Characterization of Ramie Yarn Treated with Sodium Hydroxide and Crosslinked by 1,2,3,4-Butanetetracarboxylic Acid

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ABSTRACT: Ramie yarns were treated with various concentrations of NaOH at room temperature and subsequently crosslinked with 1,2,3,4-butanetetracarboxylic acid (BTCA). The microstructure and tensile properties of the treated yarns were characterized. X-ray diffraction (XRD) and FTIR were used to study the crystalline structure of the resultant ramie yarns. The results showed that the maximum change in the structure of the alkali-modified ramie took place at 16% NaOH, which would completely transform cellulose I to cellulose II. At the same time, the crystallinity index and fiber orientation decreased to the minimum value while the absorption properties were enhanced. The average degree of polymerization ($\overline{DP}$) of the treated ramie yarns slightly decreased after NaOH treatment. Tensile properties including tenacity, breaking elongation, and modulus of the treated yarns were also investigated. Scanning electron microscopy (SEM) was used to investigate the breakage of the treated yarns. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1857–1864, 2004

Key words: crosslinking; degree of polymerization (DP); fibers; FT-IR; X-ray

INTRODUCTION

Ramie is a kind of bast fiber just like jute, linen, hemp, and sisal. It has many excellent properties when used as a textile material such as high tenacity, excellent thermal conductivity, and high water and perspiration adsorption.[1] It can be made into summer clothes and fashion items. Blending ramie with other fibers is also becoming popular for apparel fabrics with improved functional properties. However, the special molecular structure of ramie containing high crystallinity and orientation results in some undesirable properties of the ramie fiber as well as the ramie fabric such as poor elasticity, bad wrinkle recovery, itchiness, and harsh handle.[1] Over the past several years, considerable work has been done to modify the morphology and molecular structure of the ramie fiber, aiming at ameliorating the undesirable properties of ramie. Among these methods, alkali treatment was widely studied and used as a normal means to study the microstructure of the ramie fiber.[2–6]

Because the crystal structures of cellulose have already been solved,[7] it is time to use the same crystallographic conventions in the crystallinity analyses as are used in fiber diffraction studies. The structure of the cellulose in flax, hemp, jute, ramie, and cotton was studied using wide-angle X-ray scattering and ^{13}C-CP/MAS-NMR spectroscopy.[8] The characteristics, size, and orientation of the crystallization regions of the fibers were shown, consisting of the bast fibers of jute, hemp, and flax of mixtures of approximate 50% Ia and Ib cellulose. Sao et al.[6,9] measured various structure parameters of ramie such as the crystallinity and disorder parameters using the Ruland and Vonk method. They found that a simple two-phase model of completely ordered and disordered phases had little validity for ramie fiber. The existence of intermediate ordered regions had to be considered for a satisfactory explanation of the phenomenon of swelling. Some work to soften kenaf was also reported.[10,11] Fink et al.[12] recently reported on the characterization of the crystallite orientation of some regenerated cellulosic fibers with a combination of X-ray diffraction (XRD) and optical birefringence measurements. Results regarding the morphology, crystallinity, crystallite dimensions, and orientation were discussed. Wide- and small-angle X-ray scattering experiments were also performed with synchrotron and conventional radiation to investigate the structure-formation process during spinning of cellulosic fibers from *N*-methyl-morpholine *N*-oxide.[13]

Chemical crosslinking has been adopted for many years by the textile and garment industry to improve the wrinkle resistance of cellulose fabrics such as cot-

ton and rayon. The crosslinking agents being used by the textile and garment industry now are mainly *N*-methylol compounds such as dimethylol dihydroxyl ethyleneurea (DMDHEU) and modified DMDHEU with low formaldehyde levels. Formaldehyde has been found to be very toxic to human beings, and many countries have legislated laws to ban or limit the usage of the formaldehyde-containing chemicals. Poly(carboxylic acid) is a kind of nonformaldehyde crosslinking agent for cellulose and has been exensively studied to develop nonformaldehyde wrinkle-free cotton goods.[14–16] The results showed it was a very promising substitute to replace the traditional formaldehyde-containing a crosslinking agent for cotton fabrics. The most effective poly(carboxylic acid) is 1,2,3,4-butanetetracarboxylic acid (BTCA).

