

Microwave-Induced Synthesis of Carboxymethyl Hemicelluloses and Their Rheological Properties

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In this article, a facile, rapid, and efficient method was developed for the preparation of carboxymethyl hemicelluloses using microwave-induced organic reaction enhancement chemistry. The influences of the factors including reaction time, temperature, and the amount of sodium monochloroacetate and sodium hydroxide on the degree of substitution (DS) of the products were investigated. The rheological properties and the chemical structure of the resulting polymers were also studied. It was found that microwave irradiation could significantly promote the chemical reaction efficiency and accelerate the carboxymethylation of hemicelluloses with sodium monochloroacetate. Therefore, carboxymethyl hemicelluloses with higher DS of 1.02 could be obtained in much shorter time scales as compared to the conventional heating method. Results from rheological analysis indicated that carboxymethyl hemicellulose solutions exhibited shear-thinning behavior in the range of shear rates tested and showed lower viscosity and modulus in comparison with those of the native hemicelluloses due to lower molecular weight and the role of carboxymethyl groups in reducing the entanglements between hemicelluloses chains.

KEYWORDS: Hemicelluloses; carboxymethylation; microwave irradiation; rheological properties

INTRODUCTION

Hemicelluloses, comprising the noncellulose cell-wall polysaccharides of agricultural and forest residues, are considered to be inexhaustible and renewable resources for the production of bioenergy, novel biopolymers, and functional biomaterials (1). Recently, the importance of converting hemicelluloses to biodegradable and functional polymers and materials has been increasingly emphasized (2–4). Development of new bioactive and biocompatible polymers capable of exerting a temporary therapeutic function is the most strategic area in hemicellulose applications and attracts more and more attention. During the latest decade, hemicelluloses have been proposed to be suitable materials as matrixes for the preparation of hydrogels, nanoparticles, and films used in drug release systems, tissue engineering, and food packaging (3–5). In addition, hemicelluloses can also be used in chiral separations (6, 7). Therefore, these potential applications will open up new opportunities for the application of hemicelluloses in functional biomacromolecules and biomaterials (7).

In order to synthesize the functional derivatives from hemicelluloses for biomaterials, chemical modification is required. There has been increasing interest in producing novel hemicellulosic derivatives which have new properties and applications, for example, cationic hemicelluloses (8), carboxymethyl hemicelluloses (9, 10),

lauroylated hemicelluloses (11), acetylated hemicelluloses (12), and oleoylated hemicelluloses (13). Among these functional derivatives, carboxymethyl hemicelluloses, representing the properties of the ionic functions, are found to be widely used in the detergent, food exploration, paper, textile, heavy metal removal, pharmaceutical, and paint industries (14–16). In previous work, carboxymethyl hemicelluloses were obtained by conventional heating using sodium monochloroacetate and sodium hydroxide in an ethanol/water medium (17). Results indicated that the efficiency of carboxymethylation was relatively low and that the DS of the products was not more than 0.56.

Currently, microwave irradiation has received immense interest in organic chemistry due to its rapid heating and energy homogeneous penetration in comparison to those of conventional heating (18, 19). Microwave irradiation can result in almost instantaneous in core heating of materials; therefore, the reaction can be performed in a rapid and homogeneous manner. Many microwave-based simple, fast, and energy-efficient routes have been developed and applied in the synthesis or modification of polymers or materials (19). Microwave irradiation also has opened up a new way to prepare novel biopolymers and biomaterials from bioresources (21–23). However, few studies deal with the application of microwave irradiation in the modification of hemicelluloses. Microwave irradiation was first applied to enhance phthaloylation and succinylation of hemicelluloses (24). Results indicated that hemicellulose derivatives with a high DS of 1.47 could be obtained for only 5 min at 50 °C, showing a very efficient process.

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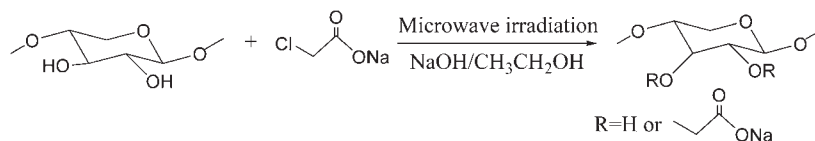


Figure 1. Reaction scheme of the carboxymethylation of hemicelluloses.

