



Preparation and characterization of sugarcane bagasse hemicellulosic derivatives containing quaternary ammonium groups in various media

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Abstract: To increase the solubility and produce cationic or ampholytic polymers as beater additives in papermaking from native hemicelluloses, quaternization of hemicelluloses were performed by reacting hemicelluloses with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHMAC) and preferably with 2,3-epoxypropyltrimethylammonium chloride (ETA) in aqueous sodium hydroxide, homogenously in dimethyl sulfoxide (DMSO), and completely heterogeneously in ethanol/water, respectively. The extent of modification was measured by degree of substitution (DS), and its value of up to 0.55 can be controlled by adjusting the molar ratio of reagent to hydroxyl functionality in hemicelluloses and the concentration of sodium hydroxide. The characterization of hemicellulosic derivatives was performed by elemental analysis, GPC, FT-IR and ¹³C NMR spectroscopy as well as thermal analysis. It was found that hemicellulosic polymer was significantly degraded in aqueous sodium hydroxide solution compared with in dimethyl sulfoxide and in ethanol/water systems under the conditions given. The thermal stability of modified hemicelluloses decreased after chemical modification, corresponding to the decreasing M_w of hemicelluloses derivatives.

Introduction

During the last few years increased attention has been paid to the exploitation of hemicelluloses as biopolymer resources because hemicelluloses are available in very large amounts in organic wastes from renewable forest and agricultural residues [1]. The variability in sugar constituents, glycosidic linkages, and structure of glycosyl side chains as well as two reactive hydroxyl groups at the xylose repeating unit of the main chain from xylans offer various possibilities for regioselective chemical and enzymatic modifications. Functionalization creates novel opportunities to exploit the various valuable properties of hemicelluloses for previously unconceived applications [2]. In particular, quaternization of the hydroxyl groups of hemicelluloses to increase the hydrophilicity is one effective approach toward increasing the water-soluble hemicelluloses and increasing the cationic charge in hemicellulosic polymers.

In general, cationic polysaccharides can be prepared by the reaction of a polysaccharide with various reagents possessing positively charged groups such as amino, imino, ammonium, sulfonium or phosphonium groups [3]. In this context, our interest was focused on cationic polysaccharides containing quaternary ammonium groups by reacting hemicelluloses with ETA or CHMAC in different media. We are interested in various procedures for the synthesis of quaternized hemicellulosic derivatives. In the present paper, a heterogeneous and a homogeneous procedure as well as a molar ratio of quaternized reagents to hydroxyl functionality in hemicelluloses were evaluated. In addition, the influence of media and the concentration of sodium hydroxide on the molecular weight (M_w) of the products were investigated in detail. The obtained hemicellulosic derivatives were characterized by means of Fourier transform infrared (FT-IR) and carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy, gel permeation chromatography (GPC), and thermal analysis.

Results and discussion

Sugar composition of SCB hemicelluloses

Sugarcane bagasse (SCB) hemicelluloses possess different sugar side chains, and their composition can vary depending on the method of isolation. Sugar analysis revealed xylose as the main neutral sugar component (55.2%). The other major sugars were found to be glucose (27.8%) and arabinose (13.0%). Uronic acids (3.0%), mainly 4-O-methyl- α -D-glucopyranosyluronic acid (MeGlcA), galactose (2.6%), and mannose (1.5%) were present in small amounts. This high amount of glucose was probably due to the degradation of cellulose by the treatment of the holocellulose with 10% KOH alkali for a longer duration.

Hemicellulosic derivatives

In a first set of experiments, the quaternization reactions were carried out in aqueous sodium hydroxide under dissolution (Fig. 1, procedure a), using molar ratios of quaternized reagent per hydroxyl functionality in hemicelluloses from 0.5 to 3.0 at a certain concentration of NaOH of 2.0% (Tab. I). In this procedure, the quaternized reaction started in a highly swollen gel-like state by pretreatment with hot water. During the reaction a water-soluble polymer was formed and hence the reaction mixture became homogeneous [4]. As observed in Tab. I (Samples 1-5), the lowest DS value of 0.09 was obtained as a molar ratio of 0.5 was used. The low DS may be due to not enough ETA reacted with hemicelluloses or the increased chances of ETA hydrolysis at high concentration of NaOH (2.0%). By increasing the molar ratio up to 2.0, a high DS value of 0.53 was achieved. With further increase in the molar ratio to 3.0, the DS of hemicellulosic derivatives was only slightly higher (0.55). The enhancement in DS can be interpreted in terms of greater availability of ETA molecules in the proximity of hemicellulosic molecules.

