Gelation of Poly(vinyl alcohol)/Water/Dimethylformamide Solutions and Properties of Dried Films

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ABSTRACT: The properties of solutions for syndiotacticity-rich poly(vinyl alcohol) (*s*-PVA)/dimethylformamide (DMF)/water systems, the gelation of the *s*-PVA solutions, and the properties of the dried *s*-PVA gel films were examined. From the results of the dissolution temperature of the polymer, the gelation temperature of the solutions, the melting temperature of the gels, and the compressive modulus of the gels, the solubility of the polymer was the highest at DMF contents of 10–20 vol %. The maximum dynamic tensile modulus of the drawn (×18) films obtained from the dried gel films with a DMF content of 10 vol % was 54.9 GPa at 20°C. The orientation of the polymer chains in the amorphous regions was higher than that in the crystalline regions. The orientation of the polymer chains in the amorphous regions for the drawn films with a DMF content of 10 vol % was higher than that for the drawn films with a DMF content of 60 vol %. The orientation of the polymer chains in the amorphous regions was considered to play an important role in the properties of high strength and high modulus. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1661–1667, 1998

Key words: poly(vinyl alcohol); dimethylformamide/water system; gelation; dry film; drawing; mechanical properties

INTRODUCTION

Poly(vinyl alcohol) (PVA) is notably soluble in viscous solvents like dimethyl sulfoxide (DMSO) in comparison with water, but water/DMSO mixtures are relatively poor solvents in the range from 30 to 60 vol % of water by volume.[1–3] The thermal and viscoelastic properties of gels for the PVA/water/DMSO system change extensively with the DMSO content.[3–5] Water/dimethylformamide (DMF) mixtures are known as solvents of PVA.[6–7] However, for PVA/water/DMF systems, there are still many indistinct points to solve. Recently, numerous investigators have made efforts to prepare PVA fibers with a high strength and high modulus. Hyon et al.[8,9] reported that the gel spinning of a solution of water/DMSO of 20/80 (v/v) was proved effective to obtain high-modulus PVA fibers.

In this article, the relationships between the solution properties of PVA/water/DMF systems, the gelation, or the thermal properties of the gels and DMF content were examined. Moreover, the production of gel films from PVA/water/DMF mixtures was attempted and the properties of the films were examined.

EXPERIMENTAL

Samples

A syndiotacticity-rich PVA (*s*-PVA) derived from vinyl trifluoroacetate was used. The degree of polymerization and the content of the syndiotactic diad were 1630 and 54.0%, respectively. Dimethylformamide (DMF) of a special grade made by

Wako Chemical Co. Ltd. (Japan) was used without further distillation.

Solution Viscosity

s-PVA was dissolved into the DMF/water mixture in a sealed test tube at about 130°C. The flow time of the mixed solvents and 0.1 g/dL s-PVA solutions were measured in an Ostwald's viscometer at 30°C.

Dissolution, Clouding, and Gelation Temperatures

Fibrous s-PVA samples were heated in a DMF/water mixture at a rate of 0.5°C/min from about 80°C and the dissolution temperature was examined. After the determination of the dissolution temperature, the clouding and gelation temperatures were examined by gradual cooling at a rate of ca. 0.5°C/min.

Melting Temperature of the Gels

After dissolution, the solutions were quenched to 40 to -75°C (quenching temperature: T_Q) and allowed to stand for 30 min, 24 h, and 360 h. The melting temperature (T_M) of the gels was determined when the solutions were heated from T_Q (= 40 to 0°C) at a heating rate of 1°C/min. In the case of gels obtained by quenching to a temperature below 0°C (-10 to -75°C), heating was initiated from 0°C. The temperature at which a gel fell to the bottom of the glass tube after air entered inside it was regarded as the melting point.

