

Rapid esterification of wheat straw hemicelluloses induced by microwave irradiation

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Abstract

Esterification of wheat straw hemicelluloses with acetyl chloride, propionyl chloride, *n*-octanoyl chloride, lauroyl chloride, palmitoyl chloride, stearoyl chloride, and oleoyl chloride, respectively, using *N*-bromosuccinimide (NBS) as a catalyst was achieved in DMF/LiCl medium by microwave irradiation. The effects of various acyl chlorides and the molar ratios of xylose units in hemicelluloses/acetyl chloride on the degree of substitution (DS) were investigated and DS reached up to 1.34 by a few minutes. ¹³C NMR studies showed that the esterification occurred preferentially at the C-3 and C-2 positions. On the other hand, microwave irradiation brought a partial degradation of the polymer, and therefore resulted in a slight decrease in thermal stability of the hemicellulosic derivatives in comparison with conventional heating technique.

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1. Introduction

Lignocellulose (mainly cellulose, hemicelluloses, and lignin) constitutes a renewable raw material widely available in the form of waste from agricultural residues such as cereal straws and sugarcane bagasse, which present a large source of natural polymers (Lundqvist et al., 2002). Hemicelluloses are a group of heteroglycans consisting of D-xylose, D-mannose, L-arabinose, D-glucose, D-galactose, and 4-*O*-methyl-D-glucuronic acid residues (Timell, 1967). In particular, xylans represent the most abundant hemicellulose-type polysaccharides constituents in the plant kingdom. The major hemicelluloses in cereal straws are

arabino-4-*O*-methylglucuronoxylan, which constitute up to 38% of the dry wheat straw (Sun, Sun, & Tomkinson, 2003). They have a backbone of β-(1 → 4)-D-xylopyranose residues which can be substituted in C-2 and/or C-3 by short and flexible side chains (Sun, Lawther, & Banks, 1996). The hemicelluloses, obtained from grasses, cereals, straws, and woods, are mainly constituted of units of α-D-glucuronic acid, or 4-*O*-methyl-α-D-glucuronic acid and occasional units of α-L-arabinofuranose, α-D-xylopyranose or α-D-galactopyranose as side chains (Bendahou, Dufresne, Kaddami, & Habibi, 2007). Other side groups are acetyl groups, phenolic acids, ferulic, and coumaric acids (Whistler & Chen, 1991).

Non-degradable, petroleum-based, polymers such as polyacrylates, polyacrylamides, and polyvinyl acetates are used extensively in applications such as thickeners, paper coatings, textile sizes, dispersants, and detergents (Shogren & Biswas, 2006). The impact of these polymers on the envi-

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ronment is considerable for two reasons: firstly, petroleum is not renewable product and, secondly, they are not recycled. Biopolymers are, however, being considered for these uses, as they are biodegradable and based on renewable resource such as wheat straw. It is known that hemicelluloses are the second most abundant renewable biopolymers and their fatty acid esters constitute potentially biodegradable films for food package (Fang, Sun, Fowler, Tomkinson, & Hill, 1999). In this way, fatty acid hemicellulose esters could be a good solution to alleviate both of these environmental problems (Sun, Sun, & Sun, 2004). More interestingly, it has been demonstrated that NBS is a novel and highly effective catalyst for acetylation of alcohols under mild reaction conditions. In addition, it is an inexpensive and commercially available reagent which is traditionally used as an oxidizing agent or brominating agent (Karimi & Seradj, 2001). The results obtained from our previous studies showed that NBS exhibited a significant effect on the rate of esterification of hemicelluloses, and 5% NBS (based on the dried hemicelluloses) accelerated faster than the tertiary amine catalysts (Sun, Sun, Tomkinson, & Baird, 2003).

