S0032-3861(96)00417-X

Polymer Vol. 37 No. 25, pp. 5649-5652, 1996

0032-3861/96/$15.00+0.00

States of water in poly(vinyl alcohol)/ poly(sodium L-glutamate) blend hydrogels

Masanobu Nagura*, Hiroshi Saitoh†, Yasuo Gotoh and Yutaka Ohkoshi
Faculty of Textile Science and Technology, Shinshu University, Ueda 386, Japan
(Received 7 December 1995; revised 2 February 1996)

Tough and rubber-like physically crosslinked hydrogels were prepared by blending of concentrated aqueous solutions of poly(vinyl alcohol) (PVA) and poly(sodium L-glutamate) (PSLG) in an autoclave under 2 atm pressure at 120°C. There are three types of water in every blend hydrogel, i.e. free water, unfrozen water (namely bound water), and frozen bound water. Unfrozen water content increases with increasing PSLG content because of the increase in the number of the ionic -COONa group, which has many bonding sites with the water molecular. Heat of thawing per unit weight of water, i.e. free and frozen bound waters, not containing unfrozen water (ΔH_w), estimated for hydrogels having various water contents, was obtained by dehydration and was smaller than that of free water. Spin lattice relaxation time (T_1), obtained by pulsed nuclear magnetic resonance measurement, decreases with increasing PSLG content. These results for ΔH_w and T_1 are caused by the interaction between water and ionic -COONa groups of the PSLG molecules. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(vinyl alcohol); poly(sodium L-glutamate); blend hydrogel)

INTRODUCTION

Recently, we obtained hydrogels, which had a high Young's modulus even in the state of relatively high water content, from a concentrated aqueous solution of poly(vinyl alcohol) (PVA) and another hydrophilic polymer such as poly(sodium L-glutamate) (PSLG)[1,2] or poly(allyl amine) HCl salt[3], by using an autoclave at elevated temperature and pressure.

The water contents of these hydrogels were higher than that of the PVA hydrogel, which was cast from a 15 wt% aqueous solution of PVA and then swollen in water, and were similar to that of a PVA hydrogel prepared by repeated freezing and thawing[4]. Young's moduli of the blend hydrogels were lower than those of hydrogel prepared from a concentrated aqueous solution of PVA by casting. These moduli were twice as large as that of PVA hydrogel prepared by repeated freezing and thawing, and increased with increasing content of another blended hydrophilic polymer although physical crosslinks formed by PVA crystallites decreased. These results mean that the increase in Young's modulus is mainly caused by the physical crosslinks of a polymer–polymer complex between PVA and the hydrophilic polymer.

Furthermore, the time dependence of the streaming potential across the hydrogel membranes was analysed as the relaxation of the polymer chains dissolved in the liquid phase of the membrane[5]. The relaxation time decreased with increasing PSLG content; it is thus clear that the crosslinks formed with the complex increase with increasing blend content.

Since it is well known that hydrophilic polymers generally have three types of absorbed water, i.e. free, frozen bound, and unfrozen water[6–8], it may be expected that the blend hydrogels obtained also have similar states of water. Many investigators have studied the state of water in chemically crosslinked PVA gels[9,10] and concluded that in these gels also three types of water exist. However, the detailed properties of the frozen bound water in the hydrogels have not yet been clarified.

In this paper, we study mainly the state of frozen bound and unfrozen water in physically crosslinked PVA hydrogels prepared by blending PVA with anionic poly(sodium L-glutamate).

EXPERIMENTAL

Chips of poly(γ methyl L-glutamate) (PMLG) (degree of polymerization 280) were placed in a methanol/water (75/25 w/w) mixture containing 1.8 wt% sodium hydroxide, and allowed to saponify for 3 h under agitation. The resulting sodium salt of PMLG, namely poly(sodium L-glutamate) (PSLG), was separated by filtration, washed with methanol, and dried *in vacuo*[11].

