Enthalpy Relaxations and Concentration Fluctuations in Blends of Polystyrene and Poly(oxy-2,6-dimethyl-1,4-phenylene)

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ABSTRACT: A series of enthalpy relaxation measurements were carried out for the pure polymers polystyrene (PS) and poly(oxy-2,6-dimethyl-1,4-phenylene) (PPE) and for homogeneous blends thereof. The data were analyzed using Moynihan's four-parameter approach.[4] For the pure components the best fit parameter values for the simple cooling/heating experiments differ somewhat from those for the annealing experiments at least partly due to thermal lag. The amount of enthalpy relaxation during annealing of the blends turned out to be considerably lower than for the corresponding homopolymers. Moreover, the annealing experiments on the blends could not be fit satisfactorily with the Moynihan model. The first observation agrees with a similar result found by Cowie and Ferguson[17] for blends of PS and poly(vinyl methyl ether). Since this effect is not present for a number of polymer blends involving polymers with comparable glass transition temperatures, it seems to be related to the large difference in glass transition temperatures of the blend components. The presence of concentration fluctuations, with a corresponding range of T_g values, is the most obvious explanation for both observations.

Introduction

In recent years, there has been a considerable effort experimentally as well as theoretically to understand and describe the relaxation behavior of amorphous polymers in the glass transition region.[1–16] Relaxation of polymers at temperatures below the glass transition temperature results in changes in many physical properties such as density and enthalpy. The whole process is of considerable practical importance, because it may lead to polymer materials becoming more brittle or in a completely different field of applications to a loss of dipole orientation as a function of time.

In this paper we will consider enthalpy relaxation in miscible polymer blends, polystyrene/poly(oxy-2,6-dimethyl-1,4-phenylene) (PS/PPE) blends in particular. One of the motivations for this study is the observation of Cowie and Ferguson[17] that the total amount of enthalpy relaxation in blends of PS and poly(vinyl methyl ether) (PVME) is much lower than for the pure components, measured at comparable undercoolings relative to the glass transition temperatures. The effect was explained by assuming that "the PVME component in the blend appears to age independently of the PS component and is responsible for essentially all of the aging effects observed". In recent years we developed a method based on enthalpy relaxations to determine the phase behavior of blends consisting of components with comparable T_g values.[18–21] For these systems, the enthalpy relaxation for the pure components and their blend as a function of aging time always turned out to be essentially the same. The effect seems therefore to be related to a difference in the glass transition temperatures of the blend components. Besides PS and PVME, one of the best known miscible polymer pairs is PS and PPE, and since the T_g values of these polymers are very different too, they form an obvious alternative pair for an enthalpy relaxation study.

Besides the amount of enthalpy relaxation, the second question that will be addressed is whether the enthalpy relaxation and recovery process in this blend can be described in a sensible manner with the four-parameter model formulated by Moynihan and co-workers.[4] The enthalpy relaxation that occurs during the annealing of polymers below the T_g is recovered during reheating and

becomes visible as a maximum in a differential scanning calorimeter scan. The position and the size of the peak depends on the thermal treatment given and on the structure of the polymer itself. This latter fact forms the basis of the alternative thermal analysis method of establishing phase behavior in blends of polymers with similar T_g values, referred to in the last paragraph. To describe the relaxation and recovery process, various related approaches are available. The four-parameter model introduced by Moynihan et al.[4] will be considered in some detail, because it is known to describe the kinetics of the glass transition and aging of pure polymers quite well. Furthermore, it was also found to work well in the case of miscible blends of poly(methyl methacrylate) (PMMA) and random copolymers of styrene and acrylonitrile (SAN).[22] But, it should be realized that these polymers have comparable T_g values, whereas our interest here is especially the effect of having polymers with very different glass transition temperatures.

