Two Calorimetric Glass Transitions in Miscible Blends Containing Poly(ethylene oxide)

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ABSTRACT: Miscible blends containing poly(ethylene oxide) (PEO) have been examined over the entire composition range using differential scanning calorimetry to explore further the reported presence of two glass transitions. Three systems, poly(ethylene oxide)−dimethyl ether (PEO−DME)/poly(methyl methacrylate) (PMMA), PEO/poly(lactide) (PLA), and PEO/poly(vinyl acetate) (PVAc), were chosen in order to study the effects of end-group chemistry, annealing time, and crystallinity on the calorimetric behavior of the blends. The molecular weight of PEO was kept low to minimize the interference due to crystallization. Two distinct glass transitions were observed in the mid-composition range for all three systems. The glass transition temperatures varied smoothly with blend composition between the glass transition temperatures of the two homopolymer components. It was found that the self-concentration model describes the composition dependence of these glass transitions well. Further investigation on selected PEO/PVAc blends showed that annealing time and degree of crystallinity had a little effect on the glass transition behavior. These results confirm that the presence of two glass transitions should not necessarily be taken as an indication of immiscibility.

Introduction

With advances in technology, it is important to prepare new materials with tunable properties. The mixing of two polymers is one of the most cost-effective and direct ways to achieve this. This has led to substantial interest in the properties of both miscible and immiscible polymer blends.

Some of the well-studied miscible polymer blend systems include poly(styrene) (PS)/poly(vinyl methyl ether) (PVME),[1,2] PS/poly(phenylene oxide) (PPO),[3–5] poly(ethylene oxide) (PEO)/poly(methyl methacrylate) (PMMA),[6–8] 1,4-polyisoprene (PI)/poly(vinylethylene) (PVE),[9,10] polycarbonate (PC)/poly(ε-caprolactone) (PCL),[11–13] and PMMA/poly(vinylidene fluoride) (PVDF).[14,15] Many studies have reported a single glass transition process, albeit significantly broadened compared to the pure homopolymer components. Conversely, two glass transitions are observed in immiscible blends and phase-separated systems more frequently compared to miscible blend systems. One might expect that in the miscible blend chains of the blend components should be homogeneously dispersed and in intimate contact with each other, leading to an equivalent compositional environment throughout the blend and therefore a single glass transition temperature. Indeed, observation of a single glass transition temperature has been considered as a criterion for establishing miscibility of two components in a blend.

In contrast, in a recent article on a PEO/PMMA blend,[16] we reported that two broad but distinct glass transition temperatures can be resolved for the composition range of 25–75% PEO in the blends. Similarly, two glass transition temperatures were also reported in polymer/solvent systems such as PS/tricresyl phosphate,[17] PS/toluene,[18] and PS dissolved in dimethyl, dibutyl, and dioctyl phthalate.[19] The presence of two glass transitions was also reported in PI/PVE blends by Sakaguchi et al.[20] and in poly(*o*-chlorostyrene)/PVME and PS/PVME blends by Miwa and co-workers.[21] In a recent study on athermal poly(α-methylstyrene)/oligomer miscible blends,[22] it was pointed out that the glass transition phenomenon in such system can be considered to be a weighted contribution from each component, and a separate glass transition can be assigned to each component in the blend depending upon the known composition. The self-concentration model of Lodge and McLeish[23] has proven to be remarkably successful in describing the dynamics of each component in miscible blends; furthermore, it provides a natural explanation of why two glass transition temperatures can be observed, even in an equilibrium one-phase polymer blend or solution.

The purpose of this paper is to report further calorimetric measurements on miscible polymer blends, to explore the presence of the two glass transition phenomenon. Furthermore, we address some of the possible complications that can arise in PEO-containing systems, including the role of the chemistry of the end groups and the crystallinity of PEO in PEO-rich mixtures. In order to study these effects, three polymer blend systems were chosen: poly(ethylene oxide)−dimethyl ether (PEO−DME)/PMMA, PEO/poly(lactide) (PLA), and PEO/poly(vinyl acetate) (PVAc). The PEO used in the previous study was hydroxyl-terminated,[16] whereas PEO−DME has methoxy end groups. This modification eliminates the possibility of hydrogen-bonding interactions between different PEO chains. From enthalpy of mixing data, it has been reported that the interaction parameter between tetramethylene glycol methyl ether (TGME), a low molecular weight analogue for PEO−DME, and PMMA is less than that for poly(ethylene glycol), an analogue for PEO.[24] Thus, if anything, PEO−DME should be more miscible with PMMA than PEO of the same molecular weight. In the case of PEO/PLA, both the components are potentially crystalline, but we select an atactic PLA to simplify matters. Several reports on PEO/PLA blends[25–30] clearly indicate that the miscibility and the crystallization behavior of these blends are dependent on the molecular weights used, and so we have selected rather modest length polymers.