Microwave heating, as an alternative to conventional heating technology, has been proved to be more rapid and efficient. The development of microwave-assisted chemistry such as synthesis, catalysis, analytical chemistry, etc., has witnessed an explosive growth during the last decade (Zhang & Hayward, 2006). In particular, there is an increasing interest in the use of microwave irradiation to speed up chemical reactions (Navarro & Stortz, 2005). Microwave radiation lies in the range of the electromagnetic spectrum between infrared and radio frequencies and corresponds to wavelengths of 1 cm to 1 m (frequencies of 30 GHz to 300 MHz). When a molecular is irradiated with microwaves it rotates to align itself with the applied field. The frequency of molecular rotation is similar to the frequency of microwave radiation and consequently the molecule continually attempts to realign itself with the changing field and energy is absorbed (Lewandowicz et al., 2000). It has been shown that through esterification of carboxylic acids and transesterification of methyl and ethyl esters with different alcohols in the absence of solvents, esters with high yield (90–97%) are obtained for a short period of time (up to 10 min) under simplified process conditions (Loupy et al., 1993). More recently, considerable efforts have been devoted to investigate the microwave-assisted reaction in the synthesis and modification of polymer materials. Especially in the derivation of nature polymers, a number of different polysaccharide esters such as ester-cellulose (Stage et al., 2002), starch acetates (Koroskyni & McCarthy, 2002), and *N*-phthaloylation of chitosan (Liu, Li, Li, & Fang, 2004), have been synthesized by the aid of microwave. In order to scale up this process, microwave heating was chosen in this study since it gives fast, uniform heating and enhanced reaction rates. The goal of the present work was to investigate the effect of the various acyl chlorides and molar proportion of the

initial substances on the degree of esterification of the products obtained. The structural features of the modified polymers were characterized by Fourier transform infrared (FT-IR) and carbon-13 magnetic resonance spectroscopy (^{13}C NMR).

2. Materials and methods

2.1. Materials

Wheat straw was collected from the farm fields at the North-Western University of Agricultural and Forestry Sciences and Technology, Yangling, China. The hemicelluloses were isolated after removal of lignin by the method described previously (Fang et al., 1999). The sugar analysis of the hemicelluloses isolated showed that xylose presented as a predominant sugar component, comprising 76.3% of the total sugars. Arabinose (9.2%) appeared as the second major sugar constituent. The uronic acids, mainly 4-*O*-methyl- α -D-glucuronic acid (5.3%) and glucose (4.8%) were present in noticeable amounts. Galactose (2.2%) and rhamnose (1.4%) were observed as minor constituents. Propionyl chloride (PC), *n*-octanoyl chloride (OC), lauroyl chloride (LC), palmitoyl chloride (PaC), stearoyl chloride (SC), and oleoyl chloride (OIC), *N*-bromosuccinimide (NBS), *N,N*-dimethylformamide (DMF), and lithium chloride (LiCl) were purchased from Aldrich Chemical Company (Beijing, China).

2.2. Preparation of hemicellulose esters

Typically, 0.66 g hemicelluloses powder (0.01 mol of hydroxyl functionality in hemicelluloses) in 10 ml of distilled water was heated to 78 °C under stirring until completely dissolved. 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 °C. To this mixture, 0.10 g LiCl, 15 ml DMF, 0.033 g NBS, and corresponding amounts of various acyl chlorides (AC, PC, OC, LC, PaC, SC, and OIC, Table 1) were added. The resulting reaction mixture was irradiated in microwave oven (Whirlpool, VIP 200) at 78 °C and was processed at 300 W for 5 min. The obtained product was cooled and then slowly poured into 120 ml ethanol with stirring. The white product that separated from the solution was filtered off and collected. The filtrate was washed thoroughly with ethanol and acetone to eliminate any colour impurities and by-products. The product was first air dried for 24 h and then further dried in a forced air oven overnight at 50 °C.

2.3. Characterization of the esterified hemicelluloses

The yield of percentages was 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 recov-

Table 1
The yield^a of esterified wheat straw hemicelluloses induced by microwave irradiation and the degree of substitution (DS)