Differential Scanning Calorimetry

After cooling the mixed solvents or s-PVA solutions to -110°C at a rate of -3 to -5°C/min and holding for 10 min at -110°C, differential scanning calorimetry (DSC) was conducted using a MAC SCIENCE DSC 3200 at the heating rate of 15°C/min. Moreover, the measurement of DSC for the films shown as follows was carried out using the same apparatus at a heating rate of 20°C/min.

Gel Films

The s-PVA solutions with a polymer concentration of 3 g/dL were chilled at 30°C for 24 h. The gel films obtained were dried at room temperature in air.

Drawing

The dry films of s-PVA were drawn in an oven at 200°C and the drawn films were annealed at 200°C for 10 min in the same oven, being fixed at both ends.

Crystallinity

The crystallinity X of the undrawn and drawn films was estimated by the following equation[10]:

$$\frac{1}{d} = \frac{X}{1.345} + \frac{1 - X}{1.269}$$

where d is the density (g/cm^3) of the films, 1.345 is the density of crystal region, and 1.269 is the density of the amorphous region.

Mechanical Properties

The dynamic compressive and tensile moduli of the gels and films were measured using a TMA 4000 apparatus from MAC Science Co. Ltd. The compressive modulus of the gels and the dynamic tensile modulus of the films were measured from 20 to 100°C and from room temperature to 220–260°, respectively. The forced longitudinal vibration (sin wave) was 2.5 (for gels) and 0.25 Hz (for films).

Birefringence

The birefringence Δn of the drawn films was estimated from the retardation determined using a Berek compensator by a Nikon OPTIPHOT POL polarizing microscope.

Infrared Dichroism

Infrared (IR) spectra were obtained using a JASCO FTIR spectrophotometer with a polarizer PL-81. The IR dichroic ratio D was estimated using the absorption at 1145 cm^{-1} known as a crystalline band of PVA and the dichroic orientation factor, F_D [= $(D - 1) \times (D + 2)$], was obtained. The orientation factor of the crystalline phases, F_{cr}, is estimated using F_D.[11]

X-ray Diffraction

X-ray diffraction curves were obtained using a Shimazu XD-610 diffractometer with CuKα radiation. The half-height width was estimated from the curves.

RESULTS AND DISCUSSION

Properties of Solutions and Gels

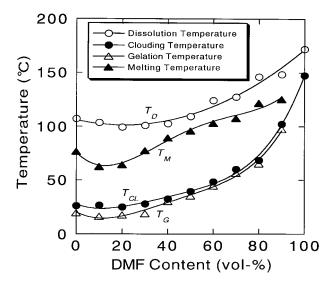Figure 1 shows the relations between the dissolution, the clouding, or the gelation temperatures

Figure 1 Relations between the dissolution temperature of PVA, the clouding, the gelling temperatures of the solutions under slow cooling, or the melting temperature of the gel and the DMF content. Polymer concentration $C = 4$ g/dL.

Figure 2 Relation between the relative viscosity of s-PVA solutions and the DMF content at 30°C. $C = 0.1$ g/dL.

(T_D, T_{CL}, T_G) and the DMF content (polymer concentration: $C = 4$ g/dL). The dissolution temperature was the smallest (about 99°C) at the content of 25 vol %. The dissolution temperature of s-PVA into DMF at the polymer concentration of 4 g/dL was 172°C. The clouding and the gelation temperatures were the smallest (25 and 16°C) at the DMF contents of 20 and 15 vol %, respectively. The s-PVA/DMF solution did not gel during slow cooling, but it generated gel-like precipitates. The difference in T_{CL} and T_G is 3–5°C in the range of DMF content of 40–90 vol % and smaller than that of a DMF content below 30 vol % and the thermal hysteresis in the former is considered to be low. Moreover, the melting temperature is shown in Figure 1 for the gels obtained by gradual cooling to 20°C and standing for 24 h and is the smallest at the DMF content of 15 vol %.

