Preparation of Conductive Polyaniline Fibers by a Continuous Forming-Drawn Processing Routine

Weijin Liu, Guang Gao

College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

ABSTRACT: Polyaniline fibers were prepared with a continuous forming-drawn processing routine that better met practical production requirements. The continuous forming drawing of the fibers was conducted successfully with the following methods. A reducing agent was added to a polymer solution during the dissolution of a polyaniline emeraldine base in N-methyl-2-pyrrolidinone (NMP). After the entire wet-spinning process was finished, the fibers were reoxidized and doped to obtain electric conductivity. The as-spun fibers were predrawn at a low drawing ratio in a warm water bath before a plasticization drawing process on a hot plate. After the fibers were predrawn, some solvent was still kept in the fibers and used as a plasticizer of the fibers so that the plasticization drawing process would be performed successfully. The spinning conditions that affected the mechanical properties and conductivity of the fibers were the content of NMP in the coagulation bath, the coagulation-bath temperature, the warm-water-bath temperature, the predrawing ratio, the hot-plate temperature, the plasticization drawing ratio, and the reoxidation and protonation treatment time. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 956–960, 2004

**Key words:** conducting polymers; fibers; mechanical properties

INTRODUCTION

An excellent conductive polymer, polyaniline (PAn) has already attracted broad interest and attention from academic circles researching polymers. During the past decade, systematic research has been conducted on its synthesis, molecular structure, and conducting mechanism. Currently, major research objectives for PAn include the study of its forming theory and processability and the production of practical PAn products. One important application area for PAn is the spinning of fibers.

PAn consists of polymers that exist in three different discrete oxidation states at the molecular level: a reduced base (leucoemeraldine), a half-oxidized base (emeraldine), and an oxidized base (permigraniline).[1] The polyaniline emeraldine base (PAn-EB) can become electrically conductive when it is doped with a protonic acid. The formation of PAn fibers has been limited by insolubility and gelation. The solution spinnability of PAn has been improved with new solvents, such as dimethyl propylene urea,[2] 1,4-diaminocyclohexane,[3] and N-methyl-2-pyrrolidinone (NMP)/2-methylaziridine.[4] A common processing routine for the formation of PAn fibers[3,5,6] is as follows: A PAn spinning solution is spun in a coagulation bath and collected to form as-spun fibers, which are soaked in a water bath for a long time to remove the solvent. Then, the as-spun fibers are dried for about 24 h. Finally, they are drawn at an elevated temperature. This processing routine stops the continuity of the forming-drawn procedure and turns it into batch spinning, which cannot meet practical production requirements. Moreover, because the strength of the as-spun fibers is very low, especially that of undrawn fibers with significant brittleness such as PAn, it is hard for this kind of fiber to withstand processes such as soaking, drying, unwinding, and redrawing and winding. During these processes, the fibers can be broken.

In this article, we report a feasible wet-spinning routine for the continuous forming drawing of PAn fibers. The following method can prevent brittle rupture during the continuous forming-drawn process of PAn fibers. With polyaniline leucoemeraldine base (PAn-LEB) as the fiber-forming polymer, the oxidation and doping of the fibers impart electric conductivity after the whole process of spinning is finished. The as-spun fibers are predrawn at a low drawing ratio in a warm water bath before the plasticization drawing process on a hot plate. After the fibers are predrawn, some solvent still remains in the fibers and is used as plasticizer of the fibers so that the plasticization drawing process can be successfully conducted at a high temperature on a hot plate. With this

