Stress Relaxation Behavior of a Compatible Polymer Blend in the Primary Transition Region

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ABSTRACT: The damped Debye lattice model for viscoelastic relaxation in the primary transition region takes into account elastic interchain interactions as well as the more usually invoked intrachain interactions. We have applied this model to compatible blends formed from atactic polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Qualitative predictions of the variation of stress relaxation behavior of the blends as a function of PPO concentration have been made. Also, predictions concerning properties of these blends upon dilution suggest very distinctive behaviors. We have measured stress relaxation master curves in the primary transition region of PS–PPO blends of various concentrations and have found that the predicted behavior is indeed observed. Furthermore, the unusual effects of dilution on the properties of these blends have been observed with dioctyl phthalate used as the diluent.

Introduction

In the original development of the theories presented by Rouse, Bueche, and Zimm (RBZ)[1] to treat the viscoelastic behavior of polymers, the chains are represented by a simple bead–spring model. Accordingly, the long molecules are conceptually divided into a number of shorter segments or submolecules which are just long enough that their distribution of end-to-end distances is Gaussian. The masses of these submolecules are considered to be concentrated at the beads shown in Figure 1A and the elasticity of the molecule is represented by the Hookean springs that hold the individual beads together.

It is important to remember that these beads do *not* represent individual chain atoms and that the springs do *not* represent individual chemical bonds. Rather, these theories suggest that the dynamics of the bead–spring model are equivalent to the dynamics of the polymer system under conditions where the resolution of molecular motion is not extreme, i.e., under conditions like those used to measure ordinary viscoelastic properties.

Loss is introduced into the model by immersing the bead–spring assembly in a friction-generating fluid. Thus, energy stored in the springs may be viscously dissipated to the fluid. Since specific interactions between polymer chains are not included, such treatments are applicable to dilute solution. The tensile stress relaxation modulus, $E(t)$, from such a model is given as

$$E(t) = 3ckT\sum_{p=1}^{Z} e^{-t/\tau_p} \tag{1}$$

where Z is the number of submolecules per polymer molecule, c is the concentration of polymer chains, k is the Boltzmann constant, T is the temperature, and τ_p is the relaxation time of the pth normal mode of the molecule. This relaxation time is itself given as

$$\tau_p = \frac{\rho\langle r^2\rangle Z^2}{6\pi^2kTp^2} \tag{2}$$

where p varies from 1 to Z, $\langle r^2\rangle$ is the mean squared end-to-end distance of the submolecule, and ρ is the friction coefficient of the bead moving through the solution.

Ferry, Landel, and Williams[2] suggested that the RBZ bead–spring model might be extended into the realm of bulk polymer behavior. In this case they argued that the friction-generating fluid would be the entire ensemble of polymer chains except for the one under consideration and concluded that two different friction factors were appropriate. A molecular weight dependent high-friction factor was employed in the rubbery and flow regions where entanglement is important; a lower valued molecular weight independent friction factor was adopted in the primary, glass-to-rubber, transition region. With this modification, they were able to account for the two large dispersions observed with high molecular weight bulk polymers.

For short relaxation times, as in the primary transition region, eq 1 may be integrated to yield (3) (and (4))

$$E(t) \simeq \frac{E_1\tau_1^{1/2}}{2}t^{-1/2}[\Gamma_{t/\tau_1}(1/2) - \Gamma_{t/\tau_1Z_1^2}(1/2)] \tag{3}$$

where E_1 is the partial modulus associated with each of the τ_p relaxation times, τ_1 is the shortest of the relaxation times, of which there are Z_1, and $\Gamma_x(^1/_2)$ is the incomplete Γ function of argument $^1/_2$. For times between the maximum and minimum relaxation times, the factor in brackets in eq 3 is constant and the time dependence is given by the $t^{-1/2}$ term. In our study of stress relaxation rates of polymers, it has been convenient to define the absolute value of the maximum negative slope of a stress relaxation master curve (plot of log $E(t)$ vs. log t) in the primary transition region as the "steepness index" (SI).[5] Clearly then the SI for the RBZ linear bead–spring model is 0.5. This value agrees well with experimental results for materials such as polyisobutylene. However, for many other materials such as poly(methyl methacrylate) (SI $\simeq$ 1.0) or polystyrene (SI $\simeq$ 1.5), there is little agreement between the behavior of the model and experimentally observed results. (It should be recalled that the SI is the slope of a log–log representation of data so that even small variations in SI correspond to enormous and easily measured variations in relaxation rates.)

