An Investigation into the High Temperature Strength and Reinforcement of Natural Rubber

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Synopsis

The failure criterion for amorphous polymers relating hysteresis at break with energy input to failure in tensile stress–strain tests was found to be obeyed only at very high or very low temperatures in natural rubber. Tensile results between about 80°C and 130°C show a high degree of scatter, and this behavior is attributed to the ability of natural rubber to crystallize at high strains. The modification of tensile properties by the addition of carbon black in natural rubber is also discussed and compared with published results from SBR. The effect of changing the degree of crosslinking on the failure properties in both dicumyl peroxide and sulfur-cured vulcanizates of natural rubber is also considered. It is found that differences in failure properties can be accounted for by the use of a crosslinking parameter from simple rubber elasticity theory in some of the failure equations.

INTRODUCTION

In earlier work,[1] a failure criterion has been well established for amorphous gum rubbers, showing that the work done or energy input to break in a tensile stress–strain test is related to the energy dissipated or hysteresis at break in the rubber by a simple power law. It was shown[1,2] that natural rubber diverges from this law at temperatures between 80° and 140°C, the hysteresis being lower than that obtained for the amorphous rubbers for the same energy input to break.

A subsequent investigation[3,4] extended this work to amorphous rubbers loaded with reinforcing carbon black filler and showed that under conditions of constant energy input, both the strains at break and the hysteresis at break of the filled and gum rubbers agreed when corrected by a factor X. This correction factor is analogous to an expression in hydrodynamic theory relating the viscosity of a liquid containing hard spherical particles to the viscosity of the liquid alone.

The investigation reported in this paper set out first to determine whether the anomalous results occurring in NR gum were also apparent in the filled vulcanizates and secondly to ascertain whether the X-factor correction

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was still applicable. The paper also considers the effect of vulcanization on the hysteresial and therefore strength properties of natural rubber.

EXPERIMENTAL

The rubber studied in this investigation was an accelerated sulfur NR vulcanizate (2.5 phr sulfur to 0.6 phr CBS) filled with 0, 30, 60, and 80 phr HAF carbon black. This was compared with a conventional SBR mix with the same concentrations of filler. In order to study the effect of changing the type and degree of crosslinking, two series of unfilled natural rubber vulcanizates were examined. The first series was vulcanized with 1, 2, and 4 phr of dicumyl peroxide. The second series was vulcanized with 1.4 and 2.5 phr sulfur, the ratio of S to CBS remaining constant. Full details of the mixing and vulcanization times are given in the Appendix.

The test pieces were in the form of rings with inner and outer diameters of 2.05 and 2.20 cm, respectively, cut from rubber sheets 0.25 cm thick using a rotating cutter. The samples were extended on an Instron tensile tester over the temperature range 21°–150°C. Below room temperature, another tensometer was employed.[5] The rate of strain was 300%/min in every case.

The experimental procedure to determine the energy input and hysteresis at break was to obtain at each temperature three tensile stress–strain curves up to failure on new samples. A fourth sample was then extended and the crosshead was reversed just below the average breaking stress of the three tensile curves. The energy input was obtained from the area under the extension curve and the hysteresis from the area between the extension and retraction curves.

RESULTS

Effect of Hysteresis

The energy input to break (U_B) in a tensile stress–strain test is related to the hysteresis or energy dissipated at break (H_B) for amorphous rubbers by the following relationship[4]:

$$\left(\frac{294}{T}\right)^{1/3} \cdot U_B = K \cdot H_B^{2/3} \tag{1}$$

where T is the temperature of test and K is a constant. The energy is reduced by the term $294/T$ to allow for the temperature dependence of rubber-like elasticity as predicted by the kinetic theory.[6] It is seen from eq. (1) that the maximum value of $U_B(294/T)$ occurs when the ratio H_B/U_B is unity, and is equal to K.[3] It is thought that this energy is obtained at a temperature near to the glass transition temperature of the polymer.[1]

The dependence of U_B on H_B is illustrated in Figure 1 for SBR with increasing amounts of HAF carbon black. The results from the filled vulcanizates lie along lines of slope approximately 2/3, but these lines are dis-
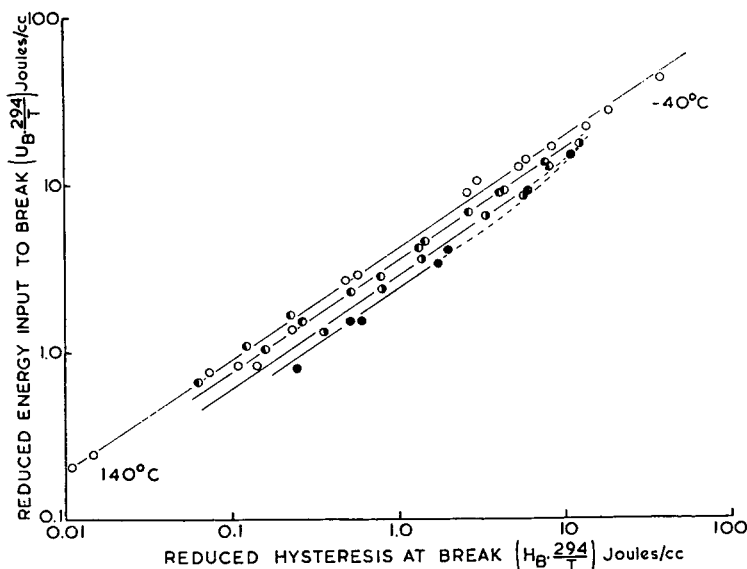
Fig. 1. Variation of reduced energy input to break with reduced hysteresis at break for SBR containing 0, 30, 60, and 80 phr HAF carbon black: (O) SBR gum; (◑) SBR + 30 phr HAF; (◐) SBR + 60 phr HAF; (●) SBR + 80 phr HAF.

