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Fabrication and characterization of novel macroporous cellulose–alginate hydrogels

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ABSTRACT

Novel macroporous hydrogels were prepared by blending of cellulose and sodium alginate (SA) solution, and then cross-linking with epichlorohydrin. The resulting cellulose/SA hydrogels were characterized by solid-state ^{13}C NMR, wide-angle X-ray diffraction (WXRD), thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM), rheological measurement, dynamic mechanical analysis (DMA) and swelling test to evaluate their structure, interior morphology, gelation time, compressive modulus, and equilibrium swelling ratio. Our findings revealed that the cellulose acted as backbone in the hydrogels, whereas SA contributed to the higher equilibrium swelling ratio. The combination of cellulose having semi-stiff chains and SA containing –COOH groups in the cross-linking hydrogel created the macroporous structure. This work provided a new pathway for preparation of hydrogel with large porous structure through incorporation of stiff polymer as support of pore wall and acidic polysaccharide as expander of pore size because of high water-absorbency.

1. Introduction

Hydrogels, attractive soft materials, have become the focus of intense activity due to the applications in the fields of food, pharmaceuticals, agriculture, personal care products, and electronics [1]. Especially, biodegradable hydrogels have potential applications as implantable carriers for drug delivery systems because of the high responsiveness to the stimulus and good biocompatibility [2,3]. Furthermore, the biodegradable hydrogels have been already proved to be safe in many medical applications [4]. Recently, several available works dealing with the preparation of biodegradable hydrogels based on both biodegradable synthetic polymers such as poly(vinyl alcohol) [5] and poly(ethylene glycol) [6], and natural polymers such as chitosan [7,8] have been reported. Moreover, the biodegradable hydrogels have been prepared from synthetic polymers and natural polymers through semi-IPN strategy [9–11]. Exciting researches have been carried out on the materials derived from natural resource [12], and the presence of polysaccharides can induce the biocompatibility, biodegradability and non-toxicity of these materials [13]. Cellulose is the most abundant natural polymer on earth [14], which is an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products [15–17]. Therefore, cellulose based materials have become one of the most important bioresource materials in the 21st century.

In our laboratory, cellulose solution has been prepared from NaOH/urea aqueous systems [18,19], and was used to fabricate cellulose membranes [18], novel fibers [20], films [21], and gels [22,23]. From the results of these works, we have discovered that cellulose can exhibit better mechanical properties than traditional water-soluble natural polymer in hydrogel matrix [24]. Sodium alginate (SA) is an acidic polysaccharide, composed of linear block copolymer of 1–4 linked β-D-mannuronic acid and α-L-guluronic acid. When metallic divalent cations such as Ca^{2+} are added into SA solution, it is readily transformed into a hydrogel [25]. Many materials based on alginate have been reported through blending [26], grafting [27] and cross-linking [28]. However, studies on hydrogels prepared from cellulose and SA in NaOH/urea aqueous systems have been never published.

It is well known that sodium alginate is a more hydrophilic polysaccharide than cellulose. Furthermore, cellulose exists as a wormlike chain in the NaOH/urea aqueous solution, suggesting character of stiffness. Therefore, we attempted to fabricate novel biodegradable hydrogel from cellulose as the backbone and SA as pore size expander. In this article, cellulose and SA were dissolved in NaOH/urea aqueous solution to construct macroporous hydrogels through chemical cross-linking. To clarify the different roles of cellulose and SA, the hydrogels were fabricated from a mixture of both the solutions with different feed ratios. The structure and morphology of the hydrogels were characterized by solid-state ^{13}C NMR, wide-angle X-ray diffraction (WXRD), thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM), and dynamic

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mechanical analysis (DMA). Moreover, the effects of feed ratio on the pore structure, the mechanical property and swelling behavior of hydrogels were investigated and discussed.

2. Experimental

2.1. Materials

Sodium alginate was an analytical-grade reagent, and was purchased from Shanghai Chemical Agents, Ltd. Co. (Shanghai, China). Its weight-average molecular weight (M_w) was determined by static laser light scattering (DAWN DSP, Wyatt Technology Co., USA) to be 2.07×10^4. Whatman CF-11 fibrous cellulose powder (catalog no. 4021050) was used as the starting cellulose. Its weight-average molecular weight (M_w) was 3.46×10^4. Epichlorohydrin (ECH, Chemical Agents, Ltd. Co. Shanghai, China) (1.18 g/ml) was of analytical-grade, and was used without further purification.

