

Synthesis and characterization of super-absorbent hydrogels based on hemicellulose

Jian Zhang,¹ Huining Xiao,² Na Li,¹ Qingwei Ping,¹ Yi Zhang³

¹Liaoning Key Laboratory of Pulp and Paper Engineering, Dalian Polytechnic University, Dalian, 116034, China

²Department of Chemical Engineering, University of New Brunswick, Fredericton New Brunswick E3B 5A3, Canada

³School of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, China

Correspondence to: H. Xiao (E-mail: hxiao@unb.ca)

ABSTRACT: A kind of novel hemicellulose-based hydrogel with excellent water absorbency was synthesized by the graft copolymerization of acrylic acid (AA), acrylic amide (AM) with hemicellulose. The various factors that influenced the water absorbency of the modified hemicellulose were studied, including AA content, hemicellulose content, neutralization degree of AA, and weight ratio (to monomer) of cross-linker and initiator. The optimal conditions were found as follows: $m(\text{AA}) : m(\text{AM}) : m(\text{hemicellulose}) = 15 : 3.5 : 1$, the neutralization degree of AA was 75%, and weight ratio (to monomers) of the cross-linker and the initiator was 0.03% and 1.0%, respectively. The maximum absorbencies toward distilled water and 0.9 wt % NaCl solution were 1128 g/g and 132 g/g, respectively. The characteristics of the hydrogels were also investigated by Fourier Transform InfraRed (FT-IR), scanning electron microscope (SEM), and atomic force microscope (AFM). The results indicated that the undulant surface and broad network structure offer the hydrogels excellent water absorbency. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42441.

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INTRODUCTION

Hydrogels are cross-linked networks of hydrophilic polymers that are capable of retaining considerable amounts of water or biological fluids without disintegration.¹ Super-absorbent hydrogels are new functional polymer materials, which can absorb a large amount of water, where the weight can reach several hundred times its own weight and have excellent water retention even under some pressure.² Moreover different functionalities can be incorporated in the physical or chemical cross-linked network to produce smart hydrogels.³ These hydrogels have exhibited potential for application in many fields such as agriculture,⁴ hygienic products,⁵ biotechnology,⁶ drug delivery,⁷ environmental protection,⁸ and numerous other applications.

The desired features of super-absorbent hydrogels are high swelling capacity. Most of the traditional water absorbing materials, such as acrylic acid (AA) and acrylamide, have been used for preparing super-absorbent hydrogels. About 90% of super-absorbents are used in disposable products; and most of them are disposed of by landfills or by incineration.⁹ Therefore, there is an environmental problem with non-biodegradable super-absorbent hydrogels.¹⁰ Meanwhile the synthetic polymer-based super-absorbent has low absorption rate under the high concentration of electrolyte, undesirable water-keeping capacity

and high cost.² Considerable attention has been paid to the naturally available resources to address the problems mentioned above. The natural resource-based absorbent has good commercial and environmental value with the advantage of low cost, renewable, and biodegradable for deriving super-absorbent hydrogels. Some kinds of natural polysaccharides material, such as starch,¹¹ cellulose,¹² wheat straw,¹³ and chitosan,¹⁴ have been widely utilized for preparing super-absorbent hydrogels owing to their eco-friendliness, biodegradability, and abundant sources.

Hemicelluloses are commonly defined as non-cellulose cell wall heterogeneous polysaccharides, composed of xylan, mannan, beta-glucan, and xyloglucan. Hemicellulose polysaccharides have been shown to have interesting properties and are promising as cheap and green constituents in films,¹⁵ hydrogels,¹⁶ food additives and emulsifiers,¹⁷ binders in paper making,¹⁸ wound dressings,¹⁹ and bio-based fuels.²⁰ Thus, increasing research activities have been directed to prepare super-absorbent hydrogels based on hemicellulose for various applications. Hemicelluloses have been used as skeletal material, on which AA and acrylamide can graft so as to form super-absorbent hydrogels.¹

Recently, some progress has been made in this field, such as hydrogels based on hemicellulose and chitosan in acidic

conditions.²¹ However there were few studies on the preparation of hydrogels base on hemicellulose with excellent water absorbability. In this work, a novel super-absorbent hydrogel containing hemicellulose with high swelling capacity was synthesized in aqueous solution via grafting polymerization. Apart from various influencing factors, the formation mechanism of hydrogels, and the swelling properties were systematically investigated.