The PVA was supplied by Kurarey Co. Ltd as Poval-120 (degree of polymerization 1700, degree of saponification 98.5 mol%). It was dissolved in water at a concentration of 12.5 wt% using an autoclave at 120°C with stirring. The PSLG (12.5 wt%) solution was made by agitation at room temperature. Mixtures of PVA with PSLG of five different weight contents, with pH values about 6, were prepared in the autoclave under 2 atm at

---

* To whom correspondence should be addressed

† Present address: Textile Research Institute of Gunma, 5-46-1, Aioi-cho, Kiryu 376, Japan

120°C. After cooling to room temperature, the mixture separated into two phases, solution and coagulation. Tough blend hydrogels with high water content were obtained by dehydrating the coagulation and then swelling in water. Hydrogels with such properties cannot be prepared from the above mixtures at usual atmospheric pressure.

D.s.c. experiments were performed on a Seiko Denshi DSC-10 in the temperature range of −80 to ~50°C at a heating rate of $5^\circ\mathrm{C\,min^{-1}}$. Pulsed nuclear magnetic resonance (p.n.m.r.) measurements were made using a Praxis II-10 instrument at 10.72 MHz. The spin–lattice relaxation time (T_1) was measured using the 90/90 pulse method, because the spin–spin relaxation time was much smaller than T_1.

Water content $C_w$was calculated from equation (1),

$$C_w(\mathrm{wt\%}) = \{(M_{\mathrm{swollen}} - M_{\mathrm{dry}})/M_{\mathrm{dry}}\} \times 100 \qquad (1)$$

where M_{swollen} and M_{dry} are respectively the mass of swollen hydrogel and of dried hydrogel.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of water content on PSLG content, determined from a high resolution n.m.r. spectrum of the D_2O solution of the dried hydrogels[1]. Water content increases with the blending of a small amount of PSLG. The fine structure of the blend hydrogel prepared by aggregation through phase separation was rougher than that of PVA hydrogel as shown in *Figure 11* of ref. 1. The water content decreases with increasing PSLG content above a PSLG content of 6 wt%. Since a hydrophilic polymer forms a complex with another hydrophilic polymer by hydrogen bonds between the polymers[12–15], in this case OH groups of PVA form the complex with peptide groups of PSLG. Consequently the hydrophilic groups of the PVA molecules are not useful as bonding sites with water; i.e., the water content decreases with increasing PSLG content. As shown below, unfrozen water increases with increasing PSLG content, namely increasing the ionic group. Thus the degree of decrease of water content by formation of a hydrogen bonded complex is larger than that of the increase of unfrozen water.

The state of water is usually investigated by using a d.s.c. instrument. Thus we also measured the thermogram of the hydrogels on heating, as shown in *Figures 2* and *3*, in which the water contents of samples are about 82 ± 5 and 59 ± 5 wt%, respectively. In the case of water content below about 50 wt% there is no peak, or a very small endothermic peak, at below 0°C. Only one endothermic peak at 0°C is observed on *Figure 2*, whereas two or three peaks are seen below 0°C in *Figure 3*. Exothermic peaks were never observed on any thermogram. According to Murase's opinion[16], an endothermic peak observed below 0°C is not due to the thawing of frozen bound water. This is because the water compartmentalized by networks in a gel forms unstable ice, which thaws below 0°C and transforms to a stable state through an endothermic process. Thus the two or three endothermic peaks are assigned to frozen bound water does not change to free water.

