

BENZYLATED HEMICELLULOSIC POLYMERS FROM *TRIPLOID POPULOUS*:  
 CHARACTERIZATION OF PHYSICOCHEMICAL, STRUCTURAL FEATURES  
 AND THERMAL STABILITY

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Chemical modification is one of the most important strategies to obtain novel biomaterials from the abundant biomacromolecules and to tailor the properties of biopolymers as desired macromolecules for specific application. In this study, a novel functional biopolymer was synthesized from *Triploid populus* hemicelluloses with benzyl chloride in dimethyl sulfoxide (DMSO) using NaOH as catalyst. Biopolymers with degrees of substitution (DS) between 0.08 and 0.34 were obtained by varying reaction temperature, reaction time, and the molar ratio of benzyl chloride to anhydroxylose unit in hemicelluloses. The chemical structure of benzylated hemicelluloses (BH) was characterized by FT-IR and <sup>13</sup>C NMR spectroscopies. The results showed that the M<sub>w</sub> and M<sub>n</sub> of BH were lower than those of the native hemicelluloses. The BH with a low DS had less thermal stability than the native hemicelluloses, whereas the BH with a high DS had higher thermal stability than the native hemicelluloses. Moreover, BH showed porous surface with small irregular slices, as evidenced by scanning electron microscope (SEM), which was ascribed to the disruption of intermolecular and intramolecular hydrogen bonds. These findings indicated that BH with hydrophobic groups could open up new opportunities for potential application in thermoplastic industries.

**Keywords:** *Triploid populus*, hemicelluloses, benzylation, thermal properties, FTIR spectroscopy, NMR

## INTRODUCTION

With growing fossil feedstock consumption for production of energy, chemicals and materials, environmental and climate issues have attracted increasing attention.<sup>1-2</sup> These problems have led to the research on the utilization of biomass, which is both sustainable and CO<sub>2</sub>-neutral. Among biomass, agricultural residues (straws, hulls, and stalks), deciduous and coniferous woods, municipal solid wastes, waste from the pulp and paper industry, and herbaceous energy

crops represent an enormous underutilized energy resource, which should be considered as a sustainable alternative of petroleum derivatives in the future.<sup>3</sup> Through conversion and effective utilization, they can be used for the production of biofuels, bioenergy, and biomaterials.<sup>4-5</sup>

The major components of the plant cell walls in biomass are cellulose (30-45%), lignin (15-30%), and hemicelluloses (20-45%).<sup>6</sup> Hemicelluloses are hetero-polysaccharide

polymers with complex structures, containing xylose, glucose, mannose, galactose, arabinose, glucuronic acid, and galacturonic acid etc., in various amounts depending on the source.<sup>7</sup> The increasing knowledge and the growing willingness to develop new biopolymer-based materials will lead to an increasing application of hemicelluloses and their derivatives, which are considered to be in-exhaustible and renewable resources for the production of bioenergy, novel biopolymers, and functional biomaterials.<sup>8-10</sup> Research on the utilization of hemicelluloses has been aimed at a potential fermentation feedstock in the production of ethanol, acetone, and xylitol, to prepare functional biomaterials, such as hydrogels, nanoparticles, and films, for special applications in papermaking, food and medicinal industry, including additives, active food packaging, wound dressings, and drug delivery.<sup>11-15</sup> Chemical modification provides an important strategy for tailoring the properties of hemicelluloses as desired macromolecules for their specific applications. Many attempts using different reaction pathways, such as etherification, esterification, oxidation, and polymerization, have been made to modify hemicelluloses in order to improve their physical-chemical characteristics.<sup>16-19</sup> The potential utilization of hemicelluloses-based or derived products in an industrial and biomedical context is beyond dispute and will stimulate further basic and applied research.

Since benzylated carbohydrates (glucose, sucrose, starch, gum, and cellulose) were initially reported by Gomberg and Buchler in 1922, benzylation has been thought to be an important reaction approach towards increasing the water resistance of biopolymers.<sup>20</sup> The benzylation of the hydroxyl groups in renewable and biodegradable polysaccharides, such as cellulose and starch, has been extensively studied. Benzyl cellulose is soluble in various organic solvents and has unique electrical and thermal properties, e.g., melting point and thermotropic liquid crystalline characteristics.<sup>21-22</sup> Benzyl starch offers better plasticity and high mechanical properties for being used in biodegradable plastics.<sup>23-24</sup>

In the present investigation, the incorporation of benzyl groups into hemicelluloses was conducted in order to endow hemicelluloses with special features, such as hydrophobicity and good solubility in organic solvents. With the aim to develop an efficient method for preparing these functional hemicelluloses derivatives, the benzylation of hemicelluloses by using DMSO as reaction medium under variable reaction conditions was conducted in this study. Benzylated hemicelluloses (BH) were characterized by both degradative method (thermal analysis) and non-degradative techniques (gel permeation chromatography, FT-IR, <sup>13</sup>C NMR, and SEM). The obtained BH with a low degree of substitution (DS) would be potentially applied in thermoplastic industry.

