Polymer Vol. 37 No. 17, pp. 3805–3811, 1996
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0032-3861/96/$15.00+0.00

S0032-3861(96)00205-4

Study of orientation in miscible and heterogeneous poly(styrene)/poly(vinyl methyl ether) blends

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(Received 11 July 1995; revised 19 December 1995)

Molecular orientation and mechanical properties of miscible poly(styrene)/poly(vinyl methyl ether) (PS/PVME) blends were compared with those of heterogeneous PS/PVME blends prepared above their temperature of phase separation. The second moment of the orientation function and the Young's modulus of the heterogeneous systems were found to be higher than those of the corresponding miscible compositions. Furthermore, it was observed that the orientation behaviour of this blend is closely related to the spinodal mechanism of phase separation, in the range of temperatures and compositions investigated. The role of the annealing time and temperature in this process is discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: PS/PVME blends; orientation; *FT*i.r.)

INTRODUCTION

Several studies on miscible polymer blends[1–6] have shown that the orientation behaviour of these systems can be interpreted in terms of specific interactions, density of entanglements, interchain friction and chain relaxation. In comparison, immiscible blends have received little attention. However, studies by White *et al.*[7–10], for instance, on poly(propylene)/poly(ethylene) (PP/PE) and poly(propylene)/nylon 6 blends have revealed that the orientation of the PP and PE crystalline phases in these systems is independent of the blend composition and remains practically equal to that of the pure polymers. In contrast, in poly(ethylene)/poly(styrene) and poly(ethylene)/poly(carbonate) blends, the orientation of the crystalline phase of PE is significantly reduced by the addition of the second polymer[9,10].

Heterogeneous systems induced by phase separation of initially miscible blends have also been investigated by several authors[11–13]. Hsu *et al.*[11] have analysed two poly(styrene)/poly(vinyl methyl ether) (PS/PVME) compositions, containing 55 and 50% of PS, and found that the orientation of PS chains as well as the Young modulus are smaller in the heterophase than in the homogeneous state. In contrast, our preliminary results[13] with a PS/PVME blend containing 60% PS showed that these two parameters are, comparatively, higher in the heterogeneous blend, in good agreement with the mechanical results reported by Kim *et al.*[14] for the same mixture. From these studies, it can be concluded that further investigations, emphasizing the role of parameters such as the nature, size and morphology of the phase domains, are needed in order to develop phenomenological models describing the mechanisms of orientation and deformation in heterophase systems.

In the present study, the PS/PVME blend was selected because it is completely amorphous and exhibits a lower critical solution temperature, which offer the opportunity to compare its orientation behaviour in the miscible and heterogeneous states (*Figure 1*). The phase separation process of this blend has been extensively investigated by several authors and its phase diagram is well established[15–20]. In the two-phase region, the system may phase separate either by nucleation and growth or by spinodal decomposition, depending on the annealing temperature: the resulting morphology depends upon the mechanism of phase separation. At the same time, the early stage of spinodal decomposition can be followed by time-resolved light scattering, as pointed out by Hashimoto *et al.*[18–20]. The scattered intensity then increases exponentially with time, in agreement with the linear theory originally proposed by Cahn[21] and extended to polymers by de Gennes[22]. In the intermediate and late stages, however, the intensity increase deviates from this exponential behaviour.

In the present study, tensile mechanical properties and molecular orientation of PS/PVME blends have been analysed in the two-phase region and compared to those of the corresponding miscible blends.

THEORY

For a simple uniaxial mode of deformation and at small deformations, the second moment of the orientation function $\langle P_2(\cos\theta)\rangle$ is adequate for describing the state of orientation[23]. Different techniques can be used to measure $\langle P_2(\cos\theta)\rangle$. Among them, birefringence and Fourier transform infrared (*FT*i.r.) dichroism are

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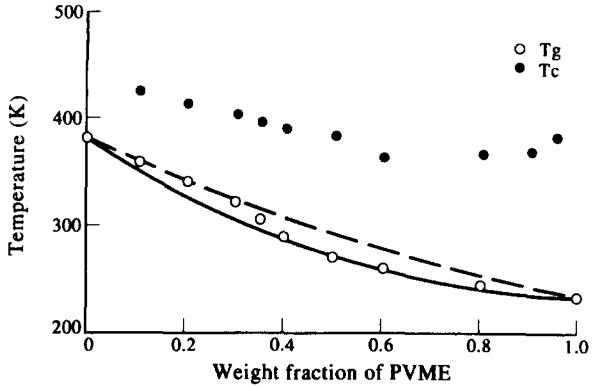

