The Influence of Solvent upon the Compatibility of Polystyrene and Poly(vinyl methyl ether)

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ABSTRACT: The compatibility behavior of cast films of polystyrene (PS)–poly(vinyl methyl ether) (PVME) mixtures is influenced by solvent. Clear films of PS–PVME mixtures are obtained upon casting from specific solvents such as toluene or benzene while visually incompatible films result upon casting from trichloroethylene and chloroform. Differential scanning calorimetry and dielectric relaxation measurements establish that the visually incompatible films have glass transitions and dielectric loss behavior characteristic of the component polymers which is indicative of two phases. The corresponding clear films do not exhibit behavior characteristic of the component polymers. Thermal analysis shows broad transitions which are composition dependent. Dielectric realxation measurements show loss peaks which are shifted in frequency and severely broadened. The evidence presented indicates some molecular mixing occurs, but it is concluded that the mixing is not as intimate as in random copolymers.

Binary mixtures of chemically dissimilar polymers generally are incompatible. Except under dilute solution conditions, such mixtures exist as two-phase systems with each phase containing a preponderance of one polymer.[1] The frequent occurrence of polymer–polymer incompatibility is attributed to the small entropy of mixing for large polymer molecules and a general tendency for polymers to have endothermic heats of mixing. Polymer pairs incompatible in one solvent usually are incompatible in a range of solvents,[2] consistent with the prediction that the solvent should play a secondary role in determining incompatibility.[3] Significantly, a few compatible polymer pairs have been reported.[4–6] These mixtures form homogeneous solutions under concentrated conditions and yield homogeneous films upon solvent casting. Whereas transitions characteristic of the component homopolymers can be detected for incompatible polymer mixtures, compatible polymer mixtures exhibit transitions and properties differing from those of the component polymers. For example, compatible polymer mixtures appear to have glass transition temperatures (T_g) that vary with mixture composition somewhat analogous to the behavior of T_g for copolymers.[4]

Although studies of polymer compatibility–incompatibility behavior have been reported,[2,5] knowledge of such phenomena still is relatively limited. The purpose of this paper is to report that the compatibility behavior of mixtures of polystyrene (PS) and poly(vinyl methyl ether) (PVME) differs from that of other polymer pairs studied to date. In solvents such as toluene, benzene, or perchloroethylene, they are visually compatible while in chloroform, methylene chloride, or trichloroethylene they are incompatible. These differences persist upon solvent evaporation. In order to gain more insight into the incompatibility behavior of PS and PVME, differential scanning calorimetry and dielectric relaxation measurements have been used to characterize PS–PVME mixtures cast from toluene and trichloroethylene.

Experimental Section

The PS polymers used in this study were a high-conversion sample bulk polymerized at 50° (PS-1) and a commercial sample, PS-690 (Dow Chemical Company, Midland, Mich.). For the former, M_n = 104,000; for the latter, M_n = 150,000. The PS-690 was used as received. The PVME (GAF, New York, N. Y.) was a commercial sample reprecipitated twice from toluene into *n*-heptane and vacuum dried before use (M_n = 524,000 after isolation). The PVME reportedly was an isotactic polymer, but infrared analysis[7] established that the degree of tacticity was low. The stereoregularity index of 0.59 for this PVME sample is barely above the value of 0.52 reported for atactic PVME.[7] Consistent with this finding only a small amount of crystalline melting was observed in the PVME. The melting temperature of 61° was low relative to that reported for highly isotactic PVME (144–164°).[7,8]

Films containing PS, PVME, and PS–PVME mixtures of various concentration ratios were cast at 25° onto aluminum or mercury surfaces from reagent grade toluene and trichloroethylene (C_2HCl_3). Initial polymer concentrations in solution were 2.5–5 g/100 ml. Reported PS–PVME concentration ratios are on a (wt %/wt %) basis. All films obtained (10–15 mils thickness) were vacuum dried at 110° for at least 2 days to maximize removal of entrapped solvent in the PS glass. Control PS films so treated showed T_g values characteristic of PS.