placed from the gum line except at low temperatures where the gum and filled results converge. At the same reduced energy input to break, the hysteresis increases with concentration of the carbon black. This additional loss of energy arises because the filler particles are inextensible and the overall strain in the sample is less than the actual strain in the rubber phase. If the strain at reversal of the crosshead is less than the breaking strain, eq. (1) has been shown not to hold,[1,3] emphasizing that it is a failure criterion. The results for NR are plotted in the same way in Figure 2. As discussed in a previous study,[1,2] the failure equation is not obeyed by NR in the temperature range 80°–140°C, the hysteresis at break being less than that predicted. This deviation was not found in noncrystallizing isomerized natural rubber as shown by the dotted line on Figure 2. The anomalous behavior is attributed to the ability of NR to crystallize at high strains in the temperature range 80°–140°C; the bulk of the polymer remains amorphous while the highly strained regions around the inherent flaws in the sample crystallize.[7] Outside this temperature range, the rubber is either predominantly crystalline at the lower temperatures or predominantly amorphous at the higher temperatures. The NR + 30 phr and NR + 60 phr carbon black results follow lines of slope approximately 2/3 at the lower temperatures, but above about 100°C, the lines through the results show a steeper slope. However, the data from the NR + 80 phr carbon black fall on a line of slope 2/3. The minimum value of U_B recorded was about 7 joules/cc at 140°C for the NR + 30 and NR + 60 phr carbon black vulcanizates; this is seven times the minimum value of energy ob-

served in the corresponding SBR rubbers.   This point will be considered in more detail later in the paper.

It was found earlier for amorphous polymers that, by dividing the hysteresis axis by a factor X which is a function of filler concentration, the filled and gum rubbers could be unified.   The factor X is given by

$$X = 1 + 2.5c + 14.1c^2 \qquad (2)$$

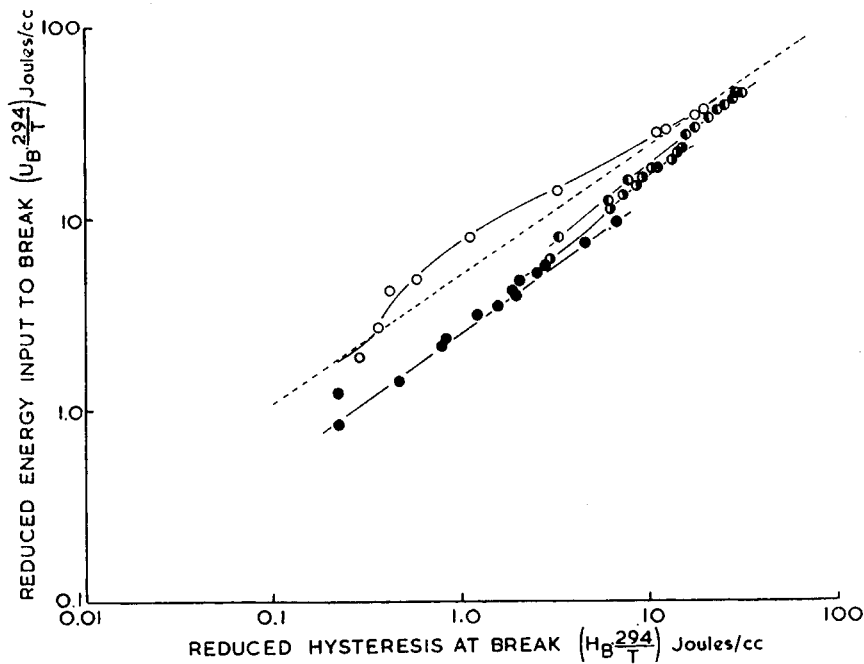where c is the volume concentration of the filler.

Fig. 2. Variation of reduced energy input to break with reduced hysteresis at break for NR containing 0, 30, 60, and 80 phr HAF carbon black.   Dotted line refers to results on isomerized natural rubber: (O) NR gum; (◐) NR + 30 phr HAF; (◑) NR + 60 phr HAF; (●) NR + 80 phr HAF.

Mullins and Tobin[8] suggested that the factor X when applied to filled vulcanizates takes account of both the disturbance of the strain distribution and the absence of deformation in that fraction of the material composed of filler.   The expression is identical to the hydrodynamic relationship derived by Guth and Gold[9] for small spherical particles in a viscous medium.   The shape of HAF carbon black particles is approximately spherical.   The general expression, therefore, for filled and unfilled vulcanizates in an amorphous polymer is given by

$$\left(\frac{294}{T}\right)^{1/3} \cdot U_B = K \cdot \left(\frac{H_B}{X}\right)^{2/3}. \qquad (3)$$

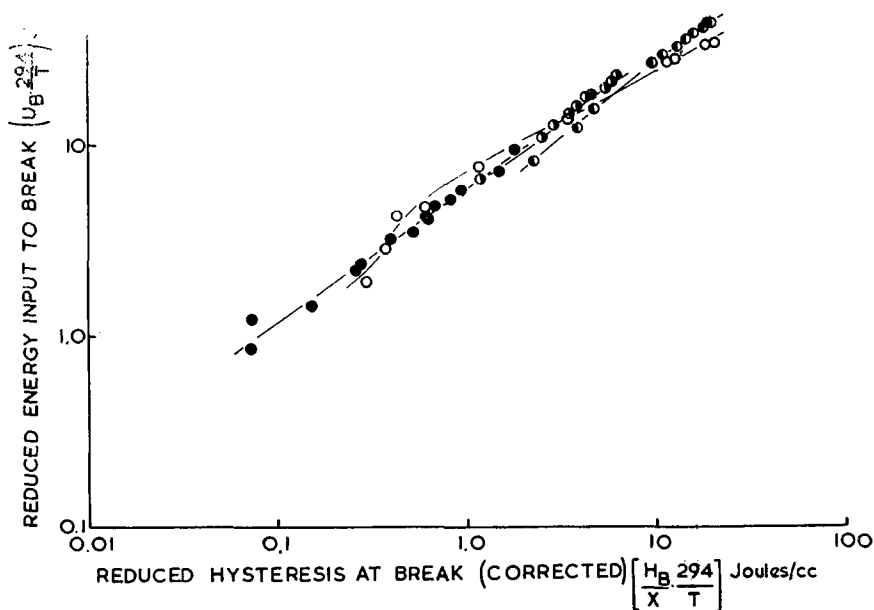Fig. 3. Variation of reduced energy input to break with reduced hysteresis at break corrected by the X-factor for NR containing 0, 30, 60, and 80 phr HAF carbon black: (O) NR gum; (◐) NR + 30 phr HAF; (◑) NR + 60 phr HAF; (●) NR + 80 phr HAF.

The filled amorphous rubbers do show some deviation from eq. (3) at the lower temperatures, as indicated by the dotted lines in Figure 1. This deviation might arise when the moduli of the filler and rubber phases of the filled vulcanizate approach parity[10] at low temperatures and hence the hydrodynamic correction becomes too large.

