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Preparation of antimicrobial polyacrylonitrile fibers: Blending with polyacrylonitrile-co-3-allyl-5,5-dimethylhydantoin

Liuyang Wang[1], Juan Xie[1], Lixia Gu (✉)[1], Gang Sun[2]

(1) State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 200051, P. R. China
(2) Division of Textiles and Clothing, University of California, Davis, California 95616
E-mail: Gulx@dhu.edu.cn; Fax: +86-21-62373928

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Summary

Polyacrylonitrile-co-3-allyl-5,5-dimethylhydantoin (Cop7-1) was prepared by a free radical polymerization process. The copolymer was blended with polyacrylonitrile (PAN) in a NaSCN aqueous solution, and the mixture was employed as a spinning solution. Rheological behavior of the spinning solution was studied. The PAN/Cop7-1 blend fibers were prepared through a two-stage wet spinning process. Tensile strengths of the blend fibers were lightly lower, but breaking elongations were higher than regular PAN fibers. Moisture regain and antistatic properties of the blend fibers were improved, while the thermal stability of the blend fibers decreased slightly. However, after treatment with 1% regular chlorine bleach, the blend fibers showed good antibacterial ability.

Introduction

Microbial threats on human health and safety have become a serious public concern in recent years. Poultry flu, foot and mouth disease, SARS [1] and many drug resistant infectious diseases are appearing more frequently, and protection of working professionals, particularly healthcare and emergency workers, from these diseases are becoming urgent needs. Use of antibacterial materials in protective clothing is a good means to improving protection against the biological threats.

N-Halamine compounds have been extensively used as effective germicides against a wide range of microorganisms in water disinfection and related applications [2-4]. Hydantoin compounds and their derivatives are widely used as precursors to prepare halamine biocides [5]. For example, 5,5-dimethylhydantoin has been grafted to cellulose, polyester, polyamide, polyacrylonitrile, and polypropylene fabrics, and the grafted hydantoin rings are then converted to the N-halamine structures after chlorination [6,7]. The thus modified textiles exhibited powerful antibacterial efficacy against gram-positive and gram-negative microorganisms, and the functions of the grafted textiles are durable and rechargeable through chlorine bleaching.

Polyacrylonitrile (PAN) is a polymer widely employed in making acrylic fibers. Acrylic fibers have advantages such as high tensile strength, good abrasion resistance, good insect resistance and easy-dyeing [7], which make the fibers popular in apparel as well as in out-door applications. Addition of antibacterial functions on acrylic fibers is important and necessary. Many research efforts have been spent on improving antimicrobial properties of the fibers [8-13], and the most successful ones are adding biocides directly into matrix of the fibers [14-15]. Many biocides are small molecules and are easy to leach out of the surface of fibers, especially in the process of washing, and losing the functions quickly. Improving durability of biocidal functions on acrylic polymers has been a challenge.

Recently, researchers reported that 3-allyl-5,5-dimethylhydantoin (ADMH) could copolymerize with acrylonitrile in a radical polymerization process, and the copolymer showed excellent antibacterial ability after chlorine bleaching [16]. In this paper, we report progresses of preparing a copolymer (Cop7-1) and blending the copolymer with polyacrylonitrile in an aqueous solution containing 45% NaSCN. The solution of polyacrylonitrile/Cop7-1 blend was extruded into fibers through a spinneret following a two-stage wet spinning process. Mechanical, electrical and antibacterial properties of the blend fibers as well as their thermal stability were investigated.

Experimental

Materials

Allyl bromide, potassium hydroxide, potassium persulfate, and 5,5-dimethylhydantoin were purchased from ACROS (Pittsburgh, PA, USA). Acrylonitrile, purchased from Zhangxing chemical reagent Co. Ltd., was distilled before use. Polyacrylonitrile with the viscosity-average molecular weight of 52,000 and a composition of 91.2% acrylonitrile (AN), 7.8% methylacrylate and 1.0% methylallylsulfonate was obtained from Shanghai Jinshan polyacrylonitrile Corporation, China. The other reagents are used without further purification.