Esterification conditions				Esterified hemicelluloses		
Molar ratio ^b	Irradiation time (min)	Temperature (°C)	Catalyst (NBS) (% dried hemicelluloses)	Sample number	Yield (%)	DS
1:1(X:AC)	5	78	5% NBS ^c	1	77.2	0.83
1:2(X:AC)	5	78	5% NBS	2	82.8	1.12
1:3(X:AC)	5	78	5% NBS	3	86.6	1.31
1:1(X:PC)	5	78	5% NBS	4	72.8	0.81
1:2(X:PC)	5	78	5% NBS	5	79.9	1.12
1:3(X:PC)	5	78	5% NBS	6	83.6	1.28
1:1(X:OC)	5	78	5% NBS	7	59.3	0.76
1:2(X:OC)	5	78	5% NBS	8	65.1	0.94
1:3(X:OC)	5	78	5% NBS	9	73.2	1.18
1:1(X:LC)	5	78	5% NBS	10	58.3	0.86
1:2(X:LC)	5	78	5% NBS	11	70.8	1.20
1:3(X:LC)	5	78	5% NBS	12	75.9	1.34
1:1(X:PaC)	5	78	5% NBS	13	52.1	0.78
1:2(X:PaC)	5	78	5% NBS	14	69.8	1.23
1:3(X:PaC)	5	78	5% NBS	15	73.7	1.33
1:1(X:SC)	5	78	5% NBS	16	46.0	0.67
1:2(X:SC)	5	78	5% NBS	17	57.2	0.93
1:3(X:SC)	5	78	5% NBS	18	64.3	1.11
1:1(X:OIC)	5	78	5% NBS	19	39.2	0.48
1:2(X:OIC)	5	78	5% NBS	20	49.3	0.73
1:3(X:OIC)	5	78	5% NBS	21	60.9	1.02

^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 un-reacted, the yield percentage would be 61.0% for acetylation, 54.1% for propionylation, 34.4% for octanoylation, 26.6% for lauroylation, 21.7% for palmitoylation, 19.8% for stearoylation, and 20.0% for oleoylation with a DS value of 0.0, respectively.

^b Molar ratio represents the mol of xylose units in hemicelluloses/mol of acetyl chloride (AC), propionyl chloride, (PC), *n*-octanoyl chloride (OC), lauroyl chloride (LC), palmitoyl chloride (PaC), stearoyl chloride (SC), and oleoyl chloride (OIC), respectively.

^c Abbreviation for *N*-bromosuccinimide.

ered un-reacted, the yield percentage would be 61.0% for acetylation, 54.1% for propionylation, 34.4% for octanoylation, 26.6% for lauroylation, 21.7% for palmitoylation, 19.8% for stearoylation, and 20.0% for oleoylation with a degree of substitution (DS) value of 0.0, respectively (Fang et al., 1999). The DS for a hemicellulose ester represents the moles of esterified hydroxyl groups per D-xylopyranosyl structural unit of the hemicellulosic polymer, with two hydroxyl groups per unit. The theoretical maximum of xylans is 2.0. The degree of substitution of hydroxyl groups of the products obtained was therefore determined on the basis of the yield. The un-reacted acyl chloride in the mixture of reactions was separated from the product by dissolution in 95% ethanol and acetone. 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 5.3% and 5.8%, respectively.

The chemical structure of the esterified hemicelluloses was evaluated by FT-IR and ¹³C NMR spectroscopy. The spectra were recorded from a KBr disc containing 1% finely ground samples on a Nicolet 750 FT-IR spectrophotometer in the range 4000–400 cm⁻¹. The solution-state ¹³C NMR spectra were obtained on a Bruker MSL300 spectrometer operating in the FT mode at 74.5 MHz. The un-modified hemicellulosic sample (80 mg) was dissolved in 1 ml D₂O, and the esterified product (80 mg) was dissolved 1 ml DMSO-*d*₆. The ¹³C 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 analysis of the esterified hemicelluloses was performed using thermogravimetric (TG) and differential thermogravimetric (DTG) analysis on a simultaneous thermal analyzer (SDT Q600, TA Instrument). The apparatus was continually flushed with nitrogen. The product was weighed between 9 and 11 mg and heated from room temperature to 600 °C at a rate of 10 °C/min.

