

# Dynamic mechanical and sonic velocity behaviour of polystyrene—poly(vinyl methyl ether) blends

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This paper is primarily concerned with the dynamic mechanical and sonic velocity behaviour of poly(vinyl methyl ether)—polystyrene blends. For this much studied system, it has been found that the results of both investigations can best be explained in terms of the blends consisting of essentially a two-phase morphology in which there are regions richer in polystyrene than would be the case if compatibility were total, and a completely mixed matrix of poly(vinyl methyl ether) and polystyrene. Attempts to predict whether this system might be expected to be compatible or not are also reported.

## INTRODUCTION

The investigation of compatibility in the polystyrene—poly(vinyl methyl ether) (PS—PVME) system has probably been as rigorous<sup>1–6</sup> as for any pair of allegedly compatible polymers. Bank *et al.*<sup>1</sup> have used differential scanning calorimetry and dielectric relaxation studies (20 Hz—200 kHz) to investigate this compatibility using at least partly isotactic PVME. In solvent casting experiments, they obtained visually compatible sheet from toluene, but not from chloroform or trichloroethylene. Their general conclusion was that for the compositions investigated compatibility was not complete.

It has been demonstrated<sup>2,3</sup> that in initially compatible PS—PVME sheet phase separation can be induced simply by raising the temperature to around 150°C. If the sample is now slowly cooled to room temperature, the sheet is again observed to be compatible<sup>2</sup>. It has also been reported<sup>2</sup> that a sheet cast from a solvent leading to initial incompatibility cannot be made compatible by thermal treatment. Kwei, Nishi and Roberts<sup>4</sup>, and Nishi, Wang and Kwei<sup>5</sup> have undertaken detailed investigations to ascertain whether the compatible or incompatible mixtures represent the thermodynamically preferred state. Using specific volume and interaction parameter measurements as well as diffusion and n.m.r. spin—lattice relaxation time studies, Kwei *et al.*<sup>4</sup> suggested the existence of both a lower and an upper critical solution temperature. They concluded that compatible PS—PVME films can best be described as microheterogeneous with the different types of polymer molecules extensively mixed, but not completely mixed on the segmental level. Nishi *et al.*<sup>5</sup> have studied the mechanism of thermally-induced phase separation by optical microscopy and pulsed n.m.r. techniques concluding that the components can phase separate by a spinodal mechanism or by nucleation and growth depending on both the composition and the temperature. Nishi and Kwei<sup>6</sup> have studied the effect of polystyrene molecular weight, molecular weight distribution and radiation crosslinking on the lower critical solution temperature.

In this work we are mainly concerned with dynamic mechanical behaviour and pulsed sonic velocity measure-

ments on this already well-characterized system, using samples prepared in such a way that they are likely to be at least partly phase separated.

## EXPERIMENTAL

### Materials

Commercial samples of polystyrene and poly(vinyl methyl ether) were used in this work. As the poly(vinyl methyl ether) showed no detectable crystallinity by differential scanning calorimetry, it was believed to be substantially atactic. See *Table 1* for characterization data.

### Blending

Three primary blends containing 40, 60 and 70% by weight of PVME were prepared by solution blending in toluene. The resulting approximately 2% polymer solutions were cast into glass trays and the solvent allowed to evaporate. The rather rough sheets were dried in a vacuum oven at approximately 60°C for 3 days prior to final sheeting in a hot press.

The polystyrene homopolymer was hot pressed directly at 175°C, but as the low molecular weight PVME sample was too soft to be handled by the techniques employed in this work, sheet was not prepared. The 40% by wt PVME blend and the 60 and 70% by wt PVME blends were hot pressed at 110°, 80° and 65°C, respectively. Some other blends were similarly prepared for the sonic velocity measurements. The pressing temperatures for these samples containing by weight 50, 30, 20, 10 and 5% of PVME were 110°, 110°, 110°, 120° and 140°C, respectively.

