

# On the Viscoelastic Properties of Poly(vinyl alcohol) and Chemically Crosslinked Poly(vinyl alcohol)

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Received 13 November 2000; 25 February 2001

**ABSTRACT:** Poly(vinyl alcohol)(PVA) films chemically crosslinked with glutaraldehyde(GA) in the presence of HCl were prepared by casting from aqueous solutions. The PVA and PVA gels were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA); their swelling characteristics and tensile strength were also determined. The DSC results for the gels displayed depressions of the melting and crystallization temperatures, as well as a decrease of the heat of fusion, when compared to those of PVA free of crosslinker. The DMA analysis revealed that: (1) The glass transition temperature of the wet PVA was lower than that of the dry one, indicating that the water had a plasticizing effect. (2) The gels had a lower glass transition temperature than PVA. (3) The glass transition temperature of the wet gels increased with increasing crosslink density. Possible explanations are provided for these observations. Whereas the thermogravimetric curves of PVA exhibited a single degradation peak, two degradation peaks were detected for the crosslinked PVA. The wet PVA and PVA gels displayed lower tensile strengths and higher elongations than the dried ones. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1816–1823, 2001

**Key words:** PVA; crosslinking; gel; hydrogen bond; plasticization; dynamic mechanical analysis

## INTRODUCTION

PVA is prepared via the hydrolysis of polyvinyl acetate (PVAc), during which the acetate groups are progressively replaced by hydroxyls. The higher crystallinity of PVA compared to that of the parent polymer, PVAc, can be attributed to the small size of the hydroxyl groups, which allows the chains to adopt a planar zig-zag confor-

mation under the action of hydrogen bonding.<sup>1,2</sup> PVA, which, is perhaps the simplest of the water-soluble hydrophilic polymers, has the highest glass transition temperature ( $T_g = 85^\circ\text{C}$ ), because of the high packing efficiency of the planar zig-zag conformation as crystalline aggregates caused by the hydrogen bondings between adjacent hydroxyl groups.<sup>3</sup>

PVA could be cast from water as films, sheets, and fibers with excellent mechanical properties. It was used as a membrane in dehydration processes because of its high hydrophilicity, chemical stability and excellent film-forming ability. To avoid its poor stability in aqueous solutions, it

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*Journal of Applied Polymer Science*, Vol. 82, 1816–1823 (2001)  
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was insolubilized by crosslinking or other modification reactions. Due to its biocompatibility, PVA could also be used in a variety of biomedical applications.<sup>3,10,11</sup> A PVA gel membrane could be used as a synthetic membrane for pervaporation and as a bioartificial pancreas in biomedical applications.<sup>4–11</sup>

The reaction between PVA and glutaraldehyde (GA) generates a polymer network, whose mechanical properties and swelling are affected by its degree of crosslinking.<sup>6</sup> The crosslinked structure was obtained through the reaction of the hydroxyl groups of PVA with the aldehyde groups of GA in the presence of a strong acid.<sup>12–19</sup> GA is an important reagent in the biomedical field, and has been used extensively as an agent for fixation of cells, for immobilizing enzymes, and for crosslinking proteins and polysaccharides.<sup>16,17,19</sup> Compared to other aldehydes, which are less efficient in generating chemically, biologically, and thermally stable crosslinks, GA is able to react relatively rapidly with the functional groups present, resulting in a tightly crosslinked network, containing inter- and/or intramolecular crosslinks. After the chemical modification of PVA by GA in the presence of HCl, the resulting gel can contain the crosslinker molecules as crosslinking and grafted moieties.<sup>3,5,8,16,17</sup>

In the present article, the thermal behavior and the viscoelastic properties of PVA and PVA gels have been investigated using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA). The swelling behavior and the mechanical properties of PVA gels, prepared in various reaction conditions, were also examined.

## EXPERIMENTAL

### Materials

PVA ( $M_w$  89,000–98,000, degree of deacetylation = 99%) and GA (25 wt % aqueous solution) were purchased from Aldrich Chem. Co. and used without further purification. Water was double distilled, and the other solvents used were of analytical grade.

### Film Preparation

PVA was first dissolved in water to obtain a 5 wt % solution, which was heated at 80°C for 10 min with constant stirring. For crosslinking, GA and

HCl were added. Prior to the addition of GA and HCl, the solution was cooled to room temperature. To eliminate the insoluble impurities, the polymer solutions were glass filtered. The films were prepared by casting on a glass plate and by drying at room temperature for 72 h; film thicknesses of 50–80  $\mu\text{m}$  were thus obtained.

