

Gelation of Poly(vinyl alcohol)/Phenol/Water Solutions and Gel Spinning

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SYNOPSIS

The light transmittance of the gels of poly(vinyl alcohol) (PVA)/phenol/water solutions was examined for the entire range of phenol/water content. Excellent transparency was found for the gels with phenol contents of 70–95 vol %. In full consideration of the results for the transparency and melting temperature of the gels and the viscosity and gelation ability of solutions, the PVA solutions of 75 vol % phenol content were selected for the gel spinning. The maximum dynamic moduli of drawn filaments at 25°C (room temperature) were 42 GPa (15×) for atactic PVA and 45 GPa (14×) for syndiotacticity-rich PVA. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The solution of 85% phenol and 15% water is a better solvent for atactic poly(vinyl alcohol) (*a*-PVA) than pure water.¹ The syndiotacticity rich PVA (*s*-PVA) solutions of 85% phenol and 15% water form gels.² The gels are transparent differing from *s*-PVA hydrogels that are turbid. Transparent gels are obtained from either *a*-PVA³ or *s*-PVA^{4,5} solutions of 80% dimethyl sulfoxide (DMSO) and 20% water. The transparent *a*-PVA dry gels are drawn to a high draw ratio and the drawn fibers have high modulus (about 60 GPa).⁶ The high draw ability is considered to be due to a few weak junction points in the transparent gels. The dry gels are suitable to gel spinning. The preparation of ultrahigh modulus polyethylene (PE) fibers and films from the ultradrawing of dried gels, produced by gelation from a semidilute solution, has been extensively studied in recent years.^{7–11} Matsuo and Sawatari produced ultrahigh drawn PE with a Young's modulus at 20°C of 216 GPa.¹¹

In this article the properties of PVA solutions, that is, the viscosity, gelation ability, and the structure of gels in the range of phenol contents of 0–95

vol %, were examined and the gel spin ability for the PVA solutions and the draw ability of dried gels were ascertained.

EXPERIMENTAL

Samples

Two *s*-PVAs were prepared by ammonolysis with 2,2'-diaminodiethylamine of poly(vinyl trifluoroacetate) obtained by bulk polymerization of vinyl trifluoroacetate at 60°C using benzoyl peroxide and at 30°C using 2,2'-azobis(2,4-dimethyl valeronitrile) as initiators. The degrees of polymerization (DP) are 3220 and 5000, respectively. In addition, two *a*-PVAs were used. One *a*-PVA is commercial PVA with DP 1700 and the other *a*-PVA has higher molecular weight (DP 17,900), supplied from Kuraray Co. Ltd.

Gelation Ability of Solutions

The 3 g/dL solutions of different phenol/water mixtures were prepared by dissolving the *s*-PVA with DP 3220 in the mixtures in sealed test tubes at about 130°C. The solutions were stored for 24 h at 0–60°C to examine the gelation ability.

The 1.25–5 g/dL solutions of the 85 vol % phenol,

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15 vol % water mixture were prepared by dissolving the α -PVA with DP 17,900 in the mixture in sealed test tubes at about 130°C. The solutions were stored at 0–30°C and the gelation time t_G of the solutions was determined.

Melting Temperatures of Gels

The solutions of different polymer concentrations were prepared by dissolving the α -PVA with DP 17,900 and the two s -PVAs in 85 vol % phenol/15 vol % water mixture in sealed test tubes at about 130°C. The solutions were stored for 24 h at the temperatures of 0–40°C. The apparent melting temperature of the gel was determined according to the Eldridge–Ferry's method¹² by placing the gel upside down and warming it at a rate of about 0.5°C/min.

Viscosity of Solution

The 0.3 g/dL solutions were prepared by dissolving the α -PVA with DP 1700 in the phenol/water mixture in sealed test tubes at about 130°C. The viscosities of the solutions and solvents were measured at 30°C using an Ostwald viscometer, with no correction for kinetic energy or shear rate.

