

Comparison of the Structures and Properties of Lyocell Fibers from High Hemicellulose Pulp and High α -Cellulose Pulp

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ABSTRACT: Lyocell fibers were produced from a cheap pulp with a high hemicellulose content and from a conventional pulp with a high α -cellulose content. The mechanical properties, supermolecular structure, fibrillation resistance, and dyeing properties as well as the fibril aggregation size of the high hemicellulose Lyocell fiber and high α -cellulose Lyocell fiber were compared. The results showed that the high hemicellulose spinning solution could be processed at a higher concentration, which improved the mechanical

properties and the efficiency of the fiber process. Compared with the high α -cellulose Lyocell fiber, the high hemicellulose Lyocell fiber had better fibrillation resistance and dyeing properties. Therefore, it is feasible that this cheap pulp with a high hemicellulose content can be used as a raw material for producing Lyocell fibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 636–641, 2008

Key words: fibers; structure; mechanical properties

INTRODUCTION

Lyocell fiber has attracted great attention in the field of textiles since it was developed in the mid 1970s because Lyocell fiber technology is a relatively simple and environmentally friendly way to produce regenerated cellulose fiber in comparison with the conventional viscose process. However, the development of Lyocell fiber is always slow because of its relatively high manufacturing cost. Therefore, it is crucial to reduce the cost of the Lyocell process for its further development.

Pulp material containing more than 90% α -cellulose is called high α -cellulose pulp, and the pulp material containing more than 20% hemicellulose is called high hemicellulose pulp.^{1–3} In the conventional viscose process, only high α -cellulose pulp can be used as a material to obtain a high yield of viscose fiber. Up to now, the Lyocell fiber process has still followed this convention by using this kind of pulp material. However, the cost of this kind of high α -cellulose pulp is higher than that of high hemicellulose pulp. It would be significant in industry if this cheap pulp containing high hemicellulose could

be used to produce Lyocell fiber because the cost could be reduced to some degree.

Our previous work showed that Lyocell fiber could be made not only from high α -cellulose pulp but also from high hemicellulose pulp.⁴ Moreover, the yields of Lyocell fibers from high hemicellulose pulp and high α -cellulose pulp were approximately equal because most of the celluloses and hemicelluloses could be converted into fiber in the Lyocell process.⁴

In the current work, the structures and properties of Lyocell fibers produced from the cheap pulp with a high hemicellulose content and the conventional pulp with a high α -cellulose content were compared. The aim of this work was to investigate the influence of hemicellulose on the quality of Lyocell fibers and confirm the feasibility that this cheap pulp containing high hemicellulose could be used to produce Lyocell fibers.

EXPERIMENTAL

Materials

Pulp 1 was a high hemicellulose pulp (80% α -cellulose content, degree of polymerization (DP) = 547). It was supplied by Weyerhaeuser (Covington, WA).

Pulp 2 was a high α -cellulose pulp (91% α -cellulose content, DP = 633). It was purchased from Sappi Saiccor (Durban, South Africa).

The N-methylmorpholine-N-oxide (NMMO) aqueous solution provided by BASF (Ludwigshafen, Germany) had an initial water content of 50% (w/w).

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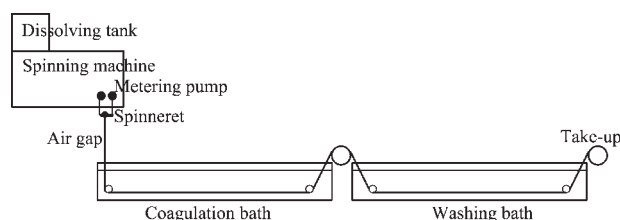


Figure 1 Schematic of the spinning process of Lyocell fibers.

n-Propyl gallate was purchased from Shanghai Chemical Corp. (Shanghai, China).

Two reactive dyes, Scarlet LS-2G and Blue P-3R, were provided by Cibacron (Uppsala, Sweden). Another reactive dye, Yellow K-6G, was obtained from YongQin Dye, Ltd. (Shanghai, China).

