Fourier transform infra-red study of uniaxially oriented poly(2,6-dimethyl 1,4-phenylene oxide)–atactic polystyrene blends

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Infra-red measurements of the dichroic ratio of absorption bands of atactic polystyrene–poly(2,6-dimethyl 1,4-phenylene oxide) blends provide a valuable method to investigate the orientation of the chains of both polymers. The results show that PPO and PS chains orient in a different way when subjected to an uniaxial strain, in spite of the compatible nature of the blend. The PPO orientational behaviour does not depend on PPO concentration in the studied concentration range (0–35%) while PS orientation regularly increases up to 25% PPO then remains constant.

INTRODUCTION

Over the last decade the interest in polymer blend systems as a way to meet new market applications with minimum development cost has increased rapidly. One of the most important compatible polymer blends is based on atactic polystyrene (PS) and poly(2,6-dimethyl 1,4-phenylene oxide) (PPO)[1].

Usually two different high polymers will not mix on the segmental level but an especially favourable interaction between two polymers may permit homogeneous blends. The compatibility of PPO and PS in all proportions[1,2] has been explained this way in agreement with thermodynamic studies[3].

PPO–PS blends exhibit improved thermal resistance and different mechanical[4] and rheological[5] properties. Two domains appear as a function of the ratio of the two polymers[6]: a brittle region exists at low PPO concentrations while a ductile behaviour is observed at high PPO ratios.

The mechanical properties are strongly influenced not only by the structure of the material but by molecular orientation and a great deal of interest exists in the molecular orientation introduced by any forming process (e.g. drawing).

The orientation of polymer chains in compatible PPO–PS blends has not yet been investigated. Infra-red spectroscopy is an attractive method of deducing the chain orientations of the different polymers in a blend using specific vibrations of the different chemical units.

The present experimental approach is designed to evaluate the orientation of PPO and PS in uniaxially stretched brittle blends as a function of draw ratio and temperature of stretching, using Fourier transform infra-red spectroscopy (*FT*i.r.).

THEORY

The use of vibrational spectroscopy as a toll to measure orientation in polymers was reviewed recently[7]. It is, however, interesting to sum up briefly the information available by infra-red dichroism measurement.

The orientation of a single unit of a polymer chain can be described by the three Eulerian angles: Θ, φ, Ψ which define the three rotations required to bring into coincidence a set of Cartesian axes in the unit with an external reference set of Cartesian axes. The orientation is then described by an orientation distribution function $f(\Theta, \varphi, \Psi)$[8]. In the case of uniaxially oriented systems, the orientation distribution of structural units is random with respect to φ and Ψ and the orientation distribution function is expressed as:

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

where $P_n(\cos\Theta)$ are the spherical harmonic functions

$$P_2(\cos\Theta)=(3\cos^2\Theta-1)/2$$

$$P_4(\cos\Theta)=(35\cos^4\Theta-3\cos^2\Theta+3)/8$$

etc....

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

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

with $R_0=2\cot g^2\alpha$· α being the angle between the dipole moment vector of the vibration and the chain axis, and Θ is the angle between the chain axis and the chain direction. The angle α can usually be obtained from theoretical considerations[9]. However, if the second moment value is known, using a well defined absorption band, the orientation of the dipole moment vector relative to the chain axis can be determined for any absorption band.

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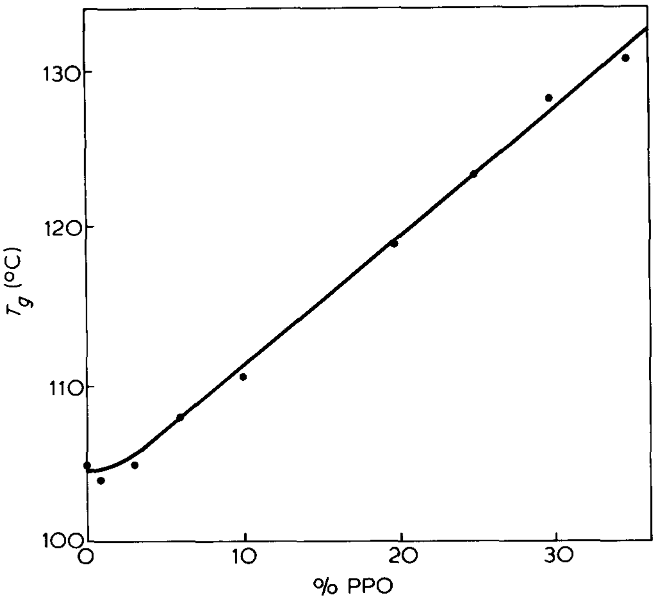

