Ageing of poly(vinyl alcohol) gels prepared from dimethylsulfoxide/water solutions

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In order to elucidate the structure of poly(vinyl alcohol) (PVA) gels, the gels studied were aged for as long as 500 days at 30°C. The original gel was formed from PVA solutions in a mixed solvent of dimethylsulfoxide (DMSO) and water by chilling at $-34°C$ for one day. The aged gel was shown to have a well grown crystal phase, in that the melting endotherm from differential scanning calorimetry could be clearly separated into two or three components, which were named A, B and C, in order of melting temperature. The enhancement of the gel modulus and the solvent exclusion observed in the aged DMSO/water gels could be atrributed to phase separation, which facilitates crystallization into the B and C components. The A component was shown not to bear a strong relationship to the high modulus and the exclusion of solvent, although it may be the most common crystallite grown from PVA solutions.

(Keywords: poly(vinyl alcohol); gels; ageing)

INTRODUCTION

Poly(vinyl alcohol) (PVA) gels from dimethylsulfoxide (DMSO)/water solutions have been attracting the attention of polymer scientists[1-14], probably because of the excellent transparency and the mechanical, adhesive and water-holding properties of the gels[3,4]. Reported values of the elastic modulus for these DMSO/water gels, ranging from 100 kPa to 1 MPa, are at the same level as those of the so-called Nanbu's gel prepared by freeze–dehydration[15] or repeated freezing[16] of aqueous solutions of PVA. Various kinds of medical applications have been proposed for Nanbu's gel[17]. The time required for Nanbu's gels to reach the same level of elastic modulus during their preparation processes is much longer than that for the DMSO/water gels. Several freezing and melting cycles are needed for Nanbu's repeated freezing method. On the other hand, the preparation method of DMSO/water gels is quite simple. However, it should be noted that DMSO has to be extracted from the DMSO/water gels for medical applications, because of its toxicity. DMSO is an indispensable component for the DMSO/water gels to keep the elastic modulus at a high level as described above.

However, the DMSO/water gel has another promising potentiality. During the past decade, much attention has been focused on high-strength/high-modulus materials made from ultra-high-molecular-weight polyethylene, motivated by the work of Smith and Lemstra[18-21]. It is anticipated that PVA will also be processed into high-strength/high-modulus materials, since the elastic modulus along the chain axis of PVA has been evaluated theoretically[22] and experimentally[23] to be almost the same as that of polyethylene. In fact, some groups have reported on fibres from the DMSO/water gels[14,24-26]. The tensile modulus of the fibres has not reached a high level comparable with that of polyethylene.

The structure and properties of PVA gels can be changed by controlling the composition of the mixed solvent DMSO/water: Watase and Nishinari expressed the compressive modulus and melting behaviour of DMSO/water gels as functions of solvent composition[1,2].

A structural model of DMSO/water gels has been proposed by Kaji *et al.*[9]. According to them, the gel structure formed at low temperatures below $-20°C$ is homogeneous, because the rate of gelation is much larger than that of phase separation. On the other hand, the structure formed at higher temperatures is somewhat complicated, because the gelation occurs in a phase-separated structure.

In this paper, we will discuss the structure and properties of the DMSO/water gel formed at a temperature below $-20°C$ in terms of crystal structure. For this, the gel was aged for a long time at 30°C so as to grow the crystallites. This process is the so-called syneresis, which is defined as volumetric shrinkage of gels accompanying solvent exclusion.

EXPERIMENTAL

Preparation of gels

The PVA powder used was from a commercial source (NH-26, kindly supplied by Japan Synthetic Chemical Inc.). The degrees of polymerization and saponification were 2600 and 99.5 mol%, respectively. Mixed solvents of DMSO and water, with DMSO/water volume ratios

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of 0/100 (pure water), 20/80, 40/60, 60/40, 80/20 and 90/10, were used. The PVA powder and the mixed solvent were dissolved within a sealed test tube (15 mm diameter and 150 mm long) by heating at 120°C for 1.5 h. The solution thus obtained was chilled in a freezer, the temperature of which was controlled at −34°C. After chilling for one day, the gel was subsequently stored at 30°C in the sealed tube. The gels will be denoted by their solvent compositions as, for example, 0/100 gel.

