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Homogeneous modification of cellulose with succinic anhydride in ionic liquid using 4-dimethylaminopyridine as a catalyst

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ABSTRACT

Cellulose, extracted from sugarcane bagasse, was successfully succinylated in ionic liquid 1-buty-3-methylimidazolium (BMIMCl) using 4-dimethylaminopyridine (DMAP) as a catalyst. Parameters investigated included the mass ratio of DMAP/succinic anhydride in a range from 0% to 15%, reaction time (from 30 to 120 min), reaction temperature (from 60 to 110 °C). The succinylated cellulosic derivatives had a degree of substitution (DS) ranging from 0.24 to 2.34. It was found that the DS of succinylated cellulosic derivatives using DMAP as a catalyst was higher than that without any catalyst under the same reaction conditions. The products were characterized by FT-IR, solid-state CP/MAS ^{13}C NMR, and thermal analysis. FT-IR and solid-state CP/MAS ^{13}C NMR spectra showed that succinoylation occurred at C-6, C-2 and C-3 positions. The thermal stability of the succinylated cellulose decreased upon chemical modification.

1. Introduction

In recent years, renewable resource has drawn much attention from the governments and researchers. Sugarcane bagasse, an abundant agricultural lignocellulosic byproduct, is a fibrous residue of cane stalks left over after the crushing and extraction of the juice from the sugarcane (Liu et al., 2007). The bagasse has been used as a fuel for the boilers by the factory or as raw materials for the manufacture of pulp and paper products, various types of building boards, and certain chemicals (Pandey, Soccol, Nigam, & Soccol, 2000; Rowell & Keany, 1991). Sugarcane bagasse has many attractive properties, including readily available, renewable, biodegradable and environmentally benign. Therefore, using resource such as sugarcane bagasse will became more and more interesting and popular.

Cellulose is the main composition of sugarcane bagasse and accounts for as high as 54% of total bagasse. It is also the most abundant renewable resource in the world. Cellulose derivatives have many important applications in fiber, paper, membrane, polymer, and paints industry (Swatloski, Spear, Holbrey, & Rogers, 2002). However, due to its polydisperse linear glucose polymer chains which form hydrogen-bonded supermolecular structures, cellulose is insoluble in water and most common organic solvents, which is a major obstacle for cellulose homogeneous modification (Finkenstadt & Millane, 1998). Over the past decades, several solvent or solvent systems such as DMAc/LiCl, DMF/N_2O_4, NMNO, and some molten salt hydrates like $LiClO_4{\cdot}3H_2O$ were reported as cellulose solvents (Heinze, Schwikal, & Barthel, 2005; Regiani, Frollini, Marson, Arantes, & El Seoud, 1999; Fischer, Thummler, Pfeiffer, Liebert, & Heinze, 2002; Heinze & Liebert 2001; Wu et al., 2004). However, they have some limitations in application because of toxicity, cost, difficulty for solvent recovery, or instability.

Recently, much attention has been focused on the use of ionic liquids as environmental benign reaction. Ionic liquids are designated as "green" solvents because they have many advantages, such as extremely low vapor pressure, are noninflammable, thermally and chemically stable, high loading capacity, and tunable polar (Zhu et al., 2006). Various chemical reaction of cellulose can be performed in ionic liquids. Homogeneous acetylation, tosylation, phthalation and carbanilation of cellulose in ionic liquids were reported (Barthal & Heinze, 2006; Granström et al., 2008; Susann & Thomas, 2006; Wu et al., 2004). It seems now the cost of ionic liquid is one of the biggest drawback before its application. Fortunately, the researchers have been realized that problem and propose solutions to this problem. It is easy to recycle ionic liquid and the recycled ionic liquid almost has same functionalization as original (Zhang et al., 2009). On the other hand, large-scale producing ionic liquid and developing technique are needed to reducing the cost of ionic liquid (Cao et al., 2009).

