

# Effect of Fillers on the Compatibility of Polymer Blends

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## Synopsis

The effects of carbon black, talc, and ultrafine silica filler, at different filler loading, on the compatibility of two binary blends was examined. These were, the mechanically compatible polyurethane (PU)/poly(vinyl chloride) (PVC) at 25/75 weight ratio, and the poly( $\epsilon$ -caprolactone) (PCL)/styrene-acrylonitrile (SAN) copolymer (with 30% AN content), at the 50/50 blend composition. For the former system, both dynamic mechanical analysis (DMA) and DSC measurements indicated that, depending on the filler surface, boundary layers are formed at the filler-matrix interface shifting the PU relaxation to higher temperatures. No significant effect was observed for the PVC component. Though the mechanical spectra are also affected, essentially no  $T_g$  shifts were observed for the PCL-SAN system. A qualitative explanation of selective filler activity towards the blend components was given by invoking the matrix-filler basic-acidic nature. Overall, the fillers had no compatibilizing effect on the blend. Using available theory both DSC and the DMA techniques agree in their estimate of the boundary layer thickness. Moduli data were also analyzed using mechanics models proposed for composite systems.

## INTRODUCTION

The aim of this experimental work was to focus on the question whether fillers can promote compatibility in polymers. There has been a suggestion in the literature<sup>1,2</sup> that such an effect has been observed, and most recently Lipatov and co-workers<sup>3</sup> reported that introduction of a filler enhances the thermodynamic compatibility of a binary polyethylene-polyurethane blend. This was ascertained by the decrease to negative values, of the thermodynamic interaction parameter  $\chi_{23}$ , with the addition of filler. It should be pointed out that if compatibilization can be achieved by the addition of suitable fillers, it would constitute a major technical achievement.

The systems chosen were the mechanically compatible blend of a rubbery polyurethane (PU)/poly(vinyl chloride) (PVC) studied before<sup>4</sup> and the binary blend poly( $\epsilon$ -caprolactone) (PCL)/styrene-acrylonitrile copolymer (SAN) containing 30 wt % acrylonitrile (AN). For this system it was reported<sup>5</sup> that changing the AN to less than 30 wt % leads to a miscible blend. Thus, compositionwise the latter system is close to conditions of miscibility. Filler parameters, which were to be examined, were type, size, and loading.

The techniques used were dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The former would give information on the effect of filler on the position and width of the relaxation spectra. In addition moduli measurements could provide data for testing various mechanics models.<sup>6,7</sup> DSC measurements would supplement the above technique providing additional data on the effective volume of fillers, more specifically,

the thickness of the matrix adhering<sup>8,9</sup> to the spherical filler particle. These data would be correlated with the DMA which, assuming certain models,<sup>10,11</sup> can also provide information on the matrix layer attached onto the filler.

## EXPERIMENTAL

### Materials and Specimens Preparation

The PCL used (PCL-700) was donated by Union Carbide Corp., and had an  $\bar{M}_w = 40,000$ . The SAN copolymer was obtained from EGA-Chemie, Europe. The PU elastomer was donated by DuPont (U.K.) and had an  $\bar{M}_n = 1-2 \times 10^5$ . Its structure was described before.<sup>4</sup> PVC was an uplasticized commercial product prepared by free-radical polymerization with  $\bar{M}_n = 3.5 \times 10^4$ .

The silica filler was Cabosil-5 (HS-5) from Cabot Corp. (U.S.A.). The spherical particles had a nominal average diameter  $\bar{d} = 80 \text{ \AA}$  and surface area<sup>12</sup>  $325 \pm 25 \text{ m}^2/\text{g}$ . Microscopic examination of the talc filler indicated that it consisted of acicular particles having an average length of  $10 \text{ }\mu\text{m}$  and forming irregular aggregates with an average diameter of  $50 \text{ }\mu\text{m}$ . Carbon black (N-375) had an average particle diameter  $\bar{d} = 240 \text{ \AA}$  and a surface area<sup>13</sup> of  $100 \text{ m}^2/\text{g}$ .

