Isolating Cellulose Nanofibers from Steam-Explosion Pretreated Corncobs Using Mild Mechanochemical Treatments

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Cellulose nanofibers (CNFs) with an average diameter 8 nm were isolated from corncobs using a stepwise method that included steam-explosion pretreatment, alkaline treatment, sodium hypochlorite bleaching, high-speed blending, and ultrasonic treatment. This mechanochemical method used only two chemical reagents in low concentrations to remove non-cellulosic components. The removal of non-cellulosic components was confirmed by Fourier-transform infrared spectroscopy. X-ray diffraction revealed an increase in crystallinity during steam explosion and subsequent mechanochemical treatments. Pretreatment by steam explosion caused the partial hydrolysis of hemicellulose and loosened the structure of raw materials, which facilitated the subsequent chemical processes. The thermal stability and morphology of samples at different stages were also investigated. Steam explosion increased the thermal stability of hemicellulose and cellulose components, as it removed a fraction of hemicellulose. High-speed blending reduced the entanglement of cellulosic fibers and created uniform size. Ultrasonic treatment was used in the final step of nanoscale fibrillation. The method used in this study is environmentally friendly and has the potential to be applied at industrial scale.

Keywords: Cellulose nanofibers; Steam explosion; Corncobs; Mechanochemical treatments; High-speed blending; Ultrasonic treatment

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INTRODUCTION

Cellulose is one of the most widely distributed and abundant natural polymers. Nanocellulose is a family of natural materials, including microfibrillated cellulose, nanocrystalline cellulose, and bacterial nanocellulose (Klemm *et al.* 2011). Nanocellulose possesses high strength and stiffness, and is abundant, biodegradable, and lightweight. These advantages make nanocellulose a promising candidate for bio-nanocomposite production (Siró and Plackett 2010). Cellulose nanofibers (CNFs) with a diameter less than 100 nm are an important type of nanocellulose. CNFs have large specific surface areas and useful mechanical properties (Bhatnagar and Sain 2005), and therefore they have been investigated for use in composites, coatings, and films.

Methods for isolating or fibrillating cellulose are essential for its use in high-value products. Various methods for preparing and isolating CNFs have been reported, and these can generally be classified as mechanical and chemical methods. Mechanical methods include: homogenization (Nakagaito and Yano 2004; Bhattacharya *et al.* 2008), grinding (Abe and Yano 2009), microfluidization (Xiang *et al.* 2016), high-speed blending (Uetani and Yano 2010), intense ultrasonication (Wang *et al.* 2016), and cryocrushing (Alemdar and Sain 2008). Chemical methods include: acidic or alkaline treatment (Yue *et al.* 2012), and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation (Saito *et al.* 2007). Mechanical isolation methods are usually more environmentally friendly than chemical methods (Wang *et al.* 2016). Various chemical or enzymatic treatments for pretreating raw materials have also been combined with intensive mechanical methods to achieve the final disintegration (Qing *et al.* 2013). In order to reduce the difficulty of fibrillation and expand the potential application of CNFs, surface modifications, such as esterification (Iwamoto and Endo 2014; Kang *et al.* 2017), acetylation (Nogi *et al.* 2006), are also applied. However, these modifications increase the use of chemical reagents and complicate the procedure.

Steam explosion has long been used as a pretreatment in the extraction of fermentable sugars from agricultural wastes to produce ethanol. Steam explosion operates under high pressure steam conditions, breaking down the cell walls of plants. It can then facilitate the hydrolysis (*i.e.* degradation) of hemicellulose to glucose or xylose (Mosier *et al*. 2005), resulting in the use of lesser amounts of chemicals.

Several recent studies have utilized steam explosion to extract and fibrillate nanocellulose. Cellulose nanofibers of diameter 10 to 50 nm were obtained from wheat straw using alkali steam explosion coupled with high shear homogenization (Kaushik and Singh 2011). In another study, banana fibers were treated with alkaline-assisted steam explosion followed by bleaching and acid hydrolysis procedures, which yielded cellulose microfibers with an average diameter of 1 µm (Deepa *et al.* 2011). Further, pineapple leaf fibers were used to isolate CNFs with widths of 5 to 60 nm using 2% NaOH and 11% oxalic acid assisted steam explosion in combination with bleaching (Cherian *et al.* 2010).

Other mechanical treatments such as high-speed blending and ultrasonication have also been used in this field. These mechanical processes play different roles in the isolation of cellulose, as they process *via* different mechanisms. Wood pulp can be fibrillated by high-speed blending, due to the agitation effect. Ultrasonication has a cavitation effect that can fibrillate microcellulose on the nanoscale, within limited local regions of lignocelluloses. Thus, combining steam explosion, high-speed blending, and ultrasonication could be a promising approach for isolating CNFs.

