

Phase Behavior of Polycarbonate Blends with Selected Halogenated Polymers

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Synopsis

Bisphenol A polycarbonate is shown to be miscible with a vinylidene chloride based polymer containing 13.5% by weight of vinyl chloride. On the other hand, polycarbonate is found to be immiscible with poly(vinyl chloride), poly(vinylidene fluoride), and polyepichlorohydrin.

INTRODUCTION

Miscibility of polymer-polymer mixtures is normally the result of an exothermic heat of mixing since the entropy of mixing is too small to be a significant factor in blend phase behavior.^{1,2} The interactions responsible for exothermic mixing are complex and usually cannot be predicted *a priori*; however, as more information on blend miscibility becomes available, patterns become evident which may lead to logical speculation about the phase behavior of related systems. For example, a variety of halogenated polymers are noted to be miscible with some members of the homologous series of aliphatic polyesters, polyacrylates, or polymethacrylates as summarized in Table I. The references noted identify which members of each homologous family are miscible with the halogen containing polymers shown and which are not. The three families of polymers, of course, have in common an ester

unit $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{O}- \end{array}$, as part of either the backbone or a pendant group. Based on this, one might wonder whether some of the halogenated polymers might

also be miscible with polymers containing a carbonate unit, $\begin{array}{c} \text{O} \\ || \\ -\text{O}-\text{C}-\text{O}- \end{array}$, owing to its similarity to the ester unit. This reasoning led us to investigate the phase behavior of blends of bisphenol A polycarbonate with selected halogenated polymers, and the results of this study are reported here.

MATERIALS AND PREPARATION PROCEDURES

All of the mixtures described here employed bisphenol A polycarbonate as a common component for which we used Lexan 131-111, a product of the General Electric Co., having $\bar{M}_n = 13.3 \times 10^3$ and $\bar{M}_w = 34.2 \times 10^3$.

Blends of a commercial poly(vinyl chloride) having a viscosity average molecular weight of 45,000 with polycarbonate were prepared by dissolving the two polymers in tetrahydrofuran (THF). After dissolution was complete,

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TABLE I
Summary of Phase Behavior of Various Halogenated Polymers with Three Families of
Polymers Containing Ester Units

	Aliphatic polyesters	Polymethacrylates	Polyacrylates
$\begin{array}{c} \text{--- CH}_2\text{--- CH ---} \\ \\ \text{F} \end{array}$	Not miscible ³	Unknown ^b	Unknown
$\begin{array}{c} \text{--- CH}_2\text{--- C ---} \\ \\ \text{F} \end{array}$	Not miscible ³⁻⁵	Miscible ^{c,5}	Miscible ^{5,6}
$\begin{array}{c} \text{--- CH}_2\text{--- CH ---} \\ \\ \text{Cl} \\ \\ \text{Cl}^d \end{array}$	Miscible ⁷⁻⁹	Miscible ^{10,11}	Miscible ^{11,12}
$\begin{array}{c} \text{--- CH}_2\text{--- C ---} \\ \\ \text{Cl} \end{array}$	Miscible ¹³⁻¹⁵	Miscible ^{14,16}	Not miscible ^{14,16}
$\begin{array}{c} \text{--- O--- CH}_2\text{--- CH ---} \\ \\ \text{CH}_2 \\ \\ \text{Cl} \end{array}$	Miscible ¹⁷	Miscible ¹⁷⁻¹⁹	Miscible ^{18,20}
$\begin{array}{c} \text{--- CH}_2\text{--- CH ---} \\ \\ \text{Br} \end{array}$	Miscible ²¹	Unknown	Unknown

^a Not miscible indicates that no member of this family, e.g., aliphatic polyesters, has yet been reported miscible with the indicated halogen containing polymer.

^b Unknown indicates no information available in the literature on these systems.

^c Miscible indicates that some (not all) members of this family have been reported miscible with the indicated halogen containing polymer.

^d Because of the intractability of poly(vinylidene chloride), these studies have used copolymers containing various comonomers; however, the results are believed to be indicative of the interactions with vinylidene chloride units and not primarily those of the comonomer.

the solvent was removed by two procedures to yield a film. In the first, THF was slowly evaporated at room temperature with final drying in a vacuum oven. In the second, a large quantity of acetone was added to the solution to precipitate the polymer. The precipitated powder was dried and then compression-molded into a film. In each case, all compositions were cloudy, visually heterogeneous, and did not become transparent on heating to the highest temperature possible prior to severe degradation.

