

The Role of Density and Temperature in the Dynamics of Polymer Blends

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ABSTRACT: The relative effect of volume and thermal energy on the local segmental dynamics, as reflected in the ratio of the isochoric, E_V , and isobaric, E_P , activation enthalpies, is determined for blends of polystyrene (PS) with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and with poly(vinyl methyl ether) (PVME). We find that neat PPO near T_g has the lowest value of $E_V/E_P = 0.25 \pm 0.02$ reported for any polymer, indicating volume-dominated dynamics. Addition of the lower T_g PS alleviates constraints on local motion, resulting in a weaker volume effect. The opposite situation prevails with PS/PVME blends. PS has a higher T_g , and in blends segmental relaxation of the PVME becomes more controlled by volume than for neat PVME. We also show herein that the relaxation times for the PVME/PS blends measured at various T and P superpose when plotted vs Tv^γ , where v is the specific volume and γ is a material constant. This scaling, which has previously been demonstrated for various neat glass-formers and is reported herein for the first time for a blend, enables E_V/E_P to be determined at T_g in the absence of actual measurements near T_g .

Introduction

Although polymer blends are of obvious practical utility (finding applications as diverse as those of neat polymers^{1–5}), fundamental studies of blends and mixtures can also be productive, with phenomena observed having no counterpart in pure materials. These new effects can offer stern tests of theoretical models. Much recent research on blends has focused on their relaxation behavior, both the local segmental dynamics and the global chain motions. While the latter are unique to macromolecules, segmental relaxation of polymers is of more general interest, since it underlies the global dynamics and has many properties in common with structural relaxation of simple, molecular liquids.

There are a number of extant models for blend dynamics,^{6–12} each accounting in somewhat different fashion for the salient features: thermorheological complexity, low-frequency broadening of the dispersion in the dielectric or mechanical loss spectra, dynamic heterogeneity (i.e., distinct relaxation peaks for each component), etc. Other phenomena, which may be specific to certain blends or particular measurement conditions, are not so easily described by available models; these include relaxation times that are not intermediate between those of the pure components,^{13–16} the composition independence of the relaxation times seen at very high temperatures,^{17,18} and the effect of blending on secondary relaxations.¹⁹

Accounting for the dynamics in blends obviously requires an understanding of the relaxation behavior of the neat components. Recent progress along these lines has come from the use of pressure as an experimental variable. By measuring relaxation times as a function of T and P (and thus also of volume), the relative degree to which thermal energy and density govern the dynamics can be quantified.^{20–24} The usual approach is to determine the ratio of the activation

enthalpies at constant volume, $E_V = R(d \ln \tau_\alpha/dT^{-1})|_V$, to that at constant pressure, $E_P = R(d \ln \tau_\alpha/dT^{-1})|_P$, where τ_α is the relaxation time for the glass transition. E_V/E_P can vary from 0 (corresponding to volume dominated dynamics) to unity (temperature as the control variable) and for polymers has been found to fall in the range from 0.5 to 0.8 at temperatures near T_g .^{24,25} This means that the change in local segmental relaxation time upon cooling toward the glass temperature is due to both thermal contraction of the material and its energy loss, with the latter exerting a somewhat stronger effect ($E_V/E_P > 0.5$).

A recent development is our finding that τ_α , measured for various conditions of T and P , can be superposed by plotting vs the product of the temperature times the specific volume, v , raised to a constant; i.e., $\tau_\alpha = f(Tv^\gamma)$, where γ varies among materials but is independent of T and P .^{26–28} The underlying idea is that segmental motions are thermally activated but impeded by steric constraints (jamming); this confers a density dependence to the activation energy, whereby non-Arrhenius behavior ($\log \tau_\alpha$ not proportional to T^{-1}) is observed. The magnitude of the scaling exponent γ reflects the role of volume in controlling the change in τ_α with temperature, and in principle it may be related to the intermolecular repulsive interactions.²⁶ If τ_α is a function of Tv^γ , it follows that^{26,27}

$$E_V/E_P = (1 + \gamma\alpha_P T)^{-1} \quad (1)$$

where α_P is the isobaric thermal expansion coefficient. Note that the product $\alpha_P T$ is roughly constant at T_g equal to ~ 0.2 .^{27,29} (although an evaluation of literature data suggests a weak increase with T_g). While E_V/E_P is usually determined near T_g , it varies with temperature. Equation 1 can be used to calculate E_V/E_P at any temperature since γ is a constant. The γ -scaling has recently been extended to the normal mode of polymers,^{30–32} with the same value of the exponent yielding superposition of both the normal mode relax-

