The Elastic Property of Polyvinyl Alcohol Gel with Boric Acid as a Crosslinking Agent

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ABSTRACT: The elastomers of polyvinyl alcohol gel were made from the polyvinyl alcohol polymer, with boric acid added as a crosslinking agent, in the mixed solvent of dimethyl sulfoxide and water. From the experimental results, the viscosity of polyvinyl alcohol solution is found to increase not only with an increment of boric acid content, but also with the temperature in the range of 70°C ~ 100°C, although the viscosity is decreased in the range of 30°C ~ 70°C. Moreover, the molecular mass between junctions of polyvinyl alcohol gel is calculated from the rubber elastic theory and found to be decreased with the increment of boric acid content. We also evaluated the values of Young's modulus of polyvinyl alcohol gel, E, E^*, and the elastic parameters C_1 and C_2 of the Mooney-Rivlin equation, according to Hook's law and theory of rubber elasticity. Based on these, the polyvinyl alcohol gel behaves as a good rubberlike elastic property. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3046–3052, 1999

Key words: polyvinyl alcohol; boric acid; Mooney–Rivlin; chemical gel

INTRODUCTION

Polyvinyl alcohol (PVA) polymer has been used for more than 40 years because of its unique chemical and physical properties.[1] These properties come from its hydroxyl groups. The hydrogen bonding between hydroxyl groups play an important role in the property of polyvinyl alcohol—for example, high water solubility, a wide range of crystallinity, and high crystal modulus.[2] Moreover, the polyvinyl alcohol polymer can react with borate ions to form a polymeric gel. The mechanism of PVA–borate crosslink is believed to be a didiol (two diol) complex, in which two diol units of polyvinyl alcohol chain with one borate ion to form a crosslink.[3,4] Shibayama et al. measured the correlation length of the gels from the Zimm's plot.[5] They found that the correlation length remained constant in the gel state and decreased

with an increase of temperature in the sol state. Robb et al. reported that the maximum lifetime in the PVA–borate gels was about 0.3 s and independent of the polymer, borate content, and the degree of hydrolysis of the polymer.[6] Also, the formation of complexes between polyvinyl alcohol and borate ion has a significant effect on the viscosity behavior of polyvinyl alcohol aqueous. Maerker et al. demonstrated that the solution of polyvinyl alcohol with sodium borate exhibited maximum viscosity followed by shear thinning as shear rate was increased; also occurring was significant hysteresis phenomenon at higher viscosity.[7] Kurokawa and Ochiai et al. studied the viscosity behavior of polyvinyl alcohol aqueous with borate. They found that the viscosity was dependent on the boric acid, PVA, and NaOH content.[8,9] Shibayama et al. also found that the relationship of the intrinsic viscosity ratio of polyvinyl alcohol aqueous with borate ion and the equilibrium swelling ratio of gels were in good proportional accordance.[5] However, most of these studies are concentrated on the behavior of polyvinyl alcohol

Table I   The Characteristics of Used Polyvinyl Alcohol Polymers

Sample Code	Degree of Polymerization	Viscosity (cps)	Hydrolysis (mol %)
BF-17	1,700	25–30	98.5–99.2
BF-20	2,000	35–43	98.5–99.4
BF-24	2,400	58–68	98.5–99.2
BF-26	2,600	75–86	98.5–99.2

aqueous gel but not on the polyvinyl alcohol gel from the mixed solvent.