PEO/PVAc is also an interesting miscible polymer blend system. Kalfoglou[31,32] studied PEO/PVAc blends using calorimetry, optical microscopy, and dynamic mechanical analysis and concluded that the components are completely miscible in the melt state. Munoz et al.,[33] Martuscelli and Silvestre,[34–36]

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Table 1. Properties of Polymers Used for the Study

polymer	T_g (°C)	M_n (g/mol)	polydispersity
PEO−DME	−95	400	∼1.5
PEO	−78	300	<1.1
PEO	−78	1000	<1.1
PVAc	18	12500	∼1.5
PLA	33	6800	∼1.2
PMMA	120	10000	<1.1

and Wu et al.[37] also studied the phase behavior of PEO/PVAc blends and have reported single glass transition temperatures, intermediate between those of two pure homopolymers. However, Han et al.[38] reported the presence of two glass transitions in the case of some blends of PEO, $M_n \sim 100\,000$ g/mol, and PVAc. PEO/PVAc differs from PEO/PMMA not only in the extent of the difference in glass transition temperatures between the two components but also possibly in terms of the strength of the interactions. For example, Jinghua et al.[39] suggested that the PEO ether oxygen can interact with the carbonyl carbon in PVAc due to lower steric hindrance as compared to that in PMMA, and these favorable enthalpic interactions with PVAc may assist the formation of a miscible blend in the case of PEO/PVAc.

This article reports the results of DSC measurements on these three miscible polymer blend systems. In all the three systems, two glass transitions were clearly observed in the mid-composition range. Different tests were carried out in order to study the effect of the annealing time and degree of crystallinity on the calorimetric response. The results are also compared with the predictions of the self-concentration model.

Experimental Section

Materials. Poly(ethylene oxide) (PEO), poly(ethylene oxide)−dimethyl ether (PEO−DME), and poly(vinyl acetate) (PVAc) used in this study were purchased from Sigma-Aldrich, whereas poly(methyl methacrylate) was synthesized by Davidock.[40] Atactic poly(lactic acid) (PLA) was provided generously by N. Lynd. The glass transition temperature, molecular weight, and polydispersity index (M_w/M_n) of each polymer are listed in Table 1. The molecular weight of PEO and PEO−DME was deliberately low to reduce interference from crystallization in the calorimetric response.

Blend Preparation. Blends were prepared by codissolving appropriate amounts of polymers with 0.5 wt % of the antioxidant 2,6-di-*tert*-butyl-4-methylphenol in a suitable solvent. Methylene chloride was used for PEO−DME/PMMA blends, whereas chloroform was used for both PEO/PLA and PEO/PVAc blends. Solutions were then stirred overnight, and solvent was removed by evaporation under flowing nitrogen. PEO/PLA and PEO/PVAc blends were further dried in a vacuum oven at 80 and 70 °C, respectively, above the T_g of both blend components, until constant weight was achieved. This ensured complete solvent removal from these blends. All blend compositions are reported as weight percent or weight fraction (w).

It was observed that prolonged heating of PEO−DME/PMMA blends at temperatures above $T_{g,\mathrm{PMMA}}$ resulted in some evaporation of the PEO−DME itself. Hence, an alternative route for complete solvent removal was necessary for PEO−DME/PMMA blends. A heating plate covered with a glass container was used for this purpose. The temperature of the heating plate was controlled using a temperature controller. A nitrogen blanket was maintained over the sample throughout. Blends were heated to 170 °C for 5 h, and then the assembly was allowed to cool to room temperature. It was observed that heating for longer intervals did not change the weight of the sample, indicating complete solvent removal.

