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An efficient method for the synthesis of hemicellulosic derivatives with bifunctional groups in butanol/water medium and their rheological properties

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ABSTRACT

Chemical modification is the most important method to design novel biopolymer and biomaterials from the abundant and biocompatible hemicelluloses. In this paper, an efficient method to synthesize hemicellulosic derivatives with bifunctional groups was developed by the etherification of hemicelluloses with acrylamide in the butanol/water medium. Varying the reaction condition such as reaction time, reaction temperature, and the amount of acrylamide and so on, the optimized hemicellulosic derivative with a higher total degree of substituent (DS) of 0.92 and with the 0.43 ratio of carbamoylethy groups and carboxyethyl groups was obtained. ^{13}C NMR analysis showed that the etherification occurred preferably at C-3 position of xylose. A significant degradation of the polymers occurred during the etherification. The shear-thinning of the hemicellulosic derivatives became more dramatic. The solution of the hemicellulosic derivatives showed lower viscosity and modulus as compared with the native hemicelluloses, exhibiting a less elastic behavior.

1. Introduction

Conversion of biomass is regarded as one of the most promising alternatives to fossil resources for production of renewable biomaterials, chemicals and functional biopolymers (Huber, Iborra, & Corma, 2006; Lange, 2007; Lin, He, & Sun, 2007; Wyman, 2003). Hemicelluloses are considered to be the second most abundant renewable resource of biopolymers. Recently, growing attention has been paid to using hemicelluloses as a basic, inexpensive and ton-scale accessible raw material to prepare biomaterials and synthesize a large number of novel biopolymers. There has been an interest in preparation of hemicellulosic films that are used in packaging for oxygen-sensitive products and in chiral separations (Gröndahl, Eriksson, & Gatenholm, 2004; Goksu, Karamanlioglu, Bakir, Yilmaz, & Yilmazer, 2007; Hansen & Plackett, 2008; Höije, Sternemalm, Heikkinen, Tenkanen, & Gatenholm, 2008; Okamoto, Kawashima, & Hatada, 1984). Another important area in hemicelluloses applications is the development of new bioactive and biocompatible polymers and materials for use in key applications such as drug release systems and tissue engineering, since hemicelluloses have been proposed to be suitable materials for biomedical application (Coviello, Matricardi, Marianecci, & Alhaique, 2007; Hansen & Plackett, 2008; Lindblad, Ranucci, & Albertsson, 2001; Lindblad, Sjöberg, Albertsson, & Hartman, 2007).

In order to facilitate hemicelluloses use as novel biopolymers for functional biomaterials applications, chemical modification, which is a more fundamental research, is necessary and plays a very important role in hemicelluloses utilization and application. Most researches have been focused on functionalization of hemicelluloses by chemical modification, such as quaternized hemicelluloses (Ebringerová, Hormadkova, Kacuracova, & Antal, 1994; Ren, Sun, Liu, Chao, & Luo, 2006; Schwikal, Heinze, Ebringerova, & Petzold, 2006), carboxymethyl hemicelluloses (Petzold, Schwikal, Günther, & Heinze, 2006; Ren, Sun, & Peng, 2008), lauroylated hemicelluloses (Ren, Xu, Sun, Peng, & Sun, 2008) and acylated hemicelluloses (Barthel & Heinze, 2006; Sun, Sun, Zhao, & Sun, 2004). Chemical modifications have led to stronger, more elastic and more hydrophobic or thermoplastic biopolymers, and the resulting products can be used as functional polymers (Jain, Sjostedt, & Glasser, 2000; Lima, Oliveira, & Buckeridge, 2003) and may find a variety of potential applications in preparation of novel hydrogel (Coviello et al., 2007; Lindblad et al., 2001) and selective membrane materials (Hansen & Plackett, 2008). Chemical modification creates novel opportunities to maximally exploit the various valuable properties of hemicelluloses for previously unperceived applications.

Acrylamide-based polymers have been used in numerous areas such as petroleum industry, paper industry, environmental protection and biomaterials (Al-Karawi & Al-Daraji, 2010; Renken & Hunkeler, 1999). In previous work, we synthesized the

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novel bifunctional hemicellulosic derivatives in different media (distilled water, ethanol, ethanol/acetone, isopropanol, and *N*, *N*-dimethylformamide) (Ren, Peng, & Sun, 2008), and endow hemicelluloses with carbamoylethyl groups and carboxyethyl groups. The results showed that the reaction efficiency was relatively low and the degree of substitution (DS) was not more than 0.58. It was also found that the reaction media had a significant influence on the DS of carbamoylethyl and carboxyethyl groups due to their different polarity. In this paper, we developed an efficient method for the synthesis of the bifunctional hemicellulosic derivatives with much higher DS by using butanol/water as a reaction medium. The hemicellulosic derivatives were characterized by Gel permeation chromatography (GPC), Fourier transform infrared (FT-IR), ^{13}C NMR spectroscopy, and thermogravimetric analysis (TGA) and differential thermal analysis (DTA). For better understanding the physico-chemical properties of the polymers and consequently their potential applications, the rheological behavior of hemicelluloses and their derivatives, which have rarely been investigated, were also investigated by dynamic and flow curve analysis.

