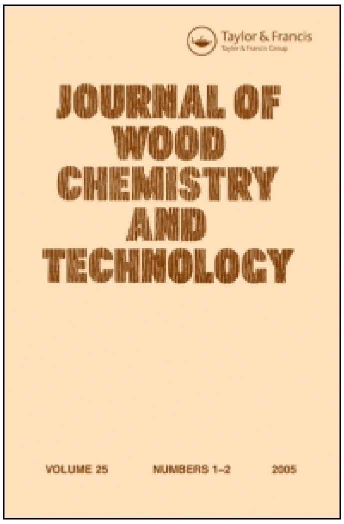
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



**Journal of Wood Chemistry and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

# Esterification of Hemicelluloses from Poplar Chips in Homogenous Solution of *N, N*- Dimethylformamide/Lithium Chloride

Runcang Sun[a]; J. M. Fanga[a]; J. Tomkinson[a]; C. A. S. Hill[b]
[a] The BioComposites Centre, University of Wales, Bangor, Gwynedd, UK [b] School of Agricultural and Forest Sciences, University of Wales, Bangor, Gwynedd, UK

**To cite this Article** Sun, Runcang , Fanga, J. M. , Tomkinson, J. and Hill, C. A. S.(1999) 'Esterification of Hemicelluloses from Poplar Chips in Homogenous Solution of *N, N*- Dimethylformamide/Lithium Chloride', Journal of Wood Chemistry and Technology, 19: 4, 287 — 306

**To link to this Article: DOI:** 10.1080/02773819909349613

**URL:** http://dx.doi.org/10.1080/02773819909349613

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 19(4), 287–306 (1999)

# ESTERIFICATION OF HEMICELLULOSES FROM POPLAR CHIPS IN HOMOGENOUS SOLUTION OF *N*, *N*-DIMETHYLFORMAMIDE/LITHIUM CHLORIDE

RunCang Sun[a,*], J. M. Fang[a], J. Tomkinson[a], and C. A. S. Hill[b]

[a]The BioComposites Centre, [b]School of Agricultural and Forest Sciences

University of Wales, Bangor, Gwynedd, LL57 2UW, UK

Downloaded At: 12:23 25 January 2011

## ABSTRACT

Hemicelluloses, extracted from the delignified poplar chips with 8.0% NaOH-1.0% $Na_2B_4O_7 \cdot 10H_2O$, were esterified with various acyl chlorides in the homogeneous *N,N*-dimethylformamide/lithium chloride system. Comparative reactions were performed with different molar ratios of acyl chloride/anhydroxylose, different concentrations of triethylamine, various reaction times, and reaction temperatures between 45°C and 75°C. The degree of substitution was controlled between 0.32 and 1.51. Under optimum conditions (sample 8, molar ratio 3:1, TEA% 280), over 75% of the hydroxyl groups in native hemicelluloses were stearoylated. The preparations were characterized by FT-IR and GPC techniques as well as their solubilities in various organic solvents. The molecular weight measurements showed minimal degradation of the hemicelluloses during the rapid reactions at 45-75°C for 30-45 min.

Copyright © 1999 by Marcel Dekker, Inc.

www.dekker.com

## INTRODUCTION

Hemicelluloses are the second most abundant polysaccharides after cellulose found in nature that are found in nearly all forms of plant life. Therefore, hemicelluloses are economically attractive as raw materials since they are available from renewable resources and waste products such as cereal straws and grasses.[1] Recent research on the technological applications of natural hemicelluloses have been receiving considerable attention since these compounds are characterized by a high stability and easy biodegradability. However, due to the hydrophilic nature of hemicelluloses, blends with hydrophobic plastics have poor mechanical properties due to the poor interfacial adhesion. The hydrophilicity of hemicelluloses results in their inability to form a continuous phase with the synthetic polymer. These shortcomings can be overcome by modifying their structure through partial hydrolysis, oxidation, reduction, etherification or esterification of the hydroxyl groups, and cross-linking. One way to improve miscibility and phase adhesion to replace the hydrophilic -OH groups of hemicelluloses with hydrophobic groups through esterification. Up to now, most hemicellulosic derivatives are prepared by heterogeneous processes which often lead to low yield, less uniform substitution, and difficulty in maintaining quality and separation of the products from the solvents.[2] The principal ester derivatives include hemicellulose acetate, propionate, octanoylate, and stearoylate.

Several procedures have been published or patented for the synthesis of cellulose derivatives in homogeneous solutions of *N,N*-dimethylacetamide (DMAc)/lithium chloride (LiCl), which was first reported by McCormick and Lichatowich in 1979.[3-6] This solvent had been previously utilized for dissolution of polyamides and chitin.[7] Subsequently, McCormick and Dawsey reported a number of synthetic transformations of cellulose to a variety of derivatives.[8,9] More recently, this procedure has been substantially improved by Samaranayake and Glasser[10], in which the acylation of cellulose in homogeneous phase (2% concentration in *N,N*-

Downloaded At: 12:23 25 January 2011

DMAc/LiCl-9%) with acid anhydrides and carboxylic acids was accomplished using *N,N*-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine. Additionally, cellulose esters with linear aliphatic acyl substituents ranging in size from C-12 (Laurie acid) to C-20 (eicosanoic acid) have been prepared in this homogeneous solution using a novel synthetic method based on the use of a mixed *p*-toluenesulfonic/carboxylic acid anhydride, and the resulting waxy cellulose esters had a high degree of substitution, between 2.8 and 2.9, and showed little degradation.[11] The researchers in our laboratories found that *N,N*-dimethylformamide (DMF), similar in structure and solubility parameter, is more effective to dissolve hemicelluloses than DMAc, even though it failed to dissolve cellulose when substituted for DMAc.[4,12] In this paper, we report supportive data for preparing esterified wood hemicelluloses in homogeneous solution of DMF/LiCl. The products are characterized by yield of esterification, degree of substitution (DS), FT-IR spectroscopy, molecular size, and solubility. The modified hemicelluloses are expected to exhibit an increased hydrophobic character due to the incorporation of long alkyl groups.