Weighing of gels

A 5 mm cube cut from the gel was weighed periodically to follow the change in polymer concentration with ageing time.

Compressive modulus measurements

Dynamic viscoelastic measurements of the gels were performed in a Thermal Analyzer System 001 (MacScience Inc., Japan) consisting of a thermomechanical analyser (TMA 4000) and a thermal analysis processing system (TAPS 1000). The compressive mode was used to measure the storage modulus (E') and the loss tangent ($\tan\delta$). The gel specimen, which was previously cut into a 5 mm cube, was introduced into a stainless cup to receive oozing solvent from the gel at high temperature, and the cup was set at the bottom of a supporting cylinder, a TMA accessory. The probe rod susceptible to compressive strain was pressed down onto the specimen through the cylinder, transferring a constant pressure of 7 g force onto the specimen. The deformation of the specimen was recorded under a sinusoidal compressive vibration with an amplitude of 5 g force and a period of 4 s (a frequency of 0.25 Hz) to estimate E' and $\tan\delta$ for each cyclic stress–strain curve. The measurement was performed in a heating process from room temperature to 130°C. A maximum scan rate of 20°C min^{-1} for our apparatus was chosen, in order to suppress evaporation of solvent from the gel as far as possible.

Differential scanning calorimetry

The Thermal Analyzer System 001 described above was also used here, now equipped with a differential scanning calorimetry module (DSC 3200) instead of the TMA 4000. Into an aluminium d.s.c. pan (5.2 mm diameter, 2 mm high and 0.1 mm thick) was sealed ca. 15 mg samples. A mixed solvent of the same weight and composition as that contained in the gel sample was used as a reference. The sample was cooled down to ca. −50°C and then heated at a rate of 10°C min^{-1} in an atmosphere of nitrogen. A ghost endotherm that appeared as an instrumental characteristic at early times in heating disappeared before the temperature reached 0°C. The same heating rate should have been used for comparative investigation between the viscoelastic and the d.s.c. measurements. However, the heating rate of 20°C min^{-1} used in the viscoelastic measurement was too fast for the d.s.c. measurement, because it raised the melting temperature of the gels to above 120°C and raised the inner pressure of the pan over the upper limit of pressure resistance of the pan (ca. 8 atm). A stainless-steel pan plated with gold was also available as a high-pressure (h.p.) d.s.c. pan (MacScience Inc.), with pressure-resistance limit of 50 atm. Unfortunately, this h.p. pan was not so sensitive as the Al pan, because the former was 75 times larger in thickness than the latter.

RESULTS AND DISCUSSION

Figure 1 shows the change of the E' modulus vs. temperature curve with ageing time, for the 60/40 gel that was formed by one-day storage at −34°C and subsequent ageing at 30°C. The ageing time indicated includes the first day of storing at −34°C. The E' modulus at 30°C, E'(30°C), slowly but extensively increased by about 10 times after 500 days of ageing. The E' curve observed at any ageing time is composed of a plateau region ranging from room temperature to ca. 70°C and a following down-slope up to ca. 110°C. The transition point from the former to the latter corresponds to the onset of melting (to be exact, dissolution) of crystallites. The E'(30°C) moduli for the gels with various solvent compositions are plotted against solvent composition (expressed as volume percentage of the DMSO content) in *Figure 2*. The curve at any ageing time has a bell shape with its maximum at 60 vol% DMSO composition.

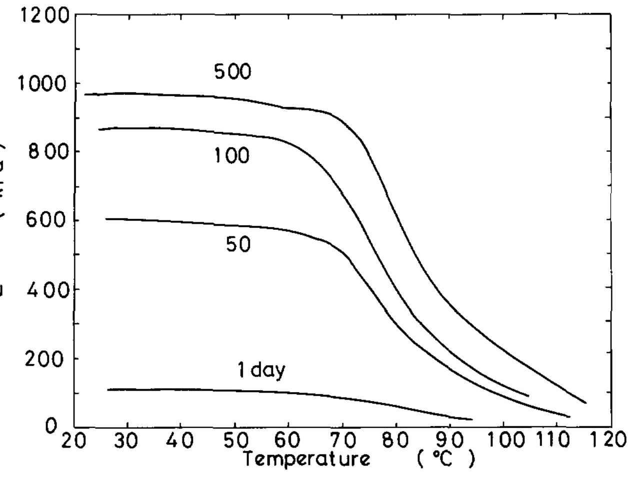

Figure 1 The E' modulus vs. temperature curves obtained from t.m.a. measurements for the 60/40 (DMSO/water volume ratio) gels. The gels were formed by one-day chilling at −34°C and some of them were subsequently aged at 30°C for the time (days) indicated. The ageing time contains the first day for gel forming