2.2. Preparation of cellulose/SA hydrogels

The cellulose solution was prepared according to our previous work [29] as follows. 3 g CF-11 was dispersed into 97 g of 6 wt% NaOH/4 wt% urea/90 wt% water mixture with stirring for 5 min, and then was stored under refrigeration (−20 °C) for 12 h. The frozen solid was thawed and stirred extensively at room temperature to obtain a transparent cellulose solution with a concentration of 3 wt%. SA was dissolved in the same solvent and stirred for 1 h at room temperature to obtain a 3 wt% polymer concentration. The cellulose and SA solutions were mixed rapidly by changing the weight ratio of cellulose to SA by w/w% of 9:1, 8:2, 7:3, 6:4 and 5:5, which was coded as Gel1 to Gel5. ECH (1 ml) as a cross-linker was added to the cellulose/SA mixture (10 g). The resultant mixtures were stirred at 25 °C for 1 h to yield a homogeneous solution, and then reacted at 60 °C for 2 h. Thus, the cellulose/SA hydrogels were created, and were taken out carefully to immerse in distilled water to remove the residual reagent for a week. During this period, distilled water was replaced three times for a day.

2.3. Characterization

Samples were cut into particle-like size after being freeze–dried and then vaccum-dried for 24 h at 50 °C before measurement of NMR. Cross-polarization/magnetic angle spinning (CP/MAS) solid-state ^{13}C NMR spectra were recorded on an Infinity Plus 400 Spectrometer (^{13}C frequency = 100.12 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, spectral width 50.000 kHz, acquisition time 20.48 ms, and the spectrum accumulated 2000 times. To characterize the structure, the hydrogel samples were ground into powder and dried in vacuum at 50 °C for 24 h. Thermo-gravimetric analysis (TGA) of the dry samples (5 mg) was carried out on a Pyris TGA linked to a Pyris diamond TA Lab System (Perkin–Elmer Co., USA) at a heating rate of 10 °C/min from 40 to 500 °C under nitrogen atmosphere. The wide-angle X-ray diffraction (WXRD) pattern of the dried sheets was recorded on a WXRD instrument (XRD-6000, Shimadzu, Japan) with Cu Kα radiation ($\lambda = 0.154$ nm). WXRD data were collected from $2\theta = 4$–40° at a scanning rate 1°/min. Scanning electron micrograph (SEM) measurements were carried out on a Hitachi X-650 microscope (Mountain View, CA, Japan). The swollen hydrogels in distilled water at 25 °C for 24 h were frozen in liquid nitrogen and snapped immediately, and then freeze–dried. The fracture surface (cross-section) of the hydrogel was sputtered with gold, and was observed and photographed.

2.4. Determination of mechanical strength

Rheology experiments of the samples were performed at 25 °C on ARES-RFS III rheometer (TA Instruments, USA). The mixture of cellulose and SA solutions (8 g) and 0.8 ml epichlorohydrin (ECH) was stirred to form a homogeneous solution. Such hybrid system was quickly transferred into rheometer for testing. The samples were first subjected to a strain sweep test in which they were deformed at different shear strains, and the modulus was recorded to define the linear viscoelastic zone in which 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 time sweep at a constant shear frequency (1 Hz) was conducted on each sample at 60 °C, to record the elastic stored modulus (G'), and viscous loss modulus (G'') for the investigation of the hydrogels. Dynamic mechanical analysis (DMA, TA instrument Q800 series) was used to determine the compressive modulus of the swollen hydrogel samples. To reach swelling equilibrium, hydrogels were incubated in distilled water for 24 h at room temperature before the test. The disk shaped samples were 1 cm × 0.5 cm (diameter × height) in dimension and were tested in compression mode at 25 °C.

2.5. Swelling measurements

The gravimetric method was employed to measure the swelling ratios of the hydrogels with different feed ratios in distilled water at 25 °C. The equilibrium swelling ratio (ESR) was calculated as

$$\mathrm{ESR} = W_s/W_d \quad (1)$$

where W_s is the weight of the swollen gel at 25 °C, and W_d is the weight of the gel in the dry state. To clarify the reswelling, the dried hydrogel samples were again immersed in distilled water to rehydrate at 25 °C. The samples were removed out from water at regular time intervals. After the surfaces of the gels had been wiped with filter papers to remove excess water, the weights of the hydrogels were recorded. The reported weight of each sample was an average value of three measurements. The results were expressed as water uptake (WU), and can be calculated by

$$\mathrm{WU} = (W_t - W_d)/W_s \times 100 \quad (2)$$

where W_t is the weight of the re-swollen gel at time t, and other symbols are the same as defined above.

3. Results and discussion

3.1. Structure of cellulose/SA hydrogels

Five types of novel cellulose/SA hydrogels with different feed ratios were prepared successfully by chemical cross-linking. The chemical composition and reaction conditions are listed in Table 1. Proposed mechanism for the cross-linking reaction of cellulose and SA with ECH in alkali aqueous solution is shown in Fig. 1. ECH was

Table 1
The preparation conditions of cellulose–SA hydrogels.

