

## A Deformational Mechanism in Particulate-Filled Glassy Polymers

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### Synopsis

The stress-strain behavior of glass bead-filled polystyrene, styrene-acrylonitrile, styrene-acrylonitrile-butadiene, and polyphenylene oxide composites is studied at various temperatures below their glass transition temperature. Earlier studies of bead-filled composites indicated that the addition of filler decreases toughness and ultimate elongation. Our results show that while this is true for certain conditions, it is also possible for such composites to have higher toughness and ultimate elongation than the unfilled matrices. A deformational mechanism, involving crazing of the matrix, is proposed which explains this behavior.

### INTRODUCTION

Rigid particulate fillers are often added to polymers to increase stiffness and abrasion resistance as well as to reduce cost and shrinkage. The stress-strain behavior of the resulting composites can be quite complicated. The response of particulate-filled rubber has been studied extensively and is fairly well understood. However, for glassy polymers containing rigid fillers, there are many unexplained phenomena. Previous studies have shown that the addition of rigid particulate fillers to polymers leads to decreased toughness and ultimate elongation which is attributed to strain magnification in the matrix.<sup>1</sup> The ultimate strain of filled elastomer systems has also been studied and can be predicted.<sup>2,3</sup> Nielsen<sup>4</sup> has derived an analogous equation to predict the ultimate strain of particulate-filled glassy matrices for composites with good adhesion. In contrast to these results, a recent paper by Nicolais and Narkis<sup>5</sup> reported that the ductility of some glassy polymers can actually be increased by the addition of rigid fillers. The purpose of this study is to investigate the deformational mechanisms active in such composites.

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## EXPERIMENTAL

Composites were prepared with polystyrene (Monsanto Co., Lustrex H-77), styrene-acrylonitrile (Monsanto Co., LNA 21-1000), styrene-acrylonitrile-butadiene (Monsanto Co., Lustran I-710), and polyphenylene oxide (General Electric Co., PPO 631-111) matrices. Glass beads (Cataphote Corp., Type 2740), with a diameter range of 0.0005 to 0.0015 in., were cleaned with refluxing isopropyl alcohol for 24 hr. For the polystyrene (PS), styrene-acrylonitrile-butadiene (ABS), and styrene-acrylonitrile (SAN) composites, the polymer was mixed with the beads on a mill roll at 170°C for approximately 10 min. The resulting mill sheet was cut and molded to about 0.1 in. in thickness in a 3 × 8 in. compression mold at 185°C and 800 psi. The polyphenyl oxide (PPO) samples were prepared by dry blending the beads with powdered polymer and compression molding at 285°C and 900 psi. Tensile specimens were cut with a high speed router to the shape designated Type I in ASTM 638-64T. Filler content was determined by burning small pieces of broken samples.

SAN, ABS, and PS specimens were annealed at 85°C, and PPO specimens at 185°C for 24 hr. All specimens were then conditioned at 23°C and 45% to 55% relative humidity for 14 days before testing. Samples were tested in tension with an Instron universal tester at temperatures ranging from -50° to 140°C. All strains were monitored with a strain gauge extensometer.

Fracture surfaces were examined with a Cambridge electron scanning microscope.

## RESULTS

Typical stress-strain curves for the styrene acrylonitrile composites at 24°C are shown in Figure 1. The modulus increases and the strength decreases as filler is added. But in contrast to theoretical predictions, the ultimate elongation of the filled polymers is greater than that of the unfilled. Although the matrix material is rather brittle, the composites appear to yield and have considerable ductility. The curves for the filled materials also have a discontinuity in the slope at a stress of about 2400 psi. The change in slope is accompanied by stress whitening over the entire gauge length. A typical fracture surface for a 20 vol-% bead-filled composite is shown in Figure 2. The clarity of the mold marks and the denuded beads indicate that the adhesion of the SAN to the glass is poor as would be expected with these materials.

The tests of SAN composites at 48°C and 65°C produced curves with essentially the same shapes as the 24°C tests. In each case, the ultimate stress, the stress at the discontinuity, and the modulus all decrease slightly with increasing temperature. Those tests run at 85°C produced curves similar to the above except that there was no clearly defined fracture. After the "zero slope region," the samples necked down and continued to elongate by viscous flow.

