Effect of Steam Pressure on Chemical and Structural Properties of Kenaf Fibers during Steam Explosion Process

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The chemical and structural properties of kenaf fibers that were treated at different steam pressures during the steam explosion process were investigated. With increased steam pressure, a higher percentage of cellulose and acid-insoluble lignin and a lower content of hemicellulose and pectin were obtained. This result was further confirmed by Fourier transform infrared (FTIR) spectroscopy. X-ray diffraction (XRD) studies revealed that the steam-exploded kenaf fibers were more crystalline than the raw kenaf fibers, and that excessive steam pressure above 3 MPa damaged the cellulose crystalline structure. Scanning electron microscopy (SEM) analysis showed a change in the surface morphology of the treated kenaf fibers. The lower content of gums and the effective defibrillation of steam-exploded kenaf fibers demonstrated the potential of steam explosion treatment in applications of kenaf fibers.

Keywords: Kenaf; Steam explosion; Chemical composition; Cellulose; Structural properties

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INTRODUCTION

Natural fiber materials, such as ramie, flax, kenaf, and bamboo, have attracted growing interest for use as textile materials because of their economic, sustainable, and renewable characteristics (Sonia and Priya Dasan 2013). Natural cellulosic fiber plays an important role in textile products.

Compared with other natural fiber materials, kenaf is relatively commercially available and economically cheap for many varied applications, *i.e.*, textiles, pulps, fabrics, building materials, biocomposites, bedding, and oil absorbing materials; it has a short plantation cycle and great flexibility in changing environmental conditions (Saba *et al*. 2015a; Saba *et al*. 2015b; Wi *et al*. 2015). Kenaf fiber is an alternative source of energy and material because of its biocompatibility, biodegradability, and excellent capability of moisture-absorption and moisture-desorption (Wang and Ramaswamy 2003). Aside from cellulose, kenaf fiber is also composed of pectin, hemicellulose, and lignin, which are called the “gums”. Individual fibers are glued by the non-cellulosic material to form the bast fibers. To improve the added value of kenaf, we have to degum the kenaf fiber to get the technical fiber bundles with certain length, fineness, and breaking strength (Amel *et al*. 2013). However, the high content of gums makes it difficult to extract fibers from kenaf bast; thus, the applications of kenaf in textiles have been restricted.

An effective method to degum the raw bast is necessary for the utilization of kenaf fibers. Mechanical, chemical (Ray and Sarkar 2001), physical-chemical (Abraham *et al*.

2013), and biological (Evans *et al*. 2003) treatments have been employed to separate fibers from the natural cellulosic fibers. Steam explosion is an effective low cost and environmentally friendly pretreatment method (Sheng *et al*. 2014). During steam explosion, saturated steam is penetrated into the fibers. When the steam pressure is released suddenly, hemicellulose is hydrolyzed, and hemicellulose-lignin bonds are also cleaved, which increases the solubility of lignin in alkaline or organic solvents (Li *et al*. 2007).

The steam explosion process successfully extracts the cellulose nanofibrils from pineapple leaf fibers. The high-pressure hydrothermal process of steam explosion individualizes the embedded cellulose of pineapple leaf fiber from a macro to nano scale, which contributes to a unique morphology of the interconnected web-like structure of nanofibers (Cherian *et al*. 2010). The pressure, time, and moisture content have significant effects on the steam explosion process. Liu *et al.* (2014) optimized the effect of the working parameters, including pressure and time, of treated corn stover to get the most glucose yield. Diop *et al.* (2015) investigated the processing conditions of dilute-acid steam explosion and changes in the cellulose fiber structure in polymer composites; there was isolation of cellulose fibers, decreased fiber length, and diminished fiber whiteness with increasing treatment severity. However, the effect of different steam pressures on the chemical and structural properties of kenaf fibers remains unclear.

In this study, steam explosion was chosen to pretreat kenaf fibers. Kenaf fibers were treated by steam explosion at different steam pressures. The effect of steam explosion on the characterization of kenaf fibers was investigated, and changes in regularity of the chemical and structural properties of kenaf fibers that were treated with different steam pressures were examined. The steam explosion treatment of kenaf fibers was evaluated by the single factor experiment of steam pressure. The chemical and structural properties of the kenaf fibers were studied by chemical composition analysis, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

Raw kenaf fibers were collected from Aksu Prefecture of Xinjiang, People’s Republic of China. Analytical grade ammonium oxalate, sodium chlorite, glacial acetic acid, and sodium hydroxide were obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Sulfuric acid (98%) was purchased from Xiangyu Chemical Industrial and Trading Co., Ltd. (Tianjin, China). All reagents were used as they were received.

