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Structure and properties of hydrogels prepared from cellulose in NaOH/urea aqueous solutions

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ABSTRACT

Hydrogels have been successfully prepared from cellulose in NaOH/urea aqueous solution by using epichlorohydrin (ECH) as a cross-linker, and via heating and freezing methods. Structure and properties of the hydrogels were measured with UV–vis spectroscopy, SEM, XRD, solid-state ^{13}C NMR, rheometry and water absorption testing. The results indicated that hydrogels prepared by heating displayed macroporous inner structure, while fiber-like structure could be observed in the hydrogels prepared by freezing. The light transparency and equilibrium swelling ratio of the hydrogels decreased, while the reswelling water uptake and the storage modulus increased, with an increase of the cellulose content. Compared with the hydrogels post-treated by freezing, the hydrogels prepared by heating displayed better light transmittance, higher equilibrium swelling ratios and reswelling water uptakes, and relatively weaker mechanical strength. Therefore, the structure and properties of the hydrogels could be adjusted by changing the cellulose content and the post-treatment methods.

1. Introduction

Hydrogels are defined as three-dimensional network of hydrophilic polymers, which can absorb and retain a significant amount of water. To obtain the network, chemical cross-linking (Denizli, Can, Rzaev, & Guner, 2004; Kiritoshi & Ishihara, 2004; Molina, Gomez-Anton, & Pierola, 2007; Zhao, Liao, Gao, & Liu, 2006), physical entanglement (Saito, Sakurai, Sakakibara, & Saga, 2003), ionic bonds (de la Torre, Torrado, & Torrado, 2003; Kang, Park, Lee, & Son, 2007; Masci, Husu, Murtas, Piozzi, & Crescenzi, 2003; Wong, Díez-Pascual, & Richtering, 2009) and hydrogen bonds (Jin, Liu, Zhang, Chen, & Niu, 2006) are used in the preparation of hydrogels. Polymer hydrogels have been widely utilized as drug delivery, food, cosmetics, high water-absorbing resin, contact lenses, corneal, implant, substitutes for skin, tendons, ligaments, cartilage, and bone, because of their excellent hydrophilicity, permeability, compatibility and low coefficient of friction (Calvert, 2009; Chang, Duan, Cai, & Zhang 2010; Chan, Whitney, & Neufeld, 2009; Liu & Fan, 2005; Yamamoto, Takahashi, & Tabata, 2003). The hydrogels from natural polymers, especially polysaccharides, are promising for application in the biomaterial field, because of their unique advantages, such as abundance, non-toxicity, biocompatibility, biodegradability, and biological functions (Cavalieri et al., 2006; Prabaharan & Mano, 2006; Yu, Lu, & Xiao, 2007; Zhai, Yoshii, Kume, & Hashim, 2002).

Cellulose is the most abundant polysaccharide available worldwide, and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products (Klemm, Heublein, Fink, & Bohn, 2005). Cellulose-based hydrogels can be obtained by chemical cross-linking of water-soluble cellulose derivatives using small difunctional molecules as cross-linker (Rodríguez, Alvarez-Lorenzo, & Concheiro, 2003; Sannino et al., 2004; Yan, Qian, & Zhu, 2001). The synthesis of cellulose-based hydrogels by radiation is also a convenient method (Chauhan, Lal, & Mahajan, 2004; Ibrahim, El Salmawi, & Zahran, 2007; Liu, Zhai, & Ha, 1999; Soderqvist Lindblad, Albertsson, Ranucci, Laus, & Giani, 2005). A new method for preparing cellulose-based hydrogels had been tried by Marsano, Bianchi, and Viscardi (2004). N-isopropylacrylamide (NIPA) monomer solution was absorbed into a dried porous hydropropyl cellulose (HPC) network and cross-linked inside the network by *N*,*N*′-methylenebisacrylamide at 25 °C. Moreover, Xie and Hsieh provided a two-step initiation and polymerization process for the preparation of PNIPAAm hydrogel-cellulose composites. All the cellulose-supported hydrogels exhibited a lower extent of phase temperature over a wider temperature range than the free PINPAAm hydrogels (Xie & Hsieh, 2003). Yoshimura, Matsuo, and Fujioka (2006) prepared novel biodegradable superabsorbent hydrogels from cotton cellulose and succinic anhydride in the presence of 4-dimethylaminopyridine as an esterification catalyst. Liu et al. (2004) reported a rapid temperature-responsive sol–gel reversible poly(N-isopropylacrylamide)-*g*-methylcellulose (PNIPAAm-*g*-MC) copolymer hydrogel. However, hydrogels pre-