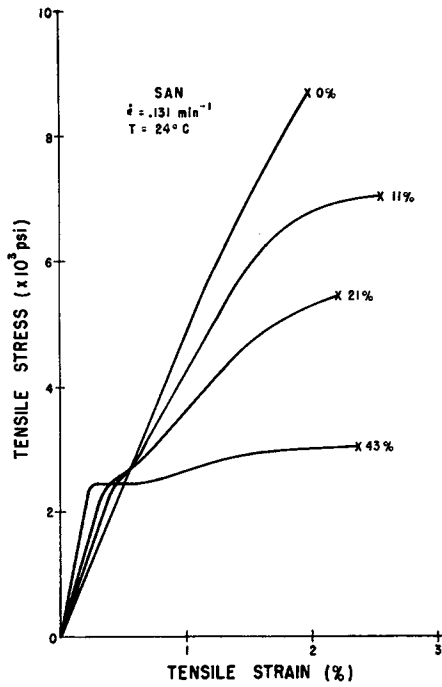


Fig. 1. Typical tensile stress-strain curves for room-temperature styrene-acrylonitrile filled with glass beads. Percentages at the ends of the curves indicate the volume fraction of filler.

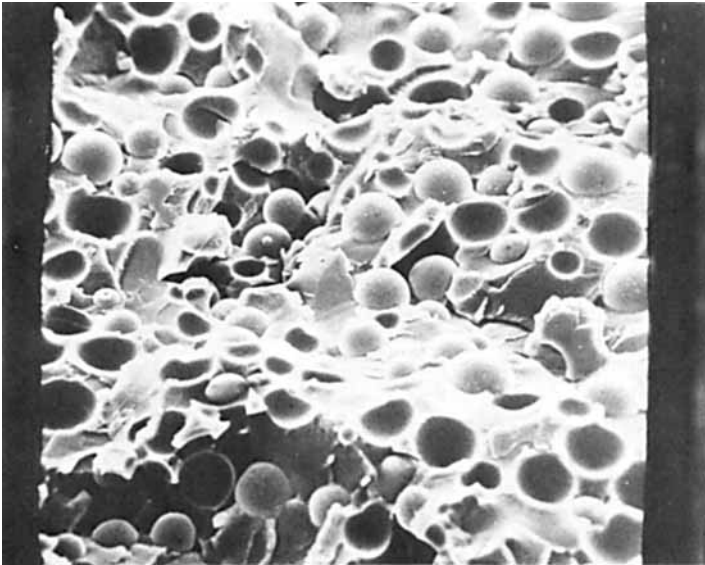


Fig. 2. Electron scanning photomicrograph of the fracture surface of a styrene-acrylonitrile composite containing 20 vol-% glass beads (210 $\times$ ).

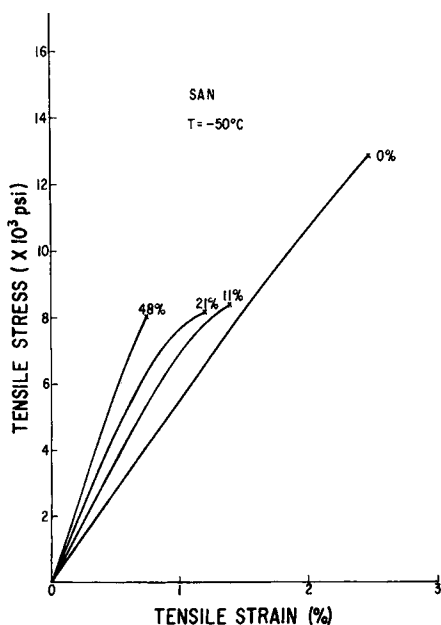


Fig. 3. Tensile stress-strain curves for  $-50^{\circ}\text{C}$  tests of styrene-acrylonitrile/glass bead composites.

Typical stress-strain curves for the  $-50^{\circ}\text{C}$  tests are shown in Figure 3. At this temperature, the SAN composites behave in a more brittle fashion and there is no detectable knee in the curves. It is also interesting to note that, in this case, the ultimate stress is the same for all the filled materials.