Downloaded At: 12:23 25 January 2011

## EXPERIMENTAL

### *Materials*

Poplar tree (*Populus nigra var. italica*), 15 years old, was harvested in November 1997, at the University Forest of the University of Wales (Bangor, UK). The tree was pealed off the outer and inner barks and then chipped and dried. The chips were ground to pass through a 0.7 mm screen. The ground sample was further dried at 60°C for 16 h. The composition (%, w/w) of the sample was 43.2% cellulose, 26.6% hemicelluloses, 21.3% lignin, 1.5% ash, and 1.8% wax on a dry basis. 4-Dimethylaminopyridine (DMAP), and triethylamine (TEA) were reagent grade. DMF solvent was dried prior to use according to conventional methods.[1]

Anhydrous LiCl was obtained by drying at 130°C for 2 h before use. Other reagent grade chemicals such as acetyl chloride (AC), butyryl chloride (BC), *n*-octanoyl chloride (OC), decanoyl chloride (DC), stearoyl chloride (SC), and oleoyl chloride (OLC) were purchased from Aldrich Chemical Company (England).

### *Extraction and Characterization of Hemicelluloses.*

The scheme for extracting the hemicelluloses from the poplar chips is illustrated in Figure 1. The ground chips were first delignified with sodium chlorite in acetic solution (pH 3.2, adjusted by 10% acetic acid) at 75°C for 4 h. The hemicelluloses were then obtained from the holocellulose by extraction with 8.0% NaOH-1.0% $Na_2B_4O_7 \cdot 10H_2O$ at room temperature for 16 h with a liquor to wood ratio of 1:22. The solubilized hemicelluloses were isolated by precipitation of the neutralized hydrolysate (pH 6.0) in 3 volumes of 95% ethanol. After filtration, the pellets of the hemicelluloses were washed with 70% ethanol and air-dried.

Downloaded At: 12:23 25 January 2011

The neutral sugars in the isolated hemicelluloses were determined by hydrolyzing of the samples with 2 M trifluroacetic acid and analysing the alditol acetates by gas chromatography (GC).[13] The content of uronic acids was assayed colorimetrically using 3-phenyphenol colour reagent according to the procedure outlined by Wedig and co-workers.[14] The content of associated lignin in the purified hemicelluloses was determined by alkaline nitrobenzene oxidation.[15] The molecular weights of the native hemicelluloses were measured according to the method described previously,[16,17] and the detection was achieved using a Knauer differential refractometer.

FT-IR spectra were obtained on a Nicolet 750 FT-IR 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 was recorded at

Downloaded At: 12:23 25 January 2011

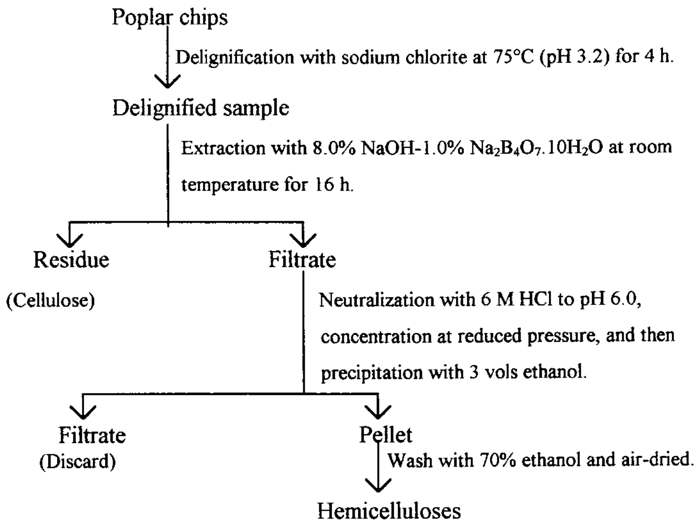


FIGURE 1. Scheme for extraction of hemicelluloses from poplar chips.

25°C from 200 mg of sample dissolved in 1.0 mL $D_2O$ after 8,000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width and a 0.85 s acquisition time were used.