Differential Scanning Calorimetry. DSC samples were prepared by sealing ∼10 mg of material in aluminum hermetic pans provided by TA Instruments. DSC experiments were carried out with a TA Instruments Q1000 equipped with a liquid nitrogen cooling system. An empty hermetic pan was used as the reference in every case. The instrument was calibrated using an indium standard (melting point −156.6 °C), and errors were found to be less than 2% in the heat flow calibration. Helium was used as a purge gas. To erase temperature history completely, all the samples were annealed at a temperature higher than the T_g of either blend component. Samples were rapidly cooled to a temperature below the T_gs of both components, at rates higher than 40 K/min over most of the temperature range. DSC scans were then obtained during heating of the sample at a specific ramp rate which was followed by a cooling cycle and second heating cycle at the same ramp rate. The glass transition temperature observed may also depend upon the cooling rate employed for the measurement. Therefore, cooling rate as well as heating rate was kept constant for each particular blend system. DSC scans obtained during second heating were compared to first heating scans and were found to be equivalent. Table 2 summarizes the various protocols used for the different blends.

Table 2. Parameters Used for DSC Measurements

blend	PEO−DME/PMMA	PEO/PLA	PEO/PVAc
annealing temp (°C)	150	100	60
annealing time (min)	5	10	10
lowest temp (°C)	−150	−100	−100
ramp rate (°C/min)	20	10	10

Results and Discussion

DSC scans (heat flow vs temperature) for PEO−DME/PMMA, PEO/PLA, and PEO/PVAc polymer blend systems, for various blend compositions, are shown in Figures 1, 2, and 3, respectively. Each figure also includes the corresponding derivative curves. The values of the glass transition temperatures and the corresponding transition widths were determined from the derivative plots. The glass transition temperature, T_g, was taken as the peak position in the derivative plot, while the entire peak width was taken as the corresponding transition width. The corresponding data are provided in Tables 3, 4, and 5 for PEO−DME/PMMA, PEO/PLA, and PEO/PVAc blends, respectively. Measurements were repeated on most of the blends, with no significant changes in the thermograms observed.

As can be seen in Figure 1, for PEO−DME/PMMA two glass transitions were readily resolved for blends containing 20%, 25%, 33%, and 45% PEO−DME. The lower and higher T_gs can be assigned to the PEO−DME and PMMA components in the blend, respectively. Crystallinity of PEO−DME was observed in pure PEO−DME and in blends with 75% and 90% PEO−DME homopolymer. It is possible that a second T_g corresponding to the PMMA component in these blends was obscured due to the melting peak. The melting point for pure PEO−DME was found to be around 0 °C. The T_gs observed for these blends vary smoothly with blend composition between the extremes of $T_{g,\mathrm{PEO-DME}}$ and $T_{g,\mathrm{PMMA}}$. In accordance with many previous reported studies on the calorimetric behavior of miscible blends, the transitions were generally broader in the blends as compared to the pure homopolymers.

Similarly, as shown in Figure 2, two glass transitions were clearly resolved for PEO/PLA blends containing 35%, 50%, and 60% PEO, and the lower T_g was assigned to PEO and the higher T_g to PLA. The variation of T_g was smooth over the range −78 °C ($T_{g,\mathrm{PEO}}$) to 33 °C ($T_{g,\mathrm{PLA}}$). Crystallinity of PEO was observed in the blends containing 70%, 90%, and pure PEO homopolymer. The transition widths in the blends were also consistently broader than the pure homopolymers (see Table 4).

A tendency toward phase separation upon prolonged aging should result in a shifting of the glass transition temperatures toward the pure homopolymer values. To test this possibility, the PEO/PLA blends that showed two glass transition temperatures were remeasured after several months storage at room temperature. Equivalent DSC thermograms were obtained, thus indicating that the PEO/PLA blends are at equilibrium.

