

Effect of High Temperature Alkali Cooking on the Constituents, Structure and Thermal Degradation of Hemp Fiber

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Received 23 May 2007; accepted 29 December 2007

DOI 10.1002/app.28008

Published online 19 March 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Degumming of hemp fiber by high temperature alkali cooking was investigated, and the effect of temperature and dosage of alkali on the constituents, structure, and thermal degradation of hemp fiber was also discussed in this work. The morphology, structure, and thermal degradation of hemp fiber after high temperature cooking were investigated through SEM, FTIR, WAXD, and TG analysis. The results indicated that the high temperature cooking process was

effective for removing hemicelluloses and lignin and could also improve the thermal stability of cellulose. Crystallinity index of the treated hemp fiber was increased, which was related to the cooking temperature and NaOH dosage. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 4058–4064, 2008

Key words: hemp fiber; high temperature; alkali cooking; structure; constituents

INTRODUCTION

Hemp is also called *Cannabis sativa*. It is an annual herbaceous plant native to Asia and widely cultivated in many parts of the world. Hemp fiber has the advantages of fineness, good moisture absorption, air permeability, radiation shielding, and antibacterial properties.^{1–3} However, decorticated hemp fibers contain 30% ± 10% gum, consisting mainly of pectin (10%), hemicellulose (18%), and lignin (6%).^{4,5} This gum should be removed as much as possible to fulfill the textile requirement (1.5% ± 2.5% residual gum). The single cell fiber of hemp was about 15–25 mm, which was too short and is not available to spin yarn.⁶ Thus, a proper degumming process that separates the fiber from nonfiber stem issues is very important to extract fibers for industrial use.

Traditionally, three methods (physical, chemical, and biological processes) for hemp degumming have been used. However, disadvantages also exist for these methods that include: low and inconsistent

quality, restriction to certain climatic regions, and producing serious contamination to environment. Furthermore, the traditional degumming processes were often time-consuming, laborious, and ineffective.⁷ As a result of these problems, a better degumming method has been sought for some time.

In a previous work,⁸ we attempted to remove non-cellulosic gummy materials from hemp using the high temperature cooking with low alkali and obtained excellent fibers. In the present work, we further investigated the effects of high temperature cooking process with low alkali content on the hemp fiber. The effect of cooking temperature and dosage of alkali on the constituents, structure, and the thermal degradation of hemp fiber was extensively discussed. Also, the morphology, structure, and thermal degradation of hemp fiber after high temperature cooking treatments were investigated through scanning electron microscope (SEM), Fourier transform infrared (FTIR), wide angle X-ray diffraction (WAXRD), and thermogravimetry (TGA).

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50573068.

Contract grant sponsor: Changjiang Scholars and Innovative Research Team in University; contract grant number: IRT0654.

Contract grant sponsor: Key Scientific Industrial Research Foundation of Zhejiang Science and Technology; contract grant number: 2005C21077.

Journal of Applied Polymer Science, Vol. 108, 4058–4064 (2008)
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EXPERIMENTAL

Materials

Hemp fiber was obtained from the quartermaster research institute of general logistics department of China People's Liberation Army. The constituents (% w/w) of the hemp bast fiber was cellulose (58.17%), hemicellulose (18.16%), lignin (6.21%), pectin (6.56%), water soluble matter (8.24%), and wax

(2.66%) based on the dry weight of raw hemp fiber. Cooking cooker (Model ZQS1) was provided by Shanxi University of science and technology machinery plant. Sodium hydroxide, sodium sulfide, sodium sulfide, benzene, ethanol, and absolute ethyl alcohol of AR grade/purity used in this article were purchased from the market.

METHODS

High temperature degumming of hemp fiber

Forty grams of hemp fibers were soaked in 200 g including 5% sodium sulfide, 0.02% anthraquinone, 2% sodium silicate, and different concentrations of sodium hydrate (5%, 7%, 9%, 11%) mixed solution for 0.5 h, then cooked in cooking cooker (Model ZQS1) at different temperatures (100, 120, 150, and 180°C) for 1 h. The degummed hemp fibers were then removed, washed with water at 80°C to remove the remaining hemicelluloses and lignin adhered to the fibers, and then thoroughly rinsed with water. The fibers were then dried to remove free water and placed in a glass container in a conditioning chamber. When the cooking temperature was selected as a variable factor, the dosage of sodium hydroxide was constant. When the dosage of sodium hydroxide was selected as a variable factor, the cooking temperature was constant.

