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Homogeneous synthesis of hemicellulosic succinates with high degree of substitution in ionic liquid

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ABSTRACT

Chemical modification is the most important means to obtain novel biopolymers and biomaterials from the abundant biomacromolecules. In this paper, hemicellulosic succinate, which is very important biomacromolecule for the preparation of functional materials, was homogeneously prepared in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid. The influence of reaction conditions used in this work on the degree of substitution (DS) was investigated, and the chemical structure and the thermal stability of hemicellulosic succinate were characterized by FT-IR and ^{13}C NMR spectroscopies as well as thermogravimetry. A high DS of up to 1.80 could be achieved at short time scale in [BMIM]Cl ionic liquid without any catalysts, which is probably due to the excellent dissolving capacity and catalytic effect of ionic liquid. These results indicate that ionic liquids open up totally new opportunities for chemically functionalization of hemicelluloses.

1. Introduction

Obtaining novel and functional biomaterials and biopolymers from biomass has attracted extensive attention because of the depletion of non-renewable petroleum-based resources. Hemicelluloses, being the second most abundant component of renewable biomass in nature, are usually non-toxic, biodegradable, biocompatible and show distinguishing and peculiar physico-chemical properties which definitely play a very important role in the preparation of functional biopolymers and biomaterials, and thus have spurred an increasing interest in recent years (Edlund, 2008; Lindblad, Sjoberg, Albertsson, & Hartman, 2007). Hemicelluloses have been proposed to be suitable biopolymers for preparation of bioactive and biomedical materials used in drug release systems and tissue engineering such as hydrogels, films and coatings (Grondahl, Eriksson, & Gatenholm, 2004; Hansen & Plackett, 2008; Lindblad, Ranucci, & Albertsson, 2001; Miyazaki et al., 2001). These potential applications and the unexploited functions will open up new window for the utilizations of hemicelluloses.

For exploiting novel functions and applications of hemicelluloses, many kinds of hemicellulosic derivatives have been developed by chemical modifications, for example, quaternized hemicelluloses (Ren, Sun, Liu, Cao, & Luo, 2007; Ren, Sun, Liu, Lin, & He, 2007), carboxymethyl hemicelluloses (Petzold, Schwikal, & Heinze, 2006; Ren, Peng, & Sun, 2008; Ren, Sun, & Peng, 2008; Ren, Xu, Sun, Peng, & Sun, 2008), lauroylated hemicelluloses (Ren, Peng, et al., 2008; Ren, Sun, et al., 2008; Ren, Xu, et al., 2008), acetylated hemicelluloses (Ren, Sun, Liu, Cao, et al., 2007; Ren, Sun, Liu, Lin, et al., 2007; Sun, Sun, & Sun, 2004; Sun, Sun, Zhao, & Sun, 2004), oleoylated hemicelluloses (Sun, Sun, & Sun, 2004; Sun, Sun, Zhao, et al., 2004) and succinoylated hemicelluloses (Sun, Min, & Sun, 2002; Sun, Sun, & Bing, 2002; Sun, Sun, Tomkinson, & Baird, 2003). The importance of succinoylated biomacromolecules and their potential applications have been increasingly emphasized, for example, water absorbing (Yoshimura, Matsuo, & Fujioka, 2006), removal of heavy metal ions (Kweon, Choi, Kim, & Lim, 2001), drug delivery (Rokhade et al., 2006), immobilization of bioactive molecules (Uyeda, 1969), and genetic attachment (Arita, Babiker, Azakami, & Kato, 2001; Salchert et al., 2004). These products also provide a reactive site upon which further modification can be carried out for other potential utilization for instance, conjugation of drugs, probes that are selected to monitor pharmacokinetics (Bruneel & Schacht, 1994; Schacht, Vermeersch, Vandoorne, Vercauteren, & Remon, 1985). In addition, the presence of carboxyl groups also enables the preparation of nano-biomaterials at the molecular level by self-assembly technology (Freudenberg et al.,

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2005). Succinoylation of hemicelluloses, which had been carried out in an aqueous solution and *N*,*N*-dimethylformamide/lithium chloride (DMF/LiCl) systems, was reported previously (Sun, Min, et al., 2002; Sun, Sun, et al., 2002; Sun et al., 2003). However, the prolonged reaction time or the relatively low degree of substitution (DS) indicated the low reaction efficiency of hemicelluloses with succinic anhydride.

