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Novel hydrophobic hemicelluloses: Synthesis and characteristic

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ABSTRACT

Novel hydrophobic hemicelluloses possessing hydrophobic groups were prepared by the benzylation of wheat straw hemicelluloses with benzyl chloride under the presence of catalyst in an ethanol/water system. In particular, the progress of the benzylation reaction was studied as a function of the volume ratio of ethanol/water from 4:1 to 6:4, the molar ratio of NaOH/anhydroxylose unit in hemicelluloses from 0.6:1 to 1.5:1, the molar ratio of benzyl chloride/anhydroxylose unit in hemicelluloses from 0.5:1 to 2.0:1, reaction temperature 50–80 °C, and reaction time 4–20 h. Benzylated hemicelluloses with the low degree of substitution from 0.09 to 0.35 were obtained depending on the experimental conditions. The incorporation of benzyl groups into the backbone of hemicelluloses was confirmed by FT-IR and ^{13}C NMR spectroscopies. The thermal stability increased after the modification of hemicelluloses due to the introduction of benzyl groups. The introduction of benzyl groups endows hemicelluloses with the hydrophobicity, which could be potentially applied in plastic industries.

1. Introduction

Hemicelluloses, being widely abundant polysaccharides in nature, represent about 25–35% of lignocellulose biomass (Kumar, Singh, & Singh, 2008; Saha, 2000). Because of their economical, biocompatible, non-toxic, biodegradable features, research activities in the utilization of hemicelluloses have been aimed at preparing functional biopolymers such as cationic or anionic hemicelluloses (Peng, Ren, & Sun, 2010; Peng, Ren, Zhong, Cao, & Sun, 2011a; Petzold, Schwikal, & Heinze, 2006; Ren, Peng, & Sun, 2008a; Ren, Sun, Liu, Chao, & Luo, 2006; Ren, Sun, & Peng, 2008b; Salam, Pawlak, Venditti, & EI-tahlawy, 2011; Schwikal, Heinze, Ebringerova, & Petzold, 2006; Schwikal et al., 2011) and biomaterials such as film and hydrogel (Edlund, 2008; Lindblad, Albertsson, Ranucci, Laus, & Giani, 2005; Peng, Ren, Zhong, & Sun, 2011c; Peng, Ren, Zhong, Peng, & Sun, 2011b; Pohjanlehto, Setala, Kammiovirta, & Harlin, 2011; Simkovic, Gedeon, Uhliarikova, Mendichi, & Kirschnerova, 2011; Stevanic et al., 2011) for special applications in papermaking, food and medicinal industry including wet end additives, active food packaging and additives, wound dressings, and drug delivery. Therefore, the utilization of hemicelluloses exhibits a new strategy for preparing environmentally friendly biomaterials and biopolymers.

The chemical modification allows hemicelluloses having special properties which can broaden their applications. Many attempts have been made to modify hemicelluloses using different reaction pathways such as etherification, esterfication, oxidation and polymerization for improving their physical–chemical characteristics. For example, acetylation (Ren, Sun, Liu, Cao, & Luo, 2007; Sun, Sun, Zhao, & Sun, 2004b), oleoylation (Sun, Sun, & Sun, 2004a), and lauroylation (Peng, Ren, Peng, Xu, & Sun, 2008; Ren, Xu, Sun, Peng, & Sun, 2008c) have been applied for improving the hydrophobicity of hemicelluloses in many literatures recently. Benzylation, which is an important reaction approach toward increasing the water resistance of the biopolymers, can endow hemicelluloses with especial features such as hydrophobicity, better solubility in organic solvents, high thermal stability, and thermoplastic properties. However, very little attention has been paid to the benzylation of hemicelluloses (Vincendon, 1998).