EXPERIMENTAL

Materials

Hemicellulose used in this work was the one isolated from prehydrolysis liquor (PHL) of the kraft-based dissolving pulp production process.²² The sugar composition (relative weight percent, w/w) in hemicellulose was as follows: 45.89% xylose, 41.10% glucose, 7.21% galactose, 5.29% mannose, 0.29% arabinose, and 0.23% rhamnose. All chemicals and reagents used for experiments and analysis were analytical grade, purchased from Sigma chemical reagent Co., Canada. Acrylic acid (AA) was purified prior to use whereas the others were used without further purification.

Preparation of Super-Absorbent Hydrogels Based on Hemicellulose

A certain amount of acrylic acid (AA, 6–18 g) was neutralized with 40 mL of NaOH solution (11.9%, 12.7%, 13.5%, 14.3%, and 15.0%) in a glass beaker under an ice bath condition. Hemicellulose (0.5–2.5 g) was dispersed in 30 mL of distilled water with a magnetic stirring at 85°C for 60 min before the solution was cooled to room temperature. Then the hemicellulose dispersion and 3.5 g of acrylamide were added to the above partial neutralized AA solution by magnetic stirring for 30 min at room temperature. The crosslinking agent *N,N*-methylenebisacrylamide (MBA, 0.002–0.02 g) was added to the above mixed solution by magnetic stirring for 10 min. Ammonium persulfate (APS, 0.1–1 g) and sodium hydrogen sulfite (NaHSO₃, 0.1–1 g) ($n_{\text{Aps}} : n_{\text{NaHSO}_3} = 1 : 1$) were dissolved in 10 mL of distilled water and then added as an initiator system under the magnetic stirring for 10 min. Then the reaction processed for 4–6 h without stirring. The super-absorbent hydrogel products were carefully washed thoroughly with deionized water and then dried to a constant mass at 40°C in a vacuum drier.

Characterization

FT-IR spectra of KBr pellets containing the hemicellulose-based hydrogel sample and the hemicellulose were obtained using a Frontier-II series FT-IR spectrometer (PERKIN-Elmer, USA). The morphology of sample, after freeze drying, was examined with JSM-6460LV scanning electron microscopy (SEM) (JEOL, Japan). The sample surface was visualized using a Veeco nanoscope III atomic force microscope (AFM) (Veeco Instruments, Santa Barbara, CA) in tapping mode using a commercial silicon tapping probe (NP-S20, Veeco Instruments) with a resonance frequency of about 273 kHz.²³

Water Absorbency Measurement

A weighted quantity of the sample was immersed in distilled water and 0.9 wt % NaCl solution at room temperature to swell, respectively. Then the swollen sample was taken out and

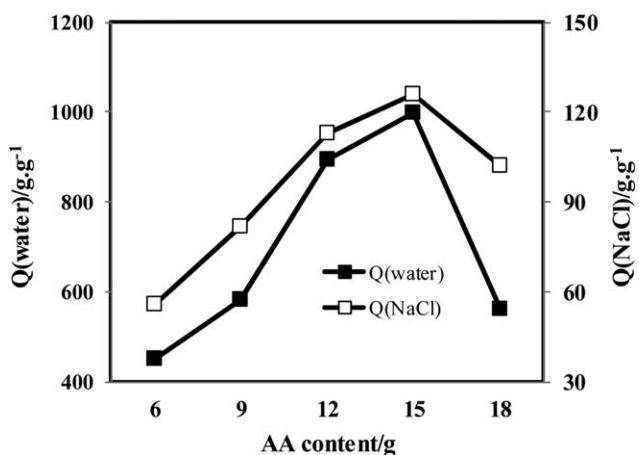


Figure 1. Effect of AA content on $Q(\text{water})$ and $Q(\text{NaCl})$.

the excess water was removed by a 100-mesh gauze. The weight of the swollen samples was measured. The liquid absorbency (Q , g/g) was calculated by the following equation [eq. (1)],

$$Q = \frac{M_2 - M_1}{M_1} \quad (1)$$

where M_2 (g) and M_1 (g) are swollen and dry weight of samples, respectively.

RESULTS AND DISCUSSION

The super-absorbent hydrogel based on hemicellulose prepared under different synthesis conditions have different absorbencies due to the different structures. The effects of different synthesis conditions on the water and 0.9 wt % NaCl absorbencies of the hemicellulose hydrogel sample were investigated, respectively.

