

Extraction and Characterization of Rice Straw Cellulose Nanofibers by an Optimized Chemomechanical Method

Bijan Nasri-Nasrabadi, Tayebeh Behzad, Rouhollah Bagheri

Department of Chemical Engineering, Isfahan University of Technology, Isfahan, Iran 8415681167

Correspondence to: B. Nasri-Nasrabadi (E-mail: bijan.nasr84@yahoo.com).

ABSTRACT: In this study, a chemomechanical method was performed to extract nanofibers from rice straw. This procedure included swelling, acid hydrolysis, alkali treatment, bleaching, and sonication. X-ray diffractometer was employed to investigate the effect of acid hydrolysis conditions and other chemical treatments on the chemical structure of the extracted cellulose fibers. It was concluded that by increasing the acid concentration and hydrolysis time, the crystallinity of the extracted fibers was increased. The optimum acid hydrolysis conditions were found to be 2M and 2 h for the acid concentration and hydrolysis time, respectively. The chemical compositions of fibers including cellulose, hemicelluloses, lignin, and silica were determined by different examinations. It was noticed that almost all the silica content of fibers was solubilized in the swelling step. Moreover, the achieved results showed that the cellulose content of the alkali treated fibers was increased around 71% compared to the raw materials. ATR-FTIR was applied out to compare the chemical structure of untreated and bleached fibers. The dimensions and morphology of the chemically and mechanically extracted nanofibers were investigated by scanning electron microscopy, field emission scanning electron microscopy, and transmission electron microscopy. The results of the image analyzer showed that almost 50% of fibers have a diameter within a range of 70–90 nm and length of several micrometers. The thermal gravimetric analyses were performed on the untreated and bleached fibers. It was demonstrated that the degradation temperature was increased around 19% for the purified fibers compared to raw materials. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40063.

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INTRODUCTION

Over the last three decades, there has been a continuously growing usage of cellulosic fibers instead of mineral and synthetic fibers as a reinforcement phase in composites.^{1,2} Although wood is the major source of cellulosic fibers, annual plants, such as wheat, rice, cotton, sisal, jute, and so forth, are also potentially a large source of cellulosic fibers.³ The reasons for the enhanced usage of these plants, in addition to saving the cost, are the ecological concerns and the ecosystem survival.^{4,5} Availability, environmental friendly, biocompatibility, low abrasiveness, and high specific stiffness and modulus are some of the most important advantages of cellulosic fibers.^{1,6,7} In contrast with glass and carbon fibers, the cellulose fibers have a high elasticity and flexibility which lead to high aspect ratio after the extraction process.⁸ The cellulose chains in plant cell walls are aggregated by hydrogen bonds, and create the cellulose micro fibrils which are the smallest structural units in plant fibers.⁹ The diameter of these semicrystalline units is from 2 to 10 nm, and their average length is >10,000 nm. Structural resistance of cellulosic fibers is owing to the existence of microfibrils in plant cell walls.² The

cellulose chains in plant cell walls are embedded in an amorphous matrix combined from hemicelluloses and lignin.¹⁰ Also, the cellulose fibrils are composed of crystalline and amorphous regions.¹¹ The purification of cellulose fibers from these regions, and consequently their reduction to diameter of nanoscale caused an increase in the reinforcement properties owing to increasing modulus, aspect ratio, and surface area of cellulose fibers.^{10,12} In biocomposites, the cellulose nanofibers form hydrogen bonds with biopolymers, such as starch, poly(vinyl alcohol), poly(lactic acid), and so forth, which cause high mechanical properties and stability of products. Moreover, less hygroscopic nature of cellulose fibers reduces barrier properties of these materials.^{13–15} Microfibrillated cellulose (MFC) is one of the terms that is typically used for extracted nanofibers using other treatments such as homogenizer,^{16,17} grinder,^{18,19} and sonication.²⁰ MFCs are in forms of highly entangled networks of nanofibers with high stiffness and numerous hydroxyl groups in their surfaces.²¹ In this study, a chemomechanical method was performed to extract nanofibers from rice straw. The chemical treatment was applied for the purification of cellulose fibers to

achieve cellulose pulp with high crystallinity. To characterize the crystallinity of chemically extracted fibers, X-ray diffraction (XRD) was performed. Chemical compositions of lignocellulosic fibers were determined by different chemical analysis methods. Afterward, the pulp was sonicated²⁰ to disintegrate cell walls and produce cellulosic networks of nanofibers. The morphology and thermal resistance of the chemically treated and ultrasonicated fibers were analyzed by scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and thermal gravimetric analysis (TGA).