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The carboxyl could be introduced to lignocelluloses which mainly contain cellulose by modification with succinic anhydride. The product usually used as absorbent for heavy metal ions such as Cu^{2+}, $Ni2^{+}$, Cr^{3+}, Fe^{3+} (Nada & Hassan, 2006). In previous literature, succinoylation of cellulose with succinic anhydride in ionic liquid were reported (Liu, Sun, Zhang, Ren, & Geng, 2006), and the reaction of cellulose with succinic anhydride is shown in Scheme 1. However, DS of prepared succinylated cellulosic derivatives were low without any catalyst. DMAP is a highly effective catalyst for acylation of alcohol. In this text, we used DMAP as a catalyst to prepare high DS of succinylated cellulosic derivatives. On the other hand, it may be possible to control the DS by controlling the temperature, reaction time and mass ratio of DMAP/succinic anhydride.

2. Experimental

2.1. Materials

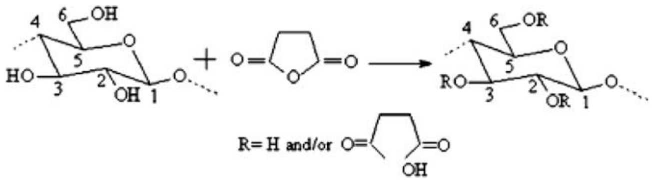
Sugarcane bagasse (SCB) was obtained from a local factory (Guangzhou, China). It was dried in sunlight and then cut into small pieces. The cut SCB was ground and screened to prepare 20–40 mesh size particles (450–900 μm). The ground SCB was further dried in a cabinet oven with air circulation for 16 h at 50 °C before use. BMIMCl was purchased from the Chemer Chemical Co., Ltd., Hangzhou, China, and used as received. All of other chemicals were of analytical-reagent grade and purchased from Guangzhou Chemical Reagent Factory, China.

2.2. Isolation of sugarcane bagasse cellulose

To isolate the cellulose, the dried SCB powder was first dewaxed with toluene–ethanol (2:1 v/v) in a Soxhlet apparatus for 6 h. The dewaxed SCB (100 g) was then soaked in distilled water (2000 ml) at 80 °C for 2 h. The insoluble residue was 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 delignify 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 extracted with 8% KOH at 25 °C for 10 h to remove the hemicelluloses. After 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. Succinoylation of cellulose with succinic anhydride in BMIMCl using DMAP as a catalyst

The succinylated cellulosic derivatives containing free carboxylic groups were prepared by reaction of SCB cellulose with succinic anhydride in BMIMCl using DMAP as a catalyst. Dried cellulose was added to BMIMCl in three-necked flask, and the mixture of cellulose/BMIMCl (containing 2.0% of cellulose by weight) was stirred at 100 °C up to 10 h to guarantee the complete dissolution of cellulose. Then succinic anhydride and DMAP catalyst were added. The mixture was then heated in oil bath under N_2 atmosphere with stirring for modification. After the required time, the resulting mixture was slowly poured into isopropanol with stirring to stop the reaction. The solid was filtered, washed thoroughly with isopropanol to eliminate ionic liquid, the un-reacted anhydride, DMAP and by-products, and then dried in vacuum at 50 °C for 16 h.



Scheme 1. Reaction of cellulose with succinic anhydride.

2.4. Determination of the degree of substitution

The degree of substitution of cellulosic preparations was determined by the back-titration method (Jeon, Viswanathan, & Gross, 1999; Stojanovic, Jeremic, Jovanovic, & Lechner, 2005). A known weight of the sample was dissolved in 10 ml of NaOH by stirring at 50 °C for 30 min. The excess of NaOH was back-titrated with standard 0.025 M HCl using phenolphthalein as the indicator. The titration was repeated three times, and the average value of the HCl volume was used for the calculations. The DS was calculated by using the following equation:

$$\mathrm{DS} = \frac{162 \times n_{\mathrm{COOH}}}{m - 100 \times n_{\mathrm{COOH}}},$$

where 162 g/mol is the molar mass of an AGU, 100 g/mol is the net increase in the mass of an AGU for each succinoyl substituted, m is the weight of sample analyzed, and n_{COOH} is the amount of COOH calculated from the obtained value of the equivalent volume of known molarity HCl according to the following equation:

$$n_{\mathrm{COOH}} = (V_{\mathrm{NaOH}} \times C_{\mathrm{NaOH}} - V_{\mathrm{HCl}} \times C_{\mathrm{HCl}})/2$$

2.5. Characterization of the native and succinylated 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 (Blakeney, Harris, & 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 their 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 cellulose was then calculated from P by multiplied by 162, the M_w of an AGU.

