Effect of Heat Treatment on the Structure and Properties of Lyocell Fibers

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ABSTRACT: Lyocell fibers were heat-treated under different conditions. The tensile strength and initial modulus of the heat-treated Lyocell fibers increased sharply, whereas the elongation at break decreased. Moreover, applying tension to the fibers during the heat treatment further improved the tensile strength and initial modulus. In addition, the crystallinity of the heat-treated fibers increased slightly, and there was no obvious change with an increase in the tension; the general orientation of the heat-treated fibers increased, the crystalline orientation little changed, and the amorphous orientation improved. Also, the improved mechanical properties of the Lyocell fibers via the heat treatment could not be preserved for long. The reason may be that the crystalline structure of the Lyocell fibers was not destroyed and no new crystallites were formed during the heat-treatment process. Therefore, the heat-treated Lyocell fibers reverted to their original state with time because there was no crosslinking point to fix the orientation, although the cellulose molecules of the amorphous region of the Lyocell fibers were more oriented by the heat treatment with tension. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1738–1743, 2006

Key words: fibers; mechanical properties; supramolecular structures

INTRODUCTION

Lyocell fiber is a kind of regenerated cellulose fiber that is spun from cellulose solutions in *N*-methylmorpholine-*N*-oxide (NMMO) by a dry–wet process.[1] The liquid crystallite can be formed in a cellulose/NMMO · H_2O solution because cellulose is a semirigid chain polymer.[2,3] However, a spinning solution of Lyocell fiber is not liquid-crystallite under the existing spinning conditions (content of cellulose $< 15\%$). Even so, the whole spinning behavior of Lyocell fiber is similar to the liquid-crystalline spinning of aramid fiber.[4] For thermoplastic aramid fiber poly(p-phenylene terephthalamide) (PPTA), the crystallinity, orientation, and density can be increased and the structure of the fiber can be improved by a heat treatment, which make the mechanical properties of aramid fiber increase greatly.[5] Therefore, the effect of the heat treatment with tension on the Lyocell fiber has been studied.

Previous work on Lyocell fiber has been focused mainly on the dissolution,[6,7] spinning,[8–10] fibrillation,[11] and structure and properties,[12–14] whereas a few studies have been reported on the investigation of the effect of the heat treatment on the structure and properties of Lyocell fiber. The work of the Thuringian Institute of Textile and Plastic Research[16] in Germany has shown that stretching swollen Lyocell filaments might be an effective way of increasing the elastic modulus of Lyocell fiber, and the elastic modulus of Lyocell fiber could increase up to 50 and 80% via the stretching of fibers swollen with water and NaOH, respectively. Nevertheless, a combination of stretching and heat treatment was not discussed. Wei et al.[17] studied the effect of a dry temperature on the mechanical properties of Lyocell fiber. The results showed that the tenacity of the fiber improved with an increase in the dry temperature, the maximum appeared at 100°C; and then the tenacity of the Lyocell fiber decreased sharply with a further increase in the temperature, whereas the effect of tension on Lyocell fiber was not investigated. In this study, a set of heat-treatment devices was fabricated, and Lyocell filaments (trade name Newcell) produced by Akzo Nobel Co. (Rudolstadt, Germany) were used as raw materials; different heat-treatment experiments were conducted to determine the effect of the heat treatment with tension on the structure and properties of Lyocell fibers. In addition, the stability of the resultant properties of the heat-treated Lyocell fiber was also investigated.

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TABLE I
Mechanical Properties of a Single Newcell Fiber

Fineness (dtex)	Tensile strength (cN/dtex)	Initial modulus (cN/dtex)	Elongation at break (%)
1.66	3.51	43.1	7.5

EXPERIMENTAL

Materials

Lyocell filaments (166 dtex/100 f; Newcell, Akzo Nobel). The mechanical properties of a single fiber are listed in Table I.

Heat-treatment equipment

A sketch of a heat-treatment device is illustrated in Figure 1.

The diameter and length of the heat pipe were 50 mm and 80 cm, respectively, and the length of the heating region was 70 cm. During the heat-treatment process, the time of the heat treatment could be regulated by the adjustment of the rate of the feed roller and draw roller, and the temperature of the heat pipe was adjusted by the temperature controller. In addition, the tension of fibers, controlled by the rate of the feed roller and draw roller, was recorded by the tensiometer.

