Influence of Alkali Treatment on the Structure of Newcell Fibers

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ABSTRACT: Alkali treatment can change the structures and properties of cellulosic fibers. The aim of this work was to study the mechanism of structural changes of Newcell fibers treated with different alkali concentrations and two treatment methods. Raman spectra showed that the molecular conformation of Newcell fibers remained unchanged. X-ray diffraction indicated that the crystal structure of Newcell cellulose II, treated with different alkali concentrations and different methods, did not change. With the increase of alkali concentration the crystallinty and crystallinity orientation index of Newcell fibers in their original length decreased slightly, whereas those of fibers in relaxed condition substantially decreased, and the crystallite size of 101 and 002 increased in both methods. The quasi-crystallite disassociation and recrystallization in the quasi-crystalline phase, during the process of alkali treatment, led to changes of crystallinity and orientation index of Newcell fibers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1731–1735, 2004

Key words: structure; X-ray; Raman spectroscopy; alkali; cellulosic fibers

INTRODUCTION

Lyocell fibers, a kind of man-made fibers, are produced through a spinning process of organic solvent without the formation of hydroxyl substitution and chemical intermediates.[1,2] The properties of Lyocell fibers differ from those of other regenerated cellulosic fibers because the raw material of Lyocell fibers is wooden paper pulp (from trees), which dissolves directly in the organic solvent *N*-methyl morpholine-*N*-oxidote without the formation of cellulose derivatives. Newcell fibers are a kind of Lyocell fibers that are regenerated cellulose fibers, whose chemical structure of cellulose II is identical to that of cellulose fibers.[3–10]

Ibbett et al.[11] studied the swelling properties of alkali-treated Tencel fibers to determine the influence of alkali concentration on the diameter of fibers or the structural shrinkage of fabrics, although the effects of alkali treatment on the structure of Newcell fibers were not included.

In this study, we adopted two alkali treatment methods (fibers in their original length and in the relaxed condition) to imitate the mercerization of cellulose fibers (i.e., cotton and hemp) and the alkali-crinkled form of regenerated cellulose fiber (i.e., rayon). Based on the experimental results, we studied the effects of alkali treatment on the molecular conformation and the morphological structure of Newcell fibers. We also analyzed the mechanism of alkali treatment on the changes of morphological structure.

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EXPERIMENTAL

Materials

Newcell filament fibers of 1.33 d/tex (supplied by Akzo Nobel GmbH, Düren, Germany) were used.

Alkali treatment

Alkali treatment in original length

Newcell fibers were fixed on spinning in natural tension, and treated with different concentrations of sodium hydroxide for 2 min at room temperature. After treatment the fibers were rinsed and dried in air.

Alkali treatment in the relaxed condition

Newcell fibers were treated with different concentrations of sodium hydroxide for 2 min at room temperature. After treatment the fibers were rinsed and dried in air.

Raman spectroscopy

The Raman instrument included a Nicolet FT-Raman 960 spectrometer (Nicolet Analytical Instruments, Madison, WI) and a liquid nitrogen–cooled Ge detec-

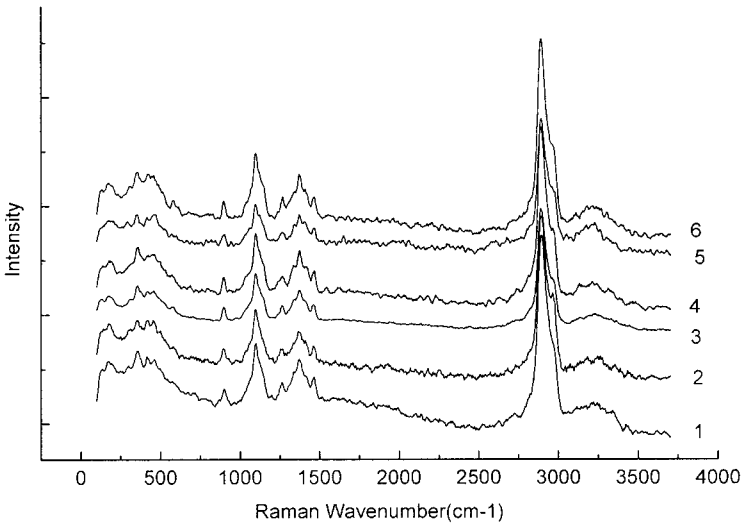

Figure 1 Raman spectra of original-length Newcell fibers treated in various alkali concentrations: (1) 0%; (2) 5%; (3) 10%; (4) 15%; (5) 18%; (6) 25%.