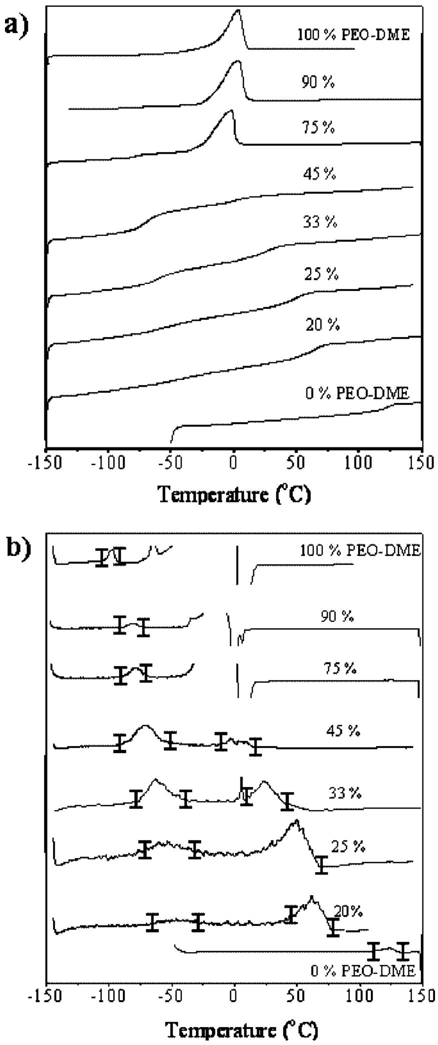

Figure 1. DSC thermograms of PEO−DME/PMMA blends for the indicated compositions obtained at a heating rate of 20 °C/min (endo down): (a) heat flow and (b) derivative curves. Bars in (b) denote the width of the peak.

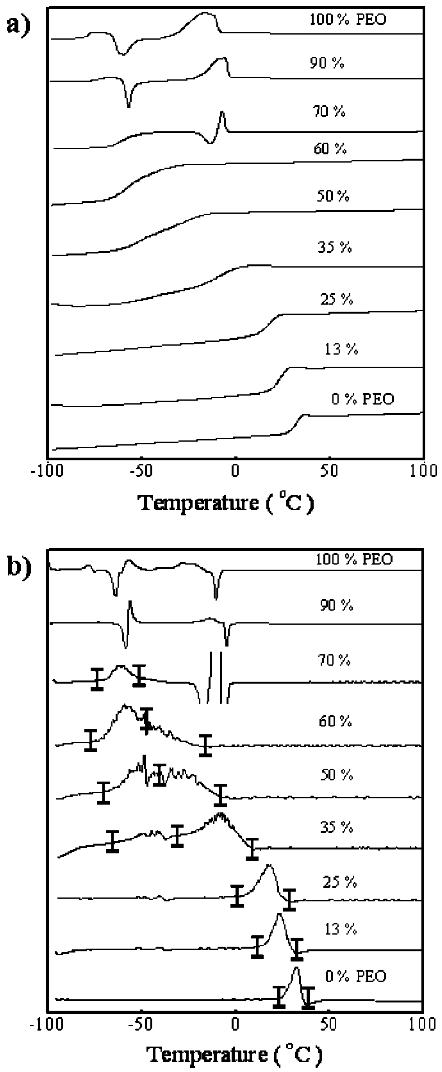

Figure 2. DSC thermograms of PEO/PLA blends for the indicated compositions obtained at a heating rate of 10 °C/min (endo down): (a) heat flow and (b) derivative curves. Bars in (b) denote the width of the peak.

As can be seen in Figure 3, for the PEO/PVAc blends, the T_gs varied smoothly between −78 °C ($T_{g,PEO}$) and 18 °C ($T_{g,PVAc}$), depending on the blend composition. Two glass transitions were observed for blends containing 40% and 50% PEO. As discussed previously, the lower T_g can be assigned to PEO and the higher T_g can be assigned to PVAc. Crystallinity of PEO was observed in the blends with $w_{PEO} > 0.50$. In those blends it is also possible that a second glass transition corresponding to PVAc was masked by PEO melting. In this system the transitions in the blends were also substantially wider than in the pure homopolymers.

The PEO/PVAc blend with 40% PEO showed two very distinct glass transition temperatures (Figure 3) using the specified experimental procedure for the DSC measurements, which involved a 10 min anneal at 70 °C to erase all thermal history and ensure blend homogeneity (see Table 2). If the blend is actually heterogeneous, thereby leading two glass transitions, a longer annealing time should result in better mixing of the two components. To confirm that this interval was sufficient, the blend was annealed at 70 °C for 10 min, 1 h, and 2 h before separate DSC measurements were taken. Figure 4 shows the DSC scans obtained after annealing the blends for different times. As shown in the figure, the blend T_gs did not change appreciably with the change in annealing time, thereby strengthening the contention that the blend is homogeneous and still shows two glass transition temperatures.