Heat-treatment mode

The Lyocell filaments were wound on a plastic tube and immersed in water for more than 2 h. Then, the tube was removed from water, and the filaments were heat-treated by passage through the heat pipe in the wetting state. Finally, the heat-treated fibers were put into a desiccator for 1 day, and then the properties and structure of the fibers were tested.

Mechanical properties of Lyocell fibers

The mechanical properties of Lyocell fibers were measured with an XQ-1 tensile tester (China Textile University, Shanghai, China). The sample length was 20 mm, and the extension rate was set at 4 mm/min. The statistical results came from more than 25 measurements for each specimen. All measurements were performed at 20°C and 65% relative humidity.

Wide-angle X-ray diffraction (WAXD)

A WAXD investigation was performed on a D/Max-γB diffractometer (Rigaku, Tokyo, Japan; Cu Kα wavelength = 0.154 nm) under the following experimental conditions: 40-kV voltage, 40-mA current, 8°/min scanning speed, and 6–40° scanning scale. The obtained data were analyzed with peak-fit software to calculate the crystallinity.

Birefringence measurements

Birefringence measurements of Lyocell fibers were performed on an Olympus XP51 optical polarized light microscopy with the aid of a model CTB Berek compensator (Olympus Co., Tokyo, Japan).

Determination of the orientation factor

The azimuthal intensity distribution of the equatorial reflections at 21.7° was used for determining the crystalline orientation factor (f_c) according to the following equation: $f_c = 1 - W_{1/2}/180$, where $W_{1/2}$ is the half-width of the azimuthal intensity distribution for the meridional reflection at the (002) plane. The amorphous orientation factor (f_a) was calculated with the Stein equation:

$$\Delta n = \alpha f_c \Delta n_{co} + (1 - \alpha) f_a \Delta n_{ao} \quad (1)$$

where Δn is the total fiber birefringence; α is the degree of crystallinity; and Δn_{co} and Δn_{ao} are the characteristic birefringences of the crystallite phase and the amorphous phase, respectively. $\Delta n_{co} = \Delta n_{ao} = 0.050$ is assumed.[18]

RESULTS AND DISCUSSION

Effect of the heat treatment on the structure and properties of Lyocell fibers

In this work, Lyocell fibers were first heat-treated and kept at a constant length with different treatment

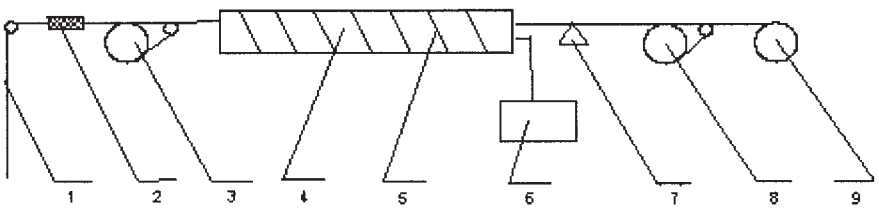

Figure 1 Sketch of the heat-treatment device: (1) Lyocell fibers, (2) tension bar, (3) feed roller, (4) heat pipe, (5) resistance coil, (6) temperature controller, (7) tensiometer, (8) draw roller, and (9) take-up machine.

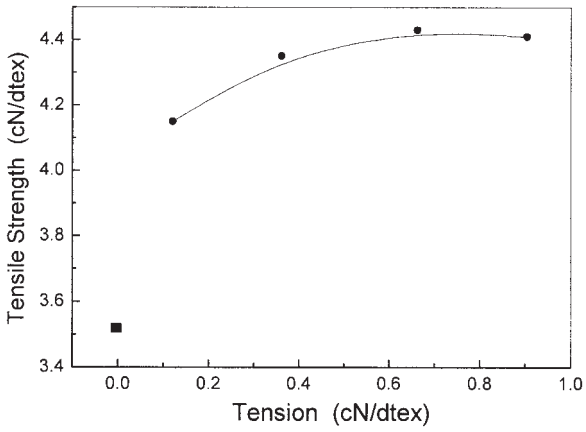

Figure 2 Effect of tension on the tensile strength of the Lyocell fiber.

