Rheological and Thermal Properties of Poly(vinyl alcohol)–Ethylene Glycol–Water Gels

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ABSTRACT: Effects of ethylene glycol (EG) on rheological and thermal properties of poly(vinyl alcohol) (PVA) gels were studied by longitudinal vibration measurements and differential scanning calorimetry. Elastic modulus of PVA gels as a function of EG content showed a maximum around 0.35 mol fraction (mf) EG, while the melting temperature and the heat absorbed on forming one mol of junction zones increased monotonously with increasing EG content. It was suggested that junction zones of PVA gels become more heat resistant by the addition of EG, however, the number of junction zones becomes maximum around 0.35 mf EG. The results were compared with those for PVA–dimethyl sulfoxide–water gels reported previously.

KEY WORDS Poly(vinyl alcohol) / Gel / Differential Scanning Calorimetry / Rheology / Ethylene Glycol /

It is well-known that poly(vinyl alcohol) (PVA) aqueous solution does not form a strong gel, and its rheological properties change remarkably with time lapse.¹ Repeating cycles of freeze-thaw^{2–5} and mixing with dimethyl sulfoxide (DMSO)^{6,7} make a strong gel of PVA. Ethylene glycol (EG) changes the structure of water, and also interacts with hydroxyl groups in gel forming polymer such as agarose. Rheological and thermal properties of agarose gels were found to be influenced strongly by the addition of EG.^{8,9}

Recently, a zipper model approach was proposed to understand the relationship between the structure of junction zones and the heat capacity of thermo-reversible gels.¹⁰ According to the zipper model approach, the heat capacity C of a gel consisting of $\mathcal{N}$ zippers is written as

$$\frac{C}{k} = \mathcal{N} \left(\log \frac{G}{x} \right)^2 \left[\frac{2x}{(1-x)^2} \right.$$

$$\left. + \frac{N(N+1)x^N[-x^{N+1} + (N+1)x - N]}{[1 - (N+1)x^N + Nx^{N+1}]^2} \right] \quad (1)$$

where N is the number of parallel links in a single zipper, ε is the energy required to open a link, G is the rotational freedom of a link, $x = G \exp(-\varepsilon/kT)$, and T is the absolute temperature. In a differential scanning calorimetry (DSC) measurement, the heat flow difference dq/dt between sample and reference is recorded as a function of temperature. Here, q and t represent the heat and time respectively. Since $dq = CdT$, or $dq/dt = CdT/dt$, the number $\mathcal{N}$ represents the number of zippers per total mass of the gel sample. Since eq 1 is based on equilibrium statistical thermodynamics, it is necessary to choose the scanning rate dT/dt as slow as possible.

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EXPERIMENTAL

DSC Measurements

DSC measurements were done with a Seiko DSC 10 calorimeter. Approximately 45 mg of the sample was sealed into the DSC pan hermetically, and the reference pan was filled with exactly the same amount

(± 0.1 mg) of solvent. The temperature was raised from 5°C to 140°C at 2°C min⁻¹, and lowered at the same rate. To examine the state of water in gels, the temperature was lowered by liquid nitrogen to -120°C, and kept for 10 min, and then raised at 2°C min⁻¹.

Rheological Measurements

Preparation of cylindrically molded gels was described previously.^{2,3,6} The gels were kept at 4°C for three days and then at the measurement temperature for 30 min. The cylindrical gels were subjected to longitudinal vibrations of 2.5 Hz. Young's storage and loss moduli were determined at once by

a phase sensitive circuit.

PVA Samples

The degree of polymerization (*DP*) and the degree of saponification (*DS*) for PVA used in this study were 1700 and 99.9 mol% respectively. The PVA samples were given by Kuraray Co. Ethylene glycol of a reagent

Figure 1. Temperature dependence of the storage Young's modulus E' (solid curve) and mechanical loss tangent $\tan \delta$ (broken curve) for PVA–EG–water gels, PVA concentrations: $\blacktriangle$, 20 wt%; $\triangle$, 15 wt%; $\blacksquare$, 12 wt%; $\bullet$, 10 wt%; $\diamond$, 8 wt%; $\square$, 7 wt%; $\circ$, 5 wt%; ∇ , 3 wt%. EG contents: (A) 1 mf; (B) 0.794 mf; (C) 0.458 mf; (D) 0.321 mf; (E) 0.222 mf; (F) 0.147 mf; (G) 0.087 mf.

grade (Wako Junyaku Kogyo Co.) was used without further purification.