Corncobs are a common agricultural waste material in China, and they are currently underutilized, often being burned, resulting in a waste of natural resources and air pollution. A small number are used as raw materials to produce chemical by-products. Using corncobs as a source for producing CNFs would add value. Shogren *et al.* (2011) repeatedly bleached ground corncobs with 1 M NaOH and 0.6% NaClO at 80 °C for 2 h, then homogenized the sample eight times at a pressure of 1000 bar. The resulting aqueous cellulose gel predominantly contained CNFs with diameters of 30 to 60 nm. While many studies have isolated CNFs from natural sources, they typically involve considerable use of chemical reagents, as well as employing complicated processes that are unsuitable for industrialization.

The aim of the current study was to use corncobs to establish a stepwise method that simplified the chemical process and decreased the use of chemicals to prepare cellulose nanofibers without surface modification. Steam explosion was used to pretreat raw corncobs. Mild chemical treatments involving only two chemical reagents at room temperature were used to remove non-cellulosic components. Subsequent mechanical treatments including high-speed blending and ultrasonication were used to isolate CNFs. The morphologies, fiber sizes, crystallinities, and thermal stabilities of the CNFs were then measured. The role of each mechanical and chemical treatment in the overall process is discussed. This study will provide insight about the impact of steam-explosion pretreatment on structural and chemical constituents of corncobs, and the advantages of using steam-explosion pretreated materials to isolate CNFs. Understanding of morphological changes in each step also will aid in optimizing the preparation of CNFs for follow-up studies.

EXPERIMENTAL

Materials

Corncobs (CC) collected from the Henan province of China were ground and sieved through a 60-mesh screen. Sodium hydroxide (NaOH) and sodium hypochlorite (NaClO) of analytical grade were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China).

Steam-Explosion Pretreatment

Approximately 20 g of dry corncob powder was placed in a self-designed steam-explosion reaction apparatus. Approximately 500 mL of water was poured in the container to supply steam under high temperatures. A tripod with copper mesh on top was used to suspend the raw material above the water. Steam cooking was conducted under optimum conditions at 200 °C for 30 min; then an electromagnetic ball valve with a diameter of 25 mm triggered the explosion, and the depressurization happened in 0.01 seconds. The resulting steam-exploded samples were thoroughly washed with water to remove soluble species arising from degradation.

Fig. 1. Procedure for preparing cellulose nanofibers from corncobs

Preparation of CNFs

Figure 1 shows the procedure for preparing the CNFs. The pretreated samples were treated with 2 wt.% NaOH solution in a liquid/solid ratio of 20:1 for 12 h to hydrolyze hemicellulose, and then rinsed with water until obtaining a pH of 7. The samples were then bleached with 3 wt.% NaClO solution in a liquid/solid ratio of 10:1 and at pH 11 to 13 (adjusted by adding a small amount of NaOH) for approximately 6 h to remove lignin. Both the above chemical treatments were carried out at room temperature. The samples were then thoroughly washed with water.

The bleached samples were mixed with water to obtain 0.5 wt.% suspensions before further treatment. The suspensions were first blended in a high-speed blender (VK-6001, OROWA, Germany) at 48000 rpm for 1 min, then treated using an ultrasonic cell disruptor in an ice water bath (XO1200D, Nanjing Atpio Instrument Manufacturing Co. Ltd., China). Ultrasonication at an output power of 1000 W was carried out for 2 s with a subsequent rest time of 3 s, intervals which were repeated for 30 min to obtain the CNFs. To analyze the impact of steam explosion on the subsequent procedures, raw corncobs were subjected to alkaline treatment without steam-explosion pretreatment, and then bleached following the same procedures. The letters S, A, B, H, and U hereafter indicate steam explosion, alkaline treatment, bleaching, high-speed blending, and ultrasonication, respectively. Samples were named with these letters according to the treatments they received. For example, CC-SABHU indicates a corncob sample treated with steam explosion, alkaline treatment, bleaching, high-speed blending, and ultrasonication in that order. Samples obtained after each stage of the process were characterized before further use.

Characterization

Fourier-transformed infrared (FT-IR) spectroscopy

FT-IR spectroscopy was used to characterize the changes in functional groups during different treatments. Spectra were recorded using a FT-IR spectrometer (VERTEX 70, Bruker, Germany). Because changes of chemical structure in CC mainly happened during steam explosion and the subsequent chemical treatments, samples from raw corncobs (CC), steam-exploded corncobs (CC-S), alkaline-treated corncobs (CC-SA), and bleached corncobs (CC-SAB) were analyzed. Samples were dried in an oven at 60 °C for 12 h, then ground into a powder. Spectra were recorded from KBr pellet samples in the wavenumber range 4000 to 400 cm^{-1}, with a resolution of 0.4 cm^{-1}.

Thermal gravimetric analysis (TGA)

The thermal stability of samples after different treatments were determined by TGA using a TG 209 F1 Libra® instrument (Netzsch, Germany). Samples were dried at 80 °C in an oven for 12 h before analysis. Measurements were performed under a nitrogen atmosphere, with a gas flow rate of 20 mL/min. The heating range was from room temperature to 600 °C, at a heating rate of 5 °C·min^{-1}.