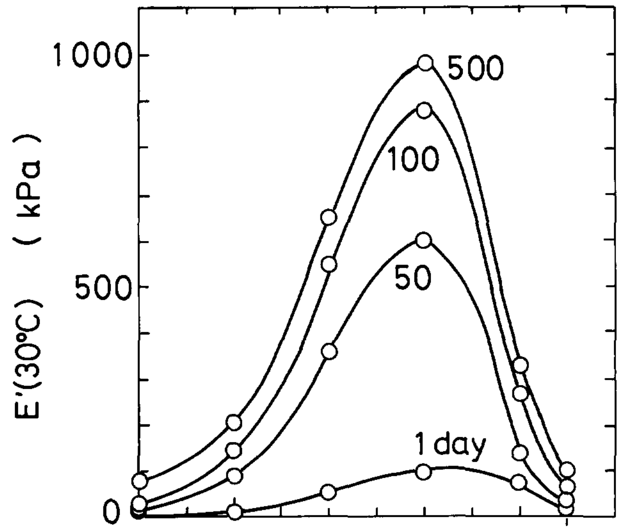

Figure 2 The modulus obtained at 30°C, E'(30°C), vs. solvent composition curves at indicated ageing times (days). The composition is expressed by volume percentage of DMSO in the solvent

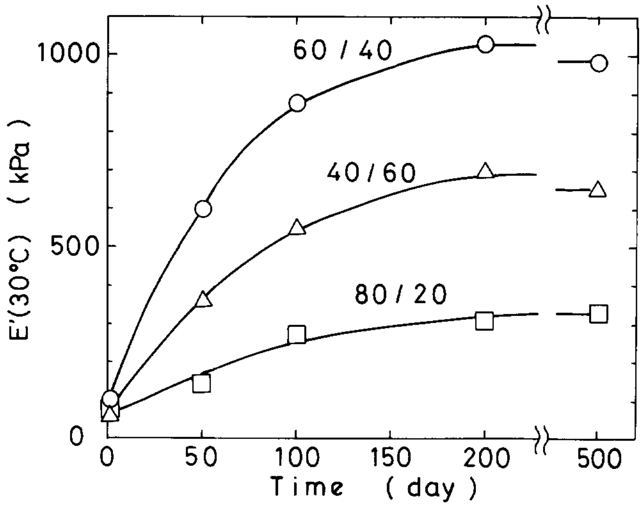

Figure 3 Changes in E'(30°C) with ageing time for the 40/60, 60/40 and 80/20 gels

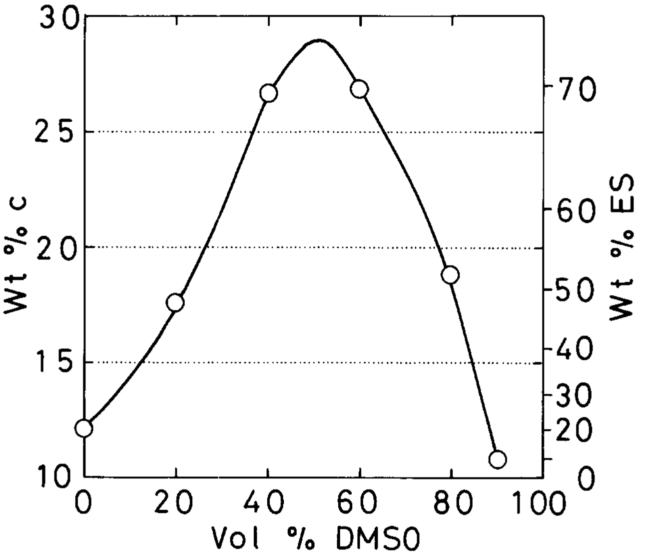

Figure 4 Polymer concentration c of the gels aged for 500 days as a function of solvent composition. The ordinate on the right side shows the weight percentage of the excluded solvent (ES)

The value of 60 vol% corresponding to 27.6 mol% DMSO is reported to be the most favourable composition for facilitating gelation and crystallization of PVA molecules[1,2]. *Figure 3* shows the E'(30°C) modulus obtained from *Figure 2* as a function of ageing time for the three gels, 40/60, 60/40 and 80/20. It takes 200 days of ageing for the gels to reach the equilibrium modulus.

