Enhanced hydrophobicity and thermal stability of hemicelluloses by butyrylation in [BMIM]Cl ionic liquid

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ABSTRACT

To enhance the hydrophobicity and thermal stability of hemicelluloses for the production of functional biopolymer, hemicelluloses was homogeneously butyrylated with butyryl chloride in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid using triethylamine as a neutralizer. This efficient method to prepare butyrylated hemicelluloses was confirmed by FT-IR, ^{1}H, and ^{13}C NMR spectroscopies. The results showed that the biopolymers with degrees of substitution (DS) between 0.91 and 1.89 were accessible in this completely homogeneous system by changing reaction conditions. The preferred reaction parameters that resulted in the highest DS (1.89) were as follows: 2:1 molar ratio of butyryl chloride to hydroxyl groups, 90 °C, and 120 min. The hydrophobicity and thermal stability of the prepared hemicellulosic derivatives were investigated by thermogravimetric analysis (TGA). The results indicated that the hydrophobicity of the butyrylated hemicelluloses was increased by increasing the value of DS. The thermal stability of the butyrylated hemicelluloses was increased while the derivative with a high DS value and decreased with a low DS value. The enhanced hydrophobicity and thermal stability of the butyrylated hemicelluloses with a high DS value make it beneficial for the production of functional biopolymer.

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1. Introduction

Since the late 1960s, petroleum-based materials had been broadly used, such as plastics, paints, and synthetic rubbers. In light of depletion of petroleum reserves, continuously increasing oil prices, and the growing environmental concerns, it is necessary to shift society's dependence away from petroleum to renewable biomass resources (Ragauskas et al., 2006). This growing willingness to develop new biopolymer-based materials has led to an increasing application of hemicelluloses and their derivatives (Cunha and Gandini, 2010; Gírio et al., 2010; Daus and Heinze, 2010; Daus et al., 2011).

Native hemicelluloses which are generally considered to be branched polymers composed of polysaccharides. Hemicelluloses can be converted into a variety of low molecular chemicals such as furfural (Sádaba et al., 2011), ethanol (Gírio et al., 2010), and xylitol (Delgenes et al., 1998). Hemicelluloses are also attractive as biopolymers, which can be utilized in their native or modified forms in various areas (Ebringerová, 2005). There are several disadvantages need to overcome when hemicellulosic polymers used for plastic films or coating materials (Hansen and Plackett, 2008) in large-scale, such as compatibility with the traditional plastics,

thermal stability, and lower water vapor permeability (Hansen and Plackett, 2008). Recent researchers have been interested in synthesis new hemicelluloses derivatives, such as acylated hemicelluloses (Gröndahl et al., 2003; Tserki et al., 2005), lauroylated hemicelluloses (Ren et al., 2008), oleoylated hemicelluloses (Sun et al., 2004), and carboxymethylated hemicelluloses (Petzold et al., 2005). These works are mostly focus on transferring hydroxyl groups of hemicelluloses into functional groups, which create novel opportunities to exploit the various valuable properties for previously unconceived applications. In these modified polysaccharides, the hydrophobicity, water absorption, mechanical properties, and their biodegradability depend on the degree of substitution (DS), and side-chain length (Kapusniak and Siemion, 2007). For example, the hydrophilic nature of hemicelluloses is a major constraint that limits the use of hemicellulosic polymer-based material (Fredon et al., 2002). Chemical modification, such as esterification with long-chain fatty acids, is an approach to produce thermoplastic and waterproof materials (Cunha and Gandini, 2010). Moreover, bio-based products obtained through a green chemistry approach are biodegradable (Buchanan et al., 1993; Komarek et al., 1993) and offer interesting alternatives to petrochemical plastics, depending on their satisfactory properties, such as biocompatibility and non-toxicity (Höije et al., 2005; Peng et al., 2011).

Many researchers have made their efforts to increase the DS, including finding appropriate solvents (Fort et al., 2007) and reaction reagents (Sun et al., 1999), optimization of reaction conditions

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(Ren et al., 2008), and using catalyst (Karimi and Maleki, 2003; Belmokaddem et al., 2011). Our team firstly prepared wheat straw hemicellulosic esters with butyryl chloride (BC) in a homogenous solution of *N,N*-dimethylformamide/lithium chloride and the highest DS reached up to 1.59 (Fang et al., 1999). In 2007, wheat straw hemicelluloses were successfully acetylated with acetic anhydride using iodine as a novel catalyst in 1-butyl-3-methylimidzolium chloride ([BMIM]Cl) ionic liquid and the highest DS was 1.53 (Ren et al., 2007a). The increase of the DS value of the esterified hemicelluloses was attributed to the homogenous system and the high efficiency catalyst used. However, there still seems to be a lot of room for improvement in the functionalization of hemicelluloses with a high DS value.

In the present study, in order to enhance the hydrophobicity and thermal stability of hemicelluloses for the production of functional biopolymer, hemicelluloses was homogeneously butyrylated with butyryl chloride in [BMIM]Cl using triethylamine as a neutralizer. Various reaction parameters, such as molar ratio of butyryl chloride to triethylamine and hydroxyl groups, reaction temperature, and reaction time, were optimized to prepare the butyrylated hemicelluloses with a high DS value.

