Study on PVA Hydrogel Crosslinked by Epichlorohydrin

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SYNOPSIS

Poly(vinyl alcohol) hydrogel was prepared by using epichlorohydrin as a crosslinking agent. The molecular weight between crosslinks was calculated. The swelling behavior, as well as mechanical properties, of the hydrogels were examined by weighing and tensile testing, respectively. Values of equilibrium water content of more than 95% were reached while Young's modulus and tensile strength of the hydrogels were about 10^5 dyn/cm^2. Crystallization was introduced by drying the hydrogels at 90°C. The dried hydrogel samples were used for swelling kinetic study, then reequilibrated with water and subjected again to tensile testing. Due to the formation of microcrystalline domains in the PVA hydrogel network after annealing, hydrogels with greatly enhanced Young's modulus, tensile strength, and elongation at break were obtained and their equilibrium water content values remained still high, i.e., 87 and 93%.

INTRODUCTION

Hydrogels have a unique position in medical, pharmaceutical, and related fields because of their high water content. They are used for membranes, contact lenses, and materials for drug delivery systems.[1,2] The copolymers containing 2-hydroxyethyl methacrylate and *N*-vinyl-2-pyrrolidone have found wide applications in preparing hydrogels.[3,4] Crosslinked poly(vinyl alcohol) (PVA) as a hydrogel has attracted particular attention because of its high degree of swelling in water, inherent low toxicity, good biocompatibility, and desirable physical properties.

PVA can be crosslinked by different physical or chemical methods to give rise to the formation of hydrogel. Peppas and Merrill investigated the crosslinking of aqueous PVA solution by electron beam or γ-ray irradiation,[5] and the method by which PVA hydrogel is obtained by repeatedly freezing and thawing PVA solution has proven successful.[6-8] Chemical methods by adding crosslinking agents such as boric acid or dialdehyde[7,9,10] have also been used for preparing PVA hydrogel.

Epichlorohydrin acts as a bifunctional molecule toward hydroxyl groups in basic medium. PVA can be obviously crosslinked with this molecule. We report here the preparation of PVA hydrogels using epichlorohydrin as crosslinking agent. The swelling behavior, as well as mechanical properties, of these PVA hydrogels are also examined.

EXPERIMENTAL

Materials

PVA used in this study is a commercial product of Sichuan Vinylon Factory, Chongqing, China, that has a degree of polymerization of 1700 with a saponification value of 99%. Before use, PVA was washed with distilled water and then dried at 60°C. Epichlorohydrin and KOH are commercial products of analytical grade and were used without further purification.

Crosslinking

An aqueous solution of PVA with a concentration of 9.5% (w/w) was prepared. In 100 g of this solution, X (mL) epichlorohydrin was added. The solution was mixed in a three-neck flask, then 10 mL KOH solution with a KOH content slightly more than an equivalent of X (mL) of epichlorohydrin was slowly added and homogenized throughout. The

Journal of Applied Polymer Science, Vol. 46, 783–786 (1992)
 CCC 0021-8995/92/050783-04

solution was moved in a glass model having a dimension of 200 × 150 × 3 mm and kept for 2 days at ambient temperature to obtain a crosslinked PVA film with a thickness of 3 mm. After crosslinking, the hydrogel film was boiled in a water bath for about 6 h. During this process, the water was changed several times. Then, the film was washed with distilled water until the washing water became neutral. Three samples with $X = 2$, 4, and 6 mL were prepared in the same way.

Swelling and Mechanical Properties

Hydrogel samples of size of roughly 50 × 60 × 3 mm were dried under vacuum at 90°C for 24 h. Then, the samples were kept in a desiccator until their weights reached constant values. The equilibrium water content (EWC) was calculated as

$$\mathrm{EWC} = 100\,(m - m')/m \quad (1)$$

and the degree of swelling (DS) as

$$\mathrm{DS} = (m - m')/m' \quad (2)$$

where m and m' denote the weights of PVA hydrogel and dried PVA hydrogel, respectively.

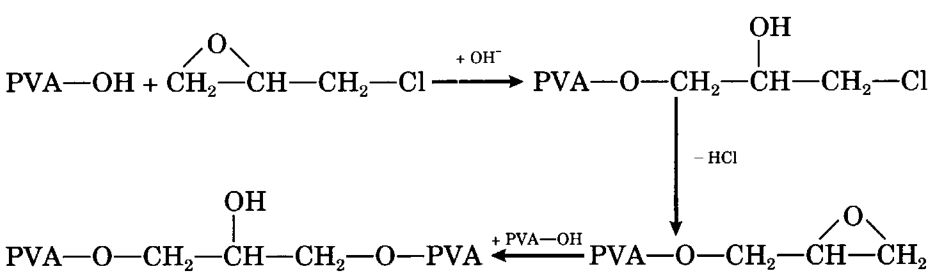
To measure the rates of swelling in distilled water, dried hydrogels having roughly the same size were used. The swelling as a function of time was followed by weighing the increase of water absorption. When the equilibrium was reached, the values of EWC and degree of swelling, which were different from their values before drying, were again calculated according to relations (1) and (2).

