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Preparation of polyacrylonitrile and polyethyleneglycol blend fibers through electrospinning

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Polyacrylonitrile (PAN)/ Polyethyleneglycol (PEG) blend nanofibers were prepared by electrospinning blend solutions of PEG and PAN in N, N-dimethylformamide (DMF). The surface morphology, thermal properties and crystal structure of electrospun PAN/PEG nanofibers were characterized using Fourier transform infrared spectroscopy (FT-IR), wide-angle x-ray diffraction (WAXD), scanning electron microscopy (SEM), Thermo gravimetric analyses (TGA) and differential scanning calorimetry (DSC). SEM image showed that the scope of the diameters was 320-480nm. The diameters of the blend fibers decreased with the increasing of PEG content. FT-IR indicated that intermolecular interactions are formed between two different polymers, which influence the thermal and crystalline properties of electrospun blend nanofibers.

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1. Introduction

Owing to its comparatively low-cost manufacturing and easy deployment even on a laboratory bench, electrospinning technology has launched polymer micro- and nanofibers, and broadens the realms of nanotechnology and materials science [1]. Since the electrospun fiber mats have a number of characteristics such as high specific surface area, high aspect ratio, and high porosity, their applications in various fields such as optoelectronics, sensor technology, catalysis, filtration, and medicine are expected. So far, most of common single polymers have been electrospun into fibers [2, 3].

Polymer blending is an effective and an economically viable way for the preparation of new materials with desired properties. This method is usually cheaper and less time consuming for the creation of polymeric materials with new properties than the development of new monomers and new polymerization routes. An additional advantage of polymer blends is that the properties of the materials can be tailored by combining component polymers [4, 5].

Polyacrylonitrile (PAN), manufactured by wet spinning using organic solvent or aqueous solution of inorganic salt, is one of the most important fiber-forming polymers and has been widely used because of its outstanding physical and chemical properties [6]. However, it also has some disadvantages, such as low dye affinity, low moisture regain, and high static charge due to the lack of segmental mobility resulting from intensive molecular orientation of the highly polar nitrile groups [7]. The method of blending to modify PAN has been widely studied. In recent years, a lot of studies have been found in the literature concerning the combination of AN-based polymers and natural polymers. Most of the work, to our knowledge, has been focused on graft copolymerization of acrylonitrile (AN) and natural polymers, such as silk fibroin [8, 9], casein [10, 11], and wool keratin [12, 13, 14] etc. However, there is still no report about the preparation and characterization of PAN/PEG composite nanofibers, which may combine both the advantages of PAN such as light weight, flexibility, and of PEG such as high hydrophilicity, processability, and biocompatibility.

This study is mainly concerned with the miscibility characterization of PAN/PEG blend nanofibers. We prepared the PAN/PEG blend fibers up to 30% PEG content by an electrospinning process. The effect of PEG content on the structural change and miscibility of the blend fibers was investigated.

2. Experimental

The PAN ($M_w=5.5\times10^{4)}$ employed in this study was purchased from Shanghai petroleum Chemical Co., Ltd (Shanghai, China). PEG was also obtained from Shanghai Reagent (China). It has a quoted number average molecular weight =20,000 g/mol and used without further purification. *N*, *N*-dimethylformamide (DMF; Fisher) was used as a solvent, because it is an appropriate co-solvent for PAN and PEG polymers. PAN and PEG were dissolved in DMF, by stirring for 12 h at 70 ℃, to obtain blend solutions for electrospinning. The blend ratios of PAN/PEG were controlled through varying the relative weight ratios of each component as 100/0, 90/10, 80/20 and 70/30. The total polymer concentration was set to be 10 wt%.

Composite solutions were fed through a capillary tip (diameter = 0.5mm) using a syringe (30 ml). The anode of the high voltage power supply was clamped to a syringe needle tip and the cathode was connected to a metal collector. During electrospinning, the applied voltage was

14 kV, the distance between the tip and collector was 17 cm, and the flow rate of the spinning solution was 1 ml/h.