*Table 1* Polymer characterization data

	Polystyrene <sup>a</sup>	Poly(vinyl methyl ether) <sup>b</sup>
Density (kg/m <sup>3</sup> )	1060	1042
$\bar{M}_n \times 10^{-3}$	124	11

<sup>a</sup>Supplied by BDH Ltd; <sup>b</sup>Lutonal M40, kindly donated by BASF

Table 2 Homopolymer solubility parameters

Polymer	$\delta$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>	Source
Polystyrene	8.9	Experimental values (average) from ref 13
	9.1	Small <sup>14</sup> calculation
	9.1	Hoy <sup>15</sup> calculation
Poly(vinyl methyl ether)	7.9	Ref 16
	8.0	Small <sup>14</sup> calculation
	8.6	Hoy <sup>15</sup> calculation

Techniques

The dynamic mechanical measurements were performed using a Rheovibron Dynamic Viscoelastomer (model DDV-II-B) at a frequency of 11 Hz and at a rate of heating of about 1°–2°C/min. For sonic velocity measurements, a Morgan Pulse Propagation Meter (model PPM-5R) was used<sup>7</sup> at a frequency of 15 kHz. Samples were about 8 cm long, 1 cm wide and 0.1 cm thick.

RESULTS AND DISCUSSION

Compatibility predictions

Methods exist which may be used to predict in an approximate fashion whether or not a given pair of polymers are likely to be compatible. Two of these have been applied to the PS–PVME system. Schneier<sup>8</sup> has calculated heats of mixing for a number of polymer pairs selected from lists of supposedly compatible and incompatible pairs published by Bohn<sup>9</sup>. It may be argued<sup>10,11</sup> that the heat of mixing is an approximate measure of the free energy of mixing and may be used as an indicator of possible compatibility. Equation (1) is a modification of an equation suggested by Gee<sup>12</sup> for the swelling of vulcanized rubbers:

$$\Delta H_m = [V_l(\delta_l - \delta_r)^2(1 - \bar{v}_l)^2]^{1/2} \quad (1)$$

Here,  $\Delta H_m$  is the heat of mixing and  $V$  and  $\delta$  are the molar volume and the solubility parameter of the liquid ( $l$ ) and the rubber ( $r$ ). The term  $(1 - \bar{v}_l)$  is the volume fraction of rubber in the swollen network at equilibrium. For two component polymer systems, equation (1) may be rewritten:

$$\Delta H_m = [V_1(\delta_1 - \delta_2)^2(1 - \bar{v}_1)^2]^{1/2} \quad (2)$$

The subscripts 1 and 2 refer to the two components of the blend. Schneier<sup>8</sup> has shown that from equation (2) the following relation, which is also applicable to two component polymer blends, may be deduced:

$$\Delta H_m = \{ \bar{x}_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \times [\bar{x}_2 / (1 - \bar{x}_2) M_2 \rho_2 + (1 - \bar{x}_1) M_1 \rho_1]^2 \}^{1/2} \quad (3)$$

$\bar{x}$ ,  $\rho$  and  $M$  are the weight fraction of polymer, polymer density and the monomer unit molecular weight, respectively.

Schneier<sup>8</sup> noted that the polymer pairs in the Bohn<sup>9</sup> list which were reported to be compatible in the solid state yielded values of heats of mixing from around  $1 \times 10^{-3}$  to  $10 \times 10^{-3}$  cal. It was argued<sup>8</sup>, therefore, that about  $10 \times 10^{-3}$  cal marks the upper limit of compatibility.

Equation (3) has been used to calculate heats of mixing for a range of compositions of the PS–PVME system.

Possible values of  $\delta$  for use in these calculations are shown in Table 2. Both literature values and those calculated using the theories of Small<sup>14</sup> and Hoy<sup>15</sup> are shown. As the literature solubility parameters for polystyrene cover quite a range of values, it was decided to base all subsequent calculations on Hoy's<sup>15</sup> revision of Small's<sup>14</sup> molar attraction constants. Figure 1 shows how the calculated heat of mixing varies with composition. Schneier<sup>8</sup> has stated that the choice of which polymer is taken as component 1 does not have a significant effect on the position of the maximum of the curve. Clearly this is not the case with this system. On the basis of Schneier's<sup>8</sup> criterion, incompatibility is predicted over most of the composition range.