Effect of AA Content

The effects of different AA monomers amounts on the absorbencies of the hydrogel sample were studied. The effect of AA weight ranged from 6 g to 18 g, while the AM weight was 3.5 g, hemicellulose weight was 1 g, weight ratio (to monomers) of cross-linker and initiator was 0.03% and 0.1%, and the neutralization degree of AA was 70%. The results are shown in Figure 1.

The liquid absorbency increased continuously with the increase of the AA content until the maximum liquid absorbency was reached, which was 997 g/g in distilled water and 126 g/g in 0.9 wt % NaCl solution, respectively. The optimal dosage of AA was 15 g. As the AA content increased, more and more hydrophilic groups were grafted onto the hemicellulose, which improved the liquid absorbency of the hydrogel sample. When the AA dosage was higher than 15 g, the liquid absorbency decreased due to the excessive crosslinking induced by overdosed AA, resulting in compact networks which were not beneficial to absorbencies. The optimal AA content was 15 g in the current system.

Effect of the Hemicellulose Content

The effect of the amount of hemicellulose on the water absorbency was investigated as well, while $m(\text{AA}) : m(\text{AM}) = 15 : 3.5$ (or AA 15.0 g and AM 3.5 g, the same below), the

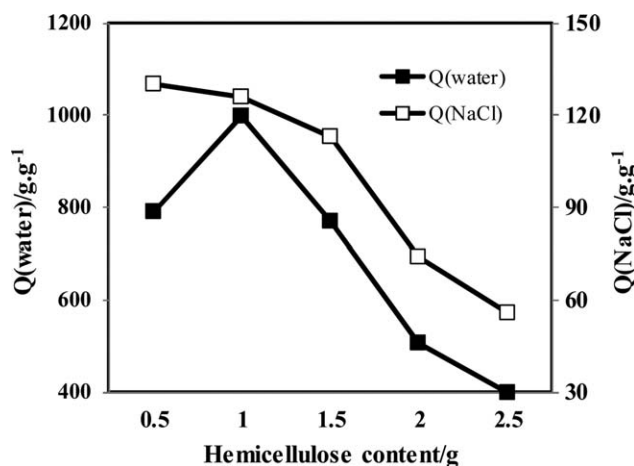


Figure 2. Effect of Hemicellulose content on $Q(\text{water})$ and $Q(\text{NaCl})$.

neutralization degree of AA was 70%, the weight ratio (to monomers) of cross-linker and initiator was 0.03% and 0.1%.

With the increase of hemicellulose content, the water absorbency increased first then decreased gradually. However the 0.9 wt % NaCl absorbency decreased slowly as the hemicellulose content increased (Figure 2). The less hemicellulose was used, the easier for more monomers to be grafted. With the increasing of hemicellulose content, the amount of grafting was declined at the content of hemicellulose above 1.0 g in the current system. At a higher content of hemicellulose, the polymeric network would become closer as mentioned above which made the water absorbency of the sample decreased gradually. When the hemicellulose content was 0.5 g, the 0.9 wt % NaCl absorbency reached the maximum, while the water absorbency was not so good. Results showed that when the hemicellulose content was 1 g, the water absorbency was improved. Therefore, the optimum hemicellulose content was 1 g. The best monomer mass ratio was $m(\text{AA}) : m(\text{AM}) : m(\text{hemicellulose}) = 15 : 3.5 : 1$.

Effect of Neutralization Degree of AA

According to the Flory's network theory, the fixed charges on polymer network of super-absorbent hydrogel play an important role in the swelling capability.²⁴ Therefore, besides the network structure, hydrophilic group is also an important factor on the absorbencies of polymer. The effect of the neutralization degree of AA, which was neutralized by different amounts of NaOH, was studied. While $m(\text{AA}) : m(\text{AM}) : m(\text{hemicellulose}) = 15 : 3.5 : 1$, weight ratio (to monomers) of cross-linker and initiator was 0.03% and 0.1%, respectively.