In this study, the microstructure and tensile properties of the ramie yarns treated with various concentrations of NaOH were characterized. The response of the NaOH treatment with respect to the subsequent BTCA treatment was also investigated.

EXPERIMENTAL

Materials

Scoured and bleached ramie yarn was purified by refluxing with ethanol/benzene (1/1) for 24 h, followed by a sufficient rinse with ethanol, and finally dried at 50°C in a vacuum oven. The BTCA used was reagent grade supplied by Aldrich (St. Louis, MO). Sodium hydroxide (NaOH) of analytic grade and sodium hypophosphite monohydrate (SHP) were supplied by ACR Organics (Pittsburgh, PA).

Yarn treatment

For NaOH treatment, the ramie yarn hank was immersed in a NaOH solution at concentrations ranging from 4 to 20% for 10 min at room temperature (25°C). It was then rinsed with distilled water, neutralized with 2% acetic acid, finally rinsed again with distilled water until neutral, and dried in a 50°C vacuum oven. For BTCA treatment, the ramie yarn was immersed in the solution containing 4% BTCA and 2.67% SHP for 5 min and then was passed through a two-rolled padder at about 80% wet pickup. The padded yarn sample was dried in an oven at 60°C for 10 min and subsequently cured at 180°C for 2 min. The cured sample was washed with 5 g/L Na_2CO_3 at 50°C for 5 min to remove the unreacted chemicals, then rinsed and finally air-dried under the standard condition (21 ± 1°C, 65 ± 2% RH).

Characterization methods

Several analytical techniques were used to obtain information concerning the microstructure of the treated samples and the resulting changes in the fiber structure. The yarn samples were ground in a Wiley mill and then made into KBr disks. The transmission infrared spectra were obtained from a Perkin–Elmer FTIR spectrometer with 96 scans for each sample. A Cambridge Mark II scanning electron microscope (SEM) was used to analyze fiber samples taken from both the treated and control ramie yarns. Analyses were conducted in the broken cross-sectional direction of the fibers.

A Philips analytic X-ray diffractometer PW 3710 was used to collect the XRD diagram of the samples with the following components involved: Cu tube anode, 40 kV generator tension, 55 mA generator current, and wavelengths of $\alpha_1 = 1.54060$ Å and $\alpha_2 = 1.54439$ Å. For investigation of the crystallinity and crystallite dimension, powder diffraction was adopted. Yarn samples were ground in a Wiley mill and then pressed into pellets of 0.5-cm diameter. A 2θ scan was started from 6° to 36°.

For the determination of the crystallite orientation, the meridianal [040] reflection was selected. The treated yarns were untwisted, combed, and made into bundles of well-parallelized fibers. The bundles were mounted on poly(methyl methacrylate) sample holders and scanned in the transmission mode. The orientation scans were obtained by keeping the 2θ fixed and rotating the sample through 360° in a plane perpendicular to the radiation direction. The values of Hermans crystallite orientation factors and the average angle of orientation (α) were determined from the following equations:

$$f_c = 1/2 \ (\overline{3 \cos^2\alpha} - 1)$$

where

$$\overline{\cos^2\alpha} = \frac{\int_0^{\pi/2} I(\alpha)\cos^2\alpha \sin\alpha d\alpha}{\int_0^{\pi/2} I(\alpha)\sin\alpha \, d\alpha}$$

Birefringence of the fiber taken from the treated yarn was determined using a compensation method using a Berek compensator combined with an Olympus polarizing microscope, and it was used to estimate the average orientation of the fiber. Based on the two-phase model of ramie cellulose, the birefringence of the fiber can be written as

