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

Part II *The effect of the gel pressing temperature*

T. TANIGAMI*, H. SUZUKI, K. YAMAURA, S. MATSUZAWA
Department of Materials Chemistry, Faculty of Textile Science and Technology,
Shinshu University, Ueda, Nagano 386, Japan
E-mail: tanigam@giptc.shinshu-u.ac.jp

It was reported in our previous paper that a relatively high-strength and high-modulus drawn poly(vinyl alcohol) (PVA) film could be obtained from aged gel sheet. In this paper, the effect of pressing temperature, at which the original PVA/dimethylsulphoxide/water gel was pressed into the gel sheet, on the tensile properties (modulus and strength) of the finally obtained drawn film is reported. The properties of the drawn films are discussed in relation to the structure of the undrawn films and the gel sheet, by birefringence and molecular orientation measurements, differential scanning calorimetry, and X-ray diffraction methods. As a result, the content of the low melting-temperature crystal component in the pressed gel is shown to be the most effective factor affecting the properties of the drawn film.

1. Introduction

A new method for preparing high-strength and high-modulus poly(vinyl alcohol) (PVA) film was proposed previously [1]. In this method, the PVA gel that is prepared by chilling a PVA solution (10 wt %) in a mixed solvent of dimethylsulphoxide (DMSO) and water (DMSO : water = 80 : 20 (vol/vol)) at −34 °C for 1 day is pressed into a gel sheet. For ageing, it is then stored in water at 10 °C for several months. This aged gel sheet is dried and then drawn at 200 °C. The highest achievable tensile strength and the modulus of the drawn film were 2.8 and 72 GPa, respectively. This method is called the gel-ageing method.

Another type of PVA, with a higher average molecular weight value than the PVA material used in the previous paper, was selected as the next PVA material in this series of our work. The average degree of polymerization of the materials was 2600 in the previous paper and 5000 in this paper. We hoped that even such a small increase in molecular weight would result in higher tensile properties, as the high-strength and high-modulus fibres could be produced from ultra-high molecular weight polyethylene [2]. However, the effect of the molecular weight could not be discussed in this paper.

In the previous paper, the original bulk gel was moulded into the gel sheet at 70 °C [1]. This temperature almost corresponded to the peak of the DSC melting endotherm. It is noted that the endotherm of the gel before moulding had another higher temperature peak. In the present work, the original gel was pressed at various temperatures between 60 and 90 °C, corresponding to the broad melting range of the gel, to study the effect of the pressing temperature on the tensile properties of the final product of the drawn film.

2. Experimental procedure

2.1. Sample preparation

The PVA material used was a product of Unithica Chemical Co. (P-5000) with an average degree of polymerization of 5000. A solution of PVA in a mixed solvent of DMSO/water (vol/vol = 80 : 20 (5 wt %)) was prepared in a flask at 120 °C for 1 h. The solution was subsequently kept at 70 °C for 24 h. It was then poured into a stainless steel container which had been previously cooled at 0 °C. After keeping the container at 0 °C for 5 min, it was stored in a refrigerator at −34 °C for 24 h to transform the solution into the gel, termed the original gel. The gel sheet was moulded from the original gel thus obtained, aged, dried, and drawn by the same method as described in the previous paper [1]. The pressing of the original gel was performed at four temperatures: 60, 70, 80 and 90 °C. The gel-ageing temperature was selected as 10 °C. The solvent for ageing was water. It should be noted that, in the previous paper, the gel was pressed at 70 °C and aged at 10, 30 and 50 °C, in water and in the mixed solvent.

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* Author to whom all correspondence should be addressed.

2.2. Measurements

Density, tensile properties, differential scanning calorimetry (DSC), X-ray diffraction, and birefringence measurements were performed as described in the previous paper [1].

The molecular orientation of the *b*-axis (the fibre axis) with respect to the drawing direction of the film was described by the following orientation function

$$F_{cr} = (3\langle\cos^2\theta\rangle - 1)/2 \tag{1}$$

where θ is the angle between the *b*-axis and the drawing direction, and $\langle\cos^2\theta\rangle$ defines the average value of $\cos^2\theta$. The function was evaluated according to Hibi *et al.*'s method [3]. The orientation function of a transition moment whose axis has an angle θ_j with the *b*-axis is represented by the following equation

$$F_{tm} = F_{cr}F_{\theta j} \tag{2}$$

where

$$F_{\theta j} = (3\langle\cos^2\theta_j\rangle - 1)/2 \tag{3}$$

Following Hibi *et al.*'s method, we used a transition moment corresponding to the infrared band of $1145\ \text{cm}^{-1}$, whose θ_j value was reported as $81^\circ 25'$. Furthermore, F_{tm} can be estimated through the dichroic ratio, D_{1145}, as follows

$$F_{tm} = (D_{1145} - 1)/(D_{1145} + 2) \tag{4}$$

where $D_{1145} = k_{1145,\parallel}/k_{1145,\perp}$, $k_{1145,\parallel}$ and $k_{1145,\perp}$ are the absorption coefficients at $1145\ \text{cm}^{-1}$ measured by an incident infrared ray oscillating parallel and perpendicular, respectively, to the drawing direction of the film.

