

Miscible Ternary Blends Containing Polycarbonate, SAN, and Aliphatic Polyesters

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Synopsis

Ternary blends comprising polycarbonate, (PC), poly(styrene-co-acrylonitrile) (SAN), and a polyester, either poly(1,4-butylene adipate) (PBA), poly(1,4-cyclohexanedimethylene succinate) (PCDS), or poly(ϵ -caprolactone) (PCL), were found to be miscible based on the presence of a single glass transition temperature at many compositions. For all systems, the addition of just 1% by weight polyester resulted in a miscible blend for SAN/PC ratios of 1/1 and 3/1, and a region of immiscibility was generally observed for PC-rich compositions with low polyester content. The melting point depression of PCL in the ternary and in binary mixtures was studied to obtain interaction parameters for the PCL/PC, PCL/SAN, and SAN/PC binaries. These parameters were used to calculate the locus of compositions which mark the boundary between single- and multiple-phase behavior. Agreement between the calculated and experimental boundary was only fair. PCDS was found to be the most efficient of the three polyesters studied for solubilizing PC and SAN. SAN copolymer containing 25% acrylonitrile (AN), was found to be more easily solubilized in PC by PCDS than SAN containing 13% AN.

INTRODUCTION

The past decade has seen an explosion in both the number of miscible binary polymer blends discovered and in the scientific understanding of the physical chemical processes necessary for the formation of these terns.¹⁻⁸ Recognition that miscible binary blends are most often formed by favorable, exothermic, interactions between the blend components has led to one of the more successful approaches for understanding and potentially predicting binary miscibility. This approach generally considers the sign of the heat or enthalpy of mixing, measured either directly from the heat of mixing of low-molecular weight analog materials^{1,6,9-11} or indirectly from blend properties,¹²⁻¹⁵ to be the dominant predictor of blend miscibility and suggests that the resulting binary interaction parameter must be negative, indicating an exothermic heat of mixing, for the formation of miscible binary blends.

A formalism for predicting the heat of mixing of multicomponent, low-molecular weight mixtures in terms of the binary interaction parameters between the components has long been reasonably successful for describing liquids whose heats of mixing follow van Laar parabolic composition dependence.¹⁶⁻¹⁸ Recently, this formalism has been applied to the prediction of miscibility of binary blends containing a copolymer with equal success.¹⁹

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One would reasonably expect that this same formalism could prove useful for understanding the behavior of multicomponent polymer blends.

Despite the several hundred miscible binaries reported in the literature over the last decade, only two miscible ternary blends have been reported; poly(vinylidene fluoride)/poly(methyl methacrylate)/poly(ethyl methacrylate)²⁰ and poly(vinylidene chloride-co-vinyl chloride)/poly(vinyl chloride)/poly(acrylonitrile-co-butadiene).²¹ Both of these systems use one of the ternary components, the poly(vinylidene fluoride) in the former and the poly(acrylonitrile-co-butadiene) in the latter to solubilize the other two, normally immiscible, components. This feature may, indeed, be a good reason for studying the formation of miscible ternary blends, since there are a variety of potentially useful blend products which could be formed if one could overcome the property deficiencies of the immiscible binary by addition of a solubilizing third component.

While the potential for discovering useful ternary blend products is enhanced by the extra compositional degree of freedom relative to binary materials, the problems of analysis and understanding are also increased. The purpose of this paper is to explore the protocols and problems associated with ternary systems and to provide additional insight and knowledge about thermal and phase behavior of several new miscible ternary blends based on polycarbonate (PC), poly(styrene-co-acrylonitrile) (SAN), and several polyesters, each of which is miscible with PC or SAN. As in the previous ternary blend studies,^{20,21} binary blends of PC and SAN are only partially miscible, although the blend properties are quite good,²² and the polyester is added to solubilize the mixture.

MATERIALS AND PROCEDURES

The polymers used in this research were polycarbonate (PC), supplied by the Dow Chemical Company as an experimental material with number XP-73009-00; poly(styrene-co-acrylonitrile) SAN(25) with 25% acrylonitrile, supplied also by the Dow Chemical Company under the trade name TYRIL 860; poly(styrene-co-acrylonitrile) SAN(13) with 13% acrylonitrile, supplied by R. L. Jalbert of Borg-Warner as Resin 21082-73; poly(1,4-butylene adipate) (PBA), poly(1,4-cyclohexanedimethylene succinate) (PCDS), supplied by Aldrich Chemical Company; and poly(ϵ -caprolactone) (PCL), supplied by Union Carbide Corporation under the trade name PCL-700. A summary of the thermal properties and molecular weights of these materials is presented in Table I.

Depending on the quantities of polyester available, blends were prepared either by melt blending the ingredients in a Brabender Plasticorder for 10 minutes at 60 rpm and at temperatures varying between 220°C and 270°C, depending on the composition, or by the solution casting method described below. Regardless of the method employed, all ingredients were carefully dried prior to preparation. The PC and SAN components were dried in an air oven at 100°C for 24 h and the polyester components were dried in a separate oven at 50°C for two days prior to blend preparation to remove sorbed water which could cause hydrolytic decomposition of the PC and

TABLE I
Measured Properties of Polymers Used in This Study

| Polymer | Abbreviation | Molecular wt. | T _m (°C) | T _g (°C) |
|--|--------------|---|---------------------|---------------------|
| Poly(ϵ -caprolactone) | PCL | M _n = 15500 ^a M _w = 40500 | 47 | -74 |
| Polycarbonate | PC | Molding grade | — | 149 |
| Poly(styrene-co-acrylonitrile) 13% AN | SAN(13) | M _n = 58300* M _w = 149000 | — | 104 |
| 25% AN | SAN(25) | Molding grade | — | 107 |
| Poly(1,4-butylene adipate) | PBA | — | 54 | -68 |
| Poly(1,4-cyclohexane-dimethylenesuccinate) | PCDS | — | — | -2 |

^a Provided by supplier.

polyester materials during subsequent thermal treatment.

