Miscible Blends of Poly(styrene-co-Allyl Alcohol) with Poly-ε-caprolactone

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Synopsis

Based on the single, composition-dependent glass transition criterion, poly-ε-caprolactone (PCL) was found to be miscible with each of four poly(styrene-co-allyl alcohol) (SAA) copolymers with hydroxyl contents between 1.3 and 7.7 wt %. Melting point depression of the PCL in the blends was used to evaluate the blend interaction parameter B for each miscible system. The parameter B was found to be negative and to vary with copolymer composition in a way that suggests that an optimum density of alcohol moieties in the copolymer exists for achieving maximum interaction with PCL.

INTRODUCTION

That miscible blends of homopolymeric materials result from the presence of exothermic, physical interactions between the unlike blend components is fairly well established.[1-10] Probably these interactions are likewise responsible for the formation of miscible blends of a copolymer with another polymeric material and for the miscibility limits with copolymer composition reported for various blend systems.[11-16] The possibility of designing copolymers, through appropriate choices of comonomers and comonomer compositions, to form miscible mixtures with specific materials is particularly intriguing. However, information regarding the nature of the interaction and its variation with copolymer composition is generally lacking for most miscible blends with copolymers, and the choices of comonomers and their compositions in the copolymer are largely a matter of art at this time.

For these reasons, the discovery reported here that amorphous copolymers of styrene with 2-propen-1-ol or allyl alcohol (SAA) are miscible with a crystallizable polyester, specifically poly-ε-caprolactone (PCL), is of particular interest. Four copolymer compositions are available for studying compositional effects on miscibility with PCL. The thermodynamic parameters governing the melting of PCL are well known,[17-20] and melting point depression of the PCL in the blend can be used to estimate the interaction between it and the copolymer.[21,22] These features readily permit the following study of the effects of copolymer composition on blend interaction parameters.

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MATERIALS AND PROCEDURES

All of the SAA copolymers described in Table I were provided through the courtesy of Mr. D. M. Gardener of the Monsanto Plastics and Resins Company, Indian Orchard, Massachusetts. One synthetic route used to produce these materials involves the copolymerization of styrene with allyl ester followed by saponification of the ester to form the alcohol moiety.[23] Materials designated RJ-101 and RJ-100 are commercially available from Monsanto, and that designated Filtrez 895 is available from FRP Company, Baxley, Georgia. The material designated RF9266 is not available in commercial quantities. These copolymers are primarily used to increase hardness and gloss in coating systems and as reactive intermediate polyols in urethane formulations. As indicated in Table I, their molecular weights and melt viscosities are quite low relative to those expected for thermoplastic molding compounds.

Dr. L. M. Robeson, Union Carbide Corporation, Bound Brook, New Jersey, provided the PCL-700 used in this study and described in Table I. PCL is known to be miscible with a variety of polymers including poly(vinyl chloride),[18,8,20] cellulosics,[19,20] poly(epichlorohydrin),[19] a styrene-acrylonitrile copolymer,[24] and the polyhydroxy ether of bisphenol A and epichlorohydrin known as Phenoxy.[19,20] The gross similarities between the chemical structures of Phenoxy and the SAA copolymers are responsible for the discovery of miscible SAA/PCL binaries.

The low transition temperatures and melt viscosities of the blend components preclude using conventional melt processing equipment for preparation of melt blends. Instead, blends were prepared by mixing the ingredients in a glass beaker heated with a hot plate to 100–120°C. The blends were stirred continuously for about 20 min, at which time the melts were observed to be transparent and uniform. The melts were then cooled by pouring them on a metal plate.

TABLE I
Properties of Materials Used in This Study

| Property | SAA Copolymers | | | | PCL |
	RJ-101	RJ-100	Filtrez 895	RF 9266	PCL-700
Hydroxyl content, wt %	7.7	5.7	2.5	1.3	NA
$\overline{M}_w$	1700	2340	1420[a]	2100[a]	40000[b]
$\overline{M}_n$	1150	1600	950[a]	1400[a]	20000[f]
Glass transition temp., °C	54	61	41	44	−71[c]
Melting temp., °C	NA	NA	NA	NA	63
Sp. gr. at 25°C	1.09	1.06	1.05	1.05	1.127[e]
Melt viscosity at 95°C, poises[d]	3×10^3	2×10^4	1×10^3	1×10^4	2×10^4

NA = Not applicable.

