

Preparation of Hemicellulosic Derivatives with Bifunctional Groups in Different Media

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Wheat straw hemicelluloses were converted to novel bifunctional hemicellulosic derivatives by etherification using acrylamide as reactant and sodium hydroxide as catalyst. The degree of substitution can be monitored by altering the molar ratio of acrylamide to xylose unit in hemicelluloses in the range of 1.0–10.0 and the molar ratio of sodium hydroxide to xylose unit in hemicelluloses in the range of 0.5–1.6, without changing the structure of the hemicelluloses. Comparison of the reaction in different media is discussed in detail. The optimized product with a high DS value of 0.58 was obtained by varying the condition parameters. Novel hemicellulosic derivatives containing carbamoylethyl and carboxyethyl groups could be confirmed by FT-IR, ¹H NMR, and ¹³C NMR spectroscopies. The behavior of hemicellulosic derivatives was monitored by means of thermogravimetry (TG) and differential thermal analysis (TGA). It was found that the product with a high DS had a lower thermal stability than the native hemicelluloses.

KEYWORDS: Hemicelluloses; etherification; characterization; NMR spectroscopy; thermal stability

INTRODUCTION

Hemicelluloses, the second most abundant class of polysaccharides found in nature after cellulose, are considered to be an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products. Recently, increasing knowledge of and a growing willingness to develop new biopolymer-based materials has led to an increasing application of hemicelluloses and their derivatives (1). It is particularly interesting to exploit the hemicelluloses from annual agricultural residual biomass as novel environmentally friendly materials for industries. For example, the hemicelluloses referred to as corn fiber gum are now utilized to replace food gums, thickeners, and adhesives (2). The feruloylated xylans isolated by dimethyl sulfoxide, dilute aqueous alkali hydroxide solution, hot water, and steaming can be utilized as a wound management aid (3). In addition, some of the xylan-rich hemicelluloses isolated from agricultural residues such as corn stalks, wheat straw, and bamboo leaves (4) and the 4-*O*-methylglucuronoxylan from Japanese beech wood (5) have been reported to inhibit the growth rate of sarcoma-180 and other tumors. Carboxymethylated xylan-rich wood hemicelluloses (6) have been found to activate T-lymphocytes and immunocytes and claimed as a new Chinese

antitumor drug (7). Quaternized xylan-rich sugar cane bagasse hemicelluloses (8) have been reported to strengthen properties of sheets formed from old corrugated container (OCC) pulp. A further useful functional property of arabinoxylans is their ability to retain gas in dough and protect protein foam against thermal disruption (9). These effects were related to the viscosity and film-forming properties of arabinoxylans (10).

The chemical modification of polysaccharides is the most important route to modify the properties of naturally occurring biopolymers and to use this renewable resource in the context of sustainable development. Recent research and development have been focused on the improvement of the unknown products and synthesis paths as well as on new derivatives and alternative synthesis concepts (11). On the basis of the complex structure and reactivity of hemicelluloses, chemical modification reactions continue to play a dominant role in improving the overall utilization of this biomacromolecules. An alternative path for increasing the applicability of hemicelluloses is chemically modifying them by incorporating many kinds of chemical groups on the hydroxyl groups of the xylose units in hemicelluloses. The hydroxyl groups allow the potential for esterification, etherification, oxidation, and other reactions such as hydrolysis and reduction. According to this procedure, several hemicellulose derivatives may be produced, as, for example, quaternized hemicellulosic derivatives (12–14), carboxymethyl hemicelluloses (15, 16), lauroylated hemicellulosic derivatives (17), acetylated hemicellulosic derivatives (18, 19), and oleoylated hemicellulosic derivatives (20). Quaternized and carboxymethyl hemicellulosic derivatives have in common an increase in the most common water solubility. In addition, the increase in

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solubility in organic solvents is observed in acetylated hemicellulosic derivatives, oleoylated hemicellulosic derivatives, and lauroylated hemicellulosic derivatives. However, up to now there has been no published study on hemicellulosic derivatives containing carbamoylethyl groups and carboxyl groups. Those hemicellulosic derivatives with bifunctional groups show new properties, such as hydrophilic character and inexpedient properties.

The preparation and properties of new polymers from hemicelluloses are an important part of any research program aimed at utilizing annually renewable, agriculturally derived polymers as extenders and replacements for polymers prepared from petrochemicals. In this context, the overall aim of the present research into hemicelluloses in our laboratories is to prepare the new polymers from hemicelluloses with bifunctional groups. The preferred route to the formation of these materials is by the etherification of hemicelluloses using acrylamide in the presence of a suitable alkaline catalyst, usually sodium hydroxide. In this work the optimized etherification condition could be controlled by varying the reaction parameters. Additionally, the different media were compared and are discussed in detail. The modified hemicelluloses were characterized by degree of substitution (DS) and Fourier transform infrared (FT-IR) and ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopies as well as thermal analysis.

MATERIALS AND METHODS

Materials and Reagents. Wheat straw was obtained from the experimental farm of the North-Western University of Agricultural and Forest Sciences and Technology (Yangling, China). It was first dried in sunlight and then ground to pass a 1.2 mm size screen. The ground straw was further dried again in a cabinet oven with air circulation for 16 h at 50 °C. Acrylamide and other chemicals were of analytical grade and were purchased from Guangzhou Chemical Reagent Factory, China.

Isolation and Characterization of Hemicelluloses from Wheat Straw. Ground wheat straw (50 g) was first extracted with toluene/ethanol (2:1, v/v) for 6 h and then using 1000 mL of H_2O at 75 °C for 2 h to remove water-soluble hemicelluloses. The water-soluble free sample was delignified with sodium chlorite in acidic solution (pH 3.8–4.0, adjusted by 10% acetic acid) at 75 °C for 2 h. The hemicelluloses were then obtained from the holocellulose by extraction with 10% KOH at 23 °C for 10 h with a liquor to solid ratio of 1:20 (g mL^{-1}). The hemicelluloses were recovered from the supernatant by acidification to pH 5.5 with 6 M acetic acid and then by precipitation of the neutralized hydrolysate in 3 volumes of 95% ethanol. After filtration, the pellets of the hemicelluloses were washed with acidified 70% ethanol and then air-dried.