By treating the data for the NR vulcanizates in a similar manner, the results shown in Figure 3 are obtained. The deviations from $^2/_3$ slope in the gum, 30, and 60-phr HAF-filled vulcanizates referred to above are still apparent, but, to a first approximation, the results coincide quite well. The loading of NR with 80 phr HAF carbon black appears to suppress or conceal crystallization and yields results similar to that obtained in an amorphous polymer.

Effect of Strain

Recent work on amorphous rubbers has shown a relationship between the energy input to break (U_B) and the strain at break (ϵ_B). This is illustrated in Figure 4a for SBR with increasing amounts of HAF-carbon black. As the temperature is increased, the failure points for the gum rubbers move clockwise around an envelope passing through a maximum strain $(\epsilon_{B\ max})$ at a temperature of about $0°C$. This type of graph is similar to the "failure
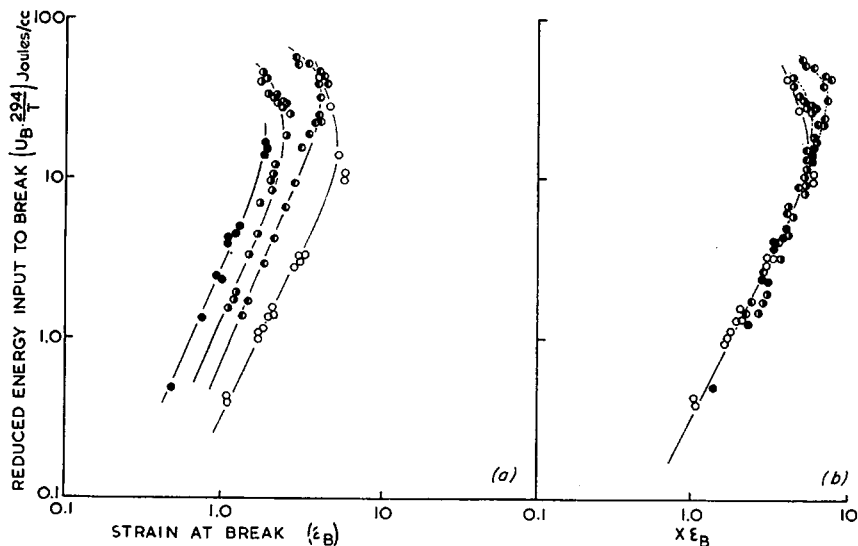
Fig. 4. Variation of reduced energy input to break with (a) strain at break and (b) strain at break corrected by the X-factor for SBR containing 0, 30, 60, and 80 phr HAF carbon black: (O) SBR gum; (◑) SBR + 30 phr HAF; (◓) SBR + 60 phr HAF; (●) SBR + 80 phr HAF.

envelope" approach of Smith[11] and others[12] who plot stress at break (σ_B) or real stress at break ($\sigma_B \lambda_B$) against the strain at break (ϵ_B). The filled rubbers lie along lines parallel to the gum rubber but are displaced slightly. It was again found that by applying the X-factor to the strain axis in Figure 4a, the gum and filled results coincided, as shown in Figure 4b, up to strains of $\epsilon_{B\ max}$, and the slope of the plot was found to be 2. At temperatures below that at which $\epsilon_{B\ max}$ occurs, the X-factor is again found to be too large to coincide the results. This is presumably due to the same reasons given for nonagreement on the hysteresis graphs. The relationship between energy and strain at break can therefore be expressed as

$$\left(\frac{294}{T}\right) \cdot U_B = A \cdot (X\epsilon_B)^2, \qquad (4)$$

where A is a constant.

This type of plot is shown for natural rubber in Figures 5a and b. The NR gum rubber follows the square law extremely well and shows none of the departures encountered in the hysteresis plots (Figs. 2 and 3). The NR + 30 phr and NR + 60 phr HAF carbon black results are shown to be confined to a small range around the position of ϵ_{Bmax}, and some scatter is evident in this region when corrected by the factor X in Figure 5b, but in general the correction by X is shown to yield fair agreement of the filled and gum results. It is interesting to note here again that, in contrast to the SBR results, the NR values of U_B and ϵ_B for the 30 and 60 phr carbon
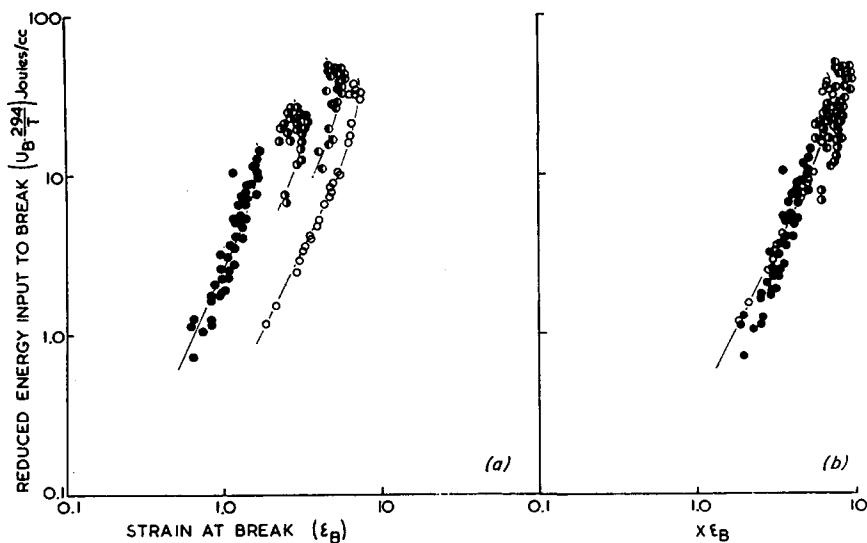
Fig. 5. Variation of reduced energy input to break with (a) strain at break and (b) strain at break corrected by the X-factor for NR containing 0, 30, 60, and 80 phr HAF carbon black: (O) NR gum; (◑) NR + 30 phr HAF; (◐) NR + 60 phr HAF; (●) NR + 80 phr HAF.

black-filled vulcanizates remain high even at temperatures approaching 140°C.