Polyvinyl alcohol gel, which is prepared from the mixed solvent of dimethyl sulfoxide (DMSO) and water, has attracted a lot of attention from polymer scientists[3–8] because of its good transparency, adhesive, and water-holding properties.[9,10] Some papers have reported that the mechanical properties of polyvinyl alcohol gel from the mixed solvent (dimethyl sulfoxide and water) are the same as those of polyvinyl alcohol gel from a repeated frozen aqueous solution of polyvinyl alcohol.[7,8,11,12] But the time for preparing the polyvinyl alcohol aqueous gel is longer than that of polyvinyl alcohol gel from the mixed solvent.[3] In other words, polyvinyl alcohol gel is much easier to prepare from the mixed solvent. However, if polyvinyl alcohol gel is used for medical applications, dimethyl sulfoxide is required to be extracted from the gel because of its toxicity.[3] In our previous article, the thermal and rheological properties of polyvinyl alcohol gel in the mixed solvent of dimethyl sulfoxide and water with boric acid as a crosslinking agent were studied.[26] It was found that the maximum value of gel-to-sol transition temperature, endothermic enthalpy, and dynamic modulus happened at the volumetric ratio of 6 : 4 in the mixed solvent of dimethyl sulfoxide and water. In this paper we focus on the viscosity behavior of polyvinyl alcohol in the mixed solvent, its formation of gel, and the analysis of the elastic properties of polyvinyl alcohol gel.

EXPERIMENTAL

Materials

Polyvinyl alcohol polymer was supplied from Chang Chun Petrochemical Co. Ltd. (Taiwan). Table I shows the characteristics of polyvinyl alcohol polymer.

The polyvinyl alcohol gel was prepared from the polyvinyl alcohol polymer heated in the mixed solvent of dimethyl sulfoxide and water with boric acid as a crosslinking agent. After polyvinyl alcohol polymer was fully dissolved, it was then cooled to room temperature to form a gel.

Extension Stress–Strain Measurement

Extension stress–strain measurement was carried out by the Instron T-9101 type from Hon-Da Instruments Corp. (Taiwan). Samples of polyvinyl alcohol gel (approximate dimensions 50 mm × 50 mm × 2 mm) were continuously extended at a low constant cross-head speed of 50 mm/min up to a elongation of about 200%. The increasing value of tensile forces was recorded on the moving chart. The measurements were carried out at room temperature.

Shear Viscosity Measurement

The determination of the viscosity of the polyvinyl alcohol solution was done using a Brookfield LVD-II viscometer. The spindle used was S31. The value of viscosity equals to the number on the viscometer × transfer factor.

RESULTS AND DISCUSSION

The Formation of Polyvinyl Alcohol Gel

Figure 1 shows the relationship of viscosity of the polyvinyl alcohol solution with different boric acid contents. It was found that viscosity increased with an increase in boric acid content. This is
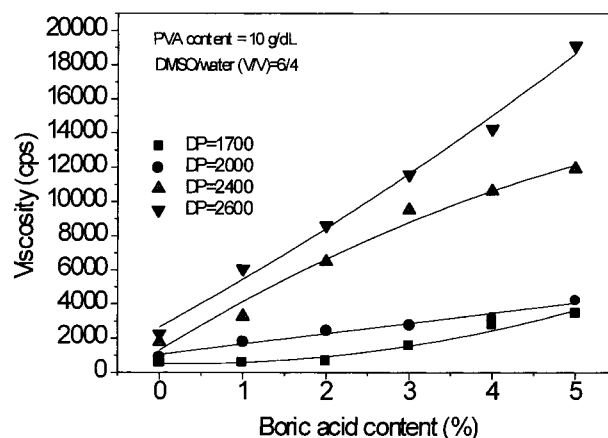

Figure 1   Relationship between the viscosity of polyvinyl alcohol solution and boric acid content.

because the degree of crosslinking is enhanced as the boric acid content is increased, leading to a higher viscosity. Figure 2 also shows the relationship of the viscosity of the polyvinyl alcohol solution to different temperatures. It was shown that the viscosity of the polyvinyl alcohol solution decreases with an increase in temperature, but it turns upward after reaching 70°C (in the range of 70°C ~ 100°C). From that, it indicates that the interaction of polyvinyl alcohol polymer with boric acid is a chemical crosslinking mechanism, and the effect of crosslinking to viscosity is manifested much more compared to that of temperature, at temperatures above 70°C. Besides, the mechanism of crosslinking of boric acid to polyvinyl alcohol was proposed by Shibayama et al. with their [11]B n. m. r. method.[2] It involved of the borate ion-aided crosslinking among polyvinyl alcohol molecules and the hydrogen bonding between the didiol complex and polyvinyl alcohol chains.[2]

