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Rapid homogeneous lauroylation of wheat straw hemicelluloses under mild conditions

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ABSTRACT

Hemicellulose-based hydrophobic biomaterials with degrees of substitution ranging from 0.46 to 1.54 were synthesized under mild conditions in homogeneous media (*N*,*N*-dimethylformamide–lithium chloride) by reacting the native wheat straw hemicellulosic polymers with lauroyl chloride using 4-dimethylaminopyridine as a catalyst. Other catalysts such as *N*-bromosuccinimide, *N*-methyl pyrrolidine, *N*-methyl pyrrolidinone, and pyridine were also investigated. Under optimum reaction conditions (2 equiv of lauroyl chloride and triethylamine per hydroxyl group, 5% 4-dimethylaminopyridine, 40 °C, 35 min), a high DS value of 1.54 was obtained. The biomaterials were characterized by FT-IR spectroscopy and ^{13}C NMR spectroscopy as well as by thermal analysis. The results showed that the lauroylation occurred preferably at the C-3 hydroxyl group of β-D-Xyl*p* units in the hemicelluloses, and the thermal stability of the hydrophobic polymers increased by esterification.

1. Introduction

Because petroleum reserves will be exhausted within half a century, the use of lignocellulosic materials from crop residues such as cereal straws as a source of chemicals has received considerable interest in recent years. These raw materials are abundant and renewable. They may, therefore, replace environmentally unfriendly fossil hydrocarbons as novel biodegradable materials for industry.[1]

The main constituents of lignocellulosic materials are cellulose, hemicelluloses, and lignin. Cellulose is a homopolymer of β-D-glucopyranose with various degrees of polymerization, depending on its origin, and its derivatives are widely used in composite and plastic industries.[2–4] Hemicelluloses, the second most abundant class of hydrophilic polysaccharides found in nature, comprise roughly one-fourth to one-third of most plant materials.[5] The major hemicelluloses in the cell walls of crop residues are arabinoxylans or arabino-4-*O*-methylglucuronoxylans. They have a backbone of β-(1→4)-linked D-xylopyranose residues, which can be substituted in C-2 and/or C-3 by short and flexible side chains of L-arabinofuranose and D-glucuronic acid (or its 4-*O*-methyl derivatives) residues in a signal unit.[6] In addition, galactose, glucose, mannose, rhamnose next to acetyl groups, and phenolic acids such as ferulic and *p*-coumaric acids have been identified in the macromolecular structure of hemicelluloses. It should be also noted that a large proportion of the numbers of hydroxyl groups are engaged in intra- and intermolecular hydrogen bonds, and some of them are hydrogen bonded to water molecules naturally trapped in hemicellulosic structure. This hydrophilic nature of hemicelluloses is a major constraint that seriously limits the development of hemicelluloses-based materials. Chemical modification has been investigated as a way to solve this problem, and to produce waterproof materials. Esterification with fatty acid chlorides is known to result in thermoplastic and hydrophobic materials.[7]

A number of reports exist in the literature pertaining to the preparation of esters of starch or cellulose with the ultimate aim of significantly modifying the physical–chemical properties of the polymers, and imparting suitable mechanical characteristics such as to render them more useful as engineering materials than the precursor polymers.[7] However, the preparation of hydrophobic polymers from various hemicellulosic polymers through etherification[8,9] or esterification[10,11] of hydroxyl groups has received little attention in comparison to cellulose and starch.

Interestingly, Ruiz et al.[12] recently proposed an easy and rapid method to perform the direct acylation of agaroids with lauroyl chloride in an homogenous system in *N*,*N*-dimethylacetamide, giving rise to highly hydrophobic esterified products, in contrast to the natural hydrophilic hemicellulosic polymers. The products could be used as thermoplastic materials or films for food packaging. It was found that the thermomechanical features of

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the plastic films were compared to those obtained from other kinds of hydrophobic plastic films, and thus could be good candidate to replace synthetic polymers obtained from petroleum. However, a relatively high reaction temperature of 90–130 °C could result in degradation of the polymers. More recently, we developed more rapid procedure for lauroylation of hemicelluloses as plastic films under microwave irradiation.[13] The results showed that under optimum reaction conditions (a molar ratio of xylose units in hemicelluloses–lauroyl chloride 1:3, a molar ratio of xylose units in hemicelluloses–triethylamine 1:2, 5% 4-dimethylaminopyridine, 78 °C, 5 min), a high DS value of 1.63 was obtained. However, it should be noted that microwave irradiation did result in more degradation of the macromolecular hemicelluloses than the conventional heating technique.

