

# The Water State in Crosslinked Poly(vinyl alcohol)–Collagen Hydrogel and Its Swelling Behavior

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**ABSTRACT:** Poly vinyl alcohol (PVA) with pendent carboxyl group was synthesized and verified. The collagen was chemical crosslinked with the produced PVA under the help of crosslinker. Then, the PVA–collagen hydrogels were prepared through the repeated freezing–thawing. Since the water states in hydrogels play an important role in the performance of the product, thermogravimetric (TG) analysis and differential scanning calorimeter (DSC) were conducted to study the different states of water. The results indicated that the weight ratio of nonfreezable water to dry gel in PVA–collagen hydrogels was about 25%. Meanwhile, the swelling behaviors in distilled water and 0.9% saline were studied. The one-phase exponential

associate equation can fit the process very well. Calculated from the simulation equation, the swelling ratios at equilibrium in distilled water and saline were 14.353 g/g dry gel and 14.205 g/g dry gel, respectively. The results illustrated that the ions in solution would decrease the swelling ratio of the hydrogel. At the same time, the lyophilization might have slighter influence to the microstructure of hydrogels and should be more suitable for the swelling research than heat drying. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2753–2761, 2012

**Key words:** poly vinyl alcohol; collagen; hydrogel; water state; swelling behavior

## INTRODUCTION

Poly (vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer with excellent properties in both chemical and mechanical. With a history of being widely researched, PVA-based hydrogels have been applied in several fields of biomedical engineering, including the wound healing, drug delivery, and tissue scaffold. Examples of clinical research or application of PVA hydrogels are diverse, such as Masanori et al.<sup>1</sup> prepared an artificial meniscus using PVA hydrogels and run a preliminary study in animal experiment, and neither wear nor breakage happened after 1 year of observation; Hideyuki and coworkers developed a PVA hydrogel with collagen immobilized and applied as corneal scaffold<sup>2,3</sup>; Lee et al. made PVA hydrogel composite scaffold with other material and evaluated the performance as a scaffold for cartilage tissue engineering in a weight-bearing environment.<sup>4</sup> PVA is so hydrophilic that the protein cannot be easily attached, leading to the

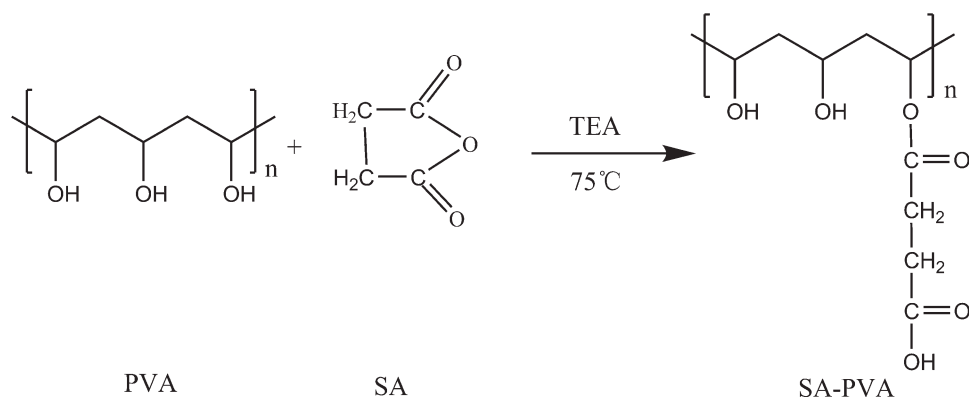
bioinert characteristic of the product and not suitable for the cell's proliferation or growth. Therefore, the bioactive materials, such as collagen and gelatin, are employed to improve the performance of PVA-based biomaterials.

As another major component of the hydrogels, the water in polymers affects their properties in several ways.<sup>5–7</sup> A better understanding of the water state in hydrogels can not only elucidate the behavior of swelling but also learn more about the internal microstructure of the polymer network. According to the literature on hydrogels, it is well established that there are three different states of water in the network, i.e., free water, intermediate water, and bound water (or nonfreezable water).<sup>5–8</sup> The distinguishing of the three physical states is mainly based on the freezing temperature. Free water can freeze at the usual freezing temperature, and the intermediate water will freeze at a lower point than free water does. These two states of water are considered as freezable water, while the bound water is classified as nonfreezable water, because it will not freeze at the usual freezing point.

There are several techniques to study the states of water in the hydrogel.<sup>7</sup> Briefly, thermoanalysis and spectroscopy are commonly employed, such as differential scanning calorimetry (DSC), thermogravimetric (TG), and Fourier transform infrared

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**Figure 1** The chemical reaction equation of PVA and SA.

spectroscopy (FTIR). Meanwhile, nuclear magnetic resonance (NMR) and X-ray diffraction are used as well.