2. Materials and methods

2.1. Material

Triploid of *Populus Tomentosa* Carr., 7 years old, was obtained from the experimental farm of Beijing Forestry University, China. The isolation process of hemicelluloses was carried out according to previous literatures (Li et al., 2009; Sun et al., 2001). Ionic liquid [BMIM]Cl ($\geq$99%) was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou, China. All chemicals used were of analytical or reagent grade and used directly without further purification.

2.2. Butyrylation of hemicelluloses

Homogeneous butyrylation of hemicelluloses was carried out in the ionic liquid [BMIM]Cl. In a typical run, hemicelluloses (0.33 g, 5 mmol of hydroxyl functionality in hemicelluloses) were dispersed in 10 g [BMIM]Cl in a 50 mL dried two-neck flask. The mixture was then placed into an oil bath and heated on a hot plate (IKA RCT basic, Germany) with vigorous magnetic stirring (600 rpm) at 95 °C for 1.5 h under a N_2 atmosphere. After the complete dissolution of hemicelluloses in [BMIM]Cl, the dissolved hemicelluloses was cooled to about 80 °C. Triethylamine was added to the cooled dissolved hemicelluloses under vigorous magnetic stirring (600 rpm) for 5 min, followed by corresponding amount of butyryl chloride (Fig. 1). Triethylamine was used as a neutralizer to counteract the HCl generated during the butyrylation process. The mixture was then placed into the oil bath at different reaction temperature and time according to the conditions listed in Table 1. At the end of the reaction, ethanol (50 mL) was slowly poured into the two-neck flask with stirring (600 rpm). After completely dispersed, water (50 mL) was added to induce precipitate. The precipitate was separated
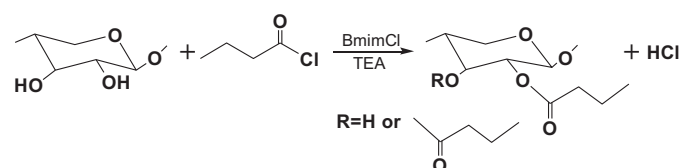

Fig. 1. Reaction of hemicelluloses OH groups with butyryl chloride.

Table 1
Degree of substitution (DS) of butyrylated hemicelluloses in the ionic liquid [BMIM]Cl.

No.	TEA/BC[a]	BC/OH[b]	Reaction temperature (°C)	Reaction time (min)	DS (%)
H_1	1:1	1:1	90	60	0.91
H_2	1:1	2:1	90	30	1.73
H_3	1:1	2:1	90	120	1.89
H_4	1:1	2:1	80	60	1.52
H_5	1:1	2:1	90	60	1.84
H_6	1:1	2:1	100	60	1.76
H_7	1:1	3:1	90	60	1.32
H_8	2:1	2:1	90	60	1.86

[a] Molar ratio of triethylamine (TEA) to butyl chloride (BC).
[b] Molar ratio of butyl chloride to hydroxyl groups (OH) in hemicelluloses.

from the solution by filtration and purified by washing with 50 mL 50% ethanol (v/v). The obtained product was then freeze-dried.

2.3. Determination of DS

The degree of hydroxyl substitution was determined by ^{1}H NMR (not shown) and Eq. (1) (Gröndahl et al., 2003; Kapusniak and Siemion, 2007). 5 mg butyrylated hemicelluloses were dissolved in 0.5 mL CDCl$_3$.

$$DS = \frac{[0.87 \times (I_{methyl}/m)]}{I_{xylan}/n} \qquad (1)$$

where 0.87 is a coefficient calculated from the results of sugar composition of the isolated hemicelluloses; I_{methyl} is the intensity of the peaks due to three protons of the terminal methyl groups in butyryl chloride chain; m is the number of protons from the methyl protons ($m = 3$); I_{xylan} is the signal intensity of six protons of the xylose unit; n is the number of protons from the xylose unit ($n = 6$).

2.4. Characterization of the native hemicelluloses and butyrylated hemicelluloses

The monosaccharides of hemicelluloses were determined by hydrolysis with dilute sulfuric acid according to the procedure described in a previous literature (Yuan et al., 2010b). The FT-IR spectra and thermal stability of the samples was performed using a Tensor 27 FT-IR (Germany) spectrophotometer and thermogravimetric analysis (STA449F3, NETZSCH Corporation, Germany) according to a previous literature, respectively (Yuan et al., 2010a). The ^{13}C NMR spectra of the samples were recorded at 25 °C on a Bruker AVIII 400 MHz spectrometer (Germany). The native hemicelluloses were dissolved in D$_2$O (δH 4.70 ppm) and the butyrylated hemicelluloses were dissolved in DMSO-d_6. The central solvent (DMSO-d_6) peak was used as an internal chemical shift reference point (δC 39.5; δH 2.49 ppm).

3. Results and discussion

3.1. Sugar composition of hemicelluloses

The sugar analysis showed the following sugar composition (relative percent, w/w): 86.3% xylose, 1.0% arabinose, 5.4% glucose, 1.6% galactose, 1.7% rhamnose. The content of glucuronic acid (GlcA) and galacturonic acid (GalA) were 3.7% and 0.4%, respectively. Though there was only 5.4% glucose in the hemicelluloses, the three hydroxyl groups which are linked on its backbone should be considered. Taking this factor into consideration, a coefficient 0.87 was multiplied to Eq. (1).