

Phase Behavior of Blends of Aliphatic Polyesters with a Vinylidene Chloride / Vinyl Chloride Copolymer

E. M. WOO,* J. W. BARLOW, and D. R. PAUL, *Department of Chemical Engineering and Center for Polymer Research, University of Texas, Austin, Texas 78712*

Synopsis

A series of aliphatic polyesters having CH_2/COO ratios from 2 to 14 in their repeat units were blended with a copolymer of vinylidene chloride containing 13.5% by weight of vinyl chloride. Blends of polyesters having $\text{CH}_2/\text{COO} < 4$ did not form completely miscible amorphous phases, whereas polyesters having $\text{CH}_2/\text{COO} \geq 4$ did form completely homogeneous amorphous phases for all temperatures below the decomposition point except for the polyester with $\text{CH}_2/\text{COO} = 14$ which showed reversible phase separation on heating, i.e., lower critical solution temperature behavior. Interaction parameters were estimated by melting point depression and by analog calorimetry. The behavior reported here is qualitatively similar to that reported earlier for blends of aliphatic polyesters with poly(vinyl chloride), polyepichlorohydrin, polycarbonate, styrene-allyl alcohol copolymers, and the hydroxy ether of bisphenol A.

INTRODUCTION

Several recent papers have reported that copolymers comprised predominantly of vinylidene chloride are miscible with poly(ϵ -caprolactone)¹⁻⁵ and with three other aliphatic polyesters containing either branched or saturated ring monomers in their repeat units.¹ Other studies^{6,7} have extended similar observations for poly(vinyl chloride) to show that this polymer is also miscible with all of the aliphatic polyesters having a ratio of methylene to ester groups, i.e., CH_2/COO , from 4 to at least 14 in their repeat units. Thus, this paper seeks to learn whether a predominately vinylidene chloride copolymer is also miscible with a wide range of aliphatic polyesters.

EXPERIMENTAL

The vinylidene chloride copolymer used contained 13.5% by weight of vinyl chloride. It is a commercial product (sold under the trademark Saran) of the Dow Chemical Co., having a weight average molecular weight of 101,000 based on GPC determination using polystyrene calibration, provided to us through the courtesy of Mr. Don Lundquist. The polyesters used are listed in Table I and further information about them has been provided earlier.⁷

* Present address: Department of Chemical Engineering, University of Washington, Seattle, WA 98195.

TABLE I
 Properties of Polyesters Used in This Study

Polyester	Repeat unit	CH ₂ /COO	Abbreviation	Source
Poly(ethylene succinate)	$-(\text{CH}_2)_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	2	PES	SPP # 150 ^a
Poly(propylene succinate)	$-(\text{CH}_2)_3-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	2.5	PPS	SPP # 592
Poly(propylene adipate)	$-(\text{CH}_2)_3-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	3.5	PPA	SPP # 594
Poly(butylene adipate)	$-(\text{CH}_2)_4-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	4	PBA	SPP # 149
Poly(ϵ -caprolactone)	$-(\text{CH}_2)_5-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-$	5	PCL	Union Carbide (PCL-700)
Poly(butylene sebacate)	$-(\text{CH}_2)_4-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	6	PBS	Synthesized ^b
Poly(hexamethylene sebacate)	$-(\text{CH}_2)_6-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	7	PHS	SPP # 124
Poly(dodecamethylene adipate)	$-(\text{CH}_2)_{12}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	8	PDOA	Synthesized
Poly(decamethylene decamethylene dicarboxylate)	$-(\text{CH}_2)_{10}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_{10}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	10	PDEDE	Synthesized
Poly(dodecamethylene dodecamethylene dicarboxylate)	$-(\text{CH}_2)_{12}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_{12}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	12	PDODO	Synthesized
Poly(hexadecamethylene dodecamethylene dicarboxylate)	$-(\text{CH}_2)_{16}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_{12}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$	14	PHEDO	Synthesized

^aSPP = Scientific Polymer Products.

^bSee Ref. 7 for details.

Blends of the copolymer, designated as P(VCl₂/VCl), with the polyesters were made by solvent casting from tetrahydrofuran (THF). Approximately 0.5 g of the two component polymers in the desired ratio were mixed with 20 cm³ of THF stirred for 4 h. The resulting solutions were poured into aluminum pans maintained at 50°C. Most of the solvent was removed overnight; however, the samples were transferred to a vacuum oven set at 60°C, where they were kept for 5 days to complete solvent removal.

