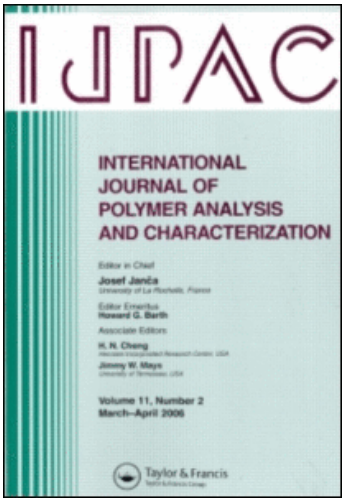


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Analysis and Characterization of Acetylated Sugarcane Bagasse Hemicelluloses

Fen Xu[a]; Run-Cang Sun[a]; Xaio-Feng Sun[b]; ZhenChao Geng[b]; Bin Xiao[b]; JinXia Sun[b]
[a] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China [b] College of Forestry, The North-Western University of Agricultural and Forest Sciences and Technology, Yangling, China

To cite this Article Xu, Fen , Sun, Run-Cang , Sun, Xaio-Feng , Geng, ZhenChao , Xiao, Bin and Sun, JinXia(2004) 'Analysis and Characterization of Acetylated Sugarcane Bagasse Hemicelluloses', International Journal of Polymer Analysis and Characterization, 9: 4, 229 — 244
To link to this Article: DOI: 10.1080/10236660490920228
URL: http://dx.doi.org/10.1080/10236660490920228

International Journal of Polymer Anal. Charact., 9: 229–244, 2004

ISSN: 1023-666X print
DOI: 10.1080/10236660490920228

Taylor & Francis
Taylor & Francis Group

Analysis and Characterization of Acetylated Sugarcane Bagasse Hemicelluloses

Fen Xu and Run-Cang Sun
State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China

Xaio-Feng Sun, ZhenChao Geng, Bin Xiao, and JinXia Sun
College of Forestry, The North-Western University of Agricultural and Forest Sciences and Technology, Yangling, China

Acetylation of sugarcane bagasse hemicelluloses with acetic anhydride using N-bromosuccinimide (NBS) as a catalyst in N,N-dimethylformamide/lithium chloride system under mild conditions was comparatively studied. The yield and the degree of substitution (DS) ranged from 68.2% and 0.37 to 78.6% and 0.82 as a function of experiment conditions. It was found that the yield and DS increased with N-bromosuccinimide concentration between 0.5 and 1.0%, reaction temperature from 18 to 80°C, and reaction time between 2 and 4 h. In comparison, other catalysts such as H_2SO_4 and four tertiary amine catalysts, pyridine, 4-dimethylaminopyridine, N-methyl pyrrolidine, and N-methyl pyrrolidinone, were also investigated. The results showed that NBS can be used as a novel and effective catalyst for acetylation of hemicelluloses under extremely mild reaction conditions. The new polymeric products were characterized by FT-IR, ^{13}C NMR spectroscopy, and thermal analysis. The thermal stability of the material was increased by chemical modification.

Received 15 March 2004; accepted 23 November 2004.

The authors are grateful for the financial support of this research from National Natural Science Foundations of China (No. 30271061 and 30430550), Shaanxi and Guangdong Natural Science funds for key projects (No. 013034 and 36567), and Ministry of Education China for a major project funding.

Address correspondence to Run-Cang Sun, The BioComposites Centre, University of Wales, Bangor, LL57 2UW, U.K. E-mail: bcs00a@bangor.ac.uk

Keywords: Sugarcane bagasse; Hemicelluloses; Acetylation; N-Bromosuccinimide

Currently, 270 million tons of petroleum and gas are globally used every year for the manufacture of plastics. The impact of these activities on the environment is considerable for two reasons: petroleum is not a renewable product and certain plastics are not recycled[1]. Therefore, the use of lignocellulosic materials from agricultural residues, such as cereal straws and sugarcane bagasse (SCB or bagasse as it is generally called), as a source of chemicals for making plastics has received considerable interest in recent years since agricultural residues are abundant and renewable. For example, about 54 million dry tons of bagasse, a fibrous residue of cane stalks left over after the crushing and extraction of juice from 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[2]. These raw materials look promising to replace environmentally unfriendly fossil hydrocarbons and, hence, to create ''green'' products[3].

After cellulose, hemicelluloses constitute the second most abundant class of polymers found in nature. They comprise roughly one-fourth to one-third of most plant materials. These by-products have been demonstrated to be a potential fermentation feedstock for the production of sugars[4], ethanol[5], and xylitol[6]. Other examples of the application of hemicelluloses include food additives, thickeners, emulsifiers, gelling agents, adhesives, and adsorbents[7].

The predominant constituents of SCB are cellulose ($\sim$40%) and hemicelluloses ($\sim$34%)[8]. The latter are polysaccharides of branched structures formed by a number of different neutral sugar units. The principal 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[9]. Because of the above heterogeneity of their chemical constituents, hemicelluloses in their native state are generally considered to be noncrystalline and are branched polymers of low molecular weight of a degree of polymerization of 80–200. Their general formulas are $(C_5H_8O_4)_n$ and $(C_6H_{10}O_5)_n$ and are respectively called pentosans and hexosans[10]. The hemicelluloses with one or two free hydroxyl groups are hydrophilic, while many synthetic polymers are hydrophobic. This result in significantly different solubility characteristics of the hemicelluloses, i.e., solubility in aqueous alkali but insolubility in virtually all organic solvents. In addition, hemicelluloses

are branched, amorphous, multi functional (consisting of different types of functional groups, e.g., OH, acetoxy, carboxyl, and methoxyl) heteropolysaccharides (composed of several different types of monosaccharides). Thus, hemicelluloses represent a different type of polysaccharide that behaves differently from cellulose and starch, which explains their infrequent use in industrial applications. However, these shortcomings can be overcome by their modification, such as etherification or esterification of the hydroxyl groups and cross-linking.

