

# Influence of dewetting on the damping properties of a filled polymer system:

## 1. Static characterization

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The effect of the interaction at the interface between filler and binder on the mechanical behaviour of the composite system has been studied. It was found that in an unreinforced filled elastomer the adhesion bonds between filler particles and the polymeric matrix play a major role in the observed increase in mechanical performance. A swelling technique and stress-strain data, were used to characterize and to estimate quantitatively the interface energy of PBCT filled with spherical A1 powder. The surface energy at the interface, calculated from the swelling of the material in different solvents, was found to be in agreement with the apparent activation energy difference obtained by shifting master curves of the initial modulus and the ultimate properties (similar to the shifting to a reference temperature by the WLF equation). Dilatometric results indicate that dewetting occurred when the strain exceeded 15%.

### INTRODUCTION

The influence of filler on the mechanical and physical properties of an elastomer depends mainly on the volume fraction of the filler<sup>1</sup> as well as on the following effects:

(a) hydrodynamic effects such as the increase of viscosity and the friction between filler particles that may occur while the material is deformed;

(b) the nature of the interaction at the interface between the filler and the binder;

(c) the stress concentration formed on the filler particle surface.

In an unreinforced filled elastomer the interactions at the interface are characterized by Van der Waals forces, which are sufficient to give a significant increase in the strength of the composite, particularly in tension<sup>2</sup>. On applying tension to adhered filler composites, dewetting occurs and the dewetted material behaves similarly to the pure elastomer. In this case, the only influence of the filler on the mechanical properties will be due to the effect of the filler on the viscosity because of the friction between filler particles.

Swelling, as well as stress-strain data, were used to obtain a deeper insight into the contribution of the above effects on the mechanical properties of an unreinforced filled elastomer, and to characterize the composite.

### BACKGROUND

#### Swelling

Introducing filler-elastomer attachments into an elastomer will increase the efficient crosslinking density of the composite which will result in higher restrictions on swelling. The decrease of the degree of swelling as a function of filler concentration depends mainly on the number of filler-elastomer attachments and to the first approximation is

independent of their strength as long as they are strong enough to withstand the internal swelling stresses. If no adhesion between filler and the binder exists, or if the bonding is not strong enough to withstand the swelling stresses, vacuoles are formed around the filler particles and a higher degree of swelling is observed. Thus, swelling data can give some indication regarding the nature of filler-binder interactions.

Assuming that the swelling is influenced by filler-binder interactions only in layers near to the filler particles surface, and from simple geometrical considerations, Kraus developed the following relation to describe the influence of the filler on swelling<sup>2</sup>. In the case of ideal adhesion between filler and binder:

$$\frac{v_{r0}}{v_r} = 1 - m \frac{\phi}{1 - \phi} \quad (1)$$

and in the case of no adhesion:

$$v_r^{-1} = \frac{v_{r0}^{-1} - \phi}{1 - \phi} \quad (2)$$

Where  $v_{r0}$  and  $v_r$  are the swelling ratios of the elastomer and the composite respectively,  $\phi$  is the volume fraction of the filler and  $m$  is a constant which describes the amount of swelling restriction due to the addition of the filler:

$$m = 3C(1 - v_{r0}^{1/3}) + v_{r0}^{-1} \quad (3)$$

where  $C$  is a constant which depends on the filler. It was found<sup>2</sup> that for carbon black reinforced rubber the value of  $C$  is 1.17–1.35 if strong enough bonds exist between the carbon black and the rubber, and  $C \approx 0.8$  if only weak bonds

are formed. In particle-filled polymers the value of  $C$  was found to be a little smaller<sup>3</sup>. If  $m = 0$ , the filler has no influence on the swelling. That happens when the swelling ratio is greater than a critical value  $-v_{rc}$ <sup>4</sup>. In this case the degree of swelling is so small, that the interface bonding does not play any role in the restriction of the swelling.

The above equations are valid only for low and medium values of filler volume fraction and do not take into consideration the interaction between filler particles<sup>5</sup>.

Other approaches to the problem of swelling of filled elastomers were given by Rigbi<sup>6</sup>, Sternstein<sup>7</sup> and Sato<sup>8</sup>. Rigbi's treatment is much more complicated and results in an upper and lower limit for the swelling. Sternstein took into consideration the stress field whereas Sato built a model on the conception of internal deformation.

#### Stress-strain data

Assuming that the material is thermorheologically simple, the well known WLF equation can be used<sup>9</sup>:

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0} \quad (4)$$

where  $a_T$  is the shift factor,  $C_1$  and  $C_2$  are constants and  $T_0$  a reference temperature. The WLF equation is valid in the range  $T_g$  to  $T_g + 100^\circ\text{C}$  (here  $T_g$  is the glass transition temperature). If only one relaxation process governs this temperature region, the apparent activation energy of this process is given by:

$$\Delta H_T = \frac{2.3 R d(\log a_T)}{d(1/T)} \quad (5)$$

Differentiation of equation (4) with respect to  $(1/T)$  results in:

$$H_T = \frac{2.3 R T^2 C_1 C_2}{(C_2 + T - T_0)^2} \quad (6)$$

With the aid of the shift factor, a master curve can be constructed. If such master curves are drawn for filled polymers with different filler contents, a family of curves, similar to those observed before shifting to a reference temperature, is obtained. It is possible to shift all these master curves to obtain one master curve which will describe a property of the materials at a reference temperature and a reference filler content<sup>10</sup>. A similar equation to the WLF may then describe the secondary shift factor  $-\log a_\phi$  as a function of filler volume fraction,  $\phi$ .

$$\log a_\phi = \frac{B_1(\phi - \phi_0)}{B_2 + \phi - \phi_0} \quad (7)$$

where  $\phi_0$  is an arbitrary reference filler volume fraction and  $B_1$  and  $B_2$  are experimental constants. The  $(-)$  sign of the WLF equation is omitted because rising filler content has the same effect as lowering the temperature and *vice versa*.

Rearrangement of equation (7) leads to:

$$\frac{\phi - \phi_0}{\log a_\phi} = \frac{\phi - \phi_0}{B_1} + \frac{B_2}{B_1} \quad (8)$$

Plotting the left term of equation (8) vs.  $\phi - \phi_0$  a straight line is obtained. The constants  $B_1$  and  $B_2$ , can be derived

from the intersection of the line with the ordinate and the slope.

The main influence of the filler on the composite's properties is due to the adhesion of the polymer to the surface of filler particles. On applying tension, dewetting occurs and, therefore, the influence of the filler decreases. Thus, comparison of the shift factor, obtained from shifting a property measured at the beginning of the straining (e.g. initial modulus), to the shift factor obtained from the shifting of the ultimate properties, may give an insight into the dewetting process. The apparent activation energy difference associated with the secondary shift factors, is a measure of the dewetting energy.