Conclusions about the phase behavior of these blends were reached using a combination of visual observations,⁸ differential scanning calorimetry (Perkin Elmer DSC-2 with a computerized data station), and dynamic mechanical behavior (automated Rheovibron).

Further information about the thermodynamics of these blends was obtained from heats of mixing of appropriate low molecular weight analogs of the polymer repeat units as described earlier⁷ and by melting point depression analysis.

RESULTS AND DISCUSSION

Visual Observations

Blends of P(VCl₂/VCl) with the various polyesters shown in Table I were heated from ambient temperatures to the point where rapid decomposition occurred, about 240°C, in a device that allowed easy visual observation of the sample.⁸ Blends with PES, PPS, and PPA (which have CH₂/COO of 3.5 or less as shown in Table I) were visually cloudy at all temperatures and were judged, therefore, to be essentially immiscible with P(VCl₂/VCl).

On the other hand, all blends containing the polyesters shown in Table I having CH₂/COO equal to 4 or more became quite transparent above the melting point of P(VCl₂/VCl), about 170°C, which is higher than the T_m of each polyester⁷ and remained so to the decomposition temperature except for PHEDO. The latter blends showed reversible phase separation on heating, or lower critical solution temperature (LCST) behavior, at the temperatures shown in Figure 1. The observed optical clarity in the melt state suggests rather strongly that polyesters having CH₂/COO of 4 or greater are miscible with P(VCl₂/VCl) as found also for PVC.⁷ For PVC, phase separation on heating was observed for a polyester with CH₂/COO = 11, and this occurred at progressively lower temperatures for polyesters with higher aliphatic contents. Interestingly, such behavior was not observed for P(VCl₂/VCl) until CH₂/COO = 14. In fact, the cloud points shown in Figure 1 are about the

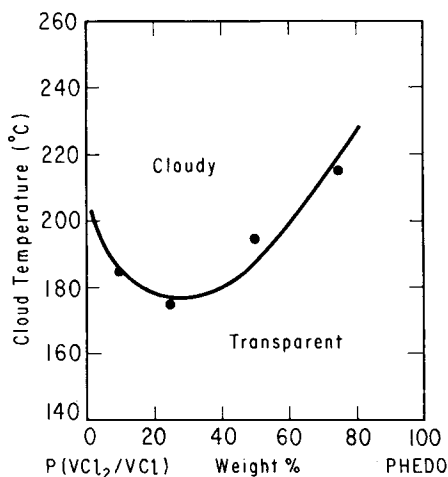


Fig. 1. Cloud point curve for P(VCl₂/VCl) blends with PHEDO.

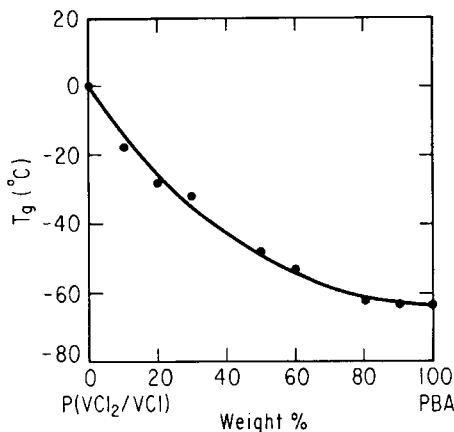


Fig. 2. Glass transition behavior for P(VCl₂/VCl) blends with PBA determined by DSC.

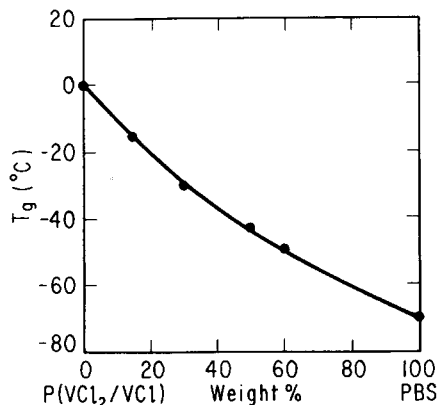


Fig. 3. Glass transition behavior for P(VCl₂/VCl) blends with PBS determined by DSC.

same or higher than those observed for PVC and for the polyester with $\text{CH}_2/\text{COO} = 11$.