Blend films were cast from solution by separately dissolving the predried components in dichloromethane to form solutions containing 2 g polymer in 10 mL of solvent. The separate solutions were then combined to prepare a casting solution with the desired composition. The solution was then poured into aluminum pans, and the dichloromethane was evaporated from the system by air drying for approximately 24 h in a hood, followed by drying *in vacuo* at 60°C for an additional 24 h.

Regardless of the mixing method employed, thin films for thermal testing were prepared by pressing the samples between Mylar release films in a compression press operated at temperatures between 175°C and 225°C, depending on the composition. Films were generally not transparent, in part the result of polycarbonate crystallization which is promoted both by low-molecular weight solvent and by the presence in the blend of polyester solvents such as PCL.^{23,24} Contributing factors to the observed opacity of the films potentially also include LCST behavior known to occur in both PC/PCL binaries²³ and SAN/PCL binaries²⁵ as well as polyester-component crystallization at high polyester levels in the blends. While none of these factors leading to opacity necessarily precludes blend miscibility, analysis of the ternary mixtures is complicated by the presence of these factors, and certain special procedures were employed to try to eliminate crystallinity as discussed, where appropriate, below.

The presence in the blend of a single composition-dependent glass transition temperature (T_g), is used in this work as the primary indicator of the formation of a miscible blend system, as is generally done in studies of binary polymer mixtures.¹⁻⁸ T_g measurements were obtained using a Perkin-Elmer DSC-2 (Differential Scanning Calorimeter), by typically first heating the film samples at 20°C/min to 230–270°C to melt out any PC crystallinity, rapidly cooling the material to 25°C, and then reheating at 20°C/min to locate the transition temperatures. This cycle was repeated several times to obtain consistent observations.

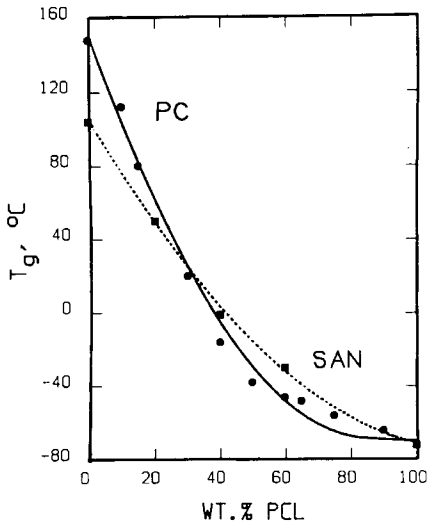


Fig. 1. Glass transition behavior of PCL/PC and PCL/SAN(25) binary blends.

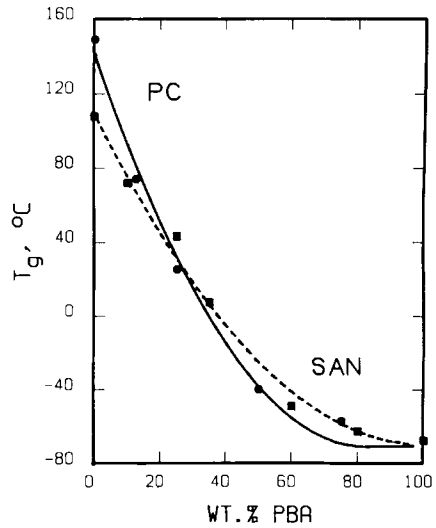


Fig. 2. Glass transition behavior of PBA/PC and PBA/SAN(25) binary blends.

BINARY BLENDS

Figures 1–4 show that each polyester/PC and polyester/SAN binary mixture studied in this work forms a miscible system throughout the entire composition range. The PC/polyester binaries are not newly discovered but are repeat determinations of the work by Cruz.^{23,24} Similarly, Chiu and Smith²⁵ reported that PCL/SAN binaries were miscible when the AN content is between 6% and 30%. While newly reported, one could also argue

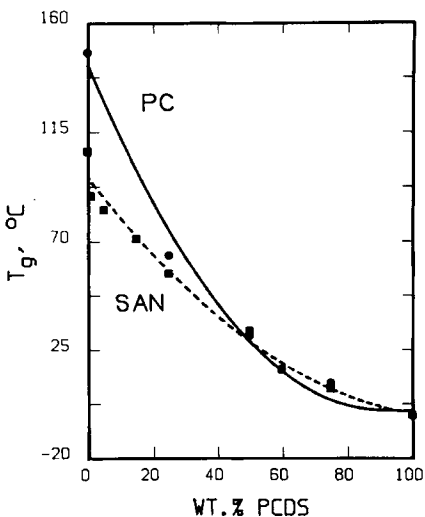


Fig. 3. Glass transition behavior of PCDS/PC and PCDS/SAN(25) binary blends.