Table 1. Influences of Reaction Conditions on the DS of Carboxymethyl Hemicelluloses

sample	temperature (°C)	reaction time (min)	molar ratio ^a (NaOH/X)	molar ratio ^b (SMCA/X)	DS ^c
1	30	20	5:5	2:1	0.21
2	45	20	5:5	2:1	0.32
3	65	20	5:5	2:1	0.87
4	85	20	5:5	2:1	0.44
5	65	4	5:5	2:1	0.31
6	65	8	5:5	2:1	0.41
7	65	12	5:5	2:1	0.63
8	65	16	5:5	2:1	0.78
3	65	20	5:5	2:1	0.87
9	65	24	5:5	2:1	0.67
10	65	30	5:5	2:1	0.48
11	65	40	5:5	2:1	0.39
12	65	20	3:5	2:1	0.44
13	65	20	4:5	2:1	0.56
3	65	20	5:5	2:1	0.87
14	65	20	6:5	2:1	0.89
15	65	20	7:5	2:1	0.91
16	65	20	8:5	2:1	0.79
17	65	20	5:5	1:2	0.56
28	65	20	5:5	1:1	0.77
3	65	20	5:5	2:1	0.87
19	65	20	5:5	3:1	0.93
20	65	20	5:5	4:1	1.02
21	65	20	5:5	5:1	0.98
22	65	20	5:5	6:1	0.96

^a Molar ratio of NaOH/X represents the molar ratio of NaOH to anhydroxylose units in hemicelluloses. ^b Molar ratio of SMCA/X represents the molar ratio of SMCA to anhydroxylose units in hemicelluloses. ^c On the basis of the assumption that all of the hemicelluloses are converted to di-etherified hemicelluloses (DS, 2.0). The DS value is 0.0 if no reaction occurred.

With the aim to develop more efficient processes for preparing functional hemicellulosic derivatives, we investigated the application of microwave irradiation in the synthesis of carboxymethyl hemicelluloses. The chemical structure, molecular weights, and thermal properties of the products were also studied. The rheological behavior of carboxymethyl hemicelluloses, which has rarely been studied, was also studied by dynamic and flow curve analysis.

MATERIALS AND METHODS

Materials. Hemicelluloses were isolated using 10% KOH at 25 °C for 10 h with a solid to liquor ratio of 1:20 (g/mL) from holocellulose obtained by delignification of wheat straw with sodium chlorite in acidic solution (pH 3.7–4.0, adjusted by 10% acetic acid) at 75 °C for 2 h. 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, and 0.8% mannose. Uronic acids, mainly 4-*O*-methyl-D-glucuronic acid (MeGlcA), were present in a noticeable amount (3.9%). Sodium monochloroacetate (SMCA) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. Sodium hydroxide and ethanol were purchased from Guangzhou Chemical Reagent Factory, China.

Preparation of Carboxymethyl Hemicelluloses. The mechanism of carboxymethylation of hemicelluloses with SMCA had been described in a previous study (17, 25), as shown in **Figure 1**. The typical procedure of the preparation of carboxymethyl hemicelluloses is as follows. Hemicellulose powder (0.66 g, approximately 10 mmol 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 down at room temperature. Subsequently, a required quantity of sodium hydroxide (accounting for 50% all amount sodium hydroxide) was added dropwise for 20 min at 30 °C, and then, ethanol and water were added to keep the total volume up to 15 mL under the condition of the 4:1 volume ratio of ethanol to water. Followed by the addition of SMCA and the remaining sodium hydroxide, we ran the microwave program (Whirlpool, VIP 200) immediately with simultaneous magnetic stirring at the required temperature. After the limited reaction time, the mixture was first cooled down and then neutralized with diluted acetic acid, and the resulting mixture was filtered and washed with 50 mL of 65% ethanol aqueous (v/v) once and 50 mL of 95% ethanol four times. The products obtained were dissolved in purified water and freeze-dried at –50 °C. The carboxymethylation of hemicelluloses was performed in duplicate, with 4% standard error. As can be seen in **Table 1**, 22 samples were prepared by changing the reaction conditions. In this experiment, a 300 W microwave irradiation power was applied for all of the procedures. The reaction times were 4, 6, 8, 10, 12, 16, 20, 24, 30, and 40 min, and the temperatures were 30, 45, 65, and 85 °C, respectively. The molar ratios of NaOH to X (anhydroxylose units in hemicelluloses) were kept from 3:5 to 8:5, and the molar ratios of SMCA to X were kept from 1:2 to 6:1.

