ELSEVIER

Carbohydrate Polymers 41 (2000) 379–387

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Acetylation of wheat straw hemicellulose B in a new non-aqueous swelling system

J.M. Fang, R.C. Sun*, J. Tomkinson, P. Fowler

The BioComposites Centre, University of Wales, Bangor, Gwynedd LL57 2UW, UK

Received 11 February 1999; received in revised form 19 May 1999; accepted 21 June 1999

Abstract

The acetylation of wheat straw hemicellulose B was carried out in a homogeneous *N,N*-dimethylformamide and lithium chloride system with acetic anhydride using 4-dimethylaminopyridine as a catalyst. The degree of substitution of hemicellulose B acetates ranged between 0.59 and 1.25 as a function of experimental conditions. Under an optimum condition (85°C, 60 h), approximately 75% of the free hydroxyl groups in native hemicellulose B were acetylated. The molecular weight measurements (31,890–34,090 g mol^{-1}) showed a controllable degradation of hemicellulose B chains during the reactions at temperature 60–85°C and duration of 2–60 h. It was found that the thermal stability of the products was increased by chemical modification. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Wheat straw; Hemicellulose B acetate; Homogeneous system; Acetylation

1. Introduction

Hemicelluloses, one of the most abundant natural polysaccharides, comprise roughly one-fourth to one-third of most plant materials, and this amount will vary according to the particular plant species, such as wheat straw 32%, barley straw 32%, oat straw 27%, rye straw 31%, rice straw 25%, sunflower husk 23%, sugarcane rind 22%, and corn cobs 37% (Sun, 1996). Over the past twenty years, studies on utilization of hemicelluloses have demonstrated to be a potential fermentation feedstock in production of ethanol, acetone, butanol, and xylitol. In previous work, we carried out the isolation and structural characterization of hemicelluloses, extracted from wheat straw (Lawther, Sun & Banks, 1995), Abaca fibre (Sun, Fang, Goodwin, Lawther & Bolton, 1998), sugar beet pulp (Sun & Hughes, 1998), and oil palm (Sun, Mott & Bolton, 1998). A simple procedure for a large scale production of hemicelluloses from wheat straw has been proposed in our laboratory and it has been successfully used in industry.

Hemicelluloses are usually defined as that polysaccharide part of plant tissue, which is accessible to the action of dilute acids and alkalis. The concept of hemicelluloses includes polymeric carbohydrates, having five and six carbon atoms in their sugar structure as repeating units comprising the polymeric chains. Hemicelluloses are branched polymers of low molecular weight of a degree of polymerization of 80–200 (Cai & Paszner, 1988). Xylans from straw and grass have the same backbone as the wood xylans, which consist of about 200 β-xylopyranose residues, linked together by 1,4-glycosidic bonds. However, they contain smaller proportions of uronic acids, but are more highly branched and contain large proportion of L-arabinofuranosyl units. The former, consisting of 4-*O*-methylglucuronic acid, attaches directly to the C-2 position of xylose, while the latter are linked mainly to the C-3 position of xylose (Puls & Schuseil, 1993).

The properties of hemicelluloses can be modified by, for example, partial hydrolysis, oxidation, reduction, etherification or esterification of the hydroxyl groups, and cross-linking. Up to now, cellulose and starch are the main starting materials for the bulk production of modified polysaccharides, and their derivatives have found use in the industrial production of food, textiles, paper and cosmetics. However, the hemicelluloses with one or two hydroxyl group are hydrophilic and synthetic polymers are usually hydrophobic, which reduce their use in industrial applications. These shortcomings can be overcome by their modification. Meanwhile, In cellulose and starch, there are three hydroxyl groups available on each monomer unit for esterification, however, in hemicelluloses or their fraction B, there are only one or two for esterification, which makes it more difficult to modify than cellulose and starch.

Over the past few years, studies on chemical modification

---

* Corresponding author. Tel.: + 1248-370588; fax: + 1248-370594.

PII: S0144-8617(99)00102-2

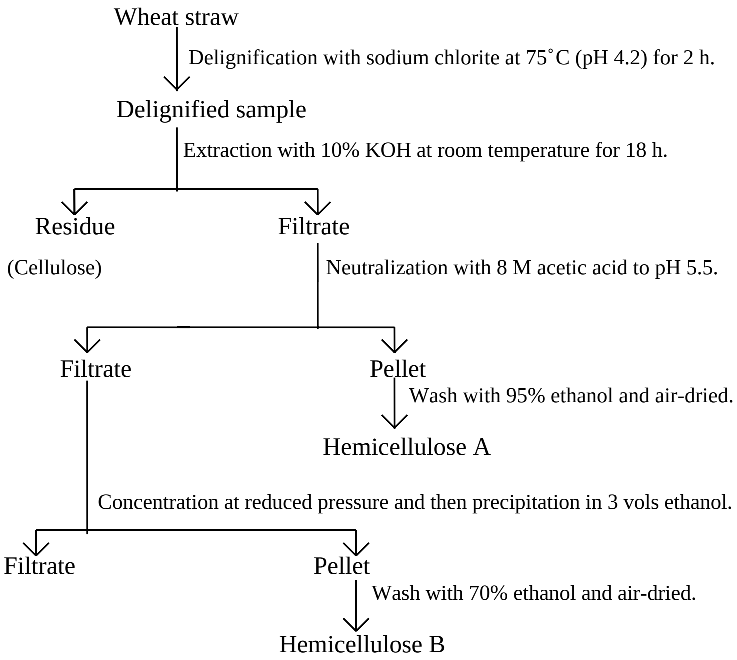

Fig. 1. Scheme for extraction of hemicellulose B from wheat straw.

of hemicelluloses have carried in heterogeneous and gel-like phase obtaining low degrees of substitution (Focher, Marzetti, Naggi & Torri, 1989). In order to improve the properties of hemicellulose derivatives, we investigated to find suitable reaction media to perform derivation reactions in homogeneous phase, 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 *N*,*N*-dimethylformamide (DMF) were found to be able to prevent the aggregation of flexible hemicellulose chains, promoting the interactions between substrate and reagents in our recent studies. Acetylation of the hydroxyl groups of hemicelluloses 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.