2. Experimental

2.1. Materials

Wheat straw hemicelluloses were isolated according to the previous paper (Ren, Sun, et al., 2008). The sugar analysis of the hemicelluloses isolated showed that xylose presented as a predominant sugar component, comprising 82.3% of the total sugars. Arabinose (9.6%) appeared as the second major sugar constituent. The uronic acids, mainly 4-*O*-methyl-D-glucuronic acid (3.9%) and glucose (2.4%), were present in noticeable amounts. Galactose (0.7%) and rhamnose (0.8%) were observed as minor constituents. Butanol, acrylamide and other chemicals were of analytical grade and purchased from Guangzhou Chemical Reagent Factory.

2.2. Synthesis of hemicellulosic derivatives

The typical procedure of the synthesis of hemicellulosic derivatives was as follow: 0.66 g of hemicelluloses (equal to 0.005 mol of anhydroxylose units in hemicelluloses) in water was heated to 60 °C under stirring until they were completely dissolved. Subsequently, the mixture was cooled at room temperature and followed by adding required quantity of sodium hydroxide and was stirred at 30 °C for 20 min, and then butanol was added, keeping on the total volume of water and butanol up to 12 ml. Followed by the addition of acrylamide at 30 °C, the mixture was stirred for 12 h. After the reaction was over, the mixture was neutralized with diluted acetic acid. The product was dialyzed (cutoff = 3500 g/mol) with distilled water and then freeze-dried. As shown in Table 1, 18 samples were prepared by changing the volume ratio of butanol to water, the molar ratio of NaOH to anhydroxylose units in hemicelluloses and the molar ratio of acrylamide to anhydroxylose units in hemicelluloses.

2.3. Chemical characteristics of the hemicellulosic derivatives

FT-IR spectra were obtained on an FT-IR 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 D_2O for native hemicelluloses and their derivates after 15,000 scans. A 60° pulse flipping angle, a 3.9-μs pulse width 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 D_2O for native hemicelluloses and their derivates.

2.4. Degree of substitution (DS) of the hemicellulosic derivatives

The DS of hemicellulosic derivatives could be characterized by ^{13}C NMR and ^{1}H NMR due to carbamoylethyl groups and carboxyethyl groups grafted onto hemicelluloses (Petzold, Günther, & Kőtteritzsch, 2008; Qi, Liebert, & Meister, 2009; Ren, Peng, et al., 2008). The total DS can be determined from the peak area of protons of methylene that connect to carbamoylethyl group and carboxyethyl group and the protons of xylose units by ^{1}H NMR. The ratio of carbamoylethyl group to carboxyethyl group could be determined by the peak intensity of ^{13}C NMR spectra for the two carbonyl peaks that connect to carbamoylethyl group and carboxyethyl group. The reaction degree could be evaluated from the relative ratio of carbamoylethyl 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.

2.5. Molecular weights

The molecular weights of the hemicelluloses and their derivatives were determined by gel permeation chromatography (GPC) on a PL aquagel–OH 50 column (300 mm × 7.7 mm, Polymer Laboratories Ltd.), calibrated with PL pullulan polysaccharide standard (average peak molecular weights of 783, 12,200, 100,000, 1,600,000). Flow rate of 0.5 ml/min was maintained. The eluent was 0.02-N NaCl in 0.005-M sodium phosphate buffer (pH 7.5). Detection was achieved with a Knauer differential refractometer. The column oven was kept at 30 °C. Hemicelluloses and their derivatives were dissolved with 0.2-N NaCl in 0.005-M sodium phosphate buffer, pH 7.5, at a concentration of 0.1%.

