

Orientation and relaxation in uniaxially stretched poly(vinyl methyl ether)-atactic polystyrene blends*

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Infrared measurements of the dichroic ratio of polystyrene and poly(vinyl methyl ether) absorption bands allow us to determine chain orientation for each component in their compatible blends. Influence of strain rate and temperature of stretching on orientation of both polymer chains in blends containing up to 25% PVME has been studied. Mechanical relaxation master curves at a reference temperature $T = T_g + 40^\circ\text{C}$ have also been determined. Results are compared to previous results obtained in PS-PPO compatible blends. Although PPO and PVME chains behave differently PS chains behaviour is similar in the two types of blends and interpreted in terms of a hindrance of relaxation of PS chains induced by a modification of friction coefficients due to the molecular interactions which are at the origin of compatibility.

(Keywords: PS; PVME; polymer blends; orientation; relaxation; FT i.r.)

INTRODUCTION

In previous work¹⁻³, we pointed out that poly(2,6-dimethyl, 1,4-phenylene oxide) (PPO) and atactic polystyrene (PS) chains orient in a different way when subjected to a uniaxial strain in spite of the compatible nature of the blend. PPO chains acquire a strong orientation independent of the composition while PS chain orientation strongly increases with PPO concentration. Results were interpreted in terms of a hindrance of relaxation of PS chains induced by interaction with a highly oriented PPO network which slowly relaxes³. The stiffness of PPO chains is quite high and it is interesting to examine the orientation behaviour of PS chains in compatible blends when the second polymer chains are more flexible than PS chains. PS-poly(vinyl methyl ether) (PVME) blends are suitable for such an analysis and the present work deals with the study of orientation and relaxation of PS/PVME blends using infra-red dichroism and dynamic shear measurements.

THEORY

Uniaxial stretching of polymer material induces anisotropy in the orientation of the molecular segments. This fact is at the origin of infra-red dichroism.

Orientation of chains can be characterized by an orientation distribution function $f(\theta)$, in the case of uniaxial stretching, where θ is the angle between the chain axis and the stretching direction. Then, $f(\theta)$ is expressed as:

$$f(\theta) = \sum_{n=0}^{\infty} (n + \frac{1}{2}) \langle P_n(\cos \theta) \rangle_{\text{av}} P_n(\cos \theta)$$

where $P_n(\cos \theta)$ are the spherical harmonic functions. Infra-red measurements on oriented materials determine

the second moment of the orientation function $\langle P_2(\cos \theta) \rangle_{\text{av}}$. For a given absorption band, the dichroic ratio $R = A_{\parallel}/A_{\perp}$ (A_{\parallel} and A_{\perp} being the measured absorbances for electric vector parallel and perpendicular to the stretching direction) is related to $\langle P_2(\cos \theta) \rangle_{\text{av}}$ by:

$$\langle P_2(\cos \theta) \rangle_{\text{av}} = (3 \langle \cos^2 \theta \rangle_{\text{av}} - 1) / 2 = \frac{R - 1 R_0 + 2}{R + 2 R_0 - 1}$$

with $R_0 = 2 \cot^2 \alpha$, α being the angle between the dipole moment vector of the vibration and the local chain axis. In a uniaxial extension, $\langle P_2(\cos \theta) \rangle_{\text{av}}$ varies between 0 for an isotropic material and 1, for a perfectly oriented sample in the stretching direction.

Orientation measurements were combined with mechanical relaxation. Dynamic shear experiments give the real ($G'(\omega)$) and imaginary ($G''(\omega)$) parts of the complex modulus. The relaxation modulus can then be calculated by the formula of Ninomya and Ferry⁵:

$$E(t) = G'(\omega) - 0.40 G''(0.40 \omega) + 0.014 G''(10 \omega)$$

with $\omega = 1/t$.

EXPERIMENTAL

Polymers used were atactic polystyrene ($M_n = 150\,000$, $M_w = 254\,000$) from CdF-Chimie Co. and poly(vinyl methyl ether) ($M_n = 45\,000$, $M_w = 90\,000$) from Poly-science.

Orientation measurements

The deformation was applied at controlled temperatures above T_g and constant strain rates using a stretching machine developed in our laboratory. After stretching, the samples were quenched at room temperature so that the orientation was frozen. Infra-red measurements were run using a 7199 Nicolet FTIR spectrometer equipped with a gold wire grid polarizer.