GLASS TRANSITION BEHAVIOR

Figures 2–4 show a single, composition dependent glass transition temperature obtained by DSC for blends of PBA, PBS, and PHS with P(VCl₂/VCl) like that observed for poly(ϵ -caprolactone) earlier,¹ which is further evidence that these blends have a single, miscible amorphous phase. As explained previously,⁷ it is rather difficult to detect the T_g by DSC for blends containing polyesters having CH_2/COO of 8 or more because of their very high crystallinity so that no thermal analysis results for these blends were attempted since the visual observations make it rather certain that these polyesters are also miscible with P(VCl₂/VCl).

However, for further support of this conclusion, limited dynamic mechanical measurements were made on selected blends with the results shown in Figures 5–8. Compositions containing significant amounts of polyester were

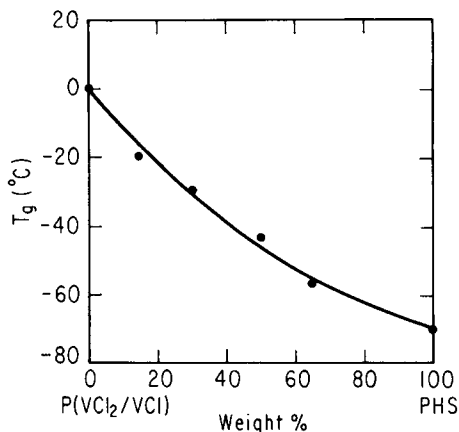


Fig. 4. Glass transition behavior for P(VCl₂/VCl) blends with PHS determined by DSC.

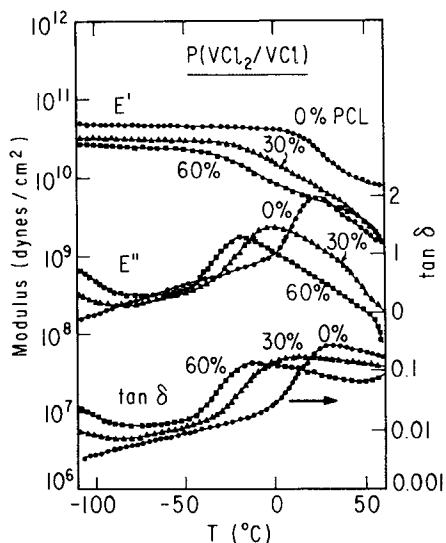


Fig. 5. Dynamic mechanical properties at 110 Hz for PCL blends.

quite brittle at room temperature, owing to high polyester crystallinity, and could not be successfully mounted in the Rheovibron. The main point to be noted in each of these figures is that addition of any of the polyesters used lowers the glass transition of the P(VCl₂/VCl). Generally speaking, the glass transition region becomes broader the larger the CH₂/COO ratio of the polyester added as noted also for PVC blends. However, no evidence for multiple T_g's is seen.

INTERACTION PARAMETERS

Estimates of the interaction parameters for these blends systems were obtained by melting point depression analysis and from the heat of mixing of low molecular weight analogs of the polymers using techniques described previously for the PVC-polyester series.⁷ In each case, this information is

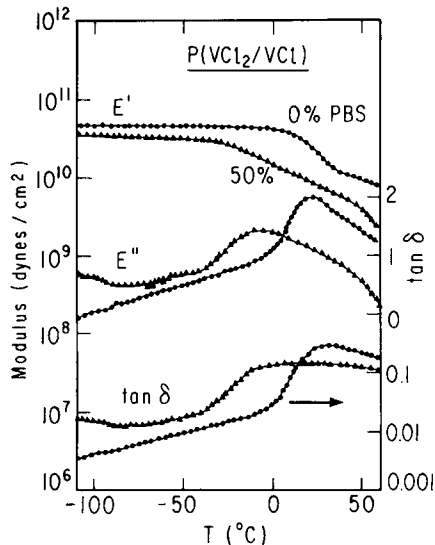


Fig. 6. Dynamic mechanical properties at 110 Hz for PBS blend.