Figure 2 shows the relation between the relative viscosity (η_{rel}: ratio of flow times of solution and solvent, polymer concentration 0.1 g/dL) of the s-PVA/water/DMF solution and the DMF content. The relative viscosity η_{rel} was the greatest at the DMF content of 40 vol %, namely, the interrelation between the relative viscosity of s-PVA and the melting temperature of the gel was not recognized. The relative viscosity η_{rel} of s-PVA dilute solutions with a DMF content of 70 to 40 vol % d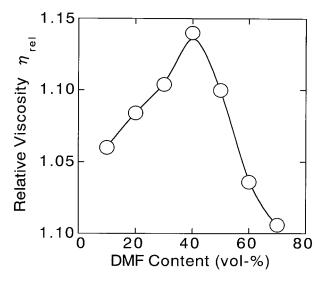ecreased with the standing time and in-creased after clouding, namely, the s-PVA dilute solutions with a DMF content over 40 vol % were unstable. The clouding time of the dilute solutions with DMF contents of 70, 60, and 50 vol % was 10, 20, and 100 min, respectively. The relative viscosity η_{rel} of s-PVA dilute solutions with a DMF content of 10–20 vol % was constant at a standing time of less than 3 h and the solutions were stable.
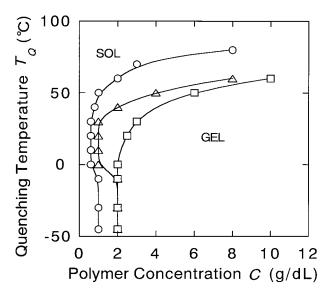
Figure 3 shows a phase diagram, that is, sol–

Figure 3 Sol–gel transition curves under quenching for s-PVA solutions. DMF content: (○) 60 vol %; (△) 40 vol %; (□) 20 vol %).
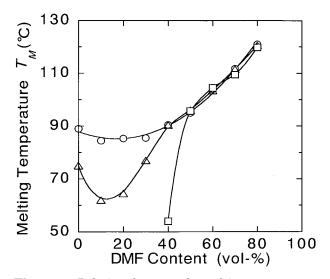
Figure 4 Relations between the melting temperature of gels obtained by quenching to 30°C and the DMF contents (C = 4 g/dL). Aging time: (□) 30 min; (△) 24 h; (○) 360 h.

gel transition curves under quenching for the s-PVA solutions with DMF contents of 20, 40, and 60 vol %. Although the critical polymer concentration of the gelation increases with increase in the quenching temperature, it was constant (DMF content of 60 vol %, 1.0 g/dL; 40 vol %, 2.0 g/dL; 20 vol %, 2.0 g/dL) at a quenching temperature below −10 to 0°C. Similar results were recognized for the PVA/water/DMSO[4,12–14] and PVA/water/ethylene glycol systems.[4] The expansion of the polymer chain in the solutions is considered to be the highest at the DMF content of 40 vol % (see Fig. 2), but the results of the dissolution temperature of the polymer, the clouding and gelling temperatures, the melting temperature (see Fig. 1), and the critical polymer concentration of the gelation (see Fig. 3) did not agree with the results shown in Figure 2. We have no interpretation of the disagreement at the present time.

Figure 4 shows the relations between the melting temperature of the gels obtained by quenching to 30°C and the DMF contents (polymer concentration C = 4 g/dL). In the case of DMF contents below 30 vol %, the effect of the standing time on the melting temperature is remarkable, that is, the propagation of the bonding points in the gel network occurs very slowly. This result coincided with the result shown in Figure 1, namely, in the region of DMF contents of 10–20 vol %, the solubility of the polymer is considered to be high. In the case of DMF contents above 40 vol %, the effect of the standing time on the melting temperature is low and the melting temperature increases with increase in the DMF content. This is considered to be due to the lowering of the solubility as shown in Figures 1 and 3. The standing time dependency of the melting temperature of the gels with a DMF content of 0–40 vol % relates to the solubility of PVA. The apparent enthalpy changes of gel melting, ΔH, estimated from the linear relation plotted by the Eldridge–Ferry method,[15] for the gels with DMF contents of 60, 40, and 20 vol % quenched at 0–40°C were about 170, 140, and 55 kJ/mol, respectively. Moreover, the compressive modulus of the gels (C = 10 g/dL) was the smallest (35 kPa) in the range of the DMF contents of 10–20 vol %. These results are coincident with those results shown in Figures 1, 2, and 4. Incidentally, the compressive modulus of the gel with a DMF content of 50 vol % was 62 kPa.