* Dedicated to Dr P. Thirion on the occasion of his retirement.

Griffiths⁶ has shown that quantitative FTi.r. spectroscopy is obtained for absorption below 0.6 absorbance unit. Hence very thin films have to be used. Casting of these films was ruled by a second main condition: PS/PVME phase diagram exhibits a lower critical solution temperature close above the blend T_g ⁷ and few solvents lead to compatible blends⁸. Eventually benzene appeared as the best solvent. A 7% solution was cast on a glass plate and dried for one day at room temperature. A thermal treatment at $T = T_g + 30^\circ\text{C}$ in an oven under vacuum followed in order to remove residual solvent and internal stresses.

To allow comparisons between blends of different compositions, stretching experiments were carried out at constant $T - T_g$ differences. This condition implies a measure of T_g . A Dupont differential scanning calorimeter was used with a $20^\circ\text{C min}^{-1}$ heating rate. On another part, this measure controlled the absence of solvent and the good compatibility in the film obtained.

Viscoelastic measurements

Dynamic shear experiments were conducted at Professeur Froelich Laboratory E.A.H.P. F 67000 Strasbourg (France). The rheometer used was a Weissenberg type RMS 605 equipped with a plate-plate system (sample diameter: 25 mm, thickness: 1.6 mm). Blends were diluted in benzene and freeze-dried. Then samples were compression moulded under vacuum at $T = T_g + 50^\circ\text{C}$ and annealed for 3 h at $T = T_g + 30^\circ\text{C}$. Frequency varied from 10^{-2} to 10^{+2} Hz and deformation from 1 to 5% according to the signal obtained.

RESULTS

Orientation in PS/PVME blends

As seen earlier, the band used for each component must be isolated and its characteristics known. Figure 1 presents the spectra of pure PS and pure PVME. Polystyrene spectra have been widely studied and according to Lefebvre *et al.*⁹ we used the ν_{18a} in plane CH bending mode of the aromatic ring at 1028 cm^{-1} . This vibration is conformationally insensitive and is not overlapped by PVME absorption bands. The dipole moment vector which is along the C_1-C_4 axis makes a 90° angle with the

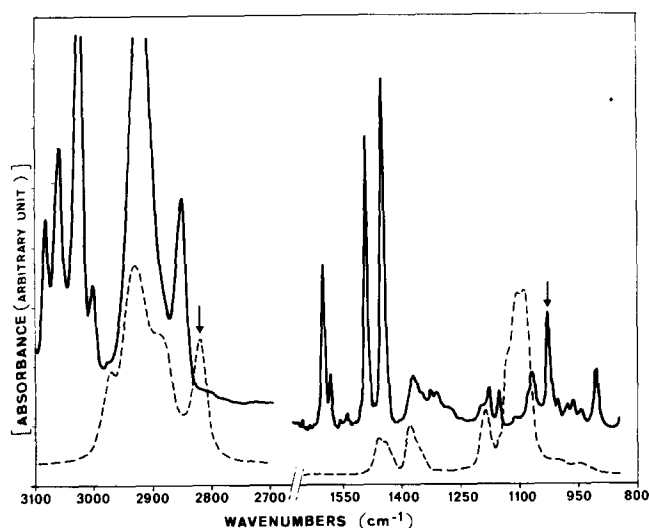


Figure 1 Infrared spectra of polystyrene (—) and PVME (---). Arrows indicate bands used for dichroic measurements

