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Extraction and Characterization of Cellulose Nanocrystals Produced by Acid Hydrolysis from Corn Husk

Piyaporn KAMPEERAPAPPUN

Division of Textile Chemical Engineering, Faculty of Textile Industries,
Rajamangala University of Technology Krungthep, Bangkok, Thailand 10210

Abstract

Corn husk is one of the agricultural residues which are abundant, inexpensive, and readily available source of renewable lignocellulosic biomass. Cellulose nanocrystals (CNCs) were extracted from corn husk by alkali and bleaching treatments followed by sulfuric acid hydrolysis treatment. The material obtained after each stage of the treatments was characterized. Morphological investigation was carried out using scanning electron microscope (SEM) and transmission electron microscopy (TEM). Fourier transform infrared (FTIR) spectroscopy showed the progressive removal of non-cellulosic materials. The crystallinity of corn husk and CNCs was also investigated using X-ray diffraction analysis (XRD). The highest crystallinity index value of this study is 68.33% for cellulose nanocrystals.

Keyword : Corn husk, Cellulose nanocrystals, Acid-hydrolysis, Extraction
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Introduction

Nowadays, the use of the bio-based industrial residues has continuously increased due to increasing amount of industrial bio-residues and the rising cost of their management. The most common products from these residues are ethanol and co-products obtained from the ethanol industry e.g. lignin, phenolic, epoxy, and isocyanate.[1-2] However, there is another interesting co-product from these bio-based industries which is cellulose nanocrystals (CNCs). Due to the low density, high aspect ratio, good mechanical properties, low thermal expansion, low toxicity, high surface concentrations of hydroxyl groups of CNCs, these materials have a great potential as nano-reinforcing fillers for industrial and biomedical applications.[3-7]

Cellulose is a semi-crystalline polymer having amorphous and crystalline regions in varying proportions depending on the plant species. Therefore, the chemical compositions and cell dimensions depend on particular plants, their origin, and extraction methods.[8-9] Until now, many researchers have reported on the extraction of CNCs from a wide variety of natural source materials, especially in agricultural wastes (e.g., rice husk[10], mulberrybark[11], pineapple leaf[12], and mango seed[13]).Various extraction processes can be used to prepare CNCs but the common method to extract the CNCs is sulfuric acid hydrolysis. CNCs are highly crystalline rod-shaped particles having at leastone dimension equal or less than 100 nm.[9,14-15] Further, although many researches reports studies about CNCs extraction from various materials, no studies on the extraction CNCs from corn husk have been conducted to date.

Corn is one of five major crops (rice, cassava, corn, sugarcane, and rubber) in Thailand. The main waste from corn production is the corn stover (the stalk and leaves after harvesting), the corn husk, and the cobs.[16] In the case of corn husks, they are often disposed using open burning. The problem with burning corn husk is it poses health and environmental hazards, therefore, the development of suitable scientific and economic method of recycling of corn husk cellulose (~42%), is very important. Corn husks are composed of lignin (~13%), ash (~4.2%), and other materials (~41%).[17] From its cellulose content, the use of corn husk as the primary source for producing cellulose fibers or nanocrystals is promising. The objective of this study was to extract CNCs from corn husk using alkali and bleaching treatments followed by sulfuric acid hydrolysis.

Materials and Experimental Procedures

Materials

The corn husk (agro-waste) was obtained from local market (Samutprakan, Thailand). Cellulose dialysis membrane tube (MWCO 12,000-

Corresponding author E-mail : piyaporn.k@rmutk.ac.th

14,000) was purchased from Membrane Filtration Products, Inc., USA. Sulfuric acid, acetic acid, sodium chlorite, sodium hydroxide were purchased from Sigma-Aldrich, USA. All other chemicals were of analytical reagent grade and used as received, without further purification.

Methods

Preparation of cellulose nanocrystals from corn husk

1) Alkali treatment

The corn husk was washed several times with distilled water and dried in an oven at 90°C for 24 hours. After washing and drying, it was ground and sieved under 40 mesh sieves and stored at room temperature. The ground corn husk was treated with 4wt% sodium hydroxide solution at 80°C for 2 hours. The solid was then filtered and washed several times in distilled water. The alkali treatment was repeated twice.

2) Bleaching process

Following alkali treatment, the bleaching treatment was carried out using 1.7w/v% sodium chlorite at 80°C for 4 hours. The mixture was allowed to cool and filtered using excess distilled water. This process was performed two times.