However, the previous water states researches are investigated according to a similar routine. First, the hydrogels are prepared and reach the equilibrium of water absorption. Then, the hydrogels are dried by water evaporation at room temperature for different time intervals<sup>9</sup> or at high temperature (60–70°C) until constant weight.<sup>5,8,10,11</sup> Subsequently, the hydrogels re-swell in water to get the samples with different water contents. Finally, the samples are tested with DSC or some other techniques. The deficiencies of the sample preparation during this procedure is that the heat drying might cause the collapse of some microstructure and is not suitable for some temperature sensitive components in the hydrogel. Meanwhile, the re-swelling of dried hydrogel is slow, neither even nor adequate. These will have influence, in some degree, to the research of water states and absorption behavior in reaching the equilibrium. One objective of the work in this article is trying to compare the sample preparation of lyophilization and heat drying. On the other hand, we are aiming to learn the water states in PVA–collagen hydrogel, which is earlier developed and might be potential in application. At the same time, the correlation between water states and swelling behavior will be discussed.

## EXPERIMENTAL

### Materials

The poly (vinyl alcohol) (PVA) was analytically pure and purchased from Kelong Chemical (Chengdu, China). The average degree of polymerization was  $1700 \pm 50$ , and the degree of hydrolyzation was 99%.

The collagen was self-prepared from porcine skin, which was developed and purified by a method we acquired.<sup>12</sup> The collagen was freezing dried and

preserved as sponge. As revealed by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE), the collagen had three main components. Two of them were close up to each other and a little higher than the standard marker of 116 kDa, while another separate one was near 200 kDa.

1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC HCl) and *N*-hydroxysuccinimide (NHS) were purchased from Medpep (Shanghai, China). The purity of both the chemicals is higher than 99%.

The other chemicals were analytical reagents, purchased from local chemistry market and had no further purification before use.

### PVA modification

The weighed PVA was added into a three-necked bottle and dissolved in dimethyl sulfoxide (DMSO) at 60°C stirring with a motor stirrer. After obtaining an even solution, a small amount of triethylamine (TEA) was added. The bottle was held in a water bath, and the temperature was kept at 75°C. Then, the succinic anhydride (SA) solution, which was prepared with SA dissolved in three times weight of DMSO, was added dropwise into the three-necked bottle. The reaction was held for about 4.5 h. The reaction diagram was shown in Figure 1. Following the reaction, the solution was cooled to room temperature and then gently poured into 20% sodium hydroxide methanol solution, while the latter solution was kept on stirring with a stirrer. The modified PVA would be solidified and precipitated in the solution. Since the outcome will be solidified as fibers or clots, they were necessary to be cut into small pieces with scissors. The new-formed solid was soft and can be cut easily. Subsequently, the product was filtrated and washed with distilled water, 0.2 mol/L hydrochloric acid, and adequate distilled water, respectively. After dried in vacuum drying oven at 50°C, the product was preserved in desiccator and marked as SA–PVA. The carboxyl group content in

SA-PVA was considered to indicate the degree of reaction, which can be adjusted by changing the ratio of SA to PVA. The degree of conversion in the reaction can be deduced with the contents of carboxyl groups in practical and in theory. Generally, the equal weight of SA and PVA (molar ratio of anhydride to hydroxy was around 0.44 : 1) would gain the content of carboxyl groups around 0.2 mmol/g, and the conversion was about 5%.

The content of carboxyl groups was determined according to a Chinese National Standard of Determination for Residual Acetic Radical Contents (or Alcoholysis) of Poly Vinyl Alcohol Resins (GB 12010.5-1989). The employed method was based on the titrations by standard solutions. The SA-PVA used in this experiment had a content of carboxyl groups at  $0.119 \pm 0.012$  mmol/g. For a better verification of the modification, both PVA and SA-PVA membranes were prepared for FTIR tests. In the FTIR curves of both samples, the hydroxyl group has a strong and wide absorption band at the range of  $3300\text{--}3400\text{ cm}^{-1}$ , and at a frequency of  $1142\text{ cm}^{-1}$ , which has been used as an assessment tool of PVA structure, because it is a semicrystalline synthetic polymer able to form some domains.<sup>13</sup> Meanwhile, the FTIR curve of SA-PVA displays a peak at  $1711\text{ cm}^{-1}$ , which can be verified as carbonyl group (C=O).

### Hydrogels preparation

To prepare the SA-PVA solution, the weighed SA-PVA was added into a conical beaker. The distilled water was added to make the PVA concentration around 10%. Then, the conical beaker was set in a water bath and heated to  $90^{\circ}\text{C}$ . Since the carboxyl group is more hydrophilic than the hydroxy group, the existence of the carboxyl groups in the SA-PVA made it easier to dissolve than the raw PVA. Stirring with a motor stirrer, the SA-PVA was dissolved to an even and viscous aqueous solution, and there was no insoluble material. The solution was ready to use when it cooled to room temperature.

The collagen sponge was accurately weighed and added to 0.1 mol/L acetic acid, stirring at  $4^{\circ}\text{C}$  with a magnetic stirrer to a concentration of 0.5%.

The SA-PVA and collagen were crosslinked with EDC and NHS. The weight ratio of PVA to collagen was 10 : 1 (based on the weight of solute), and the dosage of EDC and NHS was 1 mmol/g of the final solution. To a certain weight of SA-PVA solution, the weight of collagen solution and the dosages of EDC and NHS could be confirmed. According to the reaction principle of the EDC and NHS system, the carboxyl groups will be activated first and then reacted with the available amino groups. Thus, the NHS was added to the SA-PVA solution at first.

