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Miscibility in Binary Blends of Poly(vinylphenol) and Aromatic Polyesters

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ABSTRACT: The effect of polymer structure on blend miscibility with poly(vinylphenol) (PVPh) has been studied for a variety of polyesters that contain aromatic moieties in their backbone. In general, polyesters derived from aliphatic diols showed evidence of interaction and miscibility with PVPh. However, immiscibility was observed if the aromatic content of the polyester was very high. Polyesters derived from aromatic-containing diols generally showed little interaction and no miscibility with PVPh. Both solution-blending and melt-blending methods were utilized to prepare the blends. Good correlation between the thermal behavior and infrared results was observed. Miscibility of PVPh was observed with polyesters consisting of terephthalic acid and a mixture of ethylene glycol and 1,4-cyclohexanedimethanol moieties for copolymer compositions containing at least 20 mol % ethylene glycol. Miscibility was observed with poly(ethylene terephthalate), poly(butylene terephthalate), poly(2,2-dimethylpropylene terephthalate), poly(ethylene 2,6-naphthalenedicarboxylate), and a copolymer of terephthalic and pentanedioic acids with 1,2-propanediol and glycerol as well as with several cyclic aliphatic copolyesters containing 1,4-cyclohexanedicarboxylic acid. Miscibility of PVPh was not observed with poly(1,4-cyclohexylene dimethylene terephthalate), Ardel D100, Eastman Kodar copolyester A150, several other polyesters with high aromatic content, and two liquid crystalline polyesters.

Introduction

The science and technology of polymer blends has emerged as a major tool for designing and improving polymeric materials.[1] Virtually all classes of commercial polymers have been blended with other polymers to improve their physical and chemical properties, such as modulus, toughness, processability, barrier properties, and chemical resistance, while at the same time offering lower cost and/or added value. Polymers may be miscible and form a single homogeneous phase when blended. Alternatively, they may be immiscible and phase separate when mixed. Each class has properties that are suitable for different applications. For example, homogeneous blends retain optical clarity, which is needed for packaging and optical applications, while two-phase blends have applications ranging from rubber-toughened plastics and composites to mixtures of recycled polymers.

The degree of interaction of two polymers is best described by polymer blend thermodynamics. The fundamental thermodynamic quantity that controls polymer blend miscibility is ΔG_m, the free energy of mixing, which contains enthalpic (ΔH_m) and entropic (ΔS_m) contributions:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

At equilibrium, for a blend to be a single phase the requirement that $\Delta G_m < 0$ must be fulfilled. Additionally, the second derivative of ΔG_m with composition must be nonnegative. For high molecular weight polymers (which have large molar volumes), the combinatorial entropy terms are small. Therefore, enthalpic contributions often dominate the free energy of mixing in polymeric systems. When only dispersive or van der Waals forces are present, the enthalpy of mixing will almost always be positive or zero, ultimately leading to contributions to ΔG_m, which are unfavorable to mixing. In general, to exhibit miscibility, there needs to be some degree of interaction between the polymers, resulting in a favorable (exothermic) heat of mixing. Indeed, as is shown below, miscibility is often observed only when there is significant interaction between the constituent polymers. For immiscible polymers, the morphology and properties of the blend are determined in large part by the interaction, interface, and adhesion between the polymers. The introduction of interacting groups by chemical modification of a polymer or by copolymerization leads to negative contributions to the enthalpy of mixing. This has been shown to lead to improved miscibility of an otherwise incompatible polymer pair. Many novel and useful blends have been formed in this manner.[1]

There exists a fair amount of work in the literature concerning the miscibility of poly(vinylphenol) (PVPh) with other polymers. In general, most of the studies have used either random copolymers of styrene and vinylphenol or the VPh homopolymer itself. A number of polymers containing carbonyl groups have been found to be miscible with PVPh. Among these acceptor polymers are poly(vinyl acetate) and poly(ethylene-*co*-vinyl acetate) random copolymers,[2] main-chain aliphatic polyesters,[2] poly(*N*-vinylpyrrolidone),[3,4] aliphatic polyketones,[5] polyamides,[6] polyacrylates,[6,7] and polypeptides.[8] Other polymers that contain hydrogen bond accepting groups and have been found to be miscible with PVPh are poly(ethylene oxide),[3,9] poly(vinyl alkyl ethers),[3,10] etheric polyphosphazenes[11] and itaconates,[12] and poly(vinylpyridine).[13] PVPh was also found to be compatible with a number of other thermoplastics in a study by the Maruzen Oil Co.[14] A survey of the miscibility of PVPh with a number of classes of polymers, including polyamides, polyimides, polyurethanes, polyesters, cellulose esters, polycarbonates, and polysulfones has previously been conducted in our laboratories.[15] The present work focuses on the phase behavior of polyesters that contain aromatic moieties (see Table I) with PVPh; to date, the miscibility of these polymers has not been reported.

In some of the above studies the PVPh polymer used was of extremely low molecular weight and of broad molecular weight distribution; typically, M_w = 1500–7000.

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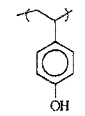
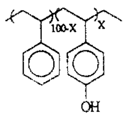
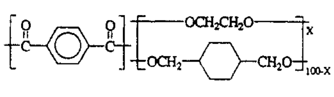
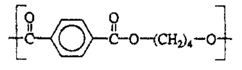
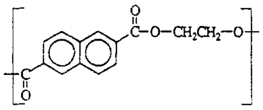
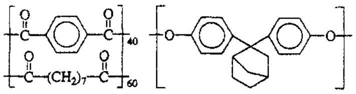
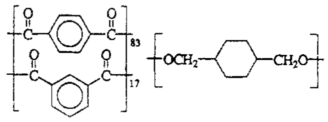
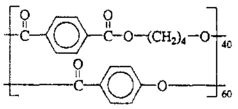
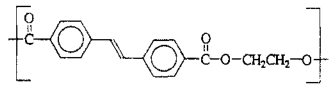
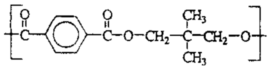
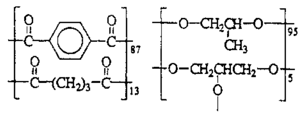
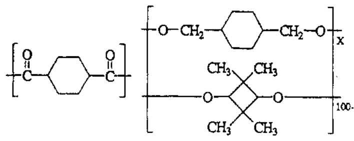
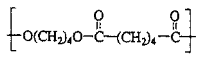
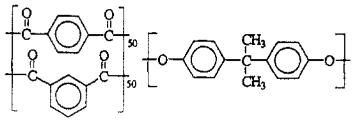
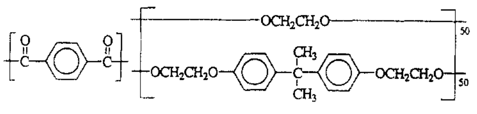
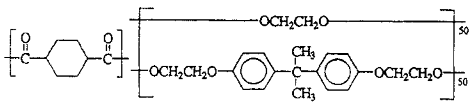
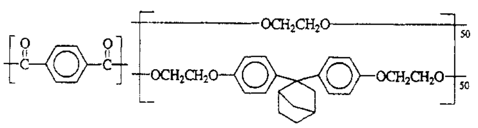
Table I. Polymer Structures and Characterization