### *Esterification of Hemicelluloses*

To 30 mL of distilled water was added 0.6 g hemicelluloses (0.009 mol of hydroxyl functionality). This mixture was heated to 80°C, with stirring, until the hemicelluloses completely dissolved (~5 min). Then a 30-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, 0.15 g of LiCl, 0.10 g of DMAP, and the corresponding amounts (molar ratio) of various acyl chlorides (AC, BC, OC, DC, SC, and OLC, Table 1) and of TEA (% of the native hemicelluloses, w/w) were added dropwise over a 10 min period, and the homogeneous reaction mixture was stirred for a period of 30, 40,

## Table 1

The Yield[a] of Esterified Hemicelluloses and the Degree of Substitution (DS).

| Esterification Conditions | | | | Esterified Hemicelluloses | | |
|---|---|---|---|---|---|---|
| Molar Ratio[b] | Temperature | Time (min) | TEA( %)[c] | Sample No. | Yield (%) | DS |
| 3: 1 (AC:X) | 45°C | 30 | 242 | 1 | 73.2 | 0.63 |
| 3: 1 (BC:X) | 75°C | 35 | 280 | 2 | 78.2 | 1.15 |
| 3: 1 (OC:X) | 75°C | 40 | 280 | 3 | 72.8 | 1.17 |
| 2: 1 (DC:X) | 65°C | 30 | 150 | 4 | 45.4 | 0.44 |
| 3: 1 (DC:X) | 75°C | 40 | 220 | 5 | 72.1 | 1.21 |
| 2: 1 (SC:X) | 65°C | 30 | 110 | 6 | 35.8 | 0.40 |
| 3: 1 (SC:X) | 75°C | 40 | 180 | 7 | 68.6 | 1.22 |
| 3: 1 (SC:X) | 75°C | 45 | 280 | 8 | 80.2 | 1.51 |
| 2: 1 (OLC:X) | 65°C | 30 | 110 | 9 | 32.9 | 0.32 |
| 3: 1 (OLC:X) | 75°C | 40 | 180 | 10 | 66.8 | 1.17 |

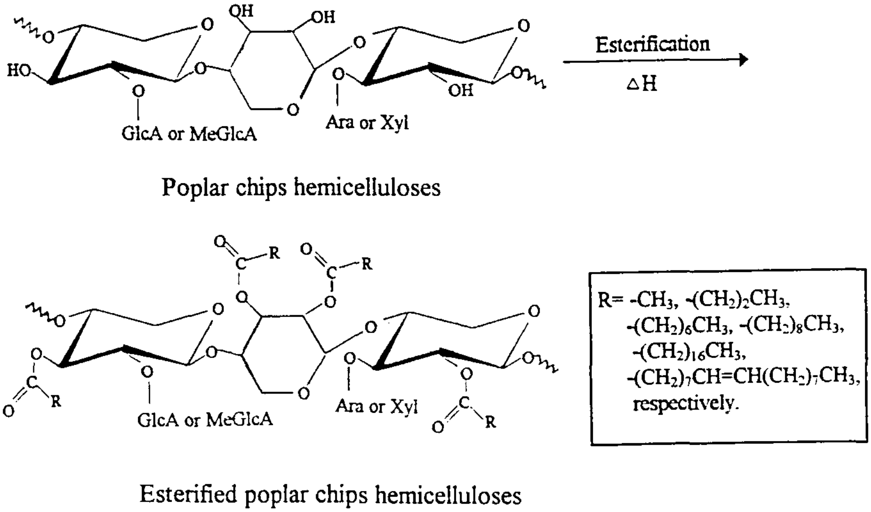
[a] Based on assumption that all of the hemicelluloses are converted to di-esterified hemicelluloses (yield, 100%; DS, 2.0). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 61.0% for acetylation, 48.8% for butyrylation, 34.4% for octanoylation, 29.9% for decanoylation, 19.8% for stearoylation, and 20.0% for oleoylation, respectively.

[b] Moar ratio represents the mole of acyl chloride/ mole of anhydroxylose (X) in hemicelluloses. AC, BC, OC, DC, SC, and OLC represent acetyl chloride, butyryl chloride, *n*-octanoyl chloride, decanoyl chloride, stearoyl chloride, and oleoyl chloride, respectively.

[c] TEA (%) represents percentage of TEA based on weight of hemicelluloses (w/w).

and 45 min. at the temperatures of 45°C, 65°C, or 75°C. The reaction was stopped at various times by cooling the reaction mixture with water. After cooling to room temperature, the homogeneous reaction mixture was slowly poured into 125 mL of 95% ethanol with stirring. Organic solvents were removed by dissolution in

Downloaded At: 12:23 25 January 2011



R= $-CH_3$, $-(CH_2)_2CH_3$, $-(CH_2)_6CH_3$, $-(CH_2)_8CH_3$, $-(CH_2)_{16}CH_3$, $-(CH_2)_7CH{=}CH(CH_2)_7CH_3$, respectively.

SCHEME 1. Esterification of hemicelluloses from poplar chips.

Downloaded At: 12:23 25 January 2011

ethanol. The white product that separated from the solution was filtered off and collected. Then it was washed with several aliquots of 95% ethanol and acetone. The resulting product was purified by Soxhlet extraction with ethanol for 6 h followed by air-dried for 24 h and then further dried in an oven at 55°C for another 16 h.

### *Characterization of the Esterified Hemicelluloses*

The yield percentages were calculated based on the assumption that all of the hemicelluloses were converted to di-esterified hemicelluloses (Scheme 1). In the case the yield percentage and the degree of substitution (DS) would be 100% and 2.0, respectively. The unreacted acyl chloride 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 would be 61.0% for acetylation, 48.8% for butyrylation, 34.4% for octanoylation, 29.9% for decanoylation, 19.8% for stearoylation, and 20.0% for oleoylation, respectively.

The molecular-average weights of esterified hemicelluloses were determined by gel permeation chromatography on a PLgel 5μ Mixed-D column. The samples were dissolved in pyridine/LiCl (0.1%, w/w) 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 pyridine/LiCl at a flow rate of 1 mL $min^{-1}$. The column was calibrated using PL pullulan polysaccharide standards. The solubility was measured at 3.0% (g/mL) concentration in different organic solvents.