tor. A Nd : YVO_4 laser provided a 1064-nm excitation source. The laser power used was about 460 mW at the samples. The scattered light was collected in backscattering with a germanium detector. The resolution of the Raman instrument was approximately 4 cm^{-1}.

X-ray diffraction

To determine the crystallinity of fibers, the powder of fibers was dispersed onto a stub and placed within the chamber of a Rigaku D/MAX-IIIB X-ray diffractometer (Rigaku Corp., Tokyo, Japan). The radiation used was Cu–K_α, with a wavelength of 0.154 nm; the X-ray unit was operated at 37.5 kV and 40 mA; angular scanning was continued from 8 to 32° at 8°/min. Crystallinity (X_c) and the size of crystallites (L_{hlk}) were obtained from eq. (1) and eq. (2), respectively, as follows:

$$X_c(\%) = \frac{I_c}{I_c + I_a} \times 100 \quad (1)$$

where X_c is the degree of crystallinity and I_c and I_a represent the integrated intensity of crystalline and amorphous regions, respectively.

$$L_{hlk} = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where L_{hlk} is the size of crystallites from the normal direction of *hlk* plane; factor K is the Scherrer constant (0.9); λ is the wavelength of the X ray; β represents half-widths of the peak, or more correctly the integral breadth in radians, considering the effect of instrument broadening (0.2); and 2θ is the Bragg angle.

The crystallite orientation index was investigated by means of a Rigaku D/MAX-IIIB X-ray diffractometer using a linear position–sensitive detector. During the measurement, each sample was rotated around the primary beam in steps of 5° (total rotation by 180°) and for each step an intensity versus scattering angle curve was measured. Crystallite orientation index (Π_c) was calculated from eq. (3), as follows:

$$\pi_c = \frac{180° - H°}{180°} \times 100 \quad (3)$$

where $H°$ is the half-width of phase intensity distribution curve of 002 plane diffraction arc.

RESULTS AND DISCUSSION

Effects of alkali treatment on molecular conformation of Newcell fibers

The Raman spectra of Newcell fibers treated with alkali at their original length are shown in Figure 1. The spectra for fibers in the relaxed condition are shown in Figure 2.

The characteristics of the Raman spectra of Newcell fibers, compared with those of other natural cellulose fibers,[12–15], are as follows: 1096–1098 cm^{-1} is the Raman contribution of ring enlargement of cellulose and –C—O, 1317–1375 cm^{-1} (weak) is that of extended vibration of –O—H, 1462 cm^{-1} (weak) is that of crimped vibration of HCH, and 2900 cm^{-1} (strong) is that of extended vibration of C—H.

Comparing the two alkali treatment methods (in original length and in the relaxed condition) and the Raman characteristic peaks of alkali treated Newcell

