Aliphatic Polyester Miscibility with Polyepichlorohydrin

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Synopsis

Based on the behavior of the glass transition for blends of polyepichlorohydrin with various aliphatic polyesters, miscible amorphous phases are formed in all cases when the ratio of aliphatic carbons to ester groups in the repeat unit is less than 10 but more than 2. This observation includes selected polyesters with branched and saturated cyclic units in their structure. Interaction parameters deduced from polyester melting point depression were all negative and showed a minimum within this range of polyester molecular structures. The composition dependence of the observed glass transitions was found to be severely influenced by the presence of polyester crystallinity in the blend when heated through the transition region.

INTRODUCTION

One aspect of recent research on polymer blends has been to discover new miscible pairs, to relate these observations to component molecular structure, and to understand the thermodynamic origin of the interaction mechanism responsible for miscibility. A fruitful approach has been to look for common structural features among reported examples of miscibility and to use these observations to construct generalizations that suggest other examples of systems which may exhibit miscibility. An excellent illustration of this is the many examples of miscibility noted among halogen-containing polymers (e.g., those based on vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, vinylidene fluoride, and chlorinated polyolefins) with those containing ester groups (e.g. polyesters, polyacrylates, and polymethacrylates) reported in the literature.[1-14]

An interesting singular example fitting this category is the observation by Brode and Koleske[15] that polyepichlorohydrin is miscible with poly(ϵ-caprolactone). Based on previous work,[2,16-18] it was clear to us that a range of other aliphatic polyesters would be similarly miscible with polyepichlorohydrin (PECH). Consequently, the purpose of this paper is to report on the validity of this speculation and to amplify on the effect polyester molecular structure has on the thermodynamic interaction parameter for these systems.

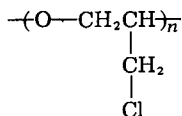## MATERIALS AND EXPERIMENTAL PROCEDURES

The polyepichlorohydrin

$$\text{--(O--CH}_2\text{CH)}_{\overline{n}}$$
$$|$$
$$\text{CH}_2$$
$$|$$
$$\text{Cl}$$

TABLE I
Summary of Polymers Used in This Work

Abbreviation	Polymer	Structure	Density (g/cm³)	Molecular weight	T_g (°C)	T_m (°C)	ΔH_f^0 (cal/g)	Source
PES 2	Poly(ethylene succinate)	$-(CH_2)_2-O-\overset{O}{C}-\overset{O}{C}-(CH_2)_2-O-$	1.32[a]	1500[a]	−15[b]	98[b]	—	SPP[c]
PEA 3	Poly(ethylene adipate)	$-(CH_2)_2-O-\overset{O}{C}-\overset{O}{C}-(CH_2)_4-O-$	1.21[a]	$\bar{M}_v = 1500$[a]	−47[b]	49.7[b]	29.2[d]	SPP
PBA 4	Poly(1,4-butylene adipate)	$-(CH_2)_4-O-\overset{O}{C}-\overset{O}{C}-(CH_2)_4-O-$	1.12[a]	$\bar{M}_v = 2500$[a]	−68[b]	57.3[b]	30.5[a]	SPP
PES 5	Poly(ethylene sebacate)	$-(CH_2)_2-O-\overset{O}{C}-\overset{O}{C}-(CH_2)_8-O-$	1.136[e]	—	−44[b]	72.6[b]	36.8[d]	—[f]
PCL	Poly(ε-caprolactone)	$-(CH_2)_5-\overset{O}{C}-O-$	1.095[a]	$\bar{M}_n = 15,500$[a] $\bar{M}_v = 40,500$ $\bar{M}_w = 46,700$	−68[b]	56.3[b]	34.6[g]	Union Carbide, PCl 700
PBS 6	Poly(butylene sebacate)	$-(CH_2)_4-O-\overset{O}{C}-\overset{O}{C}-(CH_2)_8-O-$	1.136[e]	$M_v = 2500$[e]	−62[b]	62.9[b]	37.0[h]	—[f]
PHS 7	Poly(hexamethylene sebacate)	$-(CH_2)_6-O-\overset{O}{C}-\overset{O}{C}-(CH_2)_8-O-$	1.03[a]	$\bar{M}_w = 16,500$[a]	−60[i]	66.3[b]	38.5[h]	SPP
PDOA 8	Poly(dodecamethylene adipate)	$-(CH_2)_{12}-O-\overset{O}{C}-\overset{O}{C}-(CH_2)_4-O-$	1.08[e]	$\bar{M}_v = 4,600$[e]	−58[h]	76.1[b]	39.2[h]	—[f]
PDS 9	Poly(decamethylene sebacate)	$-(CH_2)_{10}-O-\overset{O}{C}-\overset{O}{C}-(CH_2)_8-O-$	1.15[e]	$\bar{M}_v = 5,200$[e]	−58[h]	77.2[b]	39.9[d]	—[f]