Code	Cellulose (3 wt%)	SA (3 wt%)	ECH	Temperature	Time
	g	g	ml	°C	h
Gel1	9	1	1	60	2
Gel2	8	2	1	60	2
Gel3	7	3	1	60	2
Gel4	6	4	1	60	2
Gel5	5	5	1	60	2

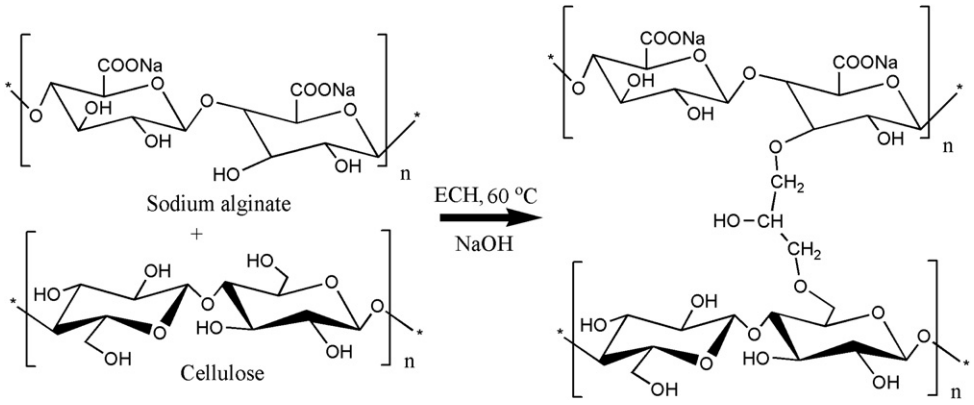

Fig. 1. Proposed mechanism for cross-linking reaction of cellulose and SA in alkali aqueous solution with ECH.

used as a cross-linker to react with the hydroxyl groups of cellulose and SA chains through nucleophilic attack of the alcoholate anion, whereas a new epoxide formed by chloride displacement [22,24,30]. The photographs of the cellulose/SA hydrogels are shown in Fig. 2. Clearly, these hydrogels exhibited good appearances, suggesting a certain mechanical strength which decreased with the increase of SA content from Gel1 to Gel5.

The solid-state ^{13}CNMR spectra have been widely applied for investigating the composition of hydrogel network. Fig. 3 shows the solid-state ^{13}C NMR spectra of cellulose/SA hydrogels (Gel5), SA, and regenerated cellulose. The assignment of the observed signals to various types of carbons is also demonstrated. In Fig. 3a, the signal at 176.7 ppm of Gel5 was due to the carboxyl carbons from SA (Fig. 3b). At 103.7 ppm the incorporation of C1′ from cellulose and C1 from SA was also observed in the spectra of Gel5. The peaks at 74.8 ppm for C4′ and 63.0 ppm for C6′ from regenerated cellulose (Fig. 3c) showed a large loss resolution in Gel5 and two shoulder peaks appeared at about 84.0 ppm and 64.5 ppm, respectively. This result indicated that cross-linking reaction had occurred in the cellulose/SA hydrogel, in good agreement with the results in the cellulose etherification reactions [31]. The intense and broad resonance centered at about 75.6 ppm is mostly attributed to resonance of other carbons in cellulose and SA.

Fig. 4a shows the WXRD patterns of the regenerated cellulose, SA, and Gel5. The diffraction peaks at $2\theta = 12$, 20, 21 and 28° were assigned to regenerated cellulose (cellulose II) and those at 16.6, 22.8° to SA [32]. However, Gel5 exhibited greater amorphous morphology than cellulose and SA. The WXRD characteristic peaks of cellulose and SA disappeared in the cellulose/SA hydrogels. This further indicated that chemical cross-linking occurred between cellulose and SA, leading to the destruction of the initial crystalline structure of cellulose and SA. TG is a powerful technique to determine the polymers' state and evaluate the inter-molecular interaction between the two polymers in the hydrogels. The TG thermograms of mixture (5:5) and Gel5, which was prepared with same weight ratio, are presented in Fig. 4b. The weight loss below 100 °C was attributed to the release of moisture from the samples. The mixture of cellulose and SA exhibited two steps of active weight loss with elevating temperature. The first step in the temperature range of 200–280 °C was assigned to the decomposition of SA. It has been reported that sodium alginate showed only one weight loss step at 200–280 °C in the course of thermal degradation [33]. The second step at 290–390 °C was caused by the onset of cellulose decomposition. However, only one sharp drop in the range from 220–380 °C occurred in the case of Gel5. It indicated that relatively high thermal stability appeared in Gel5, suggesting that the chemical cross-linking between two polymers occurred in the hydrogel.

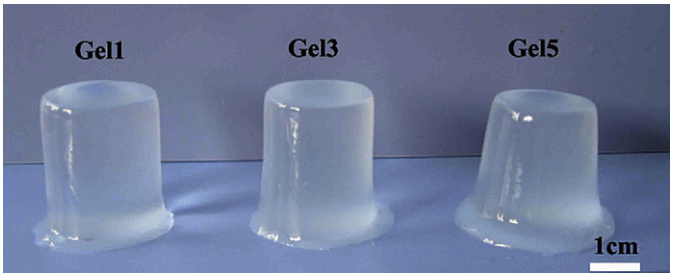

Fig. 2. The appearances of cellulose/SA hydrogels with different feed ratios.