It can be seen from Figure 3 that the liquid absorbency increased as the neutralization degree of AA increased, and reached the maximum when the neutralization degree of AA was 75%. Then it decreased with further increase of the neutralization degree of AA, and the decrease of $Q(\text{water})$ was sharper and faster than that of $Q(\text{NaCl})$. According to Flory's theory, the increasing of neutralization degree enhanced the electrostatic repulsion, ionic hydrophilic property, which is helpful to liquid absorbency.²⁵ However, further increasing the neutralization degree caused more sodium ions in the polymer network, which

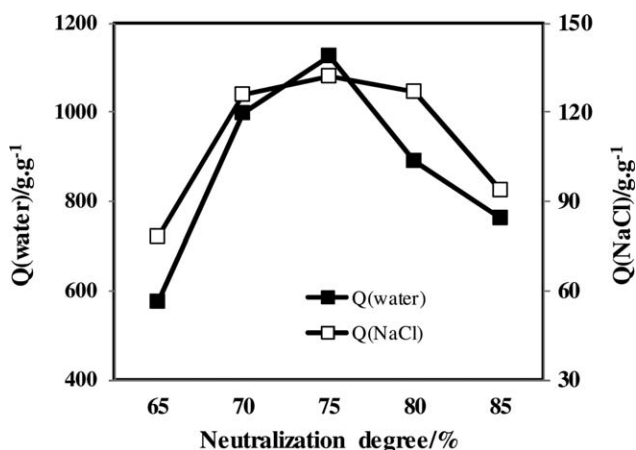


Figure 3. Effect of Neutralization degree on $Q(\text{water})$ and $Q(\text{NaCl})$.

could reduce the electrostatic repulsion and decrease the liquid absorbency. Thus the optimum neutralization degree of AA was 75%.

Effect of Cross-Linker Content

In the polymerization, increasing cross-linker could increase the nodes of network and the cross-linker density, which is favorable to the super-absorbent absorbing and retaining fluid. The effects of the cross-linker (*N,N'*-methylenebisacrylamide, MBA) weight ratio (to monomer) are shown in Figure 4. While $m(\text{AA}) : m(\text{AM}) : m(\text{hemicellulose}) = 15 : 3.5 : 1$, the neutralization degree of AA was 75%, the weight ratio (to monomers) of the initiator was 0.1%.

The liquid absorbency increased sharply when the weight ratio (to monomer) of MBA was lower than 0.03%. This demonstrated that a low amount of cross-linker was difficult for network structure to form, leading to a low liquid absorbency. When the ratio of MBA was higher than 0.03%, the liquid absorbency began to decrease with the increasing of ratio. The more cross-linker provided more cross-linking point and decreased the space of copolymer chains, which lowered the liquid absorbency.²⁶ Therefore, the optimal weight ratio of MBA was 0.03%, leading to the maximum absorbency at 1128 g/g in distilled water and 132 g/g in 0.9 wt % NaCl, respectively.

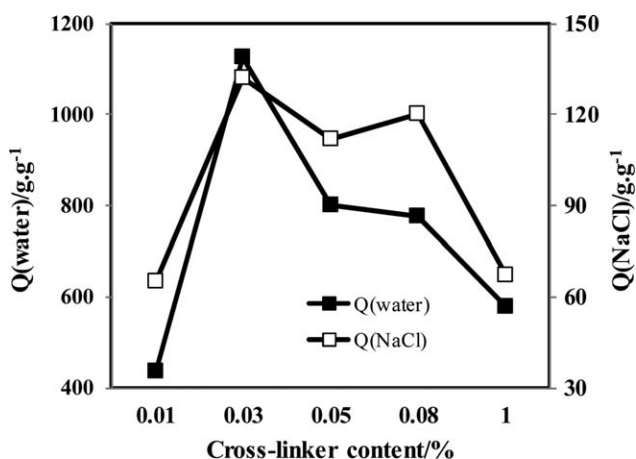


Figure 4. Effect of cross-linker content on $Q(\text{water})$ and $Q(\text{NaCl})$.

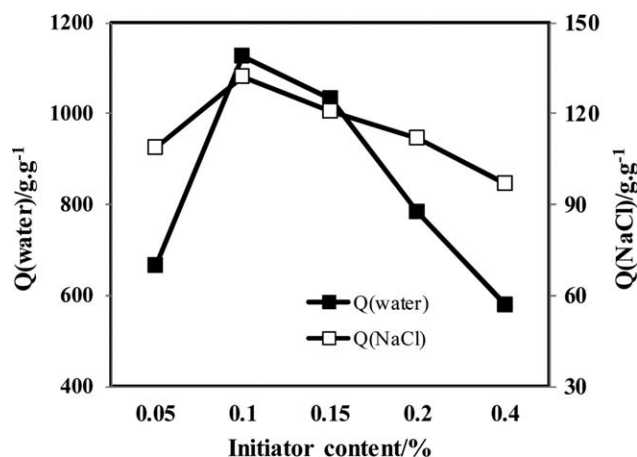


Figure 5. Effect of initiator content on $Q(\text{water})$ and $Q(\text{NaCl})$.

