

Polyblends Based on Vinyl Chloride/Propylene Copolymer

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Synopsis

Blends of vinyl chloride/propylene copolymer (VCM-P) with aromatic polycarbonate (PC) and with ABS terpolymer were studied. Particular emphasis was on characteristics of deflection temperature under load (DTUL), simply referred to as heat deflection temperature (HDT). In a binary system which contained PC and VCM-P, the HDT-composition plot exhibited an S-shaped curve, suggesting incompatibility. In contrast, a straight-line correlation, indicating compatibility, was found for VCM-P/ABS blends. These observations are consistent with dynamic measurements by viscoelastometer (Vibron Model DDV-II). Compatibility of the VCM-P/PC system was improved through incorporation of ABS copolymer, as indicated by the broadening of $\tan \delta$ peak. Electron photomicrographs revealed that, in a 50% VCM-P binary blend, polycarbonate existed in a string-like morphology which differed from the compatible ABS system where the ABS copolymer was dispersed in a form of discrete particles.

INTRODUCTION

Polyblends are classified as multicomponent or multiphase systems consisting of at least a continuous phase and a dispersed phase. Usually, one phase constitutes a rigid polymer, while the other constitutes an elastomeric material. Formation of a polyblend is one means of achieving certain specific properties which are difficult to obtain from any one of the simple components alone. A majority of PVC blends reported in the literature are centered on modification of impact strength.¹⁻³ There are few cases that involve blending of PVC with any polymer whose glass transition temperature is higher than that of PVC.⁴ The objective of this study was to increase the HDT of VCM-P copolymer by physical blending. Blends of vinyl chloride/propylene copolymers (VCM-P) and aromatic polycarbonate are interesting since the latter is known for high HDT and good impact resistance.⁵ Products made of PVC/ABS and ABS/PC compounds are commercially available, but to our knowledge there is none composed of either PVC/PC or PVC/PC/ABS systems.

A recent patent described thermoplastic molding compositions of polycarbonate, vinyl chloride polymer, and an ABS polymer or styrene/maleic anhydride copolymer or ethylene/vinyl acetate copolymer.^{6,7} It discloses that impact strength, and HDT are substantially greater than those of PVC, and hardness, tensile and flexible strength, and flame resistance are considerably better than the corresponding values of polycarbonate.

One common concern in polyblending is the problem of compatibility or miscibility, which appears to have different meaning when applied to polyblends or systems containing simple liquids. It is well known that polymer compatibility

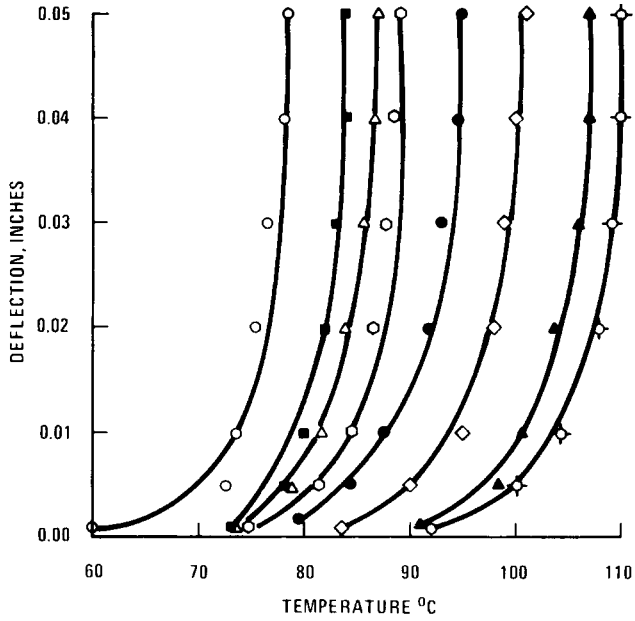


Fig. 1. Effect of blend ratio on heat deflection at 66 psi. 435 Resin/Blendex 701: (○) 100/0; (■) 80/20; (△) 70/30; (○) 60/40; (●) 50/50; (◇) 40/60; (▲) 30/70; (◊) 20/80.

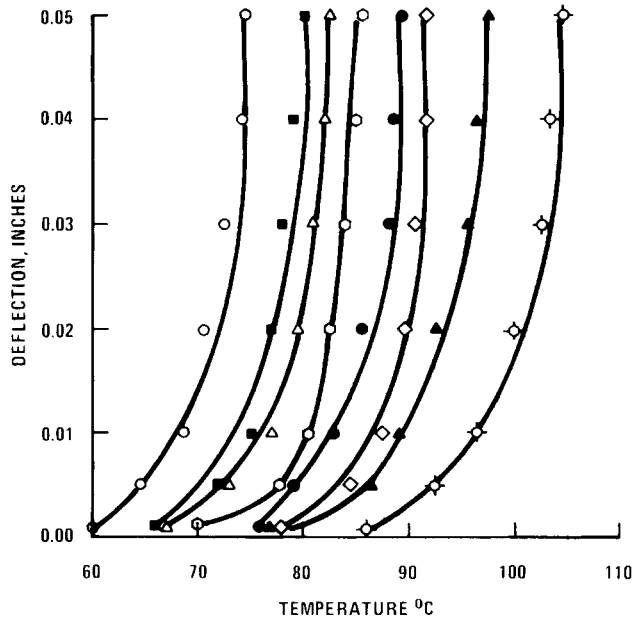


Fig. 2. Effect of blend ratio on heat deflection at 264 psi. 435 Resin/Blendex 701: (○) 100/0; (■) 80/20; (△) 70/30; (○) 60/40; (●) 50/50; (◇) 40/60; (▲) 30/70; (◊) 20/80.