Gel Spinning

The α -PVA with DP 1700 and the s -PVA with DP 3220 were dissolved in the 75 vol % phenol, 25 vol % water mixture in sealed test tubes at about 130°C. The spinning apparatus shown in the previous article¹³ was used for the gel spinning. The solutions (about 90°C) were extruded into a methanol bath of 0°C, the gel filaments were kept there for 2–3 h, then for 24 h in methanol at room temperature to extract phenol/water followed by drying.

Drawing Method

1. The filaments of α -PVA dry gel were drawn in an oven at 200°C and annealed at 200°C for 10 min.
2. The wet filaments of s -PVA gel taken out of the methanol bath were drawn to two times the original length and dried. The dry filaments were drawn in an oven at 200°C and annealed at 200°C for 10 min in the same oven fixing both ends.

Static and Dynamic Tensile Tests

Static tensile modulus and strength were measured using a Shinko Model TOM/5 tensile tester at a

crosshead speed of 10 mm/min and an original sample length of 20 mm at the temperature of 25°C and under the relative humidity of 65%.

Dynamic tensile modulus was measured using a TMA 4000 apparatus from MAC Science Co. Ltd. The storage modulus and $\tan \delta$ were measured from room temperature to 220–260°C. Forced longitudinal vibration (sine wave) was 0.25 Hz.

Birefringence

The birefringence of drawn fibers was estimated from the retardation determined using a Wetzlar Berek compensator by an Olympus POM polarizing microscope.

RESULTS AND DISCUSSION

Gelation Ability

Figure 1 shows the phase diagram of phenol/water mixtures and the transparency of gels obtained by chilling the 3 g/dL s -PVA solutions. The shaded portion in the figure is the region of phase separation, which is well-known for the phenol/water system.¹⁴ PVA dissolved homogeneously in phenol/water mixtures of all compositions at about 130°C. When 3 g/dL s -PVA solutions of different phenol/water mixtures were chilled at 0°C for 24 h, the

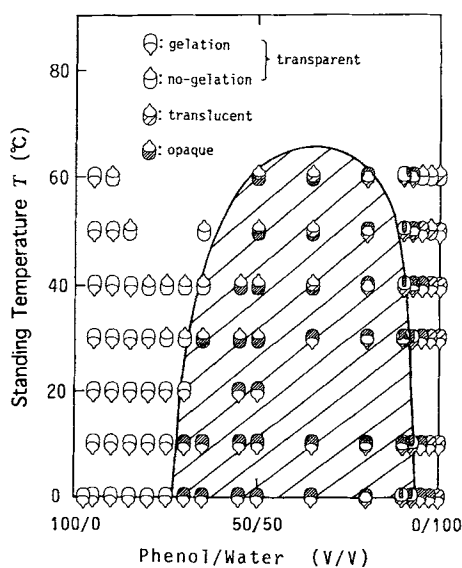


Figure 1 Phase diagram of phenol/water mixture, the gelation and transparency of gels after standing the 3 g/dL s -PVA (DP 3220) solution for 24 h at 0–60°C. The shaded portion in the figure is the region of phase separation for the phenol/water mixture.¹⁴

solutions of all compositions gelled. In the range of the water content of 80–92.5 vol %, homogeneous gels were not obtained because remarkable syneresis occurred. In the range of the water content of 2.5–25 vol %, transparent gels were obtained but slight syneresis occurred for the gel with the phenol content of 95–97.5 vol %. In the other range, translucent or opaque and apparent homogeneous gels were obtained. The transparent 3 g/dL *s*-PVA solutions with phenol contents of 7.5, 10, 20, 35, and 50 vol % changed to opaque drastically at 70, 83, 88, 79, and 63°C during slow cooling, respectively. Although the gels with the phenol content of 70 vol % were opaque at 0 and 10°C (see Fig. 1), the opaque gels changed to transparent by standing at room temperature. Bronsted-Volqvartz,¹⁵ Gee,¹⁶ and Scott¹⁷ have studied the miscibility of a poor solvent (1), a poor solvent (2), and a polymer, and found the presence of miscible and immiscible compositions. In the immiscible composition the phase separation to the polymer solution and solvent mixture occurs. The mixture of phenol content of 75 vol % is a better solvent for PVA than pure phenol and water. Thus in the mixtures other than the mixture of the phenol content of 75 vol %, phase separation is considered to occur. The opaque or syneresis gels obtained from the mixtures of the phenol contents of 7.75–65 vol % are formed by the lower solvent power.