Determination of the Degree of Substitution (DS). The DS of carboxymethyl hemicelluloses was determined by the acidometric titration method. This method had been applied to determine the DS of carboxymethyl cellulose and carboxymethyl starch (26). Two procedures performed to determine the DS of carboxymethyl hemicelluloses were as follows:

- Purity of carboxymethyl hemicelluloses: Exactly 0.5 g of carboxymethyl products was dissolved in 10 mL of water and stirred. Followed by adding 10 mL of 1 M hydrochloric acid, we agitated the mixture to completely dissolve it. Five drops of phenolphthalein indicator were added into the mixture, and then 1 M sodium hydroxide was added dropwise with stirring until the red color of the solution disappeared. Ethanol (50 mL, 95%) was slowly added into the mixture with stirring. Then, 100 mL of 95% ethanol was added, and the mixture was left to settle for 15 min before the supernatant liquid was centrifuged. The precipitate was washed with 80% ethanol four times and then washed again with 50 mL of 95% ethanol. Finally, the products were dialyzed (cutoff = 3500 g/mol) with distilled water and then freeze-dried.
- Determination of DS: The average value of DS was determined by acidometric titration (26, 27). Exactly 0.2 g of carboxymethyl hemicelluloses and 50 mL of distilled water were added to a 250 mL flask and stirred for 10 min; the pH value of the solution was adjusted up to 8.0 by acid or alkali. Then the solution was titrated with 0.05 M H₂SO₄ until the pH value of the solution decreased to 3.74. The DS value was calculated on the basis of the equations as shown below.

$$a = \frac{m'}{m}$$

$$B = \frac{2 \times M \times V}{a \times m}$$

$$DS = \frac{0.132 \times B}{1 - 0.08 \times B}$$

where *a* is the purity of the products. *m* and *m'* (g) are weights of products before and after purification, respectively, 0.132 (g·mmol⁻¹) is the molar

mass of a xylose unit, $0.08 \text{ (g}\cdot\text{mmol}^{-1}\text{)}$ is the net increase in the mass of a xylose unit for each SA substituted, M is the normality of the H_2SO_4 used, V is milliliters of H_2SO_4 used to titrate the sample, and B is the millimole per gram of H_2SO_4 consumed per gram of the products. This procedure makes the assumption that the untreated hemicelluloses do not have any carboxyl content. All of the titrations were carried out in triplicate, and standard deviations were less than 4.0%.

Characterizations of Native Hemicelluloses and the Carboxymethyl Hemicelluloses. The molecular weights of the hemicelluloses and their derivatives were determined by GPC on a PL aquagel-OH 50 column ($300 \times 7.7 \text{ mm}$, Polymer Laboratories Ltd.) and calibrated with a PL pullulan polysaccharide standard (average peak molecular weights of 783, 12200, 100000, and 1600000). A 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%.

FT-IR spectra were obtained from a Nicolet 750 spectrophotometer in the region of $400\text{--}4000 \text{ cm}^{-1}$ by the method of transmission. The carboxymethyl hemicelluloses were mixed with KBr to press a plate for measurement.

The solution-state ^{13}C NMR spectra were obtained on a Bruker spectrometer at 100 MHz . The sample (80 mg) was dissolved in 1 mL of D_2O (99.8% D) overnight at room temperature. The ^{13}C NMR spectra were recorded at 25°C after 30000 scans. Chemical shifts (δ) are expressed relative to the resonance of Me_4Si ($\delta = 0$). A 30° pulse flipping angle, a $3.9 \mu\text{s}$ pulse width, and a 0.85 s delay time between scans were used.

The dynamic rheological properties of hemicelluloses and their derivatives were measured between a 20 mm diameter steel parallel plate and a Peltier plate in an AR2000 rheometer (TA Instruments) at 25°C . All solutions were stirred for 30 min at room temperature before measurement. The flow curves were obtained in a Brookfield DVIII instrument at 25°C , hemicelluloses and carboxymethyl hemicelluloses at different concentrations of 5%, 10%, and 15% (by mass). A thin layer of paraffin oil was placed on the 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 elastic modulus (G') and loss modulus (G'') are independent of the strain amplitude. All measurements were done twice. Flow data were collected over shear rates from 10^{-1} to 10^3 s^{-1} and frequency from 10^{-1} to 10^2 rad/s , respectively. The power-law parameter n was calculated by using the equipment software.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on the DS of the Carboxymethyl Hemicelluloses. Microwave heat frequently involves a direct interaction with certain classes of absorbing molecules of polar solvents. This direct absorption can lead to localized introduction of energy to a region from the remote microwave source and raises the solution temperature. Thus, microwave heat is fundamentally different from conventional heating processes (20).

