

Homogeneous modification of sugarcane bagasse cellulose with succinic anhydride using an ionic liquid as reaction medium

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Abstract—The homogeneous chemical modification of sugarcane bagasse cellulose with succinic anhydride using 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid as a reaction medium was studied. Parameters investigated included the molar ratio of succinic anhydride/anhydroglucose units in cellulose in a range from 2:1 to 14:1, reaction time (from 30 to 160 min), and reaction temperature (between 60 and 110 °C). The succinylated cellulosic derivatives were prepared with a low degree of substitution (DS) ranging from 0.071 to 0.22. The results showed that the increase of reaction temperature, molar ratio of SA/AGU in cellulose, and reaction time led to an increase in DS of cellulose samples. The products were characterized by FT-IR and solid-state CP/MAS ¹³C NMR spectroscopy, and thermal analysis. It was found that the crystallinity of the cellulose was completely disrupted in the ionic liquid system under the conditions given. The data also demonstrated that homogeneous modification of cellulose with succinic anhydride in AmimCl resulted in the production of cellulosic monoester. The thermal stability of the succinylated cellulose decreased upon chemical modification.

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1. Introduction

Sugarcane bagasse (SCB), 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. About 54 million dry tons of bagasse is produced annually throughout the world.¹ The bagasse can be used as a fuel for the boilers by the sugar factory or as a raw material for the manufacture of pulp and paper products, various types of building boards, and certain chemicals.^{2,3}

Cellulose, the most abundant of all naturally occurring substances, is the principal structural cell wall component of all major plants and accounts for about a half of the total bagasse. It is nontoxic, renewable, biodegradable and modifiable, and has great potential as an excellent industrial material.^{3–5} Chemical modification of cellulose is one method for the production of value-added products. It is based on reactions of the free hydroxyl groups in the anhydroglucose units (AGU), resulting in the production of cellulose derivatives. However, the intrinsic lack of solubility of native cellulose in water and most organic solvent systems constitutes a major obstacle for cellulose homogeneous modification. The efficient dissolution of cellulose is a long-standing goal in cellulose research and development.⁶ A number of solvent systems, such as DMAc/

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LiCl, DMF/N₂O₄, NMNO, and some molten salt hydrates like LiClO₄·3H₂O, have been found to be efficient for cellulose dissolution. Homogeneous cellulose derivatizations, such as esterification, etherification, and other reactions, have also been reported in these solvents.^{6–10} However, there remain limitations such as toxicity, cost, difficulty of solvent recovery, or instability in processing.

In recent years, the application of ionic liquids (ILs) as alternative solvents and reaction media for a wide variety of synthetic processes has received increasing interest around the world.^{11,12} Properties of ILs, including low melting points, wide liquid ranges, and lack of vapor pressure, have encouraged researchers to explore known processes or chemical reactions using ILs in place of volatile organic solvents. In 2002, Swatloski et al.¹³ firstly reported that 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) could be used as a nonderivatizing solvent for cellulose, and the high chloride concentration and activity in ILs was found to play an important role in cellulose dissolution. However, the relatively high melting point of [C₄mim]Cl (approximately 80 °C) limits its application as a solvent or reaction medium. In 2003, 1-allyl-3-methylimidazolium chloride (AmimCl) IL, which has a low melting point (~17 °C), was synthesized and proved to have outstanding capability for dissolving cellulose.¹⁴ The chemical structure of AmimCl is shown in Chart 1. It is worth noticing that one substituent on nitrogen is alkenyl instead of saturated alkyl. As a result this IL has a lower melting point and maintains a higher thermal stability compared to other ILs substituted by saturated alkyl containing the same number of carbon atoms.¹⁰ These properties make AmimCl a promising reaction medium for cellulose functionalization. Homogeneous acetylation of cellulose with acetic anhydride in AmimCl has been successfully investigated.¹⁰ As far as the authors are aware, succinylation of cellulose using ILs as reaction media has not been reported. We therefore investigated the possibility of homogeneous cellulose succinylation in ILs. In this work, succinylation conditions of SCB cellulose in AmimCl IL, including the molar ratio of succinic anhydride (SA)/AGU in cellulose between 2:1 and 14:1, reaction temperature from 60 to 110 °C, and reaction time from 30 to 160 min, were investigated. The extent of succinylation was measured by the DS of cellulose derivatives. The modified cellulosic samples were then characterized by FT-IR and solid-state CP/MAS ¹³C NMR as well as thermal analysis.

