

# Sticky Poly(vinyl Alcohol) Hydrogels

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## SYNOPSIS

Low-temperature gelation of poly(vinyl alcohol) (PVA) solution was performed in the presence of CaCl<sub>2</sub>. The resulting PVA hydrogels showed high stickiness and excellent water-holding ability. These properties became more remarkable with increasing CaCl<sub>2</sub> concentration in solvent. Furthermore, both the peel strength on stainless steel and the degree of swelling of the PVA hydrogel drastically increased as CaCl<sub>2</sub> concentration was increased from 20 to 30 wt %. It is concluded that the sticky and water-holding properties of PVA hydrogels are intimately related to the state of hydration of Ca ions in aqueous environment. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

A number of methods have been reported for preparation of poly(vinyl alcohol) (PVA) hydrogels, including chemical methods<sup>1</sup> using a covalent cross-linking agent such as glutaraldehyde and boric acid; physical methods<sup>2</sup> using complexing agents such as titanium, aluminum, manganese, and copper; and radiation methods<sup>3-5</sup> using  $\gamma$ -ray, electron beam, and ultraviolet (uv) light. We recently reported a physical method to prepare PVA hydrogels from water alone or a mixture of water and organic solvent by low-temperature crystallization of concentrated PVA solutions.<sup>6,7</sup> Although most of the hydrogels prepared with these methods are high in water content and excellent in mechanical properties, not all of them have adhesiveness and many have poor elasticity below 0°C, because the water in the gel freezes below this point. Furthermore, the water in PVA hydrogel readily vaporizes at room temperature. If PVA hydrogels having good adhesive and water-holding properties can be prepared, they would find applications as biomaterials, for instance, in transdermal therapeutic systems. A preparation method and properties of sticky PVA hydrogels are described.

## EXPERIMENTAL

### Preparation of PVA Hydrogel

The PVA used in this study is atactic and commercially available with a viscosity-average degree of polymerization of 1,700 and a degree of saponification of 99.5 mol %. An aqueous PVA solution with polymer concentrations from 10 to 30 wt % was mixed with an aqueous CaCl<sub>2</sub> solution of different concentrations at 110°C for 1 h in an autoclave. The temperature of the admixed solutions was lowered to 60°C and samples to a thickness around 1 mm were placed on a glass plate and allowed to stand at -20°C for 24 h to prepare PVA hydrogels containing CaCl<sub>2</sub>. For simplicity, the weight concentration of CaCl<sub>2</sub> in the hydrogels is not expressed based on the total gel, but on the CaCl<sub>2</sub> solution before mixing with the PVA solution.

### Physicochemical Measurements

The water-holding ability of PVA hydrogel was estimated from the weight change that occurred when the mixture was let standing at 25°C in a relative humidity of 65%. The degree of swelling of PVA hydrogel was determined by weighing the PVA hydrogel before and after immersion in water at 37°C. The melting temperature of the PVA hydrogel was measured by Ferry's method<sup>8</sup> at a heating rate of 1°C/min. Tensile strength and elongation at break

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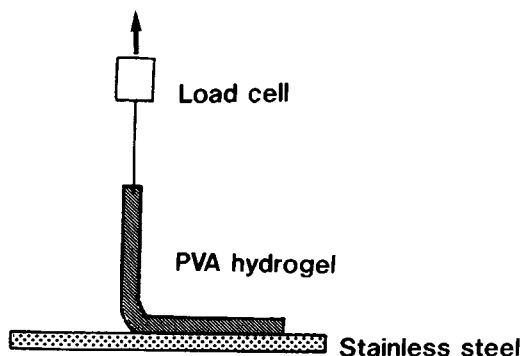
were measured with a tensile tester at a cross-head speed of 50 mm/min at 25°C and relative humidity (RH) of 65%. Dumb-bell specimens, 100 mm length  $\times$  5 mm width were cut from the gel sheet of 1 mm thickness. The peel strength of the PVA hydrogel on stainless steel was measured by the 90° peel strength method depicted in Figure 1.

The state of hydration of Ca ions in aqueous  $\text{CaCl}_2$  solution was estimated by differential scanning calorimetry (DSC). Following cooling to  $-80^\circ\text{C}$ , the samples were heated at the rate of  $10^\circ\text{C}/\text{min}$ .