To prepare the PU/PVC composite an 1% solution of PVC in butanone-2 (MEK) was prepared, the required amount of filler added and the system stirred for 24 h. Subsequently, PU was added, dissolved with stirring, followed by the required PVC component to obtain a 75 wt % of PVC in the blend. It was reported<sup>14</sup> that such a procedure enhances the matrix adhesion to the filler. A similar procedure was followed for the preparation of a 50/50 blend of SAN/PCL, using chloroform as a common solvent. The main amount of solvent was removed in a rotary evaporator, and last traces using vacuum for 4 days at  $50^\circ\text{C}$ . Thin films of the PU-PVC system were prepared by hot pressing for 2 min at  $200^\circ\text{C}$  and 3000 psi and quenching to  $0^\circ\text{C}$ . For the SAN-PCL system, conditions were  $150^\circ\text{C}$ , 1500 psi for 2 min. Filler loading for this system was 15 wt %. For the PU-PVC blend, loading was 5, 10, and 25%, and, for carbon and talc-filled blend, composites with a filler volume fraction  $\varphi_f = 0.30$ , were also prepared. At this high loading the silica-filled blend could not be melt-pressed to give a void-free film. This volume fraction corresponds to 47 and 37 wt % for the talc- and the carbon-black-filled composites, respectively.

The PCL-SAN-filled blends were brittle, and phase separation was evident with the exception of the silica-containing blend which after melt pressing gave a flexible film with a smooth surface; no polymer phase discontinuity was macroscopically evident.

Filler content in the blends will be denoted with a numeral equal to its weight percentage in the blend, followed by filler designation; Cab for Cabosil, C for carbon black, and TC for talc. Thus PU-PVC/10 Cab refers to the specific blend matrix containing 10% by wt of Cabosil.

### 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 DDVII-C, Toyo Baldwin). To obtain

TABLE I

A. Temperatures of Main Relaxations of Blend Components (°C)												
Filler type loading (wt %)	Cabosil			Carbon black			Talc					
	PU		PVC	PU		PVC	PU		PVC			
	tan δ	E''	tan δ	E''	tan δ	E''	tan δ	E''	tan δ	E''		
0	-25	-28	107	88	-25	-28	107	88	-25	-28	107	88
5	—	—	102	88.5	—	—	104	88	—	—	104	91
10	-16	-24	102	89	-14	-19.5	101	91	(-28, -20) <sup>a</sup>	(-28, -22)	104	91
25	(-10)	(-12)	102	88	-25	-25	102	93	-21	-26	105	91
$\Delta H_a^*$ (KJ/mol) × 10 <sup>-2</sup>		6.3		3.8		—		12.6		2.4		6.3

B. SAN-PCL System; <sup>b</sup> Low Temperature Relaxations (°C)											
Loading (wt %)	Cabosil			Carbon black			Talc				
	Carbon black		SAN	Carbon black		SAN	Carbon black		SAN		
	tan δ	E''	tan δ	E''	tan δ	E''	tan δ	E''	tan δ	E''	
0	-33	-41	-43	-23	-38	-19	110 <sup>c</sup>				
15	-42	(-42)	(-40, -23)	(-43, -19)							

<sup>a</sup> Parentheses signify broad relaxations centered around indicated temperature(s).

<sup>b</sup> At 50/50 composition.

<sup>c</sup> From Ref. 5.

approximate apparent activation energies for the main relaxations, measurements were also carried out at 35 Hz. The correction due to clamp extension was applied at all temperatures. During measurements, a stream of precooled argon reduced the moisture in the measuring chamber. Specimens dimensions were  $3 \times 0.3 \times 0.07 \text{ cm}^3$ . DSC measurements were carried out using a DuPont 910 Calorimeter coupled with a 990 programmer-recorder. Calibration was made with Indium standard. Sample weight was 20 mg. Samples were heated to  $130^\circ\text{C}$  prior to scanning between  $-80$  and  $120^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ .

Measurements were carried out only on the PU-PVC/Cab system, since the spherical filler allowed theory predictions to be tested. For the SAN-PCL/15 Cab system a crystallinity measurement was also carried out.

