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Preparation and characterization of hemicellulosic derivatives containing carbamoylethyl and carboxyethyl groups

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ABSTRACT

A series of novel water-soluble hemicellulosic derivatives, containing carbamoylethyl and carboxyethyl groups, were heterogeneously synthesized from wheat-straw hemicelluloses with acrylamide (AA) under alkaline conditions. The factors such as reaction temperature, reaction time, molar ratio of catalysis to xylose unit in hemicelluloses and molar ratio of acrylamide to xylose unit in hemicelluloses, were investigated. The average degree of substitution (DS) was calculated by ^{1}H NMR spectroscopy. DS values up to 0.23 in a one-step synthesis of hemicelluloses derivatives were obtained. Under optimum conditions (60 °C, NaOH to xylose unit in hemicelluloses molar ratio of 0.8, AA to xylose unit in hemicelluloses molar ratio of 8.0, reaction time of 1 h) an expected ratio of carbamoylethyl group to carboxyethyl group of 4.8 in the hemicellulosic derivatives was obtained. The structural features of the hemicellulosic derivatives were characterized by FTIR, NMR spectroscopy, and by elemental analysis. The current work provides a facile method for the synthesis of hemicellulose derivatives with bifunctional groups, which could be used as wet-end additives in the papermaking industry.

1. Introduction

Hemicelluloses, unlike cellulose, which is a unique molecule differing only in degree of polymerization and crystallinity, are non-crystalline heteropolysaccharides and classically defined as the alkali-soluble material after removal of the pectic substances.[1] After cellulose, hemicelluloses constitute the second most abundant class of polysaccharides found in nature. Hemicellulosic monomer units can be divided into hexoses and pentoses and include mainly galactose, glucose, mannose (hexoses), and arabinose and xylose (pentoses). Hemicelluloses with hexoses as monomer units occur mainly in softwoods, and in the small grains, wheat and barley, while those with pentoses as monomer units occur in hardwoods, and in the small grains, rye and oats. However, hemicelluloses differ not only in their monomer units, but also in their branching or side chains at positions C-2 and C-3.[2] The degree of polymerization (DP) of hemicelluloses is lower than the DP of cellulose. They are branched polymers of low molecular weight with a DP of 80–200.

Because of the increasing need for high-performance biocompatible polymers, the chemical modification of polysaccharides is the most important route to modify the properties of the naturally occurring biopolymers and to use this renewable resource in the context of sustainable development. Recent research and development is focused on the improvement of known products and new synthesis paths as well as on new derivatives and alternative synthesis concepts.[3] For example, to endow hemicelluloses with water-soluble and cationic functions, hemicellulosic derivatives containing cationic groups have been successfully synthesized using both homogenous and heterogeneous methods.[4–7] Carboxymethylation of hemicelluloses by applying different procedures and various slurry media (ethanol/toluene, ethanol, and 2-propanol) represents a useful way to get hemicelluloses with anionic functions.[8] In addition, esterification was used as the derivative reaction for hemicelluloses by different approaches such as the succinylation of hemicelluloses, that is, the reaction of the hemicelluloses with succinic anhydride using *N*-bromosuccinimide as a catalyst in an *N*,*N*-dimethylacetamide/lithium chloride system.[9] Acetylation of the hydroxyl groups of hemicelluloses, which seems to increase film flexibility,[10,11] is one approach toward increasing the water resistance of hemicelluloses, and sulfation of hemicelluloses can be attractive to the pharmaceutical industry as a means to produce raw materials for high-value products.[12,13]

The overall aim of the present research into hemicelluloses in our laboratories is to prepare novel and high-performance polymers from hemicelluloses as replacements for polymers prepared from petrochemicals. Thus, we investigated new reagents capable of extending the synthesis paths or yielding new structural parameters that can be applied to the reaction of hemicelluloses. An