Ionic liquids (ILs), which have been widely promoted as "green solvents", are attracting much attention for applications in the field of carbohydrate polymers due to their chemical stability, thermal stability, low vapor pressure and high ionic conductivity properties (Pinkert, Marsh, Pang, & Staiger, 2009). Homogeneous synthesis of functional carbohydrate polymers has been carried out in ILs, and high reaction efficiency can be achieved (Kubisa, 2005; El Seoud, Koschella, Fidale, Dorn, & Heinze, 2007). However, the applications of ionic liquids in preparation of functional biopolymers and materials from hemicelluloses are very limited. Completely homogeneous solutions of xylan-rich hemicelluloses had been obtained in ILs (Fukaya, Sugimoto, & Ohno, 2006), and the homogeneous chemical modifications of hemicelluloses such as the acetylation and the maleation were carried out in 1-butyl-3-methylimidazolium chloride [BMIM]Cl ionic liquid (Peng, Ren, & Sun, 2011; Ren, Sun, Liu, Cao, et al., 2007; Ren, Sun, Liu, Lin, et al., 2007). These results indicate that ILs will be desirable alternatives to conventional solvents in preparation of novel biopolymers and biomaterials from hemicelluloses. In continuation of our earlier efforts to explore efficient methods to functionalize hemicelluloses, we investigated the homogeneous succinoylation of hemicelluloses by using [BMIM]Cl ionic liquid as the reaction medium in this paper. The objective is to improve the reaction efficiency of succinoylation of hemicelluloses with succinic anhydride using IL as reaction medium, and present a more efficient process for the functionalization of hemicelluloses.

2. Experimental

2.1. Materials

Hemicelluloses were isolated using 10% KOH at 25 °C for 10 h with a solid to liquid ratio of 1:20 (g mL^{-1}) from holocellulose, which was obtained by the delignification of wheat straw with sodium chlorite in acidic solution (pH 3.7–4.0, adjusted by 10% acetic acid) at 75 °C for 2 h (Ren, Peng, et al., 2008; Ren, Sun, et al., 2008; Ren, Xu, et al., 2008). The sugar analysis showed the following sugar composition (relative molar percent): 82.3% xylose, 9.6% arabinose, 4.0% glucose, 2.4% galactose, 0.7% rhamnose, and 0.8% mannose. Uronic acids, mainly 4-*O*-methyl-D-glucuronic acid (MeGlcA), were present in a noticeable amount (3.9%). [BMIM]Cl ionic liquid was purchased from Shanghai Cheng Jie Chemical Co., Ltd. Succinic anhydride (SA) was purchased from Shaanxi Chemical Co., Ltd. Ethanol was purchased from Guangzhou Chemical Reagent Factory, China.

2.2. Homogeneous succinoylation of hemicelluloses in [BMIM]Cl ionic liquid

The typical procedure of homogeneous succinoylation of hemicelluloses with SA in [BMIM]Cl ionic liquid was shown as follows. Dry hemicelluloses (0.66 g) were added into ionic liquid (26.0 g) in a three-necked flask with a magnetic stirrer, and the mixture was stirred at 90 °C up to 1.5 h to guarantee complete dissolution of hemicelluloses under the protection of gaseous N_2. Then the required quantities of SA (the molar ratios of SA to anhydroxylose units in hemicelluloses were 2:1, 4:1, 6:1 8:1, 10:1, and 12:1) were added at 70, 80, 90, 100, 110, and 120 °C, and the reaction ran for 20, 40, 60, 80, 100, and 120 min, respectively. After the required time the mixture, which was cooled to room temperature, was precipitated with ethanol (95 wt%, 150 mL) under stirring for 60 min, and then centrifuged at 4000 rpm for 30 min. The precipitate was washed with ethanol (95 wt%, 150 mL) twice. Finally, the product was dried at 45 °C in a vacuum oven for 16 h. The succinoylation of hemicelluloses was performed in duplicate, with 4% standard error.

2.3. Determination of the DS of succinoylated hemicelluloses (SH)

The DS of SH was determined by the acidometric titration method (Bi, Liu, Wu, & Cui, 2008; Kwon et al., 1997; Ren, Peng, et al., 2008; Ren, Sun, et al., 2008; Ren, Xu, et al., 2008). Two procedures were performed to determine the DS of SH were as follows. (a) The purity of SH. SH (0.5 g) was dissolved with 10 mL of water and stirred. Followed by adding hydrochloric acid (1 M, 10 mL), the mixture was agitated to dissolve completely. Five drops of phenolphthalein indicator were added into the mixture, and then sodium hydroxide (1 M) was added dropwise with stirring until red color of the solution disappeared. Then, the mixture was poured into ethanol (95 wt%, 100 mL) under stirring and was left to settle for 15 min before the supernatant liquid was centrifuged. The precipitate was washed with 80% ethanol for four times and then washed again with ethanol (95 wt%, 100 mL). Finally, the products were dialyzed (cutoff = 3500 g mol^{-1}) with distilled water and then freeze-dried.