Effect of Temperature

The energy input and hysteresis at break for NR gum are very dependent on the temperature of test, and therefore it is informative to plot energy input to break (U_B) as a function of temperature. This is shown in Figure 6 for NR gum. At least two results are shown at each test temperature as well as the upper and lower bounds of the results. Up to about 70°C, NR gum maintains high values of energy input to break with little scatter, but between 70° and 130°C, the values of U_B decrease dramatically and show a wide variation. Corresponding results are shown for SBR in Figure 7. The wide variation of results and the dramatic drop are not seen in the case

TABLE I
Statistical Analysis of Energy Input to Break (U_B)
Values for NR Gum (2.5 phr Sulfur)

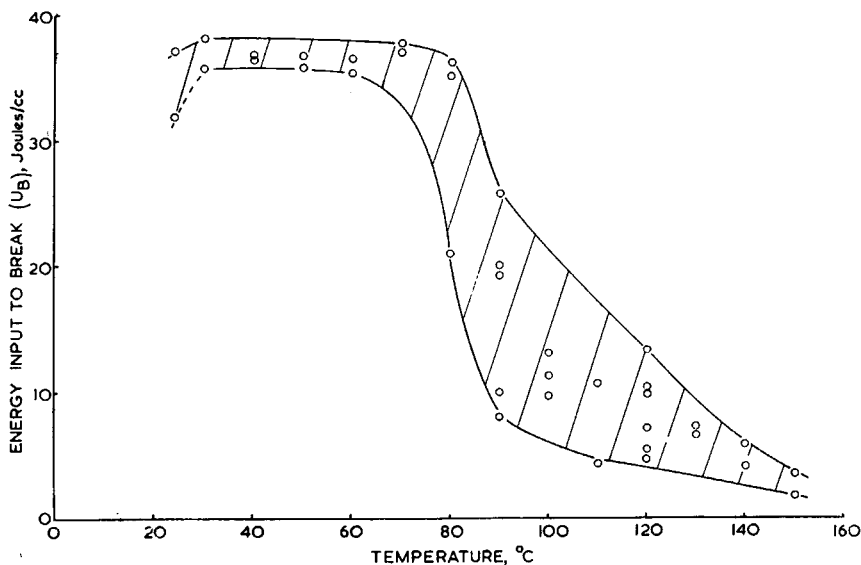| Temperature, °C	Mean U_B, joules/cc	Standard deviation, joules/cc	Variance coefficient, %
21	33.0	4.4	13
50	35.8	3.4	10
80	34.5	6.7	19
110	14.7	7.3	50
140	5.2	1.7	33

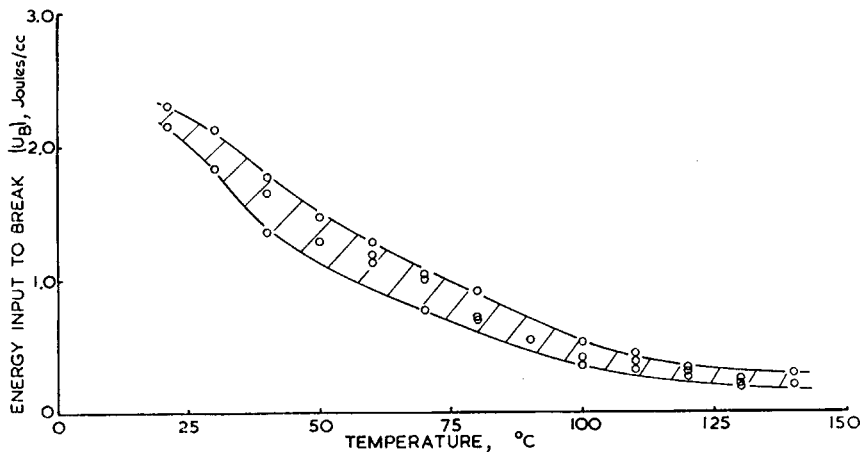Fig. 6. Variation of energy input to break with temperature for NR gum.

Fig. 7. Variation of energy input to break with temperature for SBR gum.

of the amorphous polymer, but, of course, the actual values of U_B are very much lower. The wide variation or scatter of results in the case of NR occurs over approximately the same temperature range as the deviation from the slope 2/3 line shown in Figure 2 and presumably is a reflection of the same effect, viz., crystallization.

This anomalous behavior in NR was investigated more quantitatively by obtaining 27 values of energy input to break at each of five test temperatures, 21°, 50°, 80°, 110°, and 140°C. The results were read to the nearest joule/cc and plotted in the form of a histogram, the number of times the

particular energy input to break being observed against the energy input value. This is shown in Figure 8 for the five temperatures. At 21°C, all the results except one are in the range 31–37 joules/cc. As the tempera-
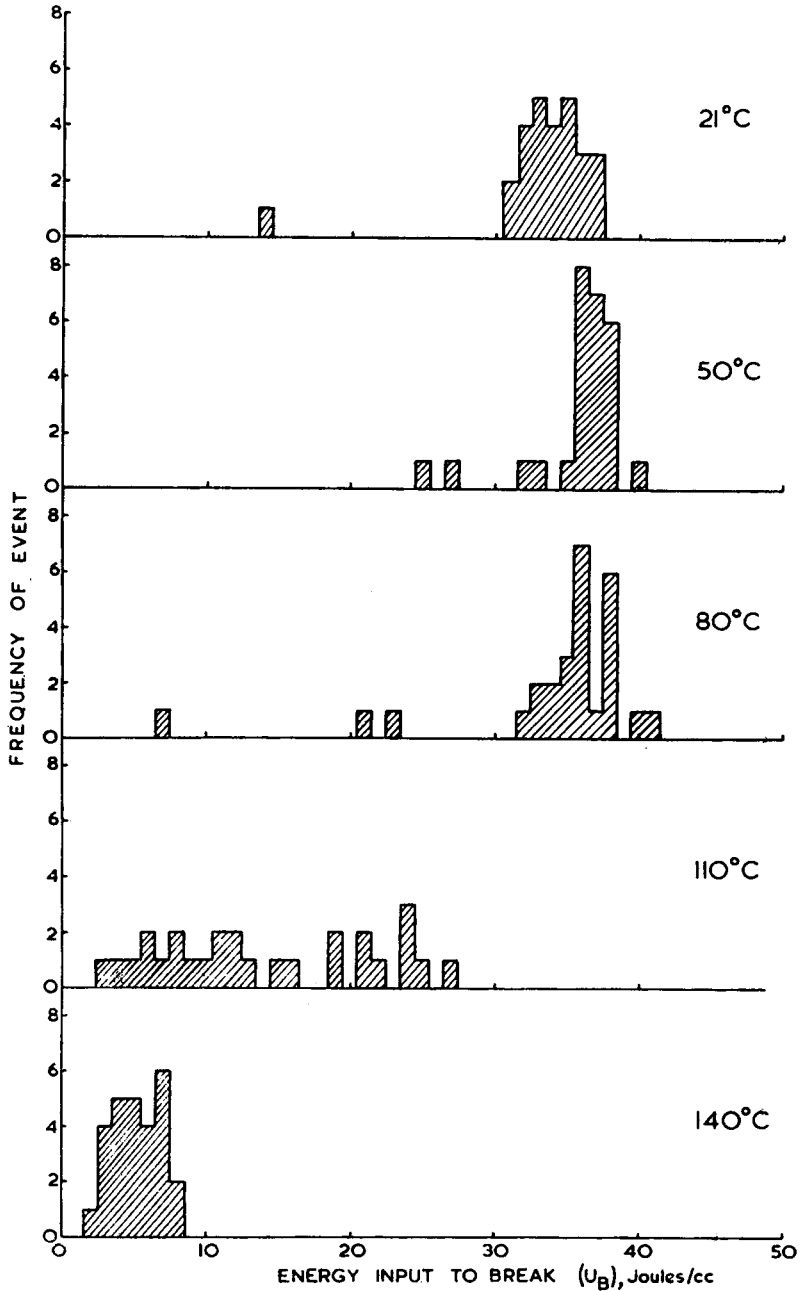

