Influence of the phase separation on the linear viscoelastic properties of a polystyrene–poly(vinyl methyl ether) blend

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The linear viscoelastic properties of a mixture of polystyrene (PS, $M_w = 2.95 \times 10^6$ g mol^{-1}, 10 wt%) and poly(vinyl methyl ether) (PVME, $M_w = 75\,000$ g mol^{-1}, $M_w/M_n = 1.6$, 90 wt%) have been investigated in the temperature range 40–190°C. From small angle light scattering (SALS) and turbidity measurements the phase separation temperature has been determined to be at 106 ± 1°C. The composition was chosen because it was close to the critical composition. Thus, phase separation is expected to occur by spinodal decomposition. At temperatures $T < T_c$ the relaxation behaviour is dominated by the relaxation of the lower molecular weight PVME. A second plateau zone which corresponds to a diluted PS is clearly resolved. Well within the phase-separated regime the frequency dependence of the storage and the loss modulus, G' and G'', is proportional to $\omega^{0.6}$.

INTRODUCTION

The rheological properties of polymer mixtures are of increasing interest, both from a practical and a theoretical point of view. Studies on mixtures of homopolymers with varying molecular weights provide crucial tests for the limits of models of the viscoelastic properties of entangled polymer melts[1–3]. The flow properties of mixtures of polymers of varying chemical nature are of interest both for homogeneous miscible systems and for heterogeneous melts. Viscoelastic studies of homogeneous miscible polymer blends like polystyrene/poly(2,6-dimethylphenylene oxide) (PS/PPO) or PS/poly(vinyl methyl ether) (PVME) might help to decide how the different chain structures contribute to the overall rheological behaviour in blends. In a recent study on mixtures of PS with low molecular weight PPO it has been shown, that the PPO behaves like a low molecular weight diluent[4]. Only at high frequencies, in the rubbery plateau close to the onset of the glass transition, do the short PPO chains contribute to the mechanical response of the system. In the present study we deal with the linear viscoelastic properties of a PS/PVME blend. We were especially interested in the behaviour near the critical point. It has been reported by Bates[5] that the transition from a heterogeneous block copolymer melt to the homogeneous melt is associated with a sudden change in the viscoelastic properties. Such an order–disorder transition especially shows up in the low frequency region. It has been observed that the storage and loss modulus, G' and G'', in the heterogeneous region obey a 0.5 power dependence on the frequency while the usual $G' \propto \omega^2$ and $G'' \propto \omega$ behaviour is observed in the homogeneous region. Recently Larson and Frederickson[6] have developed a theory which accounts

qualitatively for these experimental results. It is predicted that in block copolymer melts near the critical point the concentration fluctuations should become important for the mechanical response.

EXPERIMENTAL

A commercial PS-standard (Chrompack) $M_w = 2.95 \times 10^6$, $M_w/M_n < 1.05$ has been used. A technical grade PVME (Aldrich) has been fractionated and the highest molecular weight fraction $M_w = 75\,000$, $M_w/M_n = 1.6$, has been used in this study. The two polymers were dissolved in benzene and a transparent sample was obtained after freeze drying and subsequent drying under high vacuum at 60°C. The weight fraction of the PS was 0.1. The glass transition temperature (T_g) was measured using a calibrated PE-DSC7 instrument at a heating rate of 20 K min^{-1} to be 253 K. This value is in good agreement to literature data on PS/PVME blends of different molecular weights[7,8].

The densities (ρ) of PS and PVME in the corresponding temperature range were determined dilatometrically by Klotz[9,10] and are given by

$$\rho_{PVME} = 1.0717 - 7.67 \times 10^{-4}T + 2.8 \times 10^{-7}T^2$$
$$20°C < T < 160°C \qquad (1)$$

$$\rho_{PS} = 1.0865 - 6.19 \times 10^{-4}T + 1.36 \times 10^{-7}T^2$$
$$0°C < T < 170°C \qquad (2)$$

The volume fraction of PS in the blend (ϕ_{PS}) at 60°C is 0.098.

Small angle light scattering (SALS) data and turbidity measurements were obtained on a SALS apparatus using an expanded laser beam and subsequent collimation of the scattered light. Details on the apparatus are given elsewhere[11]. The temperature was increased in steps of
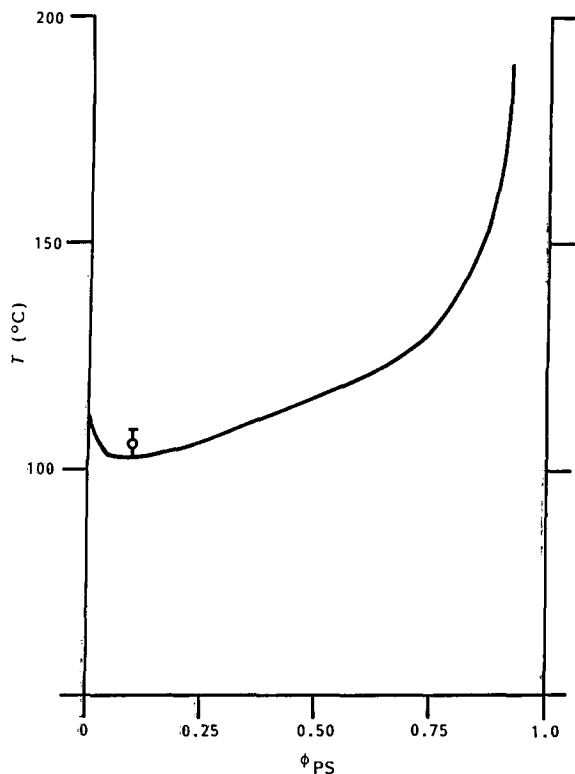
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Figure 1 Calculated spinodal curve of PS/PVME ($M_{PS} = 2.95 \times 10^6$, $M_{PVME} = 75\,000$) using the Flory–Prigogine equation of state theory[9,10]

3°C. The temperature was allowed to equilibrate at each stage for 15 min.

The dynamic mechanical measurements were run on a Rheometrics RMS-800 mechanical spectrometer in the temperature range between 39°C and 194°C. The temperature was kept constant within less than 1°C. Special care was taken to avoid 'temperature overshoot' upon heating near the phase separation temperature. Frequency sweeps were made over four decades from 0.01 to 100 rad s^{-1}.

RESULTS AND DISCUSSION

Selection of the model system

In miscible polymer blends the effect of the presence of two types of chains of different chemical nature on (viscoelastic) relaxation has to be studied. To study both the relaxation in the miscible and in the phase-separated region, we have chosen the PS/PVME system. For this system, a considerable number of thermodynamic studies have proven thermodynamic miscibility in the whole composition range at ambient temperatures and the existence of a phase-separated region at high temperatures[9,10,12,13]. In addition, PS is available as a high molecular weight material of narrow molecular weight distribution. This considerably simplifies the analysis of viscoelastic data, which are available for PS and PS/solvent systems[3,14]. The molecular weight chosen for the present study was 2.95×10^6 g mol^{-1}. The plateau modulus for PS is 3×10^5 Pa. For PVME no comparable detailed studies are available. To obtain a material which is more convenient for the linear viscoelastic studies the technical grade PVME was fractionated. A fraction with $M_w = 75\,000$ g mol^{-1} and $M_w/M_n = 1.6$ was used in this study.

From thermodynamic studies it is known that the phase diagram of blends of molecular weights comparable to those used here has its critical point at compositions 0.05–0.15 (weight fraction of PS) and at temperatures between 100°C and 110°C[13]. In addition it has been shown that for this particular system the Flory–Prigogine equation of state theory describes the system well[9]. In *Figure 1* the calculated phase diagram (spinodal curve) is shown for this particular set of molecular weights. The parameters, that have been used to calculate this phase diagram, were obtained from a system of different molecular weights which has been characterized carefully by inverse gas chromatography[9,12] ($X_{12} = -2.02$ J cm^{-3}; $Q_{12} = -0.00277$ J (cm^3·deg)$^{-1}$. The predicted critical composition is at a PS concentration of 10%. The critical temperature is around 103°C. Included in *Figure 1* is the phase separation temperature determined from turbidity measurements and by SALS.

Linear viscoelastic behaviour in the homogeneous state

A different dynamic–mechanical response is observed below and above the phase separation temperature. In addition the phase-separated region can be divided into a temperature region just above T_c and well above T_c (> 143°C). For temperatures below T_c a thermorheologically simple behaviour is observed, i.e. the time (frequency)–temperature superposition principle can be applied. For these temperatures, smooth master curves are obtained for both G' and G'' if the reduced data[14] are used according to

$$G_{red}(T_0, \omega) = G(T, \omega) \times T_0\rho_0/T_\rho \tag{3}$$

where G_{red} is the modulus ($G'(\omega)$ and $G''(\omega)$) reduced to the reference temperature T_0.

The master curves for G', G'' and the loss tangent are shown in *Figures 2* and *3*. The reference temperature is 60°C. In these figures, data for the temperatures above T_c (106–143°C) are also included. At high frequencies the data above T_c superpose the common master curves (39–106°C), while at low frequencies clear lack in
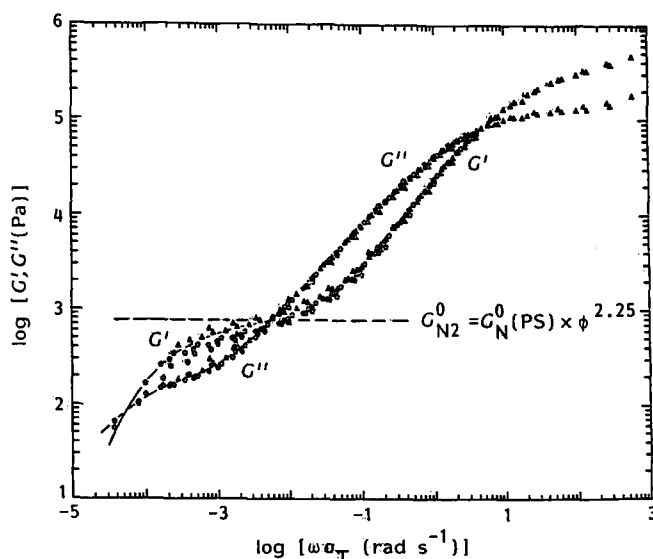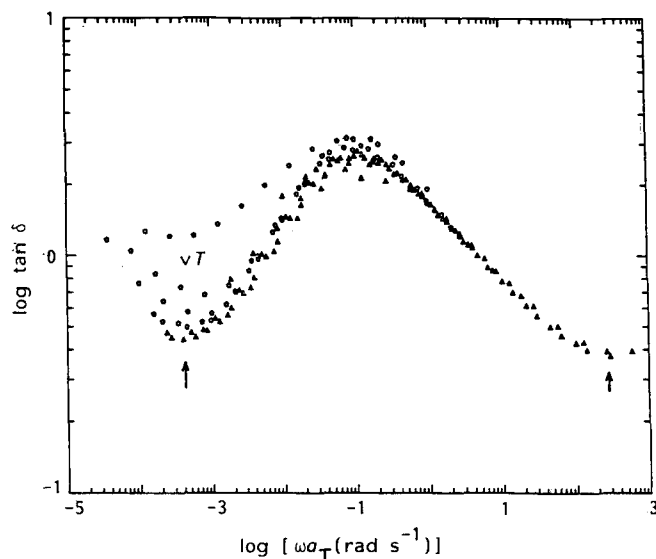

Figure 2 Viscoelastic master curve for the reduced data of G' and G'' of the PS/PVME (1:9) blend ($T_0 = 60$°C). △, Homogeneous region ($T < 106$°C); ○, phase-separated region ($T > 106$°C); – – –, calculated value for the level of the PS plateau modulus after relaxation of the PVME chains

Figure 3 Tan δ master curve of the PS/PVME (1:9) blend ($T_0 = 60°C$). Symbols as in *Figure 2*. The frequencies of the minima (arrows) have been used to estimate the values of the plateau modulus; the level of the low frequency minimum increases with temperature for $T > T_c$

superposability is observed for the storage modulus data. The lack in superposability is less pronounced for the loss modulus. The lack in superposability is also observed for the loss tangent (*Figure 3*).

The temperature dependence of the viscoelastic quantities has been analysed from the temperature dependence of the logarithmic shift factors $\log a_T$. In *Figure 4* the shift factors are plotted *versus* the reciprocal temperature. The curve was calculated according to the WLF equation[14]. The WLF constants at $T_0 = 60°C$ are $c_1 = 7.45$ and $c_2 = 166$. After reduction to T_g, the constants are $c_{1g} = 16.5$ and $c_{2g} = 75$, which are in reasonable agreement with values reported from temperature-dependent fluorescence decay measurements[8]. The transition from the homogeneous melt into the phase-separated region does not cause a discontinuity in the temperature dependence of the logarithmic shift factors. However, it must be noted that the shift factors for $T > T_c$ were obtained from the high frequency region of G' and G''.

For the highest reduced frequencies (lowest temperatures) a common rubbery plateau zone is found for the blend. The plateau modulus (G_N^0) for this zone is of the order of 4×10^5 Pa. This value has been determined from G' at the frequency where tan δ has its minimum[15] and is higher than that for PS (expected value for a rubbery PS at the same reference temperature: 1.45×10^5 Pa). No studies on narrow-distributed PVME are reported in the literature. From broad-distributed samples ($M_w = 75000$, $M_w/M_n > 2$) a value slightly higher than that for PS has been reported[16]. From our results, the plateau value for pure PVME can be estimated to be of the order of 4×10^5–4.5×10^5 Pa (at 60°C). This value is considerably larger than that of PS. Thus the molecular weight between entanglements (M_e) for PVME is of the order of 4000–6000 and much smaller than that for PS $(18000)^{14}$. In addition, this result shows that both components are well above the M_e values of the corresponding homopolymers. In this rubbery plateau zone the storage modulus is larger than the loss modulus. At frequencies of about 5 rad s^{-1}, a first crossover

between G' and G'' is observed, indicating that energy-dissipating processes are dominating. This is associated with a maximum in the loss tangent (*Figure 3*). At low frequencies a second plateau, of the order of 800 Pa, is observed. In this region a second crossover between G' and G'' occurs. At the lowest reduced frequencies a third crossover with $G'' > G'$ is observed, but this region is difficult to analyse because the data were obtained in the phase-separated region.

The overall relaxation behaviour can be explained as follows. At high frequencies both components have not relaxed and contribute to G'. The loss maximum in the mid-frequency range indicates that one of the components relaxes. At even lower frequencies this component will not contribute to the modulus and the second component, which still has not relaxed, is responsible for the occurrence of the second plateau. This behaviour is similar to the relaxation observed in melts of mixtures of homopolymers with various, strongly differing molecular weights[1]. The terminal relaxation time for the high molecular weight PS is much larger than that for the PVME. Thus it is reasonable to assume that the relaxation process which corresponds to the maximum in tan δ at 0.1 rad s^{-1} is due to the terminal relaxation of the PVME. Consequently, the second plateau is made up by the entangled PS chains diluted by the PVME, which acts like a low molecular weight solvent in this frequency range. This is true as long as no strong interactions between PS and PVME contribute to the stress relaxation.

If the binary blend is treated in this manner, the level of the second plateau G_{N2}^0 should be given similar to polymer/solvent mixtures by

$$G_{N2}^0 = G_N^0(\phi_{PS} = 1) \times \phi_{PS}^{2.25} \qquad (4)$$

where G_N^0 is the plateau modulus of a pure PS melt and ϕ_{PS} is the PS volume fraction.

The PS plateau modulus $G_N^0(\phi_{PS} = 1)$ has to be corrected for the different reference temperature and
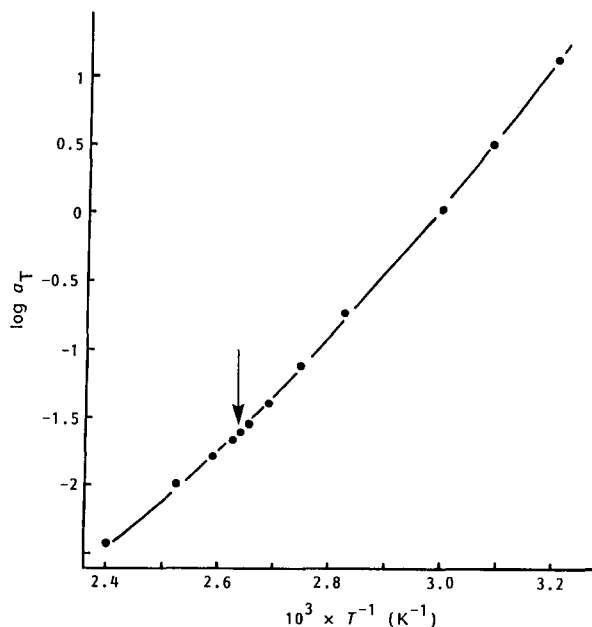
Figure 4 Logarithmic shift factors log a_T as a function of the reciprocal absolute temperature. ——, Calculated from WLF equation using the constants given in the text. The arrow indicates the critical temperature
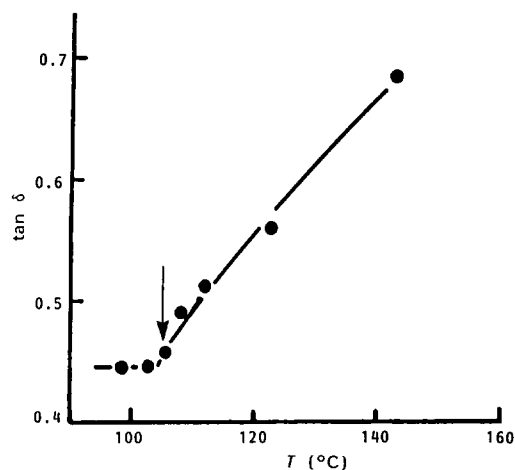
Figure 5 Variation of tan δ at the frequency of the tan δ minimum (low frequencies) with temperature. The arrow indicates the critical temperature
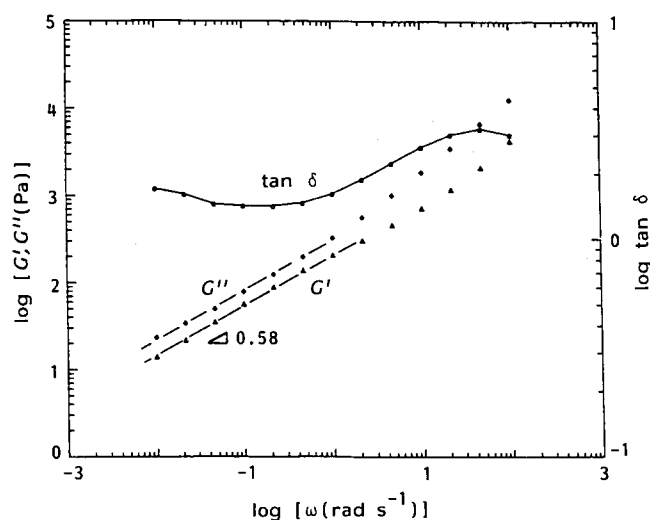
Figure 6 Isothermal frequency sweep (173°C) for G', G'' and tan δ of the PS/PVME (1:9) blend

density. Assuming no volume change upon mixing, the predicted value (eq. (4)) for the level of the second plateau is 780 Pa, which is in very good agreement with the observed value.

This analysis shows that separate relaxations for PVME and PS chains can be observed in such binary blends and that the relaxed component behaves like a low molecular diluent. From this it must be concluded that the negative enthalpic interactions which are present in PS/PVME blends have only a negligible influence on the structure of the entanglement network.

The observation of two separated relaxations for the components is only possible if the corresponding relaxation times are very different.

Behaviour in the phase-separated region

As has been discussed above, the time–temperature superposition principle is no longer valid for temperatures above T_c. The failure in superposability is not caused by a sudden change in the properties at T_c. As can be seen from *Figure 2*, the G'' data can be shifted to a smooth master curve up to temperatures as high as 143°C. For G' and, as a consequence, for tan δ the

complex behaviour is already observed at lower temperatures.

The fact that no sudden change in the properties is observed at T_c can be explained from the phase diagram given in *Figure 1*. Just above T_c the mixture decomposes into two phases that have similar compositions and properties. With increasing temperature the differences in the properties of the two phases increase. In this region the PVME-rich phase, which is present in large excess, dominates the mechanical behaviour. The G' decreases faster than predicted for the homogeneous mixture. This is associated with an increase in the minimum of the loss tangent as shown in *Figure 5*.

The most interesting behaviour is observed at 173 and 194°C. In *Figures 6* and *7* the G' and G'' curves as well as the loss tangent are given for these isotherms. At these high temperatures, within the phase-separated region, both G' and G'' are approximately parallel and a $\omega^{0.58}$ frequency dependence is observed. Correspondingly tan δ is a constant. The behaviour is more pronounced for the 193°C isotherm where a parallel behaviour is observed over four decades of frequency.

As has been stated above, a similar $\omega^{1/2}$ behaviour has been observed for the melt behaviour of phase-separated block copolymer melts while the usual $G' \sim \omega^2$ and $G'' \sim \omega$ behaviour is found in the homogeneous melt[5]. In that case a sudden change in the properties is observed at T_c, which is not the case for the blend we have investigated.

A similar $\omega^{1/2}$ power law has been reported by Winter and coworkers for some chemically crosslinking systems at the gel point[17]. In that case fractal theory has been applied to explain the uncommon power dependence at low frequencies[18] with a dimensionality of 2 at the gel point. It might be interesting for further theoretical and experimental studies to discuss the rheological properties of phase-separating polymer blends in terms of a 'fractal dimensionality' of the phase-separated system, i.e. a system which is characterized by the self similarity of the supermolecular order over a larger distance scale.

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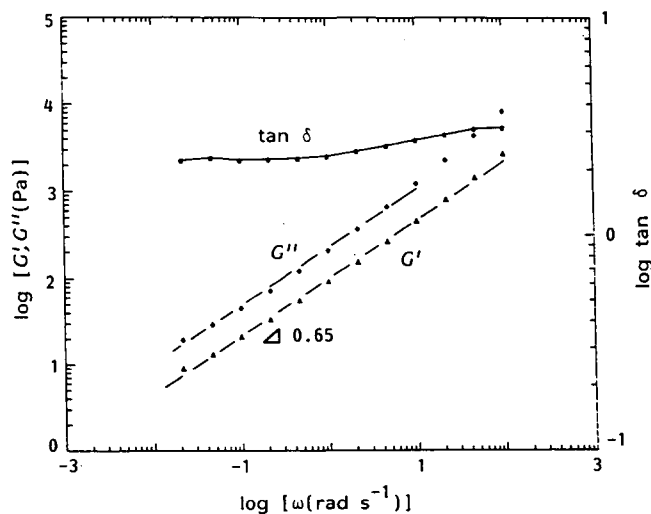
Figure 7 Isothermal frequency sweep (194°C) for G', G'' and tan δ for the PS/PVME (1:9) blend

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