Because of the difficulty of blending pure poly(vinylidene chloride),^{13,14} a copolymer was selected for blending with polycarbonate. This copolymer was obtained from the Dow Chemical Co. It is a commercial product (Saran) containing 13.5% by weight of vinyl chloride with an average molecular weight of 101,000 based on GPC determination using polystyrene calibration. This polymer represents a practical approximation to the behavior of poly(vinylidene chloride), but, as a reminder that it is a copolymer, we use

here the designation P(VCl₂/VC1). This is the same material used in some of the References^{13,14} given in Table I. Blends of P(VCl₂/VC1) with polycarbonate were made by the same two procedures described above for PVC. The films made by molding of the precipitate were quite clear and had good mechanical integrity. Corresponding blends made by solvent evaporation were somewhat less transparent. However, these samples became clear on heating above the P(VCl₂/VC1) melting temperature, about 180°C, and remained so upon rapid cooling to room temperature. This indicates that P(VCl₂/VC1) crystallinity was responsible for the opacity of the cast films.

Blends of polycarbonate with poly(vinylidene fluoride), Kynar 460N obtained from the Pennwalt Corp., were prepared by melt mixing at 275–290°C in a Brabender Plasti-Corder. The mixtures were completely opaque in the melt state after thorough mixing.

Blends of polyepichlorohydrin,¹⁷ Hydrin 100 from B. F. Goodrich Co., with polycarbonate were cast from methylene chloride solutions containing about 10% polymer. Appropriate amounts of PECH and polycarbonate were placed in beakers to which solvent was added. Because of the difficult dissolution of PECH, these mixtures were held at room temperature for 2 days and then heated with stirring and solvent makeup until all polymer in the beaker dissolved. The solutions, which appeared homogeneous, were used to form films by solvent evaporation as described previously.¹⁷

RESULTS AND CONCLUSIONS

Conclusions about the phase behavior of the blends of polycarbonate with the various halogenated polymers were reached using various observations as described below.

PVC

The physical appearance of the PVC–polycarbonate mixtures indicates immiscibility for this pair. Dynamic mechanical properties for the 50/50 composition shown in Figure 1 give more quantitative evidence. Two glass

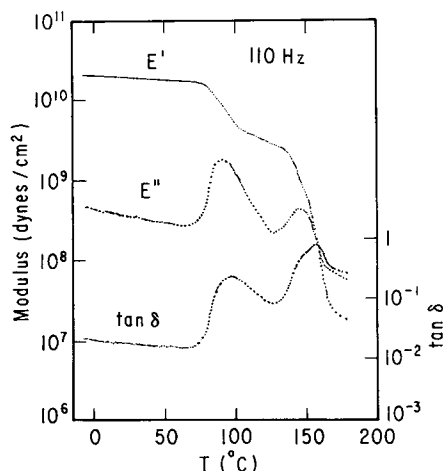


Fig. 1. Dynamic mechanical properties of a blend of poly(vinyl chloride) and polycarbonate containing 50% by weight of each component.

transition temperatures corresponding quite closely to those of pure PVC and polycarbonate phases are seen. Similar results were obtained by differential scanning calorimetry.

P(VCl₂/VC1)

In contrast to PVC, all evidence indicates that blends of P(VCl₂/VC1) with polycarbonate form a single, homogeneous amorphous phase for all proportions of the two components. For example, the lower part of Figure 2 shows the single glass transition temperature observed for these mixtures using differential scanning calorimetry (DSC). This is the expected behavior for a miscible system. However, as frequently noted for polymer mixtures, the breadth of the transition is significantly larger for blends of midrange compositions than for those of the pure components. This feature is quantified in the upper part of Figure 2 where the temperature interval over which the heat capacity increase at T_g occurred. This broadening of T_g is believed to be the result of composition fluctuations which are possible at equilibrium for homogeneous systems and not the result of "microheterogeneity" as sometimes stated if this latter term implies thermodynamic phase segregation.

Figure 3 shows other thermal information obtained by cyclic heating and cooling at 20°C/min between limits above T_m and below T_g . Addition of polycarbonate increases the temperature at which the P(VCl₂/VC1) crystallization exotherm peaks, T_c , on the heating part of the cycle. Further, the P(VCl₂/VC1) melting point and heat of fusion, or crystallinity, decreases as polycarbonate is added. Blends containing more than 25–30% polycarbonate did not crystallize at all during this protocol. These results indicate that polycarbonate kinetically impedes the process of P(VCl₂/VC1) crystallization which is expected for a miscible system where the diluent component raises the T_g strongly as polycarbonate does.

