

# 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 (<sup>13</sup>C NMR). Under the optimum preparation conditions, the highest compressive strength and strain at break of the resultant hydrogel were  $105.1 \pm 12.9$  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

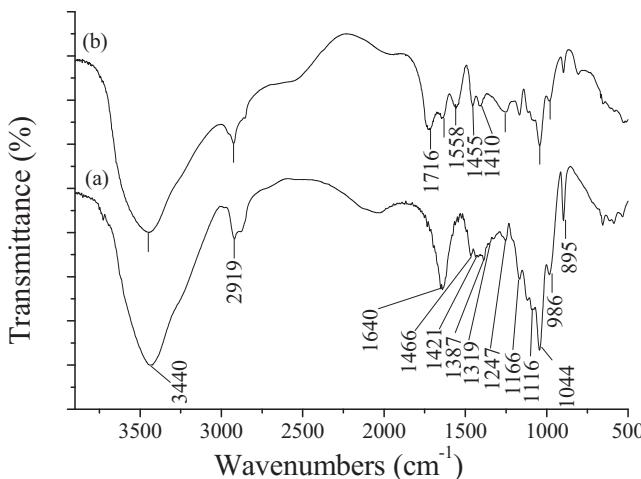
In recent years, polysaccharide (e.g. cellulose, hemicellulose, chitosan, alginate, agar etc.) based intelligent hydrogels have been widely studied because of theirs biodegradability, biocompatibility, eco-friendliness, low cost and biological functions [1–5]. Smart hydrogels could be produced by incorporating 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, Gabrielii 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 xyloans was confirmed to have a linear structure with few branches attached by the method of FT-IR, GPC, <sup>1</sup>H and <sup>13</sup>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 viscose 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 <sup>a</sup> (g/g)	NaOH/HC <sup>b</sup> (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

<sup>a</sup> Acrylic acid/hemicelluloses ratio (by weight).

<sup>b</sup> Sodium hydroxide/hemicellulose ratio (by weight).

with three times volumes of dehydrated ethanol (100%) to precipitate the hemicelluloses and then the mixture was centrifugalized at 8500 rpm for 10 min. Later, three times volumes of water were added to the above precipitate and the mixture was centrifugalized 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

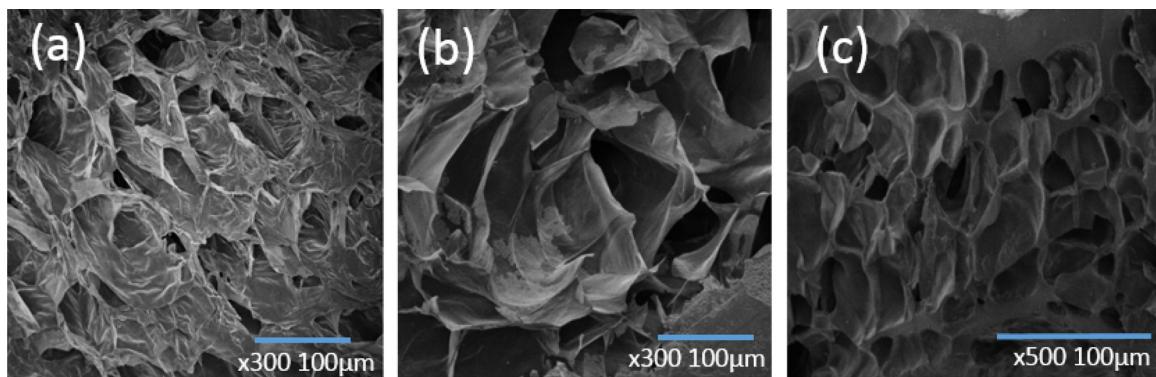
The hydrogel was formed in alkaline condition by free radical copolymerization [21]. MBA works as cross-linker and KPS/TMEDA constitute a redox initiator system. About 0.5 g hemicellulose and 0.5 g sodium hydroxide was put into 15 mL distilled water in a three-necked flask. Then the bottle was put into 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<sup>-</sup>, 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 <sup>13</sup>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



**Fig. 2.** SEM images of cross-sections of swollen samples: (a) sample 1; (b) sample 3; (c) sample 9.

was cut into the cube with dimensions of  $10 \times 10 \times 10 \text{ mm}^3$  after removal of the surface water with filter paper. Then the samples were tested at room temperature with a cross head speed of 2 mm/min. All of the tests were carried out in five times and the average was reported.