Synthesis of ADMH and Cop7-1

3-allyl-5,5-dimethylhydantoin (ADMH) was prepared according to a reported method [16]. Synthesis of Cop7-1 was conducted in a following procedure. To a 250ml three-necked flask fitted with a magnetic fixer, backflow connection, drop funnel and a thermometer, AN and ADMH with a molar ratio of 7:1 were added, respectively. Certain amount of distilled water was added to ensure that the general concentration of monomers is 1.7mol/L. Aqueous solution of potassium persulfate was dropped into the reaction system, and the concentration of the initiator used for polymerization was 5.9 mmol/L. The mixture was stirred at 72°C under nitrogen atmosphere for 2 hours. After the reaction, the unreacted AN was eliminated under reduced pressure. Then the suspension was filtered, and the precipitates were washed with large amount of water for several times, and vacuum dried at 80°C for 24 hours. The copolymer was white powder and insoluble in water. The monomers' conversion was calculated as follows:

$$C_m = \frac{M_P}{M_1 + M_2} \times 100\% \quad (1)$$

M_p was the weight of copolymer obtained. M_1 and M_2 were weights of AN and ADMH added initially.

Table 1. Synthesis of Cop7-1 and related parameters

AN/ADMH (Mol)	M_{total}/PPS (Mol)	C_m (wt)	$[\eta]^a$	$W_{ADMH}{}^b$ (wt %)
7.0	286	76.7%	2.55	18.7%

[a] Measured in dimethylformamide (DMF) at 25°C, [b] measured by elementary analysis.

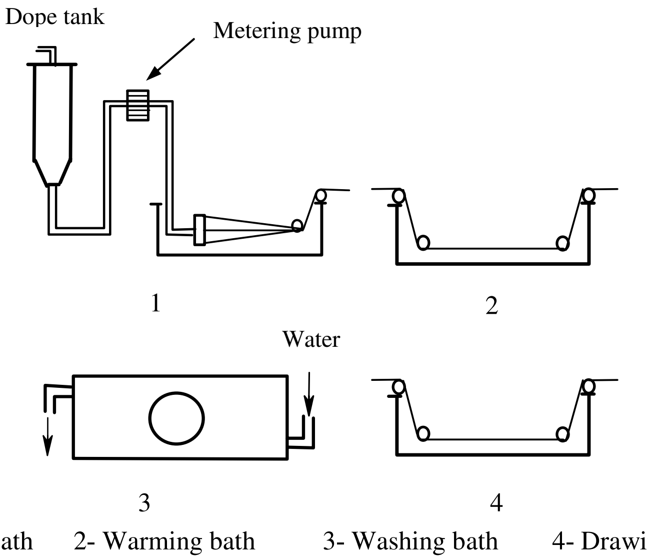
Preparation of PAN/Cop7-1 Blends

PAN and Cop7-1 powders were dissolved together in NaSCN aqueous solution with a weight ratio of PAN:Cop7-1 = 95:5, 90:10, 85:15, 80:20, 70:30, respectively. The dissolving process includes two steps: swelling and dissolving. PAN and Cop7-1 powders were initially put into 35wt% NaSCN aqueous solution and stirred at 25°C for 24 hours; then a certain amount of NaSCN was added into the solution and to ensure that the concentration of polymers was 12wt% and that of NaSCN was 45wt%. The solutions were stirred at 60°C for 5 hours, and then put into an oven to remove bobbles under reduced pressure at 29°C for 24 hours. The blended solution was slight yellow, transparent and stable even after 7 months without phase separation.

Rheological behavior of the blended solutions was studied using RS150 Haake rheometer. Shear ratios were in the range of 1~1000s^{-1}.

Preparation of blend fibers

The PAN/Cop7-1 blend fibers were prepared through a two-stage wet spinning process. The spinning process is shown in Figure 1.



1- Coagulation bath 2- Warming bath 3- Washing bath 4- Drawing bath

Figure 1. Scheme of wet spinning process

The spinning system was equipped with a dope tank, a metering pump, and spinneret with 6 holes of 0.1mm in diameter. To the dope tank the blend solution was added, and passed through 300 mesh filters to remove impurities. The pump feeding velocity was 1.5 mL/min, and take-up speed was 2.5m/min. As-spun fibers were formed in a coagulation bath (10wt% NaSCN aqueous solution, 10°C), then the fibers were warmed and drawn 1.5 times in the warming bath. After washed by hot recycled water (50~60°C), the fibers were further drawn in boiling water and air dried. The drawing ratio in boiling water varied from 4 to 7.