		Structure		$\overline{M}_v = 5{,}300^e$				
PDEDE 10 or P-10	Poly(decamethylene decamethylene dicarboxylate)	$-(CH_2)_{10}-O-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_{10}-\overset{\displaystyle O}{\overset{\|}{C}}-O-$	1.10^h	$\overline{M}_v = 5{,}300^e$	—	81.1^b	41.0^h	—[f]
PDODE 11 or P-11	Poly(dodecamethylene decamethylene dicarboxylate)	$-(CH_2)_{12}-O-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_{10}-\overset{\displaystyle O}{\overset{\|}{C}}-O-$	1.10^h	—	—	88^b	—	—[f]
PDPS	Poly(2,2-dimethyl-1,3-propylene succinate)	$-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_2-\overset{\displaystyle O}{\overset{\|}{C}}-O-$	1.17^a	1000^a	-17^b	—	—	SPP
PDPA	Poly(neopentyl glycol adipate)	$-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{\|}{C}}-O-$	—	1000^a	-47.5^b	46^b	—	Hooker Chem. Co., Rucoflex polyester S-1016-55
PCDS	Poly(1,4-cyclohexane dimethylene succinate)	$-CH_2-\langle S \rangle-CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_2-\overset{\displaystyle O}{\overset{\|}{C}}-O-$	1.16^a	6000^a	-1^b	122.6^b	—	SPP
PECH	Polyepichlorohydrin	$-\overset{H}{\underset{\overset{CH_2}{\underset{Cl}{\|}}}{C}}-CH_2-O-$	1.36^e	$700{,}000^h$	-21.5^b	—	—	B.F. Goodrich Co., Hydrin 100

[a] J. E. Harris, Ph.D. dissertation, University of Texas at Austin, 1981.

[b] Measured by DSC.

[c] SPP = Scientific Polymer Products.

[d] D. W. Van Krevelan, Properties of Polymers, Elsevier, New York, 1976.

[e] Experimental value from this laboratory.

[f] Synthesized by E. M. Woo.

[g] O. Olabisi, L. M. Robeson, and M. T. Shaw, Polymer–Polymer Miscibility, Academic, New York, 1979, p. 311.

[h] Estimated value.

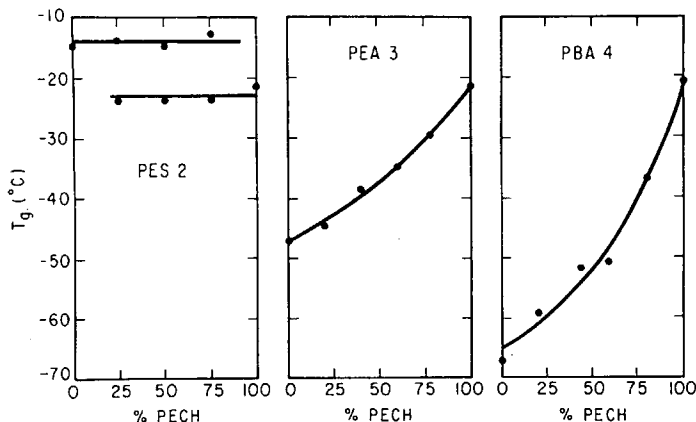[i] C. A. Cruz, Ph.D. dissertation, Univ. of Texas at Austin, 1978.