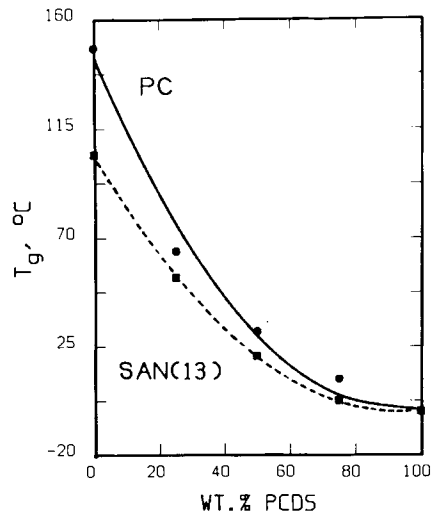


Fig. 4. Glass transition behavior of PCDS/PC and PCDS/SAN(13) binary blends.

that the structural similarities, particularly the carbonyl to aliphatic carbon ratios,¹³ of PBA and PCDS are close enough to PCL to cause miscibility of these polyesters with SAN(25) or with SAN(13) to be expected.

All binary blends containing SAN and polyester were transparent, provided the polyester content in the blend was low enough to prevent polyester crystallization. Similarly, PC-rich binary films containing less than 25% PBA, are transparent at room temperature, but opacity develops as the PBA content increases and the binary blend T_g falls sufficiently to allow the PBA to crystallize. Since PCDS is extremely slow to crystallize and does not promote PC crystallization, PCDS/PC binaries are also transparent, when processed as described above. On the other hand, the PC/PCL films tend to be slightly cloudy as formed, even at low PCL content, because of the tendency for PCL to promote PC crystallization,²³ and this cloudiness increases dramatically as the film is heated until a temperature near 250°C is reached. At this temperature, the blend becomes clear as the PC crystals are melted.

TERNARY BLENDS

Since both the polyester and PC components can crystallize under appropriate circumstances, determination of ternary blend-phase behavior from observation of blend transparency is difficult. Figures 1–4 suggest also that use of the single T_g criterion for judging the absence of multiple amorphous phases in the PC/SAN/polyester ternaries will be difficult for regions of composition where the T_g 's of the binary combinations tend to overlap. For example, the presence of a single T_g for a 40%PC/40%SAN(25)/20%PCL mixture may mean that a true single-phase solution has been obtained or may mean that a two-phase mixture exists, one phase containing the miscible 80%PC/20%PCL binary with $T_g = 35^\circ\text{C}$ and one phase containing the miscible 80%SAN(25)/20%PCL binary with the same T_g (see Fig. 1). The added complication of component crystallization in these phases effectively limits the utility of observations regarding blend transparency for providing the additional information required to judge the presence of multiple amorphous phases.

For these reasons, the presence of one T_g in ternary compositions containing large amounts of polyester will generally not constitute proof of miscibility in that composition. In addition, the instrumental difficulty associated with resolving T_g 's which are less than 20°C apart will add to the problem at the higher polyester contents (see Figs. 1–4). On the other hand, should a single T_g occur on addition of very low amounts of polyester, say less than 10%, one could argue that a miscible system has probably been formed, because no matter how one partitions the polyester into hypothetical multiple phases the T_g 's of these phases should be visible by DSC. The systems discussed below do show single T_g behavior at very low polyester content and are probably miscible in certain regions of the ternary composition diagram.

PC/SAN(25)/PCL Transition Behavior. Glass transition temperatures were measured for a variety of compositions with particular emphasis on

SAN(25) to PC weight ratios between 1/3 and 3/1. In the absence of PCL, the T_g 's of both phases were easily observed to be close to the values of the pure components. The addition of sufficient PCL, expressed as parts by weight PCL per hundred parts of the SAN(25)/PC mixture (PHR), in Figures 5-7, caused the ternary mixtures to show the single T_g behavior characteristic of a miscible system.

As indicated by Figures 5-7, strikingly different approaches to single T_g behavior were shown by the blends with increasing PCL content, depending on the SAN(25) to PC ratio employed. At the 1/3 ratio (Fig. 5), the two T_g 's are both reduced smoothly with increasing PCL until they merge to a single T_g at about 30 PHR PCL. Combined with the binary data of Figure 1, one could conclude that the PCL dissolves to the same extent in the SAN(25)-rich phase as in the PC-rich phase and that the smooth merging of the T_g 's of these phases with increasing PCL content results from the overlap of the T_g 's of these two binary phases. If this conclusion were true, one would expect to see a similarly smooth merging of T_g 's for other SAN(25)/PC ratios in the blend. Figure 6 shows that quite different T_g behavior is obtained for the 1/1 ratio. Here, two distinctly nonmerging T_g 's can be observed as the PCL content is increased to about 40 PHR, beyond which one T_g is observed.

Even more interesting is the behavior shown for the 3/1 ratio (Fig. 7). At this starting composition, one T_g is observed for PCL contents as low as 1 PHR. If two phases exist, Figure 1 suggests that one ought to be able to observe two T_g 's regardless of how the PCL, at an overall level of less than 1% by weight, is partitioned between the two phases. Consequently, one must conclude that only one amorphous phase exists for this 3/1 ratio and that PCL solubilizes the system even when present at very low levels.

A summary of T_g measurements for all ternary compositions examined is shown in the ternary diagram (Fig. 8). This diagram is not the conven-

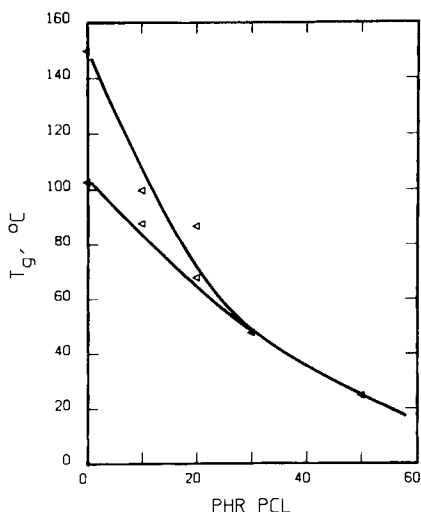


Fig. 5. Effect of PCL addition on the glass transition behavior of ternary blends containing a SAN(25)/PC ratio of 1/3.