In the present work, to reduce the degradation of the hemicellulosic polymers, we report a new method for rapid homogeneous lauroylation of wheat straw hemicelluloses under mild conditions using conventional heating process in *N*,*N*-dimethylformamide–lithium chloride (DMF–LiCl). 4-Dimethylaminopyridine (DMAP) and triethylamine (TEA) were used as a catalyst and a base, respectively. In comparison, other catalysts such as *N*-bromosuccinimide (NBS), *N*-methyl pyrrolidine (MPI), *N*-methyl pyrrolidinone (MPO), and pyridine were also investigated. The novel biomaterials have been chemically characterized by esterification yield, degree of substitution (DS), FT-IR spectroscopy, ^{13}C NMR spectroscopy, and thermal analysis.

2. Results and discussion

2.1. Yield and degree of substitution

Sugar analysis of the hemicelluloses isolated showed that xylose was the predominant component, comprising 79.1% of the total sugars. Arabinose (9.3%) appeared as the second major sugar constituent. Glucose (4.9%) and the uronic acids, mainly 4-*O*-methyl-α-D-glucuronic acid (4.2%), were also present in noticeable amounts. Galactose (1.7%) and rhamnose (0.8%) were identified as minor constituents. The results obtained by gel permeation chromatography (GPC) analysis showed that the native hemicelluloses had a weight average molecular weight (M_w) of about 28,800 g/mol with a polydispersity of 4.9, corresponding to a degree of polymerization of 216.

Esterification of hemicelluloses with lauroyl chloride (LC) in DMF–LiCl was very efficient under the mild reaction conditions given in this study. In this case, the synthesis of hydrophobic biomaterials required a preliminary activation of the native polymers by swelling in distilled water. Dissolution in DMF–LiCl allowed the acylation in a homogeneous phase, a new nonaqueous swollen system, using the lauroyl groups to exchange hemicelluloses OH protons. Next, the synthesized esters were isolated by precipitation in ethanol and purified by washing with ethanol and acetone. Due to the lack of associated unreacted lauroyl chloride in the isolated products, the DS values of lauroyl hemicelluloses were easily

Table 1
Yield[a] and the degree of substitution of lauroylated wheat straw hemicelluloses

Lauroylation conditions					Lauroylated hemicelluloses		
Molar ratio (X:LC)[b]	Reaction time (min)	Temperature (°C)	Catalyst (% dried hemicelluloses)	Molar ratio (X:TEA)[c]	Sample number	Yield (%)	DS
1:2	35	40	0	1:1	1	48.1	0.59
1:2	35	40	0	1:2	2	55.6	0.79
1:2	35	40	0	1:3	3	55.8	0.80
1:2	35	40	0	1:4	4	57.1	0.83
1:2	35	40	0	1:5	5	57.7	0.84
1:2	35	40	0	1:6	6	57.9	0.84
1:2	35	40	5% NBS[d]	1:2	7	65.5	1.06
1:2	35	40	5% DMAP[e]	1:2	8	83.2	1.54
1:2	35	40	5% MPI[f]	1:2	9	56.2	0.82
1:2	35	40	5% MPO[g]	1:2	10	57.1	0.83
1:2	35	40	5% pyridine	1:2	11	57.3	0.84
1:2	35	40	8.5% DMAP	1:2	12	81.2	1.49
1:2	35	40	10% DMAP	1:2	13	78.3	1.41
1:2	35	40	12.5% DMAP	1:2	14	77.0	1.37
1:2	35	40	15% DMAP	1:2	15	75.6	1.34
1:2	35	40	17.5% DMAP	1:2	16	72.2	1.24
1:2	35	40	20% DMAP	1:2	17	67.0	1.10
1:2	35	30	5% DMAP	1:2	18	81.7	1.50
1:2	35	50	5% DMAP	1:2	19	68.9	1.15
1:2	35	60	5% DMAP	1:2	20	64.5	1.03
1:2	35	70	5% DMAP	1:2	21	62.3	0.97
1:2	35	80	5% DMAP	1:2	22	58.5	0.87
1:2	35	90	5% DMAP	1:2	23	43.6	0.46
1:2	15	40	5% DMAP	1:2	24	66.8	1.10
1:2	40	40	5% DMAP	1:2	25	81.0	1.48
1:2	50	40	5% DMAP	1:2	26	76.9	1.37
1:2	70	40	5% DMAP	1:2	27	70.8	1.20
1:2	90	40	5% DMAP	1:2	28	59.3	0.89

[a] Based on the 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 26.6% for lauroylation with a DS value of 0.0.