Wide angle X-ray diffraction

About 1 μm of untreated and treated hemp fibers were cut and were 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 (Model D/Max-RA, Rigaku, Japan) was equipped with a scintillation counter, and linear intensities were recorded between 5° and 50° (2 θ -angle range). The crystallinity index (I_c) was determined by using eq. 1 below,⁹ where $I_{(002)}$ is the counter reading at peak intensity at a 2 θ angle close to 22° and $I_{(\text{am})}$ is the amorphous counter reading at a 2 θ angle of about 18°. It is important to note that the crystallinity index is used to indicate the order of the crystalline regions or cellulose crystals rather than the crystallinity of the fiber.¹⁰

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

To determine the % 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 % crystallinity.¹¹

The average crystallite size is calculated from the Scherrer equation 2:

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

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

Thermogravimetry

The thermal stability of raw and cooked hemp fibers were characterized using a Perkin Elmer Pyris Diamond TGA thermogravimetric analyzer. All the sample weights were about 5 mg, and all measurements were carried out under a nitrogen atmosphere with a N_2 flow of 20 mL/min. The specimens were heated up to 700°C, at the same rate of 20°C/min. The thermographs of the whole process were used for analysis.

FTIR spectroscopy

Infrared spectra of samples were measured with a Perkin-Elmer FTIR 2000 Spectrometer. 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 fiber particles 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.

Scanning electron microscopy

SEM was used to observe the areal microstructural morphology of the samples. The instrument was a JSM-5610LV SEM (Jeol, Japan) with an acceleration voltage of 20 kV. Before the scanning process, all samples were coated gold in a vacuum sputter coater, and the thickness of the gold sputter coating was 7.5 nm.

RESULTS AND DISCUSSION

Effect of NaOH dosage on the fiber constituents

According to GB5889-86,¹² chemical constituents of the raw fiber and treated fibers by high temperature cooking were tested and compared. The temperature up to 150°C was selected for investigating the effect of NaOH dosage on the constituents of hemp fibers at a high temperature, and the result was shown in Figure 1.

In raw hemp fiber, the content of cellulose, hemicellulose, and lignin was 58.16%, 18.16%, and 6.21%, respectively. After high temperature cooking, the contents of hemicellulose, pectin, and lignin obvi-

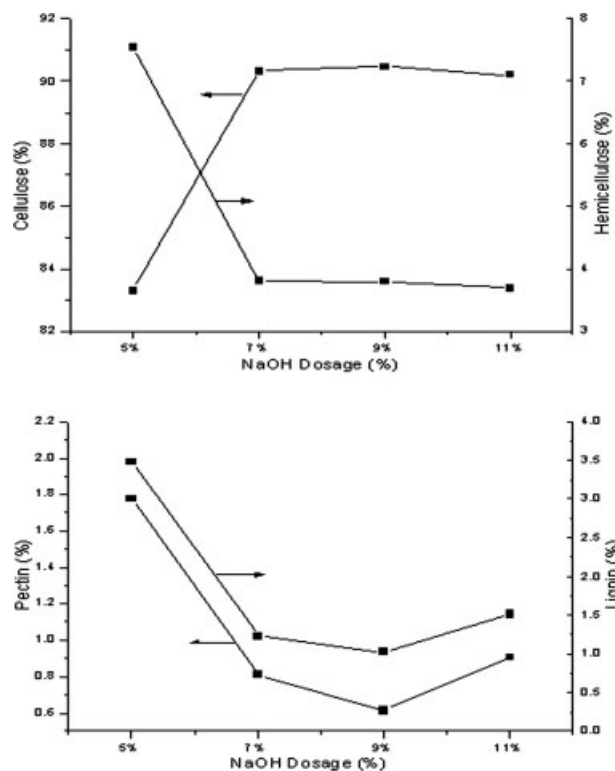


Figure 1 Effect of NaOH dosage on the constituents of hemp fibers at 150°C.

ously were decreased with the increase of NaOH dosage. High temperature cooking using 9% NaOH would remove the hemicellulose and lignin up to 79.1% and 83.5%, respectively, which indicated that the increase of NaOH dosage would increase the content of cellulose in hemp fiber. However, with the further increase of NaOH dosage, the content of cellulose would be decreased, and the contents of hemicellulose, pectin, and lignin were increased. It was likely that the more high NaOH dosage would cause damage to the supermolecular structures of cellulose at such high temperatures.