#### 2.6. Swelling behaviors of hydrogel in distilled water

The swelling behaviors of hydrogels in distilled water were determined using gravimetric method. The pre-weighted dry hydrogels were immersed into enough distilled water to uptake water to reach equilibrium swelling state. The mass of swollen hydrogel was weighted and the swelling ratio (SR) was calculated by the following equation.

$$\text{SR} = \frac{m_1 - m_0}{m_0} \quad (1)$$

where  $m_1$  and  $m_0$  are the masses of swollen and pre-weighted dry hydrogel, respectively

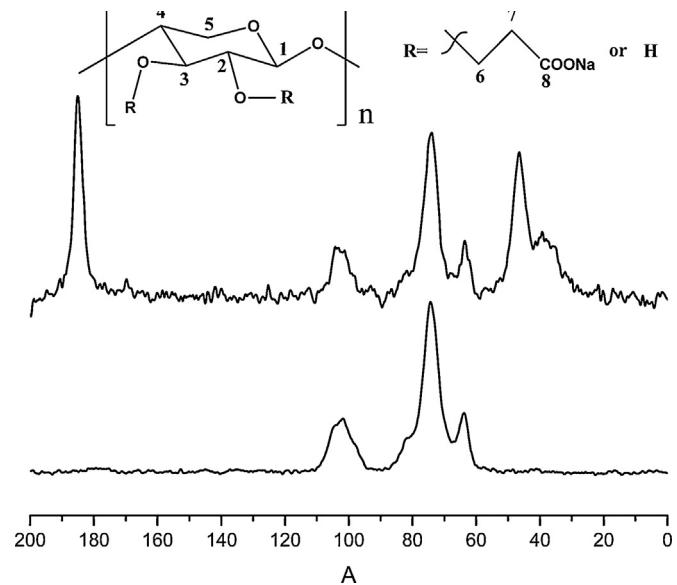
#### 2.7. Response behaviors of hydrogel to pH, salt and ethanol

Various pH values (2–10) phosphate buffer solutions were prepared and the ionic strengths were adjusted to 0.1 M using NaCl. NaCl solution was carefully prepared at different concentrations (0.005, 0.01, 0.05, 0.1, 0.5, and 1.0 M). Response behaviors of hydrogel to pH, ionic strengths and ethanol were evaluated by swelling ratio.

### 3. Results and discussion

#### 3.1. FT-IR analysis

**Fig. 1** presents the FT-IR spectra of native hemicellulose and hydrogel sample 3 (**Table 1**). In **Fig. 1a**, the adsorption peaks at 3442, 2923, 1630, 1467, 1256, 1044 and 901  $\text{cm}^{-1}$  are the characteristic adsorptions of hemicellulose polymer, which are similar as the previously reported data [29]. The absorption peaks at 3440 and 2919  $\text{cm}^{-1}$  was assigned to the stretching of the O—H groups and C—H of methyl and methylene groups, respectively. A band at 1640  $\text{cm}^{-1}$  was linked to the water adsorption and the sharp adsorption peak at 1044  $\text{cm}^{-1}$  was the characteristic absorption of xylan. The very small band at 1466  $\text{cm}^{-1}$  was indicative of a trace amount of lignin [30]. A small sharp band at 895  $\text{cm}^{-1}$  was the signal of  $\beta$ -glucosidic linkages between the sugar units, indicating that the xylose were linked by  $\beta$ -form bonds [20]. In **Fig. 1b**, there were a few new peaks at 1710, 1568 and 1454  $\text{cm}^{-1}$ , and the new peaks could be attributed to the stretching vibration of C=O, asymmetrical stretching vibration, and symmetrical stretching vibration of



**Fig. 3.** CP/MAS  $^{13}\text{C}$  NMR spectra of (a) alkaline extracted hemicellulose and (b) hydrogel sample 7 in **Table 1**.

COO<sup>−</sup>, respectively, indicating the presence of COO<sup>−</sup> groups in the hydrogel network [25].

#### 3.2. SEM analysis

The swollen hydrogel samples (samples 1, 3, 9 in **Table 1**) were freeze-dried and the cross sections were characterized by SEM. The images (**Fig. 2**) indicate that all the swollen hydrogels had macroporous structure. Compared to **Fig. 2a** (sample 1) and **Fig. 2b** (sample 3), **Fig. 2c** (sample 9) had the smallest network pores, which was consistent with the lowest swelling ratio. This was probably because more sodium ions incorporated with COO<sup>−</sup> in the network as NaOH concentration increased, thus reducing the electrostatic repulsion and resulting in the smaller pore structure [31]. The **Fig. 2b** had the largest pore size as well as the highest swelling ratio. In a word, the swelling ratio of hydrogels in distilled water was consistent with the size of the pore structure.