Krause<sup>10</sup> has outlined another approach to the prediction of compatibility for pairs of polymers which is based on the work of Scott<sup>17</sup>. The interaction parameter between molecular species of similar size is often given by equation (4)<sup>18,19</sup>:

$$\chi_{12} = \frac{V_r}{RT} (\delta_1 - \delta_2)^2 \quad (4)$$

$\chi_{12}$  is the interaction parameter between the two species which in this case are polymers and  $V_r$  is a reference volume which is taken as close as possible to the molar volume of the smaller polymer repeat unit. A value of 100 ml/mol is often taken<sup>10</sup> for this term, but in this work the molar volume of the PVME repeat unit has been used.

From Scott's work<sup>17</sup> it can be shown that the following three relations can be derived, which define the critical conditions for a mixture of a pair of polymers:

$$(\chi_{12})_{cr} = \frac{1}{2} \left( \frac{1}{x_1^{1/2}} + \frac{1}{x_2^{1/2}} \right)^2 \quad (5)$$

$$(V_1)_{cr} = x_2^{1/2} / (x_1^{1/2} + x_2^{1/2}) \quad (6)$$

$$(V_2)_{cr} = x_1^{1/2} / (x_1^{1/2} + x_2^{1/2}) \quad (7)$$

In equations (5)–(7)  $(\chi_{12})_{cr}$  is the interaction parameter at the critical point,  $(V_1)_{cr}$  and  $(V_2)_{cr}$  are the volume fractions of components 1 and 2 at the critical point and  $x_1$  and  $x_2$  are the degrees of polymerization of polymers 1 and 2 in terms of the reference volume,  $V_r$ .

Table 3 shows the calculated values of  $\chi_{12}$ ,  $(\chi_{12})_{cr}$ ,  $(V_1)_{cr}$  and  $(V_2)_{cr}$ . As  $\chi_{12}$  is greater than  $(\chi_{12})_{cr}$  incompatibility is predicted at some compositions. The greater

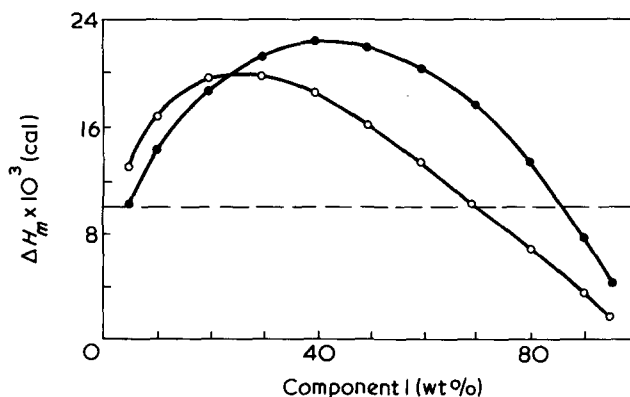
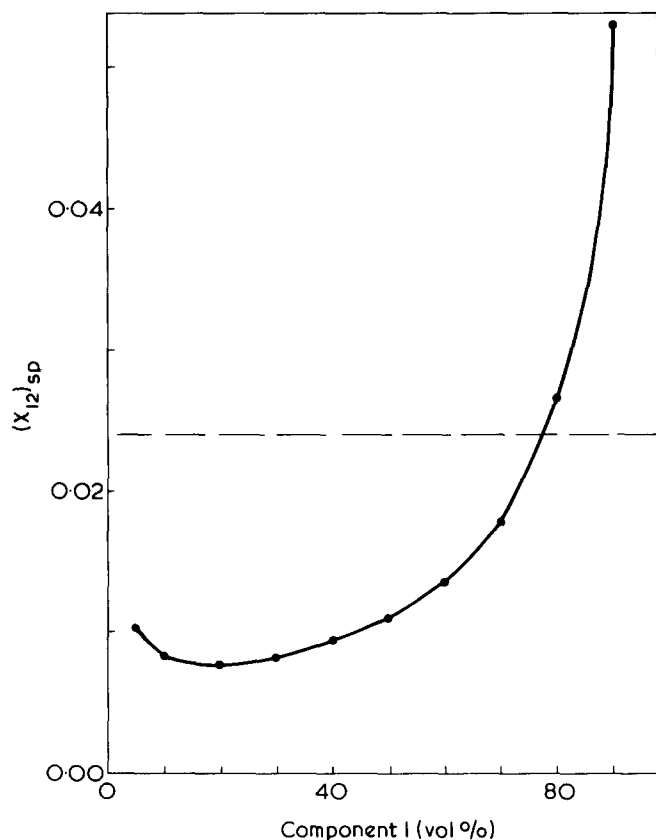