$$\Delta n = x_c f_c \Delta n_c + (1 - x_c) f_a \Delta n_a$$

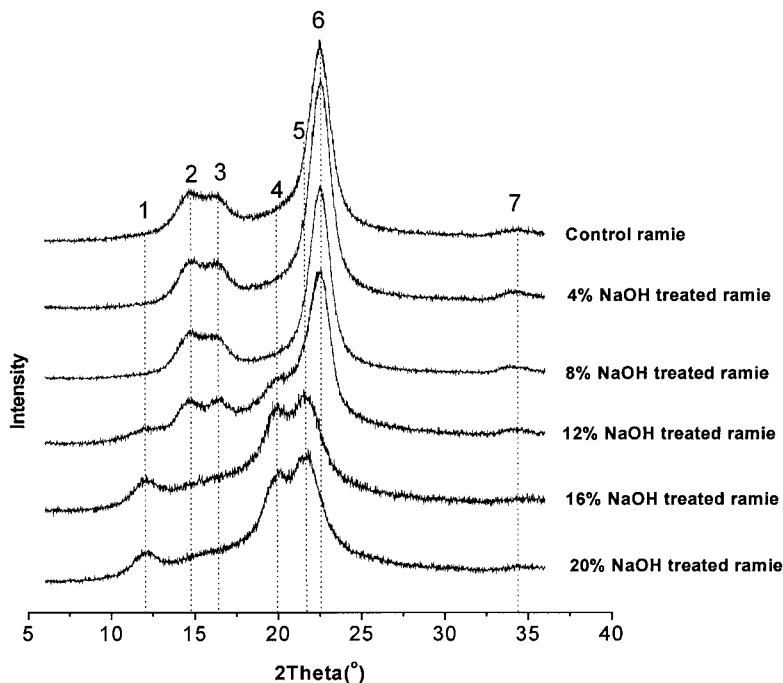where f_c and f_a are the orientation factors of the crystalline and amorphous regions, respectively; Δn_c and

Figure 1 X-ray diffraction diagram of ramie yarns treated with various concentrations of NaOH at room temperature for 10 min.

Δn_a, the birefringence of the crystalline and amorphous regions, respectively; and x_c, the crystallinity of the fiber.

Assuming that $\Delta n_c = \Delta n_a = 0.071$, then f_a is expressed as

$$f_a = \left(\frac{\Delta n}{0.071} - x_c f_c \right) \frac{1}{1 - x_c}$$

where Δn is the birefringence of the fiber; x_c, the crystallinity of the fiber; and f_c, the crystallite orientation. The average degree of polymerization ($\overline{DP}$) of the treated yarn was determined by the method of viscosity using copper diethyleneamine as the cellulose solvent, and it was calculated by the following equation[17]:

$$\overline{DP} = \frac{156 \times \eta_{sp}}{c \times (1 + 0.29 \times \eta_{sp}}$$

where $c = 0.1$ g/100 mL and

$$\eta_{sp} = \frac{t - t_0}{t_0}$$

t is the fluid time of the cellulose solution, and t_0, the fluid time of the solvent. All the results were the average of three measurements.

Yarn tensile properties were measured by an Instron, Model 4466. The gauge length was 10 cm and the crosshead speed was 30 mm/min. Each result

obtained was the average of 15 readings with the CV less than 20%.

RESULTS AND DISCUSSION

XRD investigation

The microstructure of the treated ramie fiber in terms of the crystalline structure was investigated by an XRD technique. The XRD diagram of the ramie yarns treated with various concentrations of NaOH is shown in Figure 1.

Figure 1 shows that the XRD diagram of the control ramie exhibits a sharp high peak at 2θ 23°, which is assigned to the [002] lattice plane of cellulose I. The two overlapped weaker diffraction peaks at 2θ 14.7 and 16.2° are assigned to the [101] and [101⁻] lattice planes of cellulose I. Ramie yarns treated with 4 and 8% NaOH solutions show similar diffraction diagrams as those of the control. When the NaOH concentration is increased to 12%, the two additional diffraction peaks appear at 12.0° and 19.9°, which are assigned to the [101] and [101⁻] lattice planes of cellulose II. NaOH-treated ramie, 16 and 20%, show the characteristic diffraction diagram of cellulose II. The XRD diagram (not shown) shows little change before and after being crosslinked with BTCA, indicating that the crosslinking treatment has little effect on the crystallite structure of the ramie. Since the crosslinking agent cannot penetrate into the crystalline regions, the crosslinking reaction, thus, occurs mainly in the acces-

