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Rapid Dissolution of Cellulose in Ionic Liquid with Different Methods

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1. Introduction

Cellulose, the most widespread natural polymers, can be used as a green source for fabricating biodegradable and biocompatible materials with attractive properties by chemical modification or mixing with other components (Potthast et al., 2006). Effective utilization of cellulose not only mitigates the fossil resources crisis but also protects the environment of the Earth. However, cellulose is extraordinarily difficult to be dissolved due to its considerable hydrogen bonds and partially crystalline structure.

Ionic liquids (ILs), also known as room temperature ionic liquids (RTILs), are organic salts comprised completely of ions. They are regarded as novel green solvents and have attracted tremendous attentions in analysis chemistry, electric chemistry, catalysis chemistry and organic synthesis (Forsyth et al., 2002; Turner et al., 2003) because of their unique physico-chemical properties, such as chemical and thermal stability, non-flammability and immeasurably low vapor pressure (Feng & Chen, 2008; Cao et al., 2009). Furthermore, it is feasible to modify the physicochemical properties such as viscosity, melting point, polarity and solubility of the ILs through changing the structure of cations and anions (Hermanutz et al., 2008). Recently, ILs were applied in the field of biomass research, such as dissolution and the following homogeneous modification of cellulose (Forsyth et al., 2002; Cao et al., 2010). Swatloski and his group (Swatloski et al., 2002) reported the pioneer study on the dissolving capability of a series of ILs containing 1-butyl-3-methylimidazolium ([C$_4$mim]$^+$) as cation for cellulose. Among this kind of ILs, 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl) exhibited the best solubility, which could dissolve up to 10 wt % of pulp cellulose with a degree of polymerization of (DP) of 1000 at 100 ^{o}C. Soon after, 1-allyl-3-methylimidazolium chloride ([Amim]Cl) was synthesized and found to be a powerful solvent of cellulose (Zhang et al., 2005). Cotton cellulose could be dissolved in [Amim]Cl within 120 min at 110 ^{o}C. Heinze and his co-workers (Heinze et al., 2005) tested the solubility of [C$_4$mim]Cl for cellulose and the results showed that [C$_4$mim]Cl could dissolved cotton linter (DP=1198) with the concentration of 10 wt%, though a relatively long time (12 h) was required.

In view of long treatment duration, some pretreatment or auxilary methods should be introduced to reduce the dissolution time of cellulose in ILs. Ultrasonic and microwave are the most popular activation methods or "unconventional" physical agents in the concept of "Green Chemistry" (Kardos & Luche, 2001). Ultrasonic treatment has been well established in the separation of plant materials, particularly for extraction of low molecular weight substances (Tang et al., 2005; Gadhe et al., 2006). The mechanical and chemical effects of ultrasound are believed to accelerate the extraction of organic compounds from plant materials due to disruption of cell walls and to enhance mass transfer in cell walls. Microwave heating, as an alternative to conventional heating technique, has been successfully applied in organic synthesis and carbohydrate degradation (Satge et al., 2002; Ma et al., 2009; Ramier et al., 2012) due to its thermal effects and non-thermal effects, raised from the heating rate, acceleration of ions and molecules collision, and rapid rotation of dipoles. In addition, microwave energy can easily penetrate to particle inside hence all particles can be heated simultaneously, which resolve the heat transfer resistance problem and make it more uniform and efficient than conventional heating methods (Hou et al., 2008). Consequently, it is reasonable to assume that cellulose could be rapidly dissolved in ILs using ultrasonic and microwave as pretreatment or auxilary methods to active cellulose structure. Actually Mikkola et al (Mikkola et al., 2007) and Swatloski et al (Swatloski et al., 2002) have already mentioned that ultrasonic and microwave irradiation can significantly accelerate dissolution of cellulose in ILs. Besides ultrasonic and microwave, ethanol treatment and mechanical milling were also believed to enhance cellulose dissolution rate in ILs. Mechanical milling was one of the most common mechanical pretreatment methods which can cut down the particle size and reduce molecular weight. Previous studies (Evtuguin et al., 2001; Fujimoto et al., 2005) have already applied mechanical milling to break lignocellulose structure in order to dissolve lignin from biomass matrix with organic solvents. Ethanol treatment was a new kind of pretreatment method to increase cellulose dissolution rate in our lab because it was considered to be capable of preventing cornification of cellulose fiber.

In this article, different pretreatment methods were applied to accelerate dissolution of cellulose in ILs, including mechanical milling, ethanol treatment, ultrasonic irradiation and microwave irradiation. Moreover, the effects of different pretreatment conditions on dissolution rate were also investigated, for example, the ethanol treatment time, mechanical milling time, ultrasonic and microwave irradiation power and duration. In addition, ultrasonic and microwave irradiation were also applied during the dissolution process of cellulose samples. We also investigated the influence of various reaction conditions on acceleration of cellulose dissolution and physicochemical properties of regenerated cellulose, such as degree of polymerization (DP) and crystallinity.

2. Experimental

2.1. Materials

Sugarcane bagasse, obtained from a local sugar factory (Guangzhou, China), was first dried in sunlight and then cut into small pieces. The cut SCB was ground and screened to prepare

40-60 mesh size particles. The ground SCB was dried again in a cabinet oven with air circulation for 16 h at 50 ºC.

1-Butyl-3-methylimidazolium chloride ([C₄mim]Cl) was provided by the Chemer Chemical Co., Ltd., Hangzhou, China, and used as received. All of other chemicals used were of analytical grade and obtained from Guangzhou Chemical Reagent Factory, China.

2.2. Isolation of cellulose from bagasse

The dried SCB powder was first dewaxed with toluene-ethanol (2:1 v/v) in a Soxhlet apparatus for 6 h. The dewaxed SCB was treated with distilled water (800 mL) for 2 h at 80 ºC. Further the insoluble residue was delignified with sodium chlorite at pH 3.8-4.0, adjusted by 10% acetic acid, at 75 ºC for 2 h. After filtration, the residue was sequentially washed with distilled water and 95% ethanol, and then dried in a cabinet oven at 50 ºC overnight. Finally the holocellulose obtained was extracted with 10% KOH (600 mL) at 20 ºC for 10 h to release the hemicelluloses. The residue was collected by filtration and washed thoroughly with distilled water until the filtrate was neutral, then dried in an oven at 50 ºC for 16 h.