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ation time and τ_α . This implies that both the global and local segmental relaxations are governed to the same relative degree by T and V , although their behavior is described by different functions of the variable TV^γ .

In this paper we analyze relaxation and equation-of-state data for two blends: (i) poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with atactic polystyrene (PS) and (ii) poly(vinyl methyl ether) (PVME) with PS. These blends are essentially van der Waals mixtures, having only weak interactions between the components.^{33,34} An important difference is that in the first case PS is added to a polymer (PPO) having a higher T_g , while in the second case PS is mixed with a lower T_g material (PVME). Our principal interest concerns the influence that volume and temperature have on segmental relaxation in the blends, in comparison to the neat components. Current models of blend dynamics restrict their consideration to the variation of τ_α with T , and only a few experimental studies have addressed the effect of pressure on τ_α for mixtures,^{28,35,36} block copolymers,³⁷ or blends.^{38–41} Fundamental understanding, however, requires analysis of what governs the observed dependences. At least for the two blends studied herein, we find that the effect of added PS on E_V/E_P depends on the relative T_g of the components. T_g of PS is intermediate between that of PPO (largest) and PVME and increases E_V/E_P for the former while decreasing it for the latter blend. Thus, the relative relaxation times of the components, as reflected in their neat T_g , appear to govern how blending influences the effect of volume on $\tau_\alpha(T)$. We also examine whether the $\log(\tau_\alpha) = f(Tv^\gamma)$ scaling of neat materials also applies to PVME in blends with PS.

Results

PPO/PS Blends. One of the early commercially significant polymer blends is PPO and PS (General Electric's Noryl). A limited number of studies of the dynamics in this blend have been reported. Optical and infrared birefringence measurements were used to follow chain orientation in stretched films.^{42–44} Chain relaxation of the components was found to be "coupled" due to the homogeneous phase morphology.⁴² Time-temperature shift factors for the chain dynamics are only weakly dependent on composition.⁴⁵ NMR has been used to study the component dynamics near the glass transition^{46,47} and the effect of blending on motion of the phenyl side groups in PPO/PS blends.⁴⁸ Concerning the local segmental relaxation, Robertson and Wilkes⁴⁹ reported an increased blend fragility (T_g -normalized temperature dependence of τ_α) relative to the neat components.

PVT measurements have been carried out on neat PPO and various compositions with PS,^{50,51} and in Figure 1 we show representative results for the specific volume of neat PPO as a function of temperature at pressures from ambient to 120 MPa. For the respective liquid and glassy states (but well away from the glass transition), v can be fit to quadratic functions whose intersection defines T_g . These T_g values are indicated in Figure 1 and yield the pressure coefficient of the glass transition. Results for the PPO and three blends with PS are given in Table 1. For neat PPO, $dT_g/dP = 804$ K/GPa, which is the largest pressure coefficient of T_g ever reported for any molecular liquid or polymer.²⁵

In Figure 2 the ambient pressure T_g is plotted vs composition, together with the value for neat PS (also

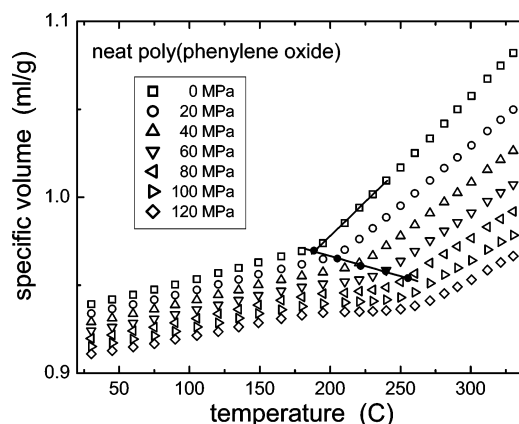


Figure 1. Specific volume vs temperature for neat PPO at the indicated pressures (data from ref 51). The solid circles represent $T_g(P)$ as determined from the intersection of the liquid and glassy $v(T)$ data. Solid lines are the isobaric ($P = 0$) and isochronal ($\tau(T_g)$) fits.

