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High strength and high modulus poly(vinyl alcohol) by the gel ageing method

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The gel ageing method was proposed for producing high strength and high modulus poly(vinyl alcohol) (PVA) materials. The PVA gel prepared from a solution in a mixed solvent of dimethylsulfoxide water (v/v) = 80:20 at −34 °C was moulded into a gel sheet and then aged in water at 10 °C for several months. The gel sheet was dried and then drawn at 200 °C. The tensile strength and the modulus of the drawn film were 2.8 and 72 GPa, respectively. These excellent properties are discussed in relation to the structures of the aged gel, the dried gel (namely the film) and the drawn film using the results from X-ray diffraction, differential scanning calorimetry and birefringence measurements. As a result, the most important process was shown to be the ageing process. If the crystallites with relatively low melting temperatures, which were called the B and C crystallites, were grown in the aged gel, the mechanical properties of the drawn film from it were as high as those described above. The orientation of the crystallites mildly caused during drying of the gel sheet was also shown to be a key structure which facilitated the high extension of the chain in the subsequent drawing process.

1. Introduction

Syneresis has been well known for many years as a term which means the gradual change in the structure of gels accompanying shrinkage of their volume and exclusion of the solvent. It should be noted here that this definition does not involve the shrinkage of gels which is caused by evaporation of the solvent from the surface of the gel in an open system. Syneresis means the shrinkage caused by inner structural change, such as a very slowly occurring phase separation of the gel network and/or crystallization. This means that the just formed gel is not in its equilibrium state. However, there have been very few papers in which one can find a description of syneresis, probably because the time scale of syneresis in almost all gels is much longer than that of the usual measurements. The structural change in the gel may be negligibly small or most scientists studying gels have no time to spare for studying syneresis. The authors have recognized the great importance of syneresis for studying the structure of poly(vinyl alcohol) (PVA) gels, when they were prepared from solutions in mixed solvents of dimethylsulfoxide (DMSO) and water at −34 °C and subsequently stored at 30 °C for ageing [1]. In a sense, the effect of ageing on the gel structure seems to be analogous to that of annealing on the crystal structure. Analysts of the crystal structure of polymers have usually used the annealing method to clarify the structure, as well as to improve the mechanical properties of the materials.

Many researchers have already attempted to produce high modulus and high strength films or fibres of atactic PVA. A fibre with a tensile strength value, σ_b of 3.4 GPa was gel spun from a solution in glycerin of an ultra high molecular weight PVA with a molecular weight of 2.2×10^6 [corresponding to a degree of polymerization (DP) of 50 000] by Mizuno *et al.* [2]. Here, the value is calculated in GPa, assuming its sample density to be 1.3 g cm^{-3}. An aqueous solution of a PVA of DP = 12 000 containing boric acid was gel spun by Sano [3] to yield a fibre of σ_b = 2.5 GPa and E = 72.2 GPa, where E is the tensile modulus. Kunugi *et al.* used the zone-drawing method [4] to obtain a fibre of E = 115 GPa from a PVA of DP = 11 800. Kanamoto *et al.* used solid state coextrusion of solution-grown crystal mats [5] to obtain a fibre of E = 50 GPa and σ_b = 1.3 GPa from a PVA of DP = 3500. Hu *et al.* obtained a fibre of E = 51 GPa and σ_b = 2.4 GPa by a gel spinning method from a DMSO solution of a PVA of DP = 4070 [6]. Cha *et al.* produced a fibre of E = 64 GPa and σ_b = 2.8 GPa by gel spinning a mixed solvent solution [DMSO:water = 80:20 (wt/wt)] of a PVA of DP = 5000 [7]. These studies seem to be motivated

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by some of the methods [8] developed for the high strength and high modulus fibres of ultra high molecular weight polyethylene (UHMWPE) which has the same planar zigzag conformation in the crystal phase as PVA. This type of conformation is one of the necessary molecular structures for high strength and high modulus fibres of flexible polymers. However, the strength and modulus of the best PVA fibres currently obtained are still lower than the highest achievable values obtained with several UHMWPE materials. This is probably attributable to the presence of hydrogen bonding in PVA which prevents the orientation of the molecule.

In this report, a new processing method is proposed for high strength and high modulus PVA materials. A gel material was used in this method, which was prepared by chilling a solution of a PVA of DP = 2600 in the DMSO : water = 80 : 20 (v/v) solvent and subsequently ageing the gel in solvents at temperatures ranging from 10 to 50 °C. The fibre was obtained by drawing the film prepared by drying the aged gel. The ageing process involved in this method is totally different from other methods. Thus, this method is called the gel ageing method. The peculiar crystallites found in the aged gels in the previous paper motivated the authors to utilize them for the high strength and high modulus fibre. Another remarkable point of the method is the use of a PVA with a relatively low molecular weight, compared with PVAs used in other methods cited above.

The three endothermic peaks corresponding to the three crystallites with different melting temperatures were found on the differential scanning calorimetry (DSC) curve of the aged gels with solvent compositions of 40 : 60, 60 : 40 and 80 : 20 [DMSO : water (v/v)] [1]. These crystallites were called A, B and C crystallites in the order of the melting temperature. The A crystallite is thought to be the ordinary one, of which the nucleus was generated in the course of cooling the original hot solution to the gelation temperature. On the contrary, the nucleation of the other two crystallites occurred in the gel phase, and their crystallization persisted over several months. The B and C crystallites were expected to be easily deformed and highly extended when the film containing them was drawn. Based on this expectation, the mechanical properties of the drawn film from the aged gel are discussed in relation to the gel structure.

2. Experimental procedure

2.1. Sample preparation

The PVA used was a commercial product of Japan Synthetic Chemical Co. (NH-26) with degrees of polymerization and saponification of 2600 and 99.5 mol %, respectively. From ^{1}H nuclear magnetic resonance (NMR) measurements, its triad tacticities were revealed: 19.1 (mm), 51.0 (mr) and 29.9 mol % (rr), where mm, mr and rr represent isotatic, heterotatic and syndiotatic triad tacticities, respectively, indicating its atactic nature.

A solution of PVA in a mixed solvent of DMSO and water with a polymer concentration of 10 wt % was prepared in a three-necked flask equipped with a condenser, a stirrer and a thermometer. The solution was heated at ~100 °C for 1 h. The DMSO content of the mixed solvent used was 80 vol %. The solution thus prepared was poured into a container made of polypropylene and chilled in a freezer at −34 °C for one day to form a gel sample about 10 mm thick.

A piece of the bulk gel thus obtained was placed in a rectangular cavity in a mould and then doubly sandwiched by a couple of poly(ethylene terephthalate) (PET) sheets 0.1 mm thick and a couple of stainless steel plates. The mould was an aluminium plate 1 mm thick, which had a punched-out 10 × 10 cm hole. The sandwiched sample was placed in a pressing machine previously heated at 75 °C. After holding the sample for 5 min, it was pressed at 200 kg cm^{-2} for 5 min and then released from pressure. The part of the sample sandwiched by the PET sheets was then chilled again at −34 °C for 1 h to cause regelation.

The gel sheets were removed from the mould and then immersed in an ageing solvent of a DMSO : water mixture at a given ageing temperature, T_a, for a given ageing time, t_a. The DMSO : water (v/v) ratios of the ageing solvents used were 0 : 100 (pure water) and 80 : 20. In the case where the ageing solvent contained DMSO, after a given ageing time, the gel was further stored in water at the same temperature as T_a for three days in order to exchange the solvent contained in the gel with water. This exchange process was added, because the evaporation rate of DMSO from the gel was much lower than that of water.

The aged gel was fixed by a wood frame (10 × 10 cm) which was made of rectangular timbers with a section of 5 × 5 mm. The sheet was dried in the atmosphere for one week and then further dried *in vacuo* at room temperature for one day. The gel sheets were called films after they were dried.

The film specimen (2 × 0.2 cm) cut from the original film was drawn to its highest achievable draw ratio at 200 °C by a manually operated drawing tool.

