Lyocell Fibers as the Precursor of Carbon Fibers

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ABSTRACT: In this work, Lyocell fibers, used as carbon fiber precursors, were investigated. Lyocell fibers used for the carbon precursors and the carbon fibers themselves were produced in our laboratory. The mechanical properties morphology and structure of the precursors and the obtained carbon fibers were studied and compared to those of rayon. The results show that Lyocell fibers have higher tenacity and modulus, and better thermal stability than rayon fibers. Scanning electron microscopy (SEM) experiments show that Lyocell precursors have round cross-sections and fewer defects in the fibers, while rayon fiber has an oval cross-section and many defects. Wide angle X-ray diffraction (WAXD) results for the Lyocell precursors indicate that the degree of crystallinity of the Lyocell precursor is higher than that of a rayon precursor. They also show that Lyocell based carbon fibers have better mechanical properties than those that are rayon-based. WAXD data of the obtained carbon fibers show that the crystallinity of Lyocell-based carbon fiber is higher than that of rayon-based carbon fiber. It is concluded that the Lyocell fibers are better precursors for carbon fibers than rayon. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1941–1947, 2003

Key words: fibers; mechanical properties; morphology; structures

INTRODUCTION

Cellulose fibers are one of the most important precursors for carbon fibers for their unique characteristics, such as low metal ion content, low density, ease of production, etc. The crystal structure in cellulose-based carbon fibers is one of disorder, which gives it a lower thermal conduction coefficient and provides materials made from it excellent thermal insulation and ablation resistance. The materials made from cellulose-based carbon fibers can be used in special fields, such as space flight and aviation. Furthermore, cellulose-based carbon fibers have good biocompatibility and can be used in medical treatment.[1]

Most cellulose-based carbon fibers are made from textile-grade rayon and viscose rayon.[2,3] Other regenerated cellulose fibers have been used as precursors of carbon fibers, such as saponified acetate rayon yarn, cuprammonium rayon, etc.[4,5] Unfortunately, all of these cellulose fibers have some defects, which reduce the properties of the obtained carbon fibers. These defects include a large void content (viscose rayon, textile rayon, saponified acetate rayon yarns, etc.) and interfilament bonding (cuprammonium rayon, etc.). The high void content and interfilament bonding of the precursors lead to weak and brittle carbon fibers, respectively, after carbonization.[6] It was claimed that polynosic rayon is an excellent precursor for carbon fibers; however, no high modulus carbon fibers have been made from it.[7] Yoneshiga et al[8] reported that, when viscose rayon fibers with a degree of polymerization ($\overline{DP}$) of cellulose higher than 450 are used as the precursor instead of conventional rayon ($\overline{DP}$ about 250), the tensile strength of the obtained carbon fibers was increased by approximately 30% after being carbonized at 800°C. Natural cellulose fibers, such as cotton and ramie, are not suitable to be used as precursors of carbon fibers, because they are discontinuous filaments, have a low degree of orientation, and are associated with impure materials such as lignin.[8,9]

In the last thirty years, Lyocell fibers, a new kind of manmade cellulose fiber, have gained attention around the world for their environmentally friendly production process and unique fiber properties,[10] and much work has been carried out on them.[11–14] Lyocell fibers are produced by dissolving cellulose directly in N-methylmorpholine-N-oxide/water, the obtained solution is extruded from an orifice, drawn in an air gap, and then precipitated in a coagulation bath.[15] Compared with rayon fibers, Lyocell fibers have unique characteristics, such as higher tenacity, higher modulus, lower shrinkage in the dry state, and lower tenacity and modulus reduction in the wet state.[16] Moreover, the cross section of Lyocell fibers is round, the molecular chains are highly oriented along the fiber axis, and the fineness of the fiber is easy to control, so superfine Lyocell can be produced.[17,24] It can be made from high $\overline{DP}$ cellulose pulp.[14] Therefore, it is reason-