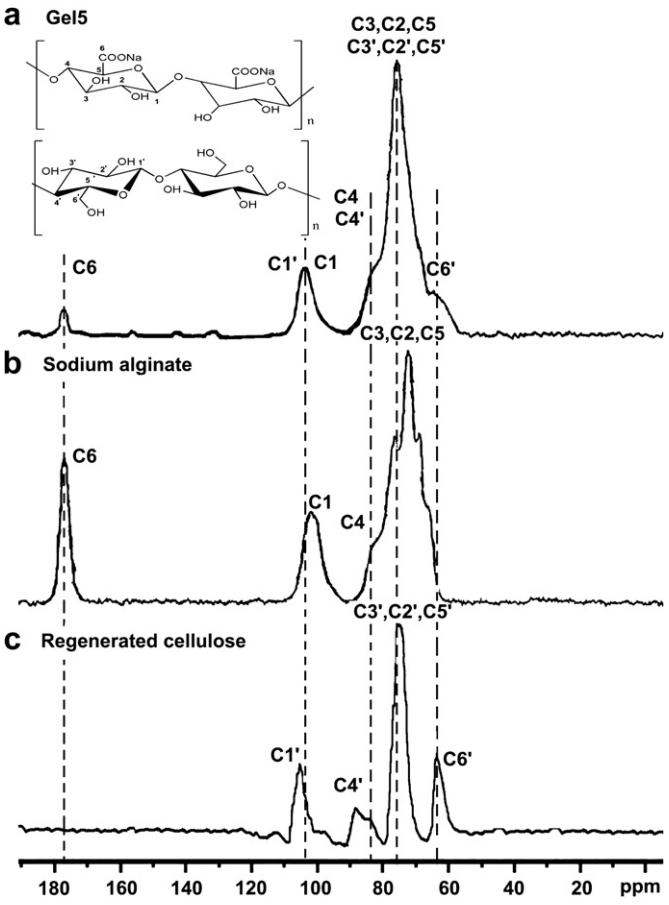

Fig. 3. ^{13}C CP/MAS solid-state NMR of Gel5 (a), SA (b) and regenerated cellulose (c).

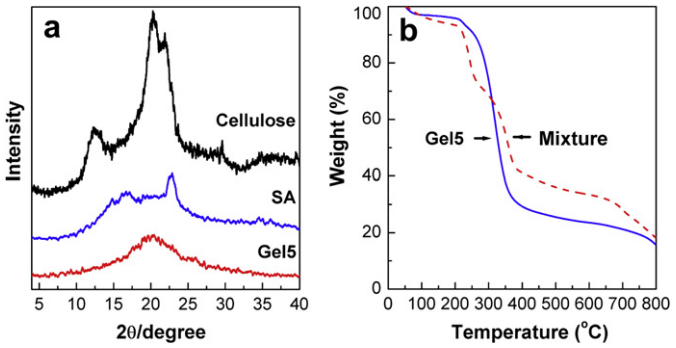

Fig. 4. (a) X-ray diffraction patterns of cellulose, SA and Gel5. (b) TG curves of mixture of cellulose and sodium alginate (5:5, weight ratio) and hydrogel (Gel5).

The interior morphologies of a series of freeze–dried, swollen hydrogels are shown in Fig. 5. The SEM images showed well-defined, interconnected, three-dimensional porous network structures. In general, the average pore size of cellulose hydrogel was about 5 to 10 μm, when cellulose chains were chemically cross-linked and regenerated from NaOH/urea aqueous solution [22]. Interestingly, the average pore size of the cellulose/SA hydrogels exceeded 200 μm, which was much larger than that of the traditional cellulose hydrogel. Moreover, the size of pores in the cellulose/SA hydrogel increased with an increase of SA content. For example, Gel1 exhibited relatively small pores with an average diameter of 200 μm, whereas Gel4 had much bigger pores with an average diameter of more than 500 μm. It was not hard to imagine that the hydrophilic SA played an important role in the enhancement of pore size. Noticeably, these pores had regular and very thin wall, suggesting the orderly aggregate of cellulose and SA chains. There was the mesh structure in the blend cellulose/SA materials, which was weaved with both alginate and cellulose [34]. Furthermore, cellulose having semi-stiff molecular chain played an important role in enhancing the strength of hydrogel, because the bulk hydrogel prepared from SA (without cellulose) was too weak to hold a lot of water. Therefore, the relatively stiff cellulose contributed to support the pore wall, whereas alginate acted as an expander of the pore size because of its high water-absorbency. The combination of cellulose and SA created the macroporous structure in the hydrogels. This work provided an effective way to construct stable hydrogel with macroporous structure by inducing both hydrophilic polysaccharide and stiff polymer into hydrogel network. These macroporous hydrogels always having higher swelling ratio, can provide fast water releasing channels [35] and act as effective enzyme-carriers [36].