Table 1. Results for PPO/PS Blends

PPO (%)	T_g (°C)	$\lim_{P \rightarrow 0}(dT_g/dP)$ (K/GPa)	E_V/E_P (at T_g)
100	188.6	840 ± 8	0.25 ± 0.02
70	153.3	692 ± 15	0.35 ± 0.02
50	124.6	555 ± 23	0.50 ± 0.04
30	112.8	483 ± 20	0.51 ± 0.03
0	100 ^a	360 ± 50^a	0.64 ± 0.05^a

^a Reference 52.

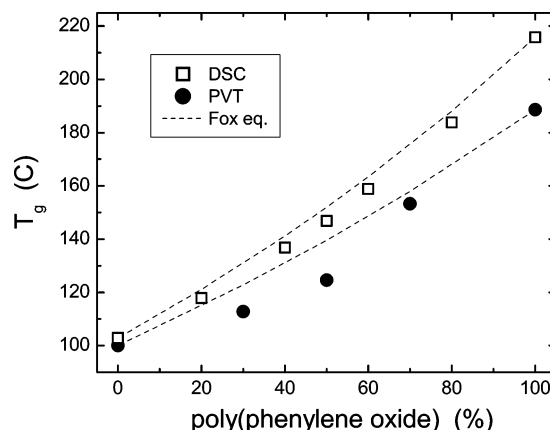


Figure 2. Composition dependence of the glass transition temperature of PPO/PS blends, determined herein from *PVT* data and as reported in ref 55 from calorimetry. The dotted lines are the respective fits to eq 2.

obtained from *PVT* data⁵²). It is common in models of blend dynamics^{8,11} to employ the Fox equation to describe the composition dependence of T_g ⁵³

$$T_g(\phi_1) = \left(\frac{\phi_1}{T_{g,1}} + \frac{1 - \phi_1}{T_{g,2}} \right)^{-1} \quad (2)$$

The fact that the Fox equation is readily implemented (no adjustable parameters) accounts for much of its popularity. Its limitations have led to modifications entailing additional parameters.⁵⁴ As seen in Figure 2, eq 2 overestimates T_g for the blends by $\leq 10\%$. Also included in the figure are DSC results⁵⁵ for a PPO/PS blend of comparable molecular weights. There is a similar negative deviation from eq 2.

The glass transition temperature determined from *PVT* measurements corresponds to the temperature at

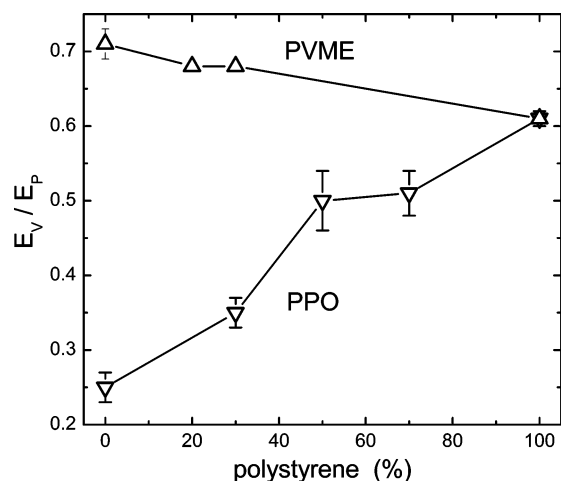


Figure 3. Activation enthalpy ratio as a function of composition for PVME/PS (Δ) and PPO/PS (∇) blends. An increasing value of E_v/E_p denotes stronger effect of thermal energy, relative to that of volume, on $\tau_\alpha(T)$.

