Nano-Carbon Black Filled Lyocell Fiber as a Precursor for Carbon Fiber

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ABSTRACT: In this work, Lyocell fibers filled with various amounts of carbon black were prepared. Wide angle X-ray diffraction (WAXD) results showed that carbon black filled Lyocell fibers still had a cellulose II crystal structure and kept the characteristic peak of carbon black at the same time. The results of mechanical properties showed a slight reduction in the carbon black filled Lyocell fiber. Moreover, the heat stabilities of the carbon black filled Lyocell fibers showed no obvious change. The residue of carbon black filled Lyocell fiber at 1000°C was higher than that of Lyocell fiber, implying higher carbon yield could be obtained for the carbon black filled Lyocell precursor. Scanning electron microscopy (SEM) experiments showed that the surface and the cross section of carbon black filled Lyocell fiber were smooth and round, which are consistent with the carbon fiber precursor. The WAXD pattern of carbon black filled Lyocell-based carbon fiber was different from that of Lyocell-based carbon fiber. The addition of carbon black transfers the diffraction peak of carbon fiber while keeping the characteristic structure of carbon black. The results of mechanical properties of carbon fibers show that, if an appropriate amount of carbon black was chosen, carbon fiber with better properties than Lyocell-based carbon fiber could be obtained by using the carbon black filled Lyocell fibers as the precursor. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 65–74, 2006

Key words: carbon black fillers; Lyocell fibers; mechanical properties; morphology; structure

INTRODUCTION

It is well known that carbon fibers can be made from cellulose, polyacrylonitrile (PAN), and pitch precursors. Although cellulose-based carbon fiber was manufactured first in the 1950s, applications are limited due to the low yield and high cost.[1] At present, the volume of cellulose-based carbon fiber is very small (approximately 1 ~ 2% of the total). However, cellulose-based carbon fiber has unique characteristics, such as low thermal conductivity, low density, high purity (low alkaline metal ion content), excellent ablation resistance, and high flexibility. Therefore, the cellulose-based carbon fiber can be used in special fields which other carbon fibers cannot satisfy, such as space flight and the aviation industry.[2] During the past several decades, numerous research studies have been carried out to improve the mechanical properties and yield of cellulose-based carbon fibers and eliminate pollution problems.[2–5]

Most cellulose-based carbon fibers are made from textile-grade rayon and viscose rayon.[6] However, the viscose rayon process is declining because of pollution problems. Lyocell fiber is a new kind of regenerated cellulose fiber, and its production process is simple and environmentally friendly.[6] Compared with rayon fiber, Lyocell fiber has higher tenacity and modulus, lower shrinkage, and better thermal stability, and the crystallinity and orientation degree of Lyocell fiber are higher than those of rayon.[2,7,8] Moreover, the cross section of Lyocell fiber is round, and the fineness of the fiber is easy to control. Peng and coworkers[2] have shown that Lyocell fiber can be used as the precursor of carbon fiber, and that the properties of Lyocell-based carbon fiber are better than those of rayon-based carbon fiber under the same processing conditions.

The carbon yield of cellulose-based carbon fibers is low (only 20% by comparison with 45% of PAN and 85% of pitch). To increase this yield, it is reasonable to propose that carbon black filled Lyocell fibers can increase the carbon yield of Lyocell-based carbon fiber. The advantages of the Lyocell process are that fiber defects, caused by foreign particles, do not impair the spinnability and that fast structure consolidation forms stable filaments, which can be utilized to produce carbon black filled Lyocell fiber.[9] At present, the carbon filled Lyocell fiber has only been studied by TITK in Germany, used for producing electrically conductive filaments.[9,10] According to the Alceru process of TITK, it is possible to fill cellulose filaments with

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finely dispersed conductive carbon black at concentrations up to > 200% with respect to the cellulose content without disturbing the fiber formation.[9] However, no work has been reported on the investigation of carbon black filled Lyocell fibers to be used as the precursor of carbon fibers until now. Zhang and coworkers[11,12] studied the effect of carbon black additives on the PAN precursor; the results showed that the addition of carbon black had a small influence on the spinnability of PAN and did not change the molecular structure of PAN. Moreover, the incorporation of carbon black can increase the amount of mesopores of the resulting activated carbon fiber. Therefore, it is feasible to prepare carbon filled Lyocell fiber for use as a precursor of carbon fiber. In this work, Lyocell fibers filled with various amounts of carbon black were prepared and studied. Based on these Lyocell fibers, carbon fibers were produced and investigated to estimate the effects of the carbon black additive on the structure and properties of Lyocell-based carbon fibers.

EXPERIMENTAL

Materials

Cotton pulp (DP = 488, α-cellulose content 98%, Baoding Chemical Fiber Co., China), *n*-propyl gallate (reagent grade, Shanghai Chemical Co., China), *N*-methylmorpholine-*N*-oxide (NMMO) aqueous solution (50 wt %) (BASF AG, Germany), and nano-carbon black dispersed aqueous solution (average particle size of carbon black < 10nm, solid content 0.4%) (Xiangfan Dongyi New Technology Development Co. Ltd, China) were used in this study.

Spinning equipment

1. A simple single filament spinning equipment without a metering pump was used in the spinning process (see Spinning Process A below).
2. Multi-filament spinning equipment with a metering pump was used in the spinning process (see Spinning Process B below).

Preparation of Lyocell fibers

Spinning process A

NMMO solution distilled to 74 wt % and a certain amount of carbon black dispersed solution were mixed and stirred for 3 h. The mixture was distilled under vacuum to remove extra water to obtain NMMO monohydrate/carbon black solution. The NMMO monohydrate/carbon black solution, cellulose pulp, and *n*-propyl gallate (antioxidant, 0.1 wt % with respect to the cellulose content) were also mixed and stirred continually for 3 h under the temperature of 100°C by using an oil bath. The mixture gradually turned into a homogeneous solution, and solutions with 10 wt % cellulose in NMMO · H_2O with different carbon black contents were obtained.