Fig. 8. The distribution of energy input to break values at five temperatures for NR gum.
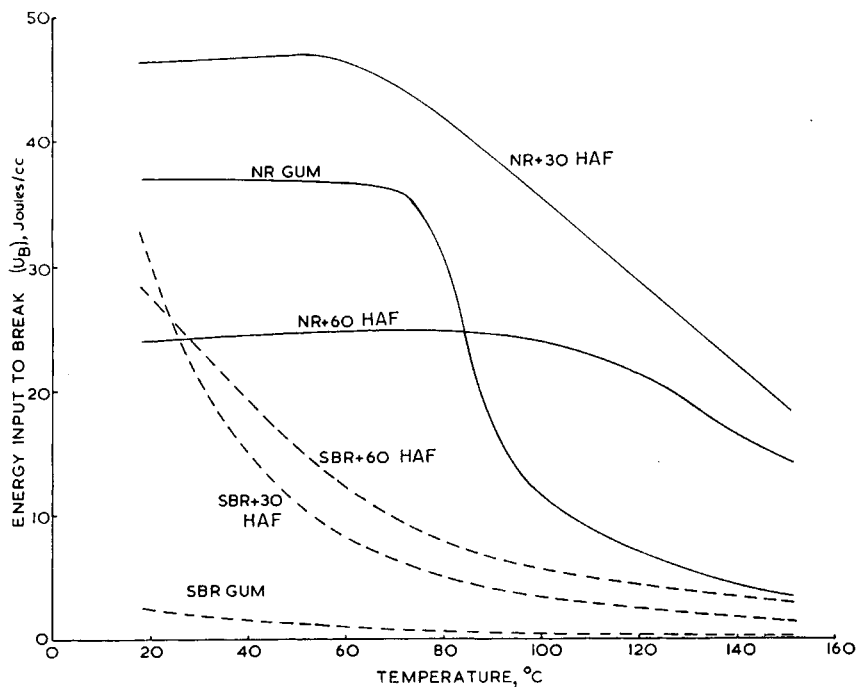
Fig. 9. Comparison of mean energy input to break with temperature for SBR and NR
containing 0, 30, and 60 phr HAF carbon black.

ture is increased to 80°C, three of the results start to break away from the
main band which at 80°C widens to cover the range 32–41 joules/cc.   At
110°C, the picture becomes vastly different, with the frequency of events
fairly evenly distributed between 3 and 27 joules/cc.   At 140°C, the results
converge again to values between 2–8 joules/cc.   The mean and standard
deviation of these results is listed in Table I.   The variance coefficient is an
index of the scatter of the results and again demonstrates the difference
between the results at room temperature (13%) and 110°C (50%).

The energy input/temperature results for NR are compared in Figure 9
with results for SBR containing 0, 30, and 60 phr HAF carbon black, but
for the sake of clarity only the mean lines through the results are shown.
It is well known that the strength of NR is about ten times that of SBR at
room temperature, but it is interesting to note that even at 140°C the
strength of NR is still above that of SBR.   The strength of the SBR + 30
phr HAF vulcanizate rises steeply as one approaches the glass transition
temperature of the polymer, but at the high temperatures, the strength of
the NR + 30 phr HAF vulcanizate is ten times that of the SBR + 30 phr
HAF vulcanizate.   In the case of the vulcanizates containing 60 phr HAF
filler, the strength of the NR vulcanizate is about six times the strength of
the SBR vulcanizate at 140°C.   The inclusion in natural rubber of 30 phr
HAF carbon black increases the energy input to break values, as compared

with the gum at all temperatures, and does not show such an abrupt drop. The further inclusion of 60 phr carbon black reduces the energy input to break values.   The graph illustrates how the unique crystallization properties of natural rubber show high temperature reinforcement well above that obtained in a synthetic polymer.

Effect of Changing Degree of Crosslinking

The variation of the failure parameters—energy input, hysteresis, and strain—with temperature has been discussed for a conventional sulfur santocure vulcanizate both unfilled and filled with carbon black.   Up to the present, the effect of changing the type or density of crosslinking on energy input or hysteresis has not been reported for either amorphous or crystalline polymers.   Smith,[13] however, has reported the variation of real stress at break with strain at break for varying degrees of crosslinking, but the study is incomplete.