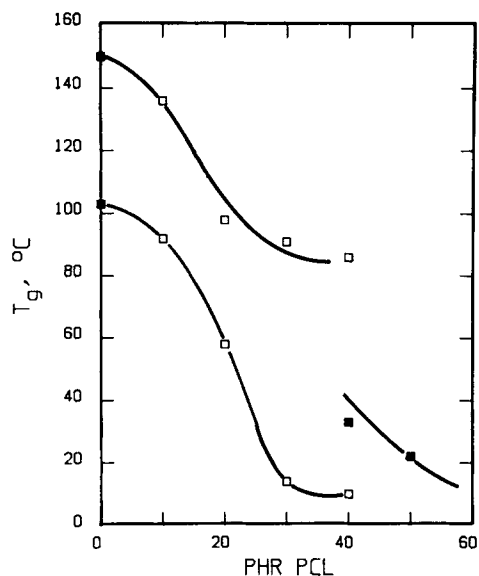


Fig. 6. Effect of PCL addition on the glass transition behavior of ternary blends containing equal parts of SAN(25) and PC.

tional ternary diagram that one normally constructs when dealing with liquid components^{16,17} because no attempt has been made to determine the compositions of phases in equilibrium. Instead, this diagram simply notes compositions where single T_g or two T_g 's are observed. From this diagram it is clear that only one T_g is observed, regardless of the PC/SAN ratio, when the PCL level in the ternary is greater than 29% by weight. No T_g corresponding to a PCL-rich amorphous phase was detected in any blend containing up to 75% by weight PCL, the limit of our investigation, a result

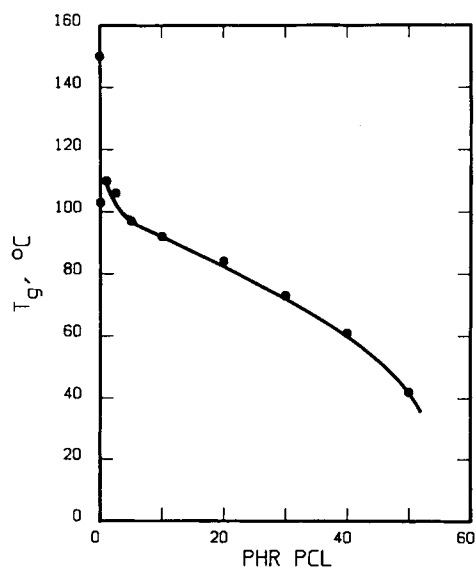


Fig. 7. Effect of PCL addition on the glass transition behavior of ternary blends containing a SAN(25)/PC ratio of 3/1.

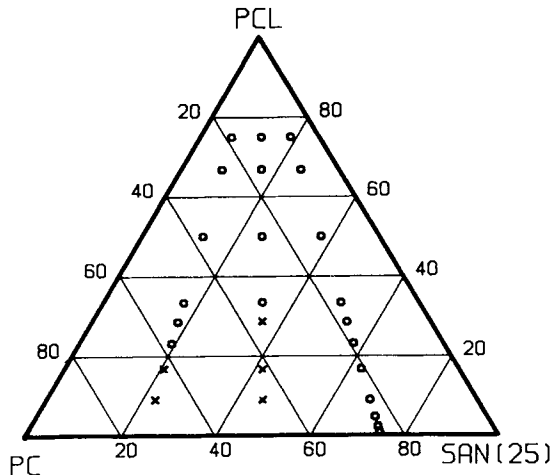


Fig. 8. Ternary diagram of the PCL/SAN(25)/PC system. (○) Indicates compositions which show single T_g behavior. (×) Indicates compositions which show two T_g 's.

consistent with the known miscibility of the PCL/SAN(25) and PCL/PC binaries.

It is also clear from the ternary diagram that the composition boundary between single T_g and two T_g behavior is distinctly nonsymmetric with respect to the SAN and PC apexes. One explanation for this behavior perhaps resides in the observation that PC is more soluble in SAN than SAN is in PC, as indicated by a previous study of PC/SAN blends which used the Fox equation to estimate phase compositions from small observed T_g shifts.²² One could expect from this work that less PCL would be required to solubilize the SAN-rich blends, as is observed, but the observation that so little PCL is required to miscibilize the 3/1 ratios is still surprising.

PCL Melting-Point Depression. As in the case of binary polymer mixtures, the melting-point depression of a crystallizable component in a ternary solution can be readily derived from existing equations,¹⁶⁻¹⁸ and a study of the melting-point depression can yield some information about interaction parameters between the blend components. The key arguments in the derivation begin with the assumption by Hildebrand and Scott¹⁶ that the heat of mixing, ΔH_{mix} , of a multicomponent system can be described in terms of binary interaction coefficients by,

$$\Delta H_{\text{mix}} = V \{ \sum_i \sum_{j \neq i} B_{ij} \phi_i \phi_j \} \quad (1)$$

where V is the system volume, B_{ij} the interaction coefficient which determines the sign and magnitude of the heat of mixing of i with j , and ϕ_i is the volume fraction of component i in the mixture. The next key assertion is that the combinatorial entropy of mixing is very small.^{1,19} This assertion requires that the change in chemical potential of component 2 relative to the pure state be equivalent to the partial molar enthalpy of component 2.

