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Ultrasonic enhance acid hydrolysis selectivity of cellulose with HCl–$FeCl_3$ as catalyst

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ABSTRACT

The effect of ultrasonic pretreatment coupled with HCl–$FeCl_3$ catalyst was evaluated to hydrolyze cellulose amorphous regions. The ultrasonic pretreatment leads to cavitation that affects the morphology and microstructure of fibers, enhancing the accessibility of chemical reagent to the loosened amorphous regions of cellulose. In this work, Fourier transform infrared spectroscopy (FTIR) was used to identify characteristic absorption bands of the constituents and the crystallinity was evaluated by the X-ray diffraction (XRD) technique. The results indicated that appropriate ultrasonic pretreatment assisted with $FeCl_3$ can enhance the acid hydrolysis of amorphous regions of cellulose, thus improving the crystallinity of the remaining hydrocellulose. It was observed that sonication samples that were pretreated for 300 W and 20 min followed by acid hydrolysis had maximum of 78.9% crystallinity. The crystallinity was 9.2% higher than samples that were not subjected to ultrasound. In addition, the average fines length decreased from 49 μm to 37 μm.

1. Introduction

The major portion of lignocellulose consists of celluloses, hemicelluloses and lignin. It is abundantly available and renewable. Cellulose is a natural polymer composed of D-glucopyranose units that are linked by β-1,4 glycosidic bonds (Degenstein, Kamireddy, Tucker, & Ji, 2013; Kamireddy, Kozliak, Tucker, & Ji, 2014). It consists of amorphous and crystalline regions. It is a very valuable natural polymer material as it can be used to produce myriad products (Ferreira, Gil, Queiroz, Duarte, & Domingues, 2011; Ragauskas, Williams, & Davison, 2006). In order to extract cellulose from cell walls, different physical and chemical pretreatment techniques are applied to convert lignocellulosic materials to valuable fuels and chemicals (Huber, Iborra, & Corma, 2006; Lange, 2007).

Microcrystalline cellulose (MCC) is such a product obtained from cellulose by the action of acid and enzymes (Mohamad Haafiz, Eichhorn, Hassan, & Jawaid, 2013; Zhang & Lynd, 2004). MCC is a fine white crystalline powder which offers a lot of advantages such as high reactivity, renewability and biodegradability (Maha, Waleed, Yvonne, Andreas, & Thomas, 2013). The most important characteristics of MCC are the dimensions and its fiber size distribution. Due to its unique physical and chemical properties, MCC has been used for many years in various industries such as pharmaceuticals, food, coatings, cosmetics and so on (Xiong, Zhang, Tian, Zhou, & Lu, 2012). Cellulose hydrolysis is the major way for high efficient utilization of biomass, e.g., conversion of renewably produced biomass to commodity chemicals and biofuels that can be used as substitute to conventional fossil fuels. Cellulose crystallinity is a parameter that used to describe relative amount of crystalline material in cellulose, is an important factor affecting the reactivity of cellulose (Kamireddy, Li, Degenstein, Tucker, & Ji, 2013; Peng, Chen, Qu, Li, & Xu, 2014). During acid treatment, cellulose in the amorphous regions is hydrolyzed faster, leaving the crystalline regions to manufacture MCC product. However, the strong acid has a poor selectivity for amorphous regions, as some of crystalline regions are also degraded. This diminishes the performance and the yield of MCC, especially when MCC is extracted from lignocellulosic feedstock with low cellulose content (Lee, Doherty, Linhardt, & Dordick, 2009; Lu & Hsieh, 2010). The hydrolysis of cellulose is usually catalyzed by dilute or concentrated sulfuric acid, although substantial effort has been devoted to the development of alternative hydrolysis schemes. This includes pretreatment with either Bronsted acids or subcritical and supercritical water, metal catalysts and enzymes (Degenstein, Kamireddy, Tucker, & Ji, 2011;

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Yamaguchi et al., 2009). Previous studies observed that extraction of MCC can be significantly improved by pretreatment of cellulose with metal ion catalysts with higher crystallinity (Kamireddy, Degenstein, Berti, & Ji, 2013b; Li et al., 2013; Li, Zhang, Zhang, Xiu, & He, 2014).