The polymer concentration c of the gels measured after 500 days of ageing was plotted against solvent composition in *Figure 4*. The c values observed after one-day storage at −34°C, not shown in the figure, were the same as the initial value of 10 wt%. These results mean that the observed solvent exclusion was induced, not in the gelation stage at −34°C, but in the ageing stage at 30°C. The curve in *Figure 4* has a similar bell shape to the curves in *Figure 2*, but the composition at its maximum is located at around 50 vol% DMSO, different from that in *Figure 2*. This deviation alone indicates that the modulus is not a function only of c. The ordinate on the right side of *Figure 4* represents the percentage of excluded solvent (ES) calculated on the basis of the initial weight of solvent. The increase in c during ageing, for example, from 10 to 27 wt% of the 60/40 gel, seems not to be large. However, this increase means that as much as 70 wt% of the solvent initially included in the gel was excluded. The change in c with ageing time was depicted for the three gels in *Figure 5*. The solvent exclusion process is apparently composed of two sequential stages. The greater part of the exclusion occurs quickly at the first stage, which is followed by slow exclusion at the second stage. No corresponding change appears on the E' vs. time curve in *Figure 3*, also indicating no proportional relationship of polymer concentration to modulus. Another important observation is that the change in c proceeds prior to that in the modulus. This will be discussed later from the view point of variety of crystallites.

The structure of the gel was studied also from d.s.c. data, shown in *Figure 6*, for the gels before ageing and after 500 days of ageing. The aged gels show clearly separable multi-peak endotherms. This multiplicity can be related to a multi-phase structure, such as coexistent polymer-rich and polymer-poor phases, which in this paper will be utilized to discuss the gel structure. The multi-peak endotherm is also explained by other kinds of factors in relation to the resultant crystal phase: one is a crystallographic factor such as the difference in chain conformation and packing, and the presence of solvation; and another is the morphological difference in crystal size or disorder in crystallites. However, we will not make a distinction between the crystallographic and morphological factors in discussing the multi-phase structure.

The 40/60, 60/40 and 80/20 gels have similar three-peak endotherms. The components corresponding to the three peaks are designated by us as A, B and C components in order of melting temperature. The 20/80 and 90/10 gels show two-peak endotherms. The 0/100 (water) gel is regarded as a different gel from the other DMSO-containing gels, since the endotherm of the former gel, even after ageing, shows a one-peak nature. The A component is characterized by its sharp peak and the C component by the independent nature of its peak position with solvent composition. The characterization of the B component seems to be difficult. If the B component is defined to be an intermediate endotherm between the A and C components, the endotherms of 20/80 and 90/20 gels would have a very small amount of or no contribution from the B component. In other words, the