[b] Molar ratio of X:LC represents the mol of xylose units in hemicelluloses/mol of lauroyl chloride (LC).

[c] Molar ratio of X:TEA represents the mol of xylose units in hemicelluloses/mol of triethylamine (TEA).

[d] Abbreviation for *N*-bromosuccinimide.

[e] Abbreviation for 4-dimethylamino pyridine.

[f] Abbreviation for *N*-methyl pyrrolidine.

[g] Abbreviation for *N*-methyl pyrrolidinone.

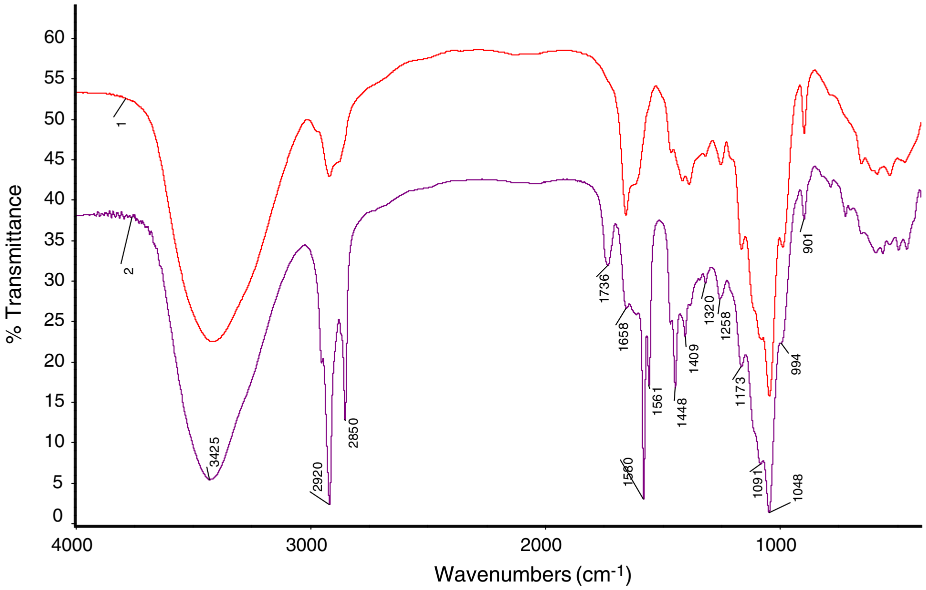

Figure 1. FT-IR spectra of unmodified wheat straw hemicelluloses (spectrum 1) and lauroylated hemicellulosic sample 2 (spectrum 2).

determined from the yield percentage of esterified hemicelluloses on the assumption that each xylose in xylan contained two free hydroxyl groups. Table 1 gives the yield percentage and degree of substitution of the lauroylated hemicelluloses. Obviously, increasing molar ratio of X:TEA (the mol of xylose units in hemicelluloses to the mol of triethylamine) from 1:1 to 1:2 resulted in a noticeable increase in lauroylation efficiency as shown by both increasing yield from 48.1 to 55.6% and DS value from 0.59 to 0.79, respectively. This increasing trend resulted from a removal of hydrochloric acid by TEA, as the addition of TEA reacts with the hydrochloric acid by forming an amine salt.[14] This observation indicates that TEA had a more significant efficiency than the pyridine as a base. However, it should be noted that the amount of ester increased slightly with the molar ratio of X:TEA raised from 1:2 to 1:3, 1:4, 1:5, and to 1:6 and became constant after 4 equiv of TEA was used. For this reason, a 1:2 molar ratio of X:TEA was chosen in the following study.