Figure 1 Phase diagram of the PS/PVME blend; (- - -) Fox equation: $T_g = T_{g1}T_{g2}/(w_1T_{g2} + w_2T_{g1})$ (—) Kwei equation: $T_g = T_g(\text{Fox}) - 85w_1w_2$

complementary methods to analyse the molecular orientation of multicomponent blends. In the case of a binary mixture, the measured birefringence, Δ, can be expressed as[24]

$$\Delta = \phi_1\Delta_1\langle P_2(\cos\theta_1)\rangle + \phi_2\Delta_2\langle P_2(\cos\theta_2)\rangle + \Delta f \quad (1)$$

where $\langle P_2(\cos\theta_i)\rangle$, Δ_i and ϕ_i are the second moment of the orientation function, the intrinsic birefringence and the volume fraction of the ith component, respectively. Δf is the form birefringence related to the difference of refractive index between the two polymers.

The second moment of the orientation function can also be calculated from *FT*i.r. measurements. The dichroic ratio D of any infrared absorption band is related to $\langle P_2(\cos\theta)\rangle$ by[25]

$$\langle P_2(\cos\theta)\rangle = (D-1)(D_0+2)/(D+2)(D_0-1) \quad (2)$$

where D, which is equal to the ratio of the absorbance for the electric vector of the incident radiation polarized parallel and perpendicular to the stretching direction, respectively, and $D_0 = 2\cot^2\alpha$, α being the angle between the transition moment vector of the considered vibration and the local chain axis. For polymer blends, the orientation of each component can be determined provided that specific bands, corresponding to vibration modes with well-defined transition moment vectors, are observed for the two polymers.

EXPERIMENTAL

Materials

Atactic poly(styrene) (PS, Pressure Chemicals, USA) having a M_w of 300 000 and a polydispersity index of 1.06, and poly(vinyl methyl ether) (PVME, Polysciences, USA) with a M_w of 44 000 and a polydispersity index of 2.3, were used in this study. These values were determined by size exclusion chromatography in tetrahydrofuran, at 298 K, using PS standards.

Films of PS, PVME and their blends were cast from benzene solutions on a glass plate. They were first air-dried for one day, and the last traces of solvent were removed under vacuum at $T_g + 30$ for 36 h. Some samples were then analysed immediately at the chosen temperature (miscible blends); others were annealed above their cloud points for a certain period of time before being quenched to room temperature and analysed (heterogeneous blends).

Birefringence and mechanical property measurements

Birefringence and mechanical property measurements were conducted using an Instron tensile tester, model 1130, with a controlled temperature sample compartment constructed in our laboratory. For the birefringence measurements, a He/Ne laser source was placed at the back of the sample compartment and a Soleil–Babinet compensator in the front. Therefore, it was possible to measure the birefringence and the stress–strain curves simultaneously, at a fixed temperature. The samples, having an initial thickness of 200 μm, a width of 3.5 mm and a length of 45 mm, were stretched at a strain rate of 5 cm min^{-1}. The birefringence measurements required a pause time which, however, did not exceed 100 s.

Infrared dichroism measurements

*FT*i.r. measurements were carried out using a Mattson Sirius 100 spectrophotometer with a rotating wire-grid polarizer (Specac, Newmarket, UK). An infrared cell, constructed in our laboratory and adapted to the sample compartment of the spectrophotometer, allowed the sample to be heated up to a given temperature and to be stretched at a constant strain rate of 5.0 cm min^{-1}. The sample was stretched up to the desired draw ratio and the stretching process was then interrupted for a period of time of about 100 s while the two polarized spectra were recorded. For each polarization, the phase correction was executed separately, and thirty scans were co-added with a maximum optical retardation of 0.52 cm, and triangulary apodized to yield a resolution of 4 cm^{-1}. Infrared dichroism was calculated from the peak height intensity measured in absorbance. All spectral manipulations were executed with software provided by Mattson. The samples had an initial width of 5.0 mm and initial length of 20 mm. The thickness was adjusted between 40 and 100 μm, depending on blend composition, in order to maintain the infrared absorbance below unit and to avoid deviations from the Beer–Lambert law.

For both birefringence and i.r. experiments, values of the orientation function reported in this paper are averages of at least three measurements on different samples with a reproducibility estimated to about 10%.