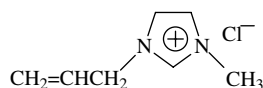


Chart 1. Chemical structure of the ionic liquid (1-allyl-3-methylimidazolium chloride).

2. Results and discussion

2.1. Modification and the degree of substitution

The yield of cellulose was found to be 49.6% of the dry SCB. The neutral sugar composition of cellulose showed that glucose was the predominant sugar component, comprising 94.8% of the total sugars, indicating a relatively high content of cellulose. Small amounts of non-cellulosic sugars, such as xylose (2.8%), galactose (1.5%), mannose (0.8%), and arabinose (0.6%), were also observed, indicating that the cellulosic preparation contained small quantities of residual hemicelluloses. The intrinsic viscosity, degree of polymerization, and molecular weight of the native cellulosic preparation were determined to be 378 mL g⁻¹, 1277, and 206,800 g mol⁻¹, respectively. In comparison, treatment of the cellulosic preparation in AmimCl at 80 °C for 10 h with a cellulose to AmimCl weight ratio of 2.0% resulted in a substantial degradation of cellulose macromolecules under the dissolving process given. This was shown by a reduction in its intrinsic viscosity, degree of polymerization, and molecular weight to 286 mL g⁻¹, 934, and 151,280 g mol⁻¹, respectively. In this case, the high chloride concentration and activity in ILs are highly effective in breaking the extensive hydrogen-bonding network present in cellulose, and play an important role in cellulose dissolution. Above the critical temperature, the ion pair in AmimCl dissociated into individual Cl⁻ and Amim⁺ ions. Free Cl⁻ ions, which are nonhydrated and in a concentration of approximately 20%, then bonded to the cellulose hydroxyl protons, and the free cations associated with the cellulose hydroxyl oxygen. This disrupted the hydrogen bonding network of cellulose and promoted its dissolution.^{15,16} ¹³C NMR studies of cellulose in ILs also showed that the cellulose was disordered in this medium, indicating that its hydrogen bonding network was indeed disrupted.¹⁷ In addition, we also found that the DP of the cellulose decreased from 1310 to 751 (data not shown) when [C₄mim]Cl was used as a solvent, suggesting that the extent of degradation of cellulose in AmimCl was lower than in [C₄mim]Cl. A similar observation on the degradation of cellulose in ILs has also been reported by Ren et al.¹⁴ The authors reported that the DP of regenerated cellulose decreased from 640 to 460 in AmimCl and to 360 in [C₄mim]Cl.

Modification of cellulose with linear chain anhydrides produces an undesired by-product, namely the corresponding carboxylic acid. This acid must be removed from the reaction following modification. However, modification with cyclic anhydrides such succinic anhydride does not yield a by-product. Furthermore, the reaction results in a pendant carboxylic moiety attached to the cellulose via a covalent ester bond, providing a site upon which further reactive chemistry is possible.

More importantly, since acylation of cellulose with a cyclic anhydride would esterify one hydroxyl group per anhydride reached, the net result would be the generation of one carboxylic acid group of equal or greater hydrophilicity of hydrogen bonding water molecules. Therefore, depending on the cellulose ester yield, the modified cellulose has a significant capacity for absorption of water as degradable absorbents.¹⁸ In addition, the esterified cellulose bearing a carboxyl group could also be used for the adsorption of metal ions from industrial wastewater.¹⁹ In the present study, the succinylation of the cellulose was carried out using AmimCl as solvent in the absence of any catalysts to esterify cellulose O–H groups. Succinic anhydride reacts with cellulose to form the monoester as shown in Scheme 1.²⁰ Solid succinic anhydride, cellulose, and the resulting products could be all dissolved in AmimCl and, therefore, a homogeneous succinylation reaction could be achieved in AmimCl IL.

