Preparation and Properties of Conductive Polyaniline/Poly-ω-aminoundecanoyle Fibers

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ABSTRACT: Historically, polyaniline (PANI) had been considered an intractable material, but it can be dissolved in some solvents. Therefore, it could be processed into films or fibers. A process of preparing a blend of conductive fibers of PANI/poly-ω-aminoundecanoyle (PA11) is described in this paper. PANI in the emeraldine base was blended with PA11 in concentrated sulfuric acid (c-H_2SO_4) to form a spinning dope solution. This solution was used to spin conductive PANI / PA11 fibers by wet-spinning technology. As-spun fibers were obtained by spinning the dopes into coagulation bath water or diluted acid and drawn fibers were obtained by drawing the as-spun fibers in warm drawing bath water. A scanning electron microscope was employed to study the effect of the acid concentration in the coagulation bath on the microstructure of as-spun fibers. The results showed that the coagulating rate of as-spun fibers was reduced and the size of pore shrank with an increase in the acid concentration in the coagulation bath. The weight fraction of PANI in the dope solution also had an influence on the microstructure of as-spun fibers. The microstructure of as-spun fibers had an influence on the drawing process and on the mechanical properties of the drawn fibers. Meanwhile, the electrically conductive property of the drawn fibers with different percentage of PANI was measured. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1458–1464, 2002

Key words: polyaniline (PANI); conductive fibers; as-spun fibers; polyaniline/poly-ω-aminoundecanoyle (PA11); wet-spinning technology; scanning electron microscopy (SEM)
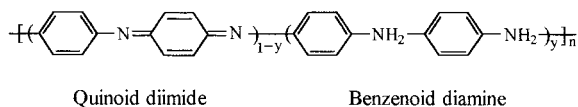
INTRODUCTION

In recent years, conducting polymers have been studied enthusiastically because of their potential application in light-emitting diodes, batteries, electromagnetic shielding, anti-static coating or fibers, gas sensors, corrosion protection, and acti-vators.[1–5] Among conducting polymers, polyaniline (PANI) continues to attract considerable attention because of its unique chemical and environmental stability in both the doped and undoped states compared with the other intrinsically conducting polymers (ICPs).[6, 7]

Undoped PANI can be schematically represented by the following formula shown in Scheme 1.[8–10] The value of y in Scheme 1 represents the oxidation state, and can be varied continuously from y = 1, which represents the completely re-

Quinoid diimide   Benzenoid diamine

Scheme 1

duced polymer (leucoemeraldine), to y = 0, which represents the completely oxidized polymer (pernigraniline). When y = 0.5, PANI is in the emeraldine base (EB). The imine atoms in any of the species can be protonated in whole or in part to give the corresponding salt.

PANI in the EB is soluble in some solvents (e.g., *N*-methyl-2-pyrrolidone [NMP], *m*-cresol, dimethyl propylene urea [DMPU], concentrated sulfuric acid [c-H_2SO_4], etc.) Thus, PANI could be processed into conductive self-standing films or complex films blended with other polymers in a solution or even be spun into conductive fibers.[11–15] Hsu and co-workers[16, 17] reported that the conductive fibers could be spun from the dope solution of PANI in 1,4-diaminocyclohexane by wet-spinning technology and that the electrical conductivity of the monofilament doped by HCl or H_2SO_4 was 10^2 S · cm^{-1}. Chacko and Gregory et al.[18,19] found that the gel easily occurred when PANI was dissolved in NMP and that the stability of the solution was greatly improved when it was dissolved in DMPU. The conductive fibers could thus be spun from the stable solution and the conductivity was also 10^2 S · cm^{-1}. Electrically conductive polyblends fibers of PANI and poly(*p*-phenylene terephthalamide) (PPTA) have been prepared by blending the polymers in concentrated sulfuric acid, and the tensile strength of the conductive fibers greatly increased because of existence of PPTA.[20] Production of the conductive polyaniline fibers has been achieved in the laboratory, but currently this production is a great challenge in the conductive fiber industry.

The microstructure of as-spun fibers will affect the fiber physical properties and aftertreatment, and the composition of coagulation bath is one of important factors that affect the microstructure of as-spun fibers. Thus, to improve spinning technology, it is essential to study the effect of acid concentration in the coagulation bath on the structure of as-spun fibers. In addition, the different mixture ratio for a multicomponent blending system is also one of the factors that affect the microstructure of as-spun fibers.