## EXPERIMENTAL

### Materials and specimens

Specimens of polybutadiene carboxy terminated (PBCT) filled with various contents of spherical Al powder ( $3 \mu\text{m}$ ), were prepared by moulding. The list of the materials and their densities are summarized in Table 1.

Bonded end-tab specimens were used for the stress-strain experiments. The dimensions of the specimens were  $10 \times 10 \times 100 \text{ mm}$  and  $10 \times 10 \times 60 \text{ mm}$ . The tabs were made from steel (SAE 1020). After phosphotization the tabs were put in the mould and adhered to the specimens as a result of the polymerization.

Examination of particle size was conducted on a Fisher Sub-Sieve Sizer. Densities were determined according to ASTM-D-792-66. Shore A hardness determination (ASTM-2240) on the upper and lower side of the specimens showed that no filler deposition occurs during the polymerization.

### Procedure

The torsion moduli and the volume changes during tension were determined using a Gehaman apparatus (ASTM-D-1053) and a dilatometer described in ref 11. The dimensions of the specimen for the dilatometric examination were  $25 \times 25 \times 130 \text{ mm}$ . This large specimen was used because the material is almost incompressible. The results were fed into a computer program to calculate the volume changes, Poisson's ratio and the experimental error<sup>11</sup>.

The equilibrium swelling was measured in toluene and heptane by weighing the sample after equilibrium was reached (7 days) and after extraction in a vacuum oven at  $80^\circ\text{C}$ . By assuming that the filler is inert to swelling, the swelling volume ratio,  $VR$ , is given by:

$$VR = \frac{\rho_p}{(1 - \phi)\rho_s} \left( \frac{W}{W} - 1 \right) + 1 \quad (9)$$

Where  $W$  and  $W_p$  are the sample weights at equilibrium swelling and after drying and  $\rho_p$  and  $\rho_s$  are the densities

Table 1 List of the materials and their densities

	Material					
	B-1	B-2	B-3	B-4	B-5	B-6
Vol% of filler	0	5	15	25	40	25 (30 $\mu\text{m}$ )
Density	0.9310	1.0177	1.2053	1.3586	1.6496	1.3593

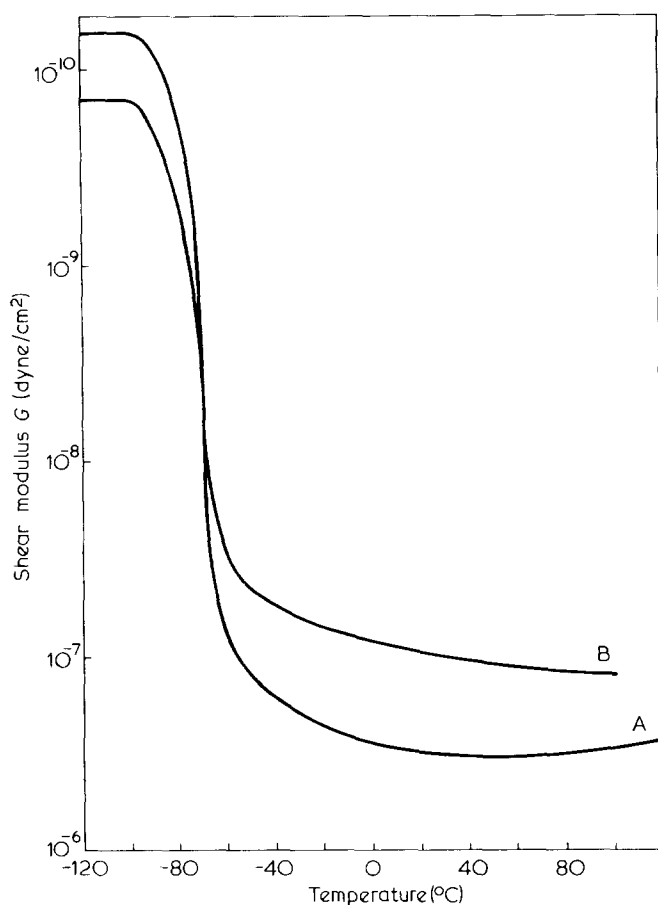


Figure 1 Torsion modulus vs. temperature for B-1 (A) ( $\phi = 0\%$ ) and B-4 (B) ( $\nu = 25\%$ )

of the composite and the solvent, respectively. The swelling ratio  $\nu_r$  is then:

$$\nu_r = \frac{1}{VR} \quad (10)$$

Tension stress-strain experiments were carried out on a Universal Instron machine at three different constant rates of straining (0.1 and 1.0 and 10.0 cm min<sup>-1</sup>) and at -75°, -60°, -50°, -40°, -25°, 0° and +25°C. The specimens were held at the testing temperature for at least 1/2 h to ensure a constant temperature throughout the samples. Because of the relatively short crosshead walk of the Instron, shorter specimens (60 mm) were also used, after it was found that the same results were obtained as with the longer specimens (100 mm). As the gauge length of bonded end-tab specimens remains essentially constant, the strain could be derived directly from the crosshead movement<sup>10</sup>. Stresses calculated on the original cross-sectional area of the specimen,  $\sigma_0$ , were converted into the true stresses,  $\sigma$ , by multiplying by the principle extension ratio, based on the fact that Poisson's ratio is almost 0.5. From the corrected stress-strain curves, the initial modulus,  $E_0$ , the ultimate stress  $\sigma_b$  and strain  $\epsilon_b$  were derived. The strain energy density to failure,  $W_b$ , was calculated from the area of the stress-strain curve:

$$W_b = \int_0^{\epsilon_b} \sigma_0 de \quad (11)$$

$E_0$ ,  $\sigma_b$ ,  $\epsilon_b$  and  $W_b$  were then superimposed using the WLF equation (4) with  $C_1 = 8.86$ ,  $C_2 = 101.6$  and  $T_0 = -25^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Glass transition temperature

The torsion modulus of the unfilled elastomer B-1 and the B-4 composition, representing the filled materials, are described in Figure 1. It can be seen that the glass transition temperature is almost unaffected by the addition of the filler. According to Yannas<sup>12</sup>,  $T_g$  is given by:

$$T_g = T_i - 4.4 \quad (12)$$

where  $T_i$  is the temperature at which the relaxation modulus equals to 10<sup>9</sup> dyne cm<sup>-2</sup>. The  $T_g$  was found to be -77°C.  $T_g$  is influenced by the molecular mobility. This mobility is affected by the filler as a result of viscosity changes or due to changes in the efficient crosslinking density. Thus a shift of  $T_g$  may give some indication of interface interactions. On the other hand, if  $T_g$  remains unchanged, the mobility of the chain molecules has no major effect on  $T_g$ , as also observed in other systems<sup>13</sup>.