abbreviation	structure	molecular weight characterization
PVPh		M_w 67.5K; M_n 37.9K[a]
P(S-VPh(X))		
X = 22		M_w 95.6K; M_n 48.4K[a]
X = 42		M_w 157K; M_n 66.2K[a]
PCT (X = 0)		IV 0.775[b]
T-C(17)E (X = 17)		IV 0.750[b]
T-C(29)E (X = 29)		IV 0.775[b]
T-C(50)E (X = 50)		IV 0.791[b]
T-C(66)E (X = 66)		IV 0.740[b]
PET (X = 1)		IV 0.621[b]
PBT		
PEN		
T(60)A-Nb		
T(17)I-C (Kodar A150)		
TB-(60)Hb		
S-E		
T-Ne		
T(13)G-P(5)GL		IV 0.4[c]
Cy-Cb(X)C (X = 30) Cy-C (X = 100)		
PBA		
T(50)I-BPA (Ardel D100)		
T-E(50)BPAE		
Cy-E(50)BPAE		
T-E(50)Nbe		

[a] GPC, polystyrene equivalents, protected phenol. [b] Inherent viscosity measured in 60 wt % phenol/40 wt % 1,1,2,2-tetrachloroethane, 25 °C, 0.5 wt %. [c] Inherent viscosity measured in phenol/chlorobenzene (1/1), 25 °C, 0.5 wt %.

Molecular weight effects are known to be very important in the phase behavior of polymer blends. A lowering of the molecular weight is often accompanied by an increase in the miscibility of the polymers, owing to the larger contribution of the combinatorial entropy term in eq 1 at lower molecular weights. The molecular weights of high-performance polymers and blends are typically much higher than those for which many of these previous PVPh blend studies have been conducted.[2,3,5,7a,b,8,9,13,14] Therefore, to ensure that the phase behavior observed in the present study is representative of the thermodynamic miscibility that would be found in practical polymers having higher molecular weights, a high-molecular-weight PVPh was prepared and used throughout the experiments.

The experimental approaches used are differential scanning calorimetry (DSC), solid-state NMR spectroscopy, and FTIR spectroscopy. These allow us to determine the phase behavior of the blends as well as to examine the molecular origins of the observed behavior.

Experimental Section

The polymers studied, including structures and available characterization data, are listed in Table I. The polyester nomenclature has been generalized so that the first part of the abbreviation, separated by a hyphen, represents the diacid monomer of the polyester. The symbols after the hyphen represent the diol portions of the copolyester. The number in parentheses gives the mole percent of the monomer that follows. Thus, T-C(*X*)E is a copolymer prepared from terephthalic acid (T) and a mixture of ethylene glycol (E) and *X* mol % of 1,4-cyclohexanedimethanol (C).

The blends of each of the polymers with poly(vinylphenol) were prepared either by solution- or melt-blending techniques, as indicated in Table II. The solution technique involved dissolving each polymer separately in a solvent common to both. Then the solutions were combined in the appropriate ratios and were either precipitated into a nonsolvent (hexane) or were knife-cast. Following coating or precipitation, the blends were dried, typically at 60–70 °C under vacuum for 48 h, before investigation by thermal analysis. The melt mixed blends were prepared by grinding each polymer to a fine powder using a Retsch grinder (with liquid nitrogen cooling, when necessary). The powders were mixed by hand in a 1:1 weight ratio and were dried under vacuum for at least 24 h at 105 °C immediately prior to extrusion. Melt extrusion was done using a Microtruder laboratory extruder (from Randcastle, Inc.) equipped with a single $^1/_4$-in. screw and a 2-in. slit die. The screw speed was 75 rpm and the extrusion temperatures for each blend are listed in Table II. Use of this type of extruder allowed for small sample quantities to be mixed, typically in the range of 4–20 g per blend.

The glass transition temperatures (T_g) and melting points (peak values) (T_m) were determined at a heating rate of 20 °C/min by DSC for each homopolymer and blend on a Perkin-Elmer DSC7. The onset, midpoint, and, for homopolymers and single-phase blends, the magnitude of the change in heat capacity at the T_g