3. Results and discussion

Our primary studies showed that as the time and temperature increase, the average degree of polymerization of the native hemicelluloses decreases with the microwave energy of 300 W. At a 10 min reaction time and temperature 110 °C, the average degree of polymerization of the polymers dropped from 216 to 93, indicating a significant depolymerization taking place under the microwave irradiation, while at 78 °C and duration of the process 5 min no obvious depolymerization of the polymer was observed (data not shown). In comparison, we observed that reaction time for 5 min and temperature of 78 °C had no significant effect on the DS, whereas the amounts of acyl chlorides were important. Therefore, a 5 min reaction time and temperature of 78 °C were optimized as the reaction duration and temperature in this study. To investigate

the effect of microwave irradiation on the yield and DS of esterified hemicelluloses, various acyl chlorides at different molar ratios of xylose (X) units in hemicelluloses/acyl chlorides 1:1, 1:2, and 1:3 in the presence of the optimum reaction temperature (78 °C), time (5 min), and catalyst level (5% NBS based on the dried hemicelluloses) were examined. The results for the yield and DS are displayed in Table 1. Due to the lack of associated un-reacted acyl chloride in isolated products, the DS values of the hemicellulose esters were determined from the yield percentage of esterified hemicelluloses on the assumption of each xylose in xylan containing two free hydroxyl groups. It is evident that when the molar ratio of xylose units in hemicelluloses/acetyl chloride (AC) increased from 1:1, to 1:2, and to 1:3 the yield of the acetylated hemicelluloses raised from 77.2 to 82.8 and to 86.6%, respectively, and hence the DS of the hydroxyl groups for a given reaction time increased from 0.83 to 1.12 and to 1.31. On the other hand, under conventional heating conditions for a time of 48 h in DMF/LiCl solvent system the obtained acetylated hemicelluloses had a degree of substitution of 0.97 at 70 °C and 1.37 at 85 °C (Sun, Fang, Tomkinson, & Jones, 1999). Generally, speaking, the reaction is accelerated under microwave conditions mainly due to the speed with which a mixture can be heated and the high temperature easily obtained in vessels. DMF is a good solvent for reaction in microwave since it absorbs microwave radiation very well and heats up rapidly. Similarly, increasing molar ratios of xylose unit/PC, OC, LC, PaC, SC, and OIC from 1:1 to 1:3 resulted in a significant increment of esterification reaction efficiency as shown by an increase in the DS values from 0.81 to 1.28, 0.76 to 1.18, 0.86 to 1.34, 0.78 to 1.33, 0.67 to 1.11, and 0.48 to 1.02, respectively. This could be interpreted in terms of greater availability of the hemicellu-

losic molecules at higher concentration of the esterifying agent (Fang et al., 1999). These current results indicated that a rapid reaction of hemicelluloses with various acyl chlorides in DMF was achieved under microwave irradiation, and 5 min of microwave heating were sufficient to realize products with DS up to 1.34.

Fig. 1 illustrates the FT-IR spectra of un-modified wheat straw hemicelluloses (spectrum 1) and lauroylated hemicelluloses (spectrum 2, sample 10). The absorptions at 1666, 1258, 1172, 1095, 1048, and 900 cm^{-1} seen in the spectrum 1 are indicative of the native hemicelluloses. A sharp band at 900 cm^{-1} is originated from β -glucosidic linkages between the sugar units, indicating that the xylose residues forming the backbone of the macromolecule are linked by β -form bonds. The prominent absorption at 1048 cm^{-1} is attributed to C—O contributions in glycosidic linkages. The intense band at 1666 cm^{-1} is originated from the absorbed water. The region between 1467 and 1172 cm^{-1} is due to the C—H and C—O bond stretching frequencies. A strong broad band belonging to hydrogen-bonded hydroxyls appears at 3409 cm^{-1} and the symmetric C—H vibration band at 2920 cm^{-1} (Sun et al., 2004). In comparison, an obvious decrease in the intensity of the characteristic band of hydroxyl group at 3409 cm^{-1} is undoubtedly due to the partial disappearance of hydroxyls present in hemicelluloses. This decrease in intensity occurs with the apparition of a band at 1740 cm^{-1} characteristic of carbonyl ester groups. A band at 1172 cm^{-1} in lauroylated hemicelluloses arises from the C—O—C ester stretching vibration. In addition, the presence of the aliphatic fatty chains of lauroyl ester is also observed on one hand from the absorbance at 2920 and 2852 cm^{-1} corresponding to the symmetric and asymmetric C—H stretching, and on the other hand from the appearance of a small peak at