2.3. Pretreatment of cellulose

2.3.1. Mechanical ball milling

Dry cellulose samples were subjected to ball milling for 6, 12, 18, and 24 h, respectively, on PM 0.4L planet ball mill machine (PM 0.4L Nanjing Chishun Science & Technology Co., Ltd, China). Ball milled samples were dried in an oven at 50 ºC for 6 h.

2.3.2. Ethanol treatment

Residue collected from alkali treatment of holocellulose was washed with distilled water and 95% ethanol and then dispersed in 95% ethanol and subjected to mechanical agitation for 4, 6, 8, and 10 h, respectively, to make cellulose adsorb sufficient ethanol. Then the sample was filtrated by Buchner funnel and dried in cabinet oven with air circulation for 8 h at 55 ºC

2.3.3. Ultrasonic irradiation

10 g of cellulose sample was suspended in 95% ethanol solvent with mechanical agitation. It was irradiated with ultrasound at the power of 30W, 50W, and 70W for 10, 20, 30 and 40 min, respectively, at room temperature (25 ºC). Ultrasonic treated samples were filtrated and dried in oven for 8 h at 55 ºC.

2.3.4. Microwave irradiation

10 g of cellulose sample was suspended in 95% ethanol solvent with mechanical agitation and then subjected to microwave oven (XH-100B, Beijing Xianghu Technology Development

Co., Ltd., China) for 200, 400, 600 W microwave irradiation with 20, 30, 40 min at room temperature and 50 ºC, respectively. Microwave treated samples were filtrated and dried in oven for 8 h at 55 ºC.

2.4. Dissolution and regeneration of cellulose

2.4.1. Dissolution of cellulose without auxilary method

Cellulose or pretreated cellulose sample was added into a flask containing [C₄mim]Cl with a weight ratio of 2% (cellulose to [C₄mim]Cl). The mixture of cellulose/[C₄mim]Cl was stirred continuously in an oil bath at 110 ºC with N₂ atmosphere to form clear solution.

2.4.2. Dissolution of cellulose with ultrasonic assisted

2% dried cellulose sample with ethanol pretreatment was added into a flask with [C₄mim]Cl at 110 ºC. N₂ was purged continuously and the mixture was stirred. Then the mixture was irradiated at 110 ºC for 5, 10, 15, and 20 min, respectively, with ultrasound provided with a horn at sonic power of 20, 30, 40, 50, 60 and 75 W, respectively. After ultrasound irradiation, the mixture was stirred at 110 ºC until cellulose was completely dissolved.

2.4.3. Dissolution of cellulose with microwave irradiation

Molten [C₄mim]Cl was mixed with cellulose sample with ethanol pretreatment (2 wt%) in a three-neck flask. The flask was positioned in the microwave reactor (XH-100B) and heated by the microwave irradiation of 300W, 400W, 500W, 600W, and 700W, respectively, to a specific temperature of 85 ºC, 90 ºC, 95 ºC, 100 ºC, 105 ºC, 110 ºC, and 115 ºC, respectively, and stirred until a clear cellulose/IL solution was formed. The temperature was real-time monitored by a sensor directly contacted with the reaction medium. When a required temperature was reached it was maintained by impulse microwave irradiation at low heating power. The accuracy of temperature was ±0.2 ºC for measurement and ±1ºC for controlment.

2.4.4. Regeneration of cellulose

After complete dissolution, the cellulose/IL mixture was slowly poured into 250 mL ethanol with vigorous agitation. The precipitate was collected by filtration and washed thoroughly with ethanol to eliminate [C₄mim]Cl, and then freezen-dried for 24 h. The yield was determined from the regenerated cellulose on the basis of initial freezen-dried measurements. To reduce errors and confirm the results, all experiments were performed at least in duplicate, and the yield represents the average value.

2.5. Characterization of the native, pretreated and regenerated cellulose

2.5.1. Degree of polymerization

The cupriethylene-diamine method (British standard) was used for determining the limiting viscosity number [η] and DP of native, pretreated, and regenerated cellulose. The viscosity

DP was calculated from the following equation, $DP^{0.90} = 1.65$ [η]. Molecular weight (Mw) of cellulose was then calculated from DP by multiplied by 162, the Mw of an AGU.

2.5.2. Fourier transform infrared

The FT-IR spectra of the native and regenerated cellulose were obtained on an FT-IR spectrophotometer (Nicolet 510) using a KBr disc containing 1% finely ground samples. Thirty-two scans were taken for each sample in the range 4000~400 cm^{-1} with a resolution of 2 cm^{-1} in the transmittance mode.

2.5.3. Wide angle X-ray diffraction

The XRD spectra were recorded at room temperature with a Rigaku D/MAX-IIIA X-ray diffractometer (Japan) in the scattering angle range from 5° to 45° with 8°/min scanning speed and a 2θ step interval of 0.02°. Cellulose samples were cut into small pieces and laid on the glass sample holder, analyzed under plateau conditions. Ni-filtered Cu Kα1 radiation (λ=0.154 nm) generated at a operating voltage of 40 kV and current of 30 mA was utilized.

2.5.4. Solid-state CP/MAS ^{13}C Nuclear Magnetic Resonance

The solid-state CP/MAS ^{13}C NMR spectra were measured on a Bruker DRX-400 spectrometer with 5mm MAS BBO probe at the frequency of 100 MHz employing both Cross Polarization and Magic Angle Spinning and each experiment was recorded at ambient temperature. Acquisition time was 0.034 s, the delay time 2 s, and the proton 90° pulse time 4.85 μs. Each spectrum was obtained with an accumulation of 5000 scans.

2.5.5. Thermogravimetric analysis

Thermal analysis of the native and regenerated cellulose was performed on thermogravimetric analysis (TGA) on a thermal analyzer (SDT Q500, TA Instrument). The sample weighed between 7 and 11 mg and the scans were run from room temperature to 600 °C at a rate of 10 °C/min under nitrogen flow.