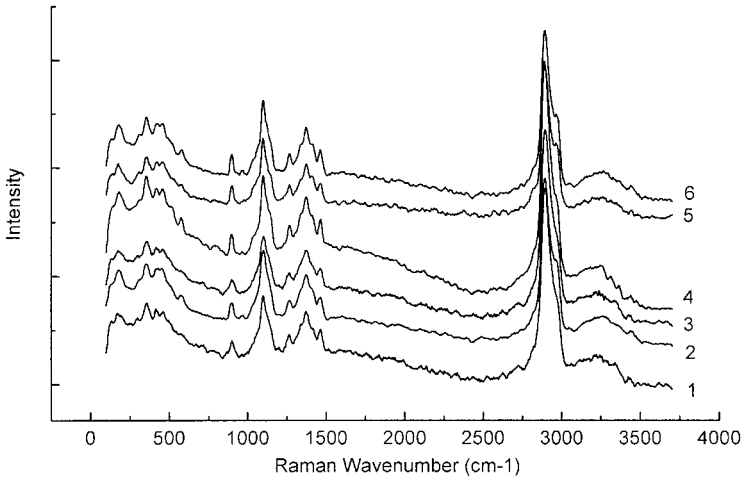

Figure 2 Raman spectra of Newcell fibers treated in the relaxed conditions in various alkali concentrations: (1) 0%; (2) 5%; (3) 10%; (4) 15%; (5) 18%; (6) 25%.

fibers, it can be seen that the peaks were not affected by treatment methods or alkali concentration. The molecular conformation of Newcell fibers remained unchanged.

Effects of alkali treatment on the morphology of Newcell fibers

Based on the XRD of relative intensity curve scanned from the equator, the diffraction intensity curve of Newcell fibers after the diffraction peak is given in Figure 3, which shows 101, $10\bar{1}$, and 002 diffraction characteristic peaks of cellulose II with diffraction angles of 11.6, 19.6, and 21.2°, respectively.[16]

The effects of alkali concentration and alkali treatment methods, on the diffraction characteristic peaks and the diffraction intensity of Newcell fibers, are shown in Figures 4 and 5 respectively. Compared with Newcell fiber, it was found that the half-widths of $10\bar{1}$ and 002 diffraction peaks decreased with increasing alkali concentration, whereas the diffraction angle remained unchanged, which indicates that the crystal structure of cellulose II was not affected by alkali concentration and treatment methods.

The crystallinity and the crystallite size change of alkali-treated Newcell fibers can be seen in Table I. Table I shows that the effects of alkali concentration and treatment methods on the crystallinity were different. The effects of alkali concentration, on the crystallinity of fibers treated at their original length were slight: the crystallinity of Newcell fibers treated at their original length decreased at a small scale. The crystallinity of alkali-treated fibers remained almost unchanged with low alkali concentration (5%) in the relaxed condition; however, with increasing alkali

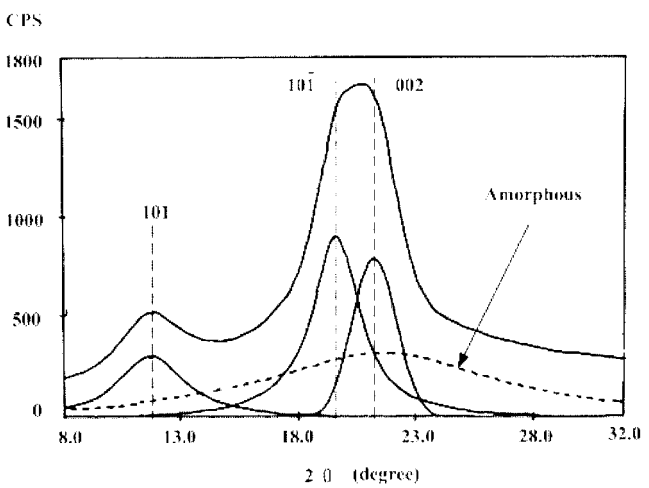

Figure 3 X-ray diffraction intensity curve of Newcell fibers.

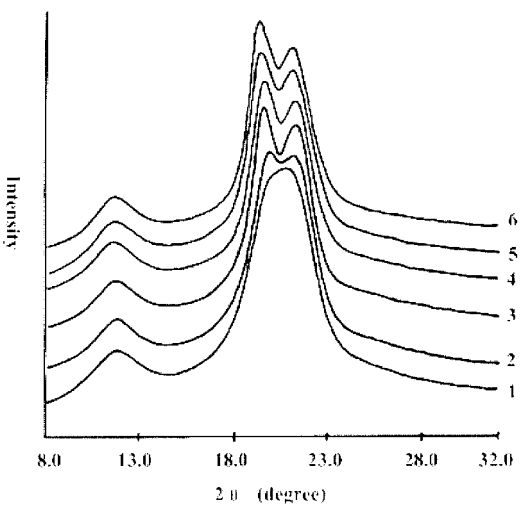

Figure 4 X-ray diffraction relative intensity curve of original-length Newcell fibers in various alkali concentrations: (1) 0%; (2) 5%; (3) 10%; (4) 15%; (5) 18%; (6) 25%.