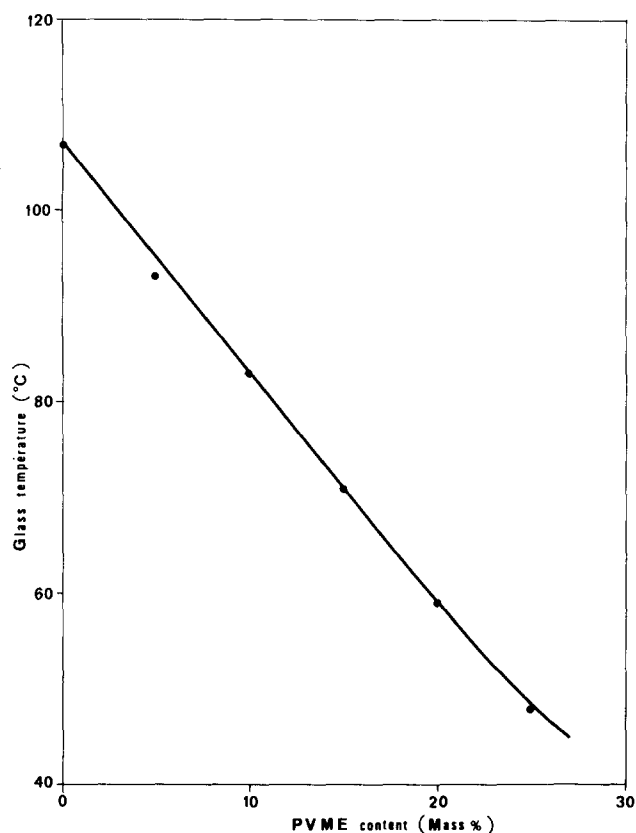


Figure 2 Glass transition temperatures of PS/PVME blends

chain axis defined in ref. 10. As for PVME, only two absorption bands are not overlapped by PS. The first one, at 1100 cm^{-1} is assigned to the C-O-C asymmetric stretching mode of the ether linkage while the second one at 2820 cm^{-1} has to be assigned to the symmetric stretching mode of the methoxy group^{11,12}. Both these modes are relative to the side chain vibrations.

In a conformational analysis of poly(alkyl vinyl ether), Abe¹³ has shown that the g^- conformation of the methoxy group is almost entirely suppressed in the poly(vinyl methyl ether) chains. Furthermore, a displacement of 20° for the t and g^+ states has been suggested from the crystallographic analysis on isotactic PVME¹⁴. Accordingly the 1100 cm^{-1} and 2820 cm^{-1} absorption bands should present a perpendicular dichroism. However, the calculation of orientation functions is impossible as the real conformational structure of the side chain of PVME in the blends cannot be exactly determined. Later, orientation of PVME chains using infra-red will only be estimated on the basis of the dichroism of these two bands.

The addition of a small amount of PVME involves a sharp decrease of the glass temperature of the blend (Figure 2) but the stretching process needs a contrast between room temperature and experimental temperature in order to freeze the orientation achieved. PVME composition in the blend is therefore limited to 25%.

Figure 3 shows the results obtained for PS at a strain rate of 0.115 s^{-1} and at stretching temperatures $T = T_g + 11.5^\circ\text{C}$. $\langle P_2(\cos \theta) \rangle$ orientation functions are plotted versus draw ratio for the different compositions studied. As pointed out elsewhere², a rectilinear relation holds between orientation function and draw ratio in the present experimental conditions. Accordingly, the slope $\frac{d\langle P_2(\cos \theta) \rangle}{d\lambda}$ is defined and gives the orientation be-

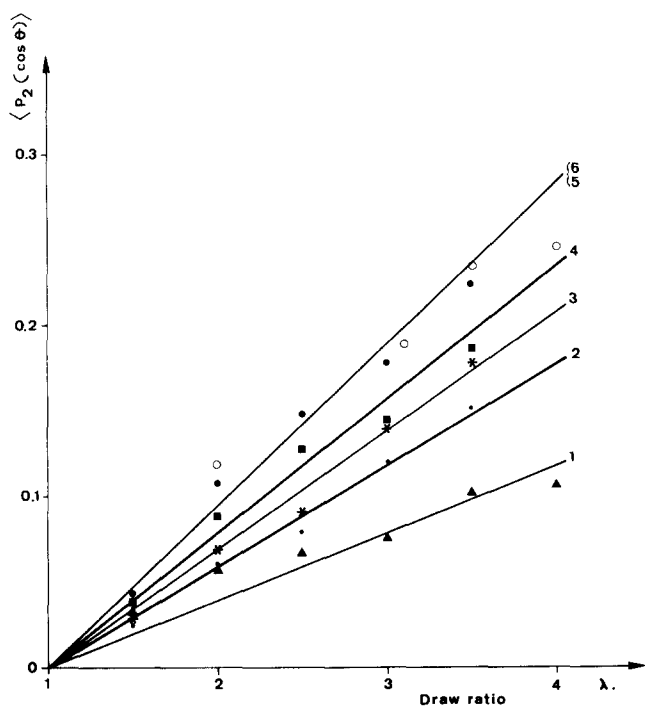


Figure 3 PS orientation in PS-PVME blends at different compositions PVME content: (1) \blacktriangle , 0%; (2) \bullet , 5%; (3) \ast , 10%; (4) \blacksquare , 15%; (5) \circ , 20%; (6) \bullet , 25%. Strain rate: 0.115 s^{-1} . Stretching temperatures: $T = T_g + 11.5^\circ\text{C}$