The preparation and properties of new polymers from hemicelluloses should thus be an important part of any research program aimed at utilizing annually renewable, agriculturally derived polymers as extenders and replacements for polymers prepared from petrochemicals. The variability in sugar constituents, glycosidic linkages, and structure of glycosyl side chains as well as two reactive hydroxyl groups at the xylose repeating unit of the main chain from xylans offer various possibilities for regioselective chemical and enzymatic modifications. Functionalization creates novel opportunities to exploit the various properties of hemicelluloses for previously unconceived applications[11]. In particular, some hemicellulosic biopolymers from higher plants and herbs represent a potential source of pharmacologically active polysaccharides. Glucuronic acid-containing (acidic) xylans isolated from annual plant residues such as bamboo leaves, corn stalks, and wheat straw as well as hardwood have been reported to markedly inhibit the growth of sarcoma-180 and other tumors, probably due to indirect stimulation of the non specific immunological host defense[12,13]. Arabino-(glucurono) xylans isolated from *Echinacea purpurea, Eupatorium perfoliatum* have been reported to have immunostimulating effects[14]. Carboxymethylated xylan-rich wood hemicelluloses[15] have been demonstrated to be active towards T-lymphocytes and immunocytes and claimed as a new Chinese antitumor drug.

Over the past few years, studies on chemical modification of hemicelluloses in our laboratory have been carried out using *N*, *N*-dimethylformamide (DMF)/lithium chloride (LiCl) solvent medium, in which the substitutions along the hemicellulose backbone can be achieved with satisfactory yields and with little depolymerization of the hemicellulose chains. Strongly polar aprotic solvents such as DMF were found to be able to prevent the aggregation of flexible hemicellulose chains and promote the interactions between substrate and reagents. Acetylation of the hydroxyl groups of hemicelluloses with acetic anhydride to increase hydrophobicity is one approach toward increasing the water resistance of hemicelluloses. Derivatization of hemicellulose hydroxyl groups may also reduce the tendency of hemicelluloses to form strong hydrogen-bonded networks and increase film flexibility.

In this work we report optimized acetylation conditions for the preparation of SCB hemicellulosic derivatives in homogenous solutions

of DMF/LiCl systems by using *N*-bromosuccinimide (NBS) as a catalyst. NBS is an inexpensive and commercially available reagent and is a novel and highly effective catalyst for acetylation of alcohols under mild reaction conditions[16]. In comparison, the potential of four other tertiary amine catalysts (*N*-methyl pyrrolidine, *N*-methyl pyrrolidinone, 4-dimethylaminopyridine, and pyridine) and 0.5% sulfuric acid were also investigated. The acetylated hemicelluloses were then characterized by chemical analysis (yield of acetylation and degree of substitution, DS), Fourier transform infrared (FT-IR) and ^{13}C nuclear magnetic resonance (NMR) spectroscopies, and thermal analysis.

EXPERIMENTAL

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 was dried prior to use according to conventional methods. Anhydrous LiCl was dried at 130°C for 2 h before use. Acetic anhydride, *N*-methyl pyrrolidine (MPI), *N*-methyl pyrrolidinone (MPO), 4-dimethylaminopyridine (DMAP), and NBS were purchased from Sigma Chemical Company (Guanzhong, China).

Isolation and Characterization of Native Hemicelluloses From SCB

SCB hemicelluloses were isolated after removal of lignin by the method described previously for wheat straw[17]. The bagasse was first delignified with sodium chlorite in acidic solution (pH 4.0, adjusted by 10% acetic acid) at 75°C for 2 h. The hemicelluloses were then obtained from the holocellulose by extraction with 10% NaOH for 10 h at 20°C with a liquor ratio of 1:20. 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 (Figure 1).

The hemicellulosic preparation was analyzed for neutral sugar and uronic acids after hydrolyzing a 10 mg sample for 2 h at 120°C in 7 mL of 2.0 M trifluoroacetic acid. The sugars released were determined by gas chromatography (GC) analysis of their alditol acetates[18]. The content of uronic acids in native hemicelluloses was estimated colorimetrically by the method of Blumenkrantz and Asboe-Hanson[19].

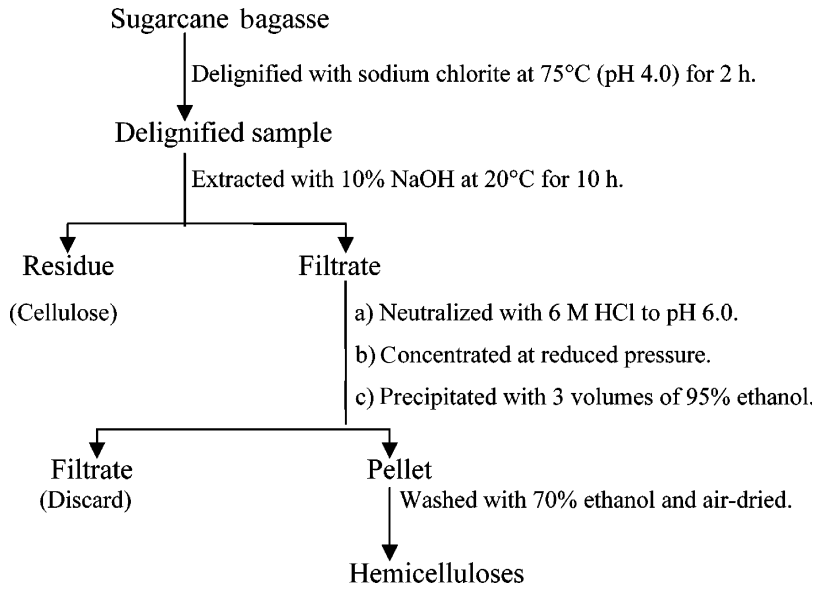


FIGURE 1 Scheme for extraction of hemicelluloses from SCB.