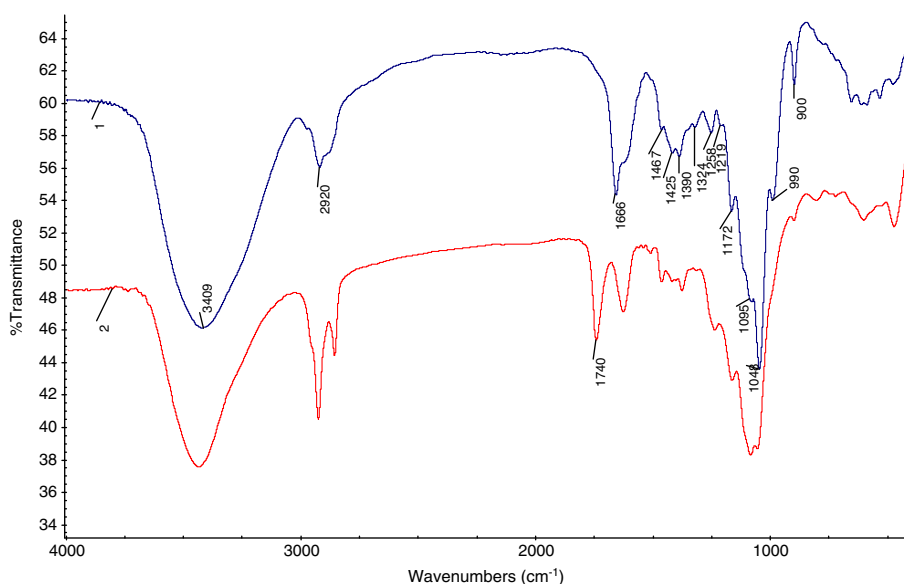


Fig. 1. FT-IR spectra of un-modified wheat straw hemicelluloses (spectrum 1) and lauroylated hemicelluloses (spectrum 2, sample 10) prepared by microwave irradiation at 78 °C for 5 min.

713 cm^{-1} relating to the linearly bonded CH_2 groups. Interestingly, the disappearance of peaks at 1800 cm^{-1} in spectrum 2 indicated that the product is free of the un-reacted acyl chloride.

Fig. 2 shows the FT-IR spectra of acetylated hemicelluloses prepared by microwave irradiation at 78 °C for 5 min with a molar ratio (X:AC) of 1:1 (spectrum 1, sample 1) and 1:2 (spectrum 2, sample 2). The similar spectral profiles indicate similar structures of the acetylated hemicelluloses. The spectra provide evidence of acetylation by showing the presence of three important ester bands at 1748 ($\text{C}=\text{O}$ ester), 1378 ($-\text{C}-\text{CH}_3$), and $-\text{C}-\text{O}$ stretching band at 1242 cm^{-1} (Saikia, Ali, Goswami, & Ghosh, 1995). However, on closer examination of the spectra, some small differences were clearly identified. Clearly, the three signals for ester bands at 1748, 1378, and 1242 cm^{-1} appear stronger in spectrum 2 than in spectrum 1, corresponding to the increase in the DS value from 0.83 in sample 1–1.12 in sample 2. Consequently, the absorbance for the un-reacted hydroxyl band at 3400 cm^{-1} decreased from spectra 1–2.

The effect of the molar ratios of X:PaC and X:OIC on the intensity of the absorption bands of the phlmitoylated and oleoylated polymers in FT-IR spectra was also examined comparatively, and their spectra are shown in Figs. 3 and 4. As illustrated, the intensity of the ester band at 1732 in Fig. 3 and 1736 cm^{-1} in Fig. 4 increased with an increase in molar ratios of X:PaC and X:OIC from 1:1 in spectrum 1–1.2 in spectrum 2, corresponding to an increment in reaction yield from 52.1% to 69.8% and from 39.2% to 49.3%, respectively. In addition, Figs. 3 and 4 also show that the absorbance for the free hydroxyl band at 3400 cm^{-1} decreased from spectra 1 to 2 with an increment in DS from 0.78 to 1.23 and from 0.48 to 0.73, respectively.