The diameter and morphology of the electrospun PAN/PEG composite fibers were determined by a JSM-5610 scanning electron microscope (SEM, Japan).

Wide angle X-ray diffraction was carried out using a BRUKER-AXC08 X-ray diffractmeter and filtered CuKα radiation. The diffraction patterns of the blend fibers of the PAN and PEG were obtained by scanning the samples in an interval of 2θ = 10-60 degrees.

Fourier transform infrared (FTIR) spectra were collected from a FTIR spectrometer (Nicolet 560) in the wavenumber range of 4000–700 cm^{-1}.

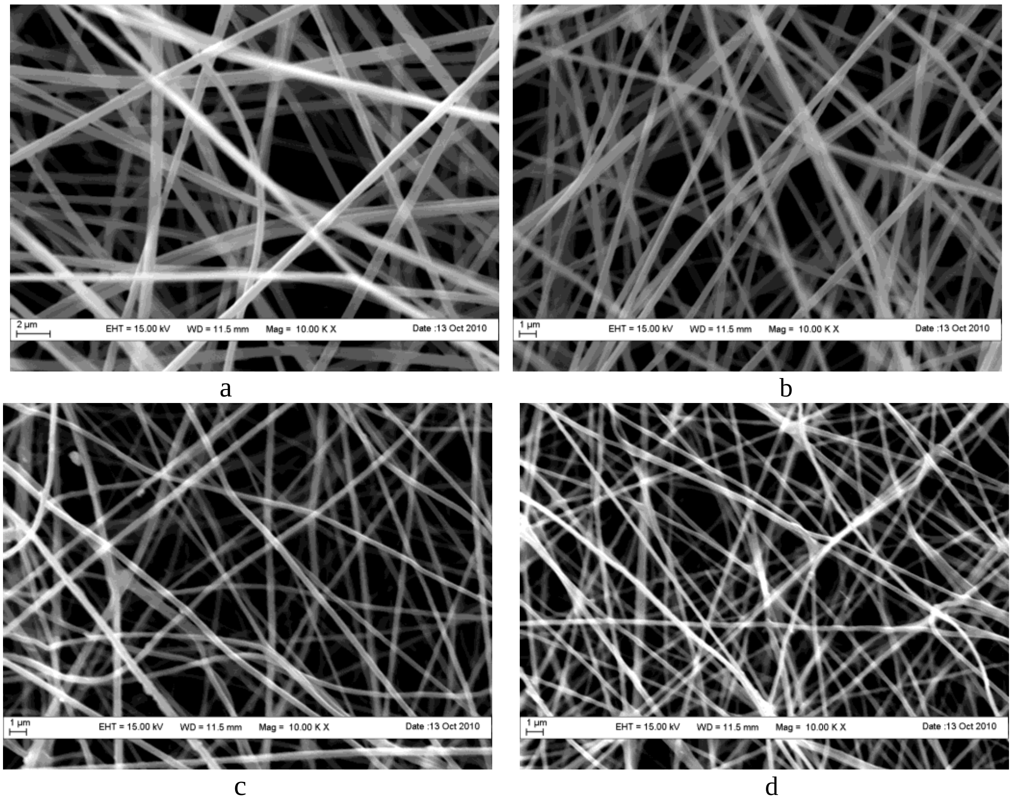
Thermal properties of electrospun fibers were evaluated using differential scanning calorimetry (DSC) from 25 to 380 at a heating rate of 20 min^{-1} in nitrogen environment.

Thermo gravimetric analyses of PAN/PEG blend fibers were performed with a TA Instruments Du Pont l090 at 20°C/min in nitrogen environment.

3. Results and discussion

Typically representative SEM photographs of all the nanofibers with different PEG contents are shown in Fig. 1. It is seen that all fibers are relatively uniform and randomly oriented, forming an interwoven network on the substrate. The average diameters of blend fibers gradually decrease form 480 to 440, 390 and 320nm when PEG concentration increases form 0 to 10, 20, 30 wt%, respectively.