Fig. 1. Glass transition behavior for blends of PECH with PES 2, PEA 3, and PBA 4.

used in this study was obtained from the B. F. Goodrich Co. and is a commercial product marketed under the designation of Hydrin 100. This polymer does not crystallize. The aliphatic polyesters used to blend with PECH are described in Table I. Several of these polymers were synthesized in our laboratory by Woo.[19] The numerical value included as part of the code for many of the polyesters refers to the ratio of CH_2 to COO units in the repeat structure which has proved to be a useful means of organizing the observations on phase behavior.

Blends of the polyesters with PECH were prepared by solvent casting from toluene solutions containing about 10% polymer by weight. Due to the difficult dissolutioning of PECH, the mixtures were heated for several hours to obtain a homogeneous solution. The solutions were poured into aluminum pans and covered with perforated foil. After an appropriate period of evaporation at room temperature, the pans were placed in a vacuum oven set at 110°C for about 48 h to complete the removal of toluene. Visual observations of blend clarity were made while heating on a hot plate following a procedure described previously.[20]

Thermal characteristics were measured using a Perkin-Elmer DSC equipped with a computerized data station. In an initial series of experiments, blends of PECH with PBA 4, PES 5, and with PBS 6 (see Table I for code designations) and the pure linear polyesters were heated at 40°C/min to above 50°C above the polyester melting point and held there for about 5 min. These samples were subsequently quenched at 320°C/min using liquid nitrogen cooling and then heated again at 40°C/min. All other samples were heated at 20°C/min and quenched to 210°K using a mechanical intercooler. Glass transitions, melting points, and heats of fusion and crystallization were recorded on subsequent heats after the first one. A separate series of experiments using cyclic heating and cooling at 10°C/min were done to obtain information for melting point depression analysis.

PHASE BEHAVIOR

Glass transition information supplemented by visual observations was used to reach conclusions concerning the phase behavior of these blends. Information
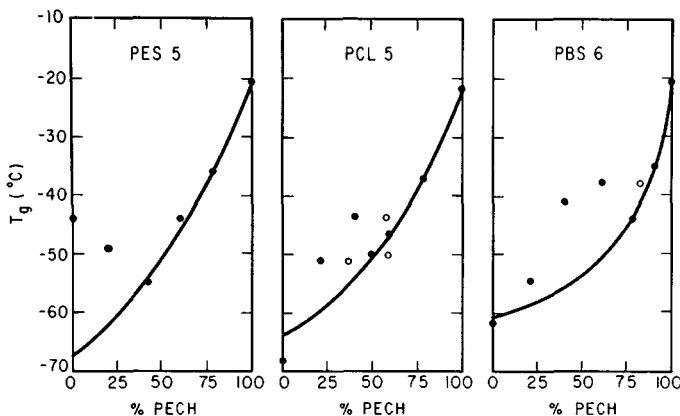
Fig. 2. Glass transition behavior for blends of PECH with PES 5, PCL 5, and PBS 6: (●) T_g values plotted vs. overall blend composition; (○) the same data plotted vs. amorphous phase compositions computed via eq. (3).

about the glass transitions of the pure component polymers is summarized in Table I for reference. Owing to their high levels of crystallinity, no glass transitions could be detected by DSC for PHS 7, PDOA 8, PDS 9, P-10, or P-11; however, a value for PHS 7 has been reported previously and it is included in Table I. Estimated values for PDOA 8 and PDS 9 are included in Table I.

The glass transition data for the various blend systems are plotted in Figures 1–5. The blends can be subdivided into three groups based on the number of glass transitions observed and how the glass transition is affected by blend composition.

Systems Showing Evidence for Multiple T_g's

Blends of PECH with PES 2 exhibit two glass transitions (Fig. 1) occurring at essentially the same temperatures as for the pure components. The blends were totally opaque at room temperature; however, they become less cloudy on heating past the melting point of PES 2 but never became as clear as the pure components even after heating to the highest possible temperature without decomposing the component polymers. Obviously, this pair is completely immiscible.

Blends with P-11 were quite cloudy at all temperatures up to the temperature range of decomposition. While only one T_g could be detected (Fig. 4), this value is essentially invariant from that of pure PECH. We believe that a second T_g corresponding to the pure polyester exists, but its magnitude is below the limits of detection owing to the high crystallinity of this component. Apparently, this pair is also completely immiscible.