Small-angle light scattering measurements

Small angle light scattering (SALS) was used to monitor the phase separation process. SALS measurements were carried out using an automated SALS system equipped with a CCD camera and a He/Ne laser source[26]. The samples were approximately 0.1 mm thick.

T_g *and* T_c *measurements*

To construct the PS/PVME phase diagram, the glass transition temperature (T_g) was determined with a Perkin–Elmer DSC-4 differential scanning calorimeter, equipped with a thermal analysis data station and calibrated with indium, at a heating rate of 20 K min^{-1}. The temperature of phase separation (T_c) was determined using a Zeiss optical microscope, a Zeiss photometer and a Mettler hot stage. The samples were heated up from room temperature to the phase separated state, at a heating rate of 2 K min^{-1}. T_c was then taken as the temperature where the intensity begins to increase (cloud point).

As can be seen in *Figure 1*, a single T_g intermediate between those of the pure components is observed at each composition, indicating the miscibility of the system in the full range of composition. The variation of T_c with composition is monotonic and almost linear in a broad range of composition, with a minimum at a critical PVME weight fraction of about 0.75 and at a temperature of 370 K, in good agreement with the data of Hashimoto *et al.*[19]. Furthermore, the miscibility window, i.e. the interval between T_g and T_c, increases from 60 K, at low PVME content, to about 120 K, at high PVME concentration.

RESULTS AND DISCUSSION

Influence of annealing temperature

The influence of the annealing temperature, T_a, on structure and orientation was first analysed with the 60% PS blend. The sample was let to demix for 15 min at different temperatures above the cloud point, and subsequently stretched at 304 K, which corresponds to $T_g + 10$ for the miscible blend.

The variation of the birefringence with strain, for samples with different annealing temperatures, is depicted in *Figure 2*. It can be noticed that the birefringence increases linearly with λ (λ = draw ratio defined by the ratio of the sample length over its initial length) but that the ultimate strain, λ_{MAX}, decreases as the temperature of annealing is increased; for example, λ_{MAX} goes from about 1.7 at $T_c + 5$ to about 1.23 at $T_c + 15$. The slope of these curves, $-d\Delta/d\lambda$, when plotted as a function of the distance to T_c (*Figure 3*), indicates that the phase separation leads to an increase of the overall birefringence, as compared to that of the miscible system. At $T_c + 30$, the birefringence increase is maximum, and about 2.5 times larger than that of the miscible one; however, a decrease is observed at $T_c + 40$. Beyond this temperature, the mechanical integrity of the sample was too poor to allow stretching. Young's modulus, E, calculated from the initial slope of the strain–stress curves, exhibits the same kind of variation with annealing temperature as the birefringence (*Figure 3*), illustrating the close relationship between these two parameters, as has been observed previously for the miscible system[27,28]. At $T_c + 30$, the modulus is maximum and more than two times larger than that of the miscible blend.

A priori, this increase of birefringence may reflect an overall increase of the orientation of the two blend components or a preferential increase in orientation of one of them. It may be related, also, to an increasing contribution of the form birefringence due to the deformation of the phase domains of the heterogeneous system. In order to verify this point, *FT*i.r. measurements were carried out. The PS orientation was analysed using the well-isolated 1028 cm^{-1} band, corresponding to the ν_{18a} vibration of the in-plane stretching mode of the C–H groups of the aromatic cycle. This vibration is conformationally insensitive with a transition moment vector perpendicular to the chain axis[2]. *Figure 4* shows the variation of the slope, $d\langle P_2(\cos\theta)\rangle/d\lambda$, of PS as a function of the distance to T_c. Original $\langle P_2(\cos\theta)\rangle$ curves are given in Abtal's thesis[29] and, for the miscible state, in ref. 28. The PS orientation of the heterogeneous blend also exhibits an increase with the annealing temperature; at $T_c + 30$, it is close to two times larger than that of the miscible system.