Morphology analysis

Field-emission scanning electron microscopy (FESEM) was used to observe the morphologies of samples after different treatments, using a FEI Quanta FEG 250 microscope (Hillsboro, OR, USA). Steam-cooked CC that were not subjected to the final explosion procedure were also observed. These observations were compared with observations for CC-S to investigate the effects of explosion procedure. Chemically-treated corncobs without pretreatment (CC-AB) were also observed, to further investigate the effects of steam explosion. Samples were diluted and sonically treated to achieve good dispersions, a droplet of which was deposited on a piece of clean mica. The water solvent was allowed to evaporate completely, and the FESEM specimen was then coated with gold to prevent charging.

Transmission electron microscopy (TEM) observations were recorded using a JEM-2100F microscope (JEOL, Tokyo, Japan), to observe the morphologies of the CNFs. A droplet of diluted CNF suspension was deposited on the surface of a clean copper grid, which was coated with a thin carbon film. For better TEM observation, the deposited CNFs were negatively stained in a 2 wt.% solution of phosphotungstic acid. The sample was then dried at room temperature before TEM observation. TEM images were used to determine the sizes of the CNFs with the Image Pro software package.

X-ray diffraction (XRD)

XRD was performed using a Bruker AXS D8 advance X-ray powder diffractometer (Karlsruhe, Germany) equipped with Cu $K\alpha$ radiation, to investigate the structures and crystallinities of samples after different treatments. The diffraction patterns were recorded between 10 and 45° 2θ. Segal's method was used to calculate the crystallinity index (Segal *et al*. 1959), according to Eq. 1,

$$I_{cr}\,(\%) = 100 \times (I_{002} - I_{am})\,/\,I_{am} \tag{1}$$

where I_{cr} is the relative degree of crystallinity, I_{002} is the maximum intensity of the 002 diffraction peak corresponding to crystalline cellulose, and I_{am} is the intensity of the amorphous region diffraction.

RESULTS AND DISCUSSION

FT-IR Analysis

FT-IR spectroscopy was used to reveal changes in the chemical structure of samples after various treatments. Figure 2 shows the FT-IR spectra of CC, CC-S, CC-SA, and CC-SAB. Corncobs consist mainly of cellulose, hemicellulose, and lignin. These three materials contain alkane, ester, aromatic, ketone, and alcohol functional groups. The disappearance or weakening of a specific peak in the FT-IR spectrum indicated the removal or partial removal of that specific functional group upon treatment. The dominant peaks between 3600 and 2800 cm^{-1} were characteristic of stretching vibrations of –OH and –CH groups, respectively (Alemdar and Sain 2008). The peak of 1732 cm^{-1} in the spectrum of CC was attributed to acetyl and uronic ester groups of hemicellulose, and ester carboxylic groups of ferulic and p-coumaric acids of lignin (Chirayil *et al.* 2014). The peak at 1608 cm^{-1} corresponded to the C=O stretching vibration of hemicellulose. The intensity of both peaks was lower in the CC-S spectrum compared to the CC spectrum. This indicates that hemicellulose was partially degraded and released from the solid matter upon steam explosion. These two peaks were almost absent in the CC-SA spectrum. Prior studies have shown that alkaline treatment can remove hemicellulose in biomass, so peaks at 1732 and 1608 cm^{-1} are rarely found. Peaks at 1253 cm^{-1} (aromatic C–O stretching) and 1515 cm^{-1} (aromatic ring vibrations) had disappeared after bleaching. This indicated the removal of lignin components, in agreement with a previous report (Andrade-Mahecha *et al.* 2015). The sharp peak at 897 cm^{-1} in all spectra was the crystalline band of cellulose (Fan *et al.* 2012), its presence indicates that cellulose was well preserved throughout the process.

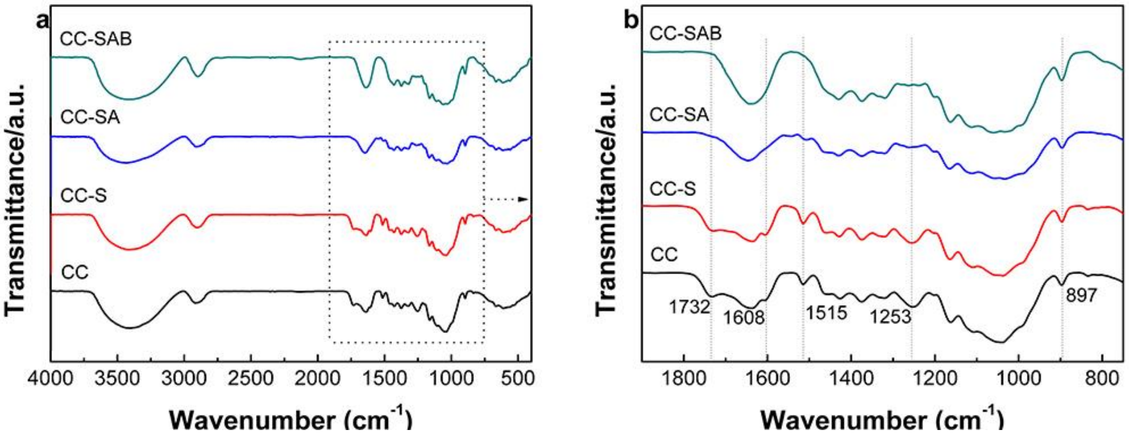

Fig. 2. (a) FT-IR spectra of samples after different treatments; (b) enlarged FT-IR spectra between specific wavenumbers