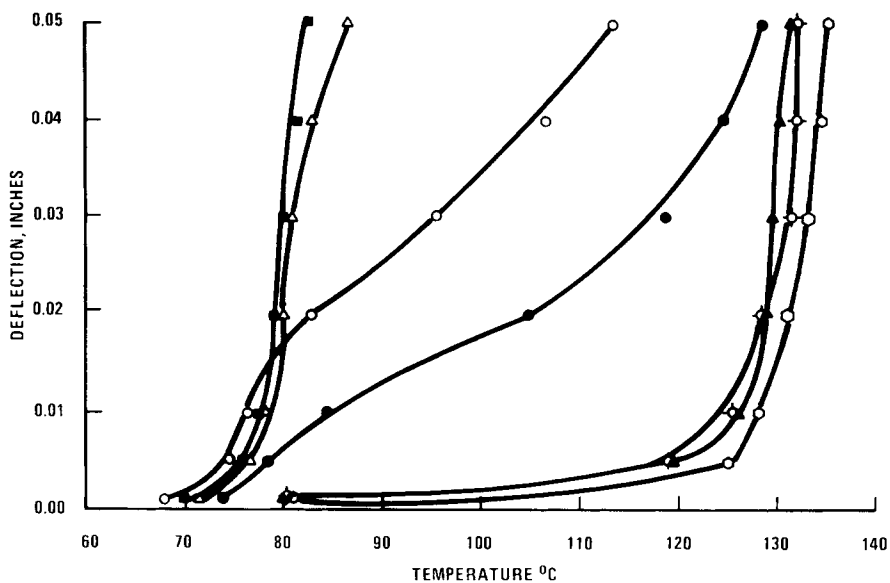


Fig. 3. Effect of blend ratio on heat deflection at 66 psi. 435 Resin/M-39: (■) 80/20; (△) 70/30; (○) 60/40; (●) 50/50; (▲) 40/60; (◇) 30/70; (○) 20/80.

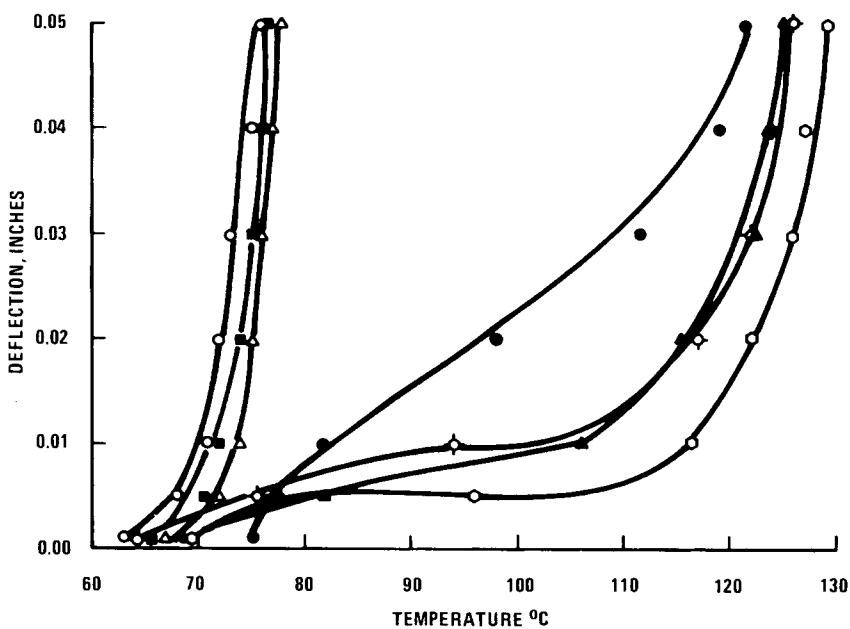


Fig. 4. Effect of blend ratio on heat deflection at 264 psi. 435 Resin/M-30: (○) 80/20; (■) 70/30; (△) 60/40; (●) 50/50; (◇) 40/60; (▲) 30/70; (○) 20/80.

is not only composition, concentration, and molecular weight dependent but is affected also by methods used to prepare specimens and testing methods.⁸⁻¹⁰ Known compatible systems based on PVC are very limited.¹¹⁻¹³ In order to be meaningful and correlatable, development of fundamental parameters is needed in defining these multiphase systems. The most often mentioned parameters include domain size, domain size distribution, and factors directly related to the degree of interphase mixing. In this paper we took a more practical approach by using HDT composition curves and dynamic measurements. Attempts were made also to characterize the system by electron microscopy.

