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# Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium

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## Abstract

The chemical modification of sugarcane bagasse cellulose with phthalic anhydride using 1-butyl-3-methylinidazolium chloride ionic liquid as reaction medium was studied. A series of phthalated cellulosic derivatives were prepared with a degree of substitution (DS) ranging from 0.12 to 2.54. It was found that the DS increased with reaction temperature from 85 to 100 °C, molar ratio of phthalic anhydride/anhydroglucose units in cellulose from 2:1 to 10:1, and reaction time from 20 to 120 min. The products were characterized by FT-IR and solid-state CP/MAS $^{13}$C-NMR spectroscopy, and thermal analysis. The results showed that modification of cellulose with phthalic anhydride using 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl) as solvent resulted in the production of cellulosic monoester, and the phthalation at C-6, C-2, and C-3 positions of the cellulose all occurred. In addition, it was found that the crystallinity of the cellulose was completely disrupted and the native cellulosic polymer was significantly degraded in the ionic liquid system under the conditions given. The thermal stability of the phthalated cellulose decreased upon chemical modification.

*Keywords:* Cellulose; Ionic liquid; Phthalic anhydride; Sugarcane bagasse; Crystallinity

## 1. Introduction

There is a growing urgency to develop novel bio-based products and other innovative technologies that can unhook widespread dependence on fossil fuel (Mohanty, Misra, & Drzal, 2002). The annually renewable agricultural residues represent an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass, and their utilizations are attracting increased interests around all over the world, particularly for the production of novel materials for environmentally friendly industrial utilizations after chemical modification (Pandey, Soccol, Nigam, & Soccol, 2000a; Richardson & Gorton, 2003).

Cellulose, the major constituent of all plant materials, forms about half to one-third of plant tissues and is constantly replenished by photosynthesis. It is non-toxic, renewable, biodegradable, and modifiable, and has great potential for an excellent industrial material (Pandey et al., 2000a; Pandey, Soccol, Nigam, & Soccol, 2000b; Richardson & Gorton, 2003). At present, cellulose is widely used as a raw material in numerous industrial applications, e.g., in the paper, paint, textile, food, and pharmaceutical industries (Focher et al., 2001; Richardson & Gorton, 2003).

In order to increase the industrial use and to fulfill the various demands for functionality of different cellulosic products, cellulose is often modified by chemical means. Chemical modification implies the substitution of free hydroxyl groups in the polymer with functional groups, yielding different cellulose derivatives. The modification of cellulose can take place in heterogeneous phase and homogeneous phase. Homogeneous functionalization of cellulose has been one focus of cellulose research for a long time (El Seoud, Marson, Giacco, & Frollini, 2000; Regiani, Frollini, Marson, Arantes, & El Seoud, 1999; Satge,

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Granet, Verneuil, Branland, & Krausz, 2004; Wu, Zhang, Zhang, & He, 2006). However, due to the stiff molecule and close chain packing via numerous intermolecular and intramolecular hydrogen bonds, cellulose is extremely difficult to dissolve in water and most organic solvents. For the homogeneous reaction, eagerly needed are suitable cellulose solvents that can dissolve cellulose and provide a feasible reaction environment. A number of solvent systems, such as DMAc/LiCl, NMNO, and molten salt hydrates like $LiX \cdot nH_2O$ ($X = I^-$, $NO_3^-$, $CH_3COO^-$, $ClO_4^-$) were investigated and proved to be efficient solvents for cellulose (Fischer, Thummler, Pfeiffer, Liebert, & Heinze, 2002). Homogeneous cellulose derivatizations, such as esterification, etherification, and other reactions, in these solvents have also been reported. However, there remain limitations such as toxicity, cost, difficulty for solvent recovery, or instability in above processing (Wu et al., 2004).

In 2002, dissolution of cellulose with ionic liquids (ILs) was firstly reported by Swatloski, Spear, Holbrey, and Rogers (2002). They investigated the solubility of cellulose in various ILs including 1-butyl-3-methylimidazolium ($[C_4mim]^+$) with different anions and found that the high chloride concentration and activity in ILs played an important role in cellulose dissolution. In 2003, another IL, 1-allyl-3-methylimidazolium chloride (AmimCl), was reported to have outstanding capability for dissolving cellulose (Ren, Wu, Zhang, He, & Guo, 2003). The utilization of ILs in the research of cellulose and cellulosic products such as paper and fiber has been increasing over the past 2 years (Turner, Spear, Holbrey, & Rogers, 2004; Przybysz et al., 2005). On the other hand, the investigation of use of ILs as reaction media for cellulose functionalization has also been reported. Homogeneous acteylation of cellulose in different ILs in the absence of any catalysts was accomplished (Heinze, Schwikal, & Barthel, 2005; Wu et al., 2004, 2006). In 2005, carboxylation of cellulose in 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$)/DMSO system was also successfully investigated (Heinze et al., 2005). As far as the authors are aware, there have been no reports of ILs as reaction media for the phthalation of cellulose. We therefore investigated the possibility of cellulose phthalation using $[C_4mim]Cl$ ionic liquid as reaction medium in the absence of any catalyst. The phthalation conditions for sugarcane bagasse (SCB) cellulose derivatives, such as reaction temperature, reaction time, and the molar ratio of phthalic anhydride/anhydroglucose units (AGU) in cellulose, were studied. The modified cellulosic samples were characterized by degree of substitution (DS), Fourier transform infrared (FT-IR), and solid-state CP/MAS $^{13}C$-NMR as well as thermal analysis.