After the dissolution of NHS, the EDC was added. Stirred for about 60 min, the collagen solution was added and kept on stirring for 4–5 h around  $25^{\circ}\text{C}$ . Since the collagen was dissolved in weak acid, the pH of the blended solution would be around 4.0–4.5, which is a suitable environment for the crosslinking. Subsequently, the hydrogels were made according to the method first reported by Peppas.<sup>14</sup> Particularly, the reacted solution was cast evenly into Petri dish ( $\Phi = 9\text{ cm}$ ) and frozen at  $-20^{\circ}\text{C}$ ; after being frozen for 10–12 h, the dishes were moved to ventilation and thawed at room temperature for 4–5 h. This freezing and thawing procedure was considered as one freezing–thawing cycle. The hydrogels were prepared after running five cycles. Following the freezing–thawing cycles, the hydrogels were soaked in distilled water, and the water was frequently changed for 3 days to remove the residual crosslinker. Finally, the hydrogels were lyophilized and preserved. Since the hydrogels were developed through repeated freezing and thawing, the freeze-drying process would have no effect on the structure or performance.

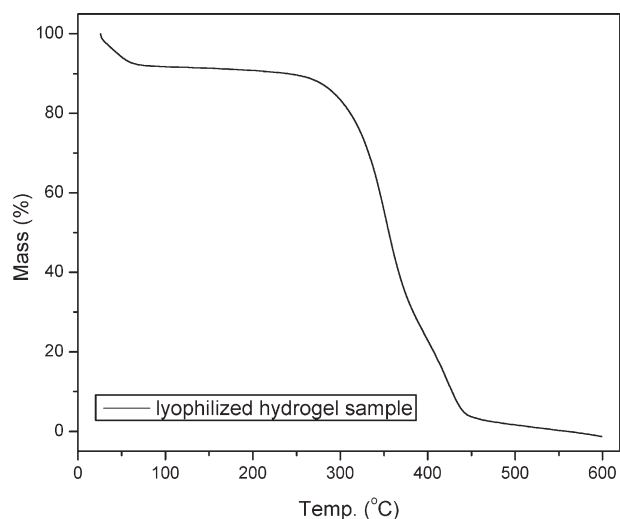
### Thermogravimetric analysis

The TG tests were run by Netzsch TG 209 F1. Through the TG tests, the water content of lyophilized hydrogel can be determined, and the thermal degradation can be observed as well. In the TG analysis, the hydrogels samples were moved to alumina crucible as soon as they were cut and prepared. The tests were run from  $25^{\circ}\text{C}$  to  $600^{\circ}\text{C}$  with a heating rate of 5 K/min and protected with nitrogen at 20 mL/min.

### Differential scanning calorimetry analysis

All the DSC data were evaluated on a Netzsch DSC 200 PC. The lyophilized PVA–collagen hydrogels were cut into pieces and accurately weighed. A small amount (among from 1 to 5  $\mu\text{L}$ ) of distilled water was sprayed to the samples to various water contents. Kept at room temperature for about 30 min, the hydrogels samples were surface-dried with absorbent paper and transferred into the aluminum pan. The pan was quickly and carefully sealed to prevent water from evaporating and precisely weighed with a Sartorius BP 210D (degree of accuracy is 0.01 mg). The water content of the hydrogels samples can be calculated according to the weight difference. The weights of hydrogel samples in the DSC tests were  $4 \pm 2\text{ mg}$ .

In the DSC determination, the samples were cooled from room temperature down to lower than  $-40^{\circ}\text{C}$  with the help of liquid nitrogen and held for about 15 min. Then, the samples were heated to



**Figure 2** The TG curve of lyophilized PVA-collagen hydrogel.

−20°C at a heating rate of 2 K/min and further heated to 25°C at a heating rate of 0.5 K/min. It is reported that a smaller heating rate will generate a better resolution of melting behavior of water.<sup>8</sup> During the test, the nitrogen was applied as protecting gas at 20 mL/min, and an empty sealed aluminum pan was used as a reference.

For a quantitative analysis of the water content in hydrogel samples, we tried to establish a calibration curve that gave the variation of the peak area (heat of fusion, J) versus the mass of distilled water (mg). The distilled water was carefully sealed in precisely weighed aluminum pan, and the weights of water samples were recorded. Then, the tests were run as the method mentioned earlier.

### Swelling behavior

The lyophilized hydrogels samples were cut into pieces, accurately weighed, and immersed into the distilled water and 0.9% sodium chloride solution, respectively. The swelling experiments were realized at 25°C in water bath. For every 20–30 min, the samples were surface-dried with the absorbent paper and weighed. After recorded for 6 h, the samples were soaked overnight and weighed at irregular intervals. The whole weighing process sustained for about 24 h. The swelling ratio,  $Q_t$ , was calculated according to the following equation.

$$Q_t = \frac{W_t - W_0}{W_0} \quad (1)$$

where,  $W_0$  is the weight of the lyophilized hydrogels,  $W_t$  is the weight of the swollen hydrogels, and  $t$  is the swelling time. Accordingly, swelling kinetics was defined by the change of  $Q_t$  versus time. For

each data point of swelling curve, three samples were assessed.