Effect of temperature on the constituents

Temperature is proposed to be very important to the chemical reactions at high temperature cooking, which may produce an effect on the reaction speed and the efficiency of cooking.¹³ Considering that cellulose may be damageable to such a high alkali dosage as 11%, the results of 9% NaOH cooking were studied in this article and shown in Figure 2.

As illustrated in Figure 2, when the hemp fibers were cooked at 100°C, the contents of hemicellulose and lignin were still higher. It indicated that these matters were difficult to remove during normal temperature cooking. But with the increasing of temperature, the content of cellulose increased, and the content of hemicellulose and lignin decreased obviously.

The cooking temperature at 150°C would remove the contents of the hemicellulose and lignin more up to 47.1% and 65.2%, respectively, than the contents at 100°C. This revealed that high temperature cooking was an effective method for removing hemicellulose and lignin from hemp fibers. The explanation for this effect of high temperature cooking may be that the peeling and hydrolysis reactions took place in alkaline condition at high temperature, the significant amounts of hemicellulose were partially hydrolyzed, and some lignin was depolymerised, giving rise to sugars and phenolic compounds that were soluble in water, and so hemicellulose and lignin were removed by these reactions.¹⁴

WAXRD results

X-ray diffraction images of the untreated and treated hemp fibers with various dosage of NaOH solution at 150°C are shown in Figure 3. The main diffraction peaks of hemp fiber appeared at 2θ -angles of 15.1°, 16.7° and 22.4° corresponding to (101), (10 $\bar{1}$), and (002) crystalline planes respectively, which was the typical crystallographic pattern of cellulose I.¹⁰ The variety of NaOH dosage caused no change to the

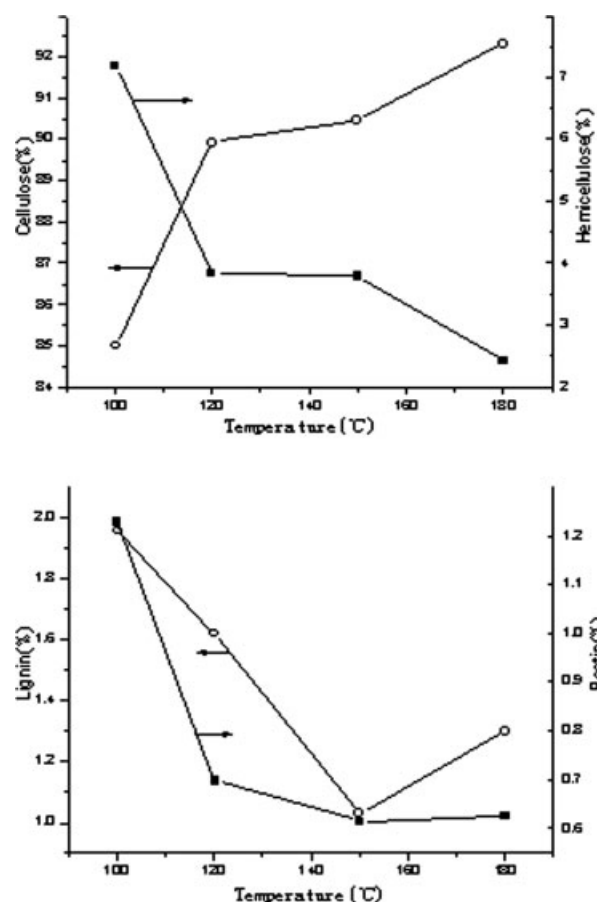


Figure 2 Effect of temperatures on the constituents of hemp fibers at 9% NaOH.