Because the reaction between hemicelluloses and fatty acid chlorides is acid- or base-catalyzed, the addition of catalyst would accelerate the rate reaction of lauroyl chloride with hemicelluloses.[15] Among the tertiary amine catalysts, such as DMAP, MPI, MPO, and DMAP, a widely used versatile hypernucleophilic acylation catalyst is much superior to pyridine, which is an effective catalyst.[16] MPI and MPO are also effective for some synthetic acylations, such as typical acylation reactions of primary and secondary alcohols.[17] However, DMAP is very expensive, which limits its industrial use. Thus, the present article describes the application of DMAP as a lauroylation catalyst only in a laboratory

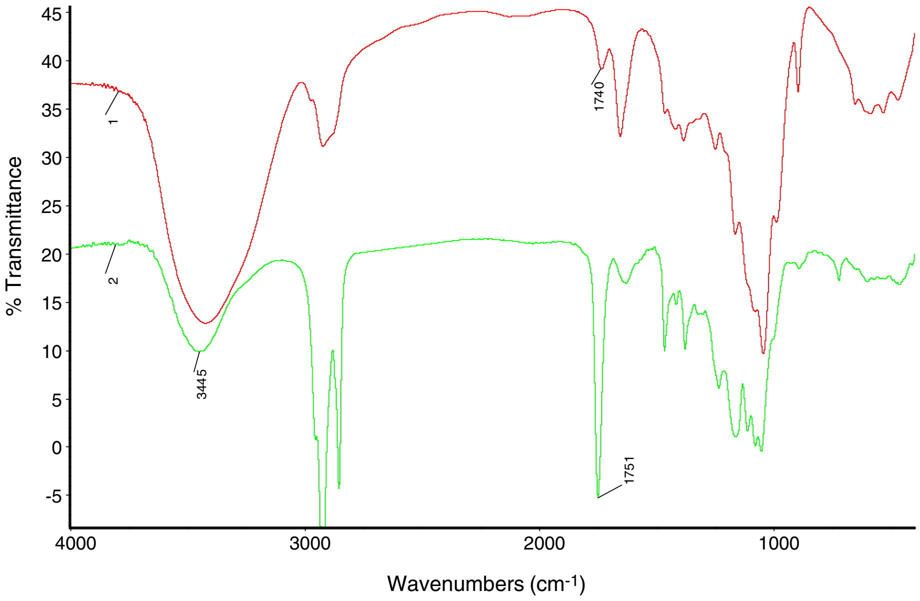

Figure 2. FT-IR spectra of lauroylated hemicelluloses prepared at 40 °C for 35 min without catalyst (spectrum 1, sample 1) and with 5% DMAP as a catalyst (spectrum 2, sample 8).

scale, and the results were compared with pyridine, MPI, MPO, and NBS, a rather cheap and commercially available reagent as a catalyst for esterification.

As shown in Table 1, all five catalysts at a concentration of 5% (% dried hemicelluloses) accelerated the reactions as shown by an increase in yield (56.2–83.2%) and DS (0.82–1.54) (samples 7–11) as compared to the control sample 2 (yield 55.6%; DS 0.79). Obviously, 5% DMAP and NBS exhibited a significant effect on the rate of lauroylation of hemicelluloses, and 5% DMAP gave the fastest rate of reaction as shown by the highest yield and DS (83.2%, 1.54). Furthermore, the effect of DMAP concentration on the yield and DS of the products was investigated, and the results are given between samples 12 and 17. Surprisingly, increasing the DMAP amounts from 5 to 8.5, 10, 12.5, 15, 17.5, and to 20% led to a decrease of yield and DS from 83.2 and 1.54 to 81.2 and 1.49, 78.3 and 1.41, 77.0 and 1.37, 75.6 and 1.34, 72.2 and 1.24, and to 67.0% and 1.10, respectively. This is a satisfactory result as DMAP is very expensive and also its recovery is a crucial economic factor. Thus, its use must be limited.

In this study, we also studied the variation of weight yield and DS as a function of factors like reaction temperature and time, while holding the molar ratios both X:LC and X:TEA at 1:2, and a DMAP concentration of 5%. As the results given in Table 1, an increase in the reaction temperature from 30 to 40 °C resulted in