3.2. Gelation behavior and mechanical properties

To monitor the gelation time of such hybrid systems and the storage modulus of the formed hydrogels, a time sweep measurement for viscoelastic properties of each system was carried out at 60 °C. Fig. 6 shows the time dependence of storage modulus (G') and loss modulus (G'') for cellulose solution with ECH (a) and five hybrid systems with different cellulose/SA weight ratios (b–f). All samples exhibited a similar rheological behavior, namely, the hybrid systems at initial time behaved as viscous liquid, G' was smaller than G'', then G' increased more rapidly than G'' with prolonging time, and G' exceeded G'', thus the system behaved as gel state. This crossover ($G' = G''$) was a well-known phenomenon in cross-linking reaction, and it could be described by the gel point ($t = t_{gel}$) [37,38]. The results indicated the transition of the cellulose/SA liquid phase to a gel state as a result of the cross-linked network formation. All gel points appeared at different times as shown in Table 2, when the hydrogel systems were prepared with different cellulose/SA feed

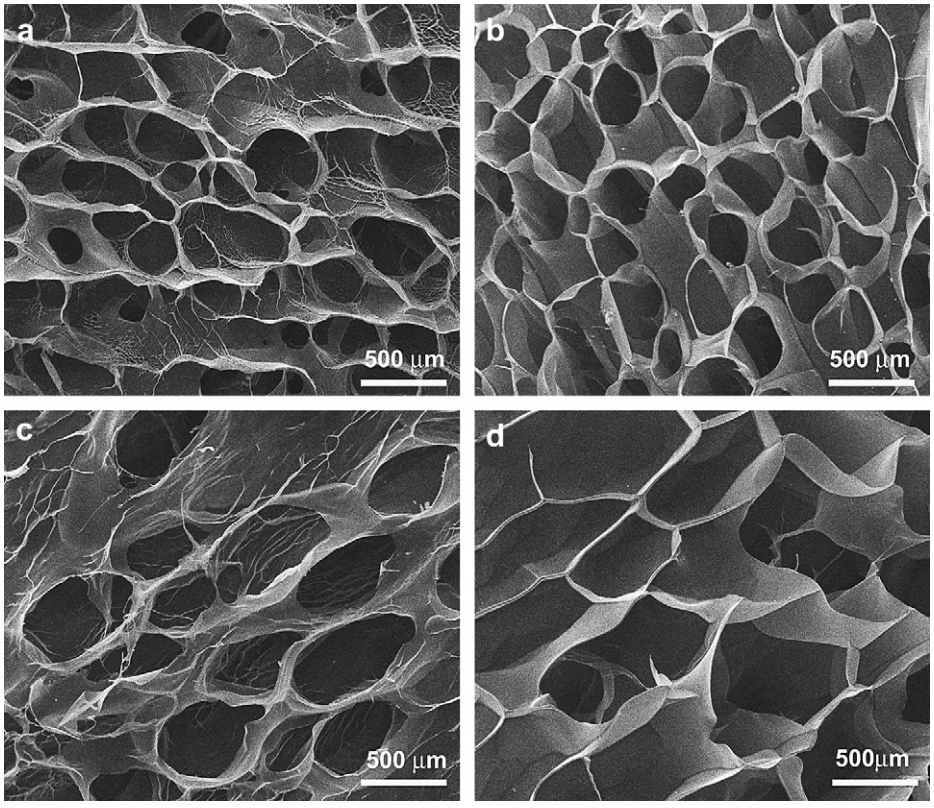

Fig. 5. SEM images of cellulose/SA hydrogels: (a) Gel1, (b) Gel2, (c) Gel3 and (d) Gel4.