which τ_α is constant; that is, $\tau_\alpha(T_g)$ is pressure-independent. This means that while $\tau_\alpha(T_g)$ may vary for different materials (usually being in the vicinity of 100 s) and the value of T_g itself is rate dependent, for a given material whose volume is measured at fixed rate the relaxation time at T_g does not change with pressure.²⁵ This means that the specific volume at $T_g(P)$ can be used to define an isochronic thermal expansion coefficient, α_τ ($\equiv v^{-1}(dv/dT)|_\tau$). Ferrer et al.²² have shown that the ratio of α_τ and the isobaric thermal expansion coefficient, α_p , provides another measure of the relative degree to which volume and temperature govern $\tau_\alpha(T)$. The activation enthalpy ratio is related to these thermal expansivities according to⁵⁶

$$E_v/E_p = (1 - \alpha_p/\alpha_\tau)^{-1} \quad (3)$$

Using eq 3, together with the assumption that $\tau_\alpha(T_g)$ is constant, allows E_v/E_p to be calculated without measurement of relaxation times. The isobaric thermal expansion coefficient above T_g is determined directly from the PVT data, while $\alpha_\tau = v(T_g)^{-1}[dv(T_g)/dT_g(P)]$. The E_v/E_p so obtained for PPO as a function of composition are plotted in Figure 3, along with the value for neat PS.⁵² The uncertainty reflects scatter in the $T_g(P)$ data.

For neat PPO, the enthalpy ratio is quite small, ≈ 0.25 , the lowest found to date for any polymer.²⁵ This indicates that the temperature dependence of the segmental dynamics of PPO is governed primarily by changes in volume, with thermal energy exerting a relatively small effect. The low value of E_v/E_p for PPO follows from the magnitude of its pressure coefficient of T_g , since this contributes to a large (negative) α_τ . Addition of the lower T_g PS increases E_v/E_p ; that is, the presence of PS makes τ_α less dependent on density. Interestingly, blending causes densification of the blend—as shown in Figure 4, the specific volume at T_g passes through a minimum vs composition. This is normal behavior for mixtures with strong specific interactions and can also arise from local packing effects.^{57,58}

PVME/PS Blends. This is one of the most studied polymer blends, due to the convenient T_g and its miscibility despite weak interactions. Dielectric spectroscopy measurements on PVME/PS^{39,59–61} are especially interesting since the dynamics of the polar PVME

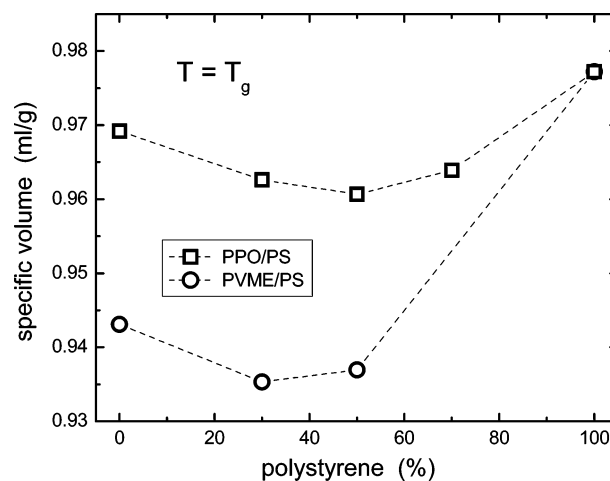


Figure 4. Composition dependence of v for PVME/PS and PPO/PS blends. Both have a negative excess volume.