(b) Determination of DS of SH. The average value of DS was determined by acidometric titration. SH (0.05 g) was dissolved in the distilled water (50 mL) with a magnetic stirrer. The pH of the solution was adjusted to 8.00 by the addition of NaOH solution. Then the solution was titrated with H_2SO_4 (0.05 M) to pH 3.74. The DS was calculated based on the equations shown below:

$$a = \frac{m'}{m}$$

$$B = \frac{2MV}{am}$$

$$DS = \frac{132B}{1 - 100B}$$

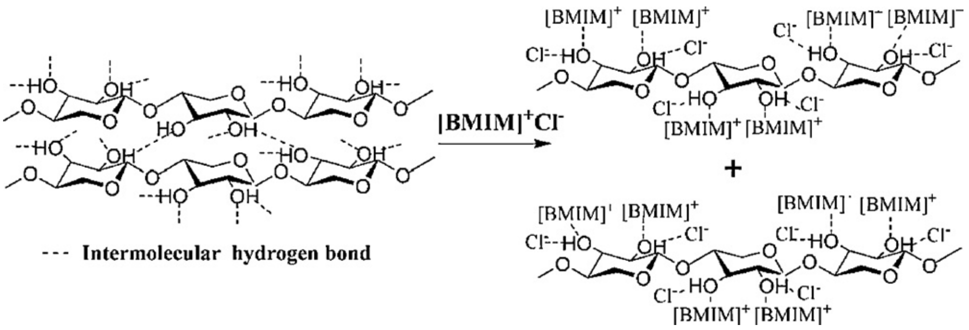
where a is the purity of SH. m and m' (g) are weights of SH after and before purified, 132 (g mol^{-1}) is the molar mass of a xylose unit, 100 (g mol^{-1}) is the net increase in the mass of a xylose unit for each SA substituted, M = molarity of H_2SO_4 used, V = L of H_2SO_4 used to titrate sample, B = mol g^{-1} of H_2SO_4 consumed per gram of the products. All the titrations were carried out in triplicates and standard deviations were less than 4.0%.

2.4. Chemical characterization of hemicelluloses and SH

FT-IR transmission spectra of hemicelluloses and SH were measured by using a Nicolet 750 spectrophotometer within the wavenumber range from 400 to 4000 cm^{-1}, and 1% finely ground samples were mixed with KBr to press a plate for measurement.

The solution-state ^{13}C NMR spectrum was obtained on a Bruker AVIII 400 MHz spectrometer operating in the FT mode at 100.6 MHz. The sample (80 mg) was dissolved in 1 mL D_2O. The ^{13}C NMR spectrum was recorded at 25 °C after 30,000 scans. A 30° pulse flipping angle, a 9.2 μs pulse width, a 1.36 s acquisition time, and 2 s relaxation delay time were used.

The molecular weights of hemicelluloses and SH were determined by gel permeation chromatography (GPC) on a PL aquagel-OH 50 column (300 mm × 7.7 mm, Polymer Laboratories Ltd.), calibrated with PL pullulan polysaccharide standard (average peak molecular weights of 783, 12,200, 100,000, 1,600,000).



Scheme 1. Proposed dissolution mechanism of hemicelluloses in [BMIM]Cl ionic liquid.

A flow rate of 0.5 mL/min was maintained. The eluent was 0.02 N NaCl in 0.005 M sodium phosphate buffer (pH 7.50). Detection was achieved with a Knauer differential refractometer. The column oven was kept at 30 °C. Hemicelluloses and SH were dissolved with 0.2 M NaCl in 0.005 M sodium phosphate buffer, pH 7.50, at a concentration of 0.1%.

Thermal analysis was performed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (Pyris Diamond TG/DTA, PE Instrument). The apparatus was continually flushed with nitrogen. The sample was weighed between 9 and 11 mg and was heated from room temperature to 600 °C at a heating rate of 10 °C/min.