Figure 2 shows the relations between the gelation time and the chilling temperature for the 85 vol % phenol solution of *a*-PVA with DP 17,900. *a*-PVA solutions of 5 g/dL gelled after the very short time of 10–20 s at 0–30°C and the activation energy of gelation was very low. *a*-PVA solutions of 1.25 g/dL gelled after 30 min at 5°C and 4 min at 0°C, respectively. In the case of solutions with lower

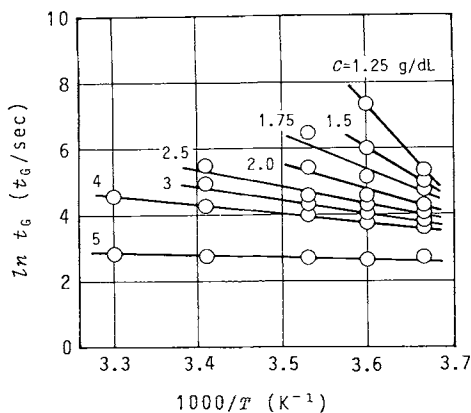


Figure 2 Relations between the gelation time and the chilling temperature for *a*-PVA (DP 17,900) solution with phenol content of 85 vol %.

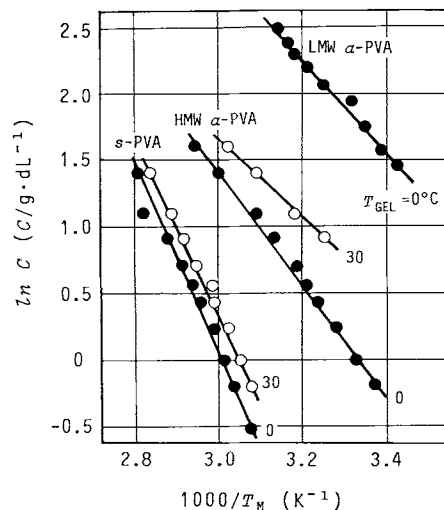


Figure 3 Eldridge-Ferry's¹² plots for LMW *a*-PVA (DP 1300),² HMW *a*-PVA (DP 17,900), and *s*-PVA (DP 5000) gels with phenol content of 85 vol %.

polymer concentration, the remarkable temperature dependency on the gelation time and the very high activation energy were found.

Melting Temperature of Gels

Figure 3 shows the relations between the polymer concentration (C) and the melting temperature (T_M) of low molecular weight (LMW) *a*-PVA (DP 1300),² high MW (HMW) *a*-PVA (DP 17,900), and *s*-PVA (DP 5000) gels obtained by chilling the solutions with the phenol content of 85 vol % at 0 and 30°C. At the same polymer concentration, the melting temperature of *a*-PVA gels obtained by chilling at 0°C increased with an increase in the molecular weight and that of *s*-PVA was higher than those of two *a*-PVAs. Linear relationships are found between $\ln C$ and $1/T_M$. The heat of fusion of a crosslink, ΔH , is estimated from the slopes of linear parts. ΔH for LMW *a*-PVA, HMW *a*-PVA, and *s*-PVA gels obtained by chilling at 0°C was 28,² 35, and 60 kJ/mol, respectively. ΔH for *a*-PVA and *s*-PVA gels obtained by chilling at 30°C was 15 and 56 kJ/mol, respectively. The ΔH for *s*-PVA are higher than those for *a*-PVA, suggesting larger crosslinks in *s*-PVA gels. ΔH for *a*-PVA hydrogels with phenol, also increased with an increase in molecular weight.