EXPERIMENTAL

Materials

Rice straw was obtained from local sources (Isfahan farms, Iran). The chemicals (NaOH, HCl, NaClO₂, H₂SO₄, and KMnO₄) were supplied by Merck, Germany.

Isolation of Nanofibers

In this study, a chemical method was used to isolate nanofibers from rice straw.¹⁷ As acid hydrolysis has more pronounced effects on the crystallinity structure of the extracted fibers,²² the influence of hydrolysis conditions (acid concentration and hydrolysis time) was examined by XRD. The steps of nanofiber preparation are presented as follows:

Swelling

First, rice straws with the length of around 4–5 cm were soaked in 17.5 wt % of sodium hydroxide solution for 2 h. Then, the swollen straws were washed with abundant distilled water and mixed by a blender for 0.5 h before being air dried at room temperature. The penetration of sodium hydroxide in the amorphous region causes the intermolecular bonds to break down owing to the internal stress in plant cell walls.²³

Acid Hydrolysis

The obtained pulp was then hydrolyzed by a diluted HCl solution to remove hemicelluloses, extractive materials, and the amorphous regions of cellulose. Hydrolysis treatments were performed in different acid concentrations (1, 2, and 3 mol) and times (1, 2, and 3 h) at 80 ± 5°C with a constant stirrer speed. After hydrolysis, pH of the pulp became neutral with distilled water followed by air drying.

Alkaline Treatment

To remove the soluble lignin, residual hemicelluloses, and pectin, the hydrolyzed pulp was treated by diluted sodium hydroxide (NaOH, 2 wt %) for 2 h at 80 ± 5°C with a constant stirring speed followed by washing and drying.

Bleaching

After alkali treatment, the rice straws were still brownish that was attributed to the existence of insoluble lignin in their structure.¹⁷ Therefore, to complete bleaching, the fibers were treated by sodium chlorite solution (20% w/v) at 50°C for 1 h. The amount of sodium chlorite was determined based on the kappa number of fibers. Then, the bleached fibers were washed by distilled water and air dried.

Sonication

A slurry of the chemically purified cellulose fibers in distilled water (125 mL, 1 wt %) was prepared; then, to fibrillate

nanofibers, the suspension was sonicated at 400 W and 20 KHz for 30 min with a cylindrical probe of 1.5 cm in diameter (Hielscher, UP400S). To control the temperature, the sonication was carried out in a water/ice bath.

Characterization of Fibers

The silica content of the untreated and swollen fibers was measured using a developed method.²⁴ In this method, the plant structure is digested with NaOH and H₂O₂ in an autoclave, and the silicon content is determined by a standard colorimetric technique. To examine the effect of chemical treatment, the chemical compositions (cellulose, hemicelluloses, and lignin) of the raw materials and alkali treated fibers were determined by NREL/TP-510–42618 standard.²⁵ In this method, the samples were hydrolyzed by a concentrated acid solution (H₂SO₄, 72% w/w) to decompose carbohydrate macromolecules into their monomers. Then, by measuring the segregated sugar units using HPLC analyzer (HPLC-RL UV–VIS Detector, Jasco), the percentages of cellulose and hemicelluloses were obtained. The lignin content in filtrate solution was measured by IR spectroscopy in 240-nm peak. To determine insoluble lignin, the solid residue of filtration was placed in an oven at 105°C for 4 h. The weight of the material in this step is the summation of the insoluble lignin and ash. Then, to measure the ash content, the mixture was placed in an oven at 575°C for 24 h. In addition, the lignin content of fibers before and after bleaching was determined by kappa number test²⁶ and was compared to the results obtained from NREL. In this procedure, 50 mg of the sample was oxidized by a mixture of 50 mL of MnO₂ (0.02M) and 20 mL of H₂SO₄ (2M) at 25°C for 3 min. Then, the UV absorption of the filtrated solution was measured at 546 nm (UV–VIS Spectrophotometer, UV-240, 1990 Shimidzu, Kyoto, Japan) and kappa number was determined by the following equation:

$$K = \frac{a}{w} \left(1 - \frac{A_e}{A_0} \right) \quad (1)$$

where K is the kappa number, a is the initial volume of MnO₂ (mL), w is the mass of moisture-free pulp (g), and A_0 and A_e are the permanganate absorbance spectral intensity at given wavelengths before and after oxidation, respectively.²⁶ The amount of NaClO₂ related to dry sample weight was measured as described in eq. (2)²⁷:

$$\text{Sodium chlorite for 1g dry sample (g)} = \frac{C \times E}{100} \quad (2)$$

C: Chlorine for 1 g dry sample (g) = kappa number × 0.25.