The FT-IR spectra of cellulose and succinylated cellulosic derivatives were recorded on a FT-IR spectrophotometer (Nicolet 510) from finely ground sample (1%) in KBr pellets in the range 4000–400 cm^{-1}. Thirty-two scans were taken for each sample with a resolution of 2 cm^{-1} in the transmission mode.

The solid-state CP/MAS ^{13}C NMR spectra of cellulose and succinylated cellulosic preparations were obtained 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 cellulose and succinylated cellulose were performed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) 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 550 °C at a rate of 10 °C per minute under nitrogen flow.

3. Result 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. The neutral sugar composition of the cellulose showed that glucose was the major sugar component in the cellulosic sample, comprising 55.7% of the total sugars. On the other hand, it should be noted that the cellulose preparation also contained significant amounts of non-cellulosic sugars, such as xylose (25.8%), arabinose (12.8%), galactose (3.2%), and mannose (1.2%), indicating that the crude cellulosic preparation contained significant quantities of residual hemicelluloses. The intrinsic viscosity, degree of polymerization, and molecular weight of the cellulosic sample were found to be 387.2 ml g^{-1}, 1309.6, and 212,152 g mol^{-1}, respectively. In comparison, dissolution of the cellulosic preparation in BMIMCl at 100 °C for 12 h with the weight ratio of cellulose to BMIMCl at 2.35% resulted in a substantial degradation of the cellulose macromolecules in the ionic liquids system as shown by reducing its intrinsic viscosity, degree of polymerization, and molecular weight to 234.6 ml g^{-1}, 750.5, and 121,580 g mol^{-1}, respectively. It is considered that the high chloride concentration and its activity in ionic liquids play an important role in cellulose dissolution, which is highly effective in breaking the extensive hydrogen-bonding network present in cellulose (Swatloski et al., 2002).

In the present study, DMAP was used as a catalyst in the succinoylation reaction of SCB cellulose in ionic liquid to improve modification efficiency. Usually, succinic anhydride reacts with cellulose O—H groups to form the monoester, as shown in Scheme 1. After cellulose was dissolved in BMIMCl, succinic anhydride and DMAP were added to the solution to achieve homogeneous reaction. The effects of DMAP dosage, reaction temperature, and reaction duration on DS of the succinylated cellulose are listed in Table 1.

The results in Table 1 clearly indicated that the DS of succinylated cellulose derivatives increased from 0.24 to 1.88 with an increment in dosage of DMAP/succinic anhydride from 0% to 8%. Obviously, DMAP could improve the efficiency of succinoylation reaction of cellulose in ionic liquid BMIMCl. However, further increasing in the DMAP dosage from 5% to 8% did not lead to substantial increments in DS. This is a satisfactory result because DMAP is a very expensive catalyst. Just as expected, a certain dosage of DMAP is necessary to achieve a high DS of succinylated celluloses.

Table 1
The degree of substitution (DS) of succinylated cellulose.

Sample	Succinoylation conditions[a]			DS
	DMAP/succinic anhydride (%)	Temperature (°C)	Reaction time (min)	
1	0	80	60	0.24
2	1	80	60	0.94
3	2	80	60	1.19
4	3	80	60	1.52
5	5	80	60	1.78
6	8	80	60	1.88
7	15	80	60	1.69
8	5	60	60	1.55
9	5	70	60	1.75
10	5	90	60	2.19
11	5	100	60	2.34
12	5	110	60	1.93
13	5	80	30	1.28
14	5	80	45	1.52
15	5	80	90	1.49
16	5	80	120	1.38

[a] Concentration of cellulose in ionic liquids during dissolution was 2.0% by weight and the molar ratio of succinic anhydride to anhydroglucose in cellulose was 4:1.