Correspondence to: W. Liu (pswjliu@scut.edu.cn).
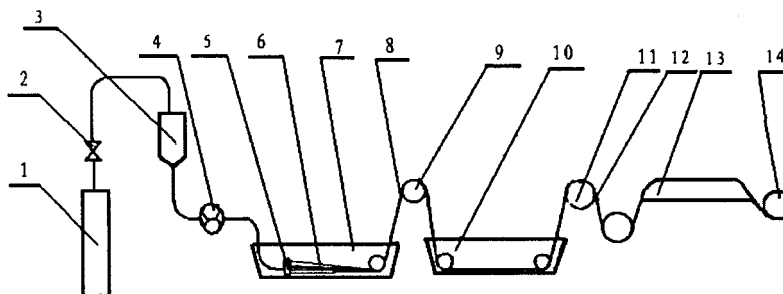
Figure 1 Flow diagram of spinning fibers: (1) buffer tank of nitrogen, (2) pressure-regulating valve, (3) dope vessel, (4) spinning metering pump, (5) spinneret, (6) dope streams, (7) coagulation bath, (8) as-spun fibers, (9) drawing roller 1, (10) warm water bath, (11) drawing roller 2, (12) predrawn fibers, (13) hot draw plate, and (14) drawing roller 3 (take-up bobbin).

method, the spinnability of PAn can be improved, and continuous forming drawing of the fibers can be conducted smoothly. As a general spinning solvent, NMP is more familiar to people and cheaper than other solvents of PAn, so NMP has been used as the solvent of PAn in this study. A solution of PAn-LEB is prepared through the addition of a reducing agent such as phenyl hydrazine to the polymer solution during the dissolution of PAn-EB in NMP. This method can prevent the formation of a gel in a PAn/NMP spinning solution. The properties of the fibers depend greatly on the spinning conditions. In this article, we report the effects of the spinning conditions on the properties of conductive PAn fibers.

EXPERIMENTAL

Synthesis of PAn

PAn-EB was synthesized through the chemical oxidation of aniline in an aqueous hydrochloric acid solution with $(NH_4)_2S_2O_8$ as an oxidant. Aniline (46.5 g, 0.5 mol) was dissolved in 500 mL of $1M$ HCl and $2.9M$ LiCl. The solution was constantly stirred in a dry-ice/acetone bath. After the solution reached $-25°C$, $(NH_4)_2S_2O_8$ (79.8 g, 0.35 mol) in 500 mL of $1M$ HCl and $2.9M$ LiCl was dripped at a rate of 1 mL/min into the aniline solution, which was being stirred. The reaction continued for 40 h with stirring at $-25°C$. The reaction mixture was filtered and washed with $1M$ HCl and methanol. Then, it was deprotonated with $0.1M$ NH_4OH. The deprotonated PAn-EB was washed with distilled water and methanol, filtered, and dried *in vacuo* at room temperature. The inherent viscosity of the polymer in 98% H_2SO_4 at 30°C was 2.04 dL/g.

Preparation of the spinning solution

The dope of PAn-LEB was prepared through the addition of a reducing agent such as phenyl hydrazine to the polymer solution during the dissolution of PAn-EB in NMP. The concentration of the dope was 15 wt

%. It was filtered under nitrogen pressure and degassed under reduced pressure at room temperature for 24 h.

Preparation of the conductive PAn fibers

The fiber spinning was conducted on the wet-spinning machine shown in Figure 1. There were 10 spinneret holes on the spinneret. The diameter and length/diameter ratio of each hole were 0.15 mm and 2, respectively. The end of the spinneret was just submerged in a coagulation bath; that is, there was no air gap. The nitrogen pressure was maintained at 150 MPa. The dope was spun into the coagulation bath, which consisted of water and NMP. The spinneret withdrawal rate was 6 m/min. The windup rate of drawing roll 1 was 5.48 m/min; that is, the apparent spin-draw ratio was -8.7%. After predrawing in a warm water bath and plasticization drawing on a hot plate, the PAn-LEB fibers were collected by a take-up bobbin. Finally, the bobbin was soaked in an aqueous solution of $FeCl_3$ and camphor sulfonic acid (CSA) for a certain period and dried at 50°C. The PAn-LEB fibers turned into conductive PAn-EB fibers. The tensile properties of the fibers were obtained with an Instron tensile tester (Bristol, UK). The electrical conductivity of the fibers was measured and calculated by the method reported by Zhang and Sun.[7]

RESULTS AND DISCUSSION

Coagulation of PAn dope streams

The effects of the NMP content in the coagulation bath on the mechanical properties of PAn-LEB fibers are presented in Table I. The coagulation bath consisted of water and NMP.