Spinning process of the Lyocell fibers

An NMMO aqueous solution with a water content of 26% (w/w), cellulose pulp, and *n*-propyl gallate (antioxidant) were put into a dissolving tank and mixed together. The mixture was heated to 100°C and stirred vigorously. At the same time, extra water in the mixture was distilled off under vacuum until the molar ratio of NMMO to water reached 1 : 1, and then a brown, transparent cellulose solution was prepared. Three solutions of different cellulose contents, that is, 11, 12, and 12.5% (w/w), were prepared.

The obtained cellulose spinning solution was transferred to a spinning machine. The temperature of the spinning machine was set at 105°C. The spinning solution was extruded through a spinneret with 100 orifices (each orifice was 80 μm in diameter) by a metering pump. The ejected spinning solution was drawn into an air gap (50 mm long) at a spinning speed of 100 m/min and then immersed in a coagulation bath to form cellulose filaments. The filaments were washed with water and dried in air. The schematic spinning process for the Lyocell fibers is shown in Figure 1.

Measurements of the mechanical properties of the Lyocell fibers

The mechanical properties of the 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 results came from more than 25 measurements of each specimen. All measurements were performed at a temperature of 20°C and 65% relative humidity.

Wide-angle X-ray diffraction (WAXD) measurements

WAXD was performed on a D/MAX-γB diffractometer (Rigaku, Tokyo, Japan; Cu Kα λ = 0.154 nm). The obtained data were analyzed with Peakfit software (Systat Software Inc., San Jose, CA) to calculate the crystallinity.

Birefringence measurements

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

Determination of the orientation factor

The azimuthal intensity distribution of the equatorial reflection at 21.7° was used for determining the crystalline orientation factor (f_c) according to the following equation:

$$f_c = 1 - W_{1/2}/180 \quad (1)$$

where $W_{1/2}$ is the full width at half-height of the azimuthal intensity distribution for the (002) plane.

Furthermore, the amorphous orientation factor (f_a) was calculated with the Stein equation:

$$\Delta n = \alpha f_c \Delta n_{co} + (1 - \alpha) f_a \Delta n_{ao} \quad (2)$$

where Δn is the total fiber birefringence, α is the crystallinity of fiber, and Δn_{co} and Δn_{ao} are the characteristic birefringences of the crystalline phase and amorphous phase, respectively. Here, it is assumed that $\Delta n_{co} = \Delta n_{ao} = 0.0545$.⁵

Measurement of the fibrillation resistance of the Lyocell fibers

The fibrillation resistance of the Lyocell fibers was determined by the wet-abrasion number, which increases nonlinearly as the fibrillation resistance increases.^{6,7} The schematic wet-abrasion test is shown in Figure 2.

The wet-abrasion number was measured as follows.^{6,7} The rotor speed was 2 m/min, and the pretension was 9.54×10^{-3} cN/dtex. A poplin cotton Ne 60 × 60 fabric was used to cover the rotating shaft, and water was dropped onto the fabric continuously. The titer of the Lyocell fiber was 2.67 dtex per filament, and each test bundle had 375 filaments. The wet-abrasion number was the mean of 25 measurements for each specimen.

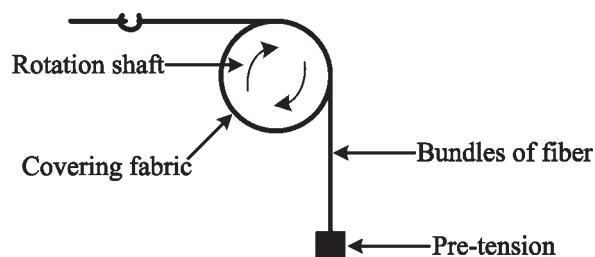


Figure 2 Schematic of the wet-abrasion test.

Measurement of the dyeing properties of the Lyocell fibers

The Lyocell fibers were dyed with the standard dyeing method (GB 2391-80) of the People's Republic of China.⁸

The dye exhaustion [E (%)] was calculated as follows:

$$X = \frac{B \times 100}{A \times n} \quad (3)$$

$$E = 100 - X \quad (4)$$

where X is the dye content in the dye residual solution (%), A is the absorbance value of the diluted dye standard solution, B is the absorbance value of the diluted dye residual solution, and n is the diluted ratio of the dye standard solution to the dye residual solution.