The homogeneous reaction in DMSO (Fig. 1, procedure b) was performed using molar ratios of quaternized reagent to hydroxyl functionality in hemicelluloses from 0.5 to 3.0 (Tab. I, samples 6-10). Obviously, with an increase in the molar ratio of ETA to hydroxyl functionality in hemicelluloses the DS of the products increased. However, above an optimum molar ratio of 2.0 the DS value decreased gradually with further increase in the molar ratios. Compared with procedure a, a DS value of

the product using the same molar ratio of 2.0 in DMSO decreased to 0.22, indicating that the reactivity depended on the reaction media.

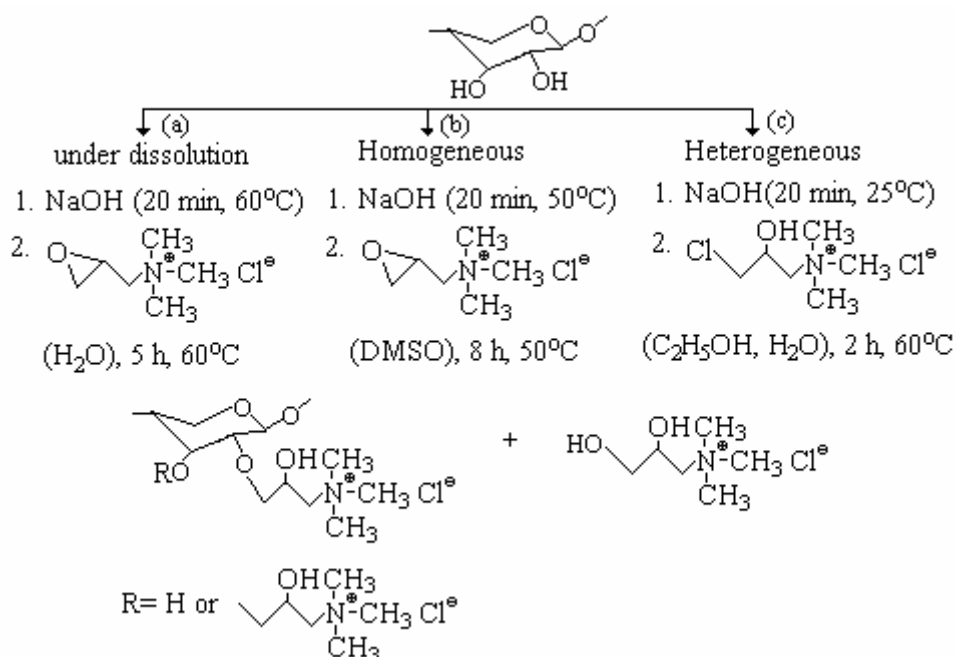


Fig. 1. Reaction scheme of the cationization of hemicelluloses with ETA or CHMAC in different media.

The quaternization heterogeneously in ethanol/water (Fig. 1, procedure c) yielded the white power products with low DS values. Applying a molar ratio of CHMAC to hydroxyl functionality in hemicelluloses from 0.5 to 3.0, products with DS values from 0.05 to 0.17 were obtained (Tab. I, samples 11-15). The product with a DS of about 0.11 was accessible by increasing the molar ratio of quaternized reagent to hydroxyl functionality in hemicelluloses to 3.0. This implied that even applying a higher molar ratio of CHMAC to hydroxyl functionality in hemicelluloses a higher DS could not be achieved in heterogeneous systems.