The obtained solution was spun at 100°C by the spinning equipment listed above after deaeration. The spinning solution was extruded through a spinneret 0.145mm in diameter, and then passed through an air gap of 50 mm in length and immersed in a coagulation bath of water to precipitate cellulose in filament form. The filaments were washed with water, wound, and dried. Then, Lyocell fibers containing various amounts of carbon black were prepared.

Spinning process B

NMMO solution distilled to 74 wt % and a certain amount of carbon black dispersed solution were mixed and stirred for 3 h. The mixture was distilled under vacuum to remove extra water to obtain 74% NMMO/carbon black solution. Then the NMMO/carbon black solution, cellulose pulp, and *n*-propyl gallate (antioxidant, 0.1 wt % with respect to the cellulose content) were mixed and transferred to a spinning tank, for which the temperature was set at 90 ~ 95°C. Then the extra water was distilled under vacuum to obtain a homogeneous cellulose/NMMO · H_2O/carbon black spinning solution. Cellulose content in the obtained spinning solution was 10 wt % in all solutions.

The spinning solution with the temperature of 90 ~ 93°C was extruded by a gear pump and then through a spinneret with 100 orifices (0.08mm in diameter). The spinning solution was passed through an air gap of 50 mm in length and immersed in water to obtain the cellulose filament.

The carbon black content of the Lyocell fiber was determined according to the initial addition content of carbon black, because no carbon black was found in the coagulation bath indicating that carbon black was retained in the Lyocell fiber completely. In this article, the carbon black content was calculated with respect to the cellulose content.

Preparation of carbon fibers

Precursors were first washed with water and afterwards with an acid aqueous solution. They were then impregnated with catalyst and preoxidized at 105, 150, 200, and 250°C for 20 min each in air. All these steps were performed in an experimental line in our laboratory. The preoxidized carbon fiber precursor was then carbonized in a laboratory scale carbonizing line under 600°C first and 1300°C afterwards in a nitrogen atmosphere for a certain time, giving carbon fibers.

Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction investigation was performed on a D/MAX-γB diffractometer (Rigaku, Japan) (CuK_α λ = 0.154nm).

Thermal gravimetric analysis (TGA)

TGA of precursors was performed on an STA 429C TGA balance (Netzsch, Germany) in a nitrogen atmosphere. The weights of samples were 5 ~ 8 mg, the scan rate was maintained at 10°C/min, and the range of temperature was 50 ~ 1000°C.

Mechanical properties of precursors and carbon fibers

The mechanical properties of Lyocell precursors were measured with an XQ-1 Tensile Tester (China Textile University, China). The sample length was 20mm, and the extension rate was set at 8 mm/min. The mechanical properties of carbon fibers were measured on an Instron5565 tester (Instron, Grove City, PA). The sample length and extension rate were set at 10mm and 1mm/min, respectively. All measurements were performed at 20°C and 65% relative humidity.

Morphological characterization

The surfaces and the cross sections of the precursors and the carbon fibers were observed using a JSM-5600LV scanning electron microscope (SEM) (JEOL Co., Japan).

Elemental analysis

The elemental analyses of the obtained carbon fibers were carried out on a VAEIO EL III element analyzer (Elmentar Analysensysteme Gob Co., Germany).

RESULTS AND DISCUSSION

WAXD of precursors

Powder WAXD patterns of Lyocell fibers containing various amounts of carbon black are illustrated in Figure 2. WAXD patterns of these fibers show intense diffraction peaks at 2θ = 11.8°, 20.2°, and 21.8°, corresponding to the characteristic peaks of (101), (10$\bar{1}$), and (002) planes of the monoclinic unit cell of cellulose. It can be seen that carbon black filled Lyocell fibers still have cellulose II crystal structure. From the powder WAXD pattern of carbon black (Fig. 3), it can be found that carbon black has characteristic diffraction peaks at 2θ = 21.8° and 26.4°. The carbon black filled Lyocell fiber also shows a diffraction peak at 2θ = 26.4°, and the intensity of this peak increases with the addition of carbon black. Furthermore, the peak composed of the (10$\bar{1}$) and (002) planes of cellulose separates gradually and the peak of the (002) plane increases with increasing of the amount of carbon black because the characteristic peak of carbon black at 2θ = 21.8° is superposed with the (002) plane of cellulose. Accordingly, it can be confirmed that carbon black has been added to the cellulose fiber and is not changed during the whole process.

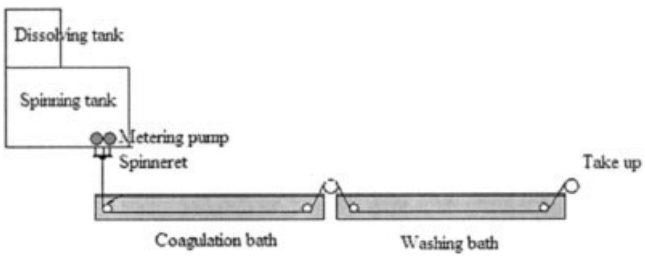

Figure 1. Schematic drawing of the multi-filament spinning equipment.

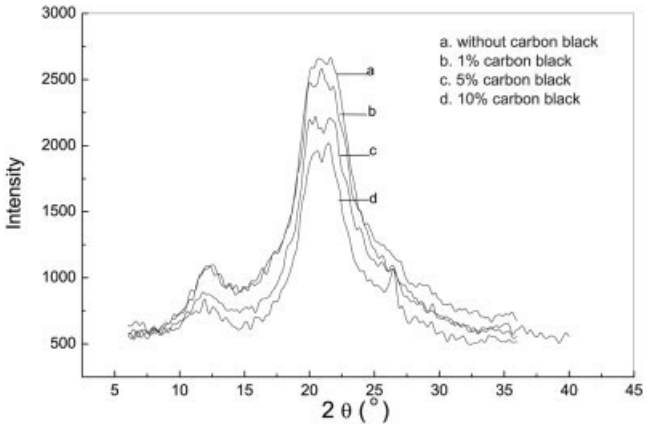

Figure 2. WAXD patterns of carbon black filled Lyocell fibers.

