Effect of High-Temperature Degumming on the Constituents and Structure of Cotton Stalk Bark Fibers

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ABSTRACT: The high-temperature degumming technology of cotton stalk bark fiber was studied, and the effects of the caustic soda concentration on the constituents, structure, and thermal degradation of the cotton stalk bark fiber were examined. The morphology, structure, and thermal degradation of the cotton stalk bark fiber after high-temperature degumming were investigated through scanning electron microscopy, Fourier transform infrared (FTIR) spectroscopy, wide-angle X-ray diffraction, and thermogravimetric analysis. The results indicate that the high-temperature degumming process was effective for removing hemicelluloses and lignin and could improve the thermal stability of the cellulose. The raw and degummed cotton stalk bark fibers both showed the structure of cellulose I, according to the FTIR spectroscopy and X-ray diffraction results. It was interesting to note that the crystallinity and crystallinity index were related to the caustic soda concentration. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: fibers; FT-IR; morphology; TEM; thermal properties

INTRODUCTION

Cotton has mainly been used as a textile material for several centuries because of its excellent wear properties. However, the planting of cotton generates a lot of residual materials, such as cotton stalk bark, cotton stalks, and cotton leaves. Although cotton stalks, which are rich in cellulose, have the potential to be used as a source for paper, industrial fuel, composites, and regenerated cellulose for rayon,[1–4] until now, cotton stalks have mostly been burned as agricultural waste.[5,6]

Previous studies have been focused on the applications of cotton stalks. As one kind of renewable energy resource, cotton stalks could be converted to bioethanol with available pretreatments to meet biofuel requirements.[1–3] Moreover, cotton stalks could also be used to obtain pulp, which is useful for the paper manufacturing industry. However, little attention has been given to cotton stalk bark.

Cotton stalk bark, composed of approximately 40% cellulose, has the potential to be used as cellulose fibers. The extraction of high-quality cellulose fibers from cottons stalk bark, with properties suitable for textiles, composites, and other fibrous applications, will help to add considerable value to cotton crops and make cotton crops more competitive as biofuel crops in the long run.[1] However, few reports are available on obtaining cellulose fibers from cotton stalk bark with properties of length, fineness, and other properties similar to common cellulose fibers in current use.

In addition to cellulose, cotton stalk bark is also rich in hemicellulose and lignin. To fully use cotton stalk bark, it is important to study a proper degumming process to extract cellulose fibers from cotton stalk bark.

In a previous work, we studied the high-temperature degumming pretreatment of hemp fiber.[7] In this study, we attempted to remove noncellulosic gummy materials from cotton stalk bark using high-temperature degumming process with a low alkali content and obtained excellent cotton stalk bark fiber. The effects of the alkali concentration on the cotton stalk bark were investigated, and the structure and properties of the natural cellulose fibers obtained from the cotton stalk bark were studied. The morphology, structure, and thermal degradation of the cotton stalk bark before and after degumming

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treatments were investigated through scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (WAXD), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

The cotton stalk bark sample was collected from Yancheng agricultural field in the People's Republic of China. The constituents (weight percentage) of the cotton stalk bark fiber were cellulose (41.05 wt %), hemicellulose (21.41 wt %), lignin (18.46 wt %), pectin (5.34 wt %), water-soluble matter (10.02 wt %), and wax (3.72 wt %) on the basis of the dry weight of the raw cotton stalk bark fiber.

A cooker (ZQS1, China) was provided by Shanxi University of Science and Technology Machinery Plant. Caustic soda, sulfuric acid, ammonium oxalic acid, benzene, absolute ethyl alcohol, sodium sulfide, anthraquinone, sodium silicate, sodium tripolyphosphate, and barium chloride (analytical reagent grade/purity) were purchased from Hangzhou Huipu Chemical Reagent Co., Ltd. (China).