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pared from unsubstituted cellulose have been scarcely reported, because of the insolubility of cellulose in aqueous solutions and in most organic solvents.

Previously, we reported that novel cellulose hydrogels were synthesized through a "one-step" method from unsubstituted cellulose, which was dissolved directly in NaOH/urea aqueous solution, by using epichlorohydrin (ECH) as cross-linker (Zhou, Chang, Zhang, & Zhang, 2007). Furthermore, the unique gelation behavior of cellulose in NaOH/urea aqueous solution has been studied, and either heating or cooling treatment could result in the gel formation (Cai & Zhang, 2006). As an extension of our previous work, we attempt to prepare hydrogels from cellulose in NaOH/urea aqueous solution by different post-treatments, i.e., heating and freezing methods. Structure and properties of the two series of hydrogels were investigated and compared.

2. Experimental

2.1. Materials

Whatman CF-11 fibrous cellulose powder (Catalogue No. 4021050) was used as the starting cellulose; the weight average molecular weight (M_w) was determined to be 3.46×10^4 by static laser light scattering. Epichlorohydrin (ECH) was analytical-grade, and was used without further purification.

2.2. Preparation of hydrogels

An aqueous solution of 6 wt% NaOH/4 wt% urea consisted of 60 g of NaOH, 40 g of urea and 900 mL of dilute water, and the resulting solution was filtered with a G2 sand filter to be used as solvent of cellulose. A cellulose solution was prepared according to our previous work (Zhang & Zhou, 2003), that is, a certain amount of CF-11 was dispersed into 100 g of solvent with stirring for 5 min and then was stored in a refrigerator (−5 to −10 °C) for 12 h. The frozen solid was thawed and stirred extensively at room temperature to obtain a colorless and transparent cellulose solution.

In a typical synthesis procedure, a certain amount of ECH was added dropwise to the 100 g cellulose solution mentioned previously, and the mixture was stirred at 25 °C for 1 h. Two post-treatment methods, heating the mixture to 50 °C for 20 h (Gel-H series) or freezing the mixture to −20 °C for 20 h (Gel-F series), were carried out for gelation of the mixtures. Hydrogels as-obtained were washed with a large amount of distilled water to remove NaOH and urea completely, and then vacuum-dried or freeze-dried by using a lyophilizer (CHRIST Alpha 1-2, Germany). According to Table 1, by changing the content of cellulose from 2 wt% to 4 wt%, and the amount of ECH from 9 mL to 5 mL, six colorless and transparent cellulose hydrogels were prepared, and coded as Gel-H2, Gel-H3, Gel-H4, Gel-F2, Gel-F3 and Gel-F4, respectively.

2.3. Characterization

Cellulose hydrogels were cut into thickness of l cm and the transmittance of hydrogels was measured over the wavelength range of 200–800 nm by using an ultraviolet–visible spectrophotometer (Shimadzu UV-160A). Scanning electron micrographs (SEM) were taken with a Hitachi S-570 microscope. The hydrogels swollen to equilibrium in distilled water at 30 °C were frozen in liquid nitrogen and snapped immediately, and then freeze-dried. The fracture surface of the hydrogel was sputtered with gold, and was observed and photographed.