## EXPERIMENTAL

### Materials

The sample of 7-year-old *Triploid populus* was harvested from an experimental farm of Beijing Forestry University. It consisted of cellulose (42%), hemicelluloses (32%), and lignin (22%) on a dry weight basis.<sup>25</sup> Hemicelluloses were obtained from *Triploid populus* according to the procedure described in a previous paper.<sup>26</sup> Hemicelluloses were isolated using 10% NaOH at 25 °C for 16 h with a solid to liquor ratio of 1:20 (g mL<sup>-1</sup>) from holocellulose, which was obtained by delignification of the extractive-free *Triploid populus* (40-60 mesh) with sodium chlorite in acidic solution (pH 3.7-4.0, adjusted by 10% acetic acid) at 75 °C for 2 h. Sugar analysis showed the following sugar composition (relative molar percent): 76.65% xylose, 12.86% glucuronic acid, 4.03% glucose, 3.38% mannose, 1.92% galactose, 1.16% arabinose. The  $M_w$ ,  $M_n$ , and  $M_w/M_n$  of hemicelluloses were 56770 g mol<sup>-1</sup>, 26460 g mol<sup>-1</sup>, and 2.14, respectively. All chemicals used in the experiment were of analytical grade, and were used without further purification.

### Preparation of BH

The procedure of BH synthesis was as follows: 0.33 g of hemicelluloses (equal to 0.005 mol of hydroxyl functionality in hemicelluloses) was dissolved in DMSO (15 mL) at 95 °C for 1.5 h to guarantee the complete dissolution of hemicelluloses, and then the mixture was cooled to room temperature; a required quantity of sodium hydroxide was added to this mixture for 20 min at room temperature, followed by the addition of benzyl chloride. As illustrated in Table 1, the benzylation reactions were conducted

under various molar ratios of benzyl chloride to anhydroxylose unit in hemicelluloses (0.5-3.0), reaction times (4-24 h), and reaction temperatures (50-80 °C), respectively. After the required reaction time, the mixtures were cooled to room temperature and then neutralized with dilute acetic acid. The resulting mixtures were precipitated by 80% (v/v) aqueous ethanol and washed with ethanol four times. The obtained products were dissolved in purified water and freeze-dried at -50 °C.

#### Determination of the DS of BH

Because each proton-benzyl group gives rise to a peak at a characteristic magnetic field strength, <sup>1</sup>H NMR is a useful technique for analyzing the DS of BH.<sup>27-28</sup> The DS was calculated by comparing experimental values with theoretical values calculated for DS ranging from 0 to 2. In this study, the DS was taken as the value that produced the closest match by <sup>1</sup>H NMR determined by dissolving the sample in

DMSO-d<sub>6</sub>. The <sup>1</sup>H NMR spectrum of BH shows two distinct zones, between 3.0 and 5.1 ppm corresponding to the signals from the six protons of anhydroxylose unit structure and the signal intensity at 7.4 ppm, regarded as the integral of the benzyl protons. The DS was obtained from the ratio of the area of the proton peak at 7.4 ppm to that of the proton peak between 3.0 and 5.1 ppm, according to the following formula:<sup>29-30</sup>

$$DS = \frac{I_{\text{benzyl}}/5}{\sum I_{\text{H}}/6 - I_{\text{OH}}/2}$$

where  $I_{\text{benzyl}}$  and  $I_{\text{H}}$  are the benzyl unit and the anhydroxylose unit, respectively; the terms 5 and 6 are the number of protons from the signal of the benzene unit and anhydroxylose unit, respectively;  $I_{\text{OH}}$  is the hydroxyl unit of anhydroxylose unit, and 2 is the hydroxyl number.

Table 1  
Benzylation of hemicelluloses under varying conditions

Sample	Molar ratio <sup>a</sup>	Molar ratio <sup>b</sup>	Temperature (°C)	Time (h)
B1	1.2:1	0.5:1	60	8
B2	1.2:1	1.0:1	60	8
B3	1.2:1	1.5:1	60	8
B4	1.2:1	2.0:1	60	8
B5	1.2:1	2.5:1	60	8
B6	1.2:1	3.0:1	60	8
B7	1.2:1	2.0:1	40	8
B8	1.2:1	2.0:1	50	8
B9	1.2:1	2.0:1	70	8
B10	1.2:1	2.0:1	80	8
B11	1.2:1	2.0:1	60	4
B12	1.2:1	2.0:1	60	12
B13	1.2:1	2.0:1	60	16
B14	1.2:1	2.0:1	60	24

<sup>a</sup>The molar ratio of NaOH to anhydroxylose unit in hemicelluloses; <sup>b</sup>The molar ratio of benzylated reagent to anhydroxylose unit in hemicelluloses