Figure 4 shows the relations between the melting temperature of the gels and the phenol (or water) content for 3 g/dL gels of *s*-PVA with DP 3220. In the range of high content of phenol, T_M decreased with a decrease in phenol content and was about 40°C at the phenol content of 75 vol %. If the weak,

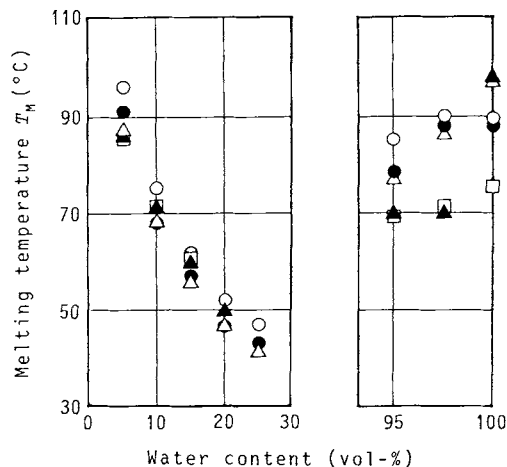


Figure 4 Relations between the melting point and the water content for 3 g/dL *s*-PVA (DP 3220) gels obtained by chilling at 0–40°C for 24 h. (○) 0°C, (●) 10°C, (△) 20°C, (▲) 30°C, and (□) 40°C.

but stable gels are obtained at the phenol content of 75 vol %, the gel spinning is considered possible.

Viscosity of Solutions

To select the optimum conditions of gel spinning, the viscosity of solutions was measured. The relative viscosity decreased steeply with a decrease in phenol content in the range of high phenol content but increased slightly in the range of low phenol content (Fig. 5). The viscosity of solution of the phenol content of 75 vol % is much higher than that of the

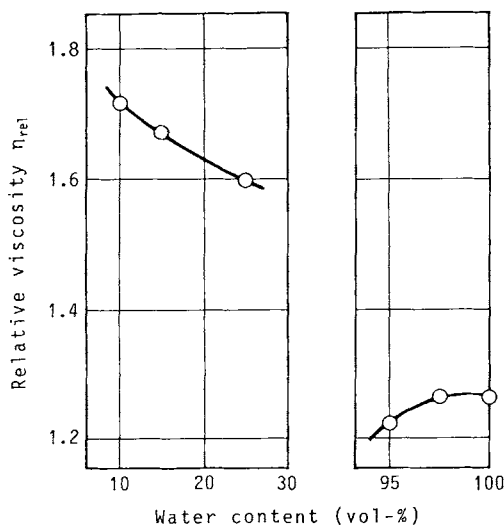


Figure 5 Relations between the relative viscosity and the water content for 0.3 g/dL *a*-PVA (DP 1700) solutions at 30°C.

aqueous solution. Therefore, the former solution is considered to be unfavorable. However, in full consideration of the results for the transparency and melting temperature of the gel, the solutions of the phenol content of 75 vol % was selected for the gel spinning in this study.

Gel Spinning and Physical Properties

As described above, the solvent mixture of 75 vol % phenol/25 vol % water system was selected for PVA gel spinning. The gel spinning was performed using the solutions of 5–10 g/dL for *a*-PVA with DP 1700 and 3–5 g/dL for *s*-PVA with DP 3220. The homogeneous filaments were obtained from 7 g/dL *a*-PVA and 4 g/dL *s*-PVA solutions. After standing in methanol for 24 h followed by drying, the filaments smelled faintly of phenol. Because the dry filaments of *s*-PVA were extremely brittle, the drawing was impossible. Therefore, the wet filaments of *s*-PVA gels taken out of methanol bath were drawn to two times the original length and dried. The maximum draw ratio of *a*-PVA filament was 19 times the original length and the total maximum draw ratio of *s*-PVA filament was 16 times. Figure 6 shows the storage modulus and $\tan \delta$ for the drawn *a*-PVA filament. The maximum dynamic moduli of drawn filaments at 25°C (room temperature) were 42 GPa (15×) for *a*-PVA and 45 GPa (14×) for *s*-PVA, respectively. The crystallinity of the drawn filaments was 45–50%. For the drawn *a*-PVA filaments, the static tensile modulus and strength were 28.5 GPa (19×) and 1.3 GPa (17×), respectively. The birefringence of drawn filament (19×) was 0.047. Although the draw ratio of the *a*-PVA filaments used for the measurement of static tensile modulus is higher than that of the dynamic

