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Modification of polyacrylonitrile nanofibers by blending with polyurethane

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Polyacrylonitrile (PAN)/ polyurethane (PU) blend nanofibers were prepared by electrospinning blend solutions of PAN and PU in N,N-dimethylformamide. The morphology, properties and structure of electrospun PAN/PAN nanofibers were characterized using Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), Thermo gravimetric analyses (TGA), mechanical properties measurement and differential scanning calorimetry (DSC). FT-IR indicated that intermolecular interactions are formed between PAN and PU and the SEM images demonstrated that point-bonded structures in the fiber mats rose with increasing PU composition. Furthermore, the elongation and tensile strength of the PAN/PU blend nanofiber mats were significantly increased compared with PAN due to the point-bonded structures.

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1. Introduction

The development of electrospinning has been rapidly increasing in the past years because it can consistently generate polymer fibers ranging from 50 to 500nm in diameter, depending on the polymer and processing conditions [1]. The nanofibers produced by electrospinning method have showed amazing characteristics such as very large surface area-to-volume ratio and high porosity with very small pore size. 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].

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 [4]. 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 [5]. 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 [6, 7], casein [8, 9], and wool keratin [10,11] etc. However, there are few reports describing PAN/PU blend nanofibers produced by electrospinning.

Researchers [12,13] have studied electrospun PU nanofibers which could be used as wound dressing, shape memory material, and so on. PU blends with cellulose acetate, polycarbonate and silver nanoparticles have been reported [14-16]. The performance of PU may be improved by blending it with appropriate polymers in view of the fact that polymer blends have provided an efficient way to fulfill new requirements for material properties. Therefore, authors try to produce the PAN and PU blend nanofibers with high strength, flexibility and hydrophilicity.

In this work, PAN/PU blends containing 0-30 wt % PU were electrospun using N,N-dimethylformamide (DMF) as the solvent. The fiber morphology, crystallization behavior, and mechanical properties of the blend fiber mats were investigated.

2. Experimental

2.1 Materials

The PAN ($Mw=5.5\times10^{4)}$ employed in this study was purchased from Shanghai petroleum Chemical Co., Ltd (Shanghai, China). PU was from Yantai Wanhua (China). It is a polyester type with a Mw of 134,800 and Mw/Mn of 2.0. N, N-dimethylformamide with purity of 99.88% was purchased from Shanghai Chemical Co.

2.2 Electrospinning

PAN and PU were dissolved in DMF, by stirring for 12 h at 70℃, to obtain blend solutions for electrospinning. The blend ratios of PAN/PU 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. All the fiber mats were dried in a vacuum oven at 40℃ for 48 h to remove the residual solvent.

2.3 Characterization and measurement

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

Fourier transforms infrared absorption spectra for the blend nanofibers were taken with a Nicolet 20sx-B FT-IR spectrometer. The scanning ranged from 4000 cm^{-1} to 700 cm^{-1} with 16 times of scanning.

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/PU blend fibers were performed with a TA Instruments Du Pont l090 at 20°C/min in nitrogen environment.

The solution viscosity was measured with a rotating viscometer (Model NDJ-8S, Shanghai Rex Instruments). The solution conductivity was tested with a conductivity instrument (Model DDSNDJ-307, Shanghai Rex Instruments).

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 PU were obtained by scanning the samples in an interval of 2θ = 10-60 degrees.

Mechanical properties were tested on an Instron 5566 Universal Testing Machine, at a gauge length of 20 mm and strain rate of 50 mm/min at room temperature, and the width of the samples was 5 mm. An average value of at least three replicates for each sample was taken.

3. Results and discussion

FT-IR spectra of the pure PAN and PAN/PU nanofibers with different PU loadings were recorded in the range 4000-600 cm^{-1}. The pure PU had been extensively studied using FTIR [17, 18]. There are several absorption bands in the curve, the band at 3342 cm^{-1} is due to the stretching vibration of OH groups in PU and the cis-NH group in –NHCO-; the band at 2950 cm^{-1} is attributed to the asymmetric stretching vibration of CH2 and CH3 groups in diketene; the band at 1731 cm^{-1} is explained by the overlap of the two C=O absorption of ester and carbamate; the band at 1600 cm^{-1} is attributed to the skeletal stretching vibration of C=C in benzene ring; the band at 1533 cm^{-1} is due to the amide II from the reaction of OH and NCO groups; the band at 1222 cm^{-1} is attributed to the stretching vibration of CO and the distorted vibration of urethano in PU; and the band at 1067 cm^{-1} is explained by the C-O-C (fatty ether).