### Dilatometric results

The volume changes during tension are shown in Figure 2 for B-1 and B-4 compositions (0 and 25% filler). While a straight line was observed for the pure elastomer, two deflection points were found for the composite. The first, at 13–14% strain, is related to the beginning of dewetting and the second, at 37% strain, to the beginning of the fracture process, as also observed during the experiment. Appearance of a critical strain for dewetting indicates that the interface bonding is relatively strong<sup>14,15</sup>. For weak interface bonds the dewetting starts with the beginning of the straining and no critical strain for dewetting is observed<sup>14,16</sup>.

The small volume changes observed in the pure elastomer and also in the composite below 14% strain are related to the fact that the material is not totally incompressible. Poisson's ratio,  $\nu$  is calculated according to the engineering equation<sup>11</sup>:

$$\frac{\Delta V}{V_0} = (1 + 2\nu)\epsilon \quad (13)$$

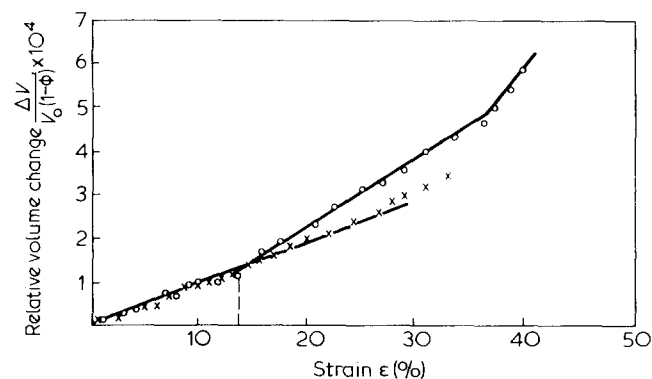


Figure 2 Volume changes for B-1 ( $\phi = 0$ ) and B-6 ( $\phi = 25\%$ ):  $\circ$ ,  $\phi = 25\%$  (B-4),  $\circ$  (B-1)

Table 2 Swelling of PBCT + Al in toluene and heptane and Kraus' constants

$v_0$	$\phi(\%)$					$m$	$C$
	0	5	15	25	40		
Heptane	0.3586	0.3612	0.3851	0.3937	0.4429	0.285	1.05
Toluene	0.1668	0.1688	0.1737	0.1789	0.2340	0.204	0.77

where  $\Delta V$  are the volume changes and  $V_0$  the initial volume, and found to be

$$\nu = 0.4996 \pm 0.00006$$

### Swelling

The swelling ratio for the materials investigated in toluene and heptane are given in Table 2 and the results according to Kraus' equation (1) are described in Figure 3.

The straight line obtained indicates the presence of filler–binder adhesion bonds. The slopes of the line were calculated by a least-square technique and are given in Table 2.

As Kraus' equations are valid only for low and medium filler concentrations, the deviation of the results obtained for PBCT + 40% Al in toluene can be understood.

When medium strength bonds between filler and binder exist [these can withstand the swelling stresses formed when a less compatible solvent is used (but  $\nu_r < \nu_{rc}$ ) yet are insufficiently strong to withstand the stress when a compatible solvent is used]  $C$  does not remain constant in different solvents. In certain solvents equation (1) is valid to describe the behaviour of the filled material, while in other solvents the material will behave according to equation (2). In this case the constant  $C$  will change depending on the compatibility of the solvent with the polymer and will decrease as the solvent becomes more compatible with the polymer.

The low value of  $C$  obtained in toluene indicates that in this compatible solvent a great part of the filler–binder attachments fail while in heptane they are strong enough to hold the swelling stresses as indicated by the high value obtained for the constant  $C$ .

One of the ways of defining a compatible solvent–polymer system is by comparing their solubility parameters. The smaller the difference between the solubility parameter of the solvent and the polymer, the more compatible is the solvent–polymer system. It was found<sup>17</sup> that the solubility parameter of PBCT is equal to that of toluene  $\delta = 8.9 \text{ (cal/cm}^3)^{1/2}$  while that of heptane is  $\delta = 7.45 \text{ (cal/cm}^3)^{1/2}$ <sup>18</sup>

The critical value of the swelling ratio is  $\nu_{rc} = 0.5$ <sup>4</sup> which is higher than that obtained for PBCT in heptane. Although heptane is not the most compatible solvent for PBCT, the degree of swelling is high enough to be influenced by filler–binder attachments.

For non-polar polymers there exists in the literature the semiempirical relation<sup>19</sup>

$$\gamma_c = 0.44\delta_p^2 \quad (14)$$

and for non-ionic liquids:

$$\gamma_c = 0.37\delta^2 \quad (14a)$$

Thus, for PBCT [ $\delta_p = 8.9 \text{ (cal/cm}^3)^{1/2}$ ] the critical surface energy was found to be  $\gamma_c = 34.9 \text{ erg/cm}^2$ , and for toluene and heptane 29.3 and 20.5  $\text{erg/cm}^2$ , respectively.

As the adhesion bonds fail in toluene but hold the swelling stresses in heptane, the strength of the interface bonds can be estimated to be within these limits. If the swollen system is treated as a mixture of two liquids, its solubility parameter can be written approximately as:

$$\delta_m = V_s\delta_s + V_p\delta_p \quad (15)$$

where  $\delta_m$ ,  $\delta_s$  and  $\delta_p$  are the solubility parameters of the mixture, the solvent and the polymer while  $V_s$  and  $V_p$  are their respective volume fractions in the mixture.

Using an improved equation instead of equation (14):

$$\gamma_c = [0.44V_p + 0.37(1 - V_p)]\delta_m^2 \quad (16)$$

the strength of the interface bonds for PBCT in toluene and heptane can be calculated to be between 24.7–30.4  $\text{dyne/cm}^2$ , in agreement with the previous results. It can be expected that dewetted specimens will swell to a higher degree. As most of the interface bonds failed in toluene, efforts were made to determine the degree and rate of swelling of prestrained ( $\epsilon = 30\%$ ) specimens in heptane. The results show a trend to a higher degree of swelling of the prestrained specimen when compared with the unstrained sample, but the difference was very small. Since the new internal surfaces formed during dewetting are free from environmental contamination, rewetting, at least to some extent, is probably taking place after the stresses are removed when the material is allowed to cure at elevated temperature. After curing of prestrained specimens for 48 h at 65°C, the same swelling was found as in the unstrained specimens. This indicates that no permanent damage, such as the breaking of chemical bonds, occurs during the straining and all the damage is due to the dewetting.