Figure 1 Glass transition of PPO blends as a function of PPO percentage

EXPERIMENTAL

The polymers used were atactic polystyrene ($\bar{M}_n$ = 149 000, $\bar{M}_w$ = 254 000) from CdF Chimie and poly(2,6-dimethyl 1,4-phenylene oxide) (M_n = 15 000, $\bar{M}_w$ = 35 000) kindly provided to us by R. P. Kambour (General Electric Co.).

Sample preparation

Films about 60μm thick were obtained by casting a 6% solution in chloroform of the two polymers in the desired proportion on a glass plate at room temperature. Samples were cut in the film and heated under vacuum to 40°C above glass transition temperature for 24 h in order to remove any solvent, residual orientation and internal stress. As expected for compatible blends, only one glass transition temperature is observed for the films with a PPO percentage up to 35%. No melting peak was detectable on the thermograms. *Figure 1* gives the variation of glass transition temperature with the percentage of PPO.

The amorphous structure of the sample was also confirmed by X-ray examination. Drawing experiments were made on an apparatus developed in our laboratory, i.e. a stretching machine operating at constant strain rate and a special oven to obtain a very good stability of the temperature all over the sample (homogeneity is ~0.05°C). The temperature of the oven was limited at 150°C and only samples containing up to 35% of PPO could be studied. A strain rate of 0.026 s^{-1} was used for all the stretching experiments. The draw ratio was defined as $\lambda = l/l_0$ (l_0 initial length of the sample, l is the length after drawing).

Infra-red dichroism

The polarized spectra were recorded using a Nicolet 7199 Fourier transform infra-red spectrometer. Single beam spectra were run and the absorbance spectra were calculated using the computer facility and a stored polarizer spectrum as reference. The polarization of the infra-red beam was obtained by the use of a Perkin–Elmer gold wire-grid polarizer, the high efficiency of which makes polarization correction unnecessary. The polarizer was set at a maximum transmission position and the samples rather than the polarizer were rotated 90° in order to obtain the two polarization measurements. Infra-red dichroism was calculated as $R = A_{\parallel}/A_{\perp}$ for $A_{\parallel}$ and $A_{\perp}$ the peak optical densities. One example of spectra and choice of arbitrary local base lines is given in *Figure 2*. This choice was made in order to minimize the influence of overlapping bands. A correct percentage of the two polymers in the blends was obtained using the absorbance values calculated from these base lines in unoriented samples.

Differential scanning calorimetry (d.s.c.)

Thermograms were obtained using a Dupont 990 differential scanning calorimeter fitted with a d.s.c. at a heating rate 20°C min^{-1}; sample weight ~10 mg.

RESULTS

The determination of the orientation function using dichroic ratio measurements requires the use of well known absorption bands. In polystyrene the vibrational modes of the benzene ring can be satisfactorily analysed in terms of the C_{2v} local symmetry of the ring[10]. We chose the out-of-plane mode $\nu^*_{17b}(B_1)$ at 906 cm^{-1} which is the only one which does not overlap any PPO absorption band. The dipole moment vector of this vibration is perpendicular to the plane of the ring and makes an angle $\alpha = 35°$ with respect to the chain axis (see *Figure 3*). This absorption band is conformationally insensitive. We have previously shown[12] that this band gives the same information about chain orientation in polystyrene than the CH_2 symmetrical stretching vibration at 2850 cm^{-1} and the ν_{18a} in plane CH bending mode of the aromatic ring at 1028 cm^{-1}. We chose three absorption bands in PPO: the asymmetric ether stretching vibration at 1190 cm^{-1}, the 1305 cm^{-1} absorption band assigned to the ν_2 (A_1) mode of the 1,2,4,6 tetrasubstituted benzene ring in the C_{2v} local symmetry, and the 865 cm^{-1} absorption band assigned to the out-of-plane ν_{11} mode of the benzene ring[13]. The 1190 cm^{-1} absorption band is very intense and cannot be used for quantitative measurements in the blends containing more than 6% of PPO. The 1305 cm^{-1} absorption band is well adapted to the study of blends containing 6% to 20% of PPO. The 865 cm^{-1} absorption band is suitable for samples containing more than 20% of PPO. All these bands overlap very weak PS bands the effect of which was negligible as discussed before. Another point to consider is how to define a chain axis in PS and PPO. Numerous conformations of the aliphatic chain are expected in atactic polystyrene because of the different configurational sequences existing in this polymer. The only way to define a chain axis compatible with all the conformations is as described in *Figure 3*. Such a chain axis gives self consistent results for 2850, 1028 and 906 cm^{-1} absorption bands[12].