#### Chemical characterization of hemicelluloses and BH

FT-IR spectra of hemicelluloses and BH were measured by using a Nicolet iN10 spectrophotometer with an MCT detector. The samples were scanned between 4000 and 650 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. The solution-state <sup>13</sup>C NMR spectra of the hemicelluloses (in D<sub>2</sub>O) and BH (in DMSO-d<sub>6</sub>) were obtained on a Bruker AVIII NMR spectrometer (400 MHz), and the parameters were set according to a previous report.<sup>31</sup> Thermal analysis of native hemicelluloses and BH was performed by TGA (DTG-60, Shimadzu, Japan). About 10 mg samples were heated in an aluminum crucible from room

temperature to 600 °C at a heating rate of 10 °C min<sup>-1</sup>, while the apparatus was continually flushed with a nitrogen flow of 30 mL min<sup>-1</sup>. The morphology changes before and after benzylation were observed by SEM. For magnification, an S-3400N (HITACHI, Japan) scanning electron microscope was operated at 10 kV acceleration voltages. Prior to taking pictures, the samples were coated with gold-palladium in a sputter coater (E-1.10, HITACHI, Japan). The molecular weights of BH were determined by gel permeation chromatography with a refraction index detector (RID) on a PL aquagel-OH 50 column (300×7.7 mm, Polymer Laboratories Ltd.) calibrated with PL pullulan polysaccharide standards (peak

average molecular weights of 738, 12 200, 100 000, and 1 600 000, Polymer Laboratories Ltd.). A 2 mg sample was dissolved in 0.005 N sodium phosphate buffer with 0.02 N NaCl (pH 7.5) at a concentration of 0.1% before measurement.<sup>32</sup>

## RESULTS AND DISCUSSION

### Effects of reaction conditions on the DS of BH

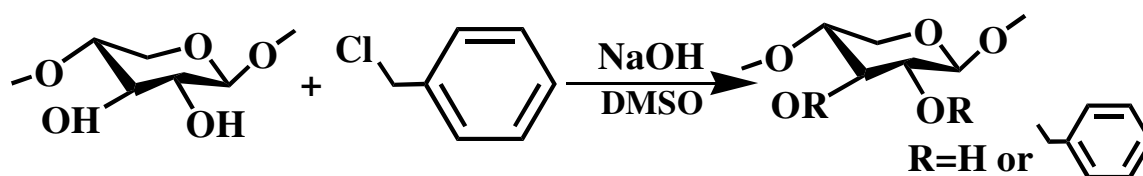
As shown in Scheme 1, benzylation is a classical Williamson reaction by nucleophilic substitution of an alkoxide ion for halide ion, which is generally carried out in a heterogeneous system. In this study, dimethylsulfoxide (DMSO) was selected as reaction medium. Compared with native hemicelluloses, BH displayed good solubility in DMSO at room temperature. In addition, the solubility of BH in DMSO increased with increasing the DS. The influence of reaction parameters (such as the molar ratio of benzyl chloride to anhydroxylose unit in native hemicelluloses, reaction temperature, and reaction time) on benzylation is shown in Figure 1.

As shown in Figure 1a (sample 1, 2, 3, 4, 5 and 6), with an increase in the molar ratio of benzyl chloride to anhydroxylose unit in hemicelluloses from 0.5:1 to 1.5:1, DS increased from 0.28 to 0.34. However, a further increase of the molar ratio from 1.5:1 to 3:1 resulted in a decrement of DS from 0.34 to 0.13, which was probably explained by the fact that a higher

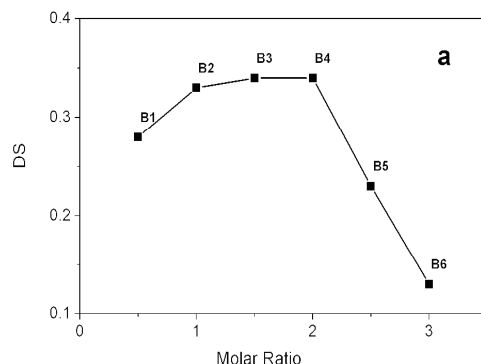
concentration of benzyl chloride led to more side reactions, especially to the degradation of hemicelluloses.

As seen from Figure 1b (samples 4, 7, 8, 9 and 10), an increase in the reaction temperature from 40 to 60 °C resulted in a marked increment of DS from 0.21 to 0.34, but a further rise of temperature to 80 °C led to a sharp decrease in DS from 0.34 to 0.16. The increase in DS could be explained by the fact that a higher reaction temperature enhanced the reactant diffusion into the hemicelluloses molecules and the compatibility of the reaction ingredients. However, higher temperature may result in the degradation of hemicelluloses and more side reactions during the benzylation of hemicelluloses, thus decreasing DS.

Reaction time showed a significant influence on BH (Figure 1c, samples 4, 11, 12, 13 and 14). The DS of the products increased from 0.08 to 0.34, when the reaction time increased from 4 to 8 h, thereafter, the DS decreased to 0.18 with an increment in reaction time up to 24 h. This observation indicated that a sufficient reaction time could provide a better reaction environment, whereas the prolonged reaction time may lead to the degradation of hemicelluloses and the occurrence of side reactions.