are monitored without interference from the relatively nonpolar PS. We have previously shown²⁷ that relaxation times for neat PVME, measured vs T at ambient P and at three temperatures for pressures up to 726 MPa,⁵⁶ superpose when expressed as a function of $Tv^{2.55}$. Scaling of the data of Floudas, who measured neat PVME as a function of pressure at various temperatures,³⁹ gives an equivalent value of γ . Since for PVME and its blends with PS considered herein, T_g is below the range of the PVT measurements, E_v/E_p cannot be extracted directly from the PVT data. Accordingly, we make use of eq 1, relating the activation enthalpy ratio to the scaling exponent γ . From PVT data for PVME in the equilibrium liquid state,⁶² $\alpha_p = 5.697 \times 10^{-4} \text{ K}^{-1}$ at $T_g = 247.6 \text{ K}$; thus, eq 1 yields $E_v/E_p = 0.73$, consistent with the value determined directly from slope of the isochoric and isobaric relaxation times vs reciprocal temperature, $E_v/E_p = 0.69$.⁵⁶ A value this large is typical of polymers, whose segmental relaxation times are usually influenced more strongly by thermal energy than by density.

For blends of PVME with 30 and 50 wt % of PS, Floudas³⁹ measured the dielectric relaxation times at ambient pressure and also determined the activation volumes, $\Delta V = RT(d \log \tau_\alpha/dP)|_T$, from measurements at pressures up to 200 MPa. From these data we obtain $\tau_\alpha(T, P)$. To express the relaxation times as a function of Tv^γ requires the equation of state for the blends. Using published PVT data⁵⁰ for blends of PVME and PS having the same composition and (high) molecular weights similar to the samples measured dielectrically, we fit the Tait equation⁶³

$$v(T, P) = (a_0 + a_1 T + a_2 T^2)[1 - 0.0894 \ln(1 + P/b_0 \exp[-b_1 T])] \quad (4)$$

with the results given in Table 2.

We then calculate v for each T and P at which τ_α is known, obtaining the master curves of the $\log \tau_\alpha(Tv^\gamma)$ shown in Figure 5. Good superposition is achieved with $\gamma = 3.0 \pm 0.05$ independent of blend composition. This is the first instance of the scaling $\log(\tau_\alpha) = f(Tv^\gamma)$ shown to be valid for a blend. The scaling exponent is significantly larger than the value of 2.55 for neat PVME. From eq 1 $E_v/E_p = 0.68 \pm 0.01$ for the blends; these data are included in Figure 3. There is a systematic increase in the degree to which volume governs the segmental dynamics with addition of PS to the PVME.

Table 2. Equation-of-State Parameters for PVME/PS Blends

PVME (%)	v_0 (mL/g)	v_1 (mL/(g °C))	v_2 (mL/(g °C ²))	b_0 (MPa)	b_1 (°C ⁻¹)
50	0.9415 ± 0.0002	$(5.30 \pm 0.04) \times 10^{-4}$	$(4.3 \pm 0.2) \times 10^{-7}$	245 ± 1	$(4.60 \pm 0.04) \times 10^{-3}$
70	0.9442 ± 0.0001	$(5.90 \pm 0.02) \times 10^{-4}$	$(3.75 \pm 0.09) \times 10^{-7}$	225.0 ± 0.6	$(4.52 \pm 0.02) \times 10^{-3}$

Figure 4 shows the specific volume at T_g for the two PVME/PS blends and the neat components. Similar to PPO/PS, there is substantial densification; that is, the excess volume is negative.

Discussion and Summary

Neat PPO has an unusually low value of $E_V/E_P = 0.25 \pm 0.02$, revealing the relative dominance of volume, as opposed to thermal energy, in determining the variation of τ_α with T . For other polymers, $0.5 > E_V/E_P > 0.8$; that is, temperature tends to be the stronger control variable.^{24,25} The latter is a consequence in polymers of a plethora of intramolecular bonds, which are insensitive to pressure. This insensitivity is evidenced by the invariance to pressure of the normal mode dielectric strength, which depends on the chain end-to-end distance.³¹ The unusually strong effect of v on the dynamics of PPO is related at least in part to the flexibility of its backbone due to the ether linkage. Volume effects are generally emphasized in flexible polymers: polysiloxanes have activation enthalpy ratios close to 0.5^{24,25} (equal influence of v and T), and for poly(propylene oxide) $E_V/E_P = 0.55$ (albeit measured for $T > T_g$).⁶⁴ The high T_g of PPO may also contribute to a low value of E_V/E_P since very generally this ratio decreases with increasing temperature. This can be seen from inspection of eq 1, noting that the product $\alpha_P T$ is an increasing function of temperature while γ is constant. It is noteworthy that most flexible chain polymers (e.g., poly(ethylene oxide), poly(propylene oxide), siloxane polymers) are low- T_g elastomers. It may be the unique circumstance in PPO of chain flexibility yet a high T_g that gives rise to the unusually strong influence of volume on the dynamics of this polymer.