3. Results and discussion

3.1. Dissolution and regeneration of cellulose with different pretreatment methods

It took quite long to completely dissolve cellulose in ILs because of the high crystallinity and tremendous hydrogen bonding in cellulose. When cellulose dissolved in ILs its crystalline structure was totally destroyed thus no bright eyeshot, which represented the crystalline structure of cellulose, could be found under polarizing microscope. Consequently, in this study we employed polarizing microscope to monitor the dissolution process and defined that dissolution of cellulose was completed when polarizing microscope was in black eyeshot. Ethanol treatment, mechanical milling, ultrasonic irradiation and microwave

irradiation were applied to pretreat cellulose for enhancement of cellulose dissolution in ILs, and the results are showed in Table 1.

No.	Pretreatment Condition				Dissolution Time	Yield
	Pretreatment	Power	Duration	Temperature		
1	-	-	-	-	11.1 h	1.18
2	Mechanical milling	-	6 h	25 °C	8.9 h	0.95
3	Mechanical milling	-	12 h	25 °C	7.6 h	0.94
4	Mechanical milling	-	18 h	25 °C	6.8 h	0.95
5	Mechanical milling	-	24 h	25 °C	6.4 h	0.94
6	Ethanol treated	-	4 h	25 °C	4.5 h	1.04
7	Ethanol treated	-	6 h	25 °C	3.8 h	1.06
8	Ethanol treated	-	8 h	25 °C	3.1 h	1.05
9	Ethanol treated	-	10 h	25 °C	2.6 h	1.06
10	Ultrasonic irradiation	30 W	20 min	25 °C	2.2 h	1.05
11	Ultrasonic irradiation	30 W	30 min	25 °C	1.5 h	1.06
12	Ultrasonic irradiation	30 W	40 min	25 °C	0.9 h	1.04
13	Ultrasonic irradiation	75 W	20 min	25 °C	1.4 h	1.02
14	Ultrasonic irradiation	75 W	40 min	25 °C	0.8 h	1.01
15	Microwave irradiation	200 W	30 min	25 °C	2.6 h	1.06
16	Microwave irradiation	400 W	30 min	25 °C	2.4 h	1.02
17	Microwave irradiation	600 W	30 min	25 °C	1.6 h	1.04
18	Microwave irradiation	200 W	20 min	50 °C	1.3 h	1.03
19	Microwave irradiation	600 W	20 min	50 °C	0.9 h	0.98

Table 1. Dissolution of cellulose in [C4mim]Cl pretreated with different methods.

Yield of regenerated cellulose was approximately between 94%~118%. On one hand, cellulose would probably absorb inorganic salt, such as impurity of IL, during dissolution process. In this case yield would increase or even beyond 100%. On the other hand, cellulose was also likely to be degraded and produced oligosaccharide or even monosaccharide which could hardly be recovered. In addition, washing step and filtration process also contributed to the losses. According to the yield of regenerated cellulose, it was reasonable to deduce that cellulose did not degraded significantly during dissolution process in ILs at 110 °C. However, yields of mechanical milling samples were relatively lower, because mechanical milling was able to degrade cellulose molecular and break the macromolecules into small fragments. In the following dissolution and regeneration process cellulose molecules were further destroyed and fragments with relatively lower molecular weights

were produced which cannot be precipitated and recovered. The same results were also discovered for samples pretreated with relatively high power of microwave.
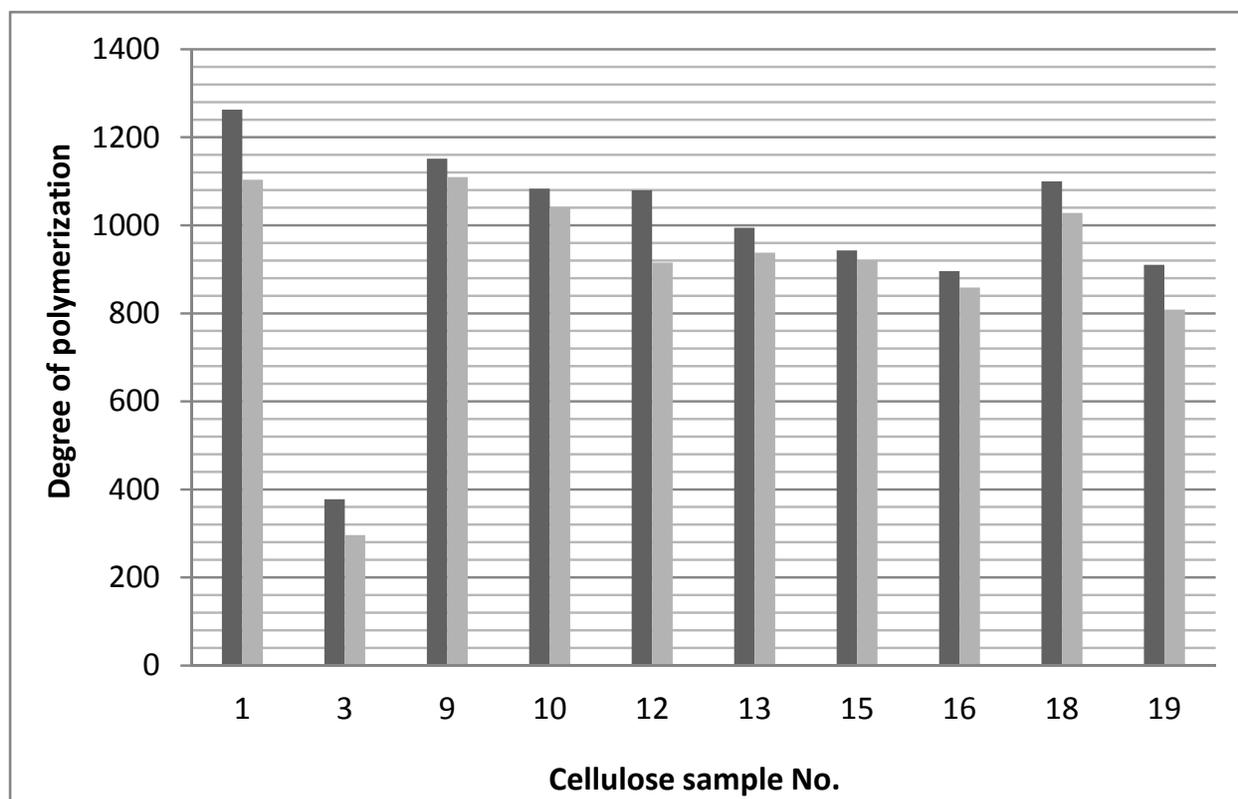

Figure 1. Degree of polymerization of pretreated and regenerated cellulose. Sample No. is in accordance with Table 1. Left bar is DP of pretreated sample, right bar is DP of regenerated sample.