The increase in reaction temperature from 60 to 100 °C resulted in a DS increase from 1.55 to 2.34. The reason for this enhancement of the succinoylation with increasing temperature was probably due to the favourable effect of temperature on mobility of the reactant molecules, diffusion of succinic anhydride into the cellulosic molecules, and swell ability of the cellulose. In contrast to the increasing trend, further increase in the reaction temperature from 100 to 110 °C led to a decrease in the DS from 2.34 to 1.93. This phenomenon may be due to the partial degradation of both native and the formed succinylated cellulosic samples at a much higher temperature.

From the data shown in Table 1, DS of cellulose derivatives reached 1.28 within 30 min, 1.52 within 45 min, 1.78 within 60 min, indicating the positive effect of reaction time. However, as the reaction duration was further increase from 60 to 120 min, DS decreased from 1.78 to 1.38. This may indicate that a sufficient time may not have been given for a substantial increase in the succinoylation. Therefore, a reaction time of 60 min was considered as optimum for reaction condition.

3.2. FT-IR spectra

Fig. 1 shows the FT-IR spectra of unmodified cellulose (spectrum a) and succinylated cellulose sample 3 (spectrum b). The absorption at 3422, 2919, 1634, 1379, 1161, 1046, and 892 cm^{-1} are associated with native cellulose in the spectrum a. The strong absorption at 3422 cm^{-1} is due to stretching of O—H groups and that one at 2919 cm^{-1} to the C—H stretching. The peak at 1634 cm^{-1} corresponds to the bending mode of the absorbed water (Sun, Sun, & Tomkinson, 2004a). The band at 1379 cm^{-1} is assigned to the O—H bending. The absorption band at 1161 cm^{-1} relates to C—O stretching in celluloses. A strong peak at 1046 cm^{-1} arises from C—O—C pyranose ring skeletal vibration (Sun, Sun, Zhao, & Sun, 2004b). A sharp band at 892 is characteristic of β-glucosidic linkages between the sugar units (Gupta, Madan, & Bansal, 1987). In spectrum b of succinylated cellulose sample 3, the absorbances at 1732 and 1567 cm^{-1} provide the evidence of succinoylation. The band at 1732 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 1732 cm^{-1}. The band at 1567 cm^{-1} corresponds to the antisymmetric stretching of carboxylic anions (Yoshimura, Matsuo, & Fujioka, 2006). Moreover, from the spectra shown in Fig. 1, the intensity of the absorption band at 1161 cm^{-1} for C—O antisymmetric stretching in ester groups increased after succinoylation. This increment indicated the formation of an ester and carboxylic acid, which suggested that the monoester of succinylated cellulose was formed in BMIMCl ionic liquid under the condition given. In addition, the intensity of the peak at 1046 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 from1309.6 cm^{-1} in native cellulose and 750.5 cm^{-1} in regenerated cellulose from the ionic liquids. As expected, the absence of peaks at 1850 and 1780 cm^{-1} in spectra of succinylated cellulose confirmed that the products are free of the un-reacted succinic anhydride (Gu & Yang, 1998).

The effects of mass ratio of DMAP/succinic anhydride in cellulose, reaction temperature, and reaction time on the DS of cellulosic preparations were also investigated by the peak intensity of succinylated cellulose samples, and their spectra are given in Figs. 2–4. As shown in Fig. 2, an increase in mass ratio of DMAP/succinic