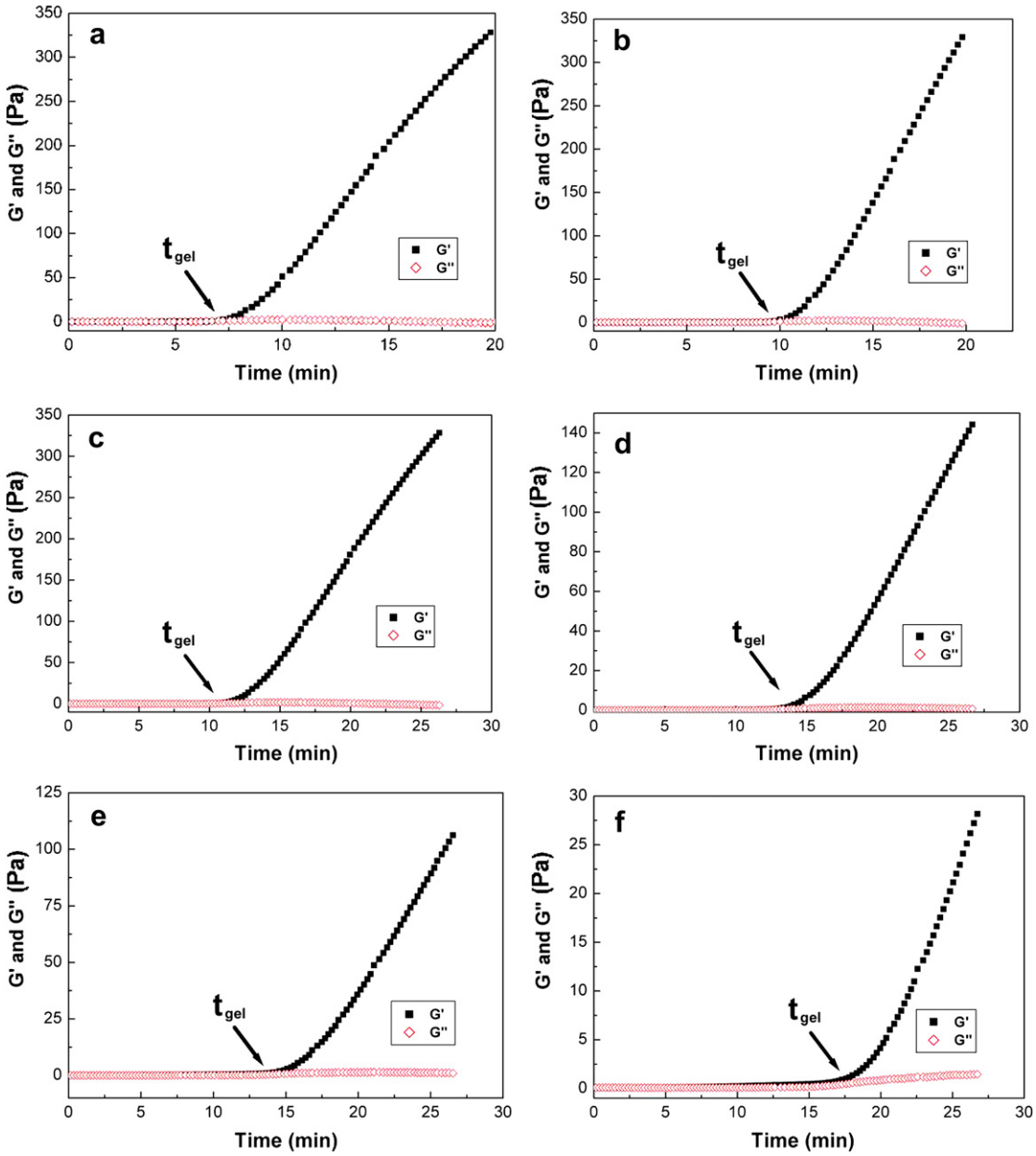

Fig. 6. The time dependence of storage modulus (G') and loss modulus (G'') for five hybrid systems: (a) cellulose hydrogel, (b) Gel1, (c) Gel2, (d) Gel3, (e) Gel4 and (f) Gel5.

ratios. The gel point of the cellulose hydrogel (without SA) was at about 7 min. The gel points of cellulose/SA hydrogel increased from 9.3 to 17.8 min, with an increase of the SA content, indicating that cellulose mainly contributed to the formation of the hydrogel network. Moreover, the maximum storage modulus of the hydrogels decreased with decrease of cellulose content. This further proved that cellulose played a key role in supporting the hydrogels, leading to the improvement of their strength.

Table 2
Physical properties of cellulose–SA hydrogels.

Code	t_{gel}	G'	Stress	ESR
	min	Pa	kPa	g/g
Gel1	9.4	666	30.9	38.2
Gel2	9.8	373	25.9	69.2
Gel3	12.3	144	19.3	82.3
Gel4	13.8	106	10.1	150.7
Gel5	16.3	28	9.3	253.7

The mechanical properties of the cellulose/SA hydrogels with different feed ratios have been determined. Fig. 7 presents the typical compressive modulus–strain curves of cellulose/SA hydrogels at room temperature. Obviously, the cellulose/SA hydrogels exhibited excellent mechanical properties. As expected, the compressive modulus of the hydrogels increased with a decrease of the SA content in the hydrogels, in the order Gel1 > Gel2 > Gel3 > Gel5. The results strongly demonstrated that cellulose contributed to enhance the mechanical properties of the cellulose/SA hydrogels. On the other hand, the strains of hydrogels increased from 59% to 86%, when the SA content was enhanced in the hydrogel. It should be emphasized that, when the weight ratio of cellulose/SA is below 5:5, it is difficult to form a bulk hydrogel with any strength from this method, because such a network was too weak to hold considerable water. Therefore, cellulose was the backbone of the hydrogel matrix, in which SA could