Over the past ten years, the benzylation of the hydroxyl groups of other renewable and biodegradable polysaccharides such as cellulose, lignocelluloses and starch, has been extensively studied. Benzylated cellulose is found to possess higher toughness owing to the steric effect of the substituting benzyl groups (Ramos, Frollini, Koschella, & Heinze, 2005; Rohleder & Heinze, 2010). Benzylated wood and pulp were used to produce thermoplastic material (da Roz & Curvelo, 2004; Hadano et al., 2004; Lu, Zhang, Rong, Shi, & Yang, 2002). In addition, benzylated ramie and sisa fibers were found to have better spinning and dyeing properties (Ferreira,

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Curvelo, & Mattoso, 2003; Liu, Sun, Liu, Lu, & Xiong, 2008). Benzylation has also offered a number of desirable properties such as better plasticity and high mechanical properties for starch used in biodegradable plastics (Li, Zhang, & Gou, 2009; Pieters, de Graaf, & Janssen, 2003; Xia, Tang, & Ding, 2010). Thus, benzylation endows polysaccharides with specific characteristics, and benzylated polysaccharides have been recommended to be applied in plastic industry.

In the present investigation, the incorporation of benzyl groups into xylan-type hemicelluloses is of interest in order to develop special chemical and physical functionality in this material especially such as hydrophobicity, solubility in organic solvents and good thermal behavior. The benzylation of xylan-type hemicelluloses under variable reaction parameters was investigated in this study for achieving the hydrophobic properties. The chemical structure change of hemicelluloses before and after modification was characterized by Fourier transform infrared (FT-IR) and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopies. Furthermore, the thermal stability of isolated hemicelluloses and benzylated hemicelluloses was also discussed. This study provides a feasible way for the preparation of benzylated hemicelluloses with the relatively low degree of substitution (DS) and they will be potentially applied in thermoplastic industry.

2. Experimental

2.1. Materials

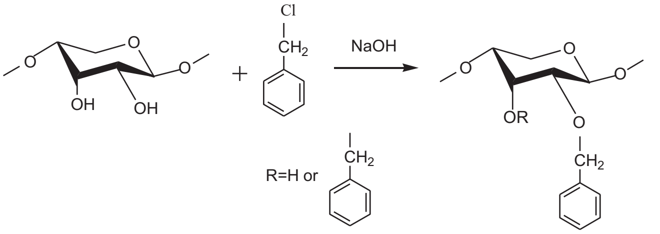
Hemicelluloses were isolated using 10% KOH at 25 °C for 10 h with a solid to liquor ratio of 1:20 (g/mL) from holocellulose obtained by delignification of wheat straw with sodium chlorite in acidic solution (pH 3.7–4.0, adjusted by 10% acetic acid) at 75 °C for 2 h. The sugar analysis showed the following sugar composition (relative wt%): 77.67% xylose, 10.16% arabinose, 2.36% glucose, 0.83% galactose. Uronic acids, mainly 4-*O*-methyl-D-glucuronic acid (MeGlcA), were present in a noticeable amount (8.97%). The molecular weight of the hemicelluloses was 28, 890 g/mol, and the polydispersity was 3.2. Benzyl chloride, sodium hydroxide, acetic acid and ethanol were analysis grade products purchased from Guangzhou Chemical Reagent Factory, China.

2.2. Preparation of benzylated hemicelluloses

The typical procedure of the preparation of benzylated hemicelluloses is as follows. 0.33 g of hemicelluloses powder (0.005 mol of hydroxyl functionality in hemicelluloses) in water (3 mL) was heated to 80 °C under stirring until dissolved (approximately 10 min), and then the mixture was cooled to room temperature. Subsequently, a required quantity of sodium hydroxide was added dropwise to this mixture for 20 min at room temperature, and then ethanol was gradually added to form heterogeneous system, and the volume of medium was set to 10 mL. Benzyl chloride was then added to the reaction mixture, and the temperature of the reaction was kept at required temperature ranging from 50 to 80 °C. Upon completion of the reaction (4, 6, 8, 10, and 20 h), the mixture was cooled down and neutralized with acetic acid and precipitated by 80% methanol, washed with 90% ethanol four times, and then dried in a vacuum oven at 45 °C for 24 h.