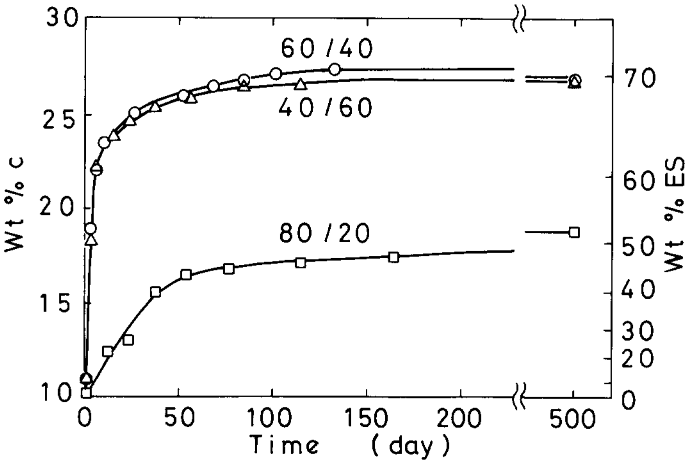

Figure 5 Changes in c with ageing time for the 40/60, and 60/40 and 80/20 gels

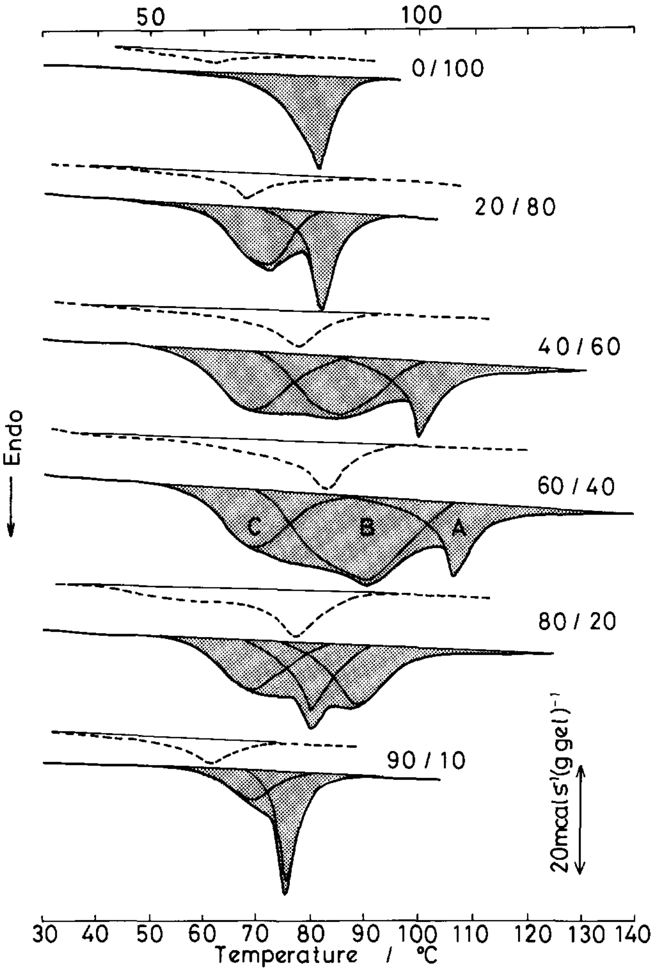

Figure 6 D.s.c. traces for the gels with solvent compositions indicated. The traces indicated by broken curves are for the gels before ageing and shaded traces are for the gels after 500 days of ageing

B component appears only in a limited solvent composition region ranging from 40 to 80 vol% DMSO, but it becomes the largest peak among the three components at a 60/40 composition. It is also possible that the endotherm on the lower-temperature side of the A component for the 20/80 and 90/20 gels is thought to be an overlapped endotherm of the B and C components. We cannot, here, derive a conclusion from this problem. However, the following discussion will not be significantly affected by this problem, whichever of the two ideas on the B and C components is adopted. The crystal component of the 0/100 gel is speculated to be similar to the A component, judging from the shape and position of the endotherm. It is concluded that the B and C components are characteristic for the DMSO/ water gels and that the A component, independently of solvent composition, occurs commonly in PVA gels.

The melting temperatures (T_m) were obtained from peak positions of the melting endotherms, as shown in *Figure 7*. $T_{m,A}$ and $T_{m,B}$ are both dependent on solvent composition, while $T_{m,C}$ is almost constant over the whole range of compositions. The total heat of fusion was also obtained from the endotherms and is expressed in *Figure 8* in units per gram of gel (ΔH) and per gram of polymer ($\Delta H'$). The ΔH and $\Delta H'$ vs. solvent composition curves for the one-day and 500-day aged gels have similar bell shapes, both bearing their maxima at around 60 vol% DMSO composition. The endothermic curves of the 500-day gels were separated into three components, and the values of heat of fusion corresponding to them, ΔH_A, ΔH_B and ΔH_C, are plotted in *Figure 9*. The variations of these values with solvent composition are clearly different from each other. The ΔH_B and ΔH_C curves are similar