Table II. Miscibility Results for Blends

polymer 2	blend ratio PVPh/poly 2	preparation method	T_{g1}/T_{g2} (onset) (°C)	T_{g1}/T_{g2} (mid) (°C)	ΔC_{p1} (J/g °C)	comments[a]
(PVPh)	pure		183	188	0.42	amorphous (A)
PBA	pure		−67	−64	0.48	crystalline (C)
	1:3	ppt from THF into hexane	−46	−37	0.45	(C)
	1:1	ppt from THF into hexane	−2	19	0.45	(A)
	3:1	ppt from THF into hexane	97	109	0.27	(A)
PET	pure		77	80	0.33	T_c = 168 °C, T_m = 249 °C
	1:1	melt at 254 °C	117	126	0.42	T_c = 200 °C, T_m = 236 °C
T-C(66)E	pure		78	82	0.28	(A)
	1:1	melt at 260 °C	122	129	0.36	(A)
T-C(50)E	pure		81	85	0.24	(A)
	1:3	ppt from 6/4 CH_2Cl_2/THF	114	125	0.32	(A)
	1:1	ppt from 6/4 CH_2Cl_2/THF	137	145	0.34	(A)
	3:1	ppt from 6/4 CH_2Cl_2/THF	145	172	0.40	(A)
T-C(29)E	pure		86	89	0.25	(A) (T_m = 236 °C)
	1:1	melt at 260 °C	136	144	0.35	(A)
T-C(17)E	pure		88	92		(C) T_m = 257 °C
	1:1	melt at 282 °C	94/158	105/165		(C) T_c = 158 °C, T_m = 264 °C
PCT	pure		92	103		T_m = 286 °C
	1:1	melt at 293 °C	96/175	107/181		T_c = 145 °C, T_m = 288 °C
PBT	pure		39	42		(C) T_m = 223 °C
	1:1	melt at 293 °C	94	103	0.34	(A) T_c = 163 °C, T_m = 216 °C
PEN	pure		119	124		(C) T_m = 260 °C (small)
	1:1	melt at 230 °C	141	149		(C) T_m = 260 °C (small)
T(60)A-Nb	pure		149	156	0.17	(A)
	1:1	melt at 293 °C	141/182	148/187		(A)
	1:3	cast from THF	135/183	144/187		(A)
	1:1	cast from THF	136/181	145/186		(A)
	3:1	cast from THF	137/183	144/187		(A)
Ardel D100	pure		183	191	0.18	T_g is too close to that of PVPh
	1:1	ppt from THF into hexane	181	188	0.37	blends were analyzed by NMR
Kodar A150	pure		89	93		(C) T_c = 166 °C, T_m = 265 °C
	1:1	melt at 277 °C	92/168	101/177		(C) T_c = 172 °C, T_m = 264 °C
T-Ne	pure		47	50	0.29	(A)
	1:1	melt at 210 °C	109	118	0.34	(A)
Cy-C	pure		60	65	0.18	T_c = 130 °C, T_m = 212 °C
	1:1	melt at 254 °C	128	135	0.26	(A)
Cy-Cb(30)C	pure		100	108	0.13	(A)
	1:1	melt at 254 °C	158	164	0.29	(A)
T(13)G-P(5)GL	pure		59	63	0.32	(A)
	1:1	melt at 210 °C	107	116	0.37	(A)
T-E(50)BPAE	pure		79	82	0.35	(A)
	1:1	melt at 254 °C	74/156	78/167		(A)
Cy-E(50)BPAE	pure		45	48	0.27	(A)
	1:1	melt at 254 °C	100	108	0.34	(A)
T-E(50)Nbe	pure		114	119	0.28	(A)
	1:1	melt at 254 °C	111/171	116/178		(A)
TB-(60)Hb	pure					liquid crystalline (LC)
	1:1	melt at 282 °C				
S-E	pure					LC, T_{m1} = 250 °C, T_{m2} = 276 °C
	1:1	melt at 282 °C				LC, T_{m1} = 251 °C, T_{m2} = 279 °C

[a] State as prepared.

(ΔC_p) were taken from the trace of the second or subsequent runs and are reported in Table II. Care was taken to ensure that semicrystalline polymers and their blends were quenched in liquid nitrogen prior to reporting their thermal data.

All FTIR spectra were obtained using a Bio-Rad (Digilab Division) FTS-7 spectrometer (3240-SPC) at a resolution of 4 cm^{-1}. The spectra were obtained at ambient temperature in a nitrogen atmosphere. Samples of the solvent-cast polymers and blends were prepared by spin-casting the 5 wt % polymer solution onto a KBr disk at ca. 1000 rpm, followed by drying at 70 °C under vacuum for several hours. FTIR spectra of the melt-processed blends were obtained by photoacoustic spectroscopy. The blends were ground to powders, and 2048 scans per sample were acquired. The data were digitally smoothed using the Savitsky–Golay smoothing algorithm. The smoothed data are plotted in the figures.

NMR spin–lattice relaxation times in the laboratory and rotating frames (T_1 and $T_{1\rho}$) were measured on a Bruker CXT-100 spectrometer, using techniques previously described.[16] The samples examined were portions of the same blends prepared for study by thermal analysis.

Results and Discussion

Solution Blends. Two blends with PVPh, prepared via solution techniques, showed a single T_g over all compositions: poly(butylene adipate) (PBA) and T-C(50)E, which is a copolymer of terephthalic acid and a 50/50 mixture of ethylene glycol and 1,4-cyclohexanedimethanol moieties. PBA is an all-aliphatic polyester, used as a comparative example; it had previously been shown to be miscible with PVPh.[2c] The blend T_g behavior is shown in Figure 1. In Figure 1a, the onset, midpoint, and end point of the glass transition region are plotted against composition and show both the composition dependence and the fact that, although only a single T_g is observed with the blends, the glass transitions are broader than those of the homopolymers. This is a common phenomenon in blends of miscible polymers.[1] In Figure 1a, the lines are drawn only as a visual guide. The plot in Figure 1b compares the T_g midpoints with the predictions of the Fox[17] and Couchman[18] equations, given below, neither of

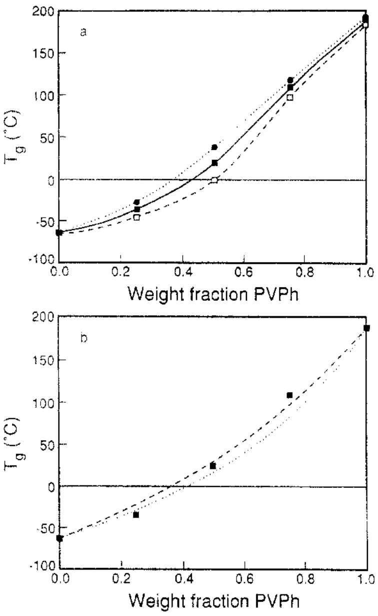


Figure 1. (a) Composition dependence of T_g for PVPh/PBA blends: (□) onset, (■) midpoint, and (●) end point of the DSC trace. (b) Theoretical fits to the data: (■) midpoint DSC data, (···) Fox equation, and (– – –) Couchman equation.

which has any adjustable parameters.

$$\text{Fox:} \quad 1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (2)$$

$$\text{Couchman:} \quad \ln T_g = \{w_1 \ln(T_{g1}) + (\Delta C_{p2}/\Delta C_{p1})w_2 \ln(T_{g2})\}/\{w_1 + (\Delta C_{p2}/\Delta C_{p1})w_2\} \quad (3)$$

Owing to the relatively large ΔC_p of PVPh, the Couchman theory predicts slightly higher T_g values at all compositions than does the Fox equation. The observed midpoints are below both theories at lower weight fractions of PVPh and above both theories at higher weight fractions of PVPh, owing to a slight sigmoidal shape to the actual T_g data for this blend. This sigmoidal shape has been observed before for this blend[2c] and for blends of PVPh with other low-T_g polymers.[9,11,12] Other theoretical expressions[19] for the composition dependence of T_g have recently proven to be successful in fitting data for blends where there is significant interaction between the components and could be used for a more complete analysis of the present data. However, given the relatively few compositions examined for most blends, little insight would be gained from this exercise.