[C4mim]Cl was one of the most widely studied ILs for cellulose dissolution, but it took 11.1 h to totally dissolve unpretreated cellulose sample at 110 °C, which significantly limited the large-scale utilization of ILs in biomass. Commercial application would be promising if the dissolution of cellulose was improved. As shown in Table 1, dissolution time decreased from 11.1 h to about 6.4~8.9 h when cellulose were subjected to mechanical milling for 6, 12, 18, and 24 h (samples 2~5), indicating the great effect of particle size on cellulose dissolution. However, the fine cellulose sample after mechanical milling would be easily agglomerated during mixing cellulose in [C4mim]Cl because of its high viscosity. Outside of agglomerates were swollen cellulose macromolecules and inside was dry sample. This kind of particles would seriously prolong the dissolution time and make it difficult to operate during dissolution process. Ethanol pretreated cellulose (samples 6~9) could be dissolved in [C4mim]Cl at 110 °C within 2.6~4.5 h. During ethanol pretreatment, free water and bound water in cellulose could be replaced by ethanol, which was able to evaporate more quickly during drying, therefore inhibiting high moisture sample become cornification. Cellulose samples after ethanol pretreatment were loosen and porous, which enabled it to open the structure and enlarge superficial area, facilitating penetration of ILs into cellulose. So ethanol pretreatment was one of the effective and feasible methods to improve cellulose dissolution. In addition, dissolution time would be further reduced when ethanol pretreated

samples were subjected to ultrasonic and microwave irradiation. It needed only 2.2 h at 110 ℃ in [C₄mim]Cl to entirely dissolve 2% cellulose pretreated with 30 W ultrasound for 20 min. When the power increased to 75 W, the sample dissolution time was reduced to 0.9 h. Further prolonging irradiation time to 40 min also decreased dissolution time to 0.8 h. The cellulose samples pretreated with microwave irradiation exhibited the similar results. It should be noted that cellulose irradiated with high microwave power at high temperature was more likely to be degraded.

Fig. 1 shows the DP of pretreated and regenerated cellulose. DP of cellulose samples after ethanol treatment, mechanical milling, ultrasonic irradiation and microwave irradiation were obviously lower than the DP of native cellulose. For ultrasonic and microwave pretreatment, enhancement of power and irradiation time further decreased the DP of cellulose, even though the decrement was marginal. For example, DP was reduced from 1083 to 994 when ultrasonic power rose from 30 W to 75 W. In addition, mechanical milling for 12 h significantly brings down DP from 1263 to 378, demonstrating the serious degradation of cellulose during mechanical milling. Moreover, DP of all the samples declined slightly after dissolution in [C₄mim]Cl at 110 ℃ and regeneration, indicating that cellulose molecules were broken into relatively low molecular fragments.

3.2. Dissolution and regeneration of cellulose assisted with ultrasonic

To further study the influence of ultrasonic irradiation on cellulose dissolution in ILs, we tried to apply ultrasonic irradiation directly during the dissolution process as not a pretreatment but an auxilary method. Results showed that it was more effective to utilize ultrasonic in dissolution process than in pretreatment, as listed in Table 2. Cellulose could be dissolved in [C₄mim]Cl within 1 h when irradiated by 30W ultrasonic for 20 min. With the same irradiation power and duration, it required 2.2 h to entirely dissolve sample when the ultrasonic was employed as pretreatment method. Enhancement of cellulose dissolution with ultrasonic was probably because ultrasound irradiation provided a greater penetration of ionic liquid into cellulose and improved mass transfer. When the dissolving system was irradiated with ultrasound, the extreme condition was probably obtained. It was said that transient temperature of at least 5000 K and pressure up to 1200 bar could be achieved, accompanied by vigorously physical agitation and shock (Kardos & Luche, 2001; Adewuyi, 2001). All of the abovementioned effects provided excellent conditions for cellulose dissolution in IL. This beneficial effect of ultrasound techniques has also been reported in isolation of cell wall polymers (Aliyu & Hepher, 2000). Cellulose dissolution time decreased from 147 (sample 24) to 120 (sample 20), 110 (sample 25) and 100 min (sample 26) with the improvement of ultrasonic power from 20 to 30, 40 and 50 W. However, further improvement of ultrasonic power (samples 26–28) did not result in the decrement in cellulose dissolution time. It seems that increase of power within small range was not as efficient as extension of duration. Compared with sample 3 obtained with one-step ultrasound irradiation, sample 11 with two-step irradiation with 5 min interval needed the same time to totally dissolve sample as well, indicating that the same ultrasound energy obtained from same power and total irradiation duration did not result in different effect on cellulose dissolution.

No.	Irradiation condition		Dissolution Time/min	Yield /%	DP
	Power /W	Duration /min[a]			
20	30	5	150	102.70	799
21	30	10	120	100.32	800
22	30	15	100	101.34	744
23	30	20	60	100.77	682
24	20	10	147	97.86	946
25	40	10	110	99.11	962
26	50	10	100	97.29	1022
27	60	10	100	101.29	-
28	75	10	99	105.19	1019
29	30	10	120	103.63	-

[a] Samples 20-28 were obtained with one-step ultrasound irradiation, while sample 29 was irradiated for 5 min, stirred for 5 min in interval, and then irradiated for another 5 min.