The preparation of new polymers from hemicelluloses or their fractions is therefore an important part of any research program aimed at utilizing annually renewable, agriculturally derived polymers as extenders and replacements for polymers prepared from petrochemicals. It is also note that the application of hemicellulose acetate would have an opportunity for the substitution of hemicellulose acetate for starch acetate and cellulose acetate.

This work presents the results of studies of acetylation under homogeneous reaction conditions in a new non-aqueous swelling system (DMF/lithium chloride (LiCl) system) by reacting the native hemicellulose B with acetic anhydride in the presence of 4-dimethylaminopyridine (DMAP) as a catalyst.

2. Experimental

2.1. Material

Wheat straw was obtained from Compak Co. (Gainsborough, England). The straw was first cut into 1–2 cm length by hand. After being dried in an oven at 55°C for 16 h, the straw was then ground to pass through a 0.7 mm screen and stored at 5°C until use. DMF solvent was dried prior to use according to conventional methods. Anhydrous LiCl was obtained by dry at 130°C for 2 h before use. Other reagent grade chemicals were used without further purification.

2.2. Isolation and characterization of hemicellulose B

Wheat straw was first delignified with sodium chlorite in acetic solution (pH 4.2, adjusted by 10% acetic acid) at 75°C for 2 h. The hemicelluloses were then obtained from the holocellulose by extraction with 10% potassium hydroxide for 18 h at room temperature with a liquor ratio of 1:20. The hemicellulose A was recovered from the supernatant by acidifying to pH 5.0 with acetic acid and then by centrifugation. Hemicellulose B was obtained from the mother liquor by precipitation with three volumes of 95% ethanol, and then filtered and washed by 70% ethanol. The fraction that remained soluble in aqueous ethanol was named hemicellulose C. After being air-dried, the resultant hemicellulose B was kept in a refrigerator at 0°C until required for analysis and acetylation (Fig. 1).

The neutral sugar composition of the isolated hemicellulose B was determined by gas chromatography (GC) analysis of their alditol acetates (Blakeney, Harris, Henry &

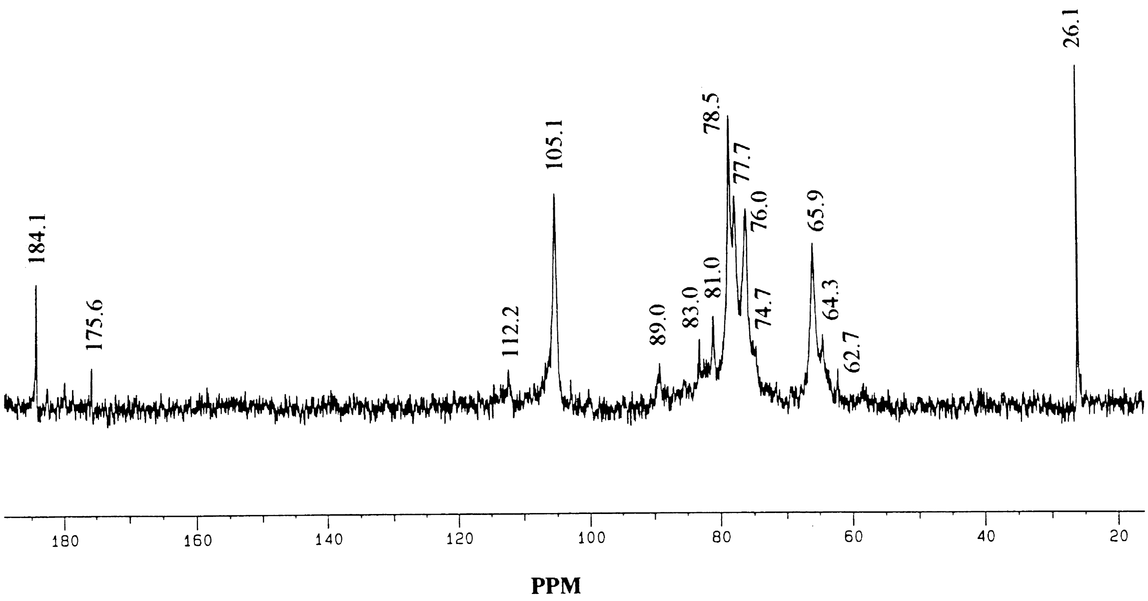

Fig. 2. ^{13}C-NMR spectrum (in D_2O) of native hemicellulose B extracted with 10% KOH at 25°C for 18 h from delignified wheat straw.

Stone, 1983). Alkaline nitrobenzene oxidation of residual lignin from hemicellulose B was performed at 170°C for 3 h. The lignin content in hemicellulose B was calculated by 2.41 multiplying the yield of phenolics, obtained by nitrobenzene oxidation (Sun et al., 1998). Methods of uronic acid analysis, determination of phenolic acids and aldehydes in nitrobenzene oxidation mixtures with high performance liquid chromatography (HPLC), and measurement of the native hemicellulosic molecular weights have been described in previous papers (Lawther et al., 1995; Sun, Lawther & Banks, 1995, 1996).