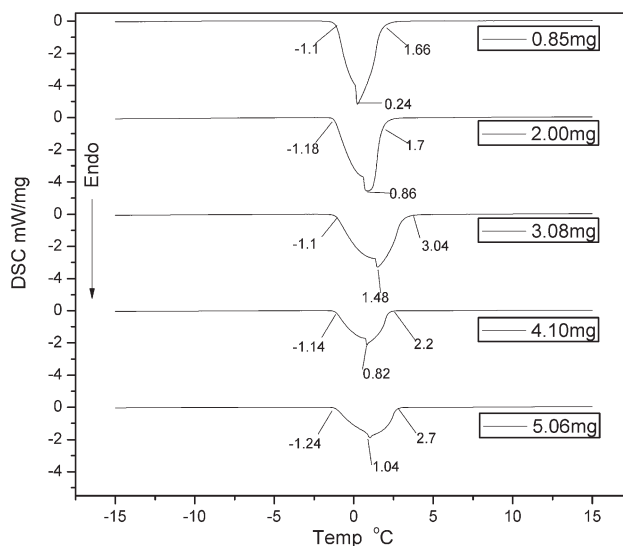
## RESULTS AND DISCUSSION

### TG analysis

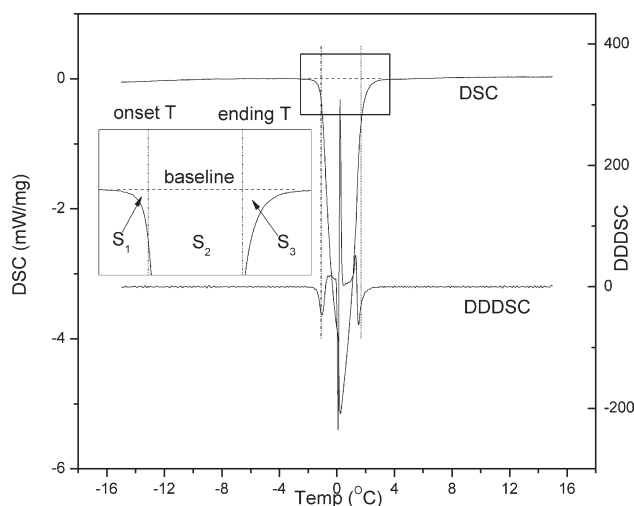
The TG data are gained by Netzsch Proteus, which is the official software provided by Netzsch. The TG curve of the lyophilized hydrogel sample is shown in Figure 2. The first weight-losing stage and flat appeared around 100°C, which means the water evaporated, and the analysis result indicates that the water content in lyophilized hydrogel sample is 8.29 wt %. The main thermodegradation begins around 330°C, and about 50 wt % of the weight is lost; while there is another weight change around 410°C, and the weight-losing percent is about 36 wt %.

### DSC analysis

The DSC data are collected and analyzed by Netzsch Soft too. The DSC curves of different amounts of distilled water are shown in Figure 3. The weights of the distilled water run in the tests range from 0.85 to 5.06 mg. Reading from the curves, the DSC peak gets lower and wider when the sample weight is increasing. The onset, peak, and ending temperatures of the phase transition are obtained by Proteus Analysis, and the results are labeled on the curves. The onset and ending temperatures are calculated according to the quadratic differential of the DSC curve (DDDSC). For example, the DDDSC curve of 0.85-mg H<sub>2</sub>O was shown in Figure 4. We can find that the curves show some consistency on the onset temperatures, which ranged from −1.10°C to



**Figure 3** The DSC curves of distilled water with different weights.



**Figure 4** A calculation sample of heat of fusion.

$-1.24^{\circ}\text{C}$ . However, the ending temperatures are at variance, varying from  $1.66^{\circ}\text{C}$  to  $3.04^{\circ}\text{C}$ . It is reported that there is a linear relationship between the area (heat of fusion) and the mass of the solvent.<sup>5,8</sup> However, the calculation is not well reported. The soft of Proteus Analysis can estimate the result between the baseline and the curve (viz.  $S_1 + S_2 + S_3$  in the insert figure of Fig. 4) but cannot give the precise area among the baseline, the curve, the onset temperature line, and the ending temperature line (viz.  $S_2$  in the insert figure of Fig. 4). Thus, we tried to determine the area by the software of OriginPro 8.0. According to the results calculated, the calibration curve of  $\Delta H$  (J) versus the weight of distilled water (mg) was plotted as shown in Figure 5.

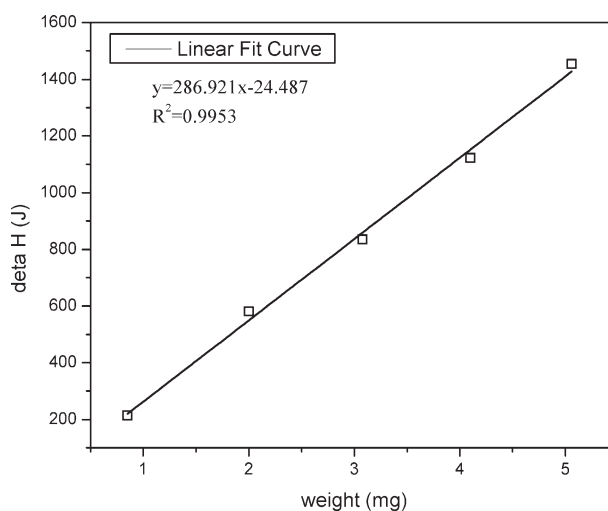
The DSC curves of PVA–collagen hydrogels with different water contents are shown in Figure 6. From the curves, we can find that the lyophilized sample does not show any transformation of heat around  $0^{\circ}\text{C}$ , but all the other samples present two peaks that are adjacent to each other. With the calculating method mentioned earlier, we obtain the areas of each peak, and the results are further used to estimate the weight of freezable water. Since the total water content in the samples can be deduced according to the preliminary weights, the characteristics and phase transition temperatures of the PVA–collagen hydrogels are listed in the Table I. Consequently, the weights of freezing water ( $W_f$ ) and non-freezable water ( $W_n$ ) are worked out, and the proportions are plotted in Figure 7.

