Blends between two types of poly(vinyl alcohol)s with different syndiotacticities

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Miscibility in the crystal phase was investigated for blends between two types of poly(vinyl alcohol)s (PVAs) with different syndiotacticities, 54 and 58 mol% of diad content. They were basically in isomorphic relation with each other, and were designated as atactic (a-) PVA and syndiotacticity-rich (s-) PVA, respectively. The melting temperature measured by differential scanning calorimetry and the crystal dispersion temperature obtained by thermomechanical measurements were used to describe the phase structure of the blends. A cocrystallized phase was found with miscible amorphous phase. Phase separation into a-PVA-rich and s-PVA-rich crystal phases was found locally at blend compositions with small contents of s-PVA. Analysis of these coexisting crystal phases by using a drawing and relaxing method was shown to be useful for discussion of the two structures in terms of the excess free energy of each crystal phase.

(Keywords: blend; poly(vinyl alcohol); syndiotacticity)

INTRODUCTION

As is well known, poly(vinyl alcohol) (PVA) is produced by hydrolysis of a variety of poly(vinyl ester)s, such as poly(vinyl acetate) (PVAc), poly(vinyl trifluoroacetate) (PVTFAc), poly(vinyl formate), poly(vinyl propionate), poly(vinyl benzoate), etc., and poly(vinyl ether)s, such as poly(vinyl trimethylsilyl ether), poly(t-butyl vinyl ether), etc.[1]. One of the most effective factors that dominate the properties of PVAs is tacticity. The tacticity of PVA is controlled by the structure and properties of the corresponding monomeric vinyl ester or vinyl ether and their polymerization conditions. Most commercially available PVAs, usually from PVAc, are called atactic (a-) polymers, since their diad syndiotacticities are usually around 50 mol%. On the other hand, syndiotacticity-rich (s-) PVA, mainly from VTFAc, is a polymer that has been extensively studied in our laboratory for the last 25 years[2]. The syndiotacticity values of PVAs that have been produced from VTFAc in our laboratory are in the range from 58 to 65% in diad content. It should be noted that we have called them syndiotacticity-rich (s-) PVAs, since their syndiotacticities deviate to the positive side from 50%. Thus the PVA produced from VTFAc will be called s-PVA in this paper, even if its diad syndiotacticity is as small as 58%. On the other hand, the PVA produced from VAc will be called a-PVA, even if its syndiotacticity is close to the above value of 58%. The nomenclature in terms of tacticity seems not to be applied so literally to PVA as to other synthetic polyolefins. For example, the term 'syndiotactic polymer' is used for the polymers with syndiotacticities higher than 95% in diad content in the case of polystyrene[3] and poly(methyl methacrylate)[4]. These peculiarities of PVA come from the fact that PVAs with syndiotacticity values close to either 100 or 0% have never been attained. Available PVAs are recognized to be in effect random mixtures of isotactic and syndiotactic sequences.

The most remarkable difference between a- and s-PVAs is revealed upon their crystallization, gelation, melting and dissolution in bulk or solvents[2]. These transition behaviours can be mainly correlated with the properties of the crystal phase, such as crystallization rate and heat of fusion. These properties seem to be higher in s-PVA than in a-PVA. For example, the observed melting temperatures of s-PVAs are usually higher than that of a-PVA[5]. It is expected that the heat of fusion Δh_f of the crystal is much higher in s-PVA than in a-PVA, indicating the higher equilibrium melting temperature of s-PVA. The Δh_f value, as well as the crystallization rate, has never been evaluated in bulk as a function of syndiotacticity. Kusanagi calculated, from the potential energy of molecular packing, the ratio of intermolecular to intramolecular hydrogen bonding in the PVA crystal lattice as a function of syndiotacticity[6]. His result showed that the intermolecular component abruptly increases over 50% syndiotacticity. The content of intermolecular component becomes 100% at 100% syndiotacticity. This result indicates that Δh_f increases with syndiotacticity, and supports the idea that a slight positive deviation in syndiotacticity from 50% (atactic) induces a large extent of change in the properties in bulk and solutions.

The difference between the two PVAs becomes more pronounced on comparing their behaviour in solutions. The crystallization rate from aqueous solutions[7] and the melting temperature of hydrogel[8] are higher in s-PVA than in a-PVA. These findings indicate the difference in affinity of the polymer molecule with water.

In this paper we report on blends of the two PVAs prepared from aqueous solutions, in order to make more clear the structural differences of the two polymers. The

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Table 1 Tacticities of the two PVAs

	Triad tacticity[a]			Diad tacticity[b]	
Sample	mm	mr	rr	m	r
a-PVA	0.21	0.50	0.29	0.46	0.54
s-PVA	0.18	0.48	0.34	0.42	0.58

[a] Measured by n.m.r.
[b] Calculated assuming Bernoullian statistics

crystallinity, solubility and degree of swelling in water have been studied in our previous paper[9]. However, the miscibility of the two PVAs in both crystal and amorphous phases has not been discussed, although the previous results showed no phase separation in the blends. As the two PVAs have the same chemical structure and crystal lattice, the usual tools for observation of miscibility used in other polymers are not effective in this case. Thus we will focus on the slight change in melting temperature with blend composition.