The NMP content in the coagulation bath had important effects on the mechanical properties of PAn-LEB fibers. Table I shows that the mechanical properties of the fibers improved with increasing content, and a 15 wt % concentration led to the highest tenacity

TABLE I
Effects of the Content of NMP in the Coagulation Bath on the Mechanical Properties of PAn-LEB Fibers

Content of NMP in the coagulation bath (wt %)	Total draw ratio	Tenacity (gpd)	Modulus (gpd)	Elongation (%)
0	1.4	0.25	16	2.3
5	2.3	0.48	48	5.6
10	3.4	1.26	60	12.3
15	4.5	2.53	71	8.6
20	3.0	1.27	58	12.6
25	2.8	1.13	58	9.2

The other conditions: temperature of the coagulation bath = 5°C; The warm-water-bath temperature = 85°C; predrawing ratio-1.3; temperature of the hot plate = 185°C.

and modulus. The diffusion rates of both NMP in the dope streams to the coagulation bath and the coagulant (water) in the coagulation bath to the dope streams decreased with increasing NMP content in the coagulation bath, and so the coagulation rate of the dope streams decreased.[8] The more slowly the dope streams coagulated, the fewer structural defects there were of the PAn as-spun fibers.[8] As-spun fibers with fewer structure defects were able to withstand a higher drawing ratio, so the total draw ratio that as-spun fibers could withstand increased with increasing NMP content in the coagulation bath (see Table I). The total draw ratio is equal to the predrawing ratio in the warm water bath times the plasticization drawing ratio on the hot plate. The fibers with higher orientation degrees and fewer structure defects had higher tenacity and modulus. However, when the content of NMP in the coagulation bath exceeded 15%, the tenacity and modulus of the fibers decreased with increasing content. Under such conditions, the diffusion rates of both the solvent and the coagulant were slow, and so the coagulation degree of the as-spun fibers was too low; such as-spun fibers could not withstand the high-stretching process. When the content of NMP in the coagulation bath reached 25%, the as-spun fibers often broke in the warm water bath as their coagulation degree was too low.

The effects of the temperature of the coagulation bath on the mechanical properties of PAn-LEB fibers are shown in Table II.

The tenacity and modulus of the fibers decreased with an increase in the coagulation-bath temperature. The effects of the coagulation-bath temperature on the coagulation of PAn dope streams were two-sided. It influenced both the phase equilibrium of the dope streams and the diffusion rate of the solvent and coagulant (water). For the spinning system of a PAn-LEB/NMP spinning solution with NMP/H$_2$O as the coagulation bath, the dissolvability of PAn-LEB in the solvent (NMP) increased with increasing temperature,

and this retarded phase separation;[8] however, the diffusion rates of the solvent and coagulant increased with increasing temperature, and this accelerated the coagulation of the dope streams. According to the postdrawing conditions and mechanical properties of the fibers, a lower temperature coagulation bath was good for the fibers.

Tables I and II show that although both the content of NMP in the coagulation bath and the temperature of the coagulation-bath influenced the postdrawing process of the as-spun fibers and the mechanical properties of the fibers, the effects of the former were greater and more obvious.