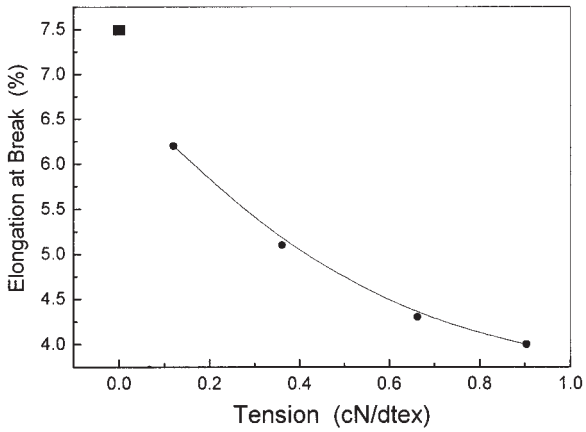

Figure 4 Effect of tension on the elongation of the Lyocell fiber.

times and temperatures, and the results show that the tensile strength and initial modulus of the treated Lyocell fibers increased sharply, whereas the elongation at break decreased. The tensile strength of the fibers reached a maximum when the treatment temperature was 160°C and the processing time was 12 s. On this basis, the Lyocell fibers were heat-treated with different tensions, and the effect of the heat treatment with tension on the structure and properties of the Lyocell fibers was investigated. The water-swollen cellulose chains showed a weaker interaction of chains that was similar to the addition of a plasticizer, which makes water-swollen Lyocell fibers exhibit a certain drawability.[19]

Figures 2–4 show the effect of the tension of the heat treatment on the tensile strength, initial modulus, and elongation of the Lyocell fibers, respectively. The tensile strength and initial modulus of the Lyocell fibers increased with increasing tension applied to the fiber during the heat treatment and then leveled off, whereas the elongation at break of the fibers decreased at the same time. The s–s curves of the Lyocell fibers heat-treated with different tensions are illustrated in Figure 5.

Figure 6 shows the effect of the tension of the heat treatment on the birefringence of the Lyocell fibers. The birefringence of the fibers improved slightly with an increase in the tension; that is, the general orientation of the Lyocell fibers increased with the tension slightly.

Figure 7 shows WAXD patterns for the heat-treated Lyocell fibers and Lyocell fibers without heat treatment, from which the crystallinity was calculated, and then the amorphous orientation was calculated from the birefringence and crystalline orientation with the Stein equation. The crystallinity and orientation of the freshly heat-treated Lyocell fibers and Lyocell fibers without the heat treatment are listed in Table II. The

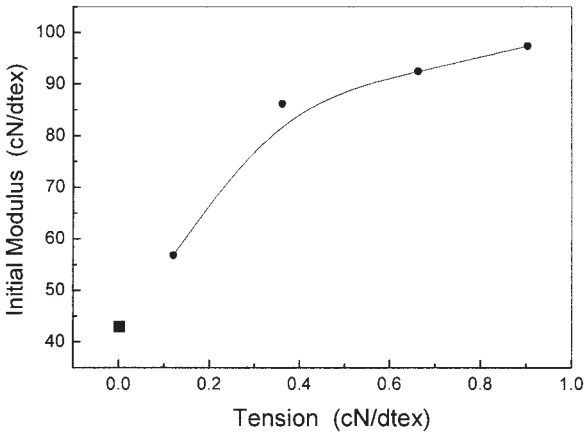

Figure 3 Effect of tension on the initial modulus of the Lyocell fiber.

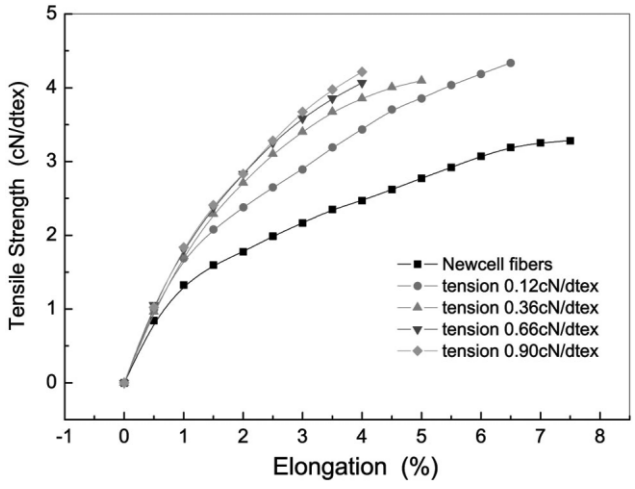

Figure 5 s–s curves of Lyocell fibers treated with different tensions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