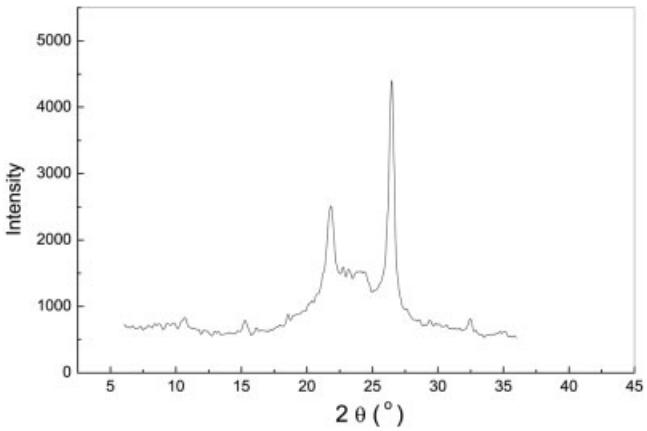

Figure 3 WAXD pattern of carbon black.

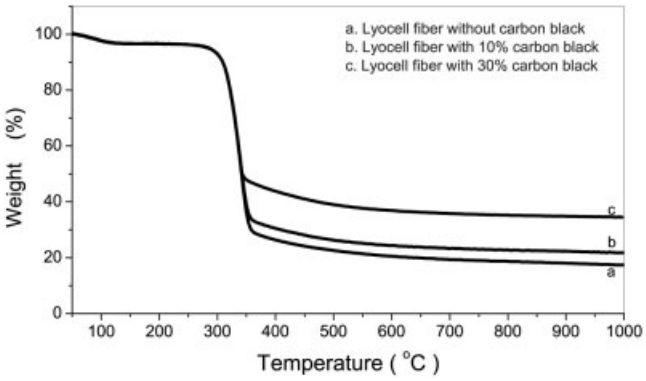

Figure 4 TGA curves of Lyocell precursors.

TGA of precursors

TGA curves for the Lyocell fibers filled with 10%, 30% carbon black and without carbon black are given in Figure 4. It may be seen that all Lyocell fibers begin to degrade at about 270°C, and the weight losses for the three Lyocell precursors take place in a narrow range of temperature from 270 to 350°C. Three curves overlap when the temperature is lower than 350°C, which shows that the three precursors have similar thermal properties. Then, the difference appears as the temperature is further increased. The residues of Lyocell fiber filled with 10% carbon black and 30% carbon black are about 21.78% and 34.53% at 1000°C, respectively, which are higher than that of Lyocell fiber (17.39%). TGA has been used to assess the suitability or performance of various precursors in terms of carbon yield.[13,14] Therefore, the above results show that the carbon yield obtained on the carbonization of the Lyocell precursor can be improved by the addition of carbon black.

Mechanical properties of precursors

The mechanical properties of carbon black filled Lyocell fibers prepared from spinning process A are listed in Table I. It can be seen that the tensile strength and the initial modulus of Lyocell fibers filled with carbon black decreases slightly, whereas the elongation at break increases. The higher the carbon black content, the higher the elongation at break of the fiber is (in our experimental range 1–10%). One of the possible reasons is that the carbon black additive acts as a solid phase lubricant among cellulose chains and can weaken the intermolecular force of cellulose. Therefore, the tensile strength and modulus of carbon black filled Lyocell fibers decrease.

It can also be found from Table I that the mechanical properties of the obtained Lyocell fibers are not very good. The reason may be that there was no metering pump in the spinning equipment listed in 1 and the diameter of the used spinneret is too big. To prepare carbon black filled Lyocell fibers with better properties, the spinning equipment described as 2 above was used for further investigating the mechanical properties of carbon black filled Lyocell fibers prepared from different spinning processes.

TABLE I
Mechanical Properties of Carbon Black Filled Lyocell Fibers Prepared by Spinning Process A

Mechanical properties	Lyocell fiber	1% carbon black filled Lyocell fiber	5% carbon black filled Lyocell fiber	10% carbon black filled Lyocell fiber
Tensile strength (cN/dtex)	2.45	2.05	2.02	1.99
Initial modulus (cN/dtex)	26.1	25.8	26.1	20.2
Elongation at break (%)	8.9	9.2	9.9	11.2

Spinning process: Pressure, 0.4 Mpa; Air gap, 5.0 cm; Coagulation bath, water; Draw ratio, 1.9; Spinneret diameter: 0.145 mm.

The tensile strength and initial modulus of carbon black filled Lyocell fibers prepared from spinning process B are listed in Tables II and III, respectively. It may be seen that the tensile strength and initial modulus of Lyocell fiber improve with the increase of the draw ratio, and reached a peak when the draw ratio was 2.60. Then the tensile strength and initial modulus decrease as the draw ratio is further increased. The same case only appears in the Lyocell fiber filled with 1% carbon black, whereas the tenacity shows the extremum when the draw ratio is 2.86. As the content of carbon black is higher than 1%, the mechanical properties of the fiber improve with the increased draw ratio in our experiment range. The

TABLE II
Tensile Strengths of Carbon Black Filled Lyocell Fibers Prepared by Spinning Process B