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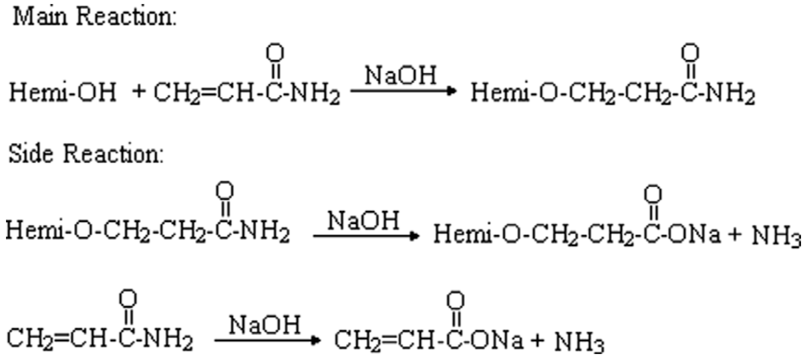

$$\text{Hemi-OH} + CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NH_2 \xrightarrow{NaOH} \text{Hemi-O-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}NH_2$$

$$\text{Hemi-O-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}NH_2 \xrightarrow{NaOH} \text{Hemi-O-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}ONa + NH_3$$

$$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NH_2 \xrightarrow{NaOH} CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}ONa + NH_3$$

Scheme 1. The main and side reactions of the etherification of hemicelluloses with acrylamide in alkaline system.

effective synthesis of bifunctional hemicelluloses containing carbamoylethyl and carboxyethyl groups under heterogeneous reaction conditions is first reported herein. The products are characterized by elemental analysis, and by FTIR and NMR spectroscopy.

2. Result and discussion

2.1. Analysis of wheat-straw hemicelluloses

On the basis of the dry weight of wheat straw, treatment of the delignified holocellulose with 10% KOH at 23 °C for 10 h yielded 34.3% of alkali-soluble hemicelluloses. The sugar composition (relative%) was found to be 82.3% xylose, 9.6% arabinose, 4.0% glucose, 2.4% galactose, 0.7% rhamnose, and 0.8% mannose. Uronic acids, mainly 4-*O*-methyl-α-D-glucuronic acid (MeGlcA), were present in a noticeable amount (3.9%). Gel-permeation chromatography (GPC) analysis showed that the native hemicelluloses had an average molecular weight of 26,800 g mol^{-1} with a polydispersity of 2.93. The FTIR and ^{13}C NMR results further confirmed the structural features of the native hemicelluloses, with a backbone of β-(1→4)-linked D-Xyl*p* units, and side chains with L-Ara*f*, D-Xyl*p*, and 4-*O*-D-Glc*p*A (or D-Glc*p*A).[11,14]

2.2. Synthesis of hemicellulosic derivatives

The polysaccharide used was wheat-straw hemicellulose with a xylose content of 82.3% (related to the total sugar content). For the etherification of hemicelluloses a procedure based on the method for the etherification of cellulose and starch[15,16] was applied. Ethanol was selected as a solvent in this reaction. To reduce the side reaction caused by a high concentration of alkali, sodium hydroxide was not added all at once, but was added in three portions during the course of the heterogeneous synthesis. The chemical functionalization of hemicelluloses is illustrated in Scheme 1. Acrylamide served as the novel etherification reagent, reacting with the hemicelluloses under alkaline conditions to form the carbamoylethyl ethers. However, the carbamoylethyl groups could be also easily saponified to carboxyethyl groups with a more highly alkaline aqueous medium (Scheme 1). Because the carbamoylethyl groups of the substituent groups could be partially saponified to carboxyethyl groups, the derivatives most likely contain bifunctional groups of carbamoylethyl and carboxyethyl by varying the reaction of conditions.

In this study, the degree of substitution was simply controlled by varying the molar ratio of acylamide to anhydroxylose units in the hemicelluloses, as well as the molar ratio of sodium hydroxide to anhydroxylose units in hemicelluloses, together with reaction temperature and reaction time. Table 1 gives the degree of substitution of the hemicellulosic preparations. Obviously, an increase of the reaction time from 3 to 6, and to 12 h at 25 °C led to the increase in the nitrogen content (N%), corresponding to an increase of the total DS value of the hemicellulosic derivatives from 0.088 to 0.161, and to 0.215, respectively. Moreover, a slight further increase in the DS value was observed, along with an

Table 1
Degree of substitution (DS) of hemicelluloses derivatives obtained by the reaction of hemicelluloses with acrylamide in various reaction systems