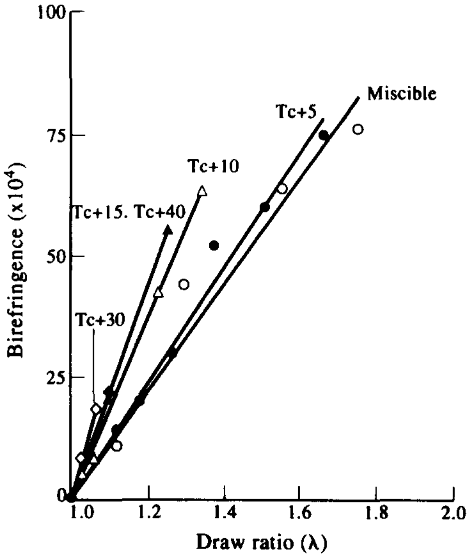

Figure 2 Birefringence Δ as a function of the draw ratio λ for the 60/40 PS/PVME blend annealed for 15 min at different annealing temperatures. The lines were drawn by a least-squares fit using a forced return to the origin

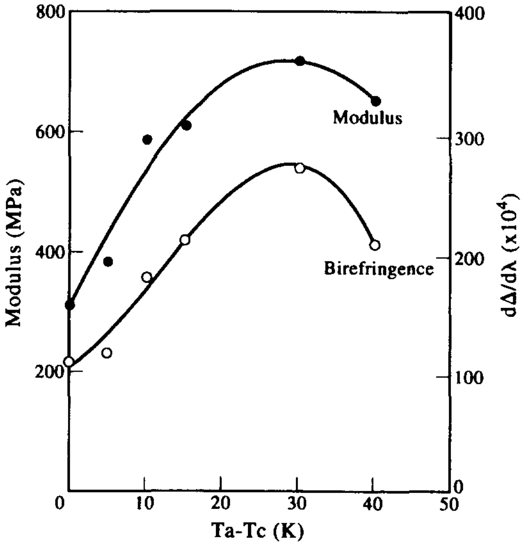

Figure 3 Initial slope of the Δ–λ curves (*Figure 2*) and Young's modulus E as a function of $T_a - T_c$, for the 60/40 PS/PVME blend ($T_c = 396$ K). The slopes were obtained from the least-squares fit

As far as PVME is concerned, a quantitative *FT*i.r. determination of its orientation is not possible since the only two isolated PVME bands in the PS/PVME infrared spectrum, at 1100 and 2820 cm^{-1}, are both related to the side chain group O–CH$_3$ whose exact conformation in the blend is not known[30]. In addition, the coupling of birefringence and *FT*i.r. measurements does not allow the characterization of the orientation of this polymer, as has been done for the miscible blends[27,28], since the contribution of the form birefringence, in comparison to the relatively modest birefringence of PVME, cannot be neglected in the heterogeneous state. However, in the range of temperatures investigated, the dichroic ratio of the 1100 and 2820 cm^{-1} bands was almost equal to unity, indicating that PVME remains practically unoriented. Therefore, the increase in the overall orientation and modulus of the heterogeneous blends can be mainly attributed to an increase of the PS chain orientation. This behaviour differs slightly from that observed in the miscible blends, at $T_g + 10$, where PVME chains also exhibit a significant orientation as a consequence of their hindered relaxation motions due to specific interactions with PS[28]. In the heterogeneous state, since the samples are stretched at about 60 K above the T_g of PVME, this polymer is expected to experience a very fast relaxation as compared to PS.

An analysis of the phases expected to be formed at equilibrium as a result of the phase separation process gives useful information about the influence of the annealing temperature on the orientation behaviour of PS/PVME blends in the immiscible region. Such data can be derived from the phase diagram (*Figure 1*). They are summarized in *Table 1* which reports the composition W, the PS content and the T_g of the two phases. From these data, it can be noted that the miscible blend is stretched 10 K above its T_g ($T - T_{gmisc} = +10$), i.e. in the rubbery state, while the major phase of the heterogeneous blends is always stretched in the glassy state, below its T_g ($T - T_{gM}$ is negative). As the temperature of annealing increases, the major phase becomes richer in PS and the difference ($T - T_{gM}$) becomes more negative. In other words, the major phase, which provides the main contribution to the resistance to deformation and to molecular orientation in the phase-separated blends, is stretched at lower temperatures as compared to its T_g, and the relaxation motions are expected to be slower. This situation leads to the observed increase in modulus and orientation (*Figures 3* and *4*), provided that the two phases are well connected, as will be discussed later. It must be noted that, in all cases, the temperature of measurement, i.e. $T_g + 10$, is below the T_g of the major phase, thus excluding any possibility for the system to evolve in the direction of a miscible state during the measurements.