Table I shows the melting temperatures of the gels (C = 4 g/dL) obtained by quenching them to the lower temperatures of 20 to −75°C. Although the melting temperatures of the gels with DMF contents of 60 vol % are independent of the quenching temperature (T_Q = 0 to −35°C), those with 15–40 vol % are dependent on it.

Figures 5 and 6 show the phase diagrams obtained from the results of the DSC for mixed

Table I Melting Temperature (T_M) of Gels (C = 4 g/dL) Obtained by Quenching to the Lower Temperatures of T_Q = 10 to −75°C

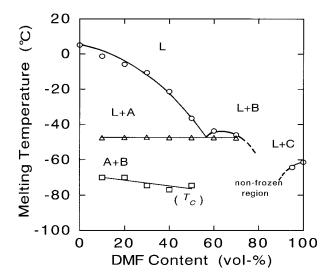| DMF Content (vol %)	Quenching Temperature T_Q (°C)				
	20	0	−20	−35	−75
	Melting Temperature T_M (°C)				
15	88.7	92.3	95.4	94.5	97.8
40	—	95.0	95.3	95.6	97.0
60	—	107.5	107.0	107.5	111.5

Figure 5 Phase diagram of the mixed solvent without s-PVA obtained from the heating DSC thermograph: (□) exothermic peak points; (△, ○) endothermic peak points; L: liquid phase; T_C: crystallization temperature; A: $H_2O(s)$; B: $DMF \cdot 3H_2O(s)$; C: DMF(s); s: solid.

Figure 6 Phase diagram of the mixed solvent with s-PVA ($C = 1$ g/dL) obtained from the heating DSC thermograph: (▲) exothermic peak points; (□, △, ○) endothermic peak points; PVA(c): crystallites of PVA; (A*) H_2O confined in polymer coils.

solvents without PVA and with PVA, respectively. During heating, first the exothermic peak in the DSC thermogram and then the endothermic peaks appeared. In the DSC thermograms of the mixed solvents with PVA in the range of DMF contents of 0–60 vol %, the endothermic peak points were recognized at ca. 0°C (see Fig. 6). However, no peak points appeared in the DSC thermograms of the mixed solvents without PVA (see Fig. 5). Therefore, the endothermic peaks were considered to correspond to the melting of water molecules confined in the polymer coils. The results for the melting temperatures of the gels shown in Table I corresponded well to the phase diagram of the mixed solvents with PVA. The range of DMF content in which the solutions did not freeze increased as PVA was added to the mixed solvents. The gels with DMF contents of 15–60 vol % were located in the unfrozen regions
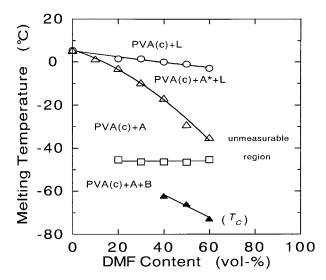
at $T_Q = 0$°C. As shown in Table I, the melting temperatures of the gels increased with increase in the DMF content at $T_Q = 0$°C, namely, in the range of DMF contents of 0–60 vol % at chilling temperatures above 0°C, the melting temperature of the gels is considered to depend on the solubility of PVA. As the PVA solutions (4 g/dL) with DMF contents of 40 and 60 vol % formed microgels at $T_Q = 0$°C, we were unable to measure the melting temperature.