Compared with the procedure a (aqueous sodium hydroxide solution as a medium), the lower DS values obtained in the heterogeneous procedure c might be explained by the fact that in the first case the charged groups were accumulated on the surface of hemicellulosic particle and the diffusion of further quaternized reagent into the inner parts was increasingly hindered. Using processes with homogeneous sequences (procedures a and b), the hemicellulosic derivatives were completely dissolved and the reaction on the “new” surface of the hemicelluloses was less impeded. Therefore, the conversion of SCB hemicelluloses to 2-hydroxypropyltrimethylammonium chloride hemicelluloses in NaOH/H₂O, DMSO, and C₂H₅OH/H₂O, were achieved with different DS values, and the reaction of hemicelluloses in NaOH/H₂O showed the highest DS value of the products.

To increase the DS value of hemicellulosic derivatives, the reaction of SCB hemicelluloses with ETA was conducted under various NaOH concentrations in the procedure a. As expected, using a concentration of 1.0% NaOH and a molar ratio of ETA to hydroxyl functionality in hemicelluloses of 2.0, a DS of 0.34 was obtained. Under comparable reaction conditions (hemicelluloses, solvent, quaternized agent,

time, and temperature), a DS of 0.53 was observed in the NaOH concentration up to 2.0%. In contrast, a further increase in the NaOH concentration to 3.0% led to products of a comparatively low DS of 0.43. Obviously, at high alkali concentration the hydrolysis of the epoxide to form diol is probably increased. Obviously, a certain NaOH concentration is necessary to activate the hemicelluloses. On one hand, the hydrolysis of the reagent should be as low as possible.

Tab. I. The DS values of hemicellulosic derivatives obtained by the reaction of hemicelluloses with ETA or CHMAC in various systems.

Quaternized condition		Hemicellulosic derivatives	
Reagent	Molar ratio ^a	Sample No	DS _N
ETA	0.5	1	0.09
ETA	1.0	2	0.28
ETA	1.5	3	0.37
ETA	2.0	4	0.53
ETA	3.0	5	0.55
ETA	0.5	6	0.05
ETA	1.0	7	0.11
ETA	1.5	8	0.13
ETA	2.0	9	0.22
ETA	3.0	10	0.21
CHMAC	0.5	11	0.05
CHMAC	1.0	12	0.17
CHMAC	1.5	13	0.14
CHMAC	2.0	14	0.12
CHMAC	3.0	15	0.11

^aRepresents molar ratio of ETA or CHMAC to hydroxyl functionality in hemicelluloses, xylose unit $M_w=132$.

To check the polymer degradation during the reaction, the weight-average molecular weight of the samples was determined by GPC. As compared with the molecular weight of the native hemicelluloses, starting hemicelluloses (M_w , 28, 900 g mol⁻¹), the M_w of hemicellulosic derivatives prepared in three media were lower than the expected values. These results demonstrated that a significant degradation of the hemicellulosic polymers occurred during the quaternization under alkaline conditions. The M_w (18, 300 g mol⁻¹) of the hemicellulosic derivatives (sample 4) synthesized in NaOH/H₂O decreased significantly compared with the M_w of hemicellulosic derivatives reacted with the same molar ratio of quaternized reagent to hydroxyl groups in hemicelluloses of 2.0 in DMSO (Sample 9, M_w , 26, 890 g mol⁻¹) and C₂H₅OH/H₂O, (Sample 14, M_w , 25, 630 g mol⁻¹), indicating that hemicellulosic polymers were degraded substantially in aqueous sodium hydroxide solution. While the hemicellulosic derivatives synthesized in DMSO had a comparatively high M_w , which might be interpreted as sodium hydroxide being restrained by DMSO from the degrading hemicelluloses.