EXPERIMENTAL

Polymers

A commercial product of Wako Pure Chemical Inc., Japan, was used as the a-PVA sample after being fully hydrolysed in our laboratory. The degree of polymerization (*DP*) was 1500 and diad syndiotacticity was 54 mol%. The s-PVA sample was synthesized from VTFAc in our laboratory. The details of the preparation were described in our previous paper[10]. *DP* and diad syndiotacticity were 1590 and 58 mol%, respectively.

Preparation of films

Solutions of the two PVAs in water with a polymer concentration of 3 wt% and five polymer/polymer ratios, 0/100, 25/75, 50/50, 75/25 and 100/0 of s-PVA/a-PVA (wt/wt), were prepared at 120°C in sealed test tubes. The solutions were then cast onto glass plates at room temperature to yield blend films. The films thus obtained were dried *in vacuo* at room temperature for one week. Some of these as-cast films were drawn to about four times their original length in air at 100°C by using a manually operated drawing tool. This draw ratio of 4× was the highest achievable under our drawing conditions for the samples. Further, some of the drawn films were relaxed to a draw ratio of 2× by swelling them in water at room temperature for one day. Some of the as-cast films were annealed at 180°C for 10 min.

Estimation of tacticity

^{1}H n.m.r. measurements for the estimation of triad tacticities, mm, mr and rr, of the neat PVA samples and the blends were performed on a Jeol JNM-A400 n.m.r. spectrometer. The samples used were ca. 0.5 wt% polymer solutions in deuterated dimethylsulfoxide. The tacticities were estimated from OH triplet signals, according to the method used by Hu *et al.*[11].

Differential scanning calorimetry

Thermodynamic studies were conducted by using a Thermal Analyzer System 001 (MacScience Inc., Japan) consisting of a differential scanning calorimeter, DSC 3200, and a thermal analysis processing system, TAPS 1000. The scans were always under a nitrogen atmosphere at a heating rate of 10 K min^{-1}.

Dynamic mechanical measurements

The same system as in d.s.c. was used, combining a thermomechanical analyser, TMA 4000, instead of the DSC 3200, to estimate the dynamic viscoelastic properties as a function of temperature. Film specimens 10 mm long and 2 mm wide were used. In addition to a constant tension of 1 MPa, a sinusoidal tensile vibration with an amplitude of 0.5 MPa and a period of 4 s, corresponding to a frequency of 0.25 Hz, was applied to the specimen to yield the tensile storage modulus E' and $\tan\delta$ for each cyclic stress–strain curve. The measurements were performed during heating from room temperature to 210°C at a rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

The triad tacticity data from n.m.r. of the two PVAs are listed in *Table 1*, with the calculated diad tacticities. The triad tacticities were measured also for the blend samples to show the difference in tacticity between the a-PVA and s-PVA samples, as shown in *Figure 1*. The observed triad tacticities, mm, mr and rr, were reasonably linear functions of blend composition. The difference in the syndiotacticity between the two PVAs was only 5% in triad (rr) and 4% in diad (r). Nevertheless, remarkable differences between the two PVAs will still be expected to appear in several macroscopic properties, such as solubility in solvents and crystallinity, as described in the 'Introduction'. Thus, blending will be a useful technique by which the syndiotacticity of PVA materials can be controlled more finely, although the properties of the materials will be much affected by the phase behaviour of the blends.

Figure 2 shows d.s.c. traces at melting for the three blends and the two neat PVAs. The most striking result was the presence of a two-peak endotherm in the s-PVA/a-PVA = 25/75 (wt/wt) blend. The 50/50 endotherm shows similar melting behaviour to that of the 25/75 blend, but a low-temperature endotherm appeared as a shoulder in the former case. The other three endotherms have similar one-peak figures. The

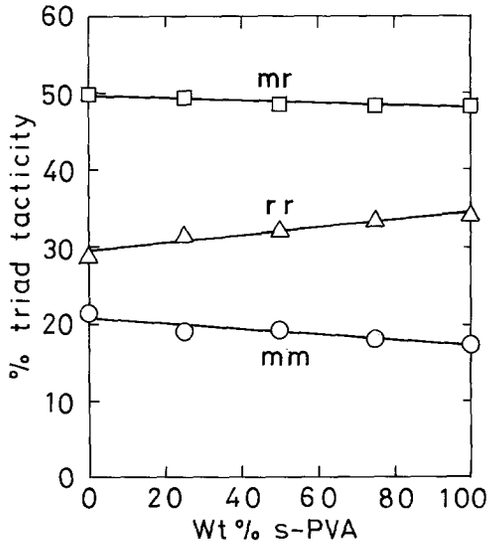

Figure 1 Triad syndiotacticity (mol%) vs. s-PVA content (wt%)