Polystyrene composites were evaluated only at  $24^{\circ}$  and  $-50^{\circ}\text{C}$ . Room temperature stress-strain curves for the polystyrene materials are shown in Figure 4. As with the SAN composites, there is a distinct knee in the curves, but in this case the stress at the knee is only about 1600 psi. Both the ultimate stress and the ultimate strain of these composites are almost independent of volume fraction and in all cases are below that of the unfilled matrix. Test results at  $-50^{\circ}\text{C}$  were comparable to those for SAN at  $-50^{\circ}\text{C}$ . That is, there are no knees in the curves, the ultimate strain decreases with volume fraction, and the ultimate stress is the same for all filled materials. The fracture surfaces of these composites are identical to those in Figure 2.

Room temperature stress-strain curves for the ABS composites are shown in Figure 5. For the materials with 11, 20, and 28 vol-% beads, there is a knee in the curves between 1700 and 1800 psi. The samples with 34 vol-% beads break at this stress level without showing any prior stress whitening.

An additional set of ABS composites made with beads treated with A-174 coupling agent had stress-strain curves similar to Figure 5 except that the stress at the knee was somewhat higher and the ultimate elongation was lower. These results are tabulated in Table I.

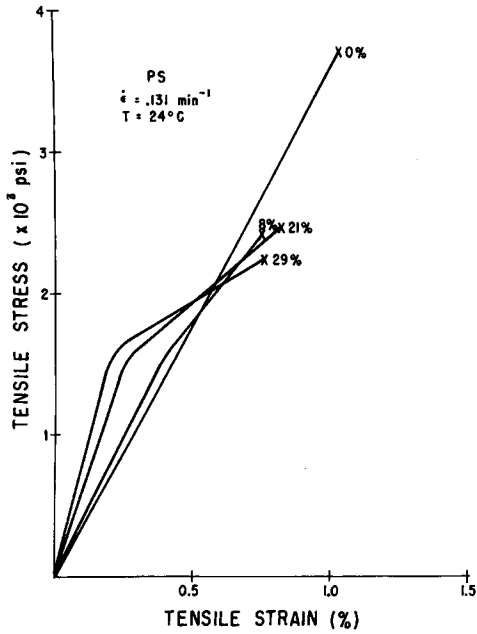


Fig. 4. Tensile stress-strain curves for room-temperature polystyrene/glass bead composites.

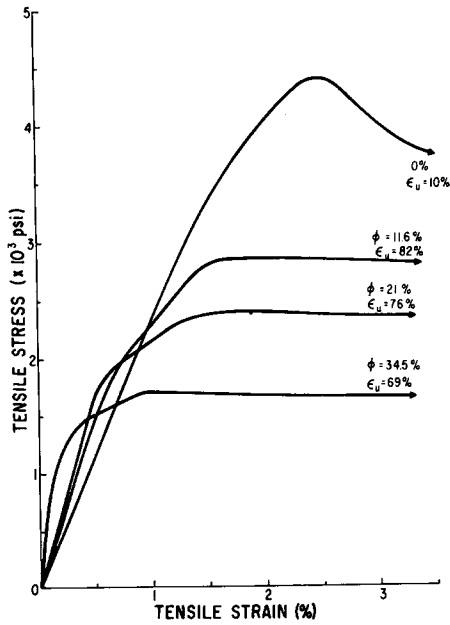


Fig. 5. Tensile stress-strain curves for room-temperature ABS/glass bead composites.

TABLE I  
Mechanical Properties Calculated from Stress-Strain Curves for Uncoupled  
and Coupled ABS Composites

$\phi$	Bead treatment	$\sigma_{yc}$ , psi	$\sigma_u$ , psi	$\epsilon_u$	$E \times$ $10^{-6}$ , psi	$W$ , in.-lb/ in. <sup>3</sup>	$\sigma_D$ , psi
0	—	4420	3450	0.105	2.40	306	—
0.116	uncoupled	2930	2860	0.82	3.16	840	1760
0.209	uncoupled	2380	2380	0.76	3.84	568	1790
0.282	uncoupled	1900	1900	0.73	4.72	442	1700
0.345	uncoupled	1700	1700	0.69	5.80	364	no knee
0.115	coupled	3180	2960	0.86	3.32	950	2440
0.144	coupled	3010	2870	0.74	3.56	703	2280
0.210	coupled	2660	2520	0.42	4.06	410	2220
0.282	coupled	2450	2180	0.22	4.90	210	no knee
0.347	coupled	2190	2050	0.15	5.40	160	no knee

The PPO composites were tested at 34°, 62°, 100°, and 140°C. Stress-strain curves for the 34°C tests are shown in Figure 6. The unfilled PPO has considerable ductility in contrast with the brittleness of the PS and SAN. However, as before, the ultimate elongation of the unfilled polymer is less than that of the filled systems. With these composites, stress whitening occurs at about 3300 psi, which corresponds to the knee in the stress-strain curve. Tests at the higher temperatures produced comparable curves with decreases in modulus, ultimate stress, and stress at the knee, as with the SAN composites.