A Perkin-Elmer differential scanning calorimeter (DSC), Model DSC-1B (Perkin-Elmer Corp., Norwalk, Connecticut), was used for all thermal analytical determinations of T_g values. A discontinuity in heat capacity, usually an increase, is associated with the glass transition; T_g is taken as the intersection of the extrapolated low temperature base line with the tangent to the heat capacity rise endotherm. Samples for DSC analysis (15–25 mg) were scanned at 20°/

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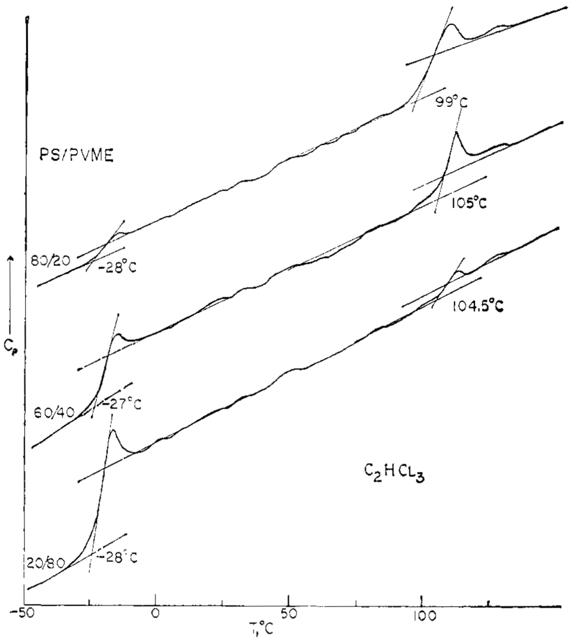

Figure 1. DSC thermograms of trichloroethylene-cast mixtures of PS–PVME. Composition ratio is given in weight per cent of the components.

min heating rate from −80 to 127°, then cooled at 10°/min. Each sample was scanned three to five times in a nitrogen atmosphere under similar conditions. The first scan was discounted to ensure uniform thermal history of each sample. Physical mixtures were used to establish the limits of detection by DSC of one homopolymer component in the presence of another. This limit was approximately 1.5 mg for PVME, and approximately 2 mg for PS under the scanning conditions employed. All samples of solvent-cast mixtures contained more than these minimum quantities of homopolymer.

Dielectric relaxation measurements were made from −25 to +150° over the frequency range 20 Hz–200 KHz. A General Radio type 716-C capacitance bridge and a two-terminal General Radio type 1690-A dielectric cell (General Radio Corp., West Concord, Mass.) were used. Film samples for these measurements were prepared as outlined above and had metal (Ag or Au) electrodes evaporated under vacuum onto their surfaces.

Results

The DSC thermograms show that the T_g value for PS falls at 102° while for PVME it falls at −29°. This is consistent with previously reported values.[9,10] PS–PVME mixtures cast from C_2HCl_3 yield films that are visibly phase separated. As shown in Figure 1, they also exhibit distinct T_g values characteristic of the homopolymer components. These transitions occur in all component ratios examined and their presence confirms the visually observed two-phase nature of PS–PVME mixtures cast from C_2HCl_3. Crystalline melting of the PVME was observed on the first run of several mixtures (80/20, 60/40, and 20/80 PS–PVME) cast from C_2HCl_3. It was not observed in subsequent runs because the PVME recrystallizes very slowly.

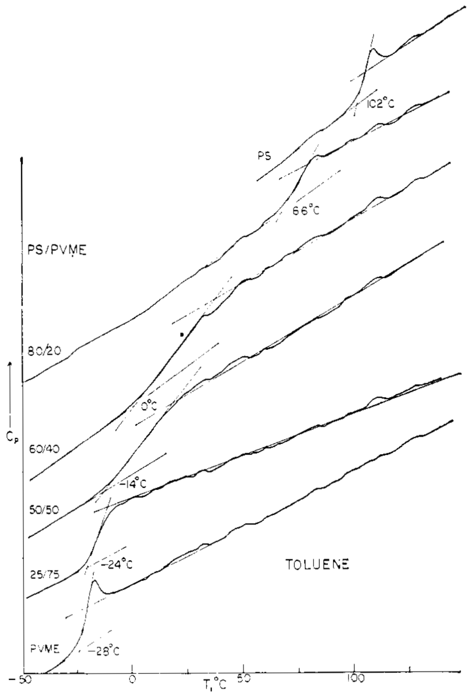

Figure 2. DSC thermograms of toluene-cast mixtures of PS–PVME. Composition ratio is given in weight per cent of the components.