Figure 1  $\Delta H_m$  (equation 3) versus wt % of component 1. ●, Polystyrene as component 1; ○, PVME as component 1

Table 3 Interaction parameters and critical point compositions<sup>a</sup>

Parameter	Value
$\chi_{12}$	0.024 (0.042) <sup>b</sup>
$(\chi_{12})_{cr}$	0.0045
$(V_1)_{cr}$ (%)	23
$(V_2)_{cr}$ (%)	77

<sup>a</sup> Component 1 is polystyrene. Temperature, 25°C. <sup>b</sup> Based on relation  $\chi_{12} \approx (\delta_1 - \delta_2)^2/6$  (see ref 10)


 Figure 2  $(\chi_{12})_{sp}$  (equation 8) versus vol % of polystyrene

the difference between  $\chi_{12}$  and  $(\chi_{12})_{cr}$ , the narrower is the range of compatibility. Even if the experimental solubility parameter value (8.9) for polystyrene is used (Table 2) with the Hoy<sup>15</sup> value of  $\delta$  for PVME, incompatibility is still predicted.

Krause<sup>10</sup> has also presented an equation to calculate  $(\chi_{12})_{sp}$ , the interaction parameter at the spinodal:

$$(\chi_{12})_{sp} = \left[ \frac{1}{2x_1(V_1)_{sp}} + \frac{1}{x_2(V_2)_{sp}} \right] \quad (8)$$

Figure 2 shows that the application of equation (8) also indicates that incompatibility is probable over most of the composition range as  $\chi_{12}$  is generally greater than  $(\chi_{12})_{sp}$ .

It must be stressed that these calculations are only approximate, but nevertheless all three measures, viz  $\Delta H_m > 10 \times 10^{-3}$  cal,  $\chi_{12} > (\chi_{12})_{cr}$  and  $\chi_{12} > (\chi_{12})_{sp}$  predict incompatibility (Figures 1 and 2) over the bulk of the composition range. All the samples prepared for this study appeared visually inhomogeneous.

#### Sonic velocity and dynamic mechanical measurements

This inhomogeneity is further emphasized by Figure 3 which is an electron micrograph of a sample containing

40% by wt of PVME. It is clear that this sample is a two-phase system composed of lighter and darker regions individual subunits of which are in the 5–25 nm diameter range. This partial aggregation of the darker regions (presumably polystyrene) to give a mottled appearance is not thought to be a sectioning artefact. The influence of this type of morphology on longitudinal sonic velocity ( $C_L$ ) and dynamic mechanical behaviour will now be discussed.

*Longitudinal sonic velocity measurements.* Figure 4 shows a plot of  $C_L$  versus composition. In earlier published<sup>7,20,21</sup> and unpublished studies of  $C_L$  versus composition, it has been noticed that when blends have a distinct two phase morphology, the curves have been S-shaped, clearly indicating the region of phase inversion. For supposedly compatible systems essentially linear plots have been obtained. It appears that the best line through the points in Figure 4 is curved, but is approximately linear over the 40% to at least 80% by wt composition range. This behaviour is readily explained in terms of the morphology shown in Figure 3. The essentially linear increase in  $C_L$  for the middle band of compositions arises because in this region the morphology consists of a PS–PVME mat-