TABLE I
Peak-fit Results of XRD Diagrams

Concentration of NaOH (%)	hkl	2θ	Peak height	Peak area	fwhm[a]	L (hkl) (nm)	Crystallinity	Cellulose I	Cellulose II
Control	101 (II)								
	$10\underline{1}$ (I)	14.68	244.4	508.1	1.324	6.72			
	$10\bar{1}$ (I)	16.19	196.1	471.7	1.531	5.82			
	$10\bar{1}$ (II)						75.0	75.0	0
	002 (II)								
	002 (I)	22.48	1407	3088	1.397	6.44			
	040	34.38	38.47	69.96	1.158	7.98			
4	101 (II)								
	$10\underline{1}$ (I)	14.78	260.8	529.0	1.291	6.89			
	$10\bar{1}$ (I)	16.26	208.2	399.4	1.221	7.3			
	$10\bar{1}$ (II)						81.0	81.0	0
	002 (II)								
	002 (I)	22.51	1671	3488	1.329	6.77			
	040	34.26	59.48	117.6	1.259	7.34			
8	101 (II)								
	$10\underline{1}$ (I)	14.71	363.7	762.8	1.335	6.67			
	$10\bar{1}$ (I)	16.18	287.4	611.0	1.353	6.59			
	$10\bar{1}$ (II)						78.5	78.5	0
	002 (II)								
	002 (I)	22.48	2019	4152	1.309	6.87			
	040	34.14	60.20	107.5	1.137	8.12			
12	101 (II)	11.92	23.99	12.63	0.3351	26.5			
	$10\underline{1}$ (I)	14.67	172.3	322.5	1.191	7.47			
	$10\bar{1}$ (I)	16.34	126.2	226.5	1.143	7.8			
	$10\bar{1}$ (II)	20.20	235.7	872.9	2.358	3.8	64.9	50.4	14.5
	002 (II)								
	002 (I)	22.44	1141	2485	1.387	6.49			
	040	34.23	33.78	53.40	1.006	9.18			
16	101 (II)	12.06	80.88	156.3	1.223	7.22			
	$10\underline{1}$ (I)								
	$10\bar{1}$ (I)								
	$10\bar{1}$ (II)	19.90	283.9	943.6	2.116	4.24	57.6	0	57.6
	002 (II)	21.74	344.0	917.3	1.698	5.29			
	002 (I)								
	040	34.91	10.69	20.84	1.242	7.45			
20	101 (II)	12.03	124.1	211.8	1.086	8.17			
	$10\underline{1}$ (I)								
	$10\bar{1}$ (I)								
	$10\bar{1}$ (II)	19.89	496.1	1466	1.881	4.76	60.2	0	60.2
	002 (II)	21.70	683.9	1918	1.785	5.03			
	002 (I)								
	040	34.81	28.50	66.17	1.478	6.26			

[a] Full-width at half-maximum.

sible regions of the fiber, that is, amorphous regions and the surface of the crystalline regions.

To calculate the crystallinity index, lattice size, and the content of celluloses I and II, a computer program was applied to separate the background and the overlapped peaks. Corrections to the diffraction traces were made for air scatter, polarization, and Compton scatter. Corrected data for the diffraction peaks in the range of 6–36 (2θ) were analyzed by the computer program which fit the envelope to a function of the form of the Cauchy equation and the background to be the profile of a polynomial. The program modified the peak and background parameters until a limiting sum of squares was reached between the observed and calculated values. The crystallinity index was the total area under the peaks evaluated as a percentage of the total area under the diffraction profiles. The lattice sizes were calculated by the Scherrer equation:

$$L(hkl) = \frac{1}{\beta} = K\lambda / \cos\theta\, d(2\theta)$$
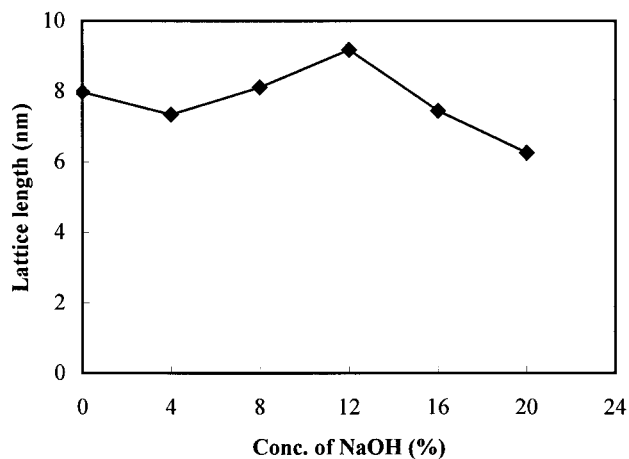
Figure 2 Lattice length of ramie treated with various concentrations of NaOH solution.

where $K = 0.9$ and $d(2\theta)$ is the half-width at half-height for the diffraction peak in radians. θ is the half-diffraction angle. The calculated crystallinity index, content of celluloses I and II, and lattice size of the treated ramie yarns are presented in Table I.