2.6. Rheological analysis of the hemicellulosic derivatives

The dynamic rheological properties of the native hemicelluloses and their derivatives were measured between a steel parallel plate (40-mm diameter) and a Peltier plate in an AR 2000 rheometer (TA Instruments) at 25 °C. All samples were dissolved in 4% NaOH aqueous solution with a magnetic stirrer for 30 min at room temperature. The flow curves were obtained in a Brookfield DVIII instrument at various concentrations and at 25 °C. A thin layer of paraffin oil was applied on top of the sample to avoid evaporation. The values of the strain amplitude were checked to ensure that all oscillatory shear experiments were performed within the linear viscoelastic regime, where the dynamic storage modulus (G') and loss modulus (G'') are independent of the strain amplitude. Flow data were collected over shear rates from 10^{-2} to 10^3 s^{-1}, frequency from 10^{-1} to 10^2 rad/s, respectively. The power-law parameters were calculated by using the equipment software.

3. Results and discussion

3.1. Effects of reaction conditions on the DS of the hemicellulosic derivatives

Hemicelluloses were first swelled in water at 60 °C for a better dissolution before modification. In the reaction, butanol was added to precipitate hemicelluloses in NaOH solution to form micro-sized particles in order to reduce the degradation of hemicelluloses during the etherification. These micro-sized particles will react with acrylamide by using butanol/water as a medium. Therefore, the properties of media will greatly affect the size and dispersion

Table 1
DS of the novel hemicellulose derivatives obtained in various reaction conditions.

Volume ratio[a]	Molar ratio[b]	Molar ratio[c]	Sample number	Total DS	Ratio[d]	DS of carbamoylethyl	DS of carboxyethyl
4:6	4:5	6:1	1	0.67	3.8	0.54	0.13
5:5	4:5	6:1	2	0.52	2.8	0.42	0.10
6:4	4:5	6:1	3	0.68	2.0	0.55	0.13
7:3	4:5	6:1	4	0.53	1.8	0.43	0.10
8:2	4:5	6:1	5	0.42	0.8	0.34	0.08
6:4	3:5	6:1	6	0.52	3.2	0.42	0.10
6:4	4:5	6:1	7	0.68	2.0	0.55	0.13
6:4	5:5	6:1	8	0.69	3.8	0.56	0.13
6:4	6:5	6:1	9	0.56	2.2	0.45	0.11
6:4	7:5	6:1	10	0.57	1.1	0.46	0.11
6:4	8:5	6:1	11	0.56	0.9	0.45	0.11
6:4	5:5	2:1	12	0.33	0.9	0.27	0.06
6:4	5:5	4:1	13	0.69	0.9	0.56	0.13
6:4	5:5	6:1	14	0.70	3.8	0.57	0.13
6:4	5:5	8:1	15	0.71	1.4	0.58	0.13
6:4	5:5	10:1	16	0.81	2.4	0.66	0.15
6:4	5:5	14:1	17	0.92	4.3	0.75	0.17
6:4	5:5	18.0	18	0.61	2.3	0.42	0.19

[a] Represents the volume ratio of butanol to water.
[b] Represents the molar ratio of NaOH to anhydroxylose units in hemicelluloses, xylose unit $Mw = 132$.
[c] Represents the molar ratio of acrylamide to anhydroxylose units in hemicelluloses, xylose unit $Mw = 132$.
[d] Represents the ratio of carbamoylethyl groups to carboxylethyl groups.

of the hemicelluloses particles, and thus influence the etherification reaction. In other words, the role of the medium in this etherification reaction is to provide miscibility and accessibility of the etherifying reagent to the reaction centers of hemicellulosic chains.

In this etherification of hemicelluloses, acrylamide was selected as etherifying reagent and reacted with hemicelluloses in an alkaline condition to form the carbamoylethyl ether of hemicelluloses. Hemicelluloses reacted with acrylamide in the presence of catalyst to form hemi–O–CH_2–CH_2–C(=O)–NH_2. In addition, the acylamino groups can be easily saponified to carboxyl groups in a higher alkaline aqueous medium at elevated temperatures (Klemn, Philipp, Heinze, Heinze, & Wagenknecht, 1998), so hemi–O–CH_2–CH_2–C(=O)–NH_2 is partially saponified into hemi–O–CH_2–CH_2–C(=O)–ONa at the high alkaline aqueous solution in this etherification. Therefore, it is likely that this etherification of hemicelluloses with acrylamide in alkaline condition can produce the bifunctional derivatives with carbamoylethyl and carboxyethyl groups.