Analysis and Measurements

FTIR spectra of the samples were taken on a Nicolet Nexus 670 FTIR spectrometer using polymer powders. ^{1}H-NMR spectra were recorded on a Bruker Avance-400 NMR spectrometer using DMSO-d_6 as a solvent. Carbon and nitrogen contents in Cop7-1 were measured using a Perkin-Elmer Series II CHNS/O Analyzer 2400. Thermogravimetric (TGA) analysis was carried out on a Perkin Elmer TGA 2050 analyzer in a temperature range of 50°C to 600°C at 10°C/min under nitrogen atmosphere. Specific electric resistance of the blend fiber was determined by using a YG321 Specific Resistance Indicator. The blend fibers were chlorinated with a NaClO aqueous solution having 1% active chlorine at 40°C for 30 minutes, then washed and dried. Antibacterial test was conducted according to a modified American Association of Textile Chemist and Colorist (AATCC) test method 100-1999 with *Escherichia coli* (*E. coli*, none pathogenic, microbiology laboratory of UC Davis) as a testing bacterium.

Results and Discussion

Synthesis of Cop7-1

Figure 2 shows ^{1}H-NMR spectrum of ADMH monomer, consistent to the reported structure [6]. The characteristic chemical shifts (ppm) of ADMH are: 1.29(6H, s, CH_3), 3.92(2H, d, N-CH_2), 4.99-5.12(1H, m, =CH), and 5.73-5.86(2H, m, =CH_2). The structure of the copolymer Cop7-1 can be confirmed by a ^{1}H-NMR spectrum (Figure 3), showing two characteristic peaks of 1.29(CH_3) and 8.33(NH, weak) of ADMH and 3.14(CH) and 2.11(CH_2) of AN. FTIR of the polymer reveals absorption bands at 2245 cm^{-1} (C≡N stretching) and 1446 cm^{-1} (CH_2 scissoring) of acrylonitrile units, and at 1709 and 1770 cm^{-1} corresponding to C=O stretching of ADMH units. These results further prove the structure of the copolymer of AN/ADMH.

The chemical composition of the copolymer was analyzed using the ^{1}H-NMR spectrum. The integrated intensities of different resonance peaks in the ^{1}H-NMR spectra are used to evaluate the content of each monomeric unit in the copolymer. Following equation 2, average molar ratio of AN unit to ADMH unit in Cop7-1 can be calculated:

$$\frac{(X + 2Y)}{3Y} = Z \qquad (2)$$

where, X and Y represent numbers of moles of AN and ADMH units in Cop7-1, respectively; Z represents the integrated intensity ratio of methylene's proton signals to that of methyl. Based on equation 2, the calculated average molar ratio of AN unit to ADMH unit in the copolymer from Figure 3 is 14.2, which can be converted to 18.3% weight content of ADMH in Cop7-1. This result is nearly consistent with the value obtained by elementary analysis (Table 1).