Table I shows that the control ramie has a crystallinity index of 75.0%. NaOH of 4 and 8% slightly increased the crystallinity index by about 5%. When the NaOH concentration was increased to 12% or higher, the crystallinity index decreased to the value below 65%, and the minimum crystallinity index, that is, 57.6%, was obtained at 16% NaOH. NaOH with a concentration lower than 12% had little effect on the transformation of the cellulose crystallite type. A 12% NaOH solution led to partial transformation of ramie cellulose from cellulose I to cellulose II. NaOH treatment of 16 and 20% resulted in a complete transformation of cellulose I to cellulose II. The lattice size calculated by the Scherrer equation is also listed in Table I.

Figure 2 shows the lattice length calculated by the diffraction of the [040] lattice plane. It is observed that the lattice length is slightly increased when the NaOH concentration is lower than 12%. It reaches the maximum value at 12% NaOH and then it decreases with a higher NaOH concentration. This is consistent with the observed experimental phenomenon that ramie fibers shrink in the NaOH solution with mercerization strength.

FTIR investigation

The FTIR spectra in Figures 3 and 4 show that there is only a little change in the absorbance at 1432 cm^{-1}, which is assigned to CH$_2$ symmetrical deformation when the NaOH concentration is lower than 16%. However, it shifts toward the low-frequency side along with a sharp decline in intensity at 16% NaOH.
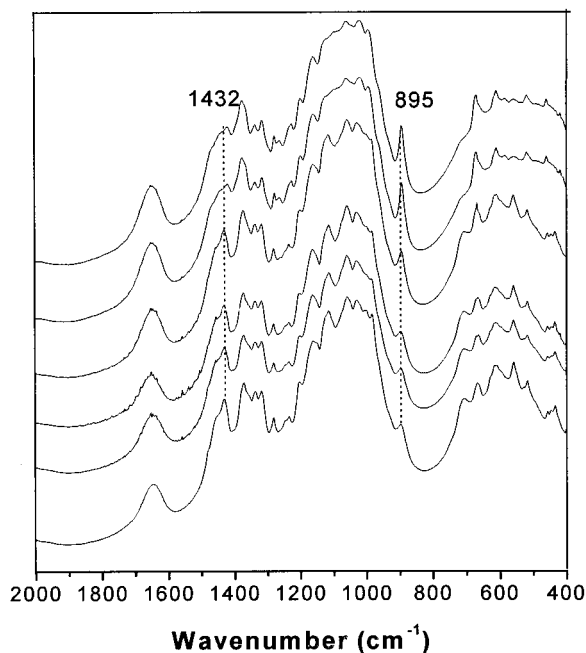

Figure 3 FTIR spectra of ramie fiber treated with 0, 4, 8, 12, 16, and 20% NaOH (from bottom to top).

The change in intensity and position of this band is correlated with the change in the environment of the C$_6$ carbon atom due to the formation or breakage of the hydrogen bond involving the atom O$_6$, which indicates the transition of the lattice between cellulose I and cellulose II.[18] The intensity at 895 cm^{-1}, which is
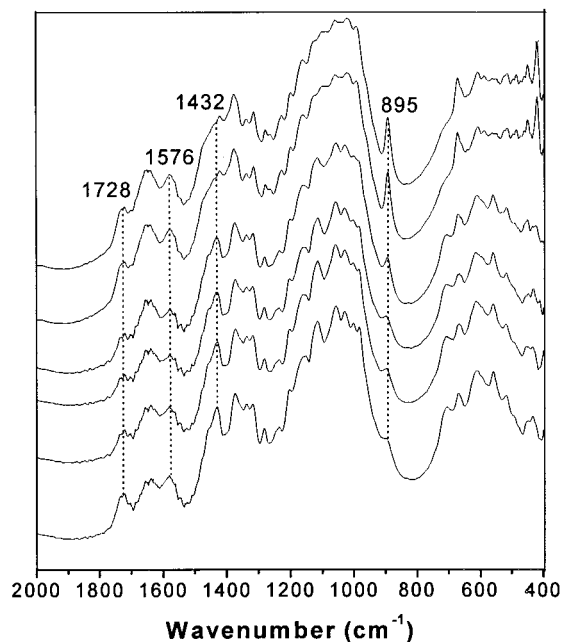