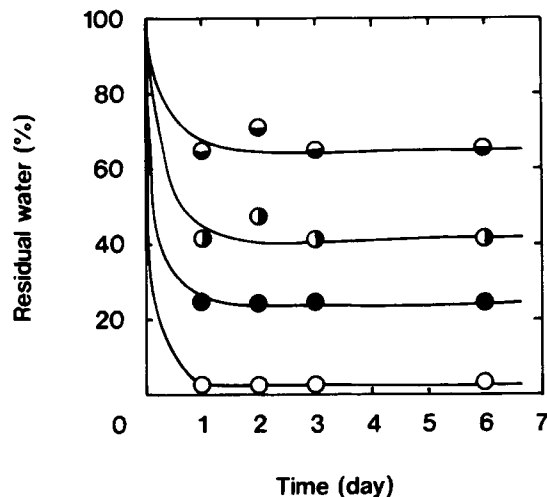
## RESULTS

The weight change of wet PVA hydrogels containing  $\text{CaCl}_2$  of different concentrations observed at 25°C and 65% RH is shown in Figure 2. As is apparent, the weight change of PVA hydrogels ceases after 1 day, regardless of the  $\text{CaCl}_2$  concentration, but the extent of weight change becomes less prominent with the increasing  $\text{CaCl}_2$  concentration. The PVA hydrogel without  $\text{CaCl}_2$  releases almost all of its water after 1 day, whereas the PVA hydrogel prepared from 30 wt %  $\text{CaCl}_2$  aqueous solution maintains 65% of its water after 6 days. Figure 3 shows the result of weight change of PVA hydrogels of various water contents, the  $\text{CaCl}_2$  concentration being kept at 30 wt %. Apparently, the weight change is slight and independent of the PVA concentration. It follows from Figures 2 and 3 that the water-holding ability is dependent on the  $\text{CaCl}_2$  concentration, but independent of the PVA concentration in the hydrogel, provided  $\text{CaCl}_2$  is present.

Tensile strength and elongation of the PVA hydrogels were measured as a function of  $\text{CaCl}_2$  concentration. The results in Figure 4 show tensile strength as well as elongation to be dependent on

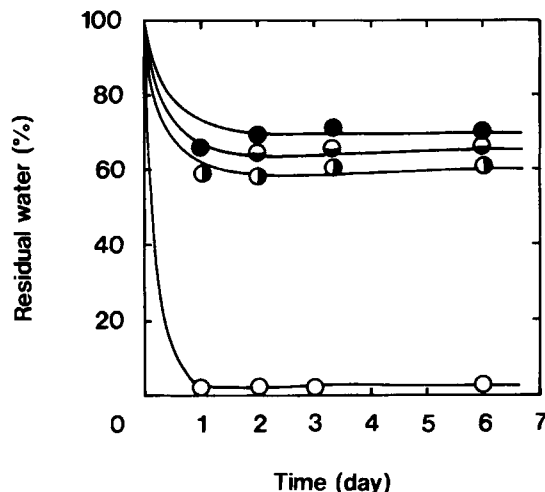


**Figure 1** Schematic diagram for the 90° peel strength measurement of PVA hydrogels.

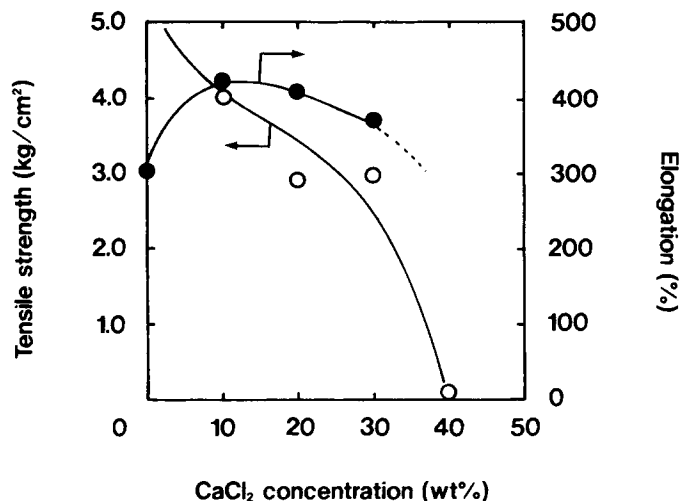


**Figure 2** Residual weight of 15 wt % PVA hydrogels as a function of drying time. [ $\text{CaCl}_2$ ]: (○), 0; (●), 10; (◐), 20; (●), 30 wt %.

the  $\text{CaCl}_2$  concentration. Tensile strength decreases drastically with increasing  $\text{CaCl}_2$  concentration, but maintains a value as high as  $3 \text{ kg}/\text{cm}^2$  at 30 wt %  $\text{CaCl}_2$  concentration. On the other hand, the elongation reaches maximum at 10 wt %  $\text{CaCl}_2$  concentration. This value is about 1.5 times as high as the elongation of PVA hydrogel without  $\text{CaCl}_2$ . The dependence of tensile strength and elongation on the PVA concentration is shown in Figure 5. With the  $\text{CaCl}_2$  concentration kept at 30 wt %, the tensile strength slowly increase with the PVA concentration up to 15 wt %, but drastically increases when the



**Figure 3** Residual weight of PVA hydrogels containing 30 wt %  $\text{CaCl}_2$  as a function of drying time. [PVA]: (●), 13; (◐), 18; (●), 20 wt %; (○), 0 wt %  $\text{CaCl}_2$ , 15 wt % PVA.