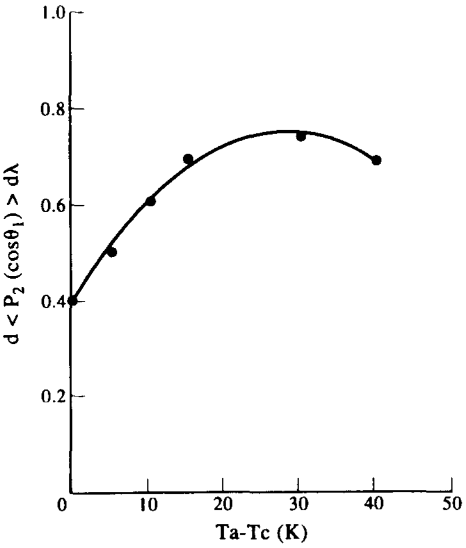

Figure 4 Initial slope of the $[\langle P_2(\cos\theta)\rangle - \lambda]$ curves as a function of $T_a - T_c$, for the 60/40 PS/PVME blend ($T_c = 396$ K)

Table 1 Weight fraction, PS percentage, and T_g of the major (M) and minor (m) phases, calculated for equilibrium conditions, for the 60/40 PS/PVME blend annealed at different annealing temperatures

$T_a - T_c$	Major phase			Minor phase			$T - T_{gM}$
(K)	W_M	%PS	T_{gM} (K)	W_M	%PS	T_{gM} (K)	(K)
Miscible	1.00	60	294	—	—	—	10
5	0.89	47	314	0.11	3.5	245	−10
10	0.80	72	326	0.20	2.5	245	−22
15	0.79	76	334	0.21	1.5	245	−30
30	0.66	90	359	0.34	1.0	245	−55
40	0.62	97	376	0.38	1.0	245	−72

Influence of the annealing time

The influence of the annealing time has also been analysed using the blend containing 60% PS. In this series of experiments, the samples were left to demix at 5 K above T_c (401 K), for different periods of time, and then stretched at 304 K which corresponds to $T_g + 10$ of the miscible blend.

Figure 5 shows the Young modulus and the slope of the birefringence curve, $-d\Delta/d\lambda$, as a function of annealing time. These two parameters increase steadily, as compared to the values for the miscible blend, and go through a maximum after about 60 min of annealing. The same trend is observed for the PS orientation which is 1.5 times larger than that of the miscible blend, after about 60 min of annealing, as illustrated in *Figure 6*. However, in the three cases, a significant decrease is observed at longer annealing times; after 200 min, the PS orientation and birefringence, but not the modulus, become again practically equal to the corresponding values for the homogeneous mixture.

This behaviour can be related to the spinodal mechanism and kinetics of the demixing process. According to this mechanism[31,32], the phase separation occurs by the growth with time of small concentration fluctuations. In the early stage, these fluctuations are relatively small and the amplitude of the predominant mode grows exponentially with time whereas its wavelength, corresponding to a developing spatially periodic structure, remains constant. In the intermediate stage, both the amplitude and the wavelength of the predominant mode vary with time, while in the late stage of decomposition, the phases have reached their equilibrium concentration, and wavelength variations only are expected. *A priori*, these different steps may be estimated by plotting the

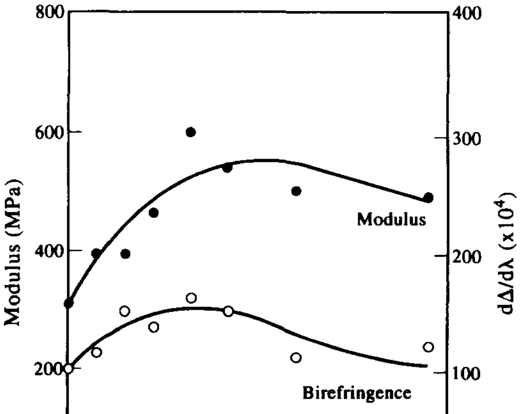

Figure 5 Initial slope of the Δ–λ curves and Young's modulus E as a function of annealing time, for the 60/40 PS/PVME blend annealed at 401 K ($T_c + 5$)

logarithm of the maximum scattered intensity, I_{max}, *versus* annealing time[18-20].