FT-IR spectra were obtained on an FT-IR (Nicolet 750) spectrophotometer using a KBr disc containing 1% finely ground samples. The solution-state ^{13}C-NMR spectrum was obtained on a Bruker 250 AC spectrometer operating in the FT mode at 62.4 MHz under total proton decoupled conditions. It is recorded at 25°C from 200 mg of sample dissolved in 1.0 ml D_2O after 8000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width and 0.85 s acquisition time were used.

2.3. Acetylation of hemicellulose B

0.6 g hemicellulose B (0.008 mol of hydroxyl functionality) was added to 30 ml DMF/LiCl (1.0%, w/w) and heated to 120°C. The mixture was stirred until completely dissolved (approximately 2 h). After temperature was lowered to the required temperature (60–90°C), 0.6 ml acetic anhydride (0.0064 mol of carboxyl functionality) and 0.15 g DMAP was added dropwise, and the homogeneous reaction mixture was stirred for 1 h at 85°C. Same amounts of acetic anhydride and DMAP was added dropwise over another period of 10 min, and the stirring was continued for a total period of 2, 4, 6, 12, 24, 36, 48, 60, and 72 h, respectively, at 85°C. Experiments 1, 2 and 4 were performed under the conditions same as others except for the temperature at 60, 70 and 90°C, respectively. After cooling to room temperature, the homogeneous reaction mixture was slowly poured in to 120 ml of 95% ethanol with stirring. The white product that separated from the solution was filtered off and collected. This filtrate was washed thoroughly with 95% ethanol and acetone. The product was first air-dried for 24 h and then further dried in an oven at 55°C for another 24 h.

2.4. Characterization of the acetylated hemicellulose B

The yield percentages were calculated based on the assumption that all of the hemicellulose B was converted to hemicellulose diacetate. In the case the yield percentage and the degree of substitution (DS) would be 100% and 2.0, respectively. The unreacted acetic anhydride in a mixture of reaction was separated from the product by dissolving in 95% ethanol and acetone. If no reaction occurred and all of the hemicellulose B was recovered unreacted, the yield percentage and the degree of substitution would be 61.0% and 0.0, respectively. The solubility was measured at 5% concentration in different organic solvents.

The molecular-average weights of acetylated hemicellulose B preparations were determined by gel permeation chromatography on a PLgel 5 μ Mixed-D column. The samples were dissolved in dimethyl sulfoxide (DMSO) at a concentration of 0.1%, and a 200 μl sample in solution was injected. The column was operated at 80°C and eluted with DMSO at a flow rate of 1 ml min^{-1}. The column was calibrated using PL pullulan polysaccharide standards.

Thermogravimetric analysis of acetylated hemicellulosic preparations was performed with a Simultaneous Thermal

Analyser (STA 625). This apparatus provides for a continuous measurement of sample weight at a range of temperatures between ambient and 600°C. Samples of approximately 10 mg weight were heated in a platinum crucible to 600°C at a heating rate of 10°C $\min^{-1}$. Provision was made for electronic differentiation of the weight signal to give the rate of weight loss. Air was used as the purge gas, and a positive pressure was maintained through the weighing chamber.

3. Results and discussion

3.1. Characterization of the isolated hemicellulose B

The yield of hemicellulose A, B and C were 7.3, 25.7 and 1.0% of the dry wheat straw, respectively. These data indicated that the hemicellulose B represented the majority of the hemicellulosic materials, which comprised 75.6% of the total hemicelluloses. The sugar analysis of the hemicellulose B showed that xylose is a predominant component sugar, which presented 73.5% of the total sugars. Arabinose (12.2%), appeared as the second major sugar component. Glucose (7.7%), galactose (5.7%), and rhamnose (1.1%) were present as minor sugar constituents. The uronic acids, mainly 4-*O*-methyl-D-glucopyranosyluronic acid (MeGlcA), were present in a noticeable amount (5.6%). The molar ratios of xylose:arabinose:MeGlcA:glucose:galactose:rhamnose were 92:15:5:8:6:1. Gel permeation chromatography (GPC) showed the native hemicellulose B had a weight-average molecular weight of 29,060 g mol^{-1} with a polydispersity of 5.4.

The ^{13}C-NMR spectrum of the native hemicellulose B (Fig. 2) substantially corresponded to those of xylans (Ebringerova, Hromadkova, Alfoldi & Berth, 1992; Focher et al., 1989; Imamura, Watanabe, Kuwahara & Koshijima, 1994; Kato, Azuma & Koshijima, 1987). The main 1,4-linked β-D-Xylp units are obviously characterized by the signals at 105.1, 78.5, 77.7, 76.0, and 65.9 ppm, which respectively attributes to C-1, C-4, C-3, C-2, and C-5 of the β-D-Xylp units. The signals at 112.2, 89.0, 83.0, 81.0, and 63.4 ppm correspond to C-1, C-4, C-2, C-3, and C-5 of α-L-Araf residues, respectively. Two signals at 62.7 and 175.6 ppm originate from the 4-*O*-methoxyl group and C-6 in 4-*O*-methoxyl group of glucuronic acid residue in the xylan, respectively. These very weak two signals are in accord with the low uronic acid content. These signals with further methylation analysis clearly showed that most of the xylose residues are linked to each other through β-(1 → 4)-linkages, and that MeGlcA, L-arabinofuranosyl residues, and a small amount of D-xylopyranosyl groups are located at C-2 and C-3 of the xylopyranosyl residues in the main chain (Sun et al., 1996). The signal at 26.1 ppm relates to $-CH_3$ in $Ar-COCH_3$, indicating the associated lignin. A signal at 184.1 ppm originates the carbonyl signal ($-CH_2COO^-$) of esterified ferulic or *p*-coumaric acids in native hemicellulose B. This esterified linkage between ferulic or *p*-coumaric acids and L-arabinofuranose was also confirmed by FT-IR absorption band at 1630 cm^{-1} (conjugated aliphatic C=C, Fig. 5). Similar results were found in bagasse hemicellulose by Kato and co-workers (1987). The authors indicated 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.