## RESULTS

### Dynamic Mechanical Measurements. PU-PVC system

The results are summarized in Figures 1-3 and Table IA. The  $\tan \delta$  spectra in Figure 1 indicate that the addition of filler broadens the rubbery PU transition at ca.  $-25^\circ\text{C}$  shifting it to higher temperatures. This effect is smaller for the high temperature PVC relaxation. At constant filler size, this relaxation decreases with filler loading (i.e., less energy is absorbed), and at similar loadings, damping decreases with decreasing size of filler. Smaller filler

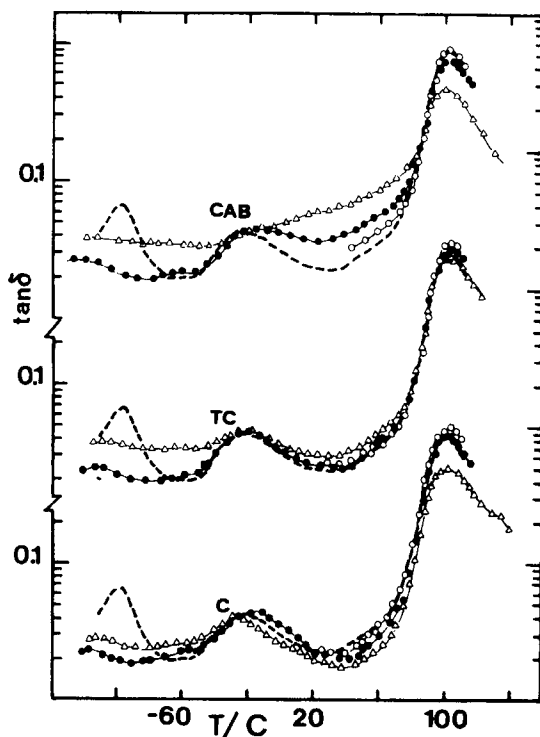


Fig. 1. Temperature dependence of damping of filled PU-PVC blend: (---) 0 wt %; (○) 5 wt %; (●) 10 wt %; (Δ) 25 wt %.

sizes, associated with high surface areas, are more effectively attached to chains leading to reduced internal friction. Similar findings were reported by other workers.<sup>6,15,16</sup> The above effects were less prominent for the rubber  $\beta$  relaxation. The main characteristic of these spectra is the raising of damping level between the main relaxations. Most effective in this respect is the silica filler which effectively washes out the  $\beta$  relaxation. It is known that the viscoelastic region following this relaxation is determined by physical entanglements.<sup>17</sup> Raising of the loss modulus plateau has also been observed<sup>18</sup> in rubbers filled with inert or reactive fillers. Silica filler is more effective in this respect because of its larger surface area and its capacity for hydrogen bonding and network formation.<sup>12</sup>

In Figure 2 it is observed that both the  $\alpha$  and  $\beta$  relaxations are increasing with filler loading. At similar loading the effect is lowest for the silica-filled system. The findings suggest that, in this case, amorphous matrix viscosity is operative, the spherical Cabosil particles offering decreased resistance to flow. Other workers reported a similar  $E''$  increase with loading.<sup>11,15</sup>

Inspection of Table IA shows a shift of the  $T_{g,PU}$ , which is highest for the silica-filled system (ca., 16°C at the highest loading). A smaller shift and splitting of this relaxation is observed for carbon- and talc-filled blends. It

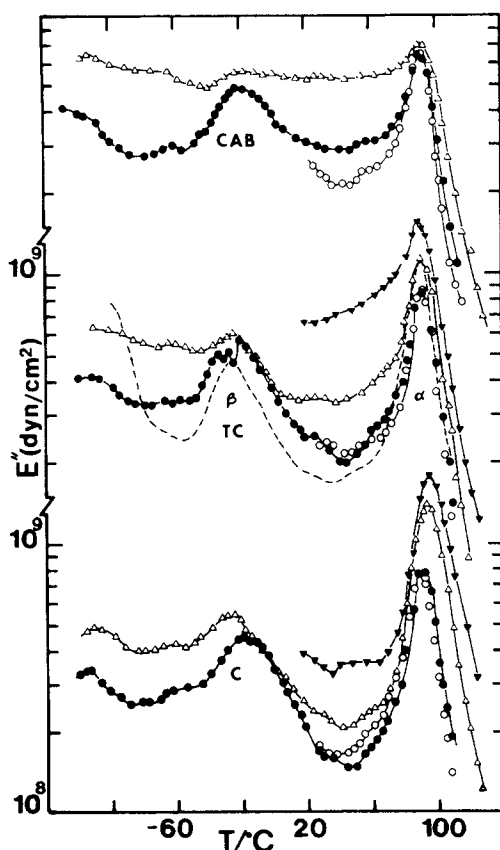


Fig. 2. Temperature dependence of loss modulus of filled PU-PVC blend: (---) 0 wt %; (○) 5 wt %; (●) 10 wt %; (△) 25 wt %; (▼) at  $\phi_f = 0.30$ .