Reading from the curves in Figure 7, we can see the changes of weight ratios of different water states and can further realize the regular pattern of water absorption in PVA–collagen hydrogels. Since the hydrogel samples are freezing-dried with low content of water (the value of  $W_h/W_g$  is  $9.31\%$ ) and do

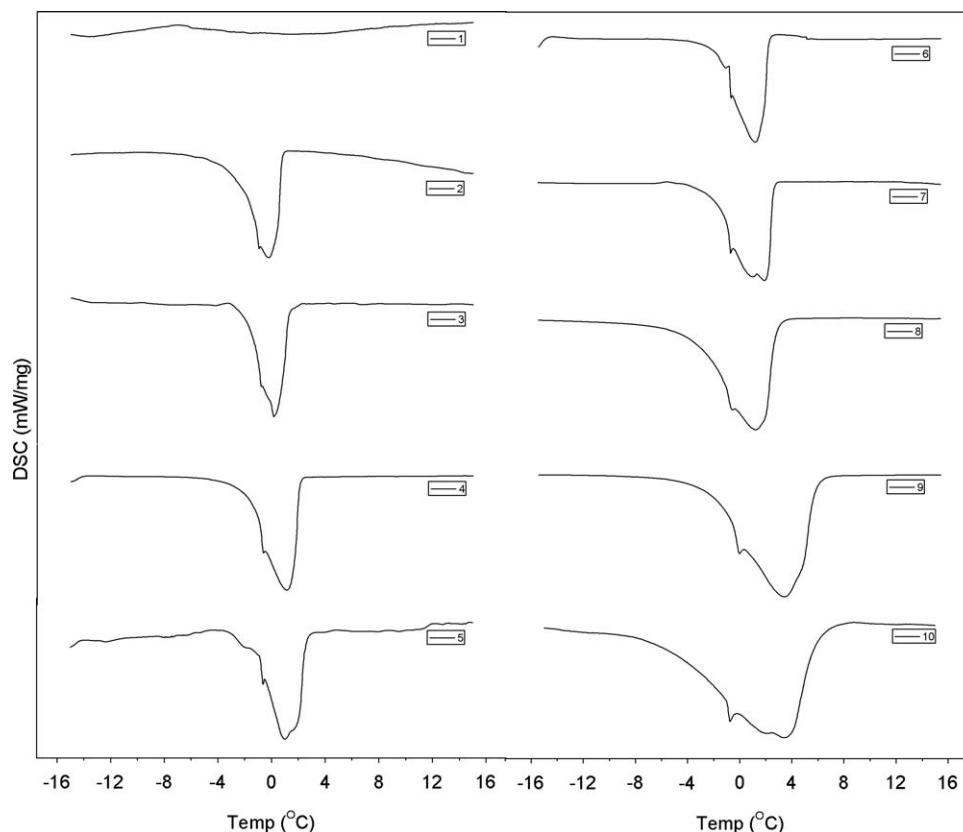
not show any phase transition in the DSC curve, the water in lyophilized sample can be considered as nonfreezable. With the increase of water absorbed in the hydrogels, i.e., when the value of  $W_h/W_g$  is climbing, the ratio of freezable water to dry gel ( $W_f/W_g$ ) increases at a similar model. However, the ratio of nonfreezable water to dry gel ( $W_n/W_g$ ) keeps in a limited range during this process. The Figure 8 illustrates the changes of  $W_n/W_h$  and  $W_f/W_h$ . The weight ratio of nonfreezable water to total water keeps on decreasing from  $100\%$  with the increasing of water content in the hydrogel samples.

The phenomena observed above can be explained by the process of water absorption in PVA–collagen hydrogels. When in contact with the hydrogel, water molecules will first bond with the hydrophilic groups in the hydrogels through hydrogen bond, leading to a stable state of nonfreezable water. The proportion of nonfreezable water is small, and the process is quick. The data and trend of  $W_n/W_g$  validate the explanation. Subsequently, the water will fill the pore among the hydrogels progressively until the absorption and swelling balance. Since the  $W_n/W_g$  is steady, the value of  $W_n/W_h$  declines and  $W_f/W_h$  rises up when the  $W_c$  is increasing. These are in consistent with the water diffusion process in three water states model.