Molar ratio[a]	Molar ratio[b]	*T* (°C)	*t* (h)	Sample no.	N%[c]	DS[d]		
						Total	Carbamoylethyl	Carboxyethyl
0.8	4.0	25	3	1	0.599	0.088	0.062	0.026
0.8	4.0	25	6	2	0.904	0.161	0.131	0.030
0.8	4.0	25	12	3	1.154	0.215	0.173	0.042
0.8	4.0	25	24	4	1.032	0.220	0.125	0.095
0.8	4.0	60	1	5	0.492	0.114	0.077	0.037
0.8	4.0	60	2	6	0.598	0.134	0.071	0.063
0.8	4.0	60	4	7	0.581	0.152	0.064	0.088
0.5	4	60	1	8	0.432	0.062	0.059	0.003
1.0	4	60	1	9	0.410	0.081	0.062	0.019
1.5	4	60	1	10	0.212	0.077	0.038	0.039
2.0	4	60	1	11	0.0793	0.041	0.012	0.029
0.8	1.0	60	1	12	0.302	0.053	0.047	0.006
0.8	2.0	60	1	13	0.484	0.085	0.061	0.024
0.8	8.0	60	1	14	1.324	0.192	0.159	0.033
0.8	10.0	60	1	15	1.356	0.230	0.161	0.069

[a] Represents the mole ratio of NaOH to xylose unit in hemicelluloses, xylose unit M_w = 132.
[b] Represents the mole ratio of AM to xylose unit in hemicelluloses, xylose unit M_w = 132.
[c] Nitrogen content (N%) was determined by the elemental analysis.
[d] Determined by ^{1}H NMR spectroscopy.

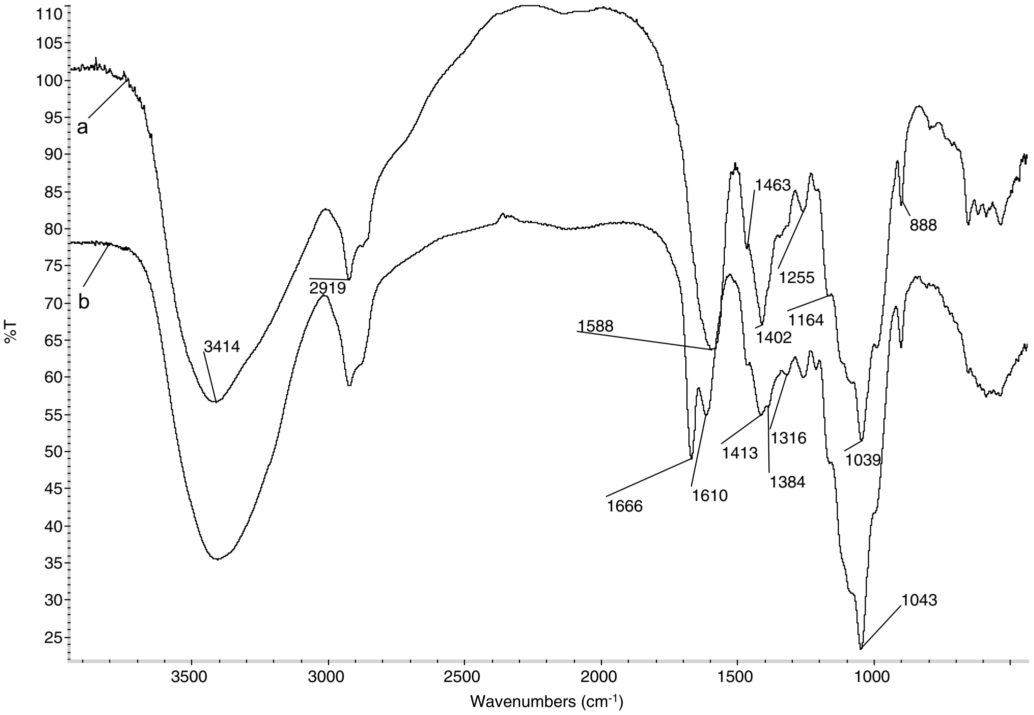

Figure 1. FTIR spectra of wheat-straw hemicelluloses (Spectrum a) and hemicellulosic derivatives (sample 14).