3) Acid hydrolysis

The acid hydrolysis treatment was conducted after alkali treatment and bleaching process using sulfuric acid concentration (64wt%) and temperature (45°C) with a range of reaction time (15-60 minutes) under continuous stirring. The ratio of the obtained cellulose to liquor was 1:20. The hydrolysis reaction was immediately quenched by adding a 8-fold quantity of chilled distilled water. The hydrolyzed material was washed by centrifugation at 10,000 rpm at 10°C for 10 minutes to remove acidic solution. The centrifugation step was repeated several times before the suspension was dialyzed againt distilled water for several days until constant pH was reached. The suspension was then sonicated for 30 minutes in ice bath to avoid overheating before kept refrigerated for futher used.

Characterization of corn husk

1) Chemical composition

The chemical constituents of the corn husk at each stage of treatment were determined accordingto TAPPI standards - cellulose and hemicellulose (TAPPI T203 OS-74), lignin (TAPPI T222 OS-83).

2) Microscopies

Scanning electron microscopy (SEM) analysis was performed using a Jeol JSM-6400 scanning electron microscope to observe the surface morphology of corn husk at different stages of treatment. All samples were air-dried and coated with a gold to avoid charging. The images were taken with an accelerating voltage of 15 kV. Transmission electron microscope (TEM) (Tecnai 20 Twin) was used to studied the size and shape of CNCs. A drop of diluted CNCs suspension (1wt%) was deposited on the carbon-coated grids and allowed to dry at room temperature. The grid was stained with a 0.5% uranyl acetate solution and dried at ambient temperature before TEM analysis was carried out with an accelerating voltage of 120 kV. The length and diameter of the CNCs was investigated using an ImageJ analyzer program.

3) Fourier Transform Infrared Spectroscopy (FTIR)

Untreated, alkali-treated, bleached, and acid-hydrolyzed corn husk samples were analyzed using a Spectrum One FTIR spectrophotometer. FTIR spectral analysis was performed in the transmittance mode in the range of 4000-400 cm^{-1}.

4) X-ray diffraction (XRD)

The crystallinity of the corn husk after different treatments was determined using an X-ray diffractometer (Bruker D-8 Discover) with CuKα radiation(λ = 0.1542 nm). The scanning range and the scanning speed were 5-40° and 5 deg/s, repectively.

Results and Discussion

1) Chemical composition of corn husk

The chemical composition of corn husk at each stage of treatment was determined and summarized in Table 1.

Table 1. Chemical composition of corn husk at each stage of treatment

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Untreated corn husk	29.3	39.7	11.4
Water soaked corn husk	30.1	39.2	11.3
Alkali treated corn husk	61.4	8.1	9.2
Bleached corn husk	97.6	1.9	0.2

The untreated corn husk are composed of 29.3wt% cellulose, 39.7wt% hemicellulose, and 11.4wt% lignin. From Table 1, it was found that the chemical composition of water soaked corn husk were not significantly changed as compared to the untreated corn husk. This can be explained that room temperature water does not significantly remove hemicellulose and lignin from corn husk. However, any remaining impurities (e.g. dirt and dust) on corn husk are removed with water. The cellulose content continuously increased upon chemical treatment. The amount of hemicellulose and lignin of untreated corn husk are higher than those of the alkali treated and bleached corn husk. The alkali treatment was efficient in removing the hemicellulose, which decreased from 39.7wt% to 8.1wt%. Hemicellulose is hydrolyzed and become water-soluble upon alkali treatment.[18] The bleaching treatment partially removed both hemicelluloses and lignin. Most of the lignin content was removed during bleaching treatment. This result can be explained that lignin reacts with sodium chlorite to get the water-soluble lignin chloride.[18]