After 1 week at 25°, the peak reappeared. Most thermograms exhibited the endothermic peaks normally observed for the homopolymers when cooled at similar rates. A number of mixtures with high PS content (80/20, 90/10 PS–PVME) were simply vacuum dried at 25° and exhibited a T_g 10–15° below the usual T_g for PS of 102°. These low T_g's are attributed to solvent retained in the PS-rich regions. Diluents, such as solvents, act as plasticizers and lower T_g.[11,12] The solvent can be removed by heating *in vacuo* at temperatures $>T_g$ of PS, and samples so treated have T_g values characteristic of PS at 102°.

Mixtures cast from toluene are markedly different from C_2HCl_3-cast mixtures. The films are clear and, therefore, visually compatible. Representative thermograms in Figure 2 show that no thermal events associated with T_g's characteristic of the homopolymer components are observed. Crystalline melting of the PVME is not detected except when the PVME content exceeds 80%. A single reproducible thermal transition, intermediate between T_g's of the homopolymers, is observed for each mixture. The transition temperatures are listed in Table I as a function of composition. As the PS content decreases, the transition temperature decreases from 102° (T_g for PS) to −28° (T_g for PVME). The transition is broad, diffuse, and does not have an endothermic peak under the experimental conditions used in this study. However, in at least one case (80/20 PS–PVME) annealing at temperatures just below the transition point yielded a small endothermic peak, similar to the effect of annealing a homopolymer.

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TABLE I
THE EFFECT OF COMPOSITION ON TEMPERATURE OF THERMAL TRANSITION OF PS–PVME MIXTURES CAST FROM TOLUENE AT 25°

% PS	Transition temp, °C
100	102
90	80
80	66
75	42
60	9
50	−14
40	−20.5
25	−24
20	−24.5
0	−28

Annealing, in general, sharpens the observed transition. We interpret these thermal transitions to be glass transitions of the toluene-cast mixtures. If the T_g's are plotted as a function of composition as given in Figure 3, the resulting curve shows a composition dependence for T_g somewhat analogous to that observed for copolymers and low molecular weight plasticizers. However, the PS–PVME system shows a poor overall fit to a number of expressions that relate T_g to copolymer composition. These expressions include the equations of Fox[13]

$$\frac{1}{T} = \frac{C_1}{T_1} + \frac{C_2}{T_2}$$

and Gordon–Taylor[14]

$$T = \frac{kC_2T_2 + C_1T_1}{C_1 + kC_2}$$

where C_1 and C_2 = weight fraction of polymer 1 and polymer 2, respectively, T_1 = T_g of polymer 1, T_2 = T_g of polymer 2, T = T_g of mixture, and k = constant.

As shown in Figure 3, a reasonable fit of the experimental data to the expressions occurs only at high PS contents (>75% PS). By varying the constant k, the Gordon–Taylor equation can be adjusted to give the best fit at high PS contents, but large deviations still occur at lower PS concentrations. The marked change in slope of the experimental curve at <60% PS content indicates the composition dependence of the transition is not uniform.