The kinetics of the processes in the glass transition region is both nonexponential and nonlinear. The relaxation toward equilibrium can be described well by the familiar Kohlrausch–Williams–Watts[23] nonexponential function $\phi(t)$ given by

$$\phi(t) = \exp[-(t/\tau_0)^\beta] \qquad (1)$$

where β is the nonexponentiality parameter ($0 < \beta < 1$). The relaxation time τ_0 is given by an expression introduced by Moynihan et al.,[4] who introduced the nonlinearity parameter in the original Gardon and Narayanaswamy[24,25] expression

$$\tau_0 = A \exp\left[\frac{x\Delta h}{RT} + \frac{(1-x)\Delta h}{RT_f}\right] \qquad (2)$$

where A is a preexponential factor, R the universal gas constant, Δh an activation enthalpy, T_f the fictive temperature defined as that temperature at which the enthalpy value would be the equilibrium value, and x the nonlinearity parameter partitioning the relaxation between purely Arrhenius and purely structure dependent through T_f. Because the relaxation depends on the specific structure, it depends on the complete thermal history and the mathematical treatment of the annealing/recovery

process requires a coherent description of cooling, annealing, and heating. A procedure to deal with all these aspects in detail was described by Hodge and Berens.[8,10] The response to cooling or heating is obtained by Boltzmann superposition of responses to each temperature step introduced to simulate the continuous cooling or heating rate. It is the value of the fictive temperature after each temperature step that determines the DSC specific heat versus temperature curve. The value of T_f after n temperature steps is given by

$$T_f(n) = T_0 + \sum_{j=1}^{n} \Delta T(j)\{1 - \exp[-(\sum_{k=j}^{n} \Delta T(k)/Q(k)\tau_0(k))^{\beta}]\} \tag{3}$$

where T_0 is the starting temperature above the glass transition temperature T_g, $Q(k)$ the cooling or heating rate, $\Delta T(j)$ the temperature jump at the jth step, and $\tau_0(k)$ given by eq 2 with T replaced by the temperature $T(k)$ obtained after k temperature jumps and T_f replaced by the fictive temperature after $k - 1$ temperature jumps $T_f(k-1)$. The parameter $\Delta h/R$ determines how the frozen-in fictive temperature of the glass, T'_f, varies with the cooling rate Q_c:

$$\frac{d(\ln Q_c)}{d(1/T'_f)} = -\Delta h/R \tag{4}$$

Thus, $\Delta h/R$ can and will be determined directly from the experimental data. An approximate value of the preexponential factor A can be obtained by the relation

$$\ln A = -\frac{\Delta h}{RT_g} + \ln \tau_0(T_g) \tag{5}$$

The four parameters β, x, A, and $\Delta h/R$ are assumed to be independent of T and T_f. The normalized heat capacity $C_p^N(T)$, defined by

$$C_p^N(T) \equiv \frac{C_p(T) - C_{p,g}(T)}{C_{p,l}(T_f) - C_{p,g}(T_f)} \tag{6}$$

where $C_{p,g}$ and $C_{p,l}$ represent the specific heat in the glassy and liquid state, respectively, and $C_p(T)$ is the relaxation part of the specific heat, is related to the fictive temperature by

$$C_{p,n}(T) = \frac{dT_f(n)}{dT} \simeq \frac{[T_f(n) - T_f(n-1)]}{[T(n) - T(n-1)]} \tag{7}$$

During annealing, T is fixed and $\Delta T(k)/Q(k)$ is replaced by a set of annealing times logarithmically evenly spaced in the interval $(0, t_a)$, where t_a is the total annealing time.

Experimental Section

Poly(oxy-2,6-dimethyl-1,4-phenylene) (PPE) was obtained from GEP, and polystyrene (PS) was prepared in our laboratory. The polymers were purified by a precipitation procedure and dried under vacuum at 313 K for at least 24 h. The molecular weights were determined by gel permeation chromatography (GPC) using chloroform as eluent. Values of M_w and M_n were calculated relative to polystyrene standards.

Blends of PPE and PS were obtained by coprecipitation from dilute toluene solution (2 wt %) into a large amount of methanol. The blends were dried under vacuum at 313 K for at least 24 h. The compositions of the blends were 25/75, 50/50, and 75/25 wt % PS/PPE. In the text they will be denoted as PS25, PS50, and PS75. Thermal analysis was performed with a Perkin-Elmer differential scanning calorimeter (DSC-7) employing a constant heating rate of 20 K/min (except one case of 10 K/min). Onset T_g values and molecular weights are shown in Table I. All samples for thermal analysis, blends as well as homopolymers, were

Table I
Molecular Weights and Glass Transition Temperatures

material	M_w	M_n	$T_{g,onset}$, K
PS	223 000	190 000	376
PS75			387
PS50			415
PS25			442
PPE	45 900	20 000	475

obtained by first pressing at room temperature the samples obtained by a precipitation procedure, followed by annealing for at least 10 min at temperatures of 50 K or more (specified below) above the respective glass transition temperatures.