The scatter of the results shown in Figure 6 could result from either crystallization or dispersion of the vulcanizing ingredients within the mix. In an attempt to throw some light on the phenomenon, the effect of changing the type and degree of crosslinking was examined.   To this end, NR
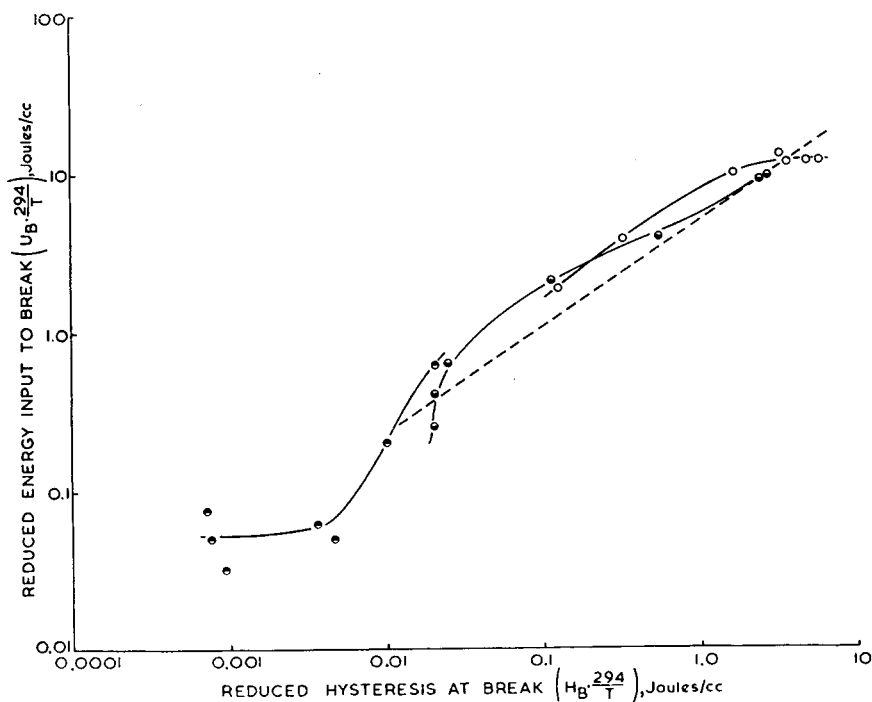

Fig. 10. Variation of reduced energy input to break with reduced hysteresis at break for three unfilled dicumyl peroxide (dicup)-cured NR vulcanizates. Dotted line represents data from isomerized natural rubber: (O) NR + 1 phr Dicup; (◓) NR + 2 phr Dicup; (◑) NR + 4 Dicup.

was vulcanized with 1, 2, and 4 phr dicumyl peroxide (Dicup) to yield car-
bon–carbon crosslinks. A dicup system was chosen because this has the
minimum of vulcanizing ingredients, and the crosslinks are nonlabile and
have no extra linkages such as the cyclic sulfides that occur as in a poly-
sulfide vulcanizing system.

Figure 10 shows the variation of energy input to break with hysteresis for
the three dicup vulcanizates over the temperature range 21°–140°C.
They are compared with data obtained from noncrystallizing NR (dotted
line of slope 2/3) previously shown in Figure 2. The data for the non-
crystallizing rubber were obtained from an isomerized NR vulcanizate
cured with sulfur in view of the fact that no data existed for isomerized NR
cured with dicumyl peroxide. However, the data already existing on
different types and degrees of crosslinking indicate that the dotted line in
Figure 10 would not be very different had an isomerized NR dicup vul-
canizate been used. The deviation from the slope 2/3 line is apparent in
all the NR vulcanizates shown in Figure 10, and it is interesting to note that
the deviation occurs at a lower energy input with increasing crosslink den-
sity.

The 4 phr dicup rubber is very weak even at 21°C. As that temperature
is increased, the hysteresis at break values become smaller still while the
U_B 294/T value remains constant at about 0.06 joules/cc. The magnitude
of the lowest recorded values of U_B has been discussed previously[3] for
amorphous polymers, but no values below 0.15 joules/cc or limiting steady
value was observed.

Lake and Thomas[14] have recently produced a theory to explain a lower
limit of tearing energies (T_0) which is related to a minimum value of U_B
($U_{B min}$). The T_0 value can be expressed as the energy required to produce
unit area of new surface and defines a fatigue limit below which the fatigue
life under repeated stressing can be virtually indefinite. It was considered
worthwhile to investigate how the values of T_0 compare with the lower limit
shown in Figure 10. Lake and Thomas calculate T_0 by considering the
energy required to rupture polymer chains lying across the path of a prop-
agating crack, this energy being calculated by the strengths of the chemi-
cal bonds. They show that for NR an average of theoretical estimates
gives $T_0 = 2 \times 10^4$ erg/cm² which is independent of the type and degree of
crosslinking. The experimental determination of T_0 for the 4 phr dicup
rubber is difficult due to its low strain at break, but as far as can be ascer-
tained[15] it is $< 3 \times 10^4$ ergs/cm². Therefore, for this vulcanizate espe-
cially, the agreement of T_0 between theory and experiment is good.

For a tensile test piece, the minimum energy input to break at very low
strains is related to T_0 by

$$U_{B min} = \frac{T_0}{2\pi c_0},\qquad (5)$$

where c_0 is the "characteristic flaw size" for NR and is given as 2.5×10^{-3}
cm. By substituting the value 2×10^4 ergs/cm² for T_0, the theoretical

value of U_{Bmin} becomes 0.13 joule/cc. Assuming that the 4 phr dicup rubber reaches a limiting value of U_{Bmin} $294/T$ (= 0.06 joule/cc) at a temperature of 120°–140°C, the experimental value of U_{Bmin} would be 0.08 joule/cc. The value given for c_0 is a standard value for an NR generally; amorphous polymers have been shown to have higher values.[16] As the 4 phr dicup vulcanizate is probably in an amorphous state signified by its low tensile strength and elongation at break, the theoretical value for U_{Bmin} could possibly be lower than 0.13 joule/cc, thus agreeing better with the experimental value of 0.08 joule/cc.
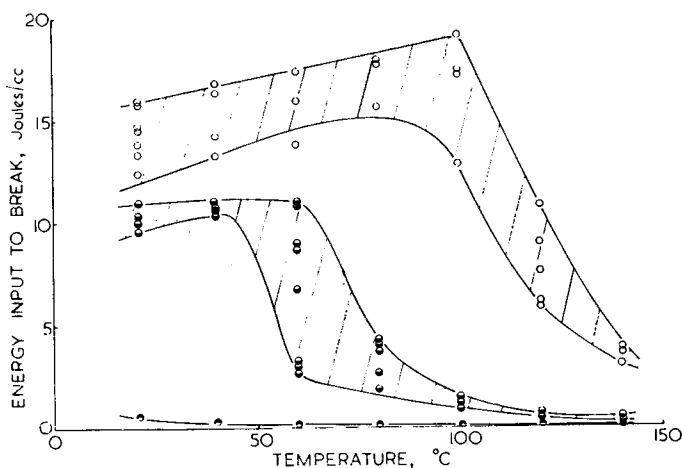

Fig. 11. Variation of energy input to break with temperature for three unfilled dicumyl peroxide-cured NR vulcanizates: (O) NR + 1 phr Dicup; (◐) NR + 2 Dicup; ◕ NR + 4 Dicup.