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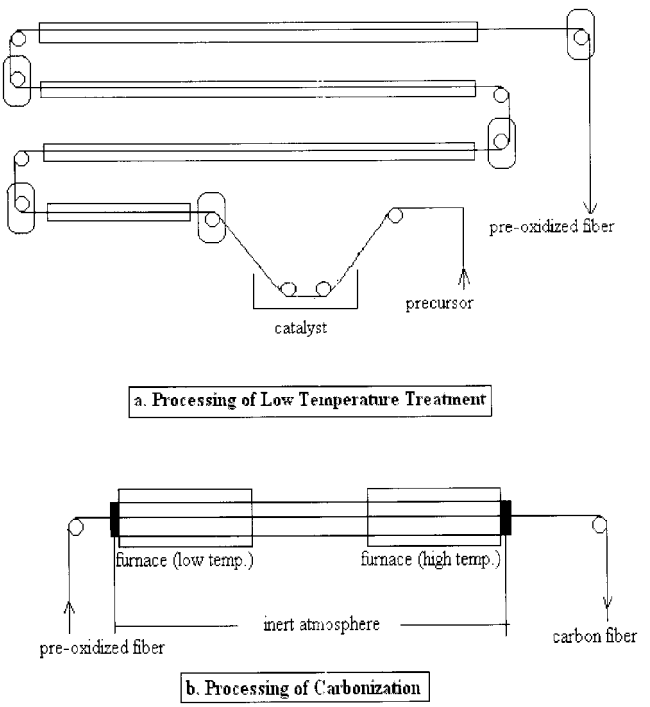

Figure 1 Schematic for the preparation of carbon fibers: (a) process of low temperature treatment; (b) process of carbonization.

able to consider that Lyocell fiber may be an excellent precursor for carbon fibers.

For this paper, we used Lyocell fibers as the precursor for carbon fiber and prepared lyocell-based carbon fibers. The properties and morphology of the precursors and the obtained carbon fibers, and their relationships were studied.

EXPERIMENTAL

Materials

Wood pulp ($\overline{DP}$ = 730, α-cellulose content 91%, Ketchikan Pulp Company, USA), *n*-propyl gallate (reagent grade, Shanghai Chemical Corporation, Shanghai, China), NH_4Cl (AR, Shanghai Chemical Corporation, Shanghai, China), and N-methylmorpholine-N-oxide (NMMO) aqueous solution (50 wt%) (BASF AG, Germany) were used in this study.

Preparation of Lyocell fibers

NMMO aqueous solution (50 wt%) was distilled under vacuum to remove a certain amount of water, and NMMO aqueous solution with a water content of 26 wt % was obtained. The NMMO aqueous solution, cellulose pulp, and n-propyl gallate (antioxidant) were mixed together; the mixture was heated to 100°C and the extra water distilled off (the final mole ratio of NMMO to water was about 1:1) under vacuum; while stirring vigorously, and a brown-yellow transparent cellulose solution was obtained. In the case of prepared cellulose solution containing NH_4Cl, a certain amount of NH_4Cl (NH_4Cl/cellulose = 1/50, w/w) was added during the mixing step. Cellulose content in the obtained cellulose solution was 9 wt % in all solutions.

The obtained solutions were transferred to a spinning tank, for which the temperature was set at 110°C. The spinning solution was extruded by a gear pump and then extruded through a spinneret with 210 orifices (80 μm in diameter). The spinning solution was drawn into an air gap of 50 mm in length and immersed in a coagulation bath to precipitate cellulose in filament form. The filaments were washed with water, wound and dried. Lyocell fibers, for use as carbon fiber precursors, were obtained.

Preparation of carbon fibers

Lyocell fibers were first washed with water and then with an acid aqueous solution. They were then impregnated with catalyst and pre-oxidized under different temperatures: the fibers were heat-treated at 105, 150, 200, and 250°C for 20 minutes in air. All of these steps were performed in an experimental line in our laboratory. The pre-oxidized carbon fiber precursor was then carbonized in our laboratory scale carbonizing line, in which the precursor was first carbonized under 800°C and then under 1300°C in an oxygen free atmosphere for a certain time. The carbonization schematic is shown in Figure 1. Carbon fibers were obtained.