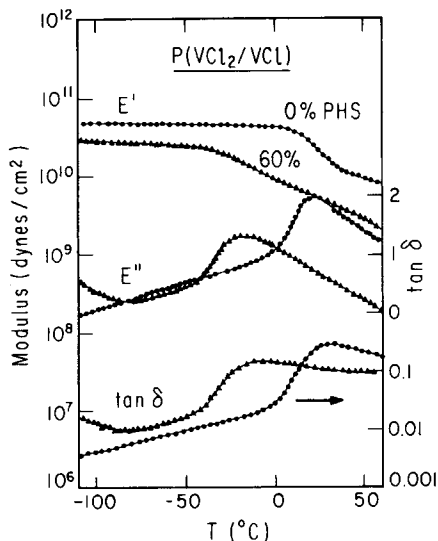


Fig. 7. Dynamic mechanical properties at 110 Hz for PHS blend.

expressed in terms of the quantity B which may be defined as follows:

$$\Delta H_{\text{mix}} = B\phi_1\phi_2 \quad (1)$$

where ΔH_{mix} is the heat of mixing per unit volume and ϕ_i is the volume fraction of component i in the final mixture.

For the calorimetry work, we selected 2,2-dichlorobutane as a convenient analog for a vinylidene chloride unit and neglected the fact that the polymer used in this study also contains vinyl chloride units. A series of monoesters with the structures shown in Figure 9 were used to simulate the polyesters. Mixtures near equal parts per volume of the two components were used to

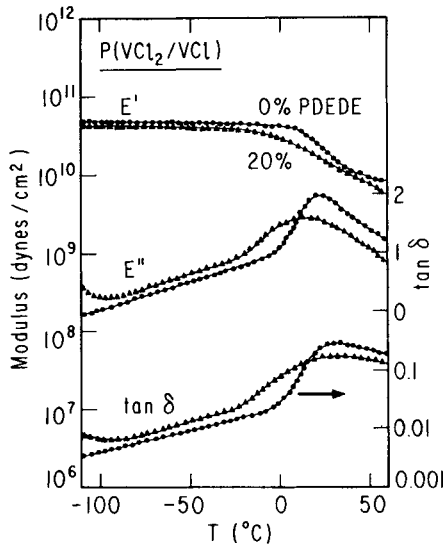


Fig. 8. Dynamic mechanical properties at 110 Hz for PDEDE blend.

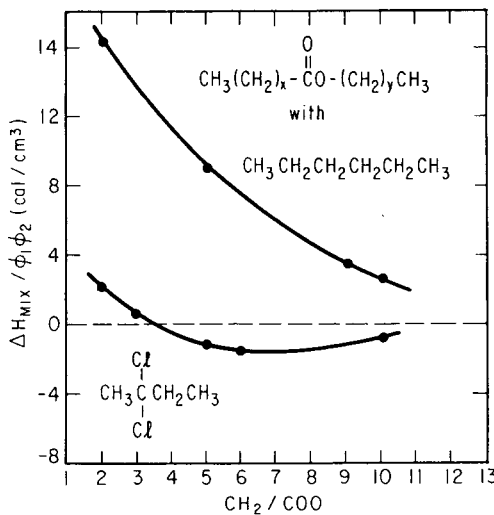


Fig. 9. Normalized heats of mixing of monoesters with hexane (upper curve) and with 2,2-dichlorobutane (lower curve).

obtain the interaction parameter via eq. (1). The upper curve in Figure 9 shows the results for mixing the various esters (plotted as $CH_2/COO = x + y + 2$) with hexane. This gives endothermic mixing in every case, but the interaction parameter appears to approach zero at high aliphatic content of the ester as might be expected and as observed earlier for a series of diesters.⁷ The lower curve shows results for mixing the monoesters with 2,2-dichlorobutane which roughly simulates blending P(VCl₂/VCl) with the various aliphatic polyesters. Interestingly, the heat of mixing is endothermic at low CH_2/COO but becomes exothermic at higher values as also observed in a simulation of the PVC-polyester series.⁷ The change in sign of the heat of

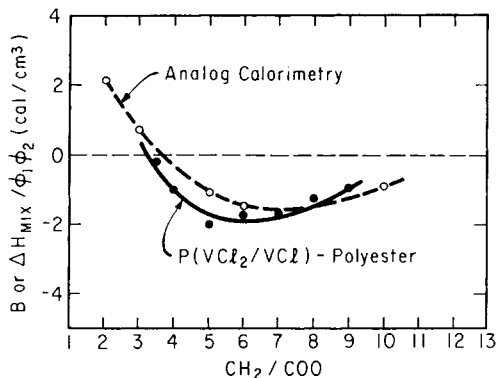


Fig. 10. Comparison of interaction parameters from melting point depression observations on blends (●) with calorimetric results from Figure 9 (○).