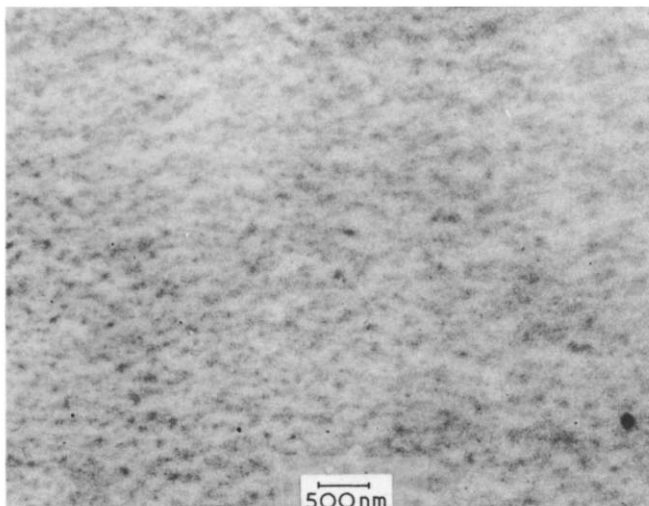
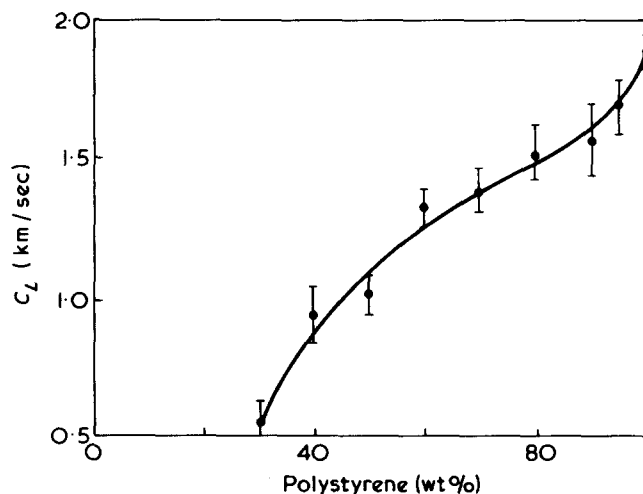


Figure 3 Electron micrograph (unstained) of a PS–PVME blend containing 60% by wt of polystyrene. X 20 000


 Figure 4 Longitudinal sonic velocity ( $C_L$ ) versus wt % polystyrene. Error bars show  $\pm$  standard deviation

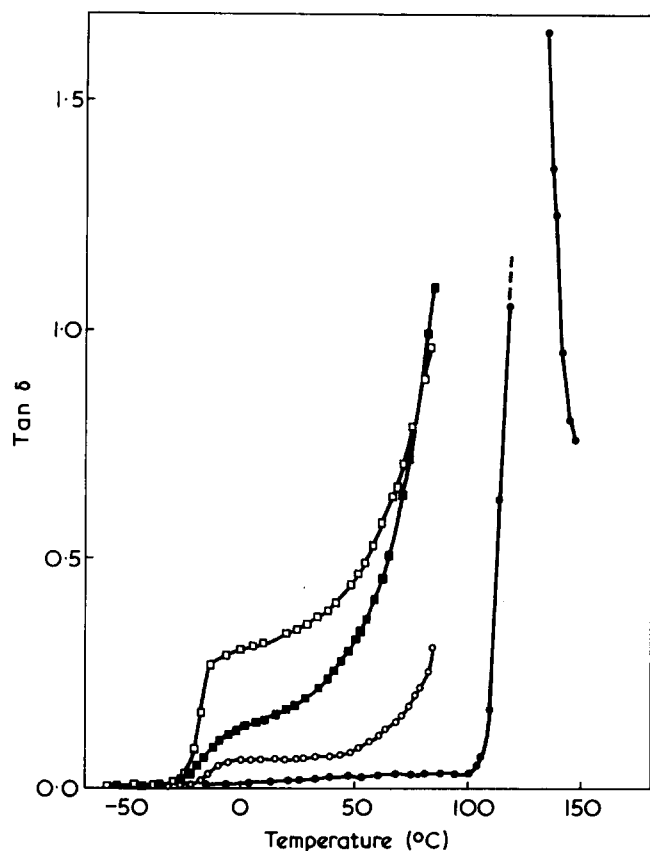


Figure 5 Tan  $\delta$  versus temperature plots of polystyrene (●) and of PS-PVME blends containing 60% (○) 40% (■) and 30% (□) polystyrene by wt. Frequency, 11 Hz

rix in which are embedded essentially continuous polystyrene-rich regions which have an approximate average diameter of 100–200 nm. In other words, over the essentially linear part of the curve the morphology remains essentially the same, but, of course, the compositions of the matrix and the polystyrene-rich domains change. Below about 40% by wt of polystyrene, the fall in  $C_L$  is attributed to the breakdown into discrete regions of this continuous polystyrene-rich phase. A similar explanation may also be offered to account for the rise in  $C_L$  at high polystyrene content if it is supposed that the PS–PVME matrix is now discontinuous. However, Figures 1 and 2 predict that the two polymers may be compatible in this region of composition.