Methods

Steam explosion treatment

Kenaf fibers were chopped to obtain a uniform size of approximately 5 cm. After being impregnated with distilled water with a fiber-to-liquor weight ratio of 1:20 at room temperature for 12 h, the kenaf fibers were divided into 10-g samples and steam-exploded in a QB-200 steam explosion reactor (Gentle Bioenergy, Hebi City of Henan Province, China) with different steam pressures of 1 MPa to 3 MPa for 3 min. The pressure was then released. The fibers were removed from the collector and washed with distilled water until the solution was neutral. The kenaf fibers were dried in a hot air oven at 75 °C for 24 h.

Chemical composition determination

The acid-soluble and acid-insoluble lignin content of kenaf fibers was determined as described (Sluiter *at al*. 2008). The water-soluble matter, pectin, hemicellulose, and cellulose content of the kenaf fibers that were treated and untreated were determined using the method described by Sun *et al.* (1998).

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the samples were recorded by a Nicolet iN10 Fourier transfer-infrared spectrophotometer (ThermoFisher Scientific, Madison, WI, USA) to examine the structural changes in the kenaf fibers. About 2 mg of fiber was milled to small particles. The fiber particles were then mixed with KBr and pressed into a small disc about 1 mm thick. The FTIR spectra were recorded at a spectral range of 4000 cm^{-1} to 400 cm^{-1} at a resolution of 2 cm^{-1}, with a total of 32 scans for each sample. The spectral outputs were recorded in the transmittance mode as a function of wavenumber.

X-ray diffraction (XRD)

The crystallinity index (CI) of the treated and untreated kenaf fibers was analyzed by a Rigaku D/max 2550 PC X-ray diffractometer (Tokyo, Japan). Powdered samples were scanned in the 2θ range of 5° to 60° at 2°/min with Cu/K1α (1.5406 Å) Ni filtered radiation with a voltage of 40 kV and an intensity of 200 mA. The crystallinity index of the fibers was calculated according to the peak height of the XRD spectra (Segal *et al.* 1959) using the following equation:

$$\text{Crystallinity index (\%)} = (I_{\text{crystalline}} - I_{\text{amorphous}} / I_{\text{crystalline}}) \times 100 \qquad (1)$$

Scanning electron microscopy (SEM)

Morphological changes in treated and untreated kenaf fibers were investigated with a JEOL JSM-6390LV scanning electron microscope (Tokyo, Japan). The samples were placed on slides and coated with gold to avoid subsequent charging before measurement by SEM.

RESULTS AND DISCUSSION

Effect of Steam Pressure on Chemical Compositions of Kenaf Fibers

Kenaf fibers were steam-exploded at pressures ranging from 1 MPa to 3 MPa for 3 min. The contents of each chemical component of kenaf fibers untreated and treated at different steam pressures were determined (Table 1). The compositions were given on the basis of the percentage of initial dry kenaf fibers before treatment. Raw kenaf fiber had the highest percentage of pectin and hemicellulose and the lowest percentage of cellulose. During the steam explosion treatment at 1 MPa to 2.5 MPa, water-soluble matter, pectin, hemicellulose, and acid-soluble lignin contents were reduced gradually, and the percentage of cellulose and acid-insoluble lignin was increased gradually as the steam pressure increased. About 60% of the pectin, 50% of the hemicellulose, and 58% of the acid-soluble lignin was removed, while the percentage of the cellulose and acid-insoluble lignin increased relative to the percentage of original weight. During steam explosion, glycosidic bonds in the hemicellulose were hydrolyzed, hemicellulose-lignin bonds were cleaved, and lignin was depolymerized. These reactions produced water-soluble sugars and phenolic compounds, leaving a residue of alpha-cellulose and lignin (Donaldson *et al.* 1988; Fernandez-Bolanos *et al.* 1999; Li *et al.* 2007). Therefore, with the hemicellulose, pectin, and acid-soluble lignin partially removed, the proportion of acid-insoluble lignin in kenaf fibers increased.