The etherification of hemicelluloses with acrylamide was optimized by varying the volume ratio of butanol to water, the molar ratio of catalysis (sodium hydroxide) to anhydroxylose units in hemicelluloses and the molar ratio of acrylamide to anhydroxylose units in hemicelluloses. Table 1 shows the extent of the chemical modification expressed as the degree of substitution (DS). The volume ratio of butanol to water plays an important role in the reaction efficiency in the etherification. The DS of carbamoylethyl groups and carboxyethyl groups firstly slightly decreased when the volume ratio of butanol to water reached up to 1:1, and then increased to a maximum DS value of 0.55 and 0.13 at the butanol/water volume ratio of 6:4, respectively; thereafter they decreased again with the increasing volume ratio. Accordingly, the total DS of the hemicellulosic derivatives showed the same trend as the DS values of carbamoylethyl groups and carboxyethyl groups with the increasing volume ratio, and a maximum value 0.68 could be obtained at the volume ratio 6:4. However, the DS value ratio of carbamoylethyl groups to carboxyethyl groups decreased from 3.8 (sample 1) to 0.8 (sample 5) with the increment in the volume ratio of butanol to water from 4:6 to 8:2. These observations may indicate that sufficient butanol can form smaller and more uniform hemicellulosic particles, and thus creates a preferable environment for the etherification. On the other hand, increasing the amount of butanol means the decease in water, which may results in the poor swelling and dissolving of hemicelluloses (Bhattacharyya, Singhal, & Kulkarni, 1995).

This reaction is a Michael addition reaction. Sodium hydroxide acts as a catalyst in the reaction, so the function of the catalyst becomes very important. The effect of catalyst on the DS of hemicellulosic derivatives shows in Table 1. The total DS and the DS of carbamoylethyl groups firstly increased to a maximum value of 0.69 and 0.56 at the molar ratio of sodium hydroxide to anhydroxylose units in hemicelluloses of 1:1, and then decreased. The DS of carboxyethyl groups reached to its maximum value of 0.13 at the molar ratio of 1:1.25. The increase in DS with the increasing molar ratio of sodium hydroxide to anhydroxylose units in hemicelluloses could be explained by sodium hydroxide making the reaction rate rise, while the decrease in the DS was mainly ascribed to the degradation of hemicelluloses and the occurrence of the side reactions at the higher alkaline concentration.

The dosage of acrylamide also affects the etherification reaction. As shown in Table 1, the total DS and the DS of carbamoylethyl groups increased with the increasing the molar ratio of acrylamide to anhydroxylose units in hemicelluloses, and reached to the maximum values of 0.92 and 0.75 at the molar ratio of 14:1. Thereafter, they significantly decreased. However, the DS of the carboxyethyl groups showed a maximum value of 0.19 at the molar ratio of 18:1. Therefore, an appropriate molar ratio of acrylamide to anhydroxylose units in hemicelluloses can facilitate the chemical reaction.

In previous studies, a series of acrylamide-grafted hemicelluloses were prepared by using different media such as alkaline aqueous solution, ethanol, isopropanol, ethanol/acetone and DMF, the DS rang from 0.04 to 0.58 (Ren, Peng, et al., 2008). In this study, we obtained the acrylamide-grafted hemicelluloses with DS up to 0.92 in butanol/water medium, which was much higher than those prepared in other media. This is possibly due to the solvent polarities and stereochemistry. The reaction efficiency increases as the polarity of the solvent decreases (Barai, Singhal, & Kulkarni, 1997). However, isopropyl alcohol and butanol with the same polarity did not produce the same DS values of hemicellulosic derivatives because smaller, uniform and better dispersing hemicellulosic particles may be formed in butanol, which can provide more reaction center and larger contact area. Therefore, a more efficient chemical reaction can be created for the synthesis of acrylamide-grafted hemicelluloses in butanol/water medium.

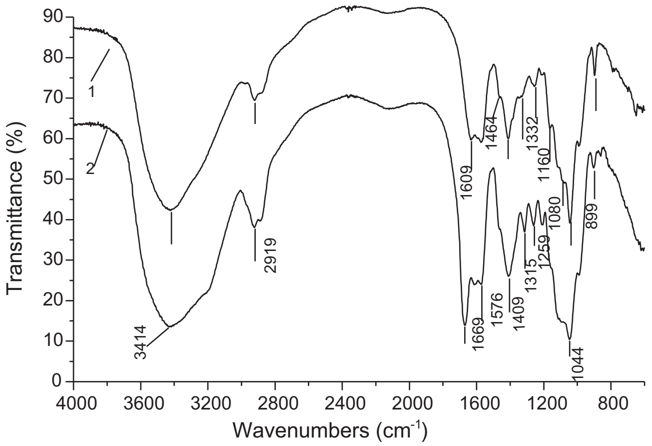

Fig. 1. FT-IR spectra of wheat straw hemicelluloses (spectrum 1) and the hemicellulosic derivatives (spectrum 2, sample 2).