increasing number of carboxyethyl groups with the duration of the reaction. When the reaction time was extended up to 24 h, the total DS values of the hemicellulosic derivative increased slightly to 0.220, but the nitrogen content and the DS values of carbamoylethyl groups decreased to 1.032 and 0.125, respectively, whereas the carboxyethyl groups increased sharply to 0.095. The reason for the decrease in the DS values for the carbamoylethyl groups could be interpreted as prolonging the duration of the reaction, which resulted in the occurrence of the side reactions, which could be seen from the data for the DS value of the carboxyethyl groups in sample 4 (0.095). The DS values and the nitrogen content of the hemicellulosic derivatives prepared for different durations of reaction when the reaction temperature was controlled at 60 °C are also shown in Table 1. The total DS value increased from 0.114 to

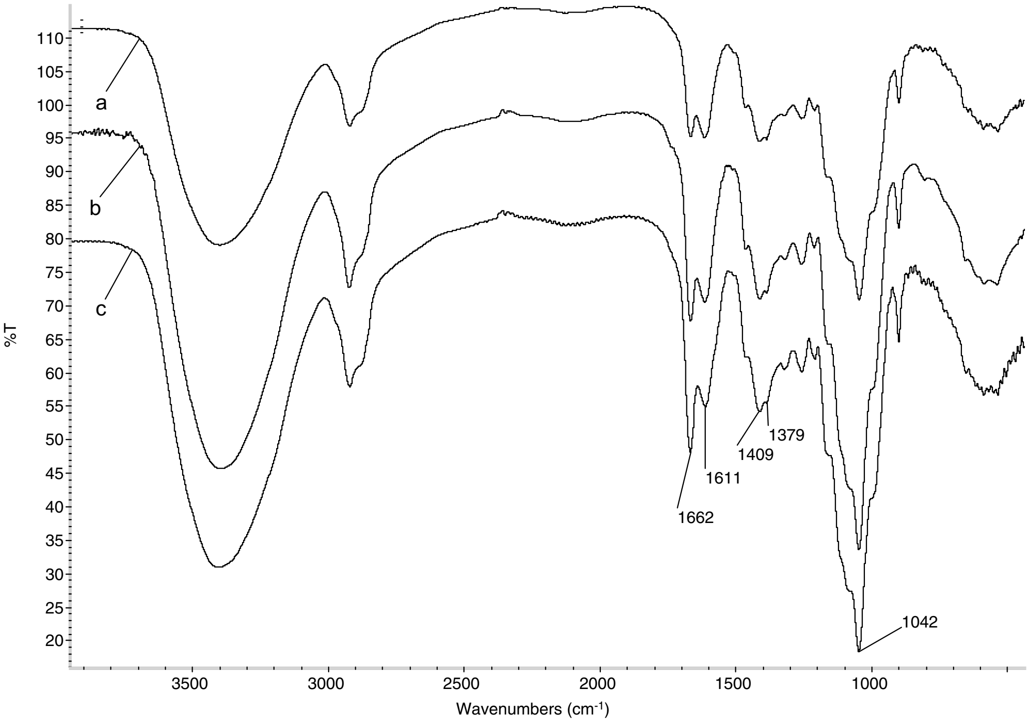

Figure 2. FTIR spectra of hemicellulosic derivatives sample 1 (Spectrum a), sample 2 (Spectrum b), and sample 3 (Spectrum c).