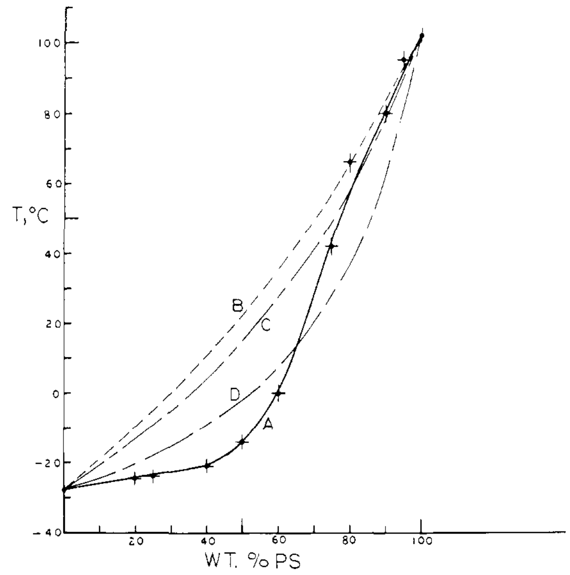

Figure 3. Plots of transition temperature of toluene-cast mixtures of PS–PVME as a function of PS concentration: A, experimental curve; B, Fox equation; C, Gordon–Taylor equation, k = 0.5; D, Gordon–Taylor equation, k = 0.25.

Consistent with the thermal analysis results, the dielectric relaxation behavior of mixtures cast from C_2HCl_3 is distinctly different from that of mixtures cast from toluene. The relaxation process for PVME homopolymer is shown in Figure 4A where the tan δ loss curve is plotted as a function of frequency at several representative temperatures. This loss peak is attributed to motion of the PVME chain backbone and is assigned to the α relaxation process. No relaxations attributable to PS are observed in this dispersion region. In the PS–PVME mixtures cast from C_2HCl_3, a loss peak observed in this region is attributed to the α relaxation process of the PVME. As shown in Figure 4B, dispersion curves of a 60/40 PS–PVME mixture cast from C_2HCl_3 behave like the PVME homopolymer with similar loss tangent frequency maximums and curve shapes at corresponding temperatures. There is no significant effect on the PVME relaxation process due to the PS in this mixture. The environment of the PVME is very similar in both cases and is consistent with the assumption of a two-phase system. Similar results were obtained with an 80/20 PS–PVME mixture.

In the toluene-cast mixtures (Figure 4C) the frequency maximum of the loss peaks is shifted to lower frequency at equivalent temperatures (or the frequency maximum is shifted to higher temperatures). The curves are broadened with an accompanying decrease in peak height. For example, comparison of the loss curves in the temperature range of 2–3° shows that the frequency maximum lies at ~2000 Hz for C_2HCl_3-cast mixtures (Figure 4B) but it is <100 Hz in the toluene-cast films. Similarly, the frequency maximum is at ~150 KHz at 23° for C_2HCl_3-cast mixture while for toluene-cast films, the maximum of the loss peak does not occur at this frequency until the temperature reaches 33°. Similar results are observed for other composition ratios. Table II shows that the frequency of the loss peak at 25° does not vary with mixture composition over the range of compositions studied. However, the peak height of the loss tangent curves at corresponding temperatures increases with increasing PVME concentration, as expected.

Discussion

The visually observed two-phase nature of C_2HCl_3-cast PS–PVME mixtures has been confirmed by both DSC and dielectric relaxation data. The homopolymer components retain their characteristic thermal transitions and dielectric loss behavior in these mixtures. In contrast, the DSC and dielectric loss data for the visually homogeneous toluene-cast mixtures differ from that of the homopolymer components. Although both

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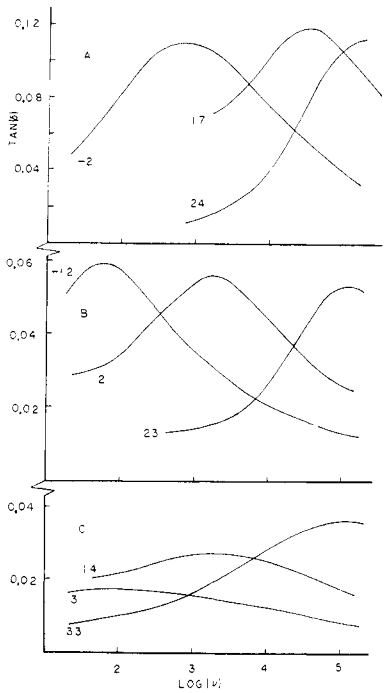

Figure 4. Dielectric loss curves of tan δ *vs.* log (ν), where ν = frequency; numbers on graph = temperature, °C: A, PVME homopolymer; B, 60/40 mixture of PS–PVME cast from trichloroethylene; C, 60/40 mixture of PS-PVME cast from toluene.