Although the main emphasis of this paper is the observation that there are two well-resolved glass transitions for all three blend systems in the mid-composition range, where there is little or no observable crystallinity, it is still interesting to consider whether the extent of crystallinity has an effect on the results. The possible effect of crystallinity was studied using PEO/PVAc blends with 60% and 75% PEO. As evident in Figure 3, both these blends showed crystallinity. The onset of PEO crystallization was found on cooling to be around −35 °C in both cases, as in the pure PEO. Hence, the crystalline fraction in the blend can be varied by changing the annealing time at this temperature. The blends were cooled to −35 °C at rate of 5 deg/min. Then, the polymer blend sample was held at −35 °C for different time intervals in order to modulate the degree of crystallinity. The crystalline fraction in the blend during DSC measurement was calculated using the difference between the area under the melting and crystallization peaks obtained during the heating cycle, using a specific heat of melting for PEO of 196.8 J/g.[41] The data corresponding to these experiments are shown in Table 6. As observed, the crystalline fraction at −100 °C increased modestly with annealing time. The 60/40 (% w/w) PEO/PVAc blend showed one T_g around −75 °C, whereas the 75/25 (% w/w) PEO/PVAc blend demonstrated one T_g around

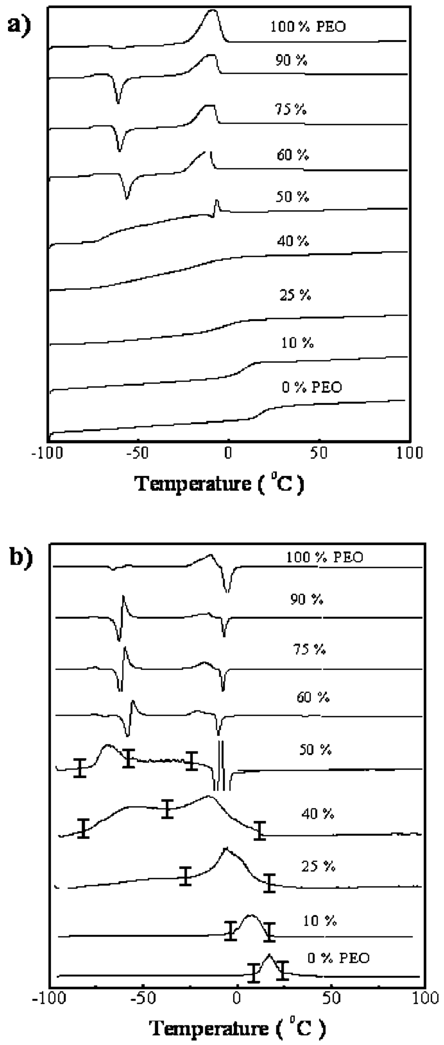

Figure 3. DSC thermograms of PEO/PVAc blends for the indicated compositions obtained at a heating rate of 10 °C/min (endo down): (a) heat flow and (b) derivative curves. Bars in (b) denote the width of the peak.

−76 °C for each different isothermal time. No significant change in the T_g value was observed for either blend with increase in the crystalline fraction.

Optical clarity is another important parameter in order to check the miscibility of blends used in this study. Photographs of PEO/PVAc 50/50 blend and PEO/PLA 50/50 blend films, prepared on a glass slide by solvent casting, are shown in Figure 5. These blends are optically clear, as was the PEO/PMMA blend reported previously,[16] which can be taken as a further indication of the miscibility of the two components.

Self-Concentration Interpretation. The presence of two glass transitions is generally taken as a signature of immiscibility of two components in a blend. If two transitions are observed, and the T_gs are close to the values of the pure components and relatively invariant to composition, immiscibility is a reasonable conclusion. But, the presence of two T_gs that are intermediate between those of the pure components, and which vary with composition, are consistent with expectation for a single-phase blend based on chain connectivity and the self-concentration model.[23] The self-concentration model is based on the realization that the environment surrounding a particular segment will be enriched in the same blend component due to chain connectivity. This results in a shift of the averaged local environment of each component relative to the bulk composition. The self-concentration model therefore anticipates different T_gs for each component

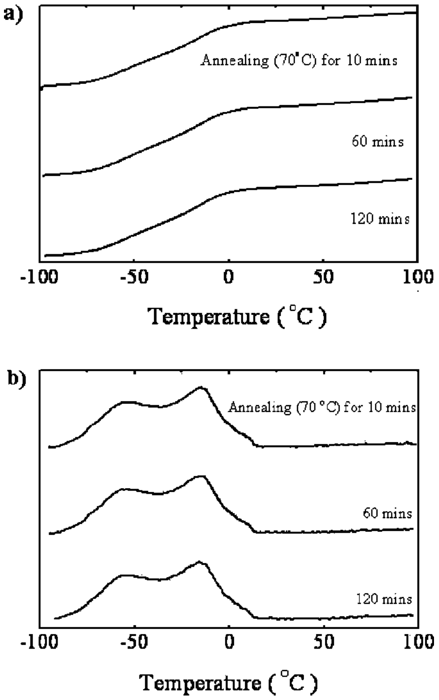

Figure 4. DSC thermograms for 40/60 PEO/PVAc blend with different annealing times at a heating rate 10 °C/min (endo down): (a) heat flow and (b) derivative curves.