Scheme 1: Reaction scheme of the benzylation of hemicelluloses



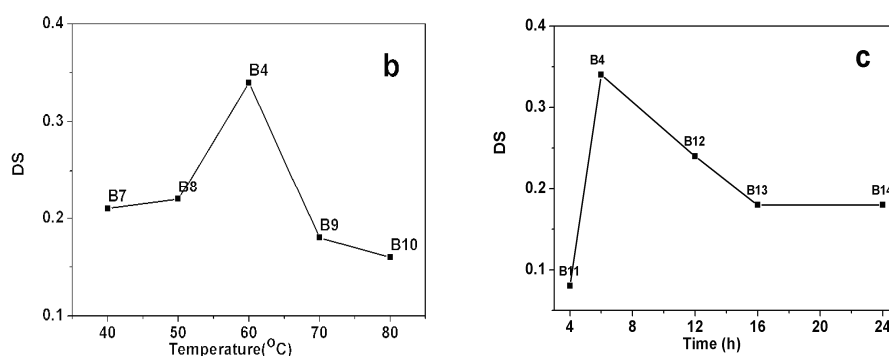


Figure 1: Effects of reaction conditions on the DS of benzylated hemicelluloses: (a) molar ratio of benzyl chloride/anhydroxylose unit in hemicelluloses; (b) reaction temperature; and (c) reaction time

### FT-IR spectra

FT-IR spectroscopy has been proven to be an effective tool for studying the molecular structures and interactions of carbohydrates.<sup>33</sup> Figure 2 illustrates the FT-IR spectra of native hemicelluloses (spectrum a) and BH (spectrum b, sample 4) prepared in DMSO solution. The absorptions at 3407, 2908, 1463, 1428, 1271, 1165, 1044, 977 and 896  $\text{cm}^{-1}$  (spectrum a) are indicative of native hemicelluloses.<sup>34</sup> The region between 1463 and 1044  $\text{cm}^{-1}$  is assigned to the

C-H and C-O bond stretching frequencies. The band at 1044  $\text{cm}^{-1}$  is assigned to xylans, indicating a dominant xylan of the native hemicelluloses. This is consistent with the results of sugar analysis. The band at 1165  $\text{cm}^{-1}$  is attributed to arabinosyl side-chains, corresponding to C-O-C vibration in hemicelluloses and the low intensity of the band at 977  $\text{cm}^{-1}$  suggests the presence of arabinosyl units attached to the xylopyranosyl constituents.<sup>35</sup>

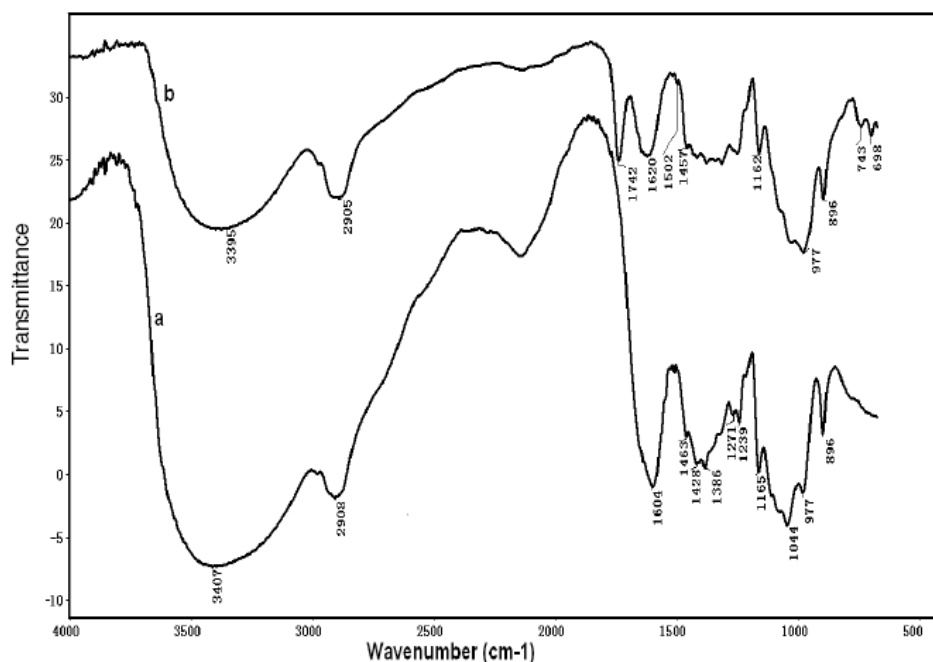


Figure 2: FT-IR spectra of native hemicelluloses (a) and BH (b, sample 4)

The sharp band at  $896\text{ cm}^{-1}$  is assigned to  $\beta$ -glycosidic linkages between the sugar units, indicating that the xylose residues forming the backbone of the macromolecule were linked by  $\beta$ -form bonds. In the carbonyl stretching region, an intensive signal at  $1604\text{ cm}^{-1}$  is attributed to glucuronic acid or 4-O-methyl-glucuronic acid carboxylate.<sup>36</sup> Another characteristic band observed at  $3407\text{ cm}^{-1}$  is assigned to the hydroxyl group stretching vibrations and a symmetric C-H vibration band was observed at  $2908\text{ cm}^{-1}$ . As compared with spectrum a, spectrum b is characterized by the presence of the bands at  $743$  and  $698\text{ cm}^{-1}$  due to an aromatic ring (aromatic C-H out-of-plane deformation and aromatic C-H deformation).<sup>37</sup> The bands at  $1502$  and  $1460\text{ cm}^{-1}$  are due to aromatic C-C axial deformation. Spectrum b clearly shows remarkable changes in chemical structure caused by the introduction of benzyl groups to the hemicelluloses chain. These new bands and the increasing intensity of the bands actually confirm that hemicelluloses have been successfully benzylated under the conditions given in this study.

