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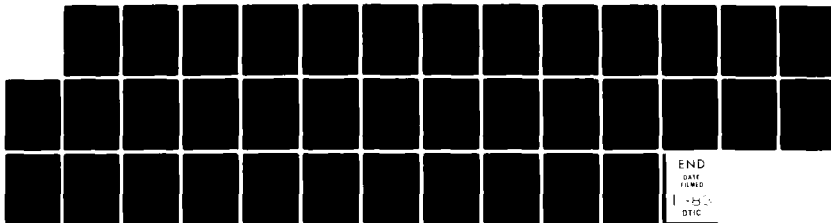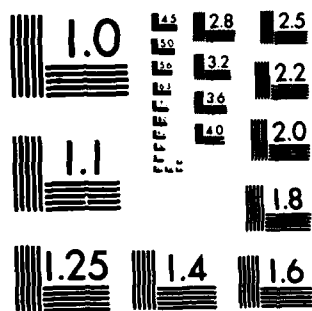
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A literature survey of the effect of the particle size of nonreinforcing fillers on the mechanical properties of elastomers and a critical evaluation of the literature results compared to new data from the authors' laboratory were made. The effect of filler content was also considered. The study demonstrated that qualitatively mechanical properties of filled elastomers in general are a complex function of the filler's particle size (surface to volume ratio) and loading (distance between particles). Quantitatively, properties were dependent on the system being studied. Relative

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modulus, relative breaking elongation, relative breaking stress and swelling ratios were functions of the reciprocal size of the filler up to a particle size of about 140 μm. With particles of larger diameter the influence on these properties was smaller. When the distance between particles is smaller than their size, interactions in the volume surrounding the particles may become the dominant variable.

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Technical Report No. 21

EFFECT OF SIZE OF NONREINFORCING FILLERS ON

MECHANICAL PROPERTIES OF ELASTOMERS

by

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INTRODUCTION

A composite propellant consists of a mixture of oxidizer and
fuel. The most widely used formulations include ammonium perchlorate
as the oxidizer and polybutadiene as the fuel. Investigations in
our laboratory are directed toward developing and understanding the
fundamental factors that control adhesion between oxidizer particles
and the fuel. When the stress is applied, poor adhesion between
these components may result in formation of voids at the filler-
matrix interface, and thus affect the uniformity of performance.

The adhesion between flat surfaces, such as coated and un-
coated plates or slides, and cured polybutadiene has been studied
as a model system for a propellant, when the emphasis of the study
was focussed on the interface alone. These studies on model
systems (Ahagon and Gent, 1975; Runge and Dreyfuss, 1979; Dreyfuss
et.al. 1981) have proven to be very helpful in elucidating the
effect of chemical bonding on adhesion.

In real systems, the oxidizer is present in the form of
particles and to gain a complete understanding studies must be
carried out with composites containing particles. The adhesion
between powdered ammonium perchlorate and polybutadiene, and ways
to improve it have been the subject of several publications, for
example, Granstein and Williams (1974), Markin and Williams (1974),
and Schwarz and Lowrey (1967). Their studies have shown that un-
modified crystalline material in these composites functions as a
nonreinforcing filler. In other studies where fundamental phenom-

ena that are not readily accessible with powdered ammonium per-
chlorate are important, glass spheres have been used as a model
for the oxidizer. In an effort to improve adhesion, surface treat-
ments have been applied to the filler. For example, in an investi-
gation of the tear strength and tensile strength of a model glass-
filled polybutadiene (Dreyfuss, et al., 1980), positive effects on
mechanical properties were observed as a result of surface treat-
ment with certain silanes. These effects correlated well with
those reported by Markin and Williams (1974) for silane treated
ammonium perchlorate particles and with predictions based on ad-
hesion studies with flat plates. The studies with glass spheres
also revealed that mechanical properties are significantly influ-
enced by the size of the particles. This paper is an updated
literature survey of the effect of nonreinforcing fillers on the
properties of composites and a comparison of the literature results
with new results from our laboratory.

Following Bueche (1962) a "reinforcing" filler is defined as
a filler which raises the modulus while still maintaining the rubber-
like qualities of the base material and which at the same time
increases the strength of low-strength rubbers. A "nonreinforcing"
filler is one which does not have these effects. For purposes of
this paper it is assumed that nonreinforcing fillers do not form
molecular bonds with the rubber even if the rubber wets the filler
surface. Accordingly, surface treated particles carrying surface

functional groups capable of bonding to the rubber are excluded from the present discussion.

RESULTS AND DISCUSSION

Mechanical properties of filled elastomers have been studied extensively as a function of the concentration of glass beads and other nonreinforcing filler particles (e.g. Bills et al. 1960; Schwarzl et al. 1965; Alter, 1965; Nielsen, 1966 and 1974; Evrard and Nottin, 1975). Properties of filled plastic materials have also been examined (e.g. Nicolais and Narkis, 1971; Migliaresi et al., 1971; Broutman and Sahu, 1971, Leidner and Woodhams, 1976). The results of the studies of plastic materials complement those with elastomers. Experimental data on the effect of particle size of "nonreinforcing" fillers on mechanical properties of com- posites are more limited (Schwarzl et al., 1965; Alter, 1965, Nielsen, 1974; Leidner and Woodhams, 1976). Depending on the system and property being studied, conclusions range from lack of effect of particle size on mechanical properties of the composite (Bills et al., 1960; Schwarzl et al., 1965), to an inverse variation of the properties with size (Alter, 1965), or its square root (Leidner and Woodhams, 1976). Most of these studies were made with par- ticles within a narrow particle size range. Eckstein and Dreyfuss (1982) expanded the size range to include particles with a mean diameter as large as 1000 µm and as small as 25 µm.

Comparison of results will be made property by property in the following.

Modulus

The increase in the Young's modulus of a composite as a function of the volume fraction of the filler, can be predicted from the Smallwood-Guth-Einstein relation (Kraus, 1965):

$$E = E_0 (1 + 2.5 \ V_F + 14.1 \ V_F{}^2) \qquad \text{(eq. 1)}$$

where E is the modulus of the filled rubber, E_0 is the modulus of the rubber matrix and V_F is the volume concentration of the filler. No dependence of the modulus on particle size is predicted. Accordingly, Schwarzl et al. (1965) found that shear moduli of NaCl filled polyurethane rubber in the glassy and rubbery states were independent of filler size. In contrast, shear moduli increased considerably with filler content. Evrard and Nottin (1975) observed that at low deformations the reinforcing properties of spherical particles in an elastomeric matrix were not related to particle size.

The values of Young's modulus reported by Eckstein and Dreyfuss (1982) for filled polybutadiene were in the same range as the theoretical one calculated from equation 1. However, contrary to theoretical predictions and the experimental observations cited above they found a small but systematic variation with particle size. This observation is in agreement with Alter's who noted a linear dependence of relative modulus on reciprocal particle size for fillers less than 0.2 μm in radius. More will be said about this below when the moduli are compared to swelling ratios on the same samples.

Swelling ratios

Swelling is equivalent in many respects to a three dimensional stretching of the elastomer. Although several theoretical treatments are available (Bills and Salcedo, 1961; Kraus, 1963; Fedors and Landel, 1966), the significance of swelling measurements of composites is not fully understood.

Kraus (1963) developed a theory for the swelling of filler-reinforced vulcanizates. His theory assumes that swelling of a crosslinked elastomer is restricted at the filler-rubber interface due to adhesion between the filler and the rubber. This theory predicts that the swelling ratio decreases with increased loading according to the following relation:

$$v_{ro}/v_r = 1 - [3c(1 - v_{ro}^{1\,3}) + v_{ro} - 1]V_F/(1 - V_F) \qquad (eq.\ 2)$$

where v_r is the volume fraction of rubber in the swollen rubber phase, v_{ro} is the same quantity referred to an otherwise analogous, unfilled vulcanizate, V_F is the volume fraction of the filler, and c is a parameter depending on the filler, but independent of V_F and v_{ro}. According to Kraus c is a measure of the ability of the filler to restrict swelling of the binder. If c = 0, there is no adhesion between the filler and the binder and then, the filler does not restrict swelling. According to Kraus the volume swelling Q is then given by:

$$Q = v_r^{-1} = (q_o^3 - V_F)/(1 - V_F) = (v_{ro}^{-1} - V_F)/(1 - V_F) \qquad (eq.\ 3)$$

where q_0 is the linear swelling coefficient of the rubber, v_r is the apparent volume fraction of rubber in the swollen gel and v_{ro} is its true value, equal to the inverse swelling ratio of the analogous gum vulcanizate. Kraus reported that the theory was obeyed for a large amount of experimental data on carbon blacks, in four different rubbers, with several vulcanizing systems, in five solvents and over a wide range of crosslinking. For these systems the average value of c was 1.17. In the few cases where the theory was not obeyed, Kraus concluded that the adhesion between the filler and the binder was poor and observed values of c well below 1.

Dick, et al. (1975) determined swelling ratios as a function of filler content for urethane rubbers containing 50-80 weight % NH_4ClO_4. In some cases the filler was treated with agents that varied the degree of adhesion between the filler and the matrix. They found that the swelling behavior followed the relation derived by Kraus. They further demonstrated that as shown in Figure 1, the nature of the variation of the swelling ratio with loading changed with the degree of adhesion between the filler and the matrix. A solvent dependence was also found.

Fedors and Landel (1966) found that the swelling ratio of a composite from glass beads and styrene butadiene rubber (SBR) decreased slowly as loading of the glass beads was increased. They supposed that since the SBR is essentially nonpolar in nature, the glass beads did not interact strongly with the SBR binder, i.e. that c = 0 in Kraus' equation. In order to explain the above decrease, they concluded tentatively that the decrease was the result of particle agglomeration or clustering. To fit Kraus' theory a value of c = 0.33 was required.

Bills and Salcedo (1961) concluded that the swelling ratio is the same with and without filler and does not vary with loading. Their treatment was based on two assumptions; namely, (1) the adhesion between filler and binder was poor so that the binder-filler bond releases on swelling and (2) the swelling of the binder,

with and without filler, is the same. They prepared samples in which concentration of glass filler in a polyurethane binder was controlled by casting into tube containers and allowing the filler to settle before curing. Their data seemed to justify their assumptions. More recently Eckstein and Dreyfuss (1982) have noted that their data can equally well be interpreted as showing a slow decrease of swelling ratio with increasing loading. Unfortunately, Bills and Salcedo (1961) based their conclusion primarily on pairs of data where one member of the pair was the "unfilled" polyurethane and the other was filled. For most of these pairs the swelling ratio for the filled sample was lower. The "unfilled" polyurethane was taken from the top part of their tube. The one set of data that has four data points shows the slow decrease noted above if the "unfilled" value is ignored. (See Eckstein and Dreyfuss, 1982).

Eckstein and Dreyfuss (1982) determined swelling ratios of polybutadiene filled with glass beads of different sizes and at different loadings. Their swelling ratios decreased slowly as the loading was increased for every particle size examined. They analyzed their results in terms of the resulting distance between neighboring particles. This distance is given by (Rehner, 1965):

$$D = d_f[(\pi/6v_f)^{1/3} - 1] \qquad \text{(eq. 4)}$$

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 glass sphere diameter. Eckstein and Dreyfuss noted that the swelling ratios initially decreased with particle size, had a minimum value for samples containing spheres of about 100 μm in diameter and then increased again. Plots of swelling ratio as a function of particle separation distance showed a systematic shift of the minimum for the curves with increasing loading of the filler; the lower the loading, the greater the distance at which the minimum occurred. Thus it appears that clustering as proposed by Landel and Fedors cannot explain the decrease of swelling ratio observed with increasing loading. It has previously been noted that the adhesion between polybutadiene and glass is unexpectedly high (Dreyfuss, et al., 1980; Runge and Dreyfuss, 1979; Wong, 1979). Since SBR also contains polymerized butadiene units, the same is probably true for SBR. Thus it seems that these data are consistent with those of Dick, et al. and in agreement with the theory of Kraus. A value c = 0 is probably not a valid assumption for describing the interaction between glass and SBR.

Eckstein and Dreyfuss (1982) also observed that the swelling ratio of glass-filled polybutadiene showed a complex dependence on particle size at constant loading. The dependence was similar to that already described for swelling ratio on interparticle distance. Alter (1965) has suggested analyzing data based on particle size in terms of the surface to volume ratio of the particle. This reduces

to an analysis in terms of the reciprocal of the diameter of the particle. When the data are plotted in this way as shown in Figure 2 and compared with corresponding modulus data plotted in the same way and also shown in Figure 2, the dependence on particle size becomes clearer. The swelling ratio curve shows an inverse relationship to the other curve at all loadings. The fact that there is an inflection in the curves for both modulus and swelling ratio for particles about 143 µm in diameter suggests that different factors are influencing properties above and below this size of filler. For example, above 143 µm it is possible that the effect of surface attachments becomes more pronounced as the particles get smaller and for any given loading the surface area increases. Below 143 µm the increasing effect of surface attachments as particles get smaller might be overshadowed by interactions in volume elements surrounding the particles. (See Figure 3) Such interactions would be more pronounced at the short distances between particles arising either from high loadings or from the smallest particles at constant loading. Alternatively, particle sizes below 143 µm may be in the range of inherent flaw sizes for the system, so that the size effect disappears. Flaw size effects will be explored further below.

In view of the foregoing discussion about all the factors that can influence the swelling behavior of composites, it is clear that equilibrium swelling measurements are sufficiently ambiguous to preclude calculation of reliable values of crosslink density.

Fracture energy

The tear quality of a rubber can be expressed by a characteristic energy which is related to the energy stored in a highly strained zone at the tip of a growing tear: as the tip grows, most of the energy is dissipated irreversibly as heat. This tearing energy varies with the nature of the rubber and of the filler. Dreyfuss, Gent, and Williams (1980) noted that the intrinsic tear strength of glass-bead-filled matrices with particles of 150 μm or less was not much different from that of the unfilled matrix. They attributed the slight enhancement observed with filled samples to a deviation of the tear path from a straight line caused by the presence of glass beads in the material. Such a deviation should result in a rougher tear path and a correspondingly higher tear strength. The enhancement of tear strength in the presence of such small particles might also result from increasing importance of a surface energy term as expressed by the relationship (Lange, 1970):

$$\gamma = \gamma_o + L/D \qquad \text{(eq. 5)}$$

where γ denotes the fracture surface energy of the composite, γ_o the fracture surface energy of unfilled matrix, L the line tension of the crack front and D the distance between the particles. At a given volume fraction of the filler, the interparticle distance becomes smaller as the size of the glass beads decreases (see Table I). It follows, thus, from equation 5 that highest fracture surface energy should be obtained with the finest particles. Broutman and Sahu (1971) attributed the enhancement of

fracture energy with increasing glass beads volume content in epoxy and polyester resins to a similar effect. Also, a study by Mullins(1963)indicated the importance of fine-particle fillers for high fracture energy.

In a study with glass beads with diameters ranging from 25 to 1000 μm Eckstein and Dreyfuss (1982) observed that the mode of fracture was a function of the particle size of the filler. With the largest particles the tear path often travelled from bead to bead. For small particles the data were in agreement with the above and clearly demonstrated that the smallest particles were the most effective in increasing tear strength of the composites. The tear strength of compounds containing the smallest particles (25 μm) increased by about 50% compared to that of unfilled poly-butadiene, while that of the composites containing larger glass beads increased by only 25%.

In presence of larger inclusions, the smaller increase in fracture energy resulted from the irregularity of the tear path and increase in the effective diamter, C, of the tip of the tear. The effective diameter, C, is defined by (Dreyfuss, Gent, and Williams, 1980):

$$C = T/2kU_b \qquad\qquad (eq.\ 6)$$

where T is the tear energy, U_b the strain energy per unit volume and k is a numerical quantity, to which a value of 2 was assigned for moderate deformations. The stored strain energy, U_b, can be calculated from the area under the stress-strain curve. The calculated values of the effective diameter, C, of the edge flaw from which fracture initiates, taken from the data of Eckstein

and Dreyfuss (1982), are given in the last column of Table I.
When the particle diameter is in the range of 14-35 μm, the
apparent size of the flaw is the same as that of the unfilled
material. In the range of sizes between 60 and 225 μm, the
effective size of the flaw seems to be of the same order of
magnitude as the diameter of the largest particles present.
With the largest beads, the calculated flaw size (528 μm) is
much smaller than the largest particle present (1411 μm). In-
stead, it correlates rather well with the mean distance between
particles (484 μm) shown in the table. 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
observed deviation of the crack front around the largest spheres
(∼1000 μm) which travels from one bead to another in a straight
line supports such a possibility.

Mechanical hysteresis ratio, H

Andrews (1961 and 1963) has pointed out that the greater
the hysteresis, the smaller the value of stress concentration
at the tip of the tear. Hysteresis arises also from possible
slippage between the rubber and the filler surfaces. Gent (1980)
predicted that the mechanical hysteresis ratio, H, given by

$$H = 3V_F/\pi \qquad \text{(eq. 7)}$$

and caused by debonding of the rubber from a spherical inclusion,
should be independent of particle size and proportional to the
volume fraction, V_F, of the particles in the composite.

Eckstein and Dreyfuss (1982) found that the hysteresis ratio does depend on particle size. The H value increased with particle size up to about 100 μm and then decreased slightly with further increase in the filler size. In each case the maximum amount of energy dissipated was lower than the theoretically predicted value from equation 7. As in the case of swelling ratios, this can be attributed to interactions of strain fields around each particle, which becomes more significant when the separation distance between particles is smaller than their diameter. As predicted by Gent's (1980) theory, the low hysteresis ratio obtained in compounds consisting of glass spheres smaller than 100 μm might be caused by rupture of the matrix near the inclusion instead of detachment of the matrix from the inclusion. The slight decrease in hysteresis ratio with particles larger than 250 μm might be caused by the presence of two competing modes of failure: dewetting and matrix rupture. Micrographs of torn surfaces in compounds containing 1000 μm spheres are consistent with these mechanisms.

Stress and strain at break

Tensile strength and elongation are the most widely studied properties of filled composites (e.g. Bills et al., 1960; Schwarzl et al. 1965; Nielsen, 1974; Smith, 1959; Nicolais and Narkis, 1971). According to the reports, rigid fillers cause a comparatively small decrease in tensile strength and a dramatic decrease in elongation at break.

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 (1967) and others (Cohan, 1950,; Cohan, 1947; Payne, 1966, Gehman, 1965) found little effect of particle size on breaking stress. Alter (1965) has reviewed much of the data. He states that up to particle radii of 0.2 μm, relative stress and elongation at break are functions of the reciprocal of the filler particle size. According to Alter (1965) 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 et al. (1965), 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. The results of Eckstein and Dreyfuss (1982) and the data of Schwarzl et al. (1965) are compared in Figures 4 and 5, where following Alter, relative stress at break, $\sigma_b/\sigma_b{}^\circ$ and relative elongation at break, $e_b/e_b{}^\circ$ are plotted versus reciprocal particle size. Here $e_b{}^\circ$ and σ° refer to the unfilled elastomer and e_b and σ_b refer to the filled elastomer.

The data in Figures 4 and 5 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 has been expended compared to that for the polyurethane data. Then it is apparent that in contrast to the

polyurethane data where the loading lines are 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 μm and 70 μm for the polybutadiene and polyurethane systems, respectively. One possible explanation of the significance of these values can be given in terms of flaw sizes, as discussed in the section on tear strength. The inflection in the relative mechanical property curves (Figures 2 and 4) may be related to inherent flaws in the rubbery matrix. If so, as shown in Figure 5, the inherent flaw size varies with the system.

The shape of the relative breaking elongation versus particle size curves are quite different from corresponding ones for the 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.

In 1976 Leidner and Woodhams developed a theoretical relationship which relates the strength at break of a composite containing spherical fillers to the size, volume fraction and interfacial adhesion between the filler and the matrix. They showed that the relative strength of a composite filled with a spherical filler is inversely proportional to the square root of the sphere diameter. Efforts to fit the data of Eckstein and Dreyfuss (1982) to this theory have been unsuccessful.

Evrard and Nottin's (1975) study on reinforcement of butadiene-styrene rubber by spherical particles (30, 75, 150μ in diameter) indicated that at high deformations the reinforcing potential increased as the particle size of the filler decreased, and as the adhesion to the matrix increased.

Nielsen (1966) suggested the following equation relating relative elongation at break and filler concentration in the case of perfect adhesion between polymer and filler particles:

$$e_b/e_b{}^\circ = 1 - V_F{}^{1/3} \qquad\qquad (eq.\ 8)$$

Since Dreyfuss et al. (1980), Runge and Dreyfuss (1979), Wong (1979) and Eckstein and Dreyfuss (1982) had observed unexpectedly large adhesion of polybutadiene to glass, and as discussed above, the swelling ratio data was also consistent with significant adhesion between the glass bead filler and polybutadiene, an attempt was made to plot the results of Eckstein and Dreyfuss (1982) according to this equation. In Figure 6 the volume fraction of glass in the elastomer is plotted as a function of the relative strain for three different sizes of the filler: 60, 145 and 225 μm in diameter. The compounds consisting of small beads (60 μm) showed higher relative strain, while the larger beads produced similar but lower relative strain values than those predicted from equation 8. With a decrease of the glass volume fraction, the relative strain converged.

Since the right-hand side of equation 8 has a fixed value which depends upon the amount of filler present in the composite, a deviation, positive or negative, of the quantity on the left-hand side from the fixed value, would imply   good or bad

adhesion, respectively. The plot of the amount of deviation, δ, of the measured relative elongation at break from the theoretical value (namely, $\delta = e_b/e_b{}^\circ - (1 - V_F{}^{1/3})$) as a function of particle size showed an inflection in the curve, occurring at a filler diameter of about 80 μm. The position of the inflection was independent of the volume fraction of the filler. A plot of the same deviation as a function of the reciprocal of particle size showed a linear dependence as the particle size increased. The deviation, and therefore the adhesion strength, decreased (see Figure 7).

SUMMARY AND CONCLUSIONS

Mechanical properties of filled elastomers are a complex function of loading (separation distance), particle size (surface/volume) and the system being studied. It has been shown that relative modulus, relative breaking elongation and stress, and swelling ratio are functions of the reciprocal size of the filler up to particle size of about 140 μm. With filler particles of larger diameter the influence on those properties is smaller. When the distance between particles is smaller than their size, the interactions in the volume surrounding the particles may become the dominant variable.

It is noteworthy that a similar complex dependence of mechanical properties on particle has been reported for alloys strengthened by dispersion of hard particles (Preston and Grant, 1961).

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TABLE I

Interparticle Separation Distance and Edge Flaw
as a Function of Particle Size[a]

Measured diameter (μm)	Mean diameter (μm)	Mean Separation distance (μm)	Edge flaw,C (μm)
No glass added	-	-	123
14-35	25	12	153
30-90	60	29	278
80-220	145	70	330
90-355	225	109	364
855-1411	1000	484	528

a) Volume fraction of glass, V_F = 0.16
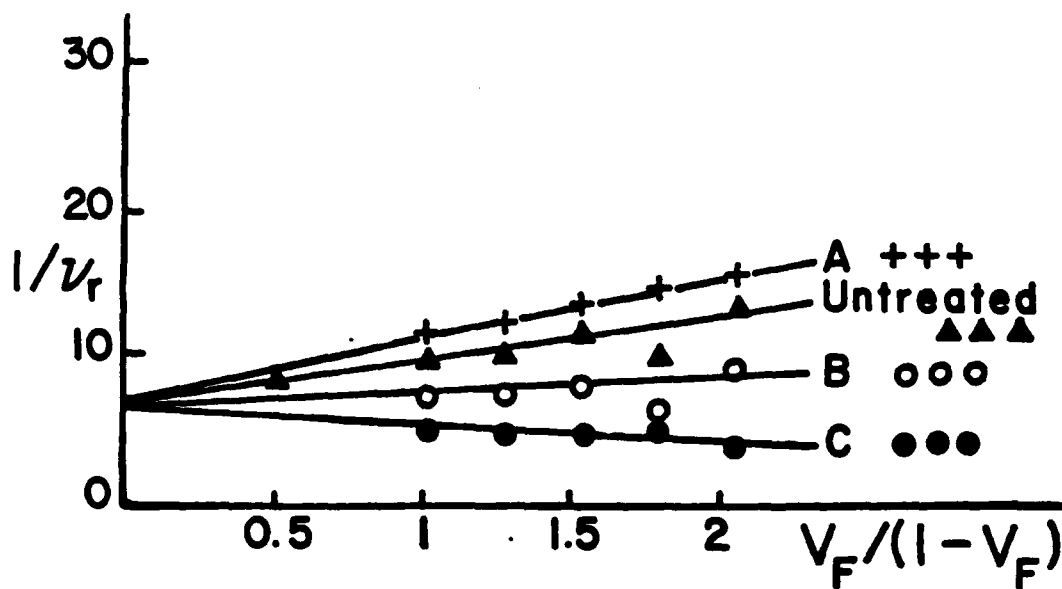
Figure 1. Variation of the swelling ratio in benzene of urethane rubbers filled with NH_4ClO_4 as a function of filler content. A, B and C are treated fillers in which the adhesion between the filler and the matrix varies in the order A < B < C. Dick, et al. (1975).
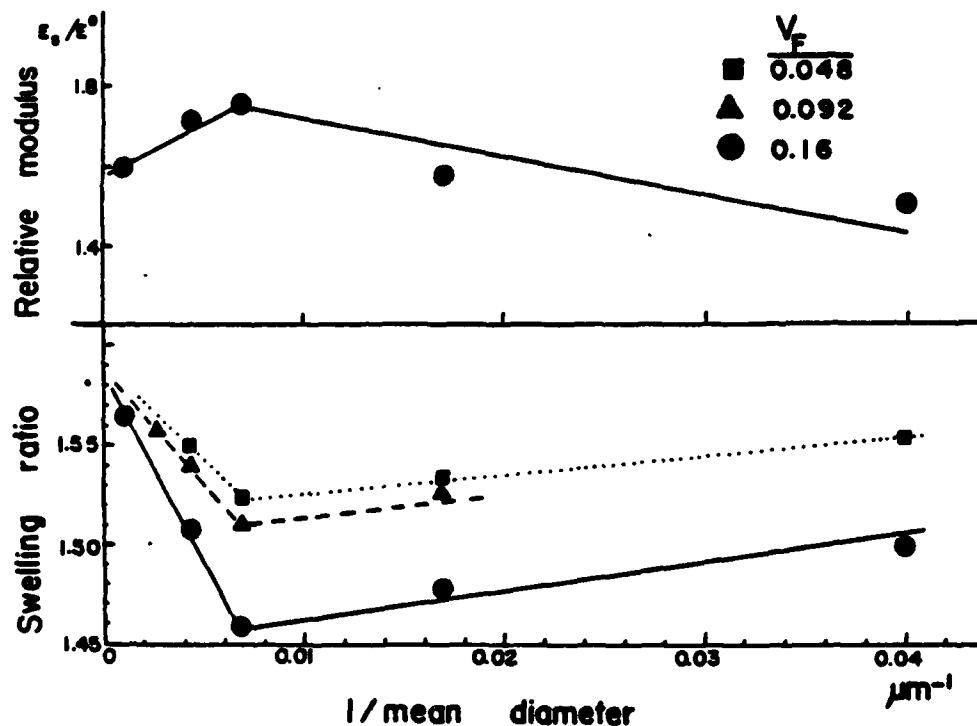
Figure 2. Relative modulus and swelling ratio as a function of
reciprocal of the mean diameter of the glass particles
in polybutadiene at the volume fraction V_F indicated
in the figure. E and E_o are moduli of the filled and
unfilled rubber, respectively. (The data could equally
well be represented by smooth curves) Eckstein and
Dreyfuss (1982).
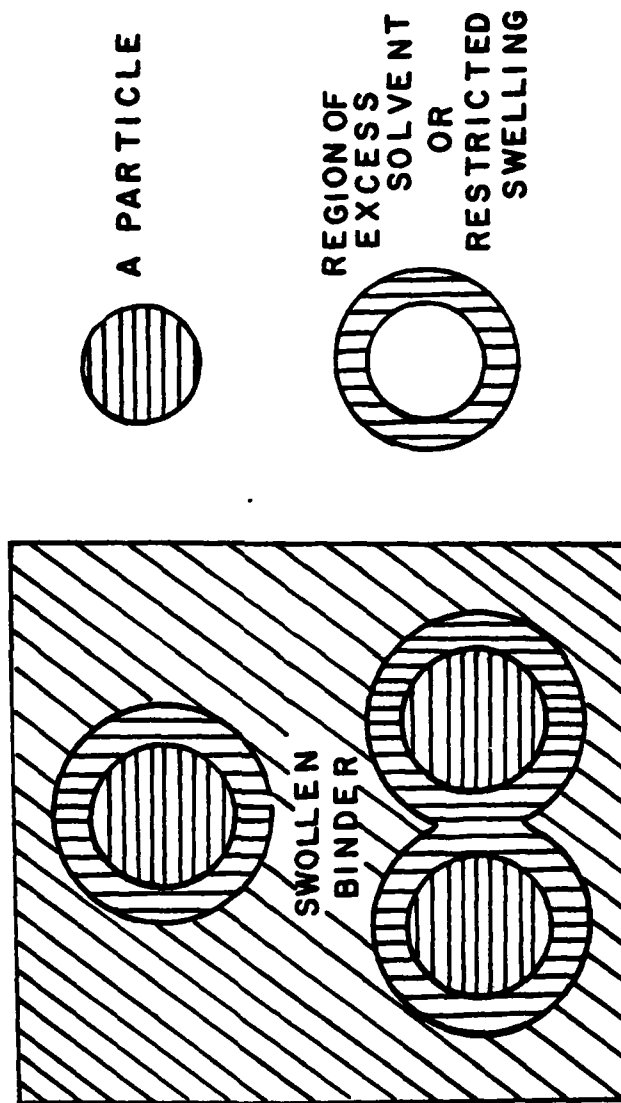
Figure 3. Schematic representation of a swollen composite showing an isolated particle with no interaction of the surrounding volume elements and two particles in close enough proximity, so that interactions can occur in the overlapping volume elements.
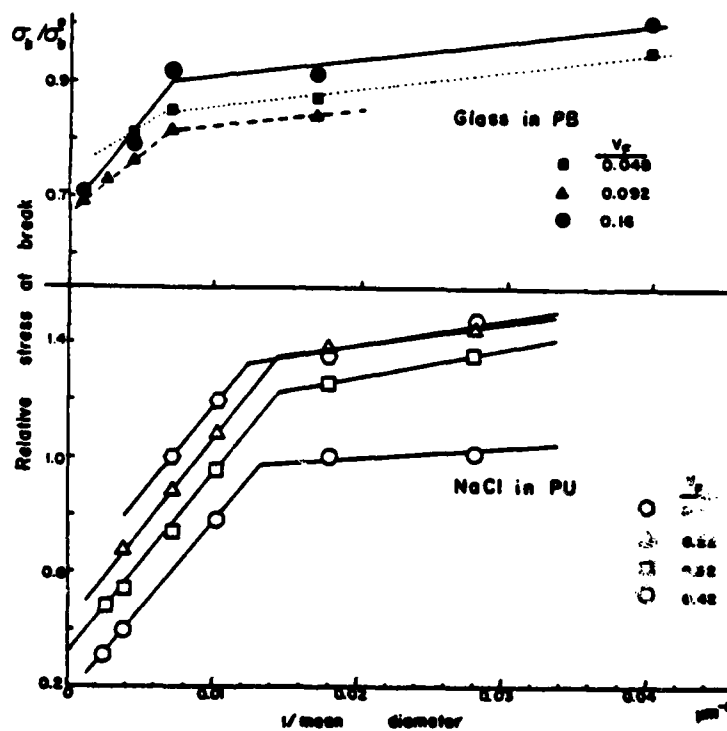
Figure 4. Relative stress at break as a function of mean diameter of glass beads in polybutadiene (PB) and of salt particles in polyurethane (NaCl in PU). σ_b and σ_b^o are the tensile strength at break of the filled and unfilled systems. Eckstein and Dreyfuss (1982).
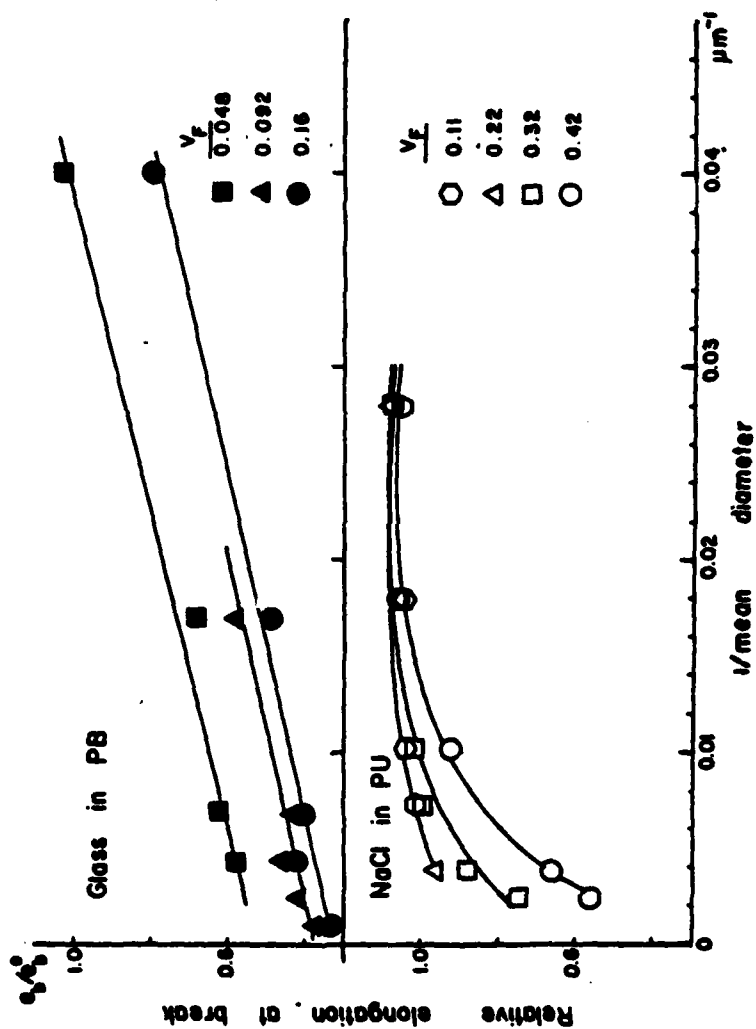
Figure 5. Relative elongation at break as a function of mean diameter of glass beads in polybutadiene (PB) and of salt particles in polyurethane (NaCl in PU). e_b and e_b° are the elongations at break of the filled and unfilled systems. Eckstein and Dreyfuss (1982).
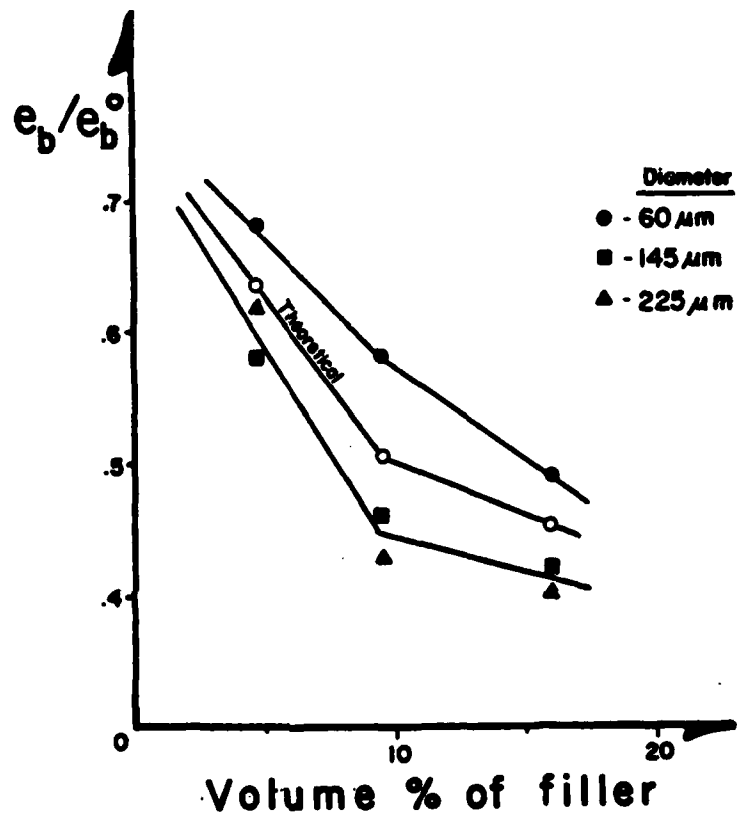
Figure 6. Theoretical and experimental curves for the elongation
at break as a function of volume fraction of glass beads
in polybutadiene, for the cases of spheres of 60, 145
and 225 μm in diameter.
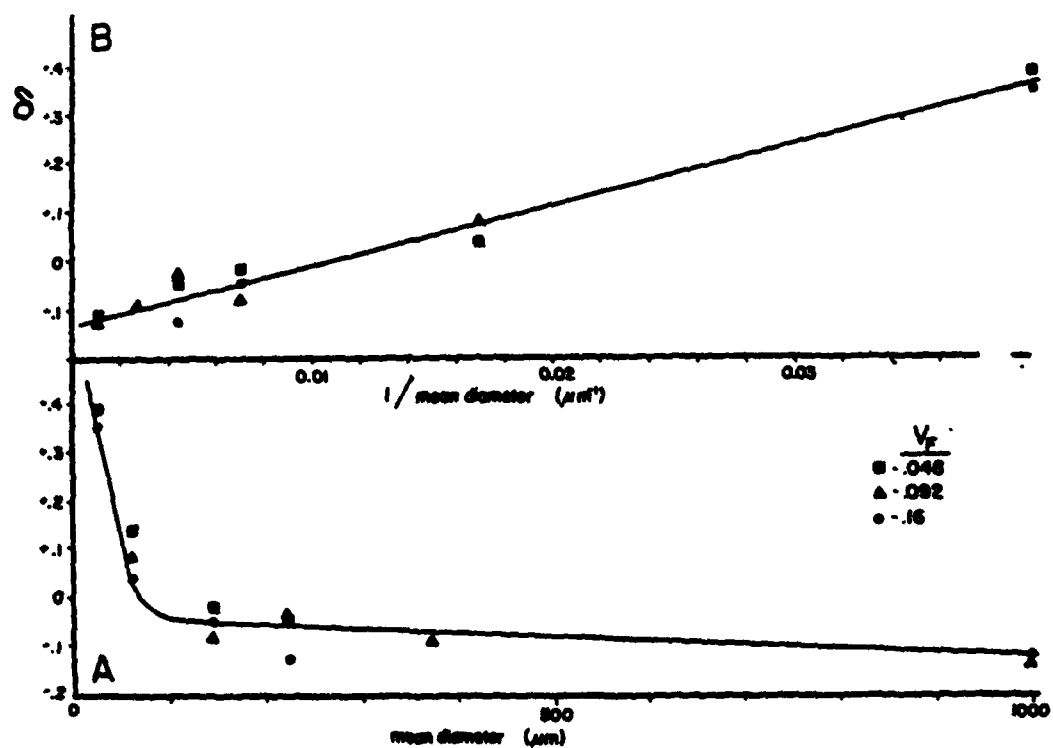
Figure 7. Plot of the amount of deviation δ, of the measured value $(e_b/e_b^\circ)_{meas}$ from the theoretical $(e_b/e_b)_{theor} = 1 - V_F^{1/3}$, so that $\delta = (e_b/e_b^\circ)_{meas} - (e_b/e_b^\circ)_{theor}$, as a function of A) particle size, B) reciprocal of particle size.

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