Blends containing P-10 were never as clear as the pure components; however, above the polyester melting point, blends rich in polyester were more clear than those rich in PECH. Only one glass transition was actually observed for any given blend (Fig. 4). For blends rich in PECH, the T_g observed occurs at essentially the same temperature as for pure PECH; however, as the polyester content increases there is an appreciable decrease in the temperature at which the transition occurs. The exact location of the T_g in this composition region
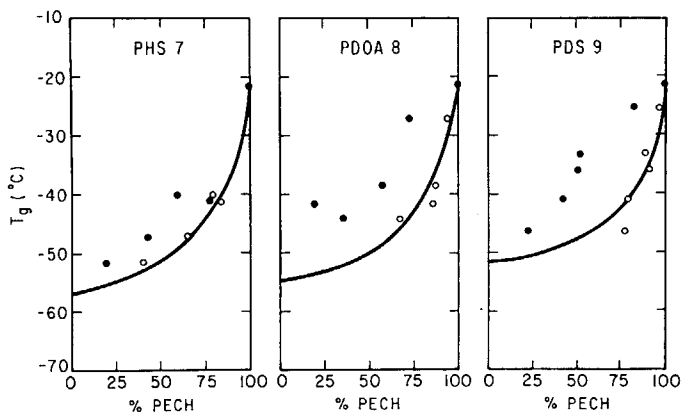
Fig. 3. Glass transition behavior for blends of PECH with PHS 7, PDOA 8, and PDS 9. Symbols have same meaning as in Figure 2.

depends on prior thermal history of the sample. Based on these observations we feel this system is close to the border of miscibility but has incomplete homogeneity.

Systems with a Single T_g Monotonic in Blend Composition

Blends of PECH with PEA 3 and with the polyesters having branched, PDPS and PDPA, or cyclic, PCDS, aliphatic structural elements within their repeat units exhibited a single glass transition which varies in a simple monotonic fashion with blend composition—see Figures 1 and 5. Based on this, each of these systems is concluded to be completely miscible.[21]

At room temperature, the PECH–PEA 3 blends are cloudy owing to the crystallinity of the polyester; however, above the melting point of the polyester all compositions became clear and remained so until heated to the temperature
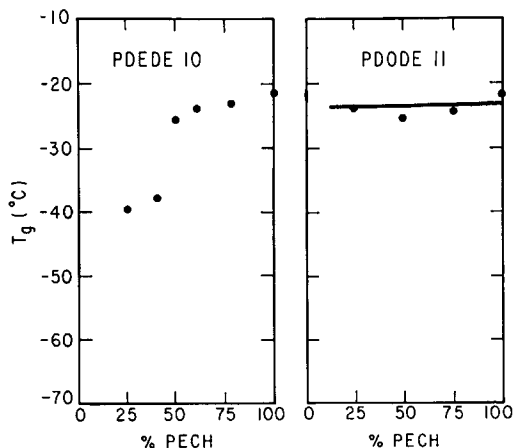

Fig. 4. Glass transition behavior for blends of PECH with PDEDE 10 and PDODE 11. In all cases, abbreviations used for the various polyesters are defined in Table I.
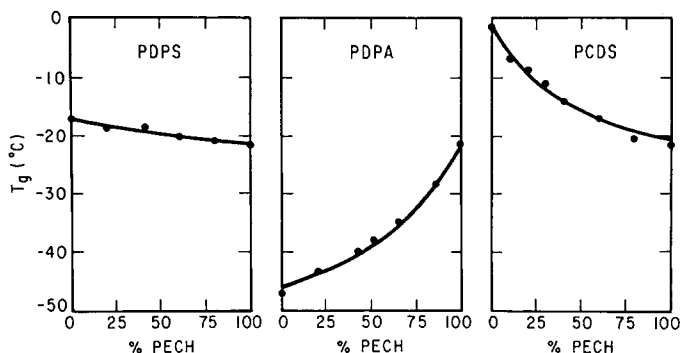
Fig. 5. Glass transition behavior for blends of PECH with various polyesters with branched or saturated cyclic units in their structures. These polyesters do not crystallize under the conditions used here.

range of decomposition. Blends of PECH with either PDPA or PDPS were clear at room temperature since these branched polyesters do not readily crystallize, and the blends remained clear on heating up to the point of decomposition. On the other hand, PCDS does crystallize slowly, and these blends were initially cloudy as cast; however, they became clear on heating above the melting point and remained so up to the point of decomposition. For this system, it was found that prolonged heating of the melt was helpful for achieving consistent glass transition behavior.

