Poly(vinyl alcohol) hydrogels prepared by freezing–thawing cyclic processing

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A novel method of preparation of strong poly(vinyl alcohol) (PVA) hydrogels was developed without utilization of chemical crosslinking or other reinforcing agents. Aqueous solutions containing 10–15 wt% PVA were frozen at −20°C for 1–24 h. They were subsequently thawed at 23°C for up to 24 h. This process was repeated four more times and the weight change and degree of swelling were measured after each freezing–thawing cycle. Strong thermoreversible hydrogels exhibiting mechanical integrity were obtained with 15 wt% solutions frozen at −20°C for 24 h and thawed at 23°C for any time period. The process of reinforcement of these thermoreversible hydrogels was a densification of the macromolecular structure. The densification process was more prominent for gels that had been exposed to up to five freezing–thawing cycles. Compressive creep studies indicated that the gel compliance was relatively constant over a wide range of stresses and decreased as the number of freezing–thawing cycles increased.

(Keywords: thermoreversible gel; hydrogel; poly(vinyl alcohol); freezing–thawing; crystallization; compressive creep)

INTRODUCTION

An aqueous solution of poly(vinyl alcohol) (PVA) will gradually gel and experience a small increase in elasticity upon standing at room temperature. While this is not a new phenomenon, recent research shows that PVA that is first heated to dissolve, then frozen and thawed repeatedly, forms a highly elastic gel[1]. This sol–gel transition produces a thermoreversible gel[2,3].

The PVA material resulting from this treatment has many unique characteristics. The gel is stable at room temperature and retains its original shape, but can be extended to five to six times its initial size. This behaviour indicates its rubbery and elastic nature and its high mechanical strength. Its properties may depend on the molecular weight of the polymer, concentration of the aqueous solution, the temperature and time of the freezing, and the number of freezing–thawing cycles. In water, the PVA gel is essentially insoluble, but undergoes significant swelling[4–7].

Development of this reinforcement technique is based on early work in our group. Indeed, as early as 1975, we studied[4] the scattering light intensity of the supermolecular PVA structure, produced from a 15 wt% aqueous solution frozen at −20°C for 45–120 min and then thawed for long periods of time. The percentage of visible light (5000 to 8000 Å) transmitted through the gel was recorded as a function of thawing and freezing time. We evaluated the properties of the supermolecular structure under the assumption that the particles that make up the gel behave as small spheres that increase in size with each freezing–thawing cycle.

It was shown that the amount of light transmitted is a function of freezing time, concentration and thawing time. The scattering intensity was found to increase gradually for those solutions that were cooled rapidly. The reasons for the increase in scattering intensity were the formation of new particles from the freezing–thawing process and a partial crystallization leading to microcrystalline structures. The microgel particles that make up the supermolecular structure increased in diameter with each freezing–thawing cycle. Before this work it was thought that crystallization only occurred at high temperatures. Our experiments proved that the supermolecular structures are dependent on temperature, freezing–thawing time and number of freezing–thawing cycles.

Lozinsky *et al.*[8] used gel chromatographic analysis to show that the PVA molecular weight distribution was the same before and after freezing–thawing took place. Watase and Nishinari[9] performed X-ray diffraction tests that demonstrated a halo effect at 26°C, indicative of PVA ordered structure and microcrystallinity. Yokoyama *et al.*[1] used X-ray diffraction to show increase of crystallites with the number of freezing–thawing cycles. However, Lozinsky *et al.*[8] investigated the PVA gel's behaviour at high temperatures and determined that the PVA crystallites melted at about 70–80°C and dissolved quickly in boiled water.

Watase and Nishinari[9] investigated the changes that occurred upon PVA immersion in water. They prepared PVA gels by freezing at 15 wt% aqueous solution at −20°C and thawing at 15°C. The degrees of hydrolysis used ranged from 96 to 99.9 mol%. After freezing–thawing and immersing in water for 96 h, the samples experienced an increase in degree of swelling. It was found that the higher the degree of hydrolysis, the lower was the degree of swelling. Nishinari *et al.*[10] also evaluated

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the weight changes of the supermolecular PVA gel made from 15% aqueous solution frozen at −40°C for hours. The gels were immersed in water for a period of seven days at 25°C. Urushizaki *et al.*[7] determined that an increase in the number of freezing–thawing cycles caused an increase in the degree of physical crosslinking.