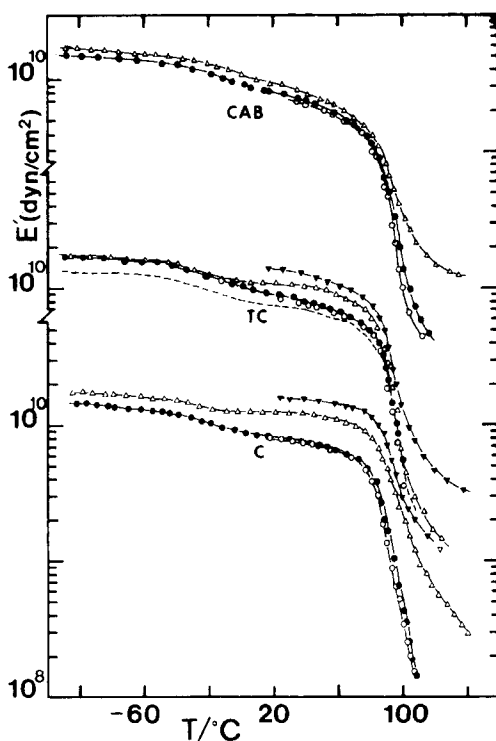


Fig. 3. Temperature dependence of storage modulus of filled PU-PVC blend: (---) 0 wt %; (○) 5 wt %; (●) 10 wt %; (Δ) 25 wt %; (▼) at  $\phi_f = 0.30$ .

seems that in the latter cases only a portion of the rubbery component is affected by the filler while the ultrafine silica filler seems to "effect" the complete rubbery mass either by network formation and/or formation of an immobilized polymer layer. A smaller shift of the  $\alpha$  PVC relaxation was observed and only for the coarser particles. A shift of relaxation spectra to higher temperatures with the addition of fillers has been reported by many workers<sup>6,19,20</sup> for pure polymers. In the present system, the fact that the increase of the  $\beta$  relaxation temperature is not associated with a concomitant reduction of the  $T_{g, \text{PVC}}$  leads to the conclusion that this shift is not due to partial miscibility phenomena but rather to the formation of immobilized layers onto the filler surface.

Apparent activation energies  $\Delta H_\alpha$  at 10% filler were also determined for both main relaxations. The results are given in Table IA. The results indicate that silica filler interferes with the low temperature relaxation to a greater extent than the coarser talc filler. This is probably associated with a more effective filler-matrix interaction of the fine filler particle. The opposite is true for the high temperature relaxation possibly due to the lubricity effect of the spherical filler. Figure 3 gives the modulus spectra at various filler levels. Stiffness is differentiated above the 10% level and above the  $\beta$  relaxation. At similar loading, stiffness is enhanced by the coarser particles. Similar findings were reported for mica-reinforced composites.<sup>21</sup>

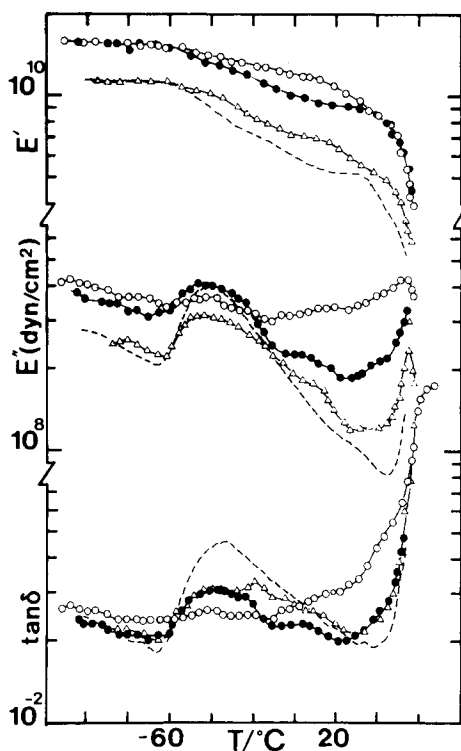


Fig. 4. Dynamic mechanical spectra of SAN-PCL at 15 wt % loading: (○) Cabosil; (●) talc; (△) carbon black; (---) unfilled matrix.