The effects of reaction time, reaction temperature, and the molar ratio of SA/AGU on the succinylation rate of cellulose were examined. The DS of the succinylated cellulose under various conditions is listed in Table 1. The data show (Table 1) that under the conditions of a molar ratio of 6:1 and reaction time of 60 min, an increase of reaction temperature from 60 to 80, 90, 100, and 110 °C led to an increment in the DS of the products from 0.071 to 0.10, to 0.13, to 0.14, and to 0.15, respectively. The reaction can be accelerated by increasing the reaction time. For example, a DS of 0.086 was achieved at 80 °C for 30 min, whereas with the same molar ratio, a DS of 0.15 was reached at 80 °C for 120 min. Increasing the molar ratio of succinic anhydride/AGU from 2 to 10 also resulted in an increment in the DS of the products from 0.080 to 0.20. When the molar ratio increased from 10 to 14, there was only a minimal increase in DS (0.02). It is very likely that excess succinic anhydride had no significant effect on the succinylation rates of cellulose in AmimC. These results indicated that it is possible to control the DS value by stoichiometric methods and by controlling the temperature and reaction duration.

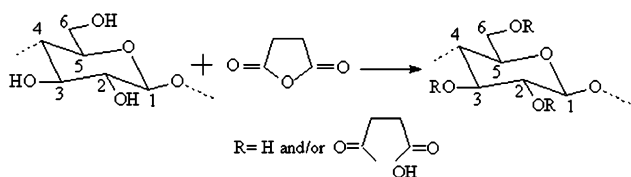
It should be noted that the efficiency of the esterification decreased with the increasing chain length of the anhydrides. For example, cellulose acetates with a degree of substitution in the range from 2.5 to 3.0 are accessible within 2 h at 80 °C in a completely homogeneous procedure. On the other hand, the esterification of cellulose with the fatty acid chloride, lauroyl chloride,

leads to cellulose laurates with DS decreasing to 0.34–1.54 under the same conditions in ILs.²¹ In other words, a steric effect on the uncatalyzed acylation reaction should be indicated, where increasing alkyl chain length of the anhydride results in a lower cellulose ester yield and DS, as occurred in our present study on the succinylation of sugarcane cellulose in AmimC. On the other hand, the succinylated cellulose with low DS values may reduce the formation of diester by cross-links of the free carboxylic group of monoesters with other hydroxyl groups of cellulose. These low DS cellulose succinates could be used as metal-ion binders and in the production of composites, especially biodegradable and/or environmentally degradable composites.

2.2. FT-IR spectra

Figure 1 shows the FT-IR spectra of unmodified cellulose (spectrum 1) and succinylated cellulose sample 14 (spectrum 2). In the two spectra, the absorbances at 3412, 2916, 1638, 1382, 1165, 1046, and 895 cm^{-1} are associated with native cellulose.^{22,23} In spectrum 2 of succinylated cellulose sample 14, the absorbance at 1727 and 1568 cm^{-1} provides the evidence of succinylation. The former band is indicative of absorption by carbonyl groups in carboxyl and esters, and the latter band derives from antisymmetric stretching of carboxylic anions.²⁰ In general, the absorption by carbonyl bonds in esters gives a peak at 1750 cm^{-1} , and one in carboxylic acids exhibits a band at 1712 cm^{-1} .^{24,25} The two bands are strongly overlapped and therefore resulted in a peak centered at 1727 cm^{-1} . Moreover, the intensity of the absorption band at 1165 cm^{-1} for C–O antisymmetric stretching in ester groups increased after succinylation. These results indicated the formation of an ester and carboxylic acid, which suggested that the monoester of succinylated cellulose was formed in AmimCl IL under the conditions given. In addition, the intensity of the broad peak at 1041 cm^{-1} for C–O–C bond stretching was slightly decreased due to the degradation of cellulose during dissolution and succinylation.