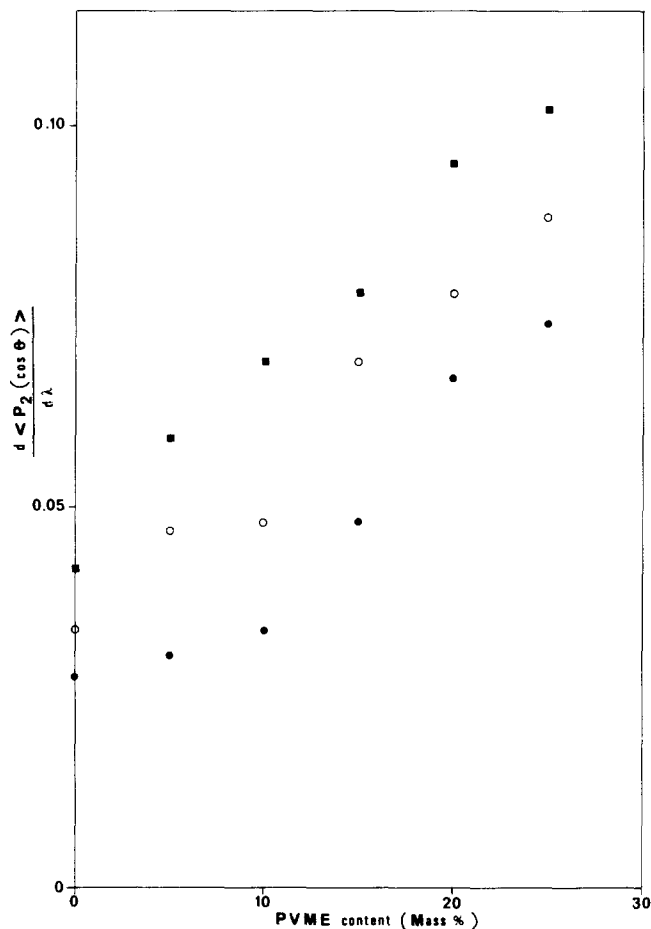


Figure 4 PS orientation versus blend composition. Stretching temperatures: $T = T_g + 11.5^\circ\text{C}$. Strain rates: (\blacksquare) 0.115 s^{-1} ; (\circ) 0.026 s^{-1} ; (\bullet) 0.008 s^{-1}

haviour of a component versus draw ratio. PS orientation increases regularly with PVME concentration.

The slope $\frac{d\langle P_2(\cos \theta) \rangle}{d\lambda}$ for polystyrene orientation versus blend composition is given in Figure 4 for three different strain rates and a stretching temperature $T = T_g + 11.5^\circ\text{C}$. The results are quite similar at $T = T_g + 20^\circ\text{C}$ (Figure 5); the main feature is the strong increase in PS orientation versus PVME concentration at given experimental conditions. Quite naturally, the absolute values of orientation achieved at $T = T_g + 20^\circ\text{C}$ are smaller than the values obtained at $T = T_g + 11.5^\circ\text{C}$. At $T = T_g + 11.5^\circ\text{C}$, there is an increase factor of 2.5 for PS orientation.

As far as PVME is concerned, almost no orientation is achieved as revealed by the very low values of the dichroic ratios of the 1100 cm^{-1} and 2820 cm^{-1} absorption bands. As an example the dichroic ratios of these two bands in the PS (75%)-PVME (25%) blend are given as a function of draw ratio in Table 1 for different strain rates and a stretching temperature of $T = T_g + 11.5^\circ\text{C}$.

Our results are in agreement with the previous work of Lu *et al.*¹⁶ who observed in a 50/50 PS/PVME blend almost no orientation for PVME chains and an increase of PS chain orientation with respect to the pure polymer. Although the experimental conditions are quite different (concentration range and strain rate), the general behaviour is similar in the two sets of measurements.