In this study, a SALS pattern was obtained in the form of a circular halo increasing in intensity as the phase separation progresses. *Figure 7* shows the variation of $\ln(I_{max})$ as a function of the annealing time at $T_c + 5$. From this plot, the early stage, which corresponds to the linear branch of the curve, can be estimated at about 35 min and, after a period of time of about 110 min, the scattered intensity remains practically constant indicating that the late stage of decomposition is reached. As a point of comparison, Kumaki and Hashimoto[20] reported, for a 70/30 PS/PVME mixture, having molecular weights comparable to those used in this study and annealed at 3 K above its cloud point, that the early stage extends for a period of about 30 min. Hashimoto *et al.*[19,33] also reported, for the 20/80 critical composition demixed at 2.4 K above its cloud point, that the late stage occurs in the time scale of 60–300 min.

These results suggest a correlation between the decomposition process and the observed variation of orientation and modulus with annealing time. In the early and intermediate stages, i.e. at relatively short times, the morphology of the blend is dominated by the growth with time of a very regular intertwined structure where the boundaries between the phases are diffuse and the domains that grow are co-continuous and well connected[18,31,34]. This morphology gives rise to long-range order and leads to enhanced mechanical properties[35]. Furthermore, since the major phase becomes progressively richer in PS, the distance between its T_g and the stretching temperature increases leading to a progressive increase of the heterogeneous blend modulus and orientation. As the phase separation approaches the late stage, i.e. for long annealing times, the interconnected structure breaks up to form discrete phase domains that grow subsequently by coalescence and the interface between the separate phases becomes relatively sharp[36,37]. This phase separation at large scale and the weak phase bonding are probably responsible for the decrease of modulus and PS orientation (*Figures 5* and *6*) observed at long times, since the stress is inefficiently transmitted through the interphase.

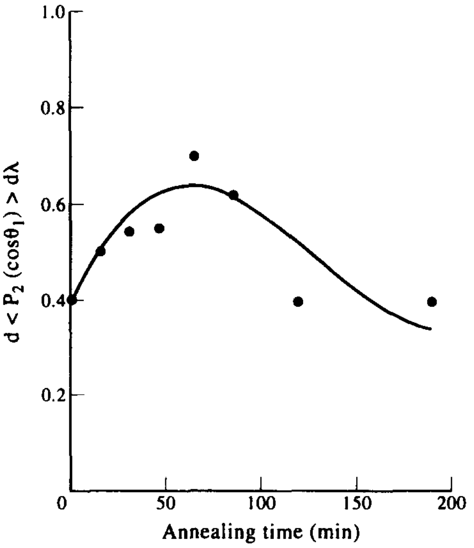

Figure 6 Initial slope of the $[\langle P_2(\cos\theta)\rangle - \lambda]$ curves for the 60/40 PS/PVME blend, as a function of annealing time

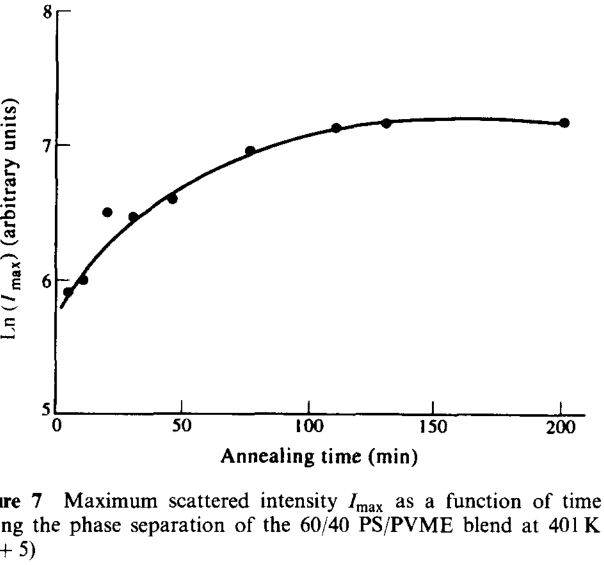

Figure 7 Maximum scattered intensity I_{max} as a function of time during the phase separation of the 60/40 PS/PVME blend at 401 K ($T_c + 5$)

In this context, the influence of annealing temperature, illustrated in *Figures 3* and *4*, can be more satisfactorily explained, in particular at high annealing temperatures. Indeed, on the basis of the difference $T - T_{gM}$ only, one would expect a higher orientation and modulus at $T_c + 40$ than at $T_c + 30$ since, at this former temperature, this difference $T - T_{gM}$ is about 20 K larger (see *Table 1*). In fact, the higher the annealing temperature, the faster the kinetics of phase separation. Therefore, after 15 min of annealing at $T_c + 40$, the late stage may have been already reached, resulting in lower modulus and orientation than those observed at $T_c + 30$.