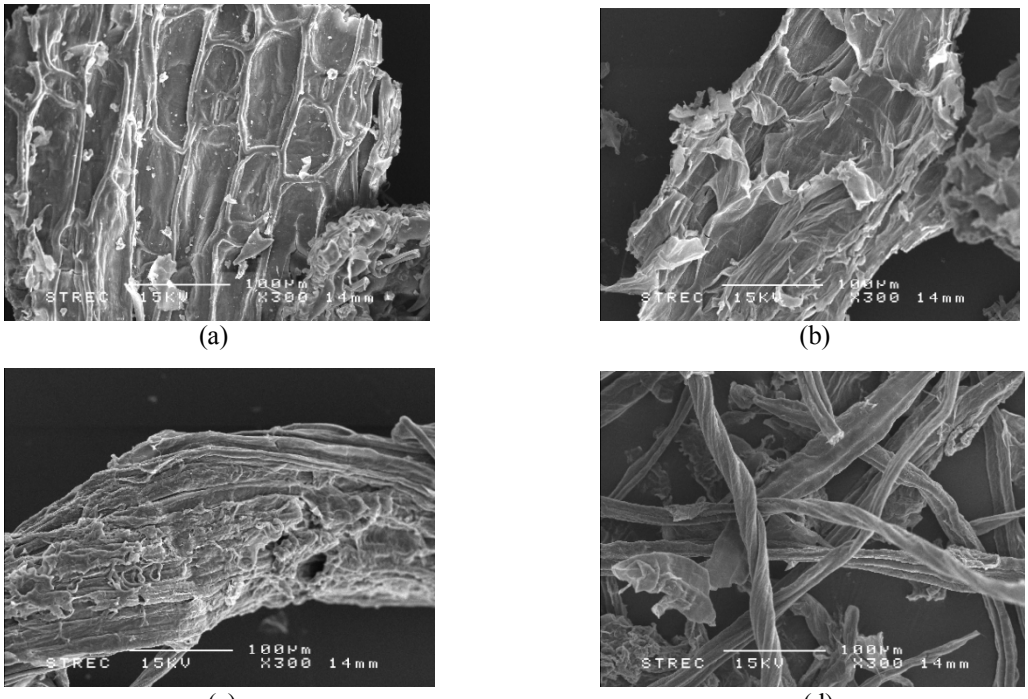
2) Morphological analysis

The visual microscopic evolution of corn husk at different stages is shown in Figure 1.

Figure 1. Photographs of ground corn husk(a) untreated corn husk (b) water soaked corn husk (c) alkali treated corn husk (d) bleached corn husk

After alkali treatment, the color of ground corn husk was changed from cream to light brown and then it turned to white color after bleaching process. This is due to the removal of non-cellulosic materials and other impurities upon chemical treatment of corn husk. The observed white color of the final product was indicated that almost pure cellulosic material is obtained and agrees with the chemical composition data.

The structure of the corn husks was investigated using SEM (Figure 2).



(a) (b)

(c) (d)

Figure 2. Scanning electron micrographs of (a) untreated corn husk (b) water soaked corn husk (c) alkali treated corn husk (d) bleached corn husk

From the SEM micrographs, it is clear that the clearer surface of water soaked corn husk is obtained compared with untreated corn husk due to remove impurities. The morphology of the corn husk changed with the chemical treatment (Figure 2). After alkali treatment, the fiber surface become rougher. This could indicate the partial removal of the outer non-cellulosic layer composed of material such as hemicellulose, lignin, pectin, wax, and other impurities contained in the corn husk. The alkali treatment helps defibrillation and the opening of the fiber bundles as shown in Figure 2(c) and this trend increased along with the bleaching treatment.[11,19] The seperated fiber into an individual form (Figure 2(d)) indicates almost all the components that bind the fibril structure of the corn husk were removed under the strong chemical treatment[10,19]

Figure 3 illustrates how the different hydrolysis times affect the morphology of cellulose nanocrystals.