[a] Estimated from melt viscosity data.

[b] See Ref. 20.

[c] See Ref. 19.

[d] By Brookfield melt viscometer, courtesy of D. Gardener.

[e] Estimated from measurements of amorphous density extrapolated to 28°C and crystalline density from Tadokoro.[47]

[f] Estimated from Ref. 20, assuming $\overline{M}_w/\overline{M}_n = 2.0$.

Glass transition temperatures T_g were measured using an R. L. Stone differential thermal analyzer. Heating rates of 10°C/min were used for all measurements. The T_g was determined after cycling the sample several times between 10°C above the highest transition and 50°C below the lowest transition, with thermograms being recorded during the heating portion of the cycle.

Heats of fusion and melting points were determined using a Perkin–Elmer DSC II differential scanning calorimeter. Blend samples were heated at 10°C/min to 100°C, where they were held for 5 min. The samples were then cooled at 320°C/min to 30°C, where they were held for 30 min prior to again heating at 10°C/min for the purpose of obtaining melting temperatures and fusion endotherm areas. The 30-min crystallization time at 30°C was found to be the shortest time in which pure PCL could achieve consistent levels of crystallinity, and these conditions were used for all blends with PCL. The melting temperature of PCL was taken as that value corresponding to the fusion endotherm peak. The fusion endotherm area, after appropriate calibration of the DSC II, was used to calculate the heat of fusion.

GLASS TRANSITION BEHAVIOR

The appearance in the blend of a single, composition-dependent T_g is the generally accepted criterion for blend miscibility. Figures 1–4 show that the PCL–SAA blends studied are miscible on this basis. The T_g observed for each of the pure SAA copolymers agrees well with those reported in Table I. The T_g of pure PCL is known to increase from −71°C in the amorphous state to −60°C in the partially crystalline state.[18] The observed values in Figures 1–4 are close
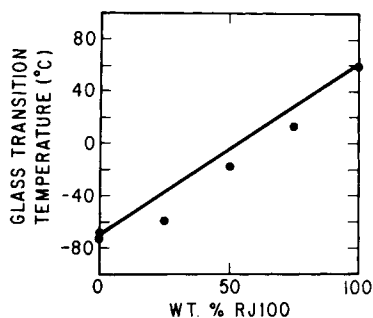

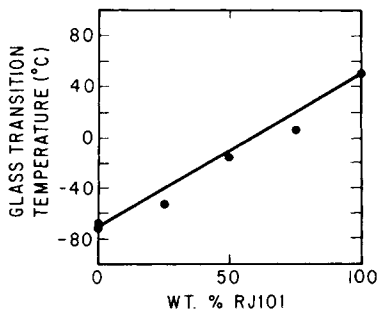Fig. 1. Glass transition behavior of PCL–RJ-100 blends.

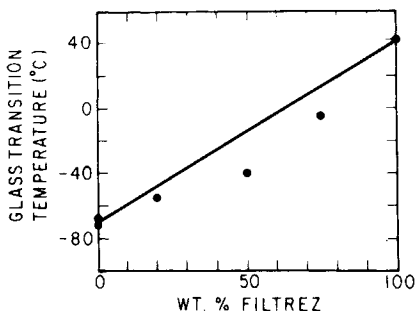Fig. 2. Glass transition behavior of PCL–RJ-101 blends.

Fig. 3. Glass transition behavior of PCL–Filtrez 895 blends.

to the reported amorphous values, and the observed variations in T_g may well be indicative of variations in the degree of crystallinity in the PCL samples.