Analysis of different blend compositions

The orientation of PS/PVME blends has been previously investigated in the miscible region, at a reference temperature of $T_g + 10$[28]. The synergestic effect observed in orientation and modulus, above a critical PVME weight fraction of 0.3, has been attributed to a change in the strength of specific interactions between PS and PVME which induces a cooperative process of orientation of the two dissimilar chains. Supposedly, up to this critical weight fraction, specific interactions are weak, the local environment of the two dissimilar chains is slightly perturbed, and the two polymers orient independently, with an orientation which differs slightly from that of the pure components. In contrast, in the intermediate range of compositions, these interactions are strong. They increase the interchain friction and the relaxation of the dissimilar chains is mutually hindered, leading to a significant increase of the orientation of the two polymers.

In order to compare the orientation behaviour of miscible and heterogeneous blends, in a broad range of compositions, samples of different PS contents have been demixed at $T_c + 5$, for a period of time 15 min, and then stretched at $T_g + 10$ (relative to the miscible blends). The variation of modulus and PS orientation as a function of the bulk composition is illustrated in *Figures 8* and *9*. It is observed that these two parameters follow the same trend in both cases, i.e. they go through a maximum at a 50% composition and they are, in the heterogeneous blends, larger than those of the miscible blends, over the full range of compositions.

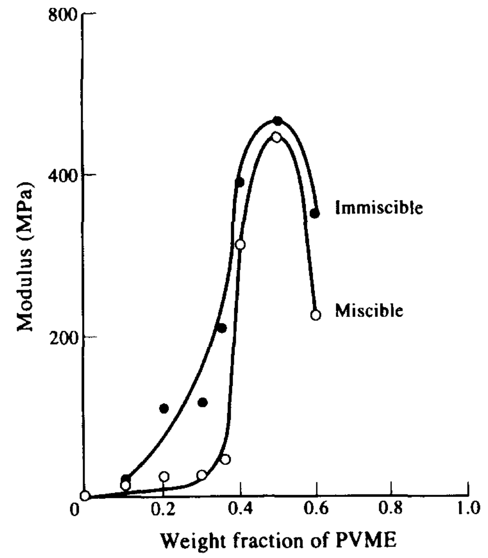

Figure 8 Young's modulus E of miscible and heterogeneous PS/PVME blends of different miscible compositions as a function of the weight fraction of PVME. The miscible blends were annealed 5 K above their cloud points for 15 min

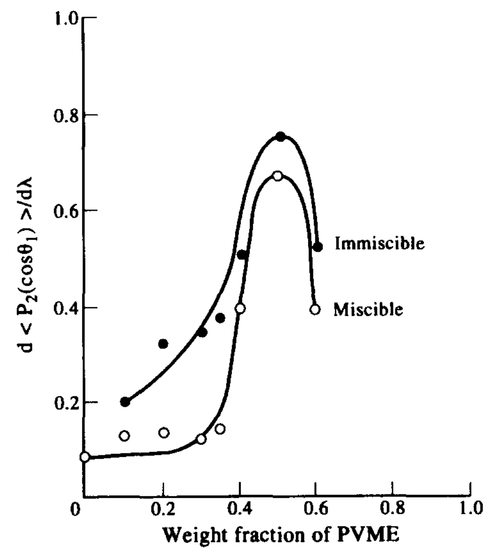

Figure 9 Initial slope of the $[\langle P_2(\cos\theta)\rangle - \lambda]$ curves of miscible and heterogeneous PS/PVME blends of different initial compositions as a function of the weight fraction of PVME. The miscible blends were annealed 5 K above their cloud points for 15 min

Table 2 Weight fraction, PS percentage, and T_g of the major phase, calculated for equilbrium conditions, for different PS/PVME miscible blends annealed 5 K above their cloud points

Miscible blend		Major phase			$T - T_{gM}$ (K)	$T - T_{gm}$ (K)
%PS	T_{gmisc} (K)	W_M	%PS	T_{gM} (K)		
90	359	0.96	94	368	1	10
80	343	0.94	85	350	3	10
70	325	0.93	75	331	4	10
65	310	0.93	71	325	−5	10
60	294	0.89	67	314	−10	10
50	275	0.78	62	300	−15	10
40	267	0.87	44	269	8	10

As has been pointed out in previous sections, this result can be related to the phase separation process which controls both the morphology and the composition of the heterogeneous blends. First, since the samples were annealed just 5 K above their T_c for a short period of time, it is expected that the phase separation process may stop at the early or intermediate stages. Consequently, the morphology of the heterogeneous blends is likely dominated by an intertwined structure where the phase domains are well connected, leading to enhanced mechanical properties. On the other hand, the composition of the phases, after phase separation at $T_c + 5$, depends on the initial composition of the miscible system.