The behavior of the T-C(50)E copolyester blend with PVPh, prepared via coprecipitation from solution, is summarized in Figures 2 and 3. Figure 2a shows a monotonically increasing T_g with PVPh content, with a rather broad transition at 75 wt % PVPh. Once again, the lines are drawn only as visual guides. A broadening of the T_g is observed in these blends, particularly for the blend containing 75 wt % PVPh. This may be revealing a degree of heterogeneity at the segmental level to which the DSC glass transition and dynamic mechanical and dielectric relaxations are sensitive.[1] There is a slightly concave-downward curvature to the compositional dependence of the T_g, which is predicted rather well by the Couchman theory, as shown in Figure 2b. This concave-downward curvature is a manifestation of the fact that, despite its higher T_g, PVPh has a ΔC_p value of nearly twice that of T-C(50)E, which leads to a weighting of the blend T_g in favor of PVPh. The composition dependence of the ΔC_p is shown in Figure 3; the line is drawn as a visual guide. Within the limits of precision of the data, the dependence is additive or slightly higher than additive.

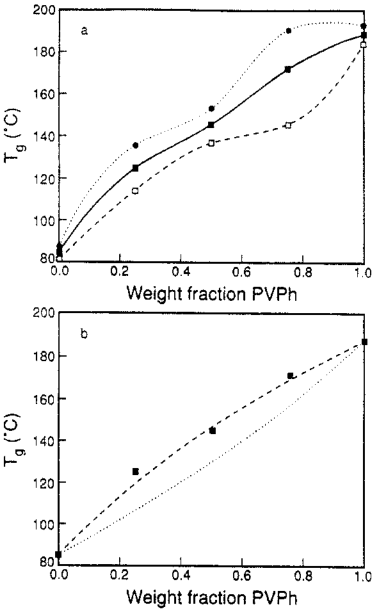


Figure 2. (a) Composition dependence of T_g for PVPh/T-C(50)E blends: (□) onset, (■) midpoint, and (●) end point of the DSC trace. (b) Theoretical fits to the data: (■) midpoint DSC data, (···) Fox equation, and (– – –) Couchman equation.

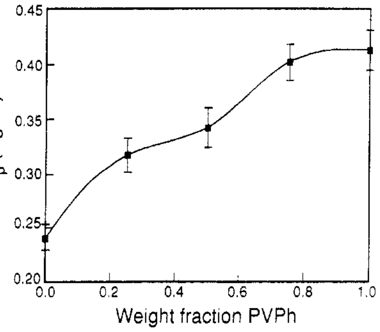


Figure 3. Composition dependence of ΔC_p for PVPh/T-C(50)E blends.

In summary, the PVPh/T-C(50)E blend system showed single-phase behavior across the composition range, with the magnitude of T_g being greater than additivity, in agreement with the Couchman theory.

Two other blends were prepared from solution and were found to exhibit no miscibility. These were blends of PVPh with T(60)A-Nb and Ardel D100. Both results were verified by preparing the blends via melt extrusion. The T_g for Ardel D100 is very close in value to that for PVPh. Therefore, the miscibility of these polymers was determined by NMR and will be discussed later.

Melt Blends. The results of the thermal analysis for the binary blends of PVPh with each of the polyesters, prepared via melt mixing, are presented in Table II. In particular, several aromatic polyesters were miscible with PVPh. PVPh was found to be miscible with poly(butylene terephthalate) (PBT), poly(2,2-dimethylpropylene terephthalate) (T-Ne), poly(ethylene 2,6-naphthalenedicarboxylate) (PEN), Cy-E(50)BPAE, a copolymer of terephthalic and pentanedioic acids with 1,2-propanediol and glycerol [T(13)G-P(5)GL], two aliphatic but cyclic copolyesters [Cy-Cb(30)C and Cy-C], and several polyesters from the T-C(X)E series. The latter will be discussed in more detail below. PVPh was not, however, miscible with PCT, Ardel D100, Eastman Kodar copolyester A150, T(60)A-Nb, T-E(50)BPAE, T-E(50)Nbe, and two liquid crystalline polyesters [TB-(60)Hb and S-E]. The structures for these are shown in Table I.

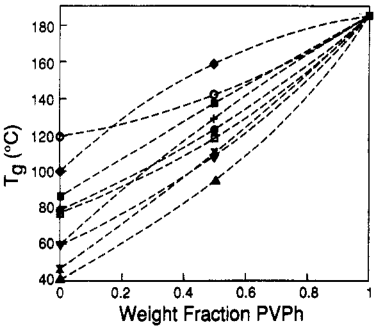


Figure 4. Composition dependence of T_g (DSC onset) for melt blends of PVPh with polyesters: (□) PET; (○) PEN; (▲) PBT; (×) T-Ne; (■) T-C(29)E; (●) T-C(66)E; (▼) T(13)G-P(5)GL; (+) Cy-C; (♦) Cy-Cb(30)C.

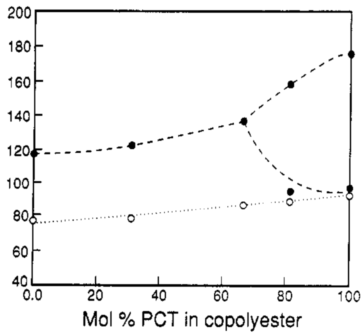


Figure 5. Composition dependence of T_g (DSC onset) for (○) the T-C(X)E copolyesters and for (●) 50/50 wt % blends of the copolyesters with PVPh.

