



Tough and multi-responsive hydrogel based on the hemicellulose from the spent liquor of viscose process

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ABSTRACT

The hemicellulose isolated from the spent liquor of a viscose process was successfully utilized to prepare hydrogels by the graft copolymerization of acrylic acid (AA) with hemicellulose. The hemicellulose and prepared hydrogel were characterized by Fourier-transform infrared (FT-IR), scanning electron microscopy (SEM), and solid-state nuclear magnetic resonance (¹³C NMR). Under the optimum preparation conditions, the highest compressive strength and strain at break of the resultant hydrogel were 105.1 ± 12.9 kPa and 34.8%, respectively. Furthermore, the maximum equilibrium swelling degree of prepared hydrogel was 192. Also, the hydrogel could rapidly respond to pH, salt and ethanol. Taken together, the prepared hydrogels had great mechanical and multi-responsive properties. Thus, the prepared hydrogels had a great potential application in drug release, water treatment and cell immobilization. In addition, the utilization of alkaline extracted hemicellulose from the viscose fiber factory has huge market potential and economic benefits.

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1. Introduction

In recent years, polysaccharide (e.g. cellulose, hemicellulose, chitosan, alginate, agar etc.) based intelligent hydrogels have been widely studied because of their biodegradability, biocompatibility, eco-friendliness, low cost and biological functions [1–5]. Smart hydrogels could be produced by incorporating different groups into the networks and they could respond to environmental stimulus, such as organic solvent, salt, pH, temperature and magnetic field [6–9]. And they could be applied in many fields, such as sensors, drug release, tissue engineering and other fields [10–13]. Among these natural polysaccharides, hemicellulose is particularly interesting as green raw materials.

Hemicellulose, the second most abundant renewable natural polysaccharides compared to cellulose, exists widely in plants [14,15]. The presence of hydroxyl and carboxylic groups on the

chains of hemicellulose makes them suitable for chemical or enzymatic modification, and hemicellulose has excellent hydrophilicity, biodegradability and biocompatibility [16–18]. Therefore, hemicellulose has become a very promising raw material for preparing smart materials. In 1998, Gabriellii and Gatenholm [19] prepared hydrogel by simply mixing birch wood hemicellulose with chitosan in acidic solution. Since 2011, Peng et al. [20] successfully grafted acrylic acid (AA) monomer onto hemicellulose, a few hemicellulose based multi-responsive hydrogels had been studied [6,9,21–23]. They isolated hemicellulose from different raw materials, such as spruce, bamboo, reed and wheat straw, by a similar method. However, the isolated hemicellulose had many side chains and high polydispersity (~10). Among these studies, the synthesized hydrogels had poor compressive strength ranging from 10 to 50 kPa, which severely limited its practical applications. In order to overcome the mechanical properties, many effects have been devoted to fabricate tough hydrogel, such as nano-composite hydrogels (e.g., enhanced by nano-cellulose, or nano-chitosan), and the use of freeze/thaw technique, but the multi-responsive properties were weakened or lost [24–27]. Therefore, how to prepare tough hemicellulose-hydrogels without losing of multi-responsive needs to be addressed.

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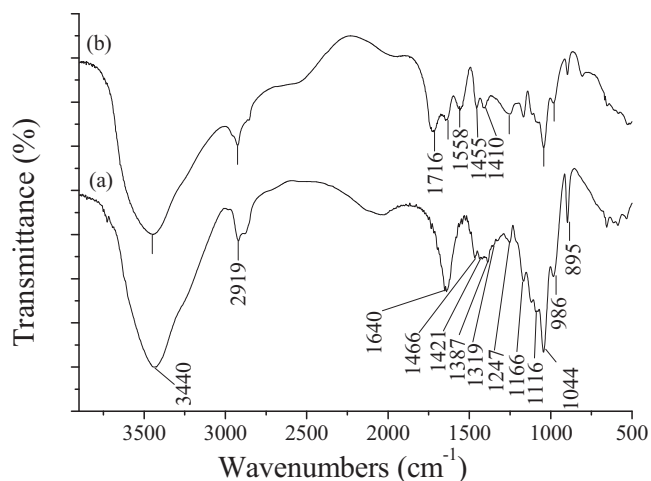


Fig. 1. FT-IR spectra of (a) alkaline extracted hemicellulose and (b) hydrogel sample 3 in Table 1.

With the rising prices of cotton pulp, many viscose fiber mills produce fibers using chemical pulp instead of cotton pulp. But, there was still remained hemicellulose in chemical pulp and it was need to be removed before using. So, as roughly calculated, about hundreds of thousands of tons waste liquor enriched with hemicellulose was produced each year in a viscose fiber mill with the annual production capacity of 50000 tons. Usually, it was abandoned or burned to generate heat and electricity. Hence, it's of significance to make better use of the alkaline extracted hemicellulose. In our previous work [28], the hemicellulose from spent liquor was isolated and characterized. The results showed that the hemicellulose contained 90.13 wt% xylan, 8.19 wt% glucan, 1.31 wt% lignin and 0.44 wt% mannan. Furthermore, the structure of isolated xyans was confirmed to have a linear structure with few branches attached by the method of FT-IR, GPC, ^1H and ^{13}C DEPTQ-NMR. Also, it had uniform (M_w (15910 g/mol)/ M_n (11920 g/mol)) = 1.33) molecular weight.