Synthesis of Novel Hemicellulosic Derivatives. The typical procedure of the preparation of hemicellulosic derivatives with bifunctional groups is as follows. An amount of 0.66 g of hemicellulose powder (0.01 mol of hydroxyl functionality in hemicelluloses) in water was heated to 80 °C under stirring until completely dissolved (approximately 10 min), and then the mixture was cooled at room temperature. Subsequently, a required quantity of sodium hydroxide was added dropwise in this mixture for 20 min at room temperature, and then different media [distilled water, ethanol, ethanol/acetone, isopropanol, butanol, and *N,N*-dimethylformamide (DMF)] were gradually added, respectively, to form a homogeneous or heterogeneous system, and the volume of medium was set to 12 mL. Acrylamide was then added in the reaction mixture, and the temperature of the reaction was kept at room temperature. After 12 h, the product was neutralized with acetic acid and washed with 95% ethanol. The product was dialyzed (cutoff = 3500 g mol^{-1}) with distilled water and then freeze-dried. As can be seen in **Tables 1** and **2**, 14 samples were prepared by changing the different reaction media, the molar ratio of acrylamide to xylose unit in hemicelluloses from 1.0 to 10.0, and the molar ratio of sodium hydroxide to xylose unit in hemicelluloses from 0.5 to 1.6.

Table 1. Degree of Substitution (DS) of Novel Hemicellulosic Derivatives Synthesized in Different Media

medium	sample	DS			
		carbamoylethyl	carboxyethyl	total	ratio ^a
NaOH/ H_2O	1	0.31	0.030	0.34	10.3
ethanol	2	0.15	0.049	0.20	3.1
isopropanol	3	0.28	0.10	0.39	2.8
ethanol/acetone	4	0.16	0.068	0.23	2.4
DMF	5	0.03	0.014	0.04	1.9

^a Represents the ratio of carbamoylethyl to carboxyethyl groups.

Table 2. Degree of Substitution (DS) of Hemicellulose Derivatives Obtained by the Reaction of Hemicelluloses with AM in Various Reaction Conditions

molar ratio ^b	molar ratio ^c	sample	DS ^a			
			carbamoylethyl	carboxyethyl	total	ratio ^d
4.0	0.5	6	0.13	0.05	0.18	2.53
4.0	1.0	7	0.29	0.09	0.38	3.12
4.0	1.2	8	0.21	0.14	0.36	1.50
4.0	1.6	9	0.16	0.20	0.35	0.80
1.0	1.0	10	0.06	0.06	0.12	1.03
2.0	1.0	11	0.12	0.11	0.23	1.04
6.0	1.0	12	0.32	0.12	0.44	2.72
8.0	1.0	13	0.36	0.14	0.50	2.60
10.0	1.0	14	0.41	0.17	0.58	2.50

^a Determined by ^1H NMR and ^{13}C NMR. ^b Represents the mole ratio of acrylamide to xylose unit in hemicelluloses, xylose unit $M_w = 132$. ^c Represents the mole ratio of NaOH to xylose unit in hemicelluloses, xylose unit $M_w = 132$. ^d Represents the ratio of carbamoylethyl groups to carboxylethyl groups.

Characterization of Hemicelluloses and Their Derivatives. The neutral sugar composition of the isolated native hemicelluloses was determined by gas chromatography (GC) analysis of their alditol acetates (21). The content of uronic acids in native hemicelluloses was estimated calorimetrically according to the method of Blumenkrantz and Asboe-Hanson (22).

FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet 510) using a KBr disk containing 1% finely ground samples. Thirty-two scans were taken for each sample recorded from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} in the transmission mode. The solution-state ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer at 25 °C from 80 mg of sample dissolved in 1.0 mL of D_2O for native hemicelluloses and their derivatives after 30000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width, and a 0.85 s delay time between scans were used. The solution-state ^1H NMR spectra were recorded on a Bruker DRX-400 spectrometer at 25 °C from 15 mg of sample dissolved in 1.0 mL of D_2O for native hemicelluloses and their derivatives.

Thermal stability of the native and modified hemicellulosic samples was determined using a simultaneous thermal analyzer (Pyris Diamond TG/DTA, PE Instrument). The sample weighed between 8 and 12 mg. The scans were run from room temperature to 600 °C at a rate of 10 °C min^{-1} under nitrogen flow. Prior to thermal analysis, the samples were dried in a vacuum at 80 °C for 24 h.

RESULTS AND DISCUSSION

Analysis of the Isolated Native Hemicelluloses. The sugar analysis showed the following sugar composition (relative percent): 82.3% xylose, 9.6% arabinose, 4.0% glucose, 2.4% galactose, 0.7% rhamnose, 0.8% mannose. Uronic acids, mainly 4-*O*-methyl- α -D-glucuronic acid (MeGlcA), were present in a noticeable amount (3.9%).

Synthesis of Novel Hemicellulosic Derivatives. Chemical modification on hemicelluloses induces physical changes because the introduction of side chains leads to different structural characteristics in the raw materials. The new hemicelluloses had improved mechanical properties in comparison with the con-

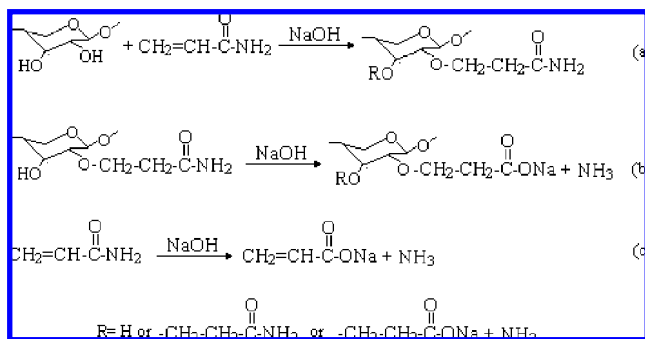


Figure 1. Etherification of hemicelluloses with acrylamide in alkaline condition.

ventional hemicelluloses. This can be achieved by appropriately selecting the chemical structure of the reactants being grafted onto hemicelluloses; the new hemicelluloses obtained could show new properties, such as hydrophilic or hydrophobic character, thermal stability, and resistance to chemical and biological agents. In this etherification reaction of hemicelluloses acrylamide was selected as etherification reagent and reacted with hemicelluloses in an alkaline condition. In other words, in this Michael addition, acrylamide can react with hemicelluloses in alkaline condition to form the carbamoyl ether of hemicelluloses. Less than 1 min was needed to dissolve completely in water at room temperature the hemicellulose ether obtained, which indicated that the hemicellulose ether showed the property of hydrophilicity. The reaction mechanism is shown in **Figure 1** on the assumption that hemicelluloses were xylan. As shown obviously, this reaction needs a catalyst to allow the formation of nucleophilic sites on hemicelluloses, and then hemicelluloses reacted with acrylamide to result in Hemi-O-CH₂-CH₂-C(=O)-NH₂ (**Figure 1a**). Moreover, the acylamino groups can be easily saponified to carboxyl groups and give carboxyethyl hemicelluloses as the stable end product in higher alkaline aqueous medium at elevated temperature (23). Therefore, the product obtained was partially saponified into Hemi-O-CH₂-CH₂-C(=O)-ONa (**Figure 1b**). More alkaline conditions could saponify acrylamide into CH₂=CH-C(=O)-ONa (**Figure 1c**). Therefore, the novel hemicellulosic derivatives may have bifunctional groups, which are carbamoyl-ethyl and carboxyethyl groups. In addition, the swelling of hemicelluloses in hot water before the etherification was necessary to increase the product yields because the diffusion of the monomer inside the hemicelluloses is easier.