3. Results and discussion

3.1. Drawn films

The tensile properties of drawn films are shown as functions of the gel-pressing temperature in Figs 1 and 2. The highest achievable values for both the modulus and the strength are somewhat lower than those reported for a PVA of *DP* = 2600 in the previous paper. The strength data in Fig. 2 show no significant variation with either the pressing temperature or the ageing time during ageing, except that the value for the unaged gel pressed at 70 °C is higher than the other values (this will not be discussed in this paper). Contrary to the strength, the modulus is shown to be a variable function of both factors, except for the gel pressed at 70 °C. This characteristic figure is a very important one for the following discussion. The finally obtained modulus values after 30 day ageing are on almost the same level (60–65 GPa). The increase in the modulus up to this final level cannot be realized without ageing for the gels which are pressed at 60, 80, and 90 °C, while the modulus of the gel pressed at 70 °C reached this level without ageing. This suggests the possibility that the most necessary factor for the gel to become a high-strength and high-modulus material by our procedure is the temperature at which the original gel was pressed into the sheet, rather than the ageing temperature, although for the gel which was pressed at unsuitable temperatures (60, 80, and 90 °C), ageing is an indispensable process.

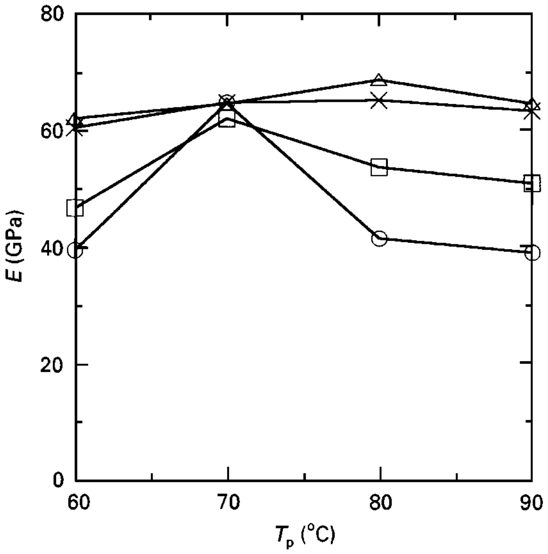

Figure 1 The tensile modulus, *E*, of the drawn film prepared from the gel sheet which was moulded by pressing at the given pressing temperature, T_p, and then aged in water for the given ageing time. Ageing times were (○) 0, (□) 10, (△) 30, and (×) 60 days.

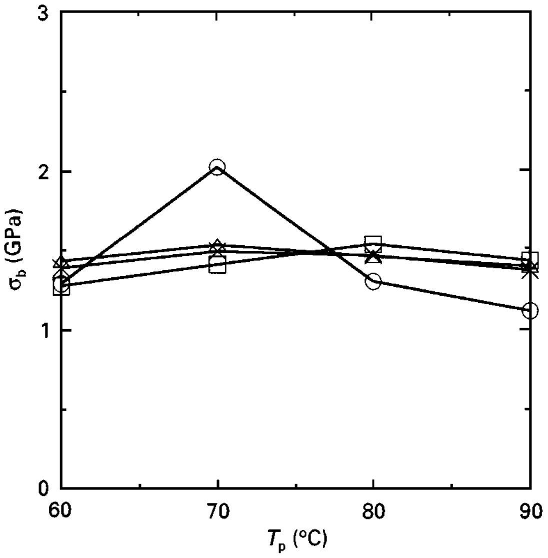

Figure 2 The tensile strength, σ_b, of the same drawn films as those in Fig. 1 as a function of pressing temperature, T_p.

In Fig. 3, the birefringence, Δn, data of the drawn films are shown as a function of the pressing temperature. The change in Δn with ageing is very analogous to that in the modulus shown in Fig. 1. In general, Δn is mainly dependent on the degree of crystallinity, X_c, and the degree of molecular orientation. In the case of PVA, Δn is an increasing function of both factors, because the birefringence of the crystal phase is larger than that of the amorphous phase. The intrinsic birefringence values for the crystal and amorphous phases have been reported by Hibi *et al.* [4] to be 51.8×10^{-3} and 43.8×10^{-3}, respectively. Therefore, which of the factors produces the Δn change is the next question. In Figs 4 and 5, the orientation factors, F_{cr}, of the crystallite estimated from the IR measurements and the

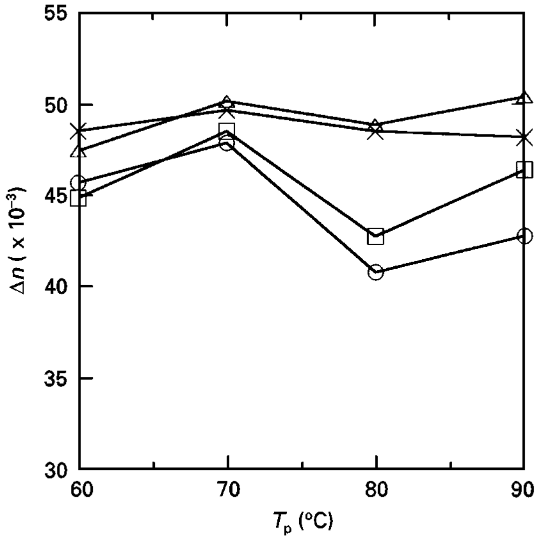

Figure 3 The birefringence, Δn, of the same drawn films as those in Fig. 1 as a function of pressing temperature, T_p.