## 2. Experimental

### 2.1. Materials

Sugarcane bagasse (SCB) was obtained from a local sugar factory (Guangzhou, China). It was dried in sunlight and then cut into small pieces. The cut SCB was ground and screened to prepare 20–40 mesh size particles (450–900 μm). The ground SCB was dried again in a cabinet oven with air circulation for 16 h at 50 °C. $[C_4mim]Cl$ ionic liquid was purchased from the Institute of Chemistry and Chemical Engineering, Heibei Normal University, and used as received. All other chemicals used were of analytical grade and purchased from Guangzhou Chemical Reagent Factory, China.

### 2.2. Isolation of crude cellulose

To isolate the cellulose, the dried and ground bagasse (100 g) was first delignified with 100 g sodium chlorite in acidic solution (pH 4.0, adjusted by 10% acetic acid) at 75 °C for 1 h, and then 50 g sodium chlorite was added to further deliginify for another 1 h. The residue was subsequently washed with distilled water and ethanol, and then dried in a cabinet oven for 16 h at 50 °C. The holocellulose obtained was treated with 10% KOH at 25 °C for 10 h to remove the hemicelluloses. At the end of the extraction, the insoluble residue (cellulose) was collected by filtration, washed thoroughly with distilled water until the filtrate was neutral, then washed with 95% ethanol, and dried in an oven at 50 °C for 16 h.

### 2.3. Characterization of the native cellulose

The neutral sugar composition of the crude cellulose obtained was determined by gas chromatography (GC) analysis of the corresponding alditol acetates. The sample (10 mg) was treated with 72% $H_2SO_4$ (0.125 ml) for 45 min at room temperature by agitation on a vortex mixture. The solution was then diluted to 1.475 ml, heated to 100 °C for 2.5 h, cooled, and neutralized with 0.32 ml of 15 M ammonia. After reduction, the resulting alditols were acetylated for GC analysis as described by Blakeney, Harris, and Stone (1983).

Viscosity of the cellulose was measured by British Standard Methods for determination of limiting viscosity number of cellulose in dilute solutions, Part 1, cupriethylenediamine (CED) method (BS 6306, Part 1, 1982). The viscosity average DP (degree of polymerization) of cellulose was estimated from its intrinsic viscosity $[\eta]$ in CED hydroxide solution, $P^{0.90} = 1.65[\eta]$, where $P$ is an indeterminate average DP (Evans & Wallis, 1999). Molecular weight ($M_w$) of the native cellulose was then calculated from $P$ multiplied by 162, the $M_w$ of an AGU.

### 2.4. Phthalation of SCB cellulose

The phthalic derivatives of cellulose containing free carboxylic groups were prepared by modification of SCB cellulose with phthalic anhydride using $[C_4mim]Cl$ as a solvent. Dry cellulose (0.405 g, equaling to 0.0025 mol of AGU and 0.0075 mol of hydroxyl functionality in cellulose) was added to 10 ml $[C_4mim]Cl$ ionic liquid in threenecked flask, and the mixture of cellulose/[$C_4$mim]Cl was stirred at 100 °C up to 12 h to guarantee the complete dissolution. The flask was continuously purged with gaseous $N_2$. Then 0.74 g (equaling to 0.005 mol of phthalic anhydride and 0.0050 mol of carboxyl functionality, molar ratio of phthalic anhydride/AGU in cellulose 2:1), 1.11 g (0.0075 mol of carboxyl functionality, molar ratio 3:1), 1.48 g (0.01 mol of carboxyl functionality, molar ratio 4:1), 1.85 g (0.0125 mol of carboxyl functionality, molar ratio 5:1), 2.22 g (0.015 mol of carboxyl functionality, molar ratio 6:1), 2.96 g (0.02 mol of carboxyl functionality, molar ratio 8:1), and 3.7 g (0.025 mol of carboxyl functionality, molar ratio 10:1) phthalic anhydride were added at the temperature of 85, 90, 95, 100, and 105 °C, respectively. The mixture was heated in oil bath under $N_2$ atmosphere with stirring for 20–120 min. The reaction was stopped after the required time by pouring the resulting mixture into 300 ml of ethanol with stirring. The solid was filtered, washed thoroughly with ethanol to eliminate IL, un-reacted anhydride, and by-products, and then dried in vacuum at 50 °C for 16 h.

### 2.5. Determination of DS of SCB cellulose phthalates

The degree of substitution of cellulose phthalates was determined by direct titration method (Jeon, Viswanathan, & Gross, 1999; Stojanovic, Jeremic, Jovanovic, & Lechner, 2005). A known weight of the sample was dissolved in 10 ml of DMSO by stirring at 75 °C for 20 min. After cooling, 5–6 drops of phenolphthalein indicator were added. This solution was titrated against 0.01 M standard NaOH solution until a permanent pale pink color was seen. The DS was calculated by using the following equation:

$$DS = \frac{162 \times n_{\mathrm{COOH}}}{m - 148 \times n_{\mathrm{COOH}}}$$

where 162 g $mol^{-1}$ is the molar mass of an AGU, 148 g $mol^{-1}$ the net increase in the mass of an AGU for each phthaloyl substituted, $m$ the dry weight of sample analyzed, and $n_{\mathrm{COOH}}$ the amount of COOH calculated from the obtained value of the equivalent volume of known molarity NaOH.

### 2.6. Characterization of the phthalated cellulosic preparations

The chemical structure of the crude cellulose and phthalic derivatives was evaluated by FT-IR and solid-state CP/MAS $^{13}$C-NMR spectroscopies. FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet 510) using a KBr disc containing 1% finely ground samples. Thirty-two scans were taken of each sample recorded from 4000 to 400 $cm^{-1}$ at a resolution of 2 $cm^{-1}$ in the transmission mode. The solid-state CP/MAS $^{13}$C-NMR spectra were recorded on a Bruker DRX-400 spectrometer at the frequency of 100 MHz with 5 mm MAS BBO probe. Acquisition time was 0.034 s. The delay time was 2 s, and the proton 90° pulse time 4.85 μs. Each spectrum was obtained with an accumulation of 5000 scans.