After polyvinyl alcohol polymer was fully dissolved in the mixed solvent of dimethyl sulfoxide and water, the solution was left standing at room temperature. It was found that the viscosity of the polyvinyl alcohol solution increased progressively with time, and finally the fluidity disappeared completely. As shown in Figure 3, the increase of viscosity of the polyvinyl alcohol solution with time can be expressed as[15]

$$\eta_t = \eta_0(1 + \alpha t) \qquad (1)$$

where η_0 is the initial viscosity of the solution, η_t is the viscosity at a time t, and α is a constant.
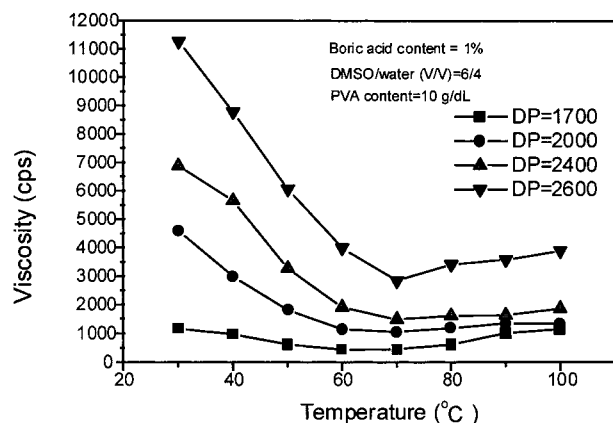

Figure 2 Relationship between the viscosity of polyvinyl alcohol solution and temperature.
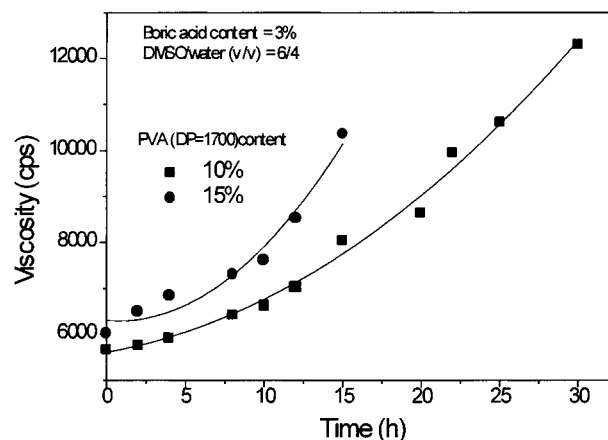

Figure 3 The viscosity of polyvinyl alcohol solution as a function of time.

The constant α is dependent on the concentration C as

$$\alpha = KC^2 \qquad (2)$$

where K is a coefficient. Since the viscosity of the polyvinyl alcohol solution increases with standing time, the viscosity will increase to some extent, which cannot be measured by static measurement due to its high viscosity (for example, 10% PVA standing after 30 h). Therefore, the solution of PVA will form a gel after a long standing period.

The Degree of Crosslinking in Polyvinyl Alcohol Gel

If the polyvinyl alcohol gel is assumed to behave as a elastomer and also if the Poisson's ratio is nearly 0.5, the modulus, E, can be expressed as the following equation[4]

$$E = 3\nu RT/V = 3\rho RT/Mc \qquad (3)$$

where ν is the number of moles of chains in network; V, the volume of the polyvinyl alcohol gel; ρ, the density of the polyvinyl alcohol gel; Mc, the molecular mass between junctions; R, the gas constant; and T, the absolute temperature. The density of the polyvinyl alcohol gels, ρ, could be determined by the floating method in xylene solvent and shown by the following equation
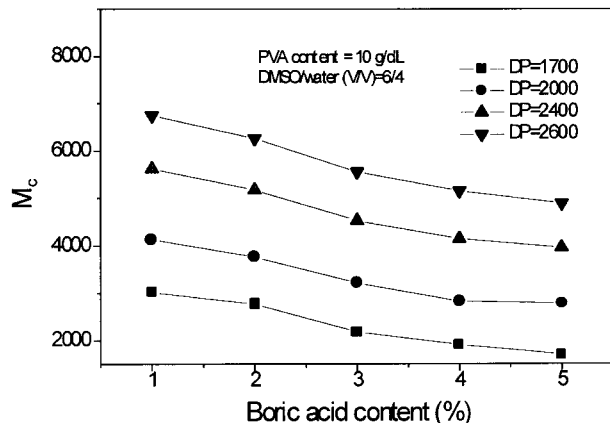
$$\rho = Wa/[(Wa - Ws)/\rho_s] \qquad (4)$$

Figure 4 Dependence of the molecular mass between junctions on the boric acid content.