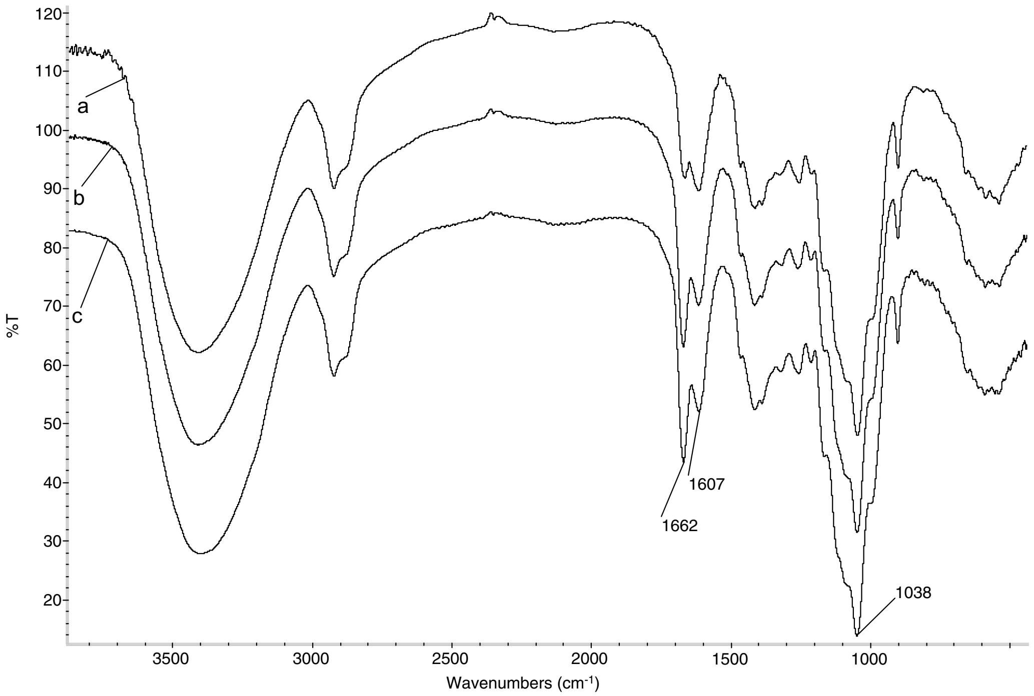

Figure 3. FTIR spectra of hemicellulosic derivatives sample 13 (Spectrum a), sample 14 (Spectrum b), and sample 15 (Spectrum c).

0.134, and to 0.152 by prolonging the reaction time from 1 to 2, and to 4 h, respectively. This increase in the DS values with duration of reaction could be due to the increased rate and time of collisions of AA with the hemicellulose molecules. In particular, the DS values of the carboxyethyl groups of hemicellulosic derivatives increased sharply compared with the increase in the DS values of

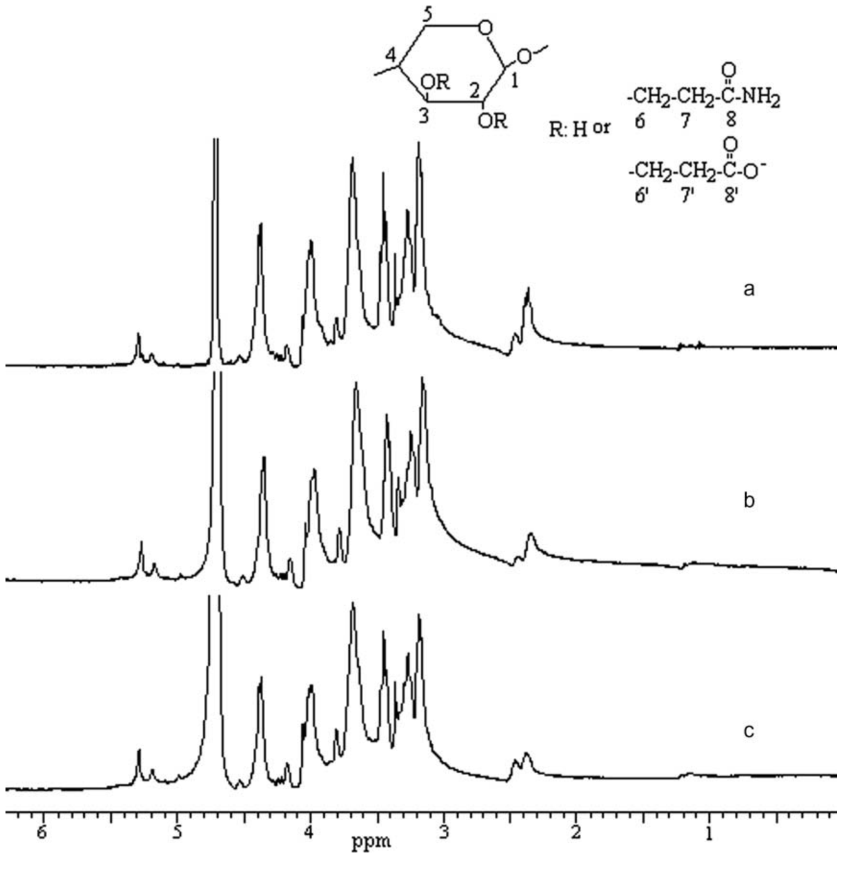

Figure 4. ^{1}H NMR spectra of hemicellulosic derivative sample 15 (Spectrum a), sample 5 (Spectrum b), and sample 9 (Spectrum c).

carbamoylethyl groups. Therefore, attempts were made to carry out the modification for 1 h so as to induce the side reaction but maintain a low DS value.