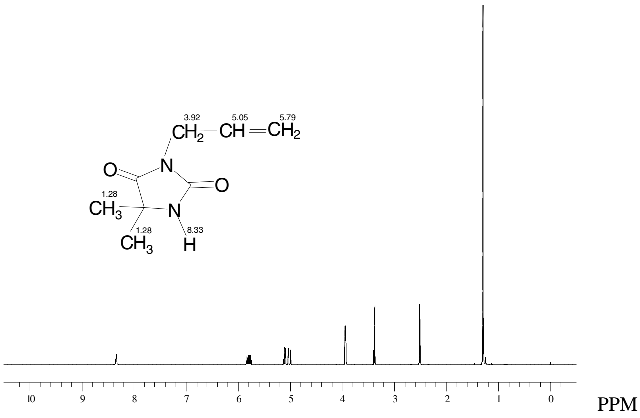


Figure 2. ^{1}H-NMR spectrum of ADMH monomer

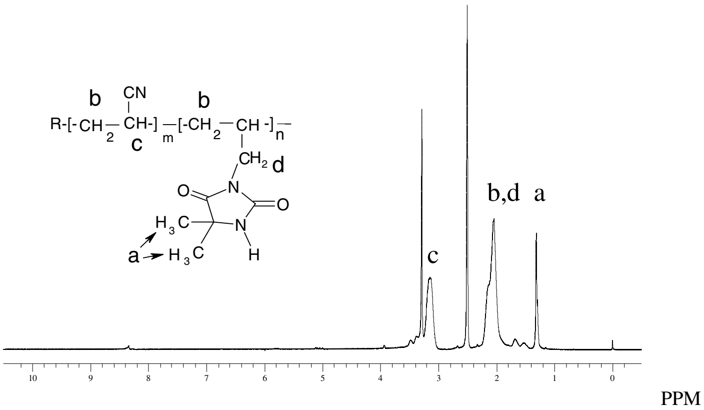


Figure 3. ^{1}H-NMR spectrum of Cop7-1

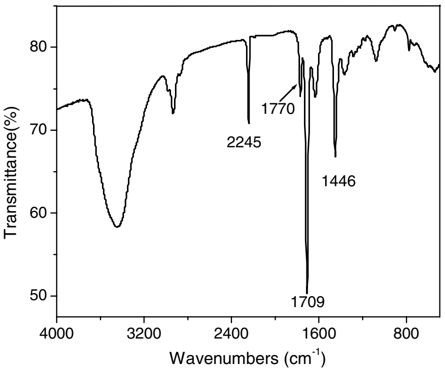


Figure 4. FTIR spectrum of Cop7-1

Rheological behavior of the spinning solutions

Apparent viscosity of the spinning solution is an important factor in control of wet spinning process. Figure 5 shows the rheological behavior of the spinning solutions. Apparent viscosities of four polymer blend solutions with compositions of AN/Cop7-1 70-30, 80-20, and 90-10 were measured under both 40°C and 60°C, respectively (Figures 5(a) and (b)). The viscosities decreased sharply initially and then flattened with the increase of shear rate. Solutions containing more Cop7-1 tended to have higher viscosity value except the solution of 90-10, which always demonstrated lower viscosity than that of PAN. Compared with nitrile group, hydantoin ring is a bulkier but less polar than nitrile side group in Cop7-1 polymer. When the content of Cop7-1 in the blend is low, the addition of ADMH monomeric unit may decrease the number of interacted sites between nitrile groups and increase the intermolecular distance. Therefore, the entanglement of the macromolecules may decrease or disappear under shear force, resulting in lower apparent viscosity than that of PAN. However, when the content of Cop7-1 is increased in the blend, apparent viscosity of the solutions should be higher than that of PAN solution because of the higher intrinsic viscosity of Cop7-1 than that of PAN.

The apparent viscosity of the blends decreased as testing temperature was raised. Figure 5(c) shows the viscosity changes of the 90-10 blend solution, and all the other solutions exhibited the same pattern. Figure 5(d) reveals the trend of decrease of apparent viscosity with the increase of testing temperature for these four different

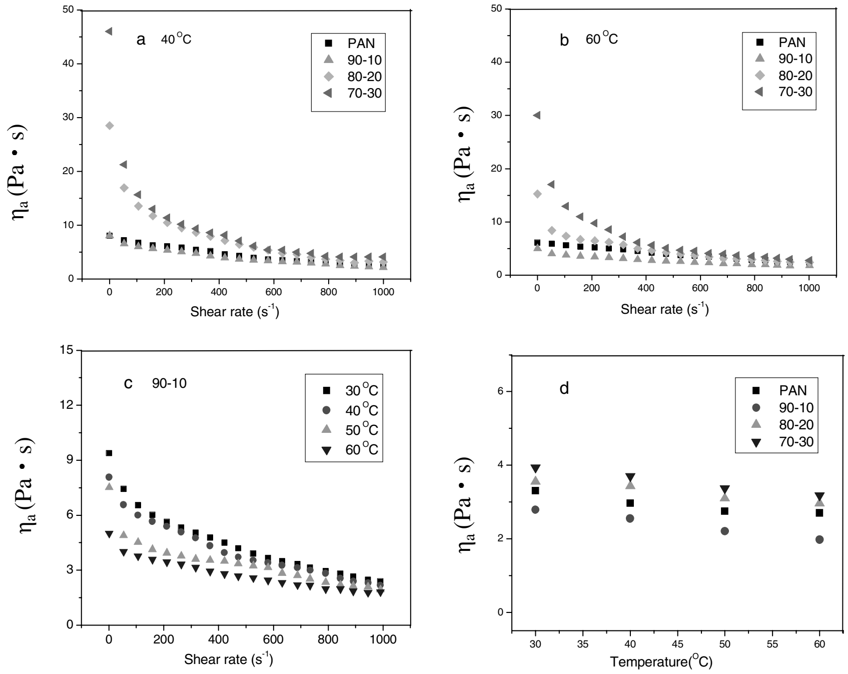


Figure 5. Rheological properties of spinning solutions. (a) and (b) Effect of shear rate on apparent viscosity for the spinning solutions at 40°C and 60°C, respectively. c) Effect of temperature on apparent viscosity for 90-10 spinning solution. d) Effect of components on apparent viscosity of spinning solutions at a shear rate of 840s^{-1}