Thermal Properties

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the various samples are shown in Fig. 3. Figures 3a and 3c show the two main weight loss ranges of 30 to 120 °C and from 200 to 400 °C in all samples. The initial weight loss resulted from the evaporation of moisture (Chandra *et al.* 2016). The second weight loss was caused by the pyrolysis of the three main materials: cellulose, hemicellulose, and lignin. There were obvious differences between the pyrolytic behaviors of these three materials. The pyrolysis of hemicellulose and cellulose occurs in the range of 220 to 315 and 315 to 390 °C, respectively (Yang *et al.* 2007). Therefore, there were two distinct pyrolytic peaks for hemicellulose and cellulose in the DTG curves. Lignin did not result in an obvious pyrolytic peak because lignin decomposes over a broader temperature range (200 to 500 °C) than the other materials (Brebu and Vasile 2010).

In Fig. 3b, the DTG curve of CC showed two pyrolytic peaks at 283 and 334 °C, which represented the maximum temperature for pyrolysis of hemicellulose and cellulose, respectively. In the DTG curve of CC-S, these two peaks were shifted to higher temperatures of 313 and 361 °C, indicating increased thermal stability for hemicellulose and cellulose upon steam explosion. For hemicellulose, this increased thermal stability could be explained by the hydrolysis process that takes place during steam explosion. In this study, hemicellulose was hydrolyzed during steam explosion into monosaccharides or water-soluble oligomers that could be washed away. Hemicellulose fractions with higher thermal stability were preferentially retained during this process, so the pyrolytic peak for hemicellulose shifted towards a higher temperature. However, the 27 °C shift observed in this study was unexpectedly high for cellulose. The hydrolysis of cellulose was not considered likely, because the steam-explosion temperature was not in the normal cellulose degradation range. The thermal stability of each component was also affected by other components in the composites, suggesting that this large temperature shift could be explained by hemicellulose. Free radicals or low molecular weight compounds may have formed during the pyrolysis of hemicellulose fractions, potentially triggering the degradation of cellulose at a lower temperature. The hemicellulose fractions used in this experiment were hydrolyzed during steam explosion, therefore losing the ability to form trigger radicals or low molecular weight compounds, therefore, increasing the thermal stability of cellulose in CC-S.

One notable pyrolytic peak was observed at around 352 °C in the DTG curve of CC-SA, which contributed to the thermal pyrolysis of cellulose. The disappearance of the pyrolytic peak of the hemicellulose was attributed to the removal of hemicellulose after alkaline treatment. Alkaline treatment also had a negative effect on the thermal stability of cellulose, with a 9 °C shift towards lower temperatures observed. Bleaching resulted in the thermal stability of cellulose in CC-SAB being even lower than CC-SA, with its pyrolytic peak observed at 331 °C. A relatively flat region was observed in the DTG curve of CC-SAB in the temperature range of 255 to 275 °C. This suggested that parts of cellulose with even lower thermal stability existed. Usually, when there is an increase in the molecular weight of a polymer there is also an increase in thermal stability. This relationship suggested that fractions of cellulose having decreased molecular weight were present in the CC-SAB. Nakasone and Kobayashi (2016) found that bleaching in 10 vol.% NaClO solution decreased the average molecular weight of sugarcane bagasse cellulose fibers. This justified the relatively flat region in the DTG curve of CC-SAB.