Table 1 shows the influences of reaction conditions on the DS of carboxymethyl hemicelluloses. In a previous investigation (17), we found that there was an increase in the DS with a reaction temperature up to 65°C . However, for further investigation the influences of microwave irradiation on the reaction at lower and higher temperatures (at 30, 45, 65, and 85°C) are discussed in this article. An increase in the reaction temperature from 30 to 65°C resulted in a DS significant increment from 0.21 to 0.87, but a further rise of temperature to 85°C led to a sharp fall in DS from 0.87 to 0.44. The increase in DS could be explained by the fact that a higher reaction temperature favors the diffusion and compatibility of the reaction ingredients, the hemicelluloses' ability to swell, and the mobility of the reactant molecules. However, the higher temperature may result in the degradation of hemicelluloses and more side reactions during the carboxymethylation of hemicelluloses (17, 24), thus decreasing the DS.

Reaction time showed a significant influence on the carboxymethylation of hemicelluloses. The DS of the products increased from 0.31 to 0.87 when the reaction time increased from 4 to 20 min; thereafter, the DS decreased to 0.79 with an increment in reaction time up to 40 min. This observation indicated that a sufficient reaction time can provide a better reaction environment, whereas the prolonged reaction time may lead to the degradation of hemicelluloses and the occurrence of a side reaction during the reaction under microwave irradiation.

In this work, we also studied the effect of the molar ratio of NaOH to X (anhydroxylose units in hemicelluloses) on DS. Increasing the molar ratio of NaOH to X from 3:5 to 7:5 could obviously promote the carboxymethylation efficiency, as shown by the increasing DS value from 0.44 to 0.91. This enhanced reaction efficiency resulted from the higher nucleophilic reactivity generated by alkalization activation and increment in the accessibility of the hemicellulosic ultrastructure. Surprisingly, increasing the molar ratio of NaOH to X from 7:5 to 8:5 led to a decrease in DS from 0.91 to 0.79. This is probably due to the partial degradation of hemicelluloses at higher NaOH concentration under microwave irradiation (17, 24). It was also observed that the DS showed a significant increase from 0.44 to 0.87 when the molar ratio of NaOH to X increased from 3:5 to 5:5, and then the DS presented a slight increase, which indicated a 5:5 molar ratio of NaOH to X was sufficient.

The amount of SMCA also showed a significant influence on reaction efficiency. An increase in the molar ratio of SMCA to X from 1:2 to 4:1 led to an increment in the DS of the products from 0.56 to 1.02; thereafter, the DS slightly decreased to 0.96. The reason for this increase is probably due to the greater availability of SMCA to hemicelluloses molecules at higher concentration. The molar ratio higher than 4:1 may lead to larger amounts of sodium glycolate which resulted from the side reaction of sodium hydroxide with SMCA (27). Therefore, the optimized product with the maximum DS value of 1.02 can be obtained in the condition of the NaOH/SMCA/X molar ratio of 1:4:1 at 65°C for 20 min.

In a previous study, carboxymethyl hemicelluloses were prepared by a conventional heating method (17). Under the optimum reaction conditions (the molar ratio of NaOH/SMCA/X of 1:4:1, 65°C), it took 75 min to obtain carboxymethyl hemicelluloses with a maximum DS of 0.56. In this study, products with a DS of 1.02 could be obtained during the period of 20 min under the same reaction conditions (molar ratio of NaOH/SMCA/X of 1:4:1, 65°C). These results suggested that microwave irradiation has the ability to markedly enhance the carboxymethylation efficiency in a shorter time in comparison to that with conventional heating. Similar results had been reported in previous works (28–30). Microwave heat involves a direct interaction with certain classes of absorbing molecules, which can lead to a localized introduction of energy to a region and a homogeneous and rapid rise in temperature (20, 22). Furthermore, it has been well established that the superheating effects caused by microwave radiation can lead to temperatures $10\text{--}30^\circ\text{C}$ in excess of the conventional boiling point of the solvent. These effects in combination with agitation and improved transport properties of molecules could lead to a significant increase in the reaction rate and the selectivity, resulting in a higher carboxymethylation efficiency of hemicelluloses within a much shorter time (20 min) (31). Therefore, microwave-irradiation-induced synthesis can provide a more efficient method for hemicellulose modification and preparation of biomaterials.