Experimental

Polymer blends were prepared on a differential two-roll mill at 375–410°F for 3 to 8 min and compression molded at 330–350°F, 4000 psi, for 3 to 5 min to a plaque of 6 in. × 6 in. × 1/4 in. for testing. Polycarbonate pellets, which are very moisture sensitive, were dried according to the manufacturer's procedure. The following formulation, based on 100 parts of VCM-P copolymer, was used for all the sample preparations: calcium stearate, 1.0; tribasic lead sulfate, 3.6; dibasic lead phosphite, 2.4; and wax 280, 1.0.

Suppliers of the materials are: vinyl chloride/propylene copolymer, Air

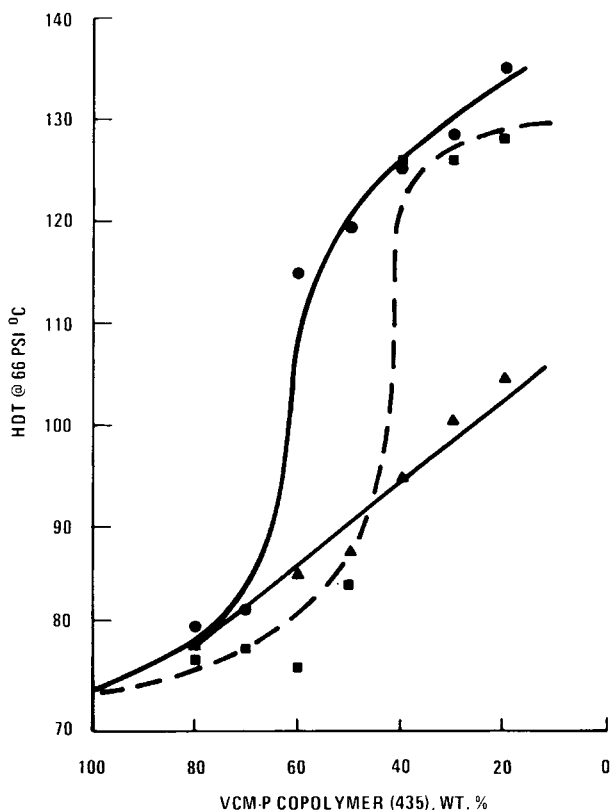


Fig. 5. HDT and composition curves for binary systems of base resin-VCM-P copolymer (435): (●) polycarbonate: Merlon M-60 (high MW); (■) polycarbonate: Merlon M-39 (low MW); (▲) ABS: Blendex 701.

TABLE I
HDT and Impact Strength for Polyblends
Ternary Systems

	Composition (435/M-39/701)	HDT, °C		Izod impact (notched), ft-lb/in.
		66 psi	264 psi	
A. Series				
1	40/40/20	101	85	0.85
2	35/45/20	104	90	0.50
3	30/50/20	123	96	0.55
4	25/55/20	121	97	0.38
5	45/40/15	100	80	0.48
6	40/45/15	108	83	0.58
7	35/50/15	115	87	0.58
B. Series				
10	50/35/15	85	79	0.32
11	50/25/25	88	84	0.52
12	50/15/35	89	83	0.66
Multicomponent Systems				
Sample no.	Composition (405/M-39/BTA-IIIN/701)	HDT, °C		Izod impact (notched), ft-lb/in.
		66 psi	264 psi	
1	25/50/10/15	119	99	5.73
2	25/45/15/15	115	92	7.03
3	25/40/20/15	104	89	4.81
4	25/45/10/20	118	93	6.60
5	25/40/15/20	108	90	4.96
6	25/35/20/20	98	88	4.39

Products and Chemicals, Inc. [435 resin: propylene 3.8%, I.V. 0.65 (ASTM D-1243-66); 405 resin: propylene 3.2%, I.V. 0.73]; Merlon M-39 (polycarbonate), Mobay Chemicals Co.; Merlon M-60 (polycarbonate) Mobay Chemicals Co.; Blendex 701 (acrylonitrile-butadiene-styrene terpolymer), Marbon Chemicals; BTA-IIIN (methacrylate-butadiene-styrene impact modifier), Marbon Chemicals; tribasic lead sulfate, NL Industries; dibasic lead phosphite, NL Industries; wax 280 (polymeric wax), Cincinnati Milicron Co.; calcium stearate, Baker Chemicals.

Specimens were imbedded in epoxy resin and sectioned. Prints were taken at 11,000 \times and enlarged to give magnification of 33,000 \times .