	Tensile strength (cN/dtex)			
Draw ratio	Lyocell fiber	1% carbon black filled Lyocell fiber	5% carbon black filled Lyocell fiber	10% carbon black filled Lyocell fiber
1.60	3.90	3.44	—	—
2.28	4.16	3.59	3.27	3.13
2.60	4.67	4.37	3.76	3.58
2.86	4.41	5.06	4.04	3.82
3.38	3.89	4.50	4.13	3.88
3.71	—	—	4.70	4.62

TABLE III
Initial Moduli of Carbon Black Filled Lyocell Fibers Prepared by Spinning Process B

	Initial modulus (cN/dtex)			
Draw ratio	Lyocell fiber	1% carbon black filled Lyocell fiber	5% carbon black filled Lyocell fiber	10% carbon black filled Lyocell fiber
1.60	35.4	30.2	—	—
2.28	40.0	33.0	27.8	25.4
2.60	45.5	35.7	29.7	27.8
2.86	42.1	48.2	32.6	29.1
3.38	40.5	48.3	34.2	31.0
3.71	—	—	37.1	35.0

possible reason is that the carbon black acts as the solid phase lubricant in the spinning process of carbon black filled Lyocell fiber, which makes the optimal draw ratio increase. The reason why there is no extremum for the Lyocell fiber filled with higher carbon black content may be that the draw ratio of the spinning process in our experiment is too small to reach the optimal draw ratio.

In addition, it can be found from Tables II and III that the tensile strength and initial modulus of carbon black filled Lyocell fibers decrease with the addition of carbon black. The higher the carbon black content is, the worse are the mechanical properties of the fiber, which is consistent with the results of spinning process A. It can also be seen that the mechanical properties of Lyocell fiber filled

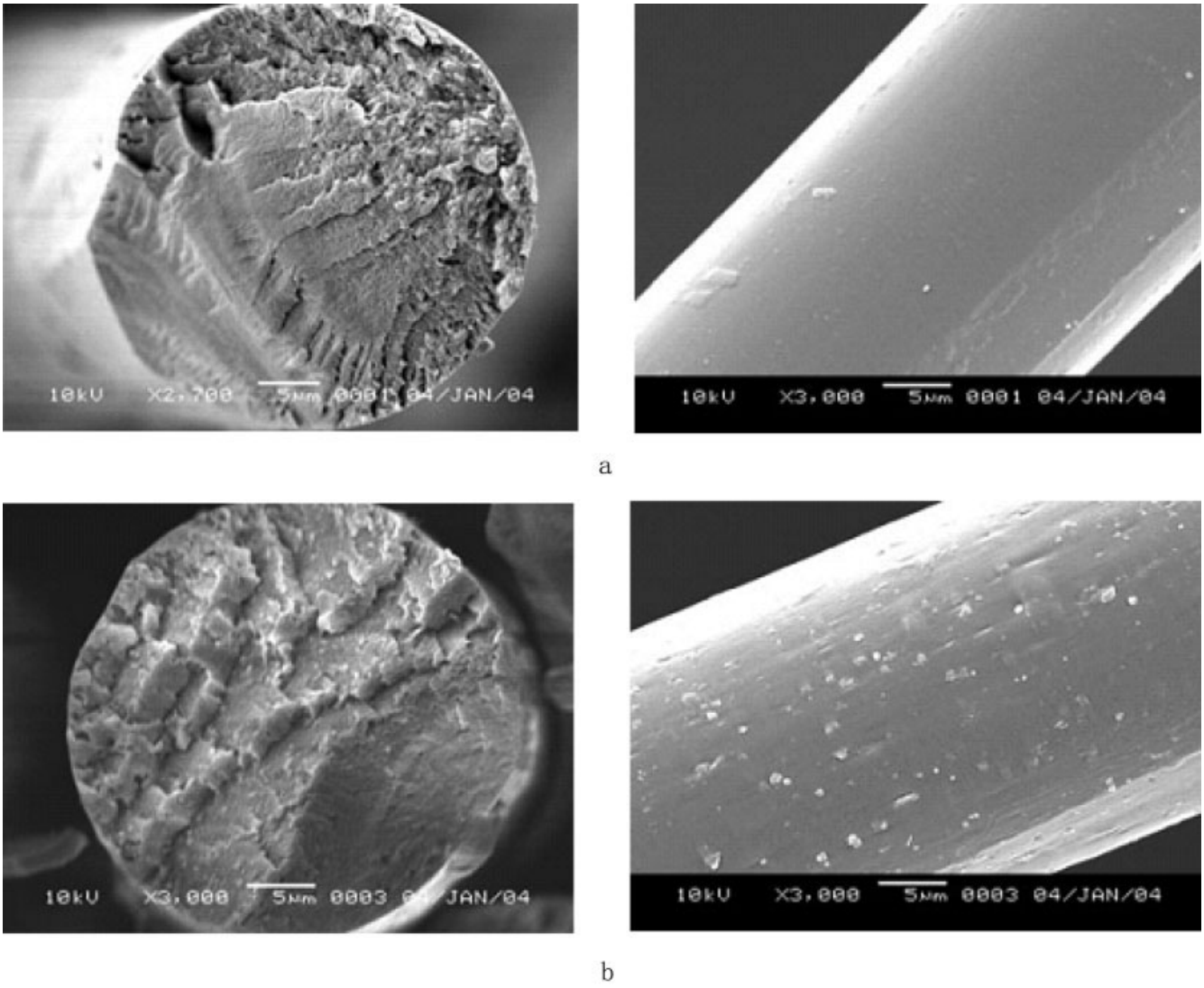

Figure 5 SEM photographs of surfaces and cross sections of Lyocell precursors prepared by spinning process A (×3000): (a) Lyocell fiber, (b) 10% carbon black filled Lyocell fiber.