Since the bonding of nonfreezable water is mainly depended on the hydrophilic groups, the hydrogels made of PVA with similar concentration and content of hydrophilic groups will have close  $W_n/W_g$ . The higher capacity of hydrophilic groups will attain a higher ratio of nonfreezable water. Takahiko and Hiroyuki prepared a series of nonmodified PVA hydrogels by repeated freezing and thawing, and the final content of nonfreezable water is as low as  $13.1\%$  for low concentration gel.<sup>9</sup> The PVA–EDTA



**Figure 5** The calibration curve of  $\Delta H$  (J) versus the weight of distilled water (mg).



**Figure 6** The DSC curves of PVA–collagen hydrogels with different water contents.

hydrogels developed with OH/anhydride group ratio of 1/0.250, which were made by Ruiz et al., arrived at a content of nonfreezable water of 24%.<sup>7</sup> Li et al. made a PVA hydrogels crosslinked with epichlorohydrin and got the  $W_n/W_g$  of 20%.<sup>11</sup> Compared with the reported results of the parallel hydrogel, the PVA–collagen hydrogel arrived at balanced nonfreezable water content around 25%, which is a little higher than the literature values. The reasons for this difference should be the

introduction of carboxyl group to the PVA molecule and the presence of collagen in the hydrogel. Both of the reasons raise the content of hydrophilic groups in the hydrogel and the “bonding sites” for water molecule.

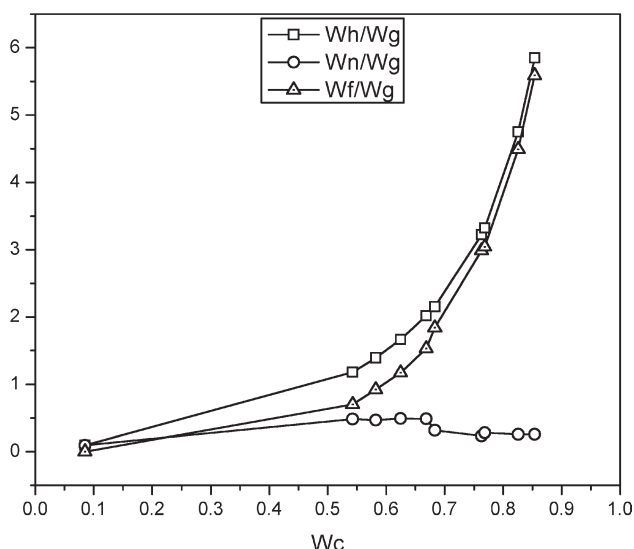
### Swelling behavior

The swelling ratios ( $Q_t$ ) of the PVA–collagen hydrogels in distilled water and saline solution at different

**TABLE I**  
Characteristics and Phase Transition Temperatures of PVA–Collagen Hydrogels

No.	$W_c$ (%)	$T_1$ (°C)	$T_2$ (°C)	$T_3$ (°C)	$\Delta H_{f1}$ (J/g)	$\Delta H_{f2}$ (J/g)
1	8.29	/	/	/	/	/
2	54.24	-1.68	-0.86	0.62	7.76	17.93
3	58.20	-1.96	-0.74	1.26	8.84	17.85
4	62.46	-1.22	-0.50	2.08	7.01	34.81
5	66.86	-3.76	-0.48	2.58	8.22	30.14
6	68.31	-2.20	-0.50	2.14	8.30	33.20
7	76.31	-2.62	-0.50	2.50	8.47	43.48
8	76.87	-1.72	-0.32	2.70	9.31	27.29
9	82.60	-1.52	-0.24	5.04	9.78	26.79
10	85.39	-6.62	-0.04	5.56	18.92	30.55

Note:  $W_c$  is short for the water content of PVA–collagen hydrogel samples calculated from weighing or TG tests.  $T_1$  and  $T_2$  correspond to the onset and ending temperatures of intermediate water’s phase transition peak, while  $T_2$  and  $T_3$  stand for the temperatures of free water’s peak.  $\Delta H_{f1}$  and  $\Delta H_{f2}$  are the enthalpy of intermediate water and free water, respectively.

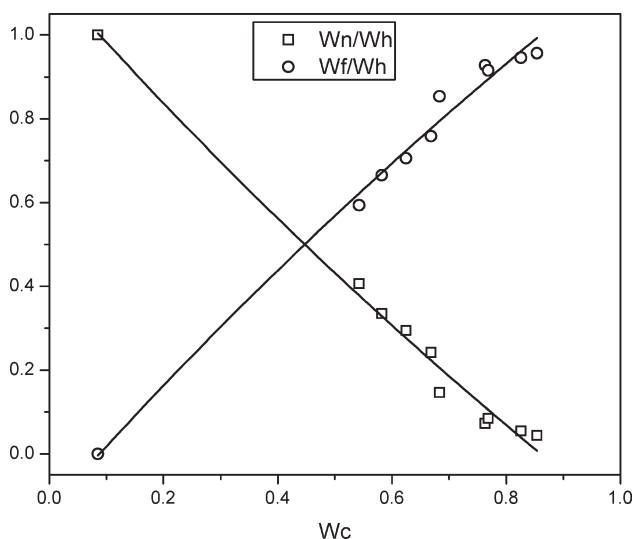


**Figure 7** The weight ratios of different states water to dry gel in PVA-collagen hydrogels.

time ( $t$ ) are shown as the points in Figure 9. For a better understanding of the swelling kinetics and to attain the swelling ratio at equilibrium ( $Q_e$ ), we try to simulate the swelling process with one-phase exponential associate equation, which can fit the process with a high degree of simulation. The equation is listed as Eq. (2), and the results of the fit are given in Figure 9 and Table II.