#### 3.3. Solid-state $^{13}\text{C}$ NMR spectra

Besides the FT-IR analysis, the additional and complementary information on the structure of hemicellulose and hydrogel was obtained using solid state  $^{13}\text{C}$  NMR. As can be seen from **Fig. 3a**, the carbon signals of hemicellulose arranged from 60 to 110 ppm mostly. The absence signals at 20 and 110–160 ppm implied that

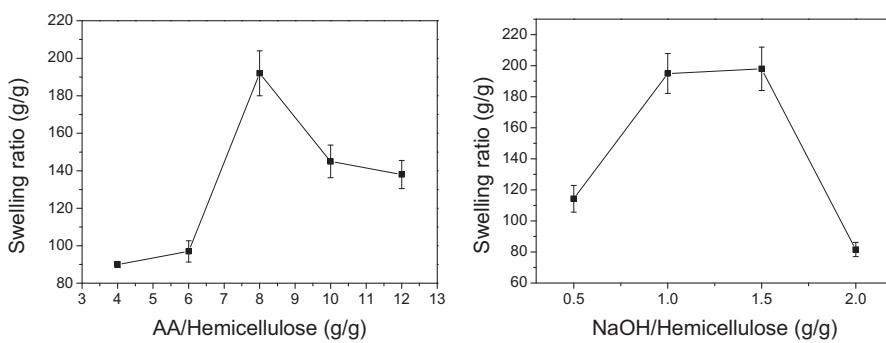


Fig. 4. Effects of AA and NaOH content on the swelling ratio of tough hydrogel in distilled water.

few acetyl groups and lignin were attached to the backbone of hemicellulose, which was agreement with our published results confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  DEPTQ-NMR [28]. The peak around 20 ppm was assigned to the  $-\text{CH}_3$  of the acetyl group and the peaks around 110–160 ppm were assigned to the carbon atoms on the benzene ring of the lignin [29]. Compared to hemicellulose spectra, hydrogel spectra (Fig. 3b) have 3 new more signals. As reported, the signals at around 185 ppm arise from the carboxylic carbons of  $\text{COONa}$ , and the signals at around 46 and 41 ppm were assigned to C-6, 7, respectively [29]. The hydrogel spectra showed that the  $\text{COONa}$  from AA was actually existed in networks and the result was in agreement with the result of FT-IR analysis (Fig. 1).

### 3.4. Compressive strength

The mechanical properties of intelligent hydrogels are important parameters, as they can limit hydrogels' application. The strain-stress data is shown in Table 1. Apparently, the stress of sample 3 and sample 7 can reach  $105.1 \pm 12.9$  kPa, which is 2 times higher than other samples. But, under the same chemical composition, the reported hemicellulose-hydrogel in literature was too weak and hard to handle [20]. When the AA content increased from 4:1 to 8:1, the compressive strength increased from  $39.9 \pm 3.1$  to  $104.3 \pm 12.5$  kPa, which was due to the higher crosslink density [27]. A highly cross-linked structure could prevent water release from the hydrogel during the stress testing and the water worked as an incompressible fluid to resist compression. When the AA content was higher than 8:1, the stress decreased abruptly from  $104.3 \pm 12.5$  to  $37.6 \pm 2.8$  kPa. The remaining liquor in reaction vessel increased as the AA content increased from 10:1 to 12:1 after the gelation process, resulting in incomplete reaction. These results differed from those reported by Peng et al. [20], who suggested that the stress increased as the AA content increased.

In the present reaction system, it was found that hemicellulose could only be dissolved in alkaline solution when NaOH/hemicellulose ratio was higher than 0.5. Therefore, in the preparation of the sample 6 the reaction was inhomogeneous, resulting in the weak formation of networks and swelling ratio. Thus, sample 6 possessed a relatively lower compressive strength of  $92.7 \pm 10.8$  kPa compared to sample 7. The stress of sample 8 and sample 9 was  $58.5 \pm 5.4$  and  $50.4 \pm 5.1$  kPa, respectively, which indicated that an over high NaOH/hemicellulose ratio also resulted in the lower compressive strength. The results might be attributed to the low molecular weight because of the degradation of hemicellulose at high NaOH concentration. Therefore, the compressive strength decreased.