### SAN-PCL system

Figure 4 gives the thermomechanical spectra of the polyblends while low temperature relaxations are given in Table IB. The main SAN relaxation at ca. 120°C<sup>5</sup> could not be obtained because of melting of the PCL phase at approx. 60°C. Both damping and loss moduli spectra indicate that, at similar loading, increasing the filler specific area affects the viscoelastic region associ-

TABLE II  
DSC Data and Boundary Layer Thickness of Silica Filled Blends

Filler loading (wt %)	Low temp relaxation				High temp relaxation			
	$T_g^a$ (°C)	$\lambda$	DSC $\Delta r^b$ (Å) at $T_g$	DMA $\Delta r^c$ (Å)		$T_g$ (°C)	$\lambda$	DSC $\Delta r$ (Å) at $T_g$
				At 30°C	At -20°C			
0	-20	0	0	0	0	80	0	0
5	-16	0.296	48	43	—	76	0.056	16
10	-16	0.415	38	36	22	78	0.190	23
25	-16	0.490	21	24	10	78	0.357	16

<sup>a</sup> Temperature where base line intersects tangent to main step.

<sup>b</sup> Determined using eqs. (3)-(4).

<sup>c</sup> Determined using eqs. (1)-(2).

ated with physical entanglements.  $E''$  and damping values are also decreased with decreasing filler size. No significant shift of the main PCL relaxation was observed; see Table IB. Some peak splitting was also observed for the coarser particles. Finally, the silica filler seems to enhance modulus (at variance with the previous system). It is possible that the decreased crystallinity of the filled blend, (see below), gives an enhanced matrix-filler wetting.

### DSC Measurements

The thermograms obtained for the PU-PVC system showed a single  $C_p$  step at the PVC  $\alpha$  transition. However, the similar step for the PU  $\beta$  transition was accompanied by a smaller "satellite" step. This effectively broadens the low temperature relaxation detected already with the DMA. For the  $\Delta C_p$  measurement only the major step was taken into account following the graphical procedure described before.<sup>9</sup> DSC results are summarized in Table II, where other calculated quantities pertinent to the discussion have been also included.

As mentioned, the SAN-PCL/15 Cab film was less brittle compared to the unfilled matrix. A crystallinity measurement showed that the addition of filler reduced crystallinity by ca. 70%. This could explain the increased film flexibility for the filled product.

### DISCUSSION

A rational approach to filler effects on mechanical spectra could be provided by considering the basic or acidic nature of the matrix and filler.<sup>22</sup> PVC having acidic character interacts with basic fillers. Thus it is expected to interact more strongly with talc than with the acidic silica filler. This could explain the  $T_{g, PVC}$  shift with the former filler but not with silica. Also, the carbonyl containing PU has hydrogen bonding capability; therefore, it will interact more effectively with Cabosil whose surface provides the acidic hydrogen. In the case of the SAN-PCL pair, the strongly acidic tertiary hydrogen of the acylonitrile moiety competes for the carbonyl group of the PCL. Thus there is less tendency for the silica filler to interact. Carbon black should show some reactivity to PU since this rubber contains carbonyl groups and has unsaturation. It is known that carbon black has free radicals interacting with the  $\pi$  electrons of the double bonds.<sup>23</sup>