2.2. Measurements

The crystallinity of the film, X_c, was estimated by the density measurement and DSC. The former was estimated by the following equation

$$1/d = X_c/d_c + (1 - X_c)/d_a \qquad (1)$$

where d, d_c and d_a are the density of the sample, the crystal level phase and the amorphous phase, respectively. The latter two density values were the reported ones ($d_c = 1.345$ g cm^{-3}, $d_a = 1.269$ g cm^{-3}) [9] whilst the sample density was measured by a flotation method at 30 °C using benzene and carbon tetrachloride as the floating solvents. The crystallinity from DSC was estimated using the reported heat of fusion of 6.87 kJ mol^{-1} VA, where VA is the vinyl alcohol unit [10].

The stress–strain curves were obtained by extension measurements at room temperature using a tensile tester (Shinko Tsushin Kogyo, Inc., TOM/5). The extension rate was 10 mm min^{-1}. The initial gauge length of the specimen was 20 mm. The width and the thickness of the specimen were measured with a microscope and a micrometer, respectively. The stress was estimated using the initial cross-section of the specimen.

The DSC was performed with a MacScience system (Thermal Analyser System 001) consisting of a differential scanning calorimeter (DSC 3200) and a thermal analysis system (TAPS 1000). The sample, packed in an aluminium pan, was heated at a rate of 20 °C min^{-1} for films and 10 °C min^{-1} for gels. These rates were the same as those in a previous study [1].

X-ray diffraction photographs were taken with a flat camera using Ni filtered CuK_α radiation generated at 30 kV and 30 mA. The X-ray generator used was made by Shimazu Seisakusyo Co. (model XD-610).

The birefringence was measured using an Olympus polarizing microscope equipped with a Berek compensator.

3. Results and discussion

3.1. Drawn films

The mechanical properties of the drawn films will be discussed first. The drawn film having the highest tensile strength and the highest tensile modulus amongst the drawn films was obtained by ageing the gel in water at 10 °C for 120 days. This ageing condition (solvent and temperature) and the film prepared under this condition are called the special ageing condition and the special film, respectively. A series of stress–strain (S–S) curves corresponding to the above case are shown with varying ageing time in Fig. 1. The films used for the tensile tests were drawn to their highest achievable draw ratios (DR_{max}), which are shown in Fig. 2c. The figure of the S–S curve is basically unchanged with ageing time. Strain hardening appears after the yield point which corresponds to a strain of between 1 and 2%. The tensile strength (the stress at the breaking point), σ_b, and the tensile modulus, E, are plotted against ageing time, t_a, in Fig. 2a, b, respectively. Each of the plotted values is an averaged value from the three observed values. The strength and the modulus increased to a maximum of 1 2.7 and 73 GPa, respectively, after 120 days of

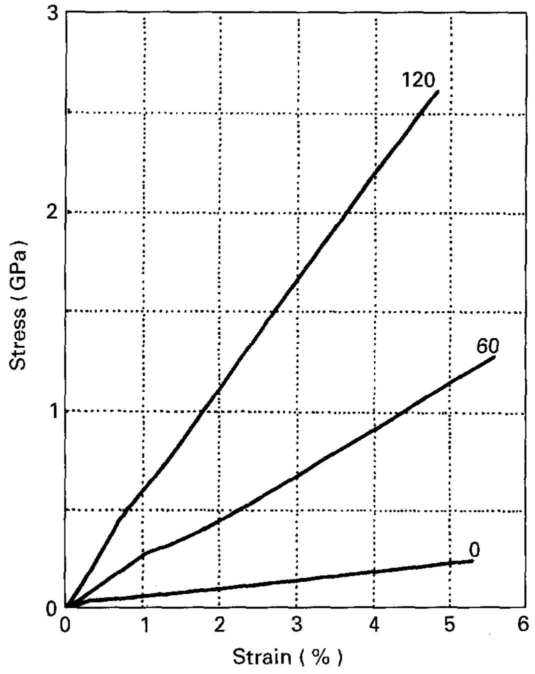

Figure 1 Stress–strain curves for the special films drawn to the draw ratios indicated in Fig. 2c. The films were prepared from the gels aged under the special condition (in water at $T_a = 10\,°\text{C}$). The ageing times (days) are shown on the curves.

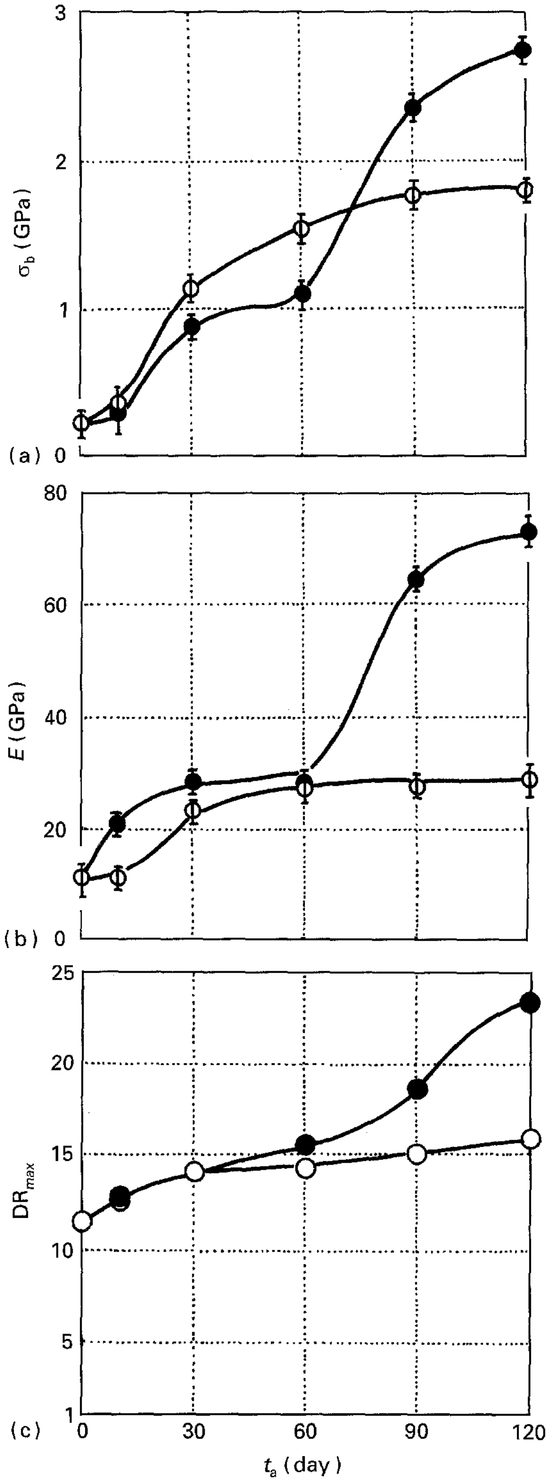

Figure 2 The tensile strength, σ_b, (a) and the tensile modulus, E, (b) of the films drawn to their highest achievable draw ratios (DR_{max}) shown in Fig. 2c, as functions of ageing time, t_a (days). The films were prepared from gels aged at 10 °C in water (●) and in the DMSO : water (v/v) = 80 : 20 solvent (○). The former films are called the special films in the text.