Methods

High-temperature degumming of cotton stalk bark fiber

With reference to the literature,[8] 40 g of cotton stalk bark fibers was soaked in a mixed solution including 20% sodium sulfide, 2% anthraquinone, 2% sodium silicate, and different concentrations of caustic soda (5, 10, or 15%) for 0.5 h at 150°C. The degummed cotton stalk bark fibers were then removed and washed with water at 80° to remove the remaining hemicelluloses and lignin adhered to the fibers; they were then thoroughly rinsed with water. Finally, the fibers were dried to remove free water and placed in a glass container in a conditioning chamber. The reagents amounts (weight percentages) were based on the dry weight of the raw cotton stalk bark fiber.

Measurements of the fiber length and linear density

In general, the fiber length measurement refers to the comb staple method, and a wool fiber length analyzer was applied. In this study, a single fiber was measured by a ruler, and the fiber linear density was measured by the cut-middles method.

Quantitative analysis of the fiber chemical components

GB5889-86 (China National Standard, 1986) was applied to quantitatively analyze ramie chemical components, such as wax, water-soluble matter, pectin, hemicellulose, lignin, and cellulose in People's Republic of China. Because the cotton stalk bark fiber and ramie had similar chemical components, this testing method was used to analyze the chemical components of the cotton stalk bark fiber.

FTIR spectroscopy

Infrared spectra of the samples were obtained with A FTIR spectrometer (2000, PerkinElmer, USA). The spectra were recorded in the transmittance mode in the 4000–400-cm^{-1} range with a 2-cm^{-1} resolution. About 2 mg of fiber was crushed into small particles in liquid nitrogen. The fibers were then mixed with KBr and pressed into a small disc about 1 mm thick. A total of 64 scans were taken for each sample.

WAXD

About 1 μm of raw and degummed cotton stalk bark fiber was cut, mixed with a very small amount of an adhesive material (Tragacanth BP), soaked in a drop of distilled water, and compressed into thin sheets and dried. A wide-angle diffractometer (D/Max-RA, Rigaku, Japan) was equipped with a scintillation counter, and the linear intensities were recorded between 5 and 50° (2θ angle range). The crystallinity index (I_c) was determined with eq. (1), where $I_{(002)}$ is the counter reading at peak intensity at a 2θ angle close to 22° and $I_{(am)}$ is the amorphous counter reading at a 2θ angle of about 18°. It is important to note that I_c is used to indicate the order of the crystalline regions or cellulose crystals rather than the crystallinity of the fiber:[9]

$$I_c = \left(I_{(002)} - I_{(\mathrm{am})}\right) \times 100/I_{(002)} \quad (1)$$

To determine the percentage crystallinity, the total diffracted area and the area under the crystalline peaks were determined by integration after absorption, Lorentz polarization effects, incoherent scatter, and air-scatter correction. The ratio of the crystalline area to that of the total diffracted area was taken as the percentage crystallinity.[10]

The average crystallite size was calculated from the Scherrer equation:

$$D_{(hkl)} = k\lambda/\beta_{(hkl)} \cos\theta \quad (2)$$

where $D_{(\mathrm{hkl})}$ is the size of the crystallite perpendicular to the (*hkl*) plane, k is the Scherrer constant (0.89), λ is the X-ray wavelength (1.54 E), and $\beta_{(hkl)}$ is the full width at half-maximum of the (*hkl*) peak (rad).

TABLE I
Effect of the Caustic Soda Concentration on the Constituents of Cotton Stalk Fibers at 150°C

NaOH concentration (%)	Constituent (%)					
	Wax	Water-soluble matter	Pectin	Hemicellulose	Lignin	Cellulose
0	3.72	10.02	5.34	21.41	18.46	41.05
5	2.91	3.36	1.98	10.99	7.22	73.54
10	1.48	1.36	0.15	3.10	1.15	92.76
15	2.35	2.41	0.59	3.90	1.43	89.32

SEM

SEM was used to observe the microstructural morphology of the samples. The instrument was a SEM (JSM-5610LV, JEOL, Japan) with an acceleration voltage of 5 kV. Before the scanning process, all samples were coated with gold in a vacuum sputter coater, and the thickness of the gold sputter coating was 7.5 nm.

