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Preparation of sugarcane bagasse hemicellulosic succinates using NBS as a catalyst

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Abstract

The chemical modification of native sugarcane bagasse hemicelluloses with succinic anhydride using *N*-bromosuccinimide as a catalyst and *N*,*N*-dimethylacetamide/lithium chloride system as solvent was studied. The parameters optimised included succinic anhydride concentration by the molar ratio of succinic anhydride/anhydroxylose units in native hemicelluloses from 1:1 to 9:1, reaction time 0.5–6 h, NBS concentration 0.5–3.0%, and reaction temperature 25–85 °C required in the process. Results were also compared with other catalysts such as pyridine, DMAP, H_2SO_4, and other two tertiary amine catalysts, *N*-methyl pyrrolidine, and *N*-methyl pyrrolidinone. The degree of substitution of succinylated hemicelluloses ranged between 0.19 and 1.39, depending on the experimental conditions. FT-IR and ^1H and ^{13}C NMR spectroscopic characterization of the esterified polymers indicated a monoester substitution. The thermal stability of the succinylated hemicelluloses decreased upon chemical modification.

Keywords: Sugarcane bagasse; Succinoylation; *N*-bromosuccinimide; Thermal stability

1. Introduction

A study on oil resources based on the production rate and oil reserves in 1994 estimated that the fossil fuels available on earth would be exhausted around the year 2040 (Chalabi, 1996). There is also an increasing awareness that fossil raw materials and fuels increase the net discharge of carbon dioxide in the atmosphere and contribute to the 'green house effect'. This has led to an increasing trend in society the use of renewable raw materials for the production of various products. Agricultural residues such as cereal straws, sugarcane bagasse (SCB or 'bagasse' as it is generally called), sugar beet pulp, coffee pulp/husk, etc. can supply renewable biomass that can be valuable in providing transport fuels or chemical feedstock.

About 54 million dry tons of bagasse, a fibrous residue of cane stalks left over after the crushing and extraction of the juice from the sugar cane, is produced annually throughout the world. Bagasse is used either 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 (Rowell & Keany, 1991). It consists mainly of cellulose (~50%), hemicelluloses (~25%), and lignin (~25%) (Pandey, Soccol, Nigam, & Socco, 2000). Cellulose is a linear homopolymer made up of microfibrils that form a para-crystalline structure stabilised by hydrogen bridges (Heredia, Jimenez, & Guillen, 1995). Lignin is an amorphous polymer made up of aromatic derivatives. Hemicelluloses are non-cellulosic heteropolysaccharides consisting of various different sugar units, arranged in different proportions and with different substituents (Aspinall & Mahomed, 1954; Glasser, Kaar, Jain, & Sealey, 2000; Timell, 1964; Whistler, 1950). They are branched polymers of low molecular weight with a degree of polymerization of 80–200. Their general formulate are $(C_5H_8O_4)_n$ and

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$(C_6H_{10}O_5)_n$ and called pentosans and hexosans, respectively (Cai & Paszner, 1988). The principle sugars in hemicelluloses are D-xylose, L-arabinose, D-glucose, D-galactose, D-mannose, D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid, D-galacturonic acid, and to a lesser extent, L-rhamnose, L-fucose, and various *O*-methylated neutral sugars. Hemicelluloses of Gramineae such as cereal straws have a backbone of (1 → 4)-linked β-D-xylpyranosyl units. The chain may be linear, but is often branched and usually has other glycosidically bound sugar units. Some xylan chains have D-glucopyranosyluronic acid units attached, but the most important acidic hemicelluloses are *O*-acetyl-4-*O*-methyl-D-glucuronoxylans and L-arabino (4-*O*-methyl-D-glucurono)xylans (Sun, Lawther, & Banks, 1996).

Recent studies on the modification of hemicelluloses have demonstrated that these polymers can be modified by means of esterification reactions to afford conventional thermoplastics (Fang, Sun, Fowler, Tomkinson, & Hill, 2000; Lindblad, Ranucci, & Albertsson, 2001). Chemical modification of hemicelluloses with long chain acyl chlorides impart water resistance to the product (Sun, Tomkinson, Liu, & Geng, 1999). Conversely, the formation of hemicellulosic succinates increases the hydrophilicity of modified hemicelluloses. In addition, high densities of hemicelluloses side-chain carboxylic groups provide useful properties such as metal chelation (Jeon, Viswanathan, & Gross, 1999). Chemical modification of dextran (Arranz, Sanchez-Chaves, & Ramirez, 1992), pullulan (Brunel & Schacht, 1994), starch (Marcazzan, Vianello, Scarpa, & Rigo, 1999; Wang, Shorgren, & Willett, 1997) with succinic anhydride have been extensively studied under highly variable reaction conditions. Such polysaccharide succinates offer a number of very desirable properties such as high viscosity, low-temperature viscosity stability, high thickening power, low gelatinization temperature, clarity of cooks, and good filming properties. Therefore, succinate derivatives have been recommended as binders and thickening agents in foods, tablet disintegrants in pharmaceuticals, surface sizing agents and coating binds in paper (Wang et al., 1997). In general, the succinoylation reactions are carried out in the presence of bases such as pyridine along with 4-dimethylaminopyridine (DMAP) as co-catalyst (Sun, Min, & Sun, 2002). However, these catalysts are rather expensive which limited their industrial application. Recently, it has been demonstrated that *N*-bromosuccinimide (NBS) is a novel and highly effective catalyst for acetylation of alcohols under mild reaction conditions (Karimi & Seradj, 2001). We, therefore, investigated the possibility of developing new catalytic system for the succinoylation of SCB hemicelluloses using succinic anhydride in the presence of NBS. *N*-bromosuccinimide is an inexpensive and commercially available reagent which is traditionally used as an oxidizing agent or brominating agent (Karimi & Seradj, 2001). We now disclose a novel and efficient protocol for the succinoylation of SCB hemicelluloses using molar ratio of succinic anhydride (SA)/anhydroxylose (AX) units in hemicelluloses between 1:1 and 6:1 and a catalytic amount of NBS (0.5–3.0%) in the *N*,*N*-dimethylformamide(DMF)/lithium chloride (LiCl) systems. The modified hemicelluloses were then characterized by Fourier transform infrared (FT-IR), and ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopies as well as thermal analysis.

2. Experimental

2.1. Materials

Sugarcane bagasse was obtained from a local sugar factory (Guanzhong, China). It was dried in sunlight and then cut into small pieces. The cut SCB was ground to pass a 1.5 mm size screen. The ground SCB was dried again in a cabinet oven with air circulation for 16 h at 50 °C. DMF solvent was dried prior to use according to conventional methods. Anhydrous LiCl was dried at 130 °C for 2 h before use. Succinic anhydride (SA), *N*-methyl pyrrolidine (MPI), *N*-methyl pyrrolidinone (MPO), DMAP, and NBS were purchased from Sigma Chemical Company (Guanzhong, China).

2.2. Isolation and characterization of the native hemicelluloses

To isolate the NBS hemicelluloses, the bagasse was first treated with distilled water at 80 °C for 2 h and then delignified with sodium chlorite in acidic solution (pH 4.0, adjusted by 10% acetic acid) at 75 °C for 2 h. The hemicellulosic preparation was then obtained from the holocellulose by extraction with 10% NaOH for 10 h at 20 °C. The hemicelluloses were recovered by precipitation of the neutralized hydrolysate in three volumes of 95% ethanol. After filtration, the pellets of the hemicelluloses were washed with acidified 70% ethanol and then air dried (Fig. 1).