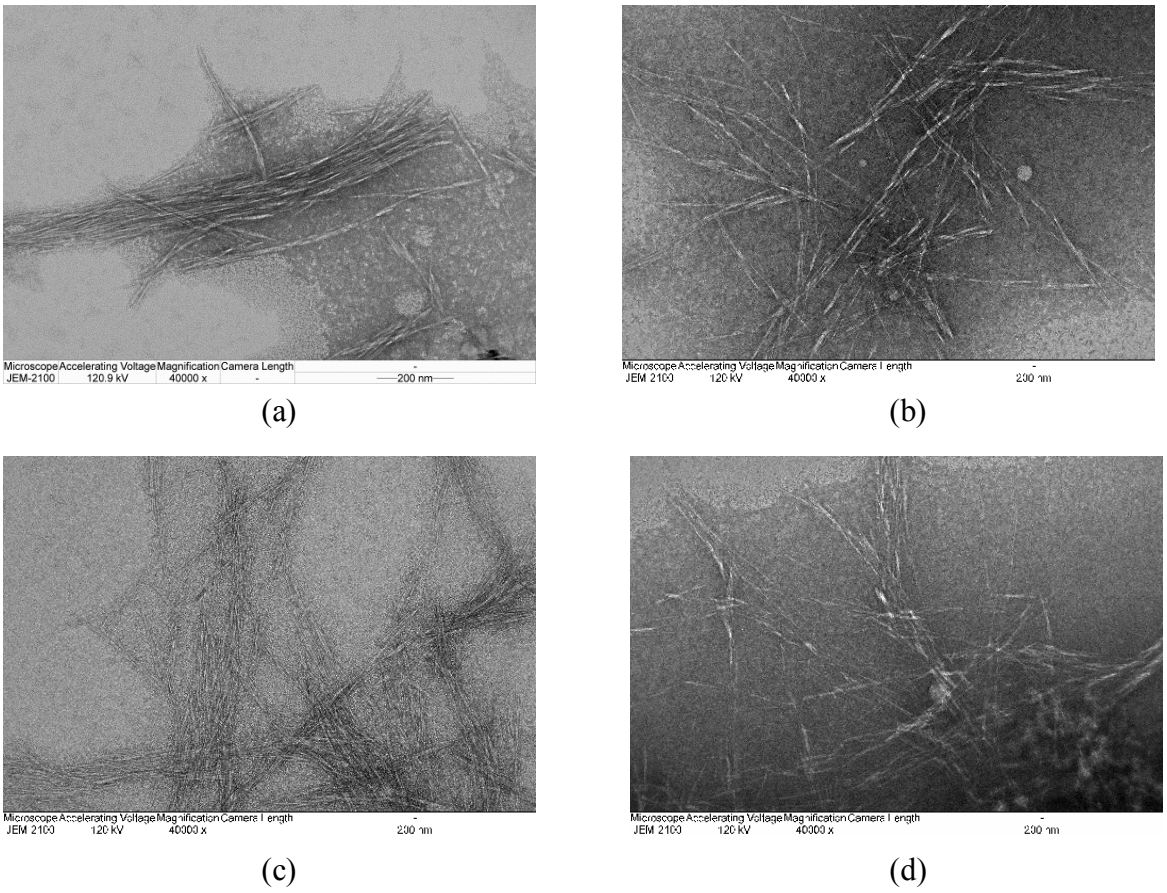


Figure 3. Transmission electron micrographs of cellulose nanocrystals extracted from corn husk fibers (a) 15 minutes (b) 30 minutes (c) 45 minutes (d) 60 minutes

All images show CNCs with a rod-like structure (Figure 3). The tendency to agglomerate can also be observed in all images. This tendency can be attributed to the drying conditions during sample preparation which involved evaporation of water. The length and diameter of CNCs were measured using ImageJ software (Table 2).

Table 2. The size of CNCs isolated by sulfuric acid hydrolysis

Hydrolysis time (minute)	Length (nm)	Diameter (nm)	L/D ratio
15	254.1 ± 41.9	11.8 ± 1.5	21.8 ± 3.7
30	235.1 ± 27.4	7.7 ± 1.3	31.6 ± 6.9
45	230.3 ± 20.9	7.4 ± 1.5	32.4 ± 7.8
60	224.6 ± 29.5	6.9 ± 0.8	32.8 ± 7.5

As can be seen in Table 2, the ranges of length and diameter for CNCs were 225-255 nm and 7-12 nm, respectively which agrees quite well with data published by Araki *et al.*[20] and Siqueira *et al.*[21], which reported that the CNCs extracted from plants show a diameter of 5-20 nm and a length of 100-300 nm.

Both length and diameter of CNCs decreased with increasing time, however, the aspect ratios of CNCs increased with hydrolysis time. This can be explained that at the early stage of the hydrolysis, the acid diffuses preferentially into the non-crystalline portions of cellulose and hydrolyzed the accessible glycosidic bonds. After that, the reaction occurs much slowly at the reducing end and at the surface of the residual crystalline regions.[22]

3) Spectroscopic analysis

The chemical structure of corn husk at each stage of treatment was analyzed using FTIR shown in Figure 4.