### <sup>13</sup>C NMR spectra

The <sup>13</sup>C NMR spectra of native hemicelluloses in D<sub>2</sub>O (a) and BH in DMSO-d<sub>6</sub> (sample 4, b) are shown in Figure 3. As seen in Figure 3a, signals between 105 and 70 ppm are characteristic of the main chain of hemicelluloses, where five major signals at 102.5, 75.9, 75.1, 73.4, and 63.3 ppm are attributed to C-1, C-4, C-3, C-2, and C-5 of the (1→4)-linked  $\beta$ -D-Xyl units, respectively.<sup>38-39</sup> The signals at 97.5, 82.7, 72.2, 71.0, 70.1, and 59.4 ppm are from C-1, C-4, C-5, C-3, C-2, and -OCH<sub>3</sub> of 4-O-methyl-D-glucuronic acid residues linked to C-2/C-3 of backbone  $\beta$ -D-Xyl units.<sup>39</sup> These results show that the native hemicelluloses were composed of 4-O-methyl-D-glucuronic acid-D-xylans. Moreover, the signal at 59.3 ppm is characteristic of the methoxyl group of 4-O-methyl-D-glucuronic acid residue in xylan, which is also in accordance with the results of the FT-IR spectra analysis above mentioned. As compared with the spectrum of native hemicelluloses in Figure 3a, the chemical changes in the structure of BH were also verified by <sup>13</sup>C NMR spectra (Fig. 3b). The signals in the range of 127.8-128.4 ppm are attributed to C-8, C-9,

and C-10 of benzyl groups and a signal at 135.8 ppm is attributed to C-7. The signals ranging from 63 to 76 ppm are attributed to C-2, C-3, C-4, and C-5 in the skeleton of hemicelluloses and the methylene group of the benzyl moiety (C-6). Interestingly, the presence of six signals at 97.6, 81.7, 72.0, 71.7, 69.7, and 59.3 ppm were assigned to C-1, C-4, C-5, C-3, C-2 and -OCH<sub>3</sub> of 4-O-methyl-D-glucuronic acid residues linked to C-3 of backbone  $\beta$ -D-Xyl units, indicating that there are no significant structural changes of the macromolecular hemicelluloses. In comparison, the signals at C-1, C-4, C-3, and C-2 from the (1→4)-linked  $\beta$ -D-Xyl units of BH slightly shifted toward the high field. The differences in  $\delta$  values of the (1→4)-linked  $\beta$ -D-Xyl units between native hemicelluloses and BH could be explained by the formation of intra-molecular and inter-molecular hydrogen bonds in the  $\beta$ -D-Xyl units. These broken hydrogen bonds increased the probability density of the electron cloud around the nucleus and engendered a shielding effect due to the incorporation of benzyl groups into the hydroxyl in DMSO, which eventually led to low intensity for the (1→4)-linked  $\beta$ -D-Xyl units of BH. Moreover, a decrease of the  $\delta$  values at 72.7 ppm for C-2 might be due to the partial substitution at the C-2 position.

### Molecular mass

Molecular mass is an important parameter to evaluate the physicochemical properties of polysaccharides, such as solubility, rheological, and thermal properties. In this study, the molecular mass distribution of native hemicelluloses (a) and BH (sample 1 (b) and sample 4 (c)) has been determined by gel permeation chromatography in an aqueous medium, as shown in Figure 4. As can be seen, the molecular mass distribution curves of b and c had two small peaks in the lower molar mass region, indicating that BH had a narrow molecular mass distribution of 1.53 and 1.71, respectively. It seems that the curve of native hemicelluloses had a high and wide peak in the higher molar mass region, as shown by the molecular mass distribution of 2.14. The  $M_w$  of native hemicelluloses was  $56\,770\text{ g mol}^{-1}$ , but the  $M_w$  values of BH decreased from  $32\,950$  to  $19\,630\text{ g mol}^{-1}$  when the DS increased from 0.28 (B1) to 0.34 (B4). The  $M_w$  and  $M_n$  of BH were lower than

those of native hemicelluloses, which might be because the hydrogen bonds among hemicelluloses chains were destroyed and the hemicelluloses were degraded during the chemical reaction process under alkaline conditions. Furthermore, the polydispersity values ranged from 1.53 to 2.14, which were indicative of molecularly uniform polymers with potential commercial utility.

### SEM analysis

To better understand how chemical modification influenced the morphology of hemicelluloses in the DMSO, a series of SEM pictures of native hemicelluloses and BH (sample 1, sample 2, and sample 4) are illustrated in Figure 5. The gradual changes (amplification factor of 0.5 k, 1.5 k, 3 k, and 8 k) of the morphology of the BH were clearly observed with

increasing the reagent molar ratios (0.5-3.0) during the reactions. The native hemicelluloses showed irregular particle with crack surfaces. However, the incorporation of benzyl groups into hemicelluloses led to significant changes of the products. BH showed amorphous and highly porous structures. The above observation indicated that with the increase in the degree of benzylation, the incorporation of benzyl groups resulted in an increasing disruption of intermolecular and intramolecular hydrogen bonds, thus destroying the rigid structure of hemicelluloses. A similar phenomenon has been investigated by other researchers who studied benzyl cellulose.<sup>41</sup> The results of the present study indicated that the starting of benzylation in the DMSO modified the structure of the native hemicelluloses fundamentally.