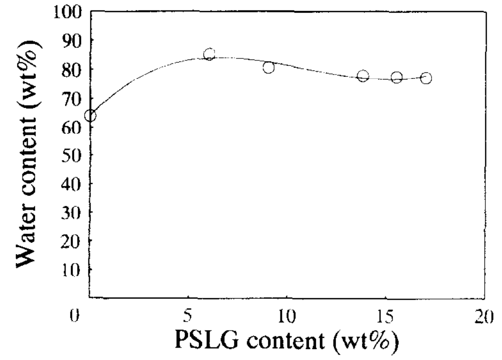

Figure 1 Dependence of water content on PSLG content

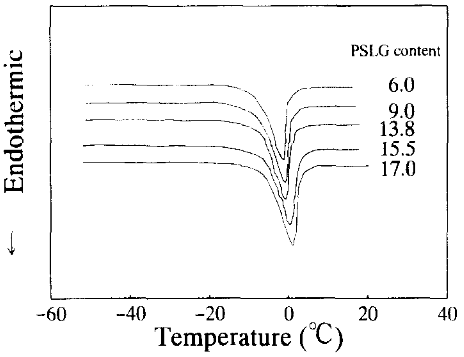

Figure 2 D.s.c. thermogram for blend hydrogels of water content of about 82 wt%

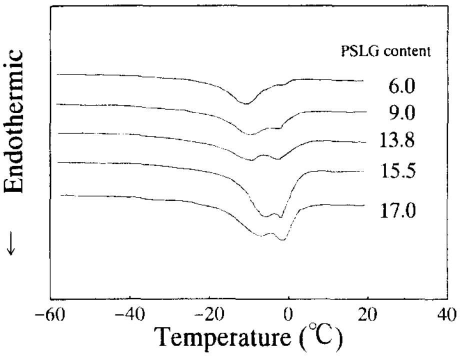

Figure 3 D.s.c. thermogram for blend hydrogels of water content of about 59 wt%

In order to elucidate the existence and content of unfrozen water in the blend hydrogels, d.s.c. thermograms were measured for hydrogels having various water contents, which were obtained by dehydration, and the heat of thawing per unit sample weight (ΔH) was calculated from the area of the endothermic peak. *Figure 4* shows the dependence of ΔH on water content for the blend hydrogel at a PSLG content of 6 wt%. With decreasing water content ΔH decreases, and water content reaches a finite value even for the hydrogel not showing any endothermic peak. Similar thermograms were observed for hydrogels containing every content of PSLG. The water content extrapolated to a zero value of ΔH corresponds to unfrozen water content in the hydrogel. The unfrozen water content and the molar ratio (α_u) between unfrozen water and monomer unit of the blend polymers are shown as functions of PSLG

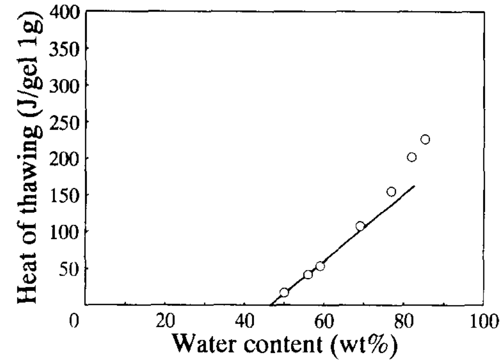

Figure 4 Dependence of heat of thawing per unit sample weight on water content

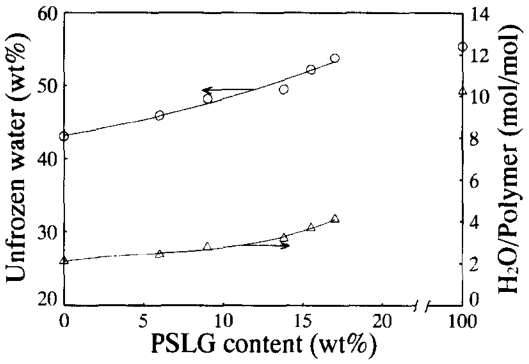

Figure 5 Dependence of unfrozen water content and molar water per repeated polymer unit on PSLG content

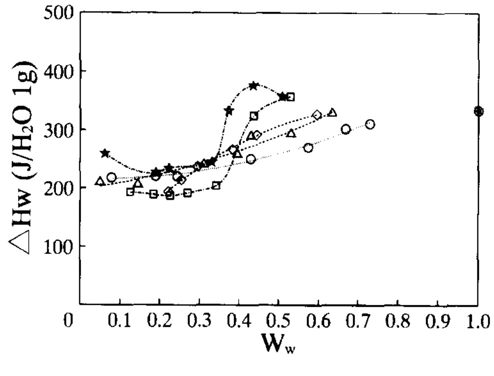

Figure 6 Dependence of heat of thawing per unit weight of water, not including unfrozen water, on weight fraction of free and bound waters (PSLG content: O, 6.0; Δ, 9.0; ◇, 13.8; □, 15.5; ☆, 17; pure water, ◎)

