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EFFECT OF SIZE OF GLASS FILLER ON THE TENSILE PROPERTIES  
AND TEAR STRENGTH OF POLYBUTADIENE

BY

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## SUMMARY

An experimental study of the tensile properties, tear strength, hysteresis, and the swelling ratio of model composite elastomeric compounds consisting of polybutadiene filled with glass beads has been carried out as a function of the size of the beads. The diameter of the beads ranged from 25 to 1000 $\mu$ m and the volume fractions examined were 0.16, 0.092 and 0.048. Mechanical properties of the filled elastomers were functions of the loading (separation distance), the particle size (surface area/volume) and the elastomer-filler systems studied.

## INTRODUCTION

Investigations in our laboratories are directed toward developing and understanding the fundamental factors that control adhesion between oxidizer particles and fuel in composite rocket propellants. Typically, oxidizer particles are solids such as  $\text{NH}_4\text{ClO}_4$  and the fuel is an elastomer such as a polyurethane derived from a polybutadiene glycol (1). One factor under intensive study is the effect of chemical bonding on adhesion. Model systems with controlled interfaces and simple materials have proven to be very helpful (2-4). In particular, as long as the emphasis of the study is focussed on the interface alone, flat surfaces, such as coated and uncoated glass plates or slides, have been useful as models for the oxidizer and cured polybutadiene has been a useful model for the fuel.

In real systems the oxidizer is present in the form of particles and to gain a complete understanding additional studies must be carried out with composites containing particles. In an investigation of the tear strength and tensile strength of model filled elastomers (5) with materials similar to those used in our adhesion studies, we found that the effects of silane treatment of the glass on mechanical properties correlated well with predictions based on our adhesion studies with flat plates. A limited survey of only two different ranges of particle sizes revealed that the properties of the resulting composites were influenced also by the size of the particles used. Clearly further consideration of chemical aspects alone could not proceed until the effect of physical aspects such as particle size were examined in our systems.

Mechanical properties of filled matrices have been studied extensively as a function of the concentration of glass beads and other nonreinforcing filler particles (e.g. 6-10). But surprisingly there is no data in which the matrix is polybutadiene. Experimental data on the effect of particle size of "nonreinforcing" fillers on the mechanical properties of composites is more limited (7,8,10). Depending on the system and property being studied conclusions range from no effect of particle size (7) to an inverse variation of the property with size (8).

The present study was undertaken to determine how glass filled polybutadiene behaves and includes a considerably extended range of particle sizes compared to previous studies. Comparison

of the earlier results with those presented in this paper and a limited discussion of theoretical considerations was also carried out.

#### EXPERIMENTAL

Glass beads were chosen as filler on the assumption that the glass surface would be inert as far as the vulcanization reaction is concerned. Five different size ranges of soda-lime beads, supplied either by Potters Industries Inc., or Petrarch Systems, Inc., have been used in the study. All beads were untreated as received and all were handled in the same way thereafter. The surfaces of the beads appeared uniformly smooth, irrespective of the source, when examined microscopically. The sizes were selected to give as broad an overall range as possible. They are summarized in Table I, with the indication of their source. The density of the glass was  $2.475 \text{ g/cm}^3$  and the refractive index 1.52. The beads were added to polybutadiene (Diene 35 NFA, Firestone Tire and Rubber Co.) usually at a concentration of 50 parts by weight per 100 parts of elastomer. The corresponding volume fraction was about 0.16 in the final product. Dicumyl peroxide (Dicup R, Hercules Inc.) was added at a concentration of 0.05 phr and crosslinking was effected by heating the mixture in a heated press for 2 hrs. at  $150^\circ\text{C}$  and a pressure of 30,000 lbs. on a 5" ram of a FHI press. Molded test sheets were prepared in this way with a thickness of 4 mm. All tests were carried out on specimens of this thickness at room temperature. A few tear tests were carried out on 9 mm samples in addition.

Tear and tensile tests were performed in a way similar to that described in (5). In order to determine the dissipation

of mechanical energy during stretching, the hysteresis ratio,  $H$ , was measured.  $H$  was calculated from the areas  $A_1$  and  $A_2$  under the loading force-displacement relations, when specimens were stretched to 20, 40, 60, 80% elongations at the rate of  $0.01 \text{ sec}^{-1}$  and then allowed to retract at the same rate back to the unstrained state. The  $H$  value was then calculated from the relationship:

$$H = (A_1 - A_2)/A_1 \quad (1)$$

Linear swelling ratio measurements were carried out on strips of about 0.5 cm wide and 8 cm long, measured along the length before ( $L_0$ ) and after ( $L_f$ ) immersion in heptane solvent for over 70 hrs. The swelling ratio,  $q$ , was calculated from the relationship:

$$q = L_f/L_0 \quad (2)$$

A few tests were carried out at bead concentrations different from 50 parts by weight per 100 parts of elastomer.

Samples were cut in same direction from molded sheets. The same sample of polybutadiene was used for all sizes of beads. The data are averages from several preparations and several samples from a given preparation. Since the beads are spherical, all samples should have equal or nearly equal anisotropy, if there is any anisotropy.

#### RESULTS AND DISCUSSION

Results and analyses of our data are arranged according to the property under discussion. In each section our results are presented first. These are followed by a comparison with selected data taken from the literature and by a limited discussion of

related theory, where available. Only nonreinforcing fillers are considered. Data for rubber-carbon black systems is omitted because factors other than particle size are probably important in such systems.

### Stress-Strain Behavior

#### Stress and Elongation at Break

Results. The treatment of data obtained from tensile fracture experiments was similar to that described previously (5). The results of the experiments are given in Table II. Data for unfilled rubber are included for comparison. In each case about seven separate measurements were made; the mean values and standard deviations are given in the table.

The presence of filler had a small but systematic effect on the tensile strength of polybutadiene. When the mean diameter of the filler particles was 25  $\mu\text{m}$ , the average breaking stress,  $\overline{\sigma}_b$ , was almost unchanged. A maximum decrease in  $\overline{\sigma}_b$  of about 30% was obtained in the presence of the three largest sizes of beads. In the concentration range studied, the effect on  $\overline{\sigma}_b$  of varying the filler concentration was negligible.

The presence of filler significantly reduced the values of breaking elongation,  $e_b$ . At a volume fraction,  $v_F$ , of 0.16 introduction of 25  $\mu\text{m}$  spheres decreased  $e_b$  by 20% while introduction of 60  $\mu\text{m}$  spheres led to a decrease of about 50%, both compared to the unfilled materials. The presence of spheres larger than 145  $\mu\text{m}$  had hardly any additional effect on  $e_b$ . For the two higher concentrations of filler particles the reduction in  $e_b$  was about the same but at  $v_F = 0.048$  the decrease in  $e_b$  was smaller.

An alternative measure of the strength in tension is given by the strain energy density at break,  $U_b$ . Approximate values of  $U_b$  were calculated from the measured breaking stress and breaking elongation, assuming that a linear stress-strain relationship was followed up to break (5). The values obtained are given in the final column of Table II. It is evident that with increase of the mean diameter of the glass beads, the  $U_b$  values decrease rapidly in a fashion similar to that of the breaking elongation,  $e_b$ . There are inflections in the curves of  $U_b$  and  $e_b$  vs. particle size occurring at a filler diameter of about 100  $\mu\text{m}$ .

