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OFFICE OF NAVAL RESEARCH Contract N00014-76-C-0408 Project NR 092-555

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Technical Report No. 7

TEAR STRENGTH AND TENSILE STRENGTH OF MODEL FILLED ELASTOMERS

by

P. Dreyfuss, A. N. Gent and J. R. Williams Institute of Polymer Science The University of Akron Akron, Ohio 44325

April 1980

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Tear Strength and Tensile Strength

of Model Filled Elastomers

P. Dreyfuss, A. N. Gent and J. R. Williams Institute of Polymer Science The University of Akron Akron, Ohio 44325

Summary

¹Measurements have been made of the tear strength, tensile strength, and energy dissipated during stretching for model filled elastomers consisting of polybutadiene with glass beads incorporated. The glass beads were pretreated with various silanes. some of which could, in principle, form covalent bonds with the polybutadiene matrix during free-radical crosslinking of the latter and some of which could not. The tear strength of the elastomer was increased by the addition of glass beads, by about 25 per cent for the largest beads, having a mean diameter of 150 µm. This effect is attributed to increased roughness of the tear path. The breaking elongation in tension was reduced by the addition of glass beads but the breaking stress was only seriously reduced for the least-well-adhering beads. The stored strain energy density at break was reduced in all cases. This is attributed to large glass beads acting as fracture nuclei in tension. Calculated sizes of a Griffith crack, 150-300 µm, are consistent with this hypothesis. Strain energy dissipated due to dewetting

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was found to be in the range 4-13 per cent of the input energy, depending upon the degree of interfacial adhesion, in addition to about 10 per cent dissipated in the unfilled material. The maximum value observed is in reasonable agreement with theoretical predictions.

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1. Introduction

There have been a number of studies of the mechanical properties of elastomers filled with solid particles, for example, glass beads, as models of rocket propellants and conventional carbon-black-filled materials (1-4). Some of these studies dealt mainly with the stiffening effect of incorporating solid particles and some were concerned also with changes in tensile breaking stress and extensibility on adding them to rubber. However, no study has yet been carried out of the tear strength, as far as the present authors are aware. Yet the resistance to a propagating tear, measured by the fracture energy T required per unit area Of the tear plane, is in many ways a more fundamental measure of the strength of a material than, say, the breaking stress $\sigma_{\rm b}$ or elongation $e_{\rm b}$ at break, for a strip in tension. This contention is based on Griffith's concept of tensile rupture as the catastrophic growth by tearing of a chance edge nick or flaw (5). If the material is linearly elastic up to the point of rupture, with Young's modulus denoted by \underline{E} , then the breaking stress and elongation at break can be expressed directly in terms of the fracture energy or tear strength \underline{T} and the depth <u>c</u> of an edge nick (5):

$$\sigma_{\rm b}^{2} = T E / \pi c, \qquad (1)$$

and

$$\mathbf{e}_{\mathbf{h}}^{2} = \mathbf{T} / \pi \mathbf{c} \mathbf{E}. \tag{2}$$

Even if the material follows a non-linear relationship between tensile stress and elongation, a corresponding relation can be derived for the elastic strain-energy density $\frac{U_{b}}{b}$ at break (6):

$$U_{\rm h} = T / 2 \, {\rm kc},$$
 (3)

where <u>k</u> is a numerical quantity, decreasing from <u>m</u> at small breaking elongations to a value of the order of unity at large breaking elongations (7). Equations (1) and (2) are then obtained as special cases of equation (3) when e_b is small.

Considerable evidence has accumulated showing that elastic materials do, indeed, undergo tensile failure by tearing apart at a stress-raising flaw, and that equations (1-3) successfully predict the tensile properties in terms of the depth \underline{c} of a flaw, the elastic modulus \underline{E} , and the tear strength, or fracture energy, \underline{T} (6,8). Moreover, \underline{T} can be measured independently in a number of ways. One convenient method is by means of the cleavage test shown in Figure 1. The tear strength \underline{T} is given in this case by (6):

$$\mathbf{T} = 2 \mathbf{F} / \mathbf{t}, \tag{4}$$

where <u>F</u> is the tear force and <u>t</u> is the width of the tear path, often about 50 per cent greater than the specimen thickness because the tear plane is not accurately perpendicular to the two surfaces of the specimen but lies at an angle of about 45° to them under the shearing action of the tear force F (9).