Thermogravimetry (TG)

The thermal stability of the raw and degummed cotton stalk bark fiber were characterized with a thermo gravimetric analyzer (Pyris 1, PerkinElmer, USA). All of the sample weights were about 5 mg, and all measurements were carried out under a nitrogen atmosphere with an N_2 flow of 20 mL/min. The specimens were heated up to 500°C at the same rate of 20°C/min. The thermographs of the whole process were used for analysis.

RESULTS AND DISCUSSION

Effect of the caustic soda concentration on the fiber constituents

According to GB5889-86 (China National Standard, 1986), the chemical constituents of the raw and degummed cotton stalk bark fibers with different caustic soda concentration were tested. Temperatures up to 150°C, from the literature,[8] were selected to investigate the effect of the caustic soda concentration on the constituents of the cotton stalk bark fibers at a high temperature, and the results are shown in Table I. As shown in Table I, the cellulose, hemicellulose, and lignin in the raw cotton stalk bark fibers were 41.05, 21.41, and 18.46%, respectively. After high-temperature degumming, the contents of hemicellulose, pectin, and lignin obviously decreased with increasing caustic soda concentration. High-temperature degumming with 10% caustic soda removed the hemicellulose and lignin up to 85.52 and 93.77%, respectively; this indicated that the increase in caustic soda concentration removed more hemicellulose and lignin and increased the cellulose content in the cotton stalk bark fiber. However, with a further increase in the caustic soda concentration, the cellulose content decreased, and the contents of hemicellulose, pectin, and lignin increased. It was likely that the higher caustic soda concentration damaged the supermolecular structures of the cellulose at higher temperatures.[7,11,12]

Fiber length and linear density measurements

Fiber length and linear density are more important for application performance. Table II shows the fiber length and linear density values of the cotton stalk bark fibers after the degumming process with different caustic soda concentrations. When caustic soda concentration was 5%, degumming was insufficient, and the fiber bundles were difficult to separate; this led easily to fiber fracture and low fiber length. However, when the caustic soda concentration was 10%, the cotton stalk bark fiber had the smallest linear density and the longest average length.

WAXD analysis

To investigate the crystal structures of the cotton stalk bark fibers, the X-ray diffraction (XRD) patterns were measured for these samples. Figure 1 shows the WAXD patterns of the raw and degummed cotton stalk bark fibers with various caustic soda concentrations at 150°C. It can be seen that the raw cotton stalk bark fiber showed a cellulose I structure (Dyer and Daul, 1985) with diffraction peaks of the 2θ angles at 15.1, 16.1, and 22.4°, which were assigned to (101), ($10\bar{1}$), and (002) planes,

TABLE II
Effect of the Caustic Soda Concentration on the Length and Linear Density of Cotton Stalk Fibers at 150°C

NaOH concentration (%)	Average length (mm)	Linear density (tex)	Average linear density (tex)
5	22.54	0.90–1.12	0.93
10	24.76	0.87–1.09	0.91
15	23.01	0.89–1.08	0.94

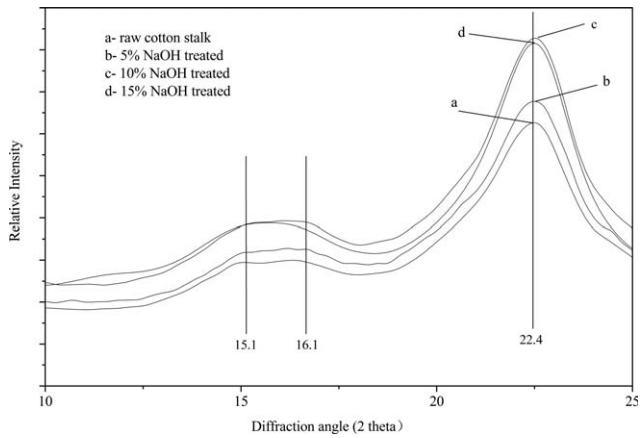

Figure 1 X-ray diffractogram of raw and treated cotton stalk fibers.

respectively. We further confirmed that different alkali concentrations did not change the cotton stalk bark fiber's crystal structure; all of the degummed cotton stalk bark fibers still maintained the structure of cellulose I.