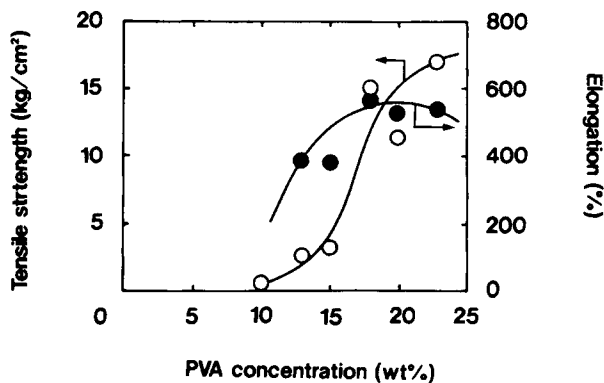
**Figure 4** Tensile strength and elongation of 15 wt % PVA hydrogels as a function of CaCl<sub>2</sub> concentration.

PVA concentration is in the range 15–25 wt %. At a PVA concentration of 25 wt %, the tensile strength reaches 17 kg/cm<sup>2</sup>, which is about 3 times as high as that of a PVA hydrogel with the PVA concentration of 15 wt %.

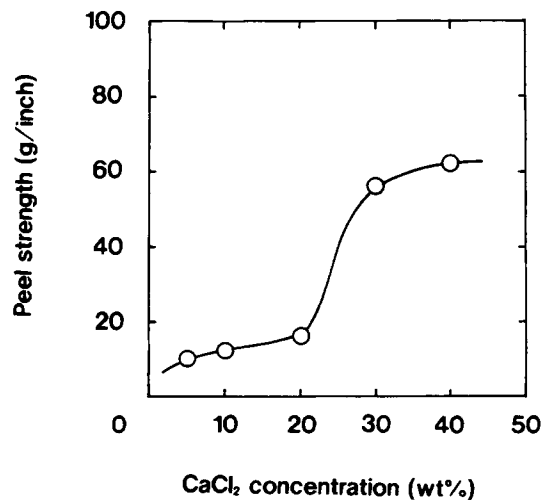
Figures 6 and 7 show the peel strength of PVA hydrogels as a function of CaCl<sub>2</sub> and PVA concentration, respectively. The peel strength measurement was conducted to obtain a quantitative measure of the hydrogel adhesiveness. Peel strength increases as the surface of PVA hydrogel becomes more adhesive. As can be seen, the concentration dependence of the peel strength is opposite that of the tensile strength. The peel strength drastically increases when the CaCl<sub>2</sub> concentration increases from 20 to 30 wt %, but exhibits a gradual increase when additional CaCl<sub>2</sub> is added. The peel strength

of PVA hydrogel prepared from 30 wt % CaCl<sub>2</sub> is 55 g/inch, about 4 times as high as that of PVA hydrogel prepared from 20 wt % CaCl<sub>2</sub>. As is obvious in Figure 7, peel strength is highly dependent on PVA concentration. Therefore, there is a steep increase in peel strength with decreasing PVA concentration, reaching 200 g/inch at a PVA concentration of 10 wt %, when the CaCl<sub>2</sub> concentration is kept at 30 wt %.

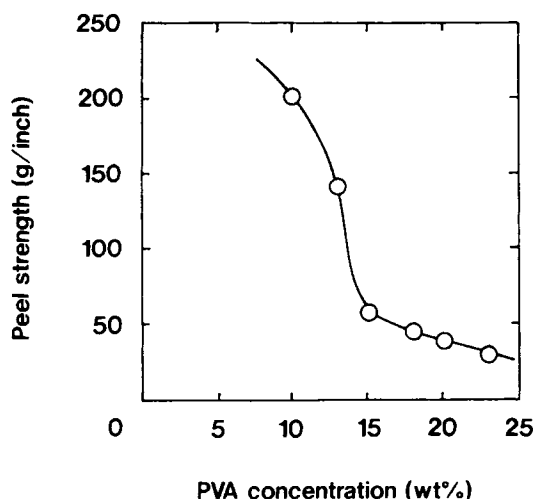
The degree of swelling of PVA hydrogels is shown in Figure 8 as a function of immersion time in water maintained at 37°C. Apparently, the degree of swelling reaches a maximum at 1 day, after which there is a gradual decrease for all PVA hydrogels.