RESULTS AND DISCUSSION

HDT Behavior

A series of binary blends based on VCM-P copolymers were prepared using PC or ABS polymer as the secondary component. We observed that characteristics of HDT behavior were quite different for the systems VCM-P/ABS and VCM-P/PC. This is seen in Figures 1 through 4. HDT curves of VCM-P/ABS

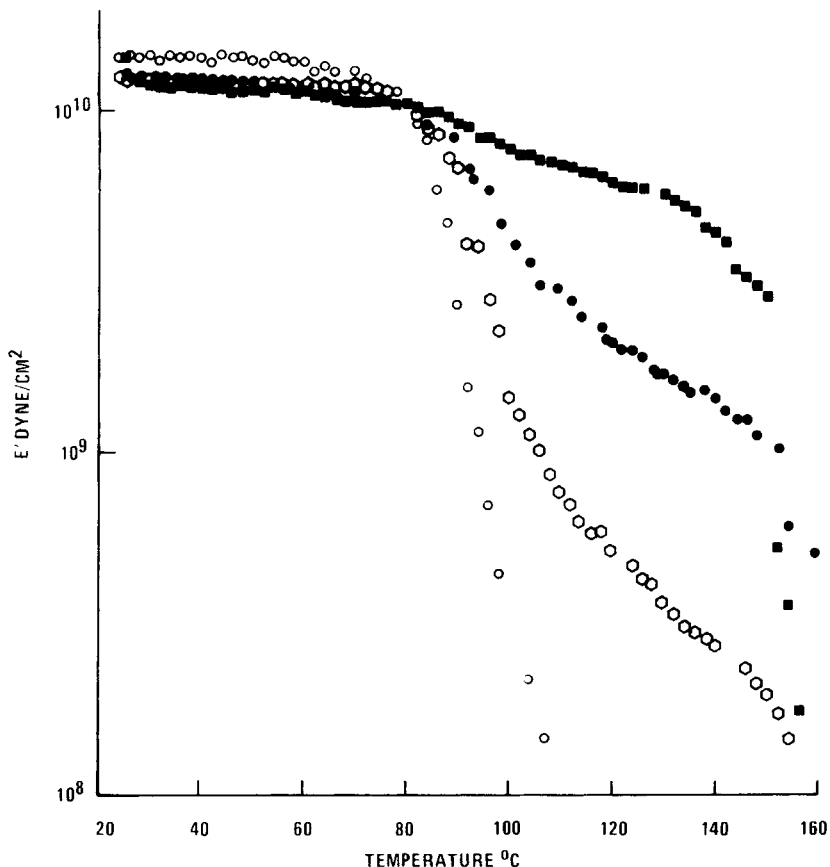


Fig. 6. Dynamic storage moduli as a function of temperature for VCM-P/PC blends: (○) 100/0; (○) 80/20; (●) 50/50; (■) 20/80.

systems are arranged in a series of parallel forms according to the blend ratio of the components. In other words, when HDT is plotted against composition, a straight-line relationship is obtained which may be approximated by the Fox equation for random copolymers (Fig. 5).¹⁴ Once the point of HDT was reached, there was almost no further resistance to deflection with temperature. By contrast, HDT in VCM-P/PC blends stayed relatively low when PC content was below 40%. HDT behavior is apparently controlled by the VCM-P phase and is not affected by the presence of PC. When the PC content was increased to 60% or over, the PC phase dominated HDT values. These results strongly suggest that phase inversion may occur around 40–60% PC level. Furthermore, in the PC system considerable heat resistance remained even after passing the point of HDT. For example, the HDT at 66 psi for the 50% PC blend was found to be 84.5°C. But to reach a deflection of 0.05 in., the temperature had to be increased to 128°C, whereas for the system containing 50% ABS, the corresponding HDT was 87.5°C and the same level of deflection was noted when the temperature had been only at 95°C.

As noted above, HDT of VCM-P copolymers are improved by blending with PC at 40% or higher. Incorporation of PC showed greater effects when HDT