The strength of all samples ranged from  $39.9 \pm 3.1$  to  $105.1 \pm 12.9$  kPa (Table 1). Under the optional conditions (AA/hemicellulose 1:4, NaOH/hemicellulose 1:1), the highest compressive strength could reach to  $105.1 \pm 12.9$  kPa. Under comparable conditions, the mechanical strength of the hydrogel

Table 2

Comparison of compressive strength of hemicellulose hydrogel from different raw material.

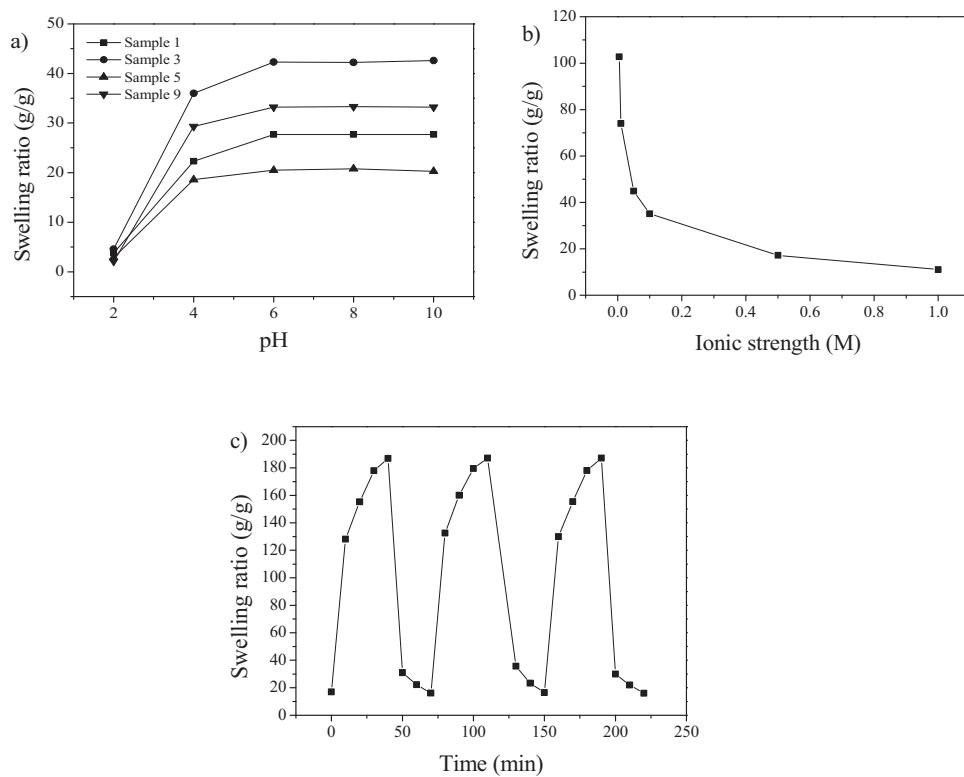
Raw Material	Compressive strength (kpa)	Reference
Wheat straw	3–10	Sun et al. [21]
Bamboo	8–55	Peng et al. [23]
Bamboo waste liquor from viscose process	Too weak	Peng et al. [20]
waste liquor from viscose process	40–105	Our work

prepared in this study was notably higher than that of multi-responsive hemicellulose hydrogel reported previously (Table 2). In literature [20,21,23], the isolation method of hemicellulose was similar but with different raw materials. And the reported hemicellulose had many side-chains and high polydispersity (~10) compared to that of hemicellulose isolated from waste liquor. In this study, the hemicellulose had special structure, which was confirmed that the xylans had the linear structure in hemicellulose with few branches. Besides, the isolated hemicellulose had a uniform molecular weight (polydispersity = 1.33). Thus, the above two characteristics of the hemicellulose material might be the key factors, causing the higher mechanical properties.

### 3.5. Swelling ratio in distilled water

The swelling ratio is an important parameter and the water uptake of hydrogels in their equilibrium swollen state is shown in Fig. 4. AA and NaOH content on the swelling ratio of hydrogel were studied, respectively. The swelling ratio increased from 90 to 192 when the AA/Hemicellulose ratio increased from 4:1 to 8:1. This is because as the AA content increased, more and more hydrophilic groups were grafted onto the hemicellulose, which could generate higher electrostatic repulsion from  $\text{COO}^-$  and expand its network to uptake much water. This results was similar to the results reported by Kipcak et al. [32]. Whereas, when the AA content was higher 8:1, the swelling ratio decreased to 136. It was probably because of the incomplete copolymerization reaction. Therefore, the suitable AA content was 8:1 in this reaction system.