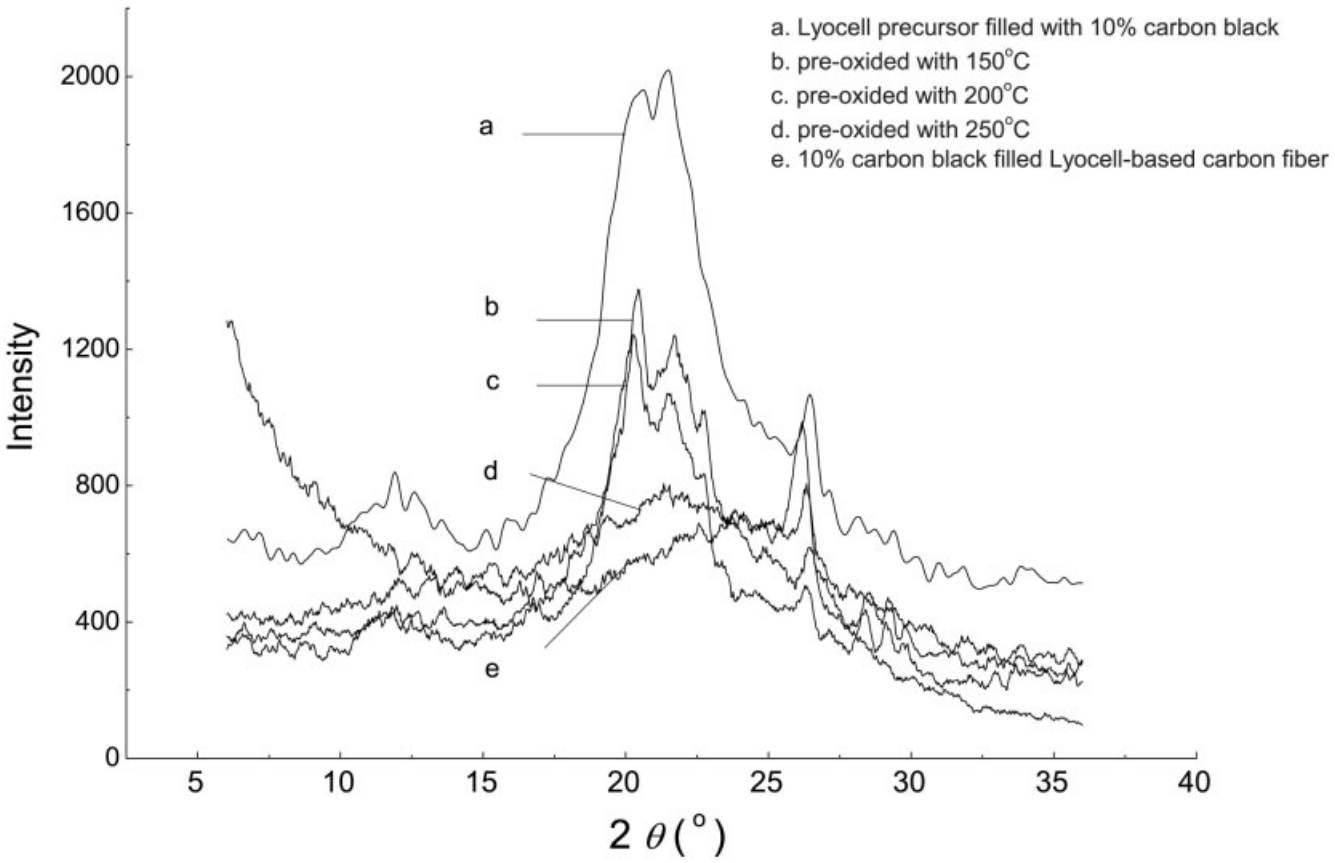

Figure 6 WAXD patterns of 10% carbon black filled Lyocell precursor and fibers treated with different temperatures of preoxidization and carbonization.

with 1% carbon black fiber are not lower than those of the Lyocell fiber when the draw ratio is more than 2.86.

Morphology of the precursors

It is known that a good precursor for carbon fiber always has the following characteristics: a round cross section, fine denier, high strength, and few physical defects. Figure 5 shows SEM photographs of Lyocell fibers filled with 10% carbon black and without carbon black that are prepared from spinning process A. We can see clearly that the surface of the carbon black filled Lyocell fiber is as smooth as the Lyocell fiber. Only some carbon black agglomerates are shown on the surface of the carbon black filled Lyocell fiber. Furthermore, the two precursors have round cross sections no matter whether carbon black is added or not. It can be seen that there are many microvoids in the cross section of the Lyocell fiber, whereas the cross section of the carbon black filled Lyocell fiber is compact and almost no microvoids can be seen. As a result, the carbon black filled Lyocell fiber is consistent with carbon fiber precursor.

WAXD of carbon black filled Lyocell fiber and fibers treated with different temperatures of preoxidization and carbonization

Figure 6 shows WAXD patterns of 10% carbon black filled Lyocell precursor and fibers treated with different temperatures of preoxidization and carbonization. It is known that Lyocell fiber has a cellulose II crystalline structure, which is a monoclinic unit cell. It can be seen that there are intense peaks corresponding to the characteristic planes of cellulose. WAXD of the samples treated at 150°C and 200°C show a reduction in peak intensity at $2\theta = 11.8°$, whereas the diffraction peaks at $2\theta = 20.3°$ and 21.8° become sharp and the intensities of these two peaks decrease markedly. It can be thought the crystalline region begins to be destroyed, whereas the change is only a quantitative change and the crystalline structure of cellulose has been unchanged due to the similar figure of these two curves.

The crystalline region of fiber treated at 250°C is badly destroyed. The X-ray diffraction peak shows no obvious crystalline peak, and 2θ is transferred to 22.0°, which means it is a qualitative change and the monoclinic unit cell of cellulose does not exist anymore.