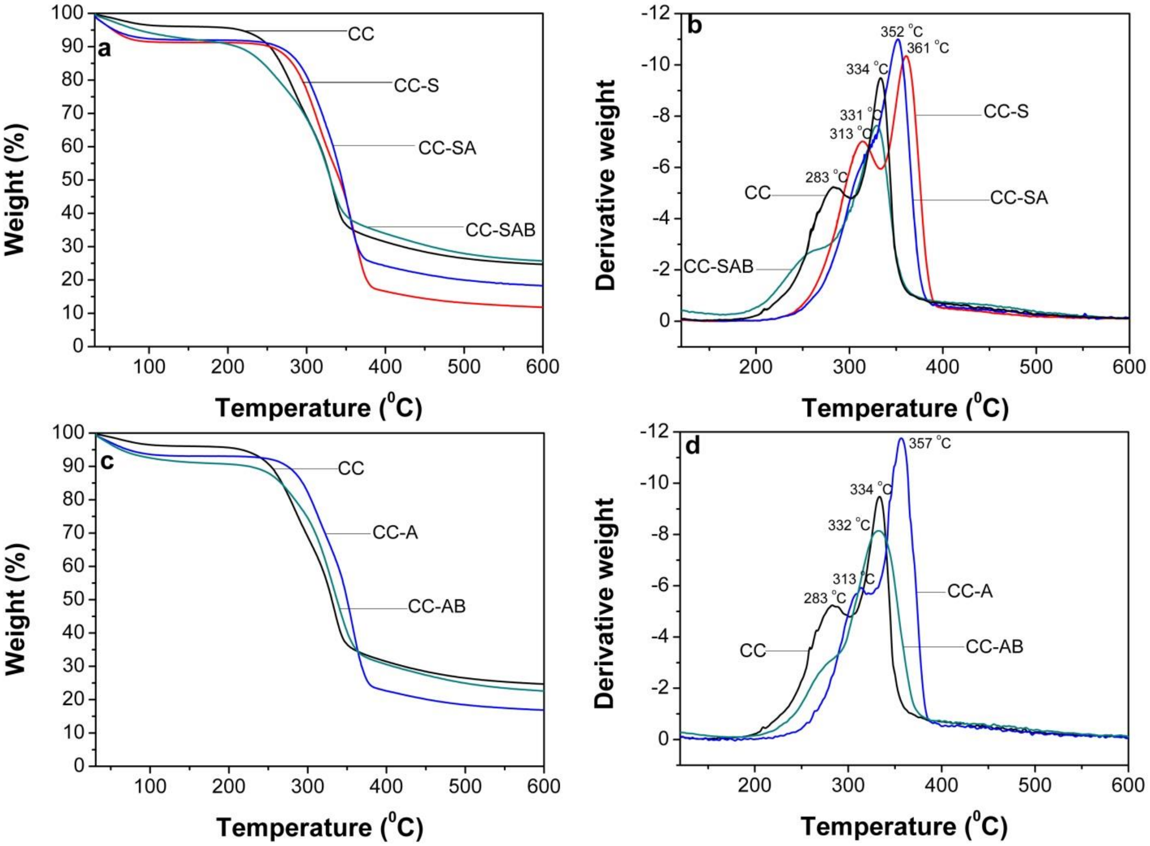

Fig. 3. TG and DTG curves of (a, b) CC, CC-S, CC-SA, and CC-SAB, and (c, d) CC, CC-A, and CC-AB.

The pyrolytic peak of hemicellulose at 313 °C was retained in the DTG curve of CC-A, even after alkaline treatment (Fig. 3d). This result indicated the incomplete removal of hemicellulose, as well as the increased thermal stability of the remaining hemicellulose, compared with the raw material. The pyrolytic peak of cellulose at 357 °C indicated that the thermal stability of cellulose in CC-A had also increased. The raw material in this study possessed a tight structure, in which cellulose fibers were held together by cementing hemicellulose and lignin. This meant that the raw material had a lower specific surface area for reaction than the steam-exploded material. Therefore, alkaline treatment in the absence of steam-explosion pretreatment could not sufficiently remove hemicellulose from corncobs under the same conditions. The pyrolytic peak of hemicellulose was absent in the curve of CC-AB, indicating that remaining hemicellulose was removed upon bleaching.

Morphologies and Diameter Distribution

FESEM images of CC are shown in Fig. 4. The cell wall structure is shown in Fig. 4a, and a higher magnification image is shown in Fig. 4b. Several minor breakages were observed in the cell wall, which were due to the pulverization procedure use to prepare the sample CC.

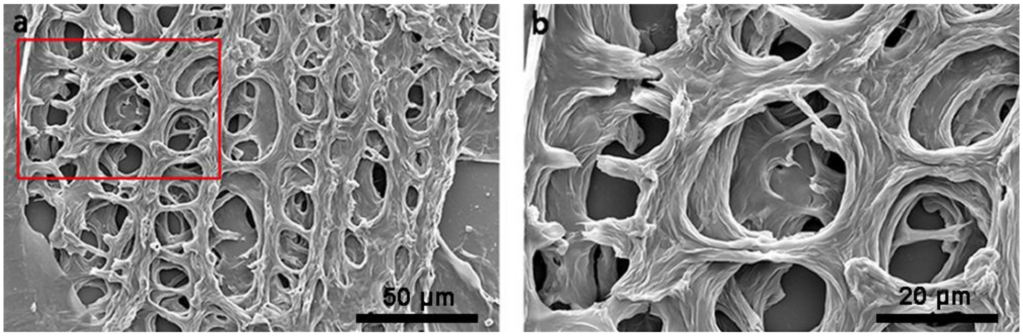

Fig. 4. (a) FESEM and (b) high magnification FESEM images of CC

A comparison of the appearance of CC-SAB and CC-AB is shown in Fig. 5. The bleached sample with steam-explosion pretreatment had a much brighter, white color than the one without the pretreatment, which indicated less lignin remaining in CC-SAB. Thus, steam explosion facilitates the subsequent chemical treatments.