To determine the frozen-in fictive temperature T'_f as a function of cooling rate Q_c, each sample (except pure PS) was kept in the calorimeter cell at 523 K for 10 min, cooled at one out of four cooling rates (-5, -10, -20, or -40 K/min) to 323 K, and immediately reheated over the same temperature range. For pure PS the same procedure was followed using the temperature range 273-473 K. The thermal history will be referred to as -40/20 with appropriate changes for cooling rate and/or heating rate. The experimental specific heat data were normalized with respect to the difference between the liquid and glassy heat capacities. For each cooling rate T'_f can be found by integrating the normalized specific heat $C_p^N(T)$ up to equilibrium temperatures. For temperatures in the equilibrium range, the integrant is a linear function of T and the temperature intercept of this line defines T'_f.

For annealing experiments the samples were likewise kept at a temperature of 523 K (except pure PS, 473 K) for 10 min to erase the thermal history. The samples were then cooled with -200 K/min to the annealing temperature T_a, annealed at this temperature for various amounts of time t_a (15-900 min), cooled with a programmed rate of -200 K/min to 323 K (except pure PS, 273 K), and finally reheated to 523 K (respectively, 473 K). After keeping the samples at 523 K (respectively, 473 K) for 5 min, a second scan was taken over the same temperature range.

The Marquardt optimization procedure[26,27] is used to obtain the best fit parameter values for A, x, and β. It amounts to minimizing the function

$$\Psi = \sum \{C_p^N(T) - C_{p,n}(T)\}^2$$

where $C_p^N(T)$ represents the experimental and $C_{p,n}(T)$ the calculated data. The starting values for x and β are 0.5, whereas the starting value of A is obtained from eq 5 with $\ln \tau_0 = 1.0$ at T_g. In the theoretical modeling of the annealing experiments, the cooling rate was taken to be -200 K/min throughout the whole cooling range. This is reasonable for the cooling toward the annealing temperature, which takes place at high temperatures. The cooling toward 323 K (respectively, 273 K) is probably much slower than the programmed -200 K/min; however, this is insignificant, since the relaxation processes have become very slow due to the annealing.

Results and Discussion

1.1. Relaxation Behavior: Cooling Experiments. In Figure 1 some selected results of the cooling experiments, without annealing, are presented. Figure 1a shows the experimental results for pure PS for the thermal histories -20/20 and -20/10, together with the theoretical optimum fit. Figure 1b shows the same data for pure PPE for the thermal history -20/20. Finally, in Figure 1c the corresponding data for the PS50 blend are shown for the thermal histories -5/20 and -20/20. There are a number of features apparent from these figures. First of all, in all cases the width of the theoretical enthalpy relaxation peaks is smaller than observed experimentally. This is at least partly due to a thermal lag effect. In a recent study by Hutchinson et al.[28] it was demonstrated that thermal lag effects can have a pronounced influence on the width of the relaxation peak. A comparison of the experimental results and the theoretical optimal fits for pure PS
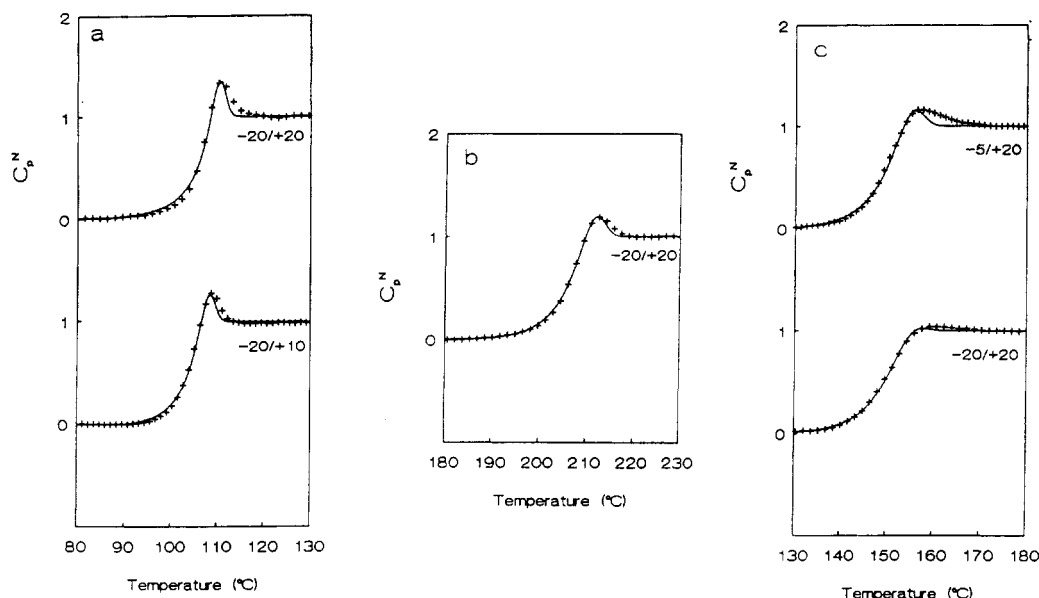
Figure 1. Experimental (symbols) and theoretical optimum fit (lines) C_p^N data for cooling experiments: (a) PS, (b) PPE, and (c) PS50.