Downloaded At: 12:23 25 January 2011

## RESULTS AND DISCUSSION

### *Characterization of the Native Hemicelluloses*

Hemicelluloses are usually defined as polymers that are solubilized from plant cell walls by alkali. Their isolation is actually a two-stage process, involving alkaline hydrolysis of ester linkages to liberate them from the lignocellulosic matrix followed by extraction into aqueous media.[18] Treatment of the delignified poplar chips with 8.0% NaOH-1.0% $Na_2B_4O_7 \cdot 10H_2O$ at room temperature for 16 h yielded 26.6% hemicelluloses based on the dried wood chips. The neutral sugar analysis showed that xylose was the predominant sugar (72.0%). Mannose (7.0%) and glucose (6.6%) were present in comparable amounts, followed by uronic acids (4.5%). The deoxysugar of rhamnose (3.2%), arabinose (3.0%), and galactose (2.3%) were present in relatively minor amounts. Gel permeation chromatography (GPC) showed the native hemicelluloses had a weight-average molecular weight of 33,600 g $mol^{-1}$ with a polydispersity of 4.5. The data obtained from the nitrobenzene oxidation showed that the native hemicelluloses contained approximately 1.5% residual lignin. A major phenolic monomer component in the oxidation mixture was found to be vanillin (0.26%, w/w), which represented approximately 37% of the total phenolic acids and aldehydes. Small amounts of acetosyringone (0.12%), vanillic acid (0.097%), syringaldehyde (0.074%), *p*-hydroxybenzaldehyde (0.045%), *p*-hydroxybenzoic acid (0.040%), syringic acid (0.025%), acetovanillone (0.017%), gallic acid (0.015%), and protocatechuic acid (0.012%) were also identified to be present in the nitrobenzene oxidation products. This relatively high amount of vanillin indicated that the lignins in the cell walls are linked to hemicelluloses mainly *via* guaiacyl units.

The structural features of the native hemicelluloses were characterized by the $^{13}$C-NMR spectroscopy (Figure 2). The spectrum was interpreted on the basis of reported data for structurally-defined arabinoxylan-type, glucuronoxylan-type and L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan.[19-22] The main 1,4-linked $\beta$-D-Xylp units were characterized by the signals at 104.9, 78.5, 77.5, 75.9, and 65.8 ppm, which attributes to the C-1, C-4, C-3, C-2, and C-5 of the $\beta$-D-Xylp units, respectively. The signals at 103.5, 74.2, and 64.3 ppm corresponded to the C-1, C-3, and C-6 of the $\beta$-D-Manp residues. The C-6, C-1, and C-4 signals in the 4-*O*-methyl-D-glucuronic acid appeared at 179.6, 100.5 and 85.8 ppm. A signal at 62.6 ppm originated from the 4-*O*-methoxyl group of glucuronic acid residue in the xylan. The configuration of the linkages, established by $^{13}$C-NMR measurements, was shown to be $\beta$ for xylopyranose (104.9 ppm) residues.[23]

### *Yield Percentage and Degree of Substitution*

The DMF/LiCl system is a highly specific solvent for dissolution of hemicelluloses, and acts as a solvent both for the starting hemicelluloses and the final products. Furthermore, the reactions in DMF/LiCl solution could be conducted within a short period of time. The yield of esterified hemicelluloses and the degree of substitution are given in Table 1. The low, moderate, and high degrees of substitution were obtained, although no attempts were made to optimize

Downloaded At: 12:23 25 January 2011

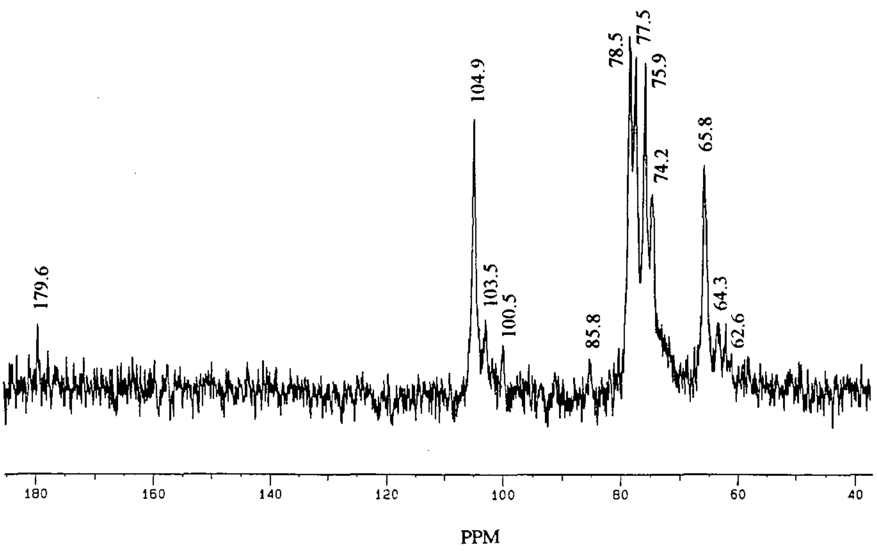


FIGURE 2. $^{13}$C-NMR spectrum (in $D_2O$) of natural hemicelluloses extracted with 8.0% NaOH-1.0% $Na_2B_4O_7.10H_2O$ at 25°C for 16 h from delignified poplar chips.