2.3. Succinoylation of hemicelluloses

The succinic derivatives of hemicelluloses containing free carboxylic groups were prepared by reaction of the SCB hemicelluloses with succinic anhydride in DMF/LiCl systems as to yield the mono-esterified carboxylic acid (Scheme 1). The details of the succinoylation of the hemicelluloses were as follows: dry hemicelluloses powder (0.66 g, equalling to 0.005 mol of anhydroxylose unit and 0.01 mol of hydroxyl functionality in hemicelluloses) in 30 ml distilled water was heated to 75 °C under stirring until completely dissolved (approximately 10 min). A 20 ml volume of DMF was added and the reaction was stirred for another 5 min. The water was removed from the swollen gel by repeated distillation under reduced pressure at 50 °C. To this mixture, 0.10 g LiCl, 15 ml DMF, and amount of the catalyst (NBS, MPI, MPO, H_2SO_4 or

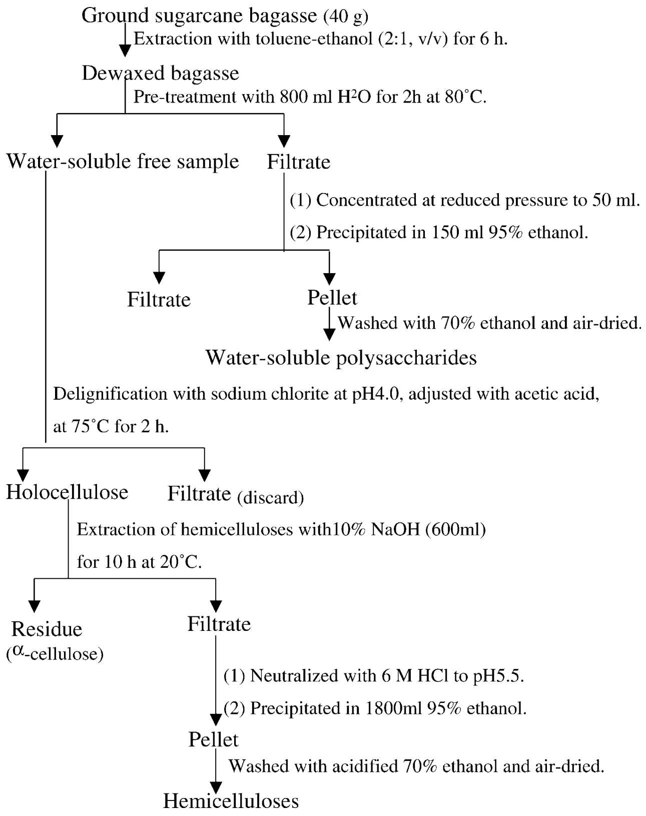


Fig. 1. Scheme for extraction of hemicelluloses from sugarcane bagasse.

DMAP) required were added, and the temperature was kept at 25, 35, 50, 70 and 80 °C, respectively. Then 0.5 g (equalling to 0.005 mol of succinic anhydride and 0.005 mol of carboxyl functionality, molar ratio 1:1), 1.0 g (0.01 mol of carboxyl functionality, molar ratio 2:1), 1.5 g (0.015 mol of carboxyl functionality, molar ratio 3:1), 3.0 g (0.03 mol of carboxyl functionality, molar ratio 6:1), and 4.5 g (0.045 mol of carboxyl functionality, molar ratio 9:1) succinic anhydride, previously dissolved in 10 ml DMF, were added over a time period of 10 min, respectively. A heating mantle was used to control the reaction temperature. The overhead stirrer was fitted for uniform and constant stirring throughout the reaction time. The reactor was fitted with reflux condenser attached with calcium chloride drying tube. The reaction was stopped at a required period (1–6 h) by cooling the resulting mixture to room temperature. Then the homogeneous reaction mixture was slowly poured into 120 ml of ethanol with stirring. The white product that separated from the solution was filtered off and collected. The filtrate was washed thoroughly with ethanol and acetone to eliminate any colour impurities and by-products. Finally, the product was first air-dried for 12 h and then further dried in an oven at 50 °C for another 12 h.

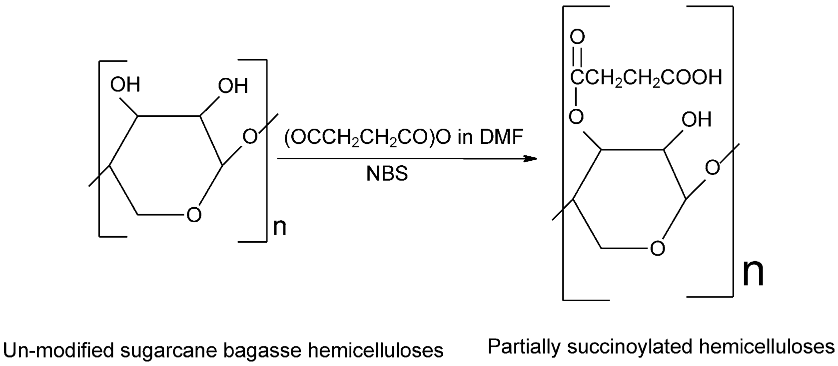
2.4. Determination of yield and degree of substitution (DS)

The yield percentages were calculated based on the assumption that all of the hemicelluloses were converted to di-esterified hemicelluloses. In the case the yield percentage and the degree of substitution (DS) would be 100% and 2.0, respectively. The unreacted succinic anhydride in a mixture of reaction was separated from the product by dissolving in ethanol and acetone. If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 39.7% with a DS value of 0.0.

2.5. Characterization of the succinylated hemicelluloses

The chemical structure of the native hemicelluloses and their derivatives was evaluated by FT-IR, and ^1H and ^{13}C NMR spectroscopies. A Nicolet 510 spectrophotometer was used to record FT-IR spectra using a KBr disc containing 1% finely ground samples. The solution-state ^1H and ^{13}C-NMR spectra were obtained on a Bruker MSL-300 spectrometer at 300 and 74.5 MHz. ^1H NMR spectra were recorded at 25 °C from 20 mg of sample dissolved in 1.0 ml D_2O for native hemicelluloses and 1.0 ml DMSO-d_6 for hemicellulosic derivatives. The ^{13}C-NMR spectra were recorded at 25 °C from 80 mg of sample dissolved in 1.0 ml D_2O for native hemicelluloses and 1.0 ml DMSO-d_6 for hemicellulosic derivatives after 30,000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width and a 0.85 s delay time between scans were used.

Thermal stability of succinylated hemicelluloses was performed using thermogravimetric analysis (TGA) and



Scheme 1. Partial succinoylation of sugarcane bagasse hemicelluloses.

differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (NETZSCH STA-409). The sample weighed between 10 and 15 mg. The scans were run from room temperature to 600 °C at a rate of 10 °C per minute under a dry air atmosphere.

3. Results and discussion

3.1. Structural characterization of the isolated native hemicelluloses

The yield of hemicelluloses was found to be 34.7% of the dry SCB. The sugar analysis showed that xylose was a predominant sugar component, comprising 82.5% of the total sugars. Arabinose (9.7%) and galactose (5.8%) appeared as the second and third major sugar constituent, respectively. The uronic acids (1.8%), mainly 4-*O*-methyl-α-D-glucopyranosyluronic acid (MeIcA), glucose (1.4%), and mannose (0.7%) were observed as minor constituents. The results obtained by gel permeation chromatography (GPC) showed that the native hemicelluloses had a weight-average molecular weight of 55,700 g mol^{-1} with a polydispersity of 12.2, corresponding to a degree of polymerization of 371. As might be expected, a relatively high M_w indicated that the 10% NaOH treatment under the condition given did not degrade the macromolecular structure of hemicelluloses to any noticeable extent.