### Swelling Test of the Gels

The water content of the gel films after swelling was calculated using the expression

$$W_c = (W_s - W_d)/W_d$$

where  $W_c$  is the water uptake in grams per gram of gel film, and  $W_s$  and  $W_d$  are the weights of the gel films after swelling and subsequent drying, respectively. The time duration for swelling was 24 h. The excess water on the swollen films was wiped out with a filter paper.

### Measurements

The dynamic mechanical analysis was conducted using a DMA 2980 instrument (TA Instruments) in the tensile mode, at a frequency of 1 Hz, by heating from  $-20$  to  $260^\circ\text{C}$  at a rate of  $2^\circ\text{C}/\text{min}$  in a nitrogen atmosphere. The cast films, with dimensions of about  $3 \times 10 \times 0.1$  mm, were subjected to sinusoidal deformations with a  $5\text{-}\mu\text{m}$  amplitude. The thermal properties were determined with a DSC 2010 instrument (TA Instruments) in a nitrogen atmosphere. Two heating scans were employed: the first was carried out to eliminate the residual water and solvent in the films, and was performed at a rate of  $20^\circ\text{C}/\text{min}$  from room temperature up to  $150^\circ\text{C}$  and kept at this temperature for 5 min. The second scan was carried out at a heating rate of  $20^\circ\text{C}/\text{min}$  from 0 to  $260^\circ\text{C}$ . To determine the crystallization temperature, the samples were heated up to  $250^\circ\text{C}$ , kept at this temperature for 5 min and then cooled down at a rate of  $10^\circ\text{C}/\text{min}$ . The thermal stability analysis was conducted by employing a TG/DTA 6200 instrument (Seiko Instruments Co., Japan) and by heating from room temperature to  $750^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$  under a nitrogen flow. The mechanical properties of the PVA networks (gels) were determined using a Texture Analyzer (Stable Micro System, U.K.). The samples for the tensile test were prepared either by conditioning them in a 50% relative humidity atmosphere for 48 h, or by drying them at  $100^\circ\text{C}$  in

**Table I Water Uptake by the PVA Gel Film for Various Glutaraldehyde Concentrations<sup>a</sup>**

Concentration of Glutaraldehyde (mol/L)	Water Content in Gels ( $W_c$ ) Grams/Gram of Gel Film
0	sol.
$6.3 \times 10^{-4}$	0.59
$2.5 \times 10^{-3}$	0.51
$5.0 \times 10^{-3}$	0.50
$8.4 \times 10^{-3}$	0.49
$1.7 \times 10^{-2}$	0.45

sol—soluble in water.

<sup>a</sup> The concentration of HCl was  $2.25 \times 10^{-1}$  mol/L. The gel film was dried in a vacuum oven for 3 h at 100°C.

a vacuum oven for 3 h. The tensile strength and the elongation were measured at an extension rate of 500 mm/min, at room temperature.

## RESULTS AND DISCUSSION

### Swelling Behavior

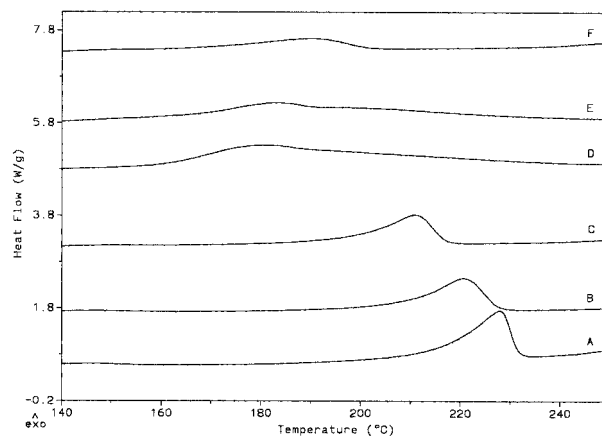
The PVA gel films were prepared by casting from aqueous solutions of PVA, GA, and HCl. The crosslinking occurred in solution at room temperature, and the degree of crosslinking was varied by changing the concentrations of GA and HCl. The results of the swelling in water are listed in Tables I and II. The extent of swelling, expressed as the amount of water uptake by the film (gr water per gr film), constitutes a measure of the degree of crosslinking. There was no significant change in the film appearance during swelling.