E: Equivalent chlorine and sodium chlorite coefficient = 0.73.

To evaluate the morphology and dimension, the fibers after the chemical and ultrasonic treatments were analyzed by SEM (ZEISS 1450EP) and FE-SEM (HITACHI-S4160), respectively. The distribution of the fibers diameter after ultrasonication was determined by an image tool analyzer program (UTHSCSA).

The extracted cellulose nanofibers from rice straw were also investigated by TEM (Zeiss model EM 10C, Germany). Images were taken at an accelerating voltage of 80 kV. Drops of dilute cellulose nanofibers suspensions were deposited on the

Table I. Chemical Composition of Rice Straw Before and After Chemical Treatment

	α - cellulose (%)	Hemicelluloses (%)	Lignin (%)	Silica (%)
Untreated fibers	46.5 [1.5]	22.5 [2.7]	29.1 [1]	1.8 [1.6]
Alkali treated fibers	79.3 [1]	4.8 [6.3]	15.9 [1.3]	0

Coefficient of variation ($=[\text{standard deviation}/\text{mean value}] \times 100$) is given in brackets.

carbon-coated grids and the excess water was absorbed by a filter paper.

XRD was performed to investigate the crystallinity of the untreated, acid hydrolyzed (at various conditions), alkali treated, bleached, and ultrasonicated fibers by a Philips instrument using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) at 40 kV and 30 mA. Scattered radiation was recorded in the angular range (2θ) of $10\text{--}30^\circ$. The crystallinity index (C_I) for cellulose fibers was calculated through the height of 200 peak (I_{200} , $2\theta = 22.6^\circ$) and the intensity peaks at $2\theta = 18^\circ$ (I_{am}) by following the segal method (eq. (3)):

$$C_I(\%) = \left(\frac{I_{200} - I_{\text{am}}}{I_{200}} \right) \times 100 \quad (3)$$

I_{200} represents both amorphous and crystalline regions.

I_{am} represents the amorphous regions.

For each sample, three specimens were tested and the average of (C_I) was reported as a result.

The chemical structure changes of bleached fibers compared to raw rice straw were analyzed at the range of $600\text{--}4000 \text{ cm}^{-1}$ using ATR-FTIR spectroscopy (Tensor 27, Bruker).²⁸

To compare the thermal stability of the untreated and bleached fibers, TGA was performed using a TG analyzer (Rheometric Scientific TGA, USA) with the heating rate of $10^\circ\text{C}/\text{min}$ conducted in a nitrogen environment.

RESULTS AND DISCUSSION

Chemical Composition of Fibers

Table I summarizes the chemical composition of the untreated and alkali-treated fibers. As it can be seen, the cellulose content is increased from 46.5[1.5] to 79.3[1] (coefficient of variation is shown in brackets) by chemical treatment (swelling, hydrolyze, and alkali treatment). The hemicellulose contents were decreased from 22.5[2.7] to 4.8[6.3] after alkali treatment. The hemicellulose with an amorphous structure, which has a low molecular weight (degree of polymerization is <200), is dissolved in alkali and acidity media.^{29,30} Thus, the major percentage of hemicelluloses is removed from the fibers after chemical purification. In addition, the lignin content was reduced from 29.1[1] to 15.9[1.3]. The results achieved from fragmental extraction of plant components show that lignin is not easily separated owing to the existence of complex network bonds between lignin and polysaccharides. Details of aggregation of lignin to other components of lignocellulosic fibers have not been determined entirely yet, but this approach is dominant that lignin–hemicelluloses bonds are more probable than lignin–cellulose bonds.³¹ Thus, by removing the hemicelluloses,