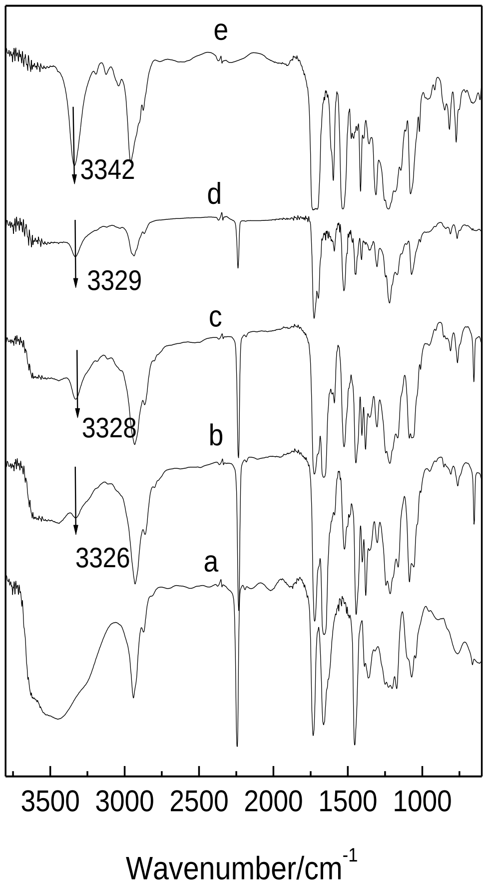


Fig. 1. FT-IR spectra of PAN/PU blend fibers with different PU loading. (a)0 wt.% (pure PAN), (b) 10 wt.%, (c) 20 wt.%, (d) 30 wt.% and (e)100 wt.%.

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 [19]. Another peak is observed in the range of 2243cm^{-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 [20].

FTIR is a useful tool for understanding the physical or chemical environment of a group in a molecule. The spectral shifts of small magnitude gave the information about the nature of the specific intermolecular interaction in materials. We observed an increase in the hydroxyl group frequencies from 3442 cm^{-1} in pure PU to 3329 cm^{-1} in the 70: 30 PAN: PU. The results suggested that there might have the formation of hydrogen bond between the PAN and PU. The spectra of PAN/PU fibers showed both characteristics peaks of electrospun PAN and PU. So this was the evidence to illustrate that there might be no other reaction between PAN and PU.

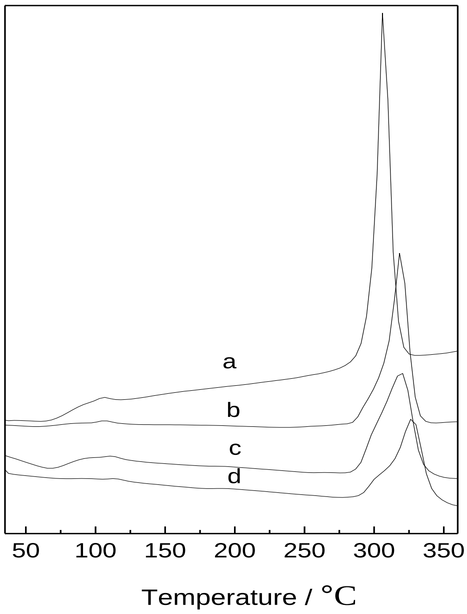


Fig. 2. DSC curves of PAN/PU nanofibers with the PU content are (a)0 wt.%, (b) 10 wt.%, (c) 20 wt.%, (d) 30 wt.%.

Generally, PAN begins to degrade when being heated near its melting point. The degradation reaction of PAN is so exothermic that it tends to obscure its melting endotherm in ordinary DSC traces. Therefore, the melting endotherm is normally not observed in PAN. When the PAN precursor is heated above 180℃, reactions such as cyclization, dehydrogenation, and oxidation take place. These reactions are exothermal, hence a sharp peak appears in the DSC curve at 260–320 ℃.