In the quaternization of hemicelluloses, NaOH acts as a catalyst, which activates hemicelluloses by alkalization to generate high nucleophilic reactivity and to increase the accessibility of the polysaccharide ultrastructure, particularly of the water-

insoluble samples, followed by the quaternized step [5-8]. Increase of NaOH concentration resulted in an increase in the number of hydroxyl groups in hemicelluloses available in the ionized form that reacted readily with the epoxide ring of cationic monomer, leading to the increase in DS values of hemicellulosic derivatives. While high amount of NaOH favoured the hydrolytic side reaction and the deetherification reaction as well as the degradation of hemicelluloses. As observed in procedure *a*, with an increase in the NaOH concentration from 0.4% to 1.0%, to 2.0%, and to 3.0%, the M_w of hemicellulosic derivatives decreased from 19,400 to 18,700, to 18,300, and to 17,700 g mol⁻¹, respectively, corresponding to an increment in DS from 0.01 to 0.34, and to 0.53 and then a decrement in DS to 0.43, respectively. Clearly, these results confirmed again that hemicelluloses were degraded in alkaline conditions. With increase in NaOH concentration the M_w of hemicellulosic polymers decreased significantly, indicating high amounts of NaOH led to the degradation of hemicelluloses.

FT-IR and ¹³C NMR spectroscopy

Fig. 2 represents the spectra of native hemicelluloses (*a*) and the product (4, DS 0.53, *b*). As observed clearly in spectrum *a*, the absorbance at 3420, 2920, 1620, 1463, 1259, 1169, 1043, 893 cm⁻¹ is associated with native hemicelluloses [9]. The broad peak at 3420 cm⁻¹ is due to the O-H stretching vibration and the symmetric C-H vibration band at 2920 cm⁻¹. A sharp band at 893 cm⁻¹ is attributed to β -glucosidic linkages between the sugars units, indicating that the xylose residues forming the backbone of the SCB hemicelluloses are linked by β -form bonds.

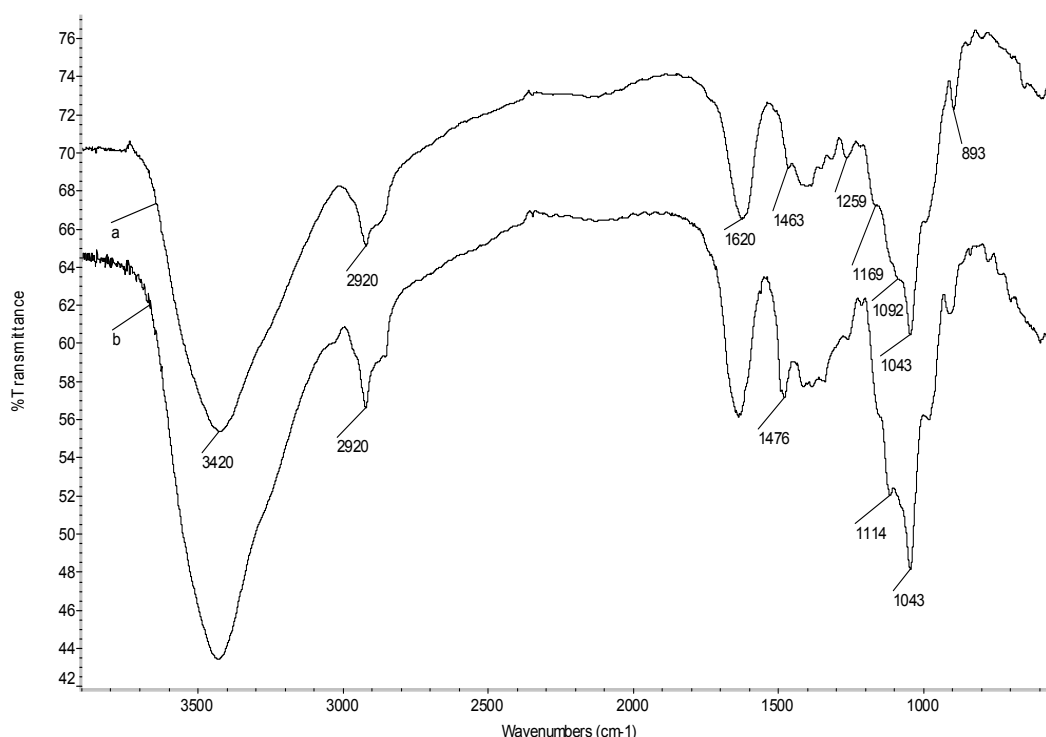


Fig. 2. FT-IR spectra of unmodified hemicelluloses (spectrum *a*) and hemicellulosic derivative sample 4 (spectrum *b*).