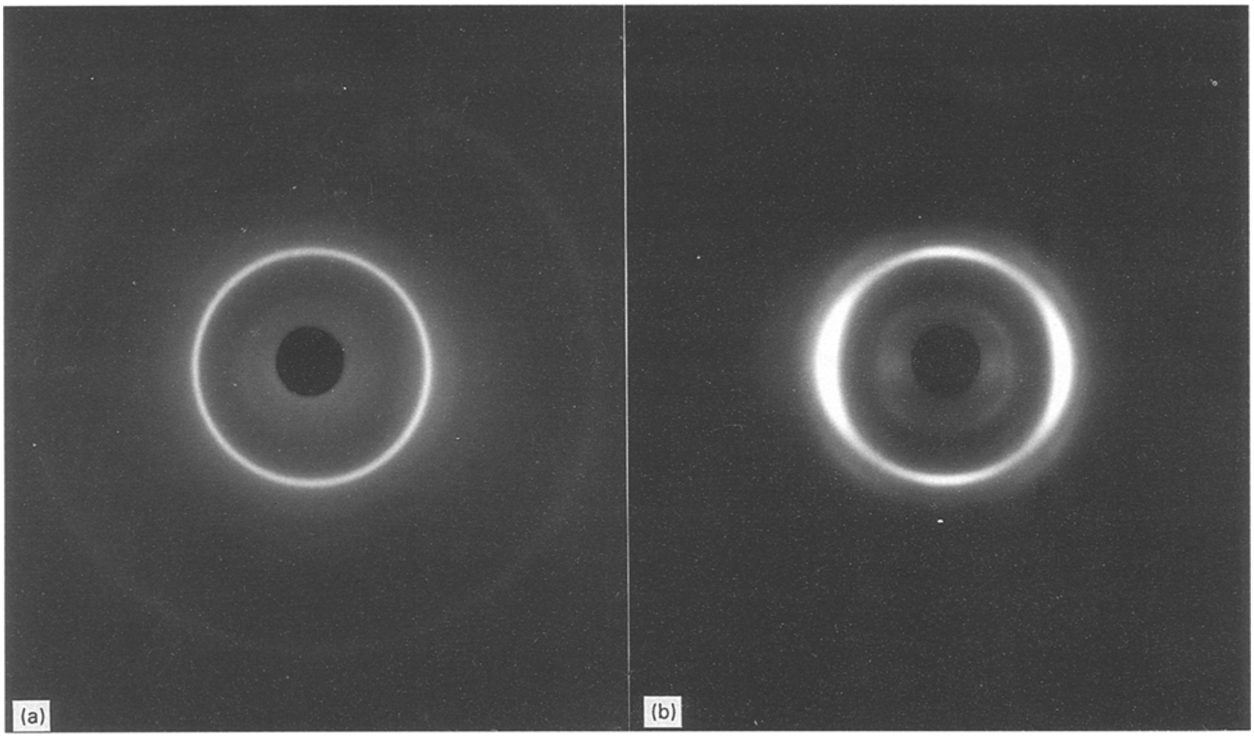

Figure 3 X-ray diffraction photographs taken with the incident beam (a) perpendicular (through view) and (b) parallel (edge view) to the film plane of the special dried film before drawing. The photograph of the edge view is set so that its vertical line is parallel to the film plane.

ageing. These values are almost the same or a little higher than those reported by Cha *et al.* who produced PVA fibres by gel spinning of the 80:20 solution [7]. It is interesting that similar results can be obtained by these two methods which are totally different with respect to the time required for producing fibres or drawn films. It took several minutes or several hours by Cha *et al*s method and several months by the authors' method to yield the drawn fibres or films.

The draw ratio is well known as one of the most important and conventional measurements of the mechanical properties of films or fibres, as shown, for example, by Furuhata *et al.* [11]. The DR_{max} of the special film is actually an increasing function of t_a, as shown in Fig. 2c. However, the $DR_{max} = 23$ times the special film after ageing of 120 days, does not seem to be high for its high mechanical properties. The DR_{max} values of Cha *et al*s high strength and high modulus fibres from a PVA of DP = 5000 were between 40 and 50 times. This difference between these results is mainly due to the novel method of drying the gel sheet employed in this paper. The circumference of the gel sheets was fixed by a wooden frame during drying. So the extension force acting against the shrinkage of the sheet must have induced molecular orientation in the directions parallel to the sheet (or film) plane. X-ray diffraction photographs of the undrawn film taken along the different incident directions are shown in Fig. 3: (a) the through view seen perpendicular to the film plane, and (b) the edge view seen parallel to the film plane. These photographs show the presence of some types of crystallite orientation in the film before drawing. This pre-orientation of the crystallites must have apparently decreased the total draw ratio.

The diffraction pattern of the edge view in Fig. 3b is different from that of a rolled PVA film, which was precisely analysed by Tadokoro *et al.* [12]. The edge view of their rolled film could be attributed to only one type of crystallite orientation: its chain axis and the (1 0 1) plane orientate parallel to the film plane. This is called here the (1 0 1) orientation. There are two possible types of interchain hydrogen bonding in the PVA crystal, as shown in Fig. 4; the two bonding directions being almost perpendicular to each other [13]. The chains are most tightly bonded laterally to the chain axes in the (1 0 1) and $(2 0 \bar{1})$ planes through these two kinds of interchain hydrogen bonding. The two planes are the candidates for the plane which orientate parallel to the direction of the applied external force. Thus, the orientation pattern is called using the name of the parallel plane, for example, the (1 0 1) orientation, as described above. The extension force applied to the film on rolling must be stronger than that on drying. The fact that only one type of orientation, the (1 0 1) orientation, was detected in the rolled film indicates that hydrogen bonding in the (1 0 1) plane is more durable against the external extension force than that in the $(2 0 \bar{1})$ plane. The latter is expected to appear only at a low level of applied force. The rolling resulting in the (1 0 1) orientation must produce serious destruction of the crystallites.

The edge view, however, cannot be explained by one pattern of orientation, although it partly resembles the pattern of the rolled film. The edge view can be explained as a mixture of two orientation patterns: one is the (1 0 1) orientation described above and the other is the $(2 0 \bar{1})$ orientation. The latter means that the $(2 0 \bar{1})$ plane and the chain axis both orientate parallel to the film plane. The two patterns are illustrated in

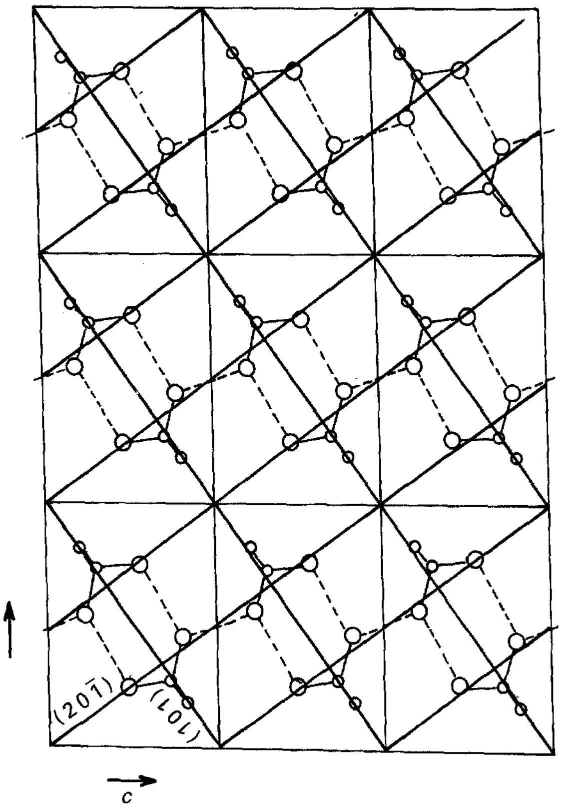

Figure 4 The two particular planes, the (1 0 1) and $(2 0 \bar{1})$ planes, in which the chains are most tightly bonded laterally to the chain axes through hydrogen bonding. The projection of the unit cell on the *a–c* plane is from Bunn's model [13]: (O) oxygen, (○) carbon, (- - - -) hydrogen bonding.

