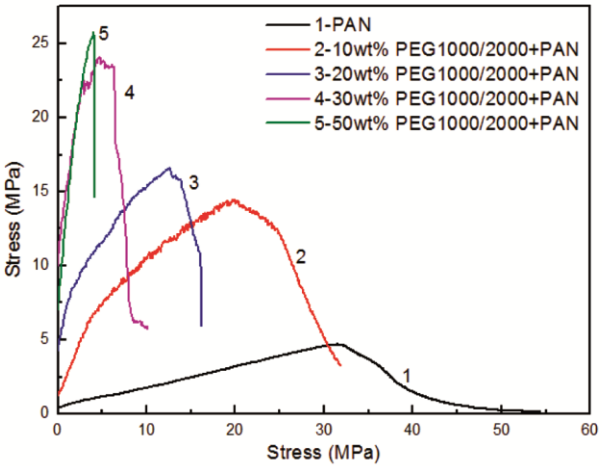

Fig. 6 — Mechanical stress-strain rate curves of electrospun PAN and PAN/PEG1000/2000 composite fibres

Table 3 — Mechanical properties of electrospun PAN and PAN/PEG1000/2000 fibres

PEG1000/ 2000 wt%	Young's modulus, MPa	Maximum tensile stress, MPa	Maximum strain rate, %
0	14.75	4.68	31.39
10	146.48	14.48	19.89
20	299.99	16.60	12.51
30	697.59	24.02	4.46
50	664.44	25.79	3.92

stress may be attributed to a better interfacial interaction between PEG and PAN[24]. The young's modulus of composite nanofibres is increased with the addition of PEG1000/2000 content, as shown in Fig. 6 and Table 3. This might be due to the stiffening occurred from the PEG dispersion in the PAN/PEG composite mats. However, the elongation-at-break decreases obviously. The decrease in ductility might be attributed to the change in fibre diameter or the presence of the PEG1000/2000 on the PAN matrix, which may restrict the segment movement of PAN chain during stretching[25,26].

4 Conclusion

Phase change temperature and enthalpy of PEG1000 and PEG2000 blends could be adjusted through their mass ratio. PEG1000/2000 (mass ratio 1:1) binary mixture has been used as PCMs to co-electrospin with PAN. PAN/PEG1000/2000 composite nano fibres have been fabricated successfully. The addition of PEG1000/2000 changes fibre shape and fibrous mats porosity. IR and XRD spectrum indicate that PAN and PEG structures are reserved in the composite fibres. Thermal characterization indicates that the PAN/PEG1000/2000 composite fibres exhibit reversible phase change behavior. The increase in PEG1000/2000 mass contents increases heat storage yields as well as decreases thermal stability and fibre ductility. In conclusion, electrospun PAN/EG1000/2000 composite nanofibres are proved to be a promising shape-stable PCM, and have potential applications in thermal energy storage fields, such as climate garment and building envelops.

Acknowledgement

The authors are thankful for the funding support by Hubei Natural Science Foundation and Fundamental Research Funds of Wuhan Textile Universities.

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