Watase and Nishinari[9] analysed the mechanical properties by evaluating the storage modulus after the gel was immersed in water for four days. It was found that the modulus and the phase lag decreased when the swelling temperature was increased from 15 to 55°C because of the melting of crystalline regions. Urushizaki *et al.*[7] also use the measured mechanical storage modulus to determine the PVA hydrogel elasticity. The elasticity was found to be a function of the number of freezing–thawing cycles. It is believed that an increase in density and chain entanglements caused the increase in rigidity as freezing–thawing cycles were increased.

Temperature effects on mechanical properties (storage modulus, loss modulus and loss tangent) were evaluated[10]. The modulus decreased as the temperature increased. Only a slight loss was experienced until the temperature was raised to 40–50°C, at which point it began to decrease rapidly. The loss tangent first decreased slightly, until it reached 50°C where it experienced an increase.

The fact that physical crosslinks are responsible for the network formation in these PVA gels is not in debate. Three basic models have been proposed in an effort to explain the mechanisms inducing the densification and physical crosslinking. These three models involve hydrogen bonding, polymer crystallite formation or a liquid–liquid phase separation process.

The main goal of this work was to perfect the technique of gel reinforcement without chemical crosslinking. This was done by studying the effect of the freezing–thawing cycle on the mechanical and physical properties of PVA gels. This involved the analysis of the effects of different experimental variables such as the PVA solution concentration, the number of freezing–thawing cycles and the temperature at which freezing occurred on the gel properties. The properties of the resulting hydrogels that were investigated included the swelling ratio, the amount of water evaporated upon drying and the compressive strength of the PVA gels produced.

EXPERIMENTAL

Gel preparation

PVA with $\bar{M}_n = 35\,420$ and $\bar{M}_w = 79\,200$ (Elvanol with degree of hydrolysis of 99.6%, E.I. duPont de Nemours & Co., Wilmington, DE) was used to prepare aqueous solutions of 10 and 15 wt% PVA by heating solutions in an oven at 90°C for a period no longer than six hours to achieve complete dissolution. After partial filling with the aqueous PVA solution, the plastic test tubes were placed at −20°C for 1–24 h. After the freezing process, they were allowed to thaw at 23 ± 1°C for up to 24 h. Up to five freezing–thawing cycles were used for the PVA gel preparation.

Gel characterization

The gels produced were removed from their plastic containers and cut in two specimens. Two tests were made on these gels: weight and volume swelling ratio determination and compressive creep. The swelling ratio was measured by determining the water uptake in the gels during their thawing period after freezing. The weight swelling ratio was determined by immersing the gels in distilled water at 37°C. The gel volume was measured by buoyancy tests in air and hexane[11].

Compressive creep experiments were used to determine the mechanical strength of the gels tested by using a dial comparator (Custom Scientific Instruments Inc., Whippany, NJ). A square piece of the swollen PVA gel was cut with a razor blade and its area was measured. This gel sample was then placed in the comparator and its initial thickness was determined. A known load (stress) was applied and the thickness (strain) was recorded as a function of time. No weight loss was observed, as the time required for this deformation was of the order of 15 s. The thickness variation was also recorded as a function of applied weight.

RESULTS AND DISCUSSION

General

Strong hydrogels with high mechanical integrity were formed when aqueous solutions of PVA were exposed to repeated freezing–thawing cycles. Experiments were made with solutions of 10 wt% and 15 wt% PVA at various freezing temperatures and number of freezing–thawing cycles. This was done to determine the optimal conditions of preparation. Initially, freezing was performed at −20°C and thawing at 23°C for both concentrations. Although both concentrations led to stable gels after two freezing–thawing cycles, stronger gels were obtained with the 15 wt% solution. Therefore, this concentration was chosen to perform the rest of the experiments.

The freezing time was varied from 1 to 24 h. Stable gels were formed even when solutions were frozen for only 1 h, but the strongest gels resulted after 24 h. The stability and strength of gels increased with an increase in freezing time. Therefore, a freezing time of 24 h was used for the remainder of the experimental studies. When the freezing temperature was changed to 0°C, the ensuing transparent gels could not hold their own weights even after four freezing–thawing cycles. The rest of the experiments were conducted at a freezing temperature of −20°C. Thus, for the final structural analysis, polymer gels were obtained from a 15 wt% aqueous solution frozen at −20°C for 24 h and thawed at 23°C for any period of time.