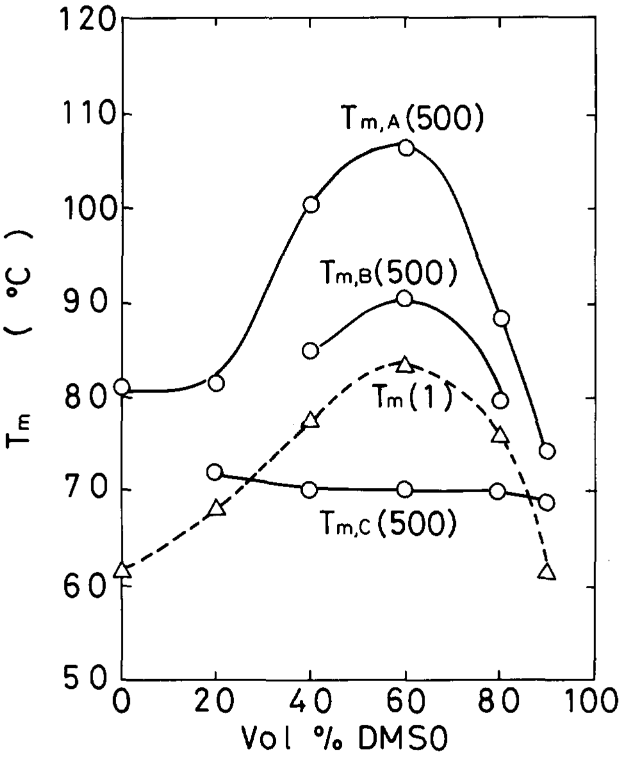

Figure 7 The melting temperatures (T_m) obtained from d.s.c. traces in *Figure 6* are plotted against solvent composition. $T_m(1)$ was obtained from the peak of the endotherm for the one-day gel. $T_{m,A}(500)$, $T_{m,B}(500)$ and $T_{m,C}(500)$ were obtained from the three peaks of the aged gel

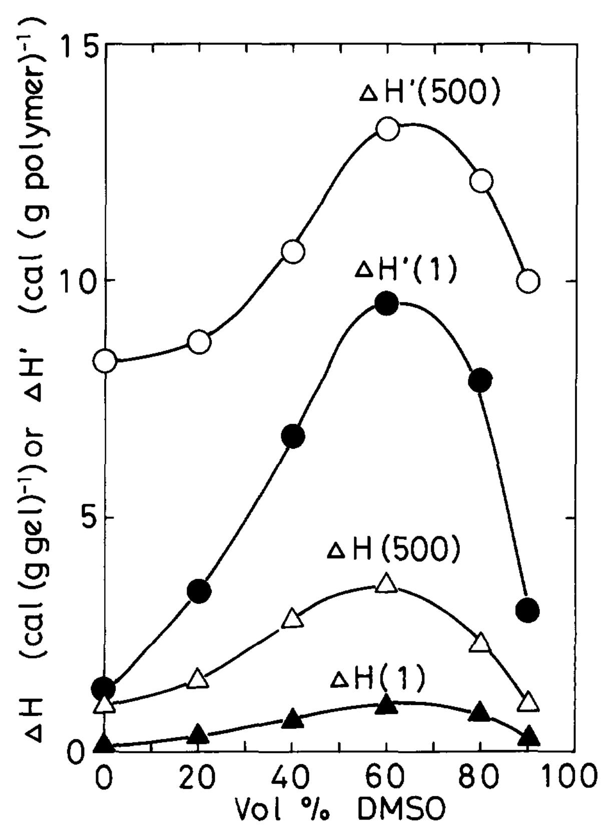

Figure 8 The heat of fusion obtained from the d.s.c. trace in *Figure 6* shown in units per gram of gel (ΔH) and per gram of polymer ($\Delta H'$). The numbers in parentheses show the time (days)