Acetylation of Hemicelluloses

A 0.66 g sample of hemicelluloses powder (0.01 mol of hydroxyl functionality in hemicelluloses) in 10 mL distilled water was heated to 80°C under stirring until completely dissolved (approximately 10 min). This was added to 10 mL of DMF, and the reaction was stirred for another 5 min. Water was removed from the swollen gel by repeated distillation under reduced pressure at 50°C. To this mixture, 0.10 g LiCl, 10 mL DMF, 15 mL acetic anhydride, and the amount of the catalyst (NBS, MPI, MPO, DMAP, or H_2SO_4) required were added. Then the homogeneous reaction mixture was stirred for a total period of 2, 4, and 6 h, respectively, at a temperature range of 18–100°C. 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 a reflux condenser attached to a calcium chloride drying tube. Upon completion of the reaction, the homogeneous reaction mixture was cooled to room temperature and the product was isolated by precipitation of the reaction solution into four volumes of 95% ethanol and purified by washing with 95% ethanol twice and acetone once to eliminate any color impurities and by-products. The product was first air-dried for 12 h and then further dried in an oven at 50°C for 16 h. All the experiments were performed in duplicate, with a 4–7% standard error of the yield.

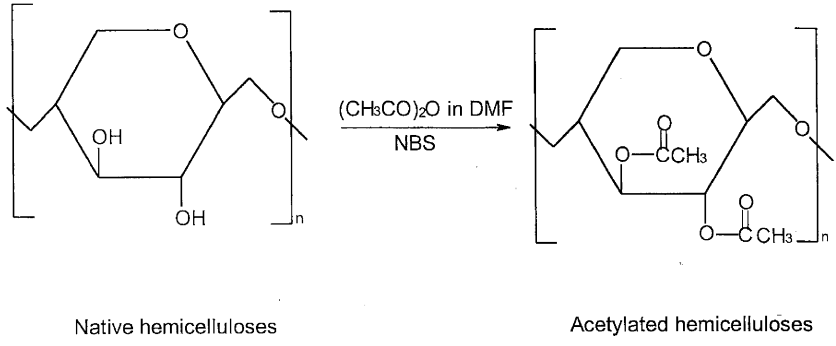
Determination of Yield and Degree of Substitution (DS)

The percent yields of the acetylated hemicelluloses were calculated based on the assumption that full conversion to di-acetylated hemicelluloses corresponds to 100% yield (Scheme 1). The degree of substitution (DS) for a hemicellulose ester is defined as the moles of substituents on the hydroxyl groups per D-xylopyranosyl structural unit of the hemicellulosic polymer. Since there are two hydroxyl groups per unit, the theoretical maximum DS is 2.0. The unreacted acetic anhydride in the mixture of reactions was separated from the product by dissolving in 95% ethanol and acetone. If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage and the degree of substitution would be 61.0% and 0.0, respectively.

Characterization of the Acetylated Hemicelluloses

The chemical structure of the acetylated hemicelluloses was evaluated by FT-IR and ^{13}C NMR. FT-IR spectra were recorded on a Nicolet 510 spectrophotometer using a KBr disc containing 1% finely ground samples. The solution-state ^{13}C-NMR spectra were obtained on a Bruker MSL-300 spectrometer operating at 74.5 MHz. The spectra of the native hemicellulosic preparation and the acetylated hemicellulosic sample 8 were recorded after 30,000 scans at 25°C from 60 mg of the sample dissolved in 0.75 mL D_2O and DMSO-d_6, respectively. A 60° pulse flipping angle, a 3.9° pulse width, and a 0.85 s time delay between pulses were used.

Thermal stability of the native and acetylated hemicelluloses was determined via thermogravimetric analysis (TGA). Measurement of calorimetric properties of the materials was performed through differential scanning calorimetry (DSC) on a simultaneous thermal analyzer



SCHEME 1 Acetylation of sugarcane bagasse hemicelluloses.

(NETZSCH STA-409). The sample weight was between 10 and 13 mg. Typically, the sample was heated from 20 to 600°C at a rate of 10°C per minute under nitrogen.

RESULTS AND DISCUSSION

Characterization of the Isolated Native Hemicelluloses

Hemicelluloses, which constituted 34.3% of the dry bagasse, were found to have the following composition: 88.6% pentosan, 1.8% uronic acid, and 1.0% lignin. Sugar analysis showed that xylose was the predominant sugar component, comprising 80.9% of the total sugars. Arabinose (9.3%) and galactose (5.6%) appeared as the second and third major sugar constituents. Uronic acids (1.8%), mainly 4-*O*-methyl-α-D-glucopyranosyluronic acid (MelcA), glucose (1.5%), and mannose (0.8%) were the minor constituents. The molar ratios of xylose : arabinose : galactose : MelcA : glucose : mannose were 83:10:5:1:1:0.7. Analysis of the isolated hemicelluloses by gel permeation chromatography (GPC) showed that the native hemicellulosic preparation had a weight-average molecular weight of 55,100 g mol^{-1} with a polydispersity of 10.5. The high molecular weight indicated that 10% NaOH extraction from SCB at 20°C did not significantly degrade the hemicellulose structure.