Figure 4 FTIR spectra of ramie yarns pretreated by different concentrations of NaOH: 0, 4, 8, 12, 16, and 20 (from bottom to top), and subsequently crosslinked by 4% BTCA.
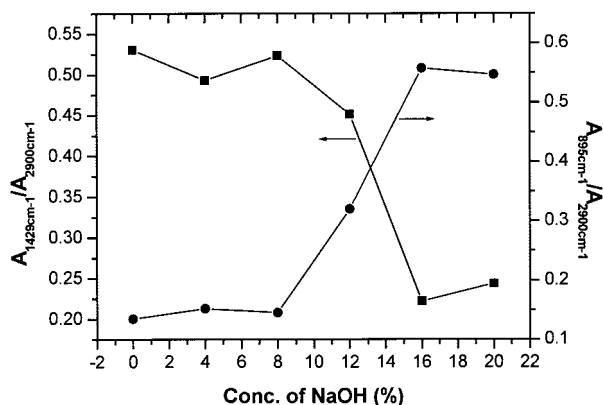
Figure 5 FTIR absorbance of ramie yarn treated with various concentrations of NaOH.

Figure 6 $\overline{DP}$ of ramie yarns treated with various concentrations of NaOH.

characteristic of the β-linkage assigned to the C_1 group frequency and is sensitive to the change in chain conformation,[19] increases with a higher NaOH concentration. The change in this band becomes most significant at 16% NaOH, as shown in Figure 5, indicating the change in the absorbance $A_{1430cm-1}/A_{2900cm-1}$ and $A_{892cm-1}/A_{2900cm-1}$. The FTIR spectra in Figure 4 show that two additional absorption peaks appear after BTCA treatment, that is, at 1728 and 1576 cm^{-1}, when compared with Figure 3. These two absorption peaks correspond to the ester bond and the carboxylate, respectively, which indicates the successful esterification of the ramie yarn. Apart from these two additional absorption peaks, there is little change of the spectra when compared with the corresponding spectra of the noncrosslinked ramie yarns.

Fiber orientation

Fiber orientation was determined in terms of both crystalline and amorphous regions with the results being shown in Table II. The data in Table II show that the average orientation index determined by the birefringence decrease with increase in the NaOH concentration and the minimum value is obtained at 16% NaOH. There is a slight reduction in the orientation index of the crystalline regions with respect to the increase in NaOH concentration as determined by the

[040] diffraction. However, the orientation index of the amorphous regions show a steady decrease in value at higher NaOH concentration, especially when the NaOH concentration is higher than 8%.

Average degree of polymerization ($\overline{DP}$)

The $\overline{DP}$ determined by the method of viscosity using copper diethyleneamine as the cellulose solvent is shown in Figure 6. The $\overline{DP}$ of the control ramie and NaOH-treated ramie ranges from 1686 to 1768. It is obvious that the alkali treatment only slightly reduced the $\overline{DP}$ of the treated ramie yarns. This may be due to the oxidative degradation of the ramie cellulose in the presence of oxygen gas.