A strong band at 1043 cm⁻¹ is assigned to C-O stretching in C-O-C linkages. An intense band at 1620 cm⁻¹ originated from the absorbed water in the isolated native

hemicelluloses. The region between 1463 and 1092 cm^{-1} relates to the C-H and C-O bond stretching frequencies [9]. Compared with the spectrum a, the spectrum b of hemicellulosic derivative sample 4 provides evidence of quaternization by the increment in the intensity of the major ether bands at 1114 and 1043 cm^{-1} . In addition, an increase in the intensity of a new band appeared at 1476 cm^{-1} (spectrum b), which can be assigned to CH_2 bending mode and methyl groups of the substituent [10]. The symmetric C-H vibration band at 2920 cm^{-1} increased, which implied that CH_3 groups have been introduced. These changes could show the proof of incorporation of reagent onto the backbone of hemicelluloses.

In the ^{13}C NMR spectrum of hemicellulosic derivative sample 2 (Fig. 3), chemical shifts assigned to the quaternized substituents could be detected. The hemicellulosic derivative N-methyl $(\text{CH}_3)_3\text{N}^+$ signals was found at $\delta 54.3$ ppm and the N-methylene $(\text{CH}_2\text{-N}^+)$ signal at $\delta 68.4$ ppm, the (CHOH) signal at $\delta 65.3$ ppm [7]. The resonances of the hemicellulosic backbone were determined between 63.1-101.8 ppm, in which the signals at 101.8, 76.5, 73.8, 72.8, and 63.1 ppm correspond to C-1, C-4, C-3, C-2, and C-5 of β -D-xylans, respectively [11, 12].