The dynamics of PPO/PS become less volume dependent with increasing concentration of PS. We expect environments enriched in PS to facilitate relaxation of PPO segments because the PS has a lower T_g . This means that PS segments will tend to have relaxed when segmental relaxation of the PPO is considered. In the limit of $\tau_\alpha(\text{PPO}) \gg \tau_\alpha(\text{PS})$, the PPO does not participate in the cooperative dynamics of the PS and thus would

be unconstrained. This is a general property of blends whose components differ significantly in T_g ^{19,65} and is exemplified by probe molecules whose dynamics are strongly correlated with the magnitude of their relaxation time relative to that of the matrix.⁶⁶ As seen herein, the mitigation of intermolecular constraints with increasing PS content leads to a decreasing effect of volume on $\tau_\alpha(T)$.

Opposite to the case of PPO, the dynamics of PVME become more volume dependent with increasing concentration of PS. The T_g of PS is higher than T_g of PVME, so that addition of PS constrains the dynamics of PVME, since PS is unrelaxed on the time scale of the PVME segmental relaxation. This means a PS-rich local environment is unaccommodating, and constraints on the local motion of a PVME segment are not easily mitigated. The result is increased fragility of PVME in blends with increasing PS concentration⁷ and, as seen herein, a stronger effect of volume on τ_α of PVME.

The idea that the relative mobility of the local environment influences the dynamics underlies the concept of "dynamic facilitation" of Garrahan and Chandler.^{67,68} In their model, jammed particles (atoms or molecules) become unjammed (i.e., constraints on their local motion are alleviated) when the particles are adjacent to a region that is already unjammed. The dynamic facilitation arising in neat materials due to dynamic heterogeneity will be more prominent in blends because of the effect of concentration fluctuations. We also note that the relative effect of volume on the blend dynamics does not depend on the excess mixing volume. Blends of both PPO/PS and PVME/PS are more dense than the weighted average of their component densities, yet the effect of blending on E_V/E_P is opposite for the two systems.

We find that the PVME segmental relaxation times in blends with PS conform to the $\log(\tau_\alpha) = f(Tv^\gamma)$ scaling previously discovered for neat materials. This scaling is especially useful herein since PVT data for $T \leq T_g$ could not be measured for PVME/PS blends due to their low (subambient) T_g . Since the scaling exponent γ is constant, eq 1 allows E_V/E_P to be determined for any temperature and pressure in the equilibrium ($>T_g$) state.

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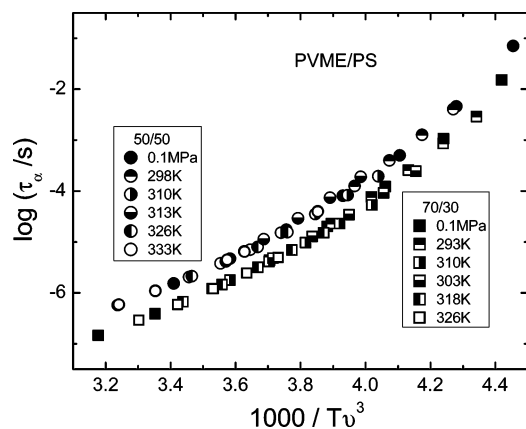


Figure 5. Specific-volume-scaled Arrhenius plots of dielectric α -relaxation times for PVME mixed with 30% (squares) and 50% (circles) PS. The scaling exponent, $\gamma = 3$, is significantly larger than the value of 2.55 for neat PVME. The experimental data are from ref 39.

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