Table 1. Chemical Compositions of the Raw and Steam-Exploded Kenaf Bast

Pressure (MPa)	Water-Soluble Matter (%)	Pectin (%)	Hemicellulose (%)	Cellulose (%)	Acid-Insoluble Lignin (%)	Acid-Soluble Lignin (%)
0*	17.25	5.45	25.24	50.68	8.05	7.58
1	5.63	4.00	23.10	61.14	9.67	4.56
1.5	5.46	2.25	22.05	61.68	9.52	4.44
2	7.23	2.34	19.18	63.4	10.05	4.34
2.5	8.23	2.53	13.76	64.95	12.10	3.50
3	16.72	4.67	11.86	55.32	12.71	3.13
*Note: Raw kenaf bast. The steam explosion process lasted 3 min.						

Steam explosion removed 60% to 70% of the water-soluble matter from the raw kenaf fibers. However, with increased steam pressure, water-soluble matter increased. With 3 MPa steam, the water-soluble matter increased to 200% of that in the 2.5 MPa treated sample. However, the cellulose content decreased dramatically when the steam pressure changed from 2.5 MPa to 3 MPa. As a polysaccharide with a high degree of polymerization, cellulose is stable in most steam explosion treatments. However, when the pressure/temperature was raised to a certain degree, the cellulose degraded, yielding increased water-soluble polysaccharides and lower cellulose content. Similar results have been found in wheat straw, where the relative percentage of the cellulose and lignin increased for some pretreatment conditions and decreased for others, depending on their level of degradation (Monschein and Nidetzky 2016). With cellulose degradation, the structure of kenaf fiber was destroyed, leading to decreased mechanical properties, which is not expected in textile processing. Therefore, pressure higher than 2.5 MPa is not suggested for the degumming of kenaf for textile purposes.

FTIR analysis

The changes in the fiber structures treated by steam explosion were revealed by FTIR analysis (Fig. 1). All samples prepared under varying steam pressures gave very similar spectral patterns. The only difference observed was the peak intensity, indicating that the treatment of steam pressures in the range of 1 MPa to 3 MPa did not result in any significant changes in the macromolecular structure of the kenaf fibers. The hydrophilic tendency of untreated and treated kenaf fibers was reflected in the broad absorption band in the 3500 cm^{-1} to 3300 cm^{-1} region, which is related to the -OH groups in the main component (Sain and Panthapulakkal 2006). The peak at 2917 cm^{-1} is due to the aliphatic C-H stretching vibration, which showed small changes in the absorbance after the steam explosion treatment, due to the partial removal of lignin from the fibers. The two peaks at 1504 cm^{-1} and 1428 cm^{-1} correspond to the aromatic peak C-C stretch from the aromatic ring of lignin (Sonia and Priya Dasan 2013). The prominent peak at 1737 cm^{-1} in the untreated kenaf fiber is attributed to either the acetyl and uronic ester groups of the hemicellulose, the ester linkage of the carboxylic group of the hemicellulose, or the ester linkage of the carboxylic group of the ferulic and p-coumeric acids of lignin and/or hemicellulose (Alemdar and Sain 2008a). The intensity of this peak decreased in the steam-treated fibers, especially at 3 MPa. This result reflects the removal of most of the hemicellulose and part of the lignin from the kenaf fibers. The absorption at 1638 cm^{-1} is principally associated with absorbed water. The decrease of the intensity of this peak in the steam-exploded kenaf fibers was due to the partial removal of hemicellulose. The absorbencies at 1058 cm^{-1} and 896 cm^{-1} are related to the C-O stretching and the C-H rocking vibrations of cellulose (Sun *et al*. 2000; Alemdar and Sain 2008b).