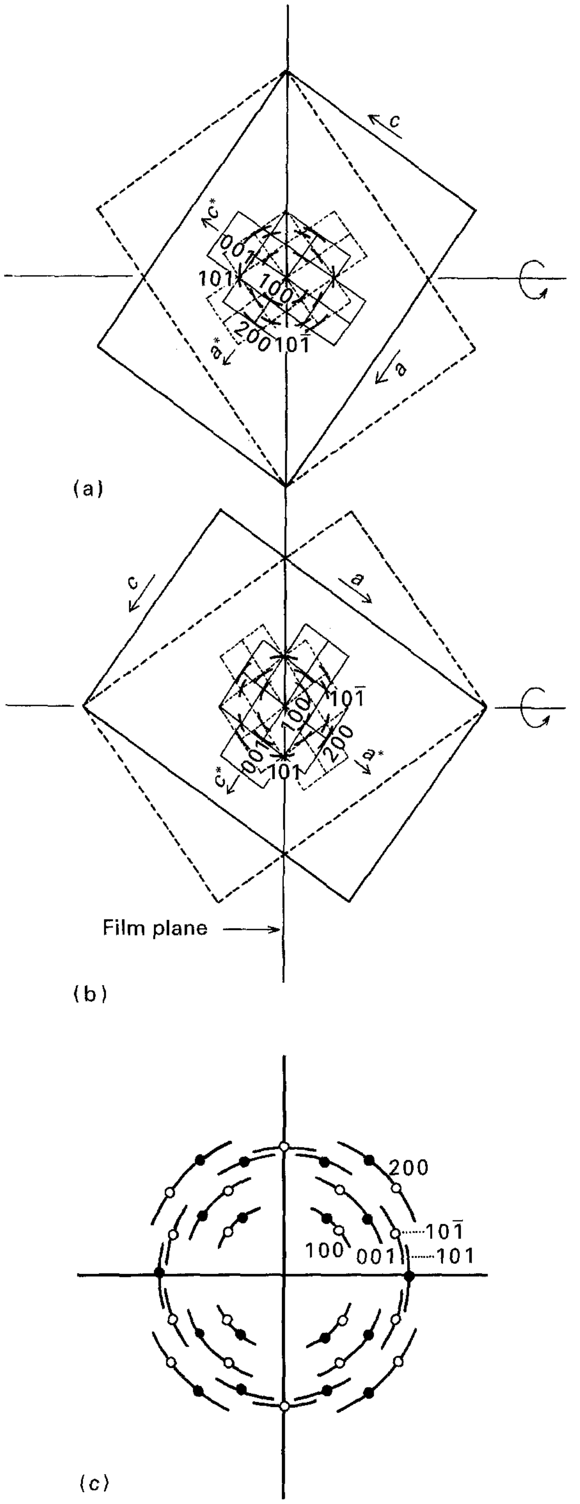

Figure 5 Schematic representation of the orientation pattern for the edge view shown in Fig. 3b. The large rectangles in (a) and (b) represent the projections of the unit cell of the PVA crystal on the *a–c* plane and the lattices superimposed on the projections are the corresponding a^*–c^* reciprocal lattices. (a) the (1 0 1) orientation pattern, (b) the $(2 0 \bar{1})$ orientation pattern, and (c) an artifact of the edge view by superimposing the (1 0 1) pattern (●) and the $(2 0 \bar{1})$ pattern (○). The crystallites illustrated in (a) and (b) randomly orientate around the normal of the film plane keeping both the chain axis and their own hydrogen bonding plane parallel to the film plane.

Fig. 5a, b, respectively. An artifact of the edge view is given in Fig. 5c by superimposing the two patterns of orientation, the (1 0 1) orientation and $(2 0 \bar{1})$ orientation, on each other. This view successfully reproduces the observed edge view in Fig. 3b, although the 0 0 1 diffraction was too weak to be detected in Fig. 3b. The characteristic strong four-point spots, two of which are located on the meridian and the other two of which are on the equator, are shown to be composed of overlapping (1 0 1) and $(1 0 \bar{1})$ reflections, comparing Figs 3b and 5c. In conclusion, the shrinkage of the film in the directions parallel to the film plane caused during drying creates a mildly orientated structure in which the $(2 0 \bar{1})$ orientation can be induced in addition to the (1 0 1) one. The observed edge view indicates that the proportion of the $(2 0 \bar{1})$ orientation is somewhat smaller than that of the (1 0 1) one. Further, the presence of the two orientations may afford the subsequent high drawability of the film, resulting in the high degrees of crystallinity and high birefringence, which will be discussed in the following sections.

The crystallinity of the special film drawn to its DR_{max} was estimated from the peak area (heat of fusion) of the melting endotherm of the DSC curve and from the density. Both estimation methods are based on the assumption that the film has a single crystal phase and a single amorphous phase. The nature of the crystal phase will be discussed in a later section based on the DSC results. The two kinds of crystallinity for the drawn special film showed a similar trend with each other, as shown in Fig. 6a, though the X_c from the heat of fusion is always higher than that from the density. The difference between the two methods will not be discussed in this study. The crystallinity of the special film after ageing for 120 days is as high as 70%, even estimated from the density.

Fig. 6b shows the birefringence, Δn, of the drawn special film as a function of ageing time. Both X_c and Δn are increasing functions of ageing time. Their values for films after ageing for 120 days are quite high. The value of Δn (51×10^{-3}) is close to the reported intrinsic birefringence of the crystal phase ($\Delta n_c = 51.8 \times 10^{-3}$) [14]. The highly orientated structure expected from this high Δn value can also be seen in the X-ray diffraction pattern of the drawn film in Fig. 7. A high degree of orientation of the crystal phase detected in the drawn film after ageing for 120 days (Fig. 7b) could also be obtained in the film from the unaged gel (Fig. 7a). This result implies that the increases in crystallinity and in the degree of orientation of the amorphous chain are the possible causes of the increase in Δn with t_a. However, in spite of the high crystallinity of this film, the extraordinarily high observed value of Δn cannot be guaranteed by a corresponding crystallinity lower than 100%. These results imply that the crystal structure in the drawn films is basically different from that of the ordinarily obtained PVA materials. One of the possible crystal structures may be the extended chain crystal that has been observed in high strength and high modulus UHMWPE fibres [11, 15–17]. Besides such a transformation from the ordinary crystal phase to the extended chain crystal phase and/or the increase in crystallinity, the increase in orientation of the amorphous polymer chain must have played an important role in increasing the birefringence.

The diffraction spots in Fig. 7b are much narrower than those in Fig. 7a. Only one film specimen was used

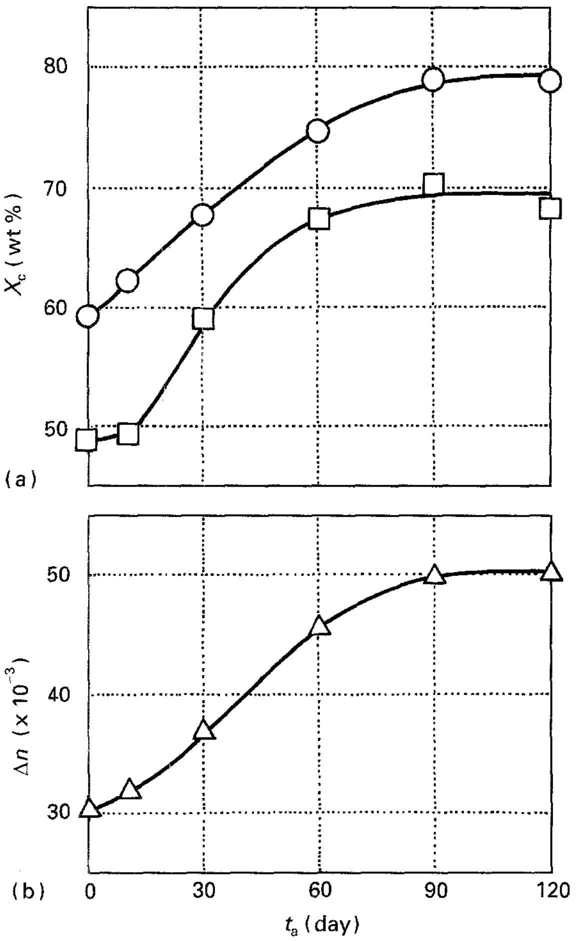

Figure 6 (a) Crystallinity, X_c, and (b) birefringence, Δn, of the special film, which means the film prepared from the gel aged in water at 10 °C, as functions of ageing time, t_a. The draw ratios of these films are shown in Fig. 2c. The crystallinity was obtained from the heat of fusion (○) and from the density (□).