polymer solutions at a shear rate of 840 s^{-1}. The decrease of the viscosity was not significant in the temperature range. The apparent viscosities of all polymer solutions moved closer at higher shear rate, which can be seen in Figures 5(a) to (c). This indicates that the blend solutions prepared are suitable for wet spinning.

Characterization of PAN/Cop7-1 blend fibers

Strong dipole-dipole interaction between nitrile groups in PAN has significant effect on its properties, such as high melting point and thermal stability of PAN. PAN is likely to decompose before melting. Decomposition of PAN undergoes cyclization among adjacent nitrile groups on the polymer chains, forming six-member and more conjugated rings [17]. Thermal stability of the blend fibers was assessed by using TGA analysis, with results shown in Figure 6. The copolymer Cop7-1 began to decompose at 266.2°C, and reached the maximum decomposition temperature at 287.5°C. PAN started to decompose at 307.5°C, and its maximum decomposition temperature was 325.2°C, obviously higher than that of Cop7-1. The lower decomposition temperature of Cop7-1 is caused by breaking of hydantoin rings from the backbone chain of the copolymer. However, the blend fibers showed improved thermal stability with values of initial and maximum decomposition temperatures increased with augment of PAN content, but each of the two values was just between the corresponding values of Cop7-1 and the PAN, as can be seen in Table 2. For all the samples, there were another major derivative peaks in the range of 345°C~460°C, also corresponding to the cyclization and decomposition of acrylonitrile units in the samples above.

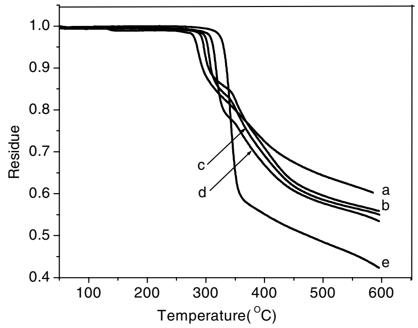


Figure 6. Thermograms of Cop7-1, PAN, and PAN/Cop7-1 blend fibers: (a) Cop7-1, (b) 70-30, (c) 80-20, (d) 90-10, (e) PAN

Table 2. Initial and maximum decomposition temperatures of Cop7-1, blend fibers and PAN

Sample	Initial decomposing temperature(°C)	Maximum decomposing temperature(°C)
Cop7-1	266.2	287.5
70-30	279.2	296.1
80-20	291.5	310.3
90-10	298.9	319.9
PAN	307.5	325.2

Mechanical properties of the blend fibers are summarized in Table 3. The drawing ratio of the blend fiber was 8.0. Compared to PAN, tensile strengths of the blend fibers dropped a little but in an acceptable range, while the breaking elongations of the blend fibers were increased, with an increase of Cop7-1 content in the blends. The bulky side groups of hydantoin rings in Cop7-1 are difficult to orientate during fiber formation in the blend fiber. Therefore, the more the copolymer is added, the smaller the orientation degree of the blend fiber gets, so that the tensile strength drops. On the other hand, existence of hydantoin rings may provide more space and be helpful for the chains to stretch under tensile effect, so the breaking elongation increased.