The effect of NaOH concentration on swelling ratio was also investigated. Increasing the concentration of NaOH, the swelling ratio increased from 113 to 196 then decreased to 83 quickly. Notably, sample 6 had a relatively lower swelling ratio compared to sample 7 because of the inhomogeneous reaction. The neutralization degree of AA increased as the dosage of NaOH increased, resulting in the enhancement of electrostatic repulsion, which was helpful to liquid absorbency [7]. However, the swelling ratio decreased sharply when the NaOH/Hemicellulose was over 1.5. This might be because of the incorporation of  $\text{Na}^+$  with  $\text{COO}^-$ , which could decrease the electrostatic repulsion and form small pores (Fig. 2c), resulting in the low absorption capacity. Although, the swelling ratio of sample 8 was slightly higher than that of sample



**Fig. 5.** The responsive properties of sample 1, 3, 5, 9 to (a) pH, all the ionic strength of buffer solution was adjust to 0.1 M using NaCl, (b) sample 3 to salt and (c) sample 3 to ethanol.

7. The press strength of sample 7 was higher than sample 8. From a mechanical properties perspective, we chose sample 7 as the best sample. Taken together, 1:1 was the optimal dosage of NaOH based on the dry weight of hemicellulose in this reaction system.

### 3.6. Response behaviors to pH, salt and ethanol

The responsive properties of prepared hydrogel to pH, salt and ethanol were characterized and the results are shown in Fig. 5. The pH response is an important parameter for multi-response hydrogel. As can be seen from Fig. 5a, the hydrogel maintained a shrinking state at pH 2 and the network rapidly expanded as the pH value increased. This was because under acid condition (pH 2), most of the COOH were unionized and resulted in little electrostatic repulsion. When the pH value was higher than 2, the swelling ratio increased sharply. Because the COOH groups dissociated into  $\text{COO}^-$ , resulting in the strong electrostatic repulsion and generating the expand network [9]. In this case, the content of carboxyl groups in the hydrogels would affect the swelling ratio. A higher AA content (samples 1, 3) could result in a more ion-sable carboxyl group in the hydrogels and in a higher swelling ratio of the hydrogels under the same pH [20]. Furthermore, with the increase of AA content (samples 3, 5), the swelling ratio decreased under the same pH due to the incomplete copolymerization reaction. Also, a higher NaOH concentration (samples 3, 9) would resulted in lower swelling ratio due to the degradation of hemicellulose. All of the results showed that the swelling ratio of different samples in buffer solution was consistent with that in distilled water. As shown in Fig. 5b, the swelling ratio decreased as the ionic strength increased and then reached a relatively low level. As we all know, the hydrogel could uptake water because of the presence of osmotic pressure between of the internal and outside of the hydrogel. Thus, increasing the ionic strength of solution could lead to the lower osmotic pressure and decrease the absorption capacity. Besides,

the increasing concentration of  $\text{Na}^+$  could cooperate with  $\text{COO}^-$  and decreased electrostatic repulsion inside the hydrogel. Both of two factors effected its swelling ratio as the increase of ionic strength. The response of hydrogel to ethanol was carried out and it exhibited good recycling properties (Fig. 5c). When the swollen hydrogel was immersed into ethanol, it shrank quickly to a relative low swelling ratio. The water could be extracted from the network in ethanol because ethanol had lower polarity and could interact easily with carboxyl groups of the hydrogel network [33]. Once it was immersed into distilled water, the shrinkage hydrogel absorbed water and expanded quickly, which was similar as reported in literature [20].

Based on the results obtained, the prepared hydrogel showed excellent mechanical properties and multi-response properties, having a great potential application in the biomedical field including in controlled drug release, cell immobilization and waste water treatment. The better use of hemicellulose derived from spent liquor of viscose process provides a good way for viscose fiber mill to treat hemicellulose waste liquor and produce high-valuable products.

## 4. Conclusions

The waste liquor from viscose process was successfully used to prepare multi-responsive hydrogel and the prepared hydrogel exhibited high mechanical properties than the ones reported. Under optimum conditions, the highest compressive strength of prepared hydrogels could reach to  $105.1 \pm 12.9$  kPa, which was about 3 times stronger than conventional hemicellulose-based pH sensitivity hydrogel. This phenomenon could probably be ascribed to the unique structure of isolated hemicellulose, including linear structure with few side chains and uniform molecular weight ( $\text{PD} = 1.33$ ). Moreover, the resultant hydrogel also presented the good responsive properties to pH, salt and ethanol.

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