$$Q_t = Q_0 + A(1 - e^{-t/k}) \quad (2)$$

With the help of the equation, we can estimate the  $Q_e$  more accurately. From the curves in Figure 9, we can realize that the  $Q/Q_e$  in both media is higher than 50% within 30 min, and the values are above 90% after soaking for about 85 min. Calculated from



**Figure 8** The weight ratios of freezable water and non-freezable water to total water in PVA-collagen hydrogels.

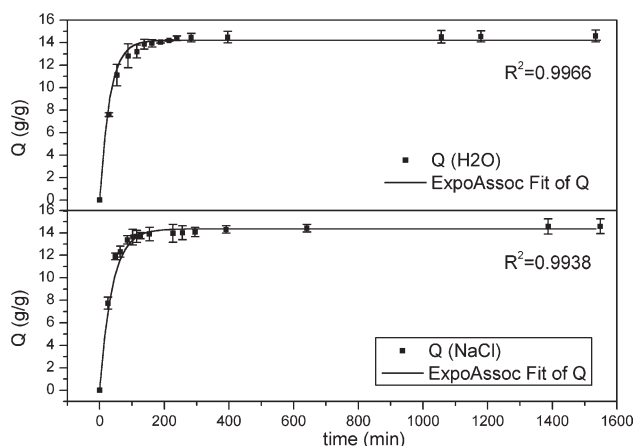
the simulation equation, the swelling ratios at equilibrium in distilled water and saline were 14.353 g/g dry gel and 14.205 g/g dry gel, respectively.

According to Gerlach et al.'s research,<sup>15</sup> the time dependence of the hydrogels' swelling process consists of three parts. The first of them is that osmotic pressure caused rapid swelling process, which lasts 1.2 s for 6- $\mu$ m thick and 80 s for 50- $\mu$ m thick PVA/PAA hydrogel layer. Because of the inadequacy of the weighing method, this part has not been detected in our work. The tendencies we observed are the second retarded part and the third relaxation part of the swelling process, as described by Gerlach. In our chemical- and physical-crosslinked PVA-collagen hydrogels, the second swelling process is mainly governed by the polymer chain mobility and the charged groups existing on the polymer. The stiff molecular backbone chain of PVA determines the mesh openings between chains and consequently the size of the water-filled regions. At the same time, the hydrophilic groups on both PVA and collagen enhance the binding of water molecule. Therefore, the lyophilized PVA-collagen hydrogels can rapidly respond in water absorption and are quickly balanced, and this microstructure in the hydrogels might be potential in biomedical application.

Guan et al. studied a series of chitosan-based hydrogels and the swelling process is fitted with Fickian equation as shown in Eq. (3).<sup>5,16</sup>

$$M_t/M_\infty = 1 - \sum [8/((2n + 1)^2\pi^2)] \times \exp[-(2n + 1)^2\pi^2(D_p t/L^2)], \quad (3)$$

where  $M_t$  and  $M_\infty$  are the mass absorbed at time  $t$  and at equilibrium,  $D_p$  is the polymer-fixed reference diffusion coefficient, and  $L$  is the initial thickness.



**Figure 9** The swelling kinetics of PVA-collagen hydrogels simulated with ExpoAssoc equation in H<sub>2</sub>O and saline at 25°C.

TABLE II  
Parameters of ExpAssoc Fit of Swelling Ratios Versus Time

Media	$Q_0$	$A$	$k$	$R^2$	$Q_e$ (g/g)
dH <sub>2</sub> O	$0.051 \pm 0.224$	$14.302 \pm 0.231$	$38.204 \pm 1.346$	0.9966	14.353
0.9% Saline	$-0.040 \pm 0.288$	$14.245 \pm 0.297$	$30.414 \pm 1.330$	0.9938	14.205

Note:  $Q_e$  means the PVA–collagen hydrogels' swelling ratio at equilibrium.

For a better comparison, we plot the swelling curves according to the method described in the reference. The Figure 10 shows the curves of swelling kinetics in both media. In Guan's research, the hydrogels were completely dried at 70°C. Then, the swelling behaviors of samples were investigated. According to the Guan's elucidation, the swelling curves of different hydrogels were all s-shape and deviated from Fickian standard curves. Consequently, the swelling behaviors of the hydrogels were defined as non-Fickian. However, the swelling curves of the PVA–collagen hydrogels we prepared show a good agreement with the Fickian equation. The reasons of this difference could be an initially retarded swelling ratio caused by the original low water content of the more compact network in Guan's hydrogels, but the microstructure in our PVA–collagen hydrogels is maintained. This microstructure can be observed in the SEM micrographs as well, as shown in Figure 11. Thus, we believe that the lyophilization is a better way than heat drying in the sample preparation of swelling research. According to the equation fit, the  $Q_e$  values of PVA–collagen hydrogels in distilled water and saline are 14.989 g/g dry gel and 14.575 g/g dry gel, respectively.