The softness of most of these blends made accurate measurement of  $C_L$  more difficult than for any other system so far investigated. However, each blend was measured at least fifteen times to ensure meaningful data.

**Dynamic mechanical measurements.** The tan  $\delta$  versus temperature dispersions for the blends and for polystyrene are shown in Figure 5. Beyond about 85°C, even the blends became too soft to handle in the Rheovibron. Figure 5 shows that for the blends there is an increase in tan  $\delta$  commencing at about –25°C for the 40% by wt PVME blend, but which occurs at progressively lower temperatures as the PVME level increases. This rise is followed by a plateau region, which is most accentuated for the lowest PVME content blend, which in turn is succeeded by a rapid rise in tan  $\delta$ . The dynamic storage ( $E'$ ) and dynamic loss ( $E''$ ) moduli versus temperature plots (Figures 6 and 7) both show unusually broad dispersions which shift to lower temperatures as the PVME level is increased. The breadth

of these dispersions is indicative of the relaxing segments being in a wide variety of environments and is consistent with the morphology deduced from Figure 3. It would appear from Figure 5 that there are at least two mechanisms involved in these transitions. Figure 7 shows a slope change at 60°–70°C suggesting that a second process is involved. This is less clear for the  $E'$  versus temperature data in Figure 6, but can at least be distinguished for the sample containing 70% by wt of PVME. If in Figure 6 the linear part of the curves at low temperature and that at higher temperature, but not above 50°C, are extrapolated to a point of interception, the position of this point on the temperature scale may be used as an index of how the low temperature component of the transitions shifts with composition. These data are plotted versus composition in Figure 8. The shift of the  $E''$  peaks with composition (Figure 7) gives a very similar trend. The peaks in Figure 7

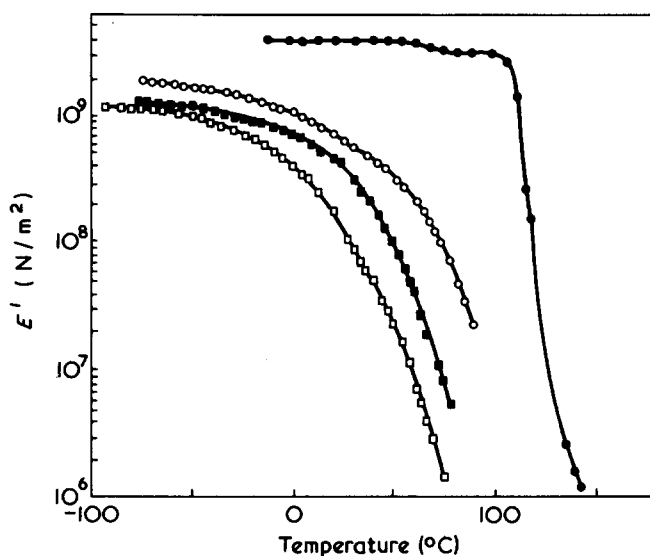


Figure 6 Dynamic storage modulus ( $E'$ ) versus temperature plots of polystyrene (●) and of PS-PVME blends containing 60% (○), 40% (■) and 30% (□) polystyrene by wt. Frequency, 11 Hz