It also could be found that the strength of the diffraction peaks at the (101), ($10\bar{1}$), and (002) planes in the samples of degummed cotton stalk bark fibers was much greater than that in the raw sample; this indicated that the crystal structure of the degummed cotton stalk bark fibers was better than that of the raw fiber. I_c, which can influence the strength and stiffness of fibers was calculated according to the Segal empirical method;[13–16] this provided a quantitative measure of the crystallinity in the fibers. Table III shows the percentage crystallinity, I_c, and crystallite size of the raw and degummed cotton stalk bark fibers with different caustic soda concentrations at 150°C. It was determined that the percentage crystallinity and I_c of the raw cotton stalk bark fibers were 52.2% and 59.8, respectively. The percentage crystallinity and I_c of the degummed cotton stalk bark fibers were higher than those of the raw material because of the removal of the lignin and hemicelluloses during degumming process. It was found that the percentage crystallinity and I_c of the cotton stalk bark fibers increased with the increase in caustic soda concentration, as shown in Table III.

TABLE III
Crystallinity and Crystallite Size of Cotton Stalk Fibers Degummed with Different Caustic Soda Concentrations

NaOH (%)	Crystallinity (%)	Crystallite index	$L_{(002)}$ (nm)	$D_{(002)}$ (nm)
0	52.2	59.8	3.2987	0.3989
5	57.4	69.6	3.3103	0.3953
10	61.3	74.9	3.9212	0.3936
15	60.9	73.4	3.9689	0.3958

Note: $L_{(002)}$ and $D_{(002)}$ mean crystallite size and interplanar distance, respectively.

However, the percentage crystallinity and I_c of the degummed cotton stalk bark fibers with 15% caustic soda were slightly less than those with 10% caustic soda. It was thought that 10% caustic soda was sufficient to remove the lignin and hemicellulose and that a higher alkali concentration could have damaged the molecular chain of the cellulose crystals. This was in line with the results of the chemical constituent analysis of cotton stalk bark fibers.[7]

The crystallite sizes of the cotton stalk bark fiber increased after alkali degumming and were found to be as high as 3.96 nm at 15% caustic soda. This was probably because the cellulose crystals underwent moderate recrystallization under the conditions of high-temperature alkali degumming with the removal of noncellulosic substances. Some authors have also reported that amorphous cellulose subjected to hydrothermal treatment above 100°C shows moderate recrystallization.[7,17–20] Also, the distance between the (002) crystalline planes slightly decreased after alkali degumming; this suggested that only the chain stacking density in this direction increased after high-temperature alkali degumming.[7]

TGA

The thermal behaviors of the raw and degummed cotton stalk bark with different caustic soda concentrations were investigated by TGA. Additionally, the location of peaks observed in the differential thermogravimetry (DTG) curve also provided information on the component and the effect of the composite components on the temperature scale. Figures 2 and 3 show the TG and DTG curves of the raw and degummed cotton stalk fibers. The DTG curves (Figure. 3) of the raw cotton stalk bark fibers showed

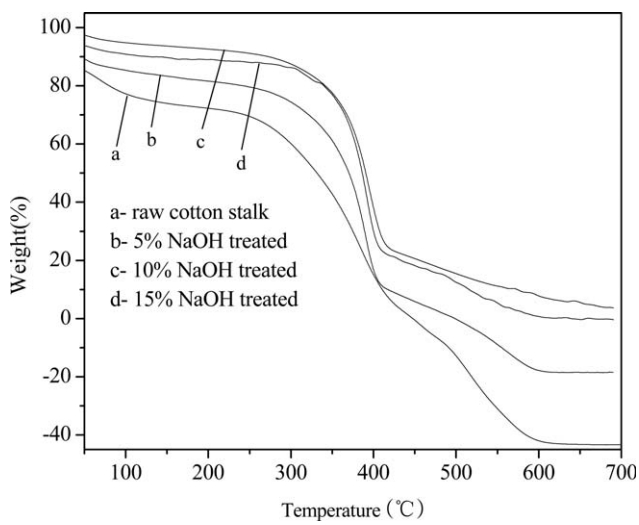

Figure 2 TG curve of raw and degummed cotton stalk fibers.