3.2. Chemical characteristics of the bifunctional hemicellulosic derivatives

3.2.1. FT-IR analyses

The wheat straw hemicelluloses and the hemicellulosic derivatives were characterized by FT-IR spectra, as shown in Fig. 1. For native hemicelluloses, the absorptions at 3414, 2919, 1464, 1409, 1259, 1160, 1044 and 897 cm^{-1} seen in spectrum 1 are indicative of the native hemicelluloses (Fang, Sun, Tomkinson, & Fowler, 2000). A sharp band at 897 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 (Gupta, Madan, & Bansal, 1987). The region between 1464 and 1044 cm^{-1} relates to the C–H and C–O bond stretching frequencies. 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} (Blumenkrantz & Asboe-Hanson, 1973).

In spectrum 2, NH_2 and OH stretching absorptions represent the strong peak around 3414 cm^{-1}, the intensities of which increases from spectrum 1 to spectrum 2. Two peaks at 1576 and 1409 cm^{-1} are ascribed to the asymmetrical and symmetrical stretching of COO groups, respectively. Amide I bands are seen at 1669 cm^{-1}, while aliphatic C–H stretching vibrations are present at 2919 cm^{-1}. –CH_2 scissoring vibrations appear at 1464 cm^{-1}. C–O stretching vibrations around 1044 cm^{-1}, typical for the xylan structure, are common to both hemicellulose and the hemicellulosic derivatives (Al-Karawi & Al-Daraji, 2010; Sun & Tomkinson, 2003). The peaks at 1669, 1590, and 1408 cm^{-1} indicate that the hemicellulosic derivatives contain carbamoylethyl and carboxyethyl groups. These observations confirm the occurrence of the etherification on hemicelluloses.

3.2.2. ^{13}C NMR analysis

Etherification is further supported by comparison the ^{13}C NMR of the hemicellulosic derivatives with the raw hemicelluloses. One-dimensional ^{13}C NMR spectra of the native hemicelluloses and the hemicellulosic derivatives were used to obtain the structural information, as shown in Fig. 2. The main (1 → 4)-linked β-D-xylopyranosyl units are obviously characterized by the signals at

