Strength of Filled Rubbers: Temperature, Rate, and Oxygen Effects*

F. BUECHE, *Physics Department, University of Dayton, Dayton, Ohio*

INTRODUCTION

The tensile strength of styrene–butadiene rubber (SBR) is seriously dependent upon temperature if the rubber contains carbon black or silica as filler.   Whereas the unfilled gum stock exhibits a fairly constant strength of about 200 psi in the temperature range of 40–90°C., the strength of the filled stocks decreases from about 3000 to 1000 psi in this same temperature interval.[1]   It was the purpose of this work to explore the rate effects pertinent to the tensile strength of SBR black- and silica-filled stocks.   Both peroxide and sulfur vulcanizates were investigated.   Measurements at various temperatures were made and can be interpreted to yield an activation energy for the breaking process.   This activation energy is found to be surprisingly high.   The strengths of the gum and filled stocks were also investigated in moderate and high vacuum at elevated temperatures.   Although the strength of the filled rubber is much increased at reduced pressure, the strength of the gum stock is essentially independent of pressure.

EXPERIMENTAL METHODS

Compounds

The various rubbers used in this work were prepared according to the recipes given in Table I.   Vulcanization was carried out between stainless-steel platens at 145°C.   All samples were vulcanized long enough so that vulcanization had become essentially complete.   Typical times were 90, 30, and 25 min. for the sulfur-black, peroxide-black, and silica stocks, respectively.

Time to Break

In these experiments, standard T-50 type samples were used.   They were usually 0.075 by 1.0 by about 0.015 in. in size.   Each sample was

TABLE I
Recipes, Parts per Hundred Parts Rubber

Materials	A	B	C	D	E
GR-S 1502	100	100	100	100	
Silastic 430					100
HAF black	30			30	
Hi-Sil 233			50		30
ZnO	5	5	4		
Stearic acid	2	2			
Nobs	0.75	0.75			
DPG	0.25	0.25			
Sulfur	1.75	1.75	3		
PBNA	1.00	1.00			
Dicumyl peroxide				1	
MBT			2		
Triethanolamine			1		
Cadox T.S. −40ᵃ					2

ᵃ 40% 2,4-dichlorobenzoyl peroxide in silicone fluid.

brought to temperature equilibrium and then a known weight was added in order to stretch it. The time taken for the sample to break under this load was then recorded. Samples which broke at the clamps were discarded.

Strength in Vacuum

The apparatus illustrated schematically in Figure 1 was employed. By tilting the evacuated tube it was possible to apply various fractions of the total weight as a stretching load. Obviously, if the weight is of magnitude W, the stretching force is $W \cos \theta$ where θ is the angle between the tube and the vertical. Friction effects were minimized by constant tapping of the tube as the angle of inclination was changed. Pressures were measured by means of McLeod gauges.
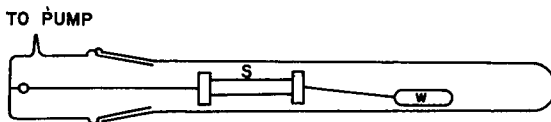

Fig. 1. A schematic diagram of the apparatus used for the vacuum tensile strength measurements. The test sample is indicated as S.

Temperature control was maintained by a heating coil wound on the outside of the tube. The oven so constructed had a temperature variation of less than 1°C. over the region of the test specimen. All measurements were made at constant temperatures to within ±1°.

Test samples for air and vacuum were run in this apparatus in the same way. The rate of tilting the tube was such that the samples took about $1/2$ min. to break. Tests were run alternately in air and vacuum on sam-

ples cut from adjacent portions of the same vulcanized sheet. Vacuum samples were usually allowed to equilibrate for 2 hrs. before the load was applied. Samples tested in air were equilibrated for about 1 hr. Twice, longer equilibration times did not change the results appreciably. Prior heating in air of the vacuum test samples did not alter the results, nor did prior pumping of the air test pieces increase their strength, provided they were maintained in air for about 20 min. before the tensile test was started.