As far as PPO is concerned, conformational calculations[14] indicate that the most stable conformational structure is as shown in *Figure 4* with the planes of the benzene rings perpendicular between them. Although the probability of the existence of higher energetical conformational states was shown not to be zero[15], we considered all the PPO chains to be in the more

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* The numbering is according to Varsanyi[11]

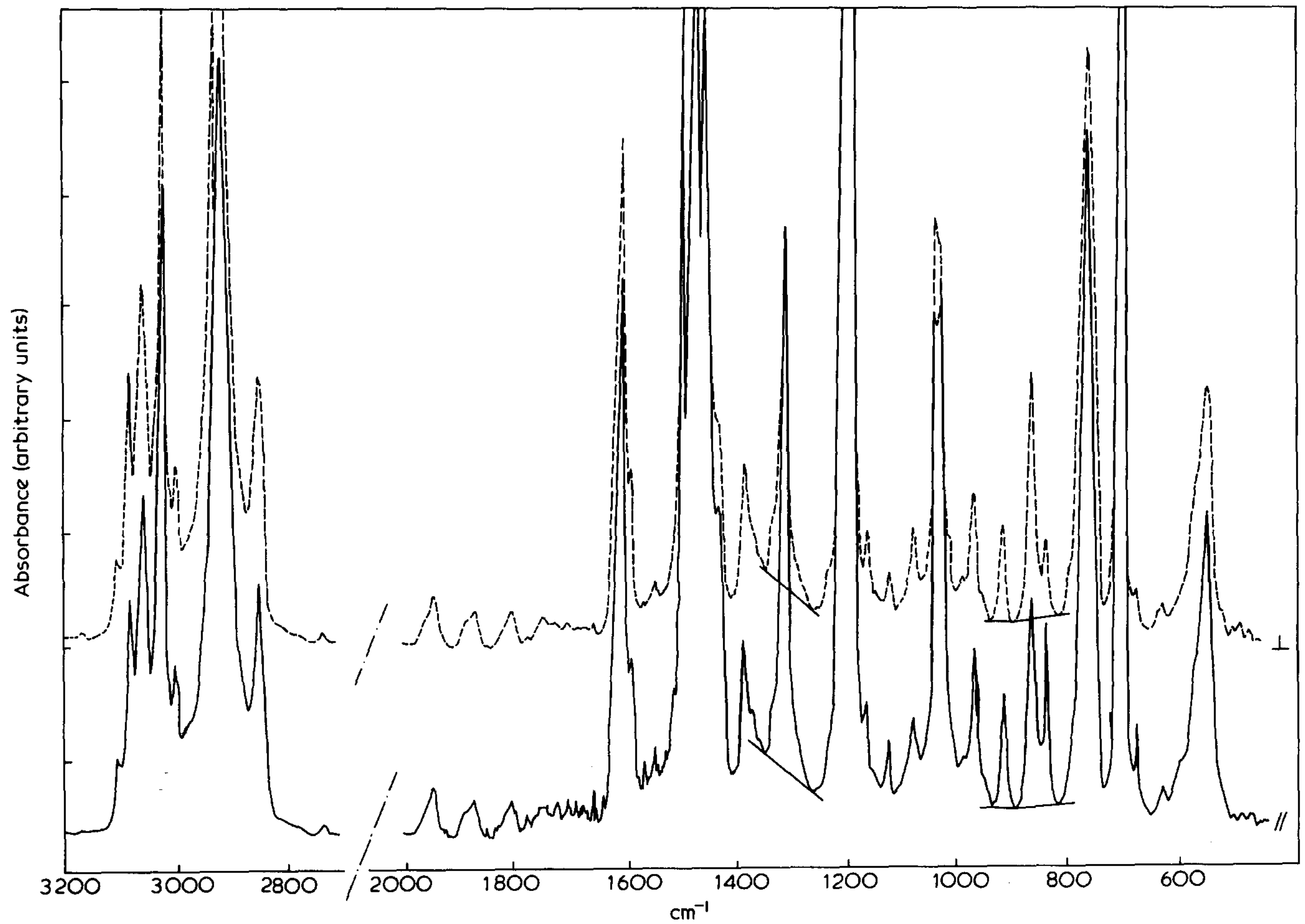

Figure 2 Infra-red spectra of oriented PPO–PS blend containing 20% PPO stretched at $T = Tg + 11.5°$ to a draw ratio $\lambda = 2.5$. Base lines are indicated as bold solid lines. The spectrum of $A_\perp$ is displaced from that of $A_\parallel$ to show the peaks more clearly

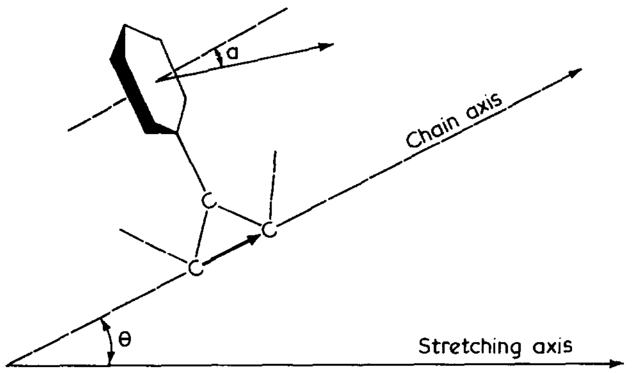

Figure 3 Orientation angles and chain axis in polystyrene

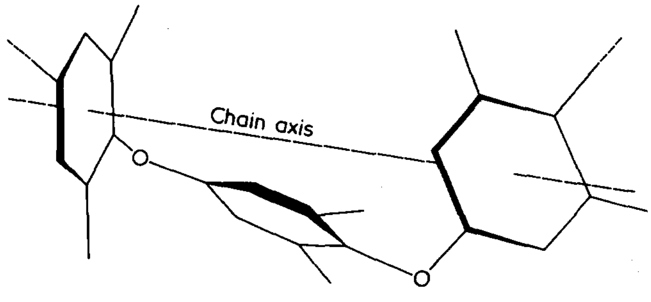

Figure 4 Chain axis in PPO

stable conformation. As shown in *Figure 4* the chain axis was defined as the broken line drawn from the centre of the first benzene ring to the centre of the third one. This choice is univocal and representative of the orientation of the central  group. It is based experimentally on the fact that the $\langle P_2(\cos\Theta)\rangle$ orientation functions obtained by the use of the 1190 cm^{-1} and 1305 cm^{-1} absorption bands are identical in the 6% PPO blends. The dipole moment vector angles α with respect to the chain axis are 20.6° and 22.4° for the 1190 cm^{-1} and 1305 cm^{-1} absorption bands, respectively. A theoretical value of $\alpha = 74°$ is obtained for the 865 cm^{-1} absorption band, in good agreement with the experimental $\alpha = 70°$ obtained from the 20% blend using the 1305 cm^{-1} absorption band as reference for the $\langle P_2(\cos\Theta)\rangle$ calculation.

The other possibilities of choice as chain axis (C_1–C_4 axis of the benzene ring or line joining the centre of two adjacent benzene rings) gave different values for the second moments calculated from the 1190 and 1305 cm^{-1} absorption bands and were rejected.

Orientation behaviour of PPO–PS blends

All the samples were stretched above the glass transition temperature. Let us first examine the results obtained with a stretching temperature $T = Tg + 11.5°$. This value was chosen to be consistent with a previous study on polystyrene orientation performed in our laboratory[16].