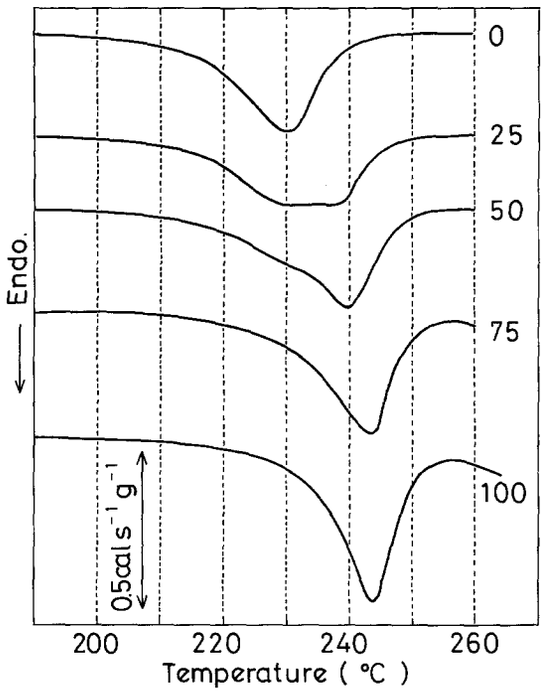

Figure 2 D.s.c. traces of as-cast films for the blends. The numbers on the curves show the s-PVA content (wt%)

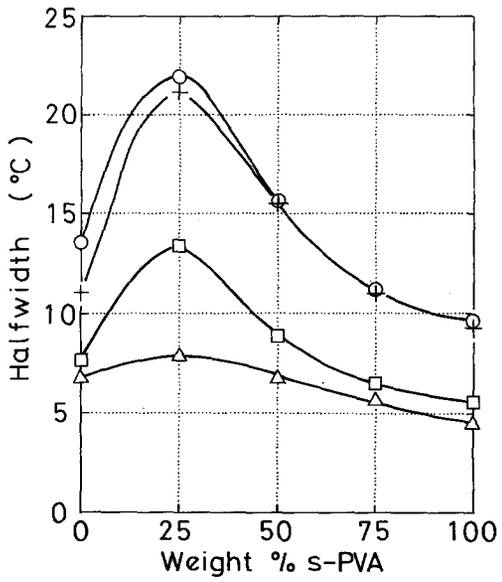

Figure 3 The halfwidth estimated from the d.s.c. melting endotherms: (○) as-cast; (+) annealed at 180°C for 10 min; (△) drawn 4×; (□) drawn 4× and subsequently relaxed to 2× draw ratio

halfwidths of these endotherms were estimated without separating the two-peak endotherm into two endotherms and are plotted by circles in *Figure 3*. This figure shows that broadening of the whole melting endotherm due to overlapping of the two endotherms is remarkable at around an s-PVA content of 25 wt%, and that the endotherm of the neat s-PVA sample is sharper than that of the neat a-PVA sample. Melting temperatures were also estimated from the peak temperatures shown in *Figure 2*, and are plotted against blend composition, as shown by circles in *Figure 4*. A large depression of the melting temperature was observed for the high-temperature component with increasing a-PVA content, whereas the low-temperature component indicates little shift with the a-PVA content. Coexistence of the two melting temperatures indicates the presence of two types of crystal phases: the high and low melting temperatures correspond to those of s-PVA-rich and a-PVA-rich phases, respectively. The heat of fusion, ΔH, was estimated from the melting endotherm in *Figure 2*, and is plotted as a function of blend composition, as shown by circles in *Figure 5*. There is no significant change with blend composition in the ΔH plots and therefore in the crystallinity plots. The crystallinity was calculated from ΔH, assuming that, regardless of the degree of syndiotacticity, the heat of fusion of the crystal was 6.87 kJ mol^{-1}, which was evaluated for a kind of a-PVA[12].