The structure of the un-modified hemicelluloses and lauroylated hemicellulosic sample 10 was also investigated by ^{13}C NMR spectroscopy by recording in D_2O and $\text{DMSO}-d_6$, respectively. The ^{13}C NMR spectrum of the native hemicelluloses (Fig. 5a) showed five major 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 β -D-Xyl residues, respectively (Imamura, Watanabe, Kuwahara, & Koshijima, 1994). The presence of arabinose was also confirmed by the presence of characteristic signals at 107.7 (C-1), 84.8 (C-4), 80.8 (C-2), 76.0 (C-3), and 61.4 (C-5) ppm in the ^{13}C NMR spectrum. The ^{13}C NMR measurements confirmed that the monomeric side chains of the L-arabinofuranosyl residues are linked to C-3 of backbone xylan. The two signals observed at 82.4 and 59.8 ppm are indicative of C-4 and the methoxyl group of a 4-O-methyl-D-glucuronic acid residue in the xylan attached at C-2 position. This revealed that the wheat straw hemicelluloses are composed mainly of L-arabino-(4-O-methyl-D-glucurono)-D-xylan (Sun et al., 1996).

In comparison with the spectrum in Fig. 5a, it can be seen that strong signals assigned to methyl and methylene groups occur in the spectrum of lauroylated hemicellulosic sample 10 between 14.9 and 38.4 ppm, of which the peak at 14.9 or 15.1 ppm arises from the methyl end of the chain, and other peaks between 22.4 and 38.4 ppm are originated from the methylene units successively farther from the methyl group (Musser & Kipatrick, 1998). The signals between 170.6 and 175.4 ppm are assigned to the carbonyl group in esterified hemicelluloses. The presence of five peaks at 102.7, 76.4, 75.0, 73.6, and 64.2 ppm is characterized by the carbon atoms C-1, C-4, C-3, C-2, and C-5 in the β -D-Xyl units of hemicelluloses, respectively. In comparison with native hemicellulosic spectrum (Fig. 5a), it should

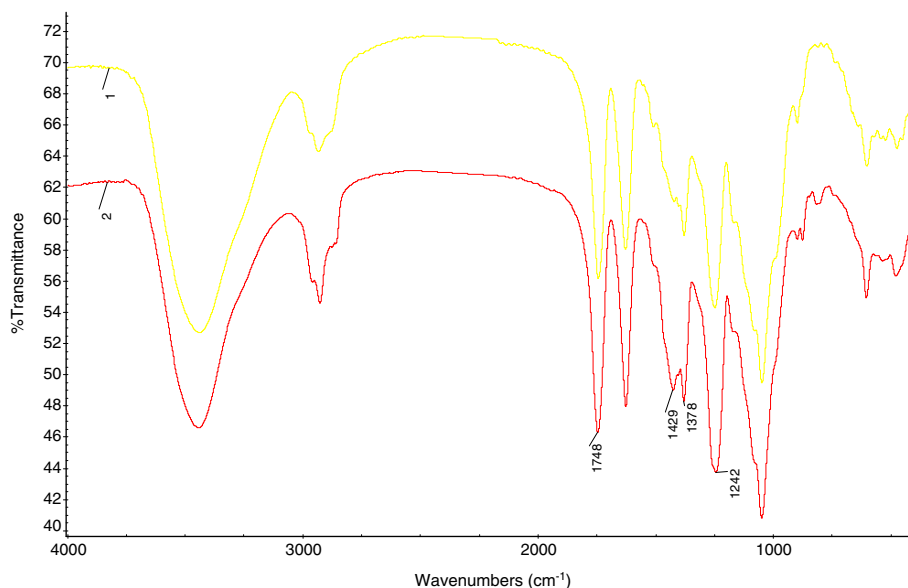


Fig. 2. FT-IR spectra of acetylated hemicelluloses prepared by microwave irradiation at 78 °C for 5 min with a molar ratio (X:AC) of 1:1 (spectrum 1, sample 1) and 1:2 (spectrum 2, sample 2).