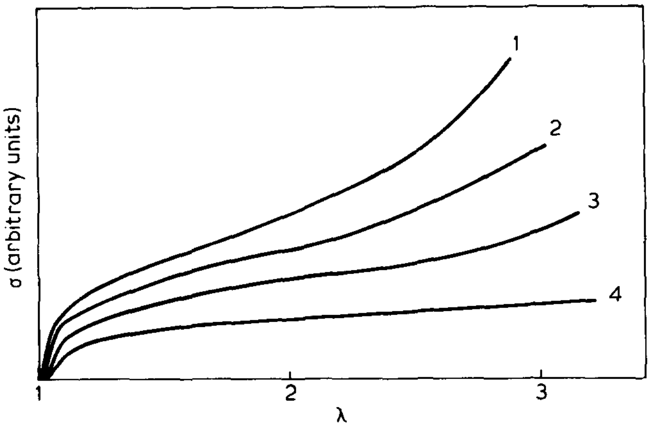

Figure 5 Strain–stress curves of PPO–PS blends stretched at $T = Tg + 11.5°$. Blends containing (1) 30% PPO; (2) 20% PPO; (3) 10% PPO; (4) 0% PPO

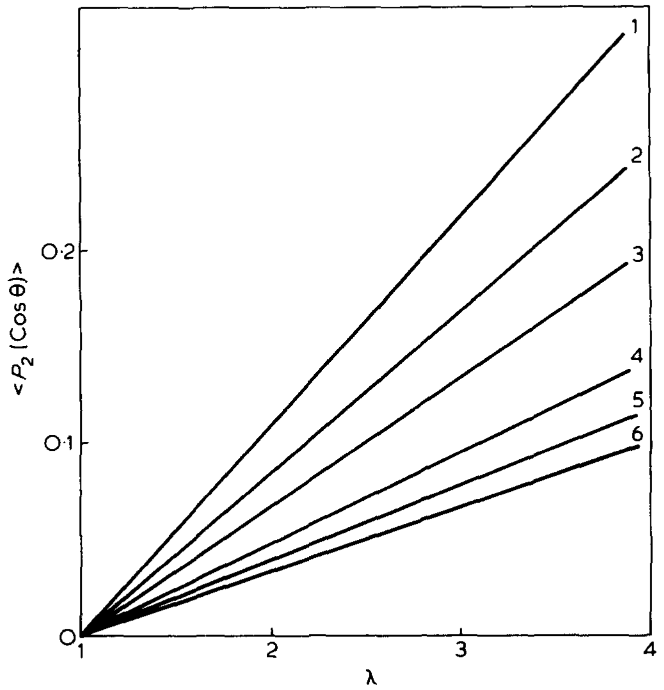

Figure 6 Orientation function of PPO and PS as a function of draw ratio. Temperature of stretching $T = Tg + 11.5°$. PPO (1) any concentration; PS (2) blends 25–35% PPO; (3) blend 20% PPO; (4) blend 10% PPO; (5) blend 6% PPO; (6) blend 0–3% PPO

A typical example of strain–stress curves obtained is shown in *Figure 5*. As expected a two-step process is observed: after a glassy stress behaviour, up to yield point, the almost linear strain–stress curve is relative to deformation in the rubbery state. An increase of the content of PPO results in an increase of the rubbery behaviour as shown by the increase of the slope of the stress–strain curve.

Figure 6 illustrates the change of the $\langle P_2(\cos\Theta)\rangle$ orientation function relative to PPO and PS chains as a function of draw ratio and PPO percentage in the blend. A linear relationship holds for both polymers and any composition of the blend between $\langle P_2(\cos\Theta)\rangle$ *versus* draw ratio.

Another way to illustrate the orientation behaviour is to plot the slope $d\langle P_2(\cos\Theta)\rangle/d\lambda$ as a function of PPO percentage as in *Figure 7*. It is apparent from these results that PPO orients in the same way up to 35%. Polystyrene orientation regularly increases up to a ratio of 25% PPO then remains constant.