The melting-temperature depression may be set down in the manner of Gibbs as:

$$T_m = T_m^\circ[1-(\delta f_c - \delta f_a)/\Delta h_f] \quad (1)$$

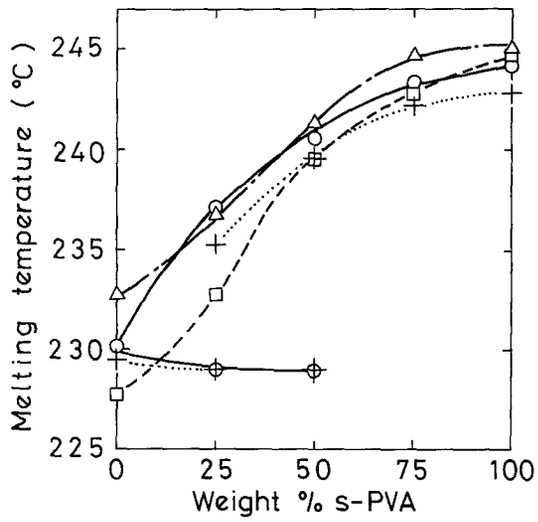

Figure 4 Melting temperatures estimated from the d.s.c. melting endotherms. The symbols are the same as in *Figure 3*

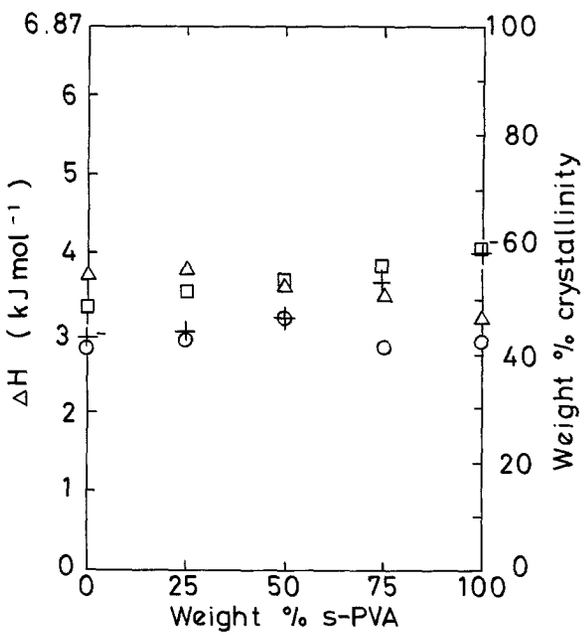

Figure 5 Heat of fusion and crystallinity estimated from the d.s.c. endotherms. The symbols are the same as in *Figure 3*

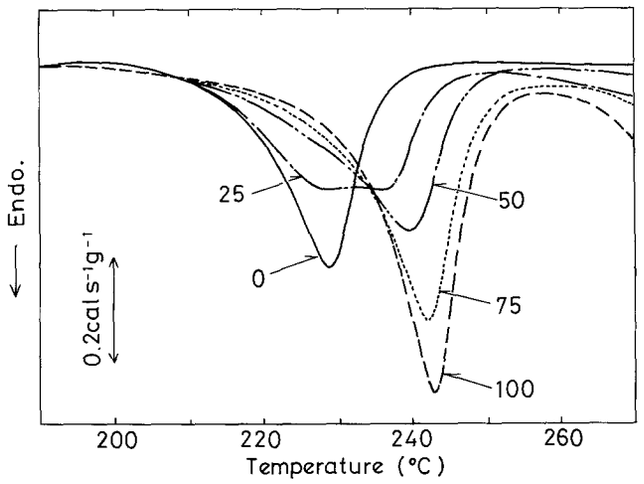

Figure 6 D.s.c. traces for the samples annealed at 180°C for 10 min. The numbers on the curves show s-PVA content (wt%)

where T_m° is the melting temperature of a crystal that has very large size and contains neither other polymer nor solvent components, T_m is the observed melting temperature, δf_c and δf_a are the excess free energy per unit volume of the crystal and amorphous phases, respectively, and Δh_f is the heat of fusion per unit volume of crystal. The excess free energy of the crystal phase is mainly due to the surface interfacial free energy of chain-folded surface and internal density defects of the crystal. These will make the δf_c term positive, resulting in the decrease in T_m. Annealing is one of the most popular ways by which δf_c is slightly reduced through crystal growth in size or improvement of crystal perfectness. Drawing is also a way to force δf_c to change through the change of the amount of defects. It is also possible that, compared with the crystal phase of the neat polymer, the amount of defects is enhanced on blending with another polymer component that is isomorphous with the mother polymer. The two PVAs, a-PVA and s-PVA, are evidently isomorphous with each other, so that they have a chance of cocrystallization. However, on cocrystallization, the heat of fusion will also be caused to change by the change in the fraction of interchain hydrogen bonding. The excess free energy of the amorphous phase is related to molecular mixing with other polymer components in the amorphous phase, residual strain energy by external force, etc. The former factor will make the δf_a term negative and the latter one will make it positive. In our blend system, s-PVA and a-PVA have similar cohesive energy density in the amorphous phase, producing a favourable enthalpy of mixing. However, the δf_a term is not so effective as to reduce the melting temperature, because there is no specific polar interaction between the two PVAs, compared with the neat PVAs. Thus, the observed depression of the melting temperature cannot be attributed to the effect of δf_a.