The ^{13}C-NMR spectrum of the native hemicelluloses (spectrum not shown) substantially corresponded to those of xylans. The main (1→4)-linked β-D-Xyl*p* units are characterized by the signals at 102.4, 75.9, 75.1, 73.4, and 63.3 ppm, which are respectively attributed to C-1, C-4, C-3, C-2, and C-5 of the β-D-Xyl*p* units [20,21]. The signals at 109.0, 86.4, 80.4, 78.3, and 61.8 ppm are assigned to C-1, C-4, C-2, C-3, and C-5 of α-L-arabinofuranosyl residues linked to β-D-xylans, respectively. Two signals at 72.0 and 70.1 ppm relate to C-4 and C-2 of the galactose residue. Signals observed at 172.9, 82.7, and 59.4 ppm, respectively, are characteristic of C-6, C-4, and methoxyl group of a 4-*O*-methyl-D-glucuronic acid residue. A very weak signal at 23.5 ppm is due to $-CH_3$ in Ar–$COCH_3$ group, indicating the associated lignin. Three signals at 181.4, 177.0, and 168.4 ppm are originated from the carbonyl signal ($-CH_2COO^-$) of the esterified ferulic or *p*-coumaric acids in native hemicelluloses. Similar results have been reported by Kato and co-workers[22] in the study of bagasse lignin-carbohydrate complex. The authors revealed 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.

Yield and Degree of Substitution

Acetylation is one of the most widely used processes for improving the hydrophobic property of polymers since acetyl groups are more

hydrophobic than hydroxyl groups. The process is routinely carried out with acetic anhydride or acetyl chloride in the presence of a tertiary amine such as DMAP or pyridine[23]. However, most of these reactions are rather expensive and the reagents are moisture sensitive[24]. Recently, it has been demonstrated that *N*-bromosuccinimide (NBS) is a more powerful catalyst for the rapid and efficient acylation of alcohols under mild and nearly neutral reaction conditions. In addition, NBS is an inexpensive and commercially available reagent[16]. Furthermore, the DMF/LiCl system acts as a solvent for both the starting hemicelluloses and the final products. As shown in Table I, NBS substantially acceler-

TABLE I Yield of acetylated hemicelluloses and degree of substitution (DS)

Acetylation conditions			Acetylated hemicelluloses		
Temperature (°C)	Reaction time (h)	Catalyst (g/100 mL solution)	Sample no.	Yield[a] (%)	DS
100	2.0	without NBS	1	68.2	0.37
100	2.0	1.0% NBS[b]	2	76.3	0.78
70	4.0	1.0% NBS	3	72.1	0.57
35	2.0	1.0% NBS	4	68.9	0.41
35	4.0	1.0% NBS	5	70.1	0.47
18	6.0	1.0% NBS	6	69.1	0.42
80	2.0	0.5% NBS	7	74.2	0.68
80	2.0	1.0% NBS	8	76.9	0.82
80	2.0	1.5% NBS	9	77.0	0.82
80	2.0	2.0% NBS	10	76.9	0.82
80	2.0	2.5% NBS	11	76.5	0.79
80	2.0	3.0% NBS	12	76.2	0.78
80	2.0	1.0% DMAP[c]	13	78.6	0.90
80	2.0	1.0% MPI[d]	14	72.6	0.60
80	2.0	1.0% MPO[e]	15	72.1	0.57
80	2.0	1.0% pyridine	16	71.0	0.51
80	2.0	0.5% H_2SO_4	17	76.0	0.77

[a]Based on assumption that all of the hemicelluloses are converted to hemicellulose diacetate (yield, 100%; DS, 2.0). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 61.0% (DS, 0.0).

[b]N-bromosuccinimide.

[c]4-dimethylamino pyridine.

[d]N-methyl pyrrolidine.

[e]N-methyl pyrrolidinone.

ated the rate of reaction in comparison with the control sample 1. Use of 1.0% NBS (1.0 g NBS in 100 mL solution) as the catalyst led to an increase in the yield by 8.1% and DS value by 0.41, which was over two times higher than the yield and the DS obtained under the same conditions without NBS (sample 1). Interestingly, an increase of NBS concentration from 0.5 (sample 7) to 1.0% (sample 8) resulted in improvements of yield from 74.2 to 76.9% and DS value from 0.68 to 0.82, respectively. However, no further increases in yield and DS were observed when the concentration of NBS was over 1.0%. This is a satisfactory result since NBS recovery is a crucial economic factor and its use must be limited. Hence the NBS concentration of 1.0% is considered optimum.

Table I also indicates that different catalytic systems can influence either the yield or the DS. The addition of 1.0% DMAP in the reaction system at 80°C for 2 h led to the highest yield (78.6%) and DS (0.90) as compared to other catalysts, such as 1.0% NBS (yield 76.9%, DS 0.82), 0.5% H_2SO_4 (yield 76.0%, DS 0.77), 1.0% MPI (yield 72.6%, DS 0.60), 1.0% MPO (yield 72.1%, DS 0.57), and 1.0% pyridine (yield 71.0%, DS 0.51). This indicated that DMAP and NBS are better catalysts than MPI, MPO, pyridine, and H_2SO_4. Although DMAP is the best catalyst studied in the acetylation of SCB hemicelluloses under the conditions given, it is expensive and not commercially available[25]. In comparison, NBS is rather cheap and commercially available. Indeed, with this catalyst, it is possible to synthesize hemicellulose acetates with a relatively low level of DS, less than 1.0. Generally, low DS hemicelluloses are recommended as environmentally friendly thermoplastics[26].