Notwithstanding these matrix-filler interactions, examination of the loss moduli spectra indicates that both binary blends remain incompatible. The low temperature  $T_g$  shifts are evidence of an immobilized boundary layer formation at the filler-matrix interface. Using the model proposed by Ziegel<sup>10</sup> for spherical particles, an estimate of this layer thickness can be obtained. An independent method is provided by the DSC technique (see below). Ziegel's equations based on dynamic mechanical data take the form

$$E_r'' = E_f''/E_m'' = 1/(1 - \varphi_e) \quad (1)$$

and

$$E_r'' = [1 - \varphi_f(1 + \Delta r/R_0)^3]^{-1} \quad (2a)$$

hence

$$\Delta r/R_0 = [(E_r'' - 1)/(E_r''\varphi_f)]^{1/3} - 1 \quad (2b)$$



where  $E_r''$ ,  $E_f''$ , and  $E_m''$  are the relative, the filled, and the unfilled matrix loss modulus, respectively,  $R_0$  is the original particle radius, and  $\Delta r$  is the boundary layer thickness at filler volume fraction  $\varphi_f$ . The increased filler radius ( $R_0 + \Delta r$ ) changes  $\varphi_f$  to an effective volume fraction  $\varphi_e$ . The above relations are derived on the assumption that the boundary layer does not contribute to energy loss. Equation (1) is general while eq. (2) is restricted to spherical particles.

The operational relationships using DSC data are based on the experimental observation that the change  $\Delta C_p$  of the specific heat  $C_p$  at the  $T_g$  decreases with filler content. This is due to immobilization of macromolecules at the boundary layer, and the fraction  $\lambda$  of these restrained molecules with respect to nonrestricted molecules is given by<sup>8</sup>

$$\lambda = 1 - \Delta C_{p,f} / \Delta C_{p,m} \quad (3)$$

where,  $\Delta C_{p,f}$  and  $\Delta C_{p,m}$  is the change of  $C_p$  of the filled and unfilled blend, respectively, at the  $T_g$ . For spherical particles the above experimental quantity can be related to the boundary layer thickness  $\Delta r$  since

$$\frac{V_{R_0+\Delta r} - V_{R_0}}{V_{R_0}} = \left[ \frac{R_0 + \Delta r}{R_0} \right]^3 - 1 = \lambda(1 - \varphi_f) / \varphi_f \quad (4)$$

Hence,

$$\Delta r / R_0 = [\lambda(1 - \varphi_f) / \varphi_f + 1]^{1/3} - 1 \quad (4a)$$

where  $V_{R_0+\Delta r}$  is the sum of volumes of filler and of the attached interface layer.

Using these models Figure 5 and Table II summarize data for various fillers. Figure 5 gives the variation of effective filler volume fraction with loading for various fillers. At constant  $\varphi_f$  silica has the highest  $\varphi_e$  and carbon the lowest. This may be due to agglomeration of carbon black particles reducing its nominal area.<sup>24</sup> DMA results and DSC data reported in Table II can be used to estimate the thickness  $\Delta r$  of the boundary layer for spherical fillers using eqs. (1)–(2) and (3)–(4), respectively. The  $\Delta r$  values are less than those reported by Lipatov<sup>8</sup>; however, they are reasonable if due consideration is

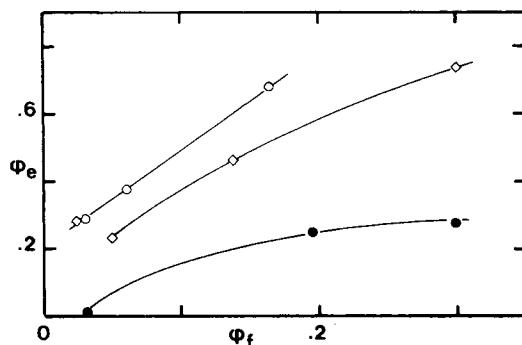


Fig. 5. Dependence of effective filler volume fraction on loading and type of filler at 25°C: (○) Cabosil; (◇) talc; (●) carbon black.