Figure 4 shows dynamic mechanical properties for polycarbonate, P(VCl₂/VC1), and two blends rich in polycarbonate exhibiting no P(VCl₂/VC1)

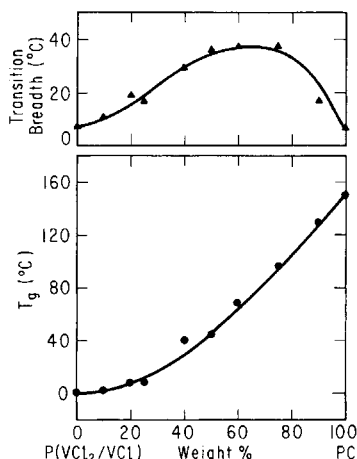


Fig. 2. Glass transition behavior of vinylidene chloride based polymer with polycarbonate as determined by DSC.

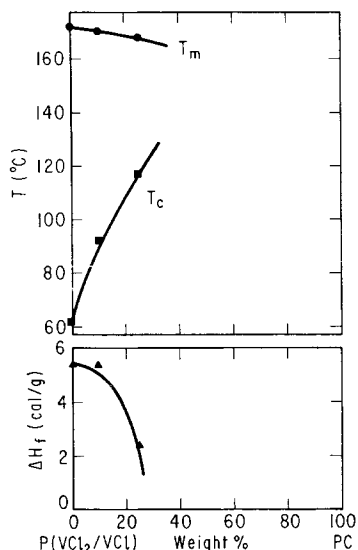


Fig. 3. Crystallization and melting behavior of blends of polycarbonate and vinylidene chloride based polymer during cyclic heating and cooling at 20°C/min.

crystallinity. Blends rich in P(VCl₂/VC1) exhibit complexities resulting from crystallization behavior and results for these compositions are not shown here for simplicity. As seen in Figure 4, addition of P(VCl₂/VC1) reduces and broadens the main transitions as expected by the DSC results shown in Figure 2. The blends have a rather significant secondary transition occurring at higher temperatures than the secondary relaxation for pure polycarbonate. A more thorough study is needed to understand this feature.

PVF₂

The blends of polycarbonate with poly(vinylidene fluoride) were obviously immiscible as judged by their complete opacity in the melt state, and no further characterization seemed necessary to document this conclusion.

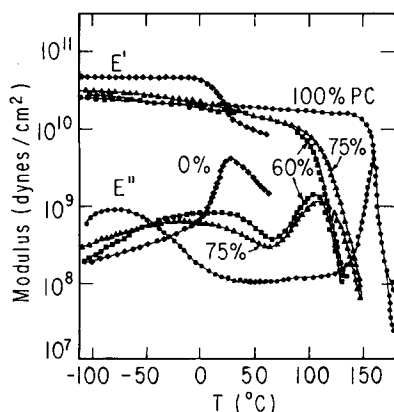


Fig. 4. Dynamic mechanical behavior of blends of polycarbonate with vinylidene chloride based polymer at 110 Hz.

PECH

Glass transition behavior of the polyepichlorohydrin-polycarbonate blends was examined using differential scanning calorimetry. Over the entire composition spectrum, two glass transitions were observed at substantially the same temperatures as those for the two pure components. Thus, these mixtures are not miscible.

SUMMARY AND DISCUSSION

The high incidence of miscible polymer pairs in Table I suggests there is a favorable interaction between halogen containing structures and those containing ester units. This observation leads us to speculate whether some of these same halogen-containing polymers might also interact favorably and, thus, be miscible with a polymer having a carbonate unit owing to the similarity of ester and carbonate groups. Of the four halogenated polymers examined, only the polymer based on vinylidene chloride proved to be miscible with bisphenol A polycarbonate. Poly(vinyl fluoride) and poly(vinyl bromide) were not studied.

It is important to point out that the above results do not provide an equal comparison of the interactions of ester and carbonate units with halogenated polymers since bisphenol A polycarbonate contains aromatic units whereas the ester-containing polymers of Table I do not. The hydrocarbon portions of the latter are all aliphatic in nature. Phase behavior is also influenced by the differences in intermolecular interactions between the halogenated polymers and the aromatic vs. aliphatic hydrocarbon units and by the differences in the *intramolecular* interactions between ester or carbonate groups and the aromatic vs. aliphatic hydrocarbon units.²² A recent study by Aubin and Prud'homme²³ has demonstrated that some aromatic polyester/chlorinated polymer pairs are miscible; however, it appears that the conditions for miscibility may be more restrictive for aromatic structures than aliphatic ones. Clarification of the latter point by calorimetry of model compounds^{13,14} would be instructive.

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