Figure 6 Stress–strain curve dependence in terms of $\sigma\lambda$ versus ε for polyvinyl alcohol gel ($DP = 1,700$).

where Wa is the weight of the polyvinyl alcohol gel in air; Ws, the weight of polyvinyl alcohol gel in xylene solvent; ρ_s, the density of xylene solvent ($\rho_s = 0.861$ g/cm^3). Figure 4 shows the relationship of the molecular weight, Mc, between polymer chains with different boric acid contents. The values of Mc were calculated from (eq) 3. It was found that the values of Mc decreased with an increase in boric acid content. Thus, it was concluded that as the degree of crosslinking increased with the increase in boric acid content, the molecular mass between junctions decreased.

Analysis of Stress–Strain Behavior of Polyvinyl Alcohol Gel

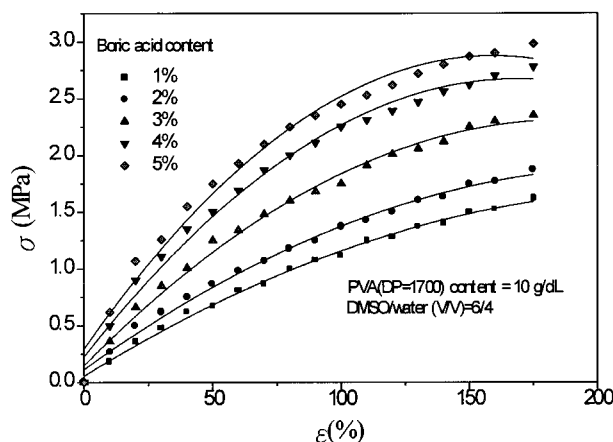Figure 5 shows the stress (σ)–strain (ε) curves of polyvinyl alcohol gel with various boric acid con-

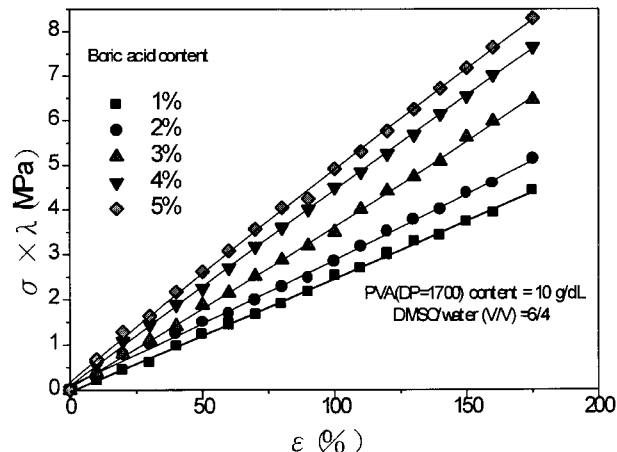**Figure 5** Stress–strain curve of polyvinyl alcohol gel ($DP = 1,700$).

tents. The stress–strain plots are not linear. In order to obtain the Young's moduli (E), the $\sigma\lambda$ was plotted versus ε, where λ is the principal extension ratio, which is equal to $\varepsilon + 1$. As seen in Figure 6, it exhibits a good linear relationship between $\sigma\lambda$ and ε. The Young's moduli (E) are therefore calculated from the slopes of these plots (as seen in Table II). It was found that the Young's moduli (E) increased with an increase in the boric acid content. This indicates that the modulus of thermoreversible gel, which is contributed to by a number of crosslinking junction zones, increased with an increase in boric acid content, if the conformations of flexible chains are assumed to be the same.