The reasons for which PVPh is miscible with some of these polyesters and not with others are not entirely clear at this time, and their elucidation is beyond the scope of the present investigation. However, it seems that the copolyesters that are derived from aliphatic diols, as opposed to aromatic diols, are more miscible with PVPh. T-E(50)BPAE does contain an aliphatic ester bond in the diol portion as well as a large aromatic moiety within the diol portion. It is interesting that replacing the terephthalic acid portion of this polyester by a 1,4-cyclohexanedicarboxylic acid unit induces miscibility. This may suggest that it is a balance of aromatic and aliphatic character that determines the miscibility with PVPh; the more aromatic character in the polyester, the more difficult it is for the favorable interactions between the ester groups and the PVPh to develop and drive miscibility of these polymers. The miscibility of poly(hydroxy ether of Bisphenol A) (Phenoxy) with aliphatic and aromatic polyesters has been examined previously.[20] Among others, Phenoxy was shown to be miscible with PBT and Kodar A150, and it was suggested that an optimum density of ester groups in the polyester was necessary for achieving maximum interaction with the Phenoxy.

The composition dependencies of the glass transition temperature for the miscible polymer pairs are summarized in Figure 4. No fits to a theoretical equation were performed since for most of the blends only the 1:1 composition was studied; the dashed lines are drawn as visual guides. This was necessary due to limited quantities of PVPh available for these experiments. The T_g vs composition curves for almost all of the miscible polyester/PVPh blends show negative deviations from additivity, with a few interesting exceptions. Blends with T-C(29)E, which is an amorphous polyester, show a slight positive deviation from additivity, and the PVPh blends with the two cycloaliphatic copolyesters, Cy-Cb(30)C and Cy-C, show strong positive deviations from additivity.

The blend of PVPh with Ardel D100 had constituent T_g values too close to be resolved by DSC. These were examined further by NMR. Nuclei that are physically close in a solid (within a few angstroms) are tightly coupled by dipolar interaction. They relax as a unit from a perturbation of the nuclear system. Thus in a polymer blend that is mixed at the molecular level, all protons relax together. Conversely, in a phase-separated blend the protons in the two types of polymers are relatively isolated and relax at different rates. Observation of different relaxation times for the protons associated with the components of a polymer blend is a clear indication that the components are phase separated. Observation of the same relaxation time for each component may be indicative of mixing, but could also be coincidental. Measurement of the proton relaxation times in the pure components can help to clarify the situation.

Two types of relaxation may be followed. The spin-lattice relaxation time T_1 characterizes the return of the nuclear system to equilibrium following a single inverting radio-frequency pulse. The spin–lattice relaxation time $T_{1\rho}$ measures the rate of relaxation of the nuclear system during a time when radio-frequency irradiation is still being applied. Generally, the value of the proton $T_{1\rho}$ for polymers is in the range 1–50 ms. The value of the proton T_1 typically is 50–500 ms. Two T_1 values in a blend indicate that phase separation is present at a scale exceeding 100–300 Å. For two $T_{1\rho}$ values, the phase separation scale exceeds 30–60 Å.[16] Measurement of proton relaxation times in polymer blends is conveniently done indirectly. After the proton nuclei have been allowed partially to relax, the proton magnetization is transferred to the carbons in the sample. The size of the resulting carbon signal is directly related to the amount of proton magnetization present at the time of transfer. In this manner the inherently high resolution of ^{13}C NMR spectra of solids taken with magic-angle spinning is utilized for measurement of proton relaxation times. Because each polymer usually gives rise to several ^{13}C NMR signals, multiple determinations of the proton relaxation times can be made in a single run. Agreement of the values obtained from different carbons in the same polymer provides a cross-check of the validity of the measurements.

The nuclear relaxation times obtained from analysis of relaxation curves of blends containing equal weights of either PVPh and Ardel D100 reveal two sets of distinct T_1 (495 ± 17 and 180 ± 10 ms) and $T_{1\rho}$ (8.2 ± 0.3 and 7.0 ± 0.5 ms) values. The errors shown were obtained from statistical analysis and should be treated as lower limits to the actual deviations of the determined relaxation times from the "true" values. The proton T_1 value of pure Ardel D100 (160 ± 13 ms) is clearly different from that of PVPh (528 ± 27 ms). The $T_{1\rho}$ values are slightly different (6.0 ± 0.4 ms for Ardel and 8.1 ± 0.4 ms for PVPh). The relaxation times obtained for the components of the blend are nearly the same as those of the pure materials. Complete phase separation of the polymers in the blends is indicated.

Blends with T-C(*X*)E Polyesters. Particular emphasis was placed on the miscibility of the copolymers of (ET) (ethylene terephthalate) with (CT) (1,4-cyclohexylenedimethylene terephthalate) of varying composition with PVPh. It was found that PVPh is miscible with PET as extruded, but phase separated with PCT. Immiscibility occurs as one introduces more (CT) component into the T-C(*X*)E copolyester. The copolymer becomes phase separated with PVPh when the PCT content in the copolyester is between about 66 and 83%. This trend is illustrated in Figure 5, where the composition dependences of T_g for the individual copolymers as well as for the 50/50 wt % blends of the copolymers with PVPh are plotted as a function of mole percent (CT) in the copolyester.

In a recent review article,[21] Coleman and Painter suggest that mixing can be predicted on the basis of a balance between the repulsive energies (expressed through the solubility parameters) and favorable specific interaction energies. The strength of these favorable specific interactions between the polymers will then determine how much unfavorable dispersive repulsion between the polymers can be tolerated before resulting in phase separation. That is, the strength of these interactions sets up the value for the critical interaction parameter, χ_c. The solubility parameters, δ_i, for the T-C(X)E copolyester series were calculated from group contributions to the molar attraction constants F^* and molar volumes V^* tabulated in the above reference (these were obtained from a data bank on organic compounds compiled by Daubert and Danner at The Pennsylvania State University[21] and are similar to those used by Small). The calculated solubility parameters for the T-C(X)E series range from 11.5 for PET to 10.4 (cal/cm^3)$^{0.5}$ for PCT. The solubility parameter for PVPh recommended[19] by the above authors is 11.0 (cal/cm^3)$^{0.5}$. Thus, since the interaction parameter is given by

$$\chi = V_r(\delta_i - \delta_j)^2/RT \qquad (4)$$

where V_r is a reference volume, the smaller the difference between the δ values for PVPh and for the polyester, the more miscibility would be predicted. One would be hard pressed to predict from these calculations which end of the T-C(X)E copolyester series would be the more miscible. Also, the authors do express the caveat that the accuracy of the calculated solubility parameters is ca. ±0.4. This, along with the fact that the reported[22] experimental δ values for PVPh range from 9.5 to 12 (cal/cm^3)$^{0.5}$, prevents us from explaining the observed differences using the above argument.