In recent years, researchers devoted efforts to integration of chemical process and high-intensity ultrasonic treatment in the production of MCC and nanocrystalline cellulose (NCC) (Zhang et al., 2013). It can modify the morphology and microstructure of fibers and enhance their accessibility to chemical reagents (Qin, Tong, Chin, & Zhou, 2011). This paper addresses the influence of ultrasonic treatment combined with metal ion catalysts on the selective acid hydrolysis of cellulose amorphous regions. A comparative study was carried out about the crystallinity, degree of polymerization (DP) and the morphological/structural characteristics of hydrocellulose, prepared in the presence or absence of ultrasonic treatment. The effect of ultrasonic treatment time catalyzed with acid was considered on the current study. The morphological and structural characteristics of the hydrocellulose were studied using scanning electron microscopy (SEM), Fourier transform infrared spectra (FT-IR), and X-ray diffraction (XRD).

2. Experimental

2.1. Materials

Dissolved Kraft eucalyptus pulp was received from Shan Dong Pulp & Paper Co., Ltd. (China). Its brightness was 86.8%ISO, and the ash content was 0.08%. Before it was used, the pulp was dispersed in water for 24 h and then filtered out. All chemicals were of analytical grade and purchased from Beijing Chemical Reagent Co. (China).

2.2. Ultrasonic pretreatment

The ultrasonic pretreatment was carried out in Ultrasonic Generator (BILON-1200Y, Bilon Biotech Co., Ltd., Xi'an, China); all sonication runs were at 20 kHz. Other conditions were as follows: the pulp consistency 1.0%, power 300 W at room temperature and with sonication treatment in range of 10–60 min by intermittent type. The water retention value (WRV) of both ultrasonic-treated and control samples were measured according to the China Standard GB/T 29286-2012.

2.3. Preparation of hydrocellulose

After the ultrasonic pretreatment, the sample of pulp (oven dry 10 g) was placed into 150 mL water of 2.5 mol/L HCl and 0.3 mol/L $FeCl_3$. The flask was heated to 80 °C in water bath and agitated for 70 min. After that, each sample was immediately washed with deionized water until the filtrate was neutral, then centrifuged to remove the water and freeze-dried. The average fines length of hydrocellulose samples both ultrasonically treated and untreated were measured by MorFi Compat. The DP was measured by the viscosity method using diluted cellulose solutions in cupriethylene diamine.

2.4. Analytical methods

The fracture surface morphology of ultrasonically of normal cellulose and hydrocellulose with or without ultrasonic pretreatment were characterized with a HITACHI S-4800 (Hitachi, Tokyo, Japan) scanning electron microscope (SEM). The samples were freeze-dried and examined at an accelerating voltage of 3 kV. The Fourier transform infrared (FT-IR) spectra of both untreated and ultrasonic pretreated samples were determined with a Bruker V70 (Germany), using a KBr disc. The crystalline structure of samples was analyzed by X-ray diffraction (XRD) on a D/max-2200 PC automatic XRD (Rigaku Co. Ltd., Tokyo, Japan) using a Ni-filtered Cu-Kα radiation source (λ = 0.1518 nm). The X-ray diffractograms were recorded from 6° to 50° 2θ by a goniometer at a scanning speed of 2°/min. The crystallinity was calculated by the total diffracted area and the area under the crystalline peaks, which were determined by integration after correcting the data for absorption. The relative crystallinity of samples was calculated by Eq. (1),

$$C_r = F_c/(F_a + F_c) \times 100\% \quad (1)$$

Where C_r is the relative crystallinity, F_a and F_c are the mass of crystalline and amorphous regions, respectively (Sun et al., 2008). Each sample was measured at least twice.