**Table II Water Uptake by the PVA Gel Film for Various Concentrations of HCl<sup>a</sup>**

Concentration of HCl (mol/L)	Water content in Gels ( $W_c$ ) Grams/Gram Gel Film
0	sol.
$7.0 \times 10^{-3}$	0.84
$1.0 \times 10^{-2}$	0.79
$2.8 \times 10^{-2}$	0.68
$1.1 \times 10^{-1}$	0.51
$2.3 \times 10^{-1}$	0.49

sol—soluble in water.

<sup>a</sup> The concentration of glutaraldehyde was  $2.25 \times 10^{-1}$  mol/L. The gel film was dried in a vacuum oven for 3 h at 100°C.

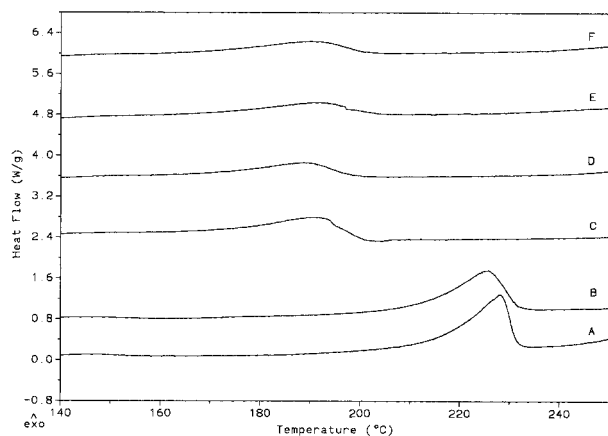


**Figure 1** DSC thermograms of PVA and PVA gels prepared by changing the concentration of glutaraldehyde. The concentration of glutaraldehyde: (A) 0 mol/L, (B)  $6.3 \times 10^{-4}$  mol/L, (C)  $2.5 \times 10^{-3}$  mol/L, (D)  $5.0 \times 10^{-3}$  mol/L, (E)  $8.4 \times 10^{-3}$  mol/L, (F)  $1.7 \times 10^{-2}$  mol/L. The concentration of HCl was  $2.25 \times 10^{-1}$  mol/L. The measurements were conducted at a 20°C/min heating rate under nitrogen.

Table I shows that the swelling of the PVA gel decreased with increasing GA content, and that the unmodified PVA completely dissolved in water. Table II shows that the swelling of the PVA gel films decreased with increasing concentration of HCl. These results are as expected.

### DSC Analysis

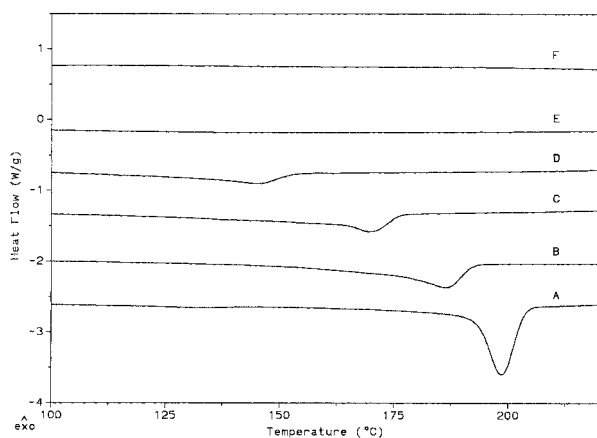
The thermal characteristics of PVA and PVA gel were examined by DSC. The results are presented in Figures 1 and 2. The pure PVA provided a relatively large and sharp melting endotherm curve with a peak around 230°C. By crosslinking with GA in the presence of HCl, the endothermic peak of PVA decreased with an accompanying depression of the melting temperature. The decrease of the heat of fusion of the chemically modified PVA is a result of the attenuation by the crosslinker molecules of the degree of crystallinity. The depression of the melting temperature is caused by the morphological effects induced by the reaction between GA and PVA.<sup>20</sup> Two kinds of reactions can occur—the crosslinking and the branching via grafting of the GA molecules. Both attenuate the hydrogen bonding and the degree of crystallinity. Figure 3 shows that the crystallization temperature and the heat of crystallization decrease with increasing GA concentration, and that for GA concentrations greater than  $8.4 \times 10^{-3}$  mol/L, one can no longer discern a crystallization process.