Simple elastomers filled with glass beads or other model fillers have been shown to be stiffer, and sometimes stronger. than the corresponding unfilled material (1-4). Large changes in stiffness have been associated with "dewetting", when the elastomer detaches from the glass beads at high strains to form vacuoles. When dewetting is pronounced, then the presence of the glass beads is stated to have no effect on the tensile properties (4). In order to study the process of fracture in glass-filled elastomers in more detail, it thus seems advisable to control the tendency of the elastomer to dewet from the glass. Glass beads have therefore been obtained with a variety of surface pretreatments. In some instances; for example, when the glass had been treated with vinyltriethoxysilane; chemical bonding to the elastomeric matrix would be expected to occur during the free-radical crosslinking of the diene elastomer itself after the glass filler had been incorporated (10,11). In other instances;

for example, when the glass had been pretreated with dimethyldiethoxysilane or had received no pretreatment at all; then no interfacial chemical bonding between the elastomeric matrix and the glass filler particles would be expected to occur when the elastomer was later crosslinked.

Model filled compounds were prepared using these treated and untreated glass beads, by mixing them into polybutadiene, together with a free-radical crosslinking agent, dicumyl peroxide. These mixes were then pressed into sheets and the elastomeric matrix crosslinked by heating. Both tensile fracture experiments and measurements of tear strength have been carried out on the resulting materials. The results are presented below.

2. Experimental details

Soda-lime glass beads were obtained from two sources: Potters Industries, Inc. (U.S. Sieve No. 140-270, density 2.48, refractive index 1.51) and Petrarch Systems, Inc. (70-140 mesh, same density and refractive index). Treated glass beads were obtained solely from Petrarch and had the same size as untreated glass from the same source.

By inspection, all of the glass beads had a wide range of sizes. Those from Potters Industries ranged from 30-95 μm

in diameter, and those from Petrarch Systems ranged from $80-220 \ \mu m$ in diameter. They also contained a small proportion of markedly non-spherical particles, some irregularly rounded like beach pebbles and some sharply pointed. The beads were added to polybutadiene (Diene 35 NFA, Firestone Tire and Rubber Company) at a concentration of 50 parts by weight per 100 parts of elastomer, corresponding to a volume fraction of about 16 per cent in the final product. This elastomer was chosen because it is a simple non-polar polymer, transparent and non-crystallizing. Dicumyl peroxide (Dicup R, Hercules Inc.) was added at a concentration of 0.05 parts by weight per hundred parts of elastomer and crosslinking was effected by heating the mixture in a heated press for 2 h at 150° C. Molded test sheets were prepared in this way with a thickness between 1 and 3 mm.

Tear tests were carried out as shown in Figure 1, using strips about 2 mm thick cut from molded sheets. The strips were about 2 cm wide and 12 cm long. They were scored with a sharp knife along the center line to a depth of about one-half of the original thickness, so that only about 1 mm of thickness remained to be torn through. The rate of tear was quite low, about 40 µm/s. All experiments were carried out at room temperature, about 24°C.



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Figure 1. Method of measuring tear strength

Tensile tests were carried out using dumb-bell shaped specimens, about 3 mm thick and 6 mm wide, cut from molded sheets with a sharp die. The nominal breaking stress $\frac{\sigma_b}{b}$ was determined from the breaking force, by dividing by the unstrained cross-sectional area of the narrow central part of the tensile specimens. It is thus not the true breaking stress, which is given by $\frac{\sigma_b(1 + e_b)}{b}$. The elongation e_b at break was determined from measurements of the elongation of the narrow central region of the tensile specimens up to break. All tensile measurements were carried out at a crosshead speed of about 8 mm/s, corresponding to a rate of elongation of about 0.2 s⁻¹.