the structure of lignin is more accessible. Other workers demonstrated that by alkali treatment before bleaching step, a significant percentage of soluble lignin content is removed.^{16,17} Also, to achieve minimum damage of degree of polymerization, less bleaching agent is needed, and hence a dilute alkali treatment is used.^{17,32,33} Results of kappa number test show that the percentage of insoluble lignin after alkali treatment is 13.9[1.1] which is reduced to 1.1[0.6] after bleaching. These results show that in the bleaching step, almost all of the remained lignin (Klason lignin) is removed. As it can be noticed, the amount of lignin for alkali treated fibers determined by kappa number test has a small deviation from the results obtained by NREL (Table I) that may be owing to versatility of these methods. The existence of silica is one of the major problems in pulping rice straw.³⁴ Results of silica determination show that after swelling, almost all silica content is removed from the fibers. The low-percentage silica in straws in this study is owing to the separation of frond from straws before use; otherwise, there is a higher content of silica.³⁵

Morphology of Fibers

Chemical treatment removes the noncellulosic materials by creating structural internal tensions caused to destruct hydrogen bonds between the cellulose microfibrils, and achieves the cellulose fibers with lower dimension compared to the untreated fibers.^{23,32,36} SEM images of the rice straw cross-section and chemically treated fibers are shown in Figures 1 and 2, respectively. Figure 1 shows some of the large and small vascular bundles of a small part of rice straw cross-section.¹⁶ Figure 2(a) shows cellulose fibers with the average dimension of $5\text{--}20 \mu\text{m}$ after the bleaching. Also, as shown in Figure 2(b, c), it can be observed that on the surface of a single micro-size fiber, there are individualized nanofiber bundles with width of nanofibers but the microfibrils still maintained their initial structure. The

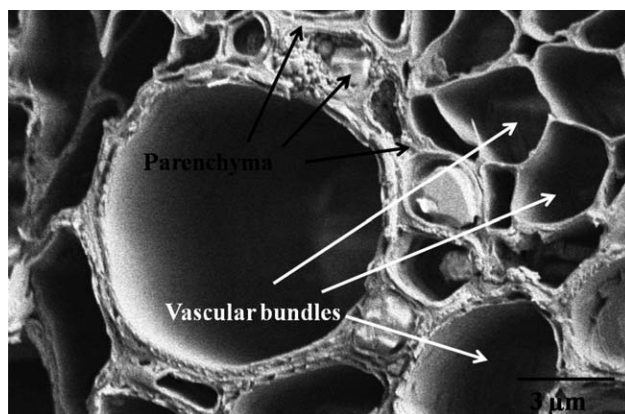


Figure 1. SEM image of a small part of rice straw cross-section.