Table 1. Thermal behavior of PAN/PU nanofibers.

PU (Wt %)	T_g (℃)	T_{cyc} (℃)
0	96.5	304
10	98.1	319
20	100.3	322
30	102.2	327

To get more insight on the thermal behavior of the blend samples, DSC measurements of PAN/PU nanofibers with the PU content are 0 wt.%, 10 wt.%, 20 wt.% and 30 wt.% were performed and the results are shown in Fig. 2. All four nanofiber samples exhibit a relatively large and sharp exothermic peak and a glass transition about 100℃. Table 1 shows the glass transition temperature (T_g), and exothermic peak temperature. With increase in PU content, the glass transition and exothermic peak shift to higher temperatures. Increases in exothermic peak temperature PAN/PU composite nanofibers (Table 1) may be caused by the inhibiting effect of PU, which hinder the recombinations between the radicals.

From Fig. 2 and Table 1, it can also be seen that pure PAN nanofibers have a glass transition temperature of about 96.5℃, while T_g of PAN/PU composite nanofibers (10, 20, 30 wt% PU) increases to 98.1, 100.3, 102.2℃, respectively. The formation of intermolecular interaction between PAN and PU may explain this phenomenon.

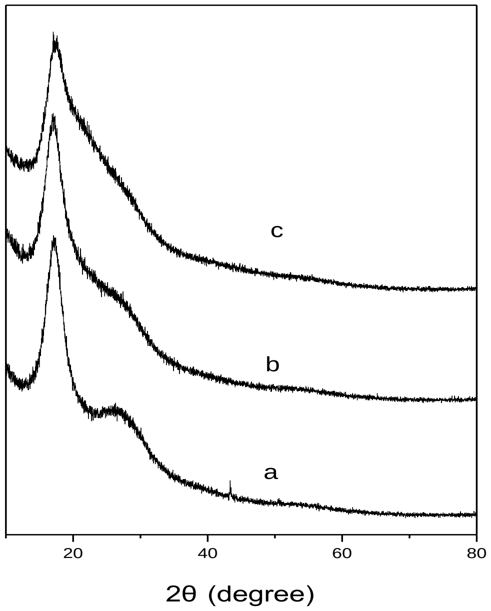


Fig. 3. WXRD patterns of PAN/PU blend fibers with different PU loadings (a)0 wt.%, (b) 10 wt.%, (c) 30 wt.%.

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/PU nanofibers with 10 and 30 wt% of PU content (curves b and c) were conducted (see Fig. 3). The XRD pattern of original PAN fiber illustrated a sharp diffraction at 2θ=16.8°, a relatively weak diffraction at 2θ=29.6°. This pattern is identical to the data-base known in the literature for PAN [17, 18]. According to these literatures, these two peaks are related to Bragg planes [010] and [300], with distances of 5.29 and 3.04Å between the planes, respectively. With increase in PU content, the peak intensity at 16.8° and 29.6° decreased. These intensity changes further corroborate the interactions between PAN and PU observed from the DSC and FT-IR analyses. As a result, the crystallinity of PAN is largely influenced by PU in the PAN/PU blend nanofibers.