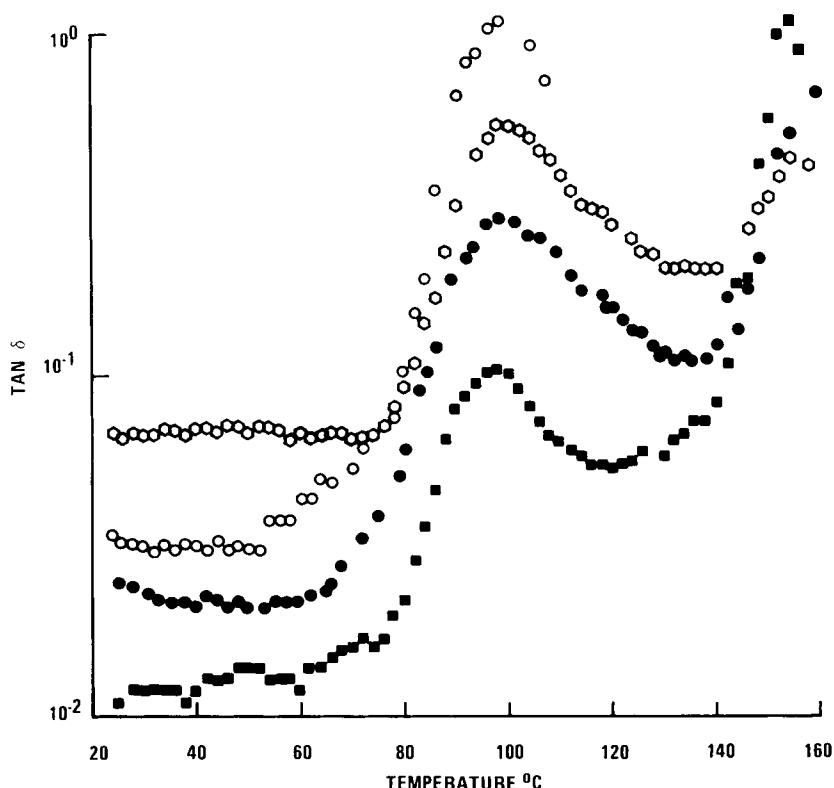


Fig. 7. Loss tangent as a function of temperature for VCM-P/PC blend: (○) 100/0; (○) 80/20; (●) 50/50; (■) 20/80.

was tested under a load of 66 psi than under 264 psi. Based on HDT and Vibron data, VCM-P/PC blends are considered to be incompatible systems. Compatibility can be improved by addition of ABS polymer to form a ternary blend. Two series of these blends were prepared, and their HDT values are presented in Table I. The first series had varied VCM-P resin contents ranging from 25% to 45%, and the HDT values at a load of 66 psi were above 100°C. When the VCM-P content was kept constant at 50% in the second series, HDT values at 66 psi were below 90°C.

The effect of molecular weight of PC on HDT of PC/VCM-P blends can be seen from Figure 5, where HDT at 66 psi was plotted against composition. The dotted lines represent blends prepared from M-39 (lower MW), while the solid lines are for blends containing M-60, a grade of high molecular weight PC. At equal composition, HDT for the M-39 blend was 85°C, compared with 114°C for an M-60 blend. However, such an effect was not observed for HDT at 264 psi until the PC level reached 60%. At this concentration the blend with M-39 and M-60 showed an HDT of 94° and 105°C, respectively. For comparison purposes, the binary system of VCM-P/ABS was included in the same plot.

Efforts were made to prepare polycarbonate blends using poly(vinyl chloride) (PVC) in the place of VCM-P. It was observed that compression-molded plaques showed visible phase separation. Since the milled sheet was uniform,

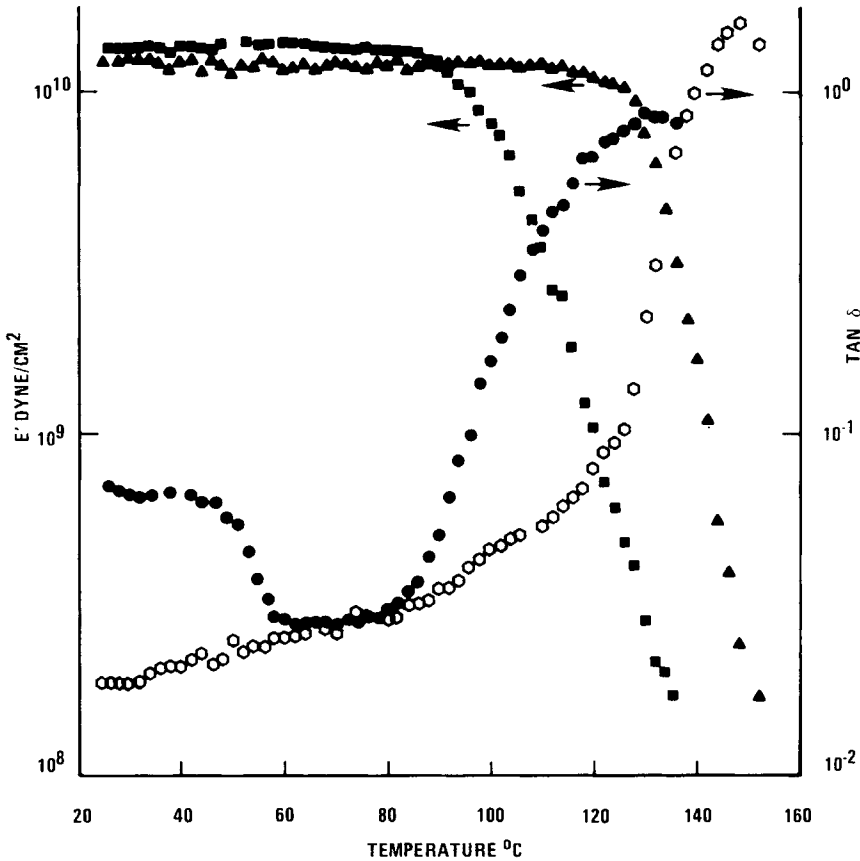


Fig. 8. Dynamic storage moduli and loss tangent as a function of temperature. VCM-P/ABS blends, Blendex 701/VCM-P: (\blacktriangle , \circ) 100/0; (\blacksquare , \bullet) 50/50.

phase separation must have occurred during the molding stage in sample preparation. With sufficient MBS added to the PVC/PC system, the physical behavior of the homopolymer blend would be expected to be comparable to that based on a vinyl chloride/propylene (VCM-P) copolymer, but we did not study that mixture in this work. Nevertheless, it was noted that blends based on PVC homopolymer were more difficult to process because of lack of flow and poor thermal stability.