We first postulate that no cocrystallization occurs in our case. Then, it is usual to estimate the equilibrium melting temperature for each blend and the neat polymers, in order to exclude morphological effects on T_m such as crystal size and defects. Unfortunately, the estimation of T_m°, usually according to the Hoffman–Weeks method[13], is not applicable to this case, because serious degradation is induced upon crystallization at high temperatures from the melt. However, we speculate that the depression due to the morphological effects is at almost the same level among all the crystal phases in our system. This is partly supported by the result that annealing at 180°C for 10 min caused no serious shift in melting temperature as shown in *Figures 6* and *4*. The heat of fusion ΔH was observed to increase at higher s-PVA contents by annealing, as shown in *Figure 5*, and the halfwidth was slightly decreased at higher a-PVA contents, as shown in *Figure 3*. The main cause of these changes should be attributed to additional crystallization in the amorphous phase and increase of the morphological factors. However, it is evident that the latter factors are not so effective to change the dependence of the melting temperature on blend composition. In conclusion, the observed depression must be caused by cocrystallization of the two PVAs. It should be noted here that the melting depression due to cocrystallization cannot be expressed so simply in an equation as by equation (1), because the heat of fusion becomes a function of blend composition.

Similar cocrystallization has been found by Starkweather in blends of low-density polyethylene (LDPE) and an ethylene/propylene/1,4-hexadiene copolymer (EPDM)[14]. (Utracki illustrated Starkweather's data in a melting temperature vs. blend composition plot and reviewed it[15].) The relationship between LDPE and EPDM polymers is quite analogous to that between the two PVAs, in view of the excess free energy due to molecular mixing in the amorphous phase. Another analogy between the two blend systems is the presence of two crystal species: the LDPE/EPDM system also showed two melting temperatures, indicating the coexistence of two types of cocrystallized phases. Starkweather gave the evidence of cocrystallization in the LDPE/EPDM system by the fact that the crystal lattice expanded slightly with blending. Expansion of the lattice cannot be a measure of cocrystallization in PVA blends, since the lattice is originally identical between the two. The atactic PVA molecule is composed of isotactic and syndiotactic sequences. Nevertheless, the chain conformation in the crystal lattice is regularly a planar zigzag[16], indicating the isomorphism of the two PVAs. The location of the hydroxyl group on the chain, syndiotactic or isotactic, is not so effective as to change the chain conformation. This means that the crystal structure of the cocrystallized PVA is identical with those of the neat PVAs.

Two types of d.s.c. traces are compared with one another in *Figure 7*: one is for the blend sample and the other is for a stacked sample of the two neat PVA films, both in the weight ratio of 25/75 (s-PVA/a-PVA). Regardless of the same total composition ratio, the ratio of the areas of the two endotherm components is quite different between the two traces. The area of the high-temperature component is almost the same as that of the low-temperature one in the blend, whereas the ratio of the areas in the case of the stacked sample seems to be apportioned into the two components in proportion to the weight ratio of the two films. The total heats of fusion were almost the same between the two d.s.c. traces: 3.1 and 3.0 kJ mol^{-1} for the stacked and the blend samples, respectively. Assuming that the two endotherm components in the blend are composed of individual pure PVAs and that the total area of the endotherm is equally divided into the two components, the crystallinities in each phase are 29% and 87% for a-PVA and s-PVA phases, respectively. In particular, the latter is an unreasonably high value. It is also unreasonable that the

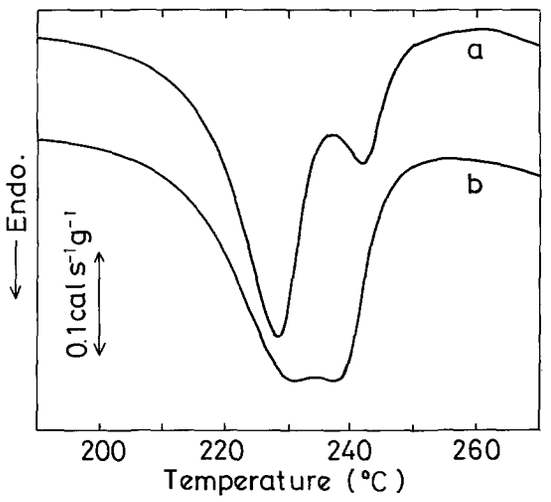

Figure 7 Comparison of two d.s.c. traces: (a) a stacked sample of the two neat PVA films and (b) a blend sample of the two PVAs, both in s-PVA/a-PVA (wt/wt) ratio of 25/75

crystallization of pure s-PVA was promoted in the presence of a-PVA molecules. Thus, the high-temperature component should contain the two PVAs as a result of cocrystallization. However, the low-temperature component may be composed mainly by a-PVA, since the depression of melting temperature was very small.