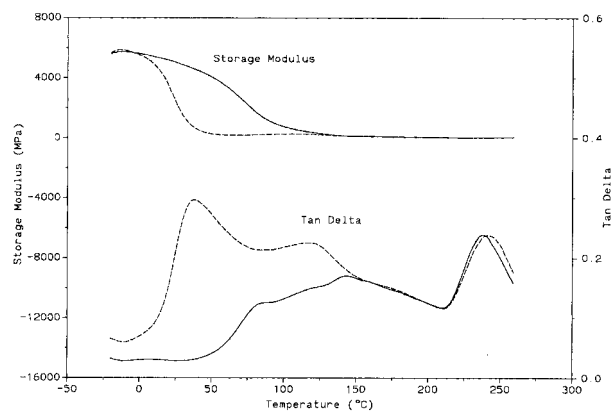
**Figure 2** DSC thermograms of PVA and PVA gels prepared by changing the concentration of HCl. The concentration of HCl: (A) 0 mol/L, (B)  $7.0 \times 10^{-3}$  mol/L, (C)  $1.0 \times 10^{-2}$  mol/L, (D)  $2.8 \times 10^{-2}$  mol/L, (E)  $1.1 \times 10^{-1}$  mol/L, (F)  $2.3 \times 10^{-1}$  mol/L. The concentration of glutaraldehyde was  $8.38 \times 10^{-3}$  mol/L. The measurements were conducted at a  $20^\circ\text{C}/\text{min}$  heating rate under nitrogen.

### DMA Analysis

The dynamic mechanical analysis is a sensitive method that can detect the molecular relaxations, including the glass transition temperature of the polymer. The dynamic mechanical properties of PVA have been previously investigated in detail,<sup>21,22</sup> and it was reported that the pure PVA



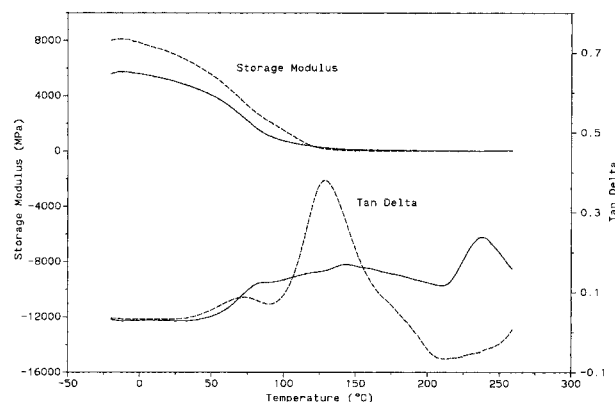
**Figure 3** DSC thermograms of PVA and PVA gels prepared by changing the concentration of glutaraldehyde. The concentration of glutaraldehyde: (A) 0 mol/L, (B)  $6.3 \times 10^{-4}$  mol/L, (C)  $2.5 \times 10^{-3}$  mol/L, (D)  $5.0 \times 10^{-3}$  mol/L, (E)  $8.4 \times 10^{-3}$  mol/L, (F)  $1.7 \times 10^{-2}$  mol/L. The concentration of HCl was  $2.25 \times 10^{-1}$  mol/L. The measurements were conducted at a  $-10^\circ\text{C}/\text{min}$  heating rate under nitrogen.



**Figure 4** Temperature dependence of storage modulus and  $\tan\delta$  for PVA (—) and moisture containing PVA (---), respectively. The measurements were conducted at a  $2^\circ\text{C}/\text{min}$  heating rate, 1-Hz frequency, and  $5\text{-}\mu\text{m}$  amplitude.

has as many as five mechanical relaxations around  $-60$ ,  $35$ ,  $80$ , and other two above  $100^\circ\text{C}$ . In the present study, the designation of the relaxations in the  $\tan\delta$  curve was borrowed from Takayanagai et al.<sup>21,22</sup> In Figure 4, the elastic modulus ( $E'$ ) and  $\tan\delta$  curve of the dry PVA and wet PVA (c.a. 5 wt % of water) are plotted against temperature, in the temperature range of  $-20$  to  $260^\circ\text{C}$ . The two peaks in the  $\tan\delta$  curve of dry PVA, located at about  $80$  and  $35^\circ\text{C}$ , are caused by relaxations in the amorphous regions of PVA. The former, the primary relaxation  $\alpha_a$ , represents the glass transition temperature of the PVA at which the micro-Brownian motions of the molecular chains become appreciable, and the elastic modulus  $E'$  decreases markedly. The latter, the  $\beta_a$  relaxation, is due to the local relaxation of the PVA main chains. The relaxations observed above  $100^\circ\text{C}$  are due to the crystalline relaxations of PVA and appear as two peaks, one around  $135^\circ\text{C}$  ( $\beta_c$  relaxation) and the other around  $237^\circ\text{C}$  ( $\alpha_c$  relaxation). The  $\alpha_c$  relaxation is caused by the melting of the crystalline domains of PVA. The  $\alpha_a$  relaxation of the wet PVA is depressed to  $35^\circ\text{C}$ , indicating a decrease in the glass transition temperature. The swelling of the polymer by water resulted in a marked increase in the free volume occupied by cavities, and thus disrupted the hydrogen bonding and increased the mobility of the polymer chains leading to a decrease of the glass transition temperature.<sup>1-3</sup>