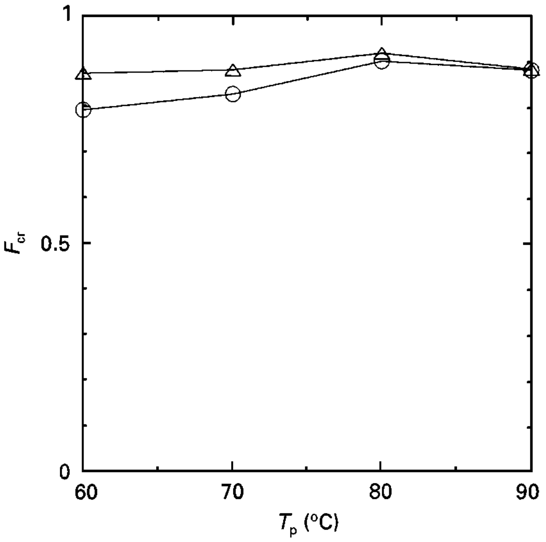

Figure 4 The orientation function, F_{cr}, of the crystal *b*-axis for some of the drawn films in Fig. 1. T_p is the pressing temperature. For key, see Fig. 1.

crystallinity, X_c, from the density measurement are, respectively, shown as functions of the pressing temperature. These results indicate that most of the Δn change can be attributed to the change in the crystallinity. The very analogous variations with ageing time are represented in Figs 1, 3, and 5. The change in the orientation factor is, however, shown to be slightly attributed to the Δn change for the film from the gel pressed at 60 °C. It is believed that the orientation factor of the amorphous molecules generally changes in accordance with the factor of the crystal phase. Therefore, the orientation factor of the molecule is not very different between the crystal phase and the amorphous one.

The draw ratio of the film is shown as a function of the pressing temperature in Fig. 6. The ratios of all the films are at a high level, ranging from 15–18, regardless of both pressing temperature and ageing time. These draw ratios are somewhat smaller than that of 23 of the drawn films having the highest achievable modulus and strength in the previous paper. The latter drawn film had almost the same values of birefringence and crystallinity as the highest achievable values in this paper. Thus, there is no significant difference in the mechanical properties between the films obtained in the previous paper and this one, although the lower strength value in this paper may be due to the slightly larger number of defects introduced in the drawn films. The latter is partly supported by the fact of the lower draw ratio. However, the difference cannot be discussed as directly relating to the difference in the molecular weight between the two PVAs, because the effect of the polymer concentration of the initial solution on the properties of the gel is still an unsolved problem for us.

The highest achievable values of Δn in the previous and this paper are both about 50×10^{-3}, corresponding to the intrinsic birefringence of the PVA crystal phase [4]. The fact that such a high value was obtained in the film where the crystallinity is substantially lower than 100% indicates the underestimation

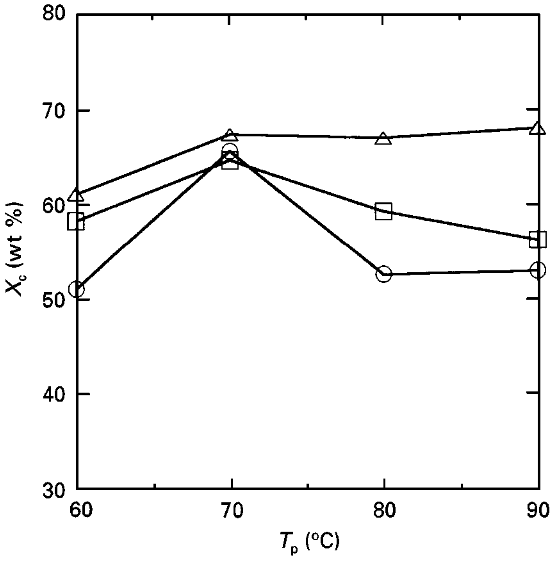

Figure 5 The crystallinity obtained from the density measurement, X_c, for some of the drawn films in Fig. 1. T_p is the pressing temperature. For key, see Fig. 1.

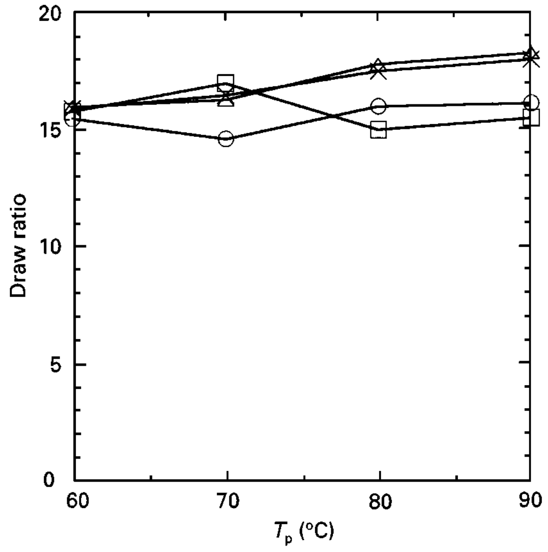

Figure 6 The draw ratio of the same drawn films as those in Fig. 1 as a function of pressing temperature, T_p. For key, see Fig. 1.