2.3. Determination of degree of substitution (DS)

The degree of substitution of benzylated hemicelluloses was calculated by elemental analysis. The nitrogen and carbon contents in the product were determined with an Elementar Vario EL (Elementar Analysensysteme GmbH, Hannover, Gemerny).



Scheme 1. Reaction scheme of benzylation of hemicelluloses with benzyl chloride.

All samples were dried at 60 °C for 24 h before measurement. To reduce errors, each experiment was performed in duplicate and mean values were presented in all the cases studied. The DS was calculated as the following equation (1).

$$\mathrm{DS} = \frac{C\% \times 132 - 60}{84 - 91 \times C\%} \tag{1}$$

where *C*% is the carbon contents of the products determined by elemental analysis, and the terms of 132 and 91 are the molecular weights (g/mol) of xylose unit in hemicelluloses and benzylated group. The terms of 60 and 84 are the carbon element in xylose unit and benzylated group.

2.4. Characterization of benzylated hemicelluloses

The chemical structure of the native hemicelluloses and benzylated hemicelluloses was evaluated by FT-IR and ^{13}C NMR spectroscopies. A Nicolet 750 spectrophotometer (Thermo Fisher Nicolet, Florida, USA) was used to record FT-IR spectra using a KBr disc containing 1% (w/w) of finely ground sample.

The solution-state ^{13}C NMR spectra were obtained on a Bruker AVIII 400 MHz spectrometer (Bruker Corporation, Rheinstetten, Gemerny) operating in the FT mode at 100.6 MHz after 15,000 scans. The isolated hemicelluloses (80 mg) and benzylated hemicelluloses were dissolved in 1.0 mL D_2O and DMSO-d_6, respectively, A 30° pulse flipping angle, a 9.2 μs pulse width, a 1.36 s acquisition time, and 2 s relaxation delay time were used.

Thermal analysis was performed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (TGA Q500, TA Instruments, New Castle, USA). The apparatus was continually flushed with nitrogen. The sample was weighed between 9 and 11 mg and was heated from room temperature to 600 °C at a heating rate of 10 °C per minute.

3. Results and discussion

3.1. Influence of reaction conditions on the DS of benzylated hemicelluloses

The benzylation of hemicelluloses is the typical Williamson reaction (nucleophilic substitution), which is shown in Scheme 1. The benzylation of biopolymers was generally carried out in a heterogeneous system. In this study the heterogeneous system (ethanol/distilled water) was, therefore, selected as reaction medium. The products obtained were light yellow powder and could not dissolve in distilled water, ethanol and acetone, but could dissolve dimethyl sulfoxide (DMSO), which are observed in Fig. 1. The reaction parameters such as temperature, time, molar ratios of benzylated reagent and NaOH to anhydroxylose unit in native hemicelluloses, and the medium characteristic, significantly affected the properties of the resulting biopolymers, and these influences are shown in Table 1.

The solvent used in this reaction inherently determines the the nucleophilicity of the nucleophile, this fact has become increasingly more apparent as more reactions are performed in etherification

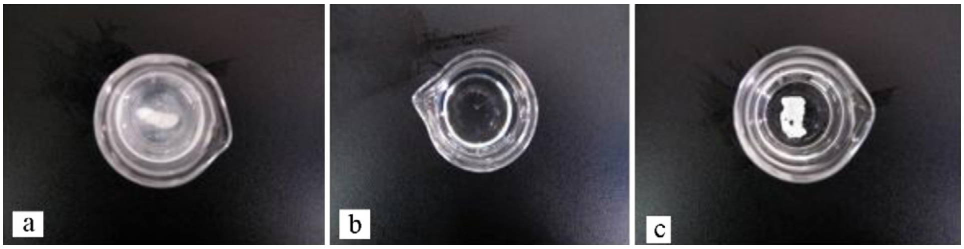


Fig. 1. The images of benzylated hemicelluloses dissolved in distilled water (a), acetone (b), and DMSO (c).