Hydrogels were freeze-dried and were cut into particle-like size, and vacuum-dried for 24 h at 50 °C before measurements of XRD and NMR. XRD measurement was carried out on an X-ray diffractometer (D/MAX-1200, Rigaku Denki, Japan). An XRD pattern with Cu Kα radiation (1.5406×10^{-10} m) at 40 kV and 30 mA was recorded in the range $2\theta = 6–40°$ at a scanning speed of 2°/min. ^{13}C cross-polarization magnetic angle spinning (CP/MAS) solid-state NMR spectra were recorded on an Infinity Plus spectrometer (^{13}C frequency = 100 MHz) with a CP/MAS unit at ambient temperature. The spinning rate and the contact time were 5.0 kHz and 5.0 ms, respectively. Pulse width was 2.10 μs, spectra width was 50,000 kHz, acquisition time was 20.48 ms, and the spectrum was accumulated 2000 times.

Table 1
Chemical composition and reactive conditions of the cellulose hydrogels.

Code	$V_{\text{cellulose}}$ (mL)	$c_{\text{cellulose}}$ (wt%)	V_{ECH} (mL)	Methods	Time (h)
Gel-H2	100	2	9	Heating	20
Gel-H3	100	3	7.4	Heating	20
Gel-H4	100	4	5	Heating	20
Gel-F2	100	2	9	Freezing	20
Gel-F3	100	3	7.4	Freezing	20
Gel-F4	100	4	5	Freezing	20

2.4. Swelling and reswelling measurements

The hydrogels were incubated in distilled water for at least 24 h at 25 °C. The swelling ratios (SR) of the hydrogels were measured gravimetrically after the sample surfaces had been wiped with moistened filter paper to remove water, and defined as

$$SR(\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where W_d and W_s are the weights of dried and swollen hydrogels, respectively.

The vacuum-dried hydrogels were immersed in distilled water to rehydrate at 25 °C. The reswelling kinetics of the hydrogels was measured gravimetrically. The samples were removed from water at regular time intervals. After the sample surfaces had been wiped with moistened filter paper to remove water, the weights of the gels were recorded. Water uptake (WU) was defined as

$$WU(\%) = \frac{W_t}{W_d} \times 100 \quad (2)$$

where W_t is the weight of the swollen hydrogel at a designated time (t) during swelling.

2.5. Rheological measurement

Viscoelastic measurements were performed on an ARES-RFS III rheometer (TA Instruments, U.S.A.). Hydrogels were prepared in the form of disks with a diameter of 30 mm and thickness of 2 mm. Samples were tested using parallel plate geometry with a diameter of 50 mm. Samples were first subjected to a strain sweep test in which they were deformed at different shear strains, and the modulus G was independent of the applied strain. A deformation of 10% was chosen in the subsequent tests to ensure that each measurement was made in linear viscoelastic region. A frequency sweep test was conducted on each sample from 0.1 to 100 Hz at 25 °C.

3. Results and discussion

3.1. Morphology and structure

Table 1 displays the reaction conditions of the cellulose hydrogels by heating and freezing methods. With increasing of cellulose content from 2 wt% to 4 wt%, the amount of ECH added into the solution decreased from 9 mL to 5 mL due to the physical cross-linking and chain entanglement of cellulose molecules. Based on