Downloaded At: 12:23 25 January 2011

conditions (molar ratio of the reactant, concentration of TEA, and reaction temperature and time) for maximum yields. There are no side products produced during these esterifying reactions and, therefore, only minor purification was required. The respective syntheses of esterified hemicelluloses were accomplished by allowing reaction of the backbone hydroxyl groups with acyl groups such as acyl halides, acid anhydrides, and carboxylic acids, in the presence of a TEA catalyst. The acyl halide pathway is effective for synthesis of some hemicellulosic esters. Acid anhydrides and carboxylic acids usually require activation for acylation.[1] In addition, due to the lack of associated unreacted acyl chloride in isolated products, the DS values of the hemicellulose derivatives were determined from the yield percentage of esterified hemicelluloses on the assumption of each xylose in xylan containing two free hydroxyl groups per xylose unit (Scheme 1). As can be seen in Table 1, the yield percentage and DS varied from 32.9% to 80.2% and 0.32 to 1.51, respectively. The lowest yield (32.9%) and DS (0.32)

Downloaded At: 12:23 25 January 2011

were obtained from sample 9 when the lowest reactant molar ratio (mole of acyl chloride : mole of anhydroxylose, 2:1), lower temperature (65°C), and lowest concentration of TEA (110%) were used, suggesting that the molar ratio of the reactant, the concentration of TEA, and the reaction temperature played a very important role for the esterification of hemicelluloses. The results also indicated that if the esterification reaction did not proceed to give a high degree of substitution, then unreacted or lightly esterified hemicelluloses were obtained. However, six samples (2, 3, 5, 7, 8, and 10) with a reactant molar ratio of 3:1 and TEA concentration of 180-280% at 75°C gave products with higher yields between 66.8% and 80.2%, corresponding to DS values between 1.17 and 1.51. Increasing molar ratios of mole of decanoyl chloride : mole of anhydroxylose from 2:1 (sample 4) to 3:1 (sample 5), TEA concentrations from 150% to 250%, reaction temperature from 65°C to 75°C, and the reaction time from 30 min. to 40 min., resulted in a significant yield increase of esterified hemicelluloses from 45.4% to 72.1% and DS value from 0.44 to 1.21, respectively. Similar observations were found between the samples 6 and 7, and 9 and 10. This could be interpreted in terms of greater availability of acyl chloride molecules in the proximity of the hemicellulosic molecules at higher concentration of the esterifying agent.[24] It is implied that the hemicellulose hydroxyls are immobile and their reaction will therefore rely on the availability of the acyl chloride molecules in the vicinity of hydroxyl groups. On the other hand, Table 1 shows that the highest degree of substitution attainable was 1.51, even with excess of the reagent. The reason for this uncompleted reaction is attributed to the high viscosity of the DMF/LiCl reaction medium which could lead to diffusion controlled kinetics.[1]

Our previous studies[12] demonstrated that DMF/LiCl served as a good solvent for hemicelluloses, allowing a variety of uniform reactions to be conducted under homogeneous conditions. That is, the most important contribution of the DMF/LiCl system for esterifying hemicelluloses is its applicability to a rather wide range of synthetic organic reactions. An added benefit of this solvent is its utility for conducting spectroscopic investigations and separations of reactants and products.[6] The complexation mechanism of DMF/LiCl with hemicelluloses is implied that hydroxyl protons on the hemicelluloses hydrogen bond to the chloride ion, which is in turn, associated with Li[DMF]$^+$ macrocation complex. This competitive hydrogen bond formation serves to disrupt the existing intra- and intermolecular hydrogen bonding, thereby enabling solubilization.[6] The homogeneous esterification of hemicelluloses in DMF/LiCl system represents a suitable and effective method for the chemical modification of hemicelluloses. The degree of substitution can be simply controlled by the molar ratio of acyl chloride/anhydroxylose unit in the hemicelluloses.

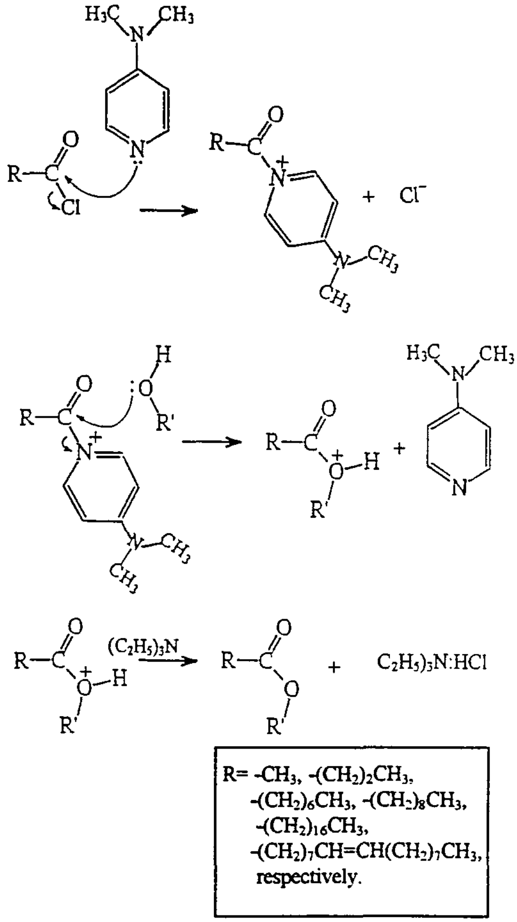
Further studies on esterification of cellulose in DMAc/LiCl system or hemicelluloses in DMF/LiCl solution indicated that the reaction mechanism involves an attacking of acyl carbon centre by nucleophile such as DMAP and a removal of hydrochloric acid by TEA (Scheme 2).[4] It was found that DMAP, a widely used versatile hypernucleophilic acylation catalyst, was $10^4$ times more active than pyridine during the esterification, and TEA, used as a base, has a more significant efficiency than the pyridine. Addition of TEA can counteract the hydrochloric acid by forming amine salt and therefore stabilize the reaction system pH between 5.5 and 6.5. These effects significantly lessen the chance of degradation of the hemicellulosic backbone by acid hydrolysis and therefore enhance the esterification.