A fundamental assumption of the RBZ theory, which was also adopted by Ferry, Landel, and Williams, is that there are no elastic interactions between the polymer chains. Tobolsky et al.[3,4] suggested a further development of the bead–spring model to take into account such interchain interactions. They defined the original RBZ linear bead–spring model as a one-dimensional system and further allowed the inclusion of interchain elastic coupling to yield a two- or a three-dimensional model as shown in Figure 1B. This so-called three-dimensional damped Debye lattice, which is also known as a three-dimensional damped torsional oscillator (DTO) model, infers that inter- and intrachain interactions should be characterized by the same force constant. This idea becomes acceptable when one recalls that the beads themselves correspond to substantial segments of the polymer chain. Thus, the intrachain force constant is expected to be reasonably low,

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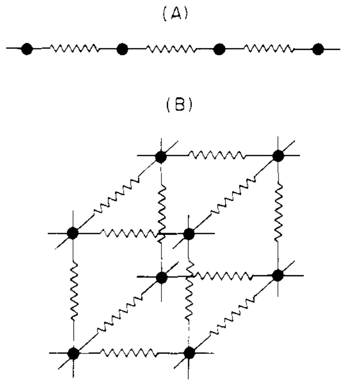

Figure 1. (A) Representation of the Rouse–Bueche–Zimm bead-spring model or the one-dimensional damped Debye lattice. (B) Representation of the three-dimensional damped Debye lattice model.

torsional modes of the polymer submolecule rather than the higher energy stretching or bending modes being involved. On the other hand, although interchain forces result from van der Waals interactions, which are known to be very weak, the force constant here can be large since it measures the ease with which an *entire submolecule* is displaced with respect to its nonbonded nearest neighbors, a process involving many van der Waals contacts.

The modulus for a three-dimensional system may be given as

$$E(t) = \frac{3E_1\tau_1{}^{3/2}}{2}t^{-3/2}[\Gamma_{t/\tau_1}(3/2) - \Gamma_{t/\tau_1 Z_1{}^2}(3/2)] \qquad (4)$$

where the symbols have been defined previously. The slope of this function when plotted as log $E(t)$ vs. log t in the region of interest is −1.5. Thus, the addition of elastic interchain coupling results in a denser distribution of relaxation times and a correspondingly higher relaxation rate. As might be expected, the slope for a two-dimensional system is −1.0. Thus, according to the damped Debye lattice model, polyisobutylene, poly(methyl methacrylate), and polystyrene would be examples of one-, two-, and three-dimensional systems, respectively.

Previous Experimental Results

In Figure 2, the stress relaxation master curves of polystyrene and polyisobutylene are compared and it is clear that at suitably reduced temperatures, polystyrene relaxes much more quickly than polyisobutylene. Since the two polymers have identical chain backbones, the difference in relaxation rates must result from the differences in the side chains.

Kelchner and Aklonis[6] questioned the possible role of π–π electronic interactions as being responsible for these differences in relaxation rates. They measured the SI of poly(vinylcyclohexane), i.e., totally hydrogenated PS. The SI was reported to be 1.35. They concluded that π–π interaction is not the main factor influencing the relaxation rates of these polymers. Rele and Aklonis[5] investigated the effect of volumes of side-chain groups on relaxation rates and concluded that the size of the side-chain substituent is not a major factor in determining relaxation rates.

Another approach to investigating the credibility of the damped Debye lattice model is to measure changes in relaxation rates as the strength of interchain interactions is varied. This can be done via plasticization or dilution of the bulk polymer with lower molecular weight materials. In the case of polystyrene, for example, with its SI near 1.5, the balance in inter- and intramolecular force constants can presumably be disrupted via dilution. Thus, the transition region is expected to broaden; i.e., SI should decrease upon dilution. Chapoy and Tobolsky[7] used dimethyl phthalate and dioctyl phthalate (DOP) as plasticizers for polystyrene. Their experimental results showed that the SI does indeed decrease with increasing concentration of the diluent. Rele and Aklonis[5] further showed that the solubility parameter was an important variable in determining effectiveness of a plasticizer in broadening the transition. When the solubility parameters of the polymer and diluent were matched, dilution did not change the strength of interchain interactions and, under these conditions, plasticization did not result in broadening of the transition. Chapoy and Pedersen[8] have come to similar conclusions.