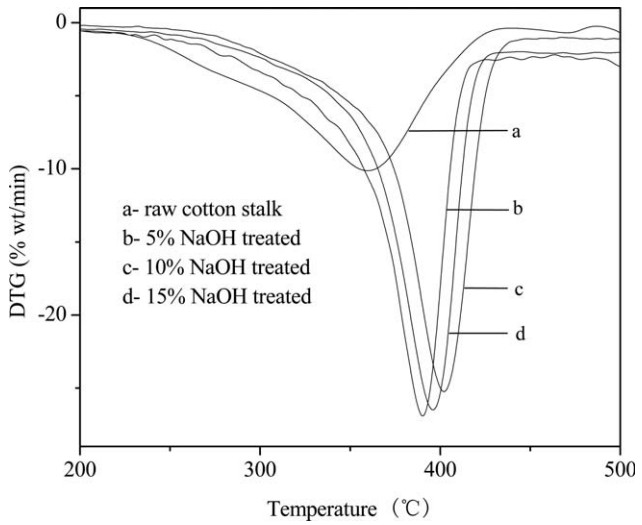

Figure 3 DTG curve of raw and degummed cotton stalk fibers at different temperatures.

an initial peak between 50 and 150°C, which corresponded to a mass loss of absorbed moisture. After this peak, the DTG curve showed three decomposition steps: (1) the first decomposition step at about 200–300°C was mainly attributed to the thermal decomposition of hemicellulose and pectin, (2) the second decomposition step at about 300–400°C was mainly attributed to the decompositions of cellulose and lignin, and (3) the final step at 400–500°C might have been mainly due to the oxidative degradation of the charred residues. The effects of various caustic soda concentrations on the DTG peak position are reported in Figure 3. The DTG maximum peak position shifted to higher temperatures after high-temperature degumming compared with the raw cotton stalk bark fibers. The main decomposition temperature increased from 359.6 (raw) to 390.3, 402.4, and 396.8°C for the 5, 10, and 15% NaOH degummed cotton stalk bark fibers, respectively. The DTG maximum peak position was consistent with the results of the X-ray crystallinity and I_c.

On the basis of the results illustrated in Figure 3, we concluded that the main decomposition temperature might have been associated with the crystalline structure of the cotton stalk bark fiber. The increasing temperature at which the maximum degradation rate of the degummed fibers occurred was likely to have resulted from a higher crystalline order, crystallinity, crystallite size, and chain stacking density of the cellulose crystalline structure. A reference also reported that a higher order of cellulose crystalline structure required a higher degradation temperature.

FTIR spectral analysis

As a relatively easy method, FTIR spectroscopy, from which the direct structural information and changes can be obtained, has been widely used in cellulose research. Infrared spectra of the raw and degummed cotton stalk bark fibers treated with different caustic soda concentrations are shown in Figure 4. According to the literature,[21,22] the absorbance peak at 897 cm^{-1} was attributed to the β-glycosidic linkages between the monosaccharides of the cotton stalk fibers. It can be seen that the absorption peaks of 3420 cm^{-1}, ascribed to the —OH group, and the absorption peaks in the fingerprint regions at 1426, 1160, and 1050 cm^{-1}, attributed to the cellulose structure, almost did not change for all cotton stalk bark fiber samples.[23,24] However, the FTIR spectrum of the raw cotton stalk bark fibers was distinctly different from those of the degummed fibers. First, the vibration peak at 1736 cm^{-1}, attributed to the C=O stretching of methyl ester and carboxylic acid, disappeared after the degumming treatment. This indicated the removal of lignin, hemicelluloses, and pectin; this was in accordance with the results of the chemical constituent analysis of the cotton stalk fibers. Second, the absorption band at 1626 cm^{-1} of the raw cotton stalk bark was drastically weakened and shifted to 1637 cm^{-1} for the degummed fibers; this was ascribed to antisymmetric COO— stretching and indicated that the used degumming methods removed the lignin effectively. Third, the absorbance peak at 1510 cm^{-1} was attributed to an aromatic C—H out-of-plane vibration in the lignin. When the cotton stalk bark was degummed with 5% NaOH, compared with the raw cotton stalk bark, this absorption peak decreased significantly, and with the increase in NaOH concentration, the absorbance peak at 1510 cm^{-1} disappeared. This indicated that