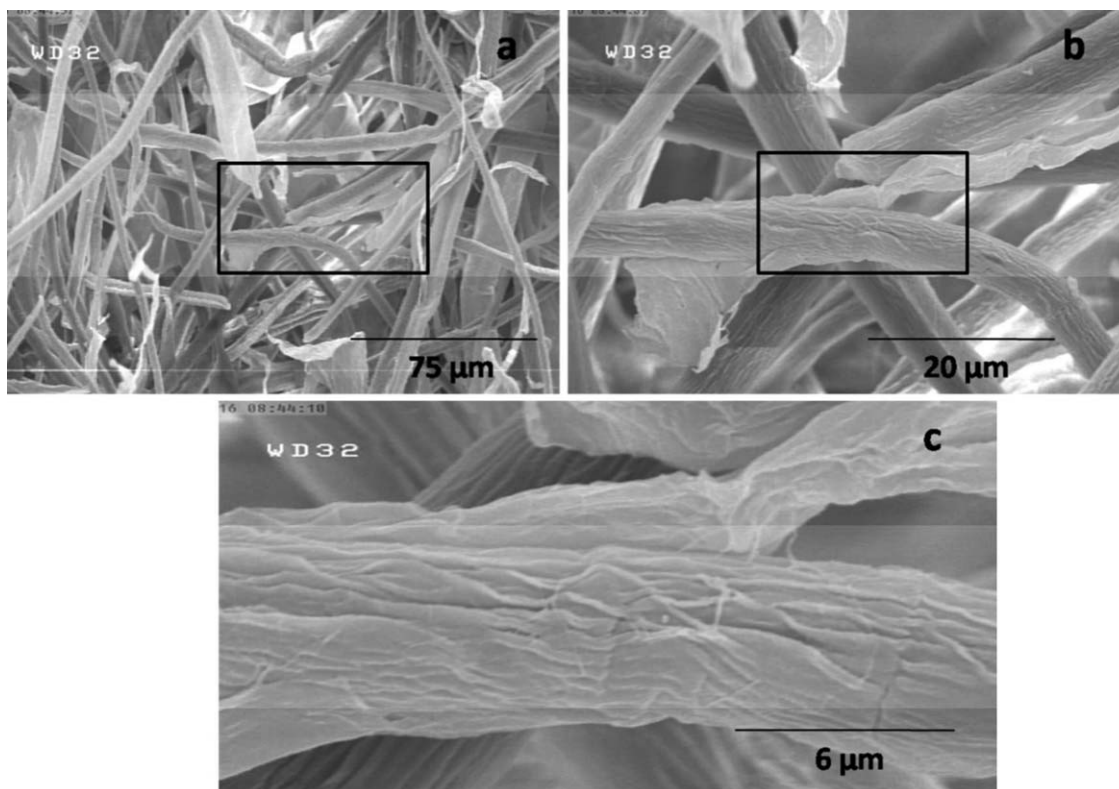


Figure 2. SEM micrographs of fibers after chemical purification.

association energy between cellulose chains is around 20 kJ/mol which is needed to break the hydrogen bonds.⁷ In this study, for individualizing microfibril bundles, the power of ultrasonication is used. The ultrasonic energy disintegrates the cellulose nanofiber bundles by combination of occurrences called cavitations, which include formation, growth, and violent collapse of these cavities. The production energy by cavities is around 10–100 kJ/mol, which is enough to destroy the intramolecular hydrogen bonds.²⁰ FE-SEM image [Figure 3(a)] shows that extracted cellulose nanofibers with uniform diameter stuck together in the form of entangled networks. The results of an

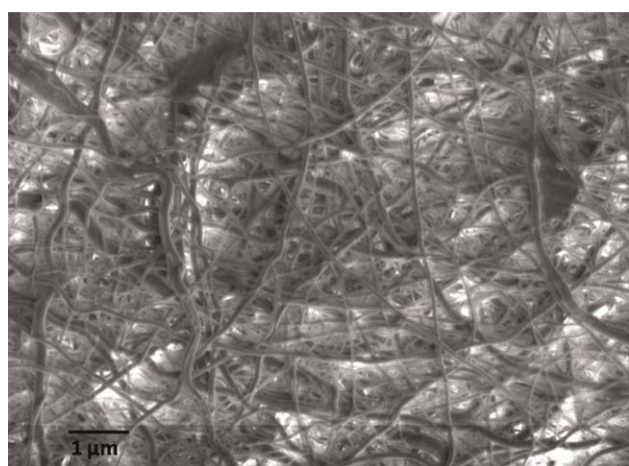


Figure 3. FE-SEM of rice straw cellulose networks of nanofibers after sonication.

image analyzer program (UTHSCSA Image Tool) portrayed that almost 50% of fibers have a diameter within a range of 70–90 nm and a length of several micrometers. Also, around 30% of fibers are >90 nm, around 10% of fibers within the range of 40–70 nm, and around 10% of them are <40 nm. During ultrasonication, a combination of cellulose microfibrils and nanofibers in the form of aqueous suspension is segregated from chemically treated fibers. A TEM image of the mechanically treated fibers is shown in Figure 4. The ultrasonication of the chemically treated fibers resulted in defibrillation of cellulose nanofibers in the form of a network of nanofibers. It is believed that the ultrasonic power (intensity and amplitude), time and temperature of treatment, primary dimension of fibers, concentration of aqueous suspension, and dimension of ultrasonicator probe are the most effective factors to extract nanofibers.^{8,37,38}

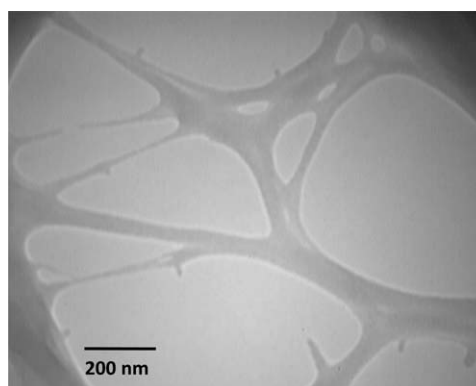


Figure 4. Transmission electron micrograph of ultrasonicated fibers.