In our previous study,[21] PANI and PANI/poly-ω-aminoundecanoyl (PA11) were blended in

c-H_2SO_4 to spin the conductive fibers, and the investigation of the morphology of the blend fibers indicated that this was an incompatible blend system. PANI penetrated into the PA11-rich domain under drawing stress, similar to fine metal wire piercing into nonconductive materials, which was valuable for improving the conductivity of the fibers. However, the mechanical properties of the conductive fibers were mainly controlled by the microstructure of the as-spun fibers and the drawing process. In this study, the effect of acid concentration in the coagulation bath and PANI percentage in the fibers on the microstructure of the as-spun fibers was studied. Also, the effect of the microstructure on the mechanical properties and drawing process was measured.

EXPERIMENTAL

Synthesis of Polyaniline

PANI powder in the EB form was synthesized by chemical oxidation of aniline with ammonium persulfate (APS) as the oxidant in HCl solution. APS (8.21 g) in aqueous 1 mol/L HCl was slowly dripped into aniline (3.02 g) in 1 mol/L HCl solution in a flask that was previously cooled at about −5 °C. The mixture was constantly stirred in an ice/salt bath for 8 h. The precipitate was washed with 0.2 mol/L HCl aqueous solution and then ethanol, dedoped with 0.1 mol/L NH$_4$OH, filtered, and dried to obtain the EB powder. The intrinsic viscosity in NMP at 30 °C was 1.26 dL/g.

Preparation of PANI/PA11 Fibers

PANI was dissolved in c-H_2SO_4 with stirring at room temperature in a flask until a homogeneously viscous solution was produced. PA11 (P40, supplied by ELF Company, France) was also dissolved in c-H_2SO_4 using the aforementioned method to produce a transparent solution. Then, the spinning dopes could be prepared by mixing the two solutions with powerful stirring for 5 h. The spinning dopes were filtered and degassed under a reduce pressure at room temperature. Fiber spinning was conducted on a wet-spinning machine shown in Figure 1, which was designed in our laboratory. There are 12 spinneret holes in the spinning head, and the diameter of each hole is 0.08 mm. The pressure of nitrogen was maintained at 250 MPa. The as-spun fibers and the drawn fibers of PANI / PA11 were ob-
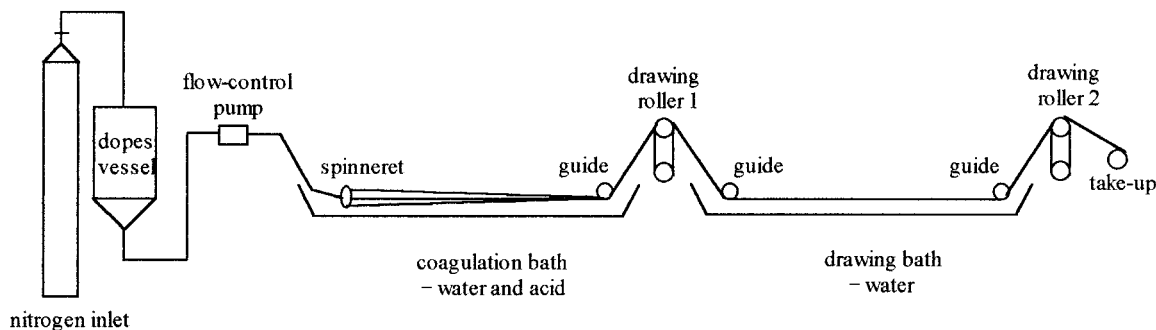
Figure 1 Flow process diagram of spinning fibers.

tained at drawing roller 1 and drawing roller 2, respectively (see Figure 1). The drawing ratio of the drawn fibers was the ratio of the velocity of drawing roller 2 to roller 1. The drawing bath was filled with recycled warm water (56 °C).

Characterization

A Camscan-4 scanning electron microscope (SEM) was employed to study the shape of the cross-section of the as-spun fibers at an accelerating voltage of 10 KV. The samples were fractured in liquid nitrogen and then gold-sputtered prior to observation.

The electrical conductivity of the fibers was measured by the four-probe technique, and the instrument was designed and assembled by us.