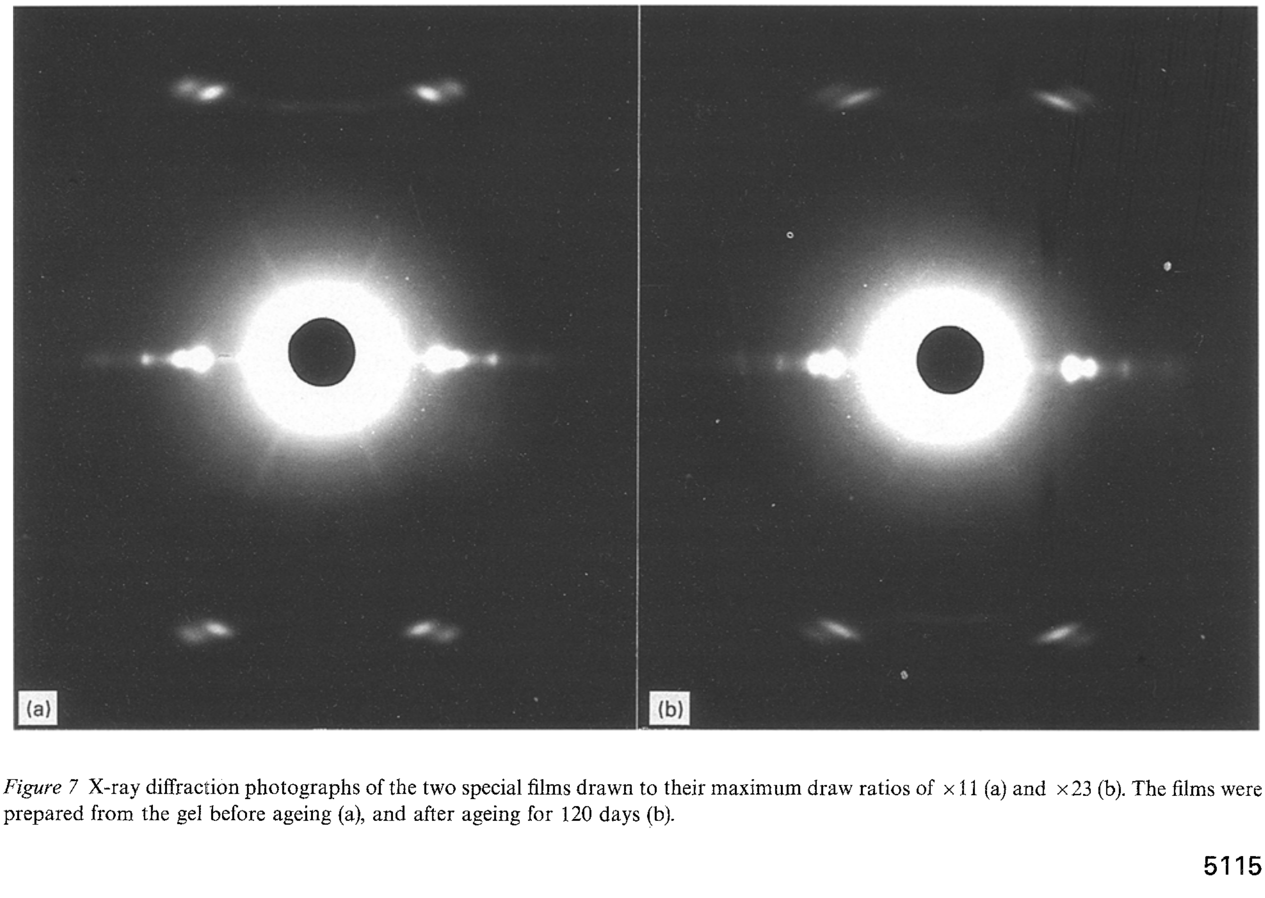

Figure 7 X-ray diffraction photographs of the two special films drawn to their maximum draw ratios of ×11 (a) and ×23 (b). The films were prepared from the gel before ageing (a), and after ageing for 120 days (b).

for both X-ray photographs. This difference indicates that the size or the degree of molecular packing in the crystal phase can be increased to a fairly high level by ageing fully and subsequent drawing.

The films from the gels aged under the other ageing conditions (at 30 and 50 °C or in the 80:20 solvent) were also drawn, and their DR_{max} and mechanical properties were compared with those of the special film, as shown in Fig. 8. It should be noted that the original gels of the drawn films shown in Fig. 8 were all aged so fully under their ageing conditions that the mechanical properties of the drawn films reached their highest achievable values. The ageing time required for ageing fully was 120 days for ageing at 10 and 30 °C and 60 days at 50 °C. The time evolution of the mechanical properties and DR_{max} of the film from the gel aged in the 80:20 solvent at $T_a = 10\,^{\circ}C$ is shown by the open circles in Fig. 2 (the results of the other films except for the special film were almost the same as those shown by the open circles in Fig. 2). The mechanical properties of the films from the gels aged under the conditions, except for the special ageing, were at a lower level than those from the special ageing. This is the reason why ageing in water at 10 °C is called special ageing.

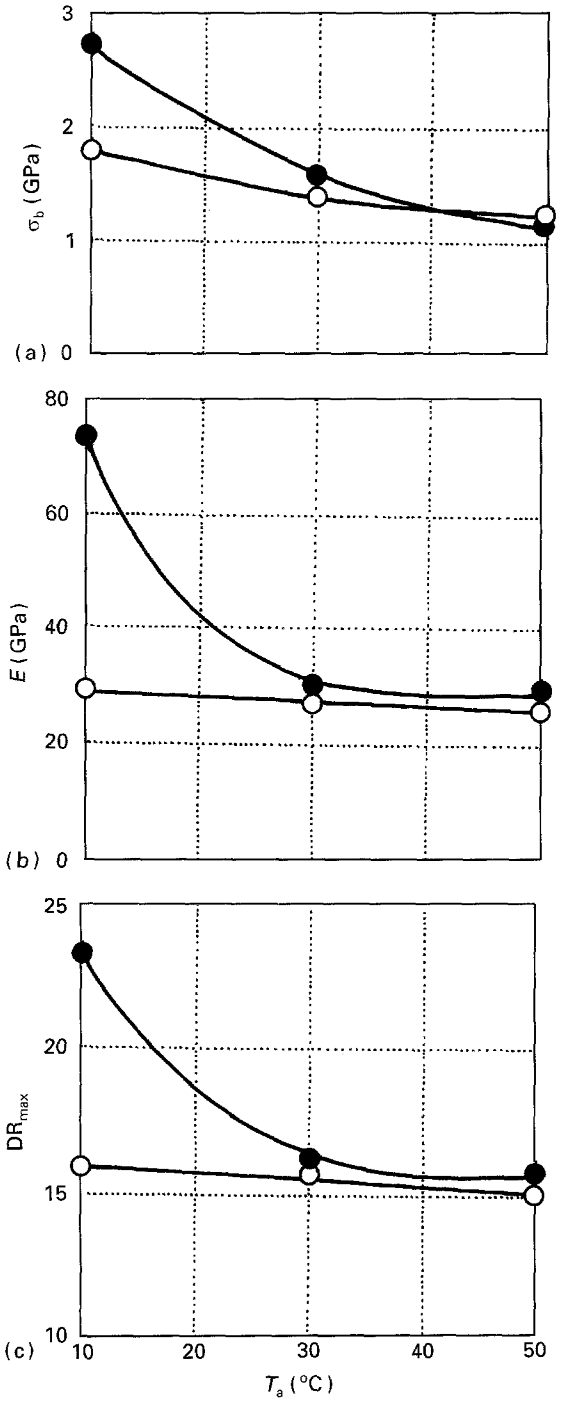

Figure 8 (a) Tensile strength, σ_b, and (b) tensile modulus, E, of the films drawn to their highest achievable draw ratios (DR_{max}) shown in (c) as functions of ageing temperature, T_a. The films were prepared from gels fully aged in water (●) and in DMSO:water (v/v) = 80:20 solvent (○).

