

# Property–Composition Dependence of Polyurethane–Poly(vinyl Chloride) Polyblends

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## Synopsis

The dynamic mechanical properties of polyblends of a polyurethane (PU) elastomer and poly(vinyl chloride) (PVC) at five compositions were studied at 110 Hz, between  $-120$  and  $120^{\circ}\text{C}$ . The study also included tensile testing at  $25^{\circ}\text{C}$ , and examination of polyblend morphology and fire-retardant properties. The results were analyzed using suitable two-phase mechanics models valid for such systems. This analysis, together with the morphological evidence and the thermomechanical spectra, indicate that these polymer alloys are essentially heterogeneous and their useful mechanical properties are due to good adhesion between the two phases. This conclusion is also corroborated by the tensile properties study. Fire retardancy is significant only above  $\sim 60\%$  by weight of PVC.

## INTRODUCTION

Blends of poly(vinyl chloride) (PVC) with various types of polyurethanes (PU) have gained considerable technological value. A survey of pertinent literature indicated that a combination of these polymers in bulk or as laminates, offers advantages in terms of increased flexibility,<sup>1</sup> tensile,<sup>2</sup> impact,<sup>3</sup> and fire-retardant properties.<sup>4</sup> Though it has been claimed<sup>5</sup> that certain PU–PVC blends are compatible, to the best of our knowledge, no systematic study on the compatibility and the effects on mechanical properties for this system has been reported. This polyblend has additional interest since chlorine containing polymers are reported<sup>6a</sup> to interact with oxygen containing polymers (e.g., polyesters) through specific forces.

The present study covers the dynamic mechanical properties of a PVC–PU elastomer blend over a wide temperature and composition range. Morphological features, tensile, and fire-retardant properties are also reported. Our aim was to assess the degree of mixing and/or interaction using the dynamic mechanical technique, in conjunction with morphological evidence. Ultimate properties could yield supplementary information with respect to possible mutual tensile reinforcement. Finally, the system could be used to test various phenomenological models proposed to predict the properties of a polyblend from those of its pure components.

## EXPERIMENTAL

### Materials and Specimens Preparation

The polyurethane used was a commercial elastomeric product with  $\bar{M}_n = 1 - 2 \times 10^5$ . The basic polymer backbone consists of short sequences of poly-

(tetramethylene oxide) (PTMO) with a MW of  $\sim 7-8 \times 10^2$ , connected with 2,4 and 2,6 toluene diisocyanate (TDI) units to tetramethylene sequences of approximately the same length. The ratio of 2,4 to 2,6 TDI units was 4:1. One molecule of trimethylpropane monoallylether per polymer molecule, provides crosslinking sites. Poly(vinyl chloride) was an unplasticized commercial product prepared by free-radical polymerization with  $\bar{M}_n = 3.5 \times 10^4$ .

Blending was affected by dissolution of the two components in a common solvent (methyl ethyl ketone) (MEK) and slow addition of the 5% solution in an excess of methanol. The product was dried at 60°C in a vacuum for 5 days. All samples used for the dynamic mechanical measurements were prepared by this procedure. Thin films were prepared by hot pressing at 300–400°F and 5000–10,000 psi, for a period of 2–3 min, depending on composition. Higher temperatures and shorter times were used for polyblends richer in PVC. For tensile testing where large quantities were required, the polymers were dissolved in MEK and the solvent removed by evaporation. The films produced were dried as described and chopped, and dumbbell test pieces were prepared by hot pressing as before, using longer times. All specimens were quenched at 0°C.

Some preliminary blending tests at 220°F using a small injection molder led to PVC degradation. To avoid the risk of possible alteration of the PVC mechanical spectra, we did not use an extruder (where the residence time of the plastic would be longer) to mix the products. Conceivably, this could be possible using suitable stabilizers. However, in this case, the interpretation of the mechanical spectra would be uncertain.

The following compositions given in terms of weight ratios of components were studied: 100P/0, 90P/10, 75P/25, 50P/50, 25P/75, 10P/90, 0P/100. The first numeral denotes the weight of PVC.

### Apparatus and Procedures

Dynamic mechanical data, loss tangent  $\tan \delta$ , and complex modulus  $|E^*|$  were obtained between  $-120$  and  $120^\circ\text{C}$  at 110 Hz, using the direct-reading viscoelastometer, (Rheovibron model DDV II-C, Toyo-Baldwin). The correction due to clamp extension was applied. The chamber was kept free of moisture by a slow stream of precooled argon. Specimens dimensions were  $3 \times 0.3 \times 0.04$  cm<sup>3</sup>.