The Scherrer equation was used to calculate crystallite thickness by using the half-width at half height of the peak assigned to (0 0 2) planes (Shakeri & Staiger, 2010)

$$L_{hkl} = K\lambda/(\beta \cos\theta) \quad (2)$$

Where L_{hkl} is the crystallite thickness, λ is the radiation wavelength, θ is the diffraction angle, and β is the full width of the diffraction peak measured at half maximum height prior to smoothing. The correction factor K, was set to 0.94.

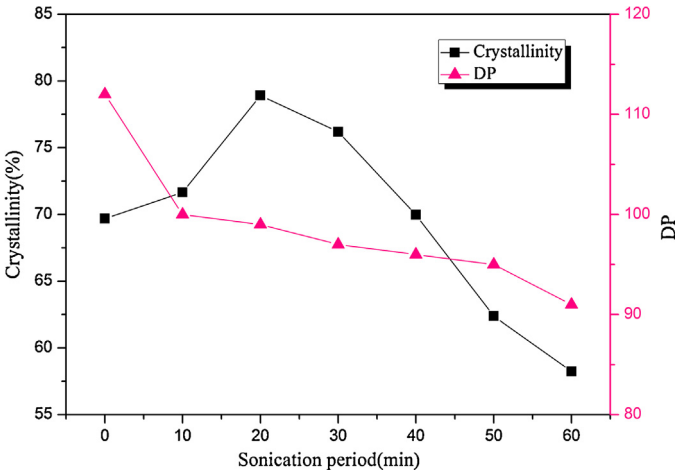

Fig. 1. Effects of different sonication period on the crystallinity and DP of hydrocellulose (other conditions: 2.5 mol/L HCl, 0.3 mol/L $FeCl_3$, 80 °C and 70 min).

3. Results and discussion

3.1. Effect of ultrasonic pretreatment on the selective acid hydrolysis of cellulose

Pulp with and without the ultrasonic pretreatment were acid hydrolyzed co-catalyzed $FeCl_3$. In order to find the optimal conditions for the ultrasonic pretreatment, the length of sonication period was investigated. From the results in Fig. 1 it could be concluded that the effect of cellulose crystallinity depended strongly on the ultrasonic time. It showed that with increasing sonication period, the crystallinity of hydrocellulose initially increased and then decreased. The maximum crystallinity of hydrocellulose was observed to be 78.9% at 20 min. The crystallinity obtained by sonication was 9.2% higher for the samples as compared to that without sonication. Thus the ultrasonic pretreatment and the metal ion catalyst had improved crystallinity by promoting the hydrolysis of amorphous region while retaining the crystalline regions. The ultrasonic treatment also influenced the DP of hydrocellulose. Studies have shown that the ultrasonic can degrade cellulose, and lead to the rupture of cellulose chain and formation of macromolecular free radicals (Yunus, Shlleh, Abdullah, & Awg

Biak, 2010). The initial DP of the dissolving pulp was 651, but the DP of hydrocellulose dropped to about 100 as the ultrasonic treatment time increased to 20 min.

It was reported that ultrasonic has the similar effects on refining. Sonication causes cavitation which leads to loosen the amorphous and defective crystalline regions of cell walls. It promotes longitudinal fibrillation, resulting in cellulose more accessible to heterogeneous catalyst for a faster hydrolysis (Li, Yue, & Liu, 2012). On the contrary, the crystalline regions were damaged slightly and retained its compact structure. The crystallinity increased until the sonication time was 20 min because a large portion of amorphous regions was hydrolyzed. However, when the sonicaton time exceed more than 20 min, significant degradation occurred even in the crystalline regions, which reduced the product crystallinity. These results indicated that ultrasonic pretreatment could enhance the selective degradation of amorphous cellulose (Liu et al., 2009). After a 20 min sonication period and hydrolysis, while the DP of remaining cellulose dropped from 112 to 99, the average fines length decreased from 49 μm to 37 μm and the crystallinity increased to 78.9%.