Mechanical properties of precursors and carbon fibers

The tensile strengths and moduli of the precursors were measured with XQ-1 Tensile Tester (China Tex-

TABLE I
Mechanical Properties of Some Cellulose Fibers

Samples	Fiber fineness (dtex)	Tenacity (cN/dtex)		Initial modulus (cN/dtex)		Extension (%)		Crystalline orientation fraction *f(x)*
		Dry	Wet	Dry	Wet	Dry	Wet	
Lyocell	1.30	6.1	5.7	74.4	62	6.4	8.3	0.95
Viscose Rayon	1.67	4.2	3.0	30.1	18.7	16	20	0.94
Polynosic[24]	1.74	4.0	3.2	100	20	14	18	0.94

TABLE II
Mechanical Properties of Carbon Fiber Precursors

	Rayon	Lyocell-I	Lyocell-II
Tenacity (cN/dtex)	3.62	4.20	6.10
Initial Modulus (cN/dtex)	30.10	36.10	74.40
Elongation at Break (%)	13.00	7.40	7.40

TABLE III
Mechanical Properties of Carbon Fibers

Carbon Fibers	Tenacity (GPa)	Modulus (GPa)
Rayon Based	0.82	79.2
Lyocell-I Based	0.94	99.7
Lyocell-II Based	1.07	96.6

tile University, Shanghai, China). The sample length was 20 mm and the extension rate was set at 3 mm/min. The mechanical properties of carbon fibers were measured on a YG-061 Tensile Tester (Laizhou Electron Instrument Limited Corporation, Sandong, Chain). The sample length and extension rate were set at 10 mm and 1 mm/min, respectively. All measurements were performed at 20°C and 65% relative humidity.

Thermal gravimetric analysis (TGA)

TGA of precursors was performed on a Perkin-Elmer (Pyris 1 TGA) in a nitrogen atmosphere; the weight of samples was 0.2–0.5 mg. The scan rate was 20°C/min.

Morphological characterization

The cross-section features of the precursors were characterized by using an OLYMPUS PM-10AD optical microscope (Japan). The surfaces of the precursors and the carbon fibers, as well as the cross-section of the carbon fibers, were observed using a JSM-5600LV scanning electric microscope (JEOL Co., Japan).

Birefringence measurement

Birefringence (Δn) measurements of the fiber samples were performed using a Model XPT-7 compensator an optical polarization microscope (Shanghai Optic Instrument Plant, Shanghai).

Wide angle x-ray diffraction (WAXD)

Wide angle X-ray diffraction investigation was performed on a D/MAX-B, Rigaku, (Japan) (CuKα λ = 0.154 nm). The obtained data were analyzed by Peakfit software to obtain the crystallinity. The crystal size (L_c) was calculated by the Scherrer equation, $L_c = \frac{k\lambda}{B\cos\theta}$, where λ is the wavelength of the X-ray, B is the half width of the diffraction peaks, and the factor k is the apparatus constant (0.89 in this case).[17,18]

Determination of the orientation factor

The azimuthal intensity distribution of the equatorial reflections at 20.7° was used for determining the crystalline orientation factor, f_{cr}, according to the method described by Sato,[19]. $f_{cr} = 1 - W_{1/2}/180$. $W_{1/2}$ is the half-width of the azimuthal intensity distribution for the meridional reflection at the (020) plane. The amorphous orientation factor was calculated by the Stein equation:

$$\Delta n = \alpha \cdot f_{cr} \cdot \Delta n_{cr}\,(\max) + (1 - \alpha) \cdot f_{am} \cdot \Delta n_{am}\,(\max),$$

where Δn is the total fiber birefringence, α is the degree of crystallinity, f_{cr} is the crystallite orientation factor, f_{am} is the amorphous orientation factor, $\Delta n_{cr}(\max)$ is the maximum birefringence of the crystallite phase and $\Delta\, n_{am}(\max)$ is the maximum birefringence of the amorphous phase. We assumed that, at an orientation factor of 1, $\Delta\, n_{cr}(\max)$ is equal to $\Delta\, n_{am}(\max)$[20] and taken to be 0.0545.[21]