The mechanical properties of the drawn fibers were measured with a Shimadzu AGS-500ND forcing instrument made in Japan. The span of two grip-holders was 200 mm, and the rising rate of upper grip-holder was 500 mm/min. The tensile strength of the drawn fibers was calculated with the following equation:

$$\phi = \frac{\bar{F}}{D} \qquad (1)$$

where, $\bar{F}$(CN) is the average of force at tensile break, which was measured five times, D (dtex) is fineness defined by the mass of 10,000 ms of fibers, and ϕ (g/d) is the tensile strength of the fibers.

RESULT AND DISCUSSION

The as-spun fiber structure generated in a wet-spinning coagulation bath was a result of the counterdiffusion of solvent and nonsolvent and the phase separation of the polymer blends of PANI and PA11. Concentration of coagulation bath was one of the factors affecting the as-spun fiber structure. The shape and structure of the cross-section of the as-spun fibers were observed with a SEM. The micrographs of the fibers with 8wt% PANI are shown in Figure 2. By contrasting the three pictures of the as-spun fibers generated in the different coagulation baths, it was shown that the cross-section void size of the as-spun fibers obviously shrank when the H_2SO_4 molar concentration in coagulation bath was changed from 0.02 to 0.11 mol/L.

The void size in the as-spun fibers was determined by the rate of diffusion and phase separation according to Fick's law of diffusion

$$J_i = -D_i\frac{dC_i}{dx} \qquad (2)$$

where J_i is flux of component i, D_i is diffusion coefficient of component i, and dC_i/dx is the gradient of concentration of component i in a coagulation bath. The change of diffusion coefficient D_i or the gradient of concentration affected the rate of diffusion controlled by flux J_i. In fact, the increase in acid concentration of coagulation bath was equal to the increase of dC_i/dx, so the flux J_i correspondingly increased, which resulted in the observed large void size.

The size of the voids impacted the fiber physical properties and the type of aftertreatments used to dry, drawing, etc. The data listed in Table I indicate that the maximum drawing ratio of the as-spun fibers increased from 3.2 to 5.0 times and the tensile strength of the drawn fibers correspondingly increased from 1.82 to 2.25 g/d when the acid concentration in coagulation bath increased from 0.02 to 0.11 mol/L. Meanwhile, when
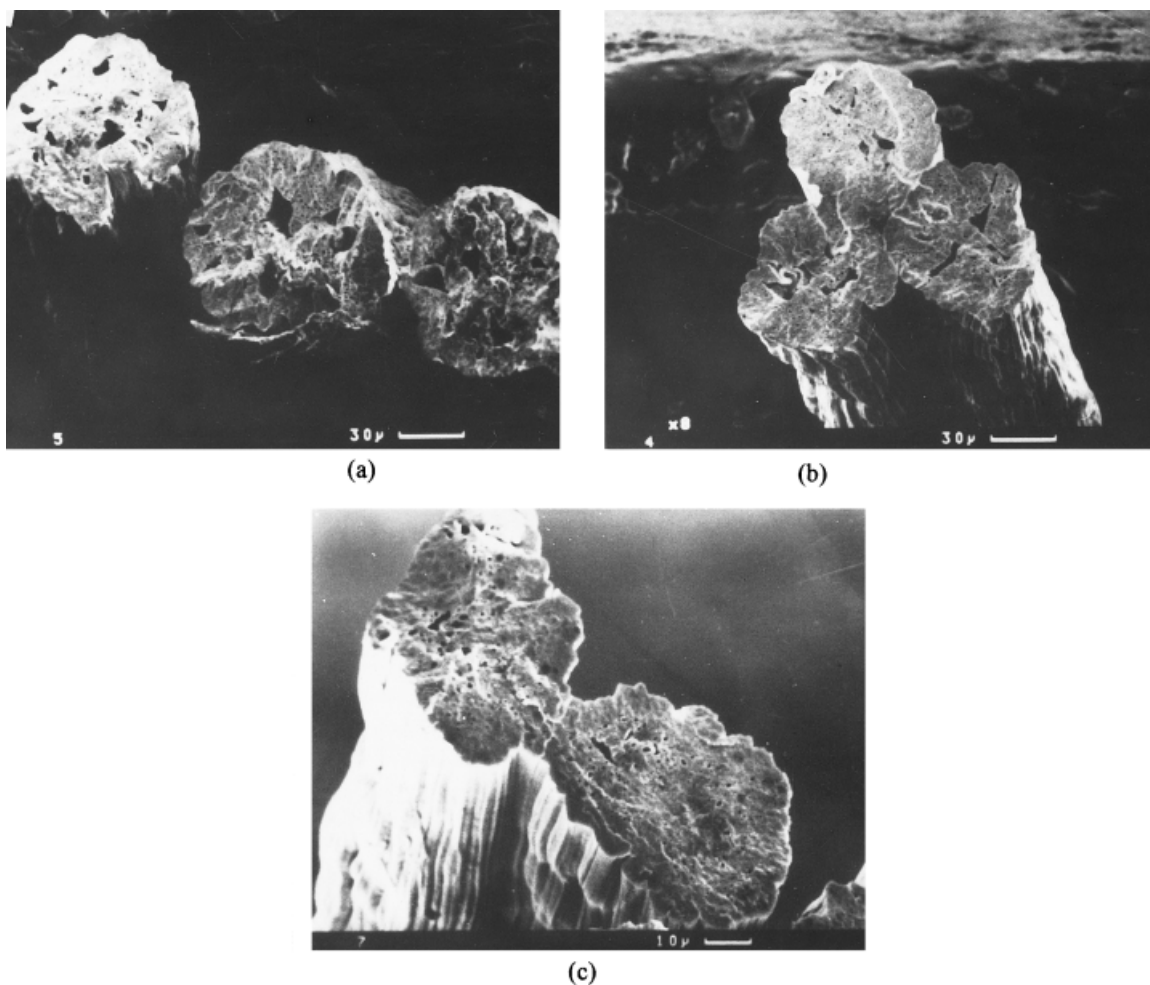
Figure 2 SEM micrographs of cross-section of as-spun fibers generated from a coagulation bath of (a) 0.02 mol/L H_2SO_4; (b) 0.06 mol/L H_2SO_4; (c) 0.11 mol/L H_2SO_4.