### Stress–strain

The stress–strain data obtained from the experiments conducted at various temperatures and rates of straining, were superimposed using the WLF equation where  $C_1$  and  $C_2$  are the 'Universal' constants and  $T_0 = -25^\circ\text{C}$ . The master curves are described in Figures 4–7. The ultimate stress, initial modulus and the strain energy density were multiplied by the factor

$$\frac{T_0}{T(1 - \phi)}$$

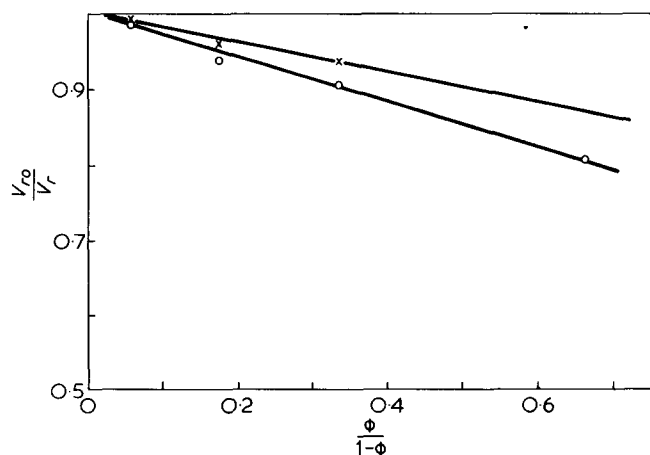


Figure 3 Swelling restriction as a function of filler content (after Kraus) X, PBCT – toluene; O, PBCT – heptane

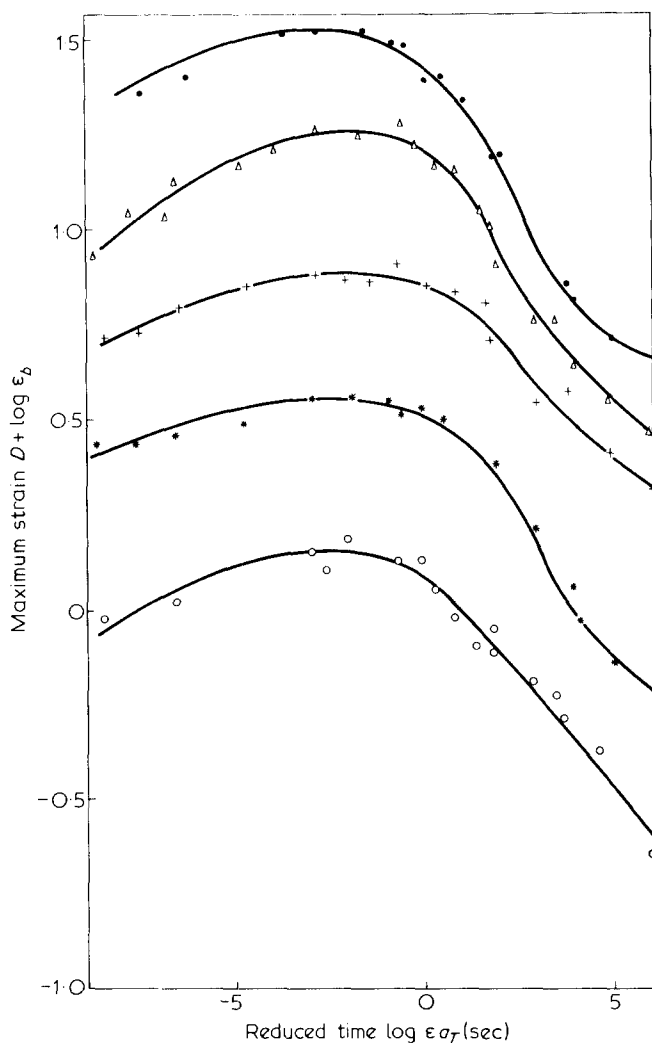


Figure 4 Maximum strain vs. reduced time

$\phi\%$		$D$
0	●	1.00
5	△	0.75
15	+	0.50
25	x	0.25
40	○	0.00

$T_0/T$  is the correction due to the theory of rubber elasticity<sup>20</sup> and  $1/1 - \phi$  is a correction for the net cross-sectional area of the binder. The correction for the density changes was neglected. Figure 8 describes the reduced stress vs. reduced strain and Figure 9 the failure envelope. Figures 4–8 show a family of curves similar to the curves obtained before shifting the stress–strain data to a reference temperature, where the parameter is the filler volume  $\phi$ . In analogy to the WLF shifting an attempt was made to shift the curve to a reference filler content  $\phi = 0$ . Figures 10–11 describe the maximum stress and the strain energy density at failure vs. the doubly reduced time; the values of the secondary shift factor,  $\log \log a_\phi$ , are given in Table 3. The shift factor,  $\log a_\phi$  can be described by an analogue WLF equation (7) and the constants  $B_1$  and  $B_2$  can be calculated from the slope and the intersection with the ordinate of the straight line obtained when the left-hand term of equation (8) is plotted vs.  $\phi$  (Figure 12). The values of  $B_1$  and  $B_2$  obtained are given in Table 3.

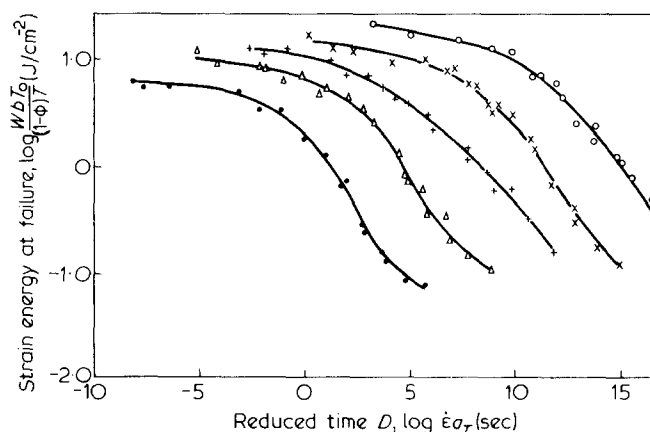
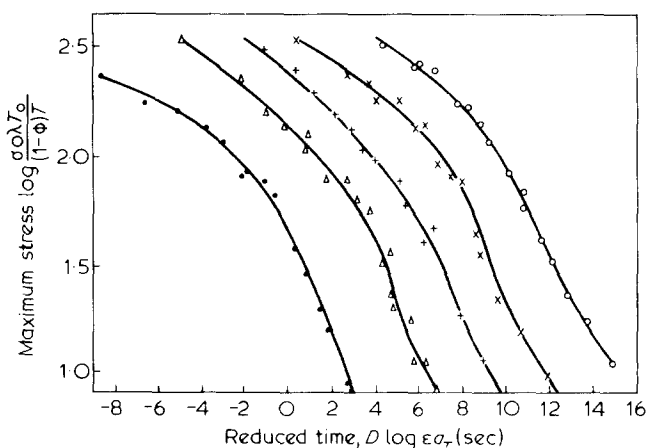
The initial modulus and reduced stress vs. reduced strain could not be shifted by the above  $\log a_\phi$  and higher values