(Ren et al., 2008b). Ethanol, as a reaction medium, was cheap and the lowest toxicity over other organic solvents, which means that its safety factor is much better than other organic solvents. In addition, the alkaline treatment after delignification of wheat straw and oven drying resulted in the insolubility of hemicelluloses in cool water and decreased the reactivity of hydroxyl groups toward the benzylation. So the pretreatment with hot water was applied to facilitate the rapid conversion of the isolated hemicelluloses into a more uniform gel. Thus in this study, benzylation of hemicelluloses was therefore carried out in an ethanol/distilled water system. Solvent conditions also significantly impact the performance of a reaction with certain solvent conditions favoring one reaction mechanism over another. Table 1 (samples 1, 2, 3, and 4) represents the influence of the ethanol/distilled water volume ratio on the DS of benzylated hemicelluloses. The role of the solvent in this reaction is to provide miscibility and accessibility of the benzylated reagent to the reaction centers of the hemicelluloses chain rather than glycolate formation, and similar phenomena was reported by Togrul and Aralan (2003). Water in the heterogeneous system acts two functions. One is to dissolve hemicelluloses, and the other is to dissolve the catalyst (NaOH). So the volume ratio of ethanol to distilled water is of great importance to the reaction efficiency. Clearly, an increase of the ethanol/distilled water volume ratio from 4:1 to 6:4 resulted in an increment of DS from 0.29 to 0.34. Low amount of water in this heterogeneous system has negative influence on the diffusion of reaction reagents into the interior of the hemicelluloses particles, leading to low reaction efficiency.

Alkaline activation with sodium hydroxide is the most important step in the hemicellulosic benzylation. Table 1 (samples 4, 5, 6, and 7) shows the effect of the molar ratio of NaOH to anhydroxylose unit in hemicellulose on the DS of the products. As an increment in the molar ratio from 0.6:1 to 1.2:1 was applied, DS increased from 0.31 to 0.34. Further increasing the molar ratio, no increase in DS was achieved, which may be due to the degradation of hemicelluloses. Clearly, the similar trend in DS was also observed in the effect of reactant on DS. An increasing DS from 0.18 to 0.35 could be achieved as the molar ratio of benzylated reagent to anhydroxylose unit in hemicellulose increased from 0.5:1 to 2.0:1. This increase in DS by increment of the reactant molar ratio could be interpreted in terms of greater availability of benzyl chloride in the proximity of the hemicellulosic molecules at higher concentration.

The results of variation in reaction temperature while holding the reactant molar ratio at 2.0:1, the NaOH molar ratio at 1.2:1, the ethanol/water volume ratio of 6:4, and a reaction duration of 8 h are given in samples 10, 11, 12, and 13 (Table 1). As expected, there was an increase in the DS from 0.30 to 0.35 with the reaction temperature increasing from 50 °C to 60 °C. Conversely, further increase in the reaction temperature from 60 to 70, and to 80 °C led to a significant decrease in the DS from 0.35 to 0.17, and to 0.09, respectively. These data revealed that a temperature (of up to 60 °C) would be expected to enhance the reactant diffusion into the hemicellulosic molecules and the compatibility of the reaction ingredients. However, a much higher temperature, such as 70 or 80 °C, would result in hemicellulose degradation, so reducing the DS.

As discussed above, all the reactions described were performed for 8 h, which may not be optimal for the reaction efficiency. Therefore, variations in the reaction time and its effect on DS were studied for five different reaction periods of 4, 6, 8, 10, and 20 h,

Table 1
Benzylated hemicelluloses obtained under variation reaction condition.