Degree of Substitution (DS) of Novel Hemicellulosic Derivatives. Carbamoyl-ethyl groups and carboxyethyl groups were grafted onto hemicelluloses, and their structures and substitutions could be characterized by ¹H NMR and ¹³C NMR. The total DS can be determined from the peak area of protons of methylene that connect to carbamoyl-ethyl groups and carboxyethyl groups and the protons of xylose unit. The ratio of carbamoyl-ethyl groups to carboxyethyl groups could be determined by the peak intensity of ¹³C NMR spectra for the two carbonyl peaks that connect to carbamoyl-ethyl groups and carboxyethyl groups. The reaction degree could be evaluated from the relative ratio of carbamoyl-ethyl groups to carboxyethyl groups. To reduce the side reaction happening and allow the main reaction to continue smoothly, this reaction was performed at room temperature for 12 h. **Table 1** shows the extent of the chemical modification expressed as degree of substitution when the reaction was carried out in different reaction media without changing the parameters of the molar ratio of sodium hydroxide to xylose unit in hemicelluloses (0.8) and the molar ratio of

acrylamide to xylose unit in hemicelluloses (4.0). Five samples obtained in different media such as alkaline aqueous solution, ethanol, isopropanol, ethanol/acetone, and DMF were performed. Clearly, when the isopropanol was used as reaction medium, a higher DS (total DS = 0.39) of novel hemicellulosic derivatives could be obtained, whereas products prepared in DMF medium had a lower DS (total DS = 0.04). The role of the solvent in this etherification reaction is to provide miscibility and accessibility of the etherifying reagent to the reaction centers of hemicellulose chains (24). The differences in the extent of this etherification can be explained by taking into consideration their solvent polarities and stereochemistries. The reaction efficiency increases as the polarity of the solvent decreases. The results obtained are in good agreement with the literature (25). Therefore, isopropanol was naturally the best choice.

To increase the DS value of novel hemicellulosic derivatives, the reaction of wheat straw hemicelluloses with acrylamide was conducted under various amounts of sodium hydroxide and acrylamide at room temperature for 12 h. These results are shown in **Table 2**. As is well-known, this reaction is a Michael addition reaction. Sodium hydroxide acts as a catalyst in this reaction, so the function of the catalyst becomes very important. The results of the influence of the molar ratio of sodium hydroxide to xylose unit in hemicelluloses on DS of products is shown from sample 6 to sample 9 and sample 3 in **Tables 1** and **2**. As the molar ratio of sodium hydroxide to xylose units in hemicelluloses increases from 0.5 to 1.6, the total DS first increased from 0.18 (sample 6) to 0.39 (sample 3) and then decreased to 0.35 (sample 9), whereas the relative ratio of carbamoyl-ethyl groups to carboxyethyl groups increased from 2.53 (sample 6) to 3.12 (sample 7) and then decreased to 0.80 (sample 9) with an increase in the molar ratio of sodium hydroxide to xylose unit in hemicelluloses. This could be explained by sodium hydroxide making the reaction rate rise, whereas a greater amount of sodium hydroxide resulted in the products being saponified. Therefore, the DS of carboxyethyl groups increased with an increment in the molar ratio of NaOH to xylose unit in hemicelluloses. Therefore, the better reaction environment of the molar ratio of NaOH to xylose unit in hemicelluloses of 1.0 created the resulting product with a total DS of 0.38 and with a carboxyethyl/carboxyethyl ratio of 3.12.

As shown in **Table 2**, the acrylamide parameter study was carried out in six different molar ratios of acrylamide to xylose unit in hemicelluloses (samples 3 and 10–14). Clearly, increasing the molar ratio of acrylamide to xylose unit in hemicelluloses from 1.0 to 10.0 resulted in a significant increment of this reaction efficiency as shown by the increase in total DS from 0.12 (sample 10) to 0.58 (sample 14). This could be interpreted in terms of greater availability of acrylamide molecules in the proximity of the hemicellulose molecules at higher concentration of the etherifying reagents. Furthermore, changing the reaction parameter of the molar ratio of acrylamide to xylose unit in hemicelluloses from 1.0 to 10.0 first significantly increased the ratio of carbamoyl-ethyl groups to carboxyethyl groups from 1.03 to 3.12 and then decreased the ratio slightly to 2.50, which indicated the degree of saponification.

FT-IR Spectra. The effect of chemical modification on the structure of the hemicelluloses was also demonstrated by FT-IR in the region of 400–4000 cm⁻¹. **Figure 2** illustrates FT-IR spectra of hemicelluloses (spectrum 1) and novel hemicellulosic derivative sample 3 (spectrum 2) prepared at room temperature for 12 h. For unmodified hemicelluloses, the absorptions at 1610, 1461, 1404, 1249, 1160, 1077, 1041, and 892 cm⁻¹ seen in spectrum 1 are indicative of the native