The very low level of orientation for PVME is corroborated by birefringence. For compatible blends of amorphous thermoplastics, a relation holds between final birefringence and individual orientation functions¹⁷:

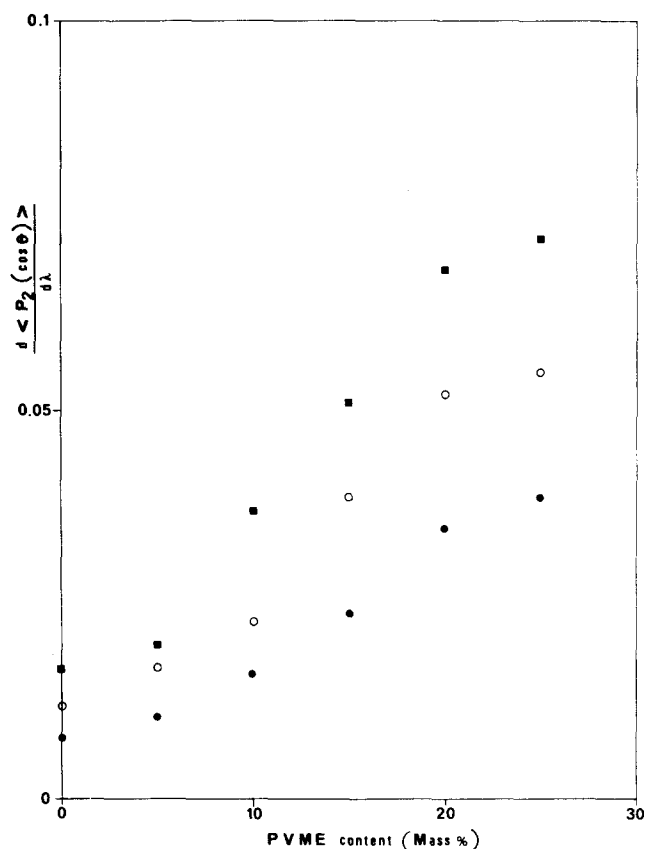


Figure 5 PS orientation versus blend composition. Stretching temperatures: $T = T_g + 20^\circ\text{C}$. Strain rates: (\blacksquare) 0.115 s^{-1} ; (\circ) 0.026 s^{-1} ; (\bullet) 0.008 s^{-1}

$$\Delta n = f_1 \Delta_i^\circ \langle P_2(\cos \theta) \rangle_1 + f_2 \Delta_2^\circ \langle P_2(\cos \theta) \rangle_2$$

where f_i , Δ_i° and $\langle P_2(\cos \theta) \rangle_i$ are the volume fraction, intrinsic birefringence and orientation function of component i , respectively.

Figure 6 illustrates the relation between birefringence and PS orientation in the PS 75%–PVME 25% blend stretched at $T = T_g + 11.5^\circ\text{C}$. Δn is plotted against $f_{\text{PS}} \langle P_2(\cos \theta) \rangle_{\text{PS}}$ where $\langle P_2(\cos \theta) \rangle_{\text{PS}}$ has been measured by infra-red dichroism. For a low level of orientation a linear relationship holds between birefringence and PS orientation with a slope of -0.12 . The slope fits the usual value of intrinsic birefringence of bulk PS¹⁸ which

Table 1 Dichroic ratios of PVME absorption bands at 1100 cm^{-1} and 2820 cm^{-1} in the PS (75%)–PVME 25% blend, as a function of draw ratio, for different strain rates and a stretching temperature of $T = T_g + 11.5^\circ\text{C}$

λ	ν	0.008 s ⁻¹		0.026 s ⁻¹		0.115 s ⁻¹	
		1100 cm ⁻¹	2820 cm ⁻¹	1100 cm ⁻¹	2820 cm ⁻¹	1100 cm ⁻¹	2820 cm ⁻¹
1.5	1.00	1.03	0.98	0.99	0.99	0.98	
2	0.97	1.02	0.97	0.98	0.97	0.97	
2.5	0.96	0.96	0.98	0.98	0.96	0.96	
3	0.97	0.96	0.96	0.96	0.95	0.96	
3.5	0.96	0.97	0.96	0.96	0.95	0.95	
4	0.97	0.95					