In an effect to gain insight into the associated lignin in nature hemicellulose B, a degradation method such as alkaline nitrobenzene oxidation was used in this study. The results showed that a major phenolic monomer component in the oxidation mixture was found to be vanillin (0.30%, w/w), which represented approximately 50% of the total phenolic acids and aldehydes. Small amounts of syringaldehyde (0.065%), *p*-hydroxybenzaldehyde (0.065%), syringic acid (0.065%), vanillic acid (0.039%), *p*-coumaric acid (0.038%), *p*-hydroxybenzoic acid (0.032%), and ferulic acid (0.023%) were also identified in the nitrobenzene oxidation products. This relatively high amount of vanillin indicated that the lignins in wheat straw cell walls are linked to hemicellulose B mainly via guaiacyl units.

3.2. Yield and degree of substitution

In order to gain a considerable conversion in subsequent reactions, an acetylation of native hemicelluloses in homogeneous system is absolutely necessary. We have found that a treatment of the polymer suspended in a dipolar-aprotic solvent such as DMF/LiCl system can lead to a highly swollen gel suspension of the polymer and activate the polymers. Similar results have been reported by Voget, Klemm and Heinze (1996) on the studies of esterification of carboxymethyl cellulose in DMF or DMSO with *p*-toluenesulfonic acid. As shown in Table 1, the yield of acetylated hemicellulose B and the degree of substitution (DS) ranged between 72.2–85.3% and 0.59–1.25, respectively. Increase of reaction temperature from 60 to 85°C resulted in an increment in the yield and DS from 72.2 to 81.7% and 0.59 to 1.06, respectively. The reason for this enhancement of acetylation by increasing temperature was probably due to the favourable effect of temperature on compatibility of the reaction ingredients, swellability of hemicellulose B, diffusion of the esterifying agent, and mobility of the reactant molecules (Khalil, Hashem & Hebeish, 1995). In contrast to the increasing trend, the acetylation yield decreased by raising the reaction temperature from 85 to 90°C. This decrement in the yield could be ascribed to the partial degradation of the native hemicellulose B at high temperature. On the contrary, enhancement of acetylation by prolonging the duration of reaction was a direct consequence of the favourable effect of time on diffusion and adsorption of the reactants between the esterifying agent and the hemicellulose B molecules. In contrast, the reaction at 85°C for 72 h in experiment 12 only gave the yield of 73.5% and a DS value of 0.64. This much lower yield of acetylation was presumed due to the significant

Table 1
The yield of acetylated hemicellulose B and the degree of substitution (DS) (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))

Sun No.	Acetylation conditions	Yield (%)	DS
1	60°C, 48 h	72.2	0.59
2	70°C, 48 h	76.2	0.78
3	85°C, 48 h	81.7	1.06
4	90°C, 48 h	78.9	0.92
5	85°C, 2 h	75.2	0.73
6	85°C, 4 h	76.2	0.78
7	85°C, 6 h	76.3	0.78
8	85°C, 12 h	76.7	0.81
9	85°C, 24 h	78.2	0.88
10	85°C, 36 h	78.5	0.90
11	85°C, 60 h	85.3	1.25
12	85°C, 72 h	73.5	0.64

degradation of some amounts of macromolecular hemicellulose B into oligosaccharides during the prolonging period of esterification for 72 h, which were solubilized in 95% ethanol and not recovered by the method used. Whereas the much lower DS may be explained by the fact that in the latter the system contained traces of water which leads to hydrolysis of the esterified hemicellulose B.

Our previous studies showed that hemicellulose B, obtained from refined wheat straw, was to be essentially a (1 → 4) linked β-D-xylan with 4-*O*-methyl-D-glucopyranosyluronic acid attached at position 2, and L-arabinofuranosyl or D-xylopyranosyl groups attached at position 3. For every six D-xylopyranosyl residues in the main chain, there is one L-arabinofuranosyl group, for every eight such D-xylopyranosyl residues, there is one D-xylopyranosyl group, and for approximately 24 such D-xylopyranosyl residues, there is one MeGlcA unit (Sun, 1996). Based on this more branched structure of hemicellulose B, for every 24 D-xylopyranosyl residues in the backbone, there are eight side chains attached at C-2 or C-3 of xylose in the main chain. This resulted in only 40 free hydroxyl groups that can be acetylated, which accounted for a maximum yield value less than 100, 93.6% and a maximum DS value less than 2.0, 1.67. In experiment 11, a maximum yield (85.3%) and a highest DS value (1.25) implied that approximately 75% of the free hydroxyl groups in native hemicellulose B were acetylated under the reaction condition used. One possible reason for this lack of complete reaction in homogeneous system is probably due to the relatively high molecular weight of the hemicellulose B substrate, which is not significantly degraded by the DMF/LiCl solvent during a period of 60 h. The second explanation for incomplete reaction is probably due to the high viscosity of the reaction medium leading to diffusion controlled kinetics (McCormick & Callais, 1987). In order to gain a complete substitution (DS, 1.67), addition of more mol of esterifying agent such as acetic anhydride per mol of free OH groups, pre-swelling or activation of the hemicelluloses before reaction are needed. An effective method for activation is to dissolve the native hemicellulose B in an aqueous solution and then removal of the water from the swollen gel by repeated distillation under reduced pressure, which may accelerate the swelling process more remarkably.