methods of analysis indicate a degree of mixing or interaction has occurred, the DSC and dielectric data present somewhat differing pictures of the extent of interaction. For example, there is no DSC evidence of characteristic T_g's of the homopolymers in the toluene-cast mixtures, and the thermal event temperature in such cases varies with mixture composition. These observations suggest a large degree of molecular mixing with a resulting polymer mixture that acts as a single phase system. The dielectric loss data indicate that interactions between the homopolymer components are occurring, but the degree of molecular mixing is not as high as suggested by the DSC results. If PS–PVME mixtures were completely compatible, *i.e.*, existed as a molecularly homogeneous single phase, the α loss peak of the PVME at a given temperature should appear at lower frequencies with increasing PS concentration. No α-relaxation process should be observed below the apparent T_g of the mixture. Such behavior was not observed over the range of PS–PVME compositions examined. As shown in Table II, the α-loss peak occurs at 20 KHz at 25° for mixtures containing 60–90% PS. Figure 3 illustrates that toluene-cast mixtures with >80% PS have apparent T_g values (DSC) >40°, well above the temperatures actually necessary to obtain the reported α-loss data. The shift in position of the PVME α-loss peak and noticeable broadening of such curves relative to that of PVME homopolymer indicate a degree of molecular mixing has been achieved, but such mixing is not as intimate as that achieved by copolymerization. Dispersal of the PVME in the PS (or PS in PVME) is incomplete thereby giving rise to a distribution of molecular environments for the PVME. This accounts for broadening of the PVME α-loss peak shown in Figure 4. In reality, the diffuse nature of the thermal event observed for toluene-cast mixtures and the marked deviation of the experimental curve in Figure 3 from theory may be thermal evidence for incomplete mixing on a molecular scale. However, any aggregation that occurs does not yield sufficiently large phase-separated regions which can be detected by thermal analysis. The only exception occurs with high PVME content mixtures (>80% PVME) where crystalline melting of the PVME is observed.

Table II

Frequency and Values of Maximum Loss Tangents for Toluene-Cast PS–PVME Mixtures (25°)

PS content, %	Frequency of max tan δ at 25°, KHz	Max tan δ at 25°
0	~300	0.126
60	20	0.0328
70	20	0.0196
80	20	0.0148
90	20	0.00620

Based upon the DSC and the dielectric relaxation data, it is concluded that different molecular environments are obtained when films containing PS–PVME mixtures are cast from toluene and C_2HCl_3. A degree of molecular mixing is achieved in films cast from toluene whereas films cast from C_2HCl_3 are heterogeneous and consist of two phases: a PS-rich phase and a PVME-rich phase. Such compatibility behavior differs from that reported for polymer pairs studied to date and indicates that for some polymer pairs the solvent can significantly influence polymer–polymer compatibility phenomena. Presumably the conformational state of these polymers in solution varies sufficiently with solvent so that the interactions responsible for compatibility phenomena are altered enough to cause the observed solvent dependence of visual compatibility. The mixture obtained upon solvent removal may not represent a true equilibrium state, but could be in a metastable state. It must be stressed that the apparent visible single-phase nature of toluene-cast PS–PVME films does not imply uniform molecular miscibility. Intimate mixing as achieved by random copolymerization has not been reached. We cannot preclude the possibility of limited homopolymer aggregation too small to be detected by thermal techniques, especially in view of the dielectric loss data. The broad (or diffuse) thermal transitions and the broadened dielectric loss curves indicate that a distribution of molecular environments exists in such films. A wide variety of intermolecular contacts are possible ranging from true molecular miscibility of PS and PVME to "micro" phase separation. By the latter we mean molecular aggregation with domains too small to be considered a phase on a macroscopic level. Molecular phases could be formed, but the effects of nearest neighbor interactions as well as intermolecular phase boundaries completely modify the normal macroscopic physical properties. Additional studies are being carried out to examine this phenomenon further and ascertain the mechanism of its occurrence.

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