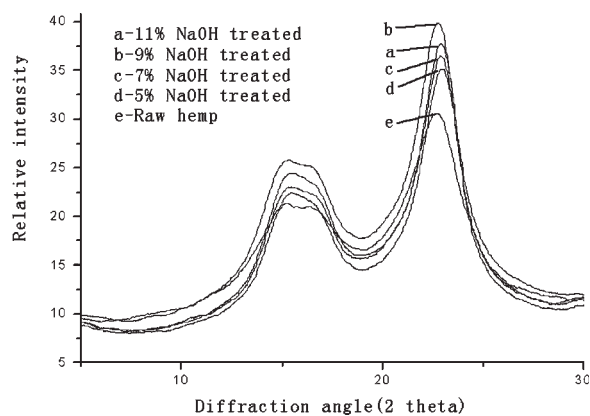


Figure 3 X-ray diffractogram of raw and treated hemp fibers.

cellulose crystal form, and alkali-treated hemp fibers still showed the characteristics of cellulose I. However, the variety of NaOH dosage caused an increase in intensity of the (002) plane, which indicated improvement in the order of the crystalline regions upon alkali treatment.¹⁵

Table I shows the crystallinity (%), crystallinity index, and crystallite size of untreated and treated fibers under different NaOH dosages at 150°C. It was determined that crystallinity (%) and crystallinity index of raw hemp fiber were 40.4% and 43.7%, respectively. The crystallinity (%) and crystallinity index of treated hemp fibers were higher than that of the raw material due to the removal of the lignin and hemicelluloses during cooking. It was found that the crystallinity (%) of hemp fiber increased with dosage of NaOH, as shown in Table I. However, the crystallinity index of hemp fiber increased until 9% NaOH and slightly decreased at 11% NaOH after high temperature cooking. The dosage of 11% NaOH was slightly higher and caused damages to the molecular chains of the cellulose crystals at high temperature cooking, which was in line with the result of the chemical constituent analysis of the hemp fiber.

Crystallite sizes of the hemp fiber increased after alkali cooking at 150°C, and it was found to be as high as 4.2 nm at 11% NaOH. This was probably because the cellulose crystals had undergone moderate recrystallization on the condition of high tempera-

TABLE I
Crystallinity and Crystallite Size of Different Dosages of NaOH-treated Fibers

NaOH(%)	Crystallinity (%)	Crystallinity index	$d_{(002)}$ (nm)	$L_{(002)}$ (nm)
Raw	40.4	43.7	0.2001	3.2
5	50.4	55.2	0.1986	3.8
7	51.6	55.3	0.1986	3.9
9	53.5	57.9	0.1988	4.0
11	54.7	57.6	0.1984	4.2

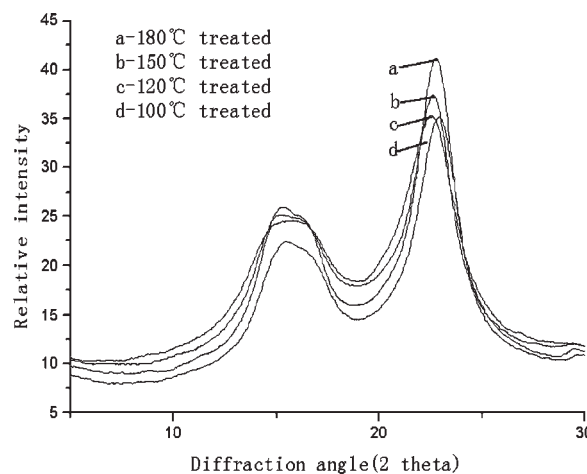


Figure 4 X-ray diffractogram of different temperature-treated hemp fibers.

ture alkali cooking with the removal of noncellulosic substances. Some authors¹⁶ had also reported that amorphous cellulose subjected to hydrothermal treatment above 100°C showed moderate recrystallization. Besides, the distance between (002) crystalline planes slightly decreased after alkali cooking, suggesting that only the chain stacking density in this direction increased after high temperature alkali cooking.

The X-ray diffraction images of the hemp fibers with different cooking temperatures at 9% NaOH are given in Figure 4. The high temperature cooking did not modify the crystalline form of the hemp cellulose. Treated hemp fibers still showed the characteristics of cellulose I.