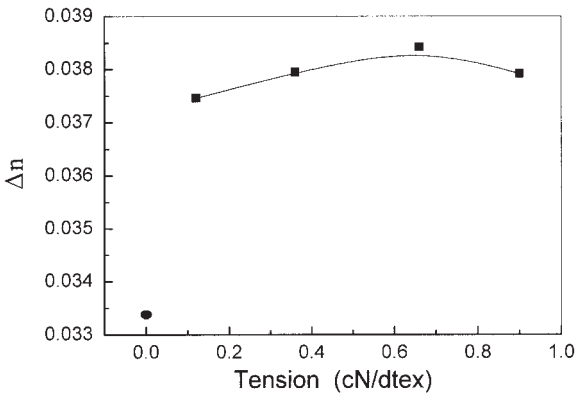

Figure 6 Effect of the tension of the heat treatment on Δn of the Lyocell fiber.

crystallinity of the heat-treated fibers increased slightly and was unchanged with an increase in the tension. In addition, the crystalline orientation of heat-the treated fiber changed little. Generally, the crystallinity of a thermoplastic crystalline polymer can be improved by the drawing process. However, the heat treatment of water-swollen Lyocell fibers with tension cannot destroy the crystallite and recrystallize because cellulose fiber is a nonthermoplastic polymer; therefore, the crystallinity of the Lyocell fibers was not improved with an increase in the tension during the heat-treatment process.

The general orientation of the treated Lyocell fibers increased, and the crystalline orientation almost remained constant, so the amorphous orientation of the fibers increased sharply. It is known that the tenacity of a fiber mainly relies on the amorphous orientation, and the modulus depends on the crystallinity and crystal orientation. For cellulose fibers, heat treatment with tension further improves the amorphous orientation, and semirigid chains are almost oriented; this increases not only the tenacity but also the modulus of the fibers.

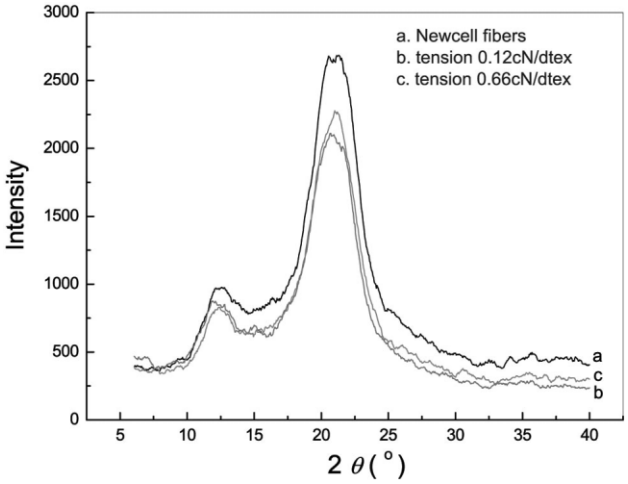

Figure 7 WAXD patterns for heat-treated Lyocell fibers and Lyocell fibers without heat treatment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Stability of the heat-treatment effect

The aforementioned results show that the tenacity and modulus of Lyocell fibers can be increased by a heat treatment, but the experimental data also show that the improved mechanical properties of heat-treated Lyocell fibers cannot be preserved for long. Figures 8 and 9 show the effect of the storage time on the tensile strength and initial modulus of heat-treated Lyocell fibers, respectively. The improved tenacity and modulus of the fibers declined with the storage time. When the storage time was more than 60 days, the mechanical properties of the Lyocell fibers were close to the state before heat treatment. To analyze the stability of the heat-treatment effect, the supramolecular structures of two heat-treated samples after 1 year of storage were studied, and the results are listed in Table II.

A comparison of the results from Table II shows that the crystallinity of heat-treated Lyocell fibers after 1 year of storage decreased slightly, and the crystalline orientation did not change. However, the general orientation, that is, the birefringence, of the fibers decreased greatly, and the amorphous orientation decreased accordingly. This indicates that the crystalline

TABLE II
Crystallinity and Orientation of Freshly Heat-Treated Lyocell Fibers and Heat-Treated Lyocell Fibers after 1 Year of Storage

		Freshly heat-treated Lyocell fibers		Heat-treated Lyocell fibers after 1 year of storage	
	Lyocell fibers without heat treatment	Heat-treated with tension of 0.12 cN/dtex	Heat-treated with tension of 0.66 cN/dtex	Heat-treated with tension of 0.12 cN/dtex	Heat-treated with tension of 0.66 cN/dtex
Δn	0.03326	0.03746	0.03842	0.03471	0.03522
α (%)	58.35	62.40	62.70	60.45	60.69
f_e	0.876	0.861	0.870	0.862	0.871
f_a	0.3699	0.5605	0.5976	0.4372	0.4462