Average Molecular Weight. In order to examine the extent of degradation of the hemicellulose polymers that occurred during carboxymethylation under microwave irradiation, the molecular weights of carboxymethyl hemicelluloses were determined by

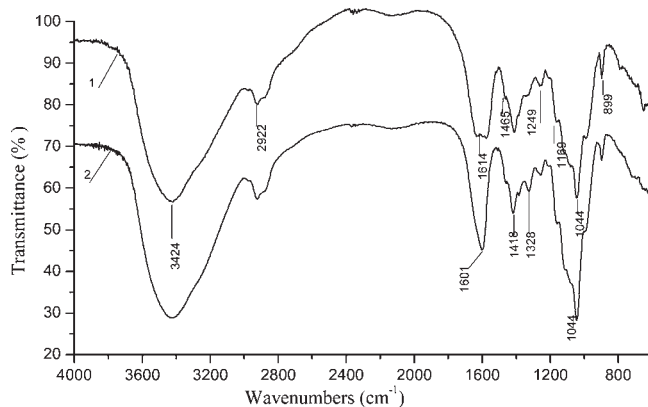
Table 2. Average Molecular Weights of the Native Hemicelluloses and Their Derivatives

sample	DS	M_w	M_n	M_w/M_n
native hemicelluloses	0	26800	9147	2.93
2	0.32	15312	5468	2.80
3	0.87	12213	4255	2.87
7	0.63	12912	4578	2.82
12	0.44	14514	5277	2.75
15	0.91	13136	4641	2.83
17	0.56	12232	4377	2.82
18	0.77	14867	5367	2.77
20	1.02	14265	5076	2.81

GPC, and their weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) are present in **Table 2**. All of the molecular weights of the carboxymethyl hemicelluloses listed in **Table 2** became lower than that of native hemicelluloses (26800 g.mol⁻¹), as shown by the M_w range from 12213 to 15312 g.mol⁻¹. In addition, carboxymethyl hemicelluloses had a relatively low index of polydispersity (2.75–2.87), which indicated that the molecular weights of hemicellulosic derivatives were more uniform. These results suggested that remarkable degradation occurred to hemicelluloses during microwave-induced synthesis of carboxymethyl hemicelluloses. Degradation of hemicelluloses and their derivatives were also observed in the case of the conventional heating method (17), which was proposed to be the etherification reaction and alkaline degradation. In addition, microwave-induced degradation may also occur to hemicelluloses and their derivatives due to the superheating effect, which has been reported in the literature (17, 32). Therefore, the degradation of hemicelluloses and their derivatives during microwave-induced synthesis can be attributed to the superheating effect of microwave irradiation, etherification reaction, and alkaline degradation.

FT-IR Spectra. FT-IR spectra of the hemicelluloses and their derivatives are shown in **Figure 2**. In **Figure 2**, the absorbance at 3424, 2922, 1614, 1465, 1249, 1169, 1044, and 899 cm⁻¹ are associated with the native hemicelluloses (spectrum 1) (33). A sharp band at 899 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 (34). The region between 1465 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 3424 cm⁻¹, and a symmetric C–H vibration band is observed at 2922 cm⁻¹ (35). In spectrum 2, the presence of new bands occurs as compared with that in spectrum 1. A strong signal at 1601 cm⁻¹ is ascribed to the COO⁻ group in carboxymethyl hemicelluloses (36). The bands around 1418 and 1328 cm⁻¹ are assigned to CH₂ scissoring and OH bending vibration, respectively. These new bands in the spectra of the hemicellulose derivatives confirmed that carboxymethylation occurred to hemicelluloses.

¹³C NMR Spectra. **Figure 3** shows the representative ¹³C NMR spectra of carboxymethyl hemicelluloses (a, sample 3) and native hemicelluloses (b). The signals of the main chain of hemicelluloses appear between 104 and 75 ppm, where the signals at 102.2, 76.0, 74.6, 73.1, and 62.9 ppm are assigned to C-1, C-4, C-3, C-2, and C-5 of the β -D-xylopyranosyl units of the hemicelluloses, respectively. The presence of arabinose was detected by the presence of characteristic signals at 109.4, 86.4, 80.2, 78.7, and 61.7 ppm, which correspond to C-1, C-4, C-2, C-3, and C-5. Acetyl CH₃ in xylan gives a signal at 23.3 ppm, as shown in **Figure 3b**. Two signals at 72.3 and 77.2 ppm represent C-4 and C-2 of the galactose residue in the xylan. Other signals observed at 176.9,

**Figure 2.** FT-IR spectra of native hemicelluloses (spectrum 1) and carboxymethyl hemicelluloses (spectrum 2, sample 4).