RESULTS AND DISCUSSION

Figures 1(A)–(G) show the temperature dependence of storage Young's modulus E' and mechanical loss tangent $\tan \delta$ for PVA–EG–water gels with various PVA concentrations, and various EG contents. E' as a function of temperature was almost independent of temperature for PVA gels with 1 mf EG (Figure 1(A)), 0.794 mf EG (Figure 1(B)) up to 85°C, and $\tan \delta$ slightly increased. Values of $\tan \delta$ were smaller for concentrated gels than for dilute gels. E' for PVA gels with 0.458 mf EG (Figure 1(C)), 0.321 mf EG (Figure 1(D)), 0.222 mf EG (Figure 1(E)), 0.147 mf EG (Figure 1(F)) increased gradually up to 55°C and then decreased with increasing temperature. At the temperature range where E' decreased rapidly around 65°C, $\tan \delta$ increased steeply indicating the commencement of internal melting of PVA gels; this is caused by the release of PVA molecular chains from the junction zones in gels consisting of the aggregation of extended PVA molecules.^{11,12} The schematic representation of PVA gel structure in water and DMSO/water consisting of junction zones and flexible chains has been proposed again recently.¹³ E' for PVA gels with a very low EG content (0.087 mf, Figure 1(G)) decreased gradually up to 55°C and then decreased rapidly beyond this temperature with increasing temperature.

The fact that E' of PVA gels containing EG showed a maximum at the EG content between 0.321 mf and 0.458 mf is understood as follows. In the presence of higher EG content than 0.458 mf, the gelation was inhibited by free EG, and in the lower EG content, the gelation was inhibited by free water. As will be discussed later, gels consist of the balance between the solubility and the crystallinity. In the presence of excessive

water, free water molecules solubilize PVA and shift this balance to the solubility side. The elastic modulus of thermo-reversible gels depends on the number and the structure of cross-linking junction zones, and on the conformation of flexible chains connecting these junction zones. A simple model, called as "reel-chain model" consisting of Langevin chains whose both ends are loosely fixed in crystalline junction regions in such a way that the segments near each end are bound densely in one of the junction region, has been proposed in order to explain the temperature dependence of elasticity of thermo-reversible gels.¹⁴ According to this reel-chain model, the segments are assumed to be released from the junction zone with increasing temperature just as thread is released from a reel. When all the segments in one of both ends are liberated from the junction zone, the chain is called a free chain in the theory of rubber elasticity, and ceases to contribute to the elasticity.¹⁵ Using this model, the elastic modulus of thermo-reversible gels can be calculated numerically by assuming the number $\mathcal{N}$ of molecular chains in a unit volume, the values of bonding energy ε , average end-to-end distance of Langevin chains r_m , an upper limit ν of the number of segments released from the junction zones before the chain ceases to contribute to the elasticity. It is, however, not possible to determine these parameters uniquely only from viscoelastic measurements. Therefore, it is desirable to combine the rheological study with other methods such as neutron or X-ray small angle scattering. It is still possible to estimate qualitatively whether these parameters increase or decrease by the change in environmental conditions. The number of cross-linking junction zones will decrease with increasing water content. The elastic modulus of thermo-reversible gels is proportional to the number of cross-linking junction zones if the conformation of flexible chains remains the

Figure 2. Double logarithmic plot of E' for PVA gels with various EG contents at 25°C vs. the concentration of PVA. EG contents: ○, 0.087 mf; ●, 0.147 mf; △, 0.222 mf; ▲, 0.321 mf; □, 0.458 mf; ■, 0.794 mf; ▽, 1 mf.

same. The presence of EG changes the ratio of entropic and energetic contributions to the elastic modulus. The entropic term increases with increasing length of flexible chains as was found in agarose gels.¹⁶ At a certain EG content between 0.321 and 0.458 mf, three main factors, the number and structure of cross-linking junction zones, the conformation of flexible chains connecting junction zones, or ϵ , r_m , v , and $\mathcal{N}$ in the above-mentioned model which determine the elastic modulus become optimum to realize the maximum of elastic modulus.