Predrawing in the warm water bath

The concentration that the PAn spinning solution could reach was not high enough (15 wt %), and the coagulation conditions adopted in the experiment were quite mild; therefore, there was a great deal of the solvent (NMP) in the as-spun fibers. The as-spun fibers were incapable of withstanding the high-stretching process because the acting force between the molecular chains was too weak. To create condition under which the fibers could withstand the high-stretching process, the as-spun fibers were predrawn at a low drawing ratio in a warm water bath so that they could dissolve before the high-stretching process. At the same time, a small amount of the solvent was kept in the predrawn fibers as a plasticizer because if it had been removed completely, it would have been difficult for the predrawn fibers to be drawn on the hot plate in the next step because of the rigid molecular chains and strong intermolecular hydrogen bonds of PAn. After the predrawing process, the amount of the residual solvent in the predrawn fibers to a great extent depended on the warm-water-bath temperature and the predrawing ratio (see Tables III and IV). During the plasticization drawing process on the hot plate, the stretchability (plasticization drawing ratio) and drawing effect of the fibers were related to the

TABLE II
Effects of the Coagulation-Bath Temperature on the Mechanical Properties of PAn-LEB Fibers

Coagulation-bath temperature (°C)	Total draw ratio	Tenacity (gpd)	Modulus (gpd)	Elongation (%)
5	4.5	2.53	71	8.6
10	4.0	2.39	67	11.5
15	4.0	2.12	64	11.0
20	3.5	1.96	60	9.1
30	3.0	1.43	55	8.3

The other conditions: content of NMP in the coagulation bath = 15%; warm-water-bath temperature = 85°C; predrawing ratio = 1.3; hot-plate temperature = 185°C.

TABLE III
Effects of the Warm-Water-Bath Temperature on the Mechanical Properties of PAn-LEB Fibers

Warm-water-bath temperature (°C)	Residual solvent in the predrawn fibers (wt %)	Total draw ratio	Tenacity (gpd)	Modulus (gpd)	Elongation (%)
70	40.3	3.6	1.66	54	10.1
80	28.7	4.9	2.41	65	8.7
85	20.8	4.5	2.53	71	8.6
90	13.9	4.0	2.38	64	8.1
95	6.6	3.0	1.32	58	9.0

The other conditions: content of NMP in the coagulation bath = 15%; coagulation-bath temperature = 5°C; hot-plate temperature = 185°C.

content of the residual solvent in the predrawn fibers, and so the warm-water-bath temperature and the predrawing ratio affected the mechanical properties of the PAn fibers.

The effects of the temperature of the warm water bath on the mechanical properties of the fibers are shown in Table III. Within the temperature range of 80–90°C, the fibers had better mechanical properties. When the temperature was greater than 90°C, the fibers often broke during the plasticization drawing process on the hot plate, and the tenacity and modulus of the fibers became quite low.

Table IV shows that too high a predrawing ratio was disadvantageous to the fibers. The purpose of predrawing was to dissolve the as-spun fibers, not to make their molecules orient. In contrast, too high a preorientation degree made it hard for the fibers to be drawn on the hot plate.

Plasticization drawing on the hot plate

The effects of the temperature of the hot plate on the mechanical properties of the fibers are shown in Table V. When the fibers were drawn within the range of 185–195°C, they had better mechanical properties. The fibers often broke during the drawing process on the hot plate when the temperature was greater than 200°C.

The tenacity and modulus of the fibers increased as the plasticization drawing ratio increased (see Table VI). However, after the plasticization drawing ratio

exceeded 3.46, the tenacity and modulus decreased with an increase in the drawing ratio because the fibers were damaged by excessive drawing stress. When the plasticization drawing ratio was 4 (i.e., the total drawing ratio was 5.2), the drawing process could not proceed normally as the fibers were often broken on the hot plate.

Conducting treatment of PAn-LEB fibers

PAn-LEB fibers entail reoxidation and protonation with an oxidant such as an aqueous solution of $FeCl_3$ and CSA to achieve electrical conductivity. The effects of the treatment time on the electrical conductivity and tenacity are shown in Table VII.