97.5, 82.5, and 59.7 ppm are the characteristic signals of C-6, C-1, C-4, and the methoxyl group of the 4-*O*-Me-GlcP_A residue, respectively. The signals at 181.5 and 173.3 ppm show the esterified ferulic linked to lignin by ester bonds (37). As compared with the spectrum of native hemicelluloses in **Figure 3b**, the new signal of the carboxyl groups appears at 178.3 ppm (38). The signals at 68.6 and 71.1 ppm are assigned to the methylene carbon atoms of the carboxymethyl groups. These observations confirmed the occurrence of carboxymethylation of hemicelluloses with SMCA.

Rheological Properties. Both dynamic viscosity and modulus are known to be good characterization tools in studying the rheological properties of some polymeric solutions (39–41). **Figure 4** shows the dynamic viscosity of solutions of native hemicelluloses and carboxymethyl hemicelluloses (sample 18) at concentrations of 5%, 10%, and 15% (w/w). Viscosity of the native hemicelluloses and carboxymethyl hemicelluloses solutions decreased with increasing shear rate at the same concentration, exhibiting a pseudoplastic or shear-thinning behavior in the range of shear rates tested. **Figure 4** also indicates that the viscosity of native hemicelluloses and their derivative solutions increased as concentration increased. This is probably due to the formation of stronger entanglements between hemicellulose chains at higher concentration. The network structure is destroyed when the shear rate increases; therefore, a shear thinning behavior is observed (42, 43). However, carboxymethyl hemicelluloses show a lower viscosity than native hemicelluloses, which indicates the lower molecular weight and weaker intermolecular interactions between carboxymethyl hemicellulose chains. In addition, the power law index (n) shown in **Figure 4** decreased from 0.698 to 0.647 for native hemicelluloses (H) and from 0.732 to 0.656 for carboxymethyl hemicelluloses (HD) when their concentrations increased from 5% to 15%, which suggested that the solutions of the native hemicelluloses and carboxymethyl hemicelluloses showed a more significant shear-thinning behavior at higher concentration due to stronger entanglements. The solutions of carboxymethyl hemicelluloses had higher power law index at the concentrations applied, indicating less obvious shear-thinning behavior.

Figures 5–7 show the frequency-dependent elastic modulus G' and loss modulus G'' of the solution of the native hemicelluloses and carboxymethyl hemicelluloses (sample 18) at concentrations of 5%, 10%, and 15% at 25 °C. At a concentration of 5% (**Figure 5**), the elastic modulus G' was obviously lower than the loss modulus G'' over the entire frequency region for the hemicellulosic derivatives solution, showing a viscous behavior (44). However, obvious elastic behavior occurred to hemicellulosic