Other measurements were carried out to determine the dissipation of mechanical energy during stretching. The hysteresis ratio \underline{H} , defined as the energy dissipated relative to the energy supplied in stretching the specimen, was determined from the areas $\underline{A_1}$ and $\underline{A_2}$ under the loading and unloading force-displacement relations when specimens were stretched to various extents at a rate of elongation of about 0.01 s^{-1} and then allowed to retract at the same rate back to the unstrained state. The hysteresis H was then calculated as follows:

$$H = (A_1 - A_2) / A_1$$
 (5)

It should be noted the same testpiece was stretched repeatedly; first, to 25 per cent elongation and back to the unstrained state, then to 50 per cent elongation and back to zero, then to 75 per cent elongation and back to zero, and finally, if the test strip did not break, to 100 per cent elongation and back to zero. Because of the prior extensions, it is probable that the measured hysteresis at the larger extensions was somewhat less than it would have been for a specimen not previously stretched at all.

3. Experimental results and discussion

Tensile properties

Values of the nominal breaking stress $\frac{z_b}{b}$ and breaking elongation e_b are given in Table 1 for all of the compounds examined. In each case about eight separate measurements were made, the mean values and standard deviations being given in the table.

The tensile breaking stresses were found to be generally higher for the compounds containing untreated glass beads and for those containing beads treated with aminopropylsilane or vinylsilane. Indeed, the values obtained were comparable to those for the unfilled material. The breaking elongations $\frac{e_b}{b}$ were also similar in magnitude for these compounds, although

they were significantly lower than the values obtained for the unfilled material. These specimens also showed little visible dewetting of the glass beads before rupture. In contrast, compounds filled with glass beads treated with dimethylsilane and octadecylsilane were found to have rather lower breaking stresses and breaking elongations than the other materials and they also exhibited substantial dewetting of the filler particles before rupture.

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No chemical bonding would be expected to take place between dimethyl- and octadecyl-groups and polybutadiene during the free-radical crosslinking of the latter. Some weakening effect of adding glass beads treated with these silanes is therefore to be expected. On the other hand, previous work has indicated that chemical bonding can occur between vinyl groups on glass and polybutadiene (10,11),so that greater strength and less dewetting would be expected in this case. It is interesting to note that aminopropylsilane-treated glass and untreated glass gave similar results to the vinylsilane-treated glass. as though a significant degree of interfacial bonding had been achieved in these cases also. It has been remarked previously that polybutadiene adheres to glass to a considerable

degree(11), much more than to simple non-polar substrates. Further study of the interfacial chemistry of polybutadiene on glass and on aminopropylsilane-treated glass is clearly called for.

An alternative measure of the strength in tension is given by the strain energy density U_{b} at break. Approximate values of U_{b} were calculated from the measured breaking stress and breaking elongation, assuming that linear stress-strain relationships were followed up to break, i.e., $U_{b} = (1/2)\sigma_{b}e_{b}$. The values obtained in this way are given in the final column of Table 1. This procedure will somewhat underestimate the true value of the work expended in stretching the specimen because the stressstrain relations become markedly concave to the strain axis near rupture when the elastomer matrix dewets from the filler. However, a correction would become necessary later if the actual work expended were to be employed for U_{b} in equation (3). This is because U there denotes strain energy <u>available</u> to propagate a tear, whereas the energy lost in dewetting can no longer be employed for rupture. Thus, the procedure followed here, although imprecise, should give more realistic values for the elastic strain energy

density available at the point of rupture than would the total energy expended in stretching the specimen to rupture.

The results show a marked decrease in $\underline{U}_{\underline{b}}$ on adding glass beads, even when the glass was pretreated with a bondable silane, and a further large decrease when the glass was pretreated with a non-bonding silane. The glass particles may be acting as fracture nuclei, as discussed in a later section.