for the shift factor were required. It should be remembered that these properties were measured at the commencement of straining, when the degree of dewetting is almost zero, while the previous ultimate properties were determined by the failure, where the dewetting reaches its maximum. Therefore, the influence of the filler on the initial properties will be much higher and a higher shift factor will be required. The minor effect that the filler has on the ultimate properties can also be seen from the low values of  $\log a_\phi$  obtained and from the fact that a failure envelope could be drawn<sup>21</sup> (see Figure 9). Landel and Smith<sup>22</sup> showed that a failure envelope could also be obtained for filled polymer, in spite of the fact that the results are more scattered. This indicates that the failure in the composite is governed by the same viscoelastic mechanism as in the pure polymer, i.e. the dewetting process.

The values of the shift factor for the initial modulus and stress vs. strain- $\log a_\phi^d$  are given in Table 3. The constant  $d$  expresses the effect of the interface bonding or wetting on the properties of the composite. The average value for this constant was found to be 4.5. Figure 13 illustrates the initial modulus vs. doubly reduced time and Figure 14 the doubly reduced stress vs. the doubly reduced strain using this shift factor.

The apparent activation energy for the viscoelastic process can then be written as:

$$\log a = \log a_T a_\phi = \frac{1}{RT_0} \frac{T_0}{T} \Delta H_T - \frac{\Delta H_\phi}{\phi} \quad (17)$$


 Figure 5 Strain energy at failure vs. reduced time. ●,  $\phi = 0, D = 0$ ; △,  $\phi = 5, D = 3$ ; +,  $\phi = 15, D = 6$ ; x,  $\phi = 25, D = 9$ ; ○,  $\phi = 40, D = 12$ 

 Figure 6 Maximum stress vs. reduced time. ●,  $\phi = 0, D = 0$ ; △,  $\phi = 5, D = 3$ ; +,  $\phi = 15, D = 6$ ; x,  $\phi = 25, D = 9$ ; ○,  $\phi = 40, D = 12$

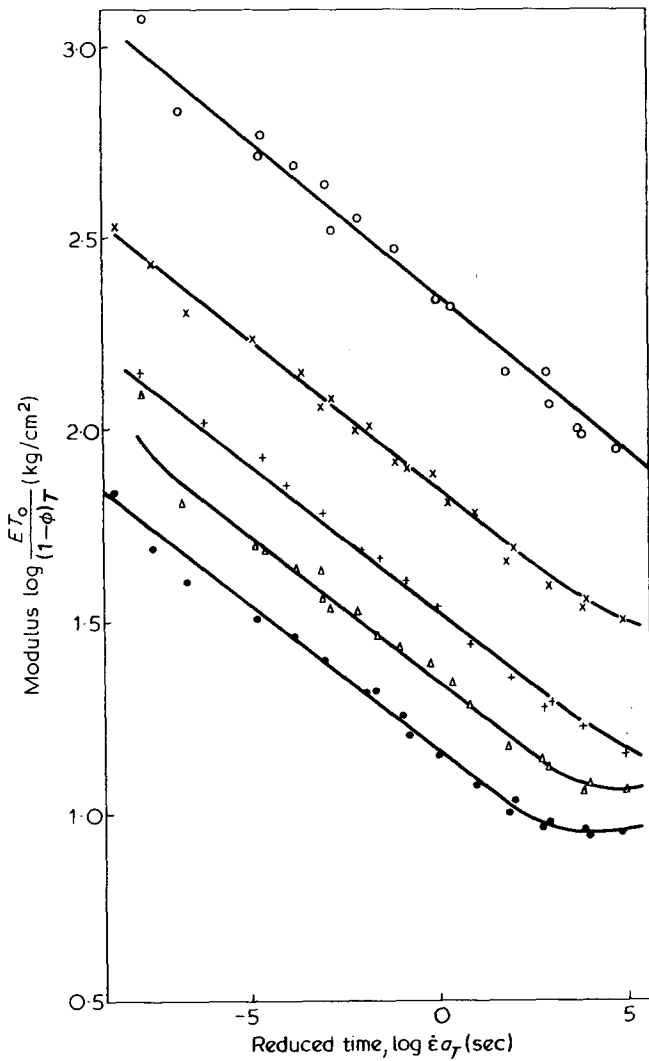


Figure 7 Initial modulus vs. reduced time. ●,  $\phi = 0$ ;  $\Delta$ , 5; +, 15; x, 25; ○, 40

where the total apparent activation energy is given by:

$$\Delta H = \Delta H_T + \Delta H_\phi \quad (18)$$

and in the limit:

$$\lim_{\phi \rightarrow 0} \frac{\Delta H_\phi}{\phi} = 0 \quad (19)$$

From equation (17), at the reference temperature,  $T_0$ , the activation energy  $\Delta H_\phi$  is given by

$$\Delta H_\phi = - \frac{2.3RT_0 d(\log a_\phi)}{d(1/\phi)} \quad (20)$$

Differentiation of equation (7) with respect to  $(1/\phi)$  results in

$$\Delta H_\phi = \frac{2.3RT_0 B_1 B_2 \phi^2}{(B_2 + \phi - \phi_0)^2} \quad (21)$$

which is similar to the apparent activation energy obtained from the WLF equation where  $\Delta H_\phi$  is a measure of the change in viscosity as a function of filler content. Thus the difference in  $\Delta H_\phi$  obtained from  $\log a_\phi (\epsilon \rightarrow \epsilon_b)$  and  $\log a_\phi^d$

( $\epsilon \rightarrow 0$ ) will be a measure of the interface bonding energy:

$$\log a_\phi^d - \log a_\phi = \frac{2.3\Delta H_\phi(d-1)}{RT_0\phi} \quad (22)$$