RESULTS AND DISCUSSION

Mechanical properties of precursors and carbon fibers

The mechanical properties of the carbon fibers depend on the mechanical properties of the precursors, as well as the oxidation process used in making carbon fibers. For a good carbon fiber precursor, excellent mechanical properties are required.[22,23] The mechanical properties of some cellulose fibers are listed in Table I. It shows that the tenacity and wet modulus of Lyocell fibers are considerably higher than those of other cellulose fibers. Moreover, by adjusting the spinning parameters, such as the diameters of the spinneret ori-

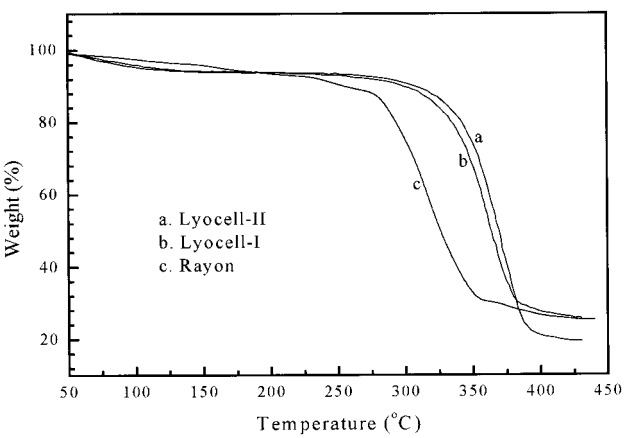

Figure 2 TGA curves of the precursors.

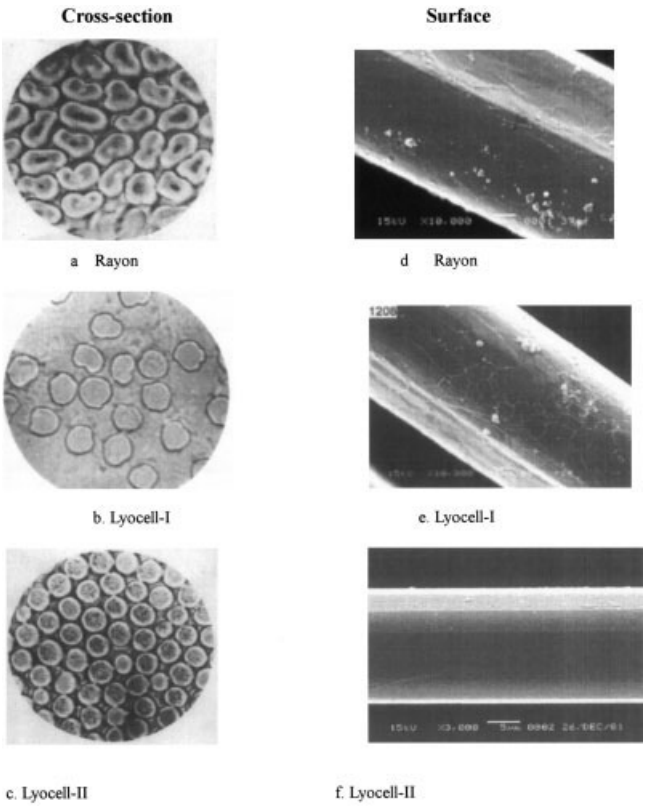

Figure 3 Morphology of the precursors: (a) Rayon; (b) Lyocell-I; (c) Lyocell-II; (d) Rayon; (e) Lyocell-I; (f) Lyocell-II.

fice, air gap, take-up speed, etc., the diameter of Lyocell fibers can be easily controlled.[24]

The mechanical properties of the precursors used for this paper are listed in Table II. It shows that rayon has the lowest tenacity and modulus, and the highest elongation at break. By contrast, both Lyocell fibers with and without NH_4Cl in the spinning solutions (Lyocell-II and Lyocell-I for short, respectively) have better mechanical properties than the rayon. In comparison of the two types of Lyocell fibers, Lyocell-II has higher tenacity and initial modulus. The modulus of Lyocell-II is more than twice that of Lyocell-I. However, the elongations at break of both Lyocell fibers are similar, because the associative character of the solvent is substantially increased with the addition of NH_4Cl to the spinning solution, and the viscosity of the solution is also enhanced.[14] Therefore, cellulose chains in the solution can be easily oriented so that the tenacity and modulus of the obtained Lyocell fibers are increased considerably.