Each of these systems was completely amorphous at the glass transition during the heating part of the DSC experiment either because the polyester did not crystallize at all or because crystallization was so sluggish that it did not occur on the cooling part of the DSC cycle. The latter was the case for the PEA 3. The extreme left part of Figure 6 shows the magnitude of the crystallization exotherm, ΔH_c, and the melting endotherm, ΔH_f, obtained for this polymer on heating in the DSC. Since the magnitude of ΔH_f and ΔH_c are the same, this means the blends were completely amorphous as the glass transition was passed.

The freedom from any polyester crystallinity at the time the glass transition occurred is the reason for the simple monotonic nature of the composition dependence of T_g for these miscible blend systems. One may expect these simple
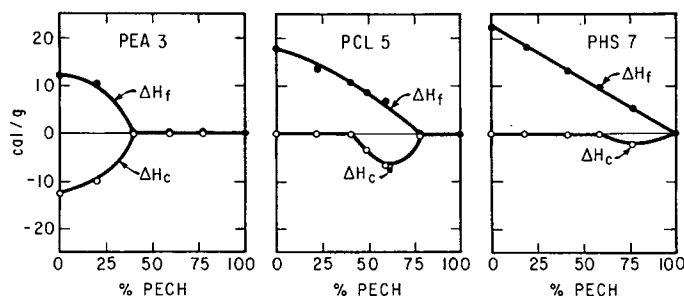

Fig. 6. Heats of fusion, ΔH_f, and crystallization, ΔH_c, for the polyesters shown when blended with PECH. Note that ΔH_f and ΔH_c are regarded as different in sign, i.e., endothermic vs. exothermic.
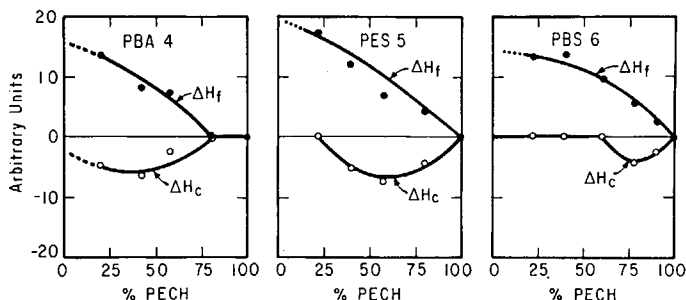
Fig. 7. Heats of fusion and crystallization for the polyesters shown when blended with PECH. Note that the units here are arbitrary in contrast to those in Figures 6 and 8.

T_g–composition plots to be described by simple relationships for mixtures or copolymers such as the Gordon–Taylor equation[8,9]

$$T_g = \frac{w_A T_{gA} + k w_B T_{gB}}{w_A + k w_B} \tag{1}$$

where k is a constant for each system and w_i and T_{gi} are the weight fractions and glass transitions for each component, respectively. For these systems the Gordon–Taylor parameter k was determined by fitting the experimental T_g data to eq. (1) in its linearized form. These values are given in Figure 9. More will be said about this plot later.

Systems with a Single T_g Not Monotonic in Blend Composition

All blends of PECH with linear polyesters having a CH_2/COO ratio between 4 and 9 exhibit a single glass transition situated between the values of the pure components, but the change in T_g with blend composition is not a simple monotonic one—see Figures 1–3. For high concentrations of the polyester component, the value of T_g observed is higher than one would expect. At room temperature all the blends were cloudy owing to polyester crystallinity; however, when heated above the melting point of the polyester, each blend became clear and remained so up to about 260°C, where decomposition became very rapid. We conclude that all of these polyesters are miscible with PECH in spite of the complex dependence of T_g on composition.