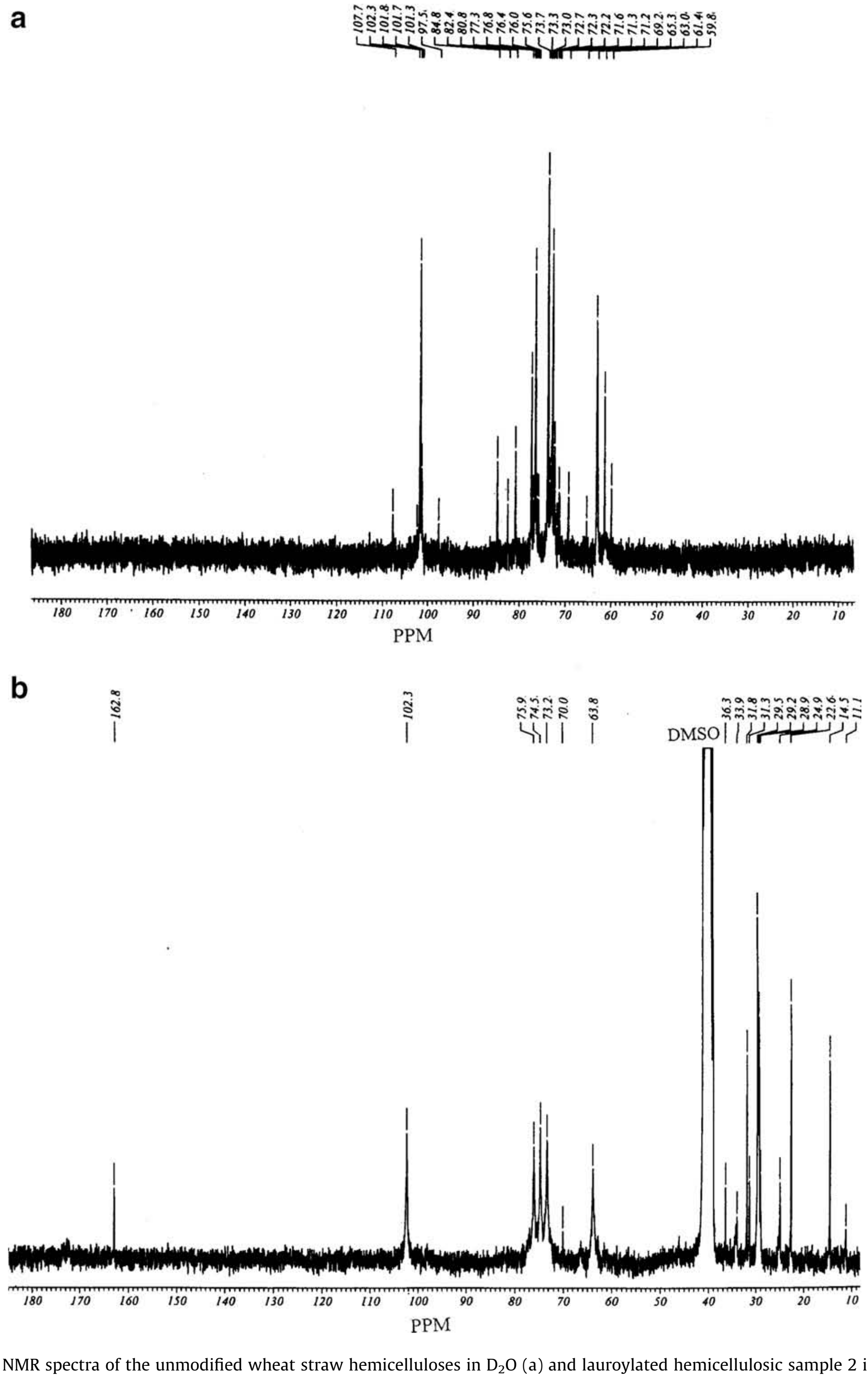

Figure 3. ^{13}C NMR spectra of the unmodified wheat straw hemicelluloses in D_2O (a) and lauroylated hemicellulosic sample 2 in DMSO-d_6 (b).

an increase in yield from 81.7% to 83.2% and DS from 1.50 to 1.54. In contrast, a further increase in the reaction temperature from 50 to 60, 70, 80, and then to 90 °C led to a decrease in the weight yield from 68.9% to 64.5%, 62.3%, 58.5,% and to 43.6%, and DS from 1.15 to 1.03, 0.97, 0.87, and to 0.46, respectively. These interesting results indicated that a temperature of 40 °C would be expected to enhance the lauroyl chloride diffusion into the hemicellulosic molecules therefore increasing the esterification rate. On the other hand, at much higher temperature, in particular 90 °C, would result in degradation and hydrolysis of the formed hemicellulosic esters. Therefore, a reaction temperature of 40 °C was considered as optimum for other samples.