Table 2. Dissolution and regeneration of cellulose in [C4mim]Cl assisted with ultrasound irradiation

No.	Microwave irradiation condition		Dissolution time/min	Yield/%
	Maximum power/W	Temperature/°C		
30	300	90	50	93.30
31	400	90	20	86.05
32	500	90	17	88.11
33	600	90	13	87.42
34	400	85	37	87.38
35	400	95	14	-
36	400	100	12.5	-
37	400	105	10.5	-
38	400	115	8.5	-

Table 3. Dissolution and regeneration of cellulose in [C4mim]Cl assisted with microwave irradiation

DP of native and regenerated cellulose is also listed in Table 2. After dissolution and regeneration, DP decreased from 1263 for native cellulose to 1103 for regenerated cellulose sample obtained without ultrasound irradiation. Ultrasound irradiation for 5, 10, 15, and 20 min led to a slight reduction of DP to 799, 800, 744 and 682, respectively. Therefore, direct utilization of ultrasonic in cellulose dissolution degraded cellulose molecular more significantly than using it as pretreatment method. However, the increase of ultrasound power from 20 to 40, 50, and 75 W resulted in an improvement of DP from 946 to 962, 1022, and 1019. The reason for this improvement is not clear and perhaps due to the reassociation and polymerisation of the radicals formed at higher ultrasound power.

3.3. Dissolution and regeneration of cellulose assisted with microwave

Microwave was also applied as a heating method instead of pretreatment to improve cellulose dissolution. Table 3 shows the results of cellulose dissolution and regeneration

under microwave heating with different power and temperature. Obviously, cellulose dissolved in [C4mim]Cl far more quickly with microwave heating than with traditional heating, like in oil bath. Cellulose could be dissolved in [C4mim]Cl within 50 min at 90 °C under 300 W microwave heating. Dissolution rate would further increase with the increment of microwave power and reaction temperature. Heating with 400W microwave at 115 °C, ethanol treated sample was completely dissolved in only 8.5 min. It should be noted that, however, the yield of regenerated cellulose were about 86~94%, lower than that heating in oil bath. The low yield suggested that degradation of cellulose was more severe under microwave heating than in oil bath.

3.4. FT-IR spectra

FI-IR characterization was employed to measure the changes of the structure of regenerated cellulose samples obtained after pretreatment and dissolution in [C4mim]Cl assisted with or without ultrasonic and microwave irradiation. Fig. 2 illustrates FT-IR spectra of native cellulose (spectrum 1) and regenerated cellulose sample 17 (spectrum 2, pretreated with 600 W microwave irradiation for 20 min at 25 °C). In these two spectra, the absorbances at 3416, 2916, 1638, 1417, 1323, 1161, 1046, and 895 cm^{-1} are associated with native cellulose (Oh et al., 2005; Liu et al., 2006). Bands in the two spectra were rather similar and no new band was displayed in spectrum of regenerated cellulose, indicating that the structure of both samples are similar and [C4mim]Cl is direct solvent for cellulose. However, there were still slightly differences in the bands in the spectra of samples dissolved with ultrasonic irradiation and microwave heating (Figures not showed). The absorption from O-H stretching moved to higher wavenumbers from 3407 cm^{-1} to 3423 cm^{-1} after regeneration, indicating the broken hydrogen bonds in cellulose. In addition, the peak for CH$_2$ bending shifted to a lower frequency from 1431 cm^{-1} to 1419 cm^{-1}, which was a hint for the splitting of hydrogen bonds in C$_6$-OH (Zhang et al., 2005).

The value of N_O'KI index, proposed by Nelson and O'connor, represents the relative changes of cellulose crystallinity. It can be calculated using the formula N_O'KI =a_{1372}/a_{2900} (Liu & Sun, 2010), in which a_{1372} and a_{2900} are the absorbance intensities of the bands at 1372 and 2900 cm^{-1} for O–H bending and C–H stretching, respectively, in FT-IR spectra of cellulose. In present study, N_O'KI of regenerated cellulose was calculated from FT-IR by the ratio of two absorbances at 2900 cm^{-1} and 1372 cm^{-1}, and the results are listed in Table 2. As seen in Table 2, N_O'KI of regenerated cellulose from ultrasonic dissolution sample increased from 0.930 to 0.963 and 1.084 when the irradiation time increase from 0 to 5 and 10 min. However, it was reduced to 0.975, 0.966 as prolonging the irradiation duration to 15 and 20 min. The N_O'KI of regenerated cellulose changed irregularly with the enhancement of ultrasonic power, and the reason need to be further studied. On the other hand, N_O'KI of regenerated cellulose from microwave heating samples rose with the enhancement of heating power and increase of temperature. It was probably because that cellulose samples with lower molecular fragments were more likely to recrystallize during regeneration. In addition, N_O'KI of the regenerated cellulose from mechanical milling samples dissolved in different temperature (110, 120, 130, and 140 °C) were also measured. Results demonstrated

that the crystallinity increase with the enhancement of temperature, similar to that of microwave heating samples.
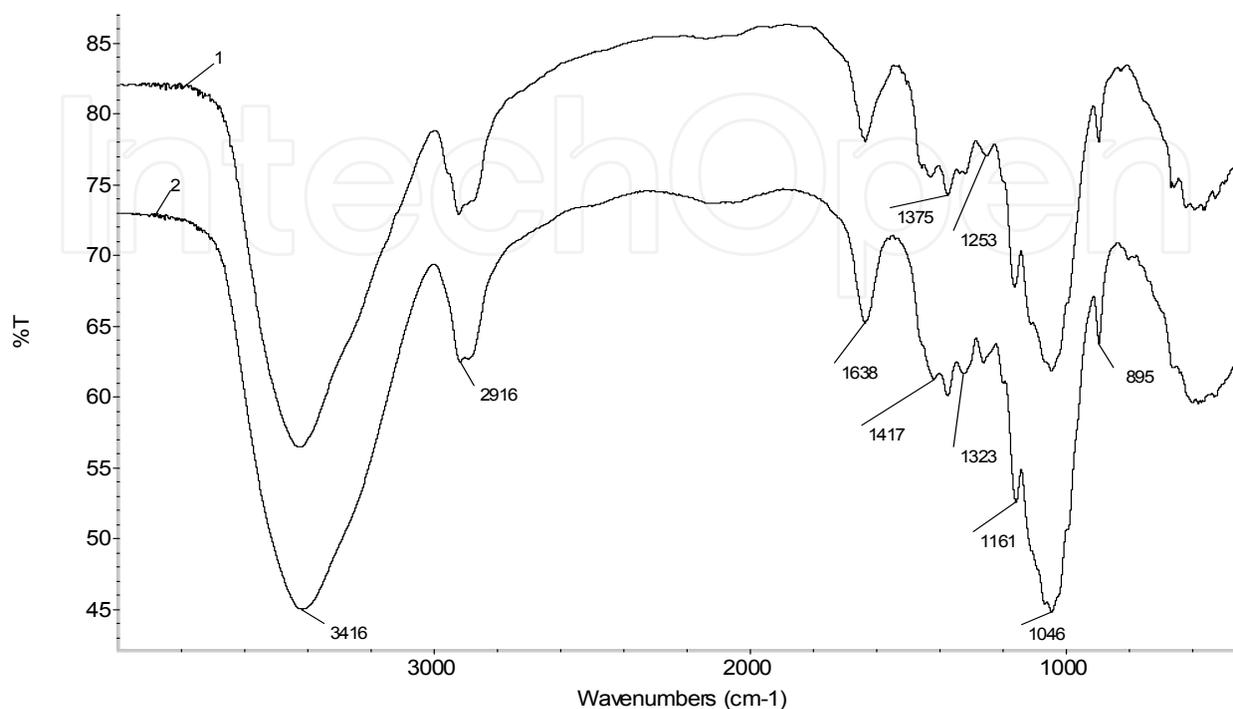