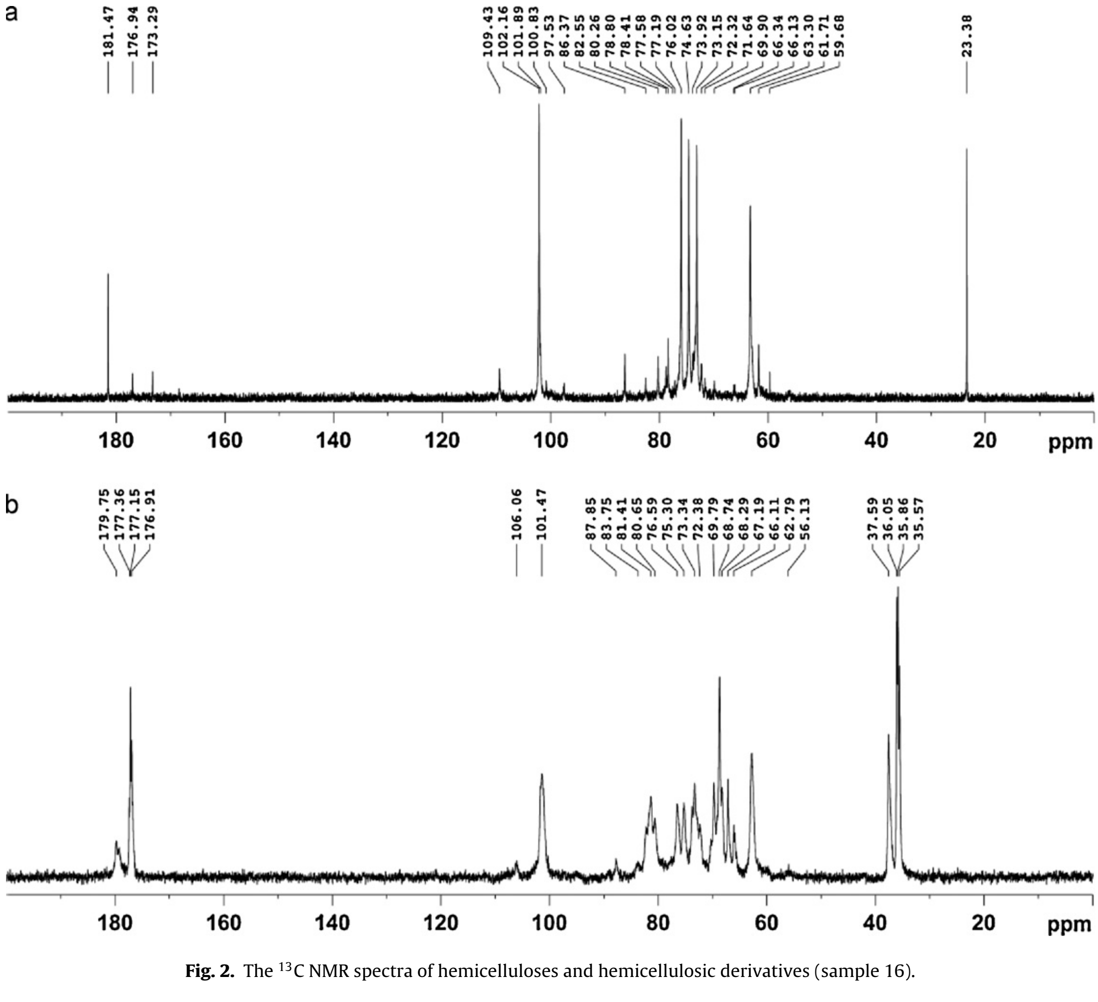

Fig. 2. The ^{13}C NMR spectra of hemicelluloses and hemicellulosic derivatives (sample 16).

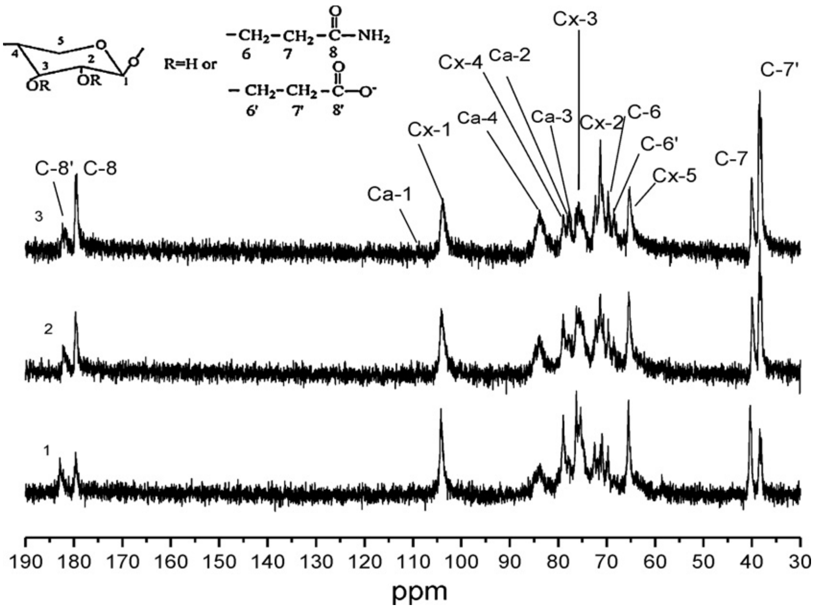

Fig. 3. The ^{13}C NMR spectra of hemicellulosic derivatives sample 5 (spectrum 1), sample 8 (spectrum 2) and sample 17 (spectrum 3).

δ101.9, δ76.0, δ73.9, δ72.3 and δ63.3, which are attributed to C-1, C-4, C-3, C-2 and C-5 of β-D-xylopyranosyl units, respectively (Schwikal & Heinze, 2007). The presence of arabinose was detected by the presence of characteristic signals at δ109.4, δ83.8, δ80.3, δ77.2 and δ61.7, which correspond to C-1, C-4, C-2, C-3 and C-5. Acetyl CH_3 on the backbone of xylan gives a signal at δ23.4. These observations illustrates that the wheat straw hemicelluloses are composed mainly of L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan. The presence of quantities of associated lignin was identified by one weak signal at δ181.5 which originates from the carbonyl group in the associated lignin.

As compared with the spectrum of native hemicelluloses in Fig. 2a, the spectrum of the hemicellulosic derivatives (Fig. 2b) shows new peaks at δ37.6, δ35.9, δ177.2, δ179.8, δ68.2 and δ65.5. Peaks at δ67.1 and δ66.1 are assigned to methylenes that are connected to the carbamoylethyl (C-6) and carboxyethyl (C-6′) groups. The resonances at δ37.6 and δ35.9 are assigned to methylenes that connect to carbamoylethyl (C-7) and carboxyethyl (C-7′) groups, respectively (Halverson, Lancaster, & Conner, 1985; McDonald & Beaver, 1979; Zurimendi, Guerrero, & Leon, 1984). The chemical shifts at δ178.2 and δ180.6 are attributed to the carbon signals of the carbonyl groups in the carbamoylethyl (C-8) and the carboxyethyl (C-8′) groups, respectively. In addition, the intensity of the peaks at δ177.2 and δ35.9 becomes stronger from curves 1 to 3 with the increasing total DS from 0.42 (sample 5) to 0.69 (sample 8) and 0.92 (sample 17), as shown in Fig. 3. Therefore, those new signals mentioned above showed that the etherification of hemicelluloses with acrylamide occurred and the carbamoylethyl and carboxyethyl groups actually were grafted onto the backbone of hemicelluloses.