The gels experienced increase in turbidity that remained even after they were immersed in water. The turbidity increased with the number of freezing–thawing cycles. Gels produced after one freezing–thawing cycle could not hold their own weight, even immediately after the freezing process at −20°C.

Swelling behaviour

The significant change of the PVA structure during freezing and the associated structural densification due to the formation of the supermolecular and semicrystalline structures were quantified by following the water uptake as a function of thawing time, after the initial freezing at 20°C for 24 h. Typical experimental results are presented in *Figure 1*, where the gel weight, W, has been normalized with respect to the weight of the frozen gel, W_0, at the end of the first freezing cycle. Since the thawing process

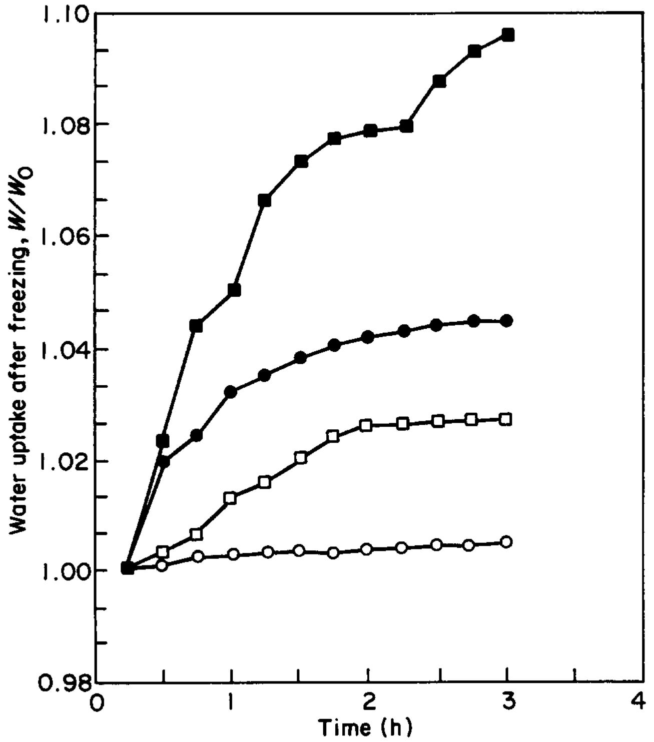

Figure 1 Water uptake of frozen–thawed PVA gels at 23°C as a function of thawing time. All gels were prepared by freezing at −20°C for 24 h and W_0 is the initial frozen weight after the first freezing process. Swelling results are presented after the second (■), third (●), fourth (□) and fifth (○) freezing–thawing cycle

is accompanied by swelling, any gels formed by physical crosslinks, microcrystallites or supermolecular structures should swell according to their structural degree with the least 'crosslinked' gels swelling the most.

In *Figure 1*, swelling results are presented for the PVA gels prepared after two, three, four and five freezing–thawing cycles. The error bars for the data were smaller than the symbol sizes of the Figure. In all cases, the water uptake increased as a function of time, slowly approaching an equilibrium value indicative of the maximum quantity of water that could be absorbed at approximately four hours. However, the equilibrium water uptake decreased with increasing number of freezing–thawing cycles, indicating that this process led to significant densification of the gel structure. In fact, after thawing of the PVA gels that had been exposed to five cycles, there was no more than 0.5 wt% change in weight, indicating a rather dense gel structure.

The process of thawing is a swelling process, where water is transported into the previously densified structure. The transport process is Fickian in nature since the first 60% of the uptake curves of *Figure 1* could be fitted to a square-root-of-time dependent expression, according to:

$$\frac{W - W_0}{W_{\max} - W_0} = 4\left(\frac{D_g t}{\pi \delta^2}\right)^{1/2} \qquad (1)$$

Here δ is the thickness of the gel sample, D is the water diffusion coefficient in the gel and $W_{\max}$ is the maximum attained value of the water uptake. The diffusion coefficients calculated from this analysis are summarized in *Table 1*. It is evident that the water diffusion coefficient decreased as the freezing–thawing cycles increased.

The gel volume, V, was also determined as a function of time, as shown in *Figure 2*. The initial volume, V_0, was determined immediately after the first freezing cycle. The ratio of the final to the initial volume was then graphed *versus* thawing time, showing the same general trend as the weight swelling ratio.