Tensile properties

The tensile properties including tenacity, breaking elongation, and modulus of the treated yarns before and after crosslinking are shown in Figure 7. There was a little increase in the tenacity of the treated yarn when the concentration of NaOH was less than 12%. It seemed that a higher concentration of NaOH caused a progressive decrease in the tenacity of the ramie yarn. The decrease in the tenacity of the slack mercerized ramie was probably attributed to the decrease in crystalline orientation as a result of the unrestrained lateral swelling of the fibrils. Warwicker[2] noted that the differential response of ramie and cotton to the slack swelling with NaOH was a function of fiber morphology rather than to differences in the fine structure. He demonstrated that ramie had a simple structure with no primary wall to exert restraint on the lateral swelling and consequent disorientation of the swollen fibrils. After slack swelling in the mercerization
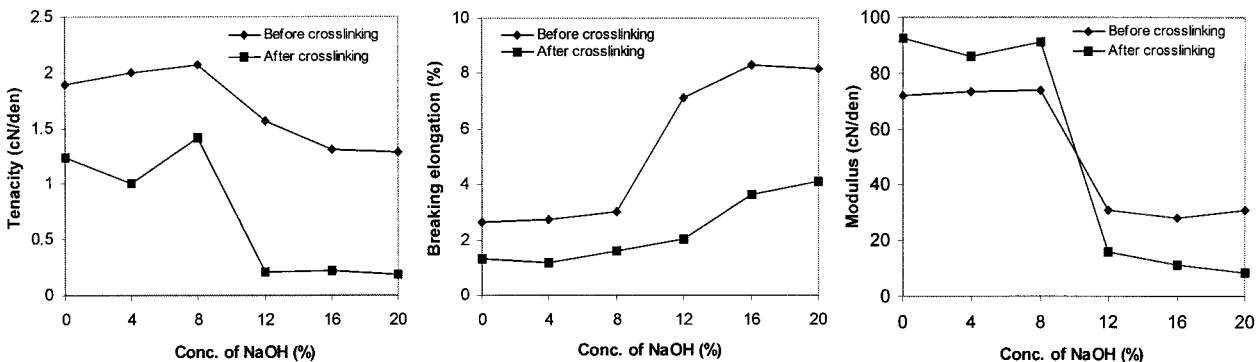
TABLE II
Orientation of Ramie Treated with Various Concentrations of NaOH

Orientation	Concentration of NaOH (%)					
	0	4	8	12	16	20
$\Delta n \times 10^2$	6.58	6.57	6.50	5.32	4.48	4.56
f_0	0.927	0.925	0.915	0.749	0.631	0.642
f_c	0.977	0.976	0.968	0.952	0.944	0.942
f_a	0.777	0.709	0.724	0.374	0.206	0.189

Figure 7 Tensile properties of ramie yarn treated with various concentrations of NaOH and subsequently crosslinked by 4% BTCA.

strength, the elongation of the treated ramie yarn was increased to about 7%, and also there was an obvious decrease in the modulus which resulted in a much softer handle. This was probably due to the decrease in fiber orientation.

When the ramie yarn was treated by the NaOH solution at a concentration higher than 12% followed by 4% BTCA treatment, it experienced a much lower tensile strength. It was also noted that at the concentration of 8% NaOH the treated yarn processed a higher tenacity than that of the crosslinked control.

The ruptured cross sections of the fiber taken from some of the treated yarns were also investigated by SEM, with the results shown in Figure 8.