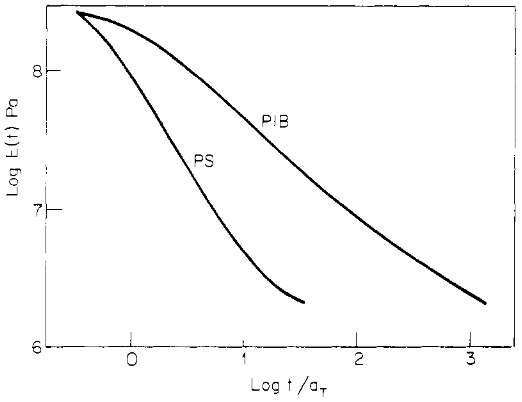

Figure 2. Stress relaxation master curves for polystyrene and polyisobutylene in the primary transition region at different reference temperatures.[5]

Polymers of other dimensionality, for example, two-dimensional systems, with SI = 1.0, have also been studied and treated according to the damped Debye lattice model. Lin and Aklonis[9] interpreted the behavior of plasticized poly(methyl methacrylate) (PMMA, SI = 1.0) according to this model. They suggested that in PMMA, interchain force constants were so much stronger than intrachain ones that dilution did not result in intrachain interactions becoming important. In this case, plasticization caused no change in SI throughout the entire range of diluent concentrations studied for all diluents investigated.

Up to this point, all previous experimental results are reasonably satisfyingly explained within the framework of the damped Debye lattice model, which expands the RBZ treatment to take into account elastic interchain interactions. As will be explained below, a critical test of this model can be achieved by taking advantage of the interesting behavior of the compatible polystyrene–poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blend.

Intrachain and Interchain Interactions in PPS-PPO Blends

Properties of blends of high molecular weight polymers have been widely studied recently,[10a] that most well-known example being the compatible mixture of PPO and atactic polystyrene. These two materials are compatible in all proportions.[10b] Films made from these blends are clear and the refractive index has been reported to increase linearly with increase in PPO content.[11] Good mechanical properties and a single glass transition temperature have also been reported[10b] for blends of these polymers in all proportions.

For materials to be compatible, the free energy of mixing, ΔG_m, has to be negative; it may be expressed as

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (5)$$

When two polymers are mixed, the entropy term, ΔS_m, is

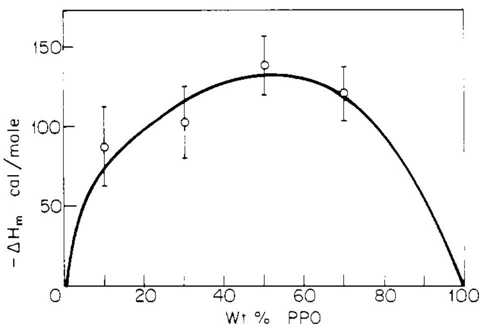

Figure 3. Enthalpy of mixing for PS with PPO as a function of PPO concentration (after Weeks, Karasz, and MacKnight[13]).

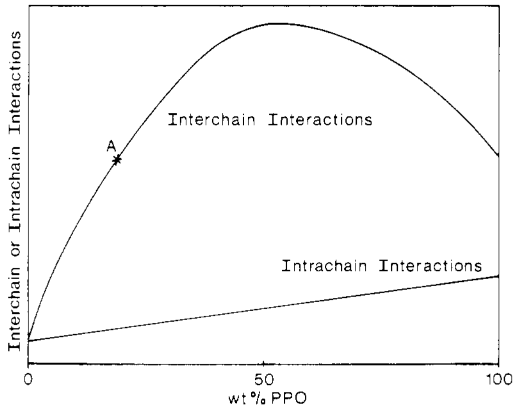

Figure 4. Qualitative representation of the strength of inter- and intrachain interactions in PS–PPO blends as a function of PPO concentration.

generally very small. Thus, the enthalpy of mixing, ΔH_m, decides the size and magnitude of ΔG_m. A negative enthalpy of mixing is expected for situations where specific interactions occur between the functional groups of the two macromolecules or where better packing of the polymer chains can be achieved.