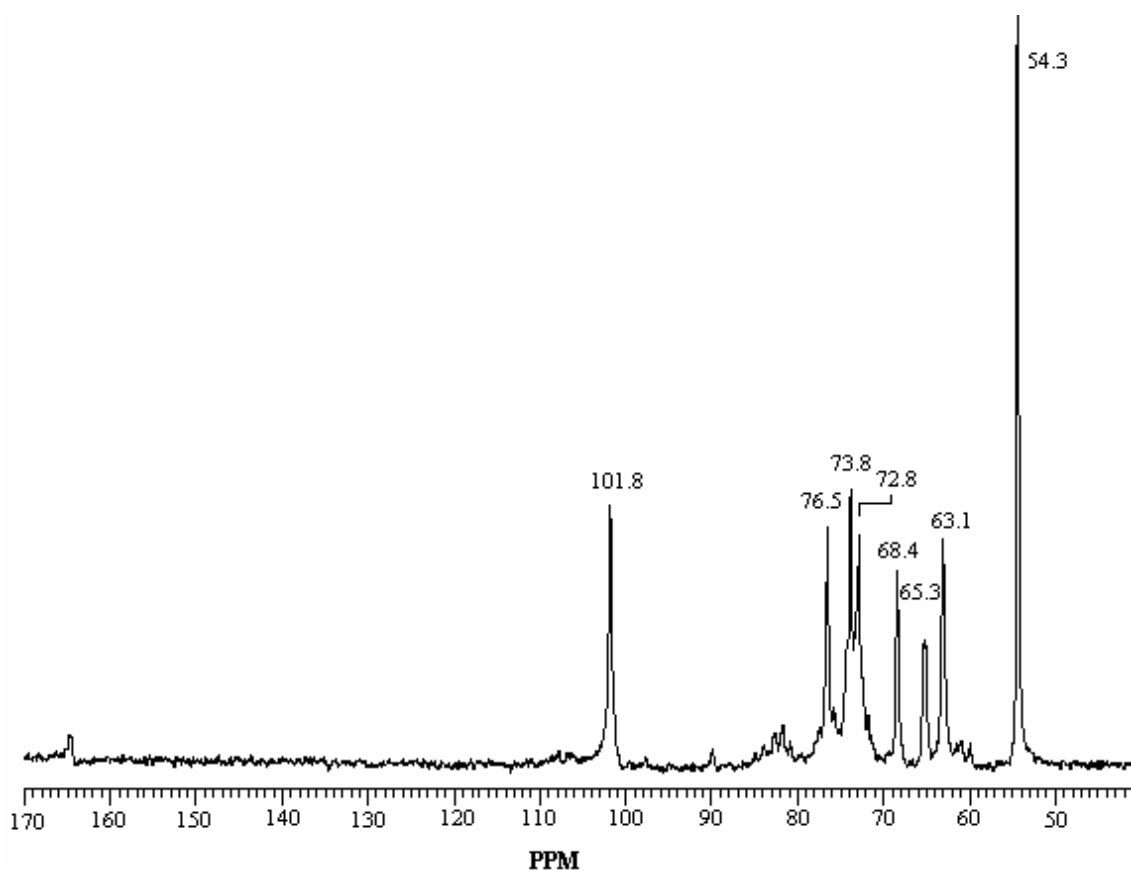


Fig. 3. ^{13}C NMR spectrum of hemicellulosic derivative sample 2.

Thermal analysis

Thermogravimetric analysis is a simple and accurate method for studying the decomposition pattern and thermal stability of polymers. Fig. 4 shows the weight loss curves for native hemicelluloses (H) and hemicellulosic derivative samples 4 and 14. For all samples studied, the early minor weight loss, which occurred between 30 and 200 $^{\circ}\text{C}$ observed for three samples, was attributed to desorption of water from the

polysaccharides. The second step spread between 200 and 250 °C. It was followed by a faster step beginning at 250 °C and ending at ~300 °C, with a maximum weight loss rate at 278 °C for sample 4, 283 °C for sample 14, and at 295 °C for native hemicelluloses, which related to the major decomposition of hemicellulosic derivative molecules. The fourth stage of weight loss ranging from 300 to 600 °C might be due to the further breakage of the polysaccharides. At 50% weight loss, the decomposition temperature occurs at 278 °C for sample 4, 290 °C for sample 14, and 294 °C for native hemicelluloses, respectively. This indicated that native hemicelluloses were more stable than modified hemicelluloses. In addition, the sample 14 and native hemicelluloses with high M_w had a slightly higher thermal stability than that of sample 4 with low M_w . This revealed that the thermal stability was paralleled to molecular weights of the polymers.

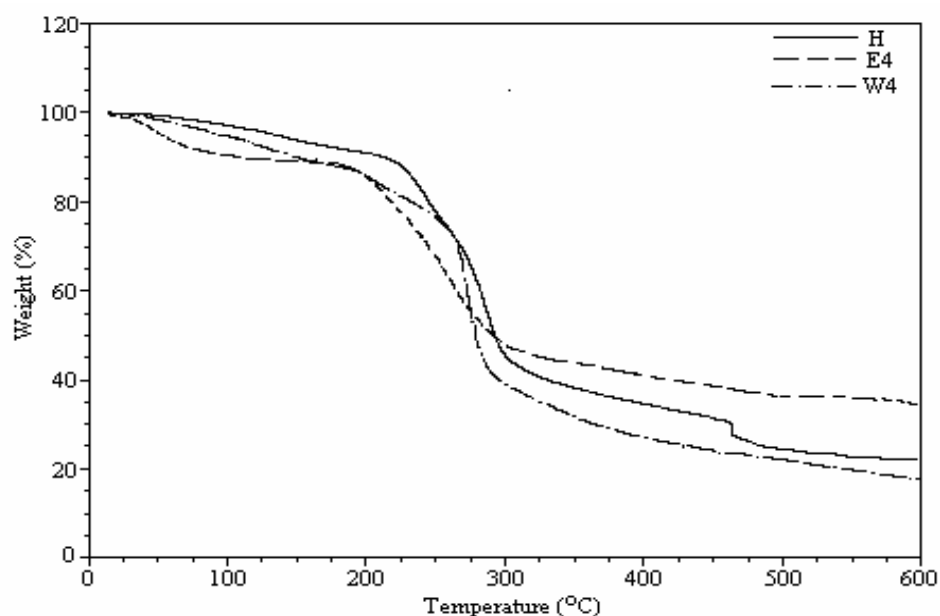


Fig. 4. Thermogram of native hemicelluloses (H) hemicellulosic derivatives sample 4 (W4) and 14 (E4) prepared in aqueous sodium hydroxide, ethanol/water, respectively.