An attempt was made to fit some of the data into a function which will best describe the experimental results. Using a bivariate curve fitting program we were able to fit the results of  $e_b$ ,  $U_b$  and  $\sigma_b$  vs. particle size,  $d_F$ , to exponential functions of the form:

$$e_b = 0.79 e^{17.1/d_F} \quad \text{with} \quad \text{correlation factor of } 0.983$$

$$U_b = 2.34 e^{27.7/d_F} \quad \text{with} \quad \text{correlation factor of } 0.963$$

$$\text{and } \sigma_b = 0.88 e^{6.8/d_F} \quad \text{with} \quad \text{correlation factor of } 0.81$$

Such a fit can be the result of pure coincidence; yet if the functions are correct it is obvious that these properties are exponentially dependent on the reciprocal of the mean particle diameter. The dependence of properties on the reciprocal of the mean particle diameter will be discussed further when these results are compared with other results taken from the literature.

Comparison with Literature. Tensile strength and elongation are the most widely studied properties of filled composites (e.g. 6-13). According to the reports, rigid fillers cause a comparatively small decrease in tensile strength and a dramatic decrease in elongation at break. The presence of filler, in addition, very often leads to a yield point in the stress-strain curve. Yielding is attributed to a dewetting effect, which is accompanied by creation of voids and dilation of the specimen. As the concentration of filler increases, the elongation at which dewetting/dilation occurs decreases (11, 14-16). Our results with glass-filled polybutadiene show the same trends except that yield points were not observed.

Reports of experimental observations on the effect of particle size on stress-strain properties of filled elastomers are few and do not agree well with each other. Oberth (17) and others (18-21) found little effect of particle size on breaking stress. Alter (8) has reviewed much of the data. He states that up to particle radii of 0.2  $\mu\text{m}$ , relative stress and elongation at break are functions of the reciprocal of the filler particle size. (Relative mechanical properties are defined as the ratio of the value for the filled to the unfilled.) According to Alter the reciprocal relationship may be viewed as a dependence on the surface area to volume ratio for the filler. At larger particle sizes according to Alter there was too much scatter to reach any conclusions. Schwarzl, Bree and Nederveen (7), who used NaCl as inert filler

in polyurethane, found that deformation at large strains was dependent on particle size but at low strains particle size dependence was not important and only filler content had a significant effect on mechanical properties. Our data and the data of Schwarzl, et al. at large strains are compared in Figures 1 and 2, where, following Alter, relative stress at break,  $\sigma_b/\sigma_b^\circ$ , and relative elongation at break,  $e_p/e_p^\circ$ , are plotted versus reciprocal particle size. The curves have arbitrarily been drawn with discontinuous slopes to emphasize the abrupt change in properties when the particle size is about 100  $\mu\text{m}$ . The smooth curve to which the lines are tangent could equally well have been drawn. Data for different loadings are given. Note that all the data are for particles with a diameter substantially greater than 0.4  $\mu\text{m}$  ( $10 \mu\text{m}^{-1}$ ), the maximum diameter examined in detail by Alter (8). The data for glass filled polybutadiene covers a particle size range from 25  $\mu\text{m}$  to 1000  $\mu\text{m}$  and a loading range from 0.17 to 0.048 volume fraction. The data for salt filled polyurethane extends from 36 to 390  $\mu\text{m}$  and 0.11 to 0.42 particle size and volume fraction, respectively. Thus the range of particle sizes and of loading has been extended by the work with polybutadiene.

The data in Figures 1 and 2 are not scattered. The results are clearly systematic functions of both loading and particle size. As loading decreases,  $\sigma_b/\sigma_b^\circ$  converges. The  $\sigma_b/\sigma_b^\circ$  scale for the polybutadiene data has been expanded compared to that for the polyurethane data. Then it is apparent that in contrast to the polyurethane data where the loading lines are nearly parallel over the whole range of particle sizes, the lines for the

largest fillers used in polybutadiene have different slopes. The larger particles have a bigger effect in reducing relative breaking stress in both systems. However, the pronounced inflection that is apparent in both sets of curves occurs at a different mean diameter. The values are 143 and 70  $\mu\text{m}$  for the polybutadiene and polyurethane systems, respectively. One possible explanation of the significance of these values will be given in terms of flaw sizes to be discussed in the section on tear strength.

The shape of the relative breaking elongation versus particle size curves are quite different from corresponding ones for relative breaking stress. There is a systematic variation with reciprocal particle size and loading but the nature of the variation is different in the two systems.

Comparison with theory. Recently Gent (22) has developed an approximate theoretical treatment for detachment of an elastomer from rigid spherical inclusions of different sizes by a tensile stress applied to the elastomeric matrix. Preliminary efforts to fit the above data to this theory have been unsuccessful.

#### Modulus

Results. The linear portion of the stress-strain curves obtained at low extensions of polybutadienes containing varying sizes of glass fillers was used to determine Young's modulus of elasticity,  $E = \sigma/e$ . The measured modulus for unfilled polybutadienes,  $E^0$ , in our study was 1.38 and those for the filled polybutadienes ranged from 2.06 to 2.3 MPa.

In the presence of the largest glass beads (1000  $\mu\text{m}$ ) Young's modulus decreased to 1.725 MPa. This might be due to void formation, or as indicated in the footnote to Table I, fragmented glass beads were found in these compounds. Their presence could have affected the E value, possibly as a result of broken fragments puncturing the surface of the specimens. Alternately, the low modulus could be caused by a "skin effect" as proposed by Nielsen and Lee (23). According to this suggestion the surface (skin) of molded polymer sheets is enriched in polymer because no part of rigid filler particles can extend out beyond the surface.

Comparison with Literature. Alter (8) finds a linear dependence of relative modulus on reciprocal particle size for fillers less than 0.2 $\mu\text{m}$  in radius. Schwarzl, Bree and Nederveen (7) found that shear moduli of NaCl filled polyurethane rubber in the glassy and rubbery states increase considerably with filler content and are independent of filler size. We find a small but apparently real dependence on particle size.

Comparison with Theory. The Smallwood-Guth-Einstein relation (24) can be used to predict the increase in the Young's modulus of a composite. According to the equation

$$E = E^{\circ}(1 + 2.5c + 14.1c^2) \quad (3)$$

where E is the modulus of the filled rubber,  $E^{\circ}$  is the modulus of the rubber matrix and c is the volume concentration of the filler. Our values for filled polybutadiene, 2.06-2.3 MPa are in the same range as the theoretical one calculated from the equation, 2.4 MPa, and the increase in the presence of filler is consistent with expectations from earlier work (6, 9, 11, 25, 26). However, contrary to theoretical predictions but in agreement with Alter's observations

(8), we find a small but systematic variation with particle size. (See Figure 6) More will be said about this below when the moduli are compared to swelling ratios on the same samples.