The highest values of E and σ_b of the special film are guaranteed by its high drawability, as shown in Fig. 8c. No significantly different pattern of the edge view was obtained for the film before and after ageing for 120 days. This means that the increase in DR_{max} with t_a depends heavily on the increase in the drawability of the chains during subsequent drawing process, rather than the orientation during drying. The crystallites are orientated without unfolding of the crystalline chains in the course of the drying process, because the shrinkage force is not strong enough to cause unfolding. The extension force applied during the following drawing process, however, causes the unfolding of the chains of the crystallites. Therefore, the drawability of the film depends on whether the unfolding occurs smoothly. The crystallites formed in the special film may have a lower number of defects or entanglements than the other films before drawing.

Fig. 9 shows a series of DSC traces of the drawn special films which were aged for different periods of time. The melting curves before and after ageing for ten days are the same as those ordinarily obtained for PVA materials. The curves after ageing for more than 30 days, however, have another melting peak at the higher temperature side of the ordinary peak; although the latter peak should be called a shoulder in some cases. The two crystallites corresponding to these two peaks are called the high (h) and low (l) melting temperature, T_m, forms. Such two-peak melting curves have been reported by Cha *et al.* [7]. The two endotherms of their DSC curve for highly drawn fibres were clearly separated peaks. Contrary to the authors' case, the area of their hT_m endotherm was smaller than that of their lT_m endotherm. The hT_m form is thought to be another kind of crystallite, namely the extended chain crystallite, as described above. This extended chain crystallite is assumed to be formed in the course of the drawing process approaching a high draw ratio of around 20 or 25 times.

The heat of fusion, ΔH, and the melting temperature determined as the peak area and peak temperature of the endotherms in Fig. 9, respectively, are plotted as functions of t_a in Figs 10 and 11, respectively. The two-peak endotherms were separated into two individual peaks to estimate the heat of fusion of the two forms (ΔH_l for the lT_m form and ΔH_h for the hT_m form), as illustrated on the curve for 30 day ageing in Fig. 9. The crystallinity values calculated from the total heat of fusion, ΔH_t ($= \Delta H_l + \Delta H_h$), have already been shown by the open circles in Fig. 6a. The ΔH_l

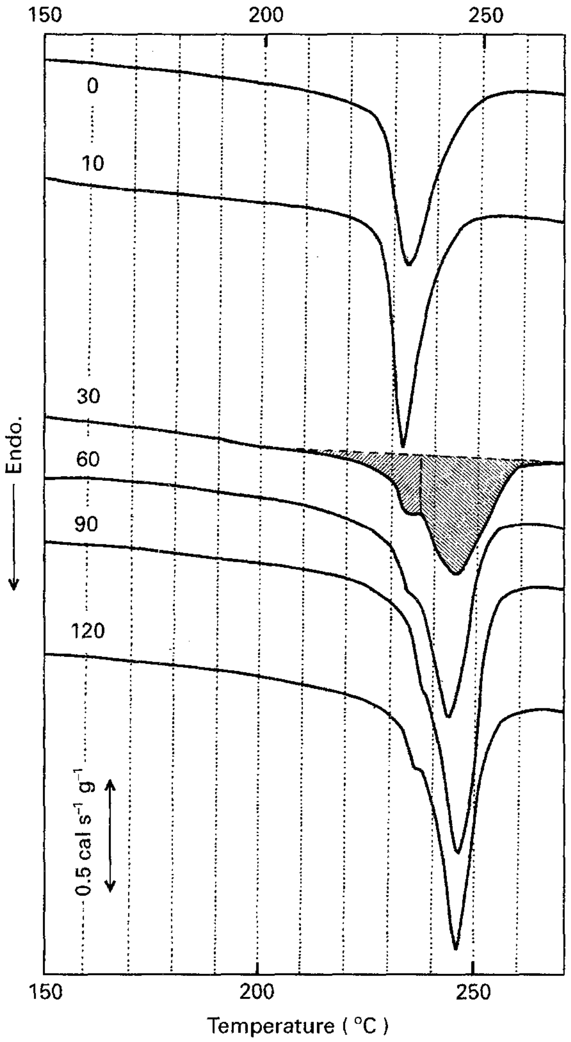

Figure 9 DSC traces for the special drawn films from the gels aged in water at 10 °C for the ageing times (days) indicated.

and the ΔH_h curves show that the fraction of the hT_m form increased with increasing t_a, whereas the T_m of the hT_m form is almost constant at all t_a. The endotherm of the hT_m form becomes sharper with increasing t_a, which indicates the increases in the size of the crystallite and/or the order of molecular packing in the crystallite. This is in accordance with the result described in Fig. 7.

Fig. 12 shows the DSC curves of the drawn films prepared from the gels aged fully under several ageing conditions. The two-peak figure of the melting endotherm for the film prepared under the special ageing condition is the most obvious amongst all the curves. The position of the major peak, probably corresponding to the hT_m peak, is higher in the film aged at higher T_a and aged in water rather than in the 80:20 solvent. However, the drawn film from the gel aged in water at the highest ageing temperature of 50 °C has a lower E and σ_b than the special film. These lower properties are supported by the lower DR_{max} in Fig. 8c, the lower crystallinity in Fig. 13a and the lower birefringence in Fig. 13b.

A series of solid curves in Fig. 14 show the DSC traces of the undrawn special films which were prepared from the gels aged for the different t_a indicated. Contrary to the drawn films in Fig. 8, the melting endotherm shows no significant change with t_a. The heat of fusion and the melting temperature of these films are shown by the open circles in Figs 10 and 11, respectively. This behaviour was also the case with all of the undrawn films used, although the melting temperature of the film slightly increased with the increase in ageing temperature. The two DSC curves for the undrawn films from the gels aged in water at 30 and 50 °C are shown by the broken lines in Fig. 14. These curves show that the hT_m form is formed in the drawing process.

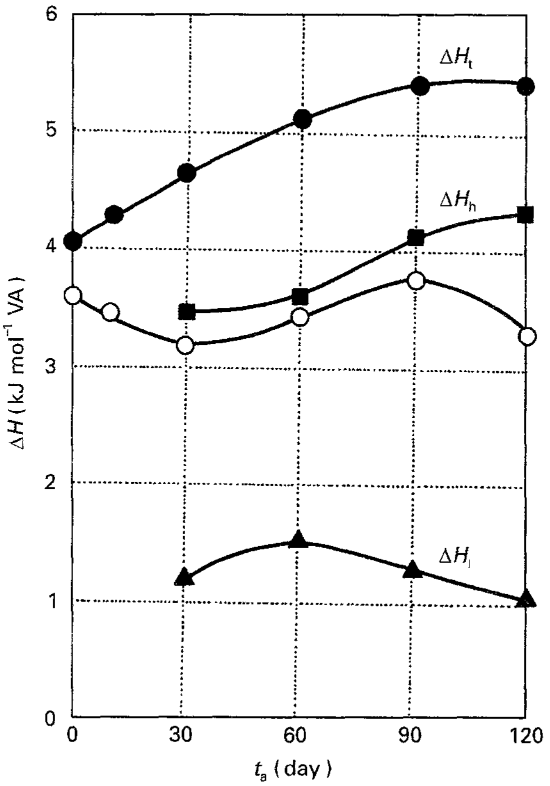

Figure 10 The heats of fusion, ΔH, of the films before (○) and after (●) drawing at 200 °C are shown as functions of ageing time, t_a. The heats of fusion of the drawn films are also shown as those of their hT_m form (■) and lT_m form (▲).

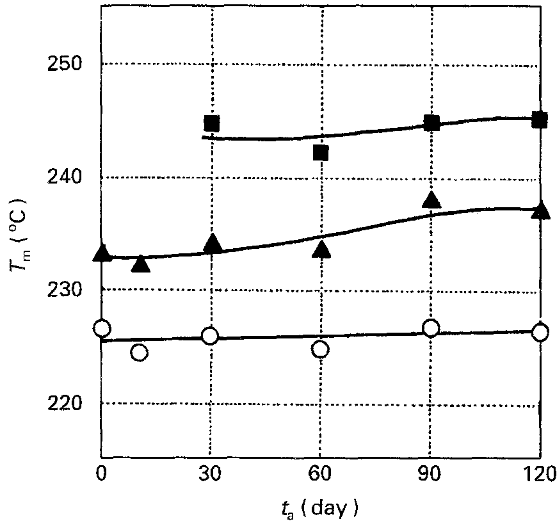

Figure 11 The melting temperature from the peak temperature of the melting endotherm, T_m, for the films before (○) and after (■, ▲) drawing at 200 °C as functions of ageing time, t_a. The drawn film had two melting temperatures, hT_m (■) and lT_m (▲).