The catalysis of NaOH apparently had other effects on this modification process. The presence of NaOH induced the modification to occur. The effect of catalysis on the DS of hemicellulosic derivatives is shown in Table 1. As can be seen, with an increase in the molar ratio of sodium hydroxide to anhydroxylose units in hemicelluloses from 0.5 to 0.8, and to 1.0, to 1.5, to 2.0, the total DS at first increased and then decreased sharply. At a molar ratio of 0.8 (NaOH:anhydroxylose unit in the hemicelluloses), the total DS (0.114, sample 5) is higher in comparison to the others. In addition, the decrease in the DS with a further increase in the molar ratio of sodium hydroxide to anhydroxylose unit in hemicelluloses was a direct consequence of the degradation of hemicelluloses and the occurrence of the side reactions at higher alkaline concentration.

Obviously, increasing the molar ratio of AA to anhydroxylose unit in hemicelluloses from 1.0 to 10.0 with a 0.8 M ratio of NaOH to anhydroxylose unit in hemicelluloses at 60 °C for 1 h resulted in a significant increase in modification efficiency as shown by the total DS values increasing from 0.053 to 0.230 and the nitrogen content increasing from 0.302 to 1.356, respectively. This increase could be interpreted in terms of the greater availability of acylamide molecules in the proximity of the hemicelluloses at higher concentration of the etherifying agent.[17] Moreover, the DS values of the carbamoylethyl groups and carboxyethyl groups also increased, respectively, with an increase in the molar ratio of AA to the anhydroxylose units in hemicelluloses. Clearly, the DS values of the carboxyethyl groups increased more rapidly compared with the increase in the DS values of the carbamoylethyl groups. That is to say, in this case the side reaction was more prevailing in the modification of hemicelluloses. In summary, the bifunctional hemicellulosic derivatives with carbamoylethyl groups and carboxyethyl groups could be synthesized by the etherification of hemicelluloses with acrylamide in an alkaline system. Different DS values of the derivatives could be obtained by varying the reaction conditions.

2.3. FTIR spectra

The FTIR spectra of wheat-straw hemicelluloses (Spectrum a) and modified hemicelluloses (Spectrum b) are shown in Figure 1. Analysis of the FTIR data showed that hemicelluloses clearly illustrated the typical signal pattern for the hemicellulosic moiety and produced a specific band in the 1200–1000 cm^{-1} region shown in Spectrum a. This region is dominated by ring vibrations overlapped with stretching vibrations of (C–OH) side groups and the (C–O–C) glycosidic bond vibration.[18] In particular, the band at 1039 cm^{-1} is dominated by a glycosidic linkage (C–O–C) contribution. The presence of the arabinosyl side chains is identified by the low-intensity shoulder at 1164 cm^{-1} corresponding to the C–O–C vibration in hemicelluloses. The absorption at 1588 cm^{-1} is principally associated with absorbed water.[19] The region between 1463 and 1164 cm^{-1} relates to the C–H and C–O bond-stretching frequencies. A strong broad bond due to hydrogen-bonded hydroxyls appears at 3414 cm^{-1}, and the symmetric C–H vibration band is found at 2919 cm^{-1}.[20]

Spectrum b shows the FTIR spectrum of a hemicellulosic derivative (Fig. 1). Clearly, the presence of a new and strong absorption band at 1666 and 1384 cm^{-1} confirms the presence of the amide I and amide III bands, respectively, in Spectrum b. The band at 1610 cm^{-1} is assigned to the COO^{-} groups.[21] The bands around 1413 and 1316 cm^{-1} are assigned to –CH$_2$ scissoring and –OH bending vibrations, respectively. Moreover, the bands between 3100 and 3500 cm^{-1} for the derivatives are ascribable to the stretching vibration of the OH and NH$_2$ groups, which became stronger than the bands of the stretching vibration of the OH groups of the hemicelluloses in Spectrum a, indicating that the hemicellulosic derivatives contained carbamoylethyl and carboxyethyl groups. This work provided a facile method for the synthesis of hemicelluloses derivatives with bifunctional groups.