The increase in yield and DS with the reaction time could be due to the increased rate and time of collisions of lauroyl chloride with hemicellulosic molecules. In this study, at a temperature of 40 °C and 5% DMAP with 2 equiv of LC and TEA per hydroxyl group in hemicelluloses, the polymers undergo partial hydrolysis by the HCl librated in situ as the reaction was performed beyond 35 min. As expected from the data in Table 1, increasing the reaction time from 15 to 35 min resulted in an increase in yield from 66.8% to 83.2% and DS from 1.10 to 1.54. In contrast, further increasing the reaction time from 40 to 50, 70, and to 90 min led to a drop of DS from 1.48 to 1.37, 1.20, and to 0.89, respectively.

2.2. FT-IR and ^{13}C NMR spectra

The FT-IR spectra of native and lauroylated hemicelluloses (sample 2) are shown in Figure 1. In the spectrum of native hemicelluloses, a strong sharp band at 1048 cm^{-1} is attributed to the C–O stretching vibrations. Another characteristic band observed at 3425 cm^{-1} is assigned to the hydroxyl group stretching vibrations. The intense band at 1658 cm^{-1} is due to absorbed water. In comparison, the spectrum of the lauroylated hemicellulosic sample 2 shows the presence of a band at 1736 cm^{-1} (C=O ester). The decrease of the band at 3426 cm^{-1}, the increasing intensity of bands at 2850 (CH_2 stretching), 2920 (CH_3 stretching), and 1550 cm^{-1} (CH bending), and the appearance of the C=O ester vibration band at 1736 cm^{-1} confirmed the efficiency of hemicellulose lauroylation. These changes could be interpreted in terms of a decrease in the concentration of hydrogen-bonded hydroxyl groups, as they were converted into ester groups. As expected, comparison of the spectra between lauroylated hemicellulosic samples 1 and 8 (Fig. 2) showed a significant increase of DS as 5% DMAP is used as a catalyst.

The chemical changes in the structure of lauroylated hemicelluloses were also verified by ^{13}C NMR spectroscopy. Figure 3 shows the ^{13}C NMR spectra of the unmodified wheat straw hemicelluloses in D_2O (a) and lauroylated hemicellulosic sample 2 in DMSO-d_6 (b). As can be seen, the spectrum of the native hemicelluloses gives five main signals at 102.3, 75.6, 73.7, 73.0, and 63.0 ppm, which are assigned to C-1, C-4, C-3, C-2, and C-5 of the (1→4)-linked β-D-Xyl units, respectively. The signals at 107.7, 84.8, 80.8, 76.0, and 61.4 ppm are attributed to C-1, C-4, C-2, C-3, and C-5 of the α-L-arabinofuranosyl residues linked to C-3 of backbone β-D-xylans, respectively.[18] The two signals observed at 82.4 and 59.8 ppm are assigned to C-4 and the methoxyl group of a 4-*O*-methyl-D-glucuronic acid residue attached at C-2 position in the xylan. This finding demonstrated that the wheat straw hemicelluloses are composed mainly of L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan.[6]

In comparison, the presence of 10 signals between 14.5 and 36.3 ppm in the esterified polymer sample 2 is originated from the methylene carbon atoms, while the occurrence of a small peak at 11.1 ppm arises from the methyl carbon atoms. A signal at 162.8 ppm is indicative of the carbonyl group in esters, confirming the occurrence of lauroylation under the mild reaction conditions. Interestingly, the presence of five peaks at 102, 3, 75.9, 74.5, 73.2, and 63.8 ppm is characterized by the carbon atoms of C-1, C-4, C-3, C-2, and C-5 in the β-D-Xyl*p* units of the lauroylated hemicelluloses, indicating that there were no significant structural changes of the macromolecular hemicelluloses under the mild lauroylation conditions used in this study. Obviously, it can be seen that the relative intensity of the signal at C-3 carbons of β-D-Xyl*p* unit decreased from native hemicelluloses to lauroylated polymers, suggesting that a partial substitution occurred at the C-3 hydroxyl group.