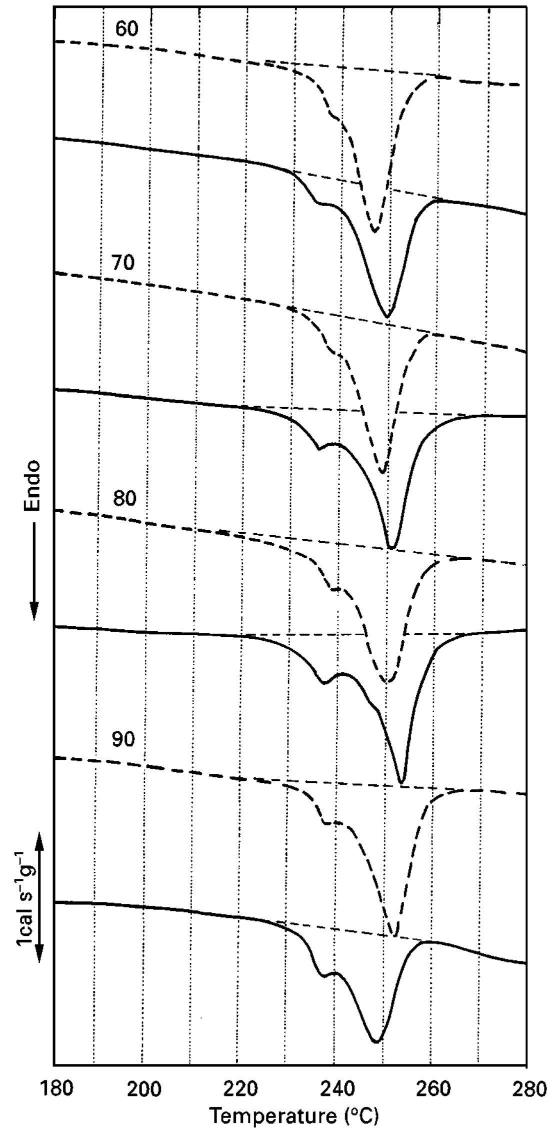

Figure 7 DSC traces of the drawn films from the gel sheets (– – –) before ageing and (——) after ageing for 60 days. The numbers in the figure represent the gel-pressing temperature, T_p.

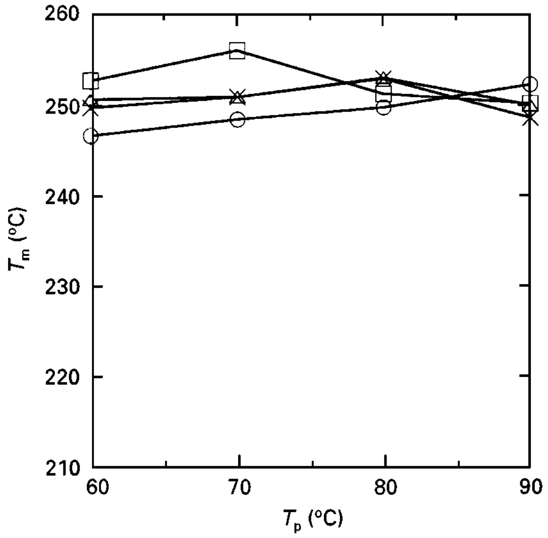

Figure 8 Melting temperature, T_m, obtained from the higher melting-peak temperature of the DSC trace of the drawn films (see Fig. 7). For key, see Fig. 1.

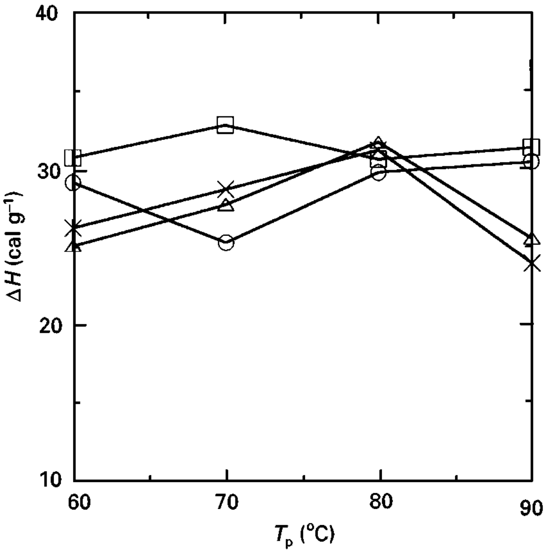

Figure 9 Heat of fusion, ΔH, obtained from the DSC trace of the drawn film is shown as a function of pressing temperature, T_p. ΔH is estimated as the whole area of the melting endotherm. For key, see Fig. 1.

of the intrinsic birefringence. Recently, rather higher birefringence (59×10^{-3}) has also been reported for the drawn films of a PVA with a higher syndiotacticity [5].

Why the films drawn from the insufficiently aged gels which were pressed at 60, 80, and 90 °C have relatively low crystallinity is the main problem that we have to solve.

DSC curves in Fig. 7 show the melting endotherms for the drawn films from the gels pressed at various temperatures. All of the curves have a similar shape: a main peak at around 250 °C and a smaller shoulder at 238 °C. No significant dependency of the curve shape on the gel-pressing temperature can be seen, nor on the ageing time. The melting temperature (the higher component) and the heat of fusion, ΔH, estimated from the whole melting endotherm, are plotted against the pressing temperature in Figs 8 and 9, respectively. Neither figure is analogous to Fig. 1. The ΔH curves in Fig. 9 should have been similar to the crystallinity curves estimated by the density measurements (in Fig. 5). The molecular orientation relaxation must have occurred during the heating run in a DSC pan, as is often the case with such very highly drawn films. The scattering of the data in Fig. 9 is due to the different degrees of relaxation between the samples during measurements. The degree of relaxation depends on the strain which is forced on the samples when they are packed into the DSC pans. This is one of the reasons why we estimated the crystallinity from the density in Fig. 5.