RESULTS

Time to Break

Data for three systems were taken: SBR + 3 0 parts HAF black vulcanized with sulfur, SBR + 30 parts HAF black vulcanized with dicumyl peroxide, and SBR + 50 parts Hi-Sil 233 vulcanized with sulfur. If the data for a given system are plotted in the form of load vs. log t where t is the time taken to break under the load in question, the curves for various temperatures are found to exhibit a natural order. The higher the temperature, the lower the curve on this type of plot. In fact, if the curves are shifted relative to each other along the log t axis, the curves overlap so as to form a single smooth curve. Hence, it appears that a temperature–time superposition applies to this type of data.

It is expected that a temperature–time superposition will be valid in any rate process for which the temperature influences only the rate constant K. In such a case, the process under consideration will be a function of the product Kt where t is the time for which the process has been going on. Even when the temperature enters the mathematical function describing the behavior in a more complicated way than this, it is still usually true that the major temperature dependence is through the rate constant.
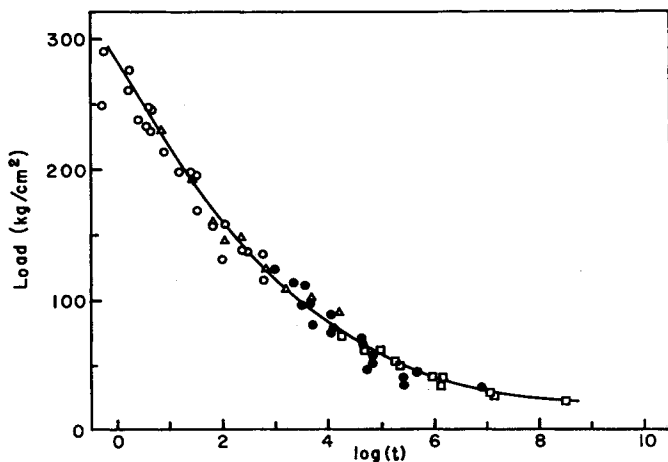

Fig. 2. Time-to-break data for the SBR–HAF–sulfur system reduced to 32.5°C. (t, min.): (O) 32.5°C; (△) 50.0°C.; (●) 68.5°C.; (□) 91.0°C.
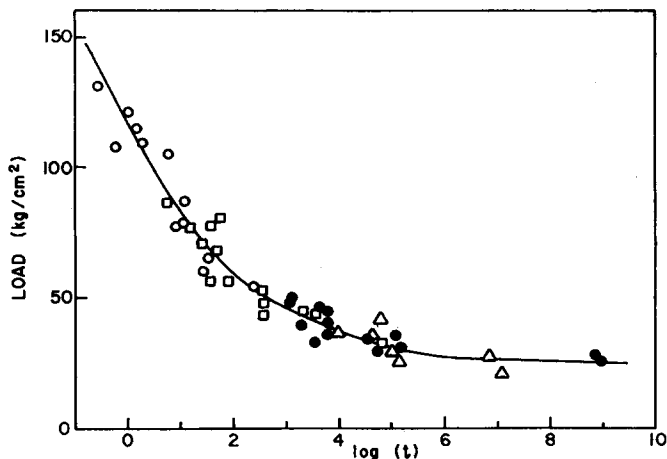
Fig. 3. Time to break data for the SBR–HAF–peroxide system reduced to 35.2°C.
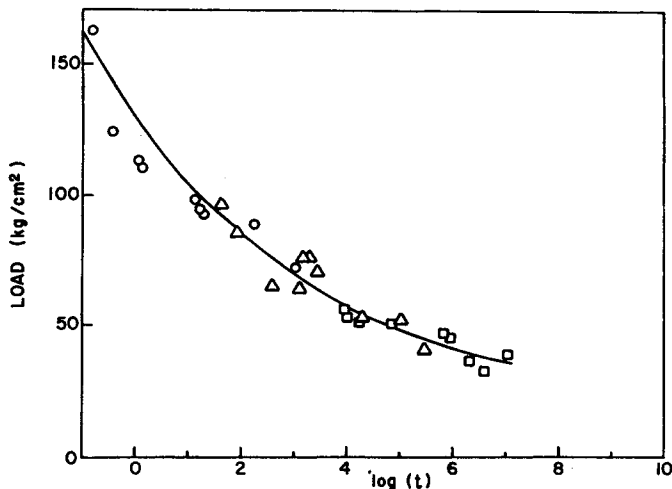(t, min.): (O) 35.2°C.; (□) 54.5°C.; (●) 77.0°C.; (△) 93.5°C.