Thermal stability of phthalated cellulose was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (SDT Q600, TA Instrument). The sample weighed between 8 and 12 mg. The scans were run from room temperature to 500 °C at a rate of 10 °C/min under nitrogen flow.

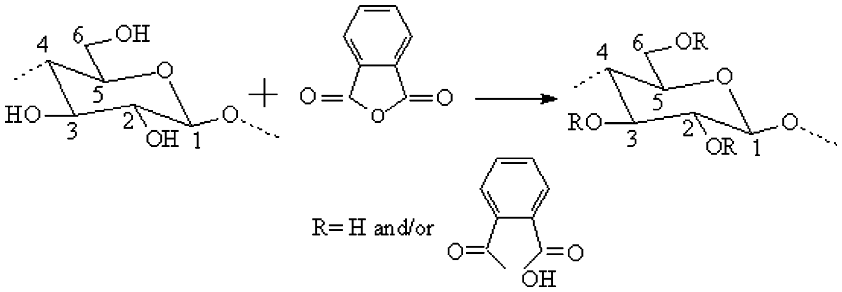
## 3. Results and discussion

### 3.1. Modification and the degree of substitution

The yield of crude cellulose was found to be 52.4% of the dry SCB, in which glucose was the main sugar component, comprising 55.7% of the total sugars. This indicated that the residue is enriched in cellulose. On the other hand, relatively high contents of xylose (25.8%) and arabinose (12.8%) as well as minor quantities of galactose (3.2%) and mannose (1.2%) were also observed in the cellulosic preparation, suggesting the cellulose sample isolated contained noticeable amounts of residual hemicelluloses. The intrinsic viscosity, degree of polymerization, and molecular weight of the native cellulosic preparation were determined to be 387.2 ml $g^{-1}$, 1309.6, and 212.150 g $mol^{-1}$, respectively.

More recently, various ILs were found to be green solvents for cellulose dissolution (Ren et al., 2003; Swatloski et al., 2002) and suitable reaction media for cellulose functionalization (Heinze et al., 2005; Wu et al., 2004). The high concentration of chloride and its activity in ILs are considered to play an important role in cellulose dissolution, which is highly effective in breaking the extensive hydrogen-bonding network present in cellulose. It was found that [$C_4$mim]Cl is one of the important ILs having outstanding capability for dissolving cellulose. In this study, we found that the dissolution of the native cellulosic sample in [$C_4$mim]Cl solution for 12 h at 100 °C resulted in significant degradation of the cellulosic polymer as its intrinsic viscosity, degree of polymerization, and molecular weight decreased from 1309.6 to 750.5 ml $g^{-1}$, 1309.6 to 750.5, and 212.150 to 121.580 g $mol^{-1}$, respectively. A similar observation on the degradation of cellulose in ILs has also been reported by Heinze et al. (2005). They found that the dissolution of spruce sulfite pulp and cotton linters in [$C_4$mim]Cl led to slight degradation, and DP of cellulose after regeneration decreased from 593 to 544 for spruce sulfite pulp and from 1198 to 812 for cotton linters, respectively.

In the present study, the phthalation of the cellulose was carried out using [$C_4$mim]Cl as solvent in the absence of any catalysts to esterify cellulose O–H groups. Though phthalic anhydride is solid, it could be dissolved in [$C_4$mim]Cl within several minutes. The reaction of cellulose with phthalic anhydride to form the monoester is shown in Scheme 1. The effects of reaction temperature, the molar ratio of phthalic anhydride/AGU in cellulose, and reaction



Scheme 1. Reaction of sugarcane bagasse cellulose with phthalic anhydride.

time were investigated, and the results are shown in Table 1. Obviously, an increase in the reaction temperature from 85 (sample 1) to 90 (sample 2), to 95 (sample 3), and to 100 (sample 4) resulted in an increment in DS of the products from 0.82 to 0.86, to 0.93, and to 1.32, respectively. The reason for this enhancement of phthalation by increasing reaction temperature was probably due to the favorable effect of temperature on mobility of the reactant molecules, diffusion of phthalic anhydride into the cellulosic molecules, and swell ability of the cellulose. In contrast, further increase in the reaction temperature from 100 to 105 °C led to a decrease in the DS from 1.32 to 1.11. This phenomenon revealed that a much higher temperature, such as 105 °C, would result in hydrolysis of the formed hemicellulosic phthalate, so reducing the DS. Therefore, a reaction temperature of 90 °C was considered as optimum for other samples.

Results from Table 1 also indicated that increasing in the molar ratio of phthalic anhydride/AGU in cellulose from 2:1 in sample 6 to 3:1 in sample 7, to 4:1 in sample 8, to 5:1 in sample 9, to 6:1 in sample 2, to 8:1 in sample 10, and to 10:1 in sample 11 led to an increment of DS values from 0.12 to 0.21, 0.50, 0.66, 0.86, 2.23, and 2.54, respectively. These increases in DS by an increment of the reactant concentration could be interpreted in terms of greater availability of phthalic anhydride molecules in the proximity of the cellulosic molecules at higher concentration of the anhydride. In addition, as the data shown in Table 1, the DS of phthalated cellulose reached 0.71 within 20 min (sample 12), 0.81 within 30 min (sample 13), 0.86 within 60 min (sample 2), 0.88 within 90 min (sample 14), and 0.89 within 120 min (sample 15) as kept the reaction temperature at 90 °C and the molar ratio of phthalic anhydride/AGU in cellulose at 6:1. This increasing trend of DS with reaction time could be due to the increasing rate and time of collisions of phthalic anhydride with cellulosic molecules.