Conclusions

Water-soluble hemicellulosic derivatives containing quaternary ammonium groups can be prepared by the quaternization reaction of hemicelluloses with CHMAC and preferably with ETA, in the presence of sodium hydroxide by using water, DMSO, and ethanol-water as the reaction media. The highest DS value (0.55) of the hemicellulosic derivatives was synthesized in aqueous sodium hydroxide solution. However, the M_w of products prepared in aqueous sodium hydroxide solution was much lower than that of the products prepared in DMSO and ethanol/water. This implied that hemicelluloses polymers were substantially degraded in aqueous sodium hydroxide. Interestingly, hemicelluloses were only slightly degraded in DMSO compared with other derivatization procedures. The evidence of quaternization of hemicelluloses was confirmed by FT-IR and ^{13}C NMR spectroscopy. The thermal stability of modified hemicelluloses decreased after chemical modification, corresponding to the decreasing M_w of hemicellulose derivatives.

Experimental

Materials

Hemicelluloses were isolated using 10% KOH at 25 °C for 10 h with a solid to liquid ratio of 1:20 (g mL⁻¹) from the holocellulose, which was obtained by delignification of sugarcane bagasse with sodium chloride in acidic solution (pH 3.7-4.0 adjusted by 10% acetic acid) at 75 °C for 2 h. Quaternized reagents [2,3-epoxypropyl trimethylammonium chloride and 3-chloro-2-hydroxypropyltrimethylammonium chloride] were purchased from Dongying fine chemicals Ltd., Shandong, China. Other chemicals were of analytical-reagent grade and purchased from Guangzhou Chemical Reagent Factory, Guangdong, China.

Synthesis of hemicellulosic derivatives in various systems

To prepare hemicellulosic derivatives 1-5 (Tab. I) in aqueous sodium hydroxide, the dried hemicelluloses (0.33 g, 0.005 mol hydroxyl functionality in hemicelluloses) were suspended in 5 mL water and heated to 60 °C for 30 min, and then a solution of sodium hydroxide, accounting for 40% to all amount sodium hydroxide, was added at 60 °C for 20 min. A solution of 5 mL ETA was then added dropwise to the hemicellulosic solution. After 30 min, the remaining sodium hydroxide was added with the total concentration of NaOH being 2.0%. The reaction mixture was additionally stirred for 5 h at 60 °C. After cooling down, the solution was neutralized with 0.1 M HCl and precipitated with 80% ethanol. The resulting hemicellulosic derivative precipitate was filtered off and washed thoroughly with 95% ethanol to remove residual reagents. The purified product was first air-dried for 12 h and then further dried in an oven at 45 °C for 24 h.

In a dimethyl sulfoxide (DMSO) system, 0.33 g of hemicelluloses (equal to 0.005 mol hydroxyl functionality in hemicelluloses) were suspended in 4 mL water, and then heated at 85 °C until the hemicelluloses dissolved completely, followed by adding 20 mL DMSO under continuous stirring. The solution was cooled down. Then 0.03 g sodium hydroxide was added. The temperature was increased to 50 °C for 20 min. ETA was added dropwise under stirring within 30 min. Then the mixture was kept at 50 °C for 8 h. After cooling to ambient temperature, the solution was slowly poured into 80 mL of 80% ethanol with stirring. The product was filtered off, washed thoroughly with 95% ethanol, dried as the method above, and named as samples 6-10 (Tab. I).