Fig. 4. Time-to-break data for the SBR–Hi-Sil–sulfur system reduced to 33.5°C.
(t, min.): (O) 33.5°C.; (△) 60.0°C.; (□) 92.0°C.

Assuming the validity of superposition in the present case, the data, when plotted as load vs. log t, give a series of curves, one for each temperature of measurement. These curves can be superposed by shifting them along the log t axis until they all form a continuous curve. This procedure is well known in the treatment of viscoelastic data and will not be detailed here.[2] The composite curves are shown in Figures 2–5 for the three systems studied. Calling K_0 the rate constant at the reference temperature (i.e., the temperature for the data to which the other data are shifted) and K the rate constant at any other temperature, one has that log (K/K_0) is given
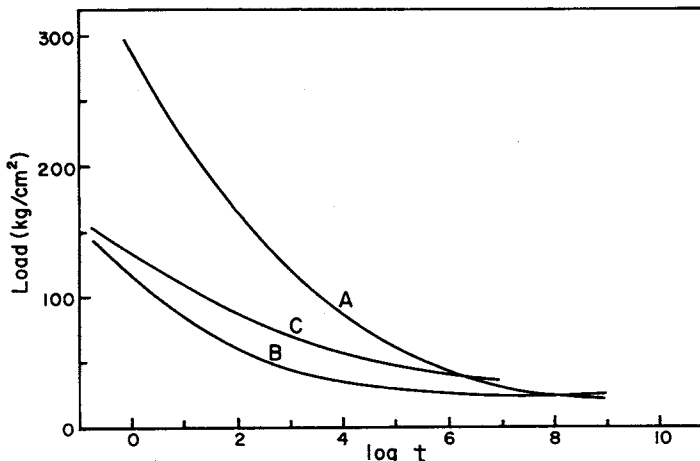
Fig. 5. Comparison of the data of Figures 2, 3, and 4, all reduced to 33°C. (t, min.).

by the amount by which the data must be shifted along the log t axis.   The values of log (K/K_0) are plotted against reciprocal temperature in Figure 6. This graph may be interpreted as follows.

If the rate constant is assumed to take the form:

$$K = A \exp \{-E/RT\}$$

one has

$$\ln (K/K_0) = (E/RT_0) - (E/RT)$$

Hence, a plot of ln (K/K_0) against $1/T$ should give rise to a straight line of slope (E/R).   In addition, the intercept at $T \to \infty$ should be (E/RT_0). It is therefore possible to compute the activation energy E from the data of Figure 6.   The two straight lines plotted in the figure yield 46 and 44 kcal./mole for the activation energy.   These values are identical within the accuracy of these measurements.

It is important to notice that all three systems exhibit the same temperature dependence for tensile strength.   One would therefore conclude that the temperature dependence of the strength of black- and silica-filled SBR is a function of neither the filler type nor the vulcanization system. This fact appears to exclude filler–rubber adhesion and crosslink scission as controlling factors in the process.   Confirmation of the fact that filler–rubber adhesion in these systems is still strong even at elevated temperatures has already been presented in studies of the Mullins softening effect.[3]   These facts indicate that the decrease in tensile strength of these filled SBR systems at high temperatures is the result of changes in the rubber matrix itself, and is not concerned with the filler per se.