Impact Strength

Addition of Blendex 701 to VCM-P had little effect on impact strength. Both binary blends with ABS and ternary blends with polycarbonate have low Izod impact strength (Table I). The effect of MBS impact modifier was then evaluated in the system consisting of VCM-P, PC, and ABS at 10%, 15%, and 20% levels. As a result of MBS addition, a number of polyblends were developed that gave a notched Izod impact strength of 4–7 ft-lb/in. while the HDT remained high at 98–119°C under 66 psi. Compositions of these blends were in the range of 25% VCM-P, 35–50% PC, 15–20% ABS, and 10–20% MBS, as shown in Table

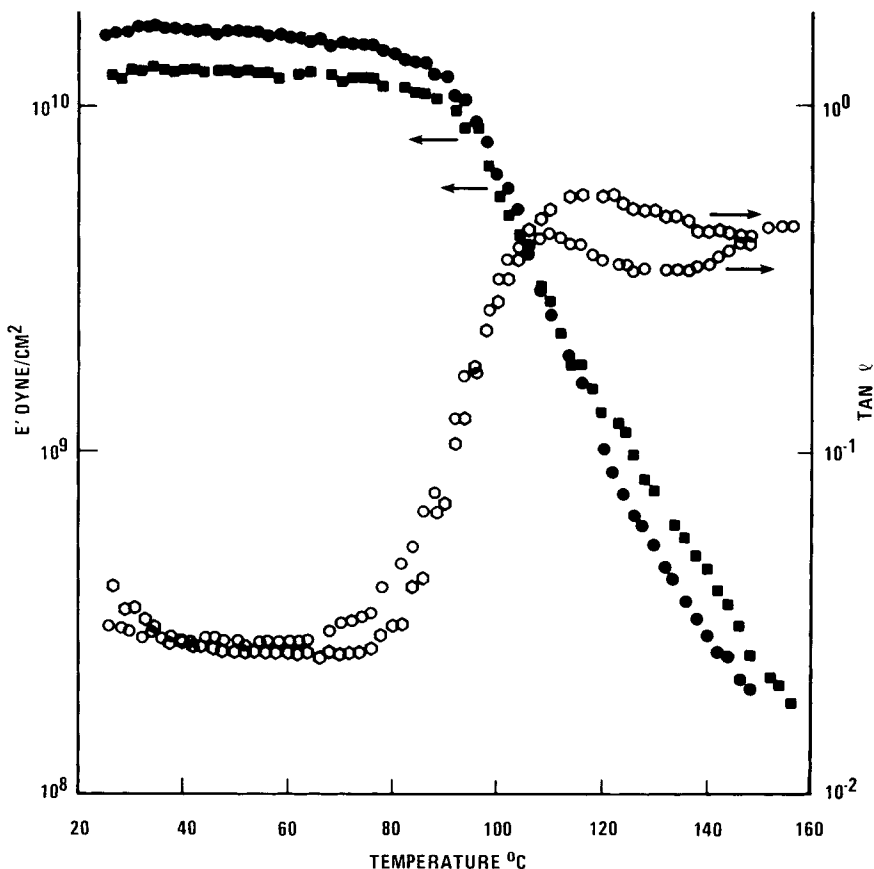


Fig. 9. Dynamic storage moduli and loss tangent as a function of temperature. VCM-P/PC/ABS: (●, ○) 50/25/25; (■, ○) 50/35/15.

I. When the VCM-P content was increased to 50%, HDT and impact strength decreased to 80°C and less than 1 ft-lb/in., respectively.

Dynamic Properties

A Vibron was used to determine compatibility of polyblends. By varying the temperature, the range of dynamic response was obtained. The loss tangent, $\tan \delta$, is read out directly from the instrument. Usually the T_g , taken at the $\tan \delta$ peak, is higher than that determined by dilatometric or thermodynamic methods because of the difference in the time scale. The relative concentration of the component may be approximated from the peak height, while the width of the peak gives some indication of the molecular weight distribution of the component. Only the dynamic storage moduli (E') and the loss tangent ($\tan \delta$) are presented here as a function of temperature at a constant frequency of 100 cps. In general, the Vibron data were found fairly consistent and in reasonable agreement with reported values. At 100 cps, the copolymer had a $\tan \delta$ peak at 100°C. PVC has a reported peak value of 93°C at 50 cps.¹⁵



Fig. 10. Cross-sectional view of VCM-P copolymer.

In the case of polycarbonate, a single $\tan \delta$ peak was observed at 154°C , in comparison with a reported value of 150°C at 1 cps.¹⁶ Both the sharp $\tan \delta$ and steep drop in E' are characteristics of a typical amorphous polymer.