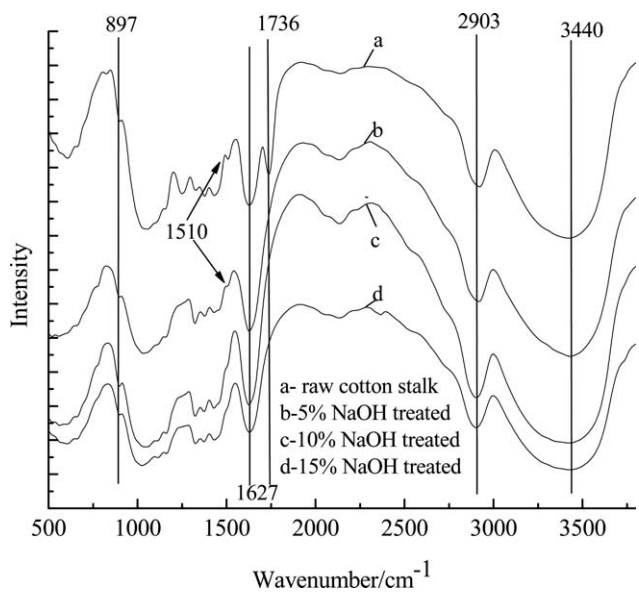

Figure 4 FTIR spectra of raw and high-temperature degummed cotton stalk fibers.