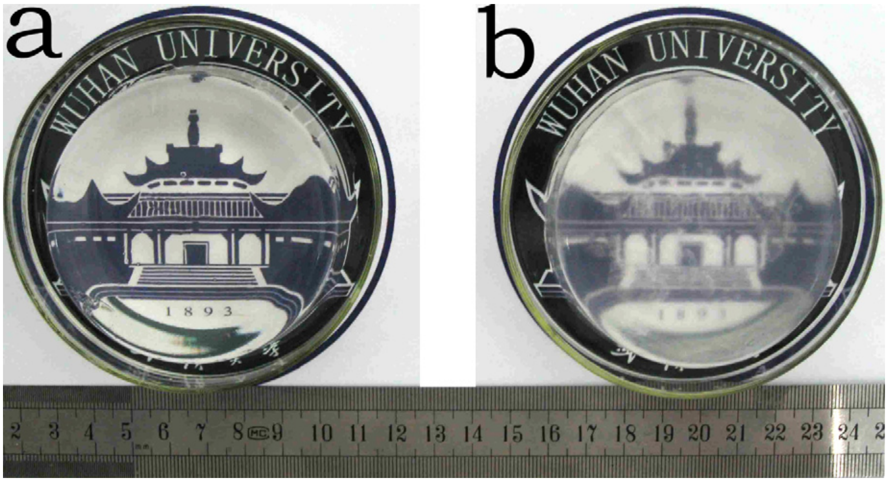

Fig. 1. Photographs of the cellulose hydrogels: (a) Gel-H2 and (b) Gel-F2.

the Williamson etherification and the alkali-catalyzed oxalkylation, cellulose dissolved in NaOH/urea aqueous solution could be chemically cross-linked by ECH to form hydrogels, and without addition of an extra base because of the basicity of the solvent system. On the other hand, physically cross-linked gels could form in the cellulose—NaOH/urea aqueous solution at either higher temperature (above 30 °C), or lower temperature (below −3 °C), or for longer gelation time (Cai & Zhang, 2006). Therefore, hydrogels treated by heating and freezing methods are thought to be both chemically and physically cross-linked. In a heating process, physical cross-linking of the hydrogels is mainly attributed to the random chain entanglement for the desolvation of cellulose molecules, forming an amorphous structure. While in a freezing process, physical cross-linking is mainly attributed to a slower and stronger self-association of the chains as a result of the strong hydrogen bonding among cellulose chains and molecules of solvent, resulting in a denser cross-linked structure. It is well known that poly(vinyl alcohol) (PVA) aqueous solution will form a gel if the cryogenic treatment is applied (Hassan & Peppas, 2000; Hassan, Ward, & Peppas, 2000; Stauffer & Peppast, 1992). These phenomena result from the formation of inter-molecular hydrogen bonds when the PVA chains come together.

Fig. 1 shows the photographs of the cellulose hydrogels (diameter × height, 7 cm × 4 cm) treated by heating (Gel-H2) and freezing (Gel-F2) methods. Clearly, the transparency of Gel-H2 is better than that of Gel-F2, but Gel-F2 displays a relative higher mechanical strength. The transmittances of ultraviolet and visible light for the cellulose hydrogel samples are shown in Fig. 2. In the wavelength range between 400 and 800 nm, all samples presented a relatively high transparency. It can be seen that the transparency of the cellulose hydrogels cross-linked with ECH decreased with increasing cellulose content. Along with the chemical composition of cellulose hydrogels, the transparency for hydrogels are basically in the order of Gel-H2 > Gel-H3 > Gel-H4 and Gel-F2 > Gel-F3 > Gel-F4. This maybe due to greater aggregation of cellulose chains when the hydrogels are prepared from relative higher concentration. However, transparency of the hydrogels from the freezing method was lower than that from heating. The freezing method may lead to the increase of crystalline regions within the three-dimensional network structure, which resulted in the loss of light transparency. The results could be confirmed by the XRD patterns of the hydrogels of Gel-H2 and Gel-F2 as shown in Fig. 3. Gel-H2 and Gel-F2 display similar diffraction peaks at $2\theta = 20^\circ$ and 22°, which correspond to the (1 1 0) and (2 0 0) planes of cellulose II crystalline form. Apparently, the crystallinity of Gel-F2 is higher than that of Gel-H2.