The crystallinity (%), crystallinity index, and crystallite size of the hemp fiber treated with different cooking temperatures at 9% NaOH are shown in Table II. It was determined that the crystallinity index of hemp fiber increased with the raise of cooking temperature, indicating that 9% NaOH did not deteriorate the crystals of the cellulose and the crystalline order of the fiber with the increase of cooking temperature. The crystallinity (%) of hemp fiber increased from 46.2 (at 100°C) to 54.2 (at 180°C). It was also found that the crystallite size of the treated hemp fiber at 002 lattice planes increased with the change of cooking temperature from 3.2 to 4.3 nm, as similarly reported by Esat Gumuskaya.¹⁴

TABLE II
Crystallinity and Crystallite Size of Different Temperature-Treated Hemp Fibers

Temperature (°C)	Crystallinity (%)	Crystallinity index	$d_{(002)}$ (nm)	$L_{(002)}$ (nm)
100	46.2	48.4	0.2000	3.2
120	51.9	51.4	0.1997	3.8
150	53.5	57.9	0.1988	4.0
180	54.2	60.5	0.1982	4.3

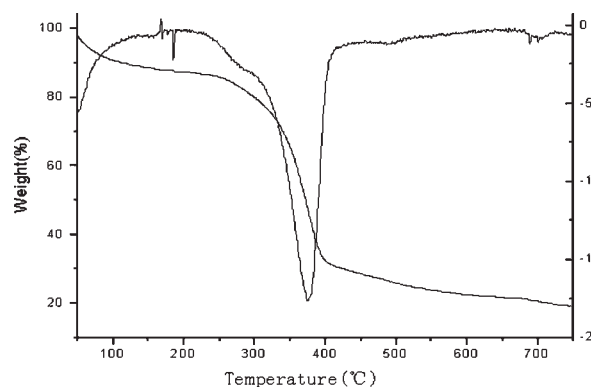


Figure 5 The TG and DTG of untreated hemp fiber.

Thermal degradation of hemp fiber

The differential thermogravimetry (DTG) curves (Fig. 5) of untreated hemp fiber shows an initial peak between 50 and 150°C, which corresponded to a mass loss of absorbed moisture of 8.92%. After this peak, the DTG curve showed three decomposition steps: (1) the first decomposition step at about 200–270°C was attributed to thermal decomposition of hemicelluloses or pectin (mass loss 3.33%); (2) the second decomposition step at about 295–400°C was attributed to cellulose and lignin decomposition (mass loss 48.43%); (3) the third step at 400–700°C (mass loss 11.63%) might be attributed to oxidative degradation of the charred residues.¹⁰

The effects of various NaOH dosage at 150°C on the DTG peak position are reported in Figure 6. The DTG maximum peak position shifted to higher temperatures after high temperature cooking compared with the untreated fibers. The main decomposition temperature increased from 374.7 (raw) to 382.7, 390.1, and 388.8°C for the 5% NaOH, 9% NaOH, and 11% NaOH treated fibers, respectively. And the DTG maximum peak position slightly shifted to lower temperature at 11% NaOH treated fibers, which was

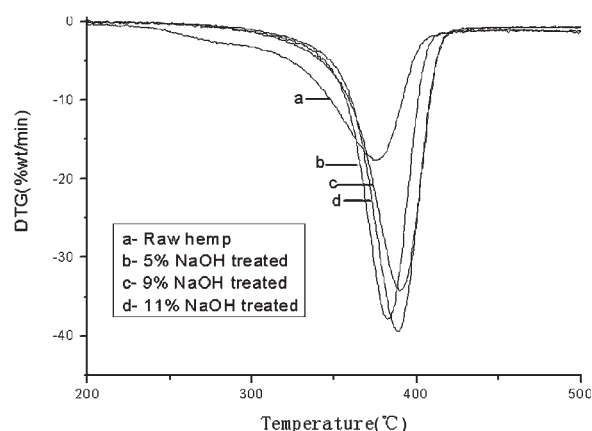


Figure 6 DTG of different dosages of NaOH-treated hemp fiber.