For a ternary mixture of components 1, 2, and 3, the partial molar enthalpy of component 2, $\Delta\bar{H}_2$, becomes

$$\Delta\bar{H}_2 = \partial\Delta H_{\text{mix}}/\partial n_2 = \tilde{V}_2 \{B_{12}\phi_1^2 + B_{23}\phi_3^2 + \Delta B\phi_1\phi_3\} \quad (2)$$

where,

$$\Delta B = B_{12} + B_{23} - B_{13} \quad (3)$$

and \tilde{V}_2 is the molar volume of component 2. When Eq. (2) is equated to the difference in chemical potential between a crystalline polymer unit and the same unit in the pure liquid state,²⁰ we obtain, assuming 2 to be the crystalline component,

$$T_m = T_m^\circ \{1 + (\Delta\bar{H}_2/\tilde{V}_2)(v_{2u}/\Delta h_{2u})\} \quad (4)$$

where v_{2u} and Δh_{2u} are volume and heat of fusion, respectively, per unit of crystalline 2, and T_m and T_m° are the melting temperatures of 2 in the blend and in the pure state, respectively. Combining Eqs. (2), (3), and (4) yields the well known result,^{20,26}

$$T_m = T_m^\circ \{1 + B(v_{2u}/\Delta h_{2u})\}(1 - \psi_2)^2 \quad (5)$$

where,

$$B = B_{12}\psi_1^2 + B_{23}\psi_3^2 + \Delta B\psi_1\psi_3 \quad (6)$$

and

$$\psi_i = \phi_i/(1 - \phi_2) \quad (7)$$

For a miscible binary blend of crystalline polymer 2 and amorphous polymer 1, $\phi_3 = 0$, $\psi_3 = 0$, $\phi_1 = (1 - \phi_2)$, $\psi_1 = 1$, and B in Eq. (5) is just B_{12} , the interaction parameter describing the heat of mixing between 2 and 1 (see Eq. 1). The generally observed decline in melting temperature with increasing content of the amorphous diluent leads to the conclusion that B_{12} and ΔH_{mix} are negative, or exothermic, for miscible binary blends.¹²⁻¹⁵

Equation (5) suggests that the parameter, B , can be evaluated in exactly the same way for a ternary mixture as for a binary mixture by determining the slope of the T_m versus the square of the amorphous volume fraction construction. Evaluation of B at several SAN/PC ratios, should then allow evaluation of the unknown interaction parameter for SAN/PC, B_{13} , via Eq. (3) and (6).

Figure 9 shows the constructions, suggested by Eq. (5), for PCL melting-point measurements in both binary and ternary mixtures. All measurements were made in the DSC-2 by heating samples at 10°C/min to 100°C, holding at that temperature for 5 min to insure melting of the PCL, cooling rapidly to 30°C, holding at that temperature for 30 min to allow the PCL to crystallize, and then reheating at 10°C/min to observe the melting tem-

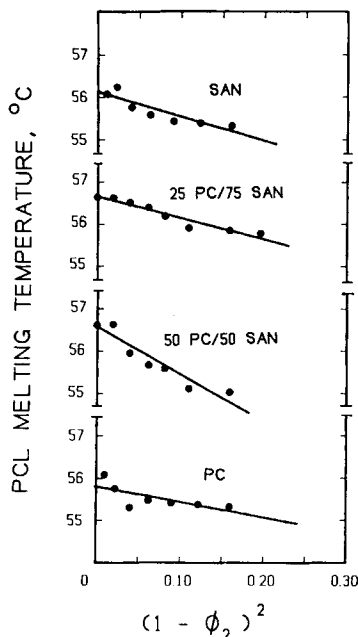


Fig. 9. Melting-point depression of PCL in both binary and ternary blends with PC and SAN(25).

perature of PCL, taken as the peak of the melting endotherm. Previous work²⁷ showed the 30 min of crystallization to be the shortest time in which PCL could achieve consistent levels of crystallinity, however the 56.6°C melting temperature observed for PCL and associated with T_m^o is somewhat lower than the 60°C melting temperature reported for PCL which has annealed for longer periods.²⁸ More extensive procedures²⁹ are available to accurately determine T_m^o , but the error associated with the present approach is small.

The B parameters, evaluated from the slopes of the lines in Figure 9 and $\Delta h_{2u}/v_{2u} = 32.4$ cal/cc,³⁰ are presented in Figure 10 as a function of the PC fraction of amorphous diluent, ψ_3 . The B values are all quite similar in magnitude, small relative to B values for other systems,^{13,27} and uncertain by at least 20% due to the numerical uncertainty associated with determining slopes. The parameter associated with the SAN/PCL binary inter-

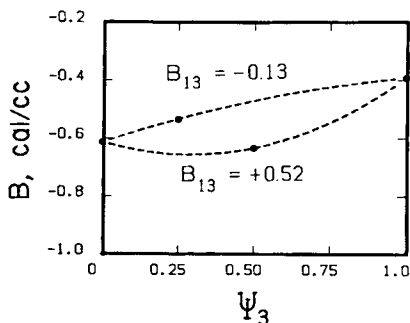


Fig. 10. Interaction parameter, B , vs. the fraction PC in the amorphous diluent for two estimates of B_{13} .