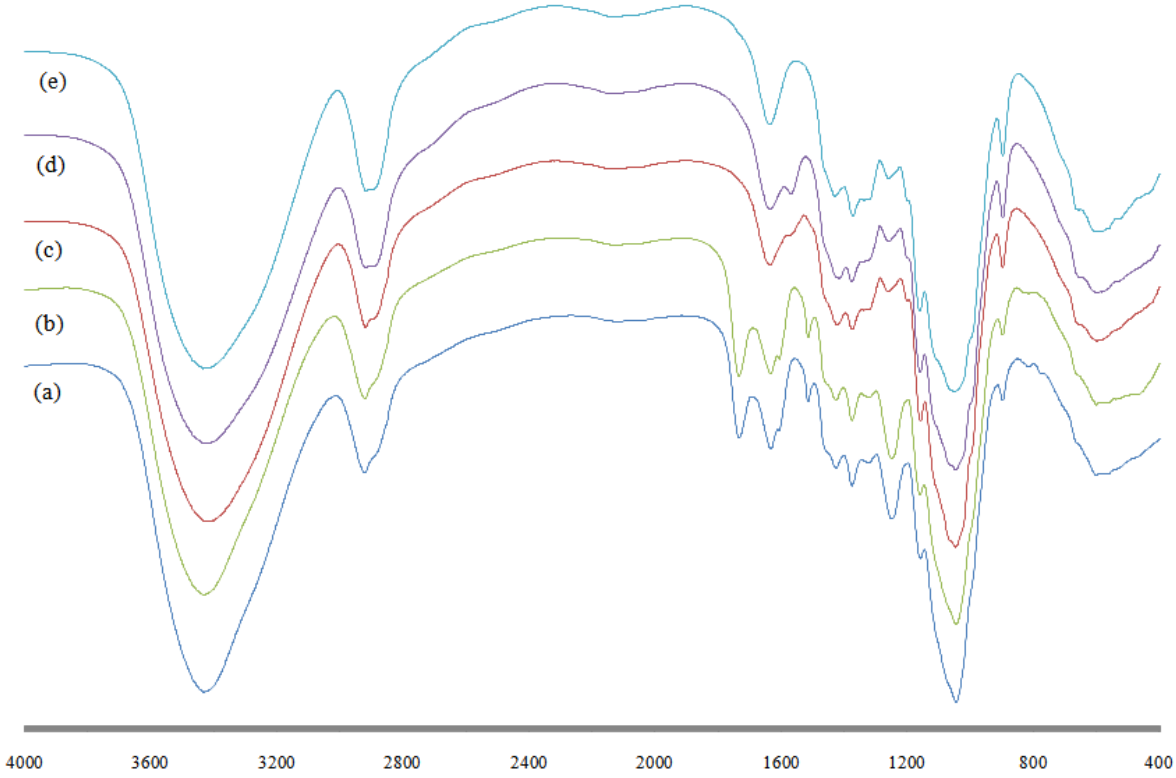


Figure 4. FTIR spectra of (a) untreated corn husk (b) water soaked corn husk (c) alkali treated corn husk (d)bleached corn husk (e) acid hydrolyzed corn husk

In the case of untreated corn husk, the peak at 3175-3490 cm^{-1} is attributed to the O-H stretching intramolecular hydrogen bonds for cellulose I. The FTIR peak at 2850-2970 cm^{-1} is due to C-H stretching. The absorption peak at 1730 cm^{-1} as present in the untreated and water soaked corn husk is attributed to the C=O stretching vibration for the acetyl and ester groups in hemicellulose or carboxylic acid groups in the ferulic and p-coumeric components of lignin (Figure 4(a)-(b)).[23] In addition, the detected peaks at 1620-1649, 1512, and 1595 cm^{-1} indicated the aromatic ring present in lignin and absorbed water. The spectra at 1250 cm^{-1} showed the characteristic of CO out of plane stretching due to aryl group in lignin.[24]Moreover, the absorption around 898 cm^{-1} and 1070 cm^{-1} refer to the C-O stretching and C-H vibration of the cellulose component.[10] The absence of the 1734 cm^{-1} and 1515 cm^{-1} peaks after chemical treatment results from removal the non-cellulosic material (Figure 4(c)-(e). Furthermore, the weak signal at 1245 cm^{-1} (Figure 4(c)-(e)) confirms that the effective removal of hemicellulose after chemical treatment.[25] It was observed that no significant difference between the spectra of bleached and acid hydrolyzed corn husk. The results indicate that the cellulose molecular structure remains unchanged following acid hydrolysis.