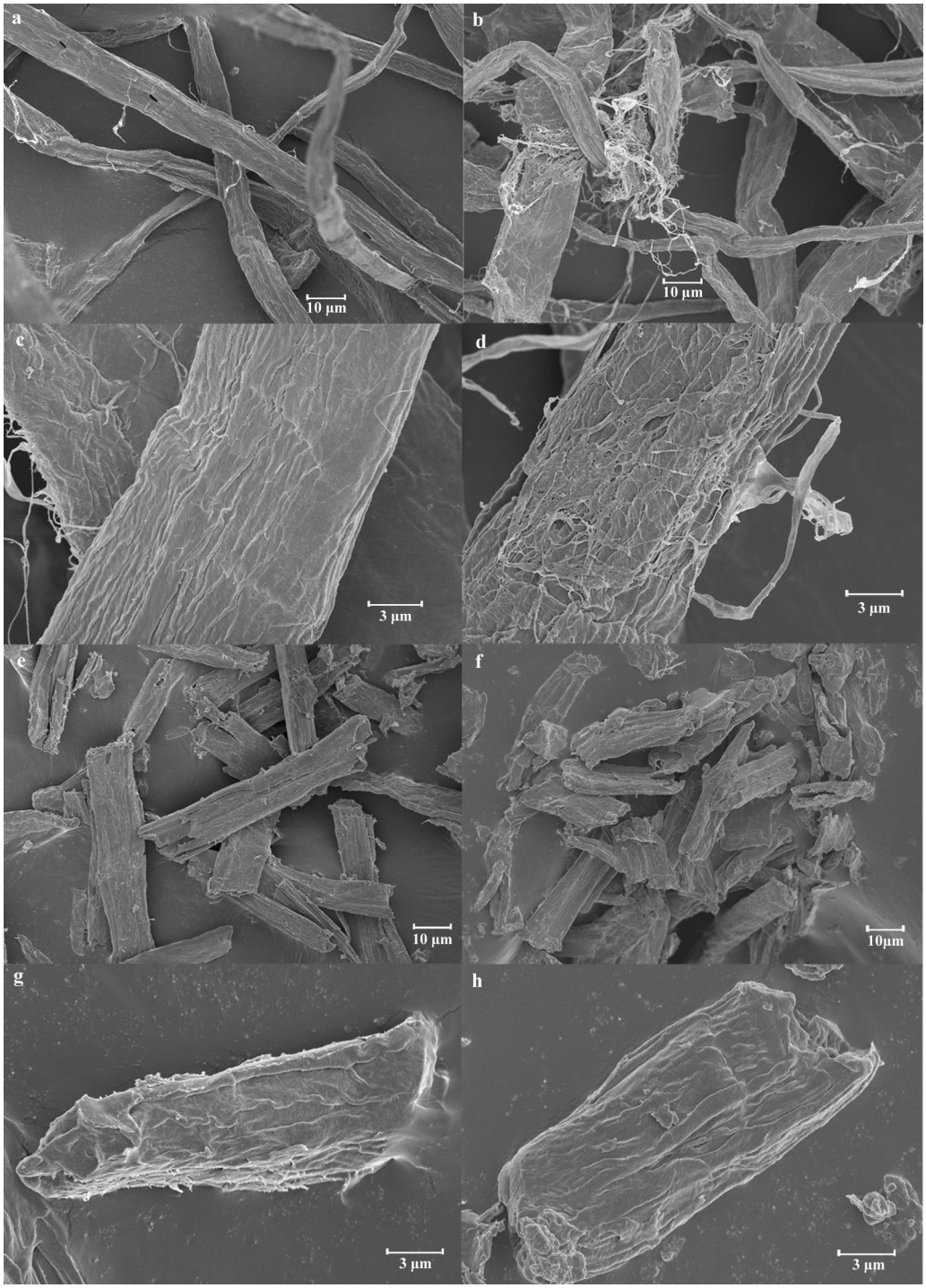

Fig. 2. SEM micrographs of the original cellulose (a, c), cellulose pretreated with ultrasonic (b, d), ultrasonically pretreated hydrocellulose (e, g), and hydrocellulose with no pretreatment (f, h).