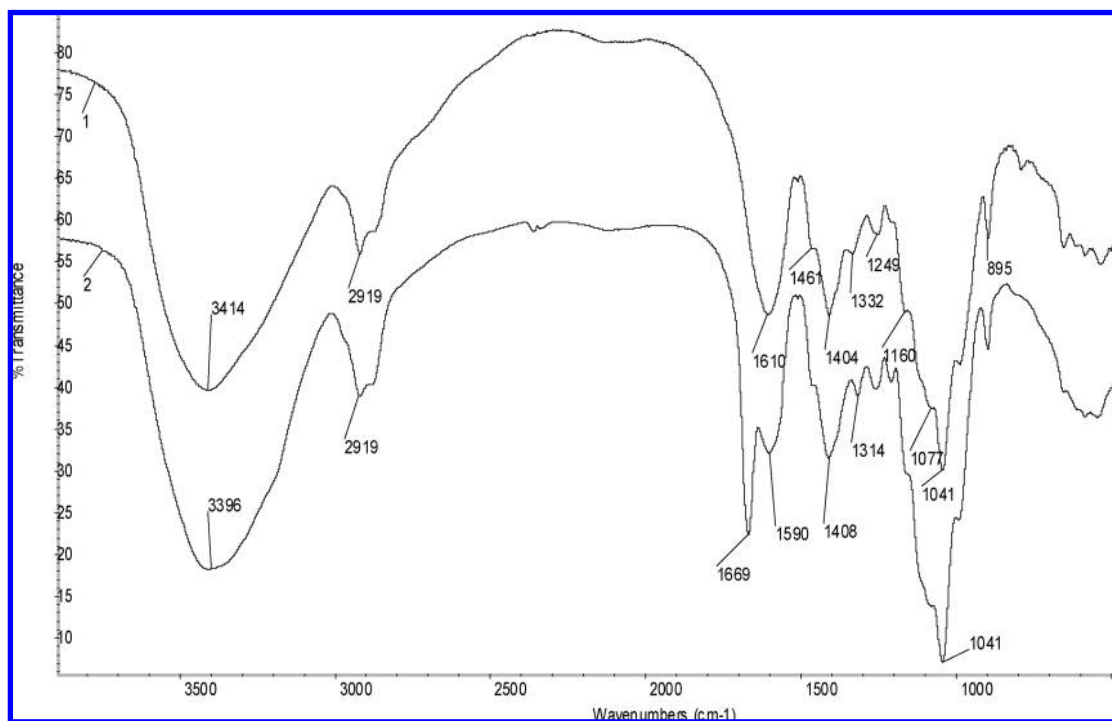


Figure 2. FT-IR spectra of hemicelluloses (spectrum 1) and modified hemicelluloses (spectrum 2, sample 9).

hemicelluloses. A sharp band at 895 cm^{-1} is assigned to 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 1041 cm^{-1} originates from C–O contributions in glycosidic linkages. The intense band at 1610 cm^{-1} is due to the absorbed water. A strong broadband belonging to hydrogen-bonded hydroxyls occurs at 3414 cm^{-1} , and a symmetric C–H vibration band is at 2919 cm^{-1} (22). Obviously, the presence of a few new bands occurs in spectrum 2 compared with spectrum 1 in **Figure 2**. Two peaks at 1590 and 1408 cm^{-1} are observed due to the asymmetrical and symmetrical stretching of —COO^- groups (26), respectively. The peak at 1669 cm^{-1} for the derivatives represents amide I (C=O stretching) bands, respectively. The peaks at 1669 , 1590 , and 1408 cm^{-1} indicate that the hemicellulosic derivatives contained carbamoylethyl and carboxyethyl groups. In addition, the bands between 3100 and 3500 cm^{-1} for the novel hemicellulosic derivatives are ascribable to the stretching vibration of OH and NH_2 groups, which became stronger than the bands of the stretching vibration of OH groups of the native hemicelluloses in spectrum 1. This suggested that strong inter- and intramolecular hydrogen bonds formed in the derivatives. Therefore, it is clearly shown that the appearance of the new bands indicates that the carbamoylethyl groups and carboxyethyl groups were grafted on the backbone of hemicelluloses.

Figure 3 illustrates the FT-IR spectra of novel hemicellulosic derivatives sample 6 (spectrum 1), sample 8 (spectrum 2), and sample 9 (spectrum 3). The similar spectral profiles indicate similar structures of the derivatives. However, on close examination of the spectra, some small differences were clearly identified. Comparison of the relative intensities at 1573 and 1669 cm^{-1} shows that the intensity at 1669 cm^{-1} apparently increased from spectrum 1 (sample 6, DS carbamoylethyl groups of 0.13) to spectrum 2 (sample 8, DS carbamoylethyl groups of 0.21) and then decreased from spectrum 2 to spectrum 3 (sample 9, DS carbamoylethyl groups of 0.16) and that the intensity at 1573 cm^{-1} increased from spectrum 1 (sample 6, DS carboxyethyl groups of 0.051) to spectrum 2 (sample 8, DS

carboxyethyl groups of 0.14) and to spectrum 3 (sample 9, DS carboxyethyl groups of 0.20). These correspond to the results of DS of novel hemicellulosic derivatives.

The effect of the molar ratio of acrylamide to xylose unit in hemicelluloses on the DS was investigated by the peak intensity of hemicellulosic derivatives, and their spectra are given in **Figure 4**. The intensities at 1669 and 1580 cm^{-1} obviously increased from spectrum 1 (sample 10) to spectrum 2 (sample 11) and to spectrum 3 (sample 13), corresponding to the increase of total DS from 0.12 to 0.23 and 0.50, the increase of DS carbamoylethyl groups from 0.063 to 0.12 and 0.36, and the increase of DS carboxyethyl groups from 0.061 to 0.11 and 0.14, respectively. Moreover, a broad absorption band around $3100\text{—}3500\text{ cm}^{-1}$ for the derivatives is ascribable to the stretching frequency of the —OH and —NH_2 groups, the intensities of which increased from spectrum 1 to spectrum 2 and spectrum 3, which indicated that more inter- and intramolecular hydrogen bonds formed in the derivatives.

^1H NMR and ^{13}C NMR Spectra. **Figure 5** shows the ^1H NMR spectrum of the native hemicelluloses. The chemical shifts of $3.2\text{—}4.4\text{ ppm}$ arise from the equatorial proton and other protons of anhydroxylose units of hemicelluloses. The methyl protons of a few acetyl groups exhibit peaks at 1.8 ppm . Anomeric protons of terminal $\alpha\text{-D-arabinofuranosyl}$ residues give a shoulder at 5.2 ppm (27). A strong signal at 4.7 ppm originates from the residual solvent (HDO).

Figure 6 shows ^1H NMR spectra of the water-soluble hemicellulosic derivatives in D_2O at $25\text{ }^\circ\text{C}$. The peaks from 2.2 to 2.6 ppm are assigned to protons of methylene that connect to carboxyethyl ($\text{H}7'$) and carbamoylethyl (H-7) groups, whereas the broad peaks from 2.8 to 4.5 ppm are attributed to another methylene ($\text{H-6, H-6}'$) of the substituents and all protons of hemicellulosic skeleton. The chemical shift of the protons of acylamino and carboxyl groups usually lay at $7\text{—}12\text{ ppm}$, which cannot be observed for their high activity. Clearly, the intensity of the peak at $2.2\text{—}2.6\text{ ppm}$ became stronger from curve 1 to curve 2 and curve 3 with increasing total DS from 0.12 (sample 10) to 0.23 (sample 11) and 0.50 (sample 13).