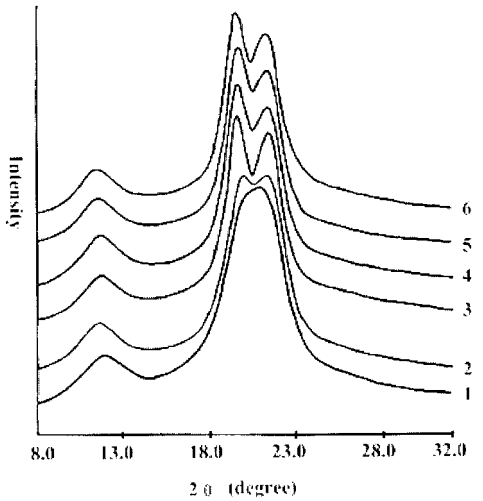

Figure 5 X-ray diffraction relative intensity curve of Newcell fibers in various alkali concentrations in the relaxed condition: (1) 0%; (2) 5%; (3) 10%; (4) 15%; (5) 18%; (6) 25%.

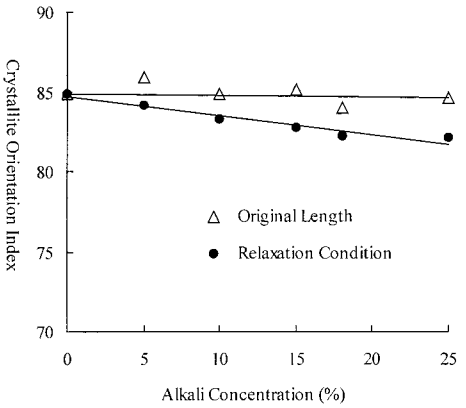

Figure 6. Effects of alkali treatment on crystallite orientation index of Newcell fibers.

concentration the crystallinity of treated fibers decreased substantially and reached its minimum at 10% alkali concentration. When the alkali concentration was between 15 and 25% the crystallinity of treated fibers did not decrease with increasing alkali concentration and was retained at about 51%.

Compared with untreated fibers, the crystallite size of $10\bar{1}$ and 002 of alkali-treated fibers increased in both methods, which meant that the crystalline region regenerated during alkali treatment processes.

The changes of crystallite orientation index of Newcell fibers are shown in Figure 6. With increasing alkali concentration, the crystallite orientation index of fibers, treated in the relaxed condition, decreased more significantly than that of the fibers treated at their original length.

TABLE I
Effects on Crystallinity and Size of Crystallites of Newcell Fibers in Alkali Treatments

Alkali treatment	Alkali concentration (%)	$L_{10\bar{1}}$ (nm)	L_{002} (nm)	Crystallinity (%)
In original length	0	3.62	4.04	56.9
	5	4.55	4.53	55.9
	10	6.00	5.58	53.7
	15	5.57	5.39	53.4
	18	5.48	5.20	53.3
	25	5.76	5.17	53.4
In relaxed condition	0	3.62	4.04	56.9
	5	4.60	4.56	56.7
	10	6.49	5.56	47.2
	15	6.04	4.93	51.1
	18	6.39	4.78	50.9
	25	6.53	5.02	50.6

Mechanism of alkali treatment on the morphology of Newcell fibers

As a typical structure of cellulose II, Newcell fibers possess many hydroxyl groups, which can form hydrogen bonds both in and between molecules. In the crystalline phase, the layered structure is very regular, so the length of hydrogen bonds between molecules is the same, and the cellulose chains spread antiparallel, which leads to a perfectly spread symmetric structure, except for some defects.[17–19] Like natural fibers, Newcell fibers have a microfibrillar structure because a portion of the molecular chains aggregate to form microcrystals while recrystallizing along the chains, whereas the remaining chains exist in the amorphous phase as links between these two phases.[20,21]

During the formation of bundle morphology, a portion of the molecular chains, which finally becomes crystal nuclei, have the chance to approach the neighboring chains parallel and aggregated easily by van der Waals force and hydrogen bonds. On the contrary, the long-distance molecular chains become the amorphous phase because they do not crystallize without hydrogen bonds.