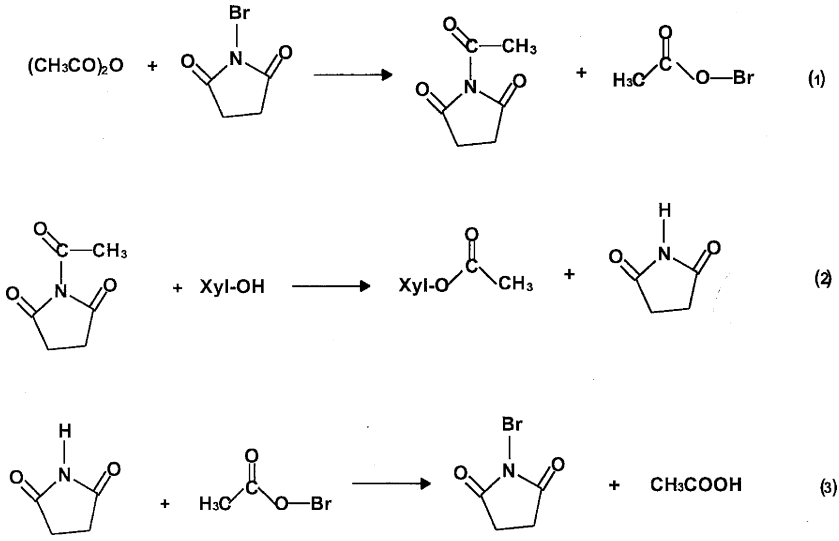
The temperature and time of reaction play a significant role in the yield and DS value of the acetylated hemicelluloses. Table I also gives the effect of reaction temperature and time on the efficiency of acetylation. As to be expected, the yield and the DS increased with increasing reaction temperature and time. At 35°C, the yield and the DS were 68.9% and 0.41 (sample 4), while at 70 and 80°C, these values increased to 72.1% and 0.57 (sample 3) and 76.9% and 0.82 (sample 8), respectively. The reasons for this increase probably include the favorable effect of temperature on compatibility of the reaction ingredients, enhanced swellability of hemicelluloses, increased diffusion of the esterifying agent, and mobility of the reactant molecules[27]. In contrast, a slight decrease in yield and DS from 80°C (sample 8) to 100°C (sample 2) resulted from hemicellulose degradation and hydrolysis of the resultant hemicellulosic acetates. Similarly, increasing reaction time from 2 to 4 h at 35°C resulted in a slight increment in yield and DS from 68.9% and 0.41 (sample 4) to 70.1% and 0.47 (sample 5), respectively. This increase in yield and DS with reaction duration could be due to the increased rate and time of collisions of acetic anhydride with SCB hemicelluloses through the formation of acetic-NBS intermediate. More importantly, a positive yield

(69%) and DS value (0.42) could be obtained under an extremely mild condition (18°C, 6 h), indicating that NBS can be used as a novel and effective catalyst for acetylation of hemicelluloses under extremely mild reaction conditions.

The actual mechanism of NBS is not clear but a plausible explanation is that NBS might act as a source for Br^+, which in turn activates the carbonyl groups of acetic anhydride to produce the highly reactive acylating agent (CH_3–CO–N–($OCCH_2CH_2CO$–). This acylating agent reacts with hydroxyl groups of hemicelluloses, which upon elimination of NBS produces acetylated hemicelluloses (Xyl–O–CO–CH_3) (Scheme 2)[16]. However, at this time the precise role of NBS is not clear and should be further studied in detail.

FT-IR Spectra

The FT-IR spectra of native and acetylated (sample 3) hemicelluloses are given in Figure 2. The absorbances at 1640, 1467, 1427, 1255, 1176, 1049, and 897 cm^{-1} in the spectrum (a) are associated with unmodified hemicelluloses. A sharp band at 897 cm^{-1} is characteristic of β-glucosidic linkages between the sugars units[28]. This confirmed that the xylose residues forming the backbone of the SCB hemicelluloses are linked by β



SCHEME 2 Mechanism of acetylation of hemicelluloses using NBS as a catalyst.

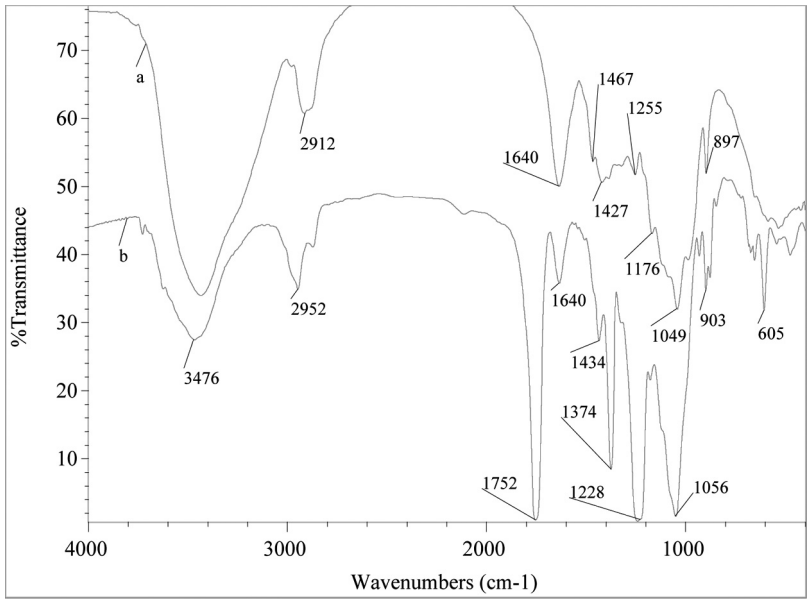


FIGURE 2 FT-IR spectra of unmodified hemicelluloses (spectrum a) and acetylated hemicellulosic sample 3 (spectrum b).