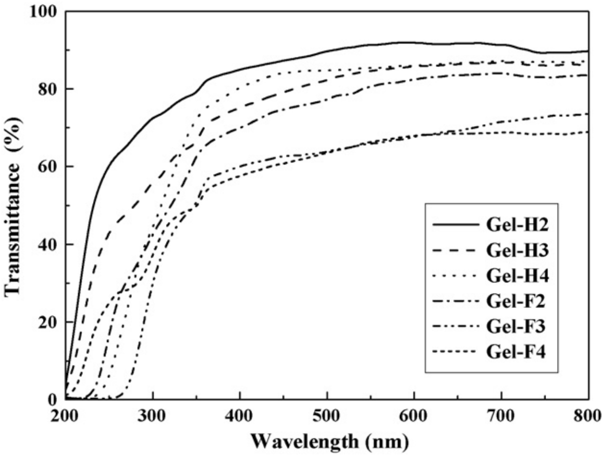

Fig. 2. The transparency of cellulose hydrogels prepared by heating and freezing methods.

Fig. 4 shows the SEM images of the cellulose hydrogels prepared by heating and freezing methods with different cellulose content. Gel-H series (post-treated by heating method) display macroporous inner structure, and the pore size decreases with an increase of the cellulose concentration. Interestingly, fiber-like structure could be observed in the fracture surfaces of the Gel-F series (post-

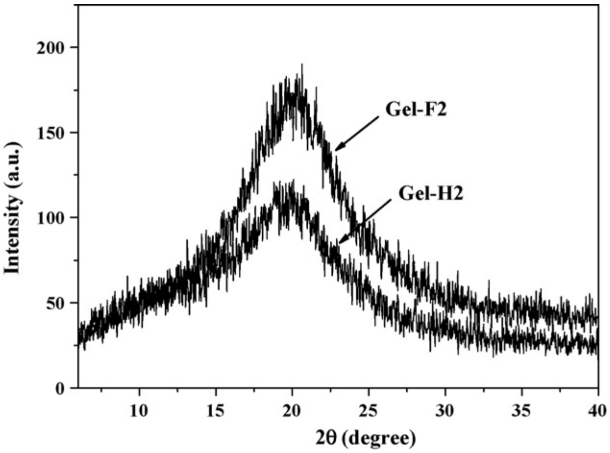

Fig. 3. XRD patterns of the cellulose hydrogels of Gel-H2 and Gel-F2.