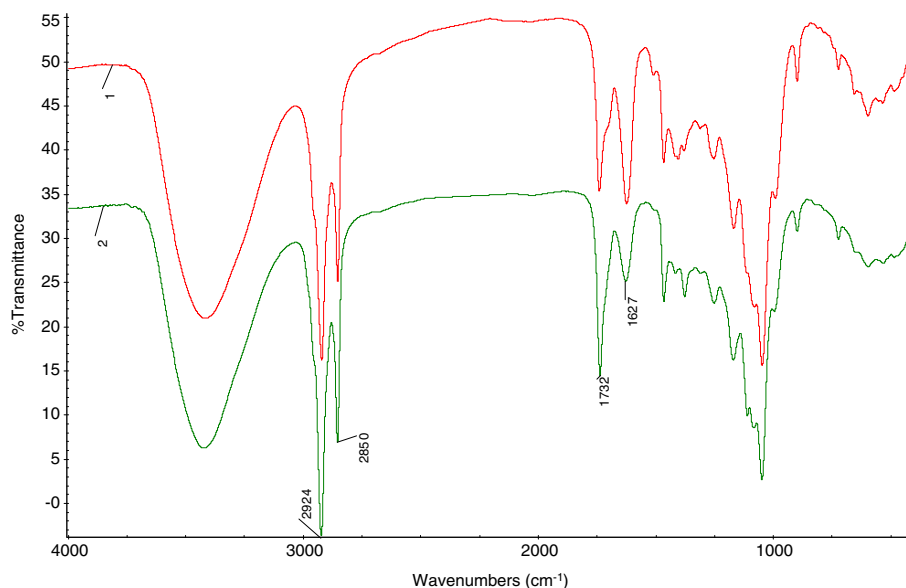


Fig. 3. FT-IR spectra of phlmitoylated hemicelluloses prepared by microwave irradiation at 78 °C for 5 min with a molar ratio (X:PaC) of 1:1 (spectrum 1, sample 13) and 1:2 (spectrum 2, sample 14).

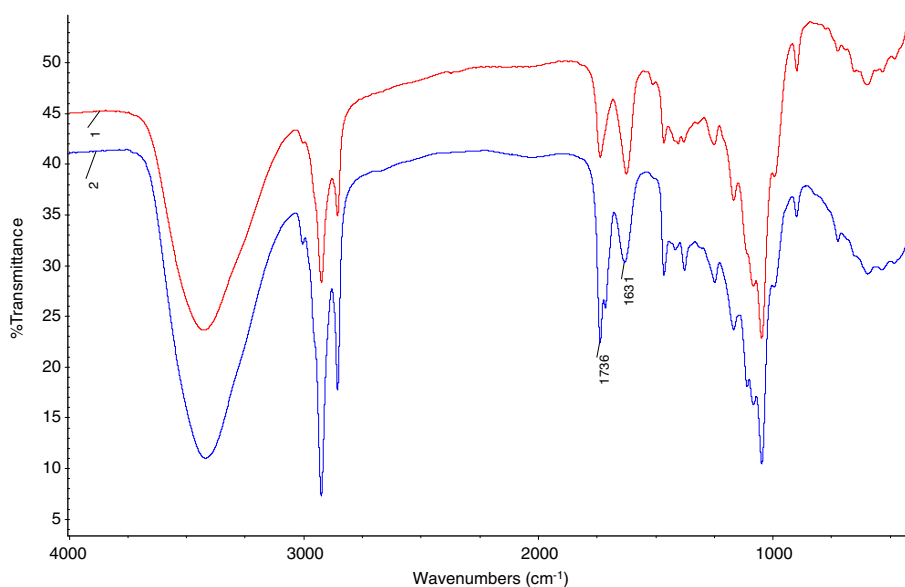


Fig. 4. FT-IR spectra of oleoylated hemicelluloses prepared by microwave irradiation at 78 °C for 5 min with a molar ratio (X:OIC) of 1:1 (spectrum 1, sample 19) and 1:2 (spectrum 2, sample 20).

be noted that the intensity of the signals at carbons C-3 and C-2 of the anhydroxylose unit decreased in the spectrum of lauroylated hemicellulosic sample 10 (Fig. 5b), implying that a partial substitution occurred at both C-3 and C-2 secondary hydroxyl groups.