It is shown clearly in Figure 8(A) that the untreated ramie broke with an axial splitting between the fibrils. Figure 8(B) shows that the ends of the break for the untreated ramie fiber is a collection of fibrils. In general, the ramie fiber has about 7° spiral angle, and the outer layer is a Z spiral followed by an S spiral layer and a core of the intermediate.[1] Hence, when the fiber is put under tension, the reversal point will tend to
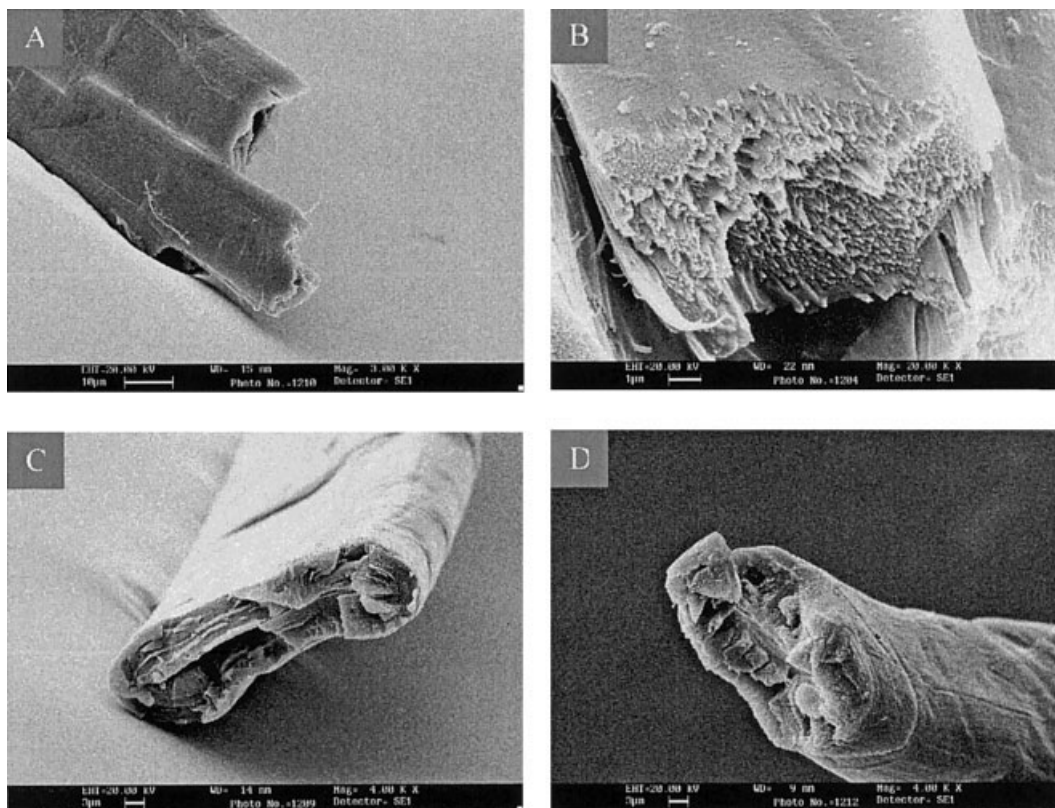

Figure 8 SEM photographs show the cross section of the broken ramie fiber: (A,B) untreated; (C) 4% BTCA crosslinked; (D) 16% NaOH pretreated and 4% BTCA crosslinked.

untwist in order to elongate the fiber, and so this generates shear stresses which cause the axial splitting between the fibrils. For the ramie fiber crosslinked with 4% BTCA, as shown in Figure 8(C), the fiber collapsed due to the high-temperature curing process. The cellulose fibrils were fastened together more firmly together by the crosslinks leading to the hindrance of axial splitting. The breaks showed distorted forms of granular across the fiber, with no axial separation linking different zones of the transverse fracture. For the 16% NaOH pretreated and 4% BTCA crosslinked ramie, the break was similar to that of the crosslinked ramie with no NaOH pretreatment, except that the cross section of the fiber became more circular due to the irreversible swelling caused by 16% NaOH, as shown in Figure 8(D).

CONCLUSIONS

Ramie yarn was treated with various concentrations of a NaOH solution ranging from 4 to 20%, and its microstructure was characterized. XRD, combined with the peak-fit technique, was used to analyze the crystalline structure of the resultant ramie yarns. The results showed that NaOH with a concentration lower than 8% caused no transformation of cellulose I to cellulose II. However, there was a little increase in the crystallinity index. NaOH with a concentration higher than 12% caused the transformation of ramie from cellulose I to cellulose II. When the NaOH concentration was higher than 16%, all the cellulose I was transferred to cellulose II. FTIR investigation further confirmed the phase change and decrystallization of the treated ramie yarns. Fiber orientation of both the crystalline and amorphous regions was also investigated with XRD and birefringence measurement. Both decreased with a higher NaOH concentration. The $\overline{DP}$ of the treated ramie yarns was determined using the method of viscosity, and the result showed that there was a slight decrease of $\overline{DP}$ with the NaOH treatment. The tenacity of the NaOH-treated yarns first increased and then decreased subsequently when the NaOH concentration was higher than 12%. At the same time, there was an increase in the breaking elongation and a tremendous decrease in the modulus, resulting in higher elasticity and a softer hand. Crosslinking treatment with BTCA resulted in an obvious decrease in the tenacity of the ramie yarn. It seemed that a low concentration of NaOH, such as 8%, could reduce the tenacity loss while a higher concentration of NaOH would result in a severe loss in tenacity due to the destruction of the fiber orientation.

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