The influence of the stretching temperature T on the slope of $\langle P_2(\cos\Theta)\rangle = f(\lambda)$ is shown in *Figure 8*. For a given draw ratio both PPO and PS orientation decrease as T increases because of an increase of chain relaxations. Furthermore a difference of the orientation behaviour of PS is observed (*Figure 9*) in samples stretched at high

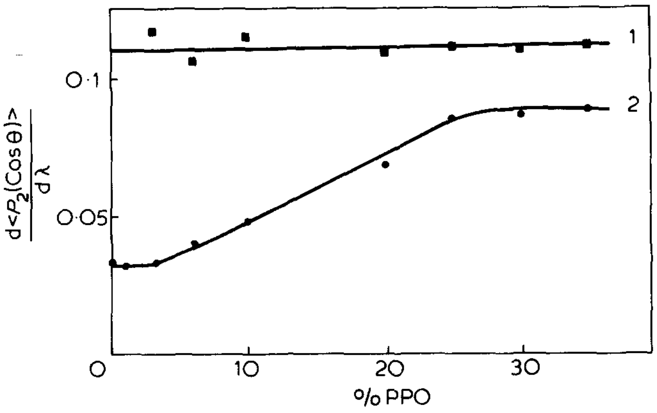

Figure 7 Slope of $\langle P_2(\cos\theta)\rangle = f(\lambda)$ as a function of PPO percentage. (1) PPO; (2) PS

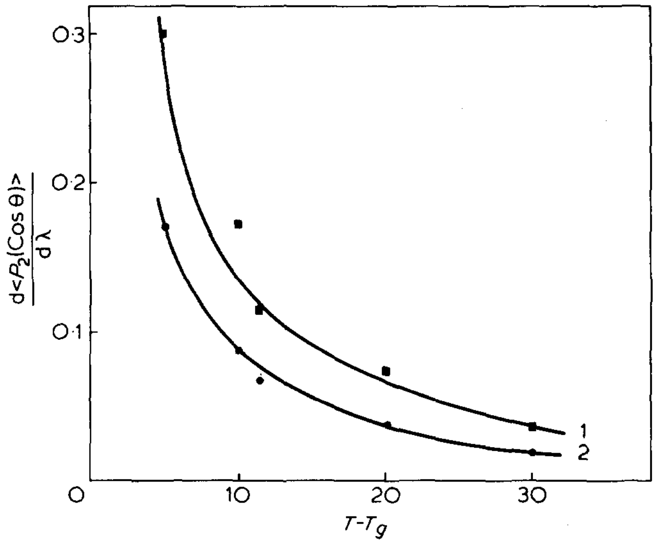

Figure 8 Slope of $\langle P_2(\cos\theta)\rangle = f(\lambda)$ as a function of stretching temperature of PPO–PS blend containing 20% PPO. (1) PPO; (2) PS

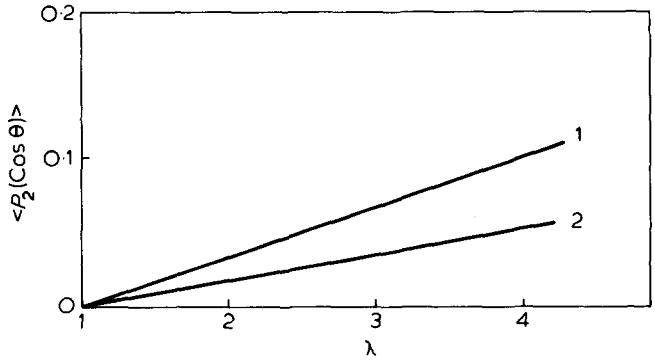

Figure 9 Orientation function of PPO and PS as a function of draw ratio. Temperature of stretching $T = Tg + 30°$. (1) PPO any percentage; (2) PS any percentage

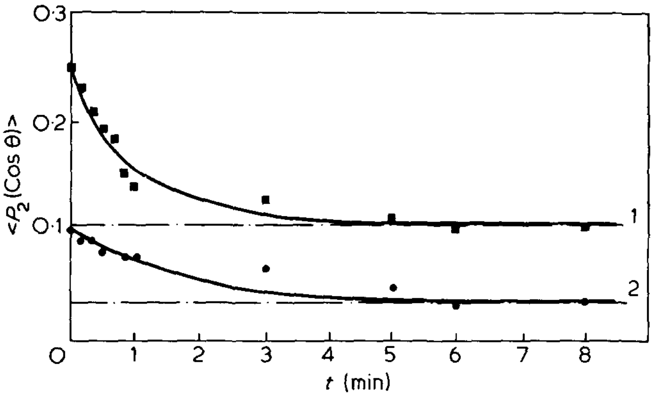

Figure 10 Evolution of orientation under stress in stretched PPO–PS blend containing 10% PPO at $T = Tg + 11.5°$ and $\lambda = 3$. (1) PPO; (2) PS