3.3. Molecular weight distribution

The average molecular weights of the hemicellulosic derivatives were determined by gel permeation chromatography (GPC). The weight-average (*M*w) and number-average (*M*n) molecular weights as well as polydispersity (*M*w/*M*n) are listed in Table 2. All of the molecular weights of the hemicellulosic derivatives are much lower than that of the native hemicelluloses. This may be due to the significant degradation of hemicelluloses during the alkaline activation and the etherification reaction. In addition, the hemicellulosic derivatives have a relatively low index of polydispersity (1.82–3.14) than the native hemicelluloses (3.23), which indicates that the hemicellulosic derivatives have a more uniform molecular weight distribution.

3.4. Rheological properties

The rheological behavior of hemicelluloses and their derivatives have rarely been investigated (Ebringerová, 2006; Ebringerová & Heinze, 2000; Xu, Willför, Holmlund, & Holmbom, 2009). For better understanding the physico-chemical properties of the polymers and consequently their possible applications, the rheological behavior of the native hemicelluloses and their derivatives was investigated in this study, as shown in Figs. 4–6. As seen from Fig. 4, viscosities of the native hemicelluloses and the hemicellulosic derivatives decrease with the increasing shear rate, implying that these solutions exhibit pseudoplastic or shear-thinning behavior in the range of shear rates tested due to the destroying of network structure of hemicelluloses. The viscosity of the native hemicelluloses solution is higher than that of the hemicellulosic derivatives solution at 5% and 10% concentration in the whole shear rate rang, as well as at 15% concentration at high shear rate (more than10 s^{-1}), which suggests that the hemicellulosic derivatives solution have weaker intermolecular interactions due to more depolymerized structure and the functional groups on the structure of macromolecule chains (Garcia, Ganter, & Carvalho, 2003; Lee & Brant, 2002). The greater slope of the curves of the hemicellulosic derivatives is also observed.

Table 2
Average molecular weight of the native hemicelluloses and the hemicellulosic derivatives.

Sample	Total DS	*M*w	*M*n	*M*w/*M*n
Native hemicelluloses	0.00	28,900	8950	3.23
5	0.42	19,317	6152	3.14
6	0.52	17,183	5934	2.10
8	0.69	18,744	6871	2.73
9	0.56	18,587	6571	1.82
15	0.71	20,142	6922	2.91
16	0.81	22,236	7022	3.17
17	0.92	19,906	7064	2.81

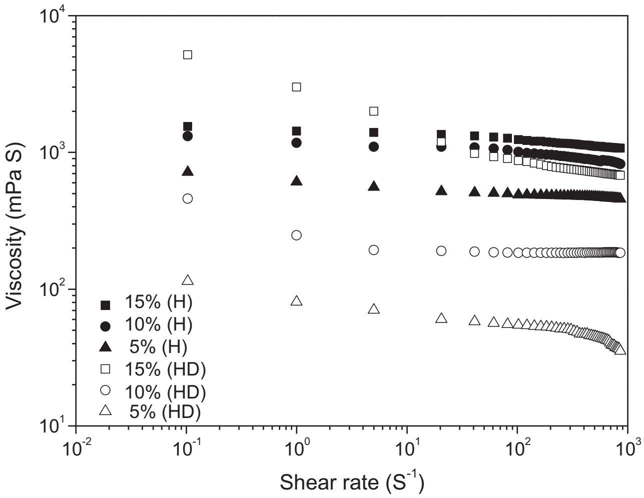

Fig. 4. Shear rate dependence of viscosity for native hemicelluloses (H) and hemicellulosic derivatives (HD, sample 13) at different concentrations.