Figure 2. FT-IR spectra of native cellulose (spectrum 1) and regenerated cellulose sample 17 (spectrum 2).

No.	Treatment condition	a_{2900} (C-H)	a_{1372} (O-H)	N_O'KI
9	ultrasonic 0 W, 0 min	0.271	0.252	0.930
20	ultrasonic 30 W, 5 min	0.271	0.252	0.963
21	ultrasonic 30 W, 10 min	0.190	0.183	1.084
22	ultrasonic 30 W, 15 min	0.154	0.167	0.974
23	ultrasonic 30 W, 20 min	0.151	0.147	0.966
30	microwave 300W, 90 °C	0.188	0.191	1.016
31	microwave 400W, 90 °C	0.229	0.240	1.048
33	microwave 600W, 90 °C	0.196	0.217	1.107
34	microwave 400W, 85 °C	0.202	0.200	0.991
35	microwave 400W, 95 °C	0.370	0.383	1.035
36	microwave 400W, 100 °C	0.248	0.257	1.036
38	microwave 400W, 115 °C	0.487	0.528	1.084

Table 4. Relative changes of crystallinity of regenerated cellulose dissolved with ultrasonic and microwave assistance, calculated from FT-IR spectra.

Temperture/^{o}C	a_{2900} (C-H)	a_{1372} (O-H)	N_O'KI
110	0.263	0.243	1.082
120	0.362	0.327	1.107
130	0.363	0.313	1.160
140	0.468	0.396	1.182

Table 5. Relative changes of crystallinity of regenerated samples from dissolution of mechanical milling cellulose at different temperature.
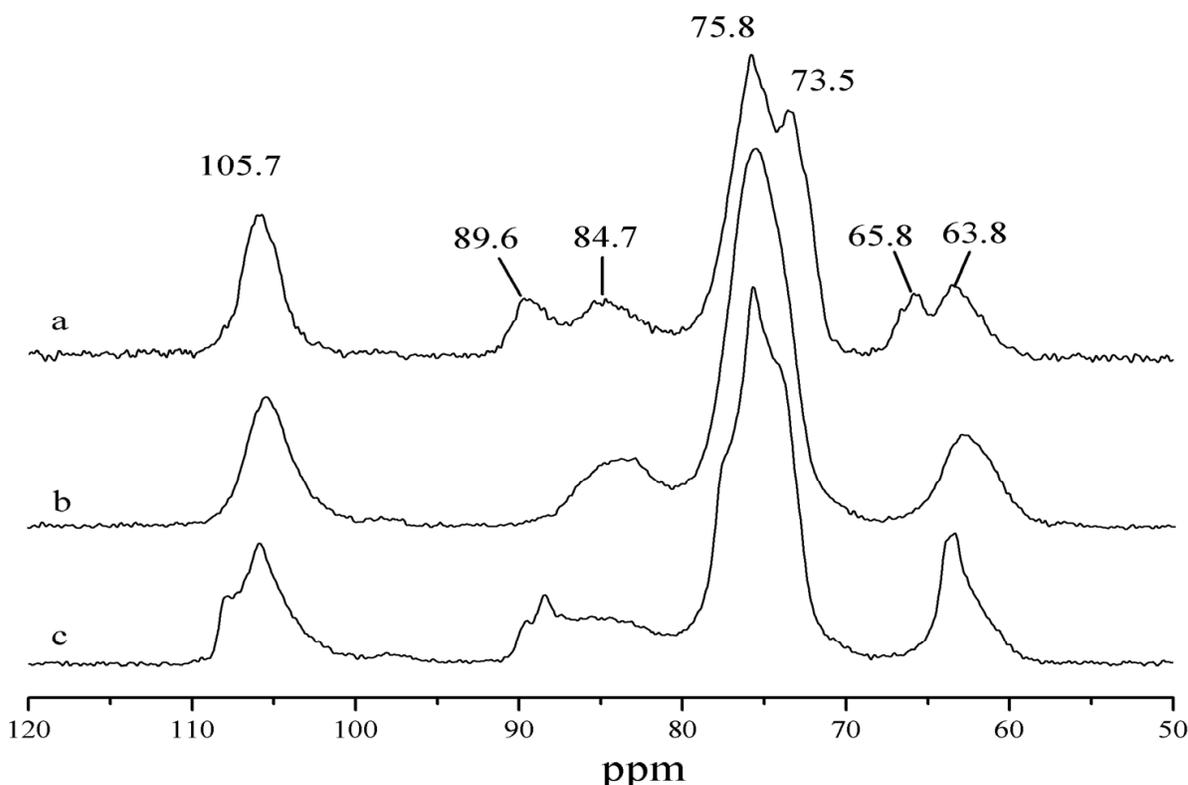

Figure 3. Solid state CP/MAS ^{13}C-NMR spectra of native cellulose (spectrum a) and regenerated cellulose sample 23 (spectrum b) and sample 38 (spectrum c).