the drawing ratio was fixed at 3.0 times, the tensile strength of the drawn fibers also increased by 0.18 g/d in the case of the increase of acid concentration from 0.02 to 0.11 mol/L. Therefore, the smaller void size was valuable for spinning, drawing, and aftertreatment. It is worth pointing out that the concentration of H_2SO_4 in the coagulation bath could not infinitely increase to reduce the void size of the as-spun fibers because the excess acidity would result in too slow formation of the as-spun fibers, or even no formation, which is also disadvantageous for the drawing process.

For a given composition of coagulation bath, the structure of the as-spun fibers was affected by

Table I   Effect of Acidic Concentration on The Drawing Process of the Fibers[a]

Acid Concentration of Coagulation Bath	Cross-section of As-spun Fibers	Maximum Drawing Ratio	Tensile Strength at Max Drawing Ratio (g/d)	Tensile Strength at Drawing Ratio of 3.0(g/d)
0.02	Shown in Fig. 1a	3.2	1.82	1.78
0.06	Shown in Fig. 1b	4.5	2.04	1.81
0.11	Shown in Fig. 1c	5.0	2.25	1.96

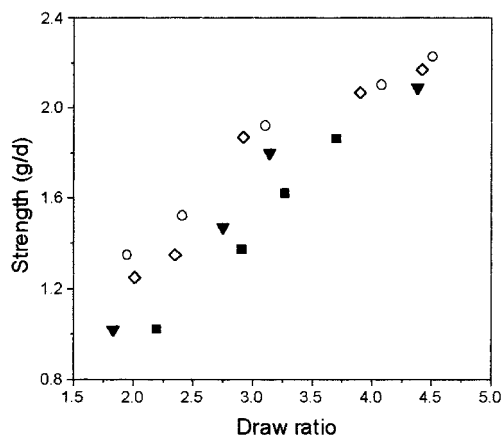[a] The fraction of PANI in the fibers was 8 wt%.
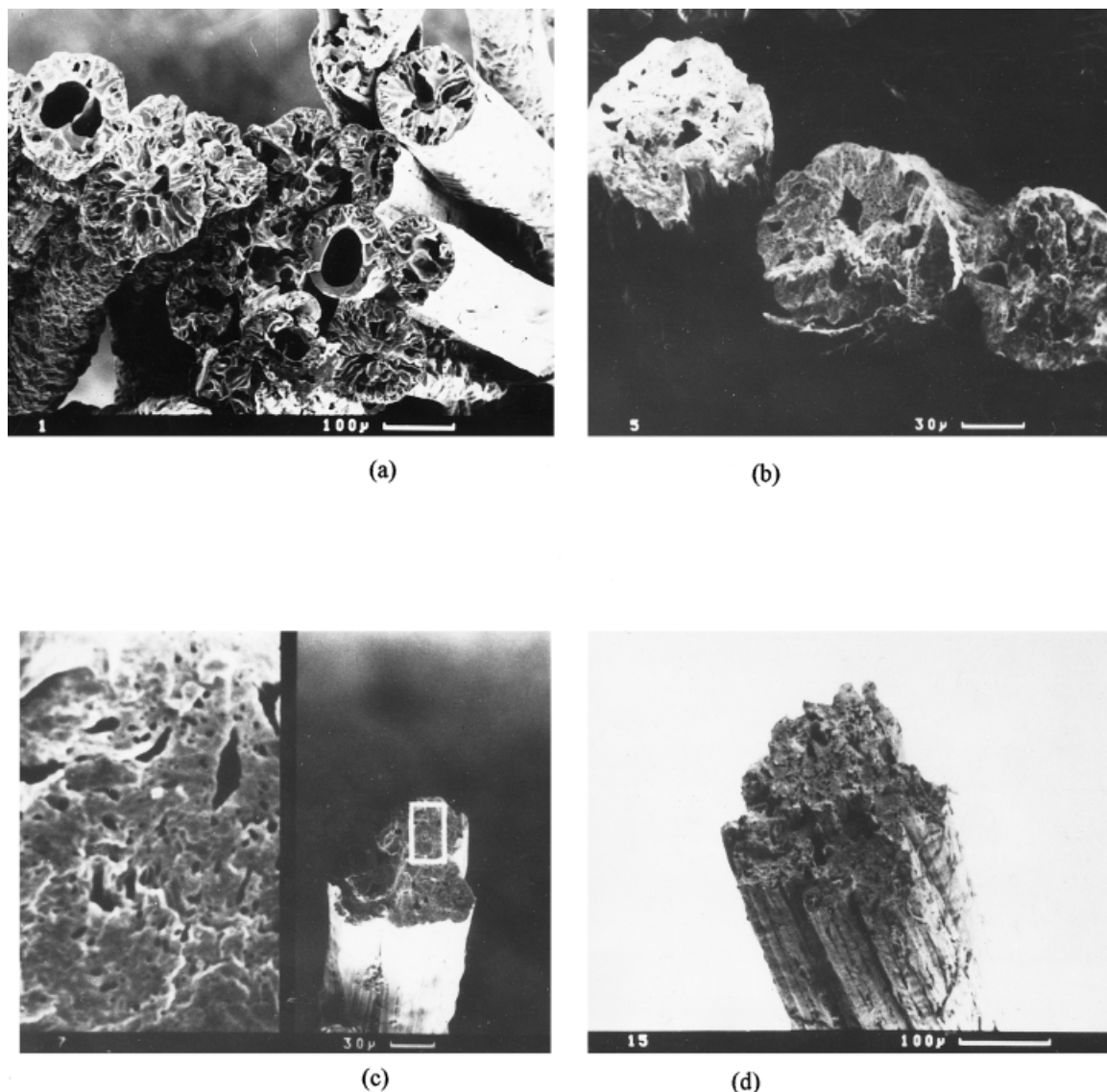
Figure 3   SEM of cross-section of as-spun fibers with PANI at (a) 0%; (b) 8%; (c) 16%; (d) and 20%. The coagulation bath was water circulated.

the percentage of PANI in the fibers. SEM micrographs of the cross-section of the as-spun fibers with different fraction of PANI are shown in Figure 3. The large void size of the cross-section of the as-spun fibers with no PANI (micrograph a) is very obvious. With the increase of PANI in the fibers, the void size shrinks. The internal void size of the as-spun fibers with 16 wt% PANI (micrograph c) is much less than that of the sample with no PANI (micrograph a). According to eq. 2, the diffusion coefficient D_i of solvent from PANI is different than that from PA11. Contrasting to PA11, the small diffusion coefficient of PANI