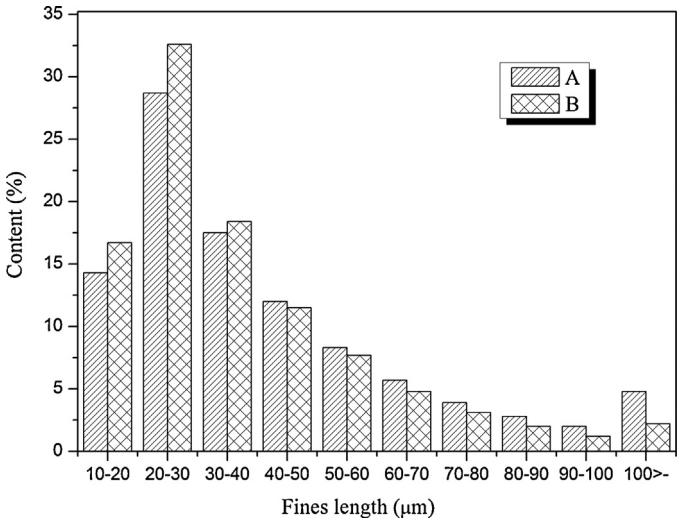

Fig. 3. Fines length distribution (A = hydrocellulose untreated, B = hydrocellulose with ultrasonic pretreated).

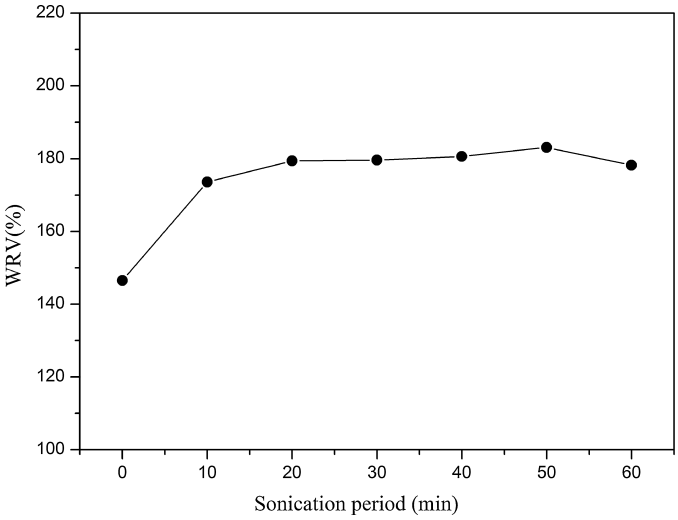

Fig. 4. The WRV of cellulose after various sonication periods.

3.2. Morphological observation

The morphology and microstructure of normal cellulose/hydrocellulose before and after the ultrasonic treatment have been characterized by MorFi Compact and SEM observation. The freeze-dried samples had a better revolution than the samples dried at room temperature. As seen from the figure (Fig. 2a and c), fibers of the original cellulose had a regular, compact and smooth surface. After the ultrasonic treatment, significant difference appeared on the fiber surface. Some erosion and large number of cracks on the surface of the fiber became apparent (Fig. 2b and d). The ultrasonic treatment increased fiber porosity, permeability, and its specific surface area. It means that acids can diffuse into the amorphous regions and some defective area of crystalline regions. The increased number of hydroxyl and Fe^{3+} ions diffused into the surface of cellulose associated with more hydrogen bonds. Then, the intermolecular hydrogen and intramolecular glycosidic fractured along with the chemical degradation of cellulose. Tang, Yang, Zhang, and Zhang (2014) reported that the asymmetric cavitation in the interface of fiber–water when treated by ultrasonic treatment can lead to the collapse of cavitation bubble. The high speed micro-jet generated by the cavitation bubble collapse will result in peeling off and erosion of the surface of fiber, increasing its surface area (Wang, Fang, & Hu, 2007; Zhou, Huang, & Wang, 2008). Such ultrasonic agitation will affect the less dense amorphous regions of cellulose more than the compact crystalline regions.