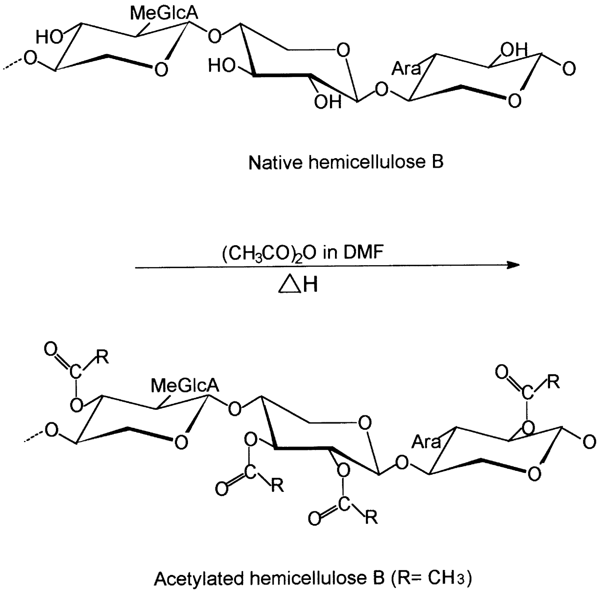

Fig. 3. Acetylation of hemicelluloses B.

Fig. 3 gives an overview of the acetylation reactions carried out under homogeneous condition in DMF. The hydroxyl groups in native hemicellulose B can be substituted by nucleophiles like halids. Therefore, the esterification reactions investigated were always carried out with anhydrides of the corresponding acids in order to exclude such side reactions. The free acetic acids formed during the acetylation, on the contrary, are not an enough strong acid to hydrolysis of the products or not nucleophilic enough to attack the acetyl ester groups (Heinze, Rahn, Jaspers & Berghmans, 1996). Further studies found that the reaction mechanism involves an attacking of acyl carbon centre by nucleophile such as DMAP and a removal of carboxylic acid (Fig. 4). In addition, DMF forms strong hydrogen bonds with hydroxyl groups of hemicellulose B, changing to some extent the original pattern of intra- and inter-molecular hydrogen bonds within and between the hemicellulose B chains. Meanwhile, the proton acceptor properties of DMF increase the nucleophilicity of hydroxyl groups, hence the reactivity towards various electrophilic agents (Focher et al., 1989).

3.3. FT-IR spectra

The hemicellulose B ester reactions were monitored by observing in the infrared spectra a reduction in the acetic anhydride carbonyl absorbance (1840–1760 cm^{-1}) and the appearance of an ester carbonyl absorbance

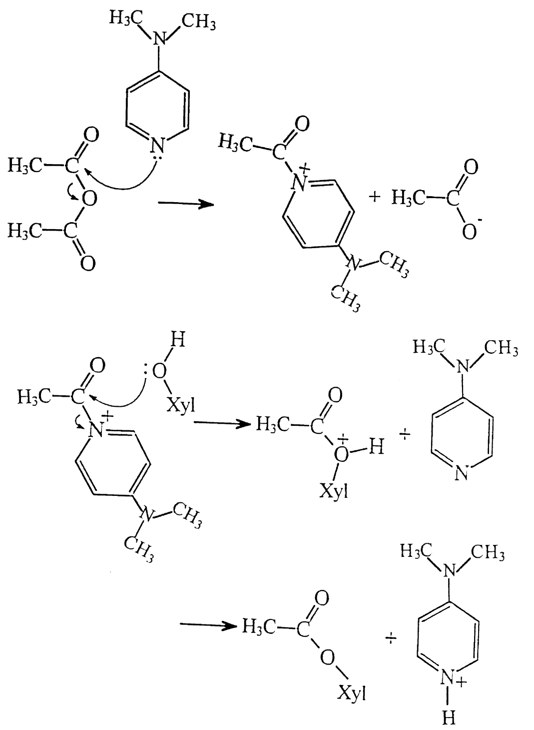

Fig. 4. Mechanism of acetylation of wheat straw hemicelluloses B.

(1760–1740 cm^{-1}). As shown in Fig. 5, the absorbances at 1638, 1580, 1467, 1414, 1342, 1268, 1170, 1129, 1045, and 897 cm^{-1} seen in the spectrum (a) are associated with native hemicellulose B (Sun et al., 1996). A sharp band at 897 cm^{-1} is characteristic of beta-glucosidic linkages between the sugars units (Gupta, Madan & Bansal, 1987). This confirmed that the xylose residues forming the backbone of the macromolecule are linked by β form bonds. The spectrum (b) of acetylated hemicellulose B (Experiment 7, 85°C, 6 h) provides evidence of acetylation by showing the presence of three important ester bands at 1752 (C=O ester), 1381 ($-C-CH_3$), and –C–O– stretching band at 1255 cm^{-1} (Saikia, Ali, Goswami & Ghosh, 1995). An increase of peak at 2959 cm^{-1} in spectrum b indicates methyl C–H stretching in acetylated hemicellulose B. The strong band at 1049 cm^{-1} may be assigned to C–O stretching in C–O–C linkages. The unreacted hydroxyl group (–O–H) bending can be seen at 1440 cm^{-1}, indicating a incomplete acetylation. The disappearance of peaks at 1840–1760 cm^{-1} in spectrum b suggested that the products are free of the unreacted acetic anhydride.

3.4. Molecular weight

The weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights and polydispersity ($\bar{M}_w/\bar{M}_n$) of hemicellulose B acetates are given in Table 2. All the molecular weights determined were to illustrate whether the extent of degradation occurred during the reaction in DMF/LiCl system. The theoretical molecular weights were based on the molecular weight of the starting hemicellulose B ($\bar{M}_w = 29,060$ g mol^{-1}) and the value of DS. It was found that the molecular weights of acetylated hemicellulose B preparations 1–3 and 5–11 were lower than the calculated values by 20%. This indicated that a slight degradation occurred in the reactions at 60–85°C during a period of 2–60 h. While the acetylated hemicellulose B preparations 4 and 12 showed much lower molecules than the calculated values. This stated that a significant amount of degradation occurred during the reaction conditions either at 90°C or under a prolonging period of 72 h at 85°C. The GPC molecular weight distribution of acetylated hemicellulose B, esterified at 85°C for 6 h (Fig. 6) ranged between 123,600 and 8,810 g mol^{-1} with a main peak at 37,500 g mol^{-1}.