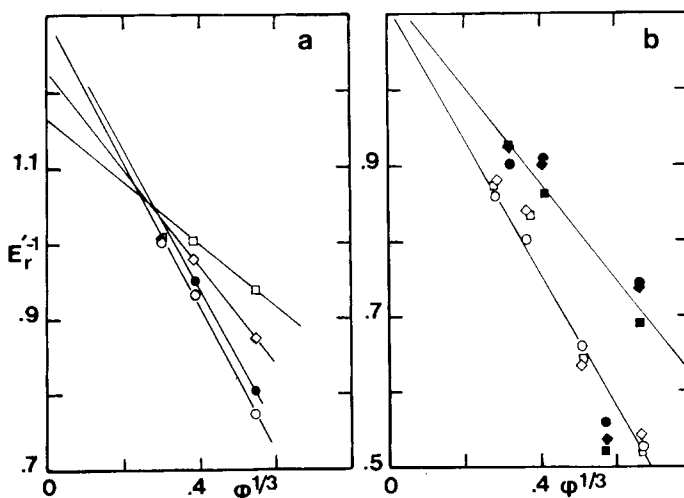


Fig. 6. (a) Testing of Narkis equation with Cabosil at various temperatures: (●) 20°C; (○) 30°C; (◇) 50°C; (□) 70°C. (b) Testing with talc (open) and carbon black (filled symbols) at 30, 50, and 70°C.

given to the fact that in our system a lesser amount of PU is available. Very satisfactory agreement between the two sets of  $\Delta r$  values is obtained using the DMA results at 30°C. This temperature was chosen since at lower temperatures due to thermal stresses<sup>25</sup>  $E_r''$  values decrease and, near the  $T_g$ 's,  $E_r''$  values are less accurate because of a steep rise in the loss moduli. Indeed an uncritical use of  $E_r''$  values at  $-20^\circ\text{C}$  leads to low values of  $\Delta r$  (see Table II). In general,  $\Delta r$  values decrease with loading, a fact explained by an increase of agglomeration. This trend was also observed for a similar system<sup>8</sup> and for polypropylene filled with silica filler.<sup>12</sup> The boundary layer associated with the PVC component has a smaller thickness. Since most of the matrix consists of PVC, it is suggested that silica because of its acid character immobilizes to a greater distance the proton accepting PU component; hence,  $\Delta r(\text{PU}) > \Delta r(\text{PVC})$ .

Considerable theoretical and experimental work has been devoted to the problem of predicting moduli of composites using pure component data.<sup>6,16,26</sup>

Modulus data were tested at constant temperature as a function of loading and at constant loading as a function of temperature. Figure 6 is a test of the Narkis semiempirical relationship<sup>27</sup> valid for spherical particles with  $K$  a constant:

$$E_r' = 1/K(1 - \phi_i^{1/3}) \quad (5)$$

According to eq. (5) a plot of  $1/E_r'$  vs.  $\phi^{1/3}$  should give a straight line with negative slope and an intercept value of  $K$ . The test is satisfactory for the spherical fillers [Fig. 6(a)], even at small loadings. Less satisfactory correlation is obtained for the nonspherical fillers [Fig. 6(b)]. In Figure 7,  $E_r'$  is calculated at 25°C using pure component data and various analytical expressions: the

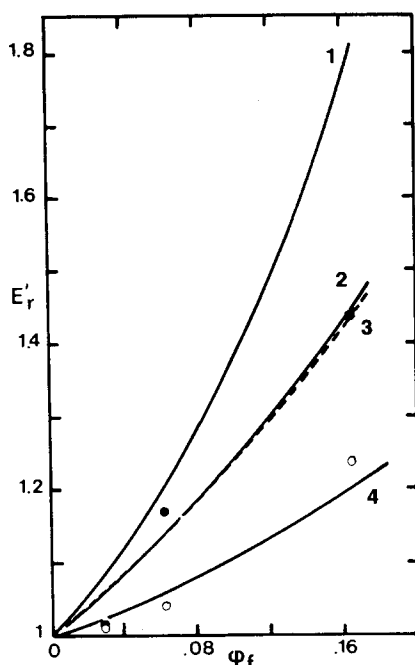


Fig. 7. Prediction of relative modulus  $E'_r$  of PU-PVC/Cab system at 25°C: (○) uncorrected experimental values; (1) eq. (6); (2) Halpin-Tsai-Nielsen equation, with random loose packing of filler; (3) eq. (7); (4) parallel phase connection; (●) data obtained after correction for thermal stresses at  $T_{g,PU} + 10^\circ\text{C}$ .