The solubility parameter of PS is 8.56 and that of PPO is 9.5.[12] This large difference in solubility parameters suggests that compatibility between these two polymers is unlikely. The fact that PS and PPO are compatible clearly indicates that there are specific interactions between the macromolecules. When this blend is formed, the strength of the interchain interactions must increase. Weeks, Karasz, and MacKnight[13] have actually measured the enthalpy of mixing for PPO and PS and their results are shown in Figure 3. It is clear that a substantial increase in interchain interaction occurs upon blending. This conclusion is also corroborated by measurements of the excess density of mixing.[14]

A further analysis of the strength of intra- and intermolecular interactions will be profitable. Since PPO has a solubility parameter substantially larger than that for polystyrene, we will conclude that intermolecular interactions in pure PPO are stronger than those in pure PS.

Turning to intramolecular interactions, we also expect the force constant characterizing intramolecular interaction to be greater for PPO than for PS since PPO has aromatic rings in the chain backbone. Furthermore, the fact that the glass transition temperature for PPO is much higher than that for pure PS is consistent with our conclusion that both inter- and intrachain interactions are stronger in PPO than in PS.

The results of this analysis are summarized in Figure 4, which is a schematic representation of the variation of strength of both inter- and intrachain interactions (force constants) for blends of PS and PPO. Concentrating on the interchain interactions, we have already argued that their strength is greater in pure PPO than in pure PS; therefore, the limits of this line are clear. A linear relationship also should be reasonable since as far as intrachain interaction is concerned, the influence of the neighbors should not be important. Next, considering interchain interactions, on the pure polystyrene side, the inter- and intrachain lines must emanate from the same point since polystyrene is an example of a three-dimensional damped Debye lattice, where the magnitudes of inter- and intrachain force constants are equal. Pure PPO, on the other hand, is essentially a two-dimensional system (SI = 0.9–1), which, according to the model, results from the interchain interactions being stronger than intrachain interactions. Thus, the interchain interaction line must terminate on the pure PPO side at a point higher than the intrachain interaction line. In the case of interchain interactions, however, a straight line connecting the two extreme points is not appropriate since, as we know, specific interchain interactions must exist which cause the blend to be compatible. Therefore, positive deviation from the straight line connecting the two extreme points is expected and is shown in the figure. Thus we see that the various factors concerning variation of strength of inter- and intrachain force constants in blends of PPO and PS are qualitatively summarized in Figure 4. Now this figure may be used to predict the behavior of the SI of blends under varying conditions.

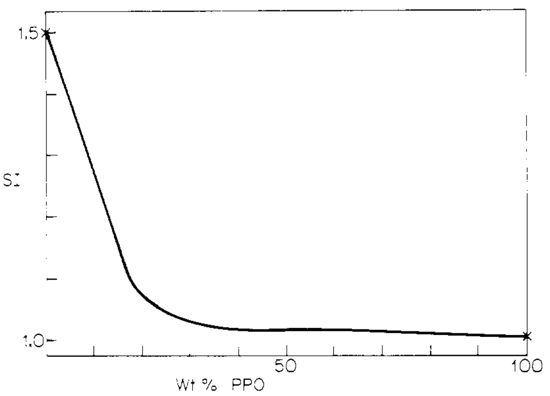

Figure 5. Predicted variation of SI with PPO concentration in PS–PPO blends according to the damped Debye lattice model.