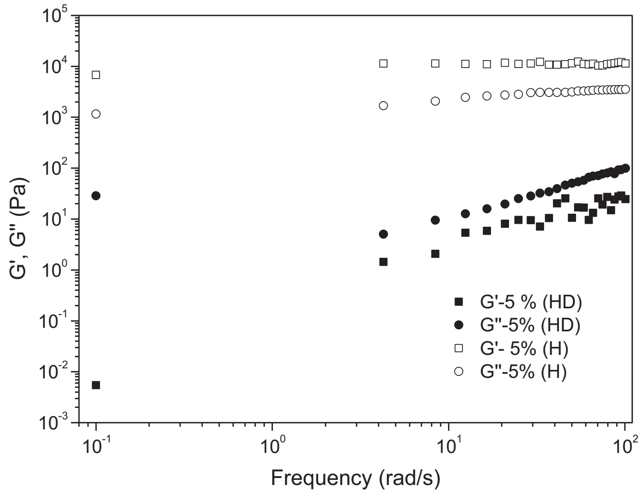

Fig. 5. Frequency dependent modulus of the solutions of native hemicelluloses and the hemicellulosic derivatives (HD, sample 13) at 5% concentration.

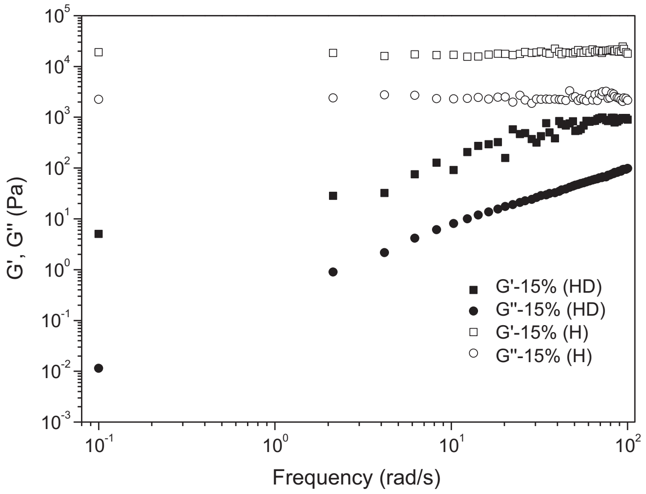

Fig. 6. Frequency dependent modulus of the solutions of native hemicelluloses and the hemicellulosic derivatives (HD, sample 13) at 10% concentration.

At the concentration of 5 wt% (Fig. 5), the elastic modulus G′ is significantly lower than the loss modulus G″ over the entire frequency region for the hemicellulosic derivatives solution, showing a viscous behavior (Lindblad, Albertsson, Ranucci, Laus, & Giani, 2005). To the contrary, the hemicellulosic derivatives solution show a stronger elastic property where G′ is above G″ throughout the applied frequency when the concentration was increased to 15% (Fig. 6), which is due to stronger molecule entanglement at higher concentration. In the case of the native hemicelluloses, the G′ is higher than G″ over the entire frequency region, indicating an elastic properties. In addition, both G′ and G″ of the native hemicelluloses solution are higher than those of the hemicellulosic derivatives solution, exhibiting a more obvious elastic behavior.

These results may be explained by the influence of molecular weight and the functional groups on the structure of macromolecule chains. The lower molecular weight as well as carbamoylethyl and carboxyethyl groups on the polymer chain may allow to reducing or preventing the associative interactions among themselves in alkaline solutions, and thus change the dynamic shear rheological properties of hemicellulosic derivatives. Similar results were reported in starch (Yoo, Kim, & Yoo, 2005). Further studies should include the determination of the distribution of the functional groups along the polymer chain in order to get comprehensive structure–property relationships. In addition, the relationships between the DS and the rheological properties of the hemicellulosic derivatives also should be clarified to further facilitate the applications of hemicelluloses in biodegradable materials.

4. Conclusions

An efficient method for synthesis of bifunctional hemicellulosic derivatives was developed by using butanol/water as the reaction medium. Under the optimum reaction condition (a 1.5:1 volume ratio of butanol to water, a 1:1 molar ratio of catalyst to anhydroxylose units in hemicelluloses and a 14:1 molar ratio of acrylamide to anhydroxylose units in hemicelluloses, at 30 °C for 12 h), a relatively higher DS value of the products up to 0.92 could be obtained, providing a facile method for the synthesis of hemicellulosic derivatives with carbamoylethyl groups and carboxyethyl groups. The molecular weights of the hemicellulosic derivatives were lower than that of the native hemicelluloses due to the significant degradation of hemicelluloses during alkaline activation in the etherification reaction. The solution of the native hemicelluloses and the hemicellulosic derivatives showed shear-thinning behavior. The hemicellulosic derivatives solution showed lower viscosity and modulus as compared with the native hemicelluloses, exhibiting a less obvious elastic behavior, which indicated the difference in macromolecule structure and the influence of the functional groups on the polymer chains.

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