The calculated values of  $\Delta H_\phi$  are given in Table 3. Both the increase in viscosity and interface bonding will contribute to  $\Delta H_\phi$ . While  $\Delta H_T$  refers to 1 mole of polymer, the con-

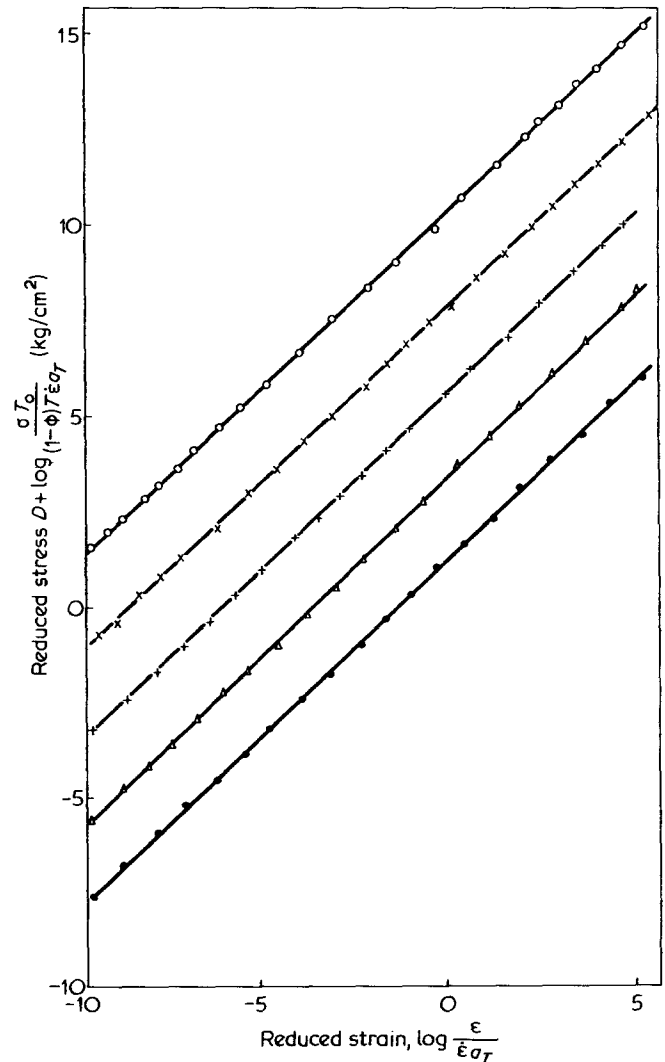


Figure 8 Reduced stress vs. reduced strain. ●,  $\phi = 0, D = 0$ ;  $\Delta$ ,  $\phi = 5, D = 2$ ; +,  $\phi = 15, D = 4$ ; x,  $\phi = 25, D = 6$ ; ○,  $\phi = 40, D = 8$

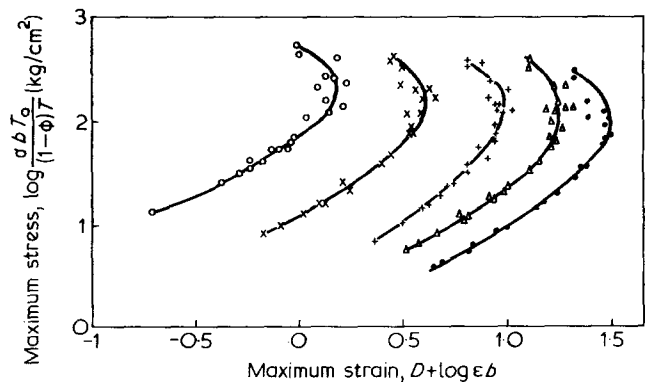


Figure 9 Failure envelope. ●,  $\phi = 0, D = 1.0$ ;  $\Delta$ ,  $\phi = 5, D = 0.8$ ; +,  $\phi = 15, D = 0.6$ ; x,  $\phi = 25, D = 0.3$ ; ○,  $\phi = 40, D = 0.0$

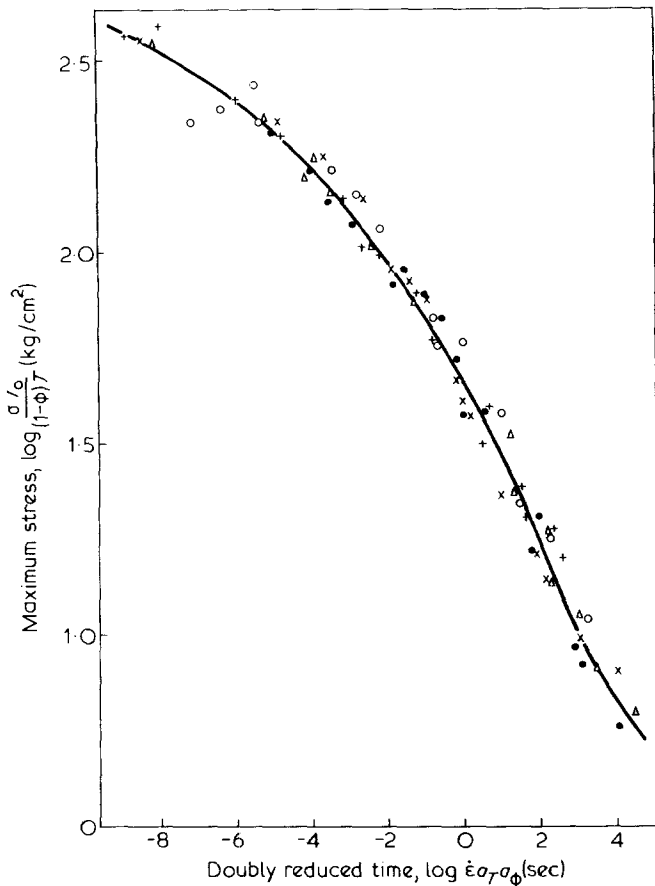


Figure 10 Maximum stress vs. doubly reduced time.  $\phi$ (%): ●, ○; △, 5; +, 16; x, 25; ○, 40

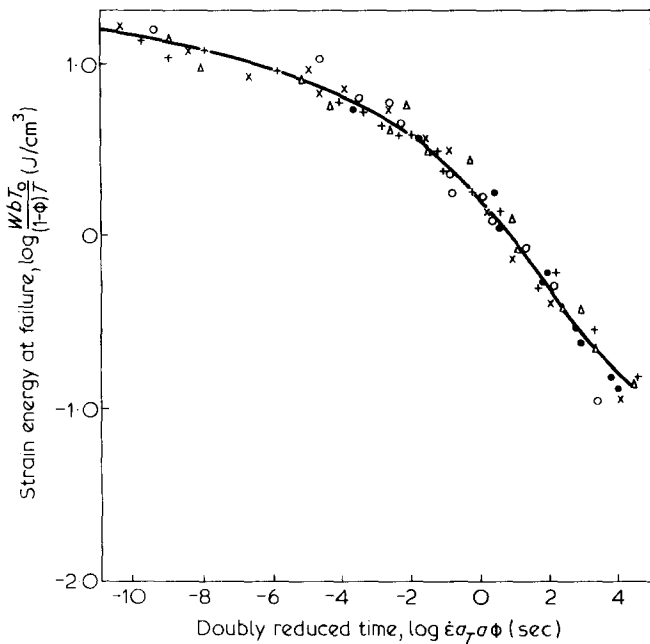


Figure 11 Strain energy at failure vs. doubly reduced time.  $\phi$  key as Figure 10

tribution of the interface bonding  $(d - 1) \Delta H_\phi$  is related to an Avogadro number of bonds.