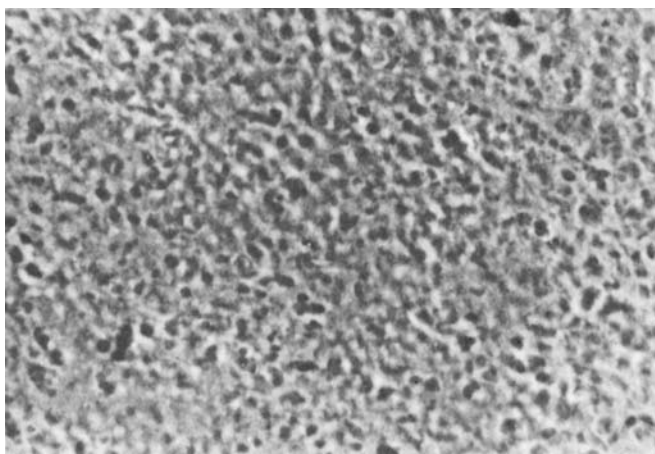
Tensile tests (see, ASTM D-638)<sup>7</sup> were made using a Zwick model 1487 tensile testing machine, at a crosshead speed of 5 mm/min at room temperature. Thin films prepared from coprecipitated components, were examined under a phase-contrast microscope (Orthoplan Leitz), with oil immersion in bright field.

Flammability tests were carried out in a mixture of oxygen–nitrogen using standard procedures (cf. ASTM D2863-70)<sup>8</sup> to determine the limiting oxygen index. This is defined as the least percentage by volume of oxygen necessary to support combustion in the atmosphere flowing around the specimen. Specimen dimensions were  $7.0 \times 0.6 \times 0.3$  cm<sup>3</sup>.

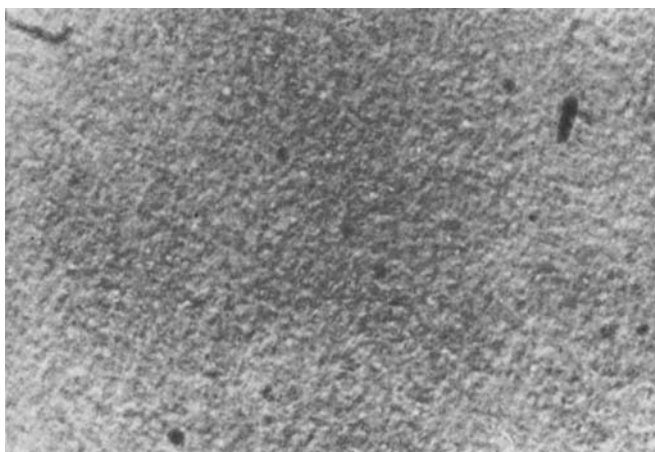
## RESULTS

### Morphology

Films prepared by coprecipitation and hot pressing were colorless, transparent but hazy. Figure 1 shows photomicrographs (a) and (b) taken with samples 50P/50 and 75P/25, respectively. They are typical of the intermediate and extreme compositions and indicate a heterogeneous polyblend with a very fine domain structure. The 25P/75 composition had a leatherlike feel, the 50P/50 was a flexible plastic, the degree of rigidity increasing with the PVC content. Films produced by solvent evaporation were opaque and phase discontinuity was more evident, especially at the intermediate compositions. Thermomechanical testing did not reveal any substantial difference between the two sets of films.



(a)



(b)

Fig. 1. Optical micrographs of PVC-PU polyblend samples, ( $\times 4000$ ). (a) 50P/50; (b) 75P/25.

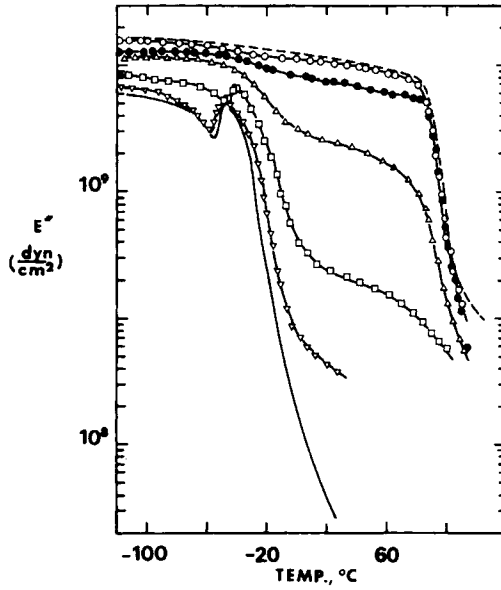


Fig. 2. Temperature dependence of storage modulus  $E'$  for various compositions: (---) 100P/0; (○) 90P/10; (●) 75P/25; (△) 50P/50; (□), 25P/75; (▽) 10P/90; (—) OP/100.