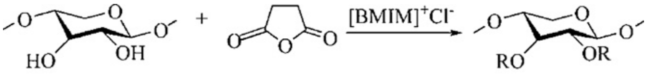
3. Results and discussion

3.1. Dissolution mechanism of hemicelluloses in ionic liquid

In view of the dissolution mechanism of cellulose in ILs, the proposed dissolving mechanism of hemicelluloses in ILs is brought forward. In the dissolving process of celluloses in ILs, the oxygen and hydrogen atoms of OH in the cellulose chain serve as electron donors and electron acceptors to form electron donor–acceptor (EDA) complexes with the cations and anions of the ionic liquids, respectively. This interaction efficiently destroyed the hydrogen bonds among different cellulose chains, resulting in the dissolution of cellulose in ionic liquids (Feng & Chen, 2008). Similarly, the hydroxyl groups in hemicelluloses can also form the electron donor–acceptor (EDA) complexes with ILs, thus resulting in the homogeneous hemicelluloses solution (Fukaya et al., 2006). Scheme 1 shows the proposed dissolution mechanism of hemicelluloses in ILs. Optical microscopy investigation clearly demonstrated that a 75-min dissolving period could create an almost homogeneous hemicelluloses solution in [BMIM]Cl IL (Peng et al., 2011). A prolonging dissolution time of 15 min (the total dissolving time was 90 min) was adopted to guarantee a complete dissolution of hemicelluloses in IL for more efficient chemical reaction.

3.2. Effects of reaction conditions on the DS of SH

Hemicellulosic succinate was prepared by the esterification of hydroxyl groups on the backbone of hemicelluloses with SA using [BMIM]Cl ionic liquid as a homogenous reaction medium. Scheme 2 shows the reaction mechanism based on the assumption that each anhydroxylose unit in hemicelluloses contains two free hydroxyl groups, and each SA molecule reacting with one free hydroxyl group will result in one carboxylic acid.



R=H or -C(=O)-CH_2-CH_2-COOH

Scheme 2. Homogeneous succinoylation of hemicelluloses with SA in [BMIM]Cl.

Table 1 shows the extent of the chemical modification expressed by DS when the reaction was carried out under various conditions. The DS of the products remarkably increased from 0.61 to 0.82, and to 1.75 when the molar ratio of SA: anhydroxylose units in hemicelluloses (H) increased from 2:1 to 4:1, and to 6:1, and a maximum DS of 1.75 was obtained with the molar ratio of SA:H of 6:1. This significant increase in DS could be interpreted in terms of the greater availability of SA molecules to hemicellulosic molecules at the higher concentration of the esterifying agent. The further increase in the molar ratio of SA:H, however, resulted in sharp decrease in DS, which is shown by the relatively low DS of 0.67 at the molar ratio of SA:H of 12:1. The reason might be the crosslinking (in the form of full ester) and other complex formations might more easily occur at higher concentration of the esterifying agent, resulting in decrease in DS (Tomasik, Wang, & Jane, 1995). Similar result was also reported and was attributed to insufficient mixing between SA and hemicelluloses (Sun, Min, et al., 2002; Sun, Sun, et al., 2002). These results indicate that SA should be employed in large excess to produce SH with a high DS.

There was an increment in the DS as the reaction temperature increased from 70 °C to 100 °C, and a maximum DS of 1.75 could be obtained at 100 °C. It is probably that a higher reaction temperature

Table 1
The DS of the succinoylated hemicelluloses obtained by the reaction of hemicelluloses (H) with SA in various reaction conditions.

Sample[a]	Molar ratio of SA/H[b]	Temperature/°C	Reaction time/min	DS[c]
1	2:1	100	60	0.61
2	4:1	100	60	0.82
3	6:1	100	60	1.75
4	8:1	100	60	1.34
5	10:1	100	60	1.09
6	12:1	100	60	0.67
7	6:1	70	60	0.83
8	6:1	80	60	1.24
9	6:1	90	60	1.52
10	6:1	110	60	1.53
11	6:1	120	60	1.21
12	6:1	100	20	0.97
13	6:1	100	40	1.80
14	6:1	100	80	1.54
15	6:1	100	100	1.35
16	6:1	100	120	0.67

[a] All samples were prepared in the same condition of 2.5% concentration of hemicelluloses in ionic liquid (based on weight).

[b] Molar ratio of succinic anhydride/xylose unit in hemicelluloses, xylose unit $M = 132$.

[c] Based on assumption that all of the hemicelluloses are converted to diesterified hemicelluloses (DS, 2.00). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the DS value would be 0.00.

favors the compatibility of the reaction ingredients, swellability of hemicelluloses, diffusion of the etherifying reagent and mobility of the reactant molecules. However, DS decreased to 1.21 when the reaction temperature further increased to 120 °C, which is probably due to the degradation of hemicelluloses and the side reaction at elevated temperature.