Moreover, the value found for E is much larger than one would expect for the activation energy for viscoelastic phenomena.   Elastic retardation and viscous flow would exhibit values of E of 15–25 kcal./mole in this
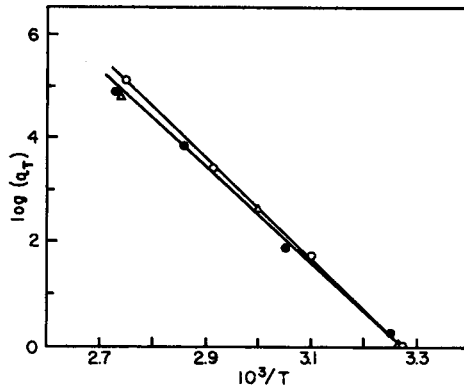
Fig. 6. An Arrhenius plot for the ratio of the rate constants $K/K_0 \equiv a_T$: (O) HAF–Sulfur; ($\triangle$) Hi-Sil; ($\bullet$) HAF–peroxide.

temperature range.[2,4] This, coupled with the fact that data for gum stocks show viscoelastic rate effects to be negligible in this temperature range for the present test rates,[1] leads one to rule out simple viscous mechanisms as the source of the rate processes observed here.

Influence of Air

The data for the tensile strength of filled SBR stocks and gum stock in air and vacuum are given in Table II. Unfortunately, these stocks were

TABLE II
Strength in Vacuum and Air

Material	Temp., °C.	Strength at 760 mm. Hg, kg./cm.²	Strength at 0.020 mm. Hg, kg./cm.²
SBR–HAF (sample 1)	120	45 ± 5	79 ± 5
	89	76	109
SBR–HAF (sample 2)	120	72	97
SBR–Hi-Sil	120	88	115
SBR–gum	120	10.6	10.9
	89	11.1	11.5
	35	13.7	
Silicone–Hi-Sil	120	37	36
	105	41	
	80	46	
	55	51	
	24	55	

not identical with those used in the time-to-break studies. Notice that the differences between the air and vacuum test pieces are much larger in general than one can explain on the basis of experimental error. Also, it is clear that the gum stock does not show any appreciable difference between
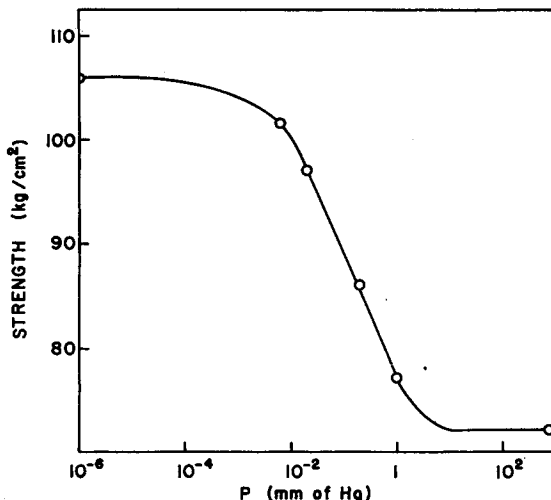
Fig. 7. The air pressure dependence for the strength of an SBR–HAF sulfur-cured stock.

its strength in air and in vacuum. Obviously, the effect in the filled stocks is highly dependent on pressure at low pressures, as is shown in Figure 7. This parallels the behavior of SBR in oxidative degradation studies, in which major changes occur only at pressures below about 0.10 mm. of Hg.[5] It is apparent from data for a sample, which had been pumped in vacuum before measurements were made in an atmosphere of commercial nitrogen, that the vacuum enhancement in strength is the result of the removal of oxygen rather than the decrease of external pressure.

Notice further that the strength of a silicone–silica stock is not changed by the removal of oxygen. This is of interest, since this material does not readily undergo oxidative degradation. It is noticed, however, that the strength of this material decreases markedly with increasing temperature.