Compared with  $Q_e$  of the hydrogels in distilled water and saline solution, no matter with the ExpoAssoc equation or the Fickian equation, the value in distilled water is a little higher than the one

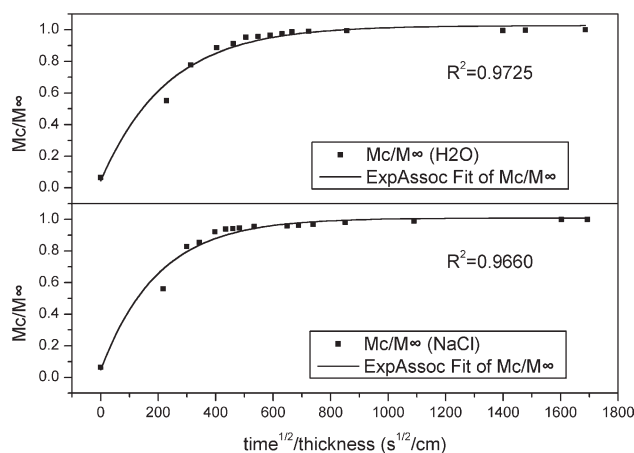


Figure 10 The swelling kinetics of PVA–collagen hydrogels simulated with Fickian equation in H<sub>2</sub>O and saline at 25°C.

in saline solution. According to the research conducted by Gerlach et al.<sup>15</sup> and the practical situation of PVA–collagen hydrogels, the ion diffusion flux induces a change of the electrical potential in the polyelectrolyte gel and the formation of a Donnan quasiequilibrium. When the inorganic ions are introduced into the hydrogels through diffusion, not only the osmotic pressure will decrease between inside and outside of the hydrogels, but also static electricity will be generated among the polymer network. The interacting static electricity, which has shielding effect, will weaken the electrostatic repulsion among the molecular chains and further decline the hydration effect.<sup>17</sup> Consequently, the swelling ratio at

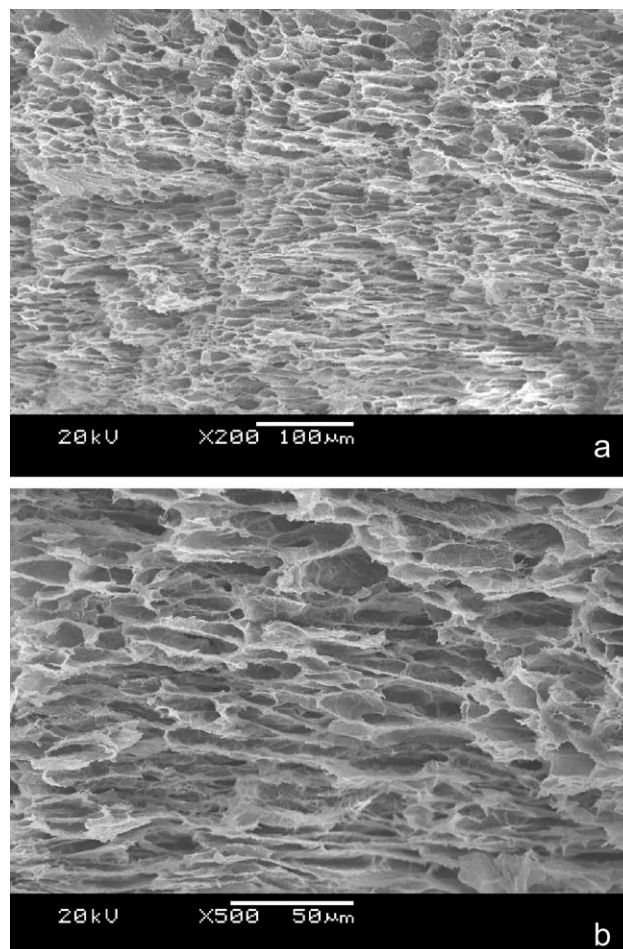


Figure 11 The scanning electron micrographs of the PVA–collagen hydrogels (a:  $\times 200$  and b:  $\times 500$ ).



equilibrium will be slightly declined in saline solution.

### CONCLUSIONS

PVA with pendent carboxyl group was synthesized and chemical crosslinked with collagen, and then the PVA-collagen hydrogels were prepared with repeated freezing and thawing. Following, the hydrogels were lyophilized for further research of water states and swelling behavior. This chemical- and physical-crosslinked interpenetrating polymer network is novel in some degree and shows some advantages in the application as biomaterial.

The water states in the hydrogels were evaluated through thermal analysis and discussed. With the results of TG and DSC tests, we carefully figured out that the freezable water content in the hydrogels is balanced around 25%. For the swelling kinetics of the hydrogels in distilled water and 0.9% saline, the one-phase exponential associate equation was employed and nicely fit. With the help of equation, we inferred the swelling ratio at equilibrium. The  $Q_e$  values in distilled water and saline were 14.353 g/g dry gel and 14.205 g/g dry gel, respectively. Meanwhile, the swelling behaviors of lyophilized PVA-collagen hydrogels in both media were in consistent with the Fickian equation to some degree. The results demonstrated that the lyophilization is suitable for the research of water states in hydrogels and swelling behavior, but neither the natural drying nor heat drying is suitable.

The lyophilized PVA-collagen hydrogels that we prepared are confirmed as a rapid response material in water absorption. The hydrogels can be close to

equilibrium in <100 min. The water states and swelling behavior indicate that the microstructure among the molecular chains makes the product potential in the application of drug carrier, scaffold, or other biomaterial.

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