

Hysteresis and Strength of Rubbers

J. A. C. HARWOOD and A. R. PAYNE,

Natural Rubber Producers'

Research Association, Welwyn Garden City, Hertfordshire, England

Synopsis

A criterion of tensile failure in terms of energy density and energy loss at break has been developed for several gum rubbers over a wide range of test temperature. A similar description of failure in filled rubbers is related to the gum criterion by a simple elastic interaction term. The upper and lower limits of the failure equation are considered in detail, and the relationships of energy density at break with temperature and ultimate strain are also discussed.

INTRODUCTION

Tensile tests are widely used for studying the physical properties of rubber. Numerous attempts have been made to discover a satisfactory criterion of failure in tensile tests, and one of these has resulted in the concept of a "failure envelope,"¹⁻⁵ a unique curve peculiar to each polymer relating the stress at break (σ_b) to the strain at break (ϵ_b) over a wide range of temperature and rate of strain. These results led Smith to the conclusions that:

(1) The ultimate properties vary with temperature, because the internal viscosity of the polymer (or molecular friction coefficient) varies with temperature.

(2) The ultimate properties vary with strain rate, because the viscous resistance to network deformation increases with the rate.

(3) The temperature dependence of factors, such as the rate of bond rupture, have no significant effect on the temperature dependence of the ultimate properties.

However, failure envelopes do not explain why a material should fail under the conditions prevailing in a particular test, nor do they give insight into the role that polymer chain network configurations play in determining ultimate strength. One factor known to influence the strength of viscoelastic materials is hysteresis.⁶⁻⁸ This is the energy dissipated by the material during deformation, and Grosch et al.^{9,10} have shown that for several rubbers a simple relation exists between the work done (or energy density) to break (U_B) and the hysteresis at break (H_B). The investigation reported in this paper extends their work of studying the effect of varying the hysteresis by changing the temperature of test. Concurrently, the

effect of varying hysteresis by swelling has been investigated by Grosch,¹¹ resulting in conclusions similar to those reported here. In addition, this paper shows that filler-loaded rubbers obey a similar failure criterion.

EXPERIMENTAL

The rubbers studied in this investigation were unfilled vulcanizates of natural rubber (NR), isomerized natural rubber (INR), acrylonitrile butadiene rubber (ABR), styrene butadiene rubber (SBR), *cis*-1,4-polybutadiene rubber (BR), and butyl rubber. A series of filled vulcanizates of ABR with 10, 20, 30, 40, 60, and 80 pphr HAF carbon black were also examined. Details of the mixing and vulcanization times are given in the Appendix.

The test samples were in the form of rings 2.75 cm. i.d. and 2.90 o.d. cut from sheets 0.25 cm. thick. At temperatures above ambient they were extended on an Instron tensile tester, but at lower temperatures another tensometer was employed.¹² The temperature range was -50 to $+150^{\circ}\text{C}$. for the gum rubbers and 21 – 150°C . for the filled vulcanizates. The rate of strain was 200%/min. in every case. An average value of the breaking stress and strain of each rubber was obtained at the test temperature. A new sample of rubber was then extended to within a few per cent of the breaking stress and then retracted to zero stress at the same strain rate. The sample was then re-extended to break and, if the breaking stress exceeded the maximum stress in the cycle by more than a few per cent, the test was rejected. An exception to this technique arose with a crystallizing polymer. The work done on stretching (U_B) was obtained by measuring the area under the load-extension curve of the cycle, and a measure of the energy lost on stretching, or hysteresis, was likewise calculated by graphical integration of the area bounded by the extension and retraction curves.

ENERGY AS A FAILURE CRITERION

Gum Rubbers

It was reported earlier^{9,10} that the energy density to break U_B is simply related to the hysteresis at break H_B by the expression

$$U_B = KH_B^{2/3} \quad (1)$$

This expression clearly shows that the more energy a rubber can dissipate on stretching, the more energy the rubber can withstand before breaking.

Figure 1 shows U_B as a function of H_B for the SBR gum vulcanizate, plotted on a double logarithmic scale. These data are described by eq. (1) over the temperature range employed. The figure also shows hysteresis and energy density measured at different maximum strains below the breaking strain at a number of test temperatures. These results clearly fall below the failure line, illustrating that eq. (1) is a sensitive criterion of failure.

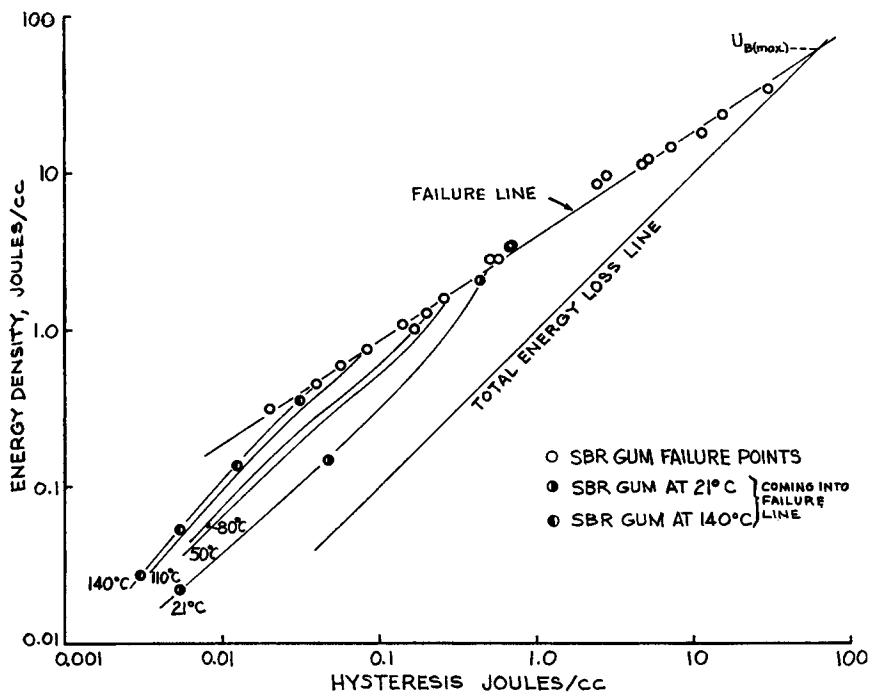


Fig. 1. Energy density as a function of hysteresis for SBR gum vulcanizate at different temperatures.