4) XRD

X-ray diffraction pattern and the crystallinity index of CNCs obtained after hydrolysis time 45 minutes were studied and compared with untreated corn husk (Figure 5 and Table 3).

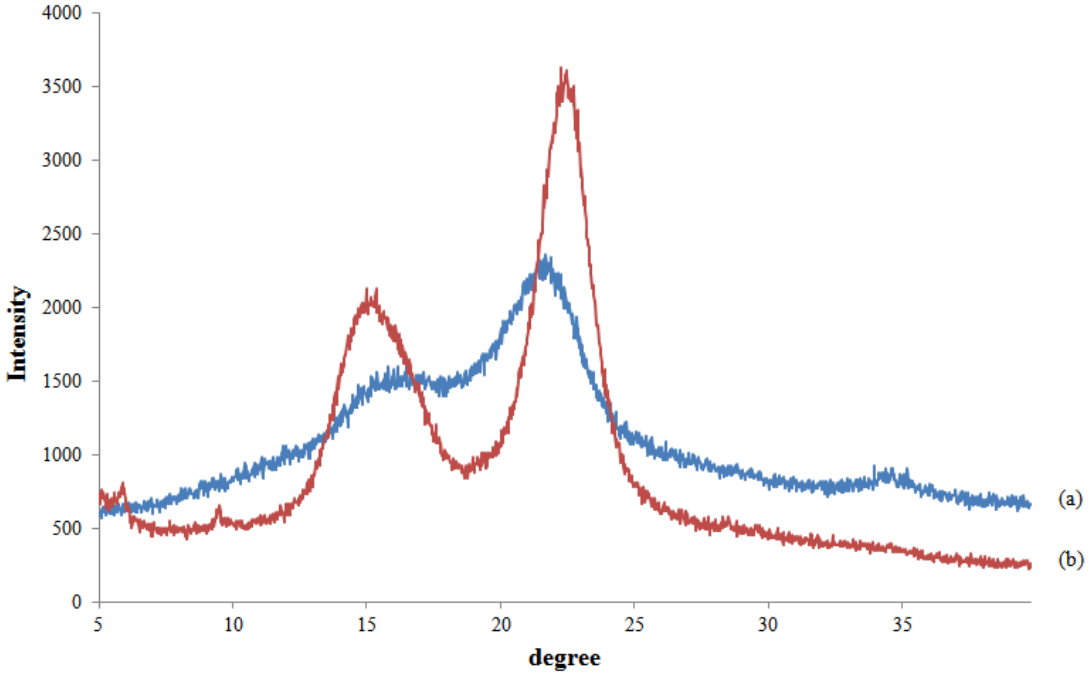


Figure 5. XRD analysis of (a) untreated corn husk and (b) CNCs extracted from corn husk

Table 3. The crystallinity index of corn husk at different stages

Sample	Crystallinity (%)
Untreated corn husk	33.86
Water soaked corn husk	36.61
Alkali treated corn husk	41.76
Bleached corn husk	55.09
Cellulose nanocrystal	68.33

The crystalline peaks around 2θ = 16°, 22°, and 35° were defined cellulose I exhibiting the hkl 110, 200, and 004 crystallographic planes, respectively.[26-27] On removing the non-cellulosic constituents of the corn husk by chemical treatment, the intensity of peak become more defined (Figure 5). The crystallinity index was determined and summarized in Table 3.

The cellulose nanocrystals show the highest crystallinity index value (68.33%) which displayed the strongest and sharpest peak at 2θ = 22°. The increased crystallinity of treated corn husk compared to untreated one was attributed to the progressive removal of amorphous non-cellulosic materials.[10] The increased crystallinity was also expected to increase their stiffness and rigidity resulting in the increased mechanical properties and reinforcing capacity of composite reinforcement.[28]

Conclusions

In this work, extraction of cellulose nanocrystals from corn husk was evaluated for the first time. The chemical composition, morphological, FTIR and XRD results confirmed that removal of hemicellulose and lignin from corn husk. The preparation condition, i.e. hydrolysis time, affects to the morphology of cellulose nanocrystals from corn husk. The obtained cellulose nanocrystals show a great potential as a reinforcing filler in biodegradable nanocomposites production.

Acknowledgments

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