The observed variations in blend T_g with composition are fairly typical insofar as the T_g tends to lie below the tie line connecting the T_g values of the pure components. This is the type of behavior expected on the basis of the Fox relation for copolymers.[25] Apparently the blend component interactions in these systems are not of sufficient strength to cause the positive deviations from tie line behavior reported for some other miscible blends.[26-28]

CRYSTALLIZATION AND MELTING BEHAVIOR

Kinetic considerations affect crystallization rates from miscible blends, with the difference between the melting point of the crystallizable component and the T_g of the blend being the main governing parameter.[29] For SAA/PCL blends with PCL weight fractions greater than 0.5, Figures 1–4 suggest that blend T_g values will be lower than −20°C, and one would expect that the reduction in crystallization kinetics should be minimal at the 30°C crystallization temperature used. Figures 5 and 6 bear out these expectations and show that the measured heat of fusion per unit mass of total sample falls very close to the line connecting that for PCL with the origin for samples which had been crystallized for 30 min at 30°C prior to measurements. These results suggest that PCL crystallizes from the blend to the same extent as it does in the pure state for the particular crystallization protocol employed. The observed heat of fusion for totally crystalline material, 32.4 cal/g,[30] indicates that the degree of crystallinity of the PCL in both the pure state and in the blend is 50%, a value in good agreement with that reported in the literature.[23]
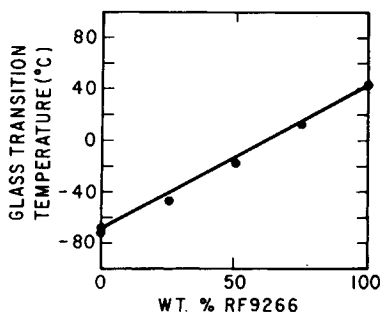

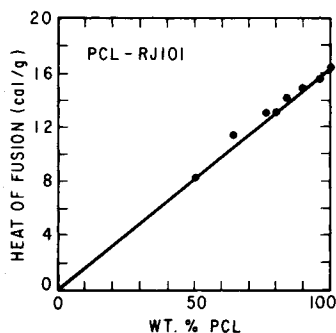Fig. 4. Glass transition behavior of PCL–RF 9266 blends.

Fig. 5. Effect of composition on PCL crystallinity in blends with RJ-101 crystallized for 30 min at 30°C.

Figures 5 and 6 further suggest that chemical reactions between the blend components have not occurred to an appreciable extent. Such reactions are known to occur between Phenoxy and polyesters,[27] and the potential chemical reactivity of the allyl alcohol moiety could, in principle, lead to similar behavior in PCL/SAA blends. The result of extensive chemical reactions should be a significant reduction in the degree of crystallinity of the PCL. That this does not occur in blends with high allyl alcohol content SAA (Fig. 5) nor in blends with low allyl alcohol content SAA (Fig. 6) suggests that chemical reactions between the blend components are not a problem at the blending and testing conditions employed in this study.

Analysis of the melting point depression of the crystallizable component in a miscible blend can be used to estimate the interaction parameter B between blend components[21,22]:

$$Y = \left(\frac{1}{T_m} - \frac{1}{T_m{}^0}\right)\frac{\Delta H_{2u}}{RV_{2u}} + \frac{\ln \phi_2}{V_2} + \phi_1\left(\frac{1}{V_2} - \frac{1}{V_1}\right) = \frac{-B}{RT_m}\phi_1{}^2 \qquad (1)$$

where component 2 is the crystallizable component, T_m^0 is its melting temperature in the pure state, $\Delta H_{2u}/V_{2u}$ is its heat of fusion per unit volume of repeat unit for 100% crystalline material, V_2 is its molar volume, and ϕ_2 is its volume fraction in the blend. Symbols with subscripts 1 refer to the correspoding quantities for the amorphous diluent, component 1. The interaction parameter B is related to the heat of mixing per unit volume, ΔH_{mix}, through

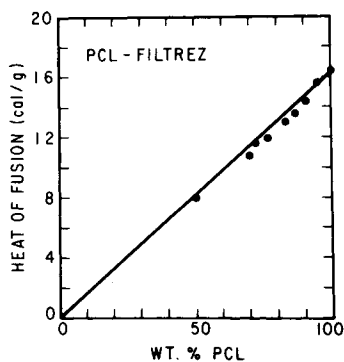$$\Delta H_{\mathrm{mix}} = B\phi_1\phi_2 \qquad (2)$$

Fig. 6. Effect of composition on PCL crystallinity in blends with Filtrez 895 crystallized for 30 min at 30°C.