Fig. 2e and g presents SEM images of cellulose samples were either ultrasonic pretreated for 20 min or not. Fig. 2f and h were not ultrasonically treated but hydrolyzed with HCl–$FeCl_3$ catalyst. The hydrocellulose samples obtained under both conditions had rod-like structure, which might indicate the acid hydrolysis of cellulose proceeded faster in the radial direction than in axial direction. Furthermore, cellulose hydrolysis assisted by ultrasonic pretreatment resulted in a narrower distribution in the average fines length of hydrocellulose as compared with hydrocellulose obtained without the ultrasonic pretreatment (Fig. 3). The fines difference observed for pulp pretreated with ultrasonication was around 49 μm and for pulp not pretreated ultrasonically was 37 μm. It is clear that the morphology and the microstructure of cellulose fibers have changed during the ultrasonic treatment, and the changes in microstructure might have increased the permeability of ultrasonic treated fibers to the acid solution.

The WRV, which depends on the aggregation structure of cellulose, the size and distribution of its pores, can reflect the ease of acid penetration into cellulose fibers (Guo, Wang, Huang, Wan, & Ma, 2011). After ultrasonic treatment, the WRV of cellulose fibers increased (Fig. 4). The value of WRV increased rapidly during the first 10 min of sonication and then decreased. This might indicate that most of the damage to the amorphous regions of cellulose has been accomplished in the first 10 min.

3.3. X-ray diffraction

The XRD diffractogram were carried out to investigate the crystallinity of the hydrocellulose for all the samples. The diffractogram for all samples presented in Fig. 5 have peaks at $2\theta = 22.23–22.72^{\circ}$, which represent a cellulose-I structure. The strong reduction, or absence, of peaks corresponding to planes (1 0 1), (0 0 2) and (0 0 4) indicate the two phase coexistence for the hydrocellulose. The crystallinity index C_r of hydrocellulose was calculated from Eq. (1), the crystallite thickness was calculated according to Eq. (2) (Luduena, Fasce, Alvarez, & Stefani, 2011). The crystallite thickness in the (0 0 2) direction (perpendicular to the fiber axis) was also determined. As shown in Table 1, the crystallinity of signified hydrocellulose was 78.9% and the crystallite thickness was 5.26 nm. These results indicated that ultrasonic cavitation damaged the amorphous regions and the surface of crystalline regions, leading to accelerate in hydrolysis of those areas. Therefore, it can

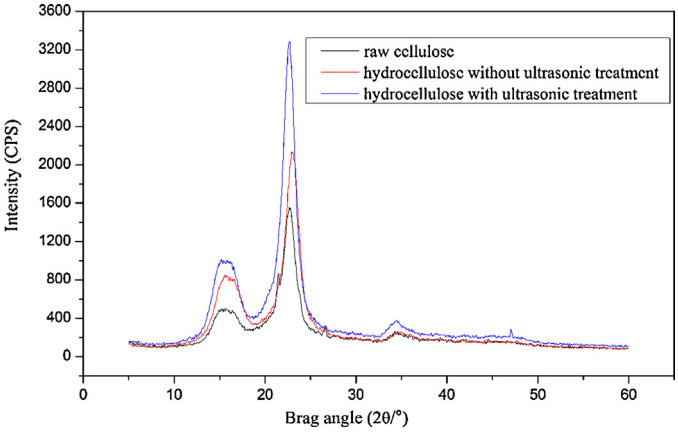

Fig. 5. X-ray diffractograms of different samples.

Table 1
Results of XRD for samples.

Sample	2θ (002)	β (002)	L_{hkl} (nm)	C_r (%)
Cellulose	22.718	1.726	4.90	58.8
Hydrocellulose	22.231	1.691	5.01	69.7
Hydrocellulose with ultrasonic treatment	22.669	1.609	5.26	78.9

be concluded that the ultrasonic pretreatment could improve the selectivity of acid hydrolysis.