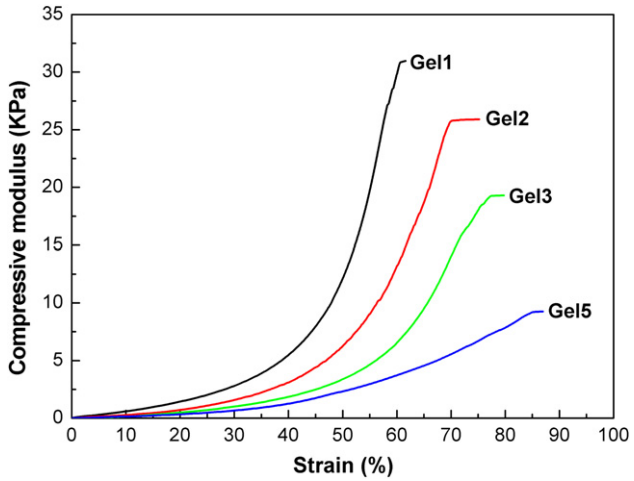

Fig. 7. Typical compressive modulus–strain curves of cellulose/SA hydrogels at room temperature.

retain a lot of water. It is anticipated that the mechanical properties of cellulose/SA hydrogels can be controlled by adjusting the content of cellulose to be consistent with their application.

3.3. Equilibrium swelling ratio and swelling behavior

Fig. 8 shows the effect of the feed ratio of the hydrogel precursors on the equilibrium swelling ratio of the cellulose/SA hydrogels at room temperature. The hydrogels exhibited high equilibrium swelling ratio in distilled water. Their equilibrium swelling ratio (ESR) is listed in Table 2. As the feed ratio of cellulose to SA in the hydrogels decreased from 9:1 to 5:5, ESR increased rapidly from 38.2 to 253.7 g/g. This result indicated directly that SA chains were more hydrophilic than cellulose and improved the hydrophilicity of the hydrogels, leading to higher equilibrium swelling ratio. The high SA content hydrogels possessed good hydrophilic properties, resulting in the enhancement of water absorbing capacity in the cellulose/SA hydrogels. This supported the conclusion that SA acted as expander of the pore sizes.

The vacuum-dried hydrogel samples were allowed to hydrate water at room temperature. Their reswelling kinetic curves are illustrated in Fig. 9. There was a typical biphasic swelling pattern,

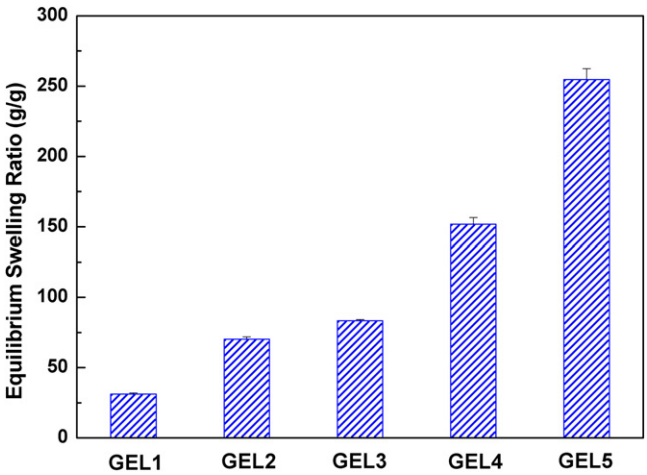

Fig. 8. Swelling properties of cellulose/SA hydrogels with different feed ratios from Gel1 to Gel5.

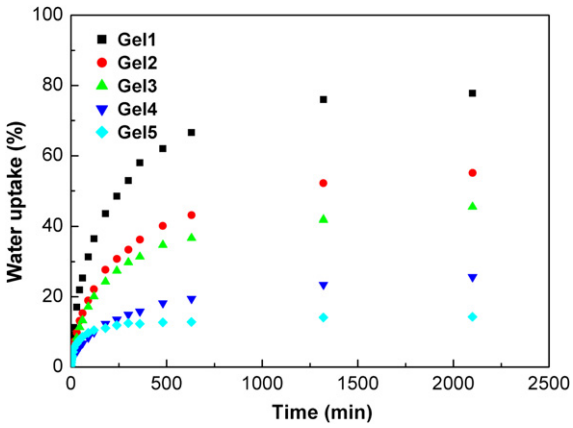

Fig. 9. Reswelling kinetics of the cellulose/SA hydrogels in distilled water at room temperature.

namely a rapid swelling followed by a slower sustained swelling (equilibrium swelling). All hydrogels swelled in water very quickly during the first 100 min; then, the swelling rates of the hydrogels became very slow, and they finally reached the swelling equilibrium in about 500–600 min. It can be found that the water uptake of all hydrogel samples cannot reach 100%. This could be explained by the fact that 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, the hydrogel samples showed lower water uptake. As the feed ratio of cellulose to SA in hydrogels decreased from 9:1 to 1:1, the water uptake decreased from 80% to 15%, because the bigger pores collapsed more easily during the vacuum-drying process.