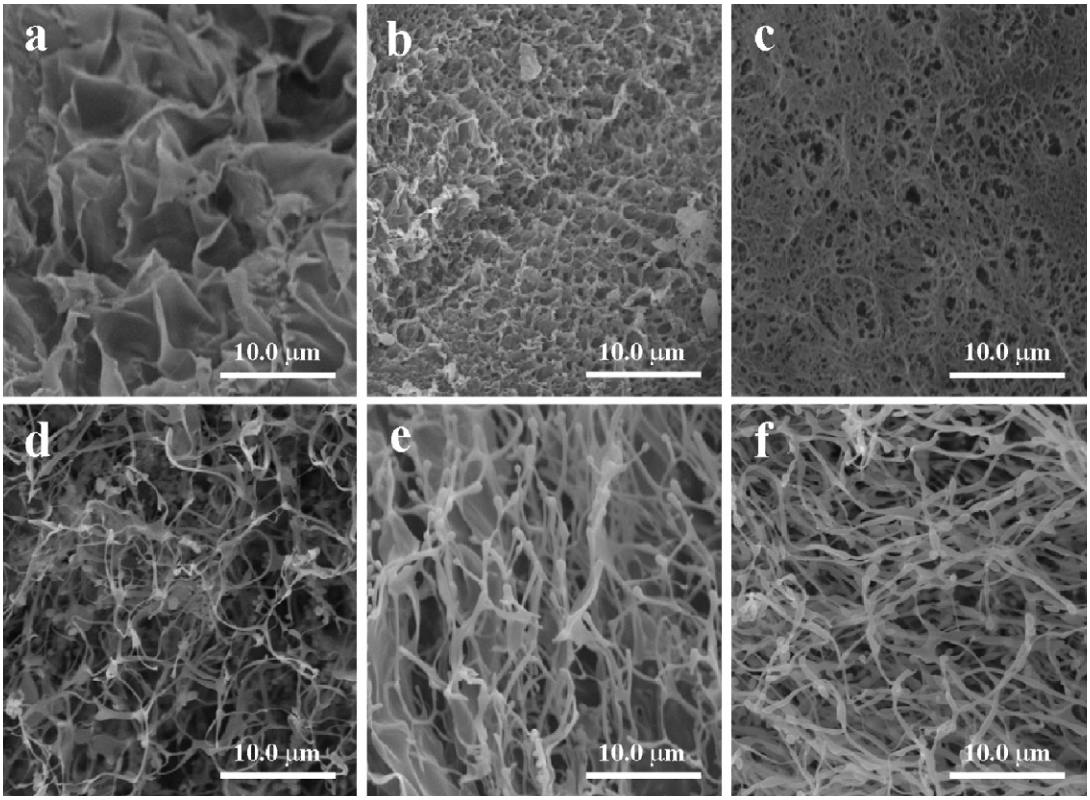

Fig. 4. SEM images of the cellulose hydrogels prepared by heating (top) and freezing (bottom) methods: (a) Gel-H2, (b) Gel-H3, (c) Gel-H4, (d) Gel-F2, (e) Gel-F3 and (f) Gel-F4.

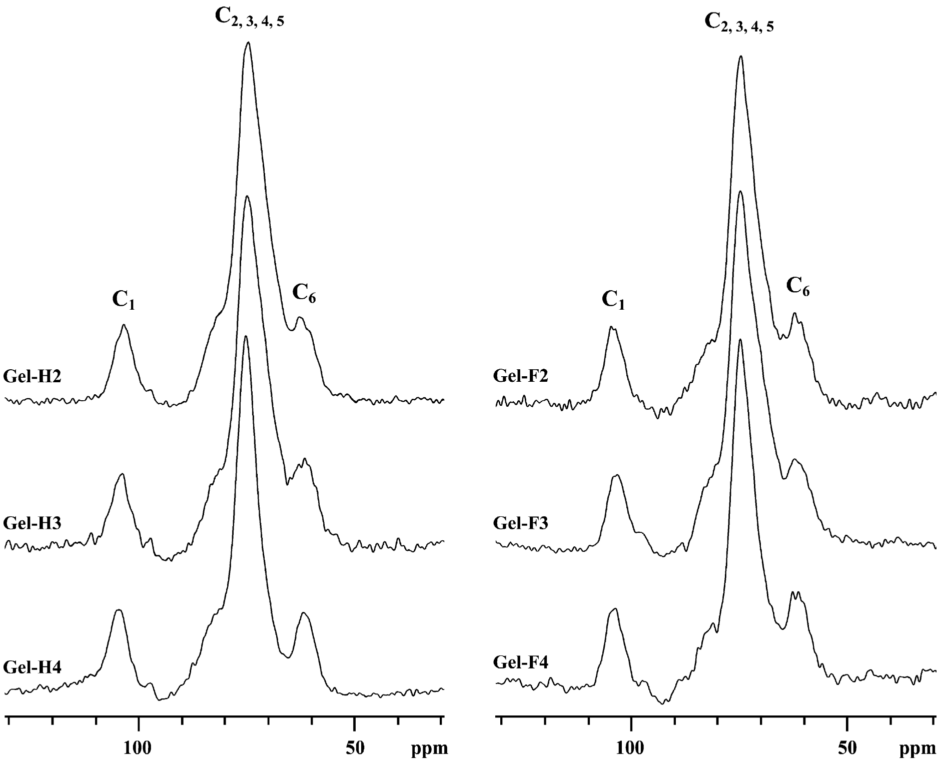

Fig. 5. ^{13}C CP/MAS solid-state NMR of the cellulose hydrogels prepared by heating method (left) and by freezing method (right).