Further analysis of the PVA gel structure was achieved by determining the true weight swelling ratio (see *Figure 3*), expressed as the actual weight of the swollen gel normalized with respect to the dry polymer ratio, W_d. Typical values of the swelling ratio varied from 7.7 to 8.6 and were indicative of highly swollen PVA gels containing from 11.6 to 13% pure PVA. When corrected for the dry weight, the PVA samples indicated that there were major structural rearrangements during the early freezing–thawing cycles. Indeed, the top curve of *Figure 3* corresponds to the data of swelling after two cycles and indicates a distinct drop of the swelling ratio after 10 h. These results agree with our turbidimetric studies reported earlier[4], where a rearrangement of the supermolecular structure was observed after long periods of time. This rearrangement may be related to further densification due to aging of the gel structure. Such

Table 1 Water diffusion coefficient, D_g, in PVA gels prepared by consecutive freezing–thawing cycles[a]

Number of cycle	$10^5 D_g$ (cm^2 s^{-1})
2	1.38
3	1.17
4	0.91
5	0.52

[a] Determined from data of *Figure 1* and equation (1)

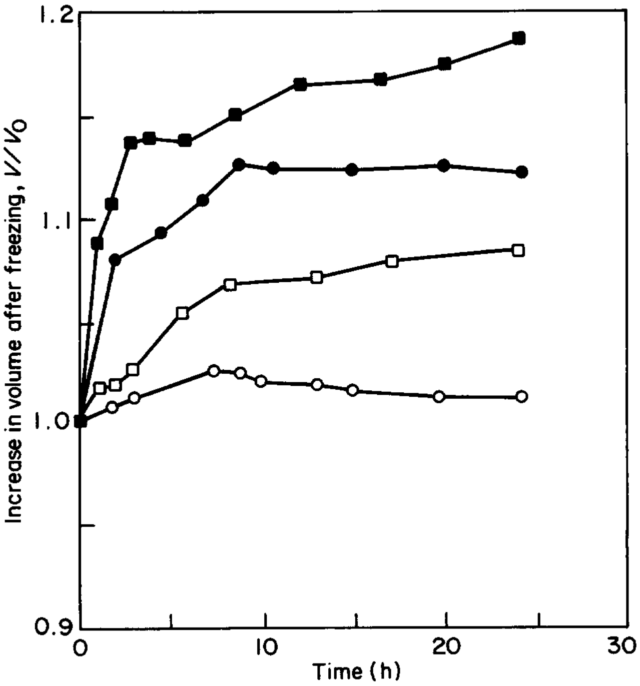

Figure 2 Increase of PVA gel volume at 23°C as a function of thawing time. All gels were prepared by freezing at −20°C for 24 h and V_0 is the initial volume after the first freezing point. Swelling results are presented after the second (■), third (●), fourth (□) and fifth (○) freezing–thawing cycle

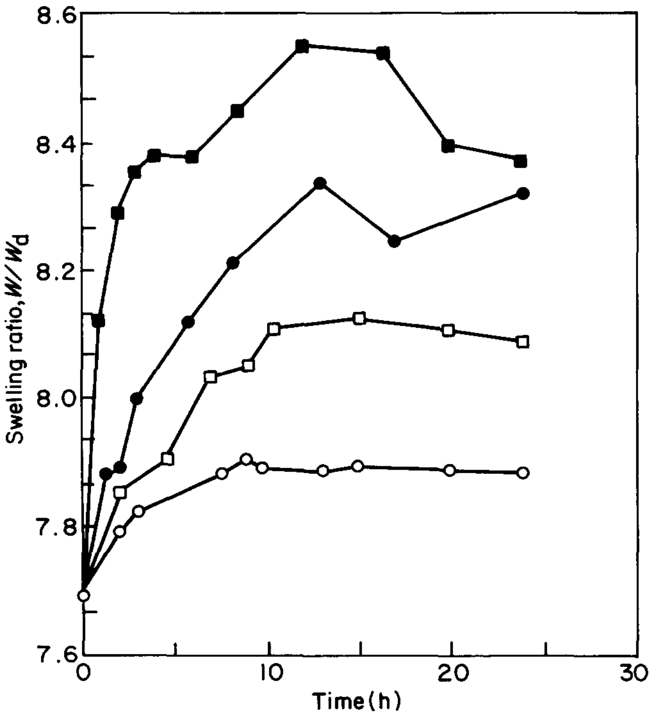

Figure 3 Weight swelling ratio of PVA samples at 23°C as a function of thawing time. All gels were prepared by freezing at −20°C for 24 h and W_d is the dry polymer weight. Swelling results are presented after the second (■), third (●), fourth (□) and fifth (○) freezing–thawing cycle