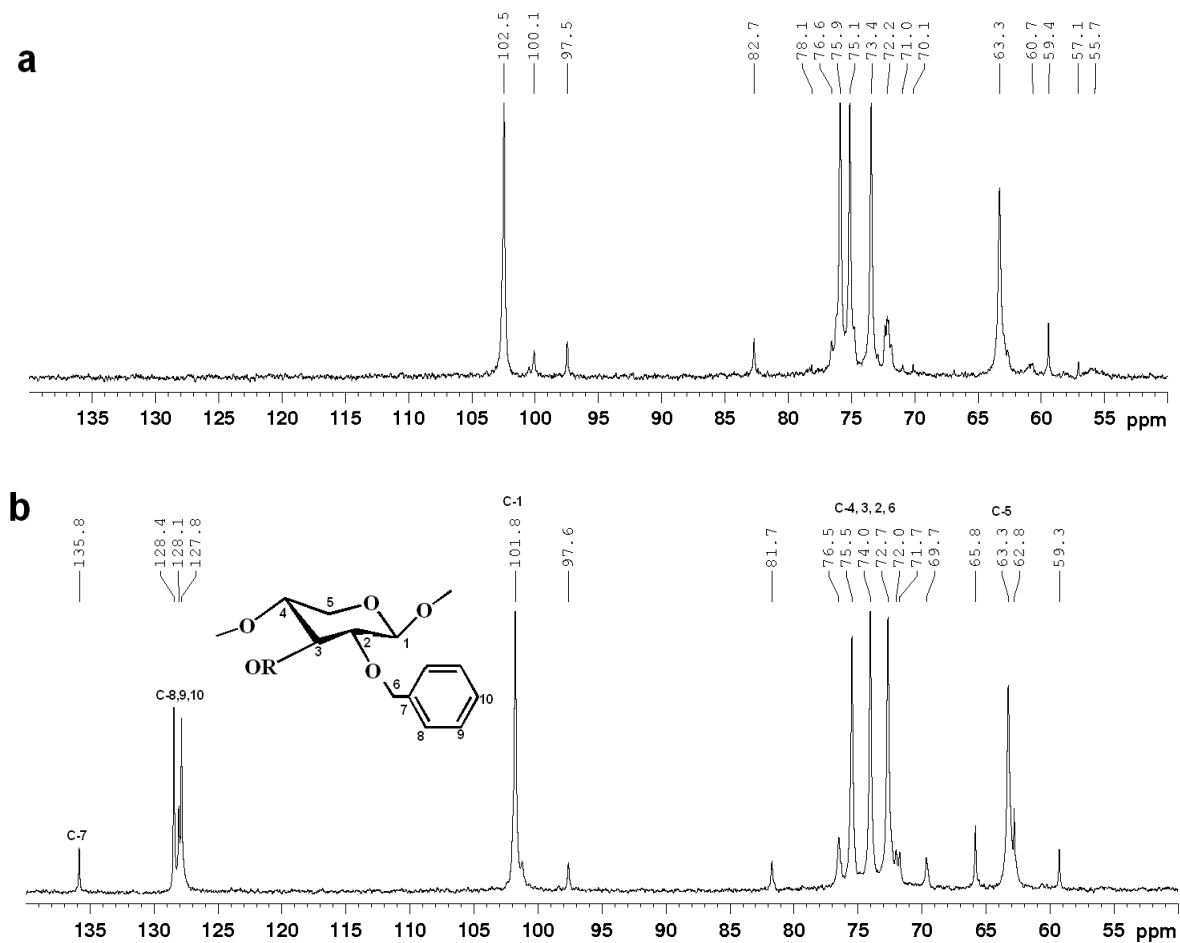


Figure 3: <sup>13</sup>C NMR spectra of native hemicelluloses (a) and BH (b, sample 4)

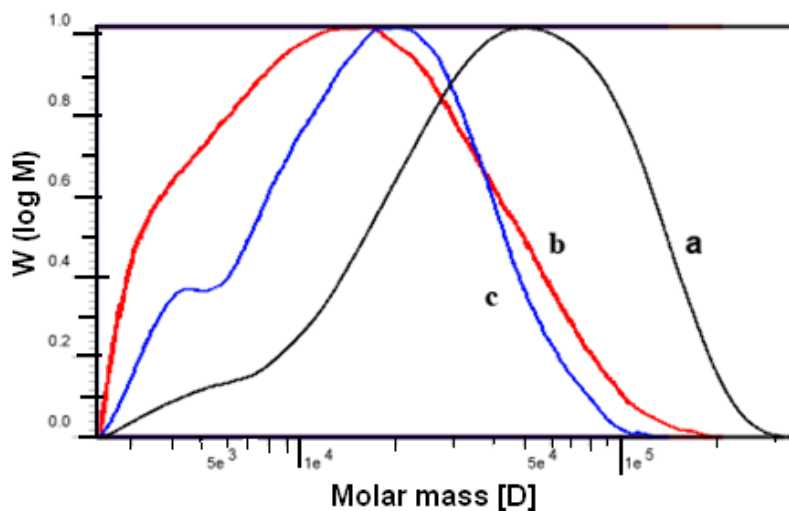


Figure 4: Molecular weight distribution curves of native hemicelluloses (a) and BH (b, sample 2; c, sample 4)