Figure 2 shows the FTIR spectra of the hemicellulosic derivatives as follows: sample 1 (Spectrum a), sample 2 (Spectrum b), and sample 3 (Spectrum c). The similar spectral profiles indicate similar structures of the modified hemicelluloses. However, on closer examination of the spectra, some differences are clearly identified. As illustrated, the intensity of the amide I at 1662 cm^{-1} and the COO^{-} groups at 1611 cm^{-1} increased with an increase in reaction time from 3 h in Spectrum a to 6 h in Spectrum b and 12 h in Spectrum c, corresponding to an increase of the carbamoylethyl groups in DS from 0.062 to 0.131, and to 0.173, and an increase in the DS of the carboxyethyl groups from 0.026 to 0.030, and 0.042, respectively. In addition, the intensity of the bands between 3100 and 3500 cm^{-1} for the stretching vibrations of the OH and NH$_2$ groups in the hemicellulosic derivatives increased with an increase in the total DS values from 0.088 to 0.161, and to 0.215, respectively. Figure 3 also shows that the absorbance for the amide and COO^{-} groups increased from Spectrum a to Spectrum b and to Spectrum c with an increase in the total DS from 0.085 to 0.192, and to 0.230.

2.4. ^{1}H and ^{13}C NMR spectra

Figure 4 shows the ^{1}H NMR spectra of hemicellulosic derivatives in D$_2$O. The peaks from 2.2 ppm to 2.6 ppm are assigned to

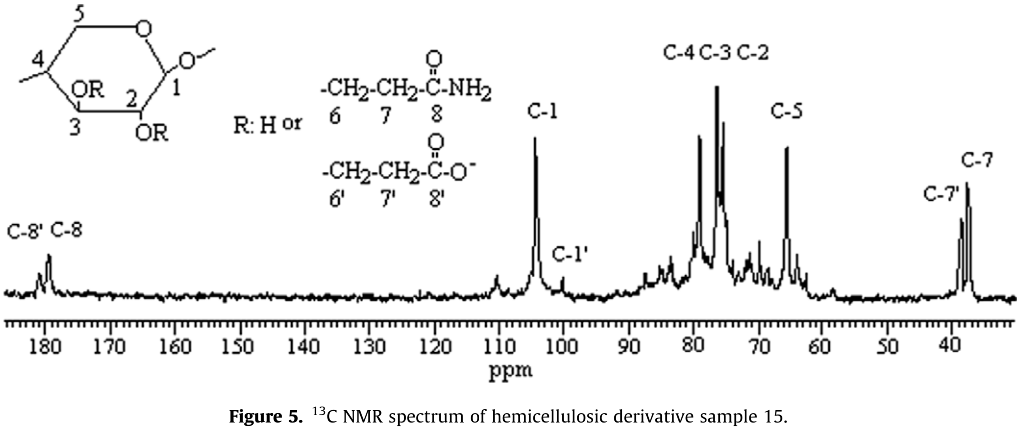

Figure 5. ^{13}C NMR spectrum of hemicellulosic derivative sample 15.

protons of the methylene group that are connected to the carbamoylethyl (H-7) and carboxyethyl (H-7′) groups. The broad peaks from 3.0 ppm to 4.6 ppm are attributed to another methylene (H-6, H-6′) of the substituents and all the protons of hemicellulosic skeleton. The total DS of the derivatives from the peak area of 2.2 ppm to 2.6 ppm and from 2.8 ppm to 4.6 ppm could be estimated, and the results are listed in Table 1. As shown in Figure 4, the signals at 2.36 and 2.42 ppm are, respectively, attributed to the carbamoylethyl (H-7) and carboxyethyl (H-7′) groups in the substituents, which indicate that the chemical modification has occurred and the carbamoylethyl groups and the carboxyethyl groups are grafted onto the backbone of hemicelluloses. Moreover, with an increase in the total DS from 0.081 (sample 9, Spectrum c) to 0.114 (sample 5, Spectrum b) and to 0.230 (sample 15, Spectrum a) the intensity of the signals between 2.2 and 2.6 ppm increased.