For preparing hemicellulosic derivative samples 11-15 (Tab. I) in C₂H₅OH/NaOH/H₂O system, dry hemicelluloses (0.33 g, 0.005 mol of hydroxyl functionality in hemicelluloses) were suspended in 5 mL H₂O and heated under reflux at 60 °C for 30 min. The mixture was cooled to room temperature and a solution of NaOH was added. After 20 min at room temperature, 21 mL ethanol was added. A solution of various amounts of CHMAC was added dropwise with a molar ratio of NaOH/CHMAC to 1.2. The mixture was stirred at 60 °C for 2 h. Upon completion of the reaction, the mixture was cooled to ambient temperature. Then the reaction mixture was neutralized with 0.1 M HCl, filtered off and thoroughly washed with ethanol until there was no chlorine ion in the filtrate. Finally, the products were dried as described in the method above. To reduce errors and confirm the results, each experiment was repeated in triplicate under the same conditions. The standard errors or deviations were observed to be 4.8-7.2%.

Determination of yield and degree of substitution

The nitrogen and carbon contents of cationic hemicellulosic derivatives were minored by a Vario EL Elemental Analyzer (Elementar, Germany). The DS of hemicellulosic derivatives was calculated from the ratio of the nitrogen to the carbon content according to the equation [5]:

$$DS = (60 \times \%N) / (14 \times \%C - 72 \times \%N)$$

Characterization of hemicelluloses and hemicellulosic derivatives

The neutral sugar composition of the isolated hemicelluloses was determined by gas chromatography (GC) analysis of their alditol acetates [13]. The content of uronic acids in native hemicelluloses was estimated colorometrically by the method of Blumenkrantz and Asboe-Hanson [14]. The molecular weights of hemicelluloses and their derivatives were examined by GPC as described previously [15]. Methods for recording FT-IR and ^{13}C -NMR spectra and thermograms have been described in a previous paper [4].

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References

- [1] Ebringerová, A.; Hromadková, A. *Biotechnol. Genet. Eng.* **1999**, *16*, 325.
- [2] Ebringerová, A.; Heinze, T. *Macromol. Rapid Comm.* **2000**, *21*, 542.
- [3] Solarek, D. B. *Modified Starches: Properties and Uses* **1986**, pp.97.
- [4] Ren, J. L.; Sun, R. C.; Liu, C. F.; Cao, Z. Y.; Luo, W. *Polym. Degrad. Stabil.* **2006**, *91*, 2579.
- [5] Schwikal, K.; Heinze, T.; Ebringerová, A.; Petzold, K. *Macromol. Symp.* **2006**, *232*, 49.
- [6] Ebringerová, A.; Hromadková, Z.; Kačuráková, M.; Antal, M. *Carbohydr. Polym.* **1994**, *24*, 301.
- [7] Haack, V.; Heinze, T.; Oelmeyer, G.; Kulicke, W. M. *Macromol. Mater. Eng.* **2002**, *287*, 495.
- [8] Zhang, L. M. *J. Appl. Polym. Sci.* **2001**, *79*, 1416.
- [9] Sun, R. C.; Sun, X. F.; Liu, Q.; Fowler, P.; Tomkinson, J. *J. Polym. Int.* **2002**, *51*, 117.
- [10] Kačuráková, M.; Ebringerová, A.; Hirsch, J.; Hromadková, Z. *J. Agr. Food Chem.* **1994**, *66*, 423.
- [11] Imanur, T.; Watanabe, T.; Kuwahara, M.; Koshijima, T. *Phytochemistry* **1994**, *37*, 1165.
- [12] Gabrelli, I.; Gatenholm, P.; Glasser, W. G.; Jain, R. K.; Kenne, L. *Carbohydr. Polym.* **2000**, *43*, 367.
- [13] Blakeney, A. B.; Harris, P. J.; Henry, R. J.; Stone, B. A. *Carbohydr. Res.* **1983**, *113*, 291.
- [14] Blumenkrantz, N.; Asboe-Hanson, G. *Anal. Biochem.* **1973**, *54*, 484.
- [15] Lawther, J. M.; Sun, R. C.; Banks, W. B. *J. Agr. Food Chem.* **1995**, *43*, 667.