### Dynamic Mechanical Properties

Figures 2 and 3 give the thermomechanical spectra of the polyblends in terms of storage  $E'$  and loss modulus  $E''$ , respectively. In Table I, more complete de-

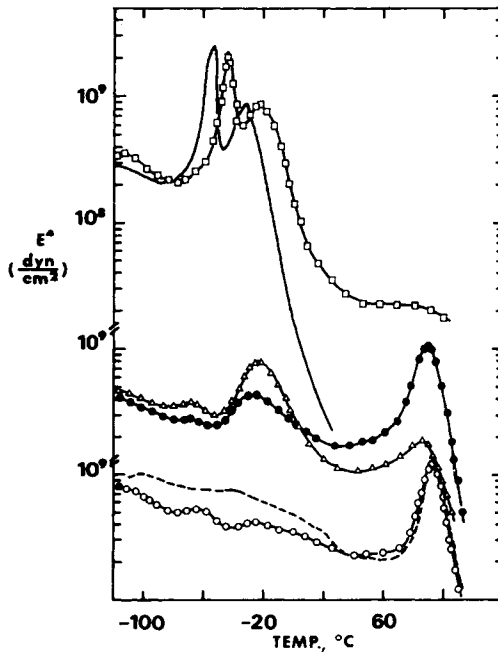


Fig. 3. Temperature dependence of loss modulus  $E''$  for various compositions: (---) 100P/0; (○) 90P/10; (●) 75P/25; (△) 50P/50; (□) 25P/75; (—) OP/100. (Curves displaced for legibility).

TABLE I  
 Temperatures of Relaxations Maxima Observed, °C

Polyblend sample	tan $\delta$			E''		
	$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$
100P/0	103	-42 <sup>a</sup>	-102 <sup>a</sup>	94	-42 <sup>a</sup>	-102 <sup>a</sup>
90P/10	103	-25	(-65) <sup>c</sup> -120 <sup>b</sup>	91	-30	(-66) <sup>c</sup> -120 <sup>b</sup>
75P/25	107	-25	(-64) <sup>c</sup> -120 <sup>b</sup>	88	-28	(-64) <sup>c</sup> -120 <sup>b</sup>
50P/50	102	-16	(-65) <sup>c</sup> -120 <sup>b</sup>	87	-25	(-66) <sup>c</sup> -120 <sup>b</sup>
25P/75	98	-11	(-55) <sup>c</sup> -116	80	-23	(-56) <sup>c</sup> -116
10P/90	—	-16	-60 -116	—	-29	-60 -116
OP/100	—	-16( $\alpha_c$ ) <sup>c</sup>	-56( $\alpha$ ) <sup>c</sup> -120 <sup>b</sup>	—	-32( $\alpha_c$ ) <sup>c</sup>	-56( $\alpha$ ) <sup>c</sup> -121 <sup>b</sup>

<sup>a</sup> Broad relaxation.

<sup>b</sup> Shoulder.

<sup>c</sup> Parentheses include very weak relaxations.

tails on the location of the main relaxations are given. The dynamic viscoelastic behavior of polyurethanes has been amply discussed.<sup>9-11</sup> The weak  $\gamma$  relaxation at around  $-120^\circ\text{C}$  involving motions of methylene sequences was observed in all compositions. The major  $\alpha$  relaxation (at  $-56^\circ\text{C}$ ) associated with the  $T_g$  of the PTMO sequences is also evident at the 25P/75 composition. An additional loss process  $\alpha_c$  has been attributed<sup>10</sup> to the crystallization of the PTMO segment. Crystallization develops during the measurements since the specimens were quenched to  $-120^\circ\text{C}$  at the start of the experiment. This explains the "hump" in the modulus-temperature curve at certain compositions (Fig. 2). Similar behavior has been observed in the case of an incompatible blend.<sup>12</sup> Examination of the spectra (Fig. 3) and Table I indicates a maximum shift of the main PU component relaxation at the 25P/75 composition. At higher PVC compositions the  $\alpha$  relaxation shifts to lower temperatures diminishing in strength. The temperature dependence of the modulus curves indicates that at the higher PVC compositions there is essentially one low-temperature main relaxation; no crystallization effects on the modulus are evident. Table I shows that this main low-temperature relaxation is shifting to higher temperatures at the intermediate compositions; see variation of  $E''_{\max}$  with composition. The main relaxations of PVC are<sup>13</sup> the  $\beta$ , a shoulder around  $-40^\circ\text{C}$ , and the main  $T_g$  relaxation at  $93^\circ\text{C}$  (Fig. 3). Of these, the  $\alpha$  peak has a higher diagnostic value in assessing possible interactions among polyblend components. Examination of the  $E''_{\max}$  shift with composition (Table I) indicates that the maximum displacement of the high-temperature relaxation takes place again at the 25P/75 composition. The modulus curves variation (Fig. 2) displays the gradual stiffening of the elastomeric PU with increasing PVC concentration. The 10P/90 blend still retains the elastomeric properties, while the 75P/25 and 90P/10 are essentially thermoplastic. At the intermediate compositions, the temperature dependence of stiffness resembles that of a block copolymer consisting of glassy and elastomeric domains.