The two-peak shape of the melting endotherm becomes more apparent in Fig. 7, compared with the corresponding data in the previous paper, because the higher melting-temperature peak shifts to a higher temperature. The T_m values from the higher melting-temperature peaks plotted in Fig. 8 are around 250 °C, which are amongst the highest melting temperatures ever found in the films and fibres produced from atactic PVA. Such a high melting temperature is not a prerequisite for high-strength and high-modulus materials, because of the possibility of containing large-sized crystallites and/or the highly constrained crystalline molecules, even before drawing. If the crystallites are constrained or of a large size, their drawing process will induce lower molecular orientation or introduce defects into the films.

3.2. Undrawn films

Fig. 10 shows the DSC traces of the undrawn films prepared from the gels pressed at the four temperatures. The melting temperature and the heat of fusion from Fig. 10 are illustrated as functions of the pressing temperature in Figs 11 and 12, respectively. These results do not show any resemblance to the behaviour observed in Fig. 1. Very little dependence of these properties on the pressing temperature and ageing time can be detected. Only a slight difference can be observed in the nature of the melting point shift with ageing time between the high-temperature region above 80 °C and the low region below 70 °C of the pressing temperature; the shift was positive for the gels pressed at 60 and 70 °C and negative for those pressed at 80 and 90 °C.

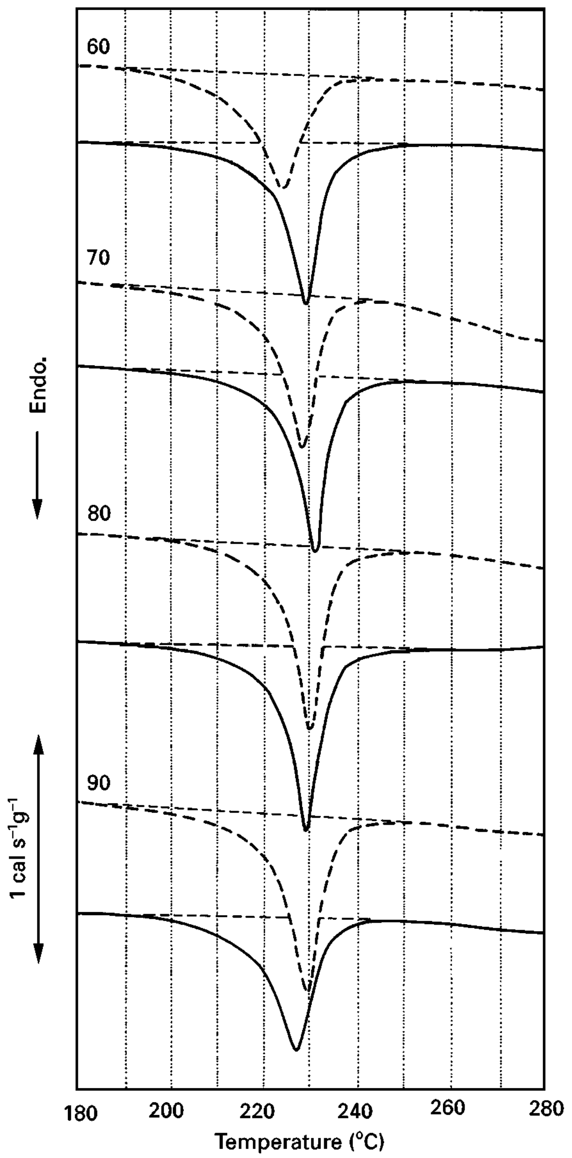

Figure 10 DSC traces of the undrawn films from the gel sheets (– – –) before ageing and (——) after ageing for 60 days. The numbers in the figure represent the gel-pressing temperature, T_p.

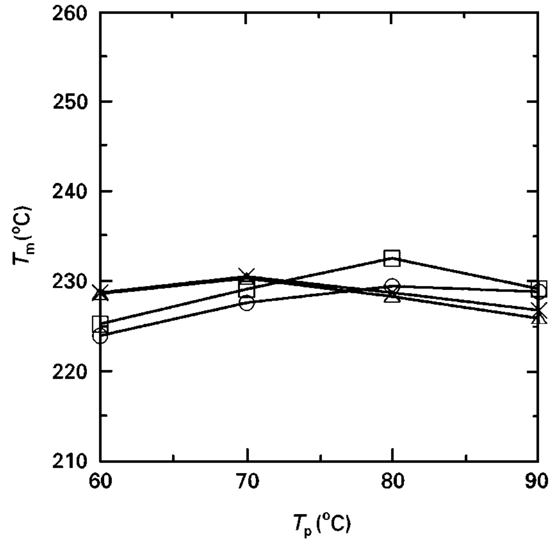

Figure 11 Melting temperature, T_m, obtained from the melting-peak temperature of the DSC trace of the undrawn films (see Fig. 9). For key, see Fig. 1.

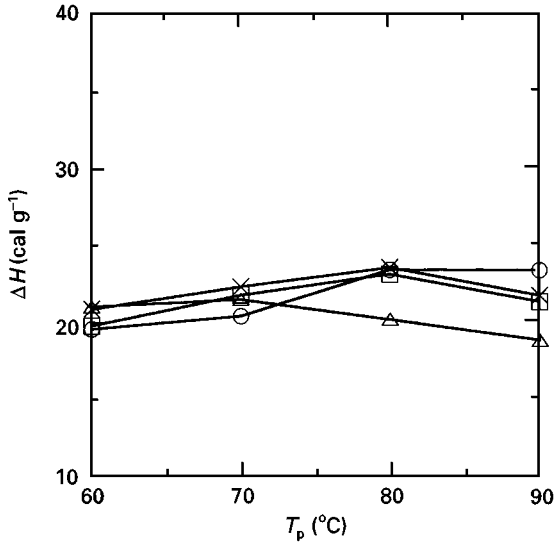

Figure 12 Heat of fusion, ΔH, obtained from the DSC trace of the undrawn film shown as a function of pressing temperature, T_p. For key, see Fig. 1.