The morphology of electrospun fibers is influenced by various parameters. In fact, one of the most significant parameters influencing fiber morphology is the solution viscosity [15,16]. When the solution viscosity is low, the jets from the needle are unstable and likely to break up and form beads on fiber surface, and it will be difficult to get a continuous nanofiber on the collector. For high viscosity solutions, the jets would not break up but rather travel and split into filaments and form fibers with increased diameter.



a b

c d

Fig. 1. SEM images of PAN/PEG nanofibers with different PEG contents. (a) 0 wt.% , (b) 10 wt.%, (c) 20 wt.% and (d) 30 wt.%.

To understand the relationship between nanofiber diameter and PEG concentration, the viscosity and conductivity were measure for all electrospinning solution and are shown in Table1 1. The viscosity of the spinning solution decreased with the addition and increasing amount of PEG (i.e., form about 997 mP for neat PAN solution to about 258 mP for spinning solution containing 30 wt% PEG), while the conductivity of spinning solution ranged between about 0.146 and 0.097mS cm^{-1}.

Table 1. Characteristics of PAN/PEG electrospinning solutions.

PEG (Wt %)	Viscosity (mPaS)	Conductivity (ms/cm)	Diameter (nm)
0	997.1	0.1465	480
10	730.2	0.1123	440
20	431.5	0.1086	390
30	258.6	0.0971	320

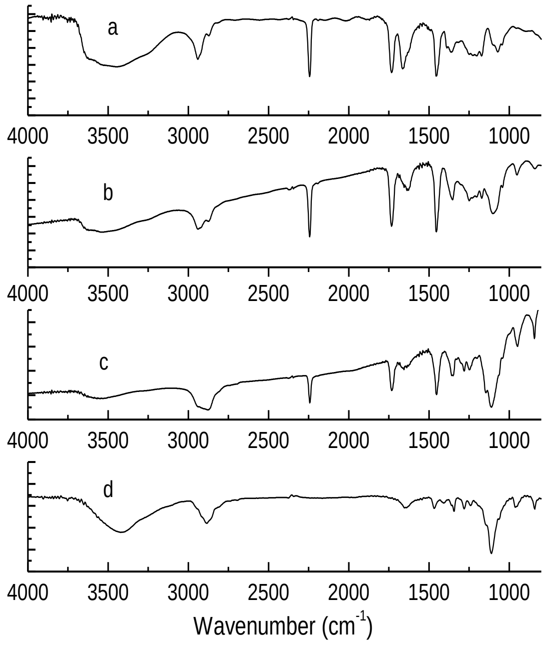


Fig. 2. FT-IR spectra of PAN/PEG blend fibers with different PEG loading. (a) 0 wt.% (pure PAN), (b) 10 wt.%, (c) 30 wt.%, and (d) 100 wt.%.

FT-IR spectra of the pure PAN and PAN/PEG nanofibers with different PEG loadings were recorded in the range 4000-700 cm^{-1}. FT-IR spectra of PAN fibers have many peaks which related to existence of CH_2, C≡N, C=O, C−O and C−H bonds. The absorption peaks are in range of 2926 cm^{-1} are related to C−H bonds in CH, CH_2 and CH_3 but in this range the second weak peak is observed which is related to C-H bonds also [17]. Another peak is observed in the range of 2243 cm^{-1} which is related to presence nitrile (C≡N) bonds and indicates the nitrile group exists in polyacrylonitrile chain. The absorption peaks in the ranges of 1733 cm^{-1} and 1170 cm^{-1} are related to C=O or C−O bonds and are resulted from presence of comonomers like MA [18].