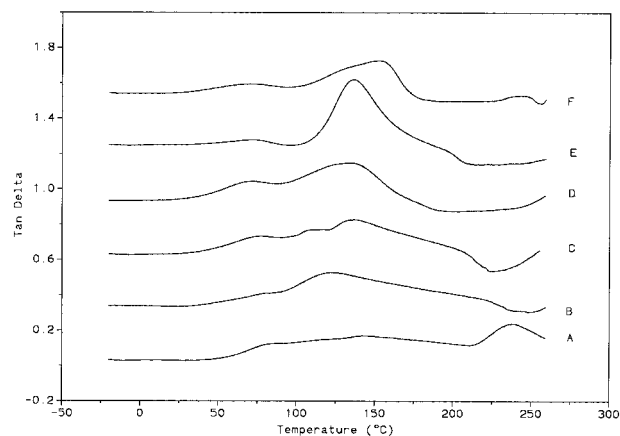
Figure 5 presents the temperature dependence of the elastic modulus  $E'$  and  $\tan\delta$  for pure and crosslinked PVA films in the range of  $-20$  to



**Figure 5** Temperature dependence of storage modulus and  $\tan \delta$  for PVA (—) and PVA gels (---). The concentration of glutaraldehyde and of HCl for the preparation of PVA gel was  $8.38 \times 10^{-3}$  mol/L and  $2.25 \times 10^{-1}$  mol/L, respectively. The measurements were conducted at a  $2^\circ\text{C}/\text{min}$  heating rate, 1-Hz frequency, and  $5\text{-}\mu\text{m}$  amplitude under nitrogen.

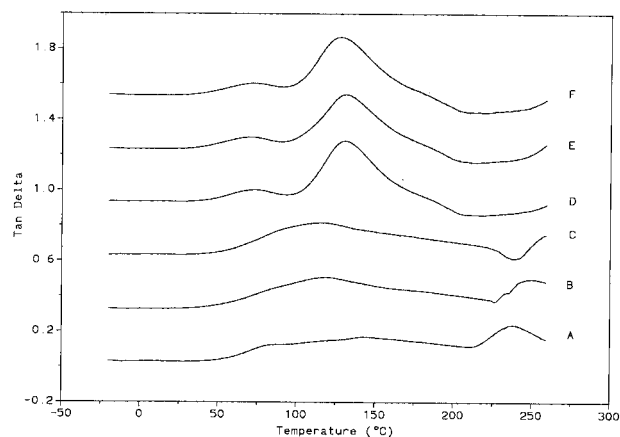
$260^\circ\text{C}$ . The peak in  $\tan \delta$  around  $85^\circ\text{C}$ , the  $\alpha_a$  relaxation, was shifted to lower temperatures for the gels, indicating a decrease of the glass transition temperature. In most cases, the glass transition temperature increases with increasing crosslink density,<sup>9,12,16–18</sup> because the crosslinking increases the rigidity of the polymer. For PVA, the hydroxyl groups contribute via hydrogen bonding to the stiffness of the polymer. When the number of hydroxyl groups is diminished by either branching because of the grafting of the crosslinker, or crosslinking, the hydrogen bonding is attenuated and the stiffness is diminished because the crosslinker induces less stiffness than the hydrogen bonding. Consequently, the crosslinked PVA can have a more flexible structure, and hence, a lower glass transition temperature than the unmodified PVA.