The nonmonotonic character of the T_g curves shown in Figures 1–3 for these systems is believed to be primarily a consequence of crystallinity of the polyester existing when the glass transition was traversed on heating in the DSC as described by Robeson et al.[22] Figures 6–8 show the observed heats of fusion, ΔH_f, and crystallization, ΔH_c, obtained during the second heating after the sample was quenched. These data are given in arbitrary units for the systems shown in Figure 7 since the thermal analysis data station was not operational when these samples were tested. All others are given in calibrated units of cal/g of the total sample. A sign convention of positive for endothermic and negative for exothermic is used throughout.

In the case of blends containing PEA 3, the polyester did not crystallize on cooling but it did on heating so $\Delta H_f + \Delta H_c = 0$, indicating no crystallinity below
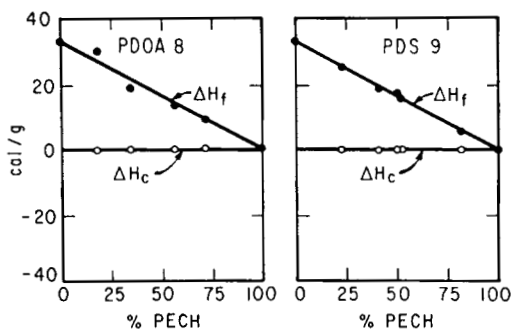
Fig. 8. Heats of fusion for the polyesters shown when blended with PECH. Note that zero values for ΔH_c indicate the polyesters crystallized completely on cooling in the DSC and did not crystallize further on heating in every case.

T_g. For all the other systems shown in Figures 6–8, crystallization of the polyester did occur on cooling in spite of the quenching conditions used. As a result, $\Delta H_c + \Delta H_f$ is greater than zero for some blend compositions especially those rich in polyester. The weight fraction of the total blend in the quenched state which is polyester crystals can be computed from

$$X_c = \frac{\Delta H_f + \Delta H_c}{\Delta H_f^0} \tag{2}$$

where ΔH_f° is the heat of fusion for the 100% crystalline polyester—values are listed in Table I. The extent of crystallinity developed during cooling is related to the crystallization kinetics for the system. This rate process is a function of chain mobility and is, therefore, influenced by the T_g of the blend. PECH has a higher T_g than all the polyesters considered here, but its value, −21.5°C, is not sufficiently high to greatly retard crystallization from its blends which is in contrast to other higher T_g polymers which have been blended with similar polyesters.[2,17,18] It is interesting to note in Figures 6–8 that the level of polyester crystallinity after quenching at a given blend composition generally increases as the CH_2/COO ratio for the polyester increases.

Crystallinity developed on cooling depletes the amorphous phase of some of the polyester component; hence, on heating, the T_g observed is that for an amorphous phase richer in PECH than the overall blend composition. This is the primary reason for the higher T_g's than expected when polyester crystallinity is present. In extreme cases, the variation in crystallinity with blend composition can actually result in a maximum in the plot of T_g vs. overall blend concentration. A second effect can also be operative which is that the T_g for some polymers, especially polyesters, is influenced by the level of crystallinity in the sample owing to restraints on chain mobility in the amorphous phase caused by the crystallites. As a result, the observed glass transition temperature may be significantly higher when such a polymer is semicrystalline than when it is completely amorphous. The results for PES 5 shown in Figure 2 seem to be an example of this effect. Similar behavior has been reported for poly(ϵ-caprolactone)[1] and for poly(ethylene oxide).[22]

In cases where ΔH_f and ΔH_c were measured in absolute units, the crystallinity of the polyester component, at the point the DSC trace passes the glass transition
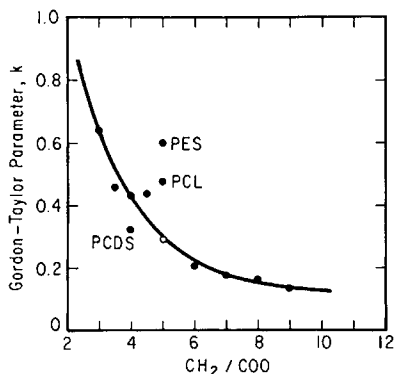
Fig. 9. Gordon–Taylor parameter deduced from regression analysis of T_g behavior as described in text. Note the distinction in the open and solid points for PCL as explained in the text.