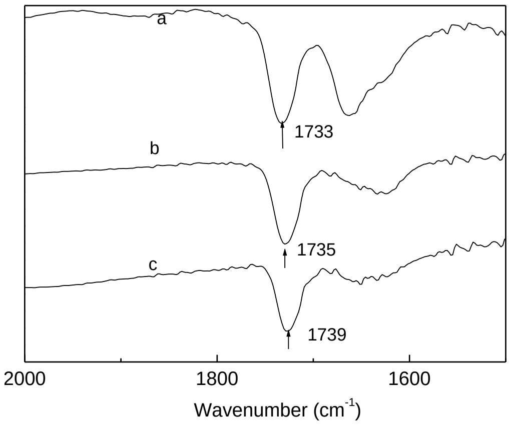


Fig. 3. FTIR spectra of the carbonyl (C=O) group in (a) PAN ; PAN/PEG blend fibers with PEG content (b) 10 wt % and (c)30 wt % .

Theoretically, PEG has the potential to form hydrogen bonds with carbonyl polymers. As we mentioned in experimental that PAN employed in this study is a copolymer, containing methylacrylate segments. That is to say, there exit carbonyl groups in the system.

If the groups involved in the hydrogen bond formation in a blend system are carbonyl and hydroxyl moieties, then the vibration frequencies of both the groups are expected to show a red shift due to hydrogen bond formation compared with the noninteracting group frequencies. In the present case, the carbonyl frequency of PAN (Fig. 3) at 1733 cm shift to low wavenumbers upon mixing PAN with PEG. The more the PEG content, the lower the wavenumbers. For PEG 30% loading composite, the carbonyl band is observed to be 1739 cm^{-1}, 6 cm^{-1} higher than the band of pure carbonyl.

We observed an increase in the hydroxyl group frequencies from 3421 cm^{-1} in pure PEG (Fig. 4) to 3569 cm^{-1} in the 70: 30 PAN: PEG. This enhancement in the AOH stretching frequencies may be attributed to the presence of intra- and intermolecular hydroxyl-hydroxyl as well as hydroxyl-ether oxygen hydrogen bonding interactions in PEG that occur at lower frequencies and the same being changed to intermolecular hydroxyl- carbonyl hydrogen bonding interactions that occur at higher frequencies in the blend system. Similar observations have also been reported in the case of miscible blends of polyvinylalcohol and polyvinylpyrrolidone. The intensity of AOH stretching band in the PEG–PAN blend is also less compared with that in the pure PEG sample. This may be indicative of weaker hydrogen bonding tendencies in the blend.

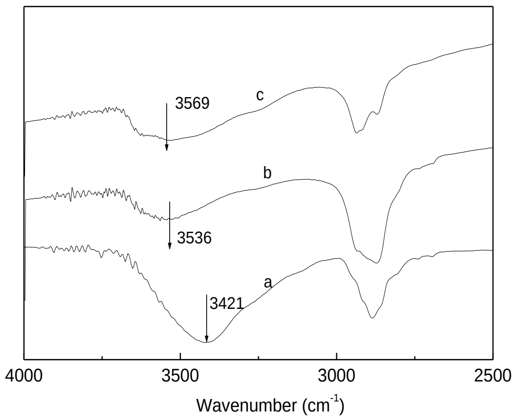


Fig. 4. FTIR spectra of the hydroxyl (0-H) group in (a) PEG; PAN/PEG blend fibers with PEGcontent (b)10 wt % and (c) 30wt % .

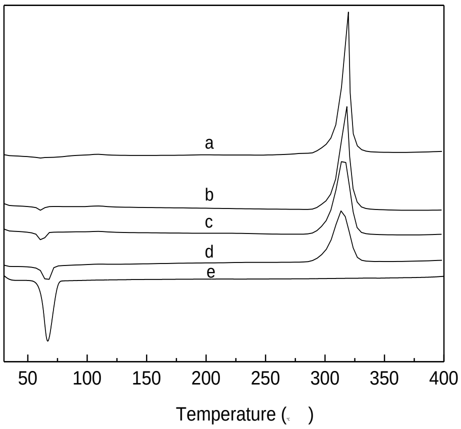


Fig. 5. DSC curves of PAN/PEG blend fibers in the range of 30-400 ℃, the PEG content are (a)0 wt.%, (b) 10 wt.%, (c) 20 wt.%, (d) 30 wt.% and (e) 100 wt.%.