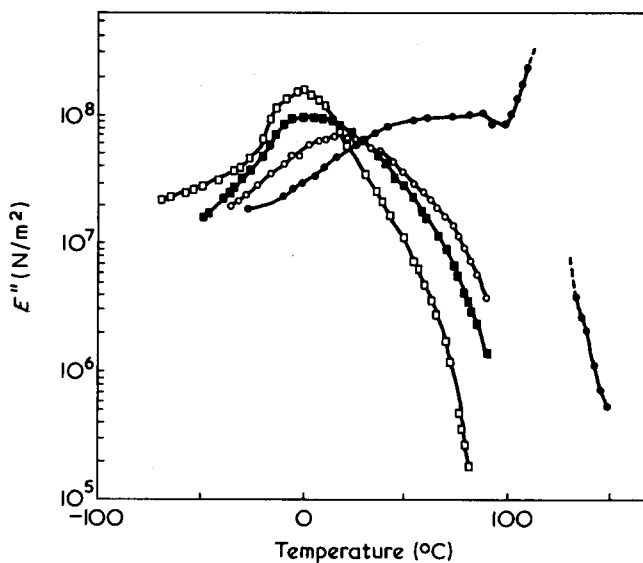


Figure 7 Dynamic loss modulus ( $E''$ ) versus temperature plots of polystyrene (●) and of PS-PVME blends containing 60% (○), 40% (■) and 30% (□) polystyrene by wt. Frequency, 11 Hz

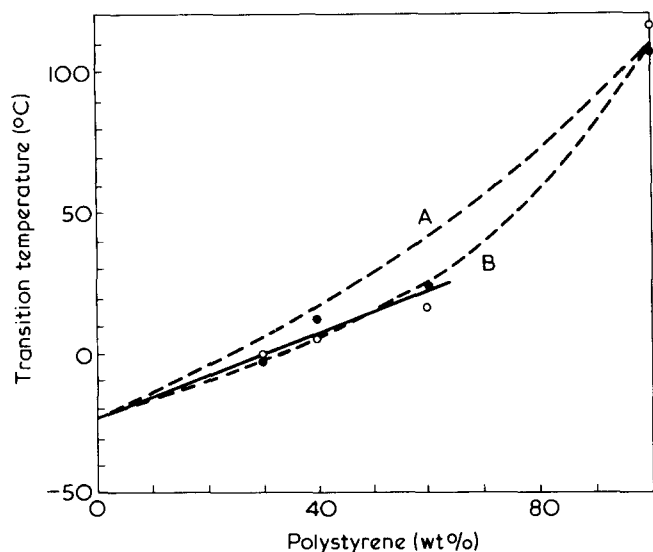


Figure 8 Transition temperature versus wt % polystyrene. ●,  $E'$  versus temperature; ○,  $E''$  versus temperature. A, Curve derived from Fox equation; B, curve derived from Gordon-Taylor equation

are thought to be sufficiently remote from the second transition not to be significantly influenced by it. The best straight line drawn through both sets of data yields a value of  $-23^{\circ}\text{C}$  for the transition temperature of pure PVME. This line does not pass through either of the data points for polystyrene. As a value of  $-29^{\circ}\text{C}$ <sup>4,22</sup> has been reported for the glass transition temperature of PVME, it is not unreasonable to suppose that this blend transition is the glass transition of an essentially compatible PS-PVME phase.

Bank *et al.*<sup>22</sup> have used differential scanning calorimetry to study transitions in PS-PVME blends. Unlike Figure 8, a plot of their transition temperature versus composition was distinctly curved over the range 0–60% by wt of polystyrene. Figure 8 shows the transition temperature–composition curves predicted by the Fox equation<sup>23</sup> and by the Gordon-Taylor equation<sup>24</sup>. The transition temperatures of the homopolymers were taken as  $-23^{\circ}\text{C}$  for PVME and  $110^{\circ}\text{C}$  for polystyrene. This latter value is intermediate between the values obtained from the  $E'$  and  $E''$  versus temperature plots. The former is a poor fit over the composition range up to 60% by wt of polystyrene, but if the constant in the Gordon-Taylor equation<sup>24</sup> is taken to be 0.4, the fit of this relation over this composition range is good.

This analysis can only be approximate because if the morphology is as supposed, then there are essentially regions of pure polystyrene. Thus, the positions of the data points

on the composition scale in Figure 8 are incorrect and the true value of the transition in PVME is higher than  $-23^{\circ}\text{C}$ .

The plateau regions in the  $\tan \delta$ –temperature dispersions in Figure 5 may arise from the zones enriched in polystyrene having a wide spectrum of compositions. For such situations, Kaplan<sup>25</sup> has predicted plateau regions. The final rapid rise in  $\tan \delta$  is thought likely to originate in the polystyrene-rich regions and consequently this rise occurs at progressively higher temperatures as the polystyrene content increases.

This overall interpretation of the morphology of PS-PVME blends is in accord with the suggestion of Bank *et al.*<sup>22</sup>.

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