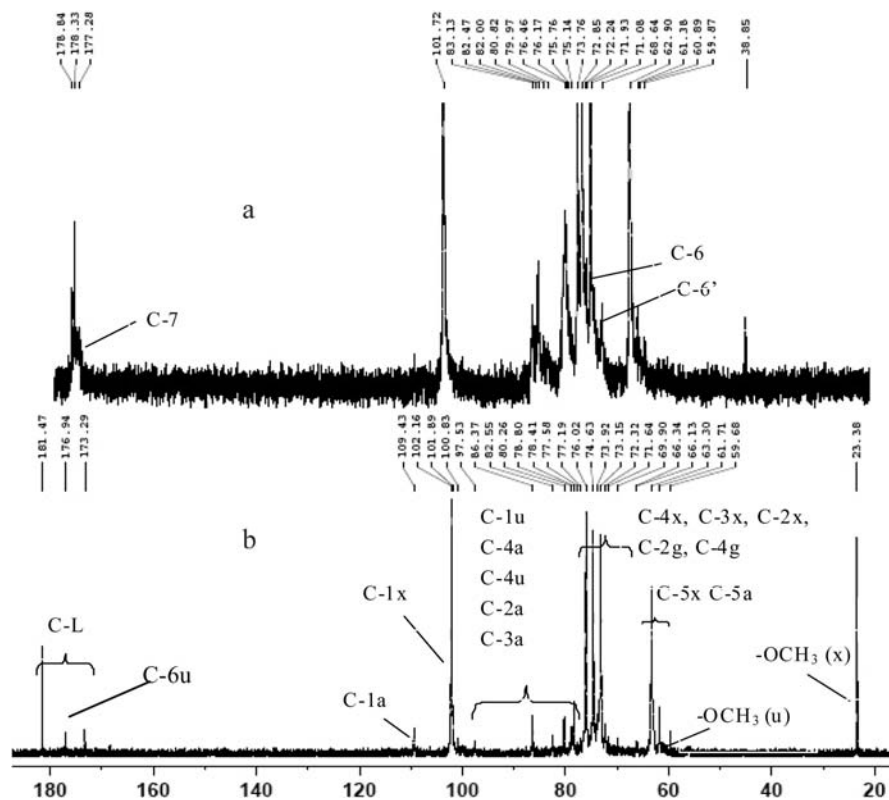


Figure 3. ^{13}C NMR spectra of hemicellulosic derivatives (a, sample 3) and native hemicelluloses (b) (X, (1 \rightarrow 4)- β -D-Xylp; U, 4-O-Me- α -D-GlcpA; a, arabinose; g, galactose).

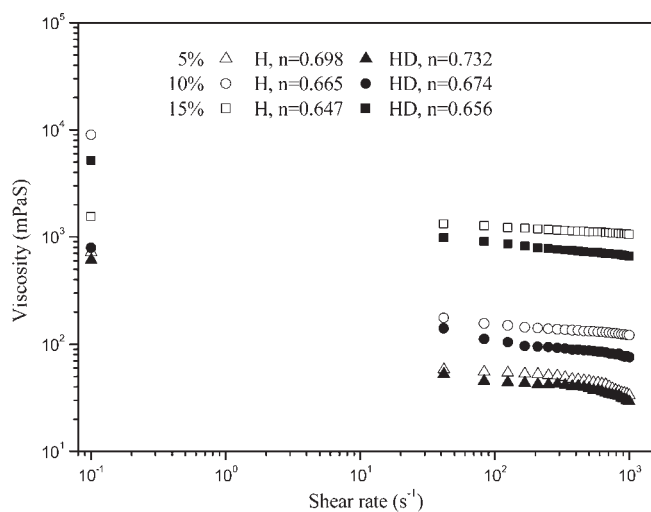


Figure 4. Shear rate dependence of viscosity for native hemicelluloses (b) and a hemicellulosic derivative (a, sample 18) at various concentrations.

derivative solutions at concentrations of 10% and 15% where G' is above G'' throughout the applied frequency (Figures 6 and 7), which is due to stronger molecule entanglement at higher concentration. However, the modulus of the native hemicellulose solutions showed a slight difference from the hemicellulosic derivatives. G' is higher than G'' over the applied frequency at concentrations of 5%, 10%, and 15%, showing elastic behavior. In addition, carboxymethyl hemicellulose solutions possessed a lower elastic modulus and a loss modulus as compared with those of native hemicelluloses solutions, which means fewer entanglements of carboxymethyl hemicellulose solutions.

These results may be explained by the difference in molecular weight and the functional groups on the structure of macromolecule

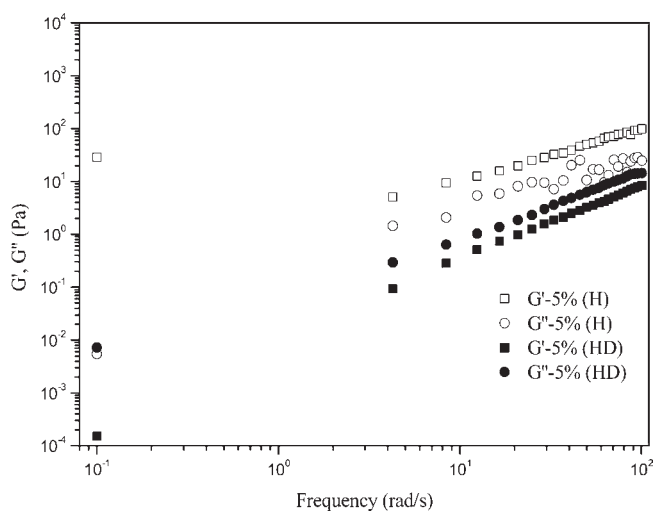


Figure 5. Frequency-dependent modulus of native hemicelluloses (H) and a hemicellulosic derivative (HD, sample 18) at 5% concentration.

chains. The carboxymethyl hemicelluloses have lower molecular weight (Table 2), and thus, the molecular entanglement is weakened. In addition, the decrease in hydroxyl groups of hemicelluloses during the reaction and the formation of carboxymethyl groups in the molecules reduce or prevent the entanglements between hemicellulose chains in alkali solution, and thus, the carboxymethyl hemicelluloses solutions show lower viscosity and modulus.