Let us start by considering how the SI should vary as polystyrene is diluted with PPO. For pure polystyrene, with an SI of 1.5, addition of PPO causes the interchain interactions to dominate intrachain interactions so that the slope of relaxation in the primary transition region is predicted to diminish with increasing PPO concentration. At some PPO concentration, perhaps that given by point A in Figure 4, the interchain interactions so dominate intrachain interactions that the system becomes a two-dimensional damped Debye lattice with an SI of 1.0. With increasing PPO content, the interchain interactions become even more dominant; however, no further change in SI is predicted by the model. Thus, the SI variation with PPO content is predicted to be as shown in Figure 5. The precise concentration where the SI becomes invariant with further PPO addition is not predicted by the model in its present qualitative form; nevertheless, the general shape of the curve is expected to be like that shown in the figure.

These simple ideas may also be extended to make predictions concerning the behavior of blends upon plasticization. If point A in Figure 4 represents the composition where interchain interaction is just strong enough that it determines the behavior of the system, then, as mentioned above, the SI will be 1.0. Dilution of blends of this com-

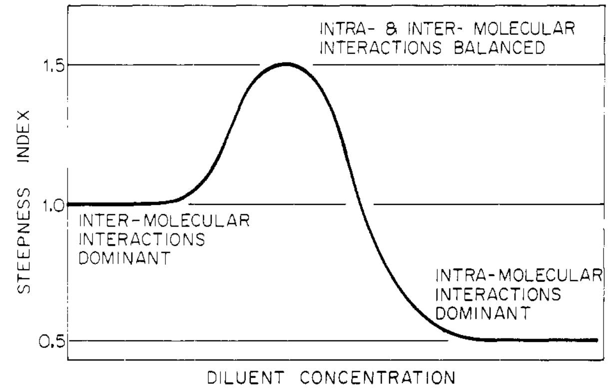

Figure 6. Predicted variation of SI with diluent concentration for a PS–PPO blend where interchain force constants barely dictate behavior.

position should reduce the interchain interaction and leave the intrachain interaction more or less unchanged. At a certain level of dilution, the interchain interaction will be reduced so as to just match the intrachain interaction and the system will be indicative of a three-dimensional damped Debye lattice. The model therefore predicts that the SI of a blend of composition A should actually exhibit an initial *steepening* of relaxation in the primary transition region upon dilution with appropriate plasticizers. Further dilution will then decrease the interchain interaction and decrease the SI from 1.5 toward 0.5. Schematically such a variation of SI with diluent concentration is shown in Figure 6.

Blends with higher percentages of PPO should show a similar SI peak upon dilution. The peak, however, should appear at higher concentrations of the diluent since the difference between the strengths of inter- and intrachain interactions increases as the weight percentage of PPO increases up to approximately 50%. As a result, it is predicted that a higher concentration of plasticizer will be needed to lower the interchain interaction to match the intrachain interaction for blends containing concentrations of PPO greater than that indicated by point A but still less than about 50%.

To our knowledge, such behavior has never been reported. However, the damped Debye lattice model clearly predicts that it should be observed for plasticized PS–PPO blends under suitable conditions. Thus, it is our opinion that this system provides an excellent opportunity to test the viability of the model in a critical manner.

Experimental Section

The polystyrene sample ($M_n = 1.10 \times 10^5$, $M_w = 2.74 \times 10^5$) was obtained from R. F. Kratz of the Koppers Co. and was purified by precipitation from a chloroform solution into a tenfold excess of methanol. It was dried in a vacuum oven for 3 days while the temperature was increased from 85 to 110 °C.

The poly(2,6-dimethyl-1,4-phenylene oxide) sample (M_n = 35 000) was supplied by Dr. Katchman of the General Electric Co. This material was purified by precipitation from a toluene solution into a tenfold excess of methanol followed by 3 days of vacuum oven drying with the temperature gradually increased from 160 to 220 °C.

The PS–PPO blends were prepared by dissolving various amounts of the two purified polymers in the same toluene solution and allowing this solution to stand overnight at room temperature. The blends were coprecipitated by dropwise addition of the solution into a tenfold excess of methanol. The samples were then dried in a vacuum oven at suitable temperatures (above T_g) for 3 days.