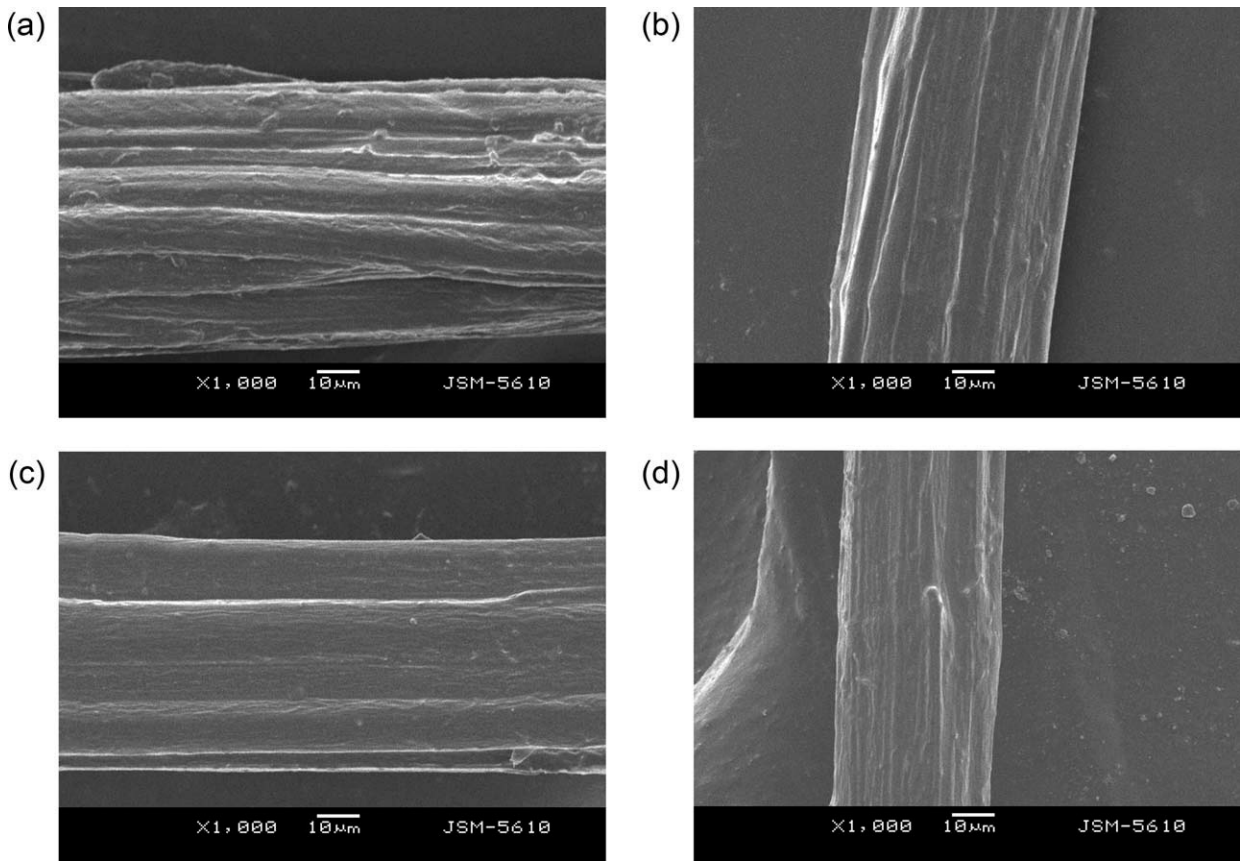

Figure 5 SEM images of cotton stalk fibers: (a) raw, (b) 5% NaOH treated at 150°C, (c) 10% NaOH treated at 150°C, and (d) 15% NaOH treated at 150°C.

high caustic soda concentration obviously reduced the lignin content in the cotton stalk bark fibers. All of these proved that pectin, hemicelluloses, and lignin were easily be removed by the degumming treatment with caustic soda.

SEM analysis

SEM images at a magnification of 1000× were obtained for the raw and degummed cotton stalk bark fibers. As shown in Figure 5(a), the raw cotton stalk bark fiber was covered with a layer consisting of hemicellulose, pectin, lignin, and wax, which could help to bind the single cells of the cotton stalk bark fibers and form optimum organizations to protect the fiber from being damaged by the ambient environment. However, the outlayer of the cotton stalk bark fibers was removed after the degumming processes, and the surface of the degummed fibers [Figure 5(b–d)] became smoother compared to that of the raw material. Figure 5(b) indicates that a low caustic soda concentration (5%) was not sufficient to remove the noncellulosic substances homogeneously. Some lignin and hemicellulose and less pectin were present on the surface of the fibers. Figure 5(c) indicates that a degumming treatment with 10% caustic soda was sufficient to remove most of the lignin and hemicellulose, and the surface topography was smoother than in the raw cotton stalk bark fiber. Figure 5(d) shows a monofilament treated with 15% caustic soda at 150°C. The noncellulosic substances were removed from the fibers, but the surface was not as smooth as that of the fiber treated with 10% caustic soda.

CONCLUSIONS

In this research, degumming treatments of cotton stalk bark fibers with different caustic soda concentrations at high temperature were conducted. On the basis of the results of length, linear density, and composition, the degummed cotton stalk bark fibers could be expected to be suitable for high-value fibrous applications. The chemical constituent analysis of the cotton stalk bark fiber and FTIR results proved that high-temperature alkali degumming was effective for removing pectin, hemicellulose, and lignin from the cotton stalk bark fibers. High-temperature alkali degumming did not change the crystalline form of the cotton stalk bark cellulose, and it still showed the characteristics of cellulose I. XRD analysis showed that the crystallinity, I_c, and crystallite size of the cotton stalk bark fiber increased after high-temperature alkali degumming. TG and

DTG analysis results suggested that the high-temperature alkali degumming treatment could improve the thermal stability of cotton stalk bark fibers.

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