Table II
Best Fit Parameters from Cooling Experiments[a]

material	$\Delta h/R$, kK	$\ln A$, s	x	β
PS	126 ± 7	−329.0 ± 0.1	0.24 ± 0.01	0.47 ± 0.01
PPE	140 ± 7	−289.0 ± 0.1	0.44 ± 0.01	0.47 ± 0.01
PS50	135 ± 10			

[a] For PS50 the best fit values of $\ln A$, x, and β varied with cooling rate (see text).

employing two different heating rates of 10 and 20 K/min, presented in Figure 1a, shows a reduced discrepancy for the former as far as the width of the peak is concerned. In this study a heating rate of 20 K/min was employed, and the thermal lag effect will influence the theoretical fitting procedure leading to values of β that are somewhat too small. Nevertheless, a set of values for β, x, and Δh can be found for PS as well as PPE that fit all the cooling experiments reasonably well, as demonstrated in parts a and b of Figure 1. These values are given in Table II.

The situation for the blend (Figure 1c) is completely different. The width of the relaxation peak is greatly enhanced, and the peak is in fact hardly present anymore for cooling rates exceeding 20 K/min. It is quite clear that this cannot be ascribed to thermal lag effects only. Most likely, it is caused primarily by concentration fluctuations, leading to a range of T'_f values. It is in accordance with the well-known fact that the breadth of the glass transition in blends is strongly increased compared to pure polymers, as long as the constituent polymers have a sufficiently different T_g. In our case the breadth ΔT is given by 5.6, 8.1, and 14.9 for PS, PPE, and PS50, respectively. Additional evidence for this conclusion will be put forward in the next section dealing with the annealing experiments. Table II presents the value of Δh determined from the cooling rate dependence of T'_f of PS50. The best fit values of $\ln A$, x, and β are not given since they depend strongly on the cooling rate and moreover the fit is, as can be seen from Figure 1c, rather poor.

1.2. Relaxation Behavior: Annealing Experiments. Figure 2 shows representative thermograms of PS and PPE annealed for 30 min at a temperature of 15 K below the glass transition temperatures (361 and 460 K, respectively). As in the case of the cooling experiments, the theoretical best fit predictions differ slightly from the
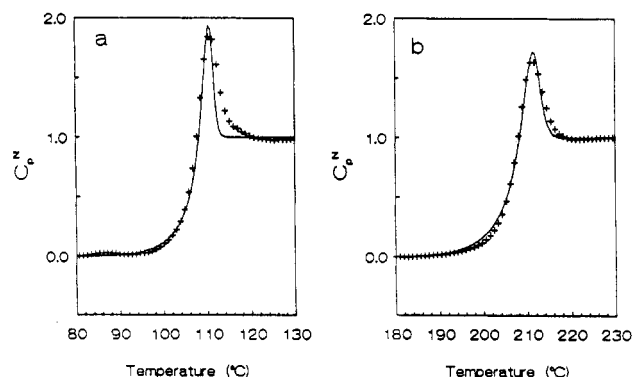

Figure 2. Experimental (symbols) and theoretical optimum fit (lines) C_p^N data for annealing experiments: (a) PS, $T_a = 361$ K, $t_a = 30$ min; (b) PPE, $T_a = 460$ K, $t_a = 30$ min.