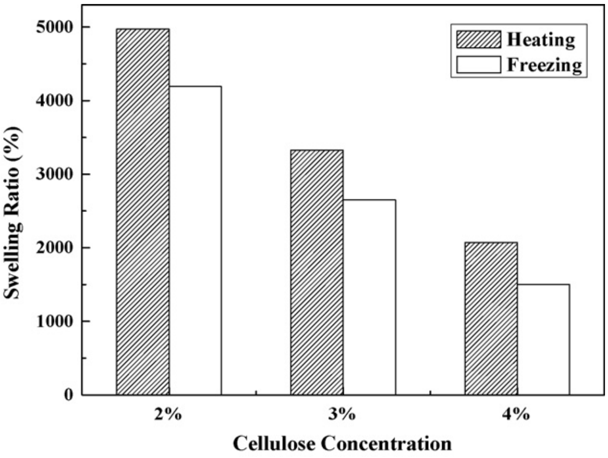

Fig. 6. Equilibrium swelling ratio of the hydrogels in distilled water as a function of the cellulose concentration at 25 °C.

treated by freezing method), which were rather different than those of Gel-H series. The fiber-like structure is probably due to a slow and strong self-association of the cellulose chains at the lower temperature, which become more obvious and orderly with increasing gelation concentration.

Solid-state NMR methods have been widely applied in high-resolution NMR studies of materials, which allow the identification, analysis and characterization of different kinds of solids and also give various information on their molecular mobility (Capitani, Del Nobile, Mensitieri, Sannino, & Segre, 2000; Delval, Crini, Bertini, Filiatre, & Torri, 2005). Fig. 5 shows the solid-state CP/MAS ^{13}C NMR spectra of the cellulose hydrogels. For all of the hydrogels, a broadening of peaks in the range 55–90 ppm could be observed. Comparing with the ^{13}C NMR spectrum of the regenerated cellulose (Zhou et al., 2007), the C_4 and C_6 signals of the hydrogels showed a large loss of resolution and became shoulder peaks of the broadening region with the increase of cross-linking agent. This could be explained by the lower mobility of carbons of anhydrous D-glucose units induced by the chemical cross-linking of cellulose with ECH. Moreover, the extent of chemical cross-linking of the hydrogels are in the order of Gel-H2 > Gel-H3 > Gel-H4 and Gel-F2 > Gel-F3 > Gel-F4, which agreed well with the addition amount of ECH and the molar ratio of ECH to cellulose.

3.2. Properties of the hydrogels

The influences of the cellulose contents and post-treatment methods on swelling ratios of the hydrogels in distilled water are found in Fig. 6. With the increase of cellulose concentration, swelling ratios of the hydrogels decreased. It is well known that the cross-linking degree is one of the important factors for determining the water absorbency of hydrogels. Except for the chemical cross-linking of cellulose by ECH, physical cross-linking of the polymer chains plays an important role in the swelling ratio of the hydrogels. With increasing cellulose concentration, physical cross-linking of the hydrogels is strengthened by more and more inter-molecular hydrogen bonds and chain entanglements, resulting in the decrease of swelling ratios. Moreover, at the same cellulose concentration, hydrogels Gel-H series displayed relatively higher swelling ratios than those of the Gel-F series. It indicated that more rigid and stable hydrogen bonding could be established by molecular rearrangement in cellulose during the freezing process. Strong interactions and partial crystallinity existed in the hydrogels obtained by freezing, which hinders the penetration of water molecules, resulting in that the swelling degree of hydrogels by freezing being lower than that of by heating.

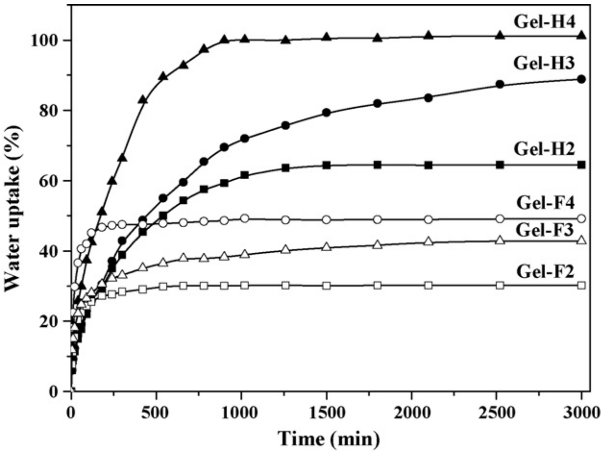

Fig. 7. Reswelling kinetics of the cellulose hydrogels in distilled water at 25 °C.