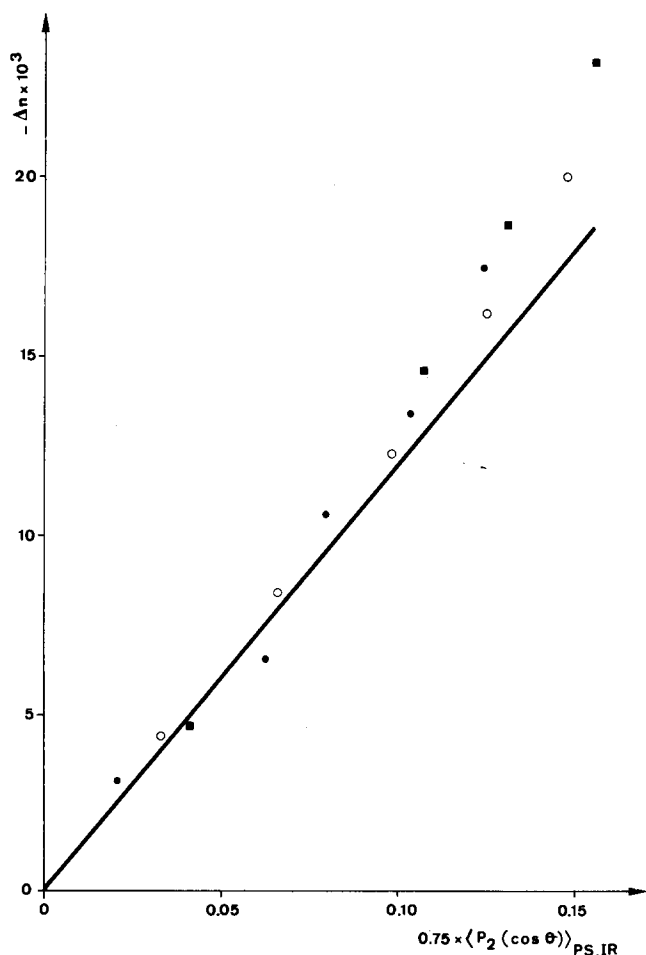


Figure 6 Birefringence versus PS orientation in the PS (75%)–PVME (25%) blend. Stretching temperature: $T = T_g + 11.5^\circ\text{C}$. Strain rates: (■) 0.115 s^{-1} ; (○) 0.026 s^{-1} ; (●) 0.008 s^{-1}

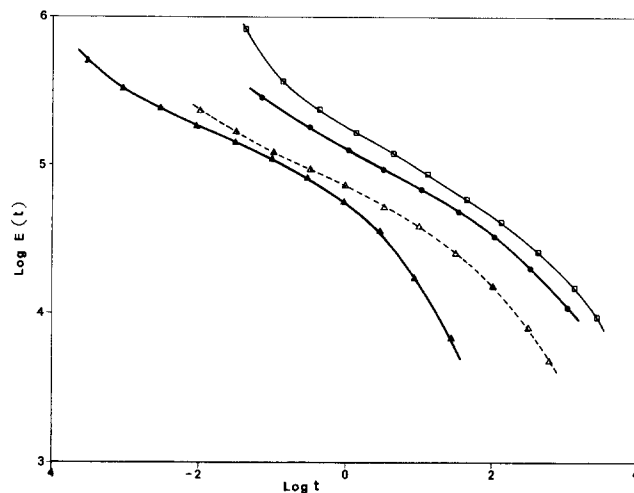


Figure 7 Master curves $\log E(t)$ versus $\log t$ for PS/PVME blends. Reference temperatures $T = T_g + 40^\circ\text{C}$. PVME content: (▲) 0%; (△) 10%; (●) 20%; (□) 25%

indicates that PVME orientation is not detectable. For PS orientation levels higher than 0.10–0.13 a deviation from linearity on the higher absolute value side of birefringence is observed. This effect is progressive and indicates that PVME begins to participate to birefringence. According to the band polarizabilities in the COCH_3 group¹⁹, a negative intrinsic birefringence can be predicted for the more stable conformations. So the appearance of a slight PVME orientation must induce an increase in the total negative birefringence of the blend.