No.	Volume ratio[a]	Molar ratio[b]	Molar ratio[c]	Temperature (°C)	Time (h)	DS
1	4:1	1.2:1	1.0:1	60	8	0.29
2	3:1	1.2:1	1.0:1	60	8	0.32
3	2:1	1.2:1	1.0:1	60	8	0.33
4	6:4	1.2:1	1.0:1	60	8	0.34
5	6:4	0.6:1	1.0:1	60	8	0.31
6	6:4	0.9:1	1.0:1	60	8	0.32
4	6:4	1.2:1	1.0:1	60	8	0.34
7	6:4	1.5:1	1.0:1	60	8	0.34
8	6:4	1.2:1	0.5:1	60	8	0.18
4	6:4	1.2:1	1.0:1	60	8	0.34
9	6:4	1.2:1	1.5:1	60	8	0.35
10	6:4	1.2:1	2.0:1	60	8	0.35
11	6:4	1.2:1	2.0:1	50	8	0.30
10	6:4	1.2:1	2.0:1	60	8	0.35
12	6:4	1.2:1	2.0:1	70	8	0.17
13	6:4	1.2:1	2.0:1	80	8	0.09
14	6:4	1.2:1	2.0:1	60	4	0.34
15	6:4	1.2:1	2.0:1	60	6	0.35
10	6:4	1.2:1	2.0:1	60	8	0.35
16	6:4	1.2:1	2.0:1	60	10	0.35
17	6:4	1.2:1	2.0:1	60	20	0.19

[a] The volume ratio of ethanol to distilled water.
[b] The molar ratio of NaOH to anhydroxylose unit in hemicelluloses.
[c] The molar ratio of benzylated reagent to anhydroxylose unit in hemicelluloses.

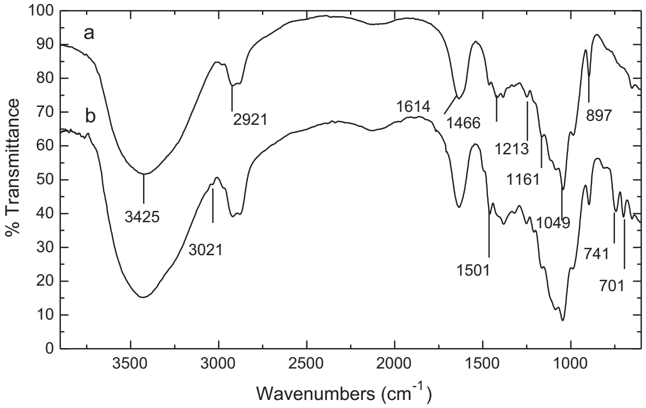


Fig. 2. FT-IR spectra of unmodified hemicelluloses (a) and benzylated hemicelluloses (b, sample 4 in Table 1).

corresponding to samples 14, 15, 10, 16, and 17 in Table 1, respectively. There was an increase in the DS with reaction time up to 6 h. Further increasing reaction time even up to 10 h, there was no increase in DS. However, as the reaction time was prolonged to 20 h, DS sharply decreased down to 0.19, which can be explained by the fact that the degradation of hemicelluloses was prevalent at long duration (Ren et al., 2008b). In view of the cost, the reaction time of 6 h was desirable.

3.2. FT-IR spectra

FT-IR spectroscopy is useful tool for identifying the structure of biopolymers since clear differences in the infrared spectra related to the intensity, shape, and location of bands (Kacurakova & Mathlouthi, 1996). Fig. 2 shows the FT-IR spectra of hemicelluloses before and after benzylation (sample 4 in Table 1). In spectrum a, the bands between 3600 cm^{-1} and 2800 cm^{-1} are due to the stretching vibrations of CH and OH, and the absorbances in the region from 1200 to 950 cm^{-1} are the C—O stretching. A sharp band at 1049 cm^{-1} is originated from typical of xylans, indicating a dominant xylan of the isolated hemicelluloses, which corresponds to the results obtained from sugar analysis. The band at 897 cm^{-1}, which corresponds to the C1 frequency or ring frequency, is characteristic of β-glycosidic linkages between the sugar units in hemicelluloses (Gupta, Madan & Bansal, 1987; Zhbankov, Andrianov, & Marchewka, 1997). The bands at 1474, 1427, 1394, and 1328 cm^{-1} represent C—H, OH or CH_2 bendings. The presence of the arabinosyl side-chains is identified by the low intensity shoulder at 1161 cm^{-1}, corresponding to the C—O—C vibration in hemicelluloses. Compared with the spectrum a, the spectrum b clearly demonstrates the remarkable changes in chemical structure caused by the introduction of benzyl groups to hemicelluloses chain. The arising intensity of aromatic moieties at the bands 3021–3580 cm^{-1} (aromatic C—H deformation) and etherifying bonds at 1049 cm^{-1} (C—O—C) was observed in spectrum b, and the bands at 1501 and 1454 cm^{-1} are due to aromatic C—C axial deformation. Furthermore, the evidence for the benzylation of hemicelluloses can be found by examining the occurrence of the presence of the bands at 741 and 701 cm^{-1} due to aromatic ring (aromatic C—H out-of-plane deformation, and aromatic C—H deformation) (Pereira, Campana Filho, & Curvelo, 1997). Hence these new bands and increasing intensity of bands actually confirms that hemicelluloses were successfully benzylated under the conditions discussed above in this study.