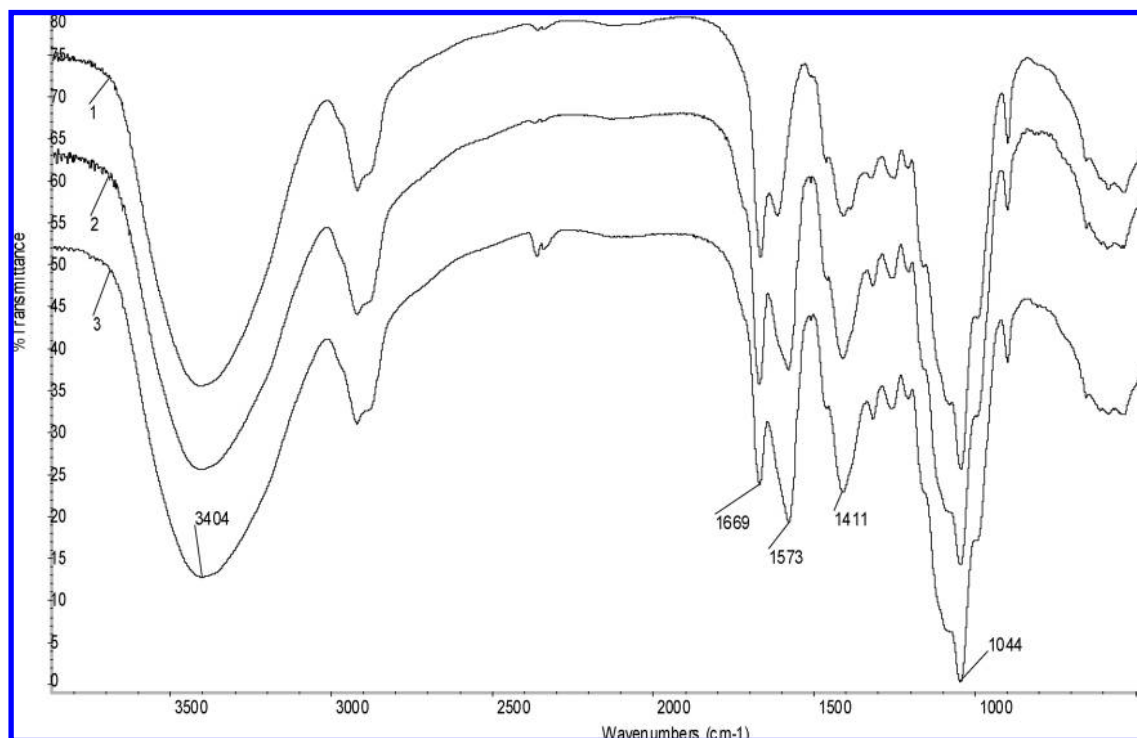


Figure 3. FT-IR spectra of modified hemicellulose sample 6 (spectrum 1), sample 8 (spectrum 2), and sample 9 (spectrum 3).

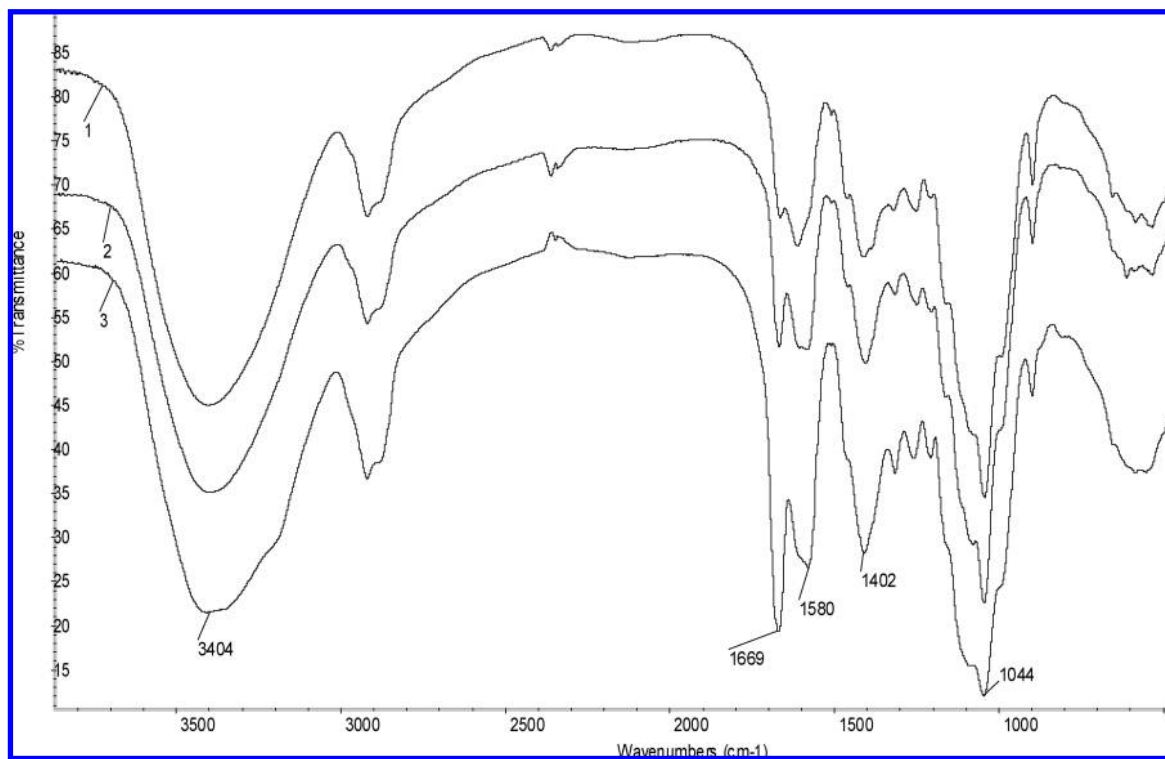


Figure 4. FT-IR spectra of modified hemicellulose sample 10 (spectrum 1), sample 11 (spectrum 2), and sample 13 (spectrum 3).

The ^{13}C NMR spectra of native hemicelluloses and novel hemicellulosic derivative sample 13 (total DS = 0.50) are shown in Figure 7. Figure 7a illustrates five major signals at 101.6, 76.2, 73.6, 72.6, and 62.9 ppm, which are attributed to the C-1, C-4, C-3, C-2, and C-5 positions of the β -D-Xylp units (28). The presence of arabinose was detected by the presence of characteristic signals at 108.4 (C-1), 84.5 (C-4), 80.7 (C-2), 77.2 (C-3), and 61.2 (C-5) ppm. The ^{13}C NMR measurements confirmed that the monomeric side chains of the L-arabinofuranosyl residues are linked to C-3 of the backbone xylan. Two signals at 71.1 and 68.4 ppm

represent C-4 and C-2 of galactose residue in the xylan, and a 57.4 ppm signal is characteristic of the methoxyl group of a 4-O-methyl-D-glucuronic acid residue in the xylan. Acetyl CH_3 in xylan gives a signal at 23.2 ppm. This revealed that the wheat straw hemicelluloses are composed mainly of L-arabino-(4-O-methyl-D-glucurono)-D-xylan (28). The presence of quantities of associated lignin was identified by one weak signal at 181.5 ppm, which originates from the carbonyl group in the associated lignin.