An important influence of reaction time on the esterification reaction efficiency can be observed in Table 1. An increase of reaction time from 20 min to 40 min led to an increment in the DS of the products from 0.97 to 1.80, thereafter DS decreased much more significantly when the reaction time was prolonged to 120 min. This observation indicates that the sufficient reaction duration facilitates the homogeneous esterification of hemicelluloses with SA in ionic liquid, whereas prolonged duration would lead to the prevailing degradation of hemicelluloses and the potential occurrence of side reaction. Hence, efforts are made to avoid the occurrence of these problems mentioned above, and a 40-min reaction time is sufficient to prepare a product with high DS.

The optimized product with a high DS of 1.80 could be obtained by using [BMIM]Cl IL as the homogenous reaction medium, and the optimum condition was the molar ratio of 6:1 (the mol of SA to the mol of anhydroxylose units in hemicelluloses), temperature of 40 °C, and reaction time of 40 min. In previous studies, succinoylated hemicelluloses were also prepared in aqueous solution and *N*,*N*-dimethylformamide/lithium chloride (DMF/LiCl) systems (Sun, Min, et al., 2002; Sun, Sun, et al., 2002; Sun et al., 2003). The succinoylated hemicelluloses with a maximum DS of 0.21 could be obtained using the aqueous solution under the optimum reaction condition. The low efficiency in succinoylation mainly was ascribed to the heterogeneous reaction system in aqueous solution (Sun, Min, et al., 2002; Sun, Sun, et al., 2002). To overcome this problem, DMF/LiCl system was employed as reaction medium (Sun, Min, et al., 2002; Sun, Sun, et al., 2002; Sun et al., 2003). Although the succinoylation was carried out in a more homogenous system, it still took a relatively long time (12 h and 2 h) to obtain succinoylated wheat straw hemicelluloses and succinoylated sugarcane bagasse hemicelluloses with the highest DS of 1.67 and 1.39, respectively, in the presence of catalysts. Comparatively, in this study, succinoylated hemicelluloses with a maximum DS value of 1.80 could be obtained in a much shorter time scale (40 min) by using [BMIM]Cl IL as reaction medium and without catalyst. In this case, [BMIM]Cl IL creates a completely homogenous system for the succinoylation of hemicelluloses with SA, which significantly promotes the reaction efficiency. Furthermore, ionic liquids may serve as catalysts to accelerate organic reactions and product formation, and many notable and impressive examples have been reported previously (Chiappe & Pieraccini, 2005; Chowdhury, Mohanb, & Scott, 2007; Dubreuil, Bourahla, Rahmouni, Bazureau, & Hamelin, 2008). Enhanced esterification had been observed in ionic liquids, and a proposed mechanism is that the carbonyl groups are activated by bonding with ionic liquid (Dubreuil et al., 2008). For these reasons, the chemical reaction efficiency is significantly promoted, and thus a high DS of 1.80 could be obtained in much shorter time scale without the presence of catalysts. Therefore, in comparison to conventional solvents, ILs can provide a more favorable reaction environment for the functionalization of hemicelluloses.

3.3. Molecular weight distribution

The average molecular weights of wheat straw hemicelluloses and their derivatives were determined by gel permeation chromatography (GPC). The weight-average (M_w) and number-average (M_n) molecular weights as well as polydispersity (M_w/M_n) are listed in Table 2. The M_w of native hemicelluloses is 26,800 g mol^{-1}, which is higher than that of DH (dissolving wheat straw hemicelluloses which were first dissolved in [BMIM]Cl and then regenerated by precipitating in ethanol, 24,369 g mol^{-1}), indicating that slight degradation occurred to native hemicelluloses during dissolving process. The depolymerization of cellulose during dissolving in ionic liquid was also reported (Fort et al., 2007; Kosan, Michels, & Meister, 2008). This may be due to that the dissociated Cl$^-$ and [BMIM]$^+$ in [BMIM]Cl weaken the glycosidic linkages in the macromolecules. Moreover, all of the M_w and M_n of succinoylated hemicelluloses are lower than that of H and DH (Table 2), which may be due to the degradation of hemicelluloses during etherification reaction in elevating temperature (70–120 °C). Table 2 also indicates the important effect of reaction temperature on the molecular weight of succinoylated hemicelluloses. The M_w of succinoylated hemicelluloses decreased from 21,863 g mol^{-1} to 16,562 g mol^{-1} when the temperature increases from 70 °C (sample 7) to 120 °C (sample 11), suggesting a more significant degradation of the macromolecules at a higher reaction temperature. Prolonging reaction time also facilitated the degradation of hemicelluloses, as indicated by a relatively low M_w (15,087 g mol^{-1}, sample 16) over a period of 120 min. The dosage of SA showed less remarkable impact on the molecular weights of succinoylated hemicelluloses, as is observed in Table 2.