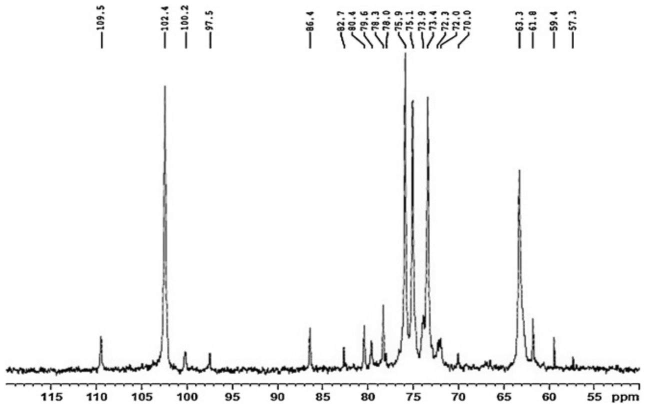


Fig. 3. ^{13}C NMR spectrum of unmodified hemicelluloses from wheat straw.

3.3. ^{13}C NMR spectra

To verify the occurrence of benzylation on hemicelluloses, ^{13}C NMR spectra of unmodified hemicelluloses and benzylated hemicelluloses (sample 4) are comparatively shown in Figs. 3 and 4. The ^{13}C NMR spectrum (Fig. 3) gives five major signals at 102.4, 75.9, 75.1, 73.4, and 63.3 ppm, corresponding to (1 → 4)-linked-β-xylan (Sun, Lawther, & Banks, 1996). The signal at 102.4 ppm corresponded to the anomeric region is a β-configuration. Signals at 109.5, 86.4, 80.4, 78.3, and 61.8 ppm originate from C-1, C-4, C-2, C-3 and C-5 of arabinofuranosyl residues linked to β-D-xylans, respectively. Such groups of arabinose signals are typical of arabinoxylan isolated from cereal straws (Sun et al., 1996). This is also in accordance with the result of FT-IR spectra analysis above. Signals at 97.5 (C-1), 82.7(C-4), 72.3(C-5), 72.0 (C-3), 70.0 (C-2), and 59.4 (—OCH_3) indicate the presence of α linked 4-*O*-MeGlcA residues (Bendahou, Dufresne, Kaddami, & Habibi, 2007). These results show that the wheat straw hemicelluloses can be structurally defined as L-arabino-(4-*O*-methyl-D-glucurono) xylan.

Comparatively, ^{13}C NMR spectrum of benzylated hemicelluloses shown in Fig. 4 indicates that two carbon signals C-3 and C-2 in xylose unit strongly shifted to higher chemical shift values ($\delta_{C\text{-}3} = 73.6$ and $\delta_{C\text{-}2} = 72.2$ ppm) due to the benzyl ether substitution. The benzylation of hemicelluloses was confirmed by the new signals in the range of 138.5–139.2 ppm (C_6H_5—) and at 128 ppm (—C=C—) (Pereira et al., 1997). More importantly, in comparison with the unmodified hemicelluloses (Fig. 3), a decrease in the intensity of the signal for C-2 at 72.2 ppm indicated that the benzylation reaction mainly occurred at C-2 position.