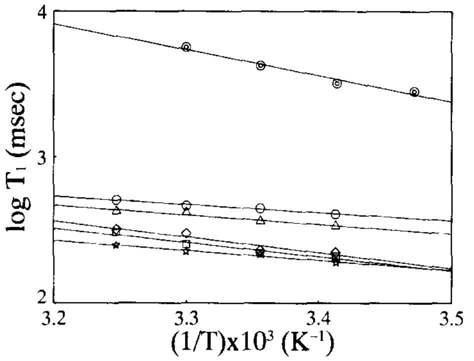

Figure 7 Dependence of reciprocal of spin lattice relaxation time on reciprocal of absolute measured temperature (PSLG content: O, 6.0; Δ, 9.0; ◇, 13.8; □, 15.5; ☆, 17; pure water, ◎)

content (*Figure 5*); both increase with increasing PSLG content.

As described above, the PVA molecule forms a complex with the PSLG molecule. Thus the hydrophilic groups of PVA and PSLG which have bonding sites with water molecules will be decreased by the formation of the conmplex between –OH groups of PVA and peptide groups of PSLG. This speculation contradicts the above results. This will be explained by the increase in the number of ionic –COONa groups, which bond with the water molecule. It is reasonable to assume that α_u is constant for the hydrogels with every water content obtained by dehydration. Thus the content of unfrozen water (m_u) in each hydrogel is calculated from equation (2),

$$m_u = f_p \times \alpha_u \times 18 \qquad (2)$$

where f_p and 18 are the mole fraction of the blend polymer in the hydrogel and the molecular weight of water, respectively. Since the weight fraction (W_w) of water, i.e. free and frozen bound waters but not including the unfrozen water, is calculated from equation (3)

$$W_w = (C_w - m_u)/100 \qquad (3)$$

for the samples of each water content obtained by dehydration, the heat of thawing (ΔH_w) per unit weight of water (not including unfrozen water) is calculated from the heat of thawing per unit weight of hydrogels (see *Figure 4*) divided by W_w. *Figure 6* shows the dependence of ΔH_w on W_w for each hydrogel. As shown in the figure, ΔH_w decreases from 334 J g^{-1} (the ΔH for free water) to about 200 J g^{-1} with decreasing W_w for the whole PSLG content of the hydrogel. This means that the water molecules crystallize incompletely in the highly dehydrated blend hydrogels, and frozen bound water certainly exists in the hydrogels. *Figure 6* shows also that ΔH_w for a hydrogel of high PSLG content is almost the same as that for free water at low W_w, because the water content is low for the hydrogel of high PSLG content, as shown in *Figure 1*.

From the d.s.c. measurements for the thawing phenomena mentioned above, it became clear that there are also three types of water in physically crosslinked blend hydrogels. These conclusions, however, do not lead to any detailed knowledge on the liquid state of the water. In order to study this state, we made p.n.m.r. measurements at 25°C. Every logarithmic free induction curve (not shown) was linear as a function of time over the whole time range. This means that the liquid water in the hydrogels at 25°C is in only one state.

Figure 7 shows the temperature dependence of the reciprocal of T_1, calculated from the slopes of the curves of the logarithm of free induction plotted against the time. Every hydrogel T_1 is smaller than that of pure water. This phenomenon indicates that the mobility of the liquid state of water in the hydrogels is more restrained by the polymers than that of pure water, because these physically crosslinked hydrogels have a very much smaller water content than that of chemically crosslinked poly(methyl methacrylic acid) hydrogel[17]. T_1 decreases with increasing PSLG content, as shown in *Figure 7*. The decrease of T_1 corresponds to the decrease in the mobility of the water. Thus we can speculate that