glucosidic bonds. The spectrum (b) of acetylated hemicelluloses provides evidence of acetylation by showing the presence of three important ester bands at 1752 (C=O ester), 1374 (–C–CH_3), and –C–O– stretching band at 1228 cm^{-1}[29]. A slight increase of peak intensity at 2952 cm^{-1} in spectrum (b) indicates methyl C–H stretching in acetylated hemicelluloses. A significant decrease in the intensity of the O–H absorption band at 3476 cm^{-1} in spectrum (b) verified that the hydroxyl groups in native hemicelluloses were substantially reduced after acetylation. Another strong band at 1056 cm^{-1} is attributed to C–O stretching in C–O–C linkages. Two small bands at 1640 and 903 cm^{-1} are assigned to the absorbed water and β-glucosidic linkages between the sugars units, respectively. As expected, the absence of absorption region 1840–1760 cm^{-1} in spectrum (b) revealed that the product is free of the unreacted acetic anhydride. Similarly, the lack of peaks at 1700 cm^{-1} for carboxylic groups indicated that the product is also free of acetic acid as a by-product.

The effect of NBS concentration and various catalysts on the intensity of the absorption bands in FT-IR spectra was also investigated and the results are given in Figures 3 and 4. Figure 3 depicts the FT-IR spectra of acetylated hemicellulosic samples 7 (0.5% NBS, spectrum (a)) and 8

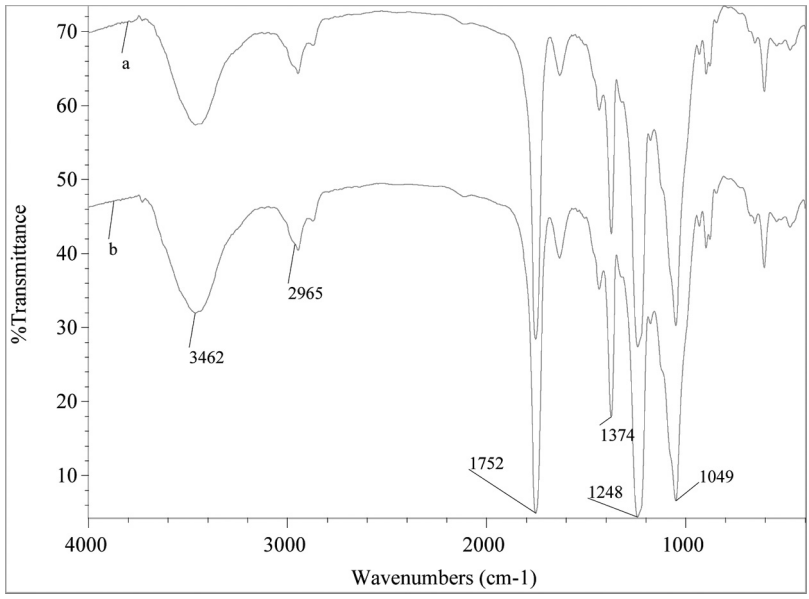


FIGURE 3 FT-IR spectra of acetylated hemicellulosic samples 7 (spectrum a) and 8 (spectrum b).

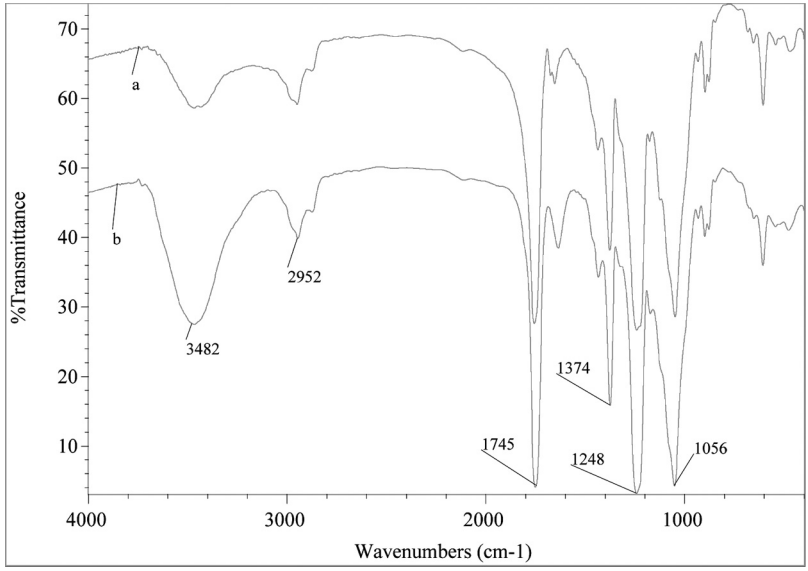


FIGURE 4 FT-IR spectra of acetylated hemicellulosic samples 13 (spectrum a) and 17 (spectrum b).

(1.0% NBS, spectrum (b)). Figure 4 shows the FT-IR spectra of acetylated hemicellulosic samples 13 (using 1.0% DMAP as a catalyst, spectrum (a)) and 17 (using 0.5% H_2SO_4 as a catalyst, spectrum (b)). Obviously, the intensity of the three ester bands at 1752 or 1745, 1374, and 1248 cm^{-1} increased with the increase of NBS concentration from 0.5 to 1.0% in Figure 3 and from spectrum (b) to (a) in Figure 4, corresponding to an increase in yield and DS in Table I. In contrast, the intensity of the band at 3462 or 3482 cm^{-1} for hydroxyl group stretching in hemicelluloses decreased with the increase of NBS concentration in Figure 3 and from spectrum (b) to (a) in Figure 4. This decreasing OH trend corresponded to the increasing level of acetylation.