Although the ΔH data from DSC in Fig. 9 are scattered, the crystallinity of the undrawn films is lower than those of the drawn films, compared to the data in Figs 9 and 12. In general, the unfolding of the chains from the chain-folded crystallite and the subsequent reorientation occur during drawing to transform the initially randomly oriented crystallites to the highly oriented structure. Through the transformation, the melting temperature and heat of fusion increase. This induces increases in the crystallinity, crystallite size and molecular packing order in the crystallite. The structure of the film before drawing is the key factor on which the finally obtained structure of the drawn films depends. The difference in the structure between the undrawn films cannot be detected from their melting temperature and heat of fusion data.

The aged gel sheet was dried with its edge fixed by a rectangular wooden flame. Therefore, the dried film thus obtained must have caused a type of molecular orientation in the film plane during drying, because the shrinkage force causes the rotation of the crystallites during drying. X-ray diffraction photographs of the two dried films before drawing are shown in Fig. 13. The orientation mode found from these photographs is the same as that found in the previous paper [1]. The orientation was analysed to be composed of the two orientation modes [1]. They were the usually observed mode when the film is strongly deformed by rolling [6] and the other mode which is caused by a mild force, such as the shrinkage force [1]. The change in the mode with ageing was not detected in all in the gel sheets pressed at different pressing temperatures.

3.3. Gels

Fig. 14 shows the DSC traces of the four gel sheets pressed at each pressing temperature and their original gel. The DSC endotherm of the original gel is composed of the two major components corresponding to the two major peaks of the endotherm: the high and low melting-temperature peaks above and below 68 °C, respectively. One of the pressing temperatures (70 °C) coincides with this critical temperature. From the DSC endotherms of the gel sheets before ageing, three groups are found according to their pressing temperatures: gel sheets pressed at 60 °C and 70 °C, and those at 80 and 90 °C. The DSC endotherm of the gel pressed at 60 °C has a very large high melting-temperature component around 75 °C and a small low-temperature component. The gel sheet pressed at 70 °C has a similar endotherm with that of the original gel. The endotherms of the two gel sheets pressed at 80 and 90 °C, respectively, became smaller than that of the original gel, and in each of the endotherms the low-temperature component is smaller than the