Table 1 Activation energy of water, not including unfrozen water

PSLG content (wt%)	Activation energy (kJ mol^{-1})
6.0	12.2
9.0	12.2
13.8	18.2
15.5	16.2
17.0	12.2

the structure of the hydrogel becomes dense with increasing PSLG content, or that the decrease in mobility is probably caused by an interaction between water molecules and the ionic groups of PSLG. We have already observed the cross-sectional structure of these hydrogels by electron microphotography in ref. 1. The fine structure of the hydrogel becomes rough with blending. This means that the decrease in the mobility of the water molecules is caused by the interaction between them and the ionic groups of PSLG. In other words, the hydrogen bonding force between the water molecules is weakened by the interaction.

Thus, estimation of the activation energy (ΔE) for the motion of water molecules is useful in order to ascertain the existence of the interaction. Values of ΔE were calculated from the plots of *Figure 7*, using equations (4) and (5):

$$\log T_1 = A - B/T \quad (4)$$

$$\Delta E = 2.303RB \quad (5)$$

where T, R and B are absolute temperature, gas constant and the slope, respectively. The ΔE obtained are shown in *Table 1*. The values for the blend hydrogels are very much smaller than 34 kJ mol^{-1}, for free water, suggesting weakness of interhydrogen bonding among water molecules as speculated above. These results also support the above discussion on d.s.c. measurements; i.e., ΔH_w of the frozen bound water is smaller than that of free water.

However, as is seen in *Figure 2*, there are only the endothermic peaks of free water in the d.s.c. thermograms for the original hydrogels. This is contrary to the p.n.m.r. results, as discussed above. This discrepancy means that, in cooling to −80°C for the d.s.c. measurements, the water restrained by the polymers in the original hydrogels changes into ice in the state of free water, and the restrained water of the slightly dehydrated state also changes into ice in the states of free and frozen bound waters.

ACKNOWLEDGEMENTS

The authors thank Kuraray Co Ltd and Ajinomoto Co. Ltd for supplying the PVA and PMLG. This work was supported by a Grant-in-Aid for Science Research from the Ministry of Education, Science and Culture of Japan.

REFERENCES

1 Nagura, M., Nishimura, H. and Ohkoshi, Y. *Kobunshi-Ronbunshu* 1991, **48**, 519
2 Nagura, M. and Eisenberg, A. *Polymer* 1991, **32**, 2205
3 Nagura, M., Arai, Y. and Ohkoshi, Y. *Senigakkai-Shi* 1992, **47**, 127
4 Nanbu, M. *Kobunshi-Kako* 1983, **32**, 523
5 Kiyono, R., Tasaka, M. and Nagura, M. *Bull. Chem. Soc. Jpn.* 1994, **67**, 3201
6 Woesser, D. E., Snowden, B. S. and Chiu, Y. *J. Colloid Interface Sci.* 1970, **34**, 283
7 Nakamura, K. and Hatakeyama, T. *Kobunshi* 1985, **41**, 369
8 Yoshida, H. *Kobunshi* 1991, **47**, 240
9 Hatakeyama, T., Yamanouchi, A. and Hatakeyama, H. *Eur. Polym. J.* 1984, **20**, 61
10 Fushimi, H., Ando, I. and Iijima, T. *Polymer* 1991, **32**, 241
11 Takahashi, T. 'Poly(amino acid)', Kodansha Science, 1974, Chap. 6
12 Osada, Y. *J. Polym. Sci. Polym. Chem. Ed.* 1979, **17**, 3485
13 Ohno, H. and Tsuchida, E. *Makromol. Chem., Rapid Commun.* 1980, **1**, 591
14 Madison, V., Lasky, J. and Currie, B. *Biopolymers* 1981, **20**, 707
15 Iliopoulos, I. and Audebert, R. *Eur. Polymer J.* 1988, **24**, 171
16 Murase, N. *Netsu-Sokutei* 1987, **14**, 13
17 Yasunaga, H. and Ando, I. *Polymer Gels and Networks* 1993, **1**, 83