The modulus E' and $\tan \delta$ for the binary blends were plotted against temperature in figures 6 and 7, respectively. The concentration of polycarbonate in these systems was at 0%, 20%, 50%, and 80%. It is apparent that the VCM-P copolymer is incompatible with polycarbonate because two $\tan \delta$ peaks are present in all cases. The peak of 98°C corresponds to the VCM-P polymer, while the one at 154°C is attributed to the polycarbonate phase. Such a two-phase incompatible behavior can also be seen from the E' plot, where two distinguishable slopes corresponding to the two transitions are detectable. In contrast to the polycarbonate system discussed, a single $\tan \delta$ peak was detected between 50 and 150°C for a 50% ABS blend, which implies that the system is compatible (Fig. 8). Moreover, an interesting case was found in a ternary system where 25% ABS was incorporated into a blend containing 25% PC and 50% VCM-P copolymer. As shown in Figure 9, only a single broad $\tan \delta$ peak was observed, indicating that the compatibility of the binary blend was indeed enhanced by

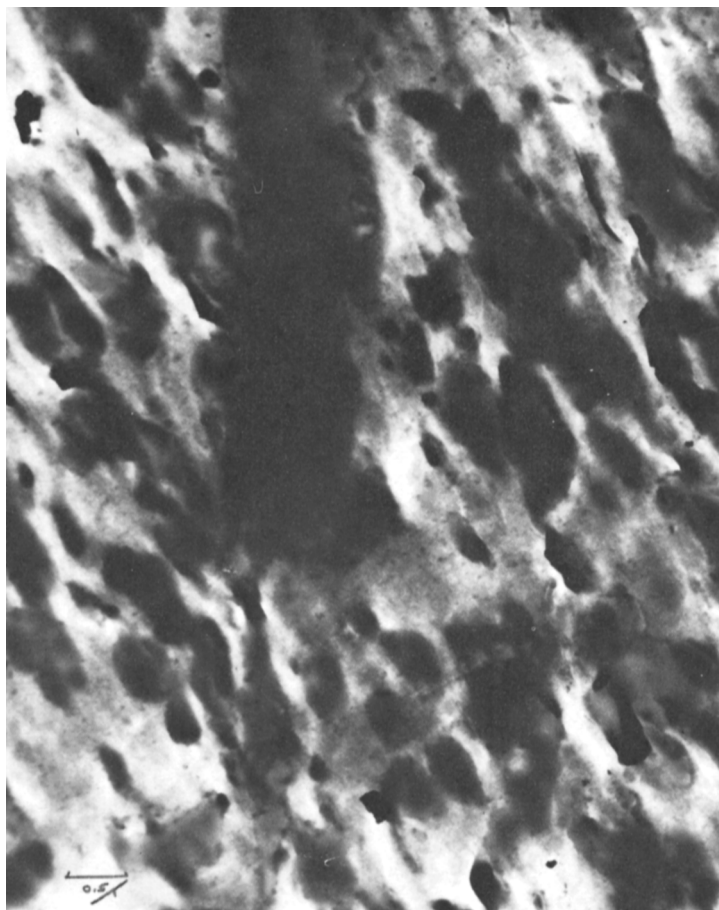


Fig. 11. Cross-sectional view of blend of VCM-P/PC at 80/20.

the presence of ABS polymer. In a similar ternary system when only 15% ABS was incorporated, as shown in the same plot, two $\tan \delta$ peaks at 110°C due to VCM-P and 156°C due to PC were still barely visible. We observed no significant differences in HDT and impact strength for the above systems (Fig. 9) containing 25% and 15% ABS.

Morphology

Electron photomicrographs were prepared for some of the blends. In Figure 10, the single phase of the VCM-P copolymer was uniform and homogeneous. Two binary systems with 20% PC and 80% PC are presented in Figures 11 and 12, respectively. At low PC level, PC particles, which were dispersed in the VCM-P phase, exhibited irregularities both in shape and size. The PC particle diameter was estimated to be about 0.5μ . An interesting feature in morphology was observed in a blend containing 20% VCM-P where PC particles existed in a form of string-like structures having a diameter of $0.1\text{--}0.2 \mu$. The length of the string, however, could not be determined since most of it was entangled