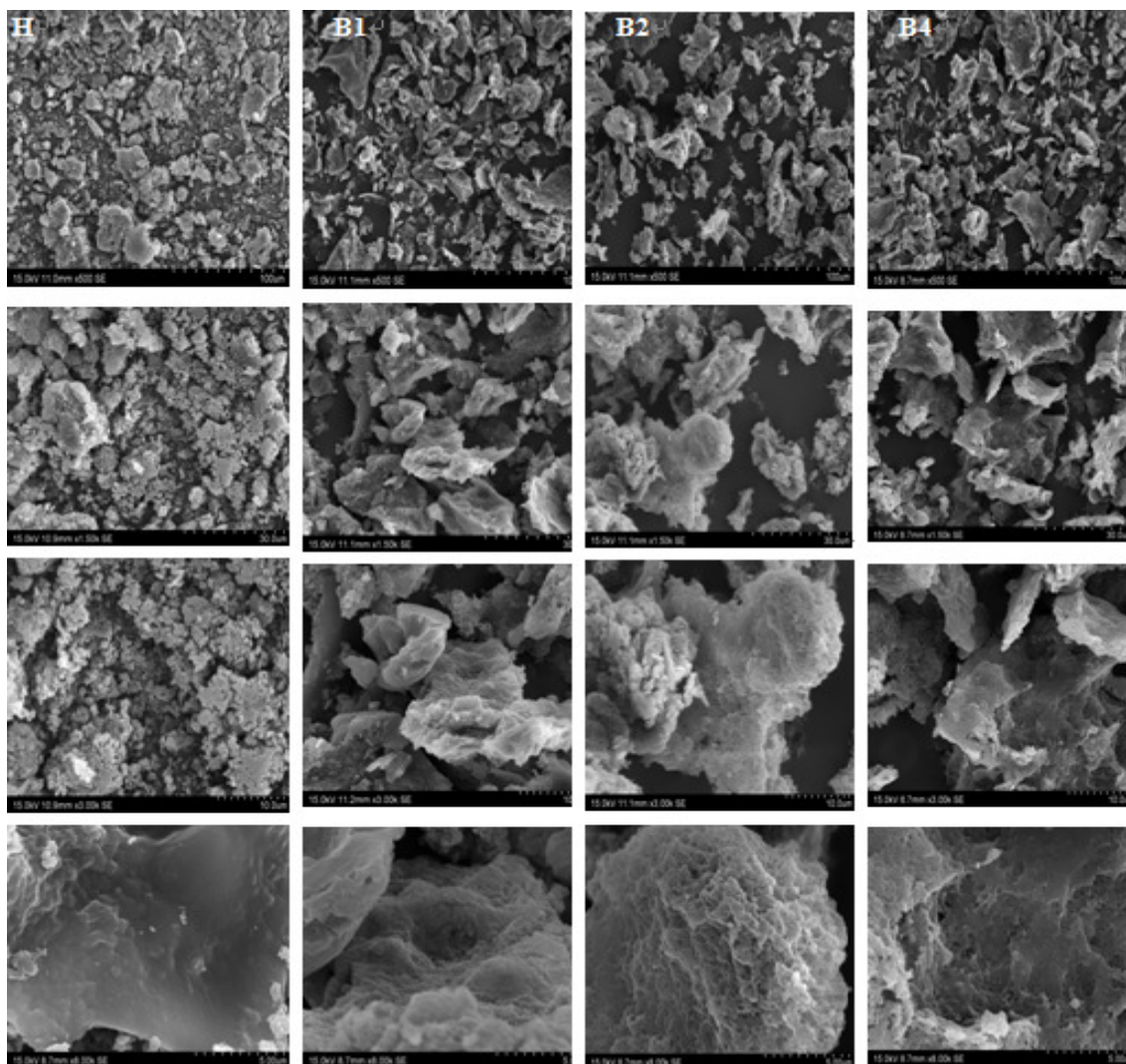


Figure 5: SEM image of native hemicelluloses and BH (sample 1, sample 2, and sample 4)



### Thermal analysis

The effect of benzylation on the thermal properties of hemicelluloses was examined by thermogravimetric (TG) and derivative thermogravimetry (DTG) in the temperature range from room temperature to 600 °C under nitrogen atmosphere. The TG curves of native hemicelluloses and BH are presented in Figure 6a. The TG curves of hemicelluloses show two degradation steps attributed to water loss and hemicelluloses degradation. Weight loss (~4.7%) was clearly observed at 264.6, 223.7 and 253.2 °C for native hemicelluloses and BH (sample 1 and sample 4), respectively, due to the evaporation of water. When weight loss reached 50%, the decomposition temperature of native

hemicelluloses and BH (sample 1 and sample 4) was recorded at 301, 297 and 301.9 °C, respectively. As shown in Figure 6b,  $T_{max}$  (the decomposition temperature corresponding to the maximum rate of weight loss) of native hemicelluloses and BH (sample 1 and sample 4) was 281.3, 266.9 and 282.8 °C, respectively. The residues at 600 °C were almost the same for native hemicelluloses and BH. These results indicated that BH with a low DS had lower thermal stability than native hemicelluloses, whereas BH with high DS had higher thermal stability than native hemicelluloses. This was mainly attributed to the introduction of benzyl groups and the destruction of hydrogen bonds from hemicelluloses.