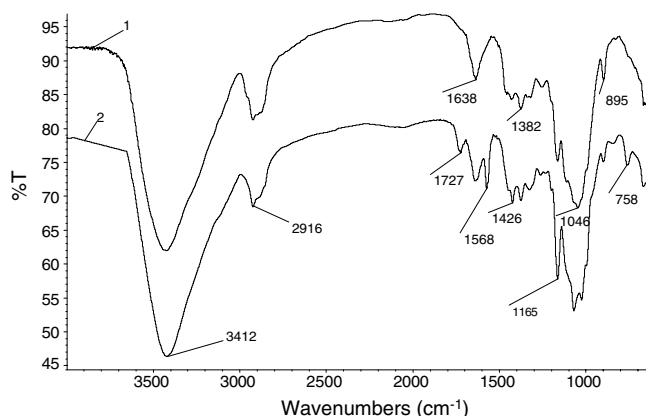
Modifying lignocellulosic fibers and wood with cyclic anhydrides such as succinic, maleic, or phthalic anhydrides in organic solvents has been suggested as a method of introducing new material properties.²⁶ Succinylation of cellulose and lignocellulosic fibers in organic solvents has been reported previously,²⁷ and the authors indicated that every succinic anhydride molecule reacting on the fiber rendered one carboxylic acid group, that is, one attached succinic acid will result in one carboxylic acid (cellulose succinate half-esters). However, there remain limitations such as toxicity, cost, difficulty as solvent recovery, or instability in processing. In this article, we have introduced the succinylation of cellulose in ionic liquids. The side reactions consist of



Scheme 1. Reaction of SCB cellulose with succinic anhydride.

Table 1. DS of succinylated cellulose using AmimCl as solvent

| Succinylation conditions | | | | Succinylated cellulose | |
|----------------------------|--------------------------|------------------|---------------------|------------------------|-------|
| Cellulose ^a (%) | Molar ratio ^b | Temperature (°C) | Reaction time (min) | Sample no. | DS |
| 2.0 | 6:1 | 60 | 60 | 1 | 0.071 |
| 2.0 | 6:1 | 80 | 60 | 2 | 0.10 |
| 2.0 | 6:1 | 90 | 60 | 3 | 0.13 |
| 2.0 | 6:1 | 100 | 60 | 4 | 0.14 |
| 2.0 | 6:1 | 110 | 60 | 5 | 0.15 |
| 2.0 | 6:1 | 80 | 30 | 6 | 0.086 |
| 2.0 | 6:1 | 80 | 90 | 7 | 0.12 |
| 2.0 | 6:1 | 80 | 120 | 8 | 0.15 |
| 2.0 | 6:1 | 80 | 160 | 9 | 0.16 |
| 2.0 | 2:1 | 80 | 60 | 10 | 0.080 |
| 2.0 | 4:1 | 80 | 60 | 11 | 0.098 |
| 2.0 | 8:1 | 80 | 60 | 12 | 0.13 |
| 2.0 | 10:1 | 80 | 60 | 13 | 0.20 |
| 2.0 | 12:1 | 80 | 60 | 14 | 0.21 |
| 2.0 | 14:1 | 80 | 60 | 15 | 0.22 |

^a Cellulose/AmimCl by weight (w/w).^b Molar ratio of succinic anhydride/AGU in cellulose.**Figure 1.** FT-IR spectra of unmodified cellulose (spectrum 1) and succinylated cellulose sample 14 (spectrum 2).

the hydrolysis of succinic anhydride and cellulosic succinate. Furthermore, the free carboxylic group of monoesters can react with other hydroxyl groups of cellulose to form cross-links and diesters. Interestingly, it was found that cellulose reacts with dicarboxylic acid anhydride to form monoester in the conditions used, and the absence of peaks at 1850 and 1780 cm^{-1} in the FT-IR spectra of the succinylated cellulose confirmed that the products are free of the unreacted succinic anhydride. However, it is possible that, with longer reaction time, cellulose-attached succinic acid may continue to react with hydroxyl group in the near surroundings to form diesters.