For miscible blends of high molecular weight materials, V_1 and V_2 are large, and those terms in eq. (1) which are inversely proportional to molar volume vanish to give, after rearrangement,

$$T_m = T_m^0 + B\left(\frac{V_{2u}}{\Delta H_{2u}}\right) T_m^0 \phi_1^2 \qquad (3)$$

from which B can be directly evaluated from a plot of T_m vs. ϕ_1^2. The heat of fusion per unit volume of repeat unit, $\Delta H_{2u}/V_{2u}$, is known to be 35 cal/cc for PCL.[31]

Figures 7 and 8 show typical PCL melting point depression behavior in blends with SAA copolymers which seems to follow eq. (3). Remarkably good straight lines result for all four blend systems plotted in this manner. The pure PCL melting point is observed to be 56°C after crystallization for 30 min at 30°C. This value is somewhat lower than the reported equilibrium melting point of 63°C.[20] Crystals of PCL are apparently subject to a certain amount of refinement on annealing at room temperature, since crystals annealed for 4 h at 30°C showed melting points of 60°C, and samples stored for two months showed the reported equilibrium value. In addition, the well-known Hoffman–Weeks theory[32] suggests that the true equilibrium melting temperature, T_m^0, is only obtained by annealing at crystallization temperatures just slightly below the
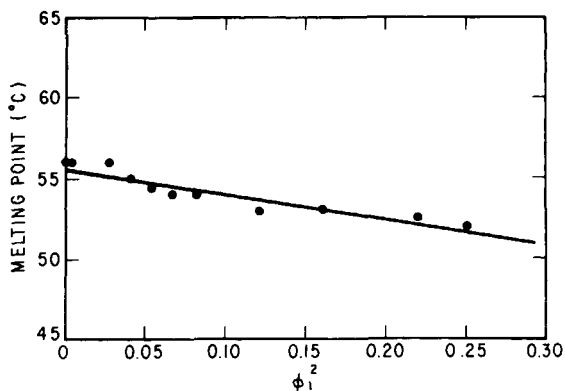

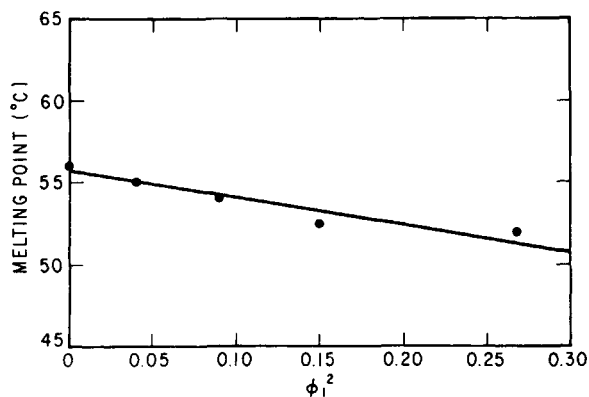Fig. 7. T_m vs. ϕ_1^2 for PCL in RJ-101.

Fig. 8. T_m vs. ϕ_1^2 for PCL in RF9266.

melting temperature. Consequently, the observed melting temperature for pure PCL, 56°C, or 329.2 K, is not the equilibrium value. For consistency with observations in Figures 7 and 8, however, $T_m^0 = 329.2$ K is used for evaluating the interaction parameter B. Some variation from the true value of B is therefore expected, but this variation is likely to be less than 10%, provided the PCL lamella thickness in the blends is similar to that in the pure state.

The lower curve of Figure 9 shows the variation in B with copolymer composition for the case where B is evaluated directly from T_m vs. ϕ_1^2 plots using eq. (3). The B parameter is found to be negative for PCL blends with each of the four SAA copolymers examined, indicating that the heats of mixing for these blends, eq. (2), are exothermic.

The SAA copolymers have low molar volumes; and some entropic contribution to melting point depression and to B, evaluated via eq. (3), is expected. To eliminate this effect, the melting point depression data were analyzed using eq. (1) and the molar volumes calculated from the data in Table I. Again, good straight lines of Y vs. ϕ_1^2 result, from which B values corrected for entropic effects can be obtained. These values are shown as the upper curve in Figure 9, and they may be a better representation of the actual enthalpic interactions between SAA and PCL.