Average values for the stress at the knee are tabulated in Table II for polystyrene, styrene-acrylonitrile, and polyphenylene oxide composites at all test temperatures where a knee exists.

TABLE II  
Tensile Stress (psi) at Which the Stress-Strain Curves  
of Glass Bead-Filled Composites Abruptly Change Slope

Temp., °C	Styrene-Acrylonitrile Composites		
	11%	21%	43%
24	2380	2390	2420
48	2020	2100	2160
65	1830	1920	1900
85	1500	1600	1600
Temp., °C	Polystyrene Composites		
	8%	21%	29%
24	1540	1530	1550
Temp., °C	Polyphenylene Oxide Composites		
	10%	25%	
34	3300	3250	
62	3180	3150	
100	3000	3050	

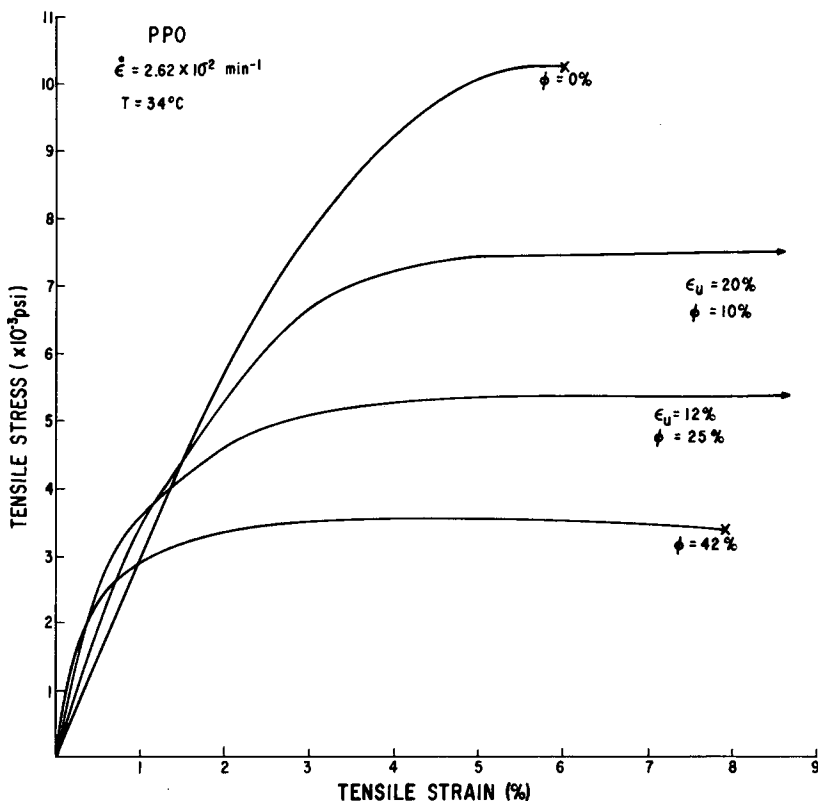


Fig. 6. Tensile stress-strain curves for polyphenylene oxide/glass bead composites at  $34^\circ\text{C}$ .

### ANALYSIS AND DISCUSSION

These composites can be divided into two distinct classes, those with a knee in the stress-strain curve and those without. The behavior of the composites without a knee is similar to that reported in the literature for particulate-filled systems. These earlier studies<sup>1-4</sup> showed that ultimate elongation decreases with volume fraction and can be estimated by

$$\epsilon_c \cong \epsilon_m(1 - \phi^{1/3}) \quad (1)$$

where  $\epsilon_c$  is the ultimate elongation of the composite,  $\epsilon_m$  is the ultimate elongation of the matrix, and  $\phi$  is the volume fraction of filler. This relationship may be compared with the appropriate experimental data in Figure 7.