The structural features of the native hemicelluloses were characterized by both ^{13}C and ^{1}H NMR spectroscopy (Figs. 2 and 3a). This method allows elucidation of the hemicellulosic backbone and can also be employed to evaluate the type of side-chain branching along the backbone. In Fig. 2 the spectrum shows five main signals at 102.4 (C-1), 73.4 (C-2), 75.1 (C-3), 75.9 (C-4), and 63.3 ppm (C-5) corresponding to (1 → 4)-linked β-D-Xyl residues (Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000; Imamura, Watanabe, Kuwahara, & Koshijima, 1994). The signals at 109.0, 86.4, 80.4, 78.3, and 61.8 ppm correspond to C-1, C-4, C-2, C-3, and C-5 of α-L-arabinofuranosyl residues linked to β-D-xylans, respectively. Such groups of arabinose signals are typical of arabinoxylan isolated from cereal straws (Sun et al., 1996). Two signals at 72.0 and 70.1 ppm originate from C-4 and C-2 of galactose residue in the xylan. Among others signals

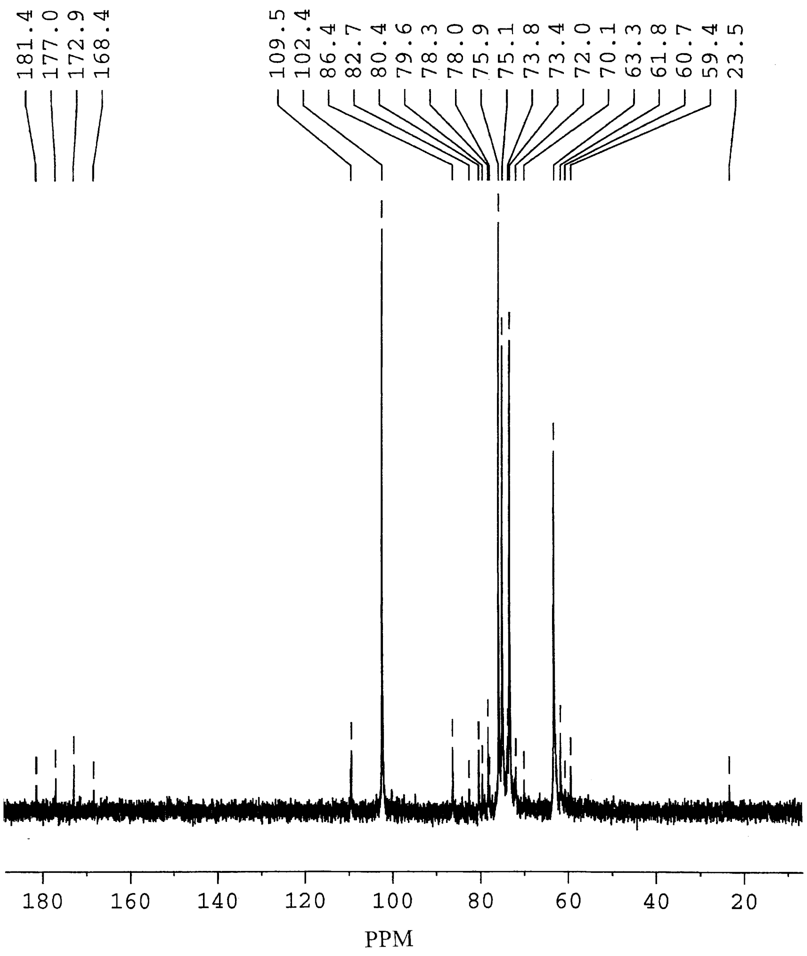


Fig. 2. ^{13}C-NMR spectrum (in D_2O) of the un-modified hemicelluloses isolated with 10% NaOH for 10 h at 20 °C from delignified sugarcane bagasse.

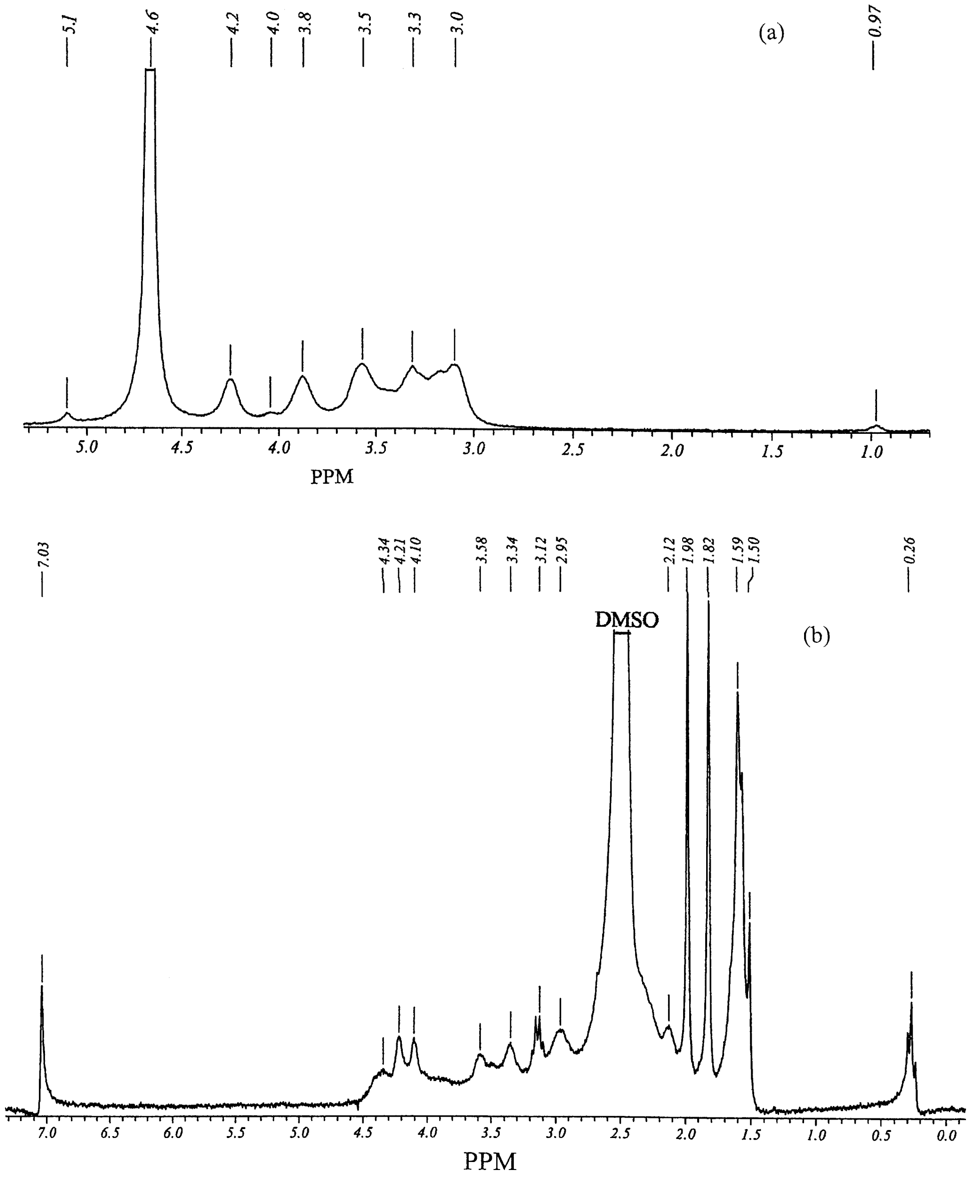


Fig. 3. ^{1}H-NMR spectra of un-modified hemicelluloses (in D_2O, spectrum (a) and the succinylated hemicellulosic sample 11 (in DMSO-d_6, spectrum (b).