Figure 2 shows the double logarithmic plot of E' for PVA gels with various EG contents at 25°C vs. the PVA concentration. Straight lines were obtained from the least squares method. The exponent n in the

Figure 3. The relation between the exponent n in the equation $E' \sim (\text{concn})^n$ for PVA gels and EG content.

equation $E' \sim (\text{concn})^n$ was determined from the slope of these straight lines, and is shown as a function of EG content in Figure 3. The value of n becomes minimum at around 0.32 mf EG. Concentration dependence of elastic modulus of the gels has been discussed by a cascade treatment of Clark and Ross-Murphy¹⁷ and by a modified rubber elasticity theory of Oakenfull.¹⁸ Both theories predict that the slope in the double logarithmic plot of the elastic modulus against the reduced polymer concentration C/C_0 , where C_0 is the critical concentration below which no gelation occurs, is steeper in dilute region than in concentrated region.¹⁹ The fact that the exponent n becomes minimum around 0.32 mf EG suggests that the critical concentration C_0 becomes minimum at around 0.32 mf EG. The effects of EG on the conformation of PVA molecules in water, and on the structure of junction zones should be determined so that we may be able to understand further details in the relation between structure and gelling prop-

erties.

Upper curves in Figure 4(A) show heating DSC curves for PVA gels with various PVA concentrations and various EG contents. An endothermic peak accompanying gel-to-sol transition appeared around 120°C, and the peak temperature shifted to higher temperatures with increasing concentration of PVA. This endothermic peak temperature will be denoted as T_m (melting temperature) here-

after. In addition to this main endothermic peak around 120°C, an endothermic shoulder was observed around 100°C, and it became more conspicuous with increasing concentration of PVA. Lower curves in Figure 4(A) are cooling DSC curves for PVA-EG-water systems with various PVA concentrations and various EG contents. A sharp exothermic peak accompanying sol-to-gel transition appeared around 70°C which is far lower

than T_m . The exothermic peak temperature will be called T_s (setting temperature) hereafter.

The reason why T_m in a heating DSC curve appears at a higher temperature than T_s in its cooling DSC curve is explained by the zipper model approach as follows: when the temperature is raised, the rotational freedom G of a parallel link which forms a zipper would start from the lower value G_g corresponding to the gel state. Then, the gel will expand, which will give rise to an increase in the rotational freedom. On the contrary, when the temperature is lowered from higher temperatures than the melting point, G will start from the higher value G_s corresponding to the sol state. Therefore, the opening of molecular zippers begins to occur at small G values in heating process, while gelation by cooling will take place with decreasing G which starts from large G values at higher temperatures. Then, the average effective value of G is small in heating and is large in cooling. As a first approximation, therefore, we can say that the melting peak temperature T_m is deter-

mined by a certain average $\bar{G}_g$ of G for gel state and the setting temperature T_s is determined by an average $\bar{G}_s$ of G for sol state. Apparently, $\bar{G}_g < \bar{G}_s$, hence, T_m is expected to be higher than T_s .

In the case of heating, the transition caused by the opening of the zippers will start as soon as the temperature arrives at the tail of the C–T curve corresponding to $G = G_g$. In cooling, on the contrary, the pair-wise coupling cannot start so easily because of the difficulty for a long molecule to find its partner in appropriate positions for the zipper construction. Hence a state like supercooling may take place in the course of cooling. It is, therefore, reasonable that the transition is sharper in cooling than in heating as has been observed for PVA–EG–water gels (Figure 4(A)) and agarose and kappa-carrageenan gels.²⁰

DSC heating curves of PVA gels with various concentrations and with various EG contents are shown in Figures 4(B)–(H). Generally, T_m shifted to higher temperatures with increasing concentration of PVA. T_m of PVA gels of the same PVA concentra-

Figure 4. Heating and cooling DSC curves for PVA–EG–water systems. PVA concentrations: a,a', 3 wt%; b,b', 5 wt%; c,c', 7 wt%; d,d', 9 wt%; e,e', 12 wt%; f,f', 15 wt%; g,g', 20 wt%. EG contents: (A) 1 mf; (B) 0.794 mf; (C) 0.458 mf; (D) 0.357 mf; (E) 0.222 mf; (F) 0.147 mf; (G) 0.087 mf; (H) 0.04 mf.