Herein, we synthesized the tough and multi-responsive hydrogels using the isolated hemicellulose from the spent liquor of a viscose process by introducing the acrylic acid (AA) monomers into hemicellulose backbone. Then, the properties (mechanical strength, and responses to pH, ionic strength, and ethanol) of the prepared hydrogel were systematically characterized. This work is of crucial importance to make better use of the waste aqueous for viscos production from the environmental and economic points of view.

2. Materials and methods

2.1. Materials

The alkaline extracted hemicellulose waste liquor was obtained from a viscose fiber factory of Tangshan Sanyou Chemical Industry Co. and the extraction process was illustrated clearly in our previous work [28]. Acrylic acid (AA), N,N-Methylene-bis(acrylamide) (MBA), potassium persulfate (KPS), N,N,N',N'-Tetramethylethylenediamine (TMEDA), sodium hydroxide (NaOH), was bought from Sinopharm Chemical Reagent Co., Ltd. All other chemicals and reagents were analytical grade and used without further purification.

2.2. Purification of hemicelluloses

The waste hemicellulose solution needs to be purified to obtain pure hemicellulose before use [28]. The waste liquor was mixed

Table 1
Stress, modulus and strain at break of hydrogels.

Sample	AA/HC ^a (g/g)	NaOH/HC ^b (g/g)	Stress (kPa)	Modulus (kPa)	Strain at break (%)
1	4	1	39.9 ± 3.1	23.4 ± 3.8	16.1 ± 0.3
2	6	1	40.6 ± 3.3	51.6 ± 5.1	26.3 ± 0.8
3	8	1	104.3 ± 12.5	72.0 ± 6.2	34.2 ± 1.2
4	10	1	59.1 ± 6.7	30.2 ± 3.2	26.7 ± 0.9
5	12	1	37.6 ± 2.8	29.8 ± 1.7	24.2 ± 0.6
6	8	0.5	92.7 ± 10.8	78.4 ± 6.8	23.6 ± 0.5
7	8	1	105.1 ± 12.9	71.9 ± 5.9	34.8 ± 1.3
8	8	1.5	58.5 ± 5.4	52.5 ± 5.2	26.9 ± 0.8
9	8	2	50.4 ± 5.1	45.1 ± 4.6	23.8 ± 0.6

^a Acrylic acid/hemicelluloses ratio (by weight).

^b Sodium hydroxide/hemicellulose ratio (by weight).

with three times volumes of dehydrated ethanol (100%) to precipitate the hemicelluloses and then the mixture was centrifuged at 8500 rpm for 10 min. Later, three times volumes of water were added to the above precipitate and the mixture was centrifuged at 8500 rpm for 20 min. The above separation and washing step was repeated until the washing solution was neutral.

2.3. Preparation of hydrogel

The hydrogel was formed in alkaline condition by free radical copolymerization [21]. MBA works as cross-linker and KPS/TMEDA constitute a redox initiator system. About 0.5 g hemicellulose and 0.5 g sodium hydroxide was put into 15 mL distilled water in a three-necked flask. Then the bottle was put into oil bath at 85 °C and stirred until a clear homogeneous hemicellulose solution obtained before the system was cooled to 50 °C. The above-mentioned hemicellulose solution was de-aired for 20 min with high purity nitrogen to exclude the oxygen. After that, 0.05 g KPS and 50 μL TMEDA was added in the de-aired solution to generate radicals for 10 min. Later, amount of AA was dropped into the solution slowly, and 5 min later, cross-linker MBA was added to the above solution. Then the reaction proceeded at 50 °C for 1 h with magnetic stirring under nitrogen gas atmosphere. After that, the resulting solution was placed at room temperature for 3.5 h without stirring to form chemically cross-linked hydrogel completely. The fresh hydrogel was immersed into distilled water for 12 h to exclude the unreacted agents, 1 M NaOH for 24 h to change COOH into COO^- , and distilled water for 12 h to exclude the NaOH and produced NaCl, respectively, with changing the distilled water at least four times. Later, the swollen hydrogels were dried to a constant mass at 40 °C. And total 9 hydrogel samples were prepared, as shown in Table 1.

2.4. Characterizations of hemicellulose and hydrogel

The molecular structure of hydrogel and hemicellulose samples were confirmed in the dry state using Fourier transform infrared spectrophotometer (FT-IR, Nicolet iN10). The cross-section morphology of samples was investigated by scanning electron microscopy (SEM, Hitachi S-4800). The swollen hydrogel was immersed in the liquid Nitrogen, freeze dried and coated a gold layer before SEM analysis. Solid-state ^{13}C NMR spectra of native hemicellulose and prepared hydrogel were obtained using a Bruker Avance 400 MHz spectrometer operating for carbon.

2.5. Mechanical testing

The compressive strength and elasticity of the hydrogel were tested using CMT6503 electromechanical material testing machine (ShenZhen SANS, China). The hydrogel at equilibrium swelling state

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