Samples were formed into 0.1 × 1.0 × 5.0 cm strips in a press at temperatures approximately 50 °C above the glass transition temperature of the blend. The stress relaxation experiments were carried out on a table model Instron equipped with an environmental test chamber especially designed to keep the temperature constant to better than ±0.05 °C. Strains were applied slowly and the modulus values were calculated as described elsewhere.[15]

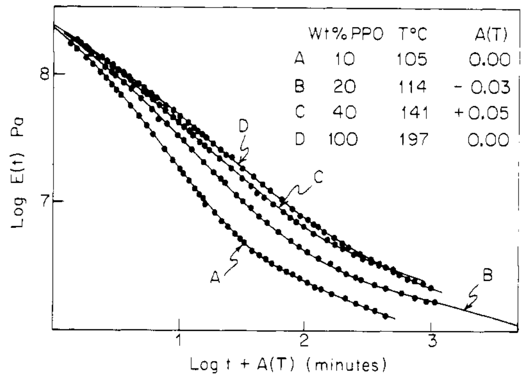

Figure 7. Stress relaxation master curves for PS–PPO blends in the primary transition region at various temperatures.

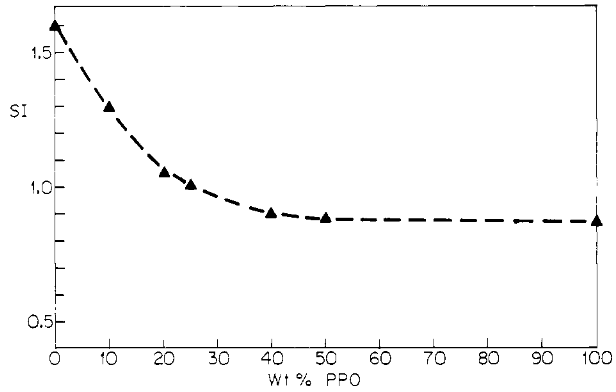

Figure 8. Experimentally determined variation of SI with PPO concentration in PS–PPO blends.

The blends containing various percentages of PPO were diluted with dioctyl phthalate (DOP) purchased from Matheson Coleman and Bell. The required amount of DOP was mixed with the blend in powdered form. This mixture was pressed to a film at temperatures approximately 55 °C over the T_g of the sample. The film was then cut into small pieces and pressed again. This mixing process was repeated many times. The resulting plasticized samples were formed into strips as described above and then subjected to stress relaxation studies. To test for adequacy of mixing, several samples were subsequently shaped into films and remixed on the press 10 times. The stress relaxation behavior of such films was also measured; in no instances were deviations greater than experimental error observed between the initially studied samples and those subjected to further mixing.

Results and Discussion

In Figure 7, we show the stress relaxation behavior in the primary transition region for several of the PS–PPO blends studied (blends studied contained 0%, 10%, 20%, 25%, 40%, and 100% PPO). The individual curves are composites of runs at several temperatures that were combined according to the time–temperature correspondence principle.[16] The reference temperature for each blend and the shift $A(T)$ applied are chosen such that the various curves emanate from the same point at short times so that changes in relaxation rate are clear. There is no particular reason for having chosen these four curves to include in the figure other than that they show clearly the regular broadening of the transition region with increasing PPO concentration.

The variation in SI with PPO concentration for PS–PPO blends is shown in Figure 8. The SI was measured merely by graphically determining the maximum slope of the raw

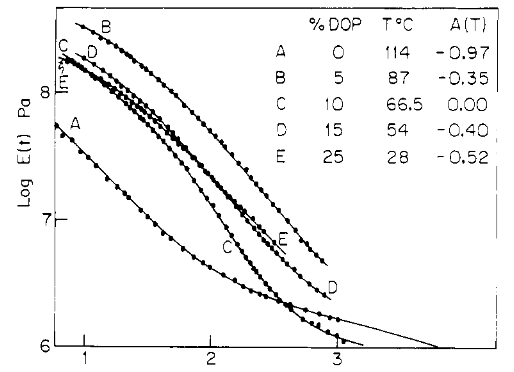

Figure 9. Stress relaxation master curves for a 20 wt % PPO blend diluted with various concentrations of DOP. The curves have the reference temperatures stated on the figure and have been shifted by the factors $A(T)$ for clarity.