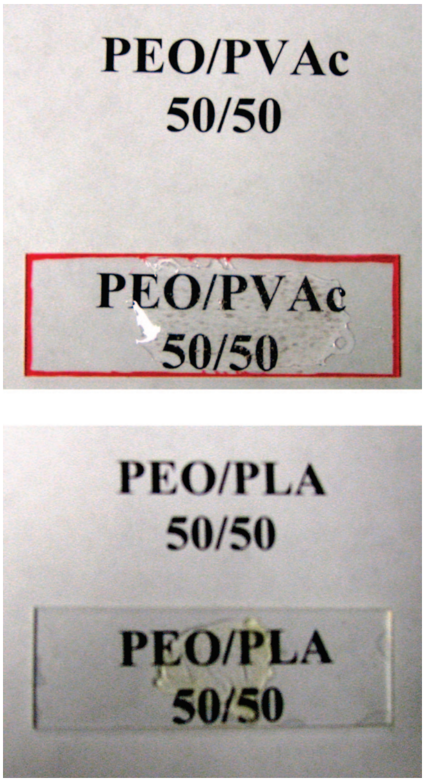

Figure 5. Optically clear solvent-cast films on a glass slide for PEO/PVAc 50/50 and PEO/PLA 50/50 blends.

in the blend. These can be estimated via the effective volume fraction of each component, ϕ_{eff}, determined by[23]

$$\phi_{\text{eff}} = \phi_s + (1 - \phi_s)\phi \tag{1}$$

where ϕ_s is the self-concentration (volume fraction) of the polymer due to chain connectivity effects and ϕ is the bulk blend

Table 3. Glass Transition Temperatures and Transition Widths for PEO−DME/PMMA Blends

	PEO−DME (°C)				PMMA (°C)			
$w_{\mathrm{PEO-DME}}$	T_g	upper limit	lower limit	ΔC_p (J/g/°C)	T_g	upper limit	lower limit	ΔC_p (J/g/°C)
0					120	131	110	0.316
0.2	−43	−30	−65	0.214	62	75	50	0.248
0.25	−51	−42	−72	0.256	51	65	37	0.292
0.33	−63	−40	−76	0.278	22	40	10	0.292
0.45	−71	−62	−84	0.553	−2	12	−4	0.191
0.75	−80	−70	−90	0.330				
0.9	−78	−68	−94	0.204				
1	−95	−90	−105	0.082				

Table 4. Glass Transition Temperatures and Transition Widths for PEO/PLA Blends

	PEO (°C)				PLA (°C)			
w_{PEO}	T_g	upper limit	lower limit	ΔC_p (J/g/°C)	T_g	upper limit	lower limit	ΔC_p (J/g/°C)
0					33	36	23	0.560
0.13					23	32	10	0.570
0.25					17	29	−5	0.571
0.35	−44	−37	−70	0.194	−8	10	−35	0.331
0.5	−52	−39	−71	0.820	−30	−2	−39	0.269
0.6	−59	−48	−80	0.441	−41	−10	−46	0.274
0.7	−63	−52	−74	1.024				
0.9	−73	−66	−83	1.080				
1	−78	−75	−84	1.295				

Table 5. Glass Transition Temperatures and Transition Widths for PEO/PVAc Blends

	PEO (°C)				PVAc (°C)			
w_{PEO}	T_g	upper limit	lower limit	ΔC_p (J/g/°C)	T_g	upper limit	lower limit	ΔC_p (J/g/°C)
0					18	25	8	0.5485
0.1					7	18	−7	0.5813
0.25					−6	21	−25	0.4625
0.4	−56	−37	−76	0.1761	−15	15	−36	0.297
0.5	−68	−56	−82	0.381	−33	−14	−51	0.185
0.6	−75	−72	−82	0.5138				
0.75	−76	−71	−82	0.6876				
1	−78	−75	−84	1.295				

Table 6. Different Annealing Times and Crystalline Fractions Obtained for Crystalline PEO/PVAc Blends[a]