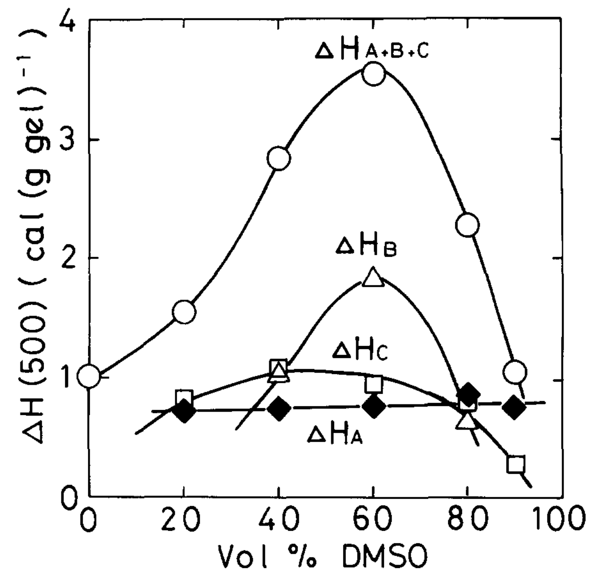

Figure 9 The heat of fusion, $\Delta H(500)$ ($=\Delta H_{A+B+C}$), for the gel after 500 days of ageing expressed in units per gram of gel, divided into the three components ΔH_A, ΔH_B and ΔH_C

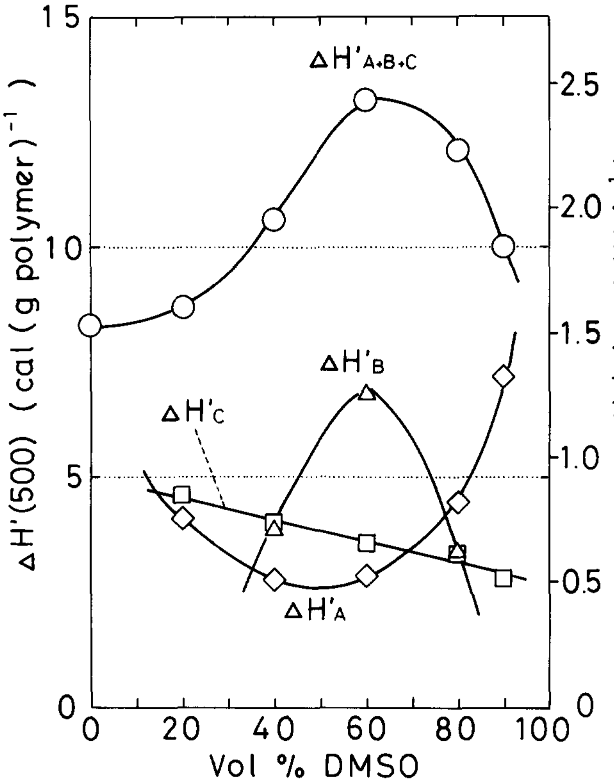

Figure 10 The heat of fusion, $\Delta H'(500)$ ($=\Delta H'_{A+B+C}$), for the gel after 500 days of ageing expressed in units per gram of polymer, divided into the three components $\Delta H'_A$, $\Delta H'_B$ and $\Delta H'_C$

to the E'(30°C) curve in *Figure 2* and to the *c* curve in *Figure 4*, respectively, with respect to their peak positions. It is thus postulated that crystallization into B and C crystallites most effectively contributes to the increase in modulus and the solvent exclusion, respectively. Contrary to these two crystallites, the A crystallite has no significant relationship to the high modulus at around 60 vol% DMSO and to the high solvent exclusion at around 50 vol% DMSO. The value of ΔH_A reduced by polymer weight, $\Delta H'_A$, more successfully represents the modest contribution of the A component to the peaked nature of the modulus and solvent exclusion, as shown in *Figure 10*. It is speculated that crystallization into the B and/or C crystallites is favoured in the gel in which syneresis proceeds, and, as a result, obstructs crystallization into the A crystallites. Nevertheless, the $T_{m,A}$ curve in *Figure 7* has a maximum at around 60 vol% DMSO. This means that the solvent composition near 60 vol% DMSO is the most favourable crystallization composition also for the A crystallite. The composition of the crystallites may be determined by the crystallization rates of the three crystallites.

The separation of endotherms of the one-day gels into three components was difficult, because the three peaks are not obvious. Their endotherms are composed of a somewhat sharp peak at the high-temperature end and a rather broad endotherm trailing from the peak to the low-temperature end. The melting temperature, $T_m(1)$, corresponding to the peak has a similar dependence on solvent composition to $T_{m,A}(500)$, as shown in *Figure 7*. The temperature distance between $T_m(1)$ and $T_{m,A}(500)$, some 20–30°C, is explained as the increase in melting temperature due to crystallization during ageing. Thus, the peak is thought to be the A component. On the other hand, the trailing part is thought to belong to the B and C components, though separation into the latter two components is impossible.