Table 1
The degree of substitution (DS) of phthalated cellulose

| Phthalation conditions | | | | Phthalated cellulose | |
|---|---|---|---|---|---|
| Cellulose[a] (%) | Molar ratio[b] | Temperature (°C) | Reaction time (min) | Sample no. | DS |
| 2.35 | 6:1 | 85 | 60 | 1 | 0.82 |
| 2.35 | 6:1 | 90 | 60 | 2 | 0.86 |
| 2.35 | 6:1 | 95 | 60 | 3 | 0.93 |
| 2.35 | 6:1 | 100 | 60 | 4 | 1.32 |
| 2.35 | 6:1 | 105 | 60 | 5 | 1.11 |
| 2.35 | 2:1 | 90 | 60 | 6 | 0.12 |
| 2.35 | 3:1 | 90 | 60 | 7 | 0.21 |
| 2.35 | 4:1 | 90 | 60 | 8 | 0.50 |
| 2.35 | 5:1 | 90 | 60 | 9 | 0.66 |
| 2.35 | 8:1 | 90 | 60 | 10 | 2.23 |
| 2.35 | 10:1 | 90 | 60 | 11 | 2.54 |
| 2.35 | 6:1 | 90 | 20 | 12 | 0.71 |
| 2.35 | 6:1 | 90 | 30 | 13 | 0.81 |
| 2.35 | 6:1 | 90 | 90 | 14 | 0.88 |
| 2.35 | 6:1 | 90 | 120 | 15 | 0.89 |

[a] Cellulose/[$C_4$mim]Cl by weight.

[b] Molar ratio of phthalic anhydride/AGU in cellulose.

### 3.2. FT-IR spectra

Fig. 1 shows the FT-IR spectra of unmodified cellulosic preparation (spectrum 1) and phthalated cellulose sample 9 (spectrum 2). The absorbances at 3426, 2919, 1632, 1370, 1159, and 1045 $cm^{-1}$ seen in spectrum 1 are associated with native cellulose. The strong absorption at 3426 $cm^{-1}$ is due to stretching of O–H groups and that one at 2919 $cm^{-1}$ to the C–H stretching. The band at 1632 $cm^{-1}$ corresponds to the bending mode of the absorbed water (Sun, Sun, & Tomkinson, 2004a). The peak at 1370 $cm^{-1}$ is attributed to the O–H bending. The absorption band at 1159 $cm^{-1}$ relates to C–O stretching in acetyl group. A strong peak at 1045 $cm^{-1}$ arises from C–O–C pyranose ring skeletal vibration (Sun, Sun, Zhao, & Sun, 2004b). In spectrum 2, the intensity of the peak at 1045 $cm^{-1}$ for C–O–C stretching slightly decreased due to the degradation of the cellulose sample during dissolution and modification, corresponding to the decreasing trend of DP from 1309.6 $cm^{-1}$ in native cellulose and 750.5 $cm^{-1}$ in regenerated cellulose from the ILs. More importantly, spectrum 2 gives evidence of phthalation. The band at 1716 $cm^{-1}$ is indicative of absorption by carbonyl group in carboxyl and esters. In general, the absorption by carbonyl bonds in esters gives peaks at 1740 $cm^{-1}$, and one in carboxylic acids exhibits a band at 1700 $cm^{-1}$ (Jayakumar, Balaji, & Nanjundan, 2000). The two bands are strongly overlapped and therefore resulted in a peak centered at 1716 $cm^{-1}$. The band at 1577 $cm^{-1}$ corresponds to the antisymmetric stretching of carboxylic anions (Yoshimura, Matsuo, &

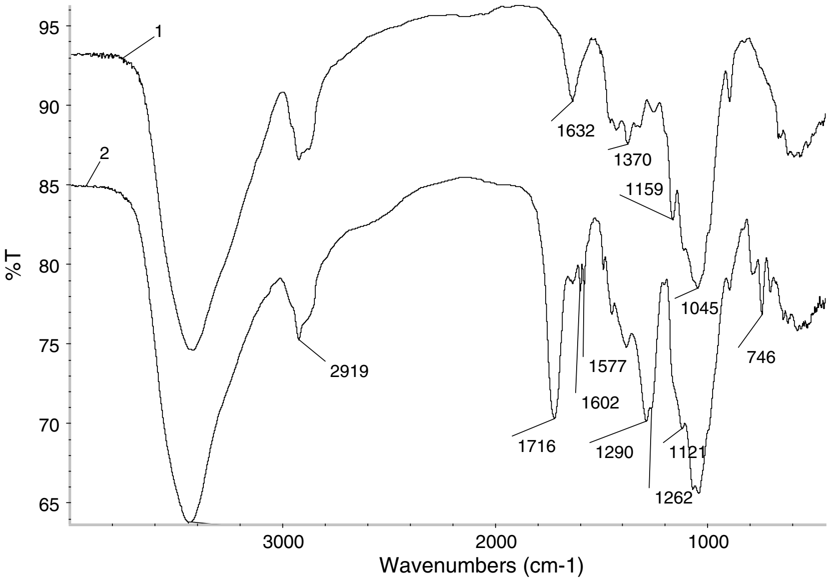


Fig. 1. FT-IR spectra of unmodified cellulose (spectrum 1) and phthalated cellulosic sample 9 (spectrum 2).