The increase in PS orientation versus PVME composition reflects a hindrance of PS orientation relaxation. It has already been shown that orientational and mechanical relaxations were closely linked². It is interesting to examine if in the case of PS/PVME blends the strong effect on polystyrene orientation has any consequence on the mechanical relaxation of the blends.

Viscoelasticity of PS/PVME blends

As seen earlier, mechanical relaxation curves can be deduced from dynamic oscillatory measurements. Frequency sweep was done at constant temperature. For a given composition, 5 to 7 different temperatures above T_g were swept. The time temperature equivalence was used to reduce results at a reference temperature. Relaxation modulus was then calculated with Ferry and Ninomya's relation.

In Figure 7, $\log E(t)$ is plotted versus time t for four different compositions at equivalent reference temperatures $T = T_g + 40^\circ\text{C}$. The choice of this temperature is arbitrary but it falls within the range of experiments so no extrapolated reduction is necessary. The hindrance in relaxation is obvious. Despite the presence of a very flexible polymer, the mechanical relaxation of the blends is strongly hindered.

It is interesting now to recall the results found previously on PS/PPO blends^{1–3}. Measurements of orientation and relaxation of each component in these blends were performed under experimental conditions comparable with the present work. Unlike PVME, PPO acquires a strong orientation, independent of composition. Polystyrene orientation increases with PPO content. It is noticeable that the range of this increase is in the same order of magnitude as in the case of PS/PVME blends.

Orientation relaxation of chains in PS/PPO blends varies similarly: whereas PPO relaxation is independent of concentration, PS orientation relaxation is hindered when PPO content increases.

DISCUSSION

The PS/PVME blends study improves the understanding of the behaviour of each component in compatible blends.

Orientation in a compatible blend cannot be related to the stiffness of the second component. Although the second component is stiffer in one case (PPO) and more flexible in the other case (PVME), polystyrene acquires a higher orientation in both blends as compared to the pure polymer. This orientation is similar in both cases.

On the other hand, variations of density of entanglements cannot be considered as at the origin of molecular behaviour, since the orientation of PPO is constant whatever its content is.

In fact PS/PVME and PS/PPO blends are thermodynamically similar and it seems necessary to explain their behaviours by the same laws. PS/PPO blends orientation and relaxation were explained³ by the existence of a rigid network of PPO hindering PS relaxation. On the contrary, PVME remains always unoriented in PS/PVME blends while PS orientation increases with the concentration of the second component. Consequently the existence of an oriented network as an hindrance to PS relaxation cannot be sustained.

Compatibility is due to strong molecular interactions. For instance, in the case of PS/PVME blends, Lu *et al.*¹⁵ pointed out the influence of compatibility on the CH out-of-plane vibration of the ring (700 cm^{-1}) in polystyrene and the COC vibration (1100 cm^{-1}) of PVME. A strong interaction between these groups induces compatibility for this pair of polymers. Similarly, there are strong interactions between the phenyl ring of PS and the phenylene ring of PPO in PS/PPO compatible blends²⁰. Interactions greatly modify molecular environment of polymer chains. Therefore, mobility of the two polymer chains is hindered and the friction coefficient of each species is increased. As final orientation is mainly governed by chain relaxation, an increase in orientation should be observed for both polymers in the blends when compared with the pure components.

In both blends—PS/PPO and PS/PVME—this observation can be done on PS when the second polymer is added. But no influence appears on PPO or PVME. In fact, in order to detect a change in chain orientation, it is necessary that the characteristic relaxation time of the polymer chain be in the time range which is covered in the experimental conditions. So, in the present case, PVME chains which have a very fast relaxation time remain unoriented while PPO chains keep the orientation that

they have acquired during stretching for their relaxation time is very long.

It would be interesting to see the change of friction coefficients induced by the compatibility in the blends. Such information can be obtained from chain diffusion experiments. Kausch and collaborators^{21,22} have shown that crack-healing of amorphous polymers slightly above T_g involves the diffusion of macromolecules across the interface. Thus such a technique should allow us to detect changes in the diffusion mechanism in the blend with respect to the pure polymer.

Preliminary results obtained on PS–PPO blends indicate a slow down of diffusion²³. Experiments are continuing in Prof Kausch laboratory on PS–PPO and PS–PVME blends to support our hypothesis.

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