observed at 172.9, 82.7, and 59.4 ppm, respectively, are characteristic signals of C-6, C-4, and methoxyl group of a 4-*O*-methyl-D-glucuronic acid residue in the xylan. The signal at 23.5 ppm relates to $-CH_3$ in $Ar-COCH_3$, indicating the associated lignin or phenolic acids. Three signals at 181.4, 177.0, and 168.4 ppm are indicative of the carbonyl signal ($-CH_2COO^-$) of the esterified ferulic or *p*-coumaric acids in native hemicelluloses. Similar results have been reported by Kato, Azuma, and Koshijima (1987). The authors demonstrated that ferulic acid is linked at C-5 of the L-arabinofuranosyl residue which is attached to the (1 → 4)-β-linked D-xylan backbone at C-3.

^{1}H NMR analysis of the native hemicelluloses revealed that signals for anomeric protons of terminal α-D-arabinofuranosyl residues at 5.1 ppm (Fig. 3a). A broad peak around 4.6 ppm is due to the residual solvent. The protons of the anhydroxylose unit in hemicelluloses are found at 3.0–4.2 ppm (Bengtsson & Aman, 1990).

3.2. Yield and degree of substitution

In our previous work (Sun, Sun, & Bing, 2002), Succinoylation of wheat straw hemicelluloses was carried out in alkaline aqueous systems, which resulted in a much lower DS, ranging between 0.017 and 0.21. The results showed that maintaining the reaction within a pH range of 8.5–9.0, a temperature between 25 and 28 °C, a 1–2 h reaction duration, and a 1:1 molar ratio of succinic anhydride to hemicelluloses, was preferable. However, in contrast to acetic anhydride, succinic anhydride has a mp of 119–120 °C and is not able to swell the hemicelluloses. Therefore, a suitable solvent or catalyst should be added to the reaction system to enhance the accessibility of the reactive hydroxyl groups of hemicelluloses to the reactants. Based on our previous study on homogeneous esterification of wheat straw hemicelluloses in the DMF/LiCl system, we found that DMF is suitable for this purpose and the reaction in DMF solution proceeds smoothly. The system acts as a solvent for both the starting hemicelluloses and the final products. In addition, the DS can be simply controlled by the molar ratio of xylose unit in hemicelluloses/succinic anhydride. Furthermore, esterification is more uniform along the polymer backbone under homogeneous solution condition. NBS, however, permits catalysis of the reaction.

In the present study, we investigated the succinoylation of SCB hemicelluloses in a DMF/LiCl system, using succinic anhydride to esterify hemicellulose O–H groups. In this case, the reaction of succinic anhydride with hydroxyl groups of hemicelluloses is rapid and irreversible. Usually, succinic anhydride reacts with hemicelluloses to form the monoester as shown in Scheme 1. The side reactions are the hydrolysis of succinic anhydride and hemicellulosic succinate. Furthermore, the free carboxylic group of monoesters may react with other hydroxyl groups of hemicelluloses to form crosslinks and diesters. However, by use of a more exotic dipolar solvent such as DMF, it was found that hemicelluloses react rapidly with dicarboxylic acid anhydride to form monoester in the presence of NBS as a catalyst. Table 1 gives the yield and DS of the succinylated hemicelluloses under the experimental conditions. Clearly, it is possible to prepare hemicellulosic succinates with different degrees of substitution (DS, defined as the moles of substituents of hydroxyl groups per anhydroxylose unit in hemicelluloses) under various reaction conditions. The theoretical maximum DS is two since each repeating anhydroxylose unit contains two hydroxyl groups. Due to the free of associated unreacted succinic anhydride in the isolated products, the DS values of the hemicellulosic succinates were calculated from the yield percentage of succinylated hemicelluloses on the assumption of each anhydroxylose unit in the polymer containing two free hydroxyl groups, and each succinic anhydride molecule reacting with one free hydroxyl group in one carboxylic acid. Obviously, as can be seen from Table 1, the yield and DS of the products depended on the molar ratio of the reactant

Table 1
The yield of succinylated hemicelluloses and the DS

Succinoylation conditions				Succinylated hemicelluloses		
Molar ratio[a]	Temperature (°C)	Reaction time (h)	Catalyst (g/100 mL DMF)	Sample no.	Yield[a] (%)	DS
1:1	50	2.0	1.0% NBS	1	45.5	0.19
2:1	50	2.0	1.0% NBS	2	46.9	0.24
3:1	50	2.0	1.0% NBS	3	48.1	0.28
6:1	50	2.0	1.0% NBS	4	59.5	0.66
9:1	50	2.0	1.0% NBS	5	59.1	0.64
6:1	50	0.5	1.0% NBS	6	56.2	0.55
6:1	50	1.0	1.0% NBS	7	57.9	0.60
6:1	50	1.5	1.0% NBS	8	58.5	0.63
6:1	50	2.5	1.0% NBS	9	60.6	0.69
6:1	50	3.0	1.0% NBS	10	61.7	0.73
6:1	50	4.0	1.0% NBS	11	62.8	0.76
6:1	50	5.0	1.0% NBS	12	65.7	0.86
6:1	50	6.0	1.0% NBS	13	65.8	0.86
6:1	50	2.0	0.5% NBS	14	60.1	0.68
6:1	50	2.0	1.5% NBS	15	63.6	0.79
6:1	50	2.0	2.0% NBS	16	70.7	1.03
6:1	50	2.0	2.5% NBS	17	64.1	0.81
6:1	50	2.0	3.0% NBS	18	60.9	0.70
6:1	25	2.0	1.0% NBS	19	56.6	0.56
6:1	35	2.0	1.0% NBS	20	58.2	0.61
6:1	70	2.0	1.0% NBS	21	57.6	0.59
6:1	85	2.0	1.0% NBS	22	56.8	0.57
6:1	50	2.0	1.0% MPI	23	59.2	0.65
6:1	50	2.0	1.0% MPO	24	58.8	0.63
6:1	50	2.0	1.0% Pyridine	25	58.5	0.62
6:1	50	2.0	0.5% H_2SO_4	26	58.0	0.61
6:1	50	2.0	1.0% DMAP	27	81.6	1.39

Based on assumption that all of the hemicelluloses are converted to diesterified hemicelluloses (yield, 100%; DS, 2.0). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 39.7% (DS, 0.0); DMF: *N,N*-dimethylformamide; NBS: *N*-bromosuccinimide; MPI: *N*-methyl pyrrolidine; MPO: *N*-methyl pyrrolidinone; DMAP: 4-dimethylamino pyridine.