on heating, can be calculated using eq. (2). By a simple material balance, the actual weight fraction of the polyester in the amorphous phase w' can be computed from the following:

$$w' = \frac{w - X_c}{1 - X_c} \tag{3}$$

where w is the total weight fraction of polyester in the blend. The observed T_g values are plotted versus the calculated amorphous phase compositions in Figures 2 and 3 for those cases where the requisite crystallinity data were available. The points are shown as open circles. The result is to shift each point to a higher fraction of PECH and to form a simple monotonic curve closer in shape to that expected for a miscible blend. The solid lines drawn in these cases are the best fit of the Gordon–Taylor equation to these adjusted data. Where this adjustment in the amorphous phase composition could not be made, viz., blends containing PBA 4, PES 5, and PBS 6, the Gordon–Taylor equation was fitted to the data for blends rich in PECH ignoring compositions which had large amounts of polyester crystallinity after quenching. Except in the case of PES 5, the polyester glass transition shown in Table I was used as part of the data base for the regression analysis to obtain the Gordon–Taylor parameter k. The value of T_g used for the polyester has a significant effect on the k obtained as can be seen for PCL in Figure 9. The solid point in Figure 9 for PCL was computed including the PCL T_g in the regression data base, whereas the open point for PCL was calculated excluding this value and using data for amorphous blends or those whose amorphous phase compositions were corrected for crystallinity.

In general, the Gordon–Taylor parameters deduced for these blends form a somewhat regularly decreasing trend as the CH_2/COO ratio for the polyester increases as seen in Figure 9. It has been suggested that k reflects the thermodynamic interaction between blend components[8,9]; however, as seen in the next section, the relation of k to polyester molecular structure is quite different from that for the interaction parameter deduced from melting point depression analysis.

MELTING POINT DEPRESSION ANALYSIS

One of the simplest approaches for gaining quantitative information about the thermodynamic interactions between polymeric components forming miscible blends is by analysis of the depression of the melting point of one of the components should one or more form a crystalline phase.   However, as pointed out by Morra and Stein,[23,24] this approach must be used with caution since the lamella thicknesses of the crystallites are usually finite and the interaction parameter may be composition-dependent.   With these limitations in mind, we have used the melting behavior of the various polyesters in blends with PECH as an estimate of the interaction parameter to gain at least a rough quantitative picture of the effect polyester molecular structure has on the thermodynamics of these systems.

A simple treatment of melting point depression using the Flory–Huggins model gives

$$\Delta T_m = T_{m2}^0 - T_{m2} = -T_{m2}^0 (V_{2u}/\Delta H_{2u})B\phi_1^2 \tag{4}$$

when both components have large molecular weights and where B = interaction energy density, ϕ_1 = volume fraction of PECH, T_{m2}^0 = melting point of the pure polyester, and $(\Delta H_{2u}/V_{2u})$ = the heat of fusion per unit volume for 100% crystalline polyester.   Information used to convert weight fractions into volume fractions and to evaluate $(\Delta H_{2u}/V_{2u})$ is given in Table I.

The melting point data for this analysis were obtained by noting the polyester melting endotherm peak during cyclic heating and cooling at 10°C/min between the limits of 220°K and 50°C above the melting point.   No attempt was made to correct these melting data for finite lamella thickness by Hoffman–Weeks plots since this would have inordinately expanded the scope of this work and because separate studies on related systems have suggested that this correction only affects the absolute value of the interaction parameter without significantly altering the trend with respect to polyester molecular structure.[19]   This approximation is only safe when care is taken to crystallize the samples in exactly the same way for each system, e.g., such as the procedure described earlier.   No evidence was found for a strong composition dependence of the interaction parameter B. Relaxation of the assumption of large molecular weights for both components changes the estimate of B by no more than 6% in the extreme case for the present systems so this effect has been ignored in these calculations in view of the other approximations made.