A number of previous studies have found that cellulose can be dissolved without derivation in high concentrations using ILs as the solvent.^{10,14,15,21,28} FT-IR spectra of cellulose before and after regeneration showed that the two spectra are quite similar. No new peaks appear in the regenerated sample, indicating that no chemical reactions occurred between IL and cellulose during the dissolution and coagulation processes of the

cellulose.¹⁵ In addition, no side reactions between IL and celluloses or the reaction agent such as acetic anhydride occurred. After only a simple distillation or freeze drying of recycled AmimC, AmimC with high purity was obtained that had the same efficiency to dissolve cellulose compared to the starting IL. In this case, the removal of water is an essential prerequisite to avoid side reactions. Furthermore, ^1H and ^{13}C NMR studies of the IL after recycling also showed no differences compared to the starting solvent,²¹ revealing again that no side reactions between IL and celluloses or the reaction agent occurred during the dissolution and modification of cellulose in IL.

The effects of reaction temperature, reaction time, and molar ratio of SA/AGU on the DS of cellulosic preparations were also investigated by the peak intensity of succinylated cellulose samples, and their spectra are given in Figures 2–4. As shown in Figure 2, an increase of reaction temperature from 60 to 90, and to 110 $^{\circ}\text{C}$ led to an increment in the intensity of the bands at 1725 cm^{-1} for C=O stretching, 1572 cm^{-1} for antisymmetric stretching of carboxylic anions, and 1166 cm^{-1} for C–O antisymmetric stretching, corresponding to an increase of the DS values in Table 1. In Figure 3, the intensity of peaks at 1727, 1576, and 1165 cm^{-1} obviously increased with an increase of reaction time, which is paralleled to the DS of succinylation. Similarly, noticeably increasing trends of the three bands at 1726, 1575, and 1169 cm^{-1} observed in Figure 4 with an increment in the molar ratios are paralleled to the increasing values of DS in Table 1.

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

In the present study, the succinylation reaction of cellulose was also studied by solid-state CP/MAS ^{13}C

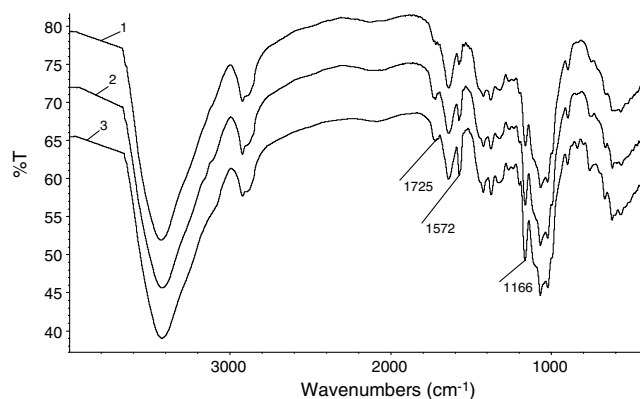


Figure 2. FT-IR spectra of succinylated cellulose prepared at 60 °C (spectrum 1, sample 1), 90 °C (spectrum 2, sample 3), and 110 °C (spectrum 3, sample 5).

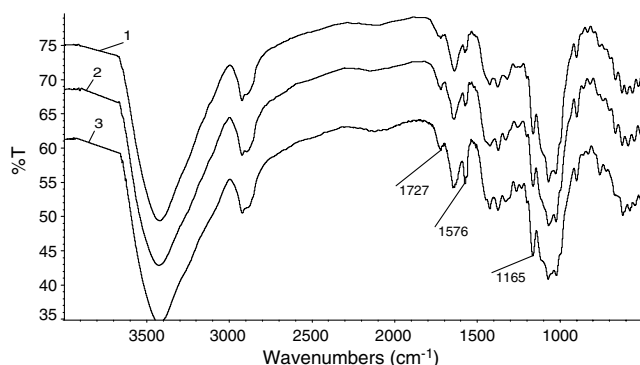


Figure 3. FT-IR spectra of succinylated cellulose prepared for 30 min (spectrum 1, sample 6), 90 min (spectrum 2, sample 7), and 160 min (spectrum 3, sample 9).