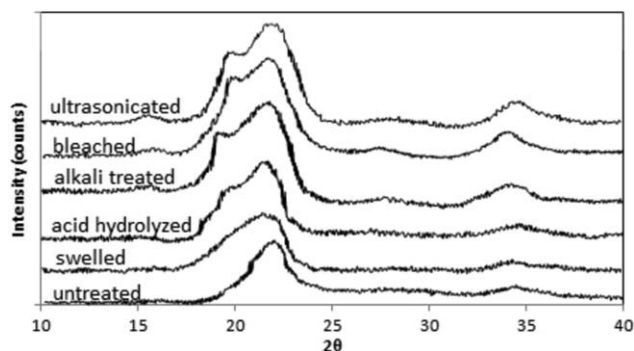


Figure 5. XRD patterns of the untreated, swelled, acid hydrolyzed (at 2M and 2 h), alkali treated, bleached, and ultrasonicated fibers.

XRD Analysis

XRD analysis on the raw rice straw, swollen, acid hydrolysis (in various conditions), alkali treated, bleached, and sonicated fibers is performed to investigate the effect of chemomechanical treatments on the crystalline structure of fibers. Figure 5 shows the crystallinity change of the treated fiber samples. The XRD pattern of the original cellulose is changed from Cellulose I (with the typical diffraction peaks at $2\theta = 14.8, 16.3,$ and 22.6°) to Cellulose II (with the typical diffraction peaks at $2\theta = 20$ and 21.7°) after swelling. This fact is owing to the rearrangement of natural cellulose chains after strong alkali treatment (NaOH, 17.5%). The bleached fiber samples have a crystallinity index of 69[2]% which is about 28% higher than the untreated samples. This could be attributed to the removal of amorphous regions (lignin, hemicelluloses, pectin, etc.) from fibers during the chemical purification. In the case of the acid-hydrolyzed fiber samples, Table 2 summarizes the crystallinity index in various hydrolysis conditions. It is found that in equal conditions (acid to pulp ratio of 25 mL/g at $80 \pm 5^\circ\text{C}$), as the acid concentration and hydrolysis time are increased up to 2M and 2 h, the crystallinity index is increased. The fiber samples treated in 2M and 2 h have the highest crystallinity ($C_I = 62[3]\%$). The increase in crystallinity can be related to the removal of amorphous regions of the fibers.^{17,22} However, with further increasing in both hydrolysis time and HCl concentration, a decrease in crystallinity is observed, which could be attributed to the decomposition of the crystallinity phase of the cellulose. Regarding the sonication, no significant change is observed in the crystallinity compared to the chemically purified cellulose fibers (Figure 5).

ATR-FTIR Analysis

ATR-FTIR spectroscopy is a suitable method for the characterization of chemical variation of lignocellulosic fibers after

Table 2. Acid-hydrolyzed Fibers at Various Times and Concentrations

	1M	2M	3M
1 h	55 [3.3]	56 [3.4]	51 [5.8]
2 h	56 [5.1]	62 [3]	48 [4.7]
3 h	58 [3.6]	50 [3.8]	43 [5.3]

Coefficient of variation ($=|\text{standard deviation}/\text{mean value}| \times 100$) is given in brackets.

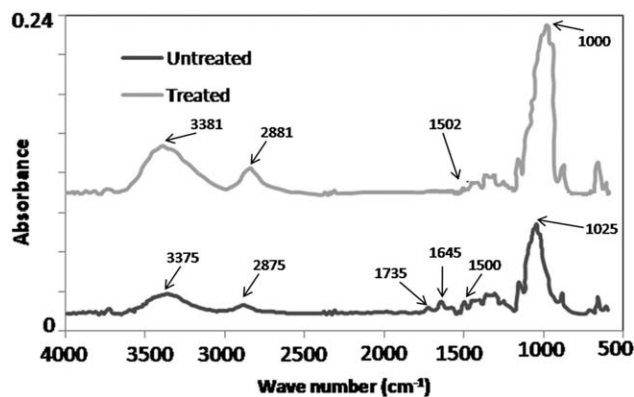


Figure 6. ATR-FTIR spectra of untreated and bleached fibers.