DISCUSSION

To interpret the results found in this study it is necessary to have an understanding of the mechanism by which fillers such as carbon black tremendously increase the strength of noncrystallizable rubbers. A possible mechanism for the strength enhancement obtained with such fillers has been presented.[1,6] It is based on the general idea that tensile failure will occur when the breaking of one chain in the sample throws enough stress onto its neighbors to cause one of them to break. The breaking of this chain in turn causes a third to break, and so on. Reasonable results for the strength of gum stocks have been predicted with the use of this picture. In addition, the effect of filler may be described with the aid of such a model as given in the following.

Refer to Figure 8(a): If the central chain breaks at point X, the newly formed free ends allow the chain to retract. If no filler is present, the final
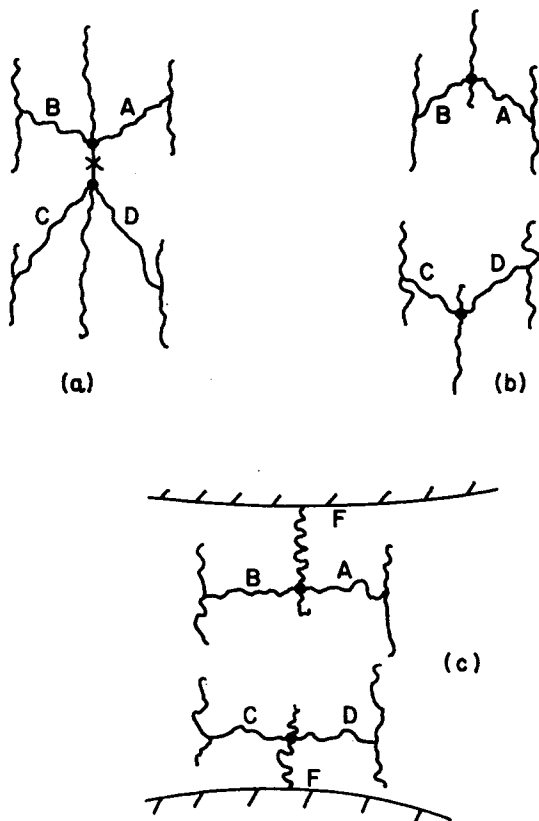
Fig. 8. Schematic diagram of the way in which a network breaks.

state of the system is something like that shown in Figure 8(b). Notice that much of the load held by the central chain has now been transferred to the near-neighbor chains by the movement of chains A, B, C, and D. However, if filler is present, the situation after the chain breaks would be more likely to appear as shown in Figure 8(c). Since points E and F are essentially fixed in space, the central chain does not retract as far as it did in 8(b). Hence, chains A, B, C, and D no longer impose as much load on the neighbor chains as was the case without filler present. The filler particles have effectively distributed the load held by the central chain to many other chains rather than just the few near-neighbor chains. This will decrease greatly the chance of a second chain's breaking as a result of the breaking of the central chain. As a consequence, the sample will be able to hold a much higher load before the break will propagate.

The explanation given above for the means by which filler increases the strength of rubbers assumes that the rubber molecules are bound tightly to the filler surface. It is to be expected that if the rubber–filler adhesion decreases, the strength of the filled rubber would decrease also. In particular systems, this may well be the cause of the decrease in strength with

increasing temperature; however, there are two good reasons for ruling out this cause for the temperature dependence of strength in the SBR systems studied here.

First, both the silica and carbon black systems exhibit the same activation energy for the process giving rise to the decrease in strength with temperature. It would seem quite unlikely that adhesion to these two far different surfaces should show the same temperature dependence. Second, measurements of the Mullins effect[3] at elevated temperatures in these systems indicate that the rubber-filler bonds are so strong that they are not easily broken at temperatures up to 90°C.