The shapes of the curves in Figure 9 suggest that B approaches zero or becomes positive at low copolymer hydroxyl contents. To check this possibility, blends of PCL with a monodisperse, 2000-molecular-weight polystyrene fraction were prepared. These blends were found to have cloudy melts and were judged on this basis to be immiscible. This result suggests that the variation of B with copolymer content at low hydroxyl levels is correct and that some exothermic interactions are necessary to guarantee miscibility even at these low levels of component molecular weight. Figure 9 also suggests that B may approach positive values as the SAA hydroxyl content is increased above about 10% by weight. This would mean that high hydroxyl contents could also lead to blend immiscibility. No SAA materials have been obtained to experimentally check this apparent upper limit in hydroxyl content for SAA miscibility with PCL.
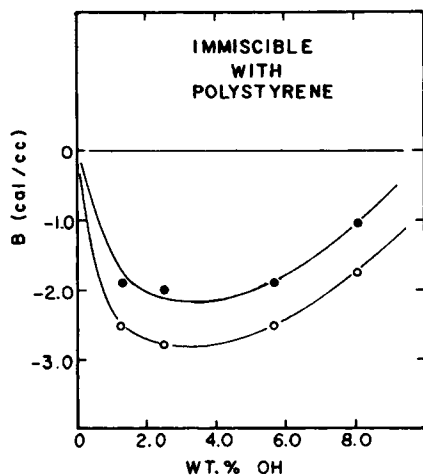

Fig. 9. Blend interaction parameters as a function of SAA hydroxyl content. Upper curve shows B obtained using eq. (1). Lower curve shows B obtained using eq. (3).

However, there are numerous examples which support the idea that miscibility only exists in certain ranges of copolymer composition,[2,8,9,13] and the apparent trend of B with composition shown here seems to be consistent with this idea and the expectation that the formation of miscible blends requires that the heat of mixing be exothermic.

DISCUSSION OF RESULTS

Because PCL is found to be immiscible with polystyrene, it is clear that the hydroxyl moiety of the SAA copolymer participates in the interaction leading to negative heats of mixing and miscibility. Hydrogen bonds are known to form between low-molecular-weight alcohols and molecules containing carbonyl oxygens,[33–36] and similar interactions between the carbonyl moiety of PCL and the hydroxyl of SAA could reasonably be expected to be responsible for the miscible behavior observed for this system, Phenoxy/polyester blends,[27,19,37,38] and mixtures of poly(styrene-co-vinylphenylhexafluorodimethylcarbinol) with polyesters.[26]

The shape of Figure 9 suggests that competing mechanisms involving the hydroxyl moieties are involved in the interaction between SAA and PCL. One possibility for this behavior could be that changes in copolymer composition change its cohesive energy density or solubility parameter relative to that for PCL and that this difference causes a positive heat of mixing contribution to partly counteract the negative heat associated with the hydrogen bond formation process. If this were the case, one could expect the solubility parameter of 3.5% hydroxyl content SAA to be the same as that for PCL, since the net exothermic contribution is maximum at this copolymer composition (see Fig. 9). The solubility parameters, as calculated by the methods of Van Krevelen, Small, and Hoy,[31] lie in the range 8.8–9.2 $(cal/cc)^{1/2}$ for PCL, 9.8–10.4 $(cal/cc)^{1/2}$ for PS, and 12–14 $(cal/cc)^{1/2}$ for poly(allyl alcohol). The solubility parameters for SAA copolymers must consequently be larger than that for PS, a value which is already larger than that for PCL, and one is forced to conclude that matching of solubility parameters has little to do with the variation of B with copolymer composition observed in Figure 9. A similar conclusion was recently reached by Aubin and Prud'homme concerning their study of miscible polyester–PVC blends.[39]

A potentially more plausible mechanism for explaining the variation of B with composition rests on the known tendency for monomeric alcohols to self-associate through hydrogen bonding to form polymeric complexes.[40–46] These materials show endothermic heats of mixing when mixed with hydrocarbons as a result of the dissociation of the hydrogen bonded complexes as required by the law of mass action. Conceivably, SAA copolymers could also be self-associated in the pure state, and the exothermic heat of mixing observed and characterized by B could be the net result of the difference between the heat evolved during formation of the carbonyl–hydroxyl hydrogen bond and the heat absorbed during the dissociation of the hydroxyl–hydroxyl hydrogen bonds between the SAA molecules. This possibility is presently being studied, and the results of this study will be reported at a later time.

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