^{13}C NMR Spectrum

The ^{13}C NMR spectrum of acetylated hemicellulosic sample 8 with a DS value of 0.82 is given in Figure 5. In comparison with the spectrum obtained from the native hemicelluloses, it can be seen that acetylation has clearly occurred as shown by two strong signals at 23.0 and 169.3 ppm, characteristic of an acetyl ester. The presence of five peaks at 99.9, 77.7, 74.9, 73.7, and 62.4 ppm are indicative of carbon atoms of C-1, C-4, C-3, C-2, and C-5 in the β-D-Xyl*p* units of hemicelluloses.

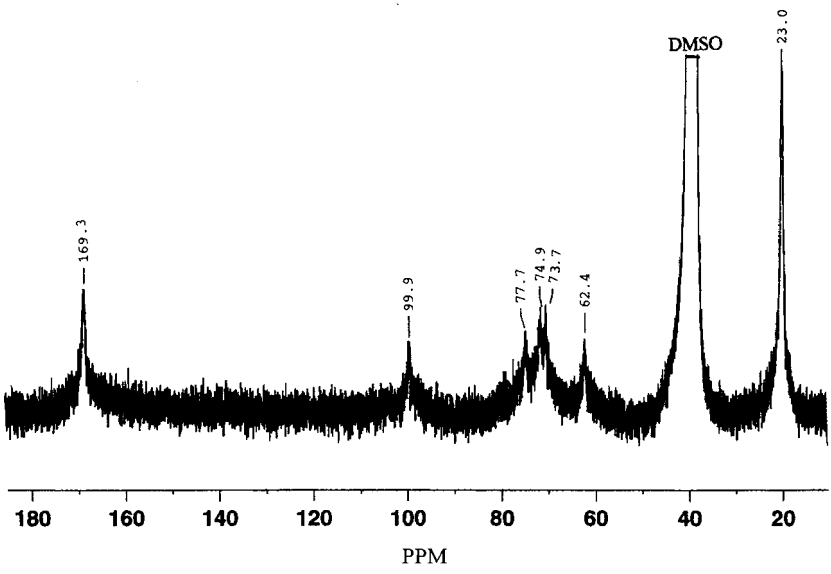


FIGURE 5 ^{13}C-NMR spectrum (in DMSO-d_6) of the acetylated hemicellulosic sample 8.

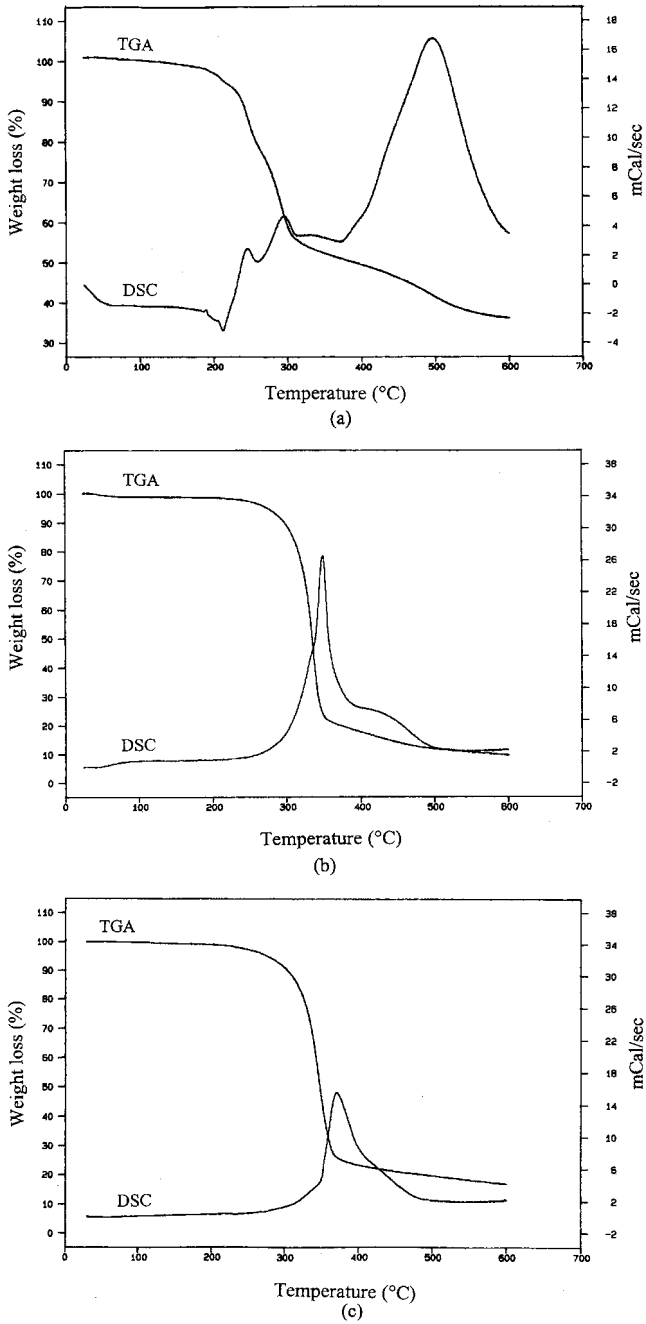


FIGURE 6 Thermograms of unmodified SCB hemicelluloses (a) and acetylated hemicellulosic samples 7 (b) and 13 (c).