Downloaded At: 12:23 25 January 2011

## *FT-IR Spectra*

FT-IR spectra of native (spectrum a) and oleoylated (spectrum b, sample 9) hemicelluloses in the frequency range of 800 to 4000 cm$^{-1}$ are illustrated in Figure 3. In the native hemicellulosic spectrum, the characteristic broad peak of hemicelluloses appeared at 1049 cm$^{-1}$, which was ascribed to the C-O stretch in hemicelluloses. A sharp band at 903 cm$^{-1}$ was attributed to the $\beta$-glucosidic linkages between the sugars units.[25] This confirmed once again that the xylose

Downloaded At: 12:23 25 January 2011



R= $-CH_3$, $-(CH_2)_2CH_3$, $-(CH_2)_6CH_3$, $-(CH_2)_8CH_3$, $-(CH_2)_{16}CH_3$, $-(CH_2)_7CH{=}CH(CH_2)_7CH_3$, respectively.

SCHEME 2. Mechanism of esterification of hemicelluloses from poplar chips.

residues forming the backbone of the macromolecule are linked by *β* form bonds. Other prominent bands corresponding to native hemicelluloses appeared at 1646, 1427, 1255, 1182, 1096, and 990 $cm^{-1}$. The esterifying reactions were monitored by observing in the infrared spectra a reduction in the acyl chloride carbonyl absorbance at 1800 $cm^{-1}$ and the appearance of an ester carbonyl absorbance at 1752 $cm^{-1}$. The FT-IR spectrum of oleoylated hemicelluloses (spectrum b) showed

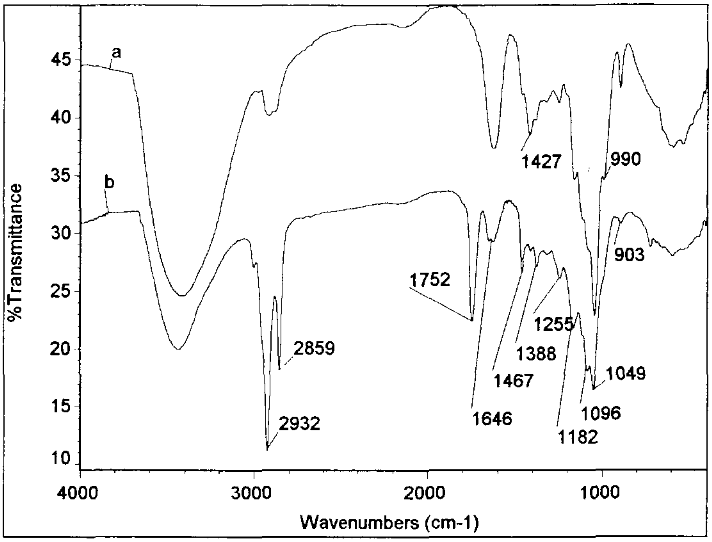


FIGURE 3. FT-IR spectra of native poplar chips hemicelluloses (spectrum a) and oleoylated hemicelluloses (spectrum b, sample No. 9).

Downloaded At: 12:23 25 January 2011

strong bands at 1752 cm$^{-1}$, 2859 cm$^{-1}$, and 2932 cm$^{-1}$, which are attributed to stretching deformation of the ester carbonyl group and the methyl/methylene groups, respectively. The strong band at 3400 cm$^{-1}$ (hydroxyl groups) of native hemicelluloses decreased significantly after the esterification reaction due to ester bond formation. The disappearance of peaks at 1800 cm$^{-1}$ in spectrum (b) indicated that the products are free of the unreacted oleoyl chloride. Additional evidence of oleoylation was indicated by the presence of ester band appearing at 1255 cm$^{-1}$ (-C-O- stretching in ester bonds).[26] The appearances of other three prominent bands at 1467, 1388, and 1182 cm$^{-1}$ in oleoylated hemicellulosic spectrum (b) were attributed to the $CH_2$ bending, C-H bending, and C-C stretching, respectively.