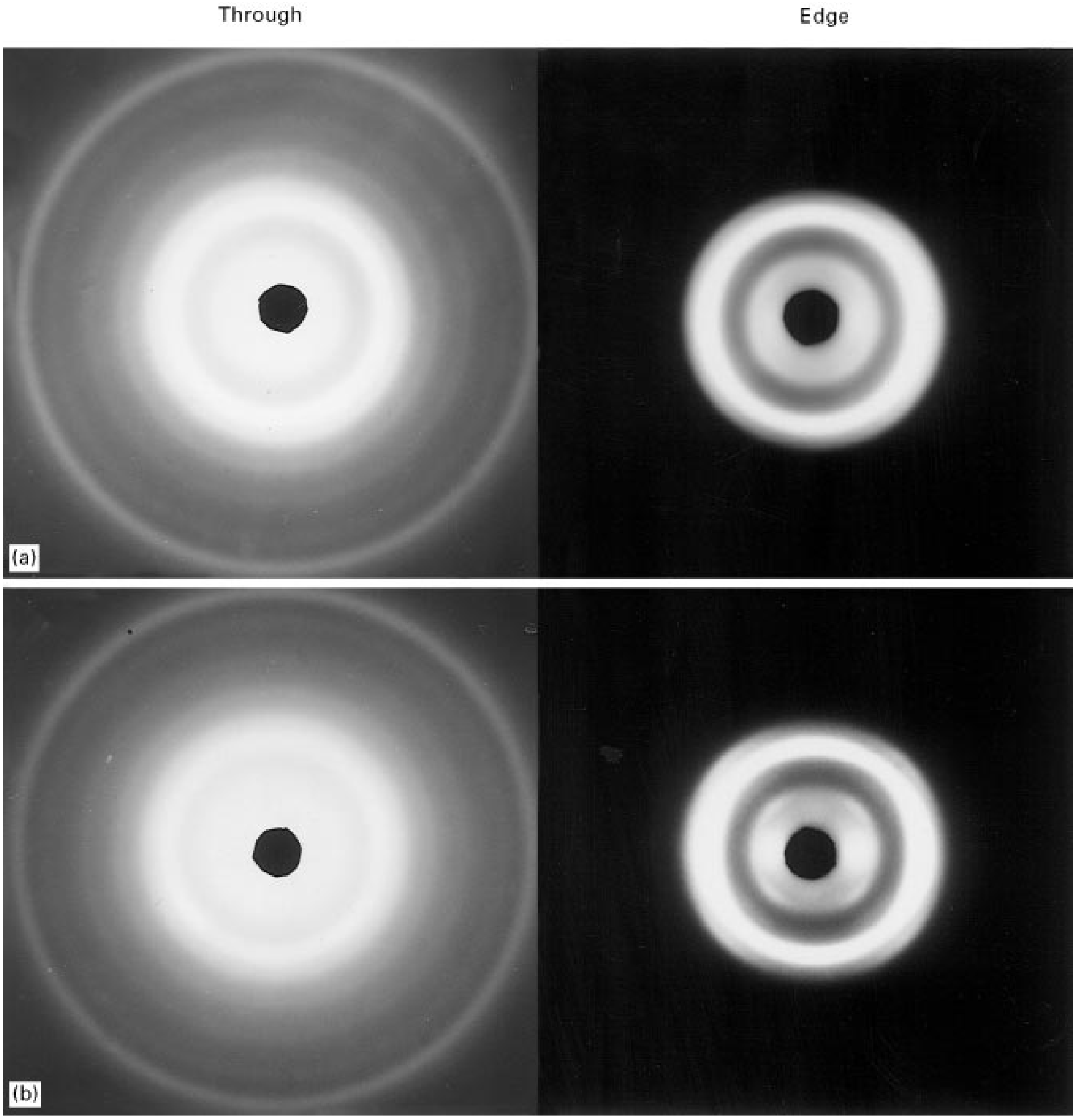

Figure 13 X-ray diffraction photographs taken with the incident beam perpendicular (through view) and parallel (edge view) to the film plane of the dried gel sheet before drawing. The photograph of the edge view is set so that its vertical line is parallel to the film plane. The gel-pressing temperature and the ageing time are as follows: (a) 70 °C and 0 day, (b) 90 °C and 0 day.

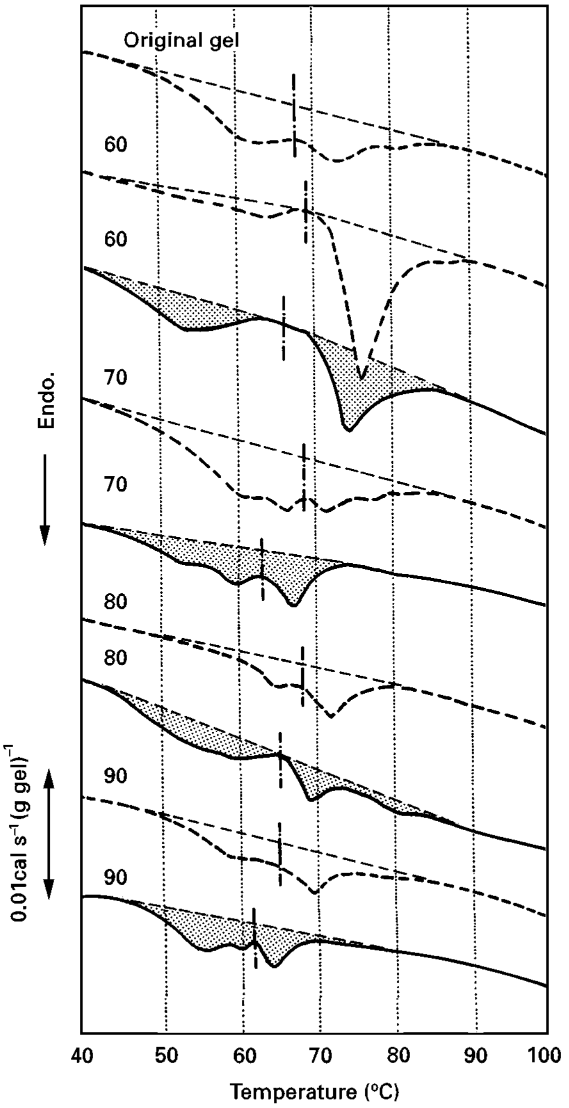

Figure 14 DSC traces of the original gel and the gel sheets (– – –) just after pressing and (——) after ageing in water for 60 days. The numbers shown in the figure are the pressing temperatures.

high-temperature one. These results can be explained by relating the pressing temperature to the melting behaviour of the original gels. The 60 °C pressing temperature is a suitable temperature for recrystallization from the original low-temperature component to the high-temperature one on pressing. The 70 °C pressing temperature is a little higher than the temperature range for recrystallization, but the melted original low-temperature component could recrystallize into the original one when the gel was recooled. Contrary to 70 °C, the 80 and 90 °C temperatures are too high for the melted low component, but not too high for the melted high component to recrystallize to the original components on cooling.

As a result, the middle temperature between the melting peak-temperature of the two components of the original gel is a suitable pressing temperature in view of the properties of the finally obtained drawn film. The pressing temperature of 70 °C, also selected in the previous paper, is not suitable, because it is located a little lower than the peak temperature of the lower component of the previous original gel. In fact, an ageing process was required in the previous work. The observation of the DSC melting endotherm of the original gel is very important for the subsequent processing of the gel.

The gel sheet just before ageing contains the solvent with the same composition as the original one (DMSO : water = 80 : 20 (vol/vol)). However, the original solvent was almost completely exchanged with the storage solvent of water during 1 or 2 days of storing (ageing). Fig. 15 shows the change in the polymer concentration with ageing time. The initial increase signifies the exchange of the solvent. The following gradual increase is due to the crystallization in the gel. Therefore, the DSC curves of the aged gels in Fig. 14 must be submitted to the melting-temperature depression effect of the solvent exchange, compared to those of the unaged gels. The change in the DSC endotherm with ageing time can be most clearly understood when the melting endotherm of the gel sheet is divided into two components, the low melting-temperature and the high melting-temperature components, as shown in Fig. 14. The ratio of the heat of fusion of the low-temperature component ($\Delta H_{\mathrm{gel,l}}$) to that of the total heat of fusion ($\Delta H_{\mathrm{gel,tot}}$) is represented as a function of pressing temperature in Fig. 16. This figure is also similar to Figs 1, 3, and 5. It can be deduced from this comparison that the chain can be so smoothly unfolded from the low-temperature component crystal, when the dried gel sheet is drawn at a high temperature, that the oriented structure thus obtained has a fairly high crystallinity. The smooth unfolding causes a small amount of entanglement and default. It is noted that the structural difference between the gel sheets previously described does not reflect on the crystallinity of the drawn sheets before drawing, because the crystallization also proceeds during the drying process of the sheets.