Evidently, as compared to the spectrum of unmodified hemicelluloses in Figure 7a, strong signals assigned to meth-

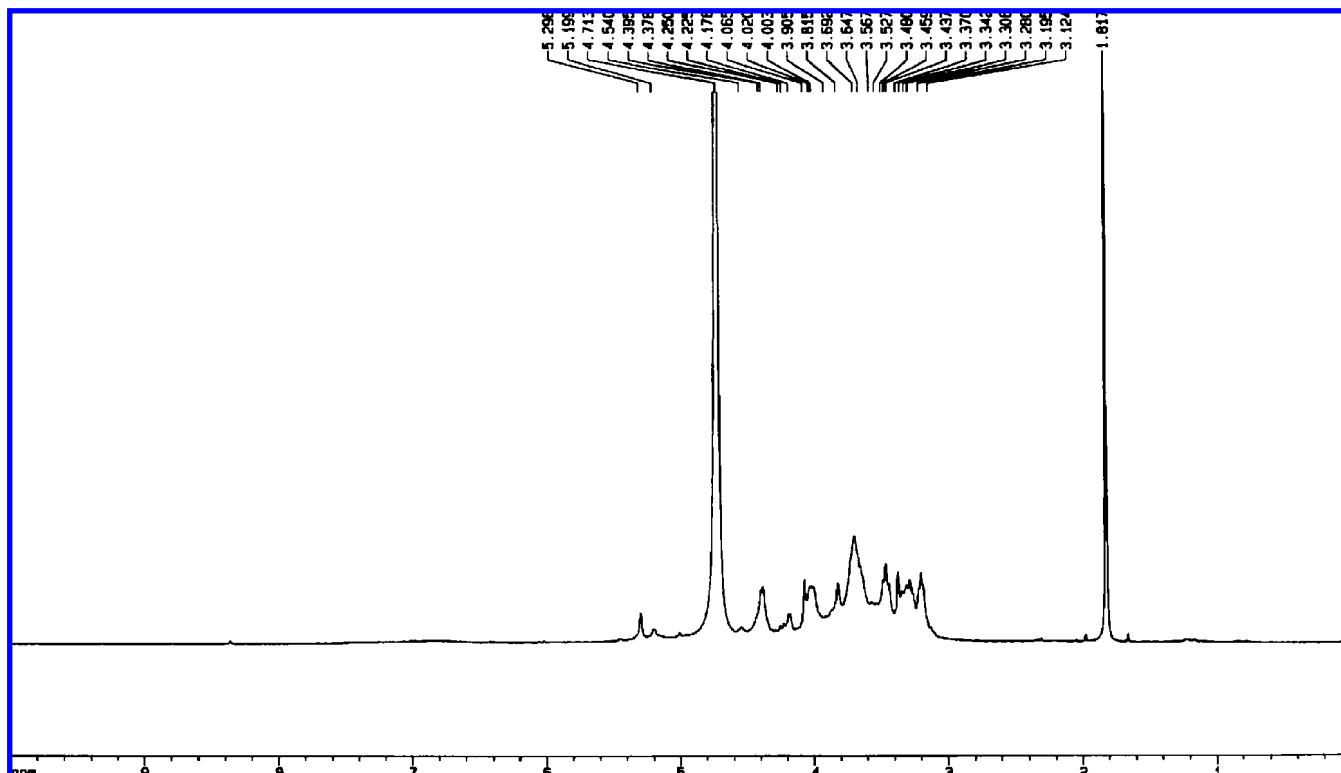


Figure 5. ^1H NMR spectrum of native hemicelluloses in D_2O at $25\text{ }^\circ\text{C}$.

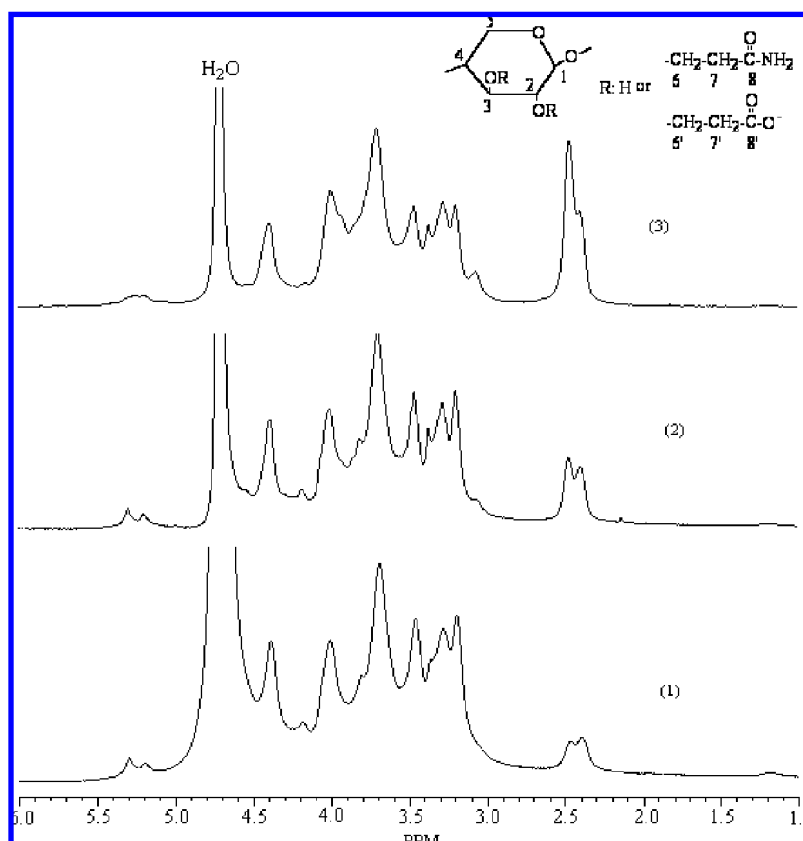


Figure 6. ^1H NMR spectra of hemicellulosic derivatives sample 10 (spectrum 1), sample 11 (spectrum 2), and sample 13 (spectrum c) in D_2O at $25\text{ }^\circ\text{C}$.

ylene peaks that connect to carbamoylethyl groups (C-7) and carboxyethyl groups (C-7') of the substituent can be seen between 34 and 40 ppm (29) in **Figure 7b**. The carbon signal of carbonyl groups in carbamoylethyl groups (C-8) and carboxyethyl groups (C-8') at 175–182 ppm revealed the presence

of carbamoylethyl and carboxyethyl groups and the occurrence of etherification in sample 13. Interestingly, the spectrum was very similar in the carbohydrate region (60–110 ppm) as compared to the spectrum of **Figure 7a** of native hemicelluloses, namely, C-1 (101.6 ppm), C-4 (76.3 ppm), C-3 (73.6 ppm),