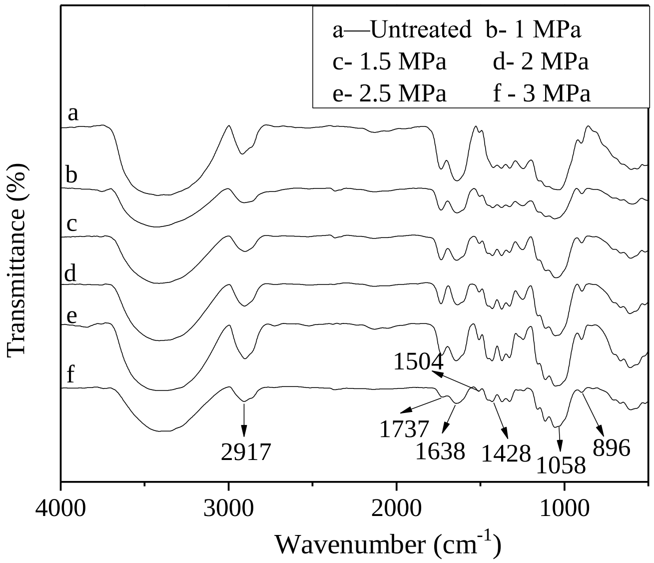

Fig. 1. FTIR spectra of kenaf fibers treated at different steam pressures

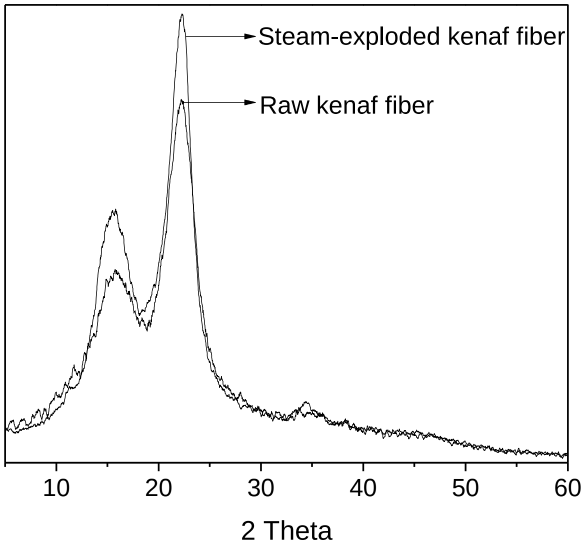

Fig. 2. X-ray diffraction patterns of raw and steam-exploded kenaf fibers

XRD Analysis

The cellulosic fibers constitute crystalline and amorphous regions. Cellulose has a well-pronounced crystalline structure due to hydrogen bonding and Van der Waals interactions between adjacent cellulose molecules. However, cellulosic fibers are surrounded by a matrix of amorphous non-cellulose polysaccharides, such as hemicellulose and lignin (Sonia and Priya Dasan 2013; Chirayil *et al*. 2014). Figure 2 shows the X-ray diffraction graphs of raw kenaf fibers and the fibers treated by steam explosion. There was no transformation of the crystalline structure because both treated and untreated fibers represented typical cellulose I patterns, which showed a peak at $2\theta = 22°$ and a shoulder in the region of $2\theta = 14°$ to 17°. By comparing the intensities of the diffraction peaks of both samples, the change in crystallinity was determined (Bondeson *et al.* 2006). More steam-exploded kenaf fibers exhibited a higher crystallinity compared with untreated fibers, which was attributed to the partial removal of the non-cellulosic polysaccharides and the dissolution of amorphous zones (Sheng *et al*. 2014).

Figure 3 shows the influence of steam pressure on the crystallinity index of kenaf fibers, in which the steam pressure of 0 MPa represented the raw kenaf fibers. The crystallinity index value of the raw kenaf fibers was 65.3%. When the pressure was less than 3 MPa, the crystallinity index increased up to 78.16% as a function of steam pressure. The crystallinity index declined at 3 MPa, indicating damage to the cell wall, as noted in the chemical composition analysis, and further demonstrated the degradation of cellulose. The results here were in good agreement with those of Abraham *et al.* (2011).

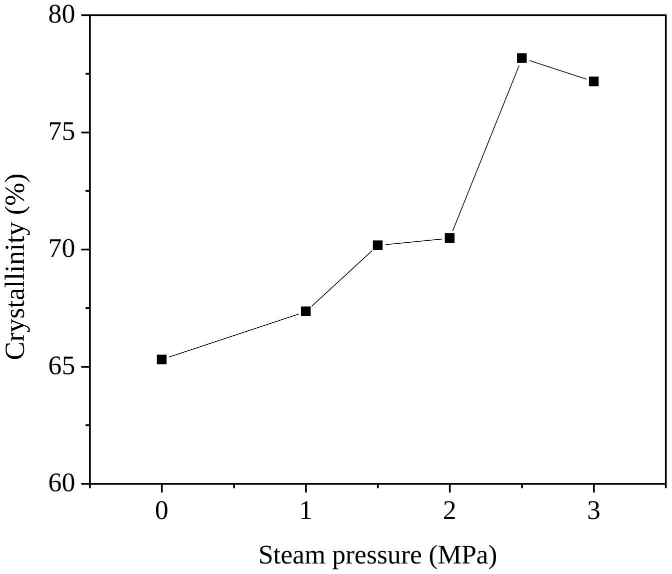

Fig. 3. The crystallinity index of kenaf fibers treated at different steam pressures