Moreover, the dye fixing [F (%)] was obtained according to the following equation:

$$Y = \frac{D \times 100}{C \times n} \quad (5)$$

$$F = E - Y \quad (6)$$

where Y is the unfixed dye content in the soaping residual solution (%), C is the absorbance value of the diluted soaping standard solution, D is the absorbance value of the diluted soaping residual solution, and n is the diluted ratio of the soaping standard solution to the soaping residual solution.

All absorbance values were measured with a UV-3000 spectrophotometer (Shimadzu, Kyoto, Japan).

Determination of the fibril size and fibril aggregation size

The fibril size and fibril aggregation size of the pulps and fibers were estimated by cross-polarization/magic-angle-spinning carbon 13 nuclear magnetic resonance spectroscopy.

The pulps and fibers were subjected to chlorite delignification followed by hydrolysis for 8 h in 2.5M HCl at 100°C, after which the spectra were recorded for wet samples (water content: 40–60 wt %) with a DSX-300 instrument (Bruker, Karlsruhe, Germany).^{9–11}

The recorded spectra were fitted by the model and method reported by Larsson and coworkers,^{9,10,12} and the fitted results were used to estimate the fibril size and fibril aggregation size.

RESULTS AND DISCUSSION

Mechanical properties of the Lyocell fibers

In this study, Lyocell fibers 1a, 1b, and 1c were made from high hemicellulose pulp with spinning solution concentrations of 11, 12, and 12.5%, respectively, whereas fiber 2 was made from high α -cellulose pulp, and the spinning solution concentration was 11%. The spinning conditions were kept as similar as possible. The mechanical properties of fibers 1a, 1b, 1c, and 2 are shown in Table I.

It can be seen from Table I that the tensile strength of fiber 1a was lower than that of fiber 2 at the same cellulose content and spinning speed because the DP value of pulp 1 was lower than that of pulp 2, and the lower molecular weight (MW) composition of pulp 1 was higher than that of pulp 2.

On the other hand, the lower MW hemicelluloses can act as plasticizers in the spinning solution. Hence, for the spinning solution of pulp 1, a higher spinning solution concentration could be used to process Lyocell fiber. It is well known¹¹ that the mechanical properties of fiber can be improved with an increase in the spinning solution concentration for wet-spinning technology. It can be confirmed from data in Table I that the mechanical properties of fibers 1b and 1c were improved and even exceeded those of fiber 2 with the spinning solution concentration increasing. Furthermore, the efficiency of the Lyocell process was also increased when the cellulose spinning solution with a higher concentration was used.

Supermolecular structure of the Lyocell fibers

Table II shows the crystallinity and orientation factors of Lyocell fibers 1a and 2. The orientation factor

TABLE I
Mechanical Properties of Lyocell Fibers 1a, 1b, 1c, and 2

Sample	Fiber 1a	Fiber 1b	Fiber 1c	Fiber 2
Cellulose content (%)	11	12	12.5	11
Titer (dtex)	2.27	2.30	2.10	2.26
Tensile strength (cN/dtex)	2.86	3.36	3.71	3.38
Initial modulus (cN/dtex)	35.7	36.7	38.10	34.00
Elongation at break (%)	7.80	8.10	8.40	7.80

TABLE II
Crystallinity and Orientation Factors of Lyocell
Fibers 1a and 2

Sample	α (%)	f_c	f_a	Δn
Fiber 1a	50	0.827	0.5273	0.03691
Fiber 2	52	0.818	0.4746	0.03663

of fiber 1a was a little higher than that of fiber 2, whereas the crystallinity of fiber 1a was slightly lower than that of fiber 2.

In the spinning solution of pulp 1, the lower MW hemicelluloses acted as plasticizers during the spinning process, and this made the cellulose molecules more easily align to form an ordered structure. Therefore, the orientation factor of fiber 1a was slightly higher than that of fiber 2.