Similar results are shown in Figure 2 for the ABR gum vulcanizate. However, at temperatures approaching the vulcanization temperature of the rubber ($140^{\circ}\text{C}.$), the failure results do not follow eq. (1), the measured hysteresis being slightly greater than that expected. Nevertheless, eq. (1) describes the failure data of the other amorphous rubbers over the complete temperature range employed and also the failure data of the slightly strain-crystallizing *cis*-1,4-polybutadiene rubber. The expression is also obeyed to a limited extent by NR, which crystallizes readily at strains above 300%, and whose optimum crystallization rate occurs at $-26^{\circ}\text{C}.$; the temperature ranges over which eq. (1) is applicable are below about $+60^{\circ}\text{C}.$ and above about $+140^{\circ}\text{C}.$ This anomalous behavior of NR and its consequential effects on strength have been described in detail in an earlier publication.¹³

The failure equations for the individual rubbers were calculated from the data by the method of least squares and are listed in Table I. The standard errors of the equation constants and the coefficient of correlation of H_B and U_B are also quoted.

It is clear that the index of H_B is $2/3$ in every case, but the constant of the equation varies with the rubber. The results for ABR and butyl differ from those quoted in an earlier publication.¹⁰ In the present investigation more data have been included in the case of butyl, but the anomalous

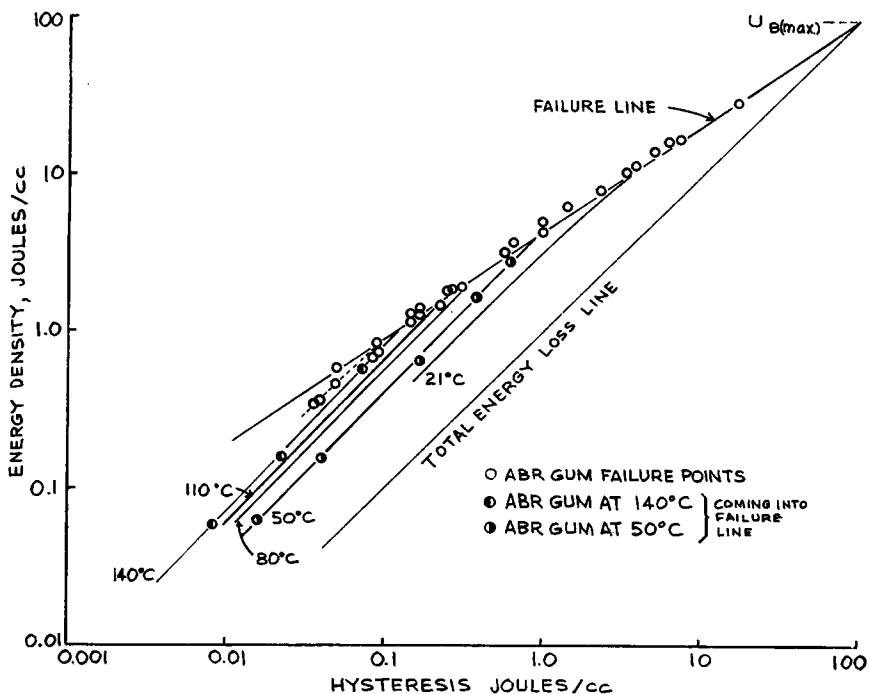


Fig. 2. Energy density as a function of hysteresis for ABR gum vulcanizate at different temperatures.

high-temperature results described earlier for ABR have been excluded. The failure equations for these two rubbers now conform with the general expression.

The failure eq. (1) can be rewritten in terms of the hysteresis ratio h :

$$U_B = K^3 h^2 \quad (2)$$

where $h = H_B/U_B$. The constant K^3 has the dimensions of energy and is the value of U_B in eq. (2) when h is unity (i.e., when $U_B = H_B$). This represents the experimental condition at which all the applied energy

TABLE I

Rubber	Failure equation	Correlation coefficient
SBR	$\log U_B = (0.668 \pm 0.010) \log H_B + (0.593 \pm 0.010)$	0.997
ABR	$\log U_B = (0.665 \pm 0.055) \log H_B + (0.666 \pm 0.036)$	0.993
BR	$\log U_B = (0.664 \pm 0.000) \log H_B + (0.653 \pm 0.014)$	0.997
Butyl	$\log U_B = (0.658 \pm 0.014) \log H_B + (0.362 \pm 0.017)$	0.995
INR (and NR)	$\log U_B = (0.670 \pm 0.017) \log H_B + (0.692 \pm 0.025)$	0.994

would be dissipated and appears to represent an upper boundary condition to eqs. (1) and (2). This is denoted in Figures 1 and 2 by $U_{B(\max)}$. Thus, eq. (2) may be expressed as

$$U_B = U_{B(\max)} h^2 \quad (3)$$

Filled Rubbers

Figure 3 shows a plot of energy density to break, U_B , versus hysteresis H_B for the ABR gum vulcanizate and vulcanizates with 20, 40, 60, and 80 pphr HAF carbon black