In summary, carboxymethyl hemicelluloses were successfully prepared in ethanol/water medium by using a microwave-induced synthesis method. Microwave irradiation could significantly promote carboxymethylation efficiency in a short time. Therefore, the products with higher DS of 1.02 could be achieved in

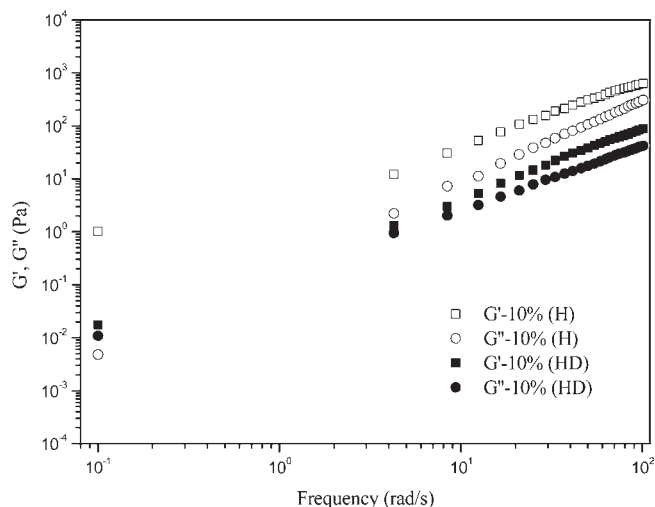


Figure 6. Frequency-dependent modulus of native hemicelluloses (H) and a hemicellulosic derivative (HD, sample 18) at 10% concentration.

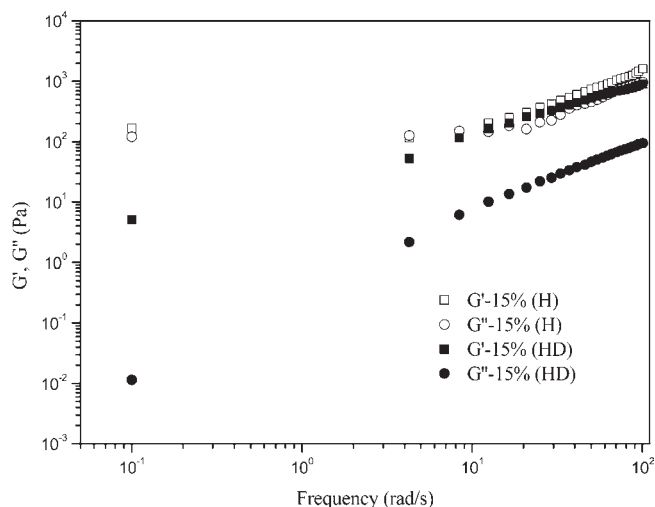


Figure 7. Frequency-dependent modulus of native hemicelluloses (H) and a hemicellulosic derivative (HD, sample 18) at 15% concentration.

much shorter time scales as compared with that with the conventional heating method. These results indicated that microwave irradiation is a rapid and efficient heating method for the functions of hemicelluloses and the preparation of materials from hemicelluloses. Degradation of the hemicelluloses and their derivatives also occurred during carboxymethylation under microwave irradiation. The carboxymethyl hemicellulose solution had lower viscosity and modulus than native hemicelluloses due to lower molecular weight and the role of carboxymethyl groups in reducing the entanglements between hemicelluloses chains. The viscosity of both native hemicelluloses and carboxymethyl hemicellulose solutions showed shear-thinning behavior throughout the applied frequency at concentrations of 5%, 10%, and 15%. The native hemicellulose solutions showed an elastic behavior at concentrations of 5%, 10%, and 15%, whereas, the solutions of the hemicellulosic derivatives showed viscous behavior at a concentration of 5% and elastic behavior at concentrations of 10% and 15%.

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