**Figure 5** Tensile strength and elongation of PVA hydrogels containing 30 wt % CaCl<sub>2</sub> as a function of PVA concentration.



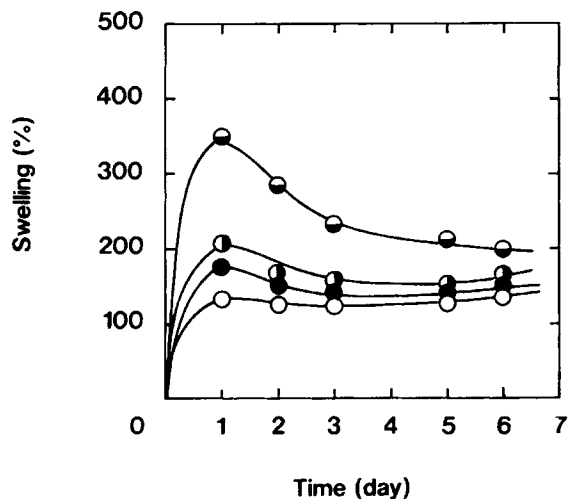
**Figure 6** Peel strength of 15 wt % PVA hydrogels as a function of CaCl<sub>2</sub> concentration.



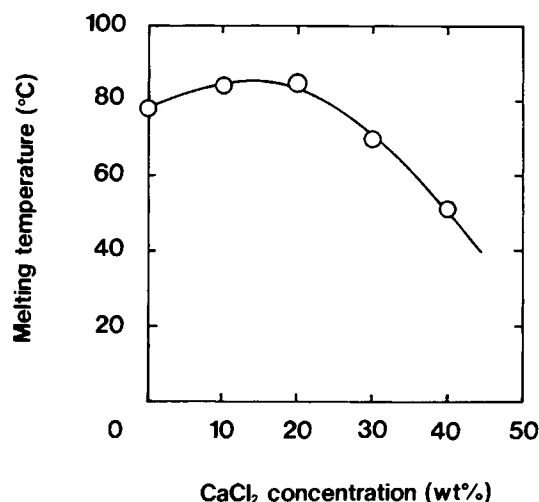
**Figure 7** Peel strength of PVA hydrogels containing 30 wt %  $\text{CaCl}_2$  as a function of PVA concentration.

The  $\text{CaCl}_2$  concentration significantly influences the degree of swelling of PVA hydrogel, especially when the  $\text{CaCl}_2$  concentration is increased from 20 to 30 wt %. This suggests that the physical structure of PVA hydrogel also changes at  $\text{CaCl}_2$  concentrations ranging from 20 to 30 wt %. No leaching of PVA was observed during the swelling experiment.

Figure 9 shows the melting temperature ( $T_m$ ) of PVA hydrogels with different  $\text{CaCl}_2$  concentrations.  $T_m$  increases only slightly up to 20 wt %  $\text{CaCl}_2$  and does not differ greatly from that of PVA hydrogel without  $\text{CaCl}_2$ . However, at  $\text{CaCl}_2$  concentrations



**Figure 8** Time course of swelling change in water at 37°C for 15 wt % PVA hydrogels containing  $\text{CaCl}_2$  of different concentrations. [ $\text{CaCl}_2$ ]: (○), 0; (●), 10; (◐), 20; (◑), 30 wt %.



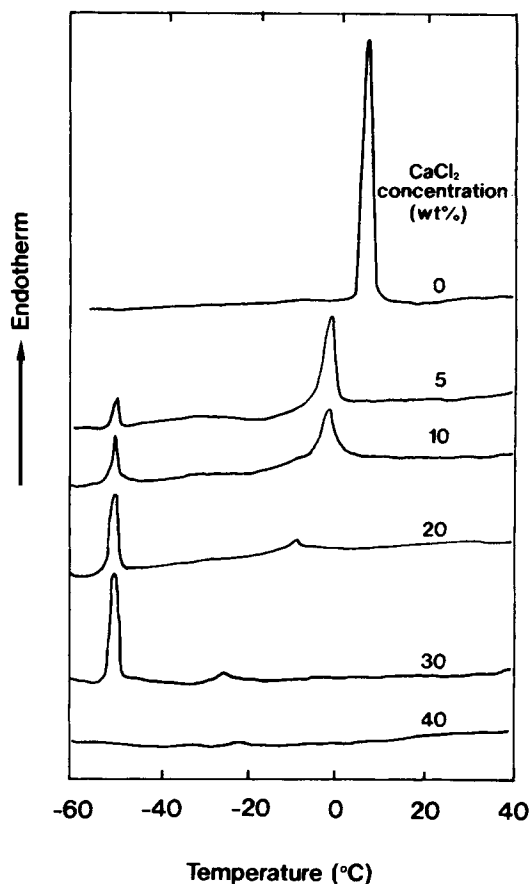
**Figure 9** Melting temperature of 10 wt % PVA hydrogels as a function of  $\text{CaCl}_2$  concentration.