Composites with a knee in the stress-strain curve have ultimate elongations much greater than predicted by the above equation. This effect must result from some inhomogeneous deformational mechanism. Experimentally, this is confirmed by the stress whitening which occurs simultaneously with the appearance of the knee. This could result either from crazing or dewetting.

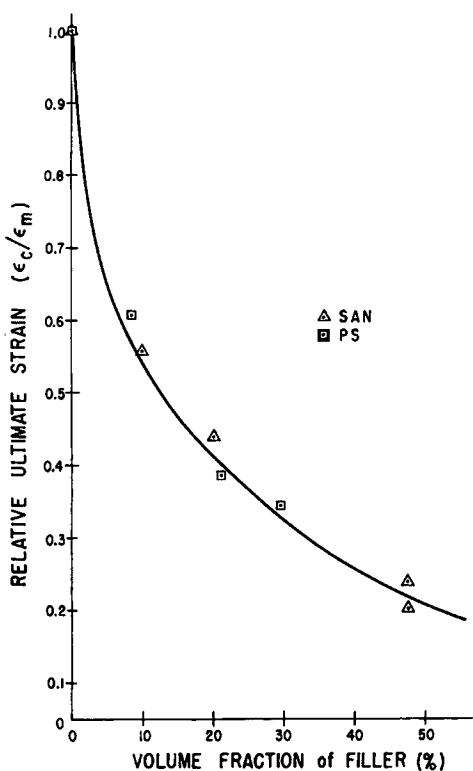


Fig. 7. Relative ultimate elongation of composites without a knee in the stress-strain curve. The solid line is the theoretical curve predicted by eq. (1).

If the knee is a result of dewetting, the modulus of the composites should change in a predictable manner. In Figure 8, experimentally determined initial moduli may be compared with three theoretical predictions.<sup>6,7,8</sup> The lowest curve, from the theory of Greszczuk, fits the data best; however, the Kerner equation, represented by the middle curve, is also a good fit. After dewetting, the modulus of the composite would be about the same as that of a foam. The equation of Greszczuk is not valid for foams, but the Kerner equation is known to work well.<sup>7</sup> The secondary modulus of the various composites may be compared with the predicted modulus of an equivalent foam in Figure 9. The theoretical prediction should be somewhat low because we have ignored the existence of the glass beads and assumed that the inclusions are voids. Despite this assumption, the experimental points are still well below the predicted value. This suggests that crazing is the predominant deformational mechanism. This hypothesis is also supported by the observation that, in sphere-filled systems, dewetting does not normally occur at such small strains.<sup>9</sup>

According to Kambour,<sup>10</sup> the crazes normally observed in thermoplastic materials are not cracks, but rather localized regions of highly oriented polymer. To investigate this hypothesis we annealed some SAN



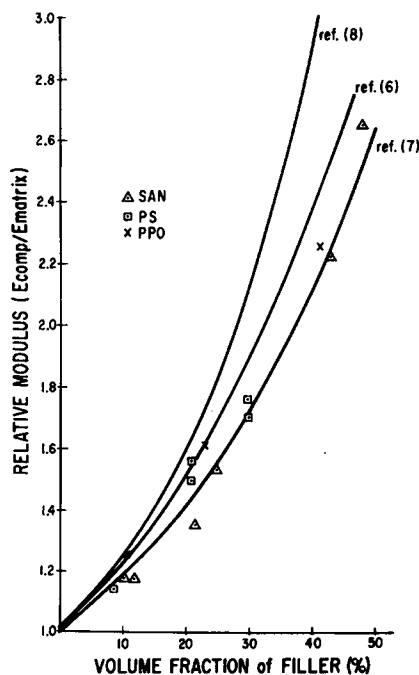


Fig. 8. Initial modulus of glass bead-filled composites compared with various theoretical predictions.

composites which had been previously loaded beyond the knee in the curve. After heating to  $10^{\circ}\text{C}$  below the glass transition temperature for as little as 5 min, the samples recovered from the previous loading and behaved almost like virgin material. This reversibility confirms that the knee in the stress-strain curve is a result of crazes since dewetting or true cracks could not heal so quickly at this temperature.