Fujioka, 2006). Interestingly, the strongly increased intensity of the bands in the range 1300–1250 $\text{cm}^{-1}$ was observed in the spectrum of modified cellulose. The band at 1262 $\text{cm}^{-1}$ relates to C–O symmetric stretching in ester and that one at 1290 $\text{cm}^{-1}$ to the C–O stretching in carboxyl. The band at 1121 $\text{cm}^{-1}$ corresponds to the C–O antisymmetric stretching in ester (Sun, Xu, Geng, Sun, & Sun, 2005). These observations revealed that an ester and carboxylic acid were formed during the reaction. In addition, the intensity of the absorption bands at 1602 $\text{cm}^{-1}$ for aromatic ring vibrations and 746 $\text{cm}^{-1}$ for out-of-plane C–H bending of the *ortho*-disubstituted benzene increased after phthalic anhydride treatment, which indicated that the phthalyl group was introduced into the cellulosic molecules (Jayakumar et al., 2000). As expected, the absence of peaks at 1850 and 1780 $\text{cm}^{-1}$ in spectrum 2 of the phthalated cellulose sample 9 confirmed that the products are free of the un-reacted phthalic anhydride (Gu & Yang, 1998).

The effects of reaction temperature, molar ratio of phthalic anhydride/AGU in cellulose, and reaction time on the DS of cellulosic preparations were also investigated by the peak intensity of phthalated cellulose samples, and their spectra are given in Figs. 2–4. As shown in Fig. 2, an increase in reaction temperature from 85 (spectrum 1, sample 1) to 95 °C (spectrum 2, sample 3) and to 105 °C (spectrum 3, sample 5) led to an increment in the intensity of the bands at 1717 $\text{cm}^{-1}$ for C=O stretching in ester and carboxyl groups, 1571 $\text{cm}^{-1}$ for antisymmetric stretching of carboxylic anions, 1280 $\text{cm}^{-1}$ for C–O symmetric stretching in ester and C–O stretching in carboxyl groups, 1125 $\text{cm}^{-1}$ for C–O antisymmetric stretching in ester, 1597 $\text{cm}^{-1}$ for aromatic ring vibrations, and 739 $\text{cm}^{-1}$ for the out-of-plane C–H bending of the *ortho*-disubstituted benzene, corresponding to an increase of the DS in Table 1.

Fig. 3 shows the FT-IR spectra of phthalated cellulosic samples 6 (molar ratio 2:1, spectrum 1), 8 (molar ratio 4:1, spectrum 2), and 10 (molar ratio 8:1, spectrum 3). The intensity of peaks at 1718, 1602, 1576, 1289, 1123, and 741 $\text{cm}^{-1}$ obviously increased with an increment in the molar ratio of phthalic anhydride/AGU in cellulose from 2:1 to 4:1, and to 8:1, which is paralleled to the increasing data of DS in Table 1. In Fig. 4, the increasing trends of the peaks at 1719, 1600, 1576, 1286, 1121, and 741 $\text{cm}^{-1}$ with an increment in reaction time from 20 (spectrum 1, sample 12) to 90 min (spectrum 2, sample 14), and to 120 min (spectrum 3, sample 15) correspond to the increasing values of DS in Table 1.

### 3.3. CP MAS $^{13}$C-NMR spectra

In the present study, the phthalation of cellulose was also studied by CP/MAS $^{13}$C-NMR spectroscopy, and Fig. 5 shows the spectra of unmodified crude cellulose (spectrum a) and phthalated cellulosic samples prepared with the molar ratio of phthalic anhydride/AGU 3:1 (spectrum b, sample 7) and 10:1 (spectrum c, sample 11). In spectrum a, the signals at 104.8 (C-1), 88.4 (C-4 of crystalline cellulose), 83.3 (C-4 of amorphous cellulose), 74.7 (C-5), 72.4 (C-2 and C-3), and 64.5 ppm (C-6) are all observed (Bardet, Foray, & Tran, 2002; Chang & Chang, 2001). In spectra b and c, the signal at 88.4 ppm for C-4 of crystal cellulose disappeared completely. Moreover, the signal for C-6 shifted from 64.5 (C-6 of crystalline cellulose) in spectrum a to 62.8 ppm (C-6 of amorphous cellulose) in spectra b and c. The changes of these two signals for C-4 and C-6 indicated that the crystalline structure was completely disrupted by breaking hydrogen bonds in α-cellulose during the dissolution and modification (Maunu, 2002). Thereafter, the structure of the cellulose was easily

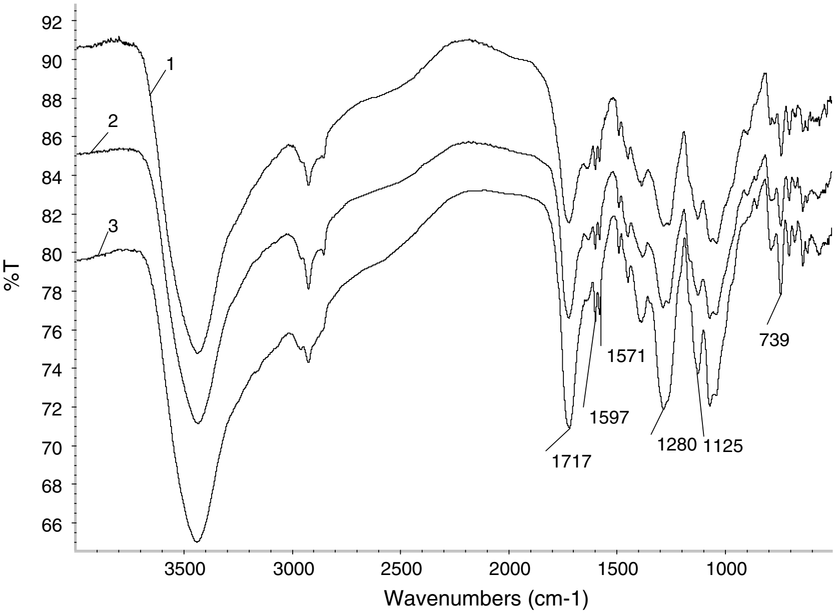


Fig. 2. FT-IR spectra of phthalated cellulosic samples 1 (spectrum 1), 3 (spectrum 2), and 5 (spectrum 3).