It is well known¹¹ that a polymer spinning solution with a lower DP value will produce a fiber with higher crystallinity. However, the experimental data showed that the crystallinity of fiber 1a was a little lower than that of fiber 2. The reason may be that the strong association between hemicellulose and cellulose reduced the average crystallinity.^{9,13}

Fibrillation resistance and dyeing properties of the Lyocell fibers

The fibrillation resistance of the Lyocell fibers was determined by the wet-abrasion number.^{6,7} The greater the wet-abrasion number was, the better the fibrillation resistance was of the Lyocell fiber. It can be seen from Table III that the wet-abrasion number of fiber 1a was about 1.5 times as large as that of fiber 2. Therefore, the fibrillation resistance of fiber 1a was better than that of fiber 2.

The dyeing properties of the Lyocell fibers were estimated with E and F .⁸ The greater the E and F values were, the better the dyeing properties were of the fiber. It can be seen from Table III that the E and F values of fiber 1a were 5–8% greater than those of fiber 2. Accordingly, the dyeing properties of fiber 1a were better than those of fiber 2.

From these experimental data, it can be concluded that the fibrillation resistance and dyeing properties of the high hemicellulose Lyocell fiber (fiber 1a)

were better than those of the high α -cellulose Lyocell fiber (fiber 2). The reason is explained in the following section.

Fibril size and fibril aggregation size

The fibril size and fibril aggregation size of the pulps and fibers were estimated by cross-polarization/magic-angle-spinning carbon 13 nuclear magnetic resonance. The spectra of the pulps and fibers 1a and 2, in combination with spectral fitting, are shown in Figure 3(a–d).

In Figure 3(a,b), two signals assigned to accessible fibril surfaces (AFS) at 83.3 and 84.2 ppm and a signal assigned to inaccessible fibril surfaces (IAFS) at 83.9 ppm are visible.¹² The relative fractions of the signal intensity from AFS and IAFS of pulps 1 and 2 were obtained through 1D WINNMR software and are listed in Table IV. According to the assumptions of the model of Larsson et al.,¹² the fibril aggregation size could be calculated from the relative fraction of the signal intensity from AFS, and the fibril size could be calculated from the relative fraction of the signal intensity from AFS and IAFS. The calculated fibril and fibril aggregation sizes of pulps 1 and 2 are listed in Table IV.

The aforementioned method was also applied to Lyocell fibers because they were constructed of clusters or bundles that were formed by fibril association,^{6,11,14} and the results are shown in Figure 3(c,d). The signals at 83 and 85.2 ppm were assigned to AFS, and the signal at 84.3 ppm was assigned to IAFS. Similarly, the calculated fibril and fibril aggregation sizes of fibers 1a and 2 are also listed in Table IV.

It can be seen from Table IV that there was no significant difference in the fibril size among the four samples. However, the difference in the fibril aggregation size was significant. The fibril aggregation size of pulp 1 and fiber 1a was 5–6 nm smaller than that of pulp 2 and fiber 2, respectively. The results show that the fibril aggregation size correlated with the hemicellulose content, and the high hemicellulose Lyocell fiber had a smaller fibril aggregation size. This may be because that hemicellulose was intimately integrated into the structure of the cellulose.^{9,13} The difference in the fibril aggregation sizes

TABLE III
Wet-Abrasion Number and E and F Values of Lyocell Fibers 1a and 2

Sample	Wet-abrasion number (s)	E (%)			F (%)		
		Scarlet LS-2G	Yellow K-6G	Blue P-3R	Scarlet LS-2G	Yellow K-6G	Blue P-3R
Fiber 1a	92	97.00	98.31	96.38	77.27	79.18	76.71
Fiber 2	57	92.48	91.87	93.21	72.28	71.94	73.14

of the Lyocell fibers would influence the fibrillation resistance and dyeing properties.

Discussion of the fibrillation resistance and dyeing properties

It has been reported^{6,14,15} that the fibrillation resistance of Lyocell fiber correlates with the size and stability of fibril aggregation. From the aforementioned results, we know that fiber 1a had a smaller fibril aggregation size because of its higher hemicellulose content.^{16–18} Furthermore, the fibril aggregation of fiber 1a was more stable because of the strong association between hemicellulose and cellulose.^{9,13} Therefore, the smaller size and more stable structure