#### Tear Strength

Results. Measurements of tear energy,  $T$ , were carried out on four strips of each compound. The values of  $T$  from 4 mm specimens varied by about  $\pm 15\%$ , even though the tear force and the width of the tear path were preaveraged along the length of each strip. The results of tear strength measurements are given in Table I. Concern that measurements of tear strength on 4 mm thick specimens would not be meaningful with beads as large as 1000 microns led us to repeat some measurements on 9 mm thick specimens. A different sample of polybutadiene, which happened to have a higher tear strength even unfilled, was used for these experiments. The conclusions from the data were the same regardless of thickness. The highest reinforcement, about 50% for 4 mm thick specimens and about 98% for 9 mm thick specimens in comparison to unfilled material, was attained in the presence of 25  $\mu\text{m}$  particles. A smaller increase of about 25% (60% for 9 mm thick specimens filled with 1000  $\mu\text{m}$  beads) was obtained in the presence of larger spheres. Overall the tear strength was only slightly dependent on the size of the glass spheres.

Comparison with Literature. Prior to the present work the effect of glass bead size on the tear strength of a composite was unclear. Dreyfuss, Gent and Williams (5) observed that the intrinsic tear strength of the glass-bead-filled-matrices was not much different from that of the unfilled matrix. They attributed the slight enhancement observed to a deviation of the tear path from a straight

line caused by the presence of the glass beads in the material. Such a deviation should result in a rougher tear path and a correspondingly higher tear strength. If this explanation is correct, a question arises with regard to the data in the present study. Why is the tear strength of compounds containing the smallest particles increased by about 50% compared to that of unfilled polybutadiene while that of composites containing larger glass beads increased only 25%? As stated above this difference was demonstrated in two slightly different polybutadienes, Diene 35NFA and Diene 35NSA, and at two different thicknesses, 4 and 9 mm.

Examination of the torn surfaces by eye or at low magnification, 5 to 13X, showed in all cases a series of troughs running across the surface in a direction of about 45° to the direction of the tear propagation. In the presence of the smaller particles the surface was comparatively smooth to the eye and very much like that of the unfilled material. The troughs were equally spaced and almost parallel. However, when magnified 10 to 13X, the surface appeared very rough (compare Figure 3A with 3B and 3C). Samples containing the largest particles had a very rough torn surface and the troughs were not parallel even when examined by eye. Instead they went in random directions, often travelling from one bead to another. It seems, therefore, that the enhancement of tear strength can be attributed to the increasing importance of a surface energy term, with small particles and to the increased irregularity of the tear path with larger inclusions.

Comparison with Theory. What is the mechanism of fracture of an elastomer in the presence of filler and how does the size of the filler influence this mechanism? Dreyfuss, Gent and Williams (5) suggested that tensile rupture in elastomers containing solid particles takes place by catastrophic tearing from an initial flaw identified with a large dewetted particle.

Using the measured tear energy,  $T$ , of the unfilled material and the tensile strain energy density,  $U_b$ , it is possible to calculate the depth  $C$  of the edge flaw from which fracture initiates from the relationship:

$$C = T/2KU_b \quad (4)$$

where  $K$  is a numerical quantity, to which a value of 2 can be assigned for moderate deformations (5). The values obtained in this way for the depth  $C$  of fracture nuclei are given in the last column of Table I. In the range of sizes between 60-225  $\mu\text{m}$  they seem to be significantly larger for the glass filled materials than for the unfilled elastomer and to be of the same order of magnitude as the diameter of the largest glass particles present. When the particle diameter was in the 14-35  $\mu\text{m}$  range then the apparent size of the flaw is the same as that of the unfilled material. With the largest beads the calculated flaw size (528  $\mu\text{m}$ ) is much smaller than the largest (1411  $\mu\text{m}$ ) beads present. Instead it correlates rather well with the mean distance between particles (484  $\mu\text{m}$ ) shown in Table I. Perhaps with very large particles the flaw size is determined by the average distance between particles instead of by the diameter of the bead.

The distance between two neighboring particles is given by (27):

$$D = d_F \left[ \left( \frac{\pi}{6v_F} \right)^{1/3} - 1 \right] \quad (5)$$

assuming that an elastic medium contains a volume fraction  $v_F$  of particles of diameter  $d_F$  arranged in a cubic lattice. The mean distances between two particles, thus calculated, are given in Table I as a function of the mean diameter of glass beads. For the 1000  $\mu\text{m}$  particles the mean distance between particles is about the same as the flaw size calculated.

#### Mechanical Hysteresis Ratio, H

Results. Experimentally determined values of the mechanical hysteresis ratio  $H$ , defined by eq. (1) are plotted vs. particle size in Figure 4. In the figure the data for rubber alone are plotted as if the size of the filler particles was 0  $\mu\text{m}$  and the loading was the same as for the other particles. The curves are extended to include this data to show that they do so naturally. Figure 4 shows that the  $H$  value increased with particle size up to about 100  $\mu\text{m}$ , and then decreased slightly with further increase of the filler size. For the unfilled material 10-12.5% of the energy expended in stretching the rubber was dissipated internally. After incorporation of the glass beads, the value rose to 11-15% in the presence of 25  $\mu\text{m}$  glass beads and to 12-22% in the presence of larger inclusions. Again there was an inflection in the plot of hysteresis versus particle size at a mean diameter of about 100  $\mu\text{m}$ . This increase in the hysteresis of the composite in comparison to unfilled material

probably results from energy dissipated in debonding of the elastomer from the surface of the filler.

Comparison with Theory. The small amount of energy dissipated in the process of dewetting for small beads supports Gent's hypothesis (22) that detachment from inclusions smaller than 100  $\mu\text{m}$  doesn't occur; instead rupture of the matrix near the inclusion becomes the preferred mode of failure at an applied stress. The smaller energy dissipated in dewetting from the largest beads ( $\sim 1000 \mu\text{m}$ ) of 0-7% implies that dewetting and matrix rupture are competing modes of failure for these compounds. In each case the maximum amount of energy dissipated is lower than the theoretically predicted value of 15% (22) for complete dewetting of 0.16 volume fraction of filler particles. This is attributed to existence of interaction of strain fields around each particle.

#### Swelling Ratios

Results. Since swelling is equivalent in many respects to a three dimensional stretching of the elastomer, the effect of particle size on the amount of swelling of glass filled compounds, at constant volume fraction of the filler was compared.

The composite compounds were immersed in heptane solvent for over three weeks, yet no desorption of rubber was observed. We believe, therefore, that polymer-filler attachments, in the systems studied, were fairly strong. Similar observations of unexpectedly large adhesion of polybutadiene to glass have been made by Dreyfuss and coworkers (3,5) and by Wong (28).

The results of swelling ratio vs. filler size are plotted in Figure 5. The swelling ratio for unfilled rubber was 1.564. The

swelling ratio decreased with particle size and had a minimum value for samples containing spheres of about 100  $\mu\text{m}$ . It then increased with further increase of the filler size until it reached a value similar to that of the unfilled material.

When the data is plotted versus reciprocal particle size, as shown in Figure 6, the dependence of swelling ratio on particle size becomes clearer. It is noteworthy that the minimum in the swelling ratio curve occurs at the same value as the maximum of the relative modulus curve, also shown in Figure 6. The swelling ratio curve shows an inverse relationship to the other curve at all loadings. The reasons for this dependence on particle size are not clear at the present time but the results suggest that different factors may be important above and below 143  $\mu\text{m}$ . It is possible that the effect of surface attachments is more pronounced with the smallest particles as a result of their greater surface area. The fact that the minimum in the curve in Figures 5 and 6 is at about 143  $\mu\text{m}$  rather than at the smallest particle diameter we studied, 25  $\mu\text{m}$ , argues against surface attachments as the exclusive factor.

Another factor could be interaction of stress fields surrounding particles at short distances from each other (27). Since, according to equation 5, the distance between particles depends on the volume fraction of the filler, swelling ratios of composites consisting of different loadings of the glass beads were measured. The results are plotted versus particle separation distance in Figure 7. The minimum for the curves of the plots of swelling ratio versus separation distance varies systematically with the loading of the filler: the lower the loading the greater the distance at which the minimum occurs.

Comparison with Literature. Although several theoretical treatments are available (29,30) the significance of swelling measurements of composites is not fully understood. Bills and Salcedo (29) concluded that the swelling ratio is the same with and without filler and does not vary with loading. In contrast Fedors and Landel (30) conclude that the swelling ratio decreases slowly with loading. Figure 8 shows a comparison of the results of these workers with the results found in this study. Since neither of the earlier studies were made with particles of known and variable particle size, correlations are hard to make. Our data indicates that the observed swelling ratio depends on both loading and particle size of filler.

The inflection in the relative mechanical property curves (Figures 1,2 and 6) may be related to inherent flaws in the rubbery matrix. If so, as shown in Figures 1 and 2, the inherent flaw size varies with the system.

#### SUMMARY AND CONCLUSIONS

Mechanical properties of filled elastomers are functions of the loading (separation distance), the particle size (surface/volume) and the system being studied. With regard to glass filled polybutadiene the following conclusions can be drawn from this study:

1. The effect of glass bead fillers on the mechanical properties of filled polybutadiene depends on the size of the filler particles and on the separation distance between them. The

properties change rapidly with increasing particle size of filler up to particle diameters of about 100  $\mu\text{m}$  and change further only slowly with further increase in bead diameter. The magnitude of the change also depends on the separation distance between the particles, which is controlled by the loading.

2. Addition of 50 parts by weight per 100 parts of polybutadiene, corresponding to a volume fraction of 0.16 in the final product, was found to increase the tear strength by 50% for beads with mean diameter of 25  $\mu\text{m}$ , while the increase in the presence of larger beads was only 25-30%. This difference is attributed to the increasing importance of a surface energy term in the case of the small beads and to increased roughness of the tear path in the case of large-glass filled materials.

3. Energy dissipation, associated with dewetting the beads on stretching the filled materials, was found to vary between 1-4% for the smallest beads and 1-10% of the input strain energy for the bigger beads.

4. Breaking stress, elongation, modulus, relative breaking stress, relative elongation, relative modulus and swelling ratio of composites are functions of the reciprocal size of the filler added. This may be interpreted as dependence on the surface area to volume ratio of the filler particles.

5. Physical properties of glass filled materials, such as breaking elongation in tension, the tensile strain energy density, mechanical hysteresis ratio or swelling ratio depend strongly on the size of the filler up to particle size of about 100  $\mu\text{m}$ .

Fillers larger than 100  $\mu\text{m}$  have only a small influence on those properties. When the distances between particles are small, the distance between particles may become the dominant variable.

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Table I  
Size of Glass Beads and the Effect of Size on Properties<sup>a</sup>

Source	Measured Diameter ( $\mu\text{m}$ )	Mean Diameter ( $\mu\text{m}$ )	Mean Distance between ( $\mu\text{m}$ )	Tear Strength		Depth of Edge Flow, C ( $\mu\text{m}$ )
				Thickness of Strip (cm)	T ( $\text{J}/\text{m}^2$ )	
No glass added				0.4	422.0 $\pm$ 0.5	123
Potters	14 - 35	25	12	0.4 0.9 <sup>b</sup>	633 $\pm$ 28.0 923	153
Potters	30 - 90	60	29	0.4	502 $\pm$ 61	278
Petrarch	80 - 220	145	70	0.4	528 $\pm$ 88	310
Petrarch	90 - 355	225	109	0.4	529 $\pm$ 88	364
Petrarch	855 - 1411 <sup>c</sup>	1135 <sup>c</sup> (1000)	484	0.4 0.9 <sup>b</sup>	554 $\pm$ 8 753 $\pm$ 9	528

<sup>a</sup> Volume fraction of glass,  $v_f = 0.16$

<sup>b</sup> These measurements were made using Diene 35 NSA, which had a higher tear strength,  $T = 465.0 \text{ J}/\text{m}^2$ , than the Diene 35 NFA used in the other measurements. The tensile properties were also different. For example, the  $v_b$  values were 0.86 and 1.125  $\text{MJ}/\text{m}^3$  for unfilled compounds from Diene 35 NFA and Diene 35 NSA, respectively.

<sup>c</sup> Some of these beads were extracted from the molded sheets by boiling pieces of the sheet in 2% Micro solution overnight. Shards ranging from 200 to 900  $\mu\text{m}$  in addition to unfragmented spheres indicated that some of the extracted beads had been broken during milling and molding. Therefore, a mean diameter of 1000  $\mu\text{m}$  was arbitrarily chosen for this sample. (Micro is a laboratory cleaning solution from International Products Corpn.)

Table II  
Tensile Properties of Glass-filled Polybutadiene

Volume fraction $v_F$	Mean diameter of glass beads ( $\mu\text{m}$ )	Volume fraction of glass			Strain energy at break, $U_b = 1/2 \sigma_b \cdot e_b$ (MJ/m <sup>3</sup> )
		Breaking stress $\sigma_b$ (MPa)	Breaking elongation $e_b$		
0.16	no glass added	$0.87 \pm 0.03$	$1.98 \pm 0.38$	0.86	
	25	$0.87 \pm 0.06$	$1.59 \pm 0.13$	0.69	
	60	$0.79 \pm 0.06$	$0.97 \pm 0.14$	0.38	
	145	$0.80 \pm 0.04$	$0.80 \pm 0.05$	0.32	
	225	$0.69 \pm 0.04$	$0.84 \pm 0.10$	0.29	
0.096	1000	$0.62 \pm 0.03$	$0.65 \pm 0.08$	0.20	
	60	$0.73 \pm 0.01$	$1.15 \pm 0.15$	0.42	
	145	$0.71 \pm 0.02$	$0.86 \pm 0.08$	0.30	
	225	$0.67 \pm 0.05$	$0.915 \pm 0.2$	0.31	
	375	$0.64 \pm 0.02$	$0.82 \pm 0.14$	0.26	
0.048	1000	$0.60 \pm 0.06$	$0.735 \pm 0.22$	0.22	
	25	$0.83 \pm 0.05$	$2.04 \pm 0.57$	0.85	
	60	$0.76 \pm 0.05$	$1.34 \pm 0.24$	0.51	
	145	$0.74 \pm 0.02$	$1.23 \pm 0.12$	0.45	
	225	$0.71 \pm 0.02$	$1.15 \pm 0.12$	0.41	

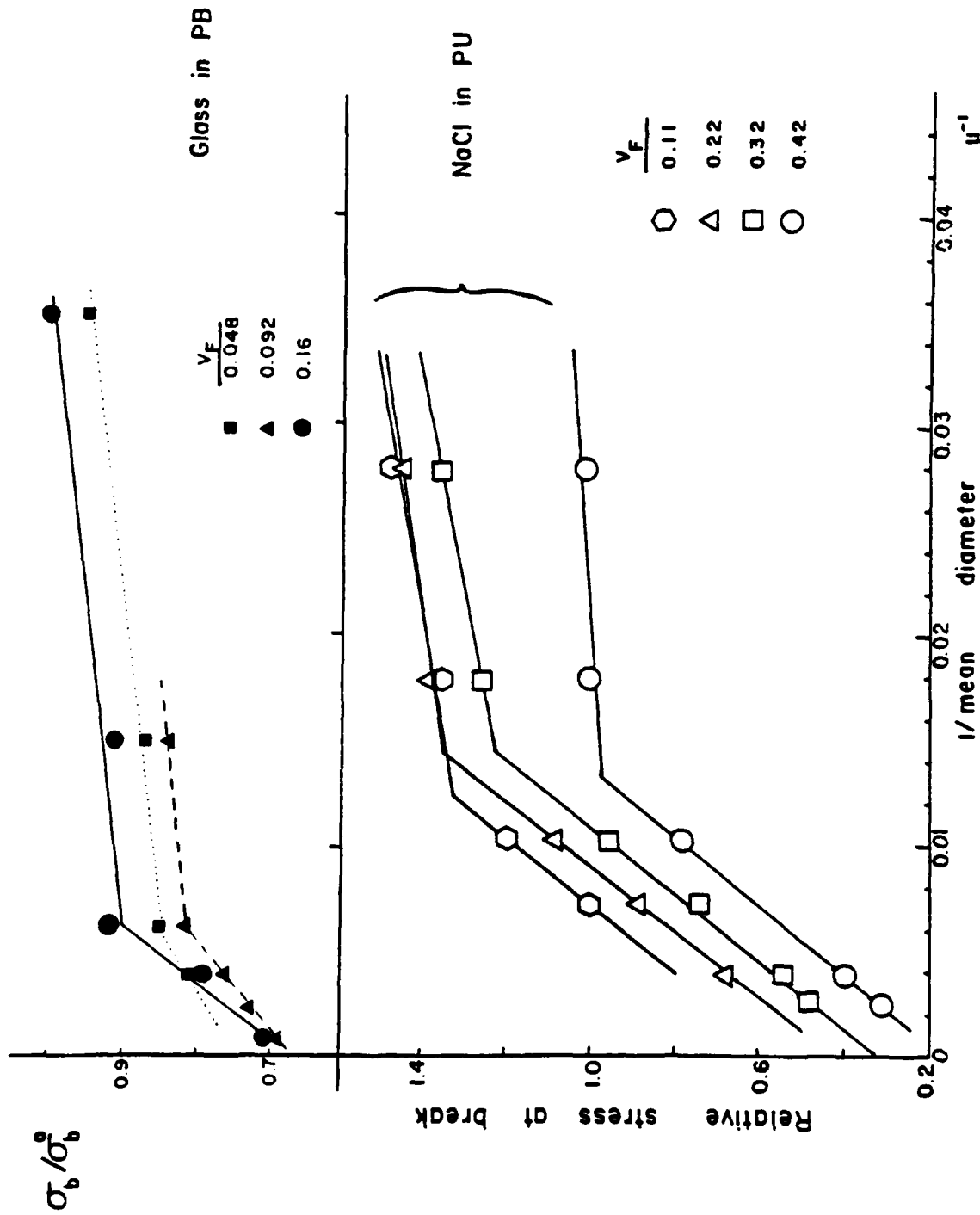


Figure 1. Relative stress at break as a function of reciprocal of mean diameter of particles of glass in polybutadiene (PB) and salt in polyurethane (NaCl in PU) (7).

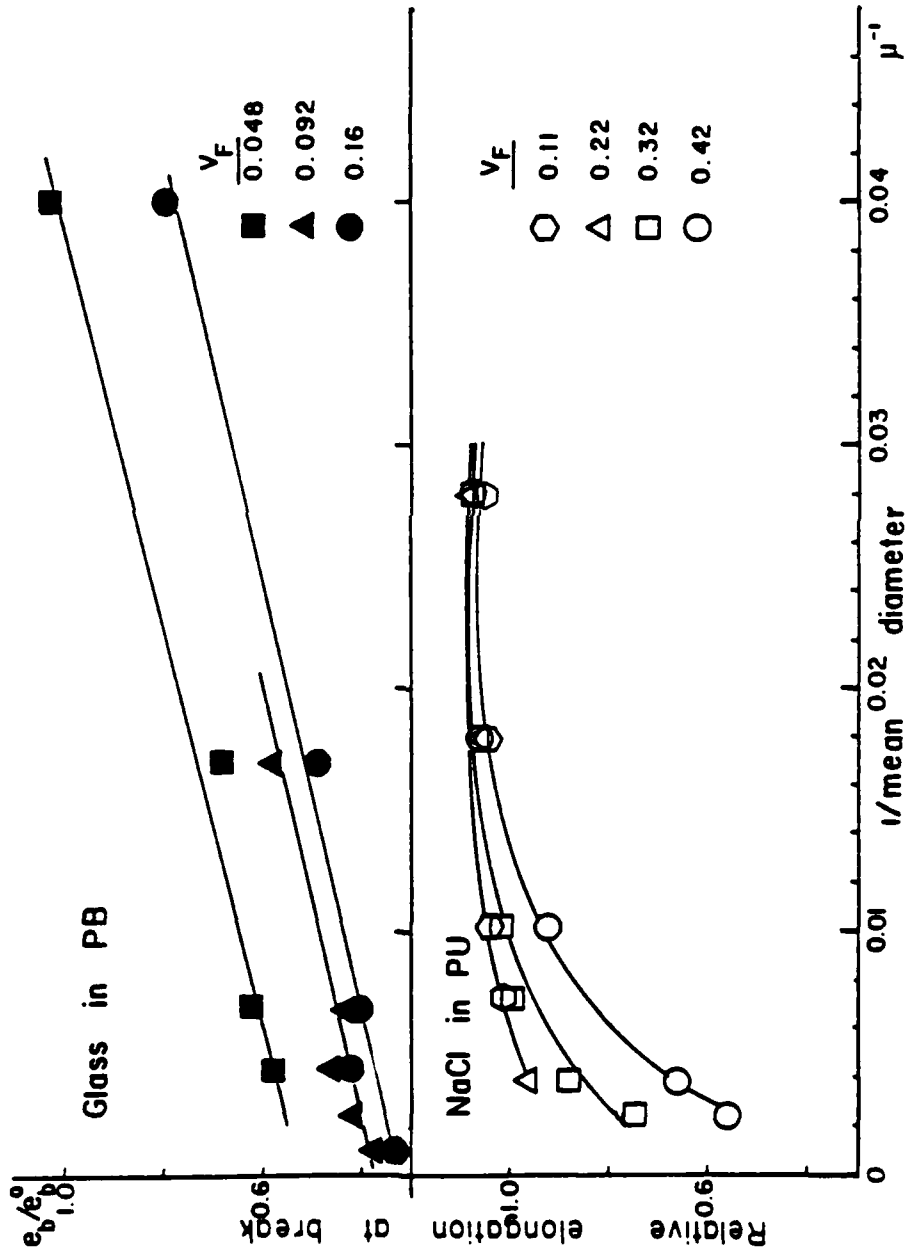
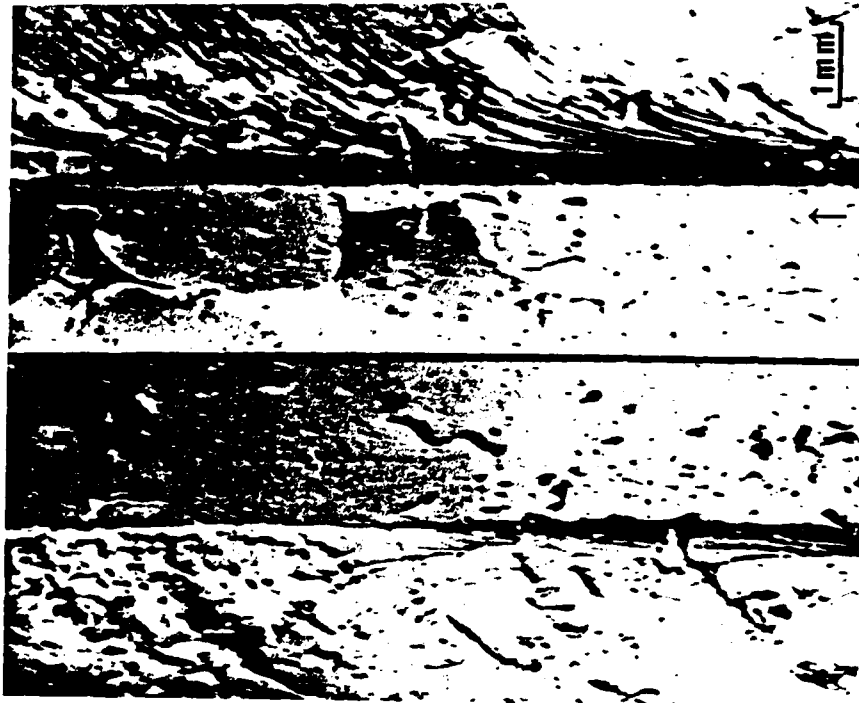
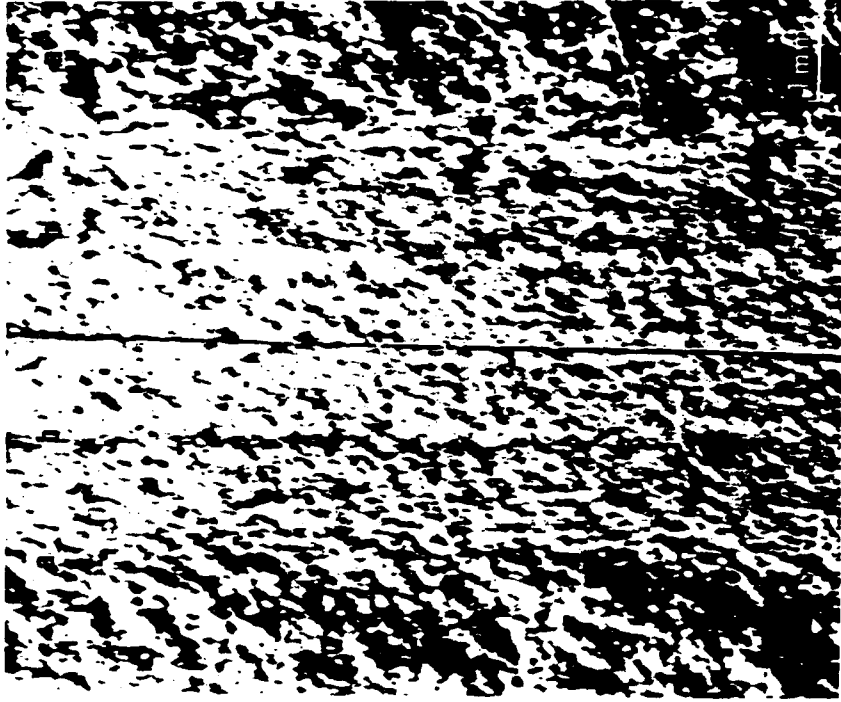


Figure 2. Relative elongation at break as a function of reciprocal of mean diameter of particles of glass in polybutadiene (PB) and salt in polyurethane (NaCl in PU) (7).

3A



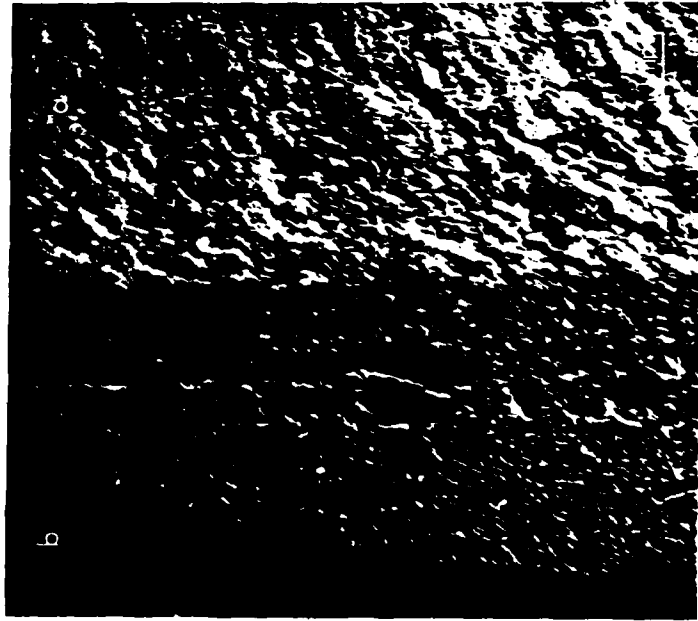
3B



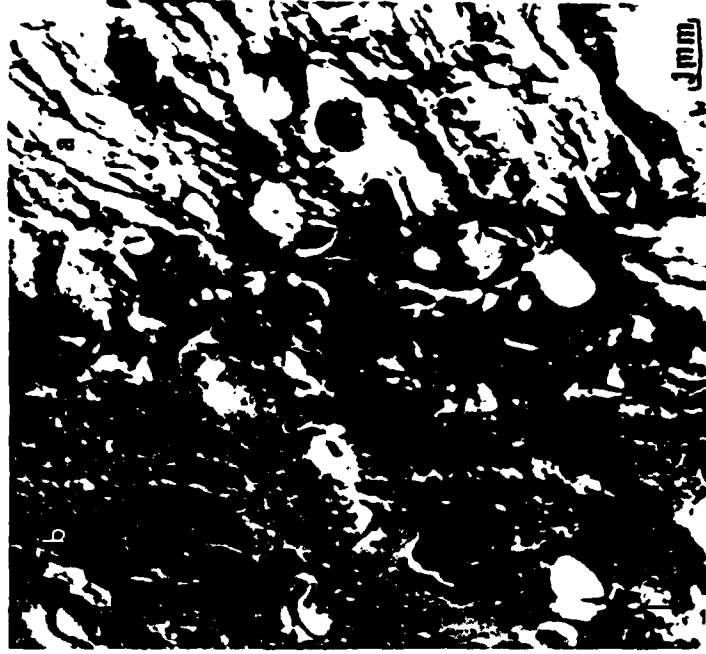
4 mm sample of unfilled polybutadiene, 13X. 4 mm sample containing 50 phr 25  $\mu$ m beads, 13X.

Figure 3. Tear surfaces of glass filled polybutadienes covered with sublimed ammonium chloride. a and b indicate the torn and cut surfaces, respectively. The arrows show the tear direction.

3C



3D



9 mm sample containing 50 phr 25 m beads, 10X. 9 mm sample containing 50 phr 1000  $\mu$ m beads, 10X.  
Figure 3. Tear surfaces of glass filled polybutadienes covered with sublimed ammonium chloride.  
a and b indicate the torn and cut surfaces, respectively. The arrows show the tear direction.

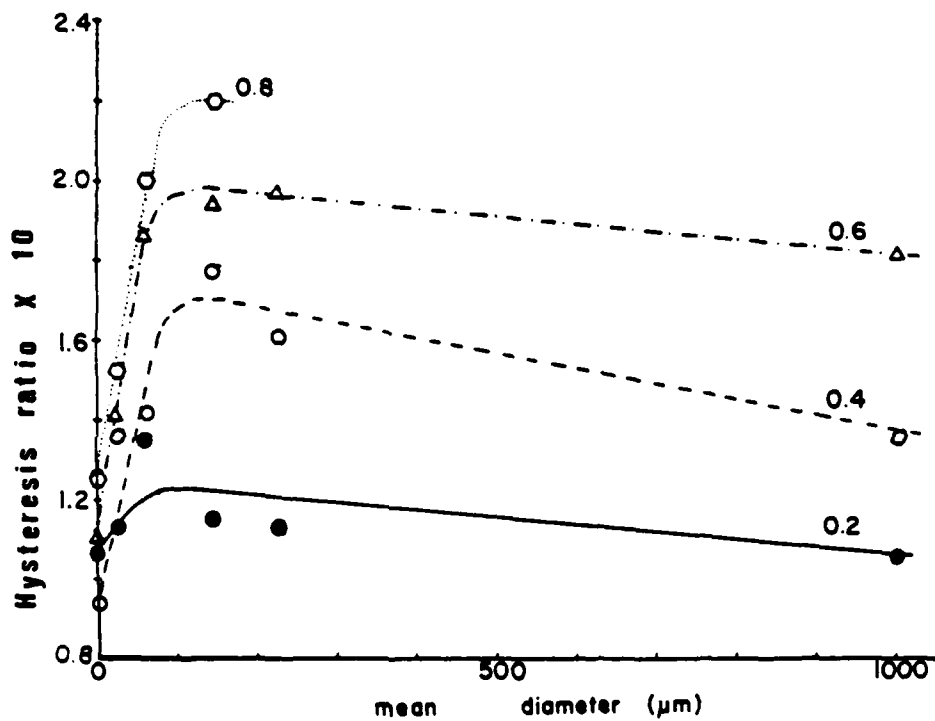


Figure 4. Hysteresis ratio versus mean diameter of glass beads. The numbers above the curves correspond to  $(l_f - l_0)/l_0$  where  $l_f$  are the lengths at highest extension and  $l_0$  are the initial lengths of the hysteresis specimens.

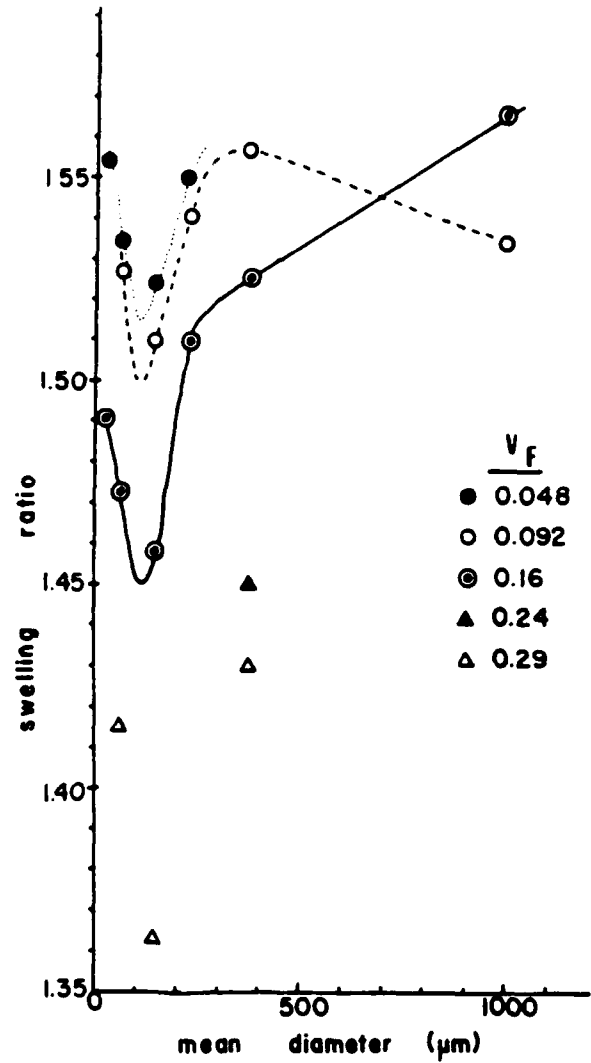


Figure 5. Swelling ratio versus mean diameter of glass beads. The numbers correspond to the volume fraction,  $v_F$ , of glass beads in the polybutadiene.

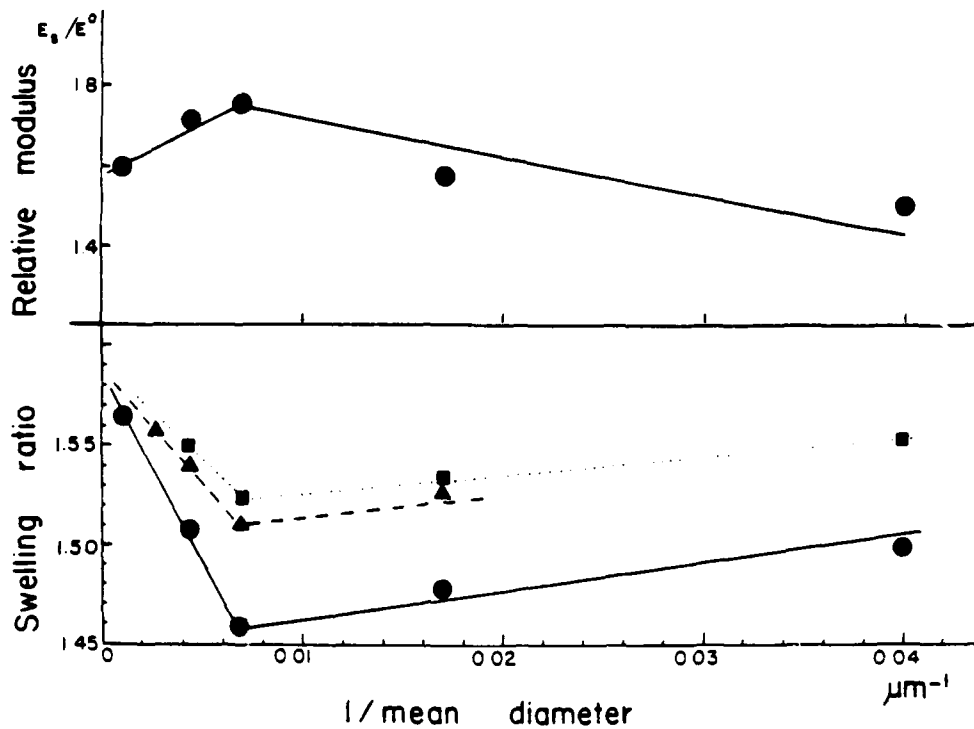


Figure 6. Relative modulus and swelling ratio as a function of reciprocal of the mean diameter of particles of glass in polybutadiene at the volume fractions  $v_F$  indicated in the figure. The symbols have the same meaning as the corresponding ones in Figures 1 and 2.

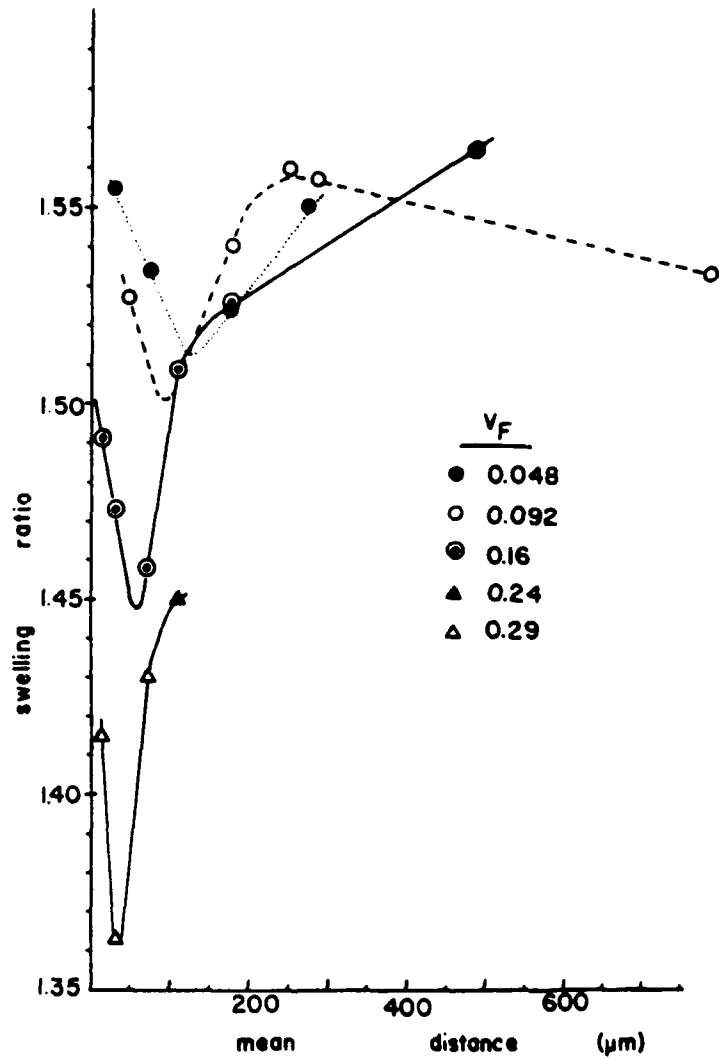


Figure 7. Swelling ratio versus mean distance between glass beads. The numbers correspond to the volume fraction,  $v_F$ , of glass beads in the polybutadiene.

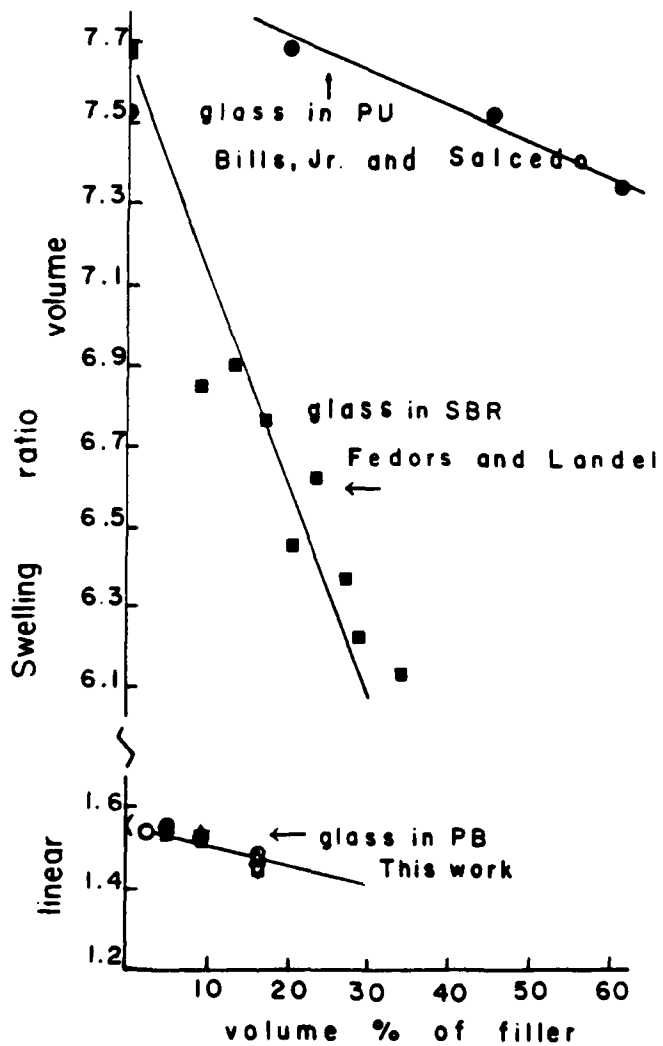


Figure 8. Comparison of swelling ratio data for polybutadiene filled with glass particles of different sizes and at different loadings with data from the literature for other systems (29,30). ● and ■ correspond to the data for glass beads in polyurethane and in SBR, respectively. ○, △, □, ▽, correspond to different loadings in polybutadiene of glass beads of 25, 60, 145 and 225 μm, respectively.

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