Table 2
Average molecular weights of the native hemicelluloses and their derivatives.

Samples	DS	M_w	M_n	M_w/M_n
H[a]	–	26,800	9147	2.93
DH[b]	–	24,369	8626	2.83
1	0.61	18,207	7329	2.48
2	0.82	18,936	7507	2.52
3	1.75	19,268	7834	2.46
4	1.34	18,346	7594	2.42
5	1.09	18,185	7448	2.44
6	0.67	18,223	7266	2.51
7	0.83	21,863	8213	2.66
8	1.24	21,160	8247	2.57
9	1.52	20,470	7916	2.59
10	1.53	18,138	7338	2.47
11	1.21	16,562	6742	2.46
12	0.97	21,382	8431	2.54
13	1.80	20,234	8288	2.44
14	1.54	18,451	7438	2.48
15	1.35	17,205	6645	2.59
16	0.67	15,087	5803	2.60

[a] Native wheat straw hemicelluloses without dissolving in [BMIM]Cl.
[b] Dissolving wheat straw hemicelluloses which were first dissolved in [BMIM]Cl and then regenerated by precipitating in ethanol.

3.4. FT-IR spectra analysis

Fig. 1 illustrates the FT-IR spectra of the native hemicelluloses isolated from wheat straw (spectrum 1) and the succinoylated hemicelluloses (spectrum 2, sample 13) prepared in [BMIM]Cl IL. For the native hemicelluloses, the absorptions at 3454, 2936, 1569, 1463, 1410, 1255, 1160, 1044, 983, and 898 cm^{-1} in spectrum 1 are indicative of the native hemicelluloses (Fang, Sun, Tomkinson, & Fowler, 2000). A sharp band at 898 cm^{-1} is assigned to β-glucosidic linkages between the sugar units, indicating that the xylose residues forming the backbone of the macromolecule are linked by β-form bonds (Gupta, Madan, & Bansal, 1987). The low intensity of the band at 983 cm^{-1} suggests the presence of arabinosyl units, which are attached only at position 3 of the xylopyranosyl constituents (Ebringerova, Hromadkova, Alfoldi, & Berth, 1992). The region between 1463 and 1044 cm^{-1} relates to the C–H and C–O bond stretching frequencies. The strong hydroxyl-stretching vibration lies at 3454 cm^{-1}, and a symmetric C–H vibration band appears at 2936 cm^{-1}. Obviously, the succinoylated hemicelluloses spectrum b is characterized by the presence of two important ester bands at 1739 and 1164 cm^{-1}. Two peaks

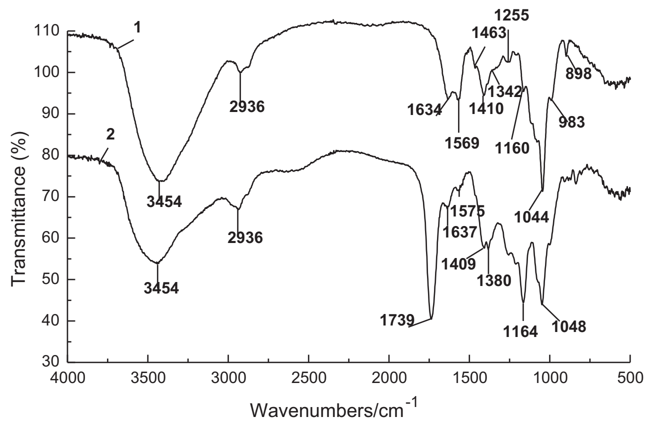


Fig. 1. FT-IR spectra of native hemicelluloses (spectrum 1) and succinoylated hemicelluloses (spectrum 2, sample 13).

at 1739 and 1164 cm^{-1} are observed due to C=O groups stretching vibrations in the C–O vibration in ester (O=C–O–CHCH$_2$–), which indicates the esterification reaction between hydroxyl groups of hemicelluloses and anhydride groups of SA (Fringant, Desbrieres, & Rinaudo, 1996). The bands at 1575 cm^{-1} and 1380 cm^{-1} correspond to the symmetrical stretching of carboxylic anions, respectively. The significant decrease in the intensity of the peak at 3454 cm^{-1} (O–H) indicates that the esterification occurred on hemicelluloses. The absence of absorption region between 1850 and 1780 cm^{-1} demonstrates that the product does not contain the unreacted SA (Hill & Mallon, 1998).