For the mechanical properties, the hydrogels were subjected to a tensile test using a Shimadzu Autograph AG-10TA (Japan) with a 10 N load cell. The measurements proceeded in air at ambient temperature with a tensile speed of 20 cm/min, and values of Young's modulus, tensile strength, and elongation at break were calculated. The hydrogel samples were cut in dumbbell form that had a cross section of (6 × 3 mm) and an effective length of 25 mm. To estimate the mechanical properties of hydrogels after annealing, samples with the same form as above were completely dried under vacuum at the temperature of 90°C, then used for tensile testing after 7 days of immersion in distilled water.

RESULTS AND DISCUSSION

Crosslinking Density

The chemical process underlying the crosslinking of PVA by epichlorohydrin is postulated as follows:



The epoxide group reacts readily with the hydroxyl group in basic medium. The reaction proceeds rather completely, and elemental analysis shows that the chloride contents in dried hydrogels are less than 1%.

In the case where 2 ml epichlorohydrin was added, formation of some viscous and insoluble substances indicates that crosslinking took place effectively; however, the crosslinking density was too low to get the film with a definite form. When 4 and 6 ml epichlorohydrin were added, respectively, crosslinked PVA hydrogels, say gel 1 and gel 2, which have the form of transparent films, were obtained.

To estimate the molecular weight between crosslinks Mc, the density of dried hydrogels are measured on a density gradient column. The same density values were found for gels 1 and 2, namely, 1.30 g/cm^3, which is slightly higher than the value of uncrosslinked PVA, 1.27 g/cm^3. Assuming the approximation that there is additivity of volume in the hydrogel, the density values of dried hydrogels can then be used for the calculation of the volume fraction of PVA in the hydrogel, Vs, and the volume fraction of PVA in solution before crosslinking, Vr:

$$Vs = \frac{(1-E)/d}{E + (1-E)/d} \qquad Vr = \frac{Mp/d}{Mp/d + Mw} \quad (3)$$

where d = density of dried hydrogel, Mp = weight of PVA added before crosslinking, Mw = weight of total water in PVA solution before crosslinking, and E is the EWC values of crosslinked hydrogels. The density of water is taken as 1 g/ml.

Bray and Merrill[11] modified Flory's equation to calculate the crosslinking density $1/Mc$ when crosslinks were introduced between polymer chains while the polymer already existed in solution:

$$\frac{1}{Mc} = \frac{2}{Mn} - \frac{v/V1[\ln(1-Vs) + Vs + X1(Vs)^2]}{Vr[(Vs/Vr)^{1/2} - (Vs/Vr)/2]} \quad (4)$$

where v = specific volume of polymer, $V1$ = molar volume of solvent, and Mn is average molecular weight of the polymer. Equation (4) is used to estimate the values of Mc for the PVA hydrogels with $v = 0.788$, $V1 = 18$, $X1 = 0.494$, and $Mn = 74{,}800$. The results are given in Table I. The high Mc values of about 20,000 indicate that the crosslinking density is not high compared with the values of 2000–12,000[11] found in other PVA hydrogels. There are on average three crosslinks per chain.

Swelling Behavior

The EWCs and degrees of swelling of PVA hydrogels are evaluated by weighing after drying the hydrogels at the temperature of 90°C; the values are given in Table I. It is interesting to note that these PVA hydrogels have quite high EWC values, i.e., 97 and 96%.

As the hydrogels are dried, shrinkage occurs. The dried hydrogels become apparently similar. However, the swelling behavior of the hydrogels are considerably affected by annealing: The degrees of swelling at equilibrium for gels 1 and 2 are decreased from the values of 32 and 24 to the values of 6.5 and 12, respectively. A comparable change in degree of swelling was found in PVA hydrogel crosslinked by electron beam irradiation.[11] The great decrease in degree of swelling after annealing is attributed to the crystallization of PVA segments that occurred during heating. When these crystallized hydrogel samples were boiled in a water bath for 10 h, the degrees of swelling of gels 1 and 2 then increased from the values of 6.5 and 12 to the values of 12 and 19, respectively, a clear indication of partial destruction of crystallization in the hydrogel network during boiling. The data in Table I show that the Mc value of gel 1 is greater than that of gel 2; therefore, segments of PVA chain in gel 1 are more susceptible to crystallization. This results in a greater decrease in degree of swelling of gel 1 compared to gel 2.

The swelling kinetic is also examined by weighing. Figure 1 is a plot of degree of swelling vs. the square root of immersion time for gels 1 and 2. In the early stage of immersion, the plot can be approximately considered linear. Urushizaki et al.[7] previously reported a similar swelling pattern for PVA hydrogels prepared by freezing and thawing the PVA solution. In this linear region, gel 2 seems to have a slightly greater rate in absorbing water, and water absorbed by the hydrogels during this time represents roughly 60% of their final water contents. The equilibrium is reached only after several days.