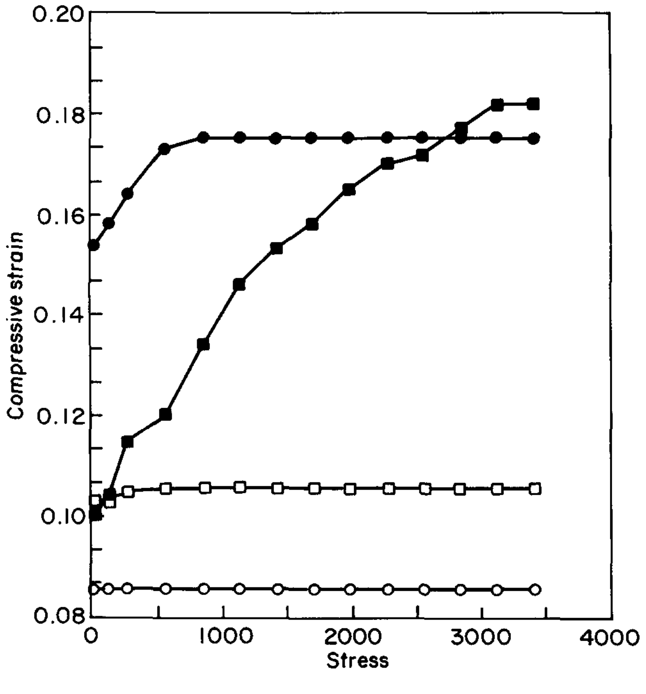

Figure 4 Compressive strain as a function of compressive stress (kPa) applied on PVA gels produced by freezing–thawing cycles. All gels were prepared by freezing at −20°C for 24 h. Results are for gels after two (■), three (●), four (□) and five (○) cycles

a process could potentially lead to semicrystalline structures.

According to the diffusion theory proposed by Peppas and Reinhart[12], the solute diffusion coefficient through gels is a function of the average molecular weight between crosslinks, $\bar{M}_c$, for gels of almost constant swelling ratios. Since the true swelling ratio varied from 7.7 to 8.6, the previous theory gives that

$$\frac{D_g}{D_w} \approx \bar{M}_c \qquad (2)$$

where D_w is the self-diffusion coefficient of water. Therefore, the data of *Table 1* in conjunction with equation (2) indicate that from the second to the fifth freezing–thawing cycle there was a decrease of 62% in the diffusion coefficient corresponding to a similar decrease in the equivalent $\bar{M}_c$. This $\bar{M}_c$ value should be viewed as a characteristic molecular weight distance between consecutive physical crosslinks (entanglements, crystallites). The decrease in $\bar{M}_c$ is indicative of the significant densification of the structure.

Compressive creep experiments

The results of compressive creep testing of various PVA gels produced after two, three, four or five freezing–thawing cycles are reported in *Figure 4*. The compressive strain increased with increasing stress up to a constant value. For loosely crosslinked PVA gels, such as those produced after two or three freezing–thawing cycles, there was a significant stress needed to achieve the maximum constant compressive strain, indicating an elastic deformation of the PVA gels during this compressive stress relaxation process. The ratio of compressive strain to stress may be viewed as equivalent to a compressive compliance that decreases with increasing number of cycles or with increasing densification.

These mechanical testing studies along with the results of the diffusional analysis provide additional evidence of the densification process during freezing–thawing.

CONCLUSIONS

In conclusion, it was possible to prepare reinforced, uncrosslinked PVA gels by freezing–thawing of aqueous PVA solutions. The strength, stability and swelling ratio of the gels were a function of the solution concentration, freezing time and number of freezing–thawing cycles. The conditions resulting in the strongest gels were freezing of a 15 wt% PVA solution at −20°C for 24 h followed by thawing at 23°C for 24 h. Investigation of the swelling ratio as a function of thawing time and freezing cycles indicated that the denser structures were observed after five freezing–thawing cycles.

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