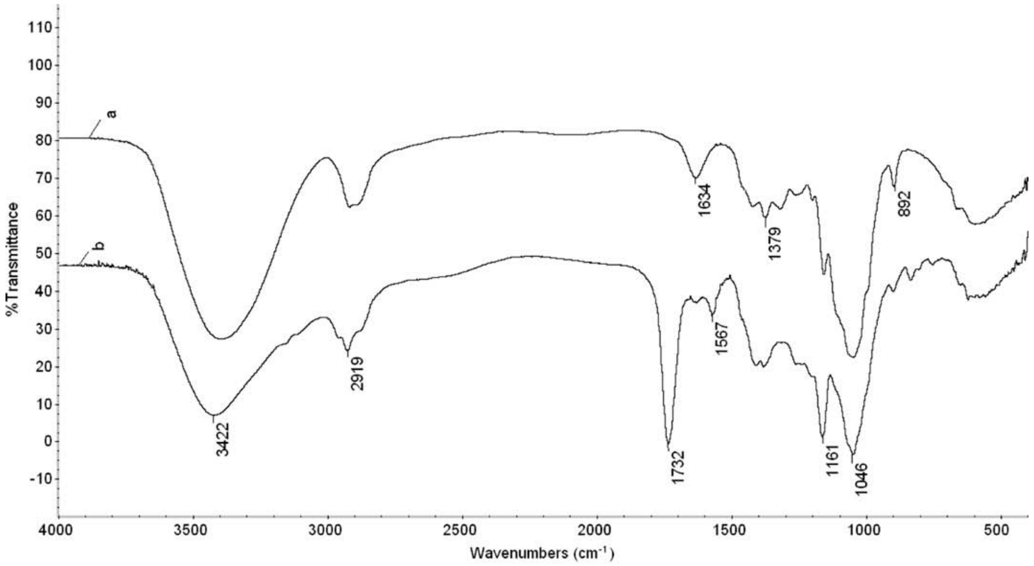


Fig. 1. FT-IR spectra of unmodification cellulose (spectrum a) and succinylated cellulose sample 3 (spectrum b).

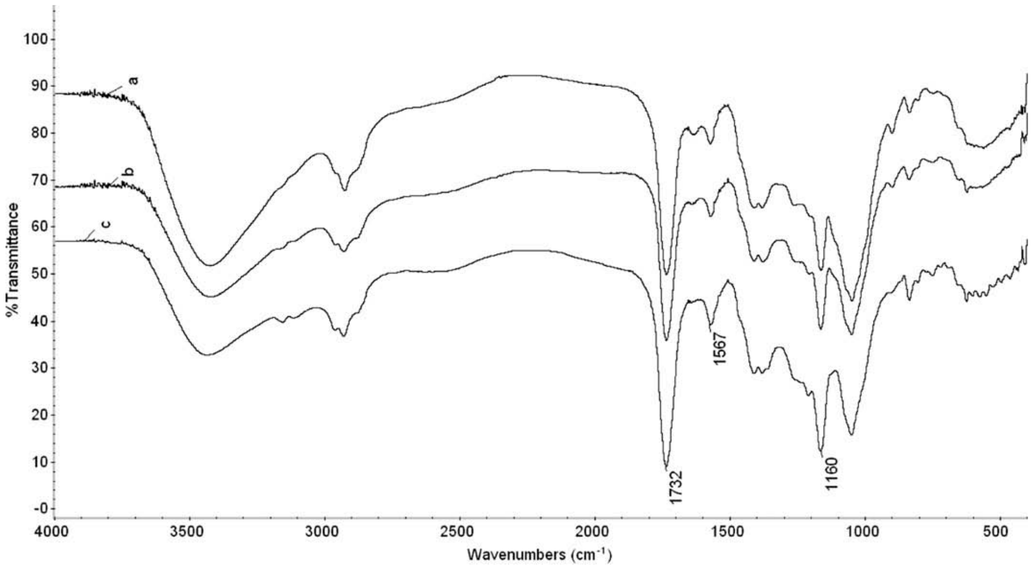


Fig. 2. FT-IR spectra of succinylated cellulose sample prepared with mass ratio of DMAP/succinic anhydride 0%, (spectrum a, sample 1), 3% (spectrum b, sample 4), and 8% (spectrum c, sample 6).

anhydride in cellulose from 0% (spectrum a, sample 1) to 3% (spectrum b, sample 4), and to 8% (spectrum c, sample 6) led to an increment in the intensity of the bands at 1732 cm^{-1} for C=O stretching in ester and carboxyl groups, 1567 cm^{-1} for antisymmetric stretching of carboxylic anions, 1160 cm^{-1} for C—O antisymmetric stretching, corresponding to an increase of the DS in Table 1. Similarly, noticeably increasing trends of the three bands at 1732, 1568, and 1161 cm^{-1} observed in Fig. 3 with an increment in reaction temperature from 60 °C (spectrum a, sample 7) to 70 °C (spectrum b, sample 8), and to 90 °C (spectrum c, sample 9) corresponded to the increasing values of DS in Table 1. In Fig. 4, the intensity of peaks at 1732, 1572, and 1161 cm^{-1} obviously increased with an increase of reaction time from 30 min (spectrum a, sample 12), to 45 min (spectrum b, sample 15), and to 60 min (spectrum c, sample 5), which was paralleled to the DS of succinoylation.