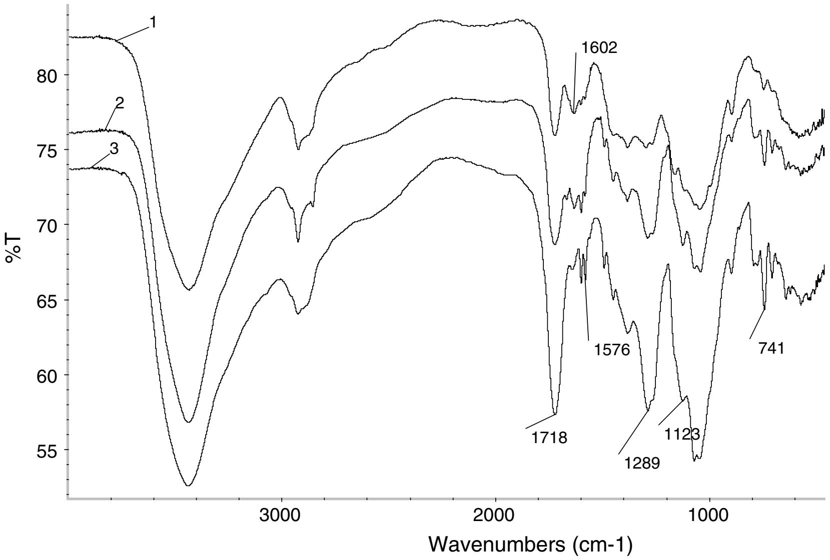


Fig. 3. FT-IR spectra of phthalated cellulosic samples 6 (spectrum 1), 8 (spectrum 2), and 10 (spectrum 3).

opened and more $\beta$-1,4 glycosidic bonds were cleaved, resulting to more reactive of the O–H groups. Evidently, the presence of the signals of the carboxylic group at 171.8 ppm, the carbonyl group at 195.1 ppm, and benzene ring at 125.5 ppm observed in modified cellulosic samples provided evidence of phthalation, and the increasing intensity of these signals from b to c was consistent with the DS values in Table 1, which indicated the reaction shown in Scheme 1 does occur. In addition, as shown in Fig. 5, the intensity of the signal for C-6 decreased after phthalation, which indicated the phthalation reaction occurred at C-6. Furthermore, the intensity of the signal at 72.4 for C-2 and C-3 also decreased from a to b and c, which indicated the phthalation at C-2 and C-3 also occurred.

### 3.4. Thermal analysis

The effect of phthalation on the thermal behavior of cellulose was also studied by TGA and DSC in the temperature range from room temperature to 500 °C at a rate of 10 °C/min under nitrogen flow. Fig. 6 shows the TGA and DSC thermograms of unmodified crude cellulose (1) and phthalated cellulose sample 11 (2). As can be seen from the figure, the native cellulose starts to decompose at 245 °C; at 50% weight loss, the decomposition temperature occurs at 339 °C. The phthalated cellulose sample 11 begins to decompose at 218 °C; at 50% weight loss, the decomposition temperature occurs at 294 °C. These decreasing trends of decomposition

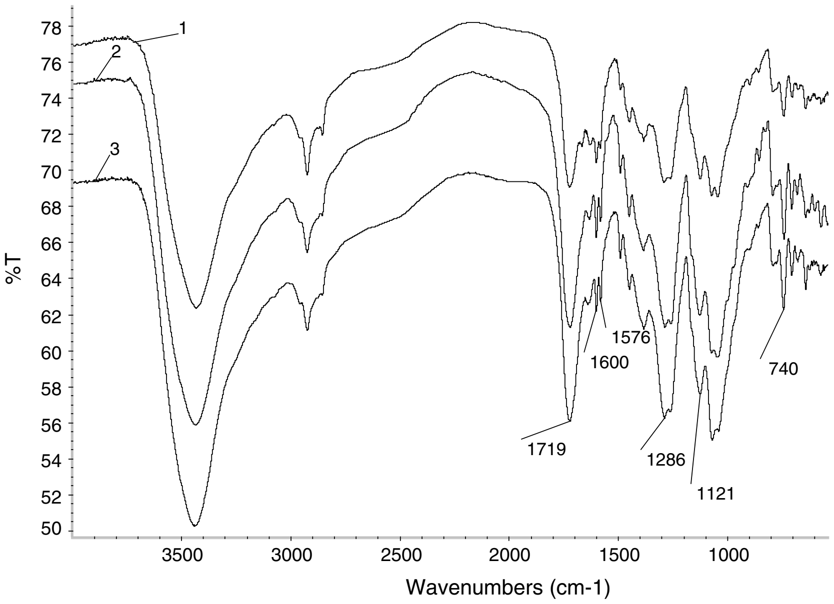


Fig. 4. FT-IR spectra of phthalated cellulosic samples 12 (spectrum 1), 14 (spectrum 2), and 15 (spectrum 3).