### Tensile Strength and Recovery

All specimens except the 10P/90, and to a lesser degree the 25P/75, showed considerable stress whitening long before failure.

Figure 4 summarizes the results for the ultimate stress  $\sigma_u$  and percentage strain

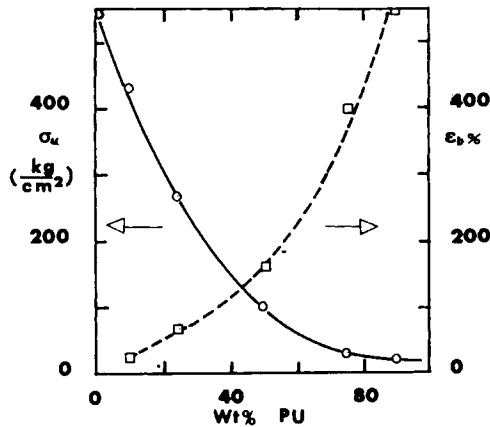


Fig. 4. Composition dependence of tensile strength  $\sigma_u$  and percentage strain at failure  $\epsilon_b$ % of polyblends at 25°C.

at failure  $\epsilon_b$ %. To compare the hysteresis properties of the polyblends, percentage relative recovery values were calculated from the ratio  $R = 100 (l_b - l_r)/l_o$ ; where  $l_b$  is the length of specimen at failure;  $l_r$  is the length after relaxation for a period of one week, and  $l_o$  is the original specimen length (distance between two fiduciary lines on the test piece). Up to 25P/75 compositions,  $R$  was about 250%, at 50P/50 it dropped to 30%, and at 75P/25 it was about 15%.

### Flammability Tests

The results are summarized in Figure 5. No significant fire retardancy is observed with up to 60 wt % of PVC. Beyond that point, fire retardancy is increasing almost linearly with PVC. Up to this composition, wet "charring" was evident.

### DISCUSSION

Morphological evidence suggests that the polyblend studied was a heterogeneous system. The heterogeneous nature of the blends induced us to test (at room temperature) various phenomenological mechanics models<sup>6b</sup> with respect to composite modulus prediction.

The results are summarized in Figure 6. The best curve fit (curve 1) to the

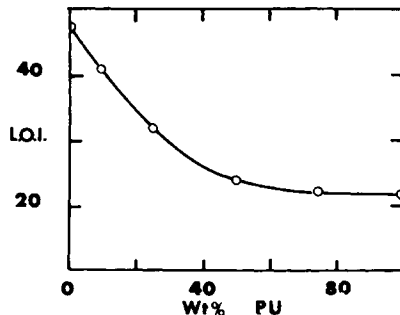


Fig. 5. Composition dependence of limiting oxygen index (LOI) of polyblends.