3.4. Thermal analysis

The effect of benzylation on the thermal properties of hemicelluloses was also studied by TGA and DTA in the temperature range from room temperature to 600 °C under nitrogen atmosphere. The

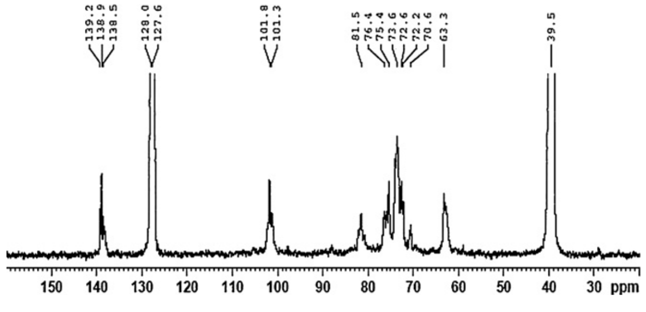


Fig. 4. ^{13}C NMR spectrum of benzylated hemicelluloses (sample 4 in Table 1).

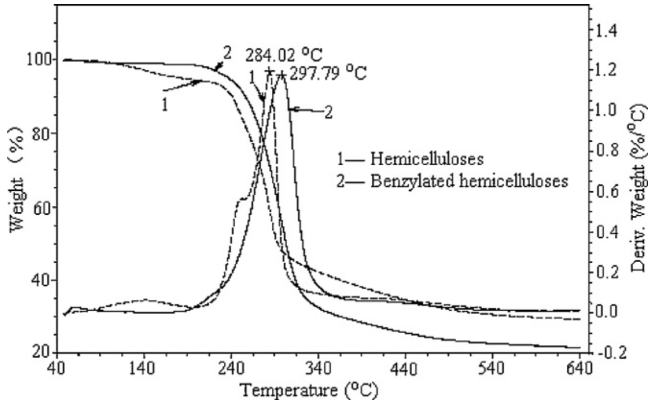


Fig. 5. TGA/DTA curves of unmodified hemicelluloses (curve 1) and benzylated hemicelluloses (curve 2, sample 4 in Table 1).

curves from the thermogravimetric analysis of benzylated hemicelluloses and isolated hemicelluloses are present in Fig. 5. Clearly, there was a noticeable weight loss (10%) beginning at 245 °C for isolated hemicelluloses and 256 °C for benzylated hemicelluloses (sample 4 in Table 1), respectively. When the weight loss arrived up to 50%, the decomposition temperature of hemicelluloses and benzylated hemicelluloses were 293 and 303 °C, respectively. The maximum decomposition rates differed, which is indicated by the $T_{\max}$ (the decomposition temperature corresponding to the maximum weight loss rate) in Fig. 5. The $T_{\max}$ was shown at 284 and 298 °C for isolated hemicelluloses and benyzlated hemicelluloses, respectively, suggesting that the thermal stability of benyzlated hemicelluloses was higher than the isolated hemicelluloses mainly due to the better thermal stability of phenyl groups. The observation about the increasing of thermal stability of benzylated hemicelluloses agreed well with the results obtained from benzylated starch (Ferreira et al., 2003).

4. Conclusion

In this study, a method to prepare hydrophobic hemicelluloses was developed by the benzylation of hemicelluloses with benzyl chloride under the presence of NaOH in an ethanol/distilled water system. By varying the reaction condition, the highest DS of benzylated hemicelluloses (0.35) was achieved at the 1.2 molar ratio of NaOH to anhydroxylose unit in hemicelluloses, the 2.0 molar ratio of benzyl chloride to anhydroxylose unit in hemicelluloses, the temperature of 60 °C, and reaction time of 6 h, in the heterogeneous system (the 6:4 volume ratio of ethanol to distilled water). FT-IR and ^{13}C NMR spectroscopies confirmed that the benzyl groups were actually grafted onto the backbone of hemicelluloses. The thermal stability of benzylated hemicelluloses was higher than that of native hemicelluloses mainly due to the introduction of benzyl groups. These features could make benzylated hemicelluloses to be potentially applied in plastics industries.

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