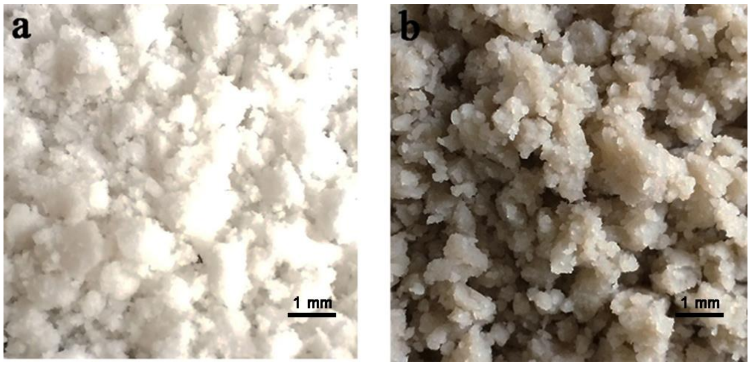

Fig. 5. Comparison of (a) CC-SAB and (b) CC-AB

The morphologies of samples after different treatments are shown in Fig. 6. The morphology of steam cooked CC that was not subjected to steam explosion is shown in Fig. 6a. The surface appeared rough, with no obvious fibrillation. The cell wall structure of the corncobs was subjected to a certain degree of damage during steam-explosion pretreatment, loosening its structure. Additionally, noticeable microfibrillated cellulose was exposed, as shown in Fig. 6b.

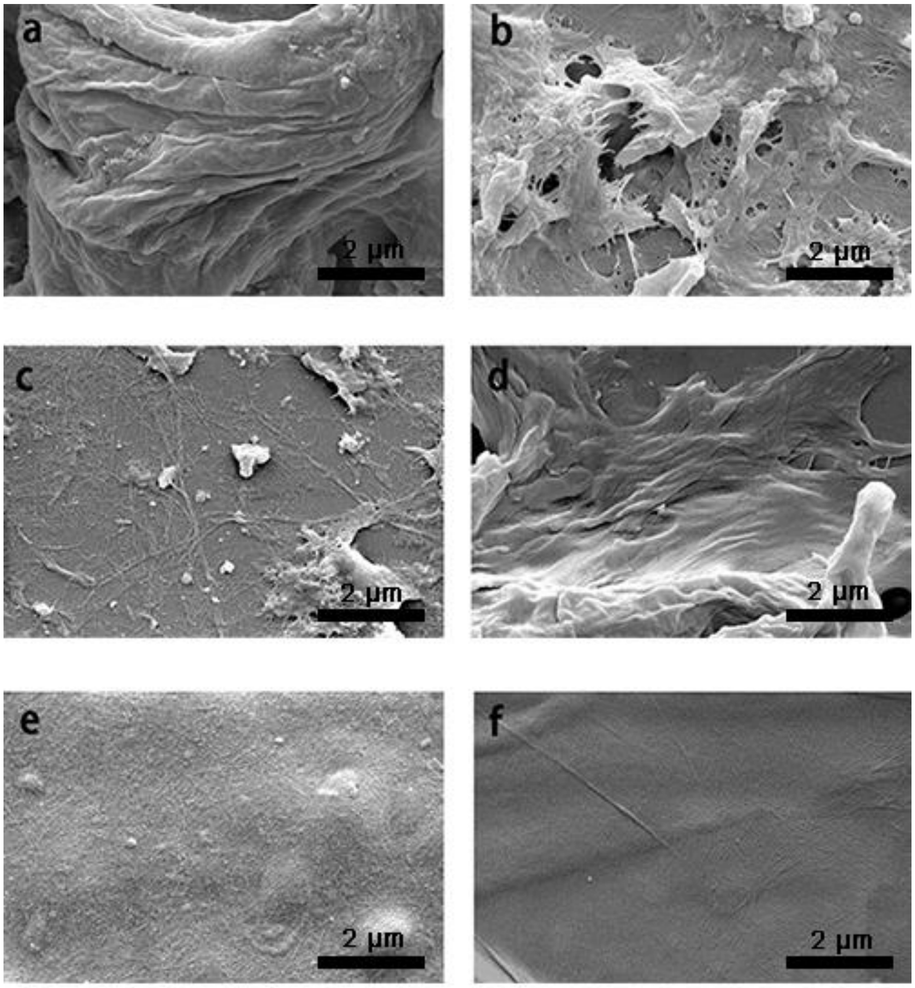

Fig. 6. FESEM images of (a) steam cooked CC, (b) CC-S, (c) CC-SAB, (d) CC-AB, (e) CC-SABH, and (f) CC-SABHU