3.5. Solubility

The acetylated hemicellulose B is more hydrophobic than the native hemicellulose B. Meanwhile, it was found that he solubility is proportional to the degree of substitution (Lepeniotis & Feuer, 1997; Rahn, Diamantoglou, Klemm, Berghmans & Heinze, 1996). Therefore, the solubility of the products was investigated only using the acetylated hemicellulose B preparation 3 as a sample. The product showed a good solubility in DMSO at ambient temperature and in pyridine at 80°C. The sample is partially soluble in chloroform and dichloromethane at 40°C. In some experiments, even at 3.0% concentration, the products did not completely dissolve in the solvents. This can be attributed to the presence of unreacted hemicellulose B or to the insolubility of the hemicellulosic diacetates. Similar results have been reported on trimethylsilyl cellulose by Rahn et al. (1996). The authors stated that samples of low DS are soluble in DMSO and *N*,*N*-dimethylacetamide (DMA), those of medium DS in tetrahydrofuran, while samples of high DS

Table 2
Weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights and polydispersity ($\bar{M}_w/\bar{M}_n$) of the acetylated hemicellulose B preparations

	Acetylated hemicellulose B preparations[a]											
	1	2	3	4	5	6	7	8	9	10	11	12
$\bar{M}_w$	31,890	32,980	33,780	28,160	32,450	32,880	33,950	33,340	33,710	34,090	32,100	23,080
$\bar{M}_n$	26,430	27,800	28,150	23,470	26,820	26,950	27,920	27,550	27,630	27,720	26,130	18,320
$\bar{M}_w/\bar{M}_n$	1.18	1.19	1.20	1.20	1.21	1.22	1.22	1.21	1.22	1.23	1.24	1.26

[a] Corresponding to the experiment Sun No. in Table 1.

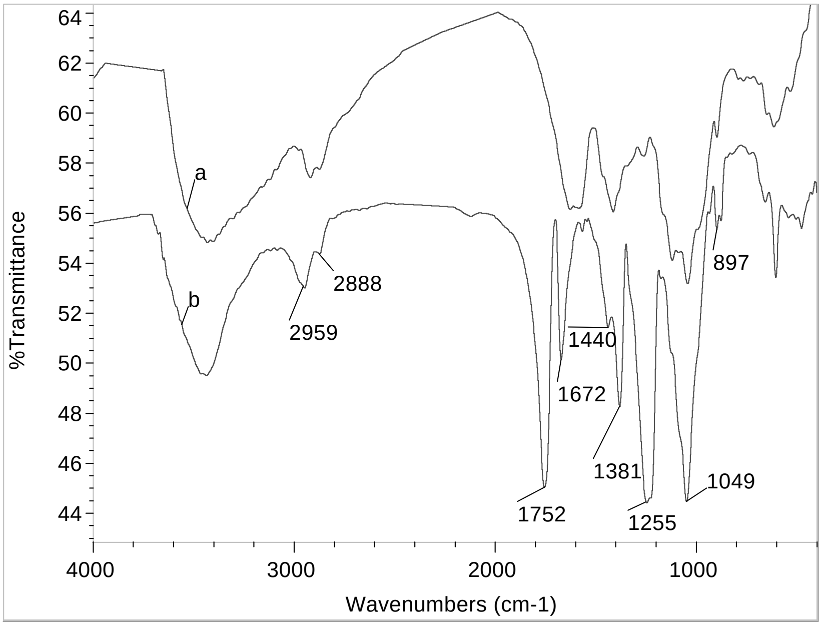

Fig. 5. FT-IR spectra of unmodified hemicellulose B (spectrum a) and acetylated hemicellulose (spectrum b, 85°C, 6 h).

can be dissolved in hexane or CCl_4 only. Thus it is presumed that there is no solvent for the whole DS range in case of acetylated hemicellulose B. The primary studies also showed that the soluble hemicellulose B acetates can form the films and membranes from the solution by casting and evaporating of the solvent. This work is being further investigated.

3.6. Thermal stability

The thermal degradation pattern of both native hemicellulose B and acetylated hemicellulose B preparation 7 (esterified at 85°C for 6 h) gave additional evidence to the relatively higher stability of the acetylated hemicellulose B (Fig. 7). The curve of native hemicellulose B (a) showed a prominent effect between 220 and 400°C with two maximum around 270 and 360°C ca. 38 and 20% of the total weight losses, respectively. While the DSC curve of the acetylated hemicellulose B (b) exhibited three thermal decomposition peaks at the relatively higher temperatures of 310, 340, and 410°C, respectively, which represented about 48, 22, and 12% of