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

The succinoylation reaction of cellulose was also studied by solid-state CP/MAS ^{13}C NMR spectroscopy. The native cellulose (spectrum a) and succinylated cellulose sample 5 (spectrum b) are shown in Fig. 5. In spectrum a, all noticeable signals are distributed in the region between 50 and 110 ppm for the carbons of carbohydrate moiety. The signals at 101.9 (C-1), 85.9 (C-4 of crystalline cellulose), 80.3 (C-4 of amorphous cellulose), 71.9 (C-5), 68.6 (C-2 and C-3), 61.8 ppm (C-6 of crystalline cellulose) and 59.5 (C-6 of amorphous cellulose) are all observed (Bardet, Foray, & Tran, 2002; Chang & Chang, 2001). In spectrum b, the signal at 85.9 ppm for C-4 of crystalline cellulose disappeared in spectrum b, and the signal for C-6 shifted from 61.8 ppm in spectrum a to 60.8 ppm in spectrum b, which indicated that the crystalline structure of the cellulose was completely disrupted by breaking hydrogen bonds

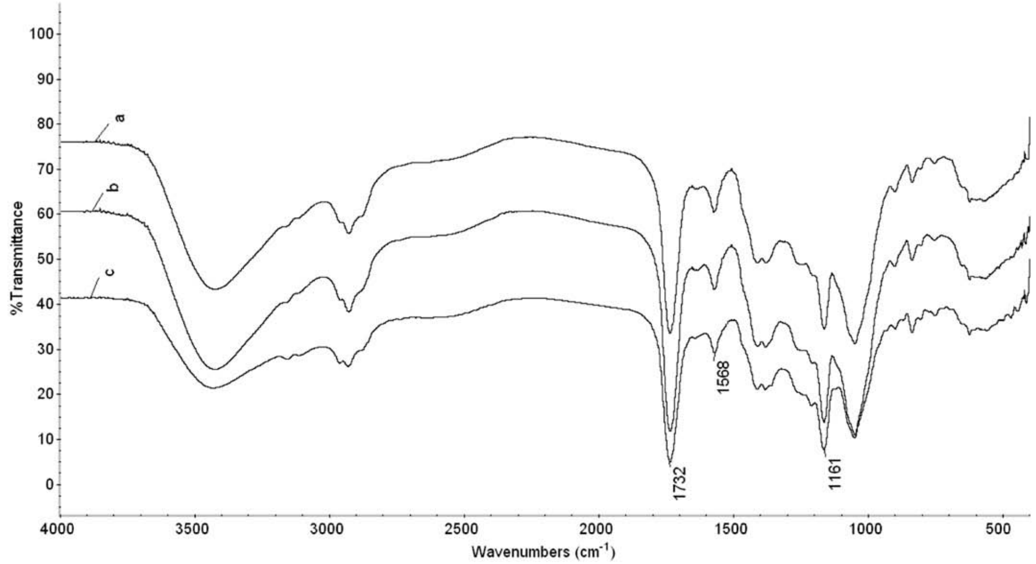


Fig. 3. FT-IR spectra of succinylated cellulose sample prepared for 60 °C (spectrum a, sample 7), 70 °C (spectrum b, sample 8), and 90 °C (spectrum c, sample 9).