[a] Molar ratio of succinic anhydride (SA)/anhydroxylose (AX) units in hemicelluloses.

agents, reaction temperature and duration, NBS concentration, and catalysts. The optimum process was started by varying one parameter at a time but keeping other constant. Results from Table 1 indicated that increasing in molar ratio of the anhydride/hemicelluloses from 1:1 in sample 1 to 6:1 in sample 4 led to a yield increment from 45.5 to 59.5% and a DS value increased from 0.19 to 0.66. These increases in yield and DS by an increment of the reactant concentration could be interpreted in terms of greater availability of succinic anhydride molecules in the proximity of the hemicellulosic molecules at higher concentration of the esterifying agent (Khalil, Hashem, & Hebeish, 1995). In contrast, as the molar ratio of the anhydride/hemicelluloses was further increased from 6:1 in sample 4 to 9:1 in sample 5, the yield and DS decreased from 59.5 to 59.1% and 0.66 to 0.64, respectively. This may result from insufficient mixing between succinic anhydride and hemicellulose phases. Also, sufficient time may not have been given for large extents of anhydride succinoylation at the higher succinic anhydride concentrations.

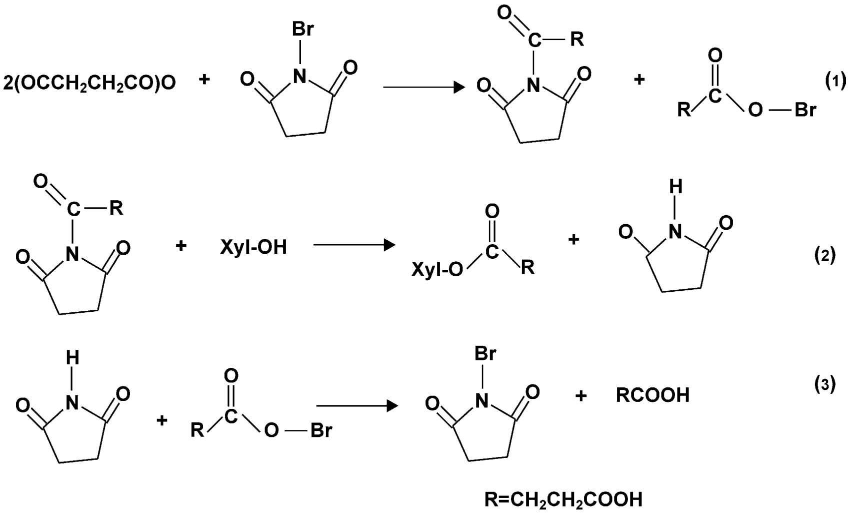
The increase in yield and DS with the reaction time could be due to the increased rate and time of collisions of succinic anhydride with hemicellulosic molecules. Hence, attempts were made to carry out the succinoylation by increasing the reaction time from 0.5 to 6 h at reactant molar ratio of 6:1, reaction temperature of 50 °C, and NBS concentration of 1.0%. As inspected from Table 1, increasing the reaction time from 0.5 h in sample 6 to 1 h in sample 7, to 1.5 h in sample 8, to 2.5 h in sample 9, to 3 h in sample 10, to 4 h in sample 11, and to 5 h in sample 12 resulted in a growth of yield from 56.2 to 57.9, 58.2, 60.6, 61.7, 62.8, and 65.7% together with an increment of DS value from 0.55 to 0.60, 0.63, 0.69, 0.73, 0.76, and 0.86, respectively. However, no significant increase in the yield and the DS was observed even after 5 h of reaction time. This could be due to maximum collisions taking place up to 5 h of reaction time and stabilising thereafter (Bhandari & Singhal, 2002).

Based on the study of acetylation of alcohols under mild reaction conditions, Karimi and Seradj (2001) reported that NBS is a novel and highly effective catalyst for acylation. In this study, the effect of NBS concentration on the yield and DS of the products was performed between samples 14 and 18. As expected, increasing the NBS amounts from 0.5% (0.5 g NBS in 100 ml DMF) in sample 14 to 2.0% in sample 16 resulted in a growth of yield from 60.1% to 70.7% and DS value from 0.68 to 1.03. Interestingly, further increase of the quantity of NBS from 2.0 to 3.0% led to a decrease in yield by 9.8% and DS by 0.33 between samples 16 and 18. This is a satisfactory result since NBS recovery is a crucial economic factor. Thus, its use must be limited.

The results of variation in reaction temperature while holding the reactant molar ratio at 6:1, NBS concentration at 1.0%, and a reaction duration of 2 h are given in samples 4 and 19–22. As can be seen from Table 1, an increase in the reaction temperature from 25 (sample 19), to 35 (sample 20), and to 50 °C (sample 4) resulted in an increment in yield from 56.6 to 58.2 and to 59.5%, and DS from 0.56 to 0.61 and to 0.66%, respectively. In contrast, further increase in the reaction temperature from 50 to 70 and to 85 °C led to a decrease in the yield from 59.5 to 57.6 and to 56.8, and DS from 0.66 to 0.59 and to 0.57, respectively. These data revealed that a temperature (of up to 50 °C) would be expected to enhance the anhydride diffusion into the hemicellulosic molecules and also the swelling of the hemicelluloses, so increasing succinoylation rates. However, at much higher temperature, such as 70–85 °C, would result in hemicellulose degradation and hydrolysis of the formed hemicellulosic succinates, so reducing the reaction yield and DS. Therefore, a reaction temperature of 50 °C was considered as optimum for other samples.

Since the reaction between hemicelluloses and succinic anhydride is acid- or base-catalysed, an addition of catalysts would accelerate the rate reaction of succinic anhydride with hemicelluloses (Rowell, Tillman, & Simonson, 1986). Pyridine-catalysed acylation is a standard method for the determination of hydroxyl compounds and other acylable substances. The mechanism involves nucleophilic catalyst with the intermediate formation of the acylpyridium ion (Connors & Albert, 1973). Although pyridine is an effective catalyst in such acylations, it is toxic, has an unpleasant odour and is not suitable for use in large scales reactions (Hill, Cetin, & Ozmen, 2000). Hofl, Steglich, and Vorbruggen (1978) reported that a tertiary amine, 4-dimethylaminopyridine (DMAP) is much superior to pyridine as a catalyst for some synthetic acylations, such as typical acylation reactions for primary and secondary alcohols, and is an effective catalyst of analytical acylation by acetic anhydride, having a specific catalytic activity about 10^4 times greater than that of pyridine. However, DMAP is very expensive, which limits its industrial use. On the other hand, NBS is a rather cheap and commercially available reagent. As far as the authors are aware, there have been no reports of its use as a catalyst for the succinoylation of hemicelluloses. The present article describes the application of NBS as a possible hemicellulosic succinoylation catalyst. Results were compared with pyridine, DMAP, H_2SO_4, and other two tertiary amine catalysts, which have also not previously been studied with respective to hemicellulosic succinoylation reactions, *N*-methyl pyrrolidine (MPI), and *N*-methyl pyrrolidinone (MPO).

As shown in Table 1, NBS, H_2SO_4, and the four tertiary amine catalysts used all accelerate the reaction as shown an increase in yield and DS (samples 4, 23–27) as compared to the control (yield 43.8; DS 0.14, data not shown). In comparison, NBS exhibited a significant effect on the rate of succinoylation of hemicelluloses (yield



Scheme 2. Mechanism of succinoylation of hemicelluloses by using NBS as a catalyst.

59.5%, DS 0.66, sample 4), and accelerated faster than MPI (yield 59.2%, DS 0.65, sample 23), MPO (yield 58.8%, DS 0.63, sample 24), pyridine (yield 58.5%, DS 0.62, sample 25), and 0.5% H_2SO_4 (yield 58.0%, DS 0.61, sample 26). DMAP showed the fastest rate of reaction (yield 81.6%, DS 1.39, sample 27). However, it should be noted that the price of DMAP is 170 times higher than that of NBS. Thus, NBS is a suitable catalyst for the hemicellulosic succinoylation if the economic point of view is taken into account.