In the process of filamentation, it is easy to form the quasi-crystalline phase, whose orientation is relatively low to moderate compared with that of the crystalline phase, which is attributed to the presence of imperfect microcrystals.[18,22] It is thus apparent that crystalline, quasi-crystalline, and amorphous phases coexist in Newcell fibers.

Based on the three-phase structure of Newcell fibers, it was supposed that alkali could permeate only into the quasi-crystalline and amorphous phases to form a hydrated layer of sodium ion, which increase the swelling of fibers and lead to quasi-crystallite dis-

association. After being washed and dried, some of the molecular chains have the chance to approach the neighboring ones in parallel. This results in the transition of quasi-crystalline phase into crystalline and amorphous phases. Thus, the change of the crystallinity depends on the transformation of quasi-crystalline phase. If the quasi-crystalline phase transforms into the amorphous phase, the crystallinity decreases.

Changes of the quasi-crystalline phase during alkali treatment were as follows: (1) crystals recrystallized on undisassociated crystal grains in the quasi-crystalline phase or on the edge of the crystalline phase; (2) small crystal nuclei formed and grew quickly in the quasi-crystalline phase; and (3) alignment changed in the quasi-crystalline phase.

All these changes led to the transition of quasi-crystalline phase into crystalline and amorphous phases. XRD results indicated that the effects of alkali concentration and treatment methods on the ratio of quasi-crystallite disassociation and recrystallization were different.

For Newcell fibers treated at their original length, the speed of quasi-crystallite disassociation was close to that of recrystallization, and the transition ratio of quasi-crystalline phase into crystalline and amorphous phases was also very close. There was a slight decrease of crystallinity after alkali treatment.

For Newcell fibers treated in the relaxed condition, when alkali concentration was low (5%), the swelling capacity of fibers was relatively small, so the crystallinity of fibers changed only slightly. However, with increasing alkali concentration, the swelling capacity increased, and a larger number of quasi-crystallites disassociated.

The reason that the speed of quasi-crystallite disassociation was greater than that of recrystallization was that the formation of bundle aggregation was difficult and the growth of crystals was relatively slow. The great tendency of transition of quasi-crystalline phase into amorphous phase caused the crystallinity of alkali-treated fibers to decrease.

The quasi-crystallite disassociation and recrystallization in the quasi-crystalline phase would affect the crystallite orientation index of the crystalline fraction. The direction of recrystallization did not occur along the fiber axis, which led to the decrease of the crystallite orientation index, although when there was crosslinking in fibers or tension along the fiber axis, the effect of alkali treatment on the crystallite orientation index was very slight.

CONCLUSIONS

1. Raman characteristic peaks of Newcell fibers were not significantly affected by alkali concentration and treatment methods. The molecular conformation of Newcell fibers remained unchanged.
2. The crystalline structure of cellulose II of Newcell fibers was not affected by alkali concentration and treatment methods.
3. The crystallinity of Newcell fibers treated at their original length was slightly affected by alkali concentration, although the crystallnity of Newcell fibers treated under relaxed conditions was significantly affected by alkali concentration, and the crystallinity substantially decreased. Compared with untreated Newcell fibers, the crystalline size of $10\bar{1}$ and 002 of Newcell fibers treated with alkali increased.
4. The orientation index of Newcell fibers decreased with increasing alkali concentration, whereas the orientation index of alkali-treated fibers at their original length decreased slightly.
5. In alkali treatment, quasi-crystallite disassociation and recrystallization occurred in the quasi-crystalline phase of fibers, which led to changes of crystallinity and orientation index.

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