Figures 6 and 7 present the temperature dependence of  $\tan \delta$  of dry PVA gels, for various concentrations of GA and of HCl, respectively. The  $\alpha_a$  relaxation of the PVA gels is shifted to lower temperatures with increasing GA and HCl concentrations, indicating a decrease of the glass transition temperature. This occurred because the strong hydrogen bonding in PVA was increasingly replaced by crosslinks, which decreased its crystallinity. Figures 8 and 9 present the temperature dependence of  $\tan \delta$  curve for wet PVA gels for various concentrations of GA and of HCl, respectively. The glass transition temperature of the wet PVA gels is shifted to higher tempera-

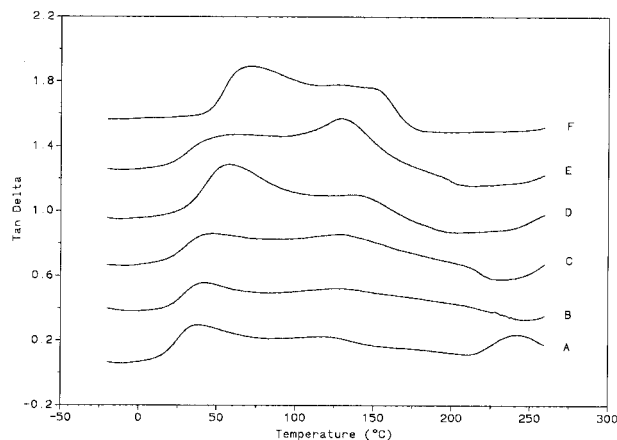


**Figure 6** Temperature dependence of loss  $\tan \delta$  for dry PVA gels prepared by changing the concentration of glutaraldehyde. The concentration of glutaraldehyde: (A) 0 mol/L, (B)  $6.3 \times 10^{-4}$  mol/L, (C)  $2.5 \times 10^{-3}$  mol/L, (D)  $5.0 \times 10^{-3}$  mol/L, (E)  $8.4 \times 10^{-3}$  mol/L, (F)  $1.7 \times 10^{-2}$  mol/L. The measurements were conducted at a  $2^\circ\text{C}/\text{min}$  heating rate, 1-Hz frequency, and  $5\text{-}\mu\text{m}$  amplitude under nitrogen.

tures when compared to the wet PVA, and the glass transition temperature of the wet PVA gel increases with increasing crosslink density. Figures 6 and 8 present the temperature dependence of  $\tan \delta$  for the dry and wet PVA gels, prepared with various GA concentrations, respectively. The

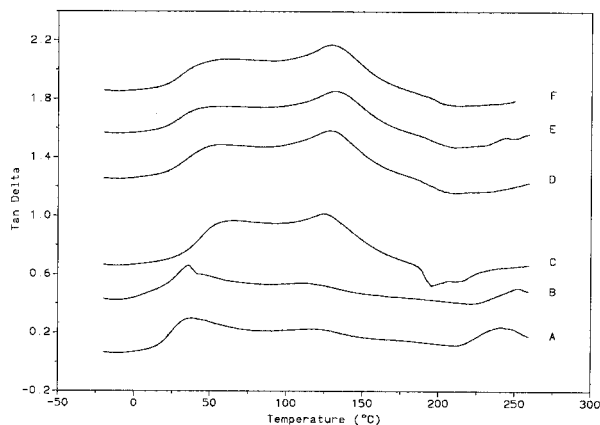


**Figure 7** Temperature dependence of  $\tan \delta$  for dry PVA gels prepared by changing the concentration of HCl. The concentration of HCl: (A) 0 mol/L, (B)  $7.0 \times 10^{-3}$  mol/L, (C)  $1.0 \times 10^{-2}$  mol/L, (D)  $2.8 \times 10^{-2}$  mol/L, (E)  $1.1 \times 10^{-1}$  mol/L, (F)  $2.3 \times 10^{-1}$  mol/L. The concentration of glutaraldehyde was  $8.38 \times 10^{-3}$  mol/L. The measurement were conducted at a  $2^\circ\text{C}/\text{min}$  heating rate, 1-Hz frequency, and  $5\text{-}\mu\text{m}$  amplitude under nitrogen.

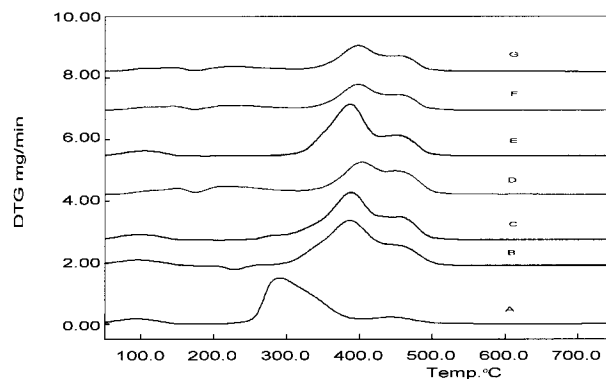


**Figure 8** Temperature dependence of  $\tan \delta$  for wet PVA gels prepared by changing the concentration of glutaraldehyde. The gel films contained c.a. 5 wt % of water. The concentration of glutaraldehyde: (A) 0 mol/L, (B)  $6.3 \times 10^{-4}$  mol/L, (C)  $2.5 \times 10^{-3}$  mol/L, (D)  $5.0 \times 10^{-3}$  mol/L, (E)  $8.4 \times 10^{-3}$  mol/L, (F)  $1.7 \times 10^{-2}$  mol/L. The measurements were conducted at a  $2^\circ\text{C}/\text{min}$  heating rate, 1-Hz frequency, and  $5\text{-}\mu\text{m}$  amplitude under nitrogen.