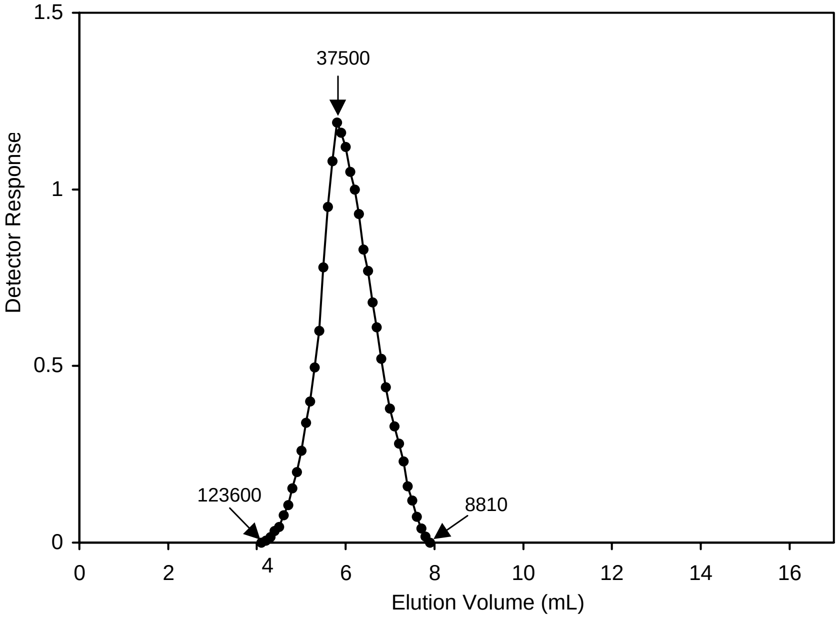

Fig. 6. GPC molecular weight distribution of acetylated hemicellulose B esterified at 85°C for 6 h.

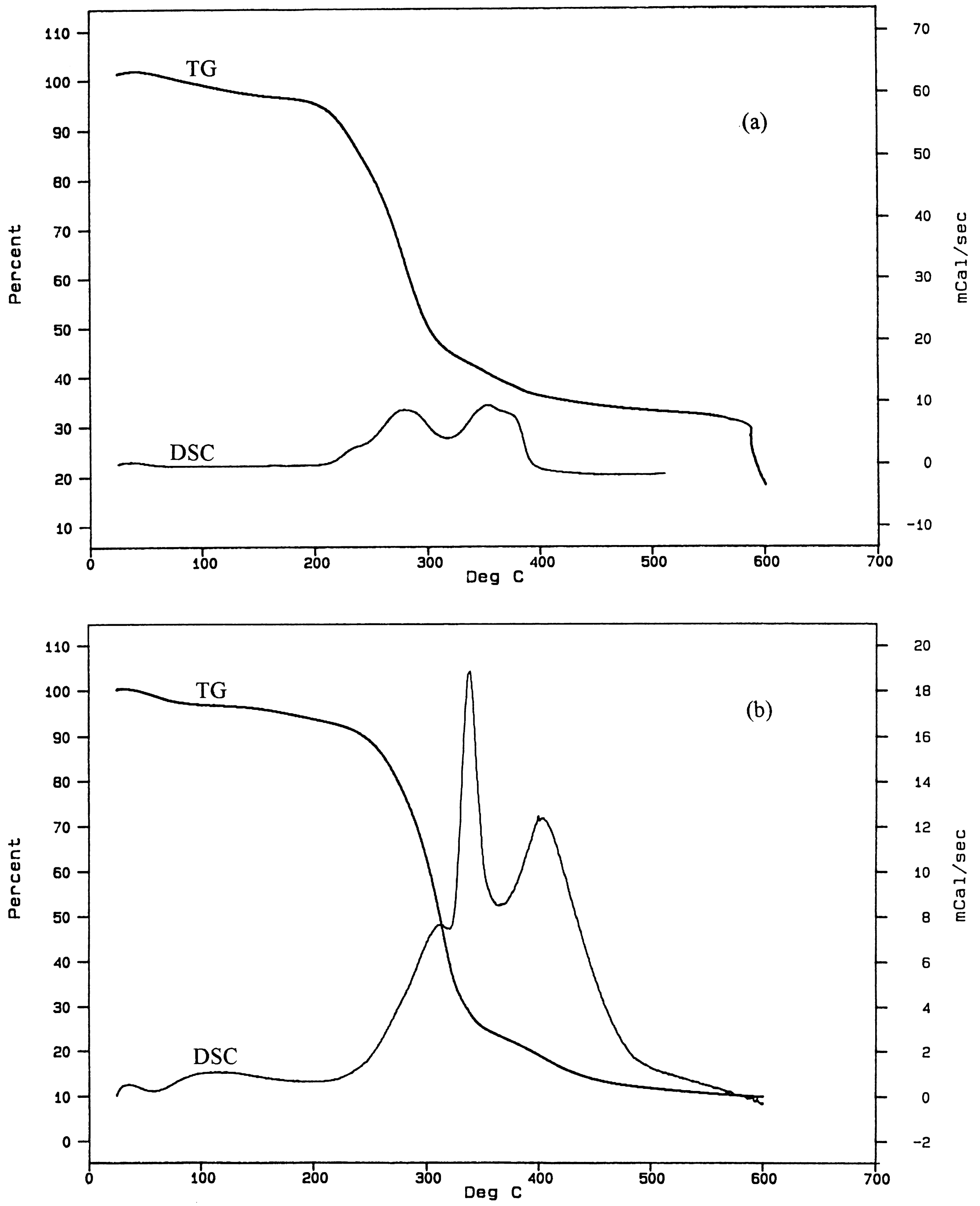

Fig. 7. Thermogram of native hemicellulose B (a) and acetylated hemicellulose B (b) esterified at 85°C for 6 h.

the total weight loss, respectively. Further, as seen from the Fig. 7, the degradation of the native hemicellulose B began at 220°C, and the total consumption completed when the temperature is around 395°C, while the total consumption of the acetylated hemicellulose B completed as the temperature arrived at 480°C, indicating an increase of the thermal stability of the esterified hemicellulose B.