As shown in *Figure 2*, the a-PVA-rich phase appeared only in a limited region of blend composition below 50% of s-PVA, while the s-PVA-rich phase clearly appeared in all blend compositions except at the pure a-PVA composition. The presence of the latter phase means that inclusion of a small amount of s-PVA within a-PVA materials will effectively cause a rise of the melting temperature by virtue of cocrystallization. The coexistence of the a-PVA-rich crystal phase with the s-PVA-rich crystal phase cannot be interpreted from our experimental results. To approach this problem, structuring from solutions, which is accompanied with evaporation of solvent, must be kinetically analysed.

Figures 8a and *8b* show the dynamic storage modulus E' and $\tan\delta$, respectively. The primary dispersion, α_a, corresponding to the glass transition can be seen at about 50°C as an abrupt decrease of E' and a sharp peak of $\tan\delta$[17]. The characteristic temperature, designated as T_{α_a}, was obtained from this peak temperature, and is plotted against blend composition in *Figure 9*. It is a reasonable result that T_{α_a} is constant among all the samples, since the blending polymer components have analogous chemical structure. The E' modulus observed at 100°C in *Figure 8a* is an increasing function of s-PVA content. The temperature of the crystalline relaxation, α_c, designated as T_{α_c}, was observed on the $\tan\delta$ curves at around 150°C[17], and is plotted against blend composition in *Figure 9*. A rise of T_{α_c} with s-PVA content is found in the higher s-PVA content region. In conclusion, the increases of E' and T_{α_c} correspond to an increase of the melting temperature of the cocrystallized phase with the high melting temperature. This means that the crystal with a higher content of s-PVA has stronger resistance to thermally or mechanically induced sliding motion of the chain along its axis, since the intermolecular hydrogen bonding increases with increasing syndiotacticity.

A change of the excess free energy could be induced in the blend samples by drawing, in order to elucidate

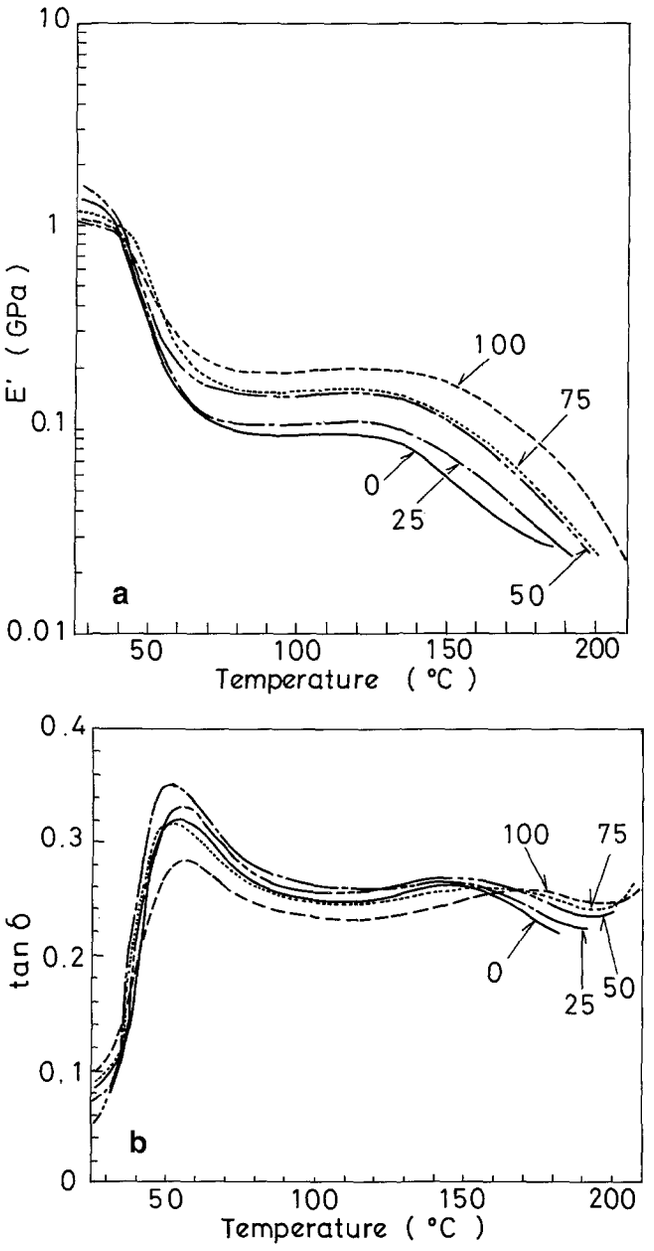

Figure 8 Thermomechanical properties of as-cast films for the blends. The numbers on the curves show s-PVA content (wt%): (a) storage modulus E'; (b) $\tan\delta$