glass transition temperature difference between the dry and wet PVA was around  $40^\circ\text{C}$ , and was caused by the replacement of the hydrogen bonding among the oxydrils of the dry PVA with the

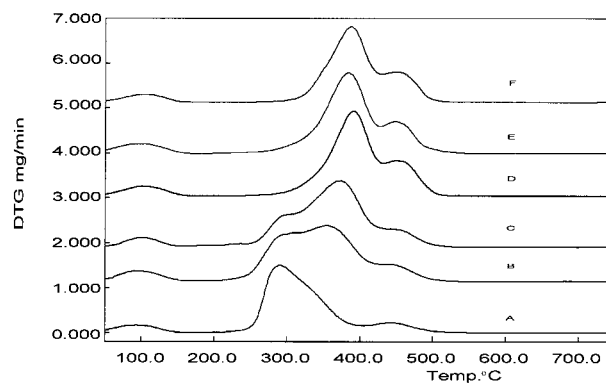


**Figure 9** Temperature dependence of  $\tan \delta$  for wet PVA gels prepared by changing the concentration of HCl. The concentration of HCl: (A) 0 mol/L, (B)  $7.0 \times 10^{-3}$  mol/L, (C)  $1.0 \times 10^{-2}$  mol/L, (D)  $2.8 \times 10^{-2}$  mol/L, (E)  $1.1 \times 10^{-1}$  mol/L, (F)  $2.3 \times 10^{-1}$  mol/L. The gel films contained ca. 5 wt % of water. The concentration of glutaraldehyde was  $8.38 \times 10^{-3}$  mol/L. Hydrated gel films contained ca. 5 wt % of water. The measurements were conducted at a  $2^\circ\text{C}/\text{min}$  heating rate, 1-Hz frequency, and  $5\text{-}\mu\text{m}$  amplitude under nitrogen.



**Figure 10** Differential thermogravimetric (DTG) thermograms of PVA gels prepared by changing the concentration of glutaraldehyde. The concentration of glutaraldehyde: A 0 mol/L, B  $6.3 \times 10^{-4}$  mol/L, C  $2.5 \times 10^{-3}$  mol/L, D  $5.0 \times 10^{-3}$  mol/L, E  $8.4 \times 10^{-3}$  mol/L, F  $1.7 \times 10^{-2}$  mol/L, G  $3.4 \times 10^{-2}$  mol/L. The concentration of HCl was  $2.25 \times 10^{-1}$  mol/L. The measurements were conducted at a  $20^\circ\text{C}/\text{min}$  heating rate under nitrogen.

hydrogen bonding between the oxydrils and water, and this decreased the crystallinity of PVA. The temperature difference between the wet and dry PVA gels became smaller with increasing crosslink density. The glass transition temperature difference between the dry and wet PVA gels, prepared with a GA concentration of  $1.7 \times 10^{-2}$  mol/L, was less than  $5^\circ\text{C}$ . This reveals that water, which is an effective plasticizer for PVA, because it appreciably lowers its glass transition temper-



**Figure 11** Differential thermogravimetric analysis (DTG) thermograms of PVA gels prepared by changing the concentration of HCl. The concentration of HCl: A 0 mol/L, B  $7.0 \times 10^{-3}$  mol/L, C  $1.0 \times 10^{-2}$  mol/L, D  $2.8 \times 10^{-2}$  mol/L, E  $1.1 \times 10^{-1}$  mol/L, F  $2.3 \times 10^{-1}$  mol/L. The concentration of glutaraldehyde was  $8.38 \times 10^{-3}$  mol/L. The measurements were conducted at a  $20^\circ\text{C}/\text{min}$  heating rate under nitrogen.