The actual role of NBS is not clear, however, a plausible explanation is that NBS might act as a source for Br^+, which in turn activates the carbonyl groups of succinic anhydride to produce the highly reactive acylating agent ($HOOC{-}CH_2{-}CH_2{-}CO{-}N{-}(O{=}CCH_2CH_2{-}C{=}O)$). This acylating agent reacts with hydroxyl groups of hemicelluloses, which upon elimination of NBS produces succinoylated hemicelluloses ($Xyl{-}O{-}CO{-}CH_2{-}CH_2{-}COOH$) (Scheme 2; Karimi and Seradj, 2001). However, at this time the precise role of NBS is not clear and the actual role of this reagent should be further studied in detail.

3.3. FT-IR spectra

Fig. 4 shows the FTIR spectra of native hemicelluloses (spectrum a) and succinylated hemicelluloses (spectrum b, sample 4). In the two spectra, a strong band at 1036 cm^{-1} is the most characteristic band for a polysaccharide, and it arises from C–O stretching in C–O–C glycosidic linkages, which was negligibly affected by succinoylation (Sun, Fang, Tomkinson, & Jones, 1999). This indicated that the β-glucosidic linkages between the sugar units were not modified by the succinoylation reaction. A strong broad band at 3436 cm^{-1} is attributed to the hydroxyl groups in both native and succinylated hemicelluloses, and its intensity decreased in the esterified derivatives due to the esterification. More importantly, the spectrum b provides

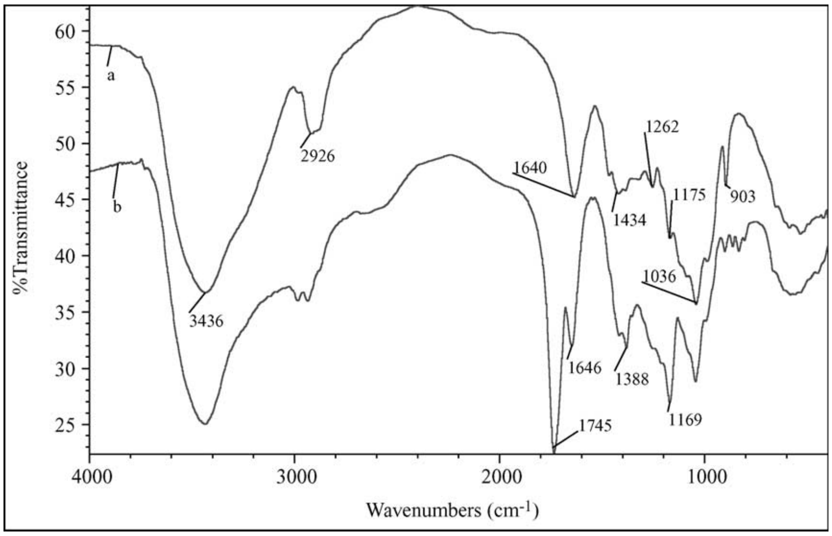


Fig. 4. FT-IR spectra of unmodified hemicelluloses (spectrum a) and succinylated hemicellulosic sample 4 (spectrum b).

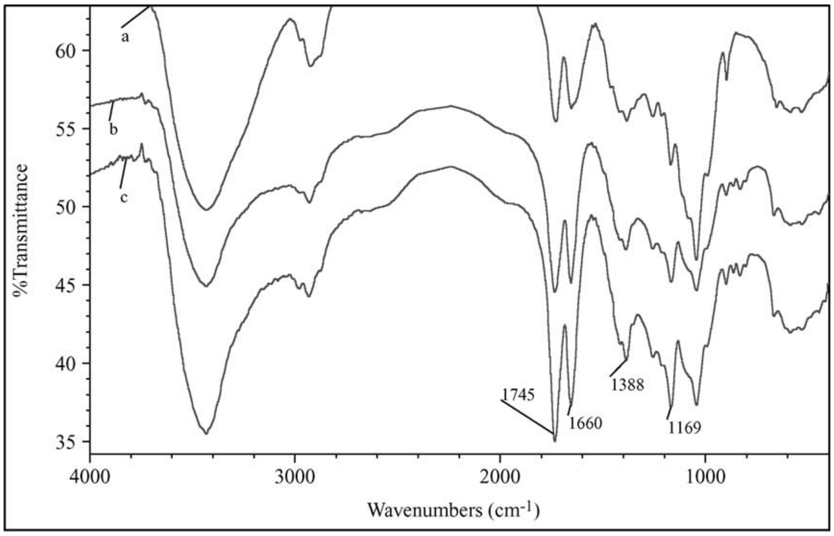


Fig. 5. FT-IR spectra of succinylated hemicellulosic samples 6 (spectrum a), 7 (spectrum b), and 11 (spectrum c).

evidence of succinoylation by showing the presence of two ester bands at 1745 and 1169 cm^{-1}. The former band at 1745 cm^{-1} is indicative of absorption by carbonyl bonds in esters. The latter band at 1169 cm^{-1} is characterized by the C–O stretching in the esters (O=C–*O*–*C*HCH$_2$–) (Fringant, Desbrieres, & Rinaudo, 1996). The stretching of the carboxylic acids forming intermolecular hydrogen occurs at 1660 cm^{-1} (Cui & Oates, 1997). These results suggested that the formation of the monoester of succinylated hemicelluloses in the homogeneous DMF/LiCl system was dominant. However, it should be noted that with longer reaction time, hemicelluloses-attached succinic acid may continue to react with hydroxyl groups in the near surrounding for crosslinks. As expected, the disappearance of peaks at 1850 and 1780 cm^{-1} in spectrum (b) of succinylated polymers confirmed that the products are free of the unreacted succinic anhydride (Wang et al., 1997).

The effect of reaction time, NBS concentration, reaction temperature, and various catalysts on the intensity of the absorption bands in FT-IR spectra was also comparatively examined, and their spectra are given in Figs. 5–8, respectively. Fig. 5 shows the FT-IR spectra of succinylated hemicellulosic samples 6 (0.5 h, spectrum a), 7 (1 h, spectrum b), and 11 (4 h, spectrum c). As illustrated, the intensity of the two ester bands at 1745 and 1169 cm^{-1} increased with an increase in the reaction time from 0.5 h in Fig. 5(a) to 1 h in Fig. 5(b), and to 4 h in Fig. 5(c), corresponding to an increment of reaction yield and DS. In Fig. 6, the intensity of the two ester bands at 1745 and 1169 cm^{-1} increased with an increment of NBS concentration from 1.5% (spectrum a) to 2.0% (spectrum b) and

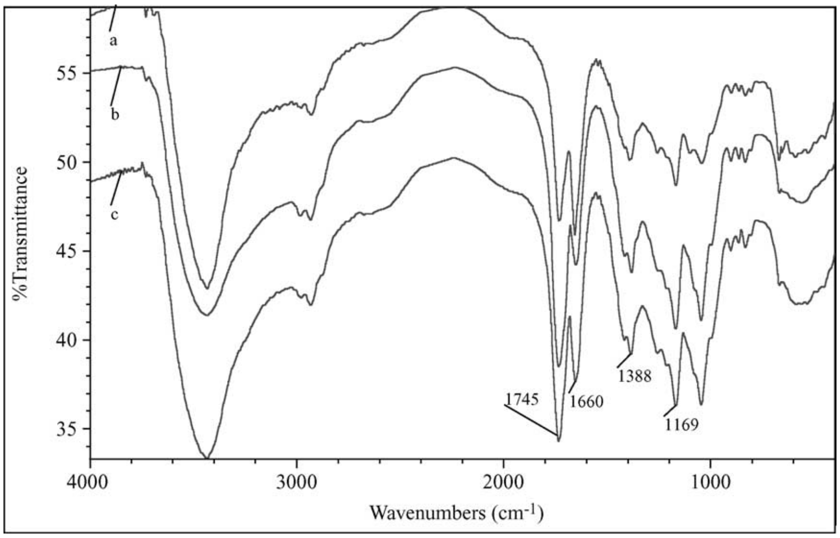


Fig. 6. FT-IR spectra of succinylated hemicellulosic samples 15 (spectrum a), 16 (spectrum b), and 17 (spectrum c).