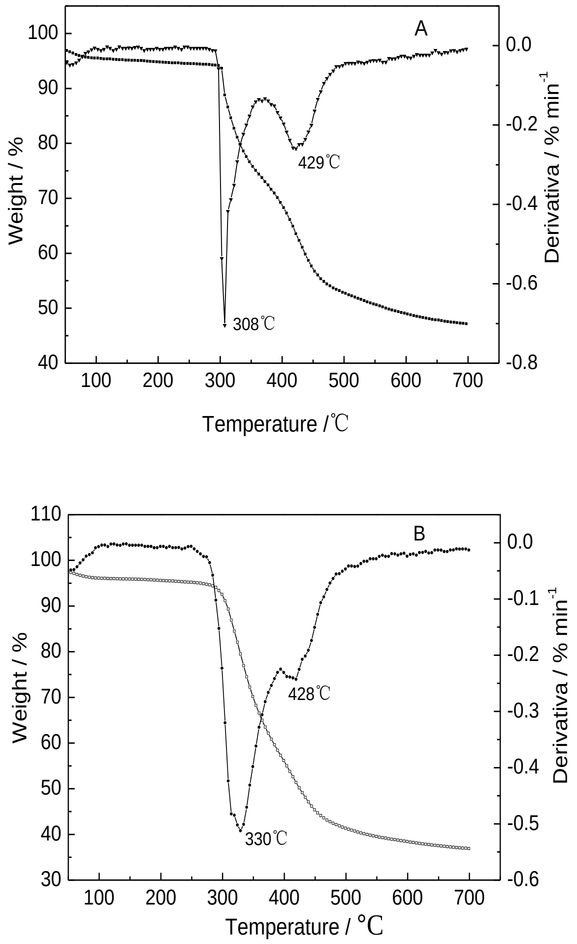
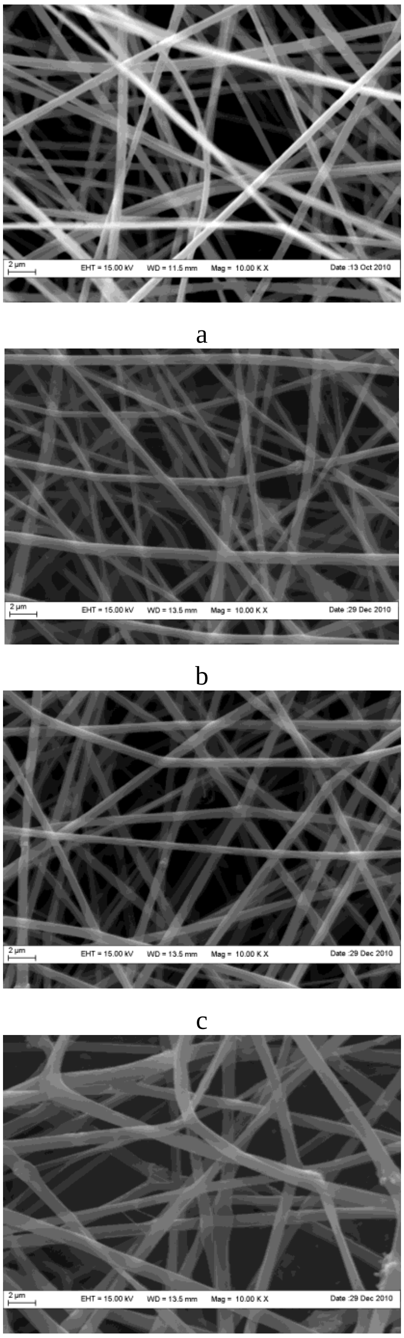


Fig. 4. TGA and DTG thermograms of (A) PAN and (B) PAN/PU blend nanofiber with 20 wt% PU.

TGA and DTG curves in Fig. 4 show the thermal stabilities of pure PAN and PAN/PU blend fiber with 20 wt % PU. There are two obvious weight loss peaks at 308 ºC and 429ºC in the TGA curve of pure PAN (Fig. 4A). The DTG minimum at 308 ºC is attributed to cyclization and the DTG minimum at 429ºC is attributed to carbonization I. For PAN/PU blend fiber, the temperature of the first weight loss peak becomes higher when with PU, while the temperature of the second weight loss peak remained almost unchanged with addaition of PU (Fig. 4B). The better thermal stability of the blend than pure PAN could be considered as additional evidence of interactions between PU and PAN.



a

b

c

d

Fig. 5. SEM images of PAN/PU nanofibers with different PEG contents. (a) 0 wt.% , (b) 10 wt.%, (c) 20 wt.% and (d) 30 wt.%.

Table 2. Characteristics of PAN/PU electrospinning solutions.