There is also preliminary evidence that, with prolonged heating at the high temperatures (ca. 260 °C), cross-reactions may occur between PVPh and the polyester. This subject will be addressed more fully in a later report. However, we conclude that the observed miscibility of these polymers is not the result of chemical reaction. This conclusion is based upon DSC results for blends containing crystalline polyesters, showing no change in melting behavior during annealing over the short time scales required for melt blending.

Infrared Results. The analysis of the infrared spectra of the blends is intended to provide information that would complement the thermal analysis results. Specific interactions between components, such as those due to hydrogen bonding, can readily be seen by FTIR.[3,4,7] The analysis will focus primarily on two portions of the IR spectrum where hydrogen bonding is likely to manifest itself. The first is the carbonyl stretch that occurs in the 1700–1800-cm^{-1} range for esters. This band provides the most quantitative information about the interaction. The second is the hydroxyl stretching mode of the PVPh, which occurs between 3000 and 3600 cm^{-1}. Frequency shifts in this band can provide information on the relative strengths of the interactions.[3]

Figure 6 shows the carbonyl stretching region (a) and the hydroxyl stretching region (b) for the pure component (PBA or PVPh) and for the 1:1 blend. The IR band of the free ester carbonyl occurs at 1729 cm^{-1}. The presence of a slight shoulder at higher wavenumbers is observed for this band. This is attributed to amorphous PBA, the primary peak being attributed to crystalline PBA. A new peak, at 1708 cm^{-1}, is seen to grow in when the PVPh is introduced, indicating a decrease in the bond order of the ester carbonyl due to hydrogen bonding to the PVPh. The free-carbonyl peak shifts slightly to higher wavenumbers, probably due to a decrease in the degree of crystallinity of the PBA in the blend. The hydroxyl stretching region for pure PVPh shows a band at 3520 cm^{-1} that is attributed to free hydroxyls and a broad band at 3364 cm^{-1} that is due to self-associated hydroxyls in the PVPh. An intermediate band, centered at 3398 cm^{-1}, appears in the spectrum of the blend and is due to hydroxyl groups that are hydrogen-bound to the PBA. The two peaks seen for pure PVPh decrease in relative magnitude upon the addition of PBA. The difference between the frequency at which the free hydroxyls absorb and the frequency at which the hydrogen-bound hydroxyls absorb is a measure of the strength of the interaction. The results for PBA/PVPh indicate that the average strength of the association between the PBA and the PVPh is less than the strength of the self-association of the hydroxyl groups in pure PVPh. This has been previously observed for blends of PVPh and esters.[3]

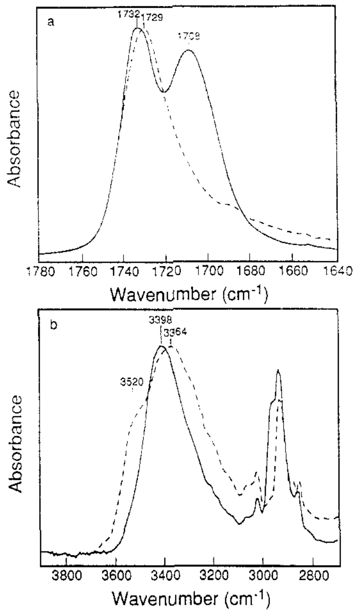


Figure 6. FTIR spectra (solid lines) for a 1:1 blend of PVPh/PBA. In (a), the carbonyl stretching region, the dashed line is pure PBA; in (b), the hydroxyl stretching region, the dashed line is pure PVPh.

Although the thermal analysis indicated that PVPh and the polyester T-C(50)2 form single-phase blends throughout the composition range when prepared via solution techniques, no evidence of hydrogen bonding was observed by FTIR. The entire spectrum of the blend was compared to that resulting from the addition of the pure component spectra. They are identical within experimental uncertainties. It is known[23,24] that solvent-induced phase separation, often referred to as the $\Delta\chi$ effect, can occur when blends are prepared from solution and can obscure the true equilibrium phase behavior of the polymer mixtures. Basically, one polymer interacts more strongly with the solvent than with the other polymer, resulting in the latter being excluded from the solution phase of the former as the polymer concentration in the solution increases during the drying process. It can readily be understood, therefore, that this effect is particularly problematic when one deals with polymers and solvents capable of hydrogen bonding. Therefore, the above discrepancy between thermal and infrared results is easily resolved. The miscible PVPh/T-C(50)E blend for thermal

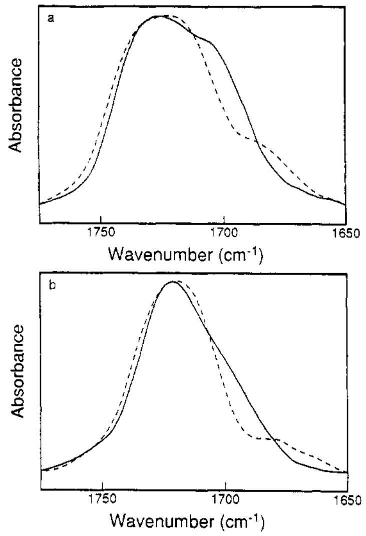


Figure 7. Carbonyl stretching region of the infrared spectra (a) for (- - -) PET and (—) a 50/50 wt % melt blend with PVPh and (b) for (- - -) PCT and (—) a 50/50 wt % melt blend with PVPh.

analysis was prepared by precipitating the mixed solution into a nonsolvent. The FTIR sample, on the other hand, was prepared by solution casting the blend onto a KBr disk. It has been shown[6] that solvent-induced phase separation is less of a problem when the precipitation method is used rather than direct solution casting. The blend examined by FTIR was in all likelihood phase separated and thus would not show any interactions between the polymers. Although one could have prepared a miscible sample for FTIR and observed the hydrogen-bound carbonyl, the data of the spin-coated blend are included to illustrate the effects of sample preparation.