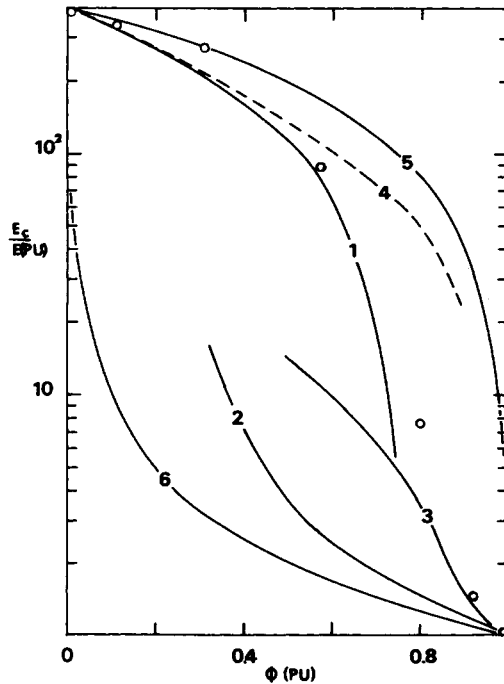


Fig. 6. Comparison of calculated and experimental  $E(\text{polyblend}/E(\text{PU}))$  values at  $25^\circ\text{C}$ : (O) experimental values; curve 1, eq. (1) with a PVC matrix,  $\Phi'_m = 0.74$ ; curve 2, Halpin-Tsai equation with a PU matrix,  $\Phi'_m = 0.74$ ; curve 3, eq. (2) with a PU matrix; curve 4, original Kerner's model with PVC matrix; curves 5 and 6 correspond to parallel and series connection, respectively.

experimental  $E_c/E(\text{PU})$  data was obtained (for up to about 70% volume fraction of PU), using the Halpin-Tsai equation<sup>14</sup> suitable for an inverse system, i.e., a PU phase dispersed in a PVC matrix with a maximum packing fraction  $\Phi'_m = 0.75$ . The equation has the form,

$$G_c/G_1 = (1 - B\Psi\Phi_2)/(1 + AB\Phi_2) \tag{1}$$

where,  $A = (8 - 10\nu_1)/(7 - 5\nu_1)$ ,  $B = (G_1/G_2 - 1)/(G_1/G_2 + A)$ , and  $\Psi = 1 + (1 - \Phi'_m)\Phi_2/\Phi'_m{}^2$ .

$G_c, G_1, G_2$  are the shear moduli of the composite, the rigid and the soft phase, respectively;  $\nu_1$  is the Poisson ratio of the rigid phase,  $\Phi_2$  is the volume fraction of the soft phase. For the particular system studied  $\nu_1 = 0.35$  and  $\nu_2 = 0.49$ .<sup>15</sup> The Poisson ratio of the composites was taken as the arithmetic mean of their components weighted as their volume fraction. The model fails when PVC is dispersed in a PU matrix (curve 2). A better prediction (curve 3) is obtained using Hashin's model<sup>16</sup> which assumes no interactions between the matrix and the dispersed phase. His model for a PU matrix is given by,

$$K_c = K_2 + (K_1 - K_2) \frac{(4G_2 + 3K_2)\Phi_1}{4G_2 + 3K_1 + 3(K_2 - K_1)\Phi_1} \tag{2}$$

where subscripts have the same meaning as before and  $K$  is the bulk modulus. In all previous expressions, bulk, shear, and Young's moduli were interconverted using the standard expression,

$$E = 2G(1 + \nu) = 3K(1 - 2\nu) \tag{3}$$

The previous analysis supports the morphological evidence that the polyblends are heterogeneous and, up to  $\Phi(\text{PU}) \approx 0.60$ , the PVC is the matrix with a strongly adhering PU phase in the form of close-packed spheres ( $\Phi'_m = 0.74$ ).<sup>14</sup> At higher PU concentrations, a PU matrix with noninteracting PVC inclusions seems to be more in accord with theoretical predictions. The experimental evidence also excludes a morphology of two partly continuous phases. For such a composite, theory predicts<sup>14,17</sup> that its  $E_c/E(\text{PU})$  values would lie between those given by curves (1) and (2).

The heterogeneous nature of the system is also supported by the dynamic mechanical spectra which do not indicate any intermediate new relaxation (shifting with composition) as would be the case for a compatible or chemically interacting system. The shift of the soft-phase relaxation at intermediate compositions to higher temperatures can be attributed to a hindering of the segmental mobility due to adhesion, or a limited solubility of the two components. Similarly, the shift to lower temperatures of the main PVC relaxation can be attributed to limited plasticization.

The successful application of the modified Kerner model (Halpin-Tsai) or the unmodified Kerner model<sup>14</sup> (curve 4), at the low PU concentration (see Fig. 6) underlines the importance of adhesion in explaining the mechanical properties of this composite system. Also, the significant  $\epsilon_b$  and relative recovery values  $R$  up to 50% by weight of PVC indicates good adhesion for the two phases.  $R$  values can reveal, in some cases, interphase integrity in a composite system.<sup>18</sup> It is also pertinent to note that PVC and polyurethane laminates show exceptional strength when bonded together by hot pressing.<sup>19</sup>

Finally, with respect to the fire-retardancy tests, it is probable that the good adhesion to PVC of the combustible PU melt, delays the formation of dry charring which is known to enhance fire retardancy. Indeed it was observed that the PU melt wetted the charred combustion product even at relatively rich PVC compositions (50–60%).

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