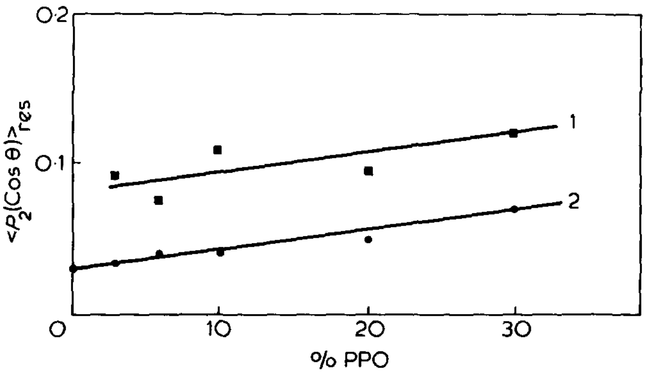

Figure 11 Residual orientation as a function of PPO percentage at $T = Tg + 11.5°$. (1) PPO; (2) PS

temperatures ($T = Tg + 30°$). A linear relationship between $\langle P_2(\cos\Theta)\rangle$ and draw ratio is still observed but results are now independant of PPO percentage. As previously observed for $T = Tg + 11.5°$, PPO chains still orient more readily than PS ones.

Orientation change after stretching

We studied the change of orientation under stress after stretching at a temperature $T = Tg + 11.5°$, and for a draw ratio $\lambda = 3$. A decrease of orientation of PPO and PS chains is observed as a function of time. *Figure 10* illustrates the results obtained with a 10% PPO blend. Both polymers seem to relax in the same way and a constant orientation level is obtained after ~5 min for any percentage. As illustrated in *Figure 11* a linear relationship holds for the residual orientation $\langle P_2(\cos\Theta)\rangle_{res}$ *versus* the PPO percentage in the blends for both PPO and PS. The positive slopes of the two straight lines are similar.

DISCUSSION

The present results show that PPO and PS chains orient in a different way when subjected to an uniaxial strain in spite of the compatible nature of the blend. The orientation of PS chains increases regularly with PPO content up to a percentage of 25% then remains constant between 25 and 35% PPO. On the other hand, PPO chains orientation remains constant all over the studied range.

Such an orientation behaviour of PS and PPO chains is quite puzzling and could be explained in two ways: (1) an increase of the PPO concentration could result in an increase of the knots of a physical network; (2) the relaxation of PS chains could be hindered by PPO chains.

The first hypothesis which involves an increase of PPO orientation as its concentration increases, is at variance with the experimental results, i.e. the PPO orientation remains constant all over the studied concentration range for a given draw ratio. The PPO network seems to be insensitive to the concentration up to 35%.

The second hypothesis relies on a change of PS relaxation time. Strain–stress curves (*Figure 5*) show that a very small slope of the curve corresponding to the rubbery region relative to PS exists. This is characteristic of a chain relaxation during drawing and very low orientation level is obtained. An increase of the slope of the $\sigma = f(\lambda)$ curve (see *Figure 5*) and of PS orientation is observed as the PPO amount increases. Both effects could be assigned to the existence of a gradual hindrance of PS chains relaxation induced by interchain interactions with PPO, during the experimental stretching time period.

When the PPO amount in the blend is above 25%, no more increase in PS orientation is observed. The experimental conditions used in this study could not detect any additional increase of hindrance to PS chains relaxation as the PPO amount increases from 25 to 35%.

At a higher temperature of stretching, both polymer chains orient independently of the blend composition. This could be explained by the fact that, in spite of an increase of relaxation, PS chains reach the terminal zone during the lasting of the experiment or by a weakening of interchain interactions at higher temperature.

Work is continuing on orientation behaviour of PS–PPO blends to obtain a better understanding of the deformation processes at the molecular level.

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