In order to describe the extension behavior of polyvinyl alcohol gel, based on the theory of rubber elasticity, the equation of rubber elasticity is expressed as[16]

$$\sigma = RT(\lambda - \lambda^{-2})V_e/V_f \qquad (5)$$

where R is the gas constant, and T and V_e/V_f are the absolute temperature and factor of elasticity, respectively. If the item of RTV_e/V_f equals to G^*, then eq. (5) is rewritten as

$$\sigma = G^* \times (\lambda - \lambda^{-2}) \qquad (6)$$

where G^* is the shear modulus. According to eq. (6), if the $\sigma/(\lambda - \lambda^{-2})$ is plotted versus λ, a straight line will be obtained. Nevertheless, the actual curve begins with a rapid nonlinear decrease in the plot of $\sigma/(\lambda - \lambda^{-2})$ versus λ, as λ increases. However, the curves will end up linear after λ

Table II   The E (MPa) and E^* (MPa) Values of Polyvinyl Alcohol Gel with Different Boric Acid Contents

| Sample Code | Boric Acid Content (%)[a] | | | | | | | | | |
| | 1 | | 2 | | 3 | | 4 | | 5 | |
	E	E^*	E	E^*	E	E^*	E	E^*	E	E^*
BF-17	2.72	2.62	2.96	2.83	3.76	3.68	4.30	4.21	4.82	4.70
BF-20	2.83	2.73	3.07	2.95	3.86	3.80	4.45	4.35	4.92	4.81
BF-24	2.92	2.82	3.19	3.08	4.01	3.91	4.57	4.44	5.03	4.90
BF-26	3.02	2.91	3.32	3.21	4.14	4.13	4.68	4.57	5.14	5.02

[a] PVA content = 10 g/dL, DMSO/water (v/v) = 6/4.

goes beyond 1.5, as seen in Figure 7. The shear moduli (G^*) are therefore obtained from the linear part of these plots after extrapolating λ to 1. The E^* values are also obtained, using the expression of $E^* = 3G^*$.[16] As seen in Table II, the E^* values are in good agreement with the values of E, since the former is a few percent smaller than the latter. This indicates that polyvinyl alcohol gels have a rubberlike elastic property.

Mooney–Rivlin plots are also used to calculate the values of the elastic parameters C_1 and C_2 from the extension stress–strain measurements. The Mooney-Rivlin equation is expressed as[17]

$$\sigma = (C_1 + C_2\lambda^{-1})(\lambda - \lambda^{-2}) \quad (7)$$

From Figure 8 it is found that the Mooney–Rivlin plots of polyvinyl alcohol gels with varying boric acid content are straight lines as λ^{-1} increases. Here, it is noticeable that the elasticity of polyvinyl alcohol gel, which comes from the micro-Brownian motion of long-chain molecules between the crosslinking junctions, is formed not only by primary chemical bonds (covalent bonds), but also by secondary bonds such as hydrogen bonds.[2] The C_1 is therefore evaluated from Figure 8 at the intercept point of the Y axis, and C_2 is calculated from the slope of these plots. As listed in Table III, both C_1 and C_2 increase with an increase in the boric acid content. Eqs. (6) and (7) may be combined to form the well-known expression of $G^* = C_1 + C_2$, hence $E^* = 3(C_1 + C_2)$. From Table III it is found that the values of $3(C_1 + C_2)$ are about 30% larger than that of E values. From that, it indicates that the elastic property of PVA gel can be correlated to the Mooney–Rivlin plot. Noticeably, the ratio C_2/C_1 is often taken as
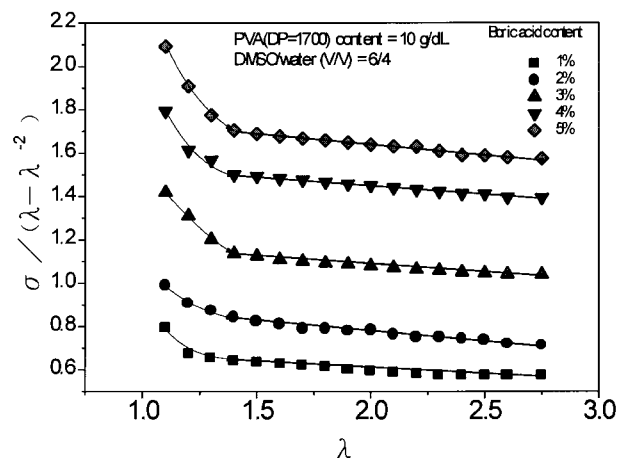