By assuming that the surface area occupied by a bond is equal to  $S_0 = 2 \times 10^{-15} \text{ cm}^2$  the surface energy at the interface,  $W_e$ , was calculated:

$$W_e = \frac{2.3 \times 4.18 \times 10 (d - 1) \Delta H_\phi}{S_0 N_0}$$

where  $N_0$  is Avogadro's number. The calculated results are summarized in Table 3.

The influence of particle size was also examined for compositions B-4 and B-6 with  $\phi = 25\%$  and particle sizes of  $3 \mu\text{m}$  and  $30 \mu\text{m}$ , respectively. No difference was found in the master curves drawn for the initial modulus of the two compositions, while a smaller value for the maximum stress and strain energy density at failure for higher particle size composition was obtained as illustrated in Figures 15 and 16.

This can be explained by the well known theory that for a bonded filler only the filler content  $\phi$  may affect the mechanical properties<sup>1</sup>. Therefore, the initial modulus of these two compositions with the same filler volume fraction is the same. At high strain where dewetting occurs, this theory no longer holds. Because larger particles show a higher tendency for dewetting<sup>16</sup>, composition B-6 will be more affected by the dewetting and, therefore, lower ultimate properties are obtained.

Table 3 Shift factor,  $\log a_\phi$ , and the corresponding apparent activation energy

$\phi$ (%)	$\log a_\phi$	$\log a_\phi^d$	$\Delta H_\phi$ (cal mol <sup>-1</sup> )	$(d-1)\Delta H_\phi$ [erg/cm <sup>2</sup> ]
0	0	0	0	0
5	0.5	2.3	26.5	3.2
15	1.3	5.4	178	21.6
25	1.9	8.4	384	46.7
40	2.6	12.8	708	86.0

$B_1 = 6.44; B_2 = 0.53; d = 4.5$

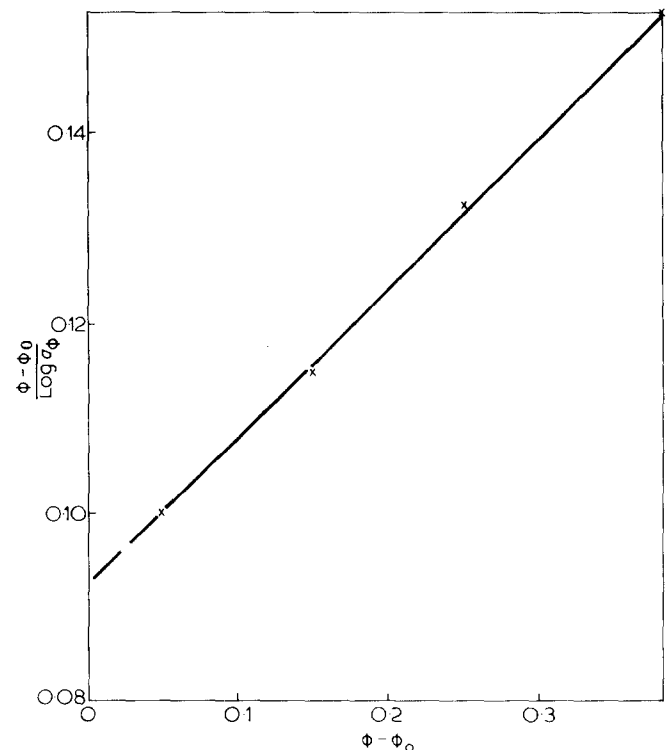


Figure 12 Plot of  $(\phi - \phi_0)/\log a_\phi$  vs.  $\phi - \phi_0$  to find the constants of the analogous WLF equation