Effect of Initiator Content

The presence of initiator is essential for inducing the free-radical grafting polymerization and crosslinking in the network or hydrogel formation. The effect of initiator weight ratio (to monomer) on water absorbencies was studied while $m(\text{AA}) : m(\text{AM}) : m(\text{hemicellulose}) = 15 : 3.5 : 1$, the neutralization degree of AA was 75%, weight ratio (to monomers) of the cross-linker was 0.03%.

It can be seen that the liquid absorbency increased with the ratio of initiator increasing and reached the maximum, then dropped (Figure 5). $Q(\text{water})$ dropped faster than $Q(\text{NaCl})$. This may be due to the fact that the less initiator would prevent the formation of more stable network structures. When the ratio of initiator was too high, the strong reaction condition led to the decrease of the main chain length or generated compact networks. Thereby the liquid absorbency of the polymer decreased. The best weight ratio (to monomer) of initiator was 0.1%.

Several hydrogels based on chitosan, xylan, and wheat straw were reported in the past. The data on water absorbency for xylan/chitosan based hydrogels,²¹ xylan-rich hemicellulose based hydrogels,¹ and wheat straw based hydrogels² were 85 g/g, 822 g/g, and 133g/g, respectively. Compared with those hydrogels, the one prepared in this work has comparable or even better water absorbency.



Figure 6. Hydrogel sample and after water absorbing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

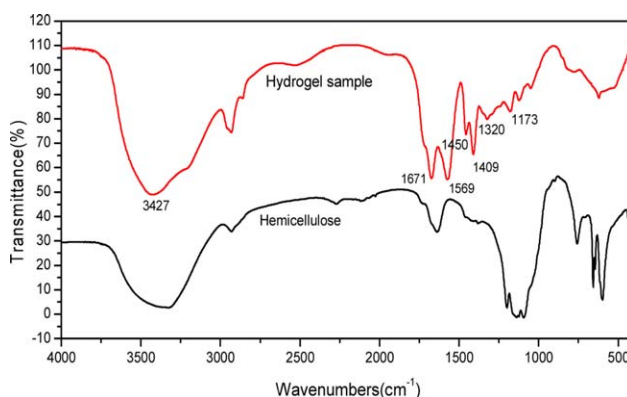
Characterization

Based on the optimum synthesis condition, the super-absorbent hydrogel based on hemicellulose was obtained. The images of hydrogel sample are shown in Figure 6. Moreover the FT-IR, SEM, and AFM characterization were carried out to reveal the formation mechanism and morphology of the hydrogels.

In Figure 6, the left one is the optical image of super-absorbent hydrogel containing hemicellulose. It was a kind of opaque, smooth, well-distributed, and high resilient hydrogel. After water absorbing, the sample became transparent and colorless without disintegration as shown in Figure 6 (right).

The mechanism of copolymerization of acrylic acid (AA) and acrylic amide (AM) onto xylose-riched hemicellulose is shown in Scheme 1. The redox initiator system consisting of persulfate and hydrosulfite generates sulfate radical anion at room temperature. Then the sulfate radical anion abstracts hydrogen from the hydroxyl group of the hemicellulose to form alkoxy radicals, leading to a graft copolymerization of AA and AM onto hemicellulose. The process is similar to those reported for cellulose or nanofiber.^{27,28} As the result, the crosslinked structure was generated in the presence of a crosslinking agent whereas the hemicellulose itself could also facilitate the crosslinking due to its multiple reactive sites.

According to the FTIR spectra of the hemicellulose and the hydrogel sample (Figure 7), the comparison of absorption peaks revealed some change of absorption, suggesting that the hemicellulose was indeed copolymerized in the hydrogel after the



Scheme 1. Mechanism of copolymerization of AA and AM onto hemicellulose.