Table 3. Mechanical properties of the blend fibers

Sample	Drawing ratio	Titer (den)	Tensile-strength (dN/tex)	Elongation (%)
70-30	8.0	5.5	2.71	26.4
80-20	8.0	7.7	2.29	25.2
90-10	8.0	8.9	2.91	24.7
PAN	8.0	8.7	2.96	18.3

Tensile speed: 10mm/min

Table 4. Moisture regain and specific electric resistance of blend fibers

Sample	Specific Resistance (Ω·cm)	Moisture Regain (%)
70-30	3.2×10^{9}	1.94
80-20	1.8×10^{11}	1.62
90-10	9.0×10^{11}	1.45
PAN	1.6×10^{13}	1.34

Moisture regain reflects hydrophilic properties of fibers, and has a great effect on the applications of fibers. Specific electric resistance is an index of spinnability for fibers. Fibers with high value of the specific resistance are easy to accumulate static charge, inhibiting spinning of fiber. Moisture regain and specific resistance of the blend fibers were both improved, as shown in Table 4. The moisture regain of the blend fibers increased after the copolymer was added; and the more Cop7-1 was added, the higher the moisture regain of the blend fiber is. Generally, the antistatic property depends on the moisture content of fiber materials [18]. As the ADMH monomer is hydrophilic in nature, the incorporation of hydantoin group increases hydrophilicity of the fibers, consequently reduces specific electric resistance of the fibers. Thus, the antistatic properties of the blend fibers were improved. Furthermore, the existence of hydantoin side chain could raise the inter-distance of adjacent chain segments, and reduce the degree of orientation, so the void fraction in the fiber matrix got increased, and this was also favorable for increase of moisture regain of blend fiber.

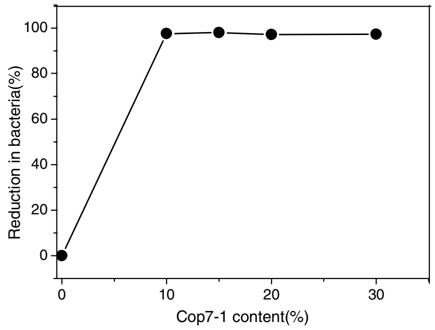


Figure 7. Effect of Cop7-1 content on the antibacterial activity of PAN/Cop7-1 blend fibers

The blend fibers can obtain antibacterial abilities after chlorination since the amide group on the hydantoin rings (on fiber surface) can be transformed into biocidal N-chloramine. The antibacterial abilities of the blend fibers were tested against *E. coli* according to the modified AATCC test method. The blend fibers were chlorinated with 1% regular chlorine bleach at 40°C for 30 minutes and washed with distilled water. The treated fibers were then contacted with 1 mL of an aqueous suspension containing 10^5–10^6 CFU/mL of *E. coli* for 2 hours, and neutralized with 100 mL of 0.03 N sodium thiosulfate solution. In order to observe the antibacterial effect, the neutralizing solution was further diluted to 10, 100, and 1000 times. Aliquots of the dilutions were placed on agar plates. Bacterial colonies on the agar plates were counted after incubation at 37°C for 24 h. The test results are shown in Figure 7. The chlorinated fibers containing 10wt% of Cop7-1 were able to achieve 97.5% bacterial reduction rate. With more Cop7-1 in the blend fiber, improvement of antibacterial ability gets mild. The antibacterial mechanism can be shown as follows:

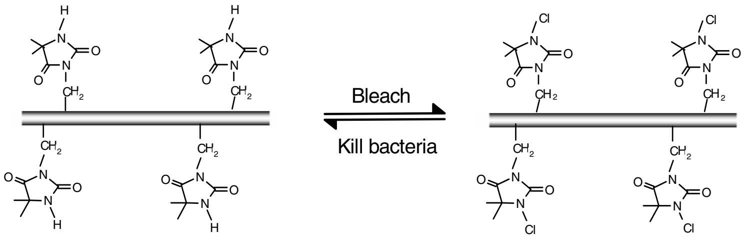


Figure 8. Sketch for antibacterial process of the blend fibers after chlorination

Conclusions

Copolymer of 3-allyl-5,5-dimethylhydantoin (ADMH) and acrylonitrile (Cop7-1) can be well prepared by radical polymerization in aqueous solution. The copolymer was blended with PAN with different blend compositions in a 45wt% NaSCN aqueous solution, and spinning solutions were prepared after removing bubbles. Fibers were prepared through a two-stage wet spinning process. The apparent viscosity of the spinning solution decreases continuously with an increase of shear rate. The decomposition temperature of the blend fiber was lower than that of PAN. When the content of Cop7-1 was increased, the blend fiber showed increased moisture regain and decreased specific resistance, as well as slightly decreased tensile strength but increased breaking elongation. After treated with 1% regular chlorine bleach, the blend fibers showed good antibacterial ability, 97.5% reduction of bacteria can be reached for fibers with 10wt% content of Cop7-1.

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