Figure 5. Eldridge-Ferry plot for PVA-EG-water gels. EG contents: $\odot$, 1 mf; $\circ$, 0.794 mf; $\bullet$, 0.458 mf, $\diamond$, 0.357 mf; $\triangle$, 0.222 mf; $\blacktriangle$, 0.147 mf; $\square$, 0.087 mf, $\blacksquare$, 0.04 mf.

tion shifted to higher temperatures with increasing EG content indicating that junction zones in PVA gels became more heat resistant with increasing EG content. This situation is different from that observed in PVA-DMSO-water gels,^{6(a)} where T_m as a function of DMSO content became maximum around 0.3 mf DMSO.

Eldridge-Ferry plot²¹ *i.e.*, the logarithm of PVA concentration vs. the inverse of T_m for PVA gels with various EG contents is shown in Figure 5. The heat absorbed on forming 1 mol of junction zones ΔH_m is proportional to the slope of straight lines in Eldridge-Ferry plot. As is clearly seen in Figure 5, ΔH_m increased with increasing EG content indicating again that junction zones in PVA gels become more heat resistant with increasing EG content.

Figure 6 shows the endothermic enthalpy ΔH estimated from the area enclosed by an endothermic peak and the baseline in Figures 4(A)–(H) as a function of PVA concentration for various EG contents. ΔH increased

Figure 6. Endothermic enthalpy as a function of PVA concentration. EG contents: a, 1 mf; b, 0.794 mf; c, 0.458 mf; d, 0.357 mf; e, 0.222 mf; f, 0.147 mf; g, 0.087 mf; h, 0.04 mf.

with increasing PVA concentration and with increasing EG content. This is again different from the case of PVA-DMSO-water gel where ΔH as a function of DMSO content became maximum around 0.3 mf DMSO (ref 6(a)).

Heating DSC curves from -120°C to 20°C for EG-water mixtures with various EG contents are shown in Figure 7. An endothermic peak observed in water alone, in EG alone, and in mixtures with 0.087 mf, and 0.222 mf EG is attributed to the melting of frozen water or EG. In addition to an endothermic peak, an exothermic peak appeared in mixtures with EG contents from

Figure 7. Heating DSC curves for EG–water systems. EG contents: a, 1 mf; b, 0.877 mf; c, 0.794 mf; d, 0.668 mf; e, 0.458 mf; f, 0.298 mf; g, 0.222 mf; h, 0.087 mf; i, 0 mf.

0.298 mf to 0.877 mf. This suggests that solvent properties of mixtures are drastically changed at around 0.3 mf EG. The heat of fusion ΔH_{mf} for frozen solvent estimated from the area enclosed by an endothermic peak and baseline in Figure 7 is shown together with the melting temperature T_{mf} as a function of EG content in Figure 8. The quantity of frozen solvent becomes minimum around 0.3 mf EG. Gels consist of the balance between the solubility and the crystallinity. Below 0.3 mf EG, the so-called “free water” solubilizes PVA, while above this EG content, free EG molecules solubilize PVA. Therefore, the number of junction zones seems to become maximum at 0.3 mf

Figure 8. Melting temperature T_{mf} and heat of fusion H_{mf} as a function of EG mole fraction. ○, T_{mf} ; ●, H_{mf} .

EG content.

E' for PVA–EG–water gels ($DP=1700$, $DS=99.9\%$, $conc=15\%$) is smaller than that for PVA–DMSO–water gels ($DP=1700$, $DS=99.9\%$, $conc=15\%$) reported in ref 6(a) at the optimum EG or DMSO content for gel formation at any temperature indicating DMSO is more effective in increasing the number of junction zones. However, PVA–EG without water forms a gel, whilst PVA–DMSO without water does not. Both DMSO and EG dissolve PVA, but the latter has hydroxyl groups which help to form junction zones by hydrogen bonds. DMSO shows a stronger interaction with water as has been shown by a flat heating DSC curve for a PVA–DMSO–water gel with 0.277 mf DMSO (Figure 6 in ref 6(a)), whilst DSC curves for EG–water systems showed an endothermic peak (Figure 7) at any EG content, which was attributed to the melting of frozen solvent. Therefore, in the presence of water, DMSO can make stronger gels than EG because it decreases much more free water than EG.

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