action, $B_{12} = -0.61$ cal/cc, is slightly more negative than that associated with the PCL/PC binary interaction, $B_{23} = -0.39$ cal/cc, a result which may be consistent with the previous observation that less PCL is needed to form the miscible ternary when the SAN to PC ratio is greater than one. Given the uncertainty in the B values, it is difficult to know whether the apparent scatter in those corresponding to the ternary compositions is real or not. If the B values have no scatter then the parabolic model [Eq. (6)], is really inappropriate for describing the phenomenon. Given the asymmetry of the miscibility boundary (Fig. 8), the B values cannot be constant but must vary with composition in some unknown way. If one, for the sake of argument, assumes the B values to be constants then the value of the interaction parameter, B_{13} , can be estimated by drawing the appropriate parabola through each of the two intermediate B values, as shown in Figure 10. That drawn through the point corresponding to $\psi_3 = 0.5$ yields, through Eqs. (3) and (6), $B_{13} = +0.52$ cal/cc while that through the other point yields $B_{13} = -0.13$ cal/cc. The average of these two determinations in $B_{13} = +0.2$ cal/cc. Since the uncertainty is larger than the value, little more can be said except that the average value seems reasonable in light of the known partial miscibility of the SAN(25)/PC binary.

Estimation of Ternary-Phase Behavior. Recently, a model for estimating the miscibility of a copolymer with another polymer was suggested¹⁹ in which the copolymer was considered a binary solution for the purpose of calculating the heat of mixing of the copolymer and the polymer via Eq. (1). The requirement for miscibility, $\Delta H_{\text{mix}} \leq 0$, was assumed to be sufficient, and the model was able to follow the limits of miscibility with varying copolymer composition observed. The PCL/SAN(25)/PC system studied here allows an experimental check on the assumption that $\Delta H_{\text{mix}} \leq 0$ is a sufficient criterion for miscibility within the limits of uncertainty associated with the B_{ij} parameters determined above.

The locus of ternary compositions is easily determined by combining Eq. (1), with $\Delta H_{\text{mix}} = 0$, and the equation of continuity, $\Sigma\phi_i = 1$, to yield,

$$\phi_2 = RB_{13}/(RB_{13} - (R + 1)(RB_{12} + B_{23})) \quad (8)$$

where,

$$\phi_3 = (1 - \phi_2)/(1 + R) \quad (9)$$

$$R = \phi_1/\phi_3 \quad (10)$$

The calculation requires specifying a value of R , from which the volume fraction of PCL, ϕ_2 , is calculated by Eq. (8), that of PC, ϕ_3 , is calculated by Eq. (9), and that of SAN, ϕ_1 , is calculated by Eq. (10). Allowing R to vary between .01 and 100 will provide nearly all compositions for which $\Delta H_{\text{mix}} = 0$.

Figure 11 compares the actual miscibility boundary obtained from T_g measurements with boundaries calculated from the B_{ij} parameters obtained from the PCL melting behavior. Since B_{13} is probably the least certain of the parameters, the boundaries are computed for several plausible choices of B_{13} , ranging from +0.2 to +0.9 cal/cc. All calculated boundaries are

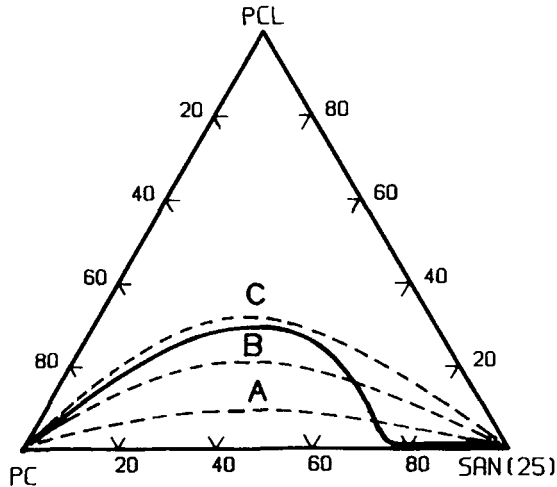


Fig. 11. Comparison of the experimentally determined two-phase region with that calculated from Eq. (1) for $B_{13} = \pm 0.9$ cal/cc (Curve C), $+0.5$ cal/cc (Curve B), and $+0.2$ cal/cc (Curve A).

parabolic with respect to composition, as expected from Eq. (1), and the calculated amount of PCL to achieve miscibility increases in the expected manner as the interaction between PC and SAN becomes increasingly positive or endothermic. The B_{13} parameters from melting-point depression studies tend to underpredict the amount of PCL required for compositions containing less than 50% SAN and to overpredict the PCL required to solubilize compositions containing more than 70% SAN, in part because the parabolic model, with composition-independent parameters, does not account for the observed asymmetry of the experimental boundary.

PC/SAN(25)/PBA Transition Behavior. The T_g behavior of PBA-containing ternary blends, summarized in Figures 12–14, is similar to that of

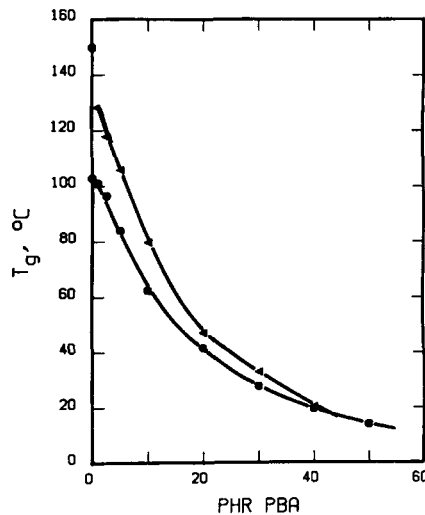


Fig. 12. Effect of PBA on the glass transition behavior of ternary blends containing SAN(25)/PC ratios of 1/1 (▲) and 3/1 (●).