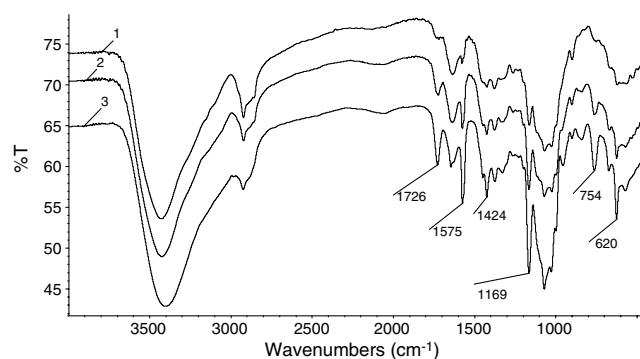


Figure 4. FT-IR spectra of succinylated cellulose prepared with molar ratio of succinic anhydride/anhydroglucose 2:1 (spectrum 1, sample 10), 10:1 (spectrum 2, sample 13) and 14:1 (spectrum 3, sample 15).

NMR spectroscopy, and the spectra of unmodified cellulose (spectrum a) and succinylated cellulose sample 12 are shown in Figure 5. In spectrum a, all noticeable signals are distributed in the region between 50 and 110 ppm for the carbon atoms of the carbohydrate moiety. The signals at 104.8 (C-1), 88.8 (C-4 of crystalline

cellulose), 83.6 (C-4 of amorphous cellulose), 74.7 (C-5), 72.4 (C-2 and C-3), and 64.5 ppm (C-6) have all been reported before.^{29,30} However, the signal at 88.8 ppm for C-4 of crystalline cellulose disappeared in spectrum b, and the signal for C-6 shifted from 64.5 ppm in spectrum a to 62.8 ppm in spectrum b, which indicated that the crystalline structure of the cellulose was completely disrupted by breaking hydrogen bonds in α -cellulose during the dissolution and functionalization.³¹ In other words, in the dissolution process, IL rapidly broke intermolecular and intramolecular hydrogen bonds and destroyed the original crystalline form. Evidently, the presence of the signals of the carboxylic group at 176.5 ppm and the methylene group at 29.3 ppm provided evidence of succinylation,³² which indicated that the reaction shown in Scheme 1 does occur.

2.4. Thermal analysis

The effect of succinylation 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⁻¹ under nitrogen flow. Figure 6 shows the TGA and DSC thermograms of unmodified cellulose (1) and succinylated cellulose sample 5 (2). As can be seen from the figure, the native cellulose starts to decompose at 234 °C, while the succinylated cellulose sample 5 begins to decompose at 213 °C. At 50% weight loss, the decomposition temperature occurs at 339 °C for native cellulose and 319 °C for sample 5. These trends 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 by Swatloski et al.¹³ during the dissolution of cellulose in the ionic liquid [C₄mim]Cl. The results showed that the original dissolving pulp started to decompose at 350–360 °C, whereas the regenerated

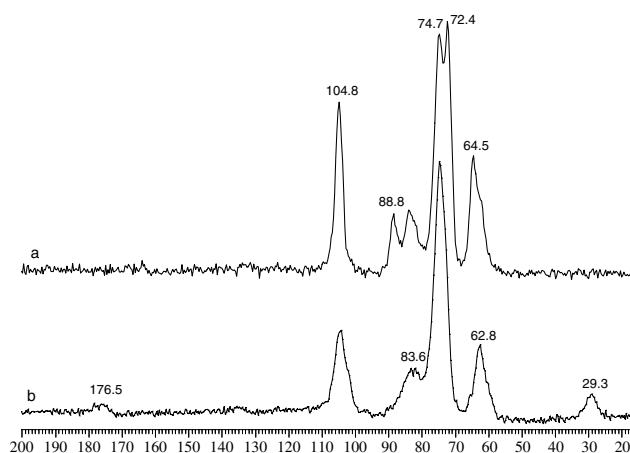


Figure 5. Solid-state CP/MAS ¹³C NMR spectra of unmodified cellulose (spectrum a) and succinylated cellulose sample 12 (spectrum b).