The conductivity increased and the tenacity of the fibers decreased with increasing treatment time. After the time exceeded 45 min, the conductivity only increased slowly but the tenacity decreased rapidly with increasing treatment time. During the conducting treatment course, reoxidation and protonation first occurred on the surface layer of the fibers. The conductivity increased as the protonation ratio increased because of longer treatment time. With a further increase in the treatment time, the reoxidation and protonation reaction transferred to the interior of the fibers. During the process, the main increase occurred in the thickness of the conductivity layer of the fibers; therefore, the increase ratio for conductivity was not high. However, oxidation and protonation changed the molecular structure and supermolecular structure of the fibers, and this greatly

TABLE IV
Effects of the Predrawing Ratio on the Mechanical Properties of PAn-LEB Fibers

Predrawing ratio	Residual solvent in the predrawn fibers (wt %)	Total draw ratio	Tenacity (gpd)	Modulus (gpd)	Elongation (%)
1.12	43.2	3.0	1.45	57	8.9
1.20	32.6	3.9	2.41	67	11.2
1.30	20.8	4.5	2.53	71	8.6
1.39	14.6	4.2	2.39	65	8.0
1.50	8.7	2.3	1.10	41	6.6

The other conditions: content of NMP in the coagulation bath = 15%; coagulation-bath temperature = 5°C; not-plate temperature = 185°C.

TABLE V
Effects of the Hot-Plate Temperature on the Mechanical Properties of PAn-LEB Fibers

Hot-Plate temperature (°C)	Tenacity (gpd)	Modulus (gpd)	Elongation (%)
180	2.08	58	8.5
185	2.53	71	8.6
190	2.49	70	8.4
195	2.37	63	8.7
200	1.98	58	8.5
205	1.51	52	8.3

The other conditions: content of NMP in the coagulation bath = 15%; coagulation-bath temperature = 5°C; warm-water-bath temperature = 85°C; predrawing ratio = 1.3; plasticization drawing ratio = 3.46.

reduced the tenacity if the fibers. We believe that it is unnecessary for the entire fiber to be made with PAn-EB. If the surface layer of the PAn-LEB fibers is reoxidized and doped, a good conductive property can be obtained. Therefore, we can determine the conducting treatment time according to practical needs.

CONCLUSIONS

PAn fibers were prepared by a continuous forming-drawn processing routine that better met practical

TABLE VI
Effects of the Plasticization Drawing Ratio on the Mechanical Properties of PAn-LEB Fibers

Plasticization drawing ratio	Tenacity (gpd)	Modulus (gpd)	Elongation (%)
1.30	0.89	31	10.1
2.30	1.55	52	9.7
2.85	2.10	60	9.5
3.46	2.53	71	8.6
3.60	2.44	64	7.8
4.00	2.21	59	6.1

The other conditions: content of NMP in the coagulation bath = 15%; coagulation-bath temperature = 5°C; warm-water-bath temperature = 85°C; predrawing ratio = 1.3; hot-plate temperature = 185°C.

TABLE VII
Effects of the Conducting Treatment Time on the Electrical Conductivity and Tenacity of the Fibers

Treatment time (min)	Tenacity (g/d)	Conductivity (S/cm)
15	2.48	10^{-2}
30	2.23	10
45	1.77	90
60	1.12	110
120	0.82	140
180	0.36	175

The other conditions: content of NMP in the coagulation bath = 15%; coagulation-bath temperature = 5°C; warm-water-bath temperature = 85°C; predrawing ratio = 1.3; hot-plate temperature = 185°C; plasticization drawing ratio = 3.46; treatment solution = 1M CSA and $FeCl_3$ aqueous solution.

production requirements. The optimum spinning conditions were as follows: 15 wt % NMP in the coagulation bath, 5°C coagulation-bath temperature, 85°C warm-water-bath temperature, 1.3 predrawing ratio, 185°C hot-plate temperature, and 3.46 plasticization drawing ratio. The tenacity and conductivity of the fibers were 1.77 g/d and 90 S/cm, respectively, for 45 min of reoxidation and protonation with an aqueous solution of 1M CSA and $FeCl_3$.

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