To get more insight on the thermal behavior of the blend samples, DSC measurements were performed and the results are shown in Fig. 5. For well resolution the curves were exhibited in two separate temperature ranges: one was 30−130°C (Fig. 6), and the other was 250−400°C (Fig. 7). The peak at around 60°C for blend films can be assigned to the melting point of PEG (Fig. 6). The melt peak of PEG became more obvious and moved to high temperatures with the increasing content of PEG (10wt.% is read at 60.0°C, 20wt.% is read at 62.2°C, 30wt.% is read at 66.4°C, pure PEG is read at 67.2°C). It is generally accepted that the *T*m corresponding to one component of the blend films would decrease owing to the increasing of lattice defects resulted from the partial miscibility of the noncrystalline phase [19].

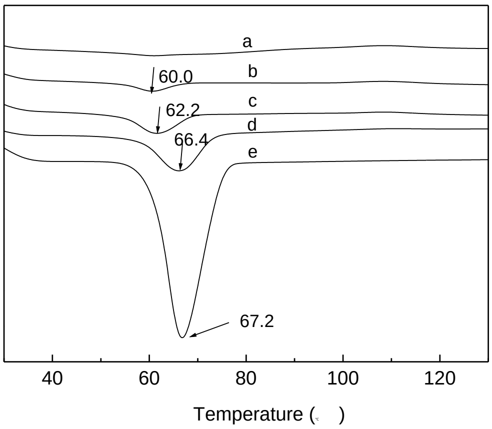


Fig. 6. DSC curves of PAN/PEG nanofibers in the range of 30-130 ℃, the PEG content are (a)0 wt.%, (b) 10 wt.%, (c) 20 wt.%, (d) 30 wt.% and (e) 100 wt.%.

The curve of the PAN homopolymer film shows a sharp exothermic peak at 319°C (Fig. 7) associated with the main reactions such as cyclization, dehydrogenation[20, 21], and oxidation of PAN when it is heated above 180°C. The exothermic peak of PAN became weaker and moved to lower temperatures with the increasing content of PEG. The results indicate that the kinetics of exothermic reaction, which is believed to be related to the cyclization of the nitrile groups, was significantly modified by blend with PEG.

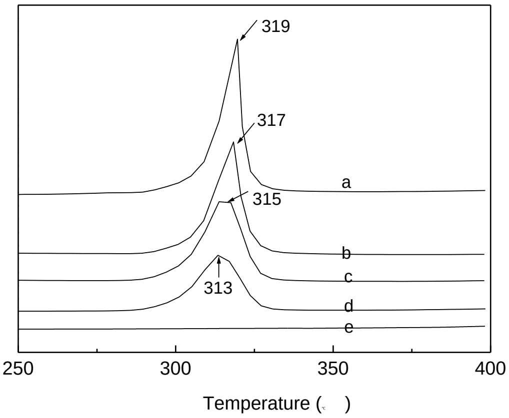


Fig. 7. DSC curves of PAN/PEG nanofibers in the range of 250-400 ℃, the PEG content are (a)0 wt.%, (b) 10 wt.%, (c) 20 wt.%, (d) 30 wt.% and (e) 100 wt.%.