Figure 5 shows the ^{13}C NMR spectrum of hemicellulosic derivative sample 15 in D_2O. The chemical shifts at 178.2 ppm and 180.6 ppm are, respectively, assigned to the carbon signal of the carbonyl groups in the carbamoylethyl (C-8) and the carboxyethyl (C-8′) groups. The resonances at 37.6 ppm and 39.2 ppm are attributed to methylenes that connect to carbamoylethyl (C-7) and carboxyethyl (C-7′) groups, respectively.[22,23] The peaks for the hemicellulose backbone are between 62.5 and 110.3 ppm. The signals at 104.3 (C-1), 78.2 (C-4), 77.8 (C-3), 75.3 (C-2), and 65.6 (C-5) ppm, correspond to (1→4) linked β-D-Xyl*p* residues.[20] Based on the results obtained by this analysis, it was concluded that hemicelluloses were indeed chemically modified, and the bifunctional groups are connected onto the backbone of the hemicelluloses.

3. Conclusions

The above results indicate that the etherification of hemicelluloses in a heterogeneous system with AA as an etherifying agent under the alkaline conditions yields water-soluble hemicellulosic derivatives with bifunctional groups, which represents more acceptable techniques of chemically modifying hemicelluloses for potential industrial applications. In this case, the low DS values of the novel hemicellulosic derivatives with carbamoylethyl and carboxyethyl groups are prepared by varying the reaction parameters such as reaction temperature and time, and the molar ratios of NaOH to anhyroxylose and AA to anhyroxylose units in hemicelluloses. The total DS and the DS of carbamoylethyl groups in the hemicellulosic derivatives increased with growth of the molar ratio of acrylamide to anhyroxylose units in hemicelluloses. Optimum conditions for the etherification process to run smoothly and to yield a product with an expected total DS (0.22, 0.19) and relatively higher ratio of carbamoylethyl group to carboxyethyl group (4.1, 4.8) were found as follows: (1) At 25 °C a molar ratio of NaOH:xylose unit in hemicelluloses of 0.8 and a molar ratio of AA:xylose unit in hemicelluloses of 4.0 for a reaction time of 12 h or (2) at 60 °C a molar ratio of NaOH:xylose unit in hemicelluloses of 0.8 and a molar ratio of AA:xylose unit in hemicelluloses of 8.0 for a reaction time of 1 h.

4. Material and methods

4.1. Materials

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 purchased from Guangzhou Chemical Reagent Factory, China.

4.2. Preparation of hemicellulosic derivatives

Wheat-straw hemicelluloses were isolated after removal of lignin by the method described in a previous paper.[11] In a typical reaction procedure, 1 g of hemicelluloses (equal to 15.15 mmol hydroxyl functionality in hemicelluloses) was suspended in 5 mL of water and heated at 85 °C for 20 min, and then the mixture was cooled to room temperature. The mixture solution was stirred at 30 °C for 60 min after the addition of required quantities of sodium hydroxide (accounting for 50% of the total sodium hydroxide). Then 16 mL of ethanol was gradually added to form uniform particles in the mixture. Sodium hydroxide accounting for 10% of the total sodium hydroxide was added over a period of 30 min. Following of the addition of AA from 0.5377 g (7.573 mmol) to 5.377 g (75.73 mmol), the temperature was raised to 60 °C for 60 min. When the reaction had progressed for 30 min, the remaining alkali was added dropwise. After reaction, the product was neutralized with acetic acid, filtered off, and then washed with 95% ethanol. The product was dialyzed with distilled water and freeze-dried.

4.3. Measurements

The neutral sugar composition of the isolated native hemicelluloses was determined by gas chromatography (GC) analysis of their alditol acetates.[24] The content of uronic acids in native hemicelluloses was estimated colorimetrically by the method of Blumenkrantz and Asboe-Hanson.[25] The method for measuring the molecular weights of the hemicelluoses has been described in a previous paper.[26] FTIR spectra were obtained on an FTIR spectrophotometer (Nicolet 510) using a KBr disc 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 derivates after 15,000 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 ^{1}H 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 derivates.

Acknowledgments

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