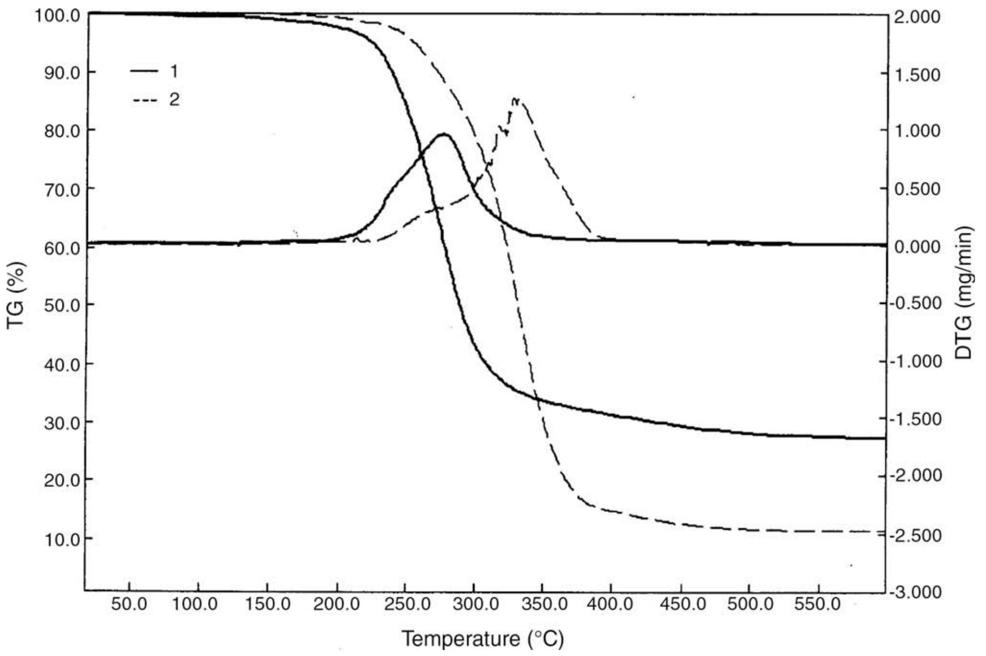

Figure 4. Thermogram of lauroylated wheat straw hemicellulosic samples 3 (spectrum 1) and 8 (spectrum 2).

2.3. Thermal properties

The results obtained from the typical thermogravimetric (TG) and differential thermogravimetric (DTG) analyses for the lauroylated wheat straw hemicellulosic samples 3 (spectrum 1) and 8 (spectrum 2) are illustrated in Figure 4. As can be seen, the samples 3 and 8 with DS values of 0.80 and 1.54 began to degrade at 215 and 250 °C, respectively. In comparison, the native hemicelluloses started to decompose at 208 °C (curve not shown). This is a rather satisfactory thermal stability of the modified wheat straw hemicelluloses. Weight loss was 50.0% when the temperature reached 258 °C for native hemicelluloses, and 292 and 338 °C for the lauroylated hemicellulosic samples 3 and 8. These data verified that the lauroylated hemicelluloses had a higher thermal stability than the unmodified polymers, and the thermal stability increased with the DS. In the DTG curves, the exothermic peaks of the native hemicelluloses (curve not shown) and the esterified hemicellulosic samples 3 and 8 occurred at 265, 278, and 338 °C, respectively. This again indicates that no significant degradation occurred during the reaction, and the thermal stability of the lauroylated hemicelluloses increased with an increment of DS.

3. Conclusions

In summary, a wide DS range of lauroylated hemicelluloses between 0.46 and 1.54 with more hydrophobic properties have been prepared in homogeneous DMF–LiCl solution under mild reaction conditions, which represents a suitable, effective, and rapid method for lauroylation of wheat straw hemicelluloses. The modified polymers are more hydrophobic than the native polymers and may be suitable for the preparation of biodegradable plastic films to replace petrochemical commodity plastics for the food packaging industry. In this ideal modification system, reaction temperature and time were reduced to a rather mild condition (40 °C, 35 min), and the hydrochloric acid produced by fatty acid chloride during the reaction could be easily removed by adding 2 equiv of TEA. Under an optimum reaction condition (2 equiv of lauroyl chloride and TEA per hydroxyl group, 5% DMAP, 40 °C, 35 min), a high DS value of 1.54 was obtained. The results obtained by thermal analysis showed that no significant degradation of the lauroylated hemicelluloses occurred during the reaction, and the thermal stability of the product was increased by lauroylation under the mild conditions.