Considering the properties of the obtained carbon fibers (listed in Table III), Lyocell-II based carbon fibers have the highest tenacity. Lyocell-I and Lyocell-II based carbon fibers have almost the same value of modulus: both are much higher than that of rayon based-carbon fibers. However, the modulus of Lyocell-I based carbon fibers is a little higher than that of Lyocell-II based, even though the modulus of Lyocell-II fibers (74.4 cN/dtex) is more than twice that of Lyocell-I fibers (36.1 cN/dtex). In the case of using Lyocell fibers as the precursors for carbon fibers, higher tenacity Lyocell fibers result in higher tenacity carbon fibers, while the modulus of Lyocell precursors has little influence on the modulus of the obtained carbon fibers, shown in Table III. Therefore, we can say that both types of Lyocell fibers are good precursors for carbon fibers: the mechanical properties of the Lyocell based carbon fibers are better than those of rayon based carbon fibers.

Thermal gravimetric analysis of precursors

The thermal properties of the precursors are very important in the production of carbon fibers, because they influence the per-oxidation, carbonization and yield ratio of carbon fibers. TGA results of the precursors are shown in Figure 2: rayon precursor has the worst thermal stability among the three precursors and began to degrade rapidly at about 270°C with the degradation finished at about 350°C. By contrast, both kinds of Lyocell fibers (Lyocell-I and II) had better thermal stability, since they began to degrade rapidly above 330°C with degradation completed at around 385°C. The weight loss of rayon, Lyocell-I and II is about 75, 80 and 74 wt%, respectively and shows little difference. Stability of both Lyocell fibers is better than

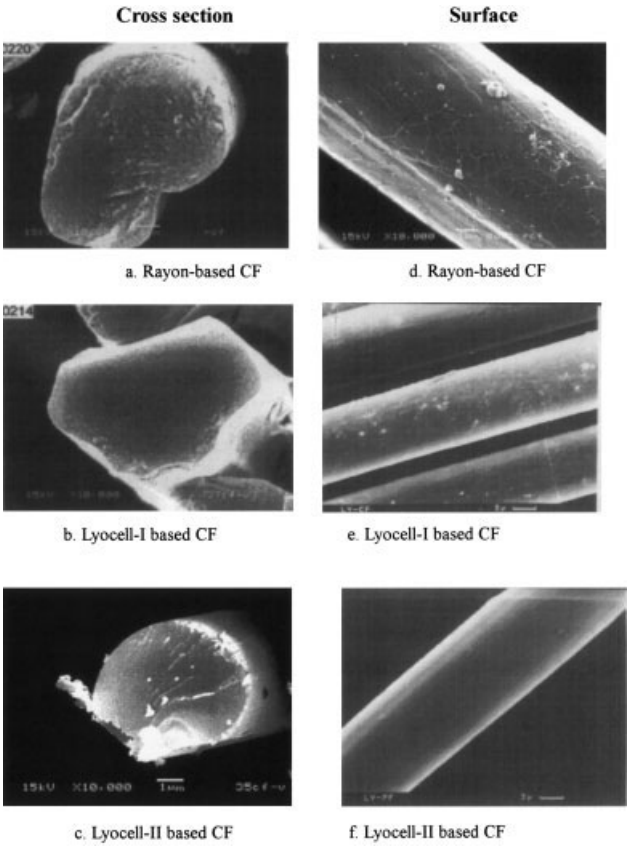

Figure 4 Morphology of carbon fibers: (a) Rayon-based CF; (b) Lyocell-I based CF; (c) Lyocell-II based CF; (d) Rayon-based CF; (e) Lyocell-I based CF; (f) Lyocell-II based CF.