mixing occurs between three and four aliphatic carbons per ester linkage in good accord with the observation of the border of miscibility for blends with the series of aliphatic polyesters. At higher CH_2/COO ratios, the heat of mixing appears to become less exothermic as it must and in a parallel fashion to that observed for the PVC-polyester analogs. In all, the analog calorimetry results seem to mimic quite well the type of thermodynamic response expected for the actual blends. That is, based on the observations noted above, we expect blends of $\text{P}(\text{VCl}_2/\text{VCl})$ with polyesters having CH_2/COO of less than 4 to exhibit endothermic mixing since these mixtures are not miscible. On the other hand, for CH_2/COO of 4 or more the blends are miscible, and this requires an exothermic heat of mixing. However, with continued increase in aliphatic content of the polyester, the heat of mixing must become less favorable for mixing since polyethylene (the limit of very high CH_2/COO) would not be miscible with $\text{P}(\text{VCl}_2/\text{VCl})$. The appearance of LCST behavior at high CH_2/COO ratios is in accord with this and reflects the less negative ΔH_{mix} suggested by Figure 9.

The interaction parameter B for each miscible blend was also estimated using the melting point depression technique described earlier for the PVC/polyester blend systems.⁷ The B values are shown by the solid points in Figure 10 vs. the CH_2/COO ratio in the polyester structure. These interaction parameters were estimated from the melting point depression of the $\text{P}(\text{VCl}_2/\text{VCl})$ component. Since the polyesters are also crystallizable, estimates of B can also be made from their melting point depression. Generally speaking, the B 's estimated from the melting point depression of the $\text{P}(\text{VCl}_2/\text{VCl})$ component were less negative than those from the melting point depression of the polyesters. This can be expected since the former is the interaction parameter at a higher temperature (ca. 170°C), and the latter is for a lower temperature (ca. 60°C). As pointed out previously, the interaction parameter for polymer blends usually decreases with increasing temperature. However, it must also be noted that values of B estimated from polyester melting involve a systematic bias caused by the alteration of the amorphous volume fraction owing to the crystallinity of the $\text{P}(\text{VCl}_2/\text{VCl})$ component at the polyester melting point. Thus, the results from the polyester melting are not reported or considered here any further.

SUMMARY

These results show that a copolymer containing predominantly vinylidene chloride units is miscible with a wide range of linear aliphatic polyesters but not all of them. None of the polyesters studied having $\text{CH}_2/\text{COO} < 4$ are completely miscible with the vinylidene chloride copolymer, whereas those having $\text{CH}_2/\text{COO} \geq 4$ do form miscible blends, based on several types of evidences, at all temperatures below the decomposition point except for the polyester having $\text{CH}_2/\text{COO} = 14$ where LCST behavior occurs. This is quite similar to the observations reported previously for blends of aliphatic polyesters with PVC except in the latter case LCST behavior commenced at somewhat lower CH_2/COO ratios.

The energetics of the interaction between the copolymer and the various polyesters was estimated by melting point depression and by measuring the heat of mixing of low molecular weight compounds having molecular structures similar to the polymers. The two estimates agree very well especially considering that the compound used for the halogenated component is not a precise analog for the vinylidene chloride copolymer. From these results, it is clear that the interactions responsible for miscibility do not involve an alpha hydrogen as proposed in the case of PVC and that intramolecular repulsion between methylene and ester units in the polyesters is strong (see heats of mixing for hexane with monoesters shown in Fig. 9) and is probably a significant factor in the tendency for heats of mixing of the halogenated component to be negative over a limited range of ester structures as explained by a recent binary interaction model.^{7,9} The latter is believed to be an issue in the similar phase behavior of these aliphatic polyesters in blends with other polymers reported previously: poly(vinyl chloride),⁷ polycarbonate,¹⁰ polyepichlorohydrin,¹¹ styrene-allyl alcohol copolymers,¹² and the hydroxy ether of bisphenol A.¹³

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