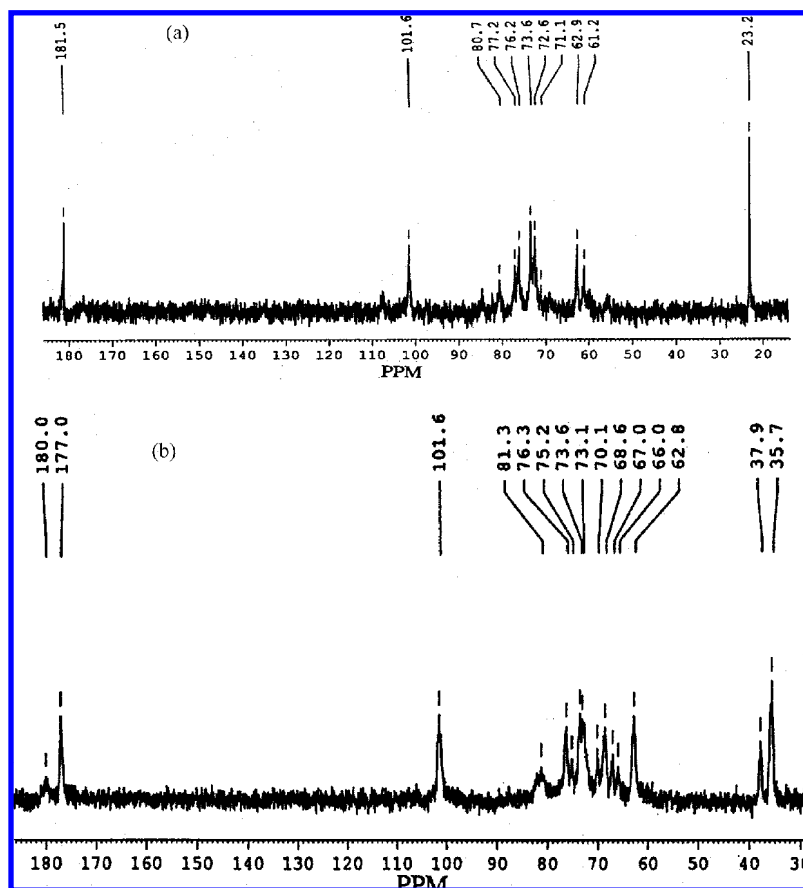


Figure 7. ^{13}C NMR spectrum of native hemicelluloses (a) and modified hemicellulose sample 13 (b) in D_2O at 25°C .

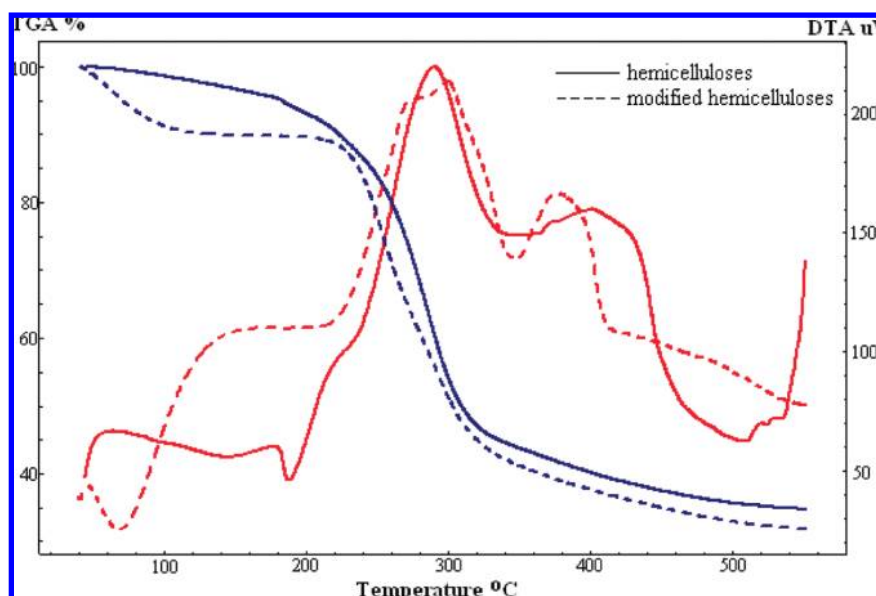


Figure 8. TGA/DTA curves of native hemicelluloses and modified hemicellulose sample 8.

C-2 (73.1 ppm), and C-5 (62.8 ppm) of xylan, indicating that the structure of the hemicellulose polymers did not significantly degrade in the alkaline condition given.

Thermal Analysis. Thermal analysis is convenient and reproducible and a useful method for characterizing heterogeneous organic material. In particular, it is a valuable analytical method to investigate the physicochemical properties of macromolecules such as hemicelluloses (30). Thermal degradability is affected by the chemical composition of the material. Figure 8 shows typical TGA/DTA curves of novel hemicellulosic

derivative sample 8 and unmodified hemicelluloses. From the analysis of thermogravimetric curves it can be observed that there was a very slight mass loss to temperatures of 228 and 223°C for native hemicelluloses and modified hemicellulose sample 8, respectively. Beyond these temperatures, there was a sharp weight loss. At 50% weight loss, the decomposition temperatures occurred at 303 and 312°C for modified hemicellulose sample 8 and native hemicellulose, respectively. The decreasing trends of decomposition temperature implied that the thermal stability of hemicelluloses decreased after chemical

modification. It was explained that acylamino groups were not stable at high temperature and more hydrogen bonds in macromolecules were destroyed during chemical modification. DTA was used to investigate the transitions of the polymers as affected by modification. As depicted in **Figure 8**, the exothermic peaks, which represent heat released from both native hemicelluloses and reaction product, were observed at 289 and 404 °C for native hemicelluloses and at 274, 300, and 378 °C for modified hemicelluloses, which indicated again that the thermal stability of modified hemicelluloses decreased.

In summary, the development of an etherification reaction of hemicelluloses makes feasible the use of acrylamide as etherifying agent and sodium hydroxide as catalyst. On the basis of the Michael addition and the saponification of acylamino groups to carboxyl groups in alkaline condition, novel hemicellulosic derivatives containing carbamoylethyl and carboxylethyl groups were heterogeneously synthesized in alkaline conditions. Hemicellulosic derivatives with total DS values of 0.12–0.58 were obtained by varying the reaction parameters. The total DS of hemicellulosic derivatives significantly increased with an increase in the amount of acrylamide. The thermal stability of the resulting products decreased after chemical modification. The products could be used as wet end additives and flocculants in papermaking and sewage treatment plants. Certainly, much more work is needed on the effects of substituent distribution on the properties of the resulting products such as viscosity behavior, solubility in water, and zeta potential in distilled water.