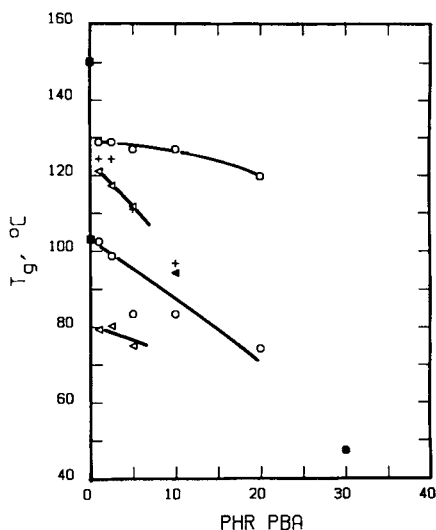


Fig. 13. Effect of PBA on the glass transition behavior of ternary blends containing SAN(25)/PC ratios of 2/3 (Δ), 1/3 (\circ), and 1/9 (+). Open symbols indicate multiple T_g behavior.

PCL-containing ternaries. Again, one sees a distinct asymmetry with respect to the SAN and PC compositions in the boundary between two T_g and single T_g behavior (Fig. 14). In contrast to the PCL-containing system, however, the boundary is shifted to higher PC content. Blends containing 50% or more SAN show single T_g behavior for PBA levels as low as 1%, as do blends which contain 90% or more PC.

As indicated by Figure 13, two distinct T_g 's are detectable in ternaries containing PC/SAN ratios of 75/25 and 60/40, but these discontinuously merge to a single T_g as the PBA content is increased beyond 17% and 5%, respectively. From Figure 2, one might expect that the appearance of a single T_g simply results from the potential overlap of the T_g 's, however the discontinuous change from two T_g to single T_g behavior, observed in Figure

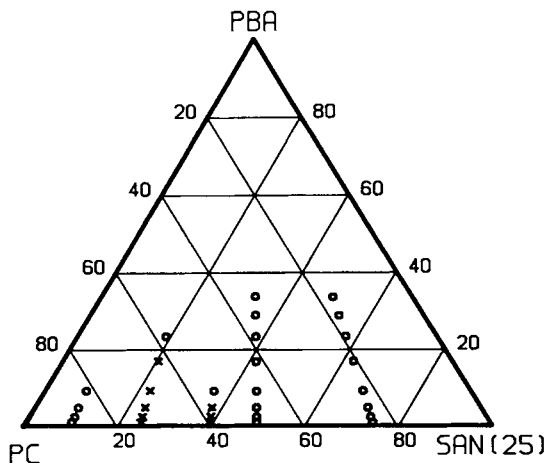


Fig. 14. Ternary diagram of the PBA/SAN(25)/PC system. (\circ) Indicates compositions with one T_g . (\times) Indicates compositions with two T_g 's.

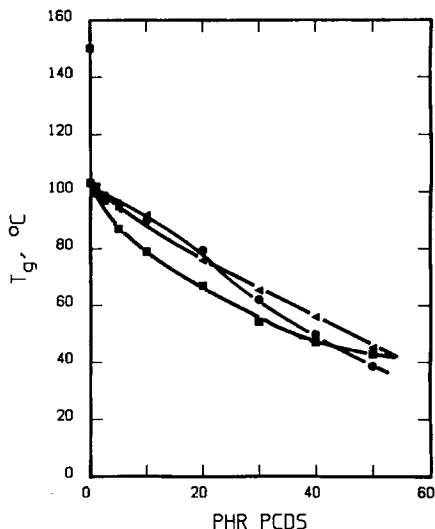


Fig. 15. Effect of PCDS on the glass transition behavior of ternary blends containing SAN(25)/PC ratios of 3/1 (●), 1/1 (▲), and 1/3 (■).

13, and the appearance of just one T_g at very low PBA contents in ternaries containing both higher and lower PC/SAN ratios seems to eliminate this simple explanation.

A comparison of Figures 8 and 14, leads to the conclusion that PBA more efficiently solubilizes the PC/SAN mixture than does PCL, and in the context of Eq. (1), one could expect that this increased efficiency results from more exothermic PBA/SAN and PBA/PC interaction parameters. Attempts were made to evaluate the B parameters from PBA melting-point depression studies, however the observed depressions were too uncertain in both the ternaries and in PC to give reliable results.

PC/SAN(25)/PCDS and PC/SAN(13)/PCDS Transition Behavior. To try to eliminate any effects which may be due to polyester crystallization and to explore further the effect of polyester structure on its efficiency for solubilizing PC/SAN(25) mixtures, ternary mixtures containing PCDS were examined. As indicated in Figure 15 and summarized in Figure 16, less than 5% addition of PCDS is sufficient to produce a single T_g regardless of the PC/SAN ratio. The three to one ratio again requires the largest amount of polyester to achieve miscibility, but this amount is only 2.4% by weight and less than 0.9% PCDS is sufficient to solubilize the 1/1 and 1/3 PC/SAN ratios.