PU (Wt %)	Viscosity (mPaS)	Conductivity (ms/cm)	Diameter (nm)
0	997.1	0.1465	480
10	1030.6	0.1523	495
20	1101.5	0.1586	500
30	1158.6	0.1967	520

Fig. 5(a–d) portray SEM images of fibers electrospun from PAN/PU blends of PAN/PU nanofibers with the PU content are 0 wt.%, 10 wt.%, 20 wt.% and 30 wt.% respectively. The fiber diameter generally increased with the amounts of PU (Fig. 5 and Table 2). The possible cause of this increased fiber diameter might be the viscosity and conductivity of the blend solutions. Therefore, the viscosity and conductivity of different systems were measured and the results are also presented in Table 2. It was clear that the viscosity of pure PAN solution is increased with the amounts of PU in the mixtures.

For pristine PAN electrospun mat (Fig. 5a), the fibers appear well-defined without any interconnection (point-bonded) among the fibers. Considering the morphology in detail, the PAN/PU nanofibers have bonding points than pure PAN nanofibers. Furthermore, junctions of fibers increased as the PU content increased. It was already reported in many literatures [21,22] that the mechanical properties of nonwoven mats increase with increasing of junctions and bundles of fibers.

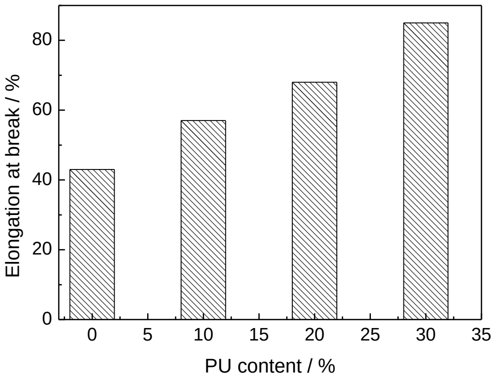


Fig. 6. Tensile strength of PAN/PU blend fibers as a function of PU content.

The mechanical behavior of electrospun fiber mats depends primarily on point-bonded structure (size and distribution) and geometrical arrangement of the fibers formed during the electrospinning process. As can it seen in Fig. 5, the fiber mats are made up of random PAN/PU fibers. Thus the point-bonded structure will more significantly affect the mechanical behavior.

The effect of PU contents on the tensile strength and the elongation at break are presented in Fig. 6 and Fig. 7. The tensile strength and the elongation at break and the tensile modulus are all increased with an increase in the PU composition. The tensile strength and the elongation at break of the neat PAN nanofiber film in this study were 1.12MPa and 43%, respectively. These two values increase to 1.53 MPa and 85% after incorporating 30wt% PU, corresponding to the improvement of 36 and 98%, respectively. The improvement in tensile properties was due to the changes in material composition and nanofibre mat morphology. It was noted that, with the blend of a high PU composition, the fibers are inter-connected together that effectively prevented the inter-fiber slippage under tensile loading, thereby leading to improved toughness. A similar result was also found from other electrospun polymer system [22].

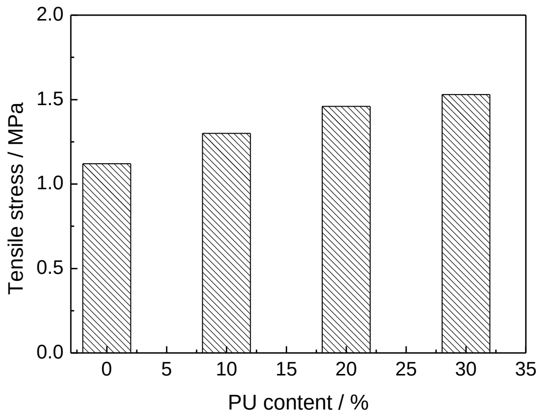


Fig. 7. Elongation to break of PAN/PU blend fibers as a function of PU content.

4. Conclusions

Various polyblends of PAN and PU dissolved in a mixture of N,N-dimethylformamide were produced by electrospinning in different ratios, with and the relationship between morphology and mechanical behavior of the resulting fiber mats was examined in detail. The surface tension, viscosity, and electrical conductivity of polymer solutions affecting electrospinning were measured, and scanning electron microscopy (SEM) along with a universal testing machine were used to examine the family of polyblends under investigation. The SEM images demonstrated that point-bonded structures in the fiber mats rose with increasing PU composition, and the mechanical properties of the fiber mats, as determined in a static tensile test, can be considered to have a strong effect by the point-bonded structure.

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