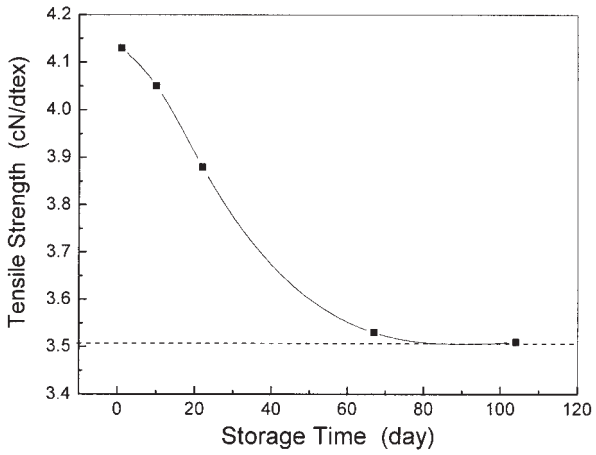

Figure 8 Effect of the storage time on the tensile strength of the heat-treated Lyocell fiber.

orientation and crystallinity of the heat-treated Lyocell fibers almost remained unchanged with an increase in the storage time; the change occurred only in the amorphous region. A possible reason is that the heat treatment with tension increased the amorphous orientation of the Lyocell fibers, but the improved tenacity and modulus of the fibers could not be fixed because there was no new crystallite formed and no physical crosslinking existed; therefore, the new oriented molecules in the amorphous phase relaxed little by little with time, and this made the tenacity and modulus of the fibers gradually revert to the state before the heat treatment.

Michels et al.[20] thought that the fiber formation of Lyocell fiber differs significantly from the spinning process of isotropic solutions or melts. They found that Lyocell fiber has a two-dimensional ordered structure comparable to the structure of liquid-crystalline polymers, the ordering in the third direction (complete formation of a meridional reflection) increases during drying with less than 60% water, and the cellulose crystallizes at the same time. That is, the crystallite of Lyocell fiber is formed by dehydration, the two-dimensional ordering of cellulose is easy to form during the spinning process, but it is difficult to form the three-dimensional ordering. The three-dimensional ordering is formed gradually with a decrease in the water content; that is, cellulose begins to crystallize when the distance between the layers of macromolecules of cellulose is shorter than that of the formation of a hydrogen bond. After the crystallite is formed, it cannot destroy the crystallite and recrystallize even if the Lyocell fiber is swollen in water and then drawn and heat-treated. It is different from the heat treatment of aramid fiber, which increases the crystallinity and crosslinking of the oriented rigid molecules and makes the mechanical properties of aramid fiber increase.

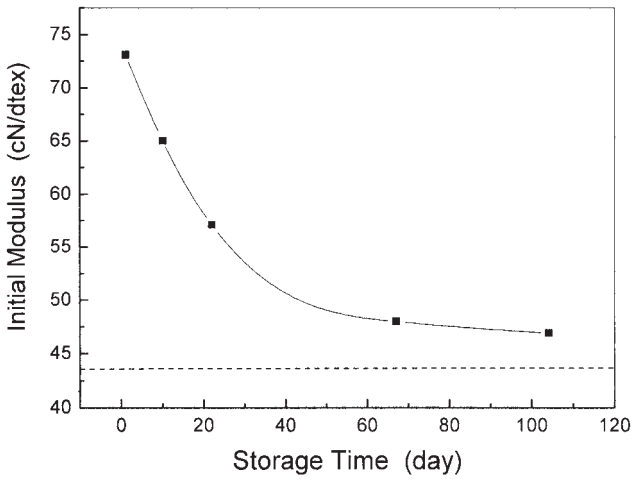

Figure 9 Effect of the storage time on the initial modulus of the heat-treated Lyocell fiber.

CONCLUSIONS

Lyocell fibers were heat-treated with a device fabricated by us. The results show that the tensile strength and initial modulus of heat-treated Lyocell fibers increase sharply, whereas the elongation at break decreases. Moreover, applying tension to the fibers during the heat treatment can further improve the tensile strength and initial modulus of Lyocell fibers. In addition, the crystallinity of heat-treated fibers increases slightly, the general orientation increases, the crystalline orientation changes little, and the amorphous orientation improves accordingly. Moreover, the improved mechanical properties of Lyocell fibers by heat treatment cannot be preserved for long; they revert to the original state by relaxation with an increase in the storage time because there is no crosslinking point to fix the orientation, although the molecules of the amorphous region of Lyocell fibers are more oriented by the heat treatment with tension.

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