In conclusion, the acetylation of the free hydroxyl groups of hemicellulose B from wheat straw in homogeneous DMF/LiCl system with acetic anhydride and using DMAP as a catalyst represents a suitable and effective method for the preparation of hemicellulose B acetates in a new non-aqueous swelling system. The total degree of substitution can be simply controlled by the reaction conditions such as reaction temperature and duration. Under an optimum reaction condition (85°C, 60 h), the product with a high DS of 1.25 can be obtained without significant degradation, in which approximately 75% of the free hydroxyl groups in native hemicellulose B were acetylated. The results obtained from the thermal analysis showed that the thermal stability of the product was also increased by chemical acetylation. In order to gain a complete substitution (DS, 1.67), addition of more mol of esterifying agents such as acetic anhydride per mol of free OH groups, pre-swelling or activation of the native hemicellulose B are needed.

Acknowledgements

The authors are grateful for the financial support of this research from the European Community under the Industrial and Materials Technologies Programme (Brite-EuRam III)-Depolymerisation, Polymerisation and Applications of Biosustainable Raw Materials for Industrial End Uses.

References

Blakeney, A. B., Harris, P. J., Henry, R. J., & Stone, B. A. (1983). A simple and rapid preparation of alditol acetates for monosaccharide analysis. *Carbohydrate Research*, *113*, 291–299.

Cai, Z. S., & Paszner, L. (1988). Salt catalyzed wood bonding with hemicellulose. *Holzforschung*, *42*, 11–20.

Ebringerova, A., Hromadkova, Z., Alfoldi, J., & Berth, G. (1992). Structural and solution properties of corn cob heteroxylans. *Carbohydrate Polymers*, *19*, 99–105.

Focher, B., Marzetti, A., Naggi, A., & Torri, G. (1989). Sulfopropylated hemicellulose: synthesis and NMR characterization. *Makromolekular Chemistry*, *190*, 129–138.

Gupta, S., Madan, R. N., & Bansal, M. C. (1987). Chemical composition of *Pinus caribaea* hemicellulose. *Tappi Journal*, *70*, 113–114.

Heinze, T., Rahn, K., Jaspers, M., & Berghmans, H. (1996). *p*-Toluenesulfonyl esters in cellulose modifications: acylation of remaining hydroxyl groups. *Macromolecular Chemical Physics*, *197*, 4207–4224.

Imamura, T., Watanabe, T., Kuwahara, M., & Koshijima, T. (1994). Ester linkages between lignin and glucuronic acid in lignin–carbohydrate complexes from *Fagus crenata*. *Phytochemistry*, *37*, 1165–1173.

Kato, A., Azuma, J., & Koshijima, T. (1987). Isolation and identification of a new ferulated tetrasaccharide from bagasse lignin–carbohydrate complex containing phenolic acid. *Agricultural Biology and Chemistry*, *51*, 1691–1693.

Khalil, M. I., Hashem, A., & Hebeish, A. (1995). Preparation and characterization of starch acetate. *Starch/Stärke*, *47*, 394–398.

Lawther, J. M., Sun, R. C., & Banks, W. B. (1995). Extraction, fractionation, and characterization of structural polysaccharides from wheat straw. *Journal of Agricultural Food Chemistry*, *43*, 667–675.

Lepeniotis, S., & Feuer, B. I. (1997). Synthesis of starch acetate: Statistical designed experiments to optimize the reaction conditions. *Chemometrics and Intelligent Laboratory Systems*, *36*, 229–243.

McCormick, C. L., & Callais, P. A. (1987). Derivatization of cellulose in lithium chloride and *N*,*N*-dimethylacetamide solutions. *Polymer*, *28*, 2317–2323.

Puls, J., & Schuseil, J. (1993). Chemistry of hemicelluloses: relationship between hemicellulose structure and enzymes required for hydrolysis. In M. P. Coughlan & G. P. Hazlewood (Eds.), *Hemicelluloses and Hemicellulases*, (pp. 4–5). London: Portland Press.

Rahn, K., Diamantoglou, M., Klemm, D., Berghmans, H., & Heinze, T. (1996). Homogeneous synthesis of cellulose *p*-toluenesulfonates in *N*,*N*-dimethylacetamide/LiCl solvent system. *Die Angewandle Makromolekulare Chemie*, *238*, 143–163.

Saikia, C. N., Ali, F., Goswami, T., & Ghosh, A. C. (1995). Esterification of high α-cellulose extracted from *Hibiscus cannabinus* L. *Industrial Crops Products*, *4*, 233–239.

Sun, R.C. (1996). Extraction, fractionation, isolation, and structural characterization of polysaccharides and lignin from wheat straw. PhD thesis, University of Wales, Bangor, pp. 5–10.

Sun, R. C., & Hughes, S. (1998). Extraction and physico-chemical characterization of pectins from sugar beet pulp. *Polymer Journal*, *30*, 671–677.

Sun, R. C., Lawther, J. M., & Banks, W. B. (1995). Influence of alkaline pre-treatment on the cell wall components of wheat straw. *Industrial Crops Products*, *4*, 127–145.

Sun, R. C., Lawther, J. M., & Banks, W. B. (1996). Fractional and structural characterization of wheat straw hemicelluloses. *Carbohydrate Polymers*, *29*, 325–331.

Sun, R. C., Fang, J. M., Goodwin, A., Lawther, J. M., & Bolton, J. (1998). Isolation and characterization of polysaccharides from Abaca fibre. *Journal of Agricultural Food Chemistry*, *46*, 2817–2822.

Sun, R. C., Mott, L., & Bolton, J. (1998). Isolation and fractional characterization of ball milled and enzyme lignins from oil palm trunk. *Journal of Agricultural Food Chemistry*, *46*, 718–723.

Voget, S., Klemm, D., & Heinze, T. (1996). Effective esterification of carboxymethyl cellulose in a new non-aqueous swelling system. *Polymer Bulletin*, *36*, 549–555.