	PEO/PVAc 60/40		PEO/PVAc 75/25	
annealing time (min)	crystalline fraction at −100 °C	T_g (°C)	crystalline fraction at −100 °C	T_g (°C)
0	0.045	−75.2	0.108	−76.0
5	0.120	−75.6	0.254	−76.5
10	0.121	−75.5	0.258	−76.3
15	0.125	−75.8	0.262	−76.1
20	0.132	−75.7	0.212	−76.3
25	0.138	−75.6	0.219	−76.3
30	0.151	−75.6	0.223	−76.4

[a] Data obtained at heating rate 5 °C/min, annealing temperature −35 °C, and lowest temperature −100 °C.

composition. The self-concentration, ϕ_s, may be taken as a fitting parameter, or estimated using the relationship

$$\phi_s = \frac{C_\infty M_0}{k\rho N_{\mathrm{av}} V} \tag{2}$$

where C_∞ is the characteristic ratio, M_0 is the molar mass of the repeat unit, k is the number of backbone bonds per repeat unit of polymer, N_{av} is Avogadro's number, and ρ is the density. The effective T_g of each component can be evaluated using the Fox equation given by[42]

$$T_g^{\mathrm{eff}}(\phi) = T_g(\phi)|_{\phi=\phi_{\mathrm{eff}}} \tag{3}$$

$$\frac{1}{T_g(\phi)} = \frac{\phi}{T_g^{\ a}} + \frac{1-\phi}{T_g^{\ b}} \tag{4}$$

According to the self-concentration model, ϕ_s is calculated on the basis of appropriate volume surrounding the polymer segment under consideration. Generally, this is taken to be on the order of the Kuhn length cubed, which typically gives values of ϕ_s between 0.1 and 0.6. Here ϕ_s was used as a parameter to account for the variation in the T_g with blend composition. In Figures 6, 7, and 8, the experimentally observed glass transition temperatures are plotted against the weight fraction of the blend component with the lower glass transition temperature, i.e., either w_{PEO} or $w_{\mathrm{PEO-DME}}$, for PEO−DME/PMMA, PEO/PLA, and PEO/PVAc, respectively.

In the case of PEO−DME/PMMA in Figure 6, the variation of T_g with composition can be well described with ϕ_s values of 0.23 for PMMA and 0.55 for PEO−DME. The self-concentration value of PMMA used to fit the data is same as predicted by the self-concentration model based on the Kuhn length, whereas the value for PEO corresponds to predictions based on two-thirds of the Kuhn length. The data can be compared with PEO/PMMA blends[16] in order to assess the possible role

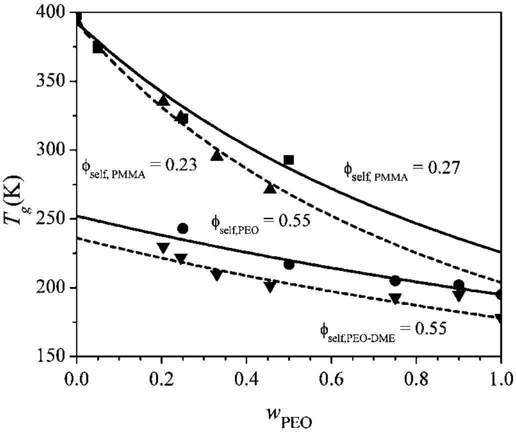

Figure 6. Variation of T_g with blend composition for PEO−DME/PMMA and for PEO-1000/PMMA. Curves represent the fits to the data with indicated values of the self-concentrations.

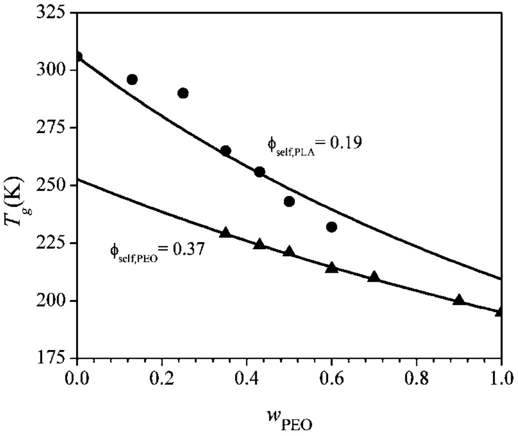

Figure 7. Variation of T_g with blend composition for PEO/PLA blends. Curves represent the fits to the data with the indicated self-concentrations.