The formation of crazes in glassy thermoplastic polymers has been studied by many researchers.<sup>10-13</sup> In unfilled materials, crazes are usually induced by strain concentrations resulting from localized defects. Because of the random nature of the defects, the stress required to initiate crazing is not well defined. If, however, there are reasonably uniform concentrations dispersed throughout the material, there is some minimum value of stress which will induce crazing near the inhomogeneities. This effect has been demonstrated by Sternstein et al.<sup>12</sup> for methyl methacrylate sheets containing holes. They observed that when the applied stress exceeded some threshold value, crazes began to form perpendicular to the lines of maximum principal stress (or strain). The threshold stress was also shown to vary linearly with temperature over the range of the experiments ( $40^{\circ}\text{C}$ ). A similar mechanism has been postulated by Strella,<sup>14</sup> Haward,<sup>15</sup> and others to explain the behavior of crazable glassy polymers filled with dispersed rubber particles. Their model requires the rubber phase to also assist in terminating the crazes.

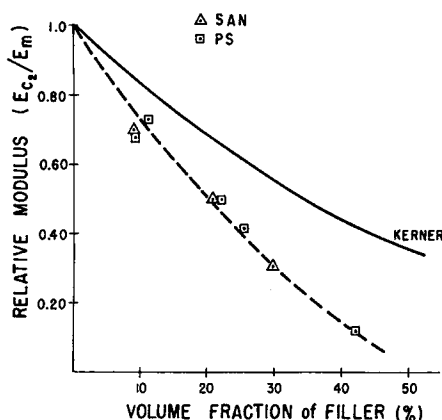


Fig. 9. Secondary modulus of composites with a knee in the stress-strain curve. The dashed curve is a smooth curve through the data, and the solid curve is the predicted modulus of an equivalent foam.

We believe a somewhat analogous process occurs in these glassy polymers filled with rigid particles and that the knee in the stress-strain curves is a manifestation of the threshold stress required to initiate crazing. The linear behavior after the knee can be explained if we assume that the formation and propagation of crazes is similar to that postulated by Halpin<sup>16</sup> for holes in viscoelastic materials.

According to the Goodier<sup>17</sup> linear elastic analysis, the maximum stress concentration caused by a rigid inclusion is about 1.5, whereas for a rubbery inclusion<sup>18</sup> it is about 2, and for a hole<sup>12</sup> it is about 3. The stress concentration effect is superposed onto shrinkage stresses, and the combination helps initiate crazing at many points in the composite at the threshold stress. The growth of the crazes might also be terminated by the glass beads. If a propagating craze encounters a glass sphere to which the matrix is not strongly adhered, interfacial debonding can effectively blunt the tip of the craze and prevent further propagation. This is analogous to the crack termination mechanism proposed by Cook and Gordon.<sup>12</sup>

For the void or rubbery inclusion, the maximum stress occurs around the equator of the sphere while for the rigid inclusion it is near the poles before debonding. This is a doubly restrictive situation. The stress concentration is lower and a smaller volume of material is involved in the initiation process. It follows that if the proposed mechanism is to be effective, the matrix material must be readily crazable. This perhaps explains why this phenomenon has not been widely reported.

Matsuo et al.<sup>20</sup> studied a model system of two rubber balls encapsulated in polystyrene. Their results indicate that the threshold stress is independent of interparticle spacing for center-to-center distances greater than 1.45 diameters and decreases by only about one third as the interparticle spacing goes to zero. Considering the statistical distribution of spacings in these "real" composites, this result is consistent with the data in Table I.

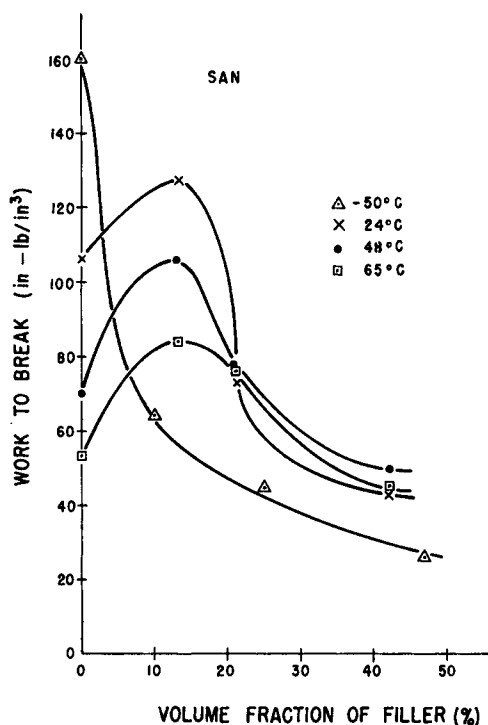


Fig. 10. Work to break for styrene-acrylonitrile/glass bead composites.