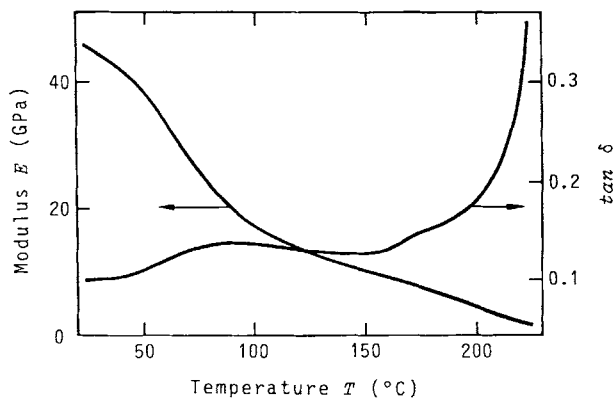


Figure 6 Storage modulus and $\tan \delta$ of a drawn *a*-PVA (DP 1700) filament (15×) as a function of temperature (spinning conditions: 7 g/dL, phenol content 75 vol %).

modulus, the former modulus is lower than the latter one. This is due to the generation of a microvoid by unreasonable drawing. Although the drawn filament had high molecular orientation, the mechanical properties were insufficient.

CONCLUSIONS

Gel spinning was performed using the PVA solutions (phenol/water 75/25) so that transparent gels and homogeneous filaments were obtained. The maximum draw ratio and maximum modulus of PVA filaments were 19 times (*a*-PVA) and 45 GPa at 205°C (14×, *s*-PVA), respectively, and lower than those for PE filaments obtained by gel spinning.

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REFERENCES

1. M. Matsumoto and K. Imai, *J. Polymer Sci.*, **24**, 125 (1957).
2. S. Matsuzawa, K. Yamaura, and H. Kobayashi, *Colloid Polym. Sci.*, **259**, 1147 (1981).
3. W.-I. Cha, S.-H. Hyon, and Y. Ikada, *Makromol. Chem.*, **193**, 1913 (1992).
4. K. Yamaura, M. Hamaguchi, N. Rokudai, S. Tamura, and S. Matsuzawa, *Sen-i Gakkaishi*, **38**, T-381 (1982) (in English).
5. K. Yamaura, M. Itoh, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **37**, 2709 (1989).
6. W.-I. Cha, S.-H. Hyon, and Y. Ikada, *J. Polym. Sci., Polym. Phys. Ed.*, **32**, 297 (1994).
7. P. Smith and P. J. Lemstra, *J. Mater. Sci.*, **15**, 505 (1980).
8. P. Smith, P. J. Lemstra, J. P. L. Pippert, and A. M. Kiel, *Colloid Polym. Sci.*, **258**, 1070 (1980).
9. P. Smith, P. J. Lemstra, and H. C. Booij, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 877 (1981).
10. C. Sawatari and M. Matsuo, *Colloid Polym. Sci.*, **263**, 783 (1985).
11. M. Matsuo and C. Sawatari, *Macromolecules*, **19**, 2036 (1986).
12. J. E. Eldridge and J. D. Ferry, *J. Phys. Chem.*, **58**, 992 (1954).
13. S. Matsuzawa, L. Sun, and K. Yamaura, *Kobunshi Ronbunshu*, **48**, 691 (1991).
14. J. Timmermans, *Z. Physik. Chem.*, **58**, 129 (1907).
15. J. N. Bronsted and K. Volqvartz, *Trans. Faraday Soc.*, **36**, 619 (1940).
16. G. Gee, *Trans. Faraday Soc.*, **40**, 468 (1944).
17. R. L. Scott, *J. Chem. Phys.*, **17**, 268 (1949).

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