Energy dissipated in stretching

Experimentally-determined values of the mechanical hysteresis ratio <u>H</u>, defined by equation (5), are given in Table 2. For the unfilled material <u>H</u> was rather small. About 10 per cent of the energy expended in stretching was dissipated internally. When bondable glass beads were incorporated the value of <u>H</u> rose to 12-16 per cent. Somewhat higher values, 14-20 per cent, were obtained for the compounds containing untreated glass beads, and non-bondable glass beads, treated with dimethylsilane, gave values for <u>H</u> of 12-17 per cent. The highest values of <u>H</u>, 17-22 per cent, were obtained for the compound containing octadecylsilane-treated beads. It is noteworthy that these beads were also the most difficult to incorporate into the elastomer, being the least readily wetted, and that the compound exhibited the most extensive dewetting of the beads on stretching.

Thus, the amount of hysteresis that can be attributed to dewetting varies from about 4 per cent to about 13 per cent, depending upon the degree of interfacial adhesion. These values may be compared to a theoretically-calculated result for abrupt and complete dewetting of the matrix from rigid spherical inclusions (12):

$$H = 3 \not 0 / \pi$$

where $\underline{\emptyset}$ denotes the volume fraction of filler particles. Thus the maximum possible contribution to mechanical hysteresis arising from dewetting for a volume fraction of 0.16 is predicted to be about 15 per cent, close to, but somewhat higher than, the experimental value obtained with the least-well-adhering particles.

Tear strength

Measurements of fracture energy, or tear strength, \underline{T} were carried out on 5 or more strips of each compound. The values obtained were found to vary by about \pm 15 per cent, even though the tear force had been averaged along the length of each strip. The mean values of tear strength are given in Table 3. They are seen to be significantly increased by adding glass beads, by about 25 per cent for the larger sized beads, but the tear strength does not appear to depend upon the degree of interfacial bonding to a significant degree.

It seems likely that the intrinsic tear strength of the filled materials is not much different from that of the elastomeric matrix. The main effect of the glass beads is apparently to cause a deviation of the tear path from a straight line, so that the tear becomes rougher and the tear strength correspondingly higher (8). A noticeable increase in roughness of the torn surface was observed in comparison with that of the unfilled material. The scale of roughness is probably set by the size of the beads; it is noteworthy that the larger glass particles gave compounds having higher tear strength. However, if the particle size is smaller than the natural tear roughness of the unfilled elastomer, then they would presumably have little influence on the tear strength by this particular mechanism of enforced deviation of the tear path.

Fracture nuclei in tension

The depth <u>c</u> of the hypothetical nick or flaw from which tensile fracture initiated may be calculated by means of equation (3), using the measured tear energy <u>T</u> and strain-energy density at break <u>U</u>_b. A value of 2 is assigned to the numerical quantity <u>k</u>, as an appropriate value for moderate deformations (7). The values obtained in this way for the depth <u>c</u> of fracture nuclei

are given in the last column of Table 3. They are seen to be significantly larger for the glass-filled materials than for the unfilled elastomer, and to be generally of the same order of magnitude as the diameter of the largest glass particles present. The only significant exception is shown by the last material, for which the filler bonding is least strong and dewetting is most pronounced. In this case, the initial fracture nucleus may be a larger flaw associated with several contiguous dewetted particles.

Nevertheless, the general correlation shown in Table 3 between the calculated flaw size and the size of the glass particles, for materials having a wide range of values of \underline{U}_{b} , strongly suggests that tensile rupture in elastomers containing solid particles takes place by catastrophic tearing from an initial flaw which may be identified with an unusually large dewetted particle. If this proposed mechanism of tensile rupture is correct, it would probably be more appropriate to calculate the depth <u>c</u> of the edge flaw from which fracture initiates using the tear energy <u>T</u> of the unfilled material, rather than the measured values for each filled material. Values of <u>c</u> calculated in this way are given in the last column of Table 3, and denoted <u>c'</u>. This procedure brings the calculated values into

closer agreement but it does not alter the general correlation noted above with the diameter of the largest glass particle present.

Clearly, when the particle diameter is smaller than the size of adventitious flaws in the elastomer, which appear to be generally about 50 μ m (13), then the observed correlation between the size of the effective fracture nucleus and the size of the filler particles will cease to hold. A study of the effect of particle size over a wider range than employed here is therefore required in order to test the proposed mechanism of tensile rupture in a critical way.