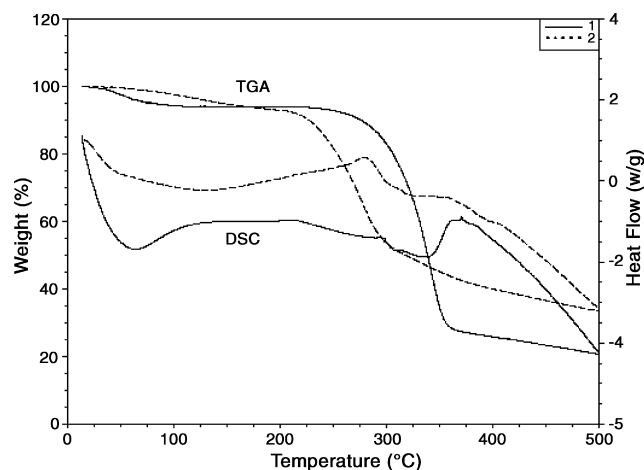


Figure 6. The thermograms of unmodified cellulose (1) and succinylated cellulose sample 5 (2).

cellulose from the IL began to decompose at 280 °C. However, the thermal stability to over 200 °C of the succinylated cellulose obtained in this study is sufficient to use it as novel and biodegradable absorbents for water and metal ions.

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.³³ The DSC curves of the unmodified cellulose and succinylated cellulose sample 5 are also given in Figure 6. Notably, the exothermic peak was asymmetric due to overlapping endothermic response from both unreacted cellulose and the reaction product.³⁴ The exothermic peak, which represents heat released from the product, was observed at a maximum temperature of 362 °C for unmodified cellulose and 281 °C for sample 5, respectively, which indicated again that a degradation of cellulose occurred during dissolution and succinylation.

3. Conclusions

The succinylation of cellulose with succinic anhydride using AmimCl ionic liquid as solvent was successfully accomplished, and carboxylic groups were introduced into cellulose. The DS of cellulose derivatives ranged from 0.071 to 0.22 and increased with the increment of reaction temperature from 60 to 110 °C, reaction time from 30 to 160 min, and the molar ratio of succinic anhydride/AGU in cellulose in a range from 2:1 to 14:1. CP/MAS ¹³C NMR spectroscopy revealed that the succinylation of cellulose in AmimCl does occur. It should be noted that cellulose was also degraded during the dissolution and succinylation in the ionic liquid under the conditions used. The thermal stability of succinylated cellulose decreased after chemical modification.

4. Experimental

4.1. Materials

Sugarcane bagasse 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. Ionic liquid AmimCl was purchased from the Institute of Chemistry and Chemical Engineering, Hebei Normal University, and used as received. All other chemicals used were of analytical grade and purchased from Guangzhou Chemical Reagent Factory, China.

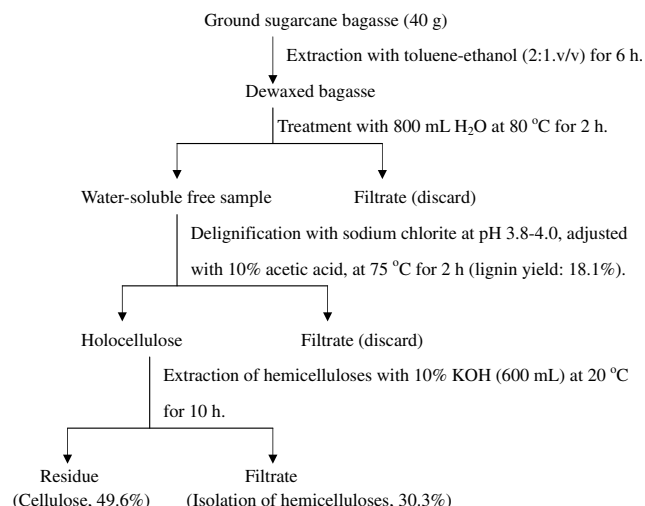
4.2. Isolation of native cellulose

To isolate the cellulose, the dewaxed bagasse (40 g) was first treated with distilled water (800 mL) at 80 °C for 2 h. The insoluble residue was delignified with sodium chlorite at pH 3.8–4.0, adjusted by 10% acetic acid, at 75 °C for 2 h. The residue was collected by filtration, 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 10% KOH (600 mL) at 20 °C for 10 h. After filtration, the residue (cellulose) was 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. The procedure for isolation of cellulose by delignification with acidified sodium chlorite is shown in Scheme 2.