If, as appears to be the case, adhesion between rubber and filler is still strong at high temperatures where the filler appears to be less effective, then some other mechanism must be sought which diminishes the ability of the filler to distribute loads at high temperatures. Notice that the filler will no longer serve its useful purpose if it comes loose from the rubber by any means whatsoever. Although breaking of the rubber–filler bond is the most direct way for this to happen, it is not the only way by which the filler can be disengaged from the rubber network. Oxidative scission of the network chains will actually accomplish the same purpose.

It is well to emphasize the fact that the breaking of chains such as the one illustrated in Figure 8 is not primarily the result of oxidative scission. This is inferred from two experimental facts. First, the energy of activation of the breaking process is about 45 kcal./mole rather than the value of about 28 kcal./mole found for the chemical stress relaxation of these same stocks at elevated temperatures. Second, and more important, the strength of the gum stock shows no dependence on air pressure, as is seen in Table II. However, the fact that the strength of the black-filled stock depends on air pressure indicates that oxidative scission is probably important in this case. The fact that the silicone stock also shows a decrease in strength at high temperatures indicates that oxidative action is not the only operative mechanism. Further work is in progress on this subject.

References

1. Bueche, F., *J. Polymer Sci.*, **33**, 259 (1958).
2. See, for example, Ferry, J. D., *Viscoelastic Properties of Polymers*, Wiley, New York, 1960.
3. Bueche, F., *J. Appl. Polymer Sci.*, **5**, 271 (1961).
4. Bueche, F., *J. Polymer Sci.*, **25**, 305 (1957).
5. Tobolsky, A. V., I. B. Prettyman, and J. H. Dillon, *J. Appl. Phys.*, **15**, 380 (1944).

Synopsis

The time taken to break under fixed load has been measured for three SBR–filler systems. Two SBR–HAF black systems were used, one vulcanized with sulfur and the other with dicumyl peroxide; the third system was an SBR–silica formulation.

Measurements at several temperatures between 30 and 100°C. allowed the computation of an activation energy for the breaking process: 45 kcal./mole for all three systems. By measuring the tensile strength of the filled stock in air and vacuum at various temperatures, it was shown that the presence of oxygen seriously decreases the strength of the filled stock at high temperatures, an effect not present in the gum stock or in silica-silicone stocks.

Résumé

On a mesuré le temps de rupture sous charge fixe pour trois systèmes charge–SBR. On a employé deux systèmes noir HAF–SBR, l'un vulcanisé au soufre et l'autre au peroxyde de dicumyle. Le troisième système est un mélange SBR–silice. Des mesures à diverses températures entre 30° et 100°C permettent l'évaluation d'une énergie d'activation pour le processus de rupture. Elle est de 45 kcal/mole pour les trois systèmes. Par mesure de la force de tension du stock soit à l'air soit sous vide a diverses températures, on a montré que la présence d'oxygène diminue fortement la force du stock a température élevée. Cet important effet ne se manifeste ni dans la gomme ni dans les stocks de silice–silicone.

Zusammenfassung

An drei SBR–Füllstoffsystemen wurde die Bruchdauer bei konstanter Belastung gemessen. Zwei SBR–HAF-Russsysteme, ein Schwefelvulkanisat und ein Dicumyl-peroxydvulkanisat, wurden verwendet. Das dritte System war eine SBR–Kiesel-säuremischung. Messungen bei mehreren Temperaturen zwischen 30 und 100°C erlaubten die Berechnung der Aktivierungsenergie für den Bruchvorgang. Diese betrug bei allen drei Systemen 45 kcal/Mol. Durch Messung der Zugfestigkeit der gefüllten Proben unter Luft und im Vakuum vei verschiedenen Temperaturen wurde gezeigt, dass die Gegenwart von Sauerstoff die Festigkeit der gefüllten Proben bei hohen Temperaturen wesentlich herabsetzt. Ein solch grosser Einfluss besteht weder bei unge-fülltem Kautschuk noch bei kieselsäuregefülltem Silikon–kautschuk.