In view of the potential for the $\Delta\chi$ effect influencing our observations of polymer miscibility, we have chosen to prepare many of the blends via a melt-blending technique. This has also permitted the expansion of the studies to include polymers that do not share a common solvent with PVPh. In the following systems both DSC and FTIR samples examined are powders of the melt-extruded blends and are not prone to problems resulting from differences in preparation techniques.

Infrared spectroscopy was performed on the melt blends of PVPh/PET, PVPh/PCT, PVPh/T-C(29)E, and PVPh/PEN to obtain information regarding the level of hydrogen bonding in the samples. Comparisons of the carbonyl regions for each of the pure polyesters and the 1:1 by weight blend with PVPh are shown in Figures 7 and 8. An indication of the ratio of interacting versus noninteracting carbonyls can be calculated by bandfitting the carbonyl region of the spectra and obtaining the relative peak areas for bound and free carbonyls. The peak areas are then corrected for differences in absorptivities, a_f (free) and a_{hb} (bound). The value for the absorptivity ratio a_{hb}/a_f used was 1.5 for these polyester blends, based on literature reports[2,4] for blends of PVPh with ester-containing polymers. These results are tabulated in Table III. It should be noted that the carbonyl bands for these polyesters are centered at 1722 cm^{-1} but are quite broad, typically ranging from 30 to 50 cm^{-1} in full-width-half-height (fwhh). This broadening can be attributed to a combination of several effects: the photoacoustic effect, partial crystallinity of the polyesters, and varied chemical environment of the carbonyl. All three blends show some degree of hydrogen bonding, even the heterogeneous blend of PVPh/PCT, although to a lesser degree than the others. For the 1:1 homogeneous blends, 42–43% of the carbonyls were found to be hydrogen-bound. These values are consistent with the results of Coleman[7] for homogeneous blends of PVPh with acrylate polymers. In the above reference, when the polymers become less miscible or phase separate, the fraction of hydrogen-bound carbonyls is seen to decrease, as is observed in the present work for the PVPh/PCT blend. The fact that a fraction of the carbonyls is hydrogen bound does, however, indicate that there are some interactions between PCT and PVPh, but apparently not enough to overcome enthalpic repulsions. The T_g values of the two phases in the PVPh/PCT blend, which are intermediate between those of the pure blend constituents, indicate partial miscibility between the two polymers. While the exact composition of the two phases cannot be quantified without knowledge of the full compositional dependence of T_g, it can be estimated assuming that the Couchman or Fox equations hold. These two equations lead to estimates that the PCT-rich phase contains ca. 8–14 wt % PVPh, while the PVPh-rich phase contains 6–11 wt % PCT. Thus, the partial miscibility of PCT with PVPh provides an opportunity for the two polymers to interact with each other and might account for the IR evidence for hydrogen bonding between them.

Figure 9 shows comparisons of the spectra in the hydroxyl frequency region for PVPh and four PVPh/polyester blends. The spectra, although smoothed, remain rather noisy in comparison with the carbonyl region. This effect is due both to lower intensity of the hydroxyl absorbance peak and to detector response in this region. Since the spectra of the single-phase blends are quite

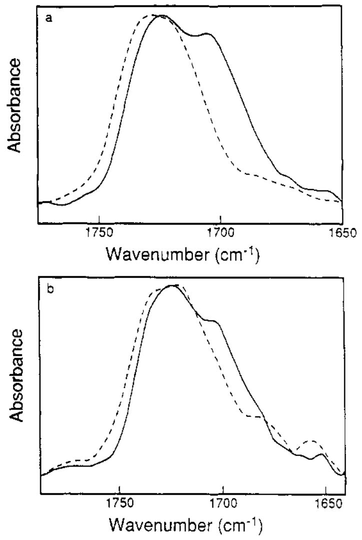


Figure 8. Carbonyl stretching region of the infrared spectra (a) for (- - -) T-C(29)E and (—) a 50/50 wt % melt blend with PVPh and (b) for (- - -) PEN and (—) a 50/50 wt % melt blend with PVPh.

Table III. FTIR Results for Polyester/PVPh Blends

blend	$\nu_{C=O}$ (cm^{-1})			% C=O hb[a]	ν_{OH} (hb) (peak) (cm^{-1})
		free (band fit)	hb (band fit)		
PVPh					3400
PET	1722				
PET/PVPh 1/1		1731	1703	41.6	3433
PCT	1722				
PCT/PVPh 1/1		1725	1700	28.7	(3433, 3367)
T-C(29)E	1724				
T-C(29)E/PVPh 1/1		1727	1702	43.2	3433
PEN	1722				
PEN/PVPh 1/1		1724	1698	43.2	3424

[a] Using a_{hb}/a_f = 1.5.[4]

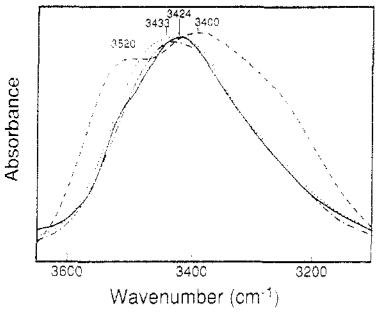


Figure 9. Hydroxyl stretching region of the infrared spectra for (- - -) PVPh, (—) PEN/PVPh 50/50 wt %, (-·-) T-C(29)E/PVPh 50/50 wt %, and (···) PET/PVPh 50/50 wt %.

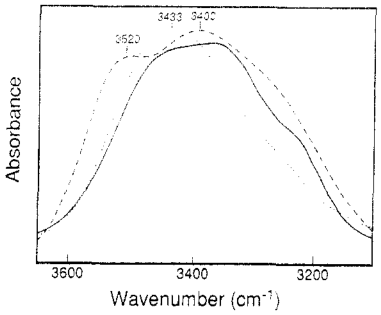


Figure 10. Hydroxyl stretching region of the infrared spectra for (- - -) PVPh, (—) PCT/PVPh 50/50 wt %, and (···) PET/PVPh 50/50 wt %.

similar to one another, the comparisons that follow are generalized for the PET, T-C(29)E, and PEN/PVPh blends versus pure PVPh. The fraction of free hydroxyls for the blends decreases relative to that found in pure PVPh, as seen by the reduction in the absorbance at 3520 cm^{-1}, indicating an increase of bound OH groups in the blends. We also note that the central peak maxima for the blends are all shifted to a higher wavenumber (ca. 3424–3433 cm^{-1}) relative to the maximum in the "bound" portion of the PVPh spectra (3400 cm^{-1}), just as was seen in the PVPh/PBA blends.