higher than 20 wt %,  $T_m$  decreases drastically reaching 50°C at a  $\text{CaCl}_2$  concentration of 40 wt %. The dependence of melting temperature of hydrogels on the  $\text{CaCl}_2$  concentration is similar to that of elongation shown in Figure 4.

## DISCUSSION

As described above, sticky PVA hydrogels could be obtained from aqueous PVA solutions containing  $\text{CaCl}_2$ . The peel strength, which is a measure of stickiness is strongly dependent on the  $\text{CaCl}_2$  concentration, similar to the tensile strength. Furthermore, the dependence of tensile strength and peel strength on  $\text{CaCl}_2$  concentration were in opposite polarity to each other. As a compromise, sticky PVA hydrogels with high strength could be obtained at concentrations of 30 wt %  $\text{CaCl}_2$  and 15 wt % PVA, as comparison of Figure 4 with Figure 6 or Figure 5 with Figure 7 indicates. In addition, the above results clearly indicate that the physical structure of PVA hydrogel changes in the  $\text{CaCl}_2$  concentration range of 20–30 wt %. This was further evidenced by the results of swelling and melting. The decrease in swelling by immersion in water for longer than 1 day may be due to further crystallization of PVA chains occurring in water at 37°C.

Divalent transient metallic salts such as titanium, zirconium, copper, and cobalt, can create complexes with PVA chains by coordinated bonds, resulting in water-insoluble gel formation.<sup>2</sup> To the contrary, when monovalent metallic salts such as sodium, potassium, thallium, and lithium, are added to aqueous



**Figure 10** DSC thermograms of water- $\text{CaCl}_2$  mixtures without PVA.

PVA solution, stable hydrogel is not formed, because these metals are precipitants of PVA. On the other hand, divalent metallic salts such as magnesium and calcium neither precipitate PVA nor create strong complex bonds with PVA, probably because of strong interaction of the metallic ions with water. Consequently, the cross-links between the PVA chains formed by these divalent metallic ions may be weak, creating a sticky transparent PVA hydrogel. The water-holding ability of PVA hydrogel containing  $\text{CaCl}_2$  could be associated with the high deliquescence and moisture regain of Ca ion, but this seems not to be the case as demonstrated below.

Differential scanning calorimetry (DSC) was performed to study the hydration of Ca ion in

aqueous  $\text{CaCl}_2$  solution without PVA. The results are shown in Figure 10. The endothermic peak of aqueous  $\text{CaCl}_2$  solution splits in two in the  $\text{CaCl}_2$  concentration range 5–30 wt %. As the  $\text{CaCl}_2$  concentration increases, the first melting peak appearing around  $0^\circ\text{C}$  shifts to lower temperatures, but the second melting peak around  $-50^\circ\text{C}$  remains unchanged. On the other hand, the peak area of the first melting temperature decreases with the increasing  $\text{CaCl}_2$  concentration, whereas the peak area of the second melting temperature increases with increasing  $\text{CaCl}_2$  concentration. This result clearly indicates that the state of hydration of Ca ion in aqueous  $\text{CaCl}_2$  solution changes with the  $\text{CaCl}_2$  concentration. When the  $\text{CaCl}_2$  concentration is low, enough free water molecules may exist in aqueous  $\text{CaCl}_2$  solution to freeze at or near  $0^\circ\text{C}$ . As a result, these solutions would produce the PVA hydrogels having physical properties similar to those prepared from water alone, without  $\text{CaCl}_2$ . On the other hand, highly concentrated solutions of  $\text{CaCl}_2$  may contain too little free water to freeze at or below  $0^\circ\text{C}$  because of the significant interaction between Ca ions and water, leading to formation of a sticky PVA hydrogel with excellent water-holding ability and high strength.

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