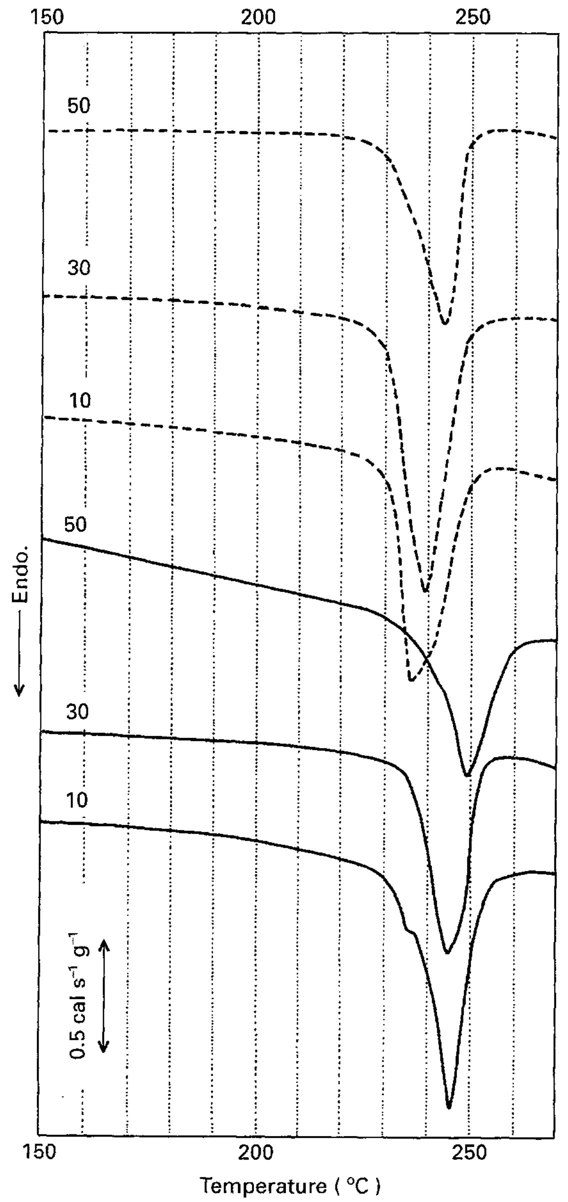

Figure 12 DSC traces of the drawn films from the gels aged fully in water (——) and DMSO : water (v/v) = 80 : 20 solvent (- - -) at the ageing temperatures (°C) indicated.

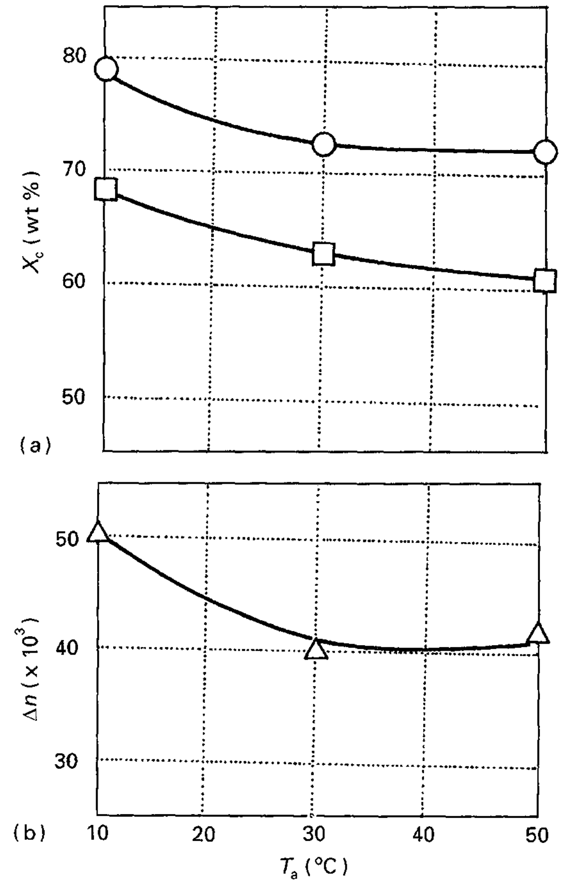

Figure 13 (a) Crystallinity, X_c, and (b) birefringence, Δn, of the drawn films prepared from the gels aged fully in water at the three ageing temperatures. The draw ratios (DR_{max}) of these films are shown by the solid circles in Fig. 8c. The crystallinity was obtained from the heat of fusion (○) and from the density (□).

3.2. Aged gels

Fig. 15 shows a series of DSC traces of the gels aged under the special condition for different periods of ageing time. The melting endotherm of the gel after ageing for 120 days is composed of the three components A, B and C, as found in the previous report. A process of pressing the melt gel and subsequent cooling at −34 °C was added between the first gelation process and the ageing process in the preparation method reported in the previous paper. This additional process is called the pressing process. Further, the gel in this report was stored in the ageing solvent from the beginning of ageing, whilst the gel in the previous paper was aged in a sealed test tube without the ageing solvent. The latter gel, however, was inevitably soaked during short ageing times (about ten days) the solvent which oozed from the gel itself. The composition of the ageing solvent was changed from the 80:20 solvent to a 0:100 composition in some cases in this report. In spite of these different points, the three endotherm components have been similarly observed in the gels prepared by the two methods.

The gel before ageing (t_a = zero days) in Fig. 15 was also the gel before the pressing process. Two components are detected on the DSC curve of this gel, although its high temperature component is detected with difficulty as a shoulder. This component is considered to be the A component which is formed in the solution, rather than in the gel phase, in the course of the cooling process of the original solution from 100 to −34 °C. On the other hand, the main component of the low temperature one of the original gel may be attributed to the B component. The endotherm of the gel aged for ten days is clearly separated into the A and B components. The area of the endotherm of the gel aged for ten days becomes smaller compared with that of the original gel. One reason for this is that the pressing process, melting at 75 °C and recooling at −34 °C, must have temporarily introduced a decrease in crystallinity. The main component which was once melted and recrystallized should be the B component, the crystallinity of which is decreased. However, such a large reduction in the endotherm area is still questionable, because a rapid reduction of ~ 40% of the weight of the original gel was observed to be completed in a one day ageing period. It should be noticed that the endothermic heat flow in Fig. 15 is normalized by the unit mass of the gel. The authors are

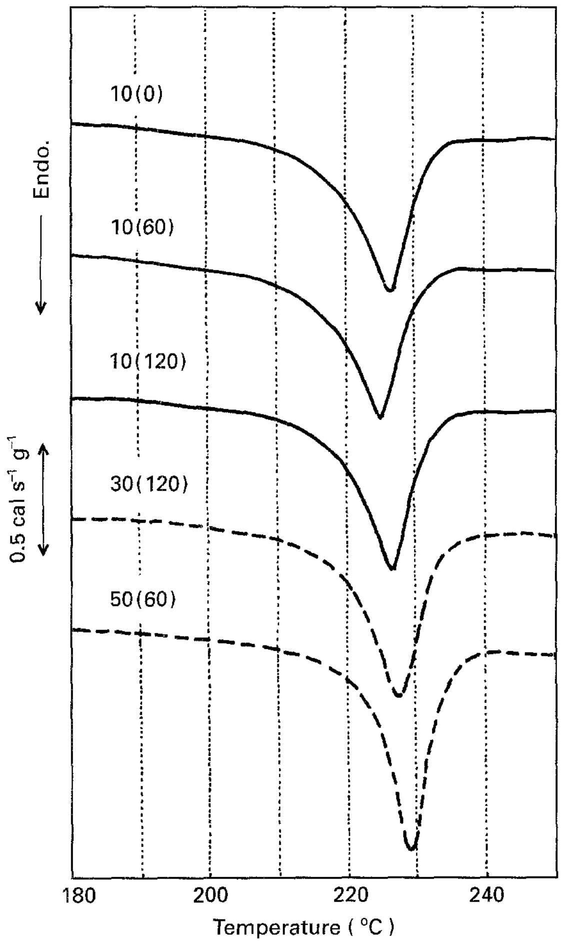

Figure 14 DSC traces of the undrawn films prepared from gels aged in water at the ageing temperatures (°C) indicated for the ageing time indicated in parentheses.

going to study in detail the change in the gel structure at the very beginning of ageing.