Figure 7   Stress–strain curve dependence in terms of $\sigma/(\lambda - \lambda^{-2})$ versus λ for polyvinyl alcohol gel ($DP = 1,700$).
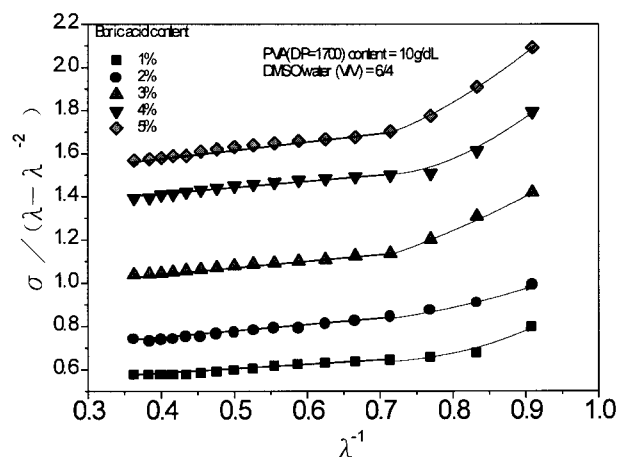

Figure 8   Mooney–Rivlin plot of polyvinyl alcohol gel ($DP = 1,700$).

Table III Mooney–Rivlin Elastic Parameters of Polyvinyl Alcohol Gel with Different Boric Acid Contents

Sample Code	Boric Acid Content (%)[a]								
	1			2			3		
	C_1	C_2	$3 (C_1 + C_2)$	C_1	C_2	$3 (C_1 + C_2)$	C_1	C_2	$3 (C_1 + C_2)$
BF-17	0.57	0.89	4.38	0.71	1.08	5.37	1.01	1.15	6.48
BF-20	0.67	1.05	5.16	0.83	1.27	6.30	1.12	1.31	7.29
BF-24	0.78	1.23	6.03	0.92	1.42	7.02	1.24	1.49	8.19
BF-26	0.89	1.38	6.81	1.04	1.59	7.89	1.32	1.62	8.82

Sample Code	Boric Acid Content (%)[a]					
	4			5		
	C_1	C_2	$3 (C_1 + C_2)$	C_1	C_2	$3 (C_1 + C_2)$
BF-17	1.27	1.30	7.50	1.35	1.39	8.28
BF-20	1.38	1.45	8.49	1.44	1.48	8.76
BF-24	1.46	1.54	9.00	1.53	1.59	9.36
BF-26	1.55	1.66	9.63	1.65	1.70	10.05

[a] PVA content = 10 g/dL, DMSO/water (v/v) = 6/4.

an important parameter not only to characterize the departure of elastomer from ideal elasticity,[13,14] but also to measure the extent of intermolecular interaction.

CONCLUSIONS

With boric acid as a crosslinking agent, the viscosity of polyvinyl alcohol solution, degree of crosslinking, and the elastic properties of polyvinyl alcohol gel were studied. It was found that the viscosity of polyvinyl alcohol increased not only with an increase of boric acid content but also with increasing temperature, in the range of 70°C $\sim$ 100°C. Also, the degree of crosslinking in polyvinyl alcohol increased with the increase of boric acid content. Thus, it led to an increase in the elastic moduli of the gel. From the stress–strain behavior of polyvinyl alcohol gel, E^* value was in good agreement with the E value. So, the polyvinyl alcohol gel has a good rubberlike elastic property. Moreover, the elastic property of polyvinyl alcohol gel can also be correlated to the Mooney–Rivlin plot. The values of $3 (C_1 + C_2)$ are about 30% larger than those of E or E^*.

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