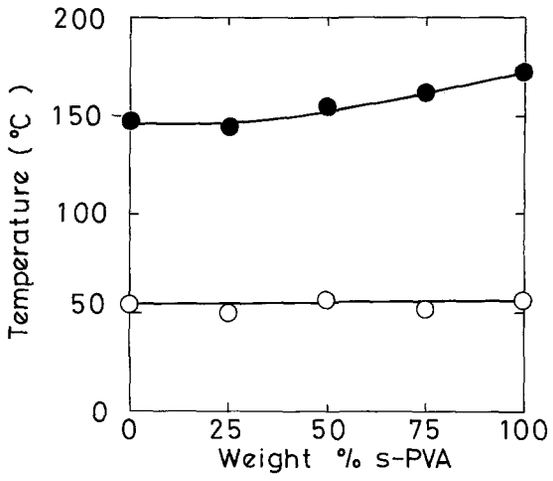

Figure 9 Two characteristic temperatures estimated from the $\tan\delta$ curve in *Figure 8b*: (○) principal dispersion temperature T_{α_a}; (●) crystal dispersion temperature T_{α_c}

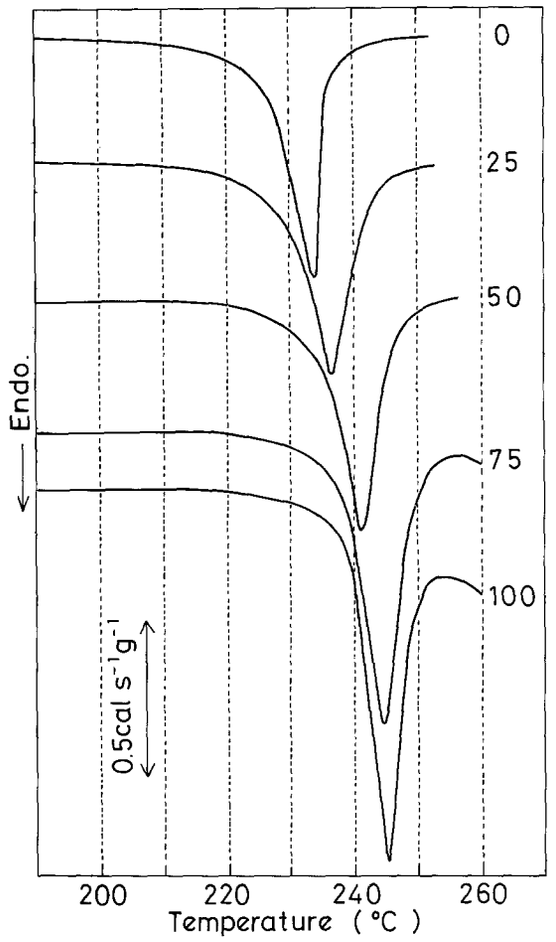

Figure 10 D.s.c. traces for the blend films drawn 4×. The numbers on the curves show s-PVA content (wt%)

the structural difference between the two coexisting crystal phases at low blending compositions. The two-peak endotherms became sharp and single peaks after drawing, as if this had been an evidence for single-phase cocrystallization in all blends, as shown by d.s.c. traces in *Figure 10* and halfwidth vs. blend composition plots in *Figure 3*. The melting temperature vs. blend composition plots are also on a curve, as shown by triangles in *Figure 4*. This curve almost overlapped the curve represented by open circles for the s-PVA-rich crystal phases of undrawn samples. The temperature shift observed for the endothermic peak of the neat a-PVA sample was remarkably large, whereas those of the s-PVA-rich phases were within the experimental error. These facts suggest that sharpening of the whole endotherm observed at low s-PVA contents is to a great extent due to the shift of the low-temperature endotherm component towards the high-temperature one. The sharpening of the individual endotherm components should also partly contribute to the sharpening of the whole endotherm. The individual sharpening is due to melting of small-size crystallites and restructuring into highly ordered crystallites. These structural changes are also detected by the increase of the halfwidth of the endotherms of single crystal phases, and by the increase in heat of fusion shown in *Figure 5*.

The melting temperature shift observed upon drawing cannot be related to the change of δf_a but to that of δf_c, because of the miscibility of the two PVAs in the amorphous phase. If a large amount of strain energy could be stored in the amorphous phase, the resultant temperature shift would have appeared equally in the melting temperatures of the two crystal phases. The decrement in δf_c by drawing should be larger in the a-PVA-rich crystal phase than in the s-PVA-rich crystal phase. It is speculated that the amount of defects including packing disorder was, before drawing, at a higher level in the a-PVA-rich crystal phase than in the s-PVA-rich crystal phase, and that the amount of defects in the former could be reduced towards the level of the latter. The crystal of a-PVA is at a higher level before drawing than that of s-PVA in terms of the packing energy of chains. This level of packing energy in the a-PVA crystal is somewhat stabilized on drawing through extension of the chains, while drawing has no significant effect on the T_m of the s-PVA crystal. This difference of the effect of drawing between the two PVAs is also due to the difference in syndiotacticity, which dominates the amount of interchain hydrogen bonding. Here, we have to state that our drawing temperature of 100°C might be too low for the s-PVA crystal phase to be extended towards a lower δf_c level.