4. Conclusion

Hydrogels having macroporous structure were fabricated successfully from cellulose and sodium alginate in NaOH/urea aqueous system through chemical cross-linking with epichlorohydrin. These hydrogels had excellent mechanical strength and high equilibrium swelling ratio in water. The introduction of SA into cellulose hydrogel increased significantly the pore size and swelling ratio. And cellulose could improve the mechanical properties of cellulose/SA hydrogel. The combination of cellulose containing semi-stiff chain and alginate containing –COOH groups created macroporous structure in the cross-linking hydrogels. In the hydrogels, cellulose contributed to support the pore wall whereas alginate acted as an expander of the pore size. This work provided a new pathway to construct macroporous hydrogels through combination of the stiff cellulose and high hydrophilic natural polymers.

Acknowledgement

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References

[1] Bingöl B, Strandberg C, Szabo A, Wegner G. Macromolecules 2008;41:2785–90.
[2] Kurisawa M, Yui N. Macromol Chem Phys 1998;199:1547–54.

[3] Zhang X, Wu D, Chu CC. Biomaterials 2004;25:4719–30.
[4] Huh KM, Bae YH. Polymer 1999;40:6147–55.
[5] Mawad D, Poole-Warren L, Martens P, Koole L, Slots T, van Hooy-Corstjens C. Biomacromolecules 2008;9:263–8.
[6] Kraehenbuehl T, Zammaretti P, Van der Vlies A, Schoenmakers R, Lutolf M, Jaconi M, et al. Biomaterials 2008;29:2766.
[7] Moura M, Figueiredo M, Gil M. Biomacromolecules 2007;8:3823–9.
[8] Qu X, Wirsén A, Albertsson AC. Polymer 2000;41:4589–98.
[9] Zhao S, Ma D, Zhang L. Macromol Biosci 2006;6:445–51.
[10] Kumashiro Y, Lee W, Ooya T, Yui N. Macromol Rapid Commun 2002;23:407–10.
[11] Chen J, Liu M, Jin S, Liu H. Polym Adv Technol 2008;19:1656–63.
[12] Kumar R, Liu D, Zhang L. J Biobased Mater Bioenergy 2008;2:1–24.
[13] Bardajee GR, Pourjavadi A, Soleyman R, Sheikn N. Nucl Instrum Methods Phys Res B 2008;266:3932–8.
[14] Klemm D, Schumann D, Udhardt U, Marsch S. Prog Polym Sci 2001;26:1561–603.
[15] Klemm D, Heublein B, Fink HP, Bohn A. Angew Chem Int Ed 2005;44:3358–93.
[16] Klemm D, Schumann D. Cellulose 2008;15:359–60.
[17] Koschella A, Heinze T, Klemm D. Macromol Biosci 2001;1:49–54.
[18] Zhou J, Zhang L. Polym J 2000;32:866–70.
[19] Cai J, Zhang L, Liu S, Liu Y, Xu X, Chen X, et al. Macromolecules 2008;41:9345–51.
[20] Cai J, Zhang L, Zhou J, Qi H, Chen H, Kondo T, et al. Adv Mater 2007;19:821–5.
[21] Qi H, Chang C, Zhang L. Green Chem 2009;11:177–84.
[22] Zhou J, Chang C, Zhang R, Zhang L. Macromol Biosci 2007;7:804–9.
[23] Cai J, Kimura S, Wada M, Kuga S. Biomacromolecules 2009;10:87–94.
[24] Chang C, Lue A, Zhang L. Macromol Chem Phys 2008;209:1266–73.
[25] Kim SJ, Yoon SG, Lee SM, Lee JH, Kim SI. Sens Actuators B 2003;96:1–5.
[26] Sakai S, Yamaguchi S, Takei T, Kawakami K. Biomacromolecules 2008;9:2036–41.
[27] Pourjavadi A, Ghasemzadeh H, Soleyman R. J Appl Polym Sci 2007;105:2631–9.
[28] Kalyani S, Smitha B, Sridhar S, Krishnaiah A. Ind Eng Chem Res 2006;45:9088–95.
[29] Zhang L, Zhou J. CN 00114486.3, 2003.
[30] Miguel ID, Rieumajou D, Betbeder D. Carbohydr Res 1999;319:17–23.
[31] Zhou J, Zhang L, Deng Q, Wu X. J Polym Sci Part A Polym Chem 2004;42:5911–20.
[32] Yang G, Zhang L, Peng T, Zhong W. J Membr Sci 2000;175:53–60.
[33] Liang CX, Hirabayashi K. J Appl Polym Sci 1992;45:1937–43.
[34] Zhou J, Zhang L. J Polym Sci Part B Polym Phys 2001;39:451–8.
[35] Zhang XZ, Chu CC, Zhuo RX. J Polym Sci Part A Polym Chem 2005;43:5490–7.
[36] Zhao Q, Sun J, Ren H, Zhou Q, Lin Q. J Polym Sci Part A Polym Chem 2008;46:2222–32.
[37] Sahiner N, Singh M, Kee DD, John VT, McPherson GL. Polymer 2006;47:1124–31.
[38] Weng L, Chen X, Chen W. Biomacromolecules 2007;8:1109–15.