Guth-Smallwood relationship<sup>28,29</sup>

$$E'_r = 1 + 2.5\varphi_f + 14.1\varphi_f^2 \quad (6)$$

and the simplified Kerner's equation<sup>17</sup>

$$E'_r = 1 + \frac{\varphi_f}{\varphi_m} \left[ \frac{15(1 - \nu_m)}{8 - \nu_m} \right] \quad (7)$$

where  $\nu$  is the Poisson ratio and the index  $m$  indicates a property of the matrix. The Halpin-Tsai-Nielsen generalized equation<sup>6</sup> was also tested with random loose packing of the filler.

The models seem to fail because no account is taken of the thermal stresses<sup>25</sup> developed at the filler-matrix interface. These are present even at 25°C since a large portion of the matrix is below the  $T_g$  of PVC. As seen in Figure 7, agreement with theory is improved if the maximum  $E'_r$  values extrapolated at around  $-10^\circ\text{C}$  are used.

A test was also made of the complete Kerner's equation<sup>17</sup> at an extended temperature range. This model assumes perfect adhesion of the matrix with the filler, a condition that one expects to be effectively ensured at low

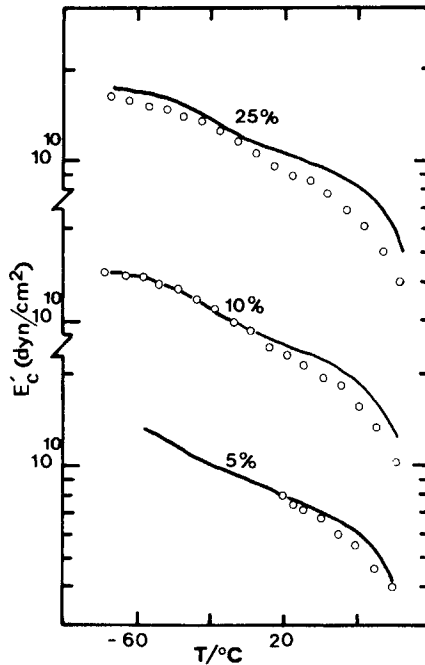


Fig. 8. Prediction of dynamic modulus  $E'_c$  of PU-PVC/Cab system using eq. (8) at an extended temperature: (○) experimental values.

temperatures. The expression has the form

$$E'_c = E'_m \left[ \frac{\varphi_f E_f}{(7 - 5\nu_m)E_m + (8 - 10\nu_m)E_f} + \frac{\varphi_f}{15(1 - \nu_m)} \right] \left/ \left[ \frac{\varphi_f E_m}{(7 - 5\nu_c)E_m + (8 - 10\nu_m)E_f} + \frac{\varphi_m}{15(1 - \nu_m)} \right] \right. \quad (8)$$

The test is seen in Figure 8 showing that data prediction is improved at low temperatures. For the above comparisons the existence of a boundary layer was not invoked. This suggests that modulus, a small strain property, is not a sensitive enough property for boundary layer studies.

Various property values used in the above calculations were;  $d(\text{matrix}) = 1.30$   $d(\text{carbon}) = 1.8$ ,  $d(\text{silica}) = 2.2$  and  $d(\text{talc}) = 2.7$   $\text{g}/\text{cm}^3$ .  $E_f = 6.87 \times 10^{11}$   $\text{dyn}/\text{cm}^2$  (from Ref. 11),  $\nu_f^{25} = 0.22$ ,  $\nu_m = 0.35$  and  $0.40$ , below and above  $T_g$ , respectively.  $\nu_c$  for the composites was assumed to be real and equal to the arithmetic mean of their components weighted as their volume fraction.

## CONCLUSIONS

1. Addition of fillers of varying surface area to a mechanically compatible or to a binary blend near its miscibility region does not lead to compatibility as conventionally defined.

2. The filler shifts the relaxation spectrum of one of the blend components. Selectivity for this seems to depend on the basic-acid interaction between the

filler and one of the matrix components. This property also influences boundary layer thickness.

3. Both dynamic loss spectra and the DSC data agree in their estimate of the boundary layer thickness. However, DMA data should be corrected to account for thermal stresses, or chosen from a temperature region where these are minimal.

The author wishes to thank Mr. A. Margaritis for the DSC measurements. The partial support of the Ministry of Industry, Energy and Technology, the General Secretariat of Research and Technology is also acknowledged.

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Received October 10, 1985

Accepted February 11, 1986