Figure 4 shows the FT-IR spectra of acetylated hemicelluloses (samples 1, spectrum (a)), decanoylated hemicelluloses (sample 4, spectrum (b)), and

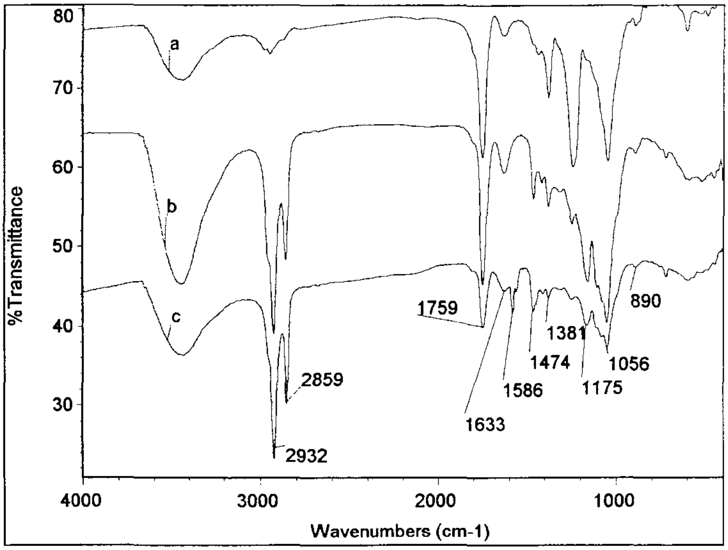


FIGURE 4. FT-IR spectra of acetylated poplar chips hemicelluloses (spectrum a, sample No. 1), decanoylated hemicelluloses (spectrum b, sample No. 4), and stearoylated hemicelluloses (spectrum c, sample No. 6).

Downloaded At: 12:23 25 January 2011

stearoylated hemicelluloses (sample 6, spectrum (c)). In spectrum (a), the acetylated hemicelluloses provides evidence of acetylation by showing the presence of three important ester bands at 1759 (C=O ester), 1381 (-C-$CH_3$), and -C-O- stretching band at 1249 cm$^{-1}$.[27] The strong band at 1056 cm$^{-1}$ may be assigned to C-O stretching in the C-O-C linkages. There are no significant differences observed in the spectra of (b) and (c) (e.g. peak shifts), indicating the similar structure of the esterified hemicelluloses. Both spectra provided evidence of decanoylation and stearoylation by showing the presence of a important ester band at 1759 cm$^{-1}$ (C=O ester). Other two large peaks at 2859 and 2932 cm$^{-1}$ indicated methyl and methylene C-H stretching in decanoylated and stearoylated hemicellulosic samples.

Downloaded At: 12:23 25 January 2011

### Table 2

Weight-Average ($\overline{M}_w$) and Number-Average ($\overline{M}_n$) Molecular Weights and Polydispersity ($\overline{M}_w/\overline{M}_n$) of the Esterified Hemicellulosic Preparations.

| | NH[a] | Esterified Hemicellulosic Preparations[b] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| $\overline{M}_w$ | 33,600 | 37,800 | 49,200 | 65,900 | 46,100 | 75,200 | 54,800 | 105,400 | 126,100 | 49,800 | 104,200 |
| $\overline{M}_n$ | 7,470 | 9,500 | 12,000 | 16,400 | 11,000 | 17,450 | 14,000 | 25,100 | 28,600 | 12,800 | 25,000 |
| $\overline{M}_w/\overline{M}_n$ | 4.5 | 4.0 | 4.1 | 4.0 | 4.2 | 4.3 | 3.9 | 4.2 | 4.4 | 3.9 | 4.2 |

[a] Represent for the native hemicelluloses.

[b] Corresponding to sample No. in Table 1.

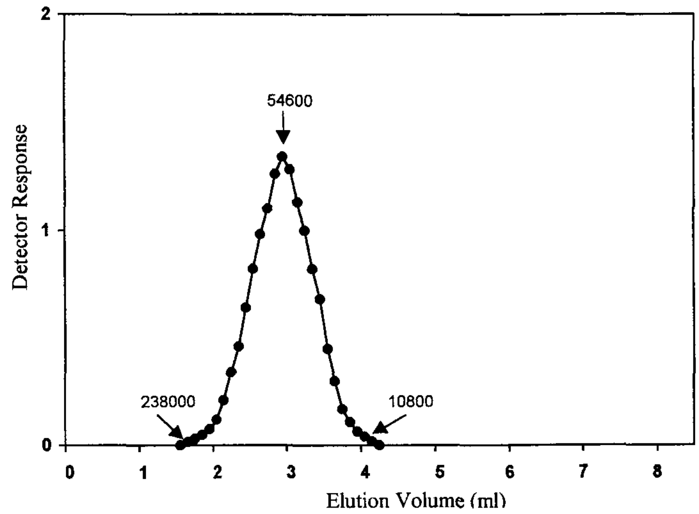


FIGURE 5. GPC molecular weight distribution of esterified hemicellulosic preparation 6.

Downloaded At: 12:23 25 January 2011

*Molecular Weight of Esterified Hemicelluloses*

The molecular weights of esterified hemicellulosic preparations were determined to illustrate the extent of degradation that occurred during the reaction in DMF/LiCl system. The weight-average ($\overline{M}_w$) and number-average ($\overline{M}n$) molecular weights and the polydispersity ($\overline{M}_w/\overline{M}_n$) of the preparations are given in Table 2. As compared to the theoretical molecular weights, which were based on the molecular weight of the starting native hemicelluloses ($\overline{M}_w$, 33,600 g mol$^{-1}$) and the DS, all of the $\overline{M}_w$ obtained by GPC from the modified hemicelluloses were lower than the expected values by 6-10%, indicating that only a slight degradation occurred during the reaction processes under the conditions given. The elution profiles of stearoylated hemicelluloses (sample 6) is shown in Figure 5. The $\overline{M}_w$ distribution ranged from 10,800 to 23,8000 g mol$^{-1}$ with a major peak at 54,600 g mol$^{-1}$.