TABLE IV
Elemental Analyses of Obtained Carbon Fibers (mass fraction, %)

Carbon fibers	C	H	N
Lyocell-based carbon fiber	96.45	0.187	1.278
10% carbon black filled Lyocell-based carbon fiber	96.28	0.211	1.196

The diffraction peak of the carbon fiber carbonized at low temperature of 600°C and high temperature of 1300°C is not very sharp, which shows that the crystallinity of the carbon fiber is low and the crystal size of the graphite crystal is small, that is, the carbon fiber has a disorderly graphite structure.

It can also be found from Figure 6 that the diffraction peak at $2\theta = 26.4°$, the characteristic peak of carbon black, always exists in carbon black filled Lyocell fiber treated with different temperatures and the resultant carbon fiber, which means that the structure of carbon black has been preserved during the process of preparing the carbon fiber.

Elemental analyses of carbon fibers

Table IV shows the results of elemental analyses of two carbon fibers. It is evident that carbon fibers with at least 96% carbon content can be prepared from both Lyocell fiber filled with 10% carbon black and without carbon black by using the same process.

WAXD of carbon fibers

Figure 7 shows the powder WAXD patterns of two kinds of carbon fibers. It can be seen that they are distinctly different. The Lyocell-based carbon fiber without carbon black shows a diffraction peak at $2\theta = 22°$, corresponding to the characteristic peak of the (002) plane of carbon fiber. However, the diffraction peak of the 10% carbon black filled Lyocell-based carbon fiber is transferred to about 24°. Furthermore, curve b has a new intense diffraction peak at $2\theta = 26.4°$, which is the characteristic peak of carbon black. Therefore, the carbon black filled Lyocell-based carbon fiber retains the original structure of carbon black and Lyocell-based carbon fiber.

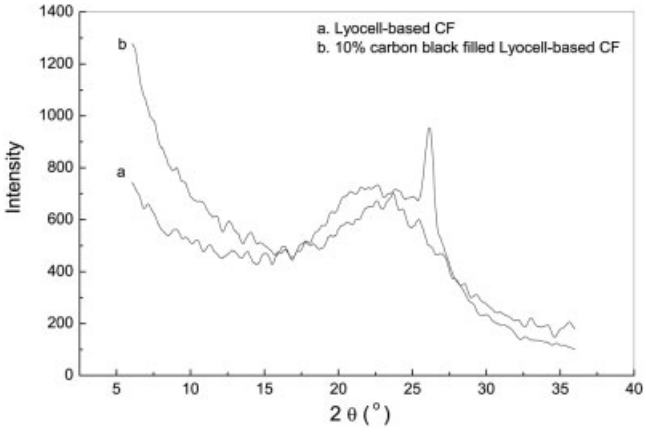

Figure 7 WAXD patterns of two carbon fibers.

TABLE V
Mechanical Properties of Carbon Fibers Using the Lyocell Fibers Prepared by Spinning Process A as the Precursors

Mechanical properties	Lyocell-based carbon fiber	1% carbon black filled Lyocell-based carbon fiber	5% carbon black filled Lyocell-based carbon fiber	10% carbon black filled Lyocell-based carbon fiber
Tensile strength (GPa)	0.22	0.16	0.26	0.27
Modulus (GPa)	13.0	9.6	16.7	18.5
Elongation at break (%)	1.1	1.1	1.2	1.1

Mechanical properties of carbon fibers

The mechanical properties of carbon fibers prepared from the Lyocell fibers filled with various amounts of carbon black, which are obtained by spinning process A, are listed in Table V. It may be seen that the higher the content of carbon black fill in the Lyocell fiber, the better the mechanical properties of the carbon fiber, except for the low addition of carbon black (1%).

By comparison with general rayon-based carbon fiber, it can be found that the mechanical properties of carbon fibers in Table V are not very good. The reason

TABLE VI
Mechanical Properties of Carbon Fibers Using the Lyocell Fibers Prepared by Spinning Process B as the Precursors

Mechanical properties	Lyocell-based carbon fiber	5% carbon black filled Lyocell-based carbon fiber	10% carbon black filled Lyocell-based carbon fiber
Tensile strength (GPa)	0.49	0.57	0.71
Modulus (GPa)	37.6	48.3	58.8
Elongation at break (%)	1.4	1.2	1.5

Spinning process of precursors: Air gap, 5.0 cm; Draw ratio, 2.6; Spinneret, 100 × 0.08 mm.