Table I Crosslinking Density and Swelling Behavior of PVA Hydrogels

	Vr	Vs	Mc	EWC	DS
Gel 1	0.062	0.023	25520	97%	32.0
Gel 2	0.062	0.031	19450	96%	24.3
Annealed gel 1	0.062	0.105	1280	87%	6.5
Annealed gel 2	0.062	0.057	6850	92%	12.7

Mechanical Properties

The values of Young's modulus and tensile strength, as well as values of elongation at break, are listed in Table II. The uncrystallized samples have Young's modulus and tensile strength on the order of 10^5 dyn/cm^2. Crystallization increases these values to more than 10^6 dyn/cm^2, and there is roughly 30% increase in the values of elongation at break. This clearly shows that crystallization can largely improve the mechanical properties of PVA hydrogels. Similar increases in these values were found previously.[11] This phenomenon is closely related to the fact that microcrystalline domains act as crosslinks. By using eq. (4), we can also estimate the Mc values for crystallized PVA hydrogels considering the microcrystalline domains as crosslinks. A much lower Mc value is found for annealed gels 1 and 2 that shows qualitatively that crystallization occurs widely in the hydrogel network. And, the lower Mc value for gel 1 clearly reveals that more microcrystalline domains are formed in gel 1 than in gel 2 during annealing, which agrees with the fact that there is a greater increase in the values of tensile strength and Young's modulus of gel 1 than that of gel 2.

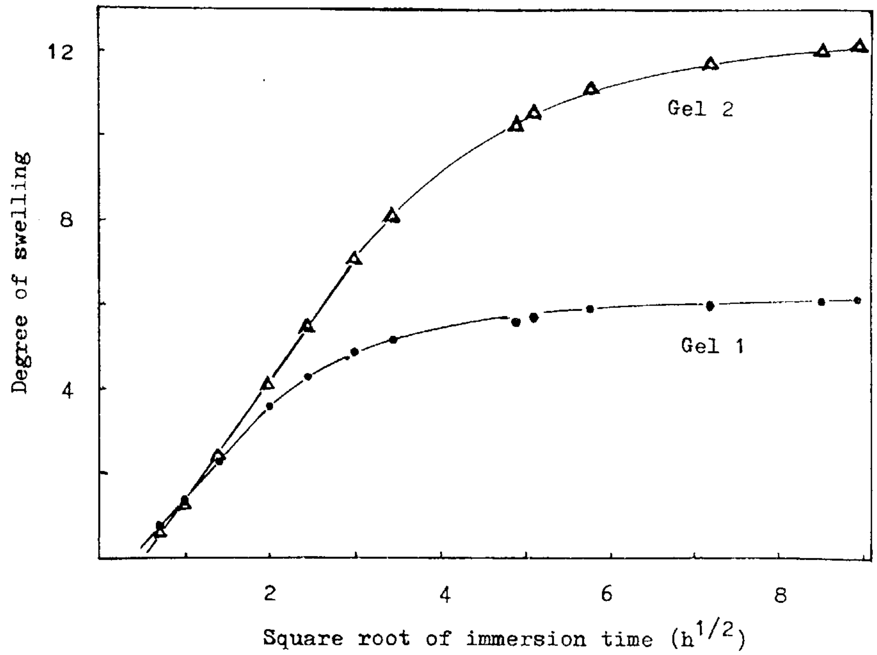


Figure 1 Swelling kinetic of PVA hydrogels.

CONCLUSION

Epichlorohydrin was effectively used as a crosslinking agent for the preparation of PVA hydrogels. The degree of swelling of these PVA hydrogels are very high. EWC values of more than 95% are reached. Even with such a high water content, mechanical properties of these hydrogels remain reasonably good. By tensile test, the values of Young's modulus and tensile strength are found to be 1.2×10^5, 0.9×10^5 and 2.2×10^5, 1.5×10^5 dyn/cm^2 for gels 1 and 2, respectively. These values are comparable with those found in previous studies[9,10,12]; however, greater values of elongation at break are obtained that are about 140 and 200% compared to the values of 20–80% in PVA hydrogels crosslinked by electron beam irradiation. The mechanical properties of the hydrogels are greatly enhanced by annealing, during which crystallization occurs among PVA segments while EWC values decrease only from 97 and 96% to 87 and 93%, respectively.

Table II Mechanical Properties of PVA Hydrogels

	E_0 ($\times 10^5$ dyn/cm^2)	Tensile Strength ($\times 10^5$ dyn/cm^2)	Elongation at Break (%)
Gel 1	1.2	0.9	140
Gel 2	2.2	1.6	200
Annealed gel 1	33.2	29.8	190
Annealed gel 2	14.0	11.4	260

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Received August 1, 1991
Accepted December 5, 1991