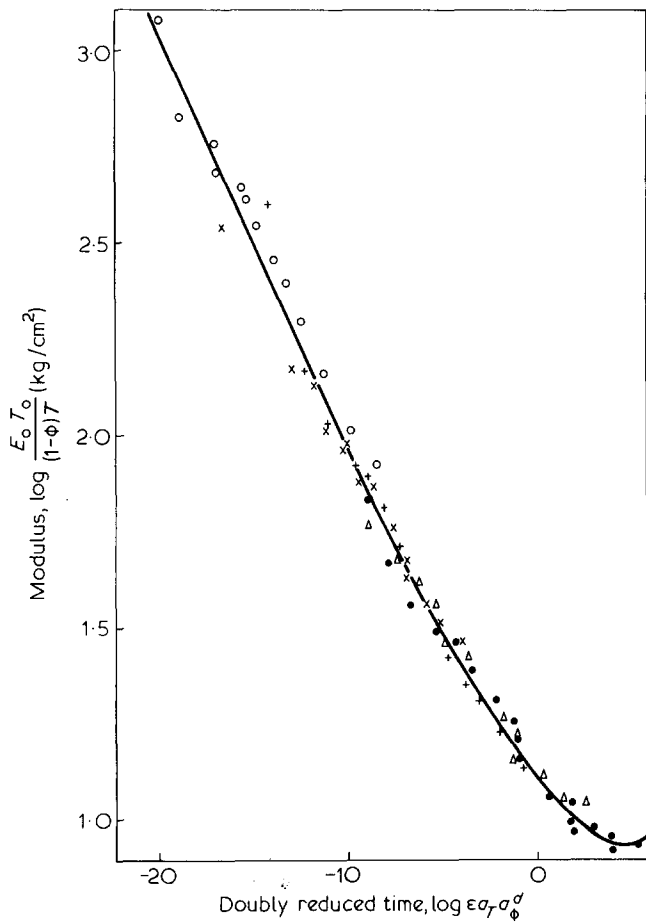


Figure 13 Initial modulus vs. doubly reduced time. Key as in Figure 10

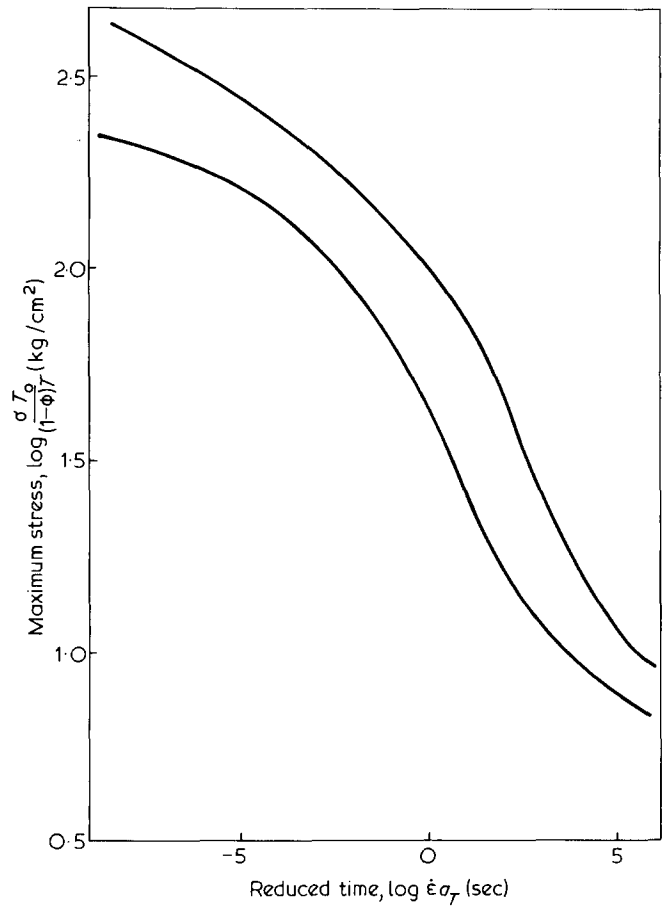


Figure 15 maximum stress vs. reduced time as a function of particle size. A, B-4(3μ); B, B-6(30μ)

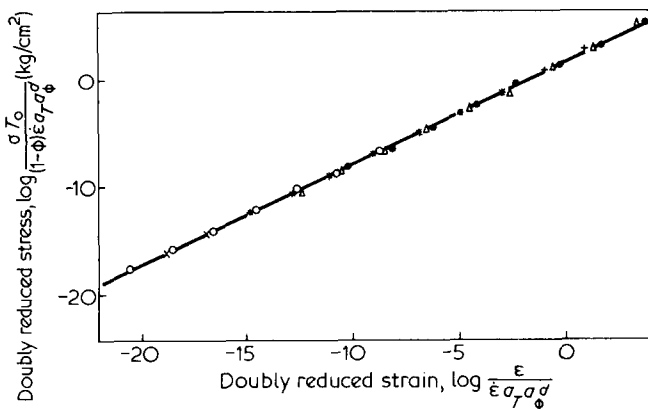


Figure 14 Doubly reduced stress vs. doubly reduced strain, Key as in Figure 10

CONCLUSIONS

A swelling technique was developed to measure the interface bonding energy of a non-reinforced filled elastomer. Using a series of solvents with different solubility parameters both the nature and a quantitative estimation of the interface bonding strength could be evaluated. For PBCT + A1 a bonding strength of 25–30 dyne/cm<sup>2</sup> was obtained.

A mechanical property of a family of materials, with different filler volume fraction, can be represented by one master curve obtained by shifting the data to a reference temperature and filler volume fraction, despite the existence of a secondary transition above  $T_g^{17,23}$ . This results in the scattering of the data at  $-40^\circ\text{C}$ . As the main purpose of

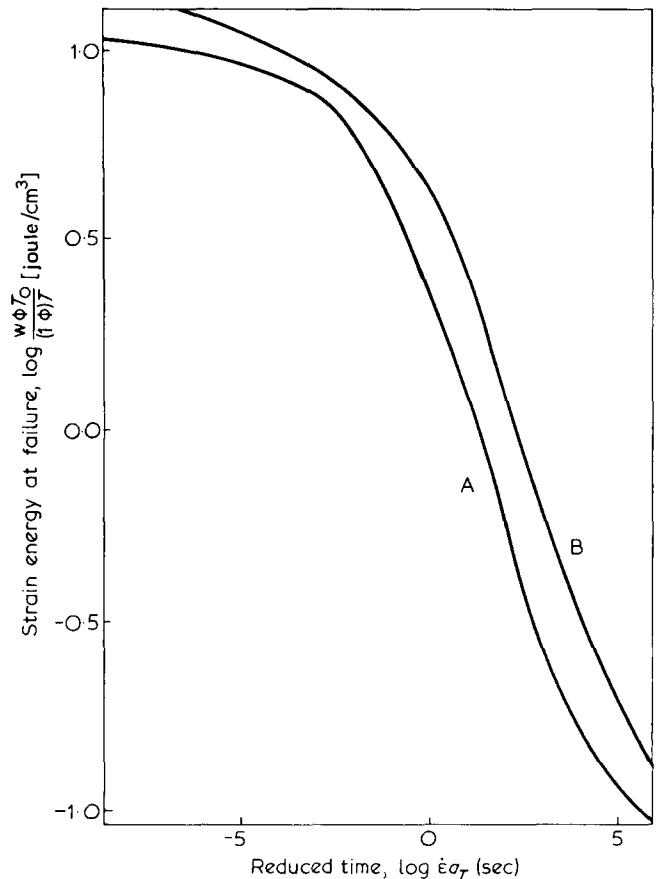


Figure 16 Strain energy at failure vs. reduced time as a function of particle sizes. A, B-6(30μ); B, B-4(3μ)



this study was to characterize the interface interaction this scattering is only of minor importance. The difference in the apparent activation energy obtained from shifting the ultimate properties and from shifting the initial modulus is an expression of the contribution of the interface bonding to the reinforcing of the composite. Comparing this shift factor with the results obtained when different particle sizes were used, it can be concluded that the wetting between the filler and the binder plays the main role in reinforcing the composite, and after dewetting occurs, the composite behaves almost like the pure elastomer. The dilatometric results indicate that the dewetting process is incomplete before the failure of the specimen but on the other hand, the low values of  $\log a_\phi$  indicate that the process is not far from completion. Therefore, the values of the constant  $d$ , listed in *Table 3* are the minimum values, but  $\Delta H_\phi$  are the maxima, so that the overall results for the surface energy are almost the same.

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