The ratio of $\Delta H_{\mathrm{gel,l}}/\Delta H_{\mathrm{gel,tot}}$ for the original gel was evaluated to be 0.55, which was a little lower than the value of the gel sheet pressed at 70 °C (0.62). It is thought that the slight increase in the ratio through

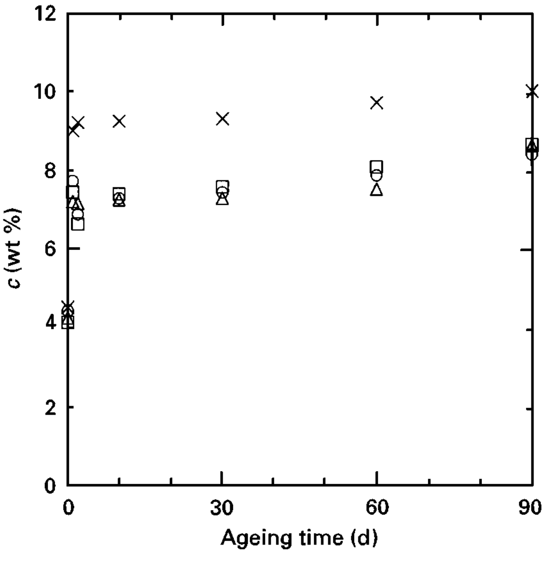

Figure 15 The change in polymer concentration of the gel sheet with ageing time. The gel sheets used were pressed at (×) 60, (△) 70, (□) 80, and (○) 90 °C.

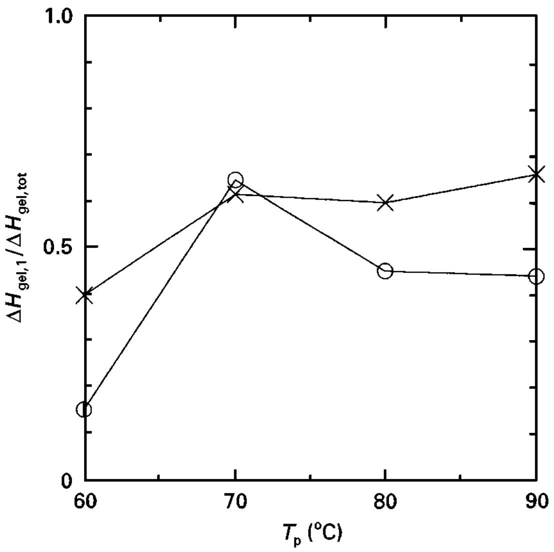

Figure 16 The ratio of the area of the lower melting-temperature component, ($\Delta H_{gel,1}$) to that of the whole melting endotherm, ($\Delta H_{gel,tot}$) of the gel sheet is shown as a function of pressing temperature. The ageing time is (○) 0 day and (□) 60 days. The whole endotherm was divided into the lower and higher melting-temperature components by the line (———) as shown in Fig. 14.

pressing indicated a substantial effect of the pressing on the structural change. If the film was obtained from the original gel without pressing, it is very difficult to draw the film up to such a high draw ratio as is obtained for the film from the pressed gel sheet. This means an increase in the uniformity of the film thickness through pressing. These results demonstrate the advantage of our method for film forming.

4. Conclusion

It has been found that the drawn film having the highest achievable modulus and strength by our method can be obtained without ageing, if the gel is moulded into the gel sheet at a suitable pressing temperature. The low melting-temperature crystal component and the high melting-temperature one were contained in our original gel. The content of the low melting-temperature components was not decreased except when the gel was pressed at the middle temperature of their melting temperatures. This temperature is the suitable pressing temperature. The inclusion of the low melting-temperature component is a necessary condition for the gel sheet to obtain the high-strength and high-modulus properties in the final form of the drawn film, without the ageing of the gel sheet. The low melting-temperature crystal must have contributed to the smooth molecular orientation when the sheet was drawn. This means no serious decrease in crystallinity.

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References

1. T. TANIGAMI, Y. NAKASHIMA, K. MURASE, H. SUZUKI, K. YAMAURA and S. MATSUZAWA, *J. Mater. Sci.* **30** (1995) 5110.
2. P. SMITH and P. J. LEMSTRA, *ibid.* **15** (1980) 505.
3. S. HIBI, M. MAEDA, S. MAKINO, S. NOMURA and H. KAWAI, *Sen-i Gakkaishi* **27** (1971) 246.
4. S. HIBI, M. MAEDA, M. TAKEUCHI, S. NOMURA, Y. SHIBATA and H. KAWAI, *ibid.* **27** (1971) 41.
5. R. FUKAE, T. YAMAMOTO, Y. IMORI, O. SANGEN and M. KAMACHI, *ibid.* **52** (1996) 434.
6. H. TADOKORO, S. SEKI, I. NITTA and R. YAMADERA, *J. Polym. Sci.* **28** (1958) 244.

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