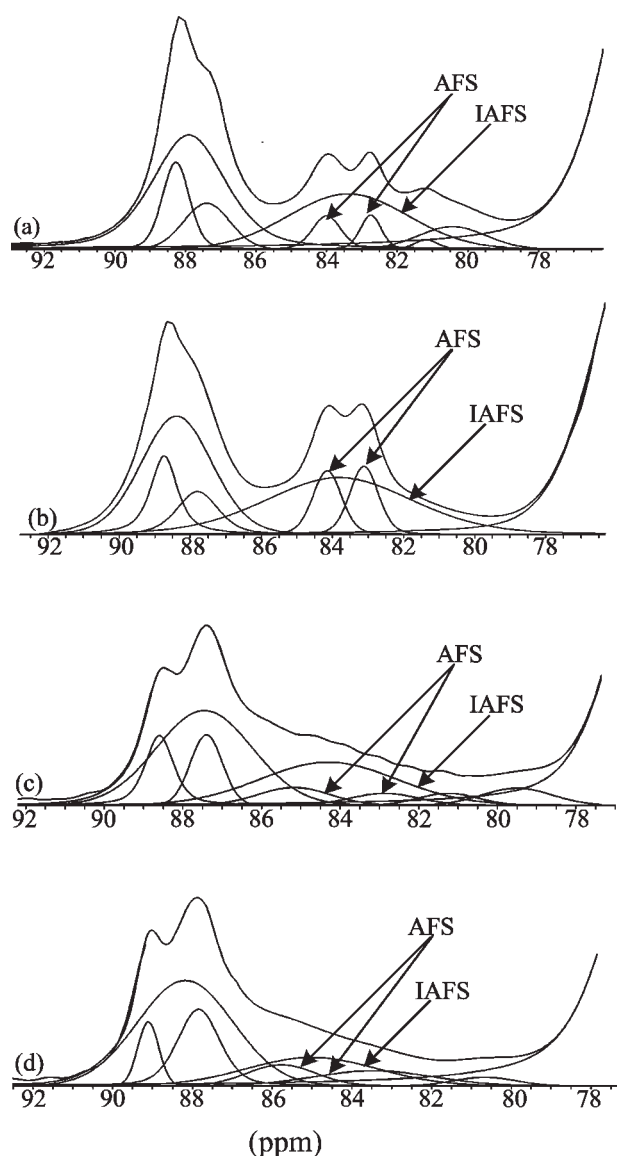


Figure 3 Results of the spectral fitting of the C4 region recorded on (a) pulp 1, (b) pulp 2, (c) fiber 1a, and (d) fiber 2.

TABLE IV
Fibril Size and Fibril Aggregation Size of the Pulps and Fibers 1a and 2

Sample	Pulp 1	Pulp 2	Fiber 1a	Fiber 2
AFS (%)	13.2	9.7	12.8	9.5
IAFS (%)	31.4	32.5	25.1	25.9
Fibril size (nm)	4.5	4.8	5.4	5.8
Fibril aggregation size (nm)	16.7	22.9	17.23	23.4

of fibril aggregation of fiber 1a, which have been confirmed in our work, would improve its fibrillation resistance.

Meanwhile, the dyeing properties of Lyocell fiber correlate with the accessible cellulose surface. The greater amorphous region and the smaller fibril aggregation size would increase the accessible cellulose surface,¹² which would improve the possibility of reaction between the cellulose fiber and dyes.^{8,12} The lower crystallinity and smaller fibril aggregation size of fiber 1a would increase the accessible cellulose surface. Moreover, the lower MW hemicelluloses in fiber 1a had an advantage over higher MW cellulose in the dyeing reaction. Therefore, the dyeing properties of fiber 1a were better than those of fiber 2.

CONCLUSIONS

The structures and properties of Lyocell fibers from a cheap pulp with a high hemicellulose content and from a conventional pulp with a high α -cellulose content were compared.

It was found that the high hemicellulose spinning solution could be processed at a higher concentration, and this improved the mechanical properties and the efficiency of the fiber process. Compared with the high α -cellulose Lyocell fiber, the high hemicellulose Lyocell fiber had better fibrillation resistance and dyeing properties, slightly higher orientation, lower crystallinity, a smaller fibril aggregation size, and a more stable structure.

Therefore, it is feasible that a cheap pulp with a high hemicellulose content could be used to produce Lyocell fiber.

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