The similarity of diffractograms obtained from the original cellulose and hydrocellulose pretreated with and without sonication indicated that neither the chemical nor ultrasonic treatment altered the main crystallite structure of cellulose. These results demonstrated that ultrasonic pretreatment can increase the crystallinity of hydrocellulose. The possibility explanation may be likely that ultrasonic accelerates cellulose hydrolysis by creating localized erosion on the solid surface, thus increasing the reaction area, and improving the accessibility of the reagents to the amorphous regions of cellulose.

3.4. FT-TR analysis

FT-IR study was conducted to determine the functional groups present in the hydrocellulose (Fig. 6). The FTIR spectra of ultrasonically pretreated hydrocellulose were similar to those of the untreated hydrocellulose and the original cellulose. The broad absorption band at 3342 cm^{-1} is associated with H-bonded OH groups. The peak detected at 2921 cm^{-1} indicates a symmetric C—H stretching vibration, and the absorption at 1645 cm^{-1} in all samples indicates the absorption of water. The peak around 1378 cm^{-1} could be attributed to C—H bending vibrations in cellulose, while the peak near 1165 cm^{-1} signifies glycosidic linkages and shows C—O, C—O—C, stretching vibration (Kumar, Negi, & Upadhyaya, 2010). Overall, although there was a slight change in the intensity of some peaks, the ultrasonic pretreated and untreated hydrocellulose essentially showed the same spectra as the original cellulose. No obvious difference could be found in the FT-IR spectra. All of the above showed that the acid hydrolysis with or without ultrasonic pretreatment did not affect the chemical structure of cellulosic fragments, and this conclusion is corroborated also by the XRD results.

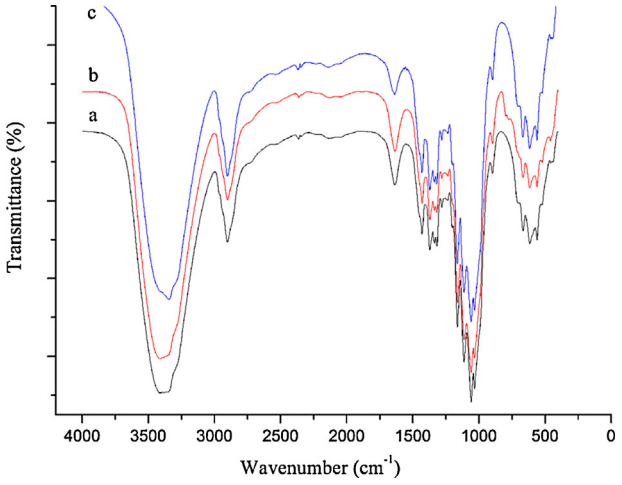

Fig. 6. FTIR spectra of the original cellulose (a), hydrocellulose after ultrasonic treatment (b) and untreated hydrocellulose (c).

4. Conclusions

In $FeCl_3$–HCl system, the ultrasonic pretreatment and metal ion catalysis acted synergistically in promoting hydrolysis of amorphous regions and retaining crystalline regions. The SEM showed that grooves, ridges and a few cracks appeared on the surface of cellulose after ultrasonic pretreatment. This fiber damage might improve the accessibility of hydroxyl and Fe^{3+} to diffuse more easily into amorphous regions of cellulose, accelerate heterogeneous reactions and improve the selective acid hydrolysis of cellulose. The ultrasonic treatment using 300 W and for 20 min increased the crystallite thickness, and the crystallinity of the product was 9.2% higher as compared with hydrocellulose obtained from pulp without ultrasonic pretreatment. In addition, the average fines length was decreased by 12 μm for ultrasonically pretreated pulp. XRD studies showed that the crystalline structure of the original cellulose was not transformed by the ultrasonic treatment. The FT-IR results demonstrated that the chemical structure of cellulose did not be changed by the ultrasonic pretreatment.

Acknowledgments

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