The variation of energy input to break with temperature is shown for the three dicup rubbers in Figure 11. About five results were obtained at each of seven temperatures between 21° and 140°C, and the upper and lower bounds are drawn through the results for the 1 and 2 phr Dicup vulcanizes. Results for the 4 phr Dicup vulcanizate were very low and scatter in the results was negligible when compared with the other two vulcanizes, so that only one mean value at each temperature for this vulcanizate is shown. The 1 phr dicup vulcanizate shows a fairly large scatter of the results over the whole temperature range, with the values of energy input to break decreasing sharply at about approximately 110°C. The 2 phr Dicup vulcanizate shows a similar behavior to that of the sulfur vulcanizate described earlier, with a low variation in values of U_B except in the region of high scatter occurring over the range 45°–80°C. The 4 phr Dicup vulcanizate shows a slightly larger value of energy input to break at 21°C than for the rest of the temperatures, and possibly had the temperature of test been reduced still further, an effect similar to that shown with the other two vulcanizes might have been observed.

Although possibly more observations at each temperature should be made in order to ascertain accurately the distribution at each temperature, the variation of energy input to break with temperature obtained by changing the degree of crosslinking is demonstrated.   The behvaior can be summarized by stating that values of the energy input to break show less scatter as the degree of crosslinking is increased, and, secondly, the temperature at which the energy input drops sharply decreases with increasing crosslinking.
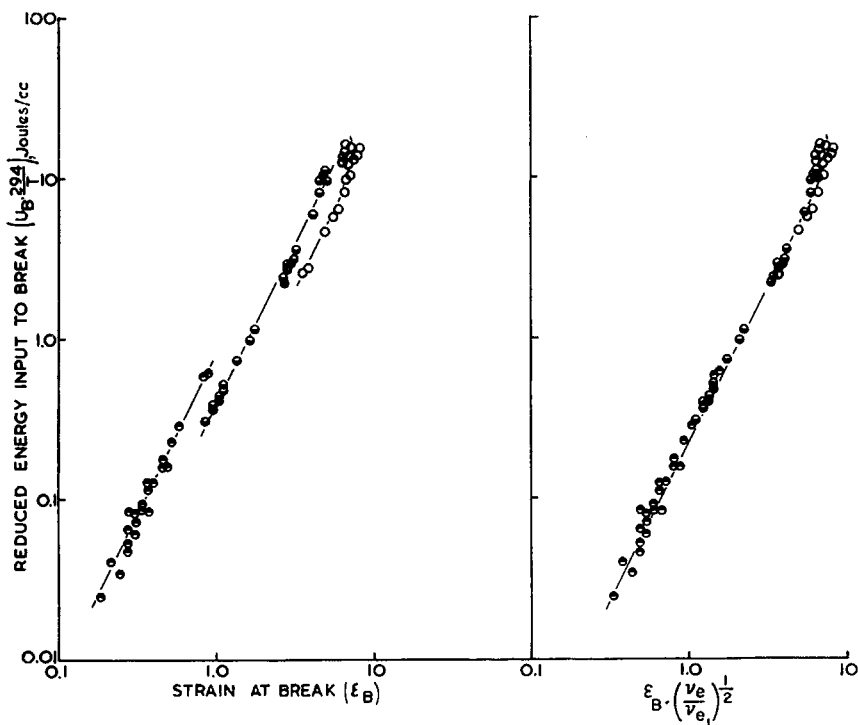

Fig. 12. Variation of reduced energy input to break with (a) strain at break and (b) strain at break multiplied by the ratio of ν_e values for three unfilled dicumyl peroxide-cured NR vulcanizates: (O) NR + 1 phr Dicup; (◐) NR + 2 phr Dicup; (◓) NR + 4 phr Dicup.

The variation of energy input to break with strain at break for the three dicup rubbers is shown in Figure 12a.   The results as shown before produce a square law relationship up to the finite extensibility of the network. It is seen that the failure lines of vulcanizates are displaced along the strain axis.   It is well known[17] that the maximum elongation of the rubber network is proportional to $N^{1/2}$ where N is the number of links in a monomer chain and is therefore inversely proportional to $\nu_e^{1/2}$, where ν_e is the number of chains per unit volume of the rubber network.   As the lines are parallel up to the maximum elongation, the strains up to this position should be in the ratios of their respective $\nu_e^{1/2}$ values.   Values of ν_e have been obtained
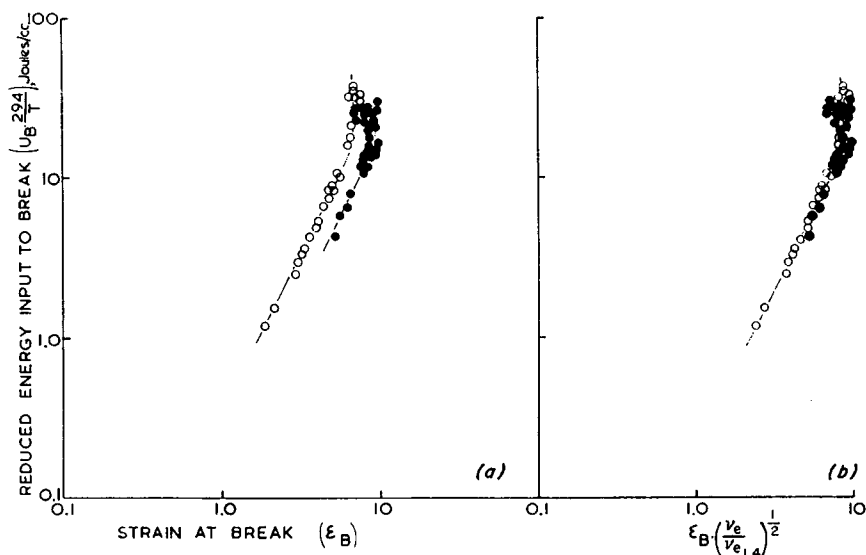
Fig. 13. Variation of reduced energy input to break with (a) strain at break and (b) strain at break multiplied by ratio of ν_e values for two polysulfide-cured NR vulcanizates: (●) NR + 1.4 phr S; (○) NR + 2.5 phr S.

by Porter[18] from measurements of C_1 in the well-known Mooney-Rivlin equation, and the ratios for the three dicup mixes are given as

$$\frac{\nu_{e4}}{\nu_{e1}} = 3.08$$

and

$$\frac{\nu_{e2}}{\nu_{e1}} = 1.67,$$

where ν_{e1} refers to the value of ν_e for the 1 phr dicup vulcanizate.