Properties of Films

Table II shows the maximum modulus of the drawn films. The films were obtained from the gels. The gels were made by chilling solutions at 30°C for 24 h and then standing them in water. The DMF in the gels was exchanged for water and the gels were dried in air. The gels contracted

Table II   Two-Dimensional Contraction of Dried Films After Exchanging Solvent to Water, Maximum Draw Ratio, and Maximum Dynamic Tensile Modulus at 20°C

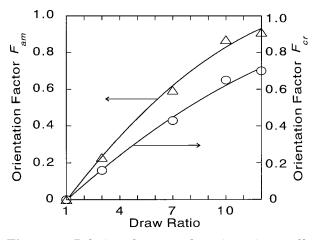|	DMF Content (vol %)							
	0	10	20	30	40	50	60	70
Contraction (%)	10.2	7.7	9.2	12.7	24.6	33.4	45.7	53.2
Draw ratio	16.5	18.0	17.0	16.5	17.5	21.5	25.0	23.0
Modulus (GPa)	39.2	54.9	41.7	38.6	31.3	33.7	39.8	27.5

Figure 7 Relations between the orientation coefficients of crystal or amorphous regions and the draw ratio for the dried films with the DMF content of 10 vol %.

during drying. The contraction of the gels with the DMF content of 10 vol % was the smallest. This result is considered to relate to the solubility of the polymers described above. Although the draw ratio of the dried films with the DMF content of 10 vol % was the smallest, the dynamic modulus at 20°C was the highest.

Figure 7 shows the relations between the orientation factors (F_{cr} or F_{am}) of the crystalline or amorphous phases and the draw ratio for the dried films with the content of 10 vol %. F_{am} was estimated using the following equation[11]:

$$\Delta n = \Delta n_{cr} F_{cr} X + \Delta n_{am} F_{am}(1 - X) + \Delta n_f$$

where Δn_{cr}, Δn_{am}, and Δn_f are the intrinsic birefringences of the crystalline (0.0518) and noncrystalline (0.0483) phases and the form birefringence (very small), respectively.[11] The noncrystalline orientation factor F_{am} was higher than the crystalline orientation factor F_{cr}. Although the crystalline orientation factor F_{cr} for the dried films with the DMF content of 10 vol % was nearly equal to that for the dried films with the DMF content of 60 vol %, the noncrystalline orientation factor F_{am} for the dried films with the DMF content of 10 vol % was higher than that for the dried films with the DMF content of 60 vol %, namely, the orientation of the amorphous regions in the uniaxially stretched s-PVA films are considered to play an important role in high strength and high modulus. The half-height width obtained from the X-ray diffraction curves increased with decrease

in the DMF content. This fact shows that the drawing of films is interfered with by the increase in the DMF content.

CONCLUSIONS

In this article, the solution properties for s-PVA/DMF/water systems, the gelation of the solutions, the properties of the gels, and the properties of the dried gel films were examined and the following results were obtained:

1. The dissolution temperature of the polymer was the lowest at the DMF content of 20 vol %.
2. The clouding and gelation temperatures of the solutions was the lowest at the DMF content of 10 vol %.
3. The compressive modulus and the melting temperature of the gels was the lowest at the DMF content of 10 vol %.
4. The maximum dynamic tensile modulus of the drawn (×18) films obtained from the dried gel films with the DMF content of 10 vol % was 54.9 GPa at 20°C.
5. The orientation of the polymer chains in the amorphous regions was high for the drawn films with the DMF content of 10 vol %.
6. The half-height width increased with decrease in the DMF content.

From the results described above, we obtained the following conclusions: The solubility of s-PVA is the highest at the DMF content of 10 vol %, the junction points in the gels and films are the lowest, the orientation of the polymer chains in the amorphous regions is the highest, and the tensile modulus of the drawn films is the highest (54.9 GPa, at 20°C).

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