Evidence for small crystallization rate at −34°C is depicted in *Figure 11*. The modulus of the 60/40 gel formed and stored at the same temperature, −34°C, remained at the initial value, while the modulus of the same gel aged at 30°C steadily increased, as shown in *Figure 3*. These results indicate that the rate of crystallization in the gel formed is negligibly small, when the gel is stored at −34°C. Thus, the crystal phase detected as melting endotherms of the one-day gel is shown to be for most part simultaneously formed on gelation. The

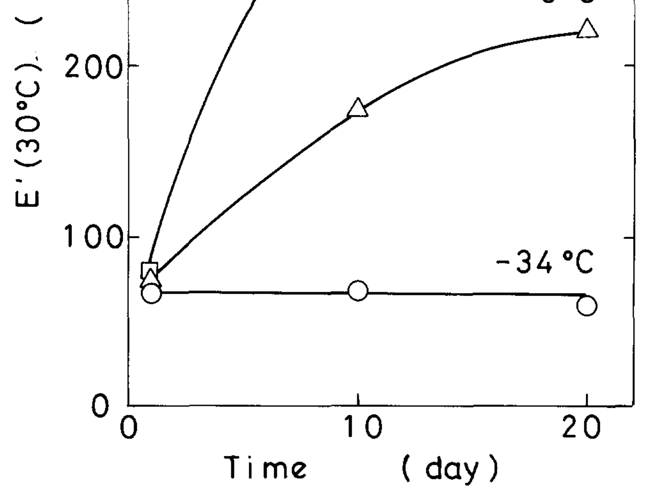

Figure 11 Changes in E'(30°C) with storage time for the 60/40 gels formed and stored at the gelation temperatures (T_{gel}) indicated

aggregation of polymer molecules caused by gelation should tentatively facilitate the crystallization. Another possible crystallization occurs in the pre-gelation stage in which the cooling stage of solution is included. We think that the A component is formed mainly in this pre-gelation stage and the B and C components are induced by gelation. In *Figure 11*, the E' data for the gels formed at 0 and 20°C are also shown in control experiments. Although, as described in the 'Introduction', the mechanism of gelation at these T_{gel} values is different from that at -34°C, the observed large increase in modulus with time at 0 and 20°C apparently indicates the larger crystallization rate at temperatures above 0°C than at -34°C. We will report in the near future on the effect of T_{gel} on the gel structure.

The syneresis in our case is caused by phase separation of the gel network according to the model by Kaji *et al.*[9]. Further, as stated above, crystallization occurs on a small scale in the gel at -34°C. Thus crystallization should proceed accompanied by phase separation in the ageing stage at 30°C. The high modulus of the aged 40/60, 60/40 and 80/20 gels is due to the condensed region formed by phase separation of the gel network. Thus, it is expected that the B and C components are formed on phase separation of the gel network. The two separated regions, condensed and loose regions of the phase-separated network, are probably composed of the B and C components, respectively. However, it is not guaranteed that crystallization is entirely linked with phase separation. As the A component does not contribute to the high modulus, the A crystallites are thought not to be incorporated into the phase-separated network, but to be isolated or loosely form another gel network. At high temperatures above the melting temperatures of the B and C components, the gel structure is retained by the network only of the A component. The high modulus of the DMSO/water gel is, thus, due to the large fractions of the B and C components.

CONCLUSION

Ageing has been shown to be a useful technique for the PVA/DMSO/water gel to elucidate its structure. It is still very difficult to analyse the structure of crystallites in the gel before ageing, because of a vague melting endotherm from d.s.c. The crystallite grown in the aged gel was detected as a clearly separable multi-peak endotherm from which the three components, A, B and C, were found. It was concluded that, on ageing, densification probably caused by phase separation of the gel network facilitated the crystallization into B and C components, and that the A component was isolated from the network made by the other components or made its own crystal network. It was speculated that the enhancement of gel modulus and the exclusion of solvent can be respectively related to the crystallization into the B and C components. In the next stage of this study we will show the change of gel structure more precisely at the early stage of ageing in terms of A, B and C components, in order to relate the structure with the gel properties such as modulus and solvent exclusion.

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