Table III
Best Fit Parameters from Annealing Experiments[a]

material	t_a, min	$\ln A$, s	x	β
PS	15	−329.1	0.23	0.57
	30	−328.6	0.25	0.58
	60	−328.4	0.26	0.57
	120	−328.8	0.28	0.57
	930	−326.1	0.34	0.59
PS50	120	−316.6	0.33	0.56
PPE	15	−288.6	0.28	0.54
	30	−288.5	0.32	0.56
	60	−288.0	0.36	0.59
	120	−288.1	0.37	0.58
	900	−286.5	0.45	0.62

[a] The values of Δh are taken from Table II.

experimental results with respect to the width of the peaks. The theoretical best fit parameters for PS are in the same range of values as found in the literature.[11,14] The values for PS as well as PPE, presented in Table III, differ somewhat from those of the cooling experiments. For a large part this is believed to be due to thermal lag effects. On the other hand, recent publications show[6] that a dependence on the thermal history of the values of β and in particular x is real. The partitioning of the relaxation times as given by eq 2 is clearly an oversimplification. Furthermore, the assumption of a temperature-independent β implies thermorheological simplicity, a property that has been questioned as well.[6] The variation of x with
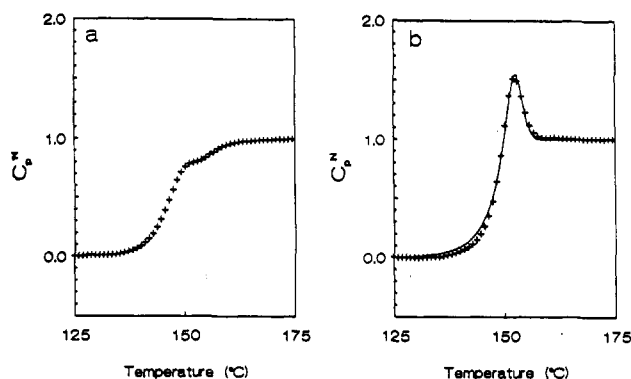
Figure 3. Experimental (symbols) and theoretical optimum fit (line) $C_p{}^N$ data for annealing experiments on PS50: (a) T_a = 400 K, t_a = 15 min; (b) T_a = 400 K, t_a = 120 min.
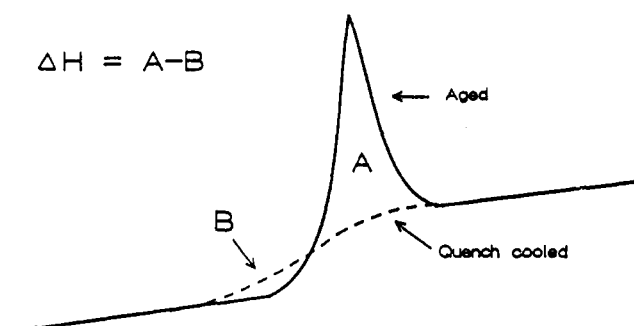

Figure 4. Illustration of the definition of enthalpy difference $\Delta H = A - B$, between aged and quench-cooled samples.

annealing time (Table III) is in excellent agreement with the published results on poly(methyl methacrylate).[6]

Figure 3 shows the thermograms of the PS50 blend, annealed at 400 K for 15 and 120 min, respectively. The second thermogram corresponding to the longest annealing time could be fitted extremely well with the theoretical model. However, this is not the case for much shorter annealing times. As can be seen from the thermogram of the sample annealed for 15 min, the enthalpy relaxation becomes visible as a shoulder on the specific heat jump. A theoretical description of this phenomenon of a pre-T_g endotherm requires a rather small value of β corresponding to a broad spectrum of relaxation times as is known to occur for instance for poly(vinyl chloride) (PVC).[9] The actual experimental curve could not be fitted very well with the theoretical model. This is again a manifestation of the presence of concentration fluctuations. As a consequence a range of T_g values is present, leading to the well-known phenomenon of a somewhat broader glass transition range in blends compared to pure components. Relatively short annealing times will result in relaxation of primarily those regions with the lowest T_g values and will subsequently lead to a relaxation endotherm at relatively low temperatures. In this way it appears as a shoulder on the ΔC_p jump. At longer annealing times all material will contribute considerably and the peak position will shift to higher temperatures. This shift to higher temperatures not only is due to higher T_g material contributing to the recovery process but is well-known to be a general phenomenon; the peak position for pure polymers shifts linearly with ln (t_a) to higher temperatures.