different chemical treatments. Figure 6 compares the ATR-FTIR spectra of untreated and bleached rice straw fiber samples. The dominant peaks between 1200 and 900 cm^{-1} are related to C—O stretching bonds. Enhancing of the peak intensity around 960 cm^{-1} after chemical treatment suggests that a typical structure of cellulose became more dominant compared to the raw materials.¹⁶ The peak at 1500 cm^{-1} in the lignocellulosic fibers is associated with the C=C stretching of aromatic groups in lignin.^{16,20} The significant decrease in this peak demonstrates the removal of lignin after chemical treatment. Also, it is clear from the curves that the peak at around 1640 cm^{-1} in the untreated fiber samples declines in the chemically treated fiber samples. Intensity of this peak depends on the absorbed water, and the decrease in its intensity is related to the removal of most of the hemicelluloses.¹⁶ The prominent peak of the untreated rice straw around 1737 cm^{-1} is related to either the acetyl and uronic groups ester of the hemicelluloses or the ester linkage of carboxylic groups of the ferulic and the p-coumaric acids of lignin or hemicelluloses.¹⁵ The peak disappears by chemical purification of the samples. The dominant peak at around 2900 cm^{-1} (Figure 6) is associated with CH-stretching vibrations.¹⁶ Intensity of this peak after chemical treatment has remarkably increased. The broad absorption band in the range of 3500–3000 cm^{-1} is attributed to the OH-stretching vibrations.³⁹ The

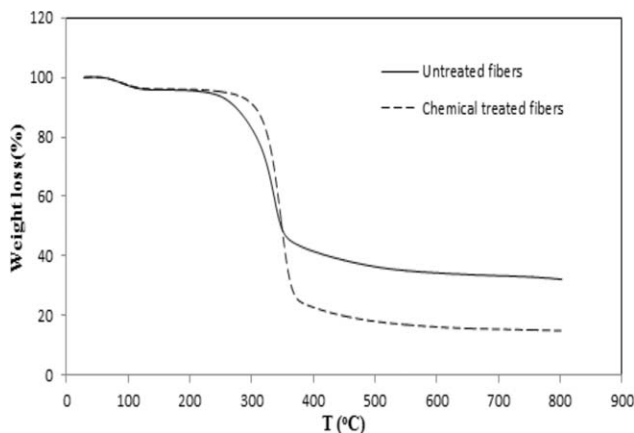


Figure 7. TGA curves of untreated and chemically treated rice straw cellulose fibers.

increase in the intensity of this peak after chemical treatment is related to enhancement of the surface moisture absorption of fiber samples.⁴⁰

Thermal Analysis

One of the most important factors in determining the ability of cellulosic fibers for different applications is thermal property. In this research, TGA was used for raw and chemically treated rice straw fibers. As shown in Figure 7, it is clear that a small weight loss occurs at around 100°C that may be the evaporation of remained humidity and low-molecular-weight components in the fibers.⁴¹ The second main event in TG curves is attributed to cellulose and hemicelluloses pyrolysis, which is shifted from 260°C for the untreated fibers to 310°C for the chemically treated ones. The resistant increase of the treated samples may be owing to the removal of almost all hemicelluloses from the untreated samples. Other research workers reported that in an inert atmosphere, pyrolysis of lignin starts at 200°C and persists till 700°C⁴² also owing to high silica content, rice straw at high temperature has a high residue.³⁶ Therefore, at above 400°C, it is observed from the curves shown in Figure 7 that the amount of remaining residual after pyrolysis in the untreated samples is higher than that in the treated one. These results are in good agreement with NREL and silica characterization of the samples.

CONCLUSIONS

In this research, a chemomechanical method was used to extract cellulose nanofibers from rice straw. Chemical characterization of fibers after alkali treatments showed that the percentage of cellulose was increased to around 71%. XRD analysis indicated that the optimum conditions for acid hydrolysis, 2M of HCl solution for acid to pulp ratio of 25 mL/g at 80 ± 5°C for 2 h resulted in the highest crystallinity of hydrolyzed fibers. TGA demonstrated that the thermal properties of the chemically treated fibers were enhanced and the degradation temperature of fibers was increased almost 19% for the bleached fibers compared to the raw materials. These increases are owing to the removal of the amorphous region from fibers. After chemical treatment, applying a process of 30-min ultrasonication with the output of 400 W produces entangled networks of nanofibers.

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