The vacuum-dried hydrogel samples were allowed to hydrate in distilled water at 25 °C, and the time kinetic curves are illustrated in Fig. 7. It can be clearly seen the swelling capabilities of all cellulose hydrogels were increased by time, but after a certain period time they showed a constant swelling behavior and the process was transformed to an equilibrium swelling state. Compared to Gel-F series, the hydrogels Gel-H series need a longer time to reach swelling equilibrium. As shown in Fig. 7, the reswelling capabilities of the Gel-H series approached 100% after a long period. However, the hydrogels Gel-F series could not swell as much as 50% due to a dense structure formed via freezing. Moreover, the desiccation stage promoted a reduction in the average distance among cross-linking sites, which caused a substantial increment in the actual cross-linking density, and in turn, an important reduction in water uptake.

The dynamic mechanical characterization was useful for understanding the structure of hydrogels and consequently their possible applications. Fig. 8 shows the linear viscoelastic frequency sweep response of the cellulose hydrogels. All of them exhibited weak frequency dependence from 0.1 to 100 rad/s with the dynamic storage modulus (*G*′), suggesting that the hydrogels were highly elastic. The storage modulus of the hydrogels increased with the increasing of the cellulose concentration. This suggested that cellulose molecular chains play an important role on the improving of mechanical strength of the hydrogels. Comparing with Gel-H series, the hydrogels prepared by freezing at the same polymer content exhibited

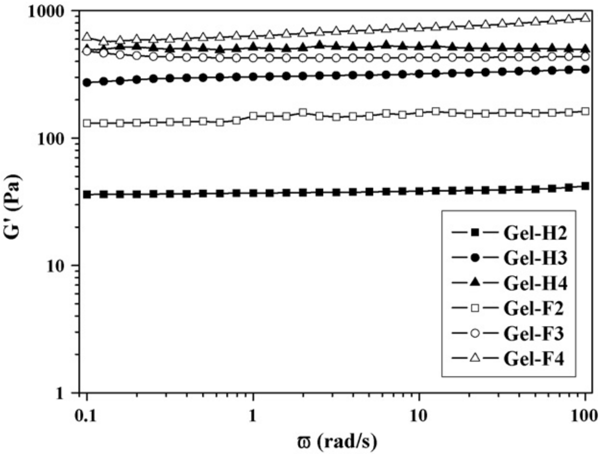

Fig. 8. Frequency dependence of the dynamic storage modulus (*G*′) of the hydrogels at a strain of 10% and at 25 °C.

much higher storage modulus. This indicated that the freezing gelation induced the formation of a compact network structure via the development of hydrogen bonding.

4. Conclusions

In summary, transparent hydrogels have been successfully synthesized from cellulose in NaOH/urea aqueous solutions by using ECH as cross-linker and by heating and freezing methods. Hydrogels prepared by heating displayed macroporous structure, while fiber-like structure could be observed in the hydrogels prepared by freezing. With the increase of the cellulose concentration, the light transparency and equilibrium swelling ratio of the hydrogels decreased, while the reswelling water uptake and the storage modulus increased. Comparing with the hydrogels post-treated by freezing, cellulose hydrogels prepared by heating displayed better light transmittance, higher equilibrium swelling ratios, higher water uptakes and relatively weaker mechanical strength. The differences are attributed to the type and extent of physical cross-linking of the cellulose molecules by heating and freezing methods, as well as the chemical cross-linking of the hydrogels.

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