Besides modeling, our main interest was the enthalpy difference, ΔH, resulting from annealing and defined by the subtracted thermogram of an aged and a quench-cooled sample following recommendations of Richardson and Savill.[29] Figure 4 shows an explicit example. For the pure components and the blend ΔH was determined as a
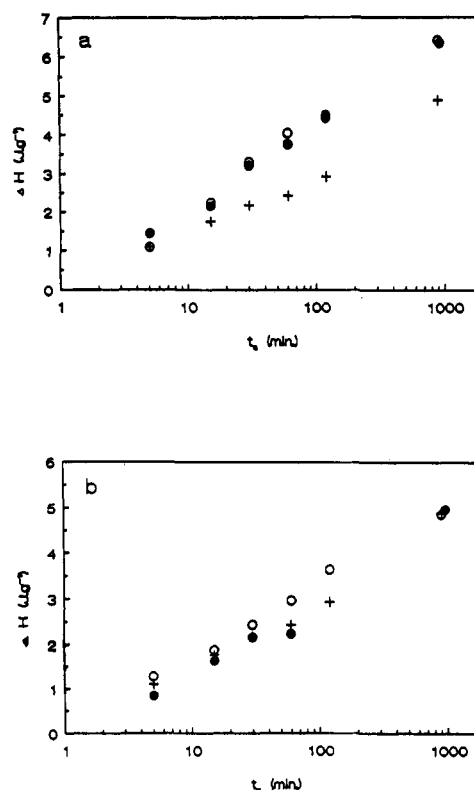

Figure 5. Enthalpy difference ΔH as a function of annealing time between aged and quench cooled samples: (a) (O) PS, T_a = 361 K; (●) PPE, T_a = 460 K; (X) PS50, T_a 400 K. (b) (O) PS75, T_a = 372 K; (X) PS50, T_a = 400 K; (●) PS25, T_a = 427 K.

function of aging time t_a for annealing temperatures satisfying $T_g - T_a$ = 15 K. Figure 5a shows the results for the pure components and the PS50 blend. The enthalpy difference for the pure components is approximately the same but is much larger than that for the blend. Since T_a is defined as 15 K below the onset T_g (defined for the quench-cooled sample), a simple explanation as before is the presence of concentration fluctuations leading to a range of T_g values, in particular T_g values way above the onset T_g. The relaxation of those domains is much slower, resulting in smaller values of ΔH. As mentioned in the Introduction Cowie and Ferguson[17] explained a similar phenomenon by assuming that the relaxation is almost completely due to the low-T_g component. Evidence that in our case the smaller values of ΔH for the blend are not due to a relaxation process dominated by the low-T_g component, PS, comes from experimental results of the PS25 and PS75 blends. Together with those of PS50, they are presented in Figure 5b. Although there is some scatter in the data there is no clear difference between the different blends. Hence, the relaxation cannot be due to the low-T_g component only. We have to conclude that the blend behaves with respect to relaxation as a pure component except that concentration fluctuations lead to a superposition of the relaxation of material with a range of T_g values. Additional support for the presence of microheterogeneities of nanometer dimensions in PS/PPE blends was presented recently by Li et al.[30] using solid NMR.

Concluding Remarks

The results in this paper provide evidence that relaxation in polymer blends can be influenced considerably by the presence of concentration fluctuations. Due to these concentration fluctuations, a range of T_g values is present, or alternatively the glass transition region is broader, and

at a given aging temperature the relaxation rate will vary from place to place. Cowie and Ferguson[17] observed that the total amount of enthalpy relaxation obtained by letting the system, PS and PVME, age until "equilibrium" is obtained was much smaller for the blend than for the pure components. They employed the enthalpic definition of T_g due to Richardson and Savill,[29] which leads to values of T_g which are considerably higher than the onset definition. For pure PVME the difference is only about 5 K; however, for the blend it is more than 23 K (281.8 K compared to 258.5 K). Aging the blend at temperatures varying from 10 to 30 K below the enthalpic T_g will in our opinion obviously lead to a reduced relaxation enthalpy because part of the material will be at or close to equilibrium to begin with. This becomes even more clear once it is realized that the breadth of the glass transition turned out to be 38 K for the blend compared to only 3.4 and 6.7 for PVME and PS, respectively.

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