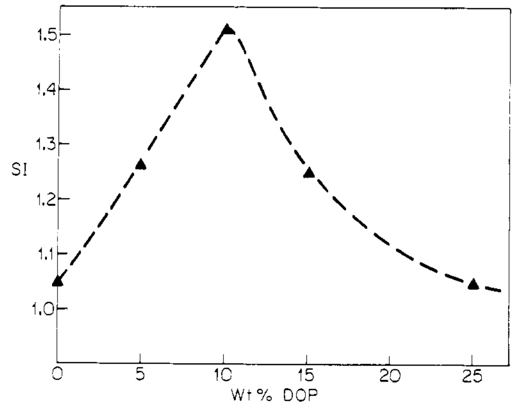

Figure 10. SI variation as a function of DOP concentration for the blend containing 20 wt % PPO.

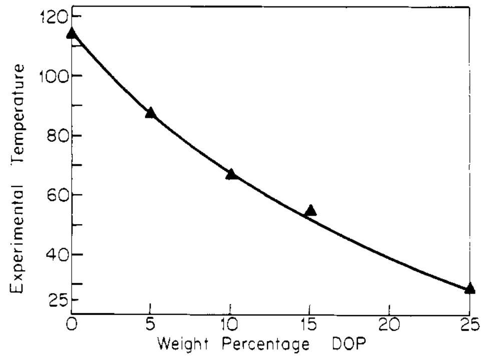

Figure 11. "Experimental temperature" vs. DOP concentration for a PS–PPO blend containing 20 wt % PPO.

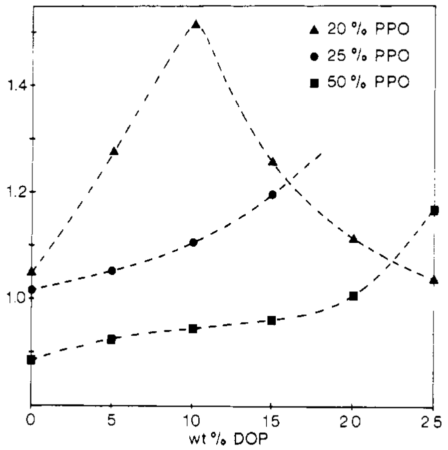

Figure 12. SI as a function of diluent concentration for three PS–PPO blends.

stress relaxation data when plotted as log (modulus) vs. log (time). This number certainly is not significant to more than ±0.1 unit. Nevertheless, the shape of the curve in Figure 8 is very similar to that in Figure 5, the schematic prediction of SI vs. PPO concentration based on the damped Debye lattice model. To be sure, small discrepancies exist; rather than having extreme values of 1.5 and 1.0, the experimentally determined behavior extends from 1.6 to 0.9. Still, the highly nonlinear character of the curve and the insensitivity to further increases in PPO concentration after approximately 25 wt % are features that were clearly predicted by the model.

In our opinion, an even more impressive success results from an analysis of experiments on a plasticized polymer blend in the primary transition region. In Figure 9, the stress relaxation behavior of blends containing 20% PPO diluted with 0, 5, 10, 15, and 25 wt % DOP is shown. These curves have been shifted by the arbitrary factors $A(T)$ listed on the figure to minimize overlap. Again, each curve is a composite of several runs, some at different temperatures that have been combined as described above. Values of the SI for these DOP plasticized blends were measured in the normal way and are presented in Figure 10. Here a dramatic increase in SI at low plasticizer concentration is observed, followed by a corresponding decrease in slopes at higher plasticizer concentrations. To our knowledge, this is the first reported example of the steepening of a master curve in the primary transition region brought about by the introduction of plasticizers. In the past, certain plasticizers have been reported that would depress the glass transition temperature without substantially affecting the shape of the relaxation curve in the transition region.[5,9] Here, as predicted by the damped Debye lattice model, a marked increase in SI is observed.

In Figure 11, the "experimental temperature", which is merely the reference temperature chosen such that all of the relaxation curves emanate from the same point at a short time, is plotted vs. weight percentage of DOP. This temperature is very much like the characteristic relaxation temperature T_i used previously by Tobolsky and others.[17] The smooth decrease in this temperature with diluent concentration is a good indication that ordinary plasticization is taking place.