**Table III Tensile Strength and Elongation of Wet and Dried PVA Gel for Various Glutaraldehyde Concentrations<sup>a</sup>**

Concentration of Glutaraldehyde (mol/L)	Wet PVA Gels		Dried PVA Gels	
	Tensile Strength (MPa)	Elongation (%)	Tensile Strength (MPa)	Elongation (%)
0	28.2	19.6	123.8	2.9
$6.3 \times 10^{-4}$	30.8	18.9	124.0	2.4
$2.5 \times 10^{-3}$	31.6	18.0	126.9	2.1
$5.0 \times 10^{-3}$	33.7	16.5	129.2	1.9
$8.4 \times 10^{-3}$	33.3	14.0	133.5	1.3
$1.7 \times 10^{-2}$	35.0	12.5	135.1	1.2

<sup>a</sup> Determined at an extension rate of 500 mm/min at room temperature. The films of wet PVA gel were conditioned in a 50% relative humidity atmosphere at room temperature for 48 h, while the films of dried PVA gel were dried in a vacuum oven at 100°C for 3 h. The concentration of HCl was  $2.3 \times 10^{-1}$  mol/L.

ature, is not equally effective for the PVA gels. This happened because, by increasing the crosslink density, the PVA gels remained with a diminishing number of hydroxyl groups and thus the water could affect, to a smaller and smaller extent, the mobility of the main chain of the polymer.

#### TGA Analysis

The thermal degradation of the PVA gels can be followed clearly from the derivative of the thermogravimetric (DTG) curves presented in Figures 10 and 11. Figure 10 presents the thermograms for various GA contents, and reveals that the thermal stability of the PVA was improved by crosslinking. The PVA gels degraded in two steps, while the pure PVA underwent a single degrada-

tion step. The weight loss in the low temperature range may correspond to the breaking of the grafted crosslinker, while the weight loss in the high temperature range to the degradation of the main chain.<sup>17</sup>

#### Mechanical Analysis

Tables III and IV provide the tensile strengths of the PVA gels for various GA and HCl concentrations, respectively. The tensile strength of the PVA gels increased with increasing GA and HCl concentrations, while their elongation decreased. The wet PVA gels containing c.a. 5 wt % water had lower tensile strengths than the dried ones, but higher elongations. This indicates that water plasticized very effectively the polymer and enhanced the mobility of the polymer backbone.

**Table IV Tensile Strength and Elongation of Wet PVA Gel and Dried PVA Gel for Various HCl Concentrations<sup>a</sup>**

Concentration of HCl (mol/L)	Wet PVA Gels		Dried PVA Gels	
	Tensile Strength (MPa)	Elongation (%)	Tensile Strength (MPa)	Elongation (%)
0	28.2	19.6	123.8	2.9
$7.0 \times 10^{-3}$	29.0	19.0	124.1	2.5
$1.0 \times 10^{-2}$	30.5	17.8	126.2	2.2
$2.8 \times 10^{-2}$	31.5	16.9	128.9	1.8
$1.1 \times 10^{-1}$	32.5	16.5	131.0	1.7
$2.3 \times 10^{-1}$	33.4	14.0	133.5	1.3

<sup>a</sup> Determined at an extension rate of 500 mm/min at room temperature. The films of wet PVA gel were conditioned in a 50% relative humidity atmosphere at room temperature for 48 h, while the films of dried PVA gel were dried in a vacuum oven at 100°C for 3 h. The concentration of glutaraldehyde was  $8.4 \times 10^{-3}$  mol/L.

## CONCLUSION

PVA gel films were prepared by chemical crosslinking with GA by employing HCl as a catalyst. The water uptake of the gel films indicated that the density of crosslinking increased with the concentrations of GA and HCl. Depressions of the melting and crystallization temperatures were observed with increasing the crosslink density. The decrease of the melting temperature and heat of fusion was caused by the decrease of the degree of crystallinity caused by the chemical modification of the hydroxyl groups of PVA by crosslinking and grafting by the crosslinker. The wet PVA had a lower glass transition temperature than the dry one, indicating that water is a plasticizing agent for PVA. The PVA gels exhibited lower glass transition temperatures than dry PVA, because of the strong attenuation of the inter- and intramolecular hydrogen bonding induced by crosslinking. For the wet PVA gels, the glass transition temperatures increased with increasing crosslink density, because the decrease of the glass transition temperature induced by the crosslinking is smaller than that induced by water. The PVA gel, which is more stable thermally than PVA, had two thermal degradation steps, implying that the PVA gels might contain both crosslinked and grafted molecules of the crosslinker. The tensile strength of PVA was increased by crosslinking, while their elongation decreased. The wet PVA gels had lower tensile strengths and higher elongations than the dried PVA gels.

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