Interestingly, even very small additions of PCDS cause the ternary blend T_g to drop to a value close to that of the SAN component. As shown in Figure 3, this phenomenon also occurs in the PC/PCDS and SAN(25)/PCDS binaries. This offset cannot be explained by any of the present theories for estimating the T_g of a blend from that of its components. Nor can it be explained by the presence of residual solvent from the casting process employed, because the same offset in T_g is obtained when these materials are melt blended instead of cast from solvent. Commensurate with this abrupt decline in T_g is an increase in the crystallinity of PC, and these blends are

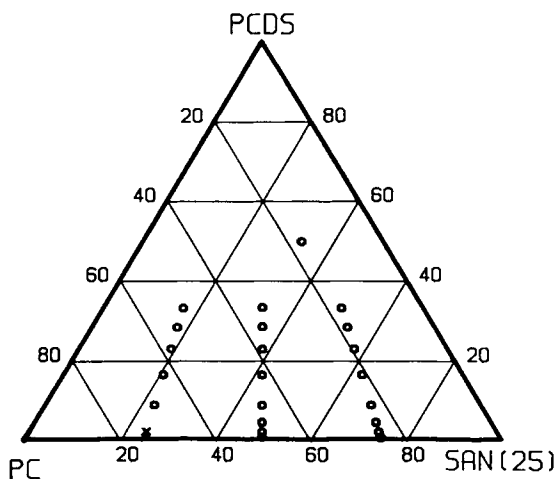


Fig. 16. Ternary diagram of the PCDS/SAN(25)/PC system. (○) Indicates compositions with one T_g . (×) Indicates compositions with two T_g 's.

cloudy due to measurable PC crystallization on addition of just 1% by weight PCDS.

The PC/SAN(13)/PCDS system (Fig. 17), shows essentially the same T_g and PC crystallization behaviors as shown by the SAN(25)-containing ternary described above. For blends with a PC/SAN ratio equal to three, 5% PCDS-containing blends are miscible when SAN(25) is used and immiscible when SAN(13) is used, and slightly higher PCDS content, between 5% and 9%, is required to solubilize the SAN(13)-containing system. To the extent that the copolymer AN content contributes to the partial miscibility of the PC/SAN binary,²² this result is expected. At other PC/SAN ratios, however, single T_g behavior is observed for SAN(13)-containing blends with PCDS concentrations as low as 1%, the limit of our investigation.

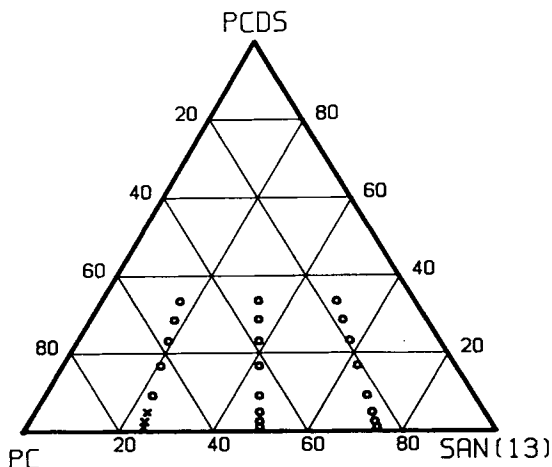


Fig. 17. Ternary diagram of the PCDS/SAN(13)/PC system. (○) Indicates compositions with one T_g . (×) Indicates compositions with two T_g 's.

SUMMARY AND CONCLUSIONS

Each of the three polyesters investigated, PCL, PBA, and PCDS, when combined with either SAN(25) or PC, is capable of promoting the single T_g behavior normally associated with the formation of a miscible binary solution. Each of these polyesters is similarly capable of promoting single T_g behavior in ternary mixtures when combined with normally immiscible PC and SAN at appropriate concentrations. Since the polyester concentrations required to promote this phenomenon are quite low in many compositions, problems associated with detection of closely spaced multiple transitions do not exist, and one can conclude that these polyesters do promote the formation of miscible ternary mixtures with PC and SAN(25).

Each ternary system investigated shows a region of compositions where two T_g 's or two amorphous phases exist. Generally, the regions of greatest immiscibility, those requiring the greatest amount of polyester to become miscible, occur at compositions rich in PC, and the transition from two-phase to single-phase behavior with increasing polyester content is often quite abrupt. Abrupt transition from two-phase to single-phase behavior is also observed for SAN-rich compositions, although the level of polyester required for this transition is relatively much less. That more PCL or other polyester is required to solubilize PC-rich compositions than is required to solubilize SAN-rich compositions is qualitatively reasonable in view of the experimental observation that B_{12} is more negative than B_{23} , however the model does not fit the miscibility boundary observed in the PCL-containing system. While it is possible to find B_{ij} parameters which will better predict the observed boundary, the parameters are so large, $B_{12} = -30$ cal/cc, $B_{23} = -0.39$ cal/cc, and $B_{13} = 7$ cal/cc in the case of PCL/SAN(25)/PC, that one must conclude that the simple model applied in this work is not adequate. Interestingly, this same problem has been observed in other attempts to apply Eq. (1) to describe the effects of polyester composition on the miscibility of polyesters with other polymers.^{9,31}

One can conclude that PCDS > PBA > PCL describes the rank order of solubilization efficiency of these polyesters with PC and SAN(25), because the least amount of PCDS is generally required to obtain a miscible ternary. PCDS and PCL both have five aliphatic carbons per ester linkage¹³ and should behave similarly in mixtures with other polymers, such as PC,¹⁰ where the interaction leading to negative B values involves the carbonyl ester. PBA has four carbons per ester linkage and could be expected to interact more strongly with PC than do the other polyesters. What is not clear, however, is the nature of the interaction between the polyester and SAN(25). Our PCL melting-point depression and miscibility boundary results suggest that this interaction is stronger than the PCL/PC interaction, and our comparison of the PCDS level required to solubilize SAN(13)/PC versus SAN(25)/PC suggests that the interaction does involve the acrylonitrile species on the SAN, but we have no information relating polyester structure to magnitude of interaction with SAN. Such information may need to be developed in order to understand the rank order observed.

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