Thermal Analysis

The TGA and DSC curves of the native hemicelluloses and acetylated hemicellulosic preparations (samples 7 and 13) are illustrated in Figure 6 (a), (b), and (c), respectively. The three samples could be differentiated by their characteristic temperature and weight loss. These different thermograms of the unmodified SCB hemicelluloses and acetylated hemicellulosic acetates were indicative of the alterations in chemical structure and thermal stability. As observed, the native hemicelluloses and two acetylated polymer samples 7 and 13 started to decompose at 200, 248, and 263°C, respectively. Similarly, at 60% weight loss the decomposition temperature of the unmodified hemicelluloses and the two acetylated polymer samples was observed at 300, 331, and 348°C, respectively. This result indicated that the thermal stability of the hemicelluloses increased by acetylation and is paralleled by the increased values of DS. DSC has been used to investigate the possibility of interaction among polymer components and to measure the extent of disruption of the hydrogen bonds as well as to quantify the heat energy[30]. As shown in Figure 6, native hemicelluloses showed a larger exothermic peak between 235 and 600°C due to the disintegration of intramolecular interaction and the decomposition of the polymer, whereas the two acetylated hemicellulosic samples produce a much smaller exothermic peak between 269 and 500°C, and 314 and 476°C, respectively. In addition, the peak area decreased substantially with an increase in DS value from 0.68 (Figure 6(b)) to 0.90 (Figure 6(c)). This implied again that the acetylation under the conditions used significantly breaks the hydrogen bonds between the molecules of the polymers.

CONCLUSION

Acetylation of the free hydroxyl groups of SCB hemicelluloses with acetic anhydride by using NBS as a catalyst in DMF/LiCl system is an elegant method to obtain polymers with low DS under extremely mild conditions. Acetylation between DS 0.37 and 0.82 could be prepared by varying NBS concentration and reaction temperature and time. An increase in the NBS concentration from 0.5 to 1.0%, reaction temperature from 35 to 80°C, and reaction time from 2.0 h to 4.0 h resulted in an increase in the product DS by 0.14, 0.41, and 0.06, respectively. The thermal stability of the products was found to be higher than the unmodified hemicelluloses, and it increased with increasing degree of substitution. Such low DS polymers could be found promising for making environmentally friendly thermoplastics.

REFERENCES

[1] Stage, C., B. Verneuil, P. Branland, R. Granet, P. Krausz, J. Rozier, and C. Petit. (2000). *Carbohydr. Polym.* **49**, 373.
[2] Rowell, R. M. and F. M. Keany. (1991). *Wood Fiber Sci.* **23**, 15.
[3] Fredon, E., R. Granet, R. Zerrouki, P. Krausz, L. Saulnier, J. F. Thibault, J. Rosier, and C. Petit. (2002). *Carbohydr. Polym.* **49**, 1.
[4] Sun, R. C., X. F. Sun, G. Q. Liu, P. Fowler, and J. Tomkinson, (2002). *Polym. Int.* **51**, 117.
[5] Olsson, L. and B. Hahn-Hagerdal. (1996). *Enzyme Microbiol. Technol.* **18**, 312.
[6] Silva, C. J. S. M. and I. C. Roberto. (2001). *Lett. Appl. Microbiol.* **32**, 248.
[7] Gabrilii, I. and P. Gatenholm. (1998). *J. Appl. Polym. Sci.* **69**, 1661.
[8] Mobarak, F., S. F. El-Kalyoubl, and N. Shukry. (1992). *Cellulose Chem. Technol.* **26**, 131.
[9] Sun, R. C., J. M. Lawther, and W. B. Banks. (1996). *Carbohydr. Polym.* **29**, 325.
[10] Cai, Z. S. and L. Paszner. (1998). *Holforschung* **42**, 11.
[11] Ebringerova, A. and T. Heinze. (2000). *Macromol. Rapid Commun.* **21**, 542.
[12] Whistler, R. L., A. Bushway, P. P. Singh, and W. Nakahara. (1976). *Adv. Carbohydr. Chem. Biochem.* **32**, 235.
[13] Hashi, M. and T. Takeshita. (1979). *Agric. Biol. Chem.* **43**, 961.
[14] Proksch, A. and H. Wagner. (1987). *Phytochemistry* **26**, 1989.
[15] Fan, X. R. and Z. H. Fen. (1987). *Acta Pharmacol. Sinica* **8**, 169.
[16] Karimi, B. and H. Seradj. (2001). *Synlett* **4**, 519.
[17] Lawther, J. M., R. C. Sun, and W. B. Banks. (1995). *J. Agric. Food Chem.* **43**, 667.
[18] Blakeney, A. B., P. J. Harris, R. J. Henry, and B. A. Stone. (1983). *Carbohyd. Res.* **113**, 291.
[19] Blumenkrantz, N. and G. Asboe-Hanson. (1973). *Anal. Biochem.* **54**, 484.
[20] Imamura, T., T. Watanabe, M. Kuwahara, and T. Koshijima. (1994). *Phytochemistry* **37**, 1165.
[21] Gabrielii, I., P. Gatenholm, W. G. Glasser, R. K. Jain, and L. Kenne. (2000). *Carbohydr. Polym.* **43**, 367.
[22] Kato, A., J. Azuma, and T. Koshijima. (1987). *Agric. Biol. Chem.* **51**, 1691.
[23] Steglich, V. and G. Hotfle. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 981.
[24] Chavan, S. P., R. Anand, K. Pasupathy, and B. S. Rao. (2001). *Green Chem.* **3**, 320.
[25] Connors, K. A. and K. S. Albert. (1973). *J. Pharmaceutical Sci.* **62**, 845.
[26] Fang, J. M., R. C. Sun, P. Fowler, J. Tomkinson, and C. A. S. Hill. (1999). *J. Appl. Polym. Sci.* **74**, 2301.
[27] Khalil, M. I., A. Hashem, and A. Hebeish. (1995). *Starch/Stärke* **47**, 394.
[28] Gupta, S. and R. N. Madan. (1987). *Tappi J.* **70**, 113.
[29] Saikia, C. N., F. Ali, T. Goswami, and A. C. Ghosh. (1995). *Ind. Crops Prod.* **4**, 233.
[30] Bilideris, C. G., T. J. Maurice, and J. R. Vose. (1980). *Starch/Stärke* **45**, 1669.