On the DSC curves of the gels aged longer than 60 days in Fig. 15 appear the A and B components of whose peak points are obviously higher than those of the immature gels and the C component which was not detected in the immature gels. The shifts of the A and B peak temperatures and the appearance of the C component must be the reason for the observed increase in the mechanical properties of the final drawn films with ageing.

This speculation is verified by comparing the DSC curves for the fully aged gels under several conditions, as shown in Fig. 16. A sharp peak is detected on the curves of the gels except for those aged in water at 10 and 30 °C. This sharp peak should be attributed to the A component. In the previous paper, the A component was defined as the component located at the high temperature end of the endotherm and its shape was remarkably sharp compared with the other components. In the strict sense of the term, the attribution done here is not based on the authors' first definition, but follows the character of the A component. This confusion is due to the fact that such sharp peaks located at the centre of the endotherm had not appeared in the previous paper. How to attribute the endotherm more clearly to the three components is also a problem that one has to solve in the future. Another important result in Fig. 16 is that the matured B and C components were observed only in the special gel. In conclusion, the necessary condition for the high strength and high modulus film is that the fully grown B and C components are contained as much as possible in the gel, resulting in restraint of the growth of the A component. The ageing in water at high T_a and in the 80:20 solvent at 10–50 °C should not be suitable conditions for the growth of the B and C components, probably because the growth rate of the A component is larger than those of the B and C components under these conditions.

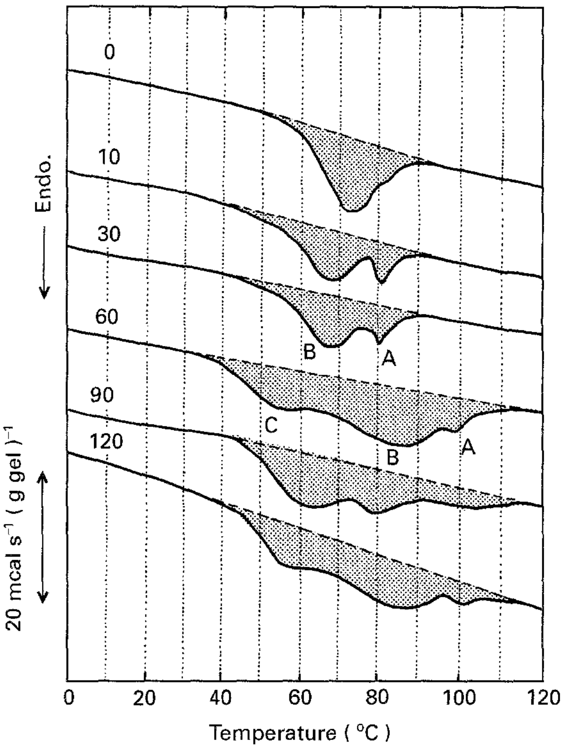

Figure 15 DSC traces for the gels aged in water at 10 °C. The numbers on the curves indicate the ageing times (days). The zero day gel is the original gel before pressing.

If the nucleation of the A components occurred in the cooling process of the original solution and can not take place once the gel phase is formed, then a more rapid quenching may be able to prevent the nucleation of the A component. Further, the best high strength and high modulus film will be obtained from these gels composed only of the B and C components. One problem involved in the method is that the media for cooling the solutions in the first and second gelation processes was the cooled air in a refrigerator. Thus, the heat conductivity might not be good compared with liquid cooling medium. This implies that the crystallization of the A crystallites would be favoured by the slow cooling rate. If one uses a liquid cooling medium, the fraction of the A component in the resultant gels would be lower than that obtained in this study.

The high drawability of the special film is thought to be due to the gel structure corresponding to the B and C components. The B and C crystallites should have a very high degree of molecular packing order and a very small number of defects, such as entanglements and vacancies. Such crystallites may be smoothly unfolded by the external extension force and recrys-

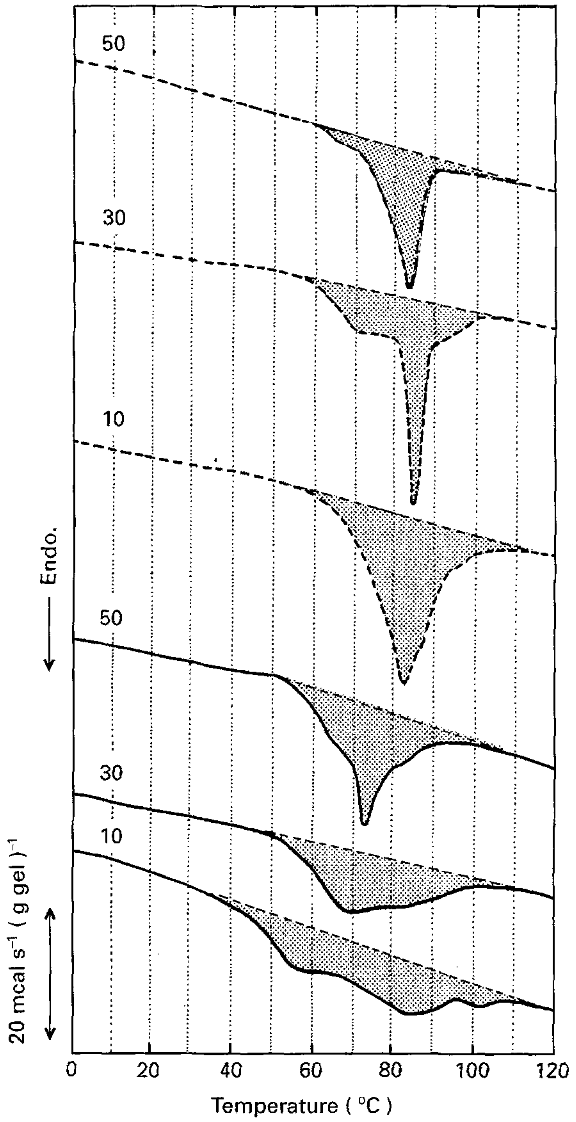

Figure 16 DSC traces for the gels aged in water (——) and in DMSO : water (v/v) = 80 : 20 solvent (- - - -) at the ageing temperatures (°C) indicated.

tallize into highly extended chain crystallites. The lower melting temperature of these components than that of the A component is thought to be related to the smaller size of the B and C crystallites than that of the A components or to the presence of totally different crystal structures for the three components. The second most important factor by which the highly extended structure can be introduced in the special film is the mild orientation of the crystallites induced in the drying process of the gel sheet. Such a mild orientation of the PVA crystallites may be difficult to induce by rolling the dried film.

4. Conclusions

High strength and high modulus PVA materials have been obtained by a gel ageing method. The method involves some structuring processes, which are important for the high mechanical properties of the resultant film. The most important process is the ageing of the gel in water at the low temperature of 10 °C, which allows low melting temperature crystallites of the B and C components to grow in the gel. The second most important process is drying the aged gel by fixing it in a frame to obtain a film with mildly orientated crystallites in the film plane. The particular orientation thus obtained facilities the extension of the chains in the subsequent drawing process. The moulding of the original gel into the gel sheet is also very important, because it facilitates the subsequent processing of the gel or film. The ageing method still has potential. The degree of polymerization of the PVA powder used in this study is not as high as those used in other studies which aimed at high strength and high modulus PVA materials. If a PVA with a higher DP is used in the ageing method, films with a higher draw ratio and thus with much better mechanical properties will be produced. The conditions of ageing, e.g. the ageing temperature, should be more precisely examined. The results indicate that ageing at temperatures below 10 °C would be more suitable for the growth of B and C components.

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