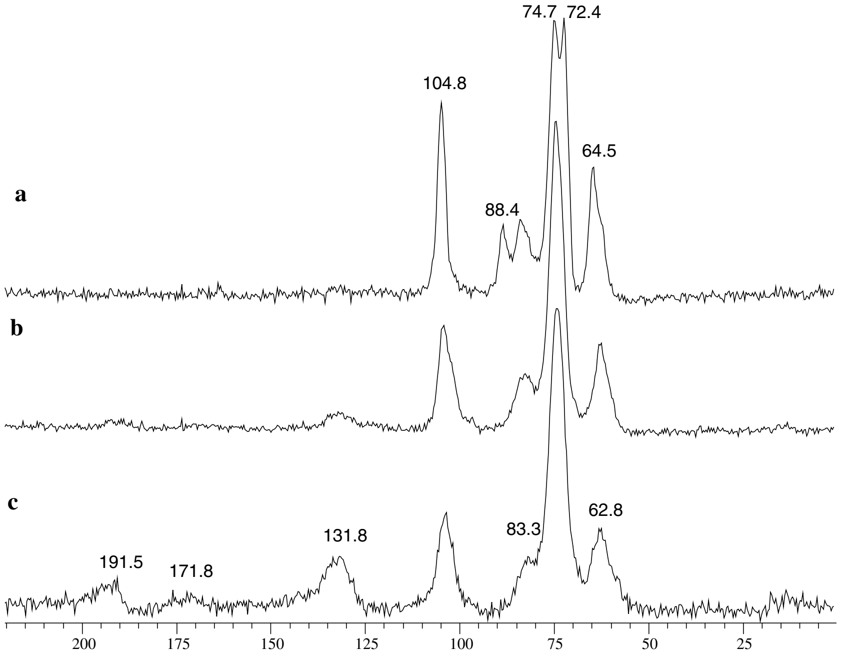


Fig. 5. Solid-state CP/MAS $^{13}$C-NMR spectra of unmodified cellulose (spectrum a) and phthalated cellulosic samples 7 (spectrum b) and 11 (spectrum c).

temperature imply that the thermal stability of phthalated cellulose is lower than that of the un-modified cellulose.

In general, DSC is used to investigate the possibility of interaction between components and measure the extent of disruption of the hydrogen bonds as well as quantify the heat energy flows (Fringant, Desbrieres, & Rinaudo, 1996). Fig. 6 also gives the DSC curves of the unmodified crude cellulose and phthalated cellulose sample 11. Notably, the exothermic peak was asymmetric due to overlapping endothermic response from both un-reacted cellulose and the reaction product (Zhuang & Steiner, 1993). The exothermic peak, which represents heat released from the product, was observed at a maximum temperature of 361 °C for unmodified cellulose and 283 °C for sample 11, respectively, which indicated that a noticeable degradation of cellulose occurred during the dissolution and modification.

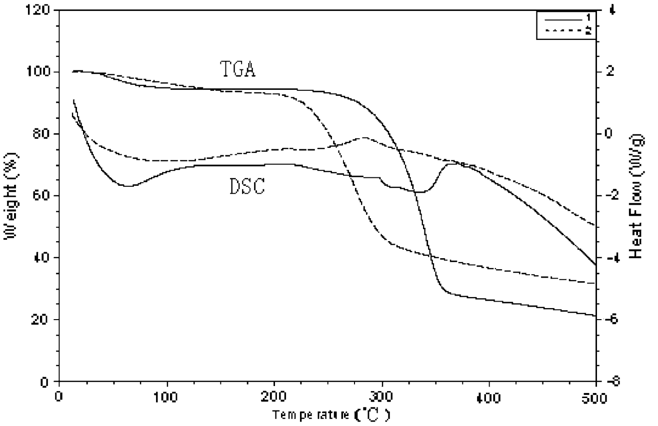


Fig. 6. The thermograms of unmodified cellulose (1) and phthalated cellulose sample 11 (2).

Based on the above studies, the modification of cellulose with phthalic anhydride using 1-butyl-3-methylinidazolium chloride ionic liquid as reaction medium was successfully accomplished, and the cellulosic derivatives bearing carboxylic groups with DS ranging from 0.12 to 2.54 were obtained. During dissolution and derivatization in [$C_4$mim]Cl, cellulose was substantially degraded. The DS of cellulose derivatives increased with the increment of reaction temperature from 85 to 100 °C, the molar ratio of phthalic anhydride/AGU in cellulose from 2:1 to 10:1, and reaction time from 20 to 120 °min. Solid-state CP/MAS $^{13}$C-NMR spectroscopy confirmed that the phthalation at C-6, C-2, and C-3 positions all occurred. The thermal stability of phthalated cellulose decreased after chemical modification.

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## References

Bardet, M., Foray, M. F., & Tran, Q. K. (2002). High-resolution solid-state CPMAS NMR study of archaeological woods. *Analytical Chemistry, 74*, 4386–4390.

Blakeney, A. B., Harris, P. J., & Stone, B. A. (1983). A simple and rapid preparation of alditol acetates for monosaccharide analysis. *Carbohydrate Research, 113*, 291–299.

Chang, S. T., & Chang, H. T. (2001). Comparisons of the photostability of esterified wood. *Polymer Degradation and Stability, 71*, 261–266.

El Seoud, O. A., Marson, G. A., Giacco, G. T., & Frollini, E. (2000). An efficient, one-pot acylation of cellulose under homogeneous reaction conditions. *Macromolecular Chemistry and Physics, 201*, 882–889.

Evans, R., & Wallis, A. F. (1999). Cellulose molecular weights determined by viscosity. *Journal of Applied Polymer Science, 37*, 2331–2340.

Fischer, S., Thummler, K., Pfeiffer, K., Liebert, T., & Heinze, T. (2002). Evaluation of molten inorganic salt hydrates as reaction medium for the derivatization of cellulose. *Cellulose, 9*, 293–300.