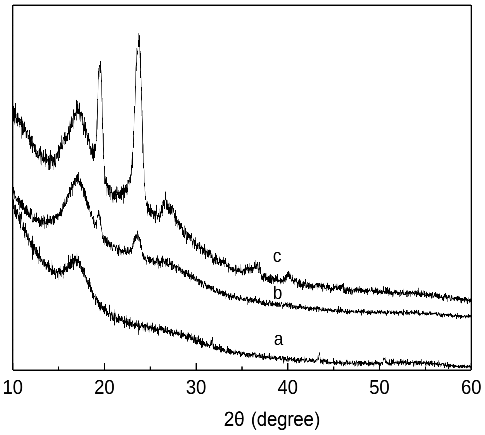


Fig. 8. WXRD patterns of PAN/PEG blend fibers with different PEG loadings (a)0 wt.%, (b) 10 wt.%, (c) 30 wt.%.

It is known that the crystal structure of the matrix has key role in determining the properties of polymer blends. The XRD characterizations of PAN (curve a) and the PAN/PEG nanofibers with 10 and 30 wt% of PEG content (curves b and c) were conducted (see Fig. 8). PAN shows only a scattering peak at 2θ=17°. The XRD patterns of the PAN/PEG nanofibers appear the both the characteristic peaks of the pure PAN and PEG. Moreover, the intensity of the peaks assigned to the PEG (19.5°, 23.4°, 26.4° and 36.6°)[22] in the composite increased with the increase of the content of PEG. The peak at 2θ=17° became strong and sharp, and there is also a new peak at 2θ=40°. These observations indicate a large influence of PEG on the crystalline of PAN in blend nanofibers and a strong interaction between the PEG and the PAN.

TGA provided quantitative information on the process of weight loss. All of the samples were pyrolyzed at the heating rate of 20℃/min in the temperature range of 50–700℃ in an N_2 atmosphere. Fig. 9 shows the TGA curves for pure PEG, pure PAN, and different mixtures of the blend nanofibers. The recorded TGA plots for pure PEG and pure PAN showed a one-stage degradation step within the range of 300−450℃. This was characterized by a weight loss of about 95% for PEG and 50% for PAN, and suggested there is a single degradative process. The blend fibers exhibited a two-step degradative process. An initial weight loss of about 10% occurred between 25 and 200℃. The second weight loss of about 50% occurred between 300 and 450 ℃. The first weight loss was caused by the loss of water and the solvent that remained in the samples. The third degradative step was caused by the complete degradation of the macromolecule. The second degradative step in blended samples demonstrated an intermediate between those of the two pure components. This suggested that the inter-macromolecular hydrogen-bonding caused interactions in the blends.

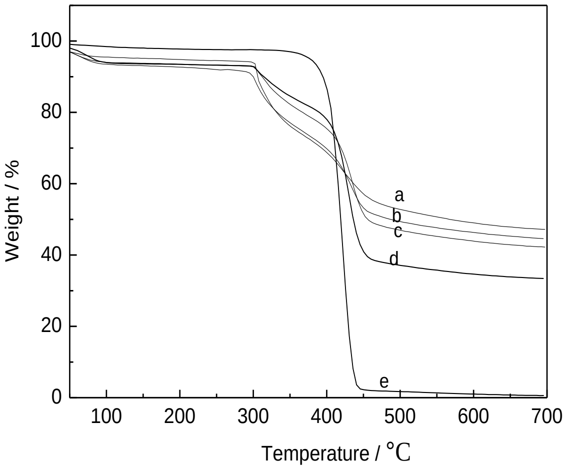


Fig. 9. TGA thermograms of PAN/PEG blend fibers with different PEG loadings (a)0 wt.%, (b) 10 wt.%, (c) 20 wt.%, (d) 30 wt.% and (e) 100wt.%.

4. Conclusions

Various PAN/PEG blend nanofibers were prepared by electrospinning composite solutions containing PEG and polyacrylonitrile (PAN) in N, N dimethylformamide (DMF). The effects of the blend weight ratio on structure and morphology of the fibers were investigated for the first time. The result indicated that the average diameter of the fiber gradually decreased with the increasing of PEG content. FTIR, DSC and TGA curves reveal that there are interactions among PAN and PEG. These interactions have profound effects on the thermal and crystalline properties of nanofibers.

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