Fig. 2 provides FT-IR spectra of succinoylated hemicellulosic samples with DS of 0.97 (spectrum 1, sample 12), 1.80 (spectrum 2, sample 13) and 0.67 (spectrum 3, sample 16), respectively. The intensity of the ester band at 1739, 1575 and 1164 cm^{-1} increased with an increase in the DS from 0.67 to 1.80. Accordingly, the intensity of the band at 3454 cm^{-1} for hydroxyl groups decreased with increasing DS.

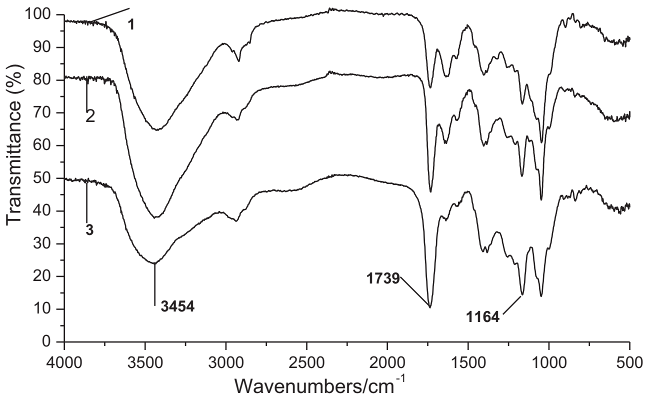


Fig. 2. FT-IR spectra of succinoylated hemicelluloses (spectra 1, 2 and 3 represent samples 12, 13 and 16, respectively).

3.5. ^{13}C NMR spectra

Fig. 3 shows representative ^{13}C NMR spectra of native hemicelluloses (a) and succinoylated hemicelluloses (b, sample 13). The signals of the main chain of hemicelluloses appear between 104 and 75 ppm, where the signals at 101.9, 76.0, 73.6, 73.1, and 62.9 ppm are assigned to C-1, C-4, C-3, C-2, and C-5 of the β-D-xylpyranosyl units of the hemicelluloses, respectively. The presence of arabinose is detected by the presence of characteristic signals at 109.4, 86.4, 80.2, 78.7, and 61.6 ppm which correspond to C-1, C-4, C-2, C-3 and C-5. Acetyl CH$_3$ in hemicelluloses gives a signal at 23.3 ppm, as shown in Fig. 3(a). The signals at 168.9 ppm represent the

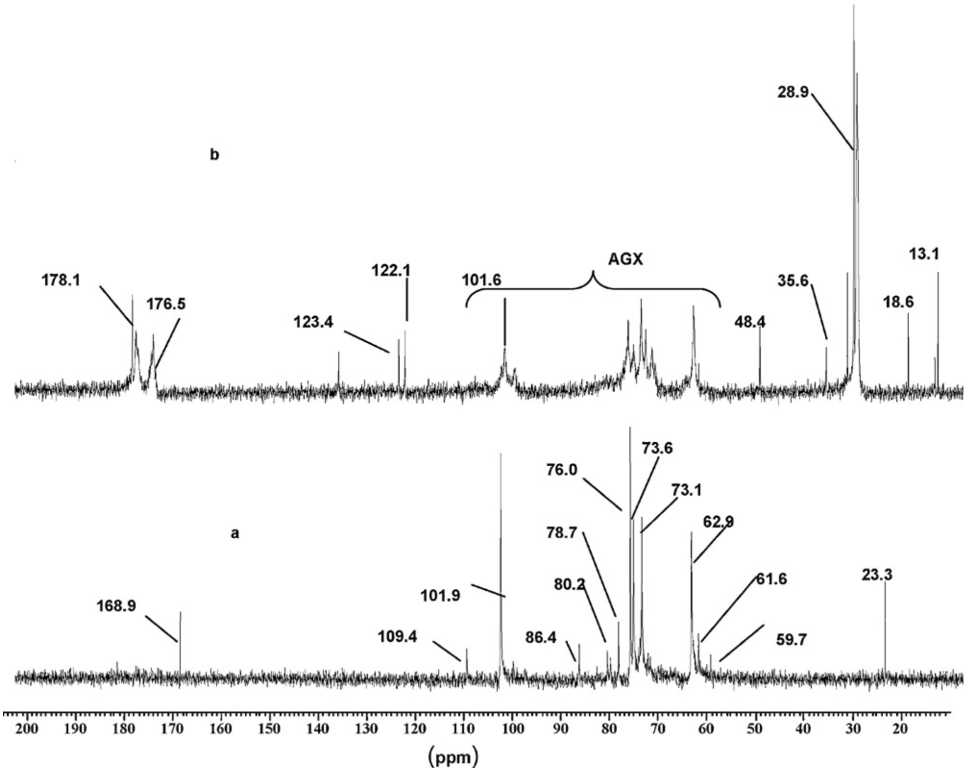


Fig. 3. The ^{13}C NMR spectra of native hemicelluloses (a) and succinoylated hemicellulose (b, sample 13). Wheat straw hemicelluloses: L-arabino-(4-O-methyl-D-glucurono)-D-xylan (AGX).