Focher, B., Palma, M. T., Canetti, M., Torri, G., Cosentino, C., & Gastaldi, G. (2001). Structural differences between non-wood plant celluloses: Evidence from solid state NMR, vibrational spectroscopy and X-ray diffractometry. *Industrial Crops and Products, 13*, 193–208.

Fringant, C., Desbrieres, J., & Rinaudo, M. (1996). Physical properties of acetylated starch-based materials: Relation with their molecular characteristics. *Polymer, 37*, 2663–2673.

Gu, X. H., & Yang, C. Q. (1998). FT-IR and FT-Raman spectroscopy study of the cyclic anhydride intermediates for esterification of cellulose: 1. Formation of anhydride without a catalyst. *Research on Chemical Intermediates, 24*, 979–996.

Heinze, T., Schwikal, K., & Barthel, S. (2005). Ionic liquids as reaction medium in cellulose functionalization. *Macromolecular Bioscience, 5*, 520–525.

Jayakumar, R., Balaji, R., & Nanjundan, S. (2000). Studies on copolymers of 2-(N-phthalimido)ethyl methacrylate with methyl methacrylate. *European Polymer Journal, 36*, 1659–1666.

Jeon, Y. S., Viswanathan, A., & Gross, R. A. (1999). Studies of starch esterification: Reactions with alkenyl-succinates in aqueous slurry systems. *Starch/Stärke, 51*, 90–93.

Maunu, S. L. (2002). NMR studies of wood and wood products. *Progress in Nuclear Magnetic Resonance Spectroscopy, 40*, 151–174.

Mohanty, A. K., Misra, M., & Drzal, L. T. (2002). Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world. *Journal of Polymers and the Environment, 10*, 19–26.

Pandey, A., Soccol, C. R., Nigam, P., & Soccol, V. T. (2000a). Biotechnological potential of agro-industrial residues. I. Sugarcane bagasse. *Bioresource Technology, 74*, 69–80.

Pandey, A., Soccol, C. R., Nigam, P., Soccol, V. T., Vandenberghe, L. P. S., & Mohan, R. (2000b). Biotechnological potential of agro-industrial residues. II. Cassava bagasse. *Bioresource Technology, 74*, 81–87.

Przybysz, K., Drzewinska, E., Stanislawska, A., Wysocka-Robak, A., Cieniecka-Roslonkiewicz, A., Foksowicz-Flaczyk, J., et al. (2005). Ionic liquids and paper. *Industrial and Engineering Chemistry Research, 44*, 4599–4604.

Regiani, A. M., Frollini, E., Marson, G. A., Arantes, G. M., & El Seoud, O. A. (1999). Some aspects of acylation of cellulose under homogeneous solution conditions. *Journal of Polymer Science Part A-Polymer Chemistry, 37*, 1357–1363.

Ren, Q., Wu, J., Zhang, J., He, J. S., & Guo, M. L. (2003). Synthesis of 1-allyl-3-methyle mazolium-based room-temperature ionic liquid and preliminary study of its dissolving cellulose. *Acta Polymerica Sinica*, 448–451.

Richardson, S., & Gorton, L. (2003). Characterisation of the substituent distribution in starch and cellulose derivatives. *Analytica Chimica Acta, 497*, 27–65.

Satge, C., Granet, R., Verneuil, B., Branland, P., & Krausz, P. (2004). Synthesis and properties of biodegradable plastic films obtained by microwave-assisted cellulose acylation in homogeneous phase. *Comptes Rendus Chimie, 7*, 135–142.

Stojanovic, Z., Jeremic, K., Jovanovic, S., & Lechner, M. D. (2005). A comparison of some methods for the determination of the degree of substitution of carboxymethyl starch. *Starch/Stärke, 57*, 79–83.

Sun, R. C., Sun, X. F., & Tomkinson, J. (2004a). Hemicelluloses and their derivatives. *ACS Symposium Series, 864*, 2–22.

Sun, J. X., Sun, X. F., Zhao, H., & Sun, R. C. (2004b). Isolation and characterization of cellulose from sugarcane bagasse. *Polymer Degradation and Stability, 84*, 331–339.

Sun, J. X., Xu, F., Geng, Z. C., Sun, X. F., & Sun, R. C. (2005). Comparative study of cellulose isolated by totally chlorine-free method from wood and cereal straw. *Journal of Applied Polymer Science, 97*, 322–335.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquids. *Journal of the American Chemical Society, 124*, 4974–4975.

Turner, M. B., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2004). Production of bioactive cellulose films reconstituted from ionic liquids. *Biomacromolecules, 5*, 1379–1384.

Wu, J., Zhang, H., Zhang, J., & He, J. S. (2006). Homogeneous acetylation and regioselectivity of cellulose in a new ionic liquid. *Chemical Journal of Chinese Universities-Chinese, 27*, 592–594.

Wu, J., Zhang, J., Zhang, H., He, J. S., Ren, Q., & Guo, M. L. (2004). Homogeneous acetylation of cellulose in a new ionic liquid. *Biomacromolecules, 5*, 266–268.

Yoshimura, T., Matsuo, K., & Fujioka, R. (2006). Novel biodegradable superabsorbent hydrogels derived from cotton cellulose and succinic anhydride: Synthesis and characterization. *Journal of Applied Polymer Science, 99*, 3251–3256.

Zhuang, J. M., & Steiner, P. R. (1993). Thermal-reactions of diisocyanate (MDI) with phenols and benzylalcohols-DSC study and synthesis of MDI adducts. *Holzforschung, 47*, 425–434.