Figure 11 shows d.s.c. traces for the drawn and subsequently relaxed samples. The most striking feature is that the halfwidth of the whole endotherm increased towards the initial halfwidth observed before drawing, especially in the 25/75 and 50/50 blends, as shown in *Figure 3*. The two-peak nature of the endotherm of the 25/75 blend was not so apparent after relaxing as

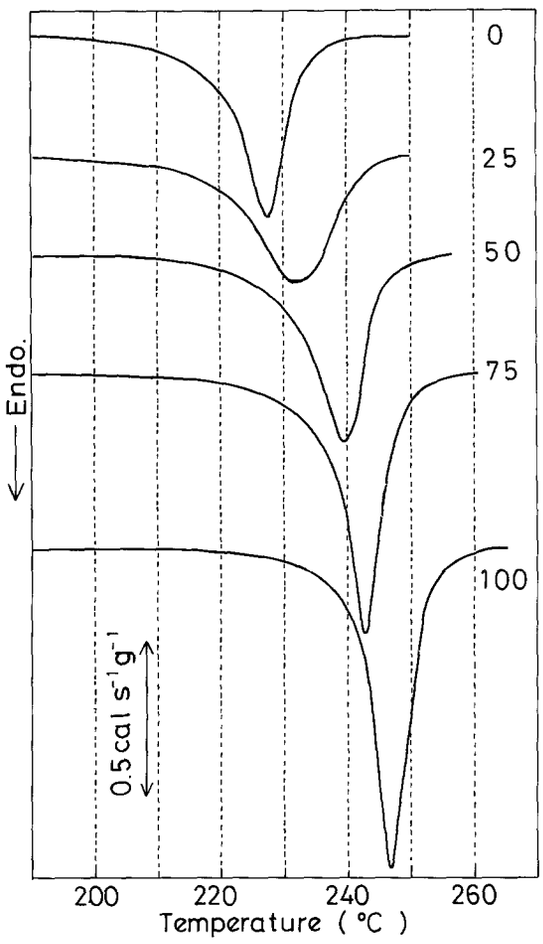

Figure 11 D.s.c. traces for the blend films drawn and relaxed. The numbers on the curves show s-PVA content (wt%)

before drawing. However, its peak melting temperature, estimated as a one-peak endotherm, is located midway between the original two melting temperatures, as shown in *Figure 4*. This is evidence that the sharp endotherm of the drawn blends consisted of two types of crystal phases. The endotherms of the single crystal phases, which appeared clearly in the two neat PVAs and the 75/25 blend, show only a small extent of reversible change in their halfwidth after relaxing. This means that the structural changes in those crystal phases caused by drawing are irreversible. Thus the reversible change in the halfwidth observed at low s-PVA contents is due to the reversible shift of the two melting temperatures, which was caused by creation and release of the δf_c term preferably within the a-PVA-rich crystal phase in the drawing and relaxing cycle. According to Bosma *et al.*, the enthalpy relaxation technique was reported to be useful for the investigation of miscibility in polymer blends with similar T_g values[18]. The blend that experienced the enthalpy relaxation by annealing at a temperature just below T_g showed two separable peaks at T_g on the d.s.c. curve, correctly indicating immiscibility of the polymers, while the d.s.c. curve for the unannealed blend has a characteristic broad change for pseudo-miscible blends. Our relaxation experiment has induced a similar result that a blend of polymers with similar T_m values has to be relaxed.

CONCLUSIONS

As expected from the structural analogy between s- and a-PVA molecules, they formed a cocrystallized phase in a blend film prepared by casting from aqueous solution. In blends with small contents of s-PVA, there were two cocrystallized phases, a-PVA-rich and s-PVA-rich crystal phases. The obtained d.s.c. endotherms, from which the above conclusion was reached, showed further that the amount of s-PVA-rich crystal phase was greater than the amount of a-PVA-rich crystal phase even for the blend with the smallest content of s-PVA (the 25/75 blend). This means that blending of a small amount of s-PVA with a-PVA will be a useful technique to produce PVA materials with higher melting temperatures from the cheaper a-PVA material. Perfect cocrystallization, namely the appearance of a single cocrystallized phase, is expected to be possible if the crystallization rates of the two PVAs can be controlled to the proper values for perfect cocrystallization by conditioning film preparation.

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