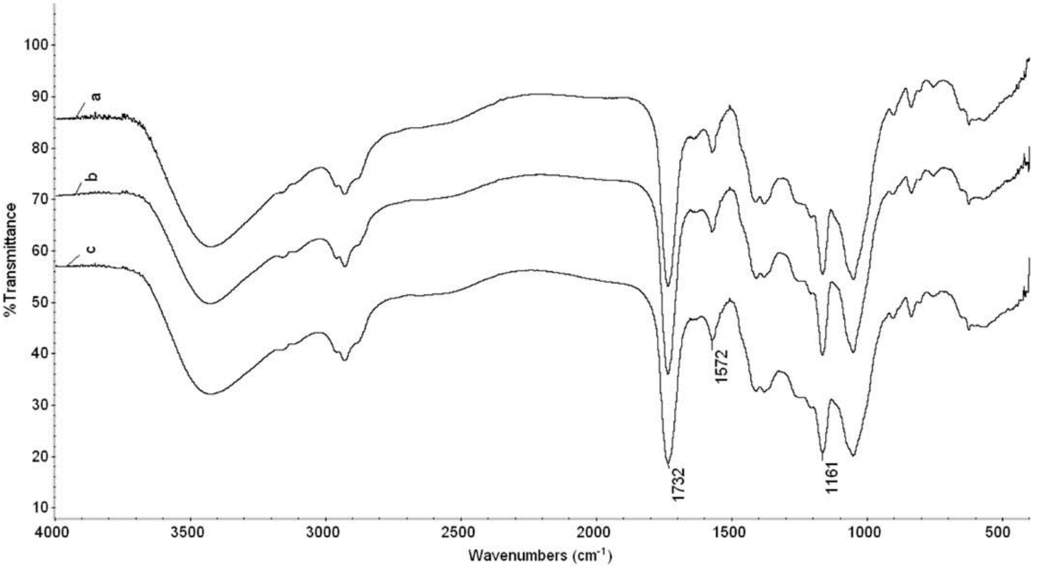


Fig. 4. FT-IR spectra of succinylated cellulose sample prepared for 30 min (spectrum a, sample 12), 45 min (spectrum b, sample 15), and 60 min (spectrum c, sample 5).

in a-cellulose during the dissolution and functionalization (Maunu, 2002).

The three free hydroxyl groups at C-6, C-2, and C-3 positions are the main reactive sites in cellulose. As shown in Fig. 5, the intensity of the signal for C-6 decreased after succinoylation, and that at 68.6 ppm for C-2 and C-3 also decreased, which indicated the succinoylation reaction occurred at C-6, C-2, and C-3 positions. Evidently, the presence of the signals of the carboxylic group at 170.5 ppm and the methylene group at 26.5 ppm provided evidence of succinoylation, which indicated the reaction shown in Scheme 1 does occur (Boonstra, Pizzi, Tekely, & Pendlebury, 1996).

3.4. Thermal analysis

The thermal characteristics of SCB cellulose and succinylated cellulosic derivatives were also studied by TGA and DSC in N_2 atmosphere. Fig. 6 shows the TGA and DSC thermograms of unmodification cellulose (a) and succinylated cellulose sample 6 (b) prepared with the DMAP as a catalyst. As can be seen from the TGA plot of native and succinylated cellulosic sample 6 in Fig. 6, there is a very slight mass loss until a temperature of 230 and 210 °C for native cellulose and succinylated cellulose sample, respectively. On further heating there is a sharp weight loss. In Fig. 6(a), the native cellulose starts to decompose at 234 °C. The succinylated cellulose sample exhibits a lower onset temperature for decomposition, but gives a higher char yield on pyrolysis, indicated by the high residuary masses after the decomposition step. At 50% weight loss, the decomposition temperature occurs at 328 °C for native cellulose and 282 °C for succinylated cellulose sample. This trend of decreasing decomposition temperature implied that the thermal stability of succinylated cellulose is lower than that of the native cellulose. Similar observations have been reported during the dissolution and modification of cellulose in the ionic liquid (Liu et al., 2007; Swatloski et al., 2002). However, the thermal sta-