4. Material and methods

4.1. Materials and reagents

Wheat straw was obtained from the experimental farm of The Northwestern University of Agricultural and Forestry Sciences and Technology, Yangling, China. The hemicelluloses were isolated from the straw after removal of lignin with sodium chlorite at pH 4.0–4.2 by the method described previously.[14] Lauroyl chloride (98%) and 4-dimethylaminopyridine (99%) were used without further purification. *N*,*N*-Dimethylformamide, lithium chloride, triethylamine, *N*-bromosuccinimide, *N*-methyl pyrrolidine, and *N*-methyl pyrrolidinone were purchased from Aldrich Chemical Company (Beijing, China) .

4.2. Chemical analyses

The neutral sugar composition of the native hemicelluloses was determined by hydrolysis with 6% H_2SO_4 for 2.5 h at 100 °C. The liberated neutral sugars were analyzed by high performance anion exchange chromatography (Dionex ICS-3000, USA) using a Dionex GP50 gradient pump, ED50 electrochemical detector, and a Carbopac^{TM} PA1column. Total uronic acids were determined colormetrically by the method of Blumenkrantz and Asboe-Hansen.[19] The method used for measuring the molecular weights of the hemicellulosic fractions and the two cellulosic preparations has been described in previous papers.[6,10]

4.3. Lauroylation of wheat straw hemicelluloses

Hemicelluloses powder (0.66 g, approximately 10 mmol of hydroxyl functionality in hemicelluloses) was swollen and activated in 8 mL of distilled water by heating to 55 °C with stirring until completely dissolved (~5 min). Then, a 20 mL volume of DMF was added and the reaction mixture was stirred for another 5 min. The water was removed from the swollen gel by repeated distillation under reduced pressure at 50–55 °C. To this mixture, 0.10 g LiCl, 15 mL DMF, different quantities of the catalyst (0, 5, 8.5, 10, 12.5, 15, 17.5, and 20% DMAP, 5% NBS, 5% MPI, 5% MPO, or 5% pyridine per weight of hemicelluloses), 2 equiv of lauroyl chloride (20 mmol), and 0–6 equiv of TEA per hydroxyl group in xylose units of hemicelluloses (Table 1) were gradually added over a time period of 5 min. The resulting reaction mixtures were stirred for a total period of 15, 35, 40, 50, 70, and 90 min at 30, 40, 50, 60, 70, 80, and 90 °C, respectively. After being cooled to room temperature, the homogeneous reaction mixture was slowly poured into ca. 100 mL of ethanol with stirring for about 5 min, and the resulting fine white powder that separated from the solution was collected by vacuum filtration. The powder was subsequently washed with ethanol and acetone to eliminate any colored impurities and by-products, as well as the unreacted LC. The product was first air dried for 12 h and then further dried in an oven overnight at 50 °C.

4.4. Determination of yield and degree of substitution

The degree of substitution for a hemicellulose ester is defined as the number of fatty chains attached per anhydroxylose unit and has been shown to have a theoretical maximum value of 2. In this study, the degree of substitution of the products obtained was determined based on the yield of the product. The unreacted LC in the mixture of reactions was separated from the product by dissolution in ethanol and acetone. The yield of percentages was, therefore, calculated 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 26.6% for lauroylation with a DS value of 0.0.[14] To reduce errors and confirm the results, each experiment was repeated in duplicate under the same conditions. The standard errors or deviations of the yield and DS were observed to be lower than 6.1% and 5.6%, respectively.

4.5. Characterization of the hemicellulosic esters

The chemical structure of the hemicellulosic derivatives was evaluated by FT-IR spectroscopy and ^{13}C NMR spectroscopy. FT-IR spectra were recorded as a KBr pellet by transmission with a FT-IR Nicolet 750 spectrophotometer within the frequency range 400–4000 cm^{-1}. The solution-state ^{13}C NMR spectra were obtained on a Bruker MSL300 spectrometer operating in the FT mode at 74.5 MHz. The unmodified hemicellulosic sample (80 mg) was dissolved in 1 mL D_2O, and the lauroylated hemicellulosic sample (80 mg) was dissolved 1 mL DMSO-d_6. The ^{13}C NMR spectra were recorded at 25 °C after 30,000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width, a 0.85 s acquisition time, and 1.2 s relaxation delay time were used.

Thermal analyses of the hemicellulosic derivatives were performed using thermogravimetric and differential thermogravimetric analysis on a simultaneous thermal analyzer (SDT Q600, TA Instrument). The apparatus was continually flushed with nitrogen. The product was weighed between 10 and 15 mg. The heating rate was set at 10 °C/min until a limit of 600 °C was reached.

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