Table 2 reports the weight fraction, the PS content and the T_g of the major phase expected for equilibrium conditions at $T_c + 5$; these values were estimated from the PS/PVME phase diagram (*Figure 1*). It can be seen that the major phase is always richer in PS than the initial mixture and, therefore, its T_g is always above that of the miscible blend. Hence, for a given bulk composition, the difference ($T - T_{gM}$) between the stretching temperature and the T_g of the major phase is always smaller than 10 K. For example, the 65/45 miscible system is stretched 10 K above its T_g, i.e. in the rubbery state, while the major phase of the corresponding heterogeneous blend is stretched in the glassy state, 5 K below its T_g (*Table 2*). This leads to higher modulus and orientation in the heterogeneous state than in the homogeneous one since the chain relaxation in the demixed blend is comparatively slower and the resistance to deformation higher.

Kim *et al.*[14] also investigated the effect of the phase separation temperature and time on the tensile and dynamic mechanical properties of PS/PVME blends. At room temperature, they found that the tensile modulus of blends containing 60 and 70% PS is higher in the heterogeneous state, and increases with the time and temperature of heat treatment, in agreement with this work. However, they pointed out that this trend is very sensitive to the stretching temperature and may even be reversed. In our opinion, this modulus inversion with the stretching temperature must be attributed to the contribution of the minor phase to the average mechanical properties of the heterogeneous blends and not to the fact that the miscible blend is stretched below its T_g. This is clearly illustrated by the dynamic mechanical results reported for the 60/40 blend; in the transition region of the minor phase, the storage modulus of the miscible blend is higher than that of the heterogeneous one, while it becomes lower in the transition region of the major phase (Fig. 11 of ref. 14). Similarly, for a blend containing 80% PS, at a stretching temperature of 50°C, the tensile modulus is lower in the miscible blend even if it is stretched in the glassy state, 30°C below its T_g (see Fig. 9 of ref. 14; the T_g value can be easily estimated from Fig. 10 of ref. 14). From another point of view, since modulus and orientation are closely related, as is illustrated from the present work, it is expected that the orientation behaviour will exhibit a similar dependence with the stretching temperature.

In contrast, the results reported by Lu *et al.*[11,12], for a 50/50 PS/PVME blend, are in disagreement with those reported here and in ref. 14. Both modulus and orientation were found to be higher in the miscible than in the heterogeneous state even if the homogeneous sample was stretched 8 K above its T_g. It must be noted, however, that the heterogeneous sample was directly cast from a chloroform solution, and not obtained by heating up the homogeneous mixture above its cloud point; this procedure may lead to macrophase separation and large phase domains with weak interfacial bonding, resulting in poor mechanical properties and relatively lower modulus and orientation values.

CONCLUSION

For immiscible polymer blends, the mechanisms of deformation and molecular orientation are intimately related to their microstructure, i.e. the composition of the phase domains, their size, and the nature of the interface. In the case of heterogeneous PS/PVME systems produced by temperature-induced phase separation, these parameters are governed by the spinodal decomposition process. In contrast to intrinsically immiscible systems, the resulting morphology is highly interconnected because the two phases are not made of pure polymer A and pure polymer B, as in the immiscible system, but are composed of a polymer A-rich phase and a polymer B-rich phase. Therefore, the two phases should exhibit adhesion and interpenetration of the dissimilar chains at the interphase. These factors can lead to enhanced mechanical properties and enable the heterogeneous blend to exhibit a high degree of orientation.

In this context, the annealing temperature and time, which control both the composition and morphology of the blend, play a crucial role. In this study, the miscible blend was always stretched in the rubbery state, 10 K above its T_g whereas, after phase separation, the major phase of the heterogeneous blend was stretched in the glassy state, at temperatures lower than its T_g. This situation has lead to higher values of modulus and orientation in the heterogeneous system. This increase was, however, attentuated by the progressive change of the blend morphology with annealing time.

ACKNOWLEDGEMENTS

The authors would like to thank the Natural Sciences and Engineering Research Council of Canada and the Department of Education of the Province of Quebec (FCAR and Action Structurante Programs) for their financial support.

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