3.5. Solid-state CP/MAS ^{13}C NMR spectra

CP/MAS ^{13}C NMR spectroscopy is one of the most effective methods to characterize lignocellulosic materials directly and is able to provide detailed information on solid samples. Fig. 3 shows the CP/MAS ^{13}C-NMR spectra of native cellulose (spectrum a) and regenerated cellulose sample 23 (spectrum b) and sample 38 (spectrum c). The region between 50 and 105 ppm is characterized for the carbons of carbohydrate. The signals from cellulose at 105.7 (C-1), 89.6 and 84.7 (C-4 of crystal cellulose and amorphous cellulose, respectively), 75.8 and 73.5 (C-2, C-3 and C-5), 65.8 and 63.8 (C-6 of crystal cellulose and amorphous cellulose, respectively) are all observed (Focher et al., 2001; Maunu, 2002; Bardet et al., 2002; Liu et al., 2007a; Liu et al., 2009). However, the spectra also exhibited differences at C-4 and C-6 signals. In spectrum b (sample 23), signals for C-4 and C-6 of crystal cellulose disappeared, indicating that the regenerated sample from ultrasonic assisted dissolution

cellulose contained mainly amorphous structure. Nonetheless, signal specific of C-4 of amorphous cellulose was degenerated and that of crystal cellulose was reappeared in spectrum c (sample 38). The two signals contributing to C-6 of crystal and amorphous cellulose were merged into one. This spectrum hinted that cellulose macromolecular formed crystalline structure in the regeneration process after dissolve in [C₄mim]Cl with relative high power of microwave heating.
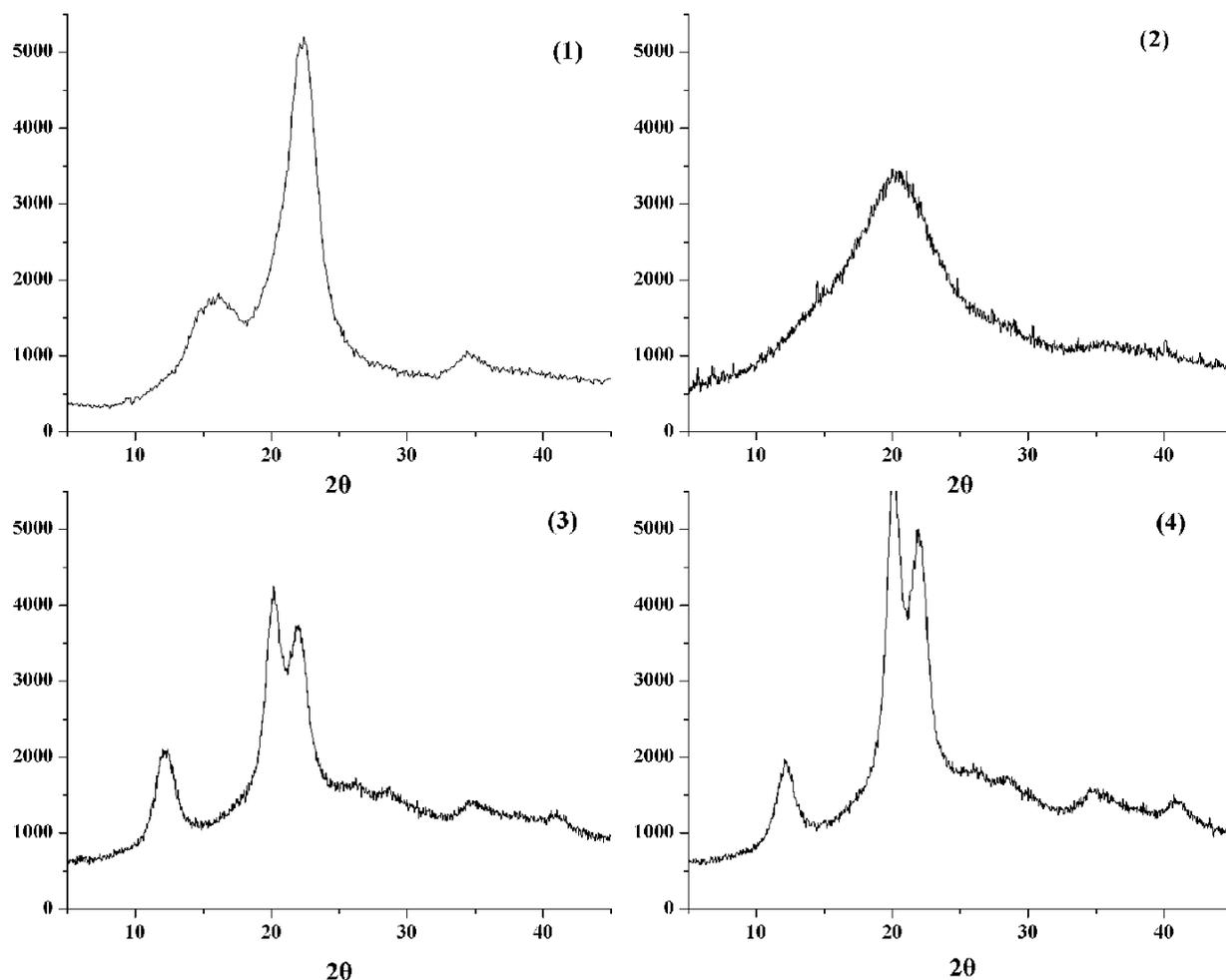

Figure 4. Wide-angle X-ray diffraction curves of native (spectrum 1) and regenerated cellulose sample 20 (spectrum 2), 31 (spectrum 3), and 34 (spectrum4).