LITERATURE CITED

- Sun, R. C.; Sun, X. F.; Ma, X. H. Effect of ultrasound on the structural and physicochemical properties of organosolv soluble hemicelluloses from wheat straw. *Ultrasound Sonochem.* **2002**, *9*, 95–101.
- Rolin, C. Pectins In *Industrial Gums: Polysaccharides and Their Derivatives*, 3rd ed.; Whistler, R. L., BeMiller, J., Eds.; Academic Press: San Diego, CA, 1993; pp 257–293.
- Lloyd, L. L.; Kennedy, J. F.; Methacann, P.; Paterson, M.; Knill, C. J. Carbohydrate polymers as wound management aids. *Carbohydr. Polym.* **1998**, *37*, 315–322.
- Whistler, R. L.; Bushway, A. A.; Singh, P. P.; Nakahara, W.; Tokuzen, R. Noncytotoxic, antitumor polysaccharides. *Adv. Carbohydr. Chem. Biochem.* **1976**, *32*, 235–275.
- Hashi, M.; Takeshita, T. Studies on anti-tumor activity of wood hemicelluloses. 2. Host-mediated anti-tumor effect of 4-*O*-methylglucuronoxylan. *Agric. Biol. Chem.* **1979**, *43*, 961–967.
- Fan, Y. R.; Feng, Z. H. Effect of carboxymethyl-modified hemicelluloses on activity of T lymphocytes and amount of immunocytes. *Acta Pharmacol. Sinica* **1987**, *8*, 166–169.
- Ebringerova, A.; Heinze, T. Xylan and xylan derivatives—biopolymers with valuable properties. 1. Naturally occurring xyans structures, procedures and properties. *Macromol. Rapid Commun.* **2000**, *21*, 542–556.
- Ren, J. L.; Sun, R. C.; Peng, F.; He, B. H.; Lin, L. Application of cationic hemicelluloses as strengthening agent in OCC pulp. *China Pulp Paper* **2007**, *26*, 14–16.
- Izydorzyc, M. S.; Biliaderis, C. G. Cereal arabinoxylans: advances in structure and physicochemical properties. *Carbohydr. Polym.* **1995**, *28*, 33–48.
- Ebringerova, A.; Hromadkova, Z. Xylans of industrial and biomedical importance. *Genet. Eng. Rev.* **1999**, *16*, 325–346.
- Heinze, T.; Liebert, T. Unconventional methods in cellulose functionalization. *Prog. Polym. Sci.* **2001**, *26*, 1689–1762.
- Ren, J. L.; Sun, R. C.; Liu, C. F.; Lin, L.; He, B. H. Synthesis and characterization of novel cationic SCB hemicelluloses with a low degree of substitution. *Carbohydr. Polym.* **2007**, *67*, 347–357.
- Schwikal, K.; Heinze, T.; Ebringerova, A.; Petzold, K. Cationic xylan derivatives with high degree of functionalization. *Macromol. Symp.* **2006**, *232*, 49–56.
- Ebringerova, A.; Hormadkova, Z.; Kacuracova, M.; Antal, M. Quaternized xyans—synthesis and structural characterization. *Carbohydr. Polym.* **1994**, *24*, 301–308.
- Petzold, K.; Schwikal, K.; Heinze, T. Carboxymethyl xylan—synthesis and detailed structure characterization. *Carbohydr. Polym.* **2006**, *64*, 292–298.
- Petzold, K.; Schwikal, K.; Günther, W.; Heinze, T. Carboxymethyl xylan—control of properties by synthesis. *Macromol. Symp.* **2006**, *232*, 27–36.
- Ren, J. L.; Xu, F.; Sun, R. C.; Peng, P.; Sun, J. X. Studies of the lauroylation of wheat straw hemicelluloses under heating. *J. Agric. Food Chem.* **2008**, *56*, 1251–1258.
- Sun, X. F.; Sun, R. C.; Zhao, L.; Sun, J. X. Acetylation of sugarcane bagasse hemicelluloses under mild reaction conditions by using NBS as a catalyst. *J. Appl. Polym. Sci.* **2004**, *92*, 53–61.
- Ren, J. L.; Sun, R. C.; Liu, C. F.; Cao, Z. N.; Luo, W. Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst. *Carbohydr. Polym.* **2007**, *70*, 406–414.
- Sun, X. F.; Sun, R. C.; Sun, J. X. Oleoylation of sugarcane bagasse hemicelluloses using *N*-bromosuccinimide as a catalyst. *J. Sci. Food Agric.* **2004**, *84*, 800–810.
- Blakeney, A. B.; Harris, P. J.; Henry, R. J.; Stone, B. A. A simple and rapid preparation of alditol acetates for monosaccharide analysis. *Carbohydr. Res.* **1983**, *113*, 291–299.
- Blumenkrantz, N.; Asboe-Hanson, G. New method for quantitative determination of uronic acids. *Anal. Biochem.* **1973**, *54*, 484–489.
- Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. Functionalization of cellulose *Comprehensive Cellulose Chemistry*; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, pp 1–66.
- Togrul, H.; Arslan, N. Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behaviour of carboxymethyl cellulose. *Carbohydr. Polym.* **2003**, *54*, 73–82.
- Bhattacharyya, D.; Singhal, R. S.; Kulkarni, P. R. A comparative account of conditions for synthesis of sodium carboxymethyl starch from corn and amaranth starch. *Carbohydr. Polym.* **1995**, *27*, 247–253.
- Bajpai, A. K.; Shrivastava, J. In vitro enzymatic degradation kinetics of polymeric blends of crosslinked starch and carboxymethyl cellulose. *Polym. Int.* **2005**, *54*, 1524–1536.
- Teleman, A.; Lundqvist, J.; Tjerneld, F.; Stalbrand, H.; Dahlman, O. Characterization of acetylated 4-*O*-methylglucuronoxylan isolated from aspen employing ¹H and ¹³C NMR spectroscopy. *Carbohydr. Res.* **2000**, *329*, 807–815.
- Sun, R. C.; Lawther, J. M.; Banks, W. B. Fractional and structural characterization of wheat straw hemicelluloses. *Carbohydr. Polym.* **1996**, *29*, 325–331.
- Halverson, F.; Lancaster, J. E.; O'Conner, M. N. Sequence distribution of carboxyl groups in hydrolyzed polyacrylamide. *Macromolecules* **1985**, *18*, 1139–1144.
- Sun, X. F.; Xu, F.; Sun, R. C.; Geng, Z.; Fowler, P.; Baird, M. S. Characteristics of degraded hemicellulosic polymers obtained from steam exploded wheat straw. *Carbohydr. Polym.* **2005**, *60*, 15–26.

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