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)
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\(^8\) 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 \(M_w = 35,420\) and \(M_n = 79,200\) (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
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, 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

![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.](image1)

![Table 1: Water diffusion coefficient, \( D_w \), in PVA gels prepared by consecutive freezing–thawing cycles.](image2)

<table>
<thead>
<tr>
<th>Number of cycle</th>
<th>( 10^3D_w ) (cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.38</td>
</tr>
<tr>
<td>3</td>
<td>1.17</td>
</tr>
<tr>
<td>4</td>
<td>0.91</td>
</tr>
<tr>
<td>5</td>
<td>0.52</td>
</tr>
</tbody>
</table>

*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.](image3)
Since the true swelling ratio varied from 7.7 to 8.6, the previous theory gives that
\[ \frac{D_z}{D_w} \approx M_e \]  
(2)

where \( D_w \) is the self-diffusion coefficient of water. Therefore, the data of Table I 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 \( M_e \). This \( M_e \) value should be viewed as a characteristic molecular weight distance between consecutive physical crosslinks (entanglements, crystallites). The decrease in \( M_e \) 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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