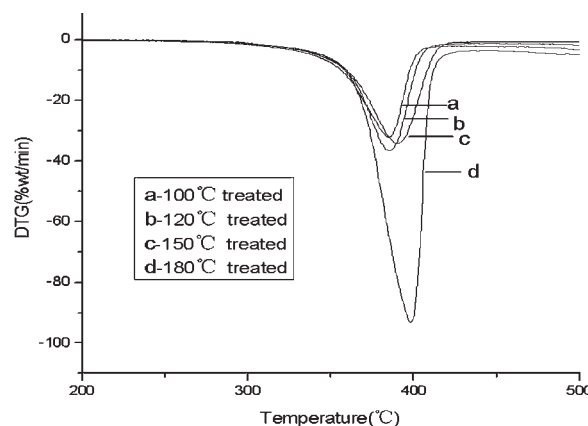


Figure 7 DTG of different temperature-treated hemp fiber.

consistent with the result of the X-ray crystallinity index.

The effects of different cooking temperatures at 9% NaOH on the DTG peak position of hemp fiber are shown in Figure 7. The main decomposition temperature shifted from 385.3 (100°C) to 385.6, 390.1, and 400.5°C for the 120, 150, and 180°C treated fibers, respectively. Based on the results illustrated in Figures 6 and 7, we could conclude that the main decomposition temperature may be associated with the crystalline structure of the hemp fiber. The increasing temperature at which maximum degradation rate of the treated fibers occurs were likely to result from a higher crystalline order, crystallinity, crystallite size, and chain stacking density of the cellulose crystalline structure. Reference 15 also reported that a higher order of cellulose crystalline structure requires a higher degradation temperature.

FTIR results

Infrared spectra of the raw and hemp fibers treated with 9% NaOH at 150°C are shown in Figure 8.

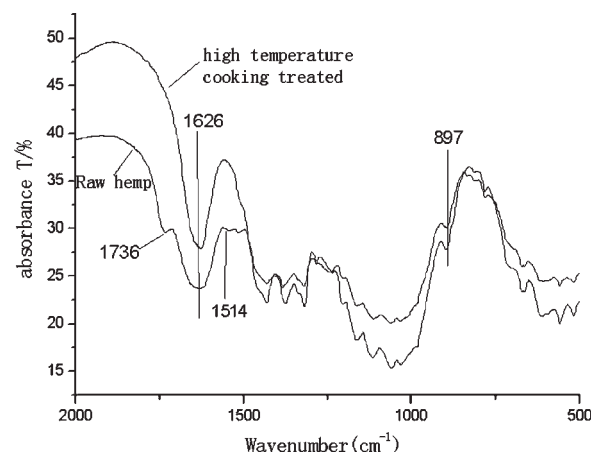


Figure 8 IR spectra of untreated and high temperature cooking treated fibers.