caused the slow diffusion of the solvent. Therefore, the addition of PANI in the spinning dopes resulted in the small void size. However, the weight fraction of PANI in the fibers was <30%, otherwise the fibers with good properties could not be obtained. As found in our experiment, when PANI was increased up to 30% under the same spinning conditions, the as-spun fibers included 12 filaments bound together because the solvent H_2SO_4 did not diffuse out in time and the nonsolvent water did not diffuse in in time.
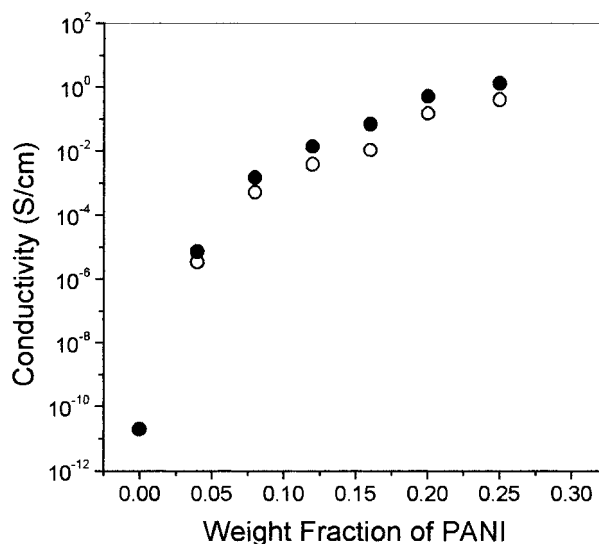
Although the addition of PANI resulted in the shrinkage of the void size in the cross-section of

Figure 4 The change of the tensile strength and the maximum drawing ratio of the bicomponent fibers with the different fractions of PANI in the fibers under the same spinning conditions. Key: (○) 0%; (◇) 8%; (▼) 12%; (■) 20%.

Figure 5 The conductive property of the drawn fibers with different drawing ratios. Key: (○) 2.7; (●) 3.7.

the as-spun fibers and the microstructure became perfect, it did not improve the drawing ratio of the as-spun fibers and the mechanical properties of the drawn fibers. The results are shown in Figure 4. When the coagulation bath was water, the as-spun fibers with no PANI could be drawn 4.5 times and the tensile strength of the drawn fibers was 2.25 g/d at the maximum drawing ratio. When the PANI was added in the spinning dopes, the maximum drawing ratio of the as-spun fibers hardly decreased except for the fibers with 20% PANI, whose maximum drawing ratio was only 3.5. However, the tensile strength of the drawn fibers decreased at a same drawing ratio. As expected, the molar mass of PANI was low and the intrinsic viscosity in NMP at 30 °C was only 1.26 dL/g; thus, the mechanical properties of the bicomponent fibers were controlled mainly by the matrix polymer PA11 instead of PANI. Therefore, the more PANI was added in the fibers, the more the tensile strength of the drawn fibers decreased.

The drawn fibers were soaked in acid solution (pH 3) for 10 min. Then they were taken out and dried prior to measurement of their conductivity. The results in Figure 5 indicate that the percentage of PANI in the fibers had an obvious influence on the conductivity. Electrical conductivity of the fibers increased from 10^{-11} S/cm for PA11 to 10^{-2} S/cm for the blending fibers with PANI of 12wt%. It was observed that only 5wt% of PANI in the fibers could give conductivity of $\sim 10^{-5}$ S/cm and 20% could give $> 10^{-1}$ S/cm. In addition, the different drawing ratios of the fibers had a slight influence on the conductive property. When the drawing ratio increased from 2.0 to 4.0 times, the conductivity of the fibers increased by one time. The drawing stress resulted in the orientation and fibrillation of PANI in the blending fibers, which is shown in Figure 6 where the dark area represents the PANI phase and the light area represents the continuous PA11 phase. PANI was separated into sections with the morphology of fibril, which was beneficial for the improvement of the electrical conductivity of the fibers.

Figure 6 Axial section SEM micrograph of monofilament with 20 wt% PANI content (magnification: ×10,000).

CONCLUSION

The as-spun fibers from PANI and PA11 were obtained by wet-spinning technology from c-H_2SO_4. Both the acid concentration in the coagulation bath and the percentage of PANI in the fibers affected the formation of the as-spun fibers. Increasing H_2SO_4 in the coagulation bath led to the shrinkage of the void size of the as-spun fibers and obviously improved the drawing process and increased mechanical properties. However, increasing PANI in the spinning dopes did not improve the drawing process and decreased mechanical properties even though it led to the shrinkage of void size of the as-spun fibers. The conductivity of the fibers ranged from 10^{-5} S/cm with 5wt% PANI to 10^{-1} S/cm with 20% PANI, and drawing stress had a slight influence on the conductivity of the drawing fibers.

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