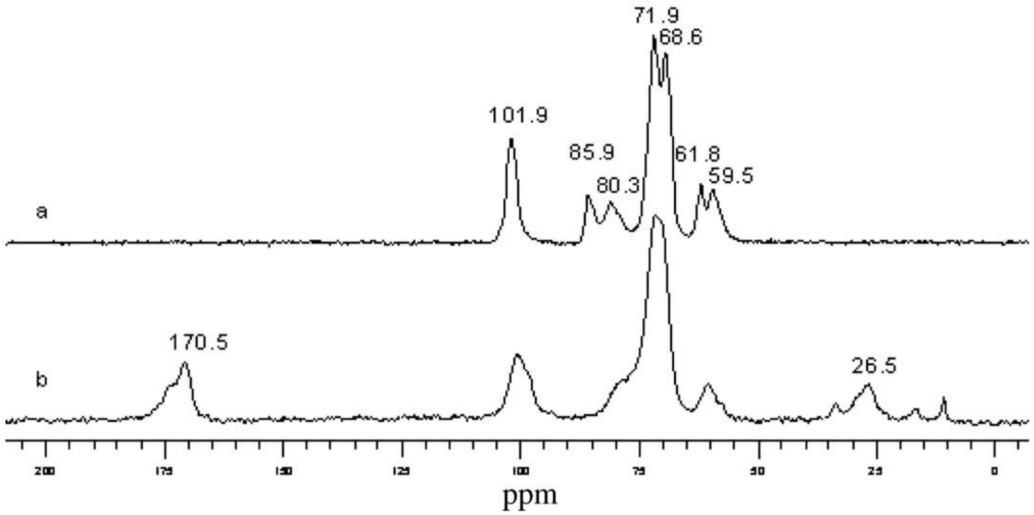


Fig. 5. Solid state CP/MAS ^{13}C NMR spectra of unmodified cellulose (spectrum a) and succinylated cellulose sample 5 with DMAP as a catalyst (spectrum b).

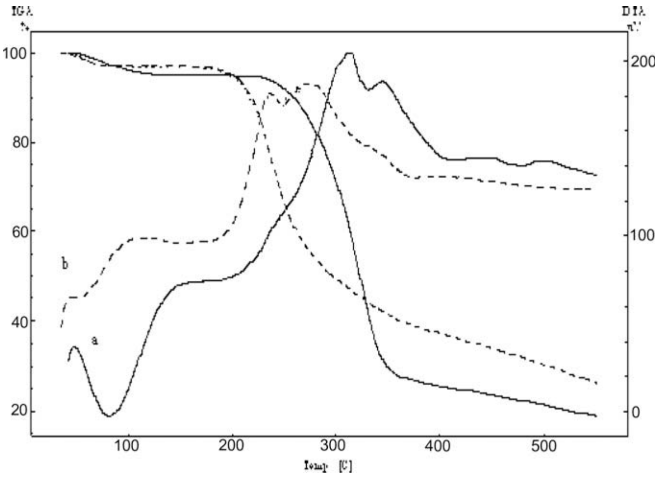


Fig. 6. Thermograms of native cellulose (spectrum a) and succinylate cellulose sample 6 (spectrum b).

bility to over 200 °C of the succinylated cellulose is sufficient to use it as novel and biodegradable absorbents for metal ions from waste water (Gu & Yang, 1998).

DTA was utilized to examine the transitions of the polymers as affected by modification. In particular, it is used to investigate the possibility of interaction between both components and measure the extent of disruption of the hydrogen bonds as well as quantify the heat energy flows (Fringant, Desbrieres, & Rinaudo, 1996). As shown in Fig. 6, the exothermic peak was asymmetric due to overlapping endothermic response from both unreacted cellulose and the reaction product (Zhuang & Steiner, 1993). The exothermic peak, which represents heat release from the product, was observed at a maximum temperature of 338 °C for unmodified cellulose and 249 °C for succinylated cellulose, respectively, which indicated again that the degradation of cellulose occurred during the dissolution and succinoylation.

In summary, the succinoylation of cellulose was successfully carried out with succinic anhydride using BMIMCl as solvent in the presence of DMAP. It was found that DMAP substantially accelerated the rate of reaction. The present method has obvious advantages on homogeneous chemical reaction. The DS of succinylated cellulose derivatives ranged from 0.24 to 2.34, which indicated that DS could be controlled by varying the condition of reaction, such as reaction temperature, reaction time and dosage of catalyst. The DS of succinylated cellulosic samples increased with the increment of reaction temperature from 60 to 100 °C, reaction time from 30 to 60 min and the weight ratio of DMAP/succinic anhydride from 0% to 8%. FT-IR and solid-state CP/MAS ^{13}C NMR spectroscopies provided the evidence of succinoylation reaction, indicating that the reaction at C-6, C-2 and C-3 positions of the cellulose occurred. The thermal stability of the succinylated cellulose decreased upon chemical modification.

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