SEM Analysis

The surface structure of the fiber contributes to fiber behavior in subsequent applications, including the interactions between the fiber and polymer matrix in composite materials (Ramesh *et al*. 2015). Scanning electron microscopy was used to evaluate the surface structure of the raw and steam-treated kenaf. Figure 4A shows the very rough surface of the untreated kenaf fibers, which presented irregular protrusions and polygonal patches of waxy and fatty acids occurring at regular intervals. As illustrated in Fig. 4B, steam treatment at 1 MPa removed the protruding debris and the polygonal patches effectively, showing a relatively smooth surface, but no defibrillization was observed. Precipitation on the fiber surface showed that hemicellulose and lignin connecting the cellulose fibrils were partially dissolved with 2 MPa steam (Fig. 4C). However, considerable cell-wall remnants of non-fibrous cells remained attached to the fiber strands.

During the higher steam pressure, of 3 MPa, more non-cellulosic material was removed, and the fiber bundles were well separated (Fig. 4D). Good separation of kenaf fibers was obtained at more severe steam explosion conditions.

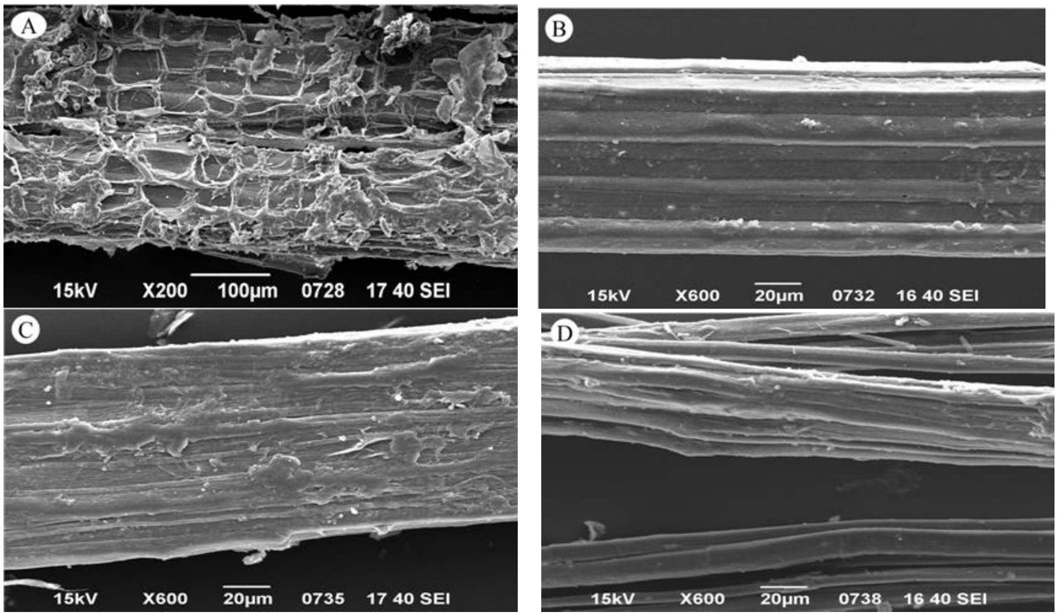

Fig. 4. SEM of untreated kenaf fibers (A) and kenaf fibers treated with 1 MPa (B), 2 MPa (C), and 3 MPa (D) steam

CONCLUSIONS

1. Kenaf fibers were treated by steam explosion with different pressures. After the steam explosion treatment, a lower percentage of hemicellulose and a higher content of cellulose were observed.
2. Excessive pressure (3 MPa and higher than 3 MPa) destroyed the cellulose structure, which was confirmed by changes in FTIR spectra and the crystallinity index (measured by XRD.
3. Fiber bundles were well separated when higher steam pressure was used.
4. Steam explosion treatment removed considerable gum and separated fibers effectively when the steam explosion conditions were severe, but a pressure higher than 2.5 MPa is not recommended for kenaf degumming.

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