The hydroxyl spectra for the miscible PET/PVPh blend and the immiscible PCT/PVPh blend are superimposed in Figure 10. Interestingly, the fraction of free hydroxyls has decreased in the PCT/PVPh (immiscible) mixture relative to those present in PVPh and is similar in magnitude to what is observed in the PET/PVPh blend. The overall shape of the PCT blend OH spectral region, however, is markedly different from those of the single-phase polyester blends and somewhat resembles that of PVPh by itself. The presence of a shoulder at ca. 3250 cm^{-1} indicates that there is still a significant self-association of phenol groups into multimers. Based on these observations in both the carbonyl and hydroxyl regions of the spectra, it is clear that interactions are occurring between PCT and PVPh that are somewhat different (or occur to a different extent) from those present in the homogeneous blends. The OH region of the infrared spectrum would be, in the first approximation, the sum of the two mixed phases present in the blend: one composed of 89–94 wt % and the other containing ca. 8–14 wt % PVPh. Thus the amount of hydroxyl groups that would participate in hydrogen bonding to ester groups is minor. Such a spectrum would look more like that of PVPh and may not be expected to be the same as for the other blends, in which the spectra are for single-phase 50/50 wt % mixtures.

It appears, therefore, that the driving force for miscibility in the blends of PVPh with these polyesters is hydrogen bonding between the carbonyl of the polyester and the phenolic hydroxyl.

Finally, in an effort to better define miscibility limits, several random styrene–vinylphenol copolymers were melt blended with two compositions of T-C(*X*)E copolymer. Since PET and PVPh are miscible, one would like to know how much styrene can be incorporated in PVPh before immiscibility with the polyesters occurs. Blends of two random copolymers were also studied: poly(styrene-*co*-vinylphenol), P(S-VPh(22)) containing 22 mol % vinylphenol [T_g = 122 °C (onset), 127 °C (mid)] and P(S-VPh(42)) containing 42 mol % vinylphenol [T_g = 141 °C (onset), 146 °C (mid)]. These were blended with PET and T-C(29)E. A single, intermediate T_g [118 °C (onset), 122 °C (mid)] was obtained for blends of T-C(29)E with P(S-VPh(42)), indicating miscibility. Neither polyester was found to be miscible with the 22 mol % VPh copolymer. The amount of VPh necessary to miscibilize polystyrene with these polyesters is much greater than that found for most polyacrylates,[7d] where less than 2% VPh units in PS are often required to produce a single phase blend.

Conclusions and Suggestions for Further Study

The results of solution and melt blending PVPh with a number of polyesters are described. Polyesters consisting of terephthalic acid and a mixture of ethylene glycol and 1,4-cyclohexanedimethanol moieties [T-C(*X*)E series] form homogeneous blends with PVPh in polyester compositions containing no more than ca. 80 mol % of the cycloaliphatic diol. Other polyesters found to be miscible with PVPh include poly(butylene terephthalate) (PBT), poly(2,2-dimethylpropylene terephthalate) (T-Ne), poly(ethylene 2,6-naphthalenedicarboxylate) (PEN), a copolymer of terephthalic and pentanedioic acids with 1,2-propanediol and glycerol [T(13)G-P(5)GL], and several cyclic aliphatic copolyesters containing 1,4-cyclohexanedicarboxylic acid [Cy-Cb(30)C, Cy-C, Cy-E(50)BPAE]. Miscibility of PVPh was not observed with poly(1,4-cyclohexylene dimethylene terephthalate) (PCT), Ardel D100, Kodar A150, several other polyesters with high aromatic content, and two liquid crystalline polyesters. Despite the opportunity for hydrogen bonding to take place between the ester carbonyl and the phenol hydroxyl, it appears that an appreciable percentage of the polyester glycol moiety must be aliphatic to achieve miscibility. Higher T_g polyesters that contain aromatic diols [T(60)A-Nb and Ardel D100] or a high aromatic content [Kodar A150, T-E(50)Nbe, and T-E(50)BPAE] showed little interaction and no miscibility with PVPh.

Intermolecular hydrogen bond formation between the hydroxyl group of the vinylphenol and the carbonyl group of the ester linkage is observed by FTIR in several of the polyester/PVPh blends studied, even those shown by thermal analysis to be only partially miscible. Homogeneous blend samples are shown, however, to have a greater fraction of hydrogen-bound groups (carbonyl and hydroxyl) than do partially miscible blends. This confirms our expectation that hydrogen bonding is a significant (although not always sufficient) driving force toward miscibility in these blends.

In general, there was a good correlation between the thermal behavior and the IR results. When there was evidence of significant interaction between the polymers by IR, substantial miscibility was seen by thermal analysis. In one case, the solution-prepared PVPh/T-C(50)E blend, there was no evidence of hydrogen bonding by IR, even though thermal analysis results indicated a single T_g at all compositions. This was attributed to the tendency of solution-cast blends (as were the FTIR samples) to undergo solvent-induced phase separation more readily than the precipitated samples (for thermal analysis). This illustrates the important role that sample preparation plays in determining the ultimate blend morphology.

Finally, several styrene–vinylphenol random copolymers were melt blended with two compositions of T-C(*X*)E copolymer. Although a complete series was not investigated, the data indicate that these polyesters [PET to T-C(29)E] are miscible with P(S-VPh(42)) but are not, however, miscible with P(S-VPh(22)).

As many of these polymers do not share a common solvent with PVPh, melt blending is required. Information on melt-blending behavior would be itself useful, as many practical blends could be made by this method. Among the important unanswered questions is whether or not hydrogen bonding with PVPh is the only interaction in these miscible systems. The possibility of chemical cross-reactions during melt processing exists and should be understood. Although this will be the subject of a future report, preliminary evidence suggests that such reactions are slow and cannot account for the miscibility observed in these blends. Also, the thermal stability of pure PVPh must be a consideration.

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