Steam-explosion treatment typically consists of two stages. First, biomass is steam cooked at high temperature and pressure. Steam penetrates loose areas, such as the cementing region which is composed of lignin, hemicellulose, and amorphous cellulose. Components having low thermal stability, such fractions of hemicellulose, are hydrolyzed in this stage. Second, hot steam that has penetrated the raw material is released in a high-speed steam flow. This produces an intense force which tears cell walls, especially in amorphous regions. Some Van der Waals forces and/or hydrogen bonds are also disrupted, which further loosens the structure of the material. In this study, it can be concluded from Figs. 6a and 6b that initial fibrillation and loosening of the structure occurred during the second stage of steam explosion. The loosened structure was more susceptible to the subsequent chemical processes, as reagents could readily infiltrate the interior of the material, and benefit from a higher contact area for reaction. Steam explosion increased the distance between fibers, making it more difficult for hydrogen bonds to be re-formed. This benefited the subsequent mechanical treatments.

After steam-explosion treatment, corncobs were treated with NaOH and NaClO to remove the remaining hemicellulose and lignin. Fig. 6c shows a FESEM image of CC-SAB. Fibers ranging greatly in diameter were exposed after chemical treatments removed cementing materials. This indicated that steam-explosion treatment decreased hydrogen bonding between cellulose fibers. The FESEM image shown in Fig. 6d demonstrates that cellulose fibers were not fibrillated in CC-AB. There are two possible explanations for this phenomenon. First, from the results seen in Fig. 5, it can be speculated that lignin as a cementing material still exists in CC-AB, meaning that the remaining lignin may have hindered the fibrillation of cellulose. Alternatively, cellulose fibers were held together by a remarkable amount of hydrogen bonds that were undisrupted by the explosion procedure.

The FESEM image in Fig. 6e provides insight into the role of high-speed blending as it relates to fiber size. Compared to Fig. 6c, a noticeable decrease in the size of the fibers can be seen in Fig. 6e. Additionally, several macro-scale particles were observed between isolated fibers in Fig. 6e. The fiber samples subjected to blending treatment were of uniform size and reduced entanglement. This is due to the high-speed blending process generating a rapid vortex in the water. Particles and fibers were pulverized or fibrillated because of the effect of agitation in this process (Uetani and Yano 2010). However, there are limitations for high-speed blending for both the degree of fibrillation and energy consumption. One-minute blend times were used in this study to reduce energy consumption, based on previous experimental observations. The morphology of CC-SABHU after being subjected to ultrasonication is shown in Fig. 6f. A further decrease in nanofiber size was observed, due to ultrasonic cavitation. Figure 1 shows that the transparency of the suspension increased following ultrasonication, when compared with a suspension of the same concentration (0.5 wt.%). The diameter of the nanofibers shown in these images were typically 5 to 10 nm.

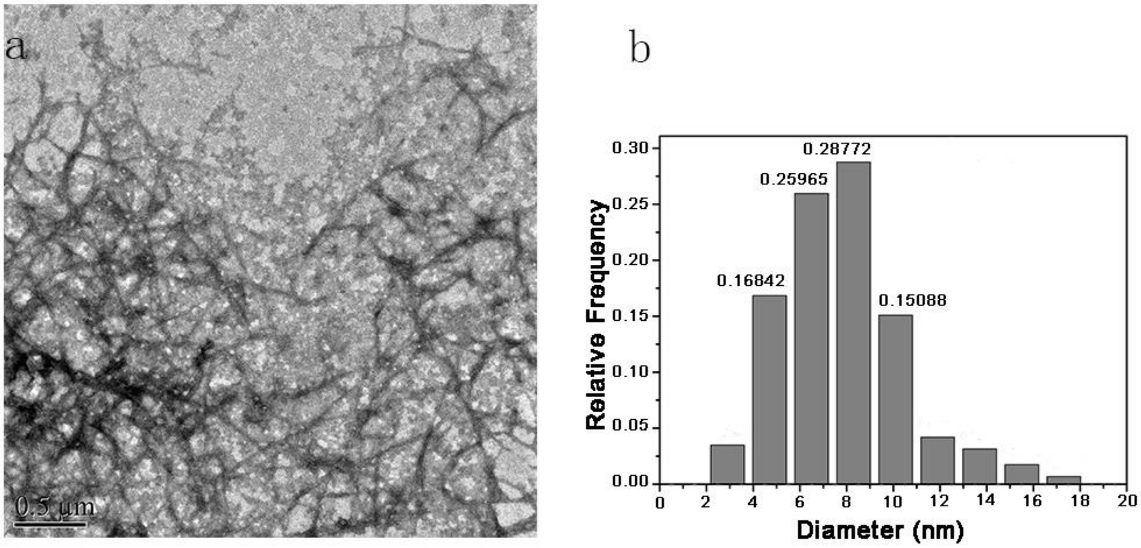

Fig. 7. (a) TEM image and (b) diameter size distribution of CNFs prepared from corncobs

The FESEM results indicated that steam explosion could expose microfibrillated cellulose from corncobs, which has not been previously reported. This was likely because the cellulose fibers of corncobs are reportedly less entangled than other materials. For example, eucalyptus fibers could not be fibrillated into such small scale using a similar continuous steam-explosion method in a previous study by the authors (Ma *et al.* 2015). After steam-explosion treatment, chemical treatments removed remaining cementing materials. Furthermore, the cell wall structure was barely visible, and numerous CNFs of 10 to 100 nm in diameter were exposed. High-speed blending disentangled the cellulose fibers to give a uniform fiber size distribution. Subsequent ultrasonication further decreased the CNF diameter distribution. CNFs were therefore obtained by combined mechanical and mild chemical treatments.