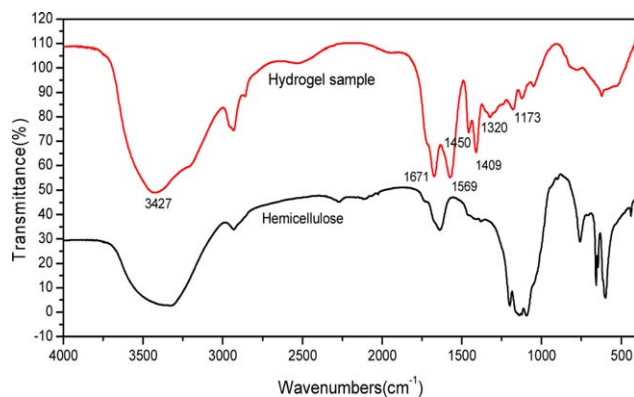


Figure 7. FT-IR spectra of hydrogel sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction. The absorption peak of 3427 cm^{-1} , attributed to hydroxyl stretching vibration, was higher in hydrogel sample than that in hemicellulose. This implied that more hydroxyl groups were incorporated into the hydrogel after the graft polymerization involving AA. The absorption peak at 1671 cm^{-1} was attributed to the stretching vibration of C=O of amide I band, the peak at 1569 cm^{-1} was corresponding to the N–H bending vibration of amide II band, the peaks at 1450 cm^{-1} , 1409 cm^{-1} , and 1173 cm^{-1} were resulted from the symmetrical stretching vibration of COO^- and the peak at 1320 cm^{-1} was attributed to the C–N bond of amide III band. From the information above, it can be concluded that AA and AM were indeed grafted onto the hemicellulose backbone during the copolymerization induced by APS and NaHCO_3 as the initiator and MBA as the cross-linker.

Figure 8 shows the morphology of the hydrogel sample further revealed by SEM. The sample exhibits an undulant surface and broad network structure. This undulant surface is convenient for the penetration of water into the hydrogel network.² This kind of surface is related to the equilibrium water absorbency

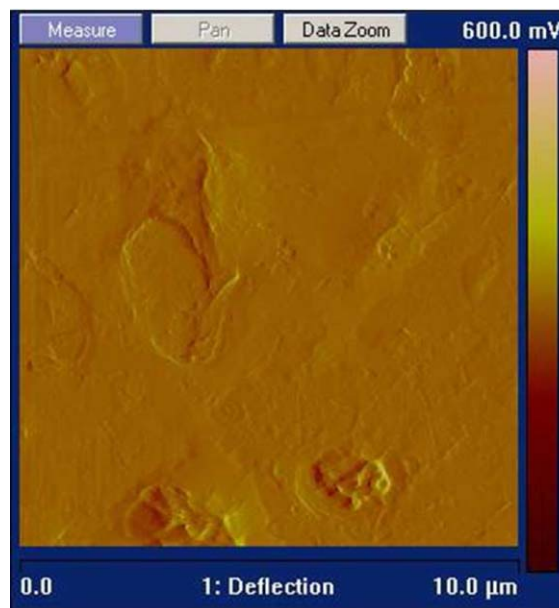


Figure 9. AFM image of hydrogel sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and swelling behaviors of the corresponding in hemicellulose hydrogel and makes the sample an excellent water absorption material.

AFM has recently been successfully used for imaging polysaccharide gels and surfaces of amorphous films.^{29,30} Figure 9 shows the AFM image of the hydrogel for the current system. As can be seen, the sample appeared to be smooth; and some sunk domains appearing in the image may well correspond to the undulant structure on the sample surface. The results are consistent with those revealed by SEM observation mentioned above.

CONCLUSION

A super-absorbent hydrogel based on hemicellulose was prepared by grafting copolymerization. The synthesis conditions were optimized, where $m(\text{AA}) : m(\text{AM}) : m(\text{hemicellulose}) = 15 : 3.5 : 1$, the neutralization degree of AA was 75%, weight ratio (to monomers) of the cross-linker and the initiator was 0.03% and 1.0%, respectively. Under the optimal conditions, the hydrogel sample attained the best liquid absorbency of 1128 g/g in distilled water and 132 g/g in 0.9 wt % NaCl solution. The resulting sample is a kind of opaque, smooth, and high resilient hydrogel with excellent water absorbency. Based on the IR, SEM, and AFM characterization, the formation mechanisms and the morphologic structure of the hydrogels were revealed. The hydrogel with undulant surface and broad network structure offer the products excellent water absorbency.

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