that of Fortisan-36 (Celanese Corporation, USA), a highly crystalline fiber regenerated from cellulose acetate, for which major pyrolytic degradation occurs between 240°C and 320°C, and the weight loss is over 90%.[25,26] Therefore, although the chemical components of Lyocell and rayon precursors are the same, their thermal properties are quite different because they have different crystal and orientation structures. Therefore, the process of producing Lyocell-based carbon fibers, especially the pre-oxidation process, should be modified from that used for producing traditional rayon-based carbon fibers, by which even better properties may be obtained. This work is underway, and the results will be published in our next paper. In this paper, the properties of carbon fibers from different precursors, under the same production process, will be discussed.

Morphology of the precursors and the obtained carbon fibers

It is known that a good precursor for carbon fiber always has the following characteristics: a round cross-section, fine denier, high strength and modulus, few physical defects, etc.[23,27,29–33] Figure 3 shows the SEM photographs of the precursors. All of the Lyocell precursors have round cross-sections and fewer defects in the cross-section [Fig. 3 (b,c)]. The surface of the Lyocell precursors is also smooth [Fig. 3 (e,f)], while the cross-section of rayon is oval and has more defects [Fig. 3a] and its surface is quite rough [Fig. 3(d)]. It is known that the defects in the precursors are directly related to the defects in the obtained carbon fibers[5,28] and the properties of the obtained carbon fibers will reflect this. This is one of the reasons that the mechanical properties of the Lyocell fibers are better than those of rayon precursors, and the proper-

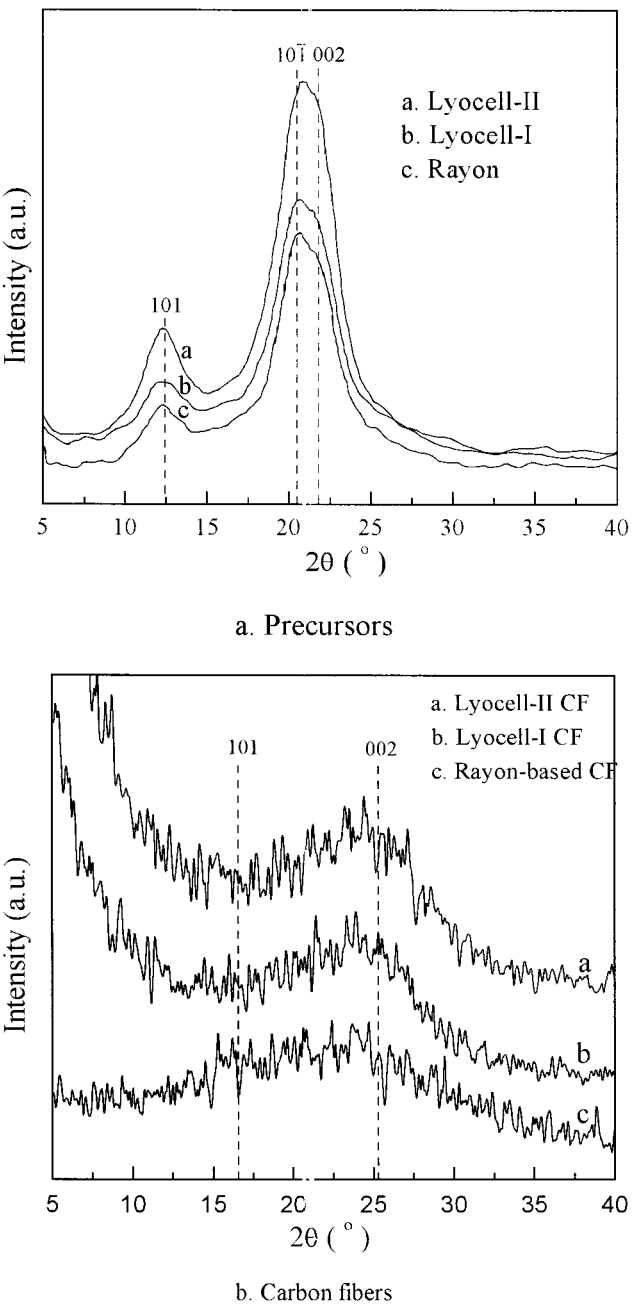

Figure 5 Powder WAXD results of (a) precursors and (b) obtained carbon fibers.