Also, as noted by Sternstein et al., the values of the threshold stress decrease linearly with temperature above ambient.

At  $-50^\circ\text{C}$ , we found the threshold stress to be poorly defined but quite high. At this temperature, the composites all broke at or slightly above the threshold stress with very little nonlinear deformation. There is almost no evidence of crazing in these samples, which suggests that the stress required to cause crazing at  $-50^\circ\text{C}$  is about the same as the brittle fracture strength of the matrix. The ultimate elongation of these composites is quite low but, as previously mentioned, is in good agreement with theoretical predictions. The above hypothesis is also consistent with the observations of Kenyon and Duffey, who studied the mechanical response of a bead-filled thermosetting resin. Their matrix material did not craze and their results were similar to our low-temperature data.

The increase in ultimate elongation which results from this crazing process also affects composite toughness. It is normally expected that work to break will decrease when a particulate filler is added to a polymer.<sup>1</sup> However, Figures 10, 11, and 12 show that for systems in which the matrix can craze, the composite toughness can actually be significantly increased by the addition of filler. The toughness of the SAN composites tested at  $-50^\circ\text{C}$  decreases sharply with increasing filler volume fraction; however, at all other temperatures investigated, the toughness of the composites

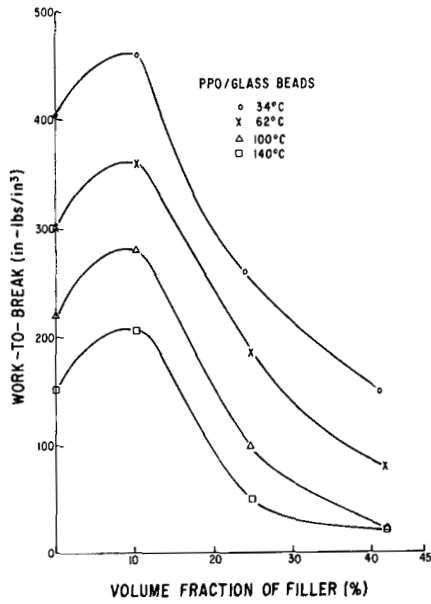


Fig. 11. Work to break for polyphenylene oxide/glass bead composites.

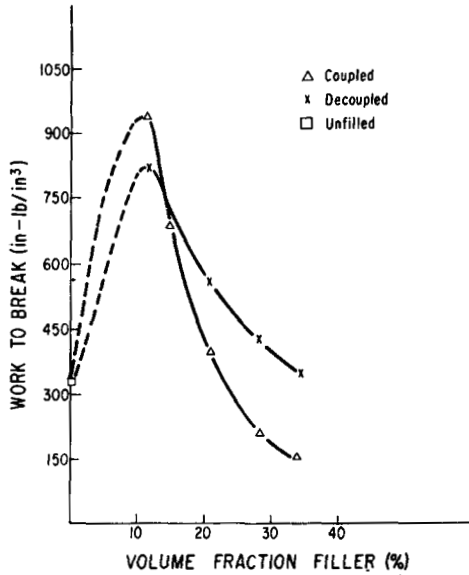


Fig. 12. Work to break for ABS/glass bead composites.

increases initially with the addition of filler and then decreases. The increase is modest for PPO and SAN but quite dramatic for ABS where the toughness can be increased by as much as a factor of 3 by adding filler.

In summary, we have found that particulate-filled composites may have ultimate elongation and toughness greater than the unfilled polymer if the

polymer is amenable to crazing. The inhomogeneous deformational mechanism responsible for this increase in properties is crazing of the matrix near the rigid inclusions. This energy-absorbing mechanism is well known in rubber-filled polymers such as high-impact polystyrene; however, extensive crazing has not previously been reported for glassy polymers filled with rigid particles. The data presented here are not to be construed as representing an optimized system but rather reflect a first encounter with such a crazing mechanism in this type of composite. Subsequent work should lead to even better particulate-filled composites. It is also possible that this mechanism can be utilized to composites reinforced with aligned fibers. A crazable matrix might significantly improve the transverse properties of such composites.

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