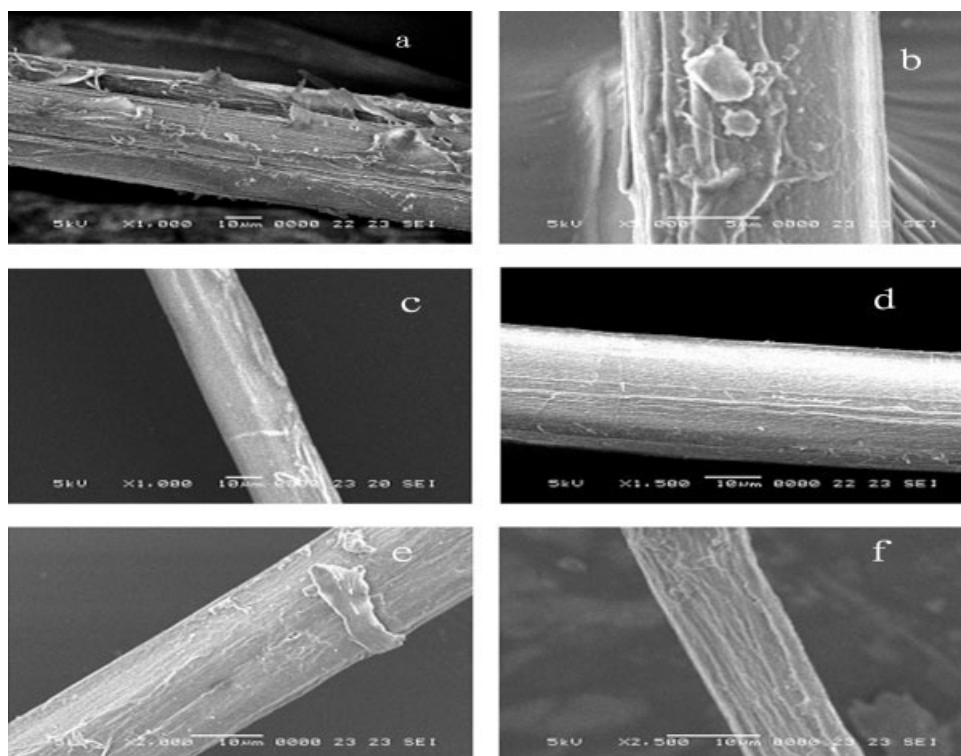


Figure 9 SEM images of hemp fiber: (a) raw, (b) 9% NaOH treated at 120°C, (c) 9% NaOH treated at 150°C, (d) 9% NaOH treated at 180°C, (e) 5% NaOH treated at 150°C, (f) 11% NaOH treated at 150°C.

With reference to the literatures,^{17,18} the absorbance peak at 897 cm^{-1} was attributed to the β -glycosidic linkages between the monosaccharides of hemp fiber. The vibration peak at 1736 cm^{-1} attributed to the C=O stretching of methyl ester and carboxylic acid in pectin disappears upon high temperature cooking treatment, indicating the removal of pectin and hemicelluloses by high temperature cooking, which accorded with the result of the chemical constituent analysis of hemp fibers. The absorbance peak at 1626 cm^{-1} was due to the bending mode of the absorbed water. The absorbance peak at 1514 cm^{-1} attributed to an aromatic C—H out-of-plane vibration in the lignin also disappears after the treatment. This indicated that the high temperature alkali cooking treatment could obviously reduce lignin content of hemp fibers. All these proved that pectin, hemicelluloses, and lignin could easily be removed by high temperature alkali cooking treatment.

SEM results

SEM images at magnifications between 1000 and 3000 were obtained for untreated and high temperature alkali cooked fibers. Figure 9(a) shows a fiber monofilament of untreated hemp covered by noncellulosic substances and the surface topography of hemp is rougher before treatment. Figure 9(b) indicates that a treatment at 120°C is not sufficient to

remove all of the noncellulosic substances from the fibers. Some pectins are still present on the surface of the fibers. Figure 9(c) indicates that treatment with 9% NaOH at 150°C is sufficient to remove all of the noncellulosic substances from the fibers. Treated fibers exhibit a considerably cleaner and smooth surface, and the hemp monofilament is 20–40 μm in diameter. Figure 9(d) shows a fiber monofilament treated with 9% NaOH at 180°C. The noncellulosic substances are removed from the fibers, but the surface is not as smooth as that of the fiber treated at 150°C. A low NaOH dose (5%) is not sufficient to remove the noncellulosic substances homogeneously. Some pectin is still present on the surface of the fibers [Fig. 9 (e)]. But with the increase of NaOH dosage, the surface of the fibers appears to be affected by alkalization at the highest dosage [Fig. 9 (f)].

CONCLUSIONS

The treatment of hemp fiber by high temperature alkali cooking has been conducted in this research. Chemical constituent analysis of hemp fiber and FTIR results prove that high temperature alkali cooking is an effective method for removing pectin, hemicellulose, and lignin from hemp fibers. The high temperature alkali cooking does not change the crystalline form of the hemp cellulose, still showing the characteristics of cellulose I. After high temperature alkali

cooking, X-ray diffraction analysis shows that the crystallinity, crystallinity index, crystallite size of the hemp fiber has been raised, which is subject to the cooking temperature and dosage of NaOH. High temperature alkali cooking treated fibers look cleaner with a highly smooth surface. TG and DTG analysis results suggest that high temperature alkali cooking treatment could improve the thermal stability of the hemp cellulose.

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