Fig. 6 gives the thermograms of modified wheat straw hemicellulosic samples 4 (spectrum 1) and 17 (spectrum 2). As can be seen, the TG analysis of the two-modified hemicellulosic samples 4 and 17 showed that approximately 40% of the weight was lost at temperatures of 260 °C, whereas the native hemicelluloses had a same weight loss at a temperature of 280 °C (the curve not shown), indicating that the decomposition rate of the esterified hemicellulosic samples

was faster than that of un-modified hemicelluloses at the temperature ranges. In addition, in the curves of propionylated and stearoylated hemicelluloses in Fig. 6, the main peak shifted toward lower temperature between 230 and 270 °C as compared to the native hemicelluloses at temperature of 290 °C, indicating a decrease of the thermal stability of the products. Similar decreasing trend was also observed in the DTG curves, in which the exothermic peaks of the propionylated and stearoylated hemicellulosic samples 4 and 17 and native hemicelluloses appeared around 185, 280, and 290 °C, respectively. This suggested again that the esterification under the conditions of microwave irradiation partially degraded the polymers by breaking the glucosidic bonds

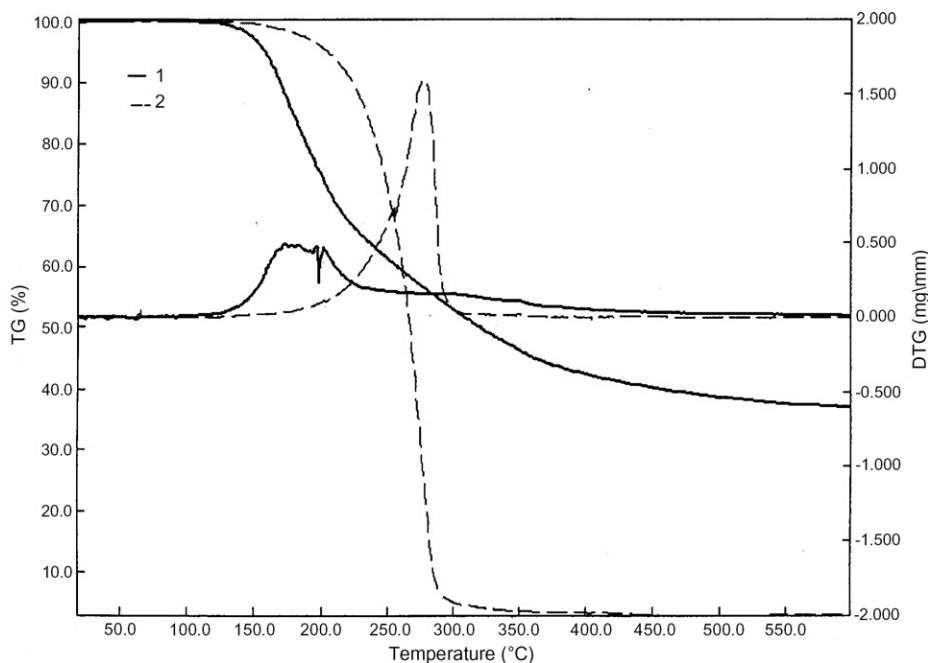


Fig. 6. Thermogram of modified wheat straw hemicellulosic samples 4 (spectrum 1) and 17 (spectrum 2).

In summary, hemicellulosic esters with DS values of 0.48–1.34 were prepared quickly and efficiently by microwave heating of hemicelluloses and acyl chlorides in DMF/LiCl medium. It improved the speed of esterification reaction remarkably and made reaction processing more smoothly. Microwave did not significantly affect the kind of acyl chlorides substituted into the native hemicelluloses. There were no obvious changes in the chemical structure of the modified polymers. However, microwave irradiation resulted in a slight degradation of hemicellulosic polymers in the esterification reactions in comparing with the conventional heating technique. Such esterified hemicelluloses might have value as food packages or biodegradable films. Certainly, much more work is needed on the effect of microwave irradiation on the molecular weight of the hemicellulosic derivatives.

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