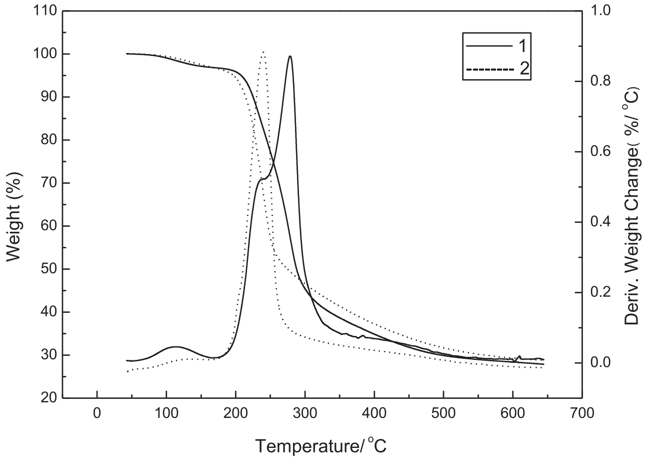


Fig. 4. Thermal Analysis of the native hemicelluloses (curve 1) and succinylated hemicellulosic sample 13 (curve 2).

esterified ferulic linked to the residual lignin by ester bonds (Sun, Mott, & Bolton, 1998). As shown in Fig. 3(b), in comparison with the spectrum obtained from the native hemicelluloses, the new signals appear at 18.6 and 35.6 ppm and two groups of bands centered at 176.5 and 178.1 ppm are indicative of the presence of methylene carbon atoms and carbonyl ester and carboxylic acid groups, respectively, corresponding to the formed monosuccinate groups (Sun, Min, et al., 2002; Sun, Sun, et al., 2002). The signals at 48.4 and 82.3 ppm arise from the –C–O group in esters.

3.6. Thermal analysis

TG/DTA curves of the native hemicelluloses and SH (sample 13) are illustrated in Fig. 4. The temperatures at 5% weight loss were 210 °C and 179 °C for the native hemicelluloses and succinoylated hemicelluloses, respectively. $T_{\max}$ (the decomposition temperature corresponding to the maximum rate of weight loss) of the native hemicelluloses and the succinylated hemicelluloses were 265 °C and 218 °C, respectively. At 50% weight loss, the decomposition temperatures of the native hemicelluloses and succinoylated hemicelluloses were 290 °C and 256 °C, respectively. The remainder weights at 600 °C were almost same for the native hemicelluloses and the succinoylated hemicelluloses, respectively. These results indicated that the thermal stability of the succinoylated hemicelluloses was lower than that of the native hemicelluloses, which can be explained by the instability of carboxylic groups and breakage of hydrogen bonds during chemical modification, as well as the lower average molecular weight.

4. Conclusion

Homogeneous esterification of hemicelluloses with succinic anhydride can be efficiently carried out in [BMIM]Cl ionic liquid without the presence of catalyst. The factors such as the molar ratio of succinic anhydride to anhydroxylose units in hemicelluloses, reaction temperature, and reaction time showed important influences on the reaction efficiency. The hemicellulosic succinates with a wide DS range between 0.61 and 1.80 could be obtained, and thus the chemical and physical properties of this important biomacromolecule can be more desirable for preparation of functional biomaterials. Results obtained from GPC indicated that degradation occurred to hemicelluloses and their derivatives in [BMIM]Cl ionic liquid. FT-IR and ^{13}C NMR analysis confirmed the structure of the hemicellulosic derivatives and their functional groups. In addition, thermal analysis showed that the thermal stability of succinoylated hemicelluloses was lower than that of the native hemicelluloses.

In comparison to conventional solvent, a higher DS of 1.80 can be achieved at shorter time scale in [BMIM]Cl ionic liquid (without any catalyst), which indicates that [BMIM]Cl is an ideal reaction medium for the functionalization of hemicelluloses. Therefore, ionic liquids create a completely homogenous system for the succinoylation of hemicelluloses, and accelerate the chemical reaction, resulting in rapid and efficient esterification of hemicelluloses with succinic anhydride.

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