Downloaded At: 12:23 25 January 2011

### *Solubility of Modified Hemicelluloses*

In general, the hydrophobic nature is not present in xylan obtained from straw or wood.[28] Introduction of hydrophobic acyl groups in the molecular structure of hemicelluloses should alter their solubility properties. Such alterations would be related to the degree of substitution. The results showed that all of the esterified hemicellulose preparations solubilized in pyridine at 80°C. Some of the preparations were also soluble in dimethylsulfoxide (DMSO) at 40°C and partially soluble in chloroform, dichloromethane, toluene, and tetrahydrofuran (THF) at room temperature. This increasing hydrophobic capacity would lead to potential use of esterified hemicelluloses in the production of plastic, especially biodegradable and/or environmentally degradable plastics, resins, films, and coatings in the food industry. The work on these areas is in progress in our laboratory.

## CONCLUSIONS

Previously unreported hemicellulosic derivatives were prepared in homogeneous solutions of DMF/LiCl by esterification of wood hemicelluloses with various acyl chlorides. The esterifying reactions could be controlled by adjusting the stoichiometry of reagents and the amounts of TEA used. The reaction conditions appeared to give low, moderate, and high degrees of substitution under mild reaction conditions with a short period of reaction. The highest degree of substitution obtained was 1.51 for the formation of stearoylated hemicelluloses under the following conditions: (molar ratio 3:1, TEA% 280, 75°C, 45 min.). The GPC analysis indicated that no significant degradation of the polymers occurred during the reaction process.

## ACKNOWLEDGMENTS

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

## REFERENCES

1. S. L. Williamson and C. L. McCormick, J.M.S.—Pure Appl. Chem., A35, 1915 (1998).
2. X. R. Fan and Z. H. Fen, Acta Pharmacol Sinica, 8, 169 (1987).
3. C. L. McCormick and D. K. Lichatowich, J. Poly. Sci.: Polym. Lett., 7, 478 (1979).
4. C. L. McCormick and T. Shen, In Macromolecular solutions, R. B. Seymour and G. S. Stahl, (Eds.), p. 101-110, Pergamon Press, New York, 1982.
5. C. L. McCormick and P. A. Callais, Polymer, 28, 2317 (1987).
6. S. L. Williamson, R. S. Armentrout, R. S. Porter and C. L. McCormick, Macromolecules, 31, 8134 (1998).
7. M. Panar and L. F. Beste, Macromolecules, 10, 1401 (177).
8. C. L. McCormick and T. Dawsey, JMS-Rev. Macromol. Chem. Phys., C30, 405 (1990).
9. C. L. McCormick and T. Dawsey, Macromolecules, 23, 3606 (1990).
10. G. Samaranayake and W. G. Glasser, Carbohydr. Polym., 22, 1 (1993).
11. J. E. Sealey, G. Samaranayake, J. G. Todd and W. G. Glasser, J. Polym. Sci. B- Polym. Physics, 34, 1613 (1996).
12. J. M. Fang, R. C. Sun, P. Fowler and J. Tomkinson, Acetylation of wheat straw hemicellulose B in a new non-aqueous swelling system. (in press) Carbohydr. Polym. (1999).

Downloaded At: 12:23 25 January 2011

13. A. B. Blakeney, P. J. Harris, R. J. Henry and B. A. Stone, Carbohydr. Res., 113, 291 (1983).
14. C. Wedig, E. H. Jaster and K. J. Moore, J. Agric. Food Chem., 35, 214 (1987).
15. J. M. Lawther, R. C. Sun and W. B. Banks, J. Agric. Food Chem., 43, 667 (1995).
16. R. C. Sun, J. M. Lawther and W. B. Banks, Ind. Crops Prod., 4, 127 (1995).
17. R. C. Sun., J. M. Fang, P. Rowlands and J. Bolton, J. Agric. Food Chem., 46, 2804 (1998).
18. L. W. Doner and K. Hicks, Cereal Chem., 74, 176 (1997).
19. R. C. Sun, J. M. Lawther and W. B. Banks, Carbohydr. Polym., 29, 325 (1996).
20. A. Kato, J. Azuma and T. Koshijima, Agric. Bio. Chem., 51, 1691 (1987).
21. A. Ebringerova, Z. Hromadkova, J. Alfoldi and G. Berth, Carbohydr. Polym., 19, 99 (1992).
22. T. Imamura, T. Watanabe, M. Kuwahara and T. Koshijima, Phytochemistry, 37, 1165 (1994).
23. S. Karacsonyi, Chem. Papers, 47, 400 (1993).
24. M. I. Khalil, A. Hashem and A. Hebeish, Starch/Stärke, 47, 394 (1995).
25. S. Gupta, R. N. Madan and M. C. Bansal, Tappi J., 70, 113 (1987).
26. C. Q. Yang and X. Wang, Textile Res. J., 66, 595 (1996).
27. C. N. Saikia, F. Ali, T. Goswami and A. C. Ghosh, Ind. Crops Prod., 4, 233 (1995).
28. M. Shigematsu, A. Goto, S. Yoshida, M. Tanahashi and Y. Shinoda, Mokuzai Gakkaishi, 40, 1214 (1994).

Downloaded At: 12:23 25 January 2011