The strains at break for the 2 and 4 phr dicup rubbers have been multiplied by the square root of this ratio in Figure 12b. Agreement between the vulcanizates on this type of plot is shown to be good, and therefore the equation of the line for different crosslink densities can be expressed as

$$\left(\frac{294}{T}\right) \cdot U_B = C \cdot \frac{\nu_e}{\nu_{e1}} \cdot \epsilon_B{}^2 \qquad (6)$$

when the rubbers are referred to the 1 phr dicup vulcanizate, where C is a constant.

The peroxide-cured rubbers used were fully vulcanized so that all the dicumyl peroxide had been reacted. In the case of polysulfidic vulcanizates, however, all the sulfur is not used efficiently in the formation of crosslinks, and therefore it is necessary to ascertain whether eq. (6) still applies. Two polysulfide vulcanizates were chosen, and energy input to

break is plotted against strain in Figure 13a. The 2.5 phr sulfur–0.6 per CBS vulcanizate is the same rubber as that used in the previous sections, and the second vulcanizate contained 1.4 phr sulfur and 0.33 per CBS. The ratio of the ν_e values for these two vulcanizates[18] is 1.65, and the strains at break of the 2.5/0.6 phr vulcanizate have been multiplied by the root of this ratio in Figure 13b. The energies to break for the 1.4 phr sulfur vulcanizate remain very high even at 140°C, and therefore the superposition can only be applied over a small region but even so agreement is shown to be good. The equation to this line can be given as

$$\left(\frac{294}{T}\right) \cdot U_B = D \cdot \frac{\nu_e}{\nu_{e1.4}} \cdot \epsilon_B{}^2 \tag{7}$$

when referred to the 1.4 phr vulcanizate, where D is a constant.

It was shown earlier in the paper that the X-factor can be applied to superimpose gum and filler data for the 2.5 phr sulfur vulcanizate, eq. (4). Equations (4) and (7) can now be combined in eq. (8), which has general applicability to all sulfur-vulcanized rubbers of constant S/CBS ratio, both gum and filled:

$$\left(\frac{294}{T}\right) \cdot U_B = D \cdot \frac{\nu_e}{\nu_{e1.4}} \cdot X^2 \epsilon_B{}^2 \tag{8}$$

when referred to the 1.4 phr sulfur vulcanizate.

CONCLUSIONS

The failure criterion relating energy input to break and hysteresis over a range of temperature for amorphous rubbers applies only at very high and very low temperatures to a strain-crystallizing polymer such as natural rubber. Between these two temperature limits, the bulk properties of the rubber are not simply related to conditions occurring locally around a flaw, as the rubber sample is neither in a uniformly crystalline nor totally amorphous state. Tensile results within this region show a high amount of scatter. This behavior therefore has important practical consequences and makes it essential to obtain a statistical distribution at any temperature rather than take the mean of a few results.

Failure data from filled amorphous rubbers agree with data from unfilled rubbers when the former are expressed independently of time and temperature and corrected by a simple expression taking account of filler concentration, which is analogous to an expression in hydrodynamic theory. This paper has shown that when data from filler-loaded NR is corrected by the same expression, they agree fairly well with gum NR data, the agreement improving with increasing concentration of carbon black filler. This work has been extended to unfilled rubbers of differing crosslink densities, and a general expression has been derived unifying these data in terms of a crosslinking parameter from simple rubber elasticity theory. The lowest recorded values of energy input to break agree approximately with the theo-

retically calculated strength determined by the tearing energy approach, assuming a flaw size of 2.5×10^{-3} cm.

The superposition of gum and filler-loaded NR data by the hydrodynamic correction only occurs when the data are expressed independently of time and temperature, so that the temperature of the filled rubber at the same reduced energy input to break is always greater than that of the gum rubber. These results support the conclusions drawn in a recent investigation[4,19] on the effect of fillers in amorphous rubbers, that is, that the filler particles, or agglomerates of the filler particles, are surrounded by a shell or region of immobilized rubber. The adhesion between rubber and filler is stronger than the cohesion of the rubber continuum, and thus the interface remains unbroken when the rubber is stretched or the temperature is raised. However, the extent of the immobile region decreases with increasing temperature. The presence of this shell or region of different viscoelastic properties from the rubber continuum changes the viscoelastic temperature response of the gum rubber by introducing additional relaxation times.[20]

In the case of NR, the effect of the filler on the viscoelastic response is such that reinforcement is still apparent at temperatures above 100°C, unlike SBR and other amorphous polymers.

Appendix

Compounding Details of Vulcanizates Used in This Study[a]

SMR5 RSS	100	100	100	100	—	—	—	—	100	100	100	100
Polysar Krylene NS	—	—	—	—	100	100	100	100	—	—	—	—
Zinc oxide	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	—	—	—
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	—	—	—
Nonox HFN	1	1	1	1	1	1	1	1	1	—	—	—
Sulfur	2.5	2.5	2.5	2.5	2	2	2	2	1.4	—	—	—
CBS	0.6	0.6	0.6	0.6	1.1	1.1	1.1	1.1	0.33	—	—	—
Dicumyl peroxide	—	—	—	—	—	—	—	—	—	1	2	4
Dutrex R	—	—	—	—	—	3	6	8	—	—	—	—
HAF	—	30	60	80	—	30	60	80	—	—	—	—
Time of cure, min	40	40	40	40	60	60	60	60	40	60	60	60
Temp of cure, °C	140	140	140	140	140	140	140	140	140	150	150	150

[a] All figures, except for time and temperature, represent parts per hundred of rubber.

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