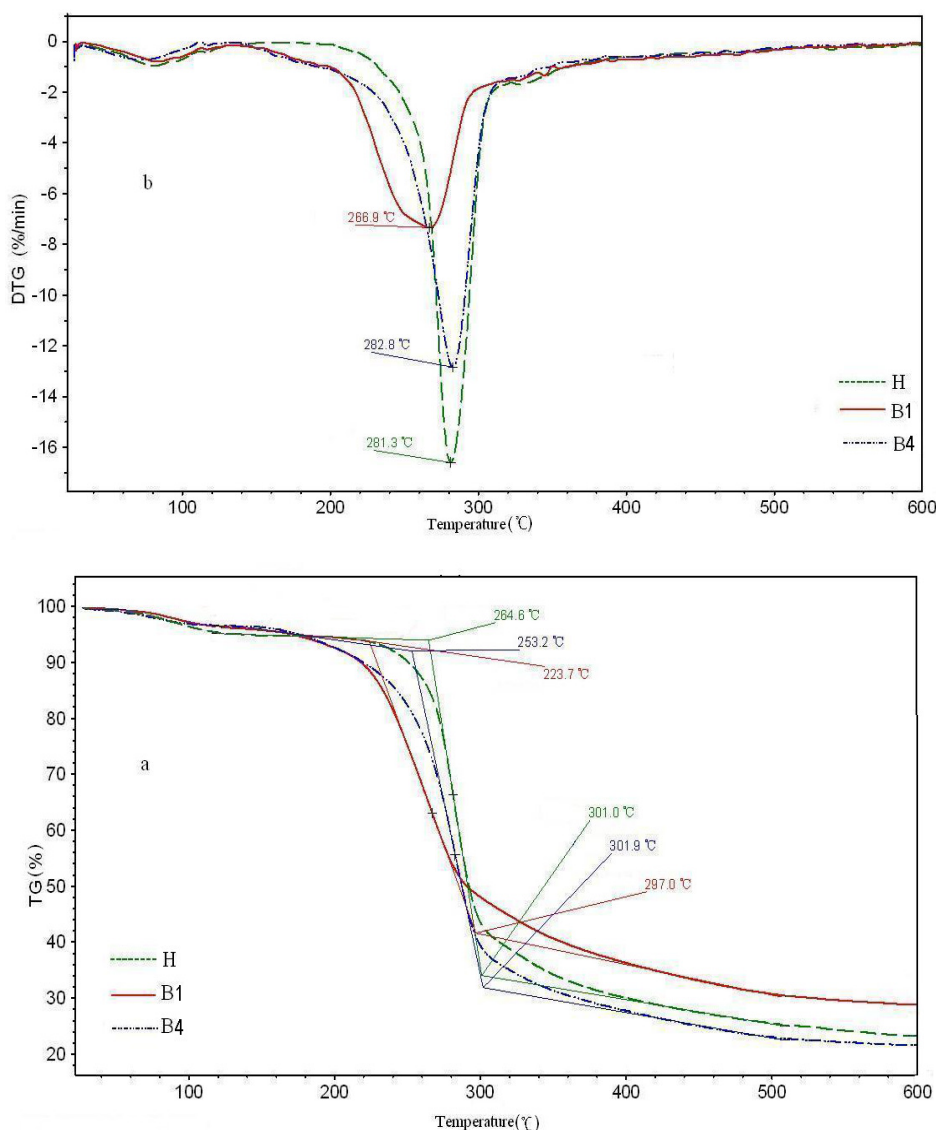


Figure 6: TGA/DTG analysis of native hemicelluloses and BH (sample 1 and sample 4)

## CONCLUSION

On the basis of the above results, the following conclusions were drawn: by varying the molar ratio of benzyl chloride/anhydroxylose unit in hemicelluloses (0.5:1-3:1), the reaction temperature (40-80 °C) and reaction time (4-24 h), BH with DS of 0.08-0.36 was successfully synthesized in DMSO. FT-IR and <sup>13</sup>C NMR spectroscopy confirmed that the benzyl groups were introduced into the backbone of hemicelluloses. SEM indicated that the BH was endowed with porous surface with small irregular slices, which was ascribed to the disruption of intermolecular and intramolecular hydrogen bonds. The molecular weight measurement showed that the M<sub>w</sub> and M<sub>n</sub> of BH were lower than those of native hemicelluloses. BH with a low DS had lower thermal stability than that of native hemicelluloses, whereas BH with a high DS had higher thermal stability than that of native hemicelluloses. During the process of benzylation of hemicelluloses, the hydrogen bonds among the hemicelluloses chains were destroyed in DMSO, and then the benzyl group was introduced into hemicelluloses. These features could make BH potentially applicable in thermoplastic industries.

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