4.3. Characterization of native cellulose

The neutral sugar composition of the SCB cellulose was determined by GC analysis of the corresponding alditol acetates. The sample (10 mg) was treated with 72% H₂SO₄ (0.125 mL) for 45 min at room temperature by agitation on a vortex mixture. The soln 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 et al.³⁵

Viscosity of the cellulose was measured by British Standard Methods for determination of limiting viscosity number of cellulose in dilute solutions, Part 1, cupri-ethylenediamine (CED) method (BS 6306, Part 1, 1982). The viscosity average DP (degree of polymerization) of the cellulose was estimated from their intrinsic viscosity $[\eta]$ in CED hydroxide solution, $P^{0.90} = 1.65[\eta]/\text{mL g}^{-1}$, where P is an indeterminate average DP.³⁶ Molecular weight (M_w) of the cellulose was then calculated from P by multiplication by 162, the M_w of an AGU.



Scheme 2. General procedure for isolation of cellulose from sugarcane bagasse.

4.4. Succinylation of SCB cellulose

The succinic derivatives of cellulose containing free carboxylic groups were prepared by reaction of SCB cellulose with succinic anhydride in AmimCl. Dried cellulose (0.405 g, equaling to 0.0025 mol of AGU and 0.0075 mol of hydroxyl functionality in cellulose) was added to 20 g AmimCl in a three-necked flask, and the mixture of cellulose/AmimCl was stirred at 80 °C for up to 10 h to guarantee the complete dissolution of cellulose. Then, the flask was continuously purged with gaseous N₂. To the cellulose/AmimCl solution, 0.50 g (equaling to 0.0050 mol of succinic anhydride and 0.0050 mol of carboxyl functionality, molar ratio of succinic anhydride/AGU in cellulose 2:1), 1.00 g (0.01 mol of carboxyl functionality, molar ratio 4:1), 2.00 g (0.02 mol of carboxyl functionality, molar ratio 8:1), 2.5 g (0.025 mol of carboxyl functionality, molar ratio 10:1), 3.0 g (0.03 mol of carboxyl functionality, molar ratio 12:1), and 3.5 g (0.035 mol of carboxyl functionality, molar ratio 14:1) succinic anhydride, previously dissolved in 5 mL AmimCl, were added at the temperatures of 60, 80, 90, 100, and 110 °C, respectively. The mixture was heated in an oil bath under N₂ atmosphere with stirring for 30–160 min. After the required time, the resulting mixture was slowly poured into 300 mL of ethanol with stirring to stop the reaction. The solid was filtered, washed thoroughly with ethanol to eliminate ILs, unreacted anhydride, and by-products, and then dried in vacuum at 50 °C for 16 h.

4.5. Determination of the degree of substitution

The degree of substitution of cellulosic preparations was determined by back titration method.^{37,38} A known

weight of the sample was dissolved in 10 mL of 0.1 M 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:

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

where 162 g mol⁻¹ is the molar mass of an AGU, 100 g mol⁻¹ is the net increase in the mass of an AGU for each succinoyl substituted, *m* is the weight of the 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:

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

4.6. Characterization of the succinylated cellulosic preparations

The chemical structure of cellulose and succinic derivatives was evaluated by FT-IR and solid-state CP/MAS ¹³C NMR spectroscopy. 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 ¹³C 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 s. Each spectrum was obtained with an accumulation of 5000 scans.

Thermal stability of succinylated 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⁻¹ under nitrogen flow.

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