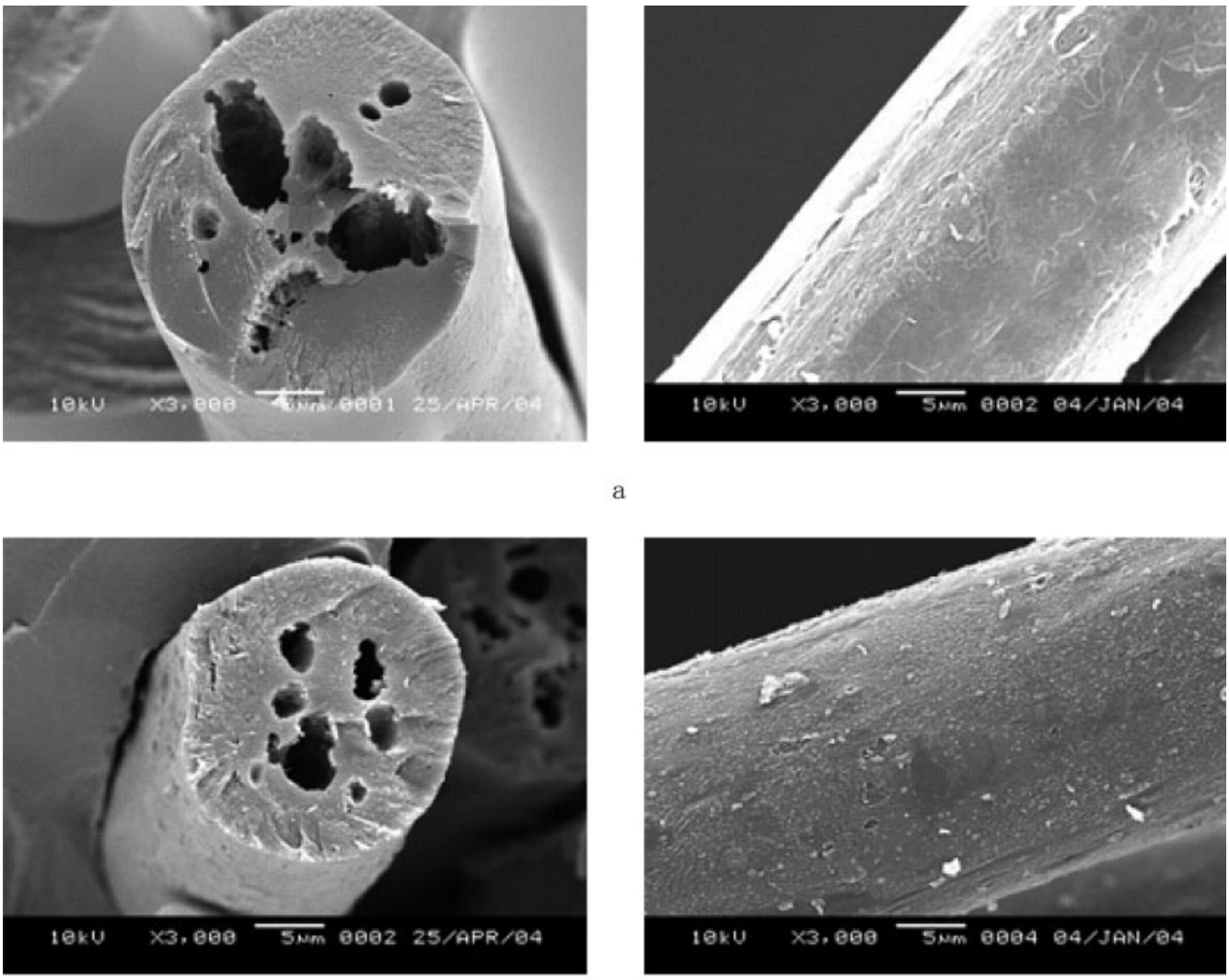

Figure 8 SEM photographs of surfaces and cross sections of Lyocell-based carbon fibers using Lyocell fibers prepared by spinning process A as the precursors (×3000): (a) Lyocell-based carbon fiber, (b) 10% carbon black filled Lyocell-based carbon fiber.

is that the Lyocell precursor is coarse due to the experimental equipment and the spinning process. Therefore, the mechanical properties of the precursor and the resultant carbon fiber are poor. To obtain carbon black filled Lyocell-based carbon fiber with better mechanical properties, the Lyocell fibers spun by process B are used to prepare the carbon fiber.

Table VI lists the mechanical properties of these carbon fibers. We can see clearly that the mechanical properties of 5 and 10% carbon black filled Lyocell-based carbon fiber are much higher than those of non carbon black filled Lyocell-based carbon fiber. Moreover, the higher the content of carbon black fill, the better the mechanical properties of the carbon fiber, which is consistent with the data of Table V. Therefore, we can draw a conclusion from Tables V and VI that it is possible to prepare carbon fiber with better properties than the Lyocell-based carbon fiber by using the carbon black filled Lyocell fiber as the precursor.

Since the addition of carbon black has little influence on the spinnability of Lyocell fiber, it may be an effective way to improve carbon yield and mechanical properties of Lyocell-based carbon fiber by increasing the content of carbon black fill in the Lyocell fiber.

The reason why the addition of carbon black can improve the mechanical properties of the resultant Lyocell-based carbon fiber has not been very clear up to now. One of the possible reasons is that there are many microvoids in the cross section of Lyocell fiber, whereas the carbon black filled Lyocell fiber is compact and almost no microvoids can be seen. We know that the morphology structure of the precursor, especially the microvoids and crevices, greatly affects the