The experimental values for B deduced in the manner described above are plotted in Figure 10 vs. the CH_2/COO ratio for the polyester component.   No values could be obtained for the branched or cyclic polyester containing blends since these produced no crystallinity using the cyclic heating/cooling scheme employed.   No data are reported for blends containing PES 5 owing to the erratic crystallization/melting behavior of this polyester even in the pure state.   In two cases, bars are shown rather than points to indicate the limits of data scatter which existed in these instances.   Multiple melting peaks occurred in some cases such as PCL; however, a consistent value of B was found by treating each peak separately.

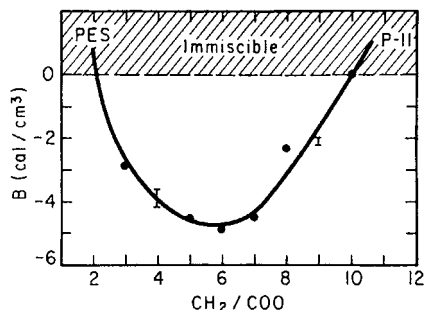The solid line constructed through the data points in Figure 10 was drawn

Fig. 10. Interaction parameters deduced from polyester melting point depression information. The curve was drawn by eye using the fact that the interaction parameter must be positive at the extreme ends of the CH_2/COO scale owing to the immiscibility with PECH of the polyesters designated in the crosshatched region.

taking into consideration that polyesters with the extreme CH_2/COO ratios of 2 and 11 were found to be completely immiscible with PECH; hence, their interaction parameters while unknown must be positive. Note that blends with polyester with $CH_2/COO = 10$ showed essentially no melting point depression and, thus, based on the T_g pattern shown in Figure 4, it is included that B must be zero or slightly positive in this case. Using these facts, the shape of the line drawn in Figure 10 is entirely reasonable and points to the fact that there is a "window" in the structure of aliphatic polyesters which forms miscible blends with PECH.[25]

SUMMARY

Based on the behavior of the glass transition temperature, it has been shown that aliphatic polyesters having three to nine aliphatic carbons per ester group in the repeat structure form completely miscible amorphous phases with polyepichlorohydrin. Linear polyesters having a CH_2/COO ratio of 2 and 11 are completely immiscible with PECH while for a ratio of 10 partial miscibility may exist. Nonlinear polyesters with aliphatic carbon to ester ratios in this range were also found to be miscible with PECH. Crystallinity of the polyester was found to alter substantially the composition dependence of the glass transition of these miscible blends; however, when the blend T_g is plotted vs. the actual composition of the amorphous phase, a more normal curve was obtained. The T_g–composition curves were adequately described by the Gordon–Taylor equation with an adjustable parameter that varied rather systematically with the structure of the polyester.

Melting point depression analysis was used to estimate the interaction parameter for PECH with the various polyesters which crystallized in a regular enough fashion. These results combined with the observations that polyesters having CH_2/COO ratios of 2 or less and 10 or more are not completely miscible with PECH lead to the conclusion that the interaction parameter exhibits a minimum and is only negative for a finite window of polyester molecular structures. These polyesters have similar miscibility windows in blends with some other polymers.[17,19,26] This pattern of behavior is not yet well understood;

however, it is clear that multiple segmental interactions must be involved in order to explain the existence of an optimum polyester structure. In addition to intermolecular interactions between structural units in polyepichlorohydrin and the CH_2 and COO units in the polyester, the intramolecular interactions between CH_2 and COO units within the polyester may be an influential factor as pointed out recently.[25] For poly(vinyl chloride)/polyester mixtures, two possible specific interactions can be envisioned both of which involve the polyester carbonyl. One considers the polarization of the PVC hydrogen α to the chlorine and subsequent hydrogen bonding with the carbonyl while the other considers a direct dipolar-type interaction between the chlorine and the carbonyl. The former mechanism would be somewhat more complex for polyepichlorohydrin than PVC owing to the fact that there are two hydrogens α to the chlorine and to the presence of the oxygen in the chain. Regardless of the exact mechanism of the interaction between the carbonyl and the polyepichlorohydrin, or PVC, there must also be competition for these sites to interact with themselves. The net heat of mixing is the result of proper consideration of all possible interactions after mixing compared to those which existed before mixing, and it is this which makes behavior like that seen in Figure 10 possible.

References

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