TABLE IV
Some Structural Parameters of Precursors

Sample	Crystallinity %	(Crystal size) (nm)			Orientation factor		Δn
		L_{101}	L_{101}	L_{002}	Crystal	Amorphous	
Rayon	45.60	3.21	2.92	4.30	0.8750	0.3764	0.0320
Lyocell-I	64.04	2.39	3.84	4.60	0.7911	0.5692	0.0377
Lyocell-II	72.56	2.23	3.70	3.84	0.8932	0.4599	0.0395

ties of Lyocell based carbon fibers are better than those of rayon based carbon fibers (Tables I and II).

Figure 4 shows SEM photographs of the obtained carbon fibers. They show that the surface of Lyocell based carbon fibers is smooth [Fig. 4 (e,f)] with fewer defects in their cross-sections [Fig. 4 (b,c)]. By contrast, the surface of a rayon based carbon fiber has ditches and flaws, and some defects in its cross-section, which are associated with the defects and ditches in the rayon precursors. By comparison of the SEM photographs in Figures 3 and 4, the morphology of the carbon fiber is shown to be directly related to the morphology of the precursors: the defects and weaknesses in the precursors will be brought into the obtained carbon fibers. Since the Lyocell fibers have fewer defects in them, they should be better carbon fiber precursors.

Crystalline structure

In order to study the structure of the precursors and the obtained carbon fibers, WAXD experiments were carried out. Figure 5 shows the results of WAXD experiments on precursors and the corresponding carbon fibers: all the precursors have cellulose II crystalline structure [Fig. 5(a)]. The crystallinity of the precursors can be calculated by using WAXD data, and the results are listed in Table IV. Both Lyocell precursors have higher crystallinity than the rayon precursor, and Lyocell-II has the highest crystallinity among them. Lyocell precursors have higher moduli than rayon. Among the three precursors, we also found that their crystal orientation factors do not differ remarkably, but the amorphous orientation factors have distinct differences. This trend is in accord with that of tensile strength. Based on the above, we deduced from Tables II and IV that crystallinity and amorphous orientation factors seem to have more important influences on a precursor's modulus and tensile strength than the other factors. The crystallinity of the precursors may contribute to the difference in their stability, and higher crystallinity is accompanied by better thermal stability. Moreover, it can be found that the orientation of Lyocell precursors is higher than that of rayon precursors, while the Lyocell-II precursor has the highest orientation among the three samples.

Figure 5(b) shows the WAXD experiment results for the obtained carbon fibers. It shows that the diffraction signal of (101) plane at $2\theta = 16.5°$ of carbon fibers is quite weak in all obtained carbon fibers, and no difference in intensity can be recognized. The diffraction signals of planes (002) at $2\theta = 25.5°$ are different; the intensity of rayon based carbon fiber is quite weak compared with that of Lyocell based carbon fibers. It can be deduced that the crystalline degree of Lyocell-based carbon fibers is higher than that of rayon based carbon fiber. This is why Lyocell based carbon fiber has better properties than rayon based carbon fiber.

CONCLUSIONS

Lyocell fibers have higher tenacity and modulus, and better thermal stability than rayon fibers. SEM experiments show that Lyocell precursors have round cross sections and fewer defects in the fibers, while rayon fibers have oval cross-sections and some defects. WAXD and birefringence results on the precursors indicate that the crystalline degree and orientation of Lyocell precursors are higher than those of rayon precursors. Lyocell based carbon fibers have better mechanical properties than do rayon based. WAXD experiments on the obtained carbon fibers show that the crystallinity of Lyocell-based carbon fibers is higher than that of rayon-based carbon fibers. It is concluded that Lyocell fibers are better precursors for carbon fibers than rayon. Since the thermal properties of Lyocell are different from those of rayon, the process of preoxidation of Lyocell should be adjusted from that used for a rayon precursor.

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