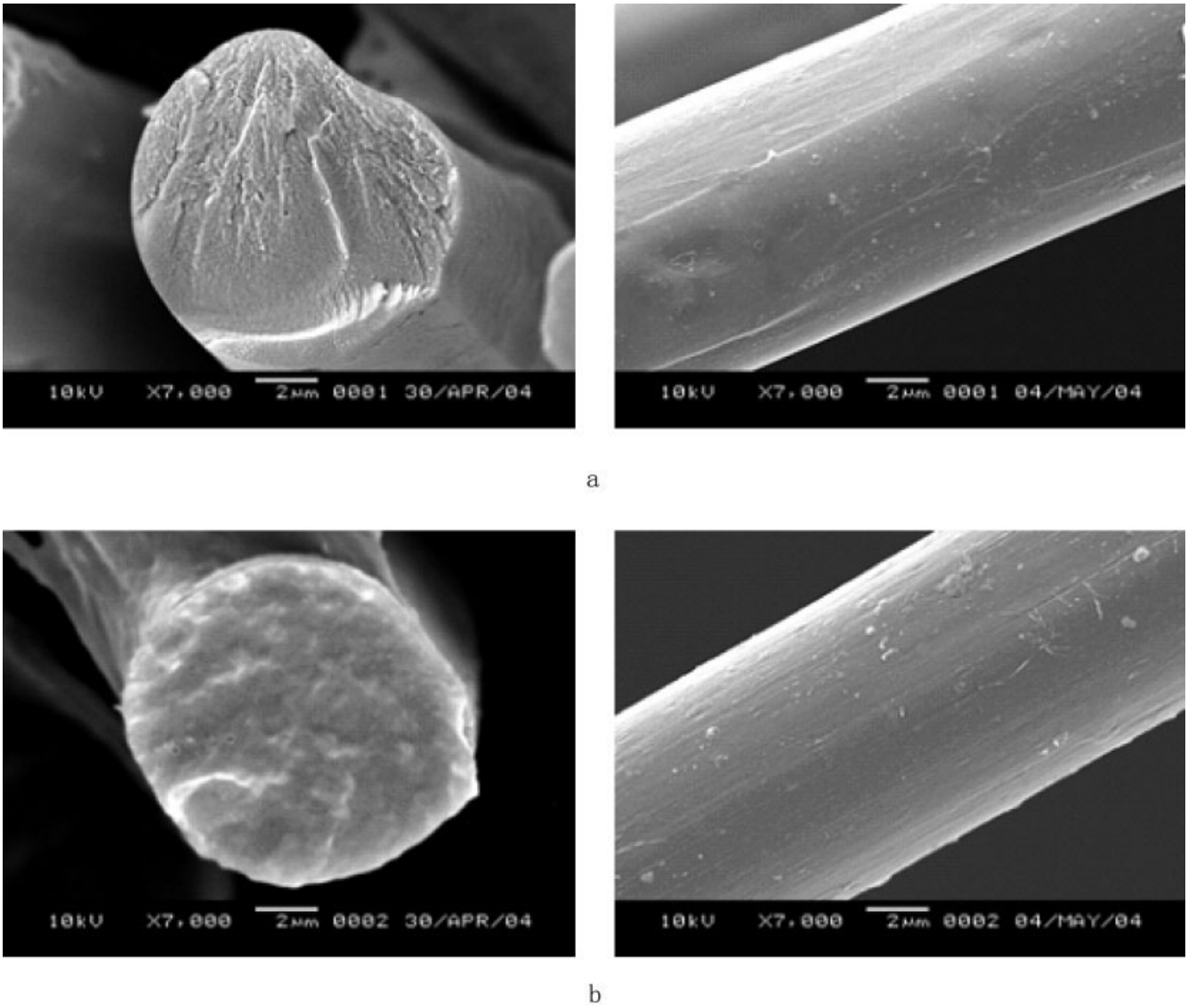

Figure 9 SEM photographs of surfaces and cross sections of Lyocell-based carbon fibers using Lyocell fibers prepared by spinning process B as the precursors (×7000): (a) Lyocell-based carbon fiber, (b) 10% carbon black filled Lyocell-based carbon fiber.

properties of the resultant carbon fiber. If the microvoids in the precursor remain in the final carbon fiber after the carbonization processes, the tensile strength of the carbon fiber would be decreased accordingly. Yin[15] thought the mechanical properties of carbon materials decreased as their porosities increased, and the correlations between the properties and the porosities were significant. Moreover, Konkin[16] thought the crevices and voids in the carbon fiber were the direct reasons for the reduction of the tensile strength. Therefore, the mechanical properties of carbon black filled Lyocell-based carbon fiber can be improved due to less voids in the precursor.

Morphology of the carbon fibers

Figure 8 shows SEM photographs of carbon fibers prepared from the Lyocell fibers obtained by spinning process A. It is evident that there are voids in the cross sections of two carbon fibers. The reason may be that the carbon fiber prepared by process A is coarse. Wu and colleagues[17] thought the coarser the precursor is, the higher the probability of voids and flaws in the precursor, and the more flaws reserved in the carbon fiber. In addition, Yue and coworkers[18] have studied the effect of fiber diameter on the structure and properties of carbon fiber. They found that coarse carbon fiber showed a hollow structure because the coarse precursor easily formed a core that tended to fuse and become hollow during the preoxidization process. It is confirmed that there are no voids in the cross section of carbon fiber with finer diameter that we have prepared with process B.

Figure 9 shows SEM photographs of carbon fibers prepared from the Lyocell fibers spun by process B. It

may be seen that the surfaces of two carbon fibers were all smooth without any obvious crevices and flaws. In addition, it also can be seen that the cross section of the non carbon black filled Lyocell-based carbon fiber is not as round as that of the carbon black filled Lyocell-based carbon fiber. Moreover, we can find by comparison of Figures 8 and 9 that the carbon fiber with compact structure and without voids can be prepared when the Lyocell precursor is fine, which also means the voids in Figure 8 are caused by the coarse precursor of the carbon fiber.

CONCLUSIONS

In this work, Lyocell fibers filled with various amounts of carbon black were prepared and used as the precursors of carbon fibers. WAXD results showed that the carbon black filled Lyocell fibers still have a cellulose II crystal structure and retain the characteristic peak of carbon black at the same time. Moreover, the heat stability of the carbon black filled Lyocell fiber is the same as that of the Lyocell fiber from TGA curves. The residues of carbon black filled Lyocell fibers at 1000°C are increased with the increase of the carbon black additive, which means that the carbon yield of carbon fiber can be increased by using the carbon black filled Lyocell fiber as the precursor. In addition, the tensile strength and initial modulus of the carbon black filled Lyocell fibers decrease slightly, whereas the elongation at break increases. SEM photographs show that the surface of the carbon black filled Lyocell fiber is as smooth as the Lyocell fiber. Furthermore, the two precursors have round cross sections no matter whether carbon black is added or not. Therefore, the carbon black filled Lyocell fiber is consistent with the carbon fiber precursor.

The carbon black filled Lyocell fiber preoxidized under different temperatures and resultant carbon fiber always have the characteristic peak of carbon black, that is, the structure of carbon black was preserved during the process of preparing the carbon fiber. The WAXD patterns of the carbon fibers show that the structure of the carbon black filled Lyocell-based carbon fiber is different from that of the Lyocell-based carbon fiber. In the range of our experiments, the higher the content of carbon black fill in the Lyocell fiber, the better the mechanical properties of the carbon fiber. Although there are some voids in the cross section of the coarse carbon fiber, the carbon fiber with compact structure and without voids is prepared when the Lyocell precursor is fine.

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