The CNFs obtained after ultrasonication were confirmed by TEM analysis. Fig. 7a clearly shows isolated CNF structures. By drying and coating the structures during SEM specimen preparation, some self-aggregation may have occurred, slightly increasing the measured size. TEM is therefore, more frequently used to evaluate the size of single nanofibers (Chen *et al.* 2015). The Image Pro software package was used to analyze the CNF diameter distribution, based on 800 measured, individual fibers. Fig. 7b shows that the diameters of approximately 70% of the fibers were between 5 and 10 nm, with an average diameter of approximately 8 nm.

XRD Analysis

Crystallinity index is a key factor for determining the mechanical and thermal properties of nanofibers. The XRD patterns of CC, CC-S, CC-SA, and CC-SAB are shown in Fig. 8. Table 1 shows the crystallinity indices of these samples, which increased as the treatment process progressed. Hydrogen bonding and Van der Waals interactions exist between adjacent cellulose chains, in contrast to the natural amorphous structures of hemicellulose and lignin. Thus, cellulose has a well-established crystalline structure (Chirayil *et al.* 2014).

Figure 8 shows that all samples exhibited major diffraction intensities at 22.5 and 15.5° 2θ, and a shoulder in the region of 19° 2θ. This suggests that all samples were cellulose I type. Differences in the XRD patterns of CC and CC-S are due to the 1.38% increase in crystallinity index, increasing from 27.31 to 28.69%. This was in agreement with the FT-IR results, showing that while hemicellulose and other amorphous components were partially degraded during steam explosion, the molecular weights of the resulting compounds were not sufficiently low enough to be washed away. Therefore, the crystallinity remained largely unchanged. The peak at 22.5° 2θ became sharper after chemical treatments, indicating the removal of non-cellulosic polysaccharides and the dissolution of amorphous zones (Cherian *et al.* 2008). The chemical treatments resulted in the crystallinity index increasing from 28.69 to 40.08%, because of the removal of non-cellulosic materials.

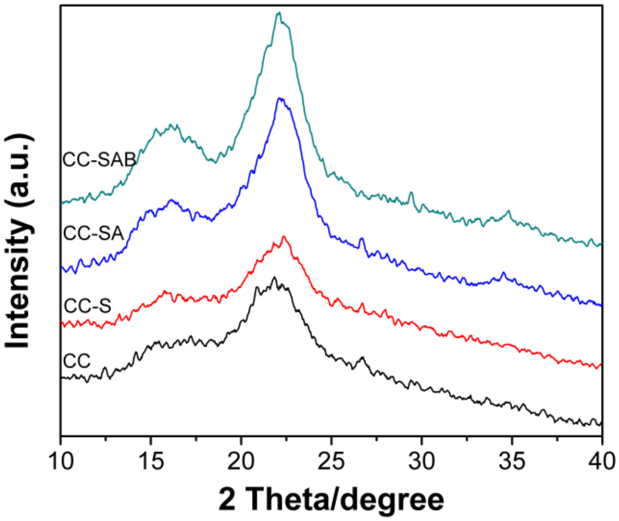

Fig. 8. XRD patterns of CC, CC-S, CC-SA, and CC-SAB

Table 1. Crystallinity Indices of Samples

Sample	Crystallinity Index (%)
CC	27.31
CC-S	28.69
CC-SA	36.17
CC-SAB	40.08

CONCLUSIONS

1. Cellulose nanofibrils (CNFs) were isolated from an abundant and low-cost natural resource, corncobs, using steam-explosion pretreatment and mild mechanochemical treatments.
2. Mechanical treatments including high-speed blending and ultrasonication were combined with mild chemical treatments involving only two chemical reagents in low concentration to remove non-cellulosic components.
3. Steam explosion loosened the cell wall structure and facilitated the removal of the remaining cementing materials, hemicellulose and lignin, during subsequent chemical treatments. The pretreatment also increased the thermal stability of remaining hemicellulose and cellulose by removing fractions of hemicellulose that could trigger the degradation of cellulose at a lower temperature.
4. High-speed blending decreased the entanglement of CNFs, yielding CNFs of uniform diameter distribution. The process of ultrasonication fibrillated cellulose fibers into nanofibers with an average diameter of 8 nm.
5. X-ray diffraction (XRD) showed that steam explosion had little effect on the crystallinity. The removal of non-cellulosic components by subsequent chemical treatments increased crystallinity.

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