3.6. Wide-angle X-ray diffraction

Wide-angle X-ray diffraction is the one of the most valuable technique to measure the crystalline structure of material. In this article wide-angle X-ray diffraction was used to characterize the influence of different pretreatment methods, ultrasonic irradiation and microwave heating on crystalline structure of regenerated cellulose. Fig. 4 exhibits the wide-angle X-ray diffractogram of native (spectrum 1) and regenerated cellulose sample 20 (spectrum 2), 31 (spectrum 3), and 34 (spectrum4). Spectrum 1 gave strong crystalline peak at 22.3° for (002) crystal plane and at 16.1° merged from peaks of (110) and (1$\bar{1}$0) crystal

plane, indicating a cellulose I crystalline structure for native cellulose (Focher et al., 2001; Oh et al., 2005). After dissolution with ultrasonic irradiation and regeneration, cellulose sample comprised mainly amorphous structure and little cellulose II crystalline structure, suggested by a broad peak at 19.8° in the diffratogram (Isogai et al., 1989), as shown in spectrum 2. However, spectrum of sample 31 and 34 displayed three obvious crystalline peaks at 12.2°, 20.2° and 22.0°. They were corresponding to (110), (1$\bar{1}$0) and (002) planes of cellulose II crytal (Zuluaga et al., 2009), respectively. Evidently, samples with microwave heating after regeneration possessed more cellulose II crystalline structure and higher crystallinity, which was in well accordance with the results of NMR spectra (Fig. 3).
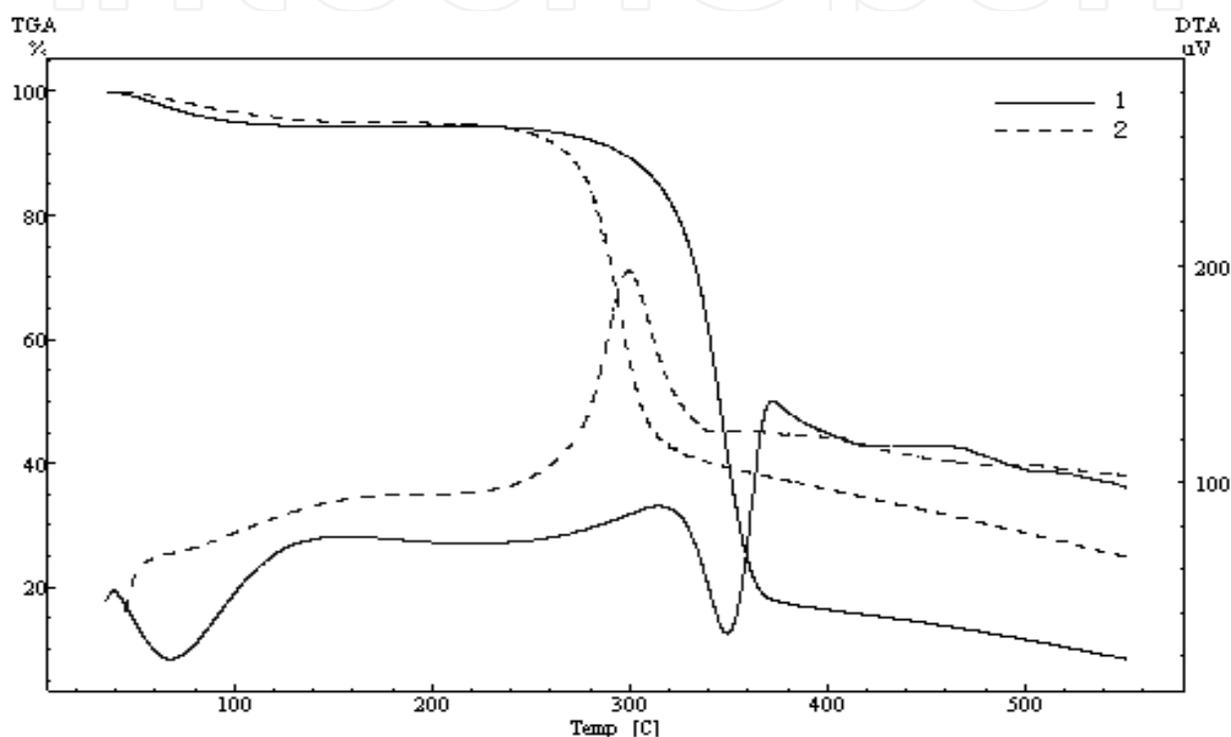

Figure 5. TGA/DTA curves of native cellulose (spectrum 1) and regenerated cellulose sample 17 (spectrum 2).

3.7. Thermal analysis

Fig. 5 shows the TGA and DTG curves of native cellulose (spectrum 1) and regenerated cellulose sample 17 (spectrum 2). The small initial drops occurring near 100 °C in both cases are due to the evaporation of retained moisture. The native cellulose starts to decompose at 228 °C, whereas the regenerated cellulose samples 17 begin to decompose at 211 °C. The decomposition temperature at 50% weight loss occurs at 342 °C for native cellulose and 330 °C for regenerated cellulose sample 17. These decreasing trends of decomposition temperature implied that the thermal stability of regenerated cellulose was lower than that of native cellulose, which was probably due to partial hydrolysis and degradation of macromolecular cellulose during pretreatment with microwave irradiation and dissolution. Similar results have been reported during the dissolution and modification of cellulose in

ionic liquid (Swatloski et al., 2002; Liu et al., 2007b; Li et al., 2011). Pyrolysis residues are primarily indecomposable inorganic salts. As seen in Fig. 5, the residual char yield of native cellulose was lower than that of regenerated cellulose sample 17. The higher pyrolysis residues of regenerated cellulose suggested that some impurities from ILs probably involved in cellulose in the dissolution process, which might be the mind reason contributed to the over 100% yield of some samples.

4. Conclusion

Ethanol treatment, mechanical milling, ultrasonic and microwave irradiation were demonstrated to be effective pretreatment methods to improve cellulose dissolution in [C$_4$mim]Cl. Cellulose sample with 75 W ultrasonic pretreated for 40 min could be dissolved within 0.8 h. Moreover, all the pretreatment methods except mechanical milling did not seriously degrade the cellulose macromolecular. DP of the native cellulose was 1263 and DP of the pretreated samples ranged from about 900 to 1150. DP of regenerated samples were between 800 and 1110. In addition, ultrasonic irradiation and microwave heating were tested to be more effective when applied during the dissolution process. The total dissolution time of the cellulose sample irradiated with 30W ultrasonic for 20 min was 60 min. Under 400 W microwave heating at 115 ^{o}C, it took only 8.5 min to dissolve cellulose sample in [C$_4$mim]Cl. The application of ultrasonic and microwave heating, especially the microwave heating, broke the cellulose macromolecular at certain degree. Regenerated samples from ultrasonic irradiated cellulose were major amorphous cellulose whereas samples from microwave heating cellulose comprised cellulose II crystalline structure.

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