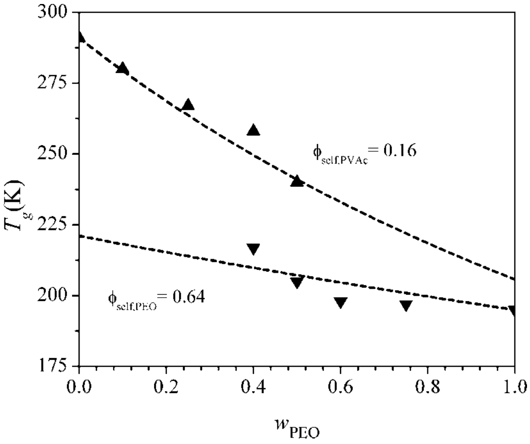

Figure 8. Variation of T_g with blend composition for PEO/PVAc blends. Curves represent the fits with the indicated self-concentrations.

of the hydroxyl end groups on the calorimetric behavior. We determined that PEO with M_n = 300 g/mol also tends to evaporate after prolonged heating at high temperature during vacuum drying. Consequently, new PEO/PMMA blends were prepared with PEO of M_n = 1000 g/mol by the solvent-casting method using methylene dichloride. The corresponding DSC curves are not shown here for the purpose of brevity, but two glass transition temperatures were observed in the mid-composition range as shown in Figure 6. (These data show some minor differences compared to the PEO/PMMA data reported earlier[16] due to evaporation of the lower molecular weight PEO.) The data for the PEO-1000/PMMA blends can be described well with the self-concentration values of 0.27 for PMMA and 0.55 for PEO, in very reasonable agreement with PEO−DME/PMMA. Note that the values of the glass transition temperatures for pure PEO−DME and PEO-1000 are different, which leads to small differences between the two blends as well.

The molecular weight of the PEO used in the previous study[16] was kept deliberately low ($M_n \sim 300$ g/mol) to minimize the interference due to PEO crystallization during calorimetric measurements. At such low molecular weights, the end-group contribution to the miscibility of polymers can become significant. For example, self-association of the hydroxyl end groups by hydrogen bonding might lead to clustering of PEO in the blends. This possibility can be eliminated by using PEO−DME instead of PEO. As seen in Figure 6, a similar variation of T_g was observed in both cases. Also, the values of the self-concentration are also very similar, which indicates that the end groups do not play any particular role in the observation of two glass transitions in this system.

In the case of PEO/PLA blends, self-concentration values of 0.19 for PLA and 0.37 for PEO provide the best fits to the data, as shown in Figure 7, whereas as shown in Figure 8, $\phi_{s,PVAc}$ = 0.16 and $\phi_{s,PEO}$ = 0.64 fits the data for the PEO/PVAc blends. The value for the higher T_g component, i.e. ϕ_{PVAc}, was found to be close to the theoretically predicted value of 0.23.[23]

In each case, the value of the self-concentration obtained for the component with the lower T_g is higher than that for the component with the higher T_g as expected from the self-concentration theory.[23] However, the value for $\phi_{s,PEO}$ is found to be different in each case. In an earlier reported study on dilute blends of PI[43] and dilute blends of PS,[44] it was observed that the value of the self-concentration for PI and PS, respectively, is dependent on its partner in the blend. Similar differences in the self-concentration values for PEO were observed when it is blended with PMMA, PVAc, and PLA.

Two glass transition temperatures might also be seen in the case of phase-separated mixtures with two well-defined phases with intermediate compositions ϕ' and ϕ''. In this work the possibility of presence of two phases can be ruled out because of the optical clarity of the blends in which two glass transitions are observed. Furthermore, the compositions of the two phases should be a strong function of temperature (i.e., distance from the critical point), which should make the measurements very sensitive to thermal history.

Summary

Differential scanning calorimetry was used to study three miscible blend systems containing low molecular weight PEO. Two glass transitions were observed in the mid-composition range in all three systems examined, PEO−DME/PMMA, PEO/PLA, and PEO/PVAc. The self-concentration model anticipates the presence of two different effective glass transitions. The compositional dependence of the glass transition was well described with reasonable self-concentration values. The calorimetric behavior of the PEO−DME/PMMA was found to be similar to the PEO/PMMA blend system. This indicates that the end groups do not play a significant role in the observation of two glass transitions. Also, crystallinity and annealing time changes did not affect the glass transition temperatures in selected PEO/PVAc blends, which indicate that the blends were at equilibrium and still showed two glass transition temperatures. Thus, the rule of thumb that two glass transitions indicate immiscibility need not always hold. If there is sufficient difference in the glass transition temperatures of two homopolymers, then one should expect to see two distinct glass transition temperatures, at least over limited range of composition, for miscible blends as well.

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