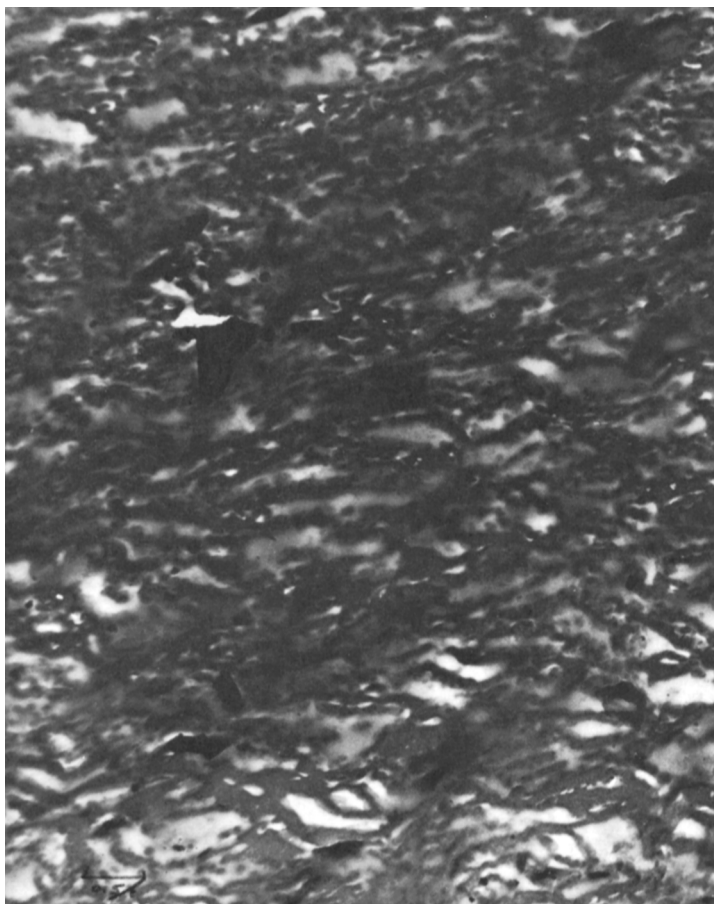


Fig. 12. Cross-sectional view of blend of VCM-P/PC at 20/80.

without clear definition. Furthermore, the morphology of a 60% PC blend was very similar to that observed for the 80% PC blend, whereas a 40% PC blend was, in fact, close to the 20% PC system in terms of morphology. The last photo was taken of a 50% ABS binary blend (Fig. 13). Apparently, the fine ABS particles, with a diameter of 0.1μ , were more uniformly dispersed in a discrete form throughout the VCM-P phase. Morphology studies of ternary and multicomponent systems are far more complex than single- or two-phase systems. No electron photographs are presented because of the uncertainty of identifying single components.

CONCLUSIONS

1. Polyblends based on VCM-P/ABS appear compatible, while the VCM-P/PC system is definitely not. The HDT-composition plot for the latter exhibited an S-shaped curve, in contrast to a straight line for VCM-P/ABS.

2. Since deformation in an HDT test is inversely proportional to the modulus, the experimental HDT and HDT-composition curves may be used to give some indication of compatibility, at least for the binary systems studied here.

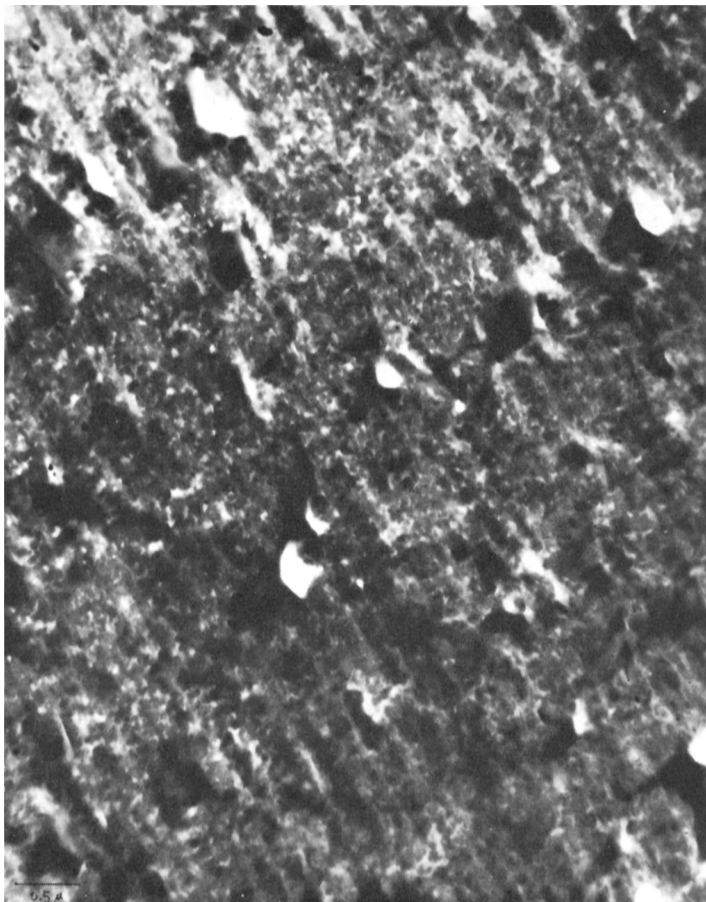


Fig. 13. Cross-sectional view of blend of VCM-P/ABS at 50/50.

3. The HDT behavior in VCM-P/PC systems can be best explained as a phase inversion phenomenon. However, in view of the wide difference in melting temperature between VCM-P copolymer and polycarbonates, it is suggested that the string-like morphology of polycarbonates may still exist as a discontinuous phase functioning as a reinforcing fiber or filler in the VCM-P copolymer matrix, provided that the level of polycarbonate is sufficiently high and there are strong bonding forces between the interphases.

4. Using a multicomponent system, the results indicate that VCM-P-based polyblends can be prepared with high HDT and some impact strength. Further improvement on the system may depend upon the selection of a more effective HDT modifier so that the VCM-P content in the blend can be increased to 50% or over without adverse effect in other physical properties.

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