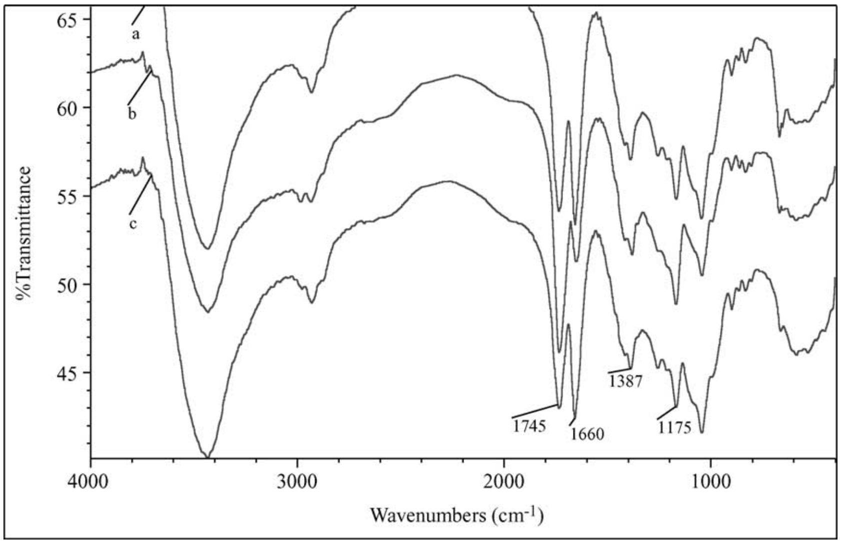


Fig. 7. FT-IR spectra of succinylated hemicellulosic samples 19 (spectrum a), 20 (spectrum b), and 21 (spectrum c).

then decreased to 2.5% (spectrum c), which is paralleled to the yield and DS of the succinoylation. Similar increasing or decreasing trends of ester bonds at 1745 and 1169 cm^{-1} with increments of reaction temperature from 25 to 35 and to 70 °C, and with different catalysts were also observed between the samples as shown by the spectra shown in Figs. 7 and 8, respectively.

3.4. ^1H and ^{13}C NMR spectra

The ^1H NMR spectrum of the succinylated hemicellulosic sample 11 is shown in Fig. 3b. The new intensive signals, occurring at 1.50–1.59 ppm, are attributed to the methylene protons connecting the carboxylic group ($HO-CO-CH_2-CH_2-$). Other new two peaks at 1.8 and 2.0 ppm are originated from methylene protons connecting the ester group ($-O-CO-CH_2-CH_2-$) of the hemicellulsic succinate (Aburto et al., 1997). The protons in H-bonded carboxylic acid group give a small peak at 7.0 ppm. The peaks between 3.0 and 4.3 ppm represent the protons of the anhydroxylose units in hemicelluloses.

The ^{13}C NMR spectrum of succinylated hemicellulosic sample 20 with a DS value of 0.61 is given in Fig. 9. In comparison with the spectrum obtained from the native hemicelluloses shown in Fig. 2, it can be seen that the presence of eight signals between 14.0 and 35.7 ppm is attributed to the methylene carbon atoms. A signal at 162 ppm and several bands between 170 and 179 ppm are indicative of the occurrence of carbonyl ester and carboxylic acid groups, respectively, corresponding to the formed monosuccinated groups. The signals at 51.3 and

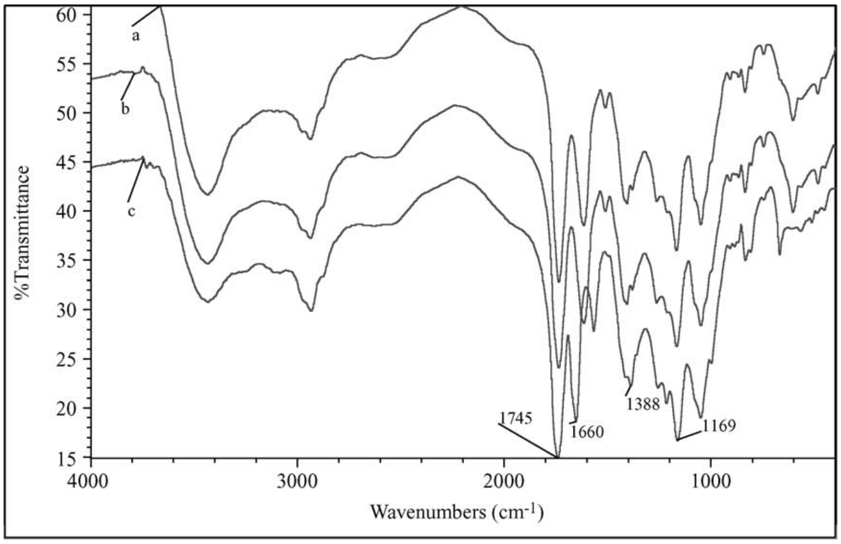


Fig. 8. FT-IR spectra of succinylated hemicellulosic samples 25 (spectrum a), 23 (spectrum b), and 27 (spectrum c).

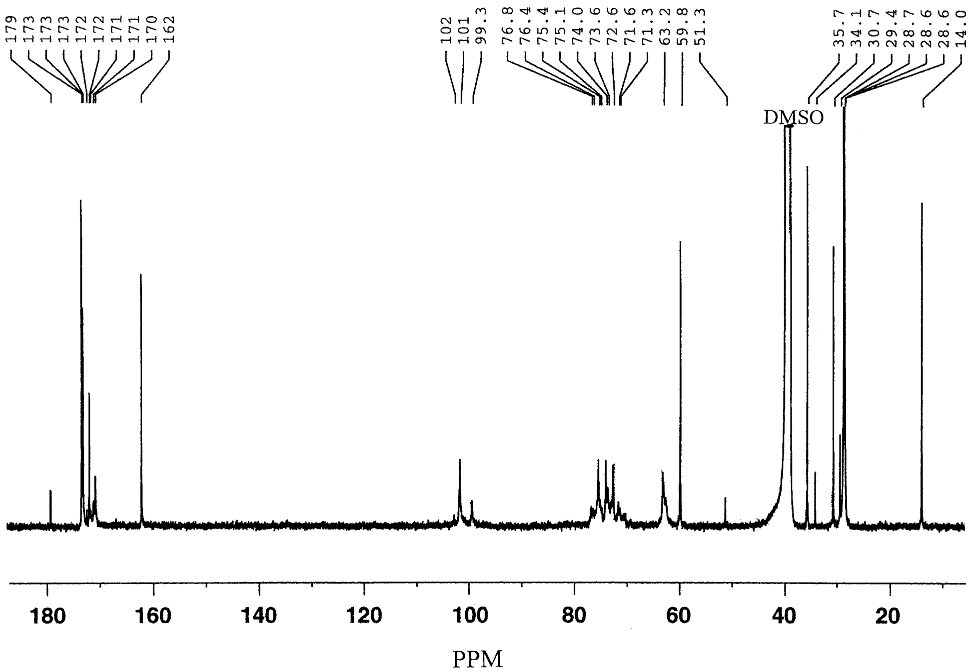


Fig. 9. ^{13}C-NMR spectrum (in DMSO-d$_6$) of the succinylated hemicellulosic sample 20.

59.8 ppm are due to the –C–O group in esters. The presence of five peaks at 101, 76.4, 75.4, 75.1, and 63.3 ppm relate to carbon atoms of C-1, C-4, C-3, C-2, and C-5 in the β-D-Xyl*p* units of hemicelluloses.

3.5. Thermal analysis

The effect of succinoylation on the thermal behavior of SCB hemicelluloses was also studied by TGA and DSC in the temperature range from 25 to 600 °C. Fig. 10 presents the TGA and DSC thermograms of native hemicelluloses (a) and succinylated polymer samples 1 (b) and 11 (c). As observed, the unmodified hemicelluloses and succinylated polymer samples 1 and 11 are stable up to 200, 196, and 193 °C, respectively. Beyond these temperatures, thermal degradation takes place, depending mainly on the DS of the hemicelluloses. For example, the greatest weight loss point of native hemicelluloses occurred at 270 °C, while it exhibited at 241 and 230 °C for succinylated hemicellulosic samples 1 and 11, respectively. At 50.0% weight loss the decomposition temperatures of native and succinylated polymer samples 1 and 11 were observed at 400, 276, and 255 °C, respectively. These results revealed that the unmodified hemicelluloses appeared to be more stable than succinylated polymers. In addition, in comparison with the temperature of onset of active pyrolysis, the succinylated hemicellulosic sample 11 with a DS of 0.76 showed to be the least thermally stable, starting to decompose from 193 °C, indicating that the thermal stability of the succinylated polymers decreased with an increment of DS. This lower thermal stability of the succinylated polymers was probably due to the disintegration of intramolecular interactions such as hydrogen bonds between polymer chains and higher amounts of carboxylic acid groups after esterification. However, this thermal stability of the succinylated hemicelluloses over to 190 °C is rather satisfactory.

DSC was 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 (Bilideris, Maurice, & Vose, 1980; Fringant et al., 1996). As illustrated in Fig. 10, the native hemicelluloses showed a larger exothermic peak between 235 and 600 °C due to the disintegration of intramolecular interaction and the decomposing of the polymer, whereas the two succinylated hemicellulosic samples gave a much smaller exothermic peak between the corresponding temperatures. This suggested that succinoylation significantly breaks the hydrogen bonds between the polymer chains under the conditions given.

Based on the above studies, it can be concluded that succinoylation of hemicelluloses with succinic anhydride by using NBS as a catalyst in DMF/LiCl system was an efficient chemical modification for obtaining the polymers with carboxylic groups. The total DS can be simply controlled by the reaction conditions. The preferred reaction parameters that resulted in the highest DS were as follows: 6:1 reactant molar ratio, 50 °C, 5 h, 2.0% NBS. An increase in the molar ratio of succinic anhydride/anhydroxylose unit in native hemicelluloses from 1:1 to 6:1, reaction time from 0.5 to 5 h, NBS concentration from 0.5 to 2.0%, and reaction temperature

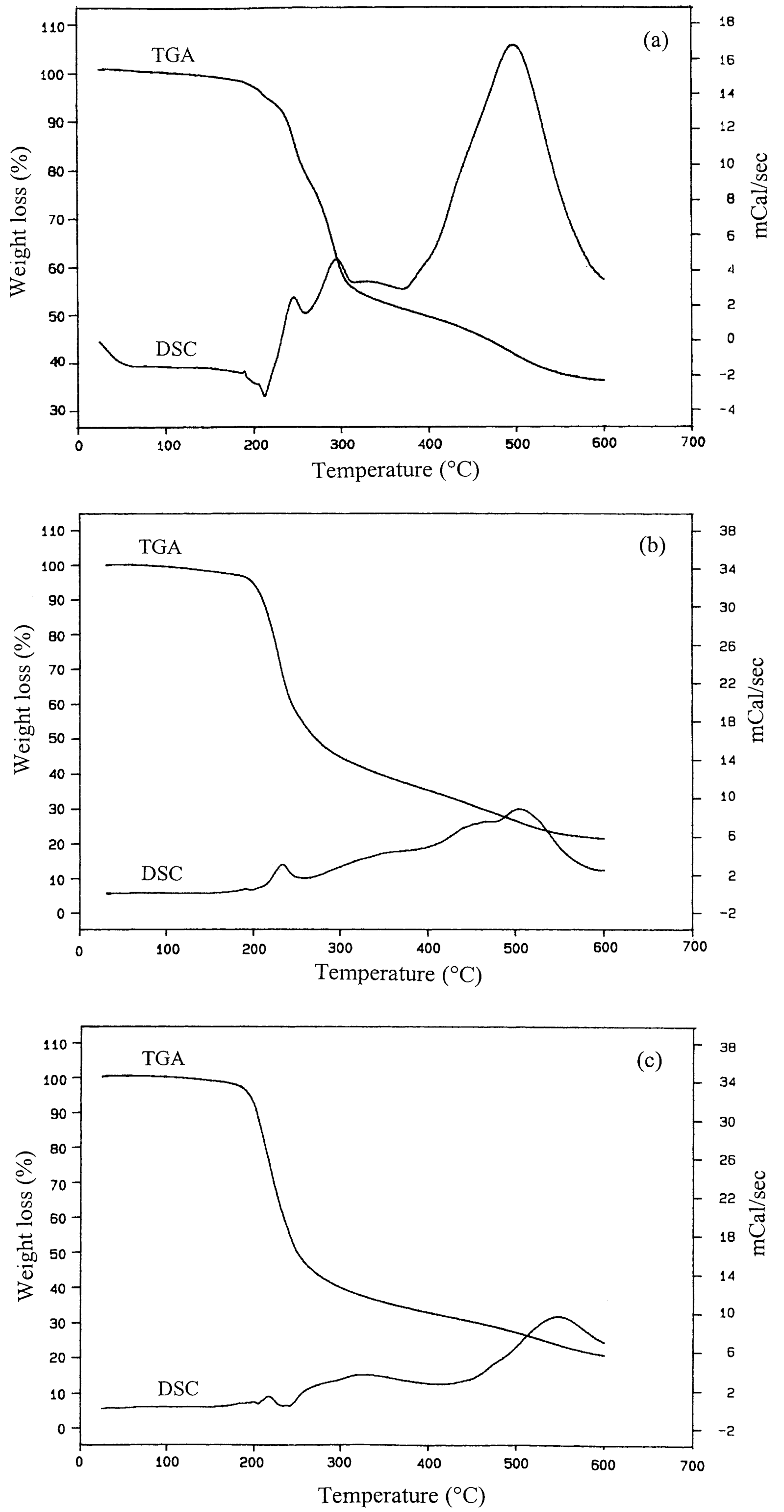


Fig. 10. Thermogram of native hemicelluloses (a) and succinylated hemicellulosic samples 1 (b) and 11 (c).

from 25 to 50 °C led to an increment of product yield by 30.8, 16.9, 17.6, and 5.1%, respectively. The thermal stability of the products decreased by chemical modification.

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