4. <u>Conclusions</u>

(i) Addition of 16 per cent by volume of glass beads to polybutadiene was found to increase the tear strength significantly, by about 25 per cent for beads with a mean diameter of 150 μ m. This effect was largely independent of the degree of interfacial bonding between the glass beads and the elastomer. It is attributed to an increased roughness of the tear path in the glass-filled materials.

(ii) The strain-energy density at break was found to be much lower for the glass-filled materials than for the

unfilled elastomer, especially with unbonded glass beads. It is suggested that unusually large beads will act as fracture nuclei in tension. In agreement with this hypothesis the size of Griffith flaws, calculated from tensile and tear measurements, was found to be quite similar to the diameter of the largest beads.

(iii) The tensile breaking stress was increased by adding bondable glass beads and decreased by adding non-bondable beads. These changes probably reflect corresponding differences in Young's modulus \underline{E} . Indeed, it can be inferred from Equation (1) that the bondable beads have a greater stiffening effect than the non-bondable beads, as would be expected, and that this effect can outweigh the larger flaw size \underline{c} associated with the presence of glass beads.

(iv) Energy dissipation, associated with dewetting the beads on stretching the filled materials, was found to vary between about 4 per cent and 13 per cent of the input strain energy, depending upon the degree of interfacial adhesion. The maximum amount of energy dissipated is thus close to a theoretically-predicted value of 15 per cent, for complete dewetting of 16 volume per cent of filler particles.

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Table 1: Tensile properties of glass-filled polybutadiene. Volume fraction of glass is 0.16

Mean diameter of glass beads	<u>Glass</u> treatment	<u>Nominal</u> <u>breaking</u> <u>stress</u>	<u>Breaking</u> elongation	<u>Strain energy</u> <u>density at</u> <u>break</u>
<u>d</u> (µu)		<u>σ</u> (MPa)	e _b	U _b (MJ/m ³)
	Effect of a	dding untre	ated glass	
(No glass added)	-	0.85 <u>+</u> 0.03	2.06 <u>+</u> 0.18	0.88
60	none	0.81 <u>+</u> 0.04	1.73 <u>+</u> 0.04	0.70
150	none	0.87 <u>+</u> 0.015	1.38 <u>+</u> 0.10	0.60
	Effect o	of silane tr	eatment	
150	none	0.87 <u>+</u> 0.015	1.38 <u>+</u> 0.10	0.60
150	AS	1.00 <u>+</u> 0.025	1.23 <u>+</u> 0.15	0.62
150	VS	0.88 ₅ ±0.01	1.18 <u>+</u> 0.05	0.52
150	DMS	0.80 ₅ ±0.01	0.95 <u>+</u> 0.08	0.38
150	OS	0.57 <u>+</u> 0.008	1.34 <u>+</u> 0.10	0.38

Note:

- AS: Aminopropyltriethoxysilane
- VS: Vinyltriethoxysilane
- DMS: Dimethyldiethoxysilane
- OS: Octadecyltriethoxysilane

<u>Mean diameter</u>	<u>Glass</u>	Max	cimum elor	gation	
<u>of glass beads</u>	treatment	0.25	0.5	0.75	1.0
<u>a</u> (µm)		<u></u>			
(None)	-	0.12	0.09	0.09	0.09
60	none	0.16	0.20	0.17	0.17
150	none	0.16	0.14	0.14	-
150	AS	0.12	0.12	-	-
150	VS	0.16	0.12	-	-
150	DMS	0.12	0.17	-	-
150	OS	0.22	0.22	0.17	-

Table 2: Mechanical hysteresis \underline{H} on stretching to specified elongations and retracting

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Table 3: Tear strength of glass-filled polybutadiene.

Volume fraction of glass is 0.16

Mean diameter of glass beads <u>d</u> (µm)	<u>Glass</u> treatment	<u>Tear strength</u> <u>T</u> (J/m^2)	$\frac{c = T/4U_{b}}{(um)}$	<u>c'</u> (µm)
(None)	-	405	115	115
60	none	440	155	145
150	none	520	215	170
150	AS	530	215	165
150	vs	490	235	195
150	DMS	400	265	265
150	os	560	370	265

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