Figure 10 is reminiscent of Figure 6, the predicted SI behavior as a function of diluent concentration based on the damped Debye lattice. Although the model predicts that the SI should go down to 0.5 at high dilutions, we cannot test this feature since our apparatus has no low-temperature capability and thus experiments on highly plasticized systems are not possible at this time. The lowest value of SI observed was approximately 1.0 for the 25 wt % DOP diluted system. Nevertheless, as predicted by the model for the blend containing the minimum amount of PPO necessary to produce a two-dimensional system, dilution did result in the very surprising SI behavior like that shown in Figure 6.

One further test of the model is also feasible at this point. From Figure 8 and the schematic Figure 4, it is clear that at PPO concentrations greater than approximately 20 wt %, interchain interaction should even more strongly dominate the material behavior than at 20% PPO. Under these conditions, the model predicts that the incorporation of the diluent should be less effective in modifying the SI. The peak in the SI should still be observed but now at higher diluent concentrations. Experiments to test this prediction were carried out with samples containing 25 and

50 wt % PPO. A summary of results is shown in Figure 12. It is clear that under these conditions, the incorporation of the plasticizer is indeed much less effective in varying the SI than for the 20 wt % PPO blend. From these data, it can be anticipated that a peak in SI similar to that observed with the 20 wt % PPO blend would be observed at DOP concentrations higher than those that can be used in our laboratory. Thus, once again the predictions of the damped Debye lattice model have been observed experimentally for the PPO-PS system.

Conclusions

We have used the behavior of the compatible polystyrene-poly(2,6-dimethyl-1,4-phenylene oxide) blend in the primary transition region to investigate the credibility of the damped Debye lattice model. We have studied the properties of blends that contained various amounts of PPO and have also investigated the behavior of several of these blends plasticized with dioctyl phthalate.

On the basis of information concerning the enthalpy of mixing, the excess density of mixing, polymer backbone structure, and the glass transition temperatures of blends of these two polymers, we have deduced how intra- and intermolecular interactions (force constants) vary with the amount of PPO in the blends. Using this information, we have shown that the damped Debye lattice model qualitatively predicts many aspects of the behavior of PS-PPO blends in the primary transition region. Experimentally, all of these predictions were found to be correct. This being the case, we may conclude that the damped Debye lattice is indeed a very powerful model to use in rationalizing viscoelastic behavior in the primary transition region. Fundamentally, these results show that interchain interactions, which can conveniently be disregarded in solution, are of primary importance in bulk and the influence of these interactions on viscoelasticity relaxation in the primary transition region is often profound.

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Registry No. PS, 9003-53-6; PPO, 24938-67-8; 2,6-dimethylphenol homopolymer, 25134-01-4.

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Evidence for Critical Double Points in Blends of Polystyrene and Poly(*o*-chlorostyrene)

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ABSTRACT: Theoretical and experimental evidence is put forward to prove that both UCST and LCST behavior can be found in blends of polystyrene and poly(*o*-chlorostyrene). Vapor sorption results combined with known results of heat of mixing experiments lead to the conclusion of the rather uncommon UCST behavior. Existing data of T_g measurements show that the PS/PoClS system is extremely sensitive to a small change in molar mass. A decrease in molar mass of PS of less than 4000 transforms an only partially miscible system into a system that is miscible throughout the entire experimental temperature range from 150 to 400 °C. The enhanced sensitivity is shown to be related to the existence of a critical double point in the system under consideration and as such provides additional proof for the existence of both UCST and LCST in PS/PoClS blends. The last section is devoted to a model calculation, using Flory's equation of state theory. It shows in a most convincing way the enhanced sensitivity near a critical double point.

Soon after the discovery of the LCST phenomenon in polymer solutions, Flory and co-workers formulated a mean field theory that could explain this behavior.[1,2] The so-called equation of state theory shows that for nonpolar polymer solutions one should expect phase separation upon heating and upon cooling. A lower critical solution temperature (LCST) is associated with the first one and an upper critical solution temperature (UCST) with the latter one. A UCST was of course well-known and could be explained by the Flory-Huggins theory.[3-5] In order to explain the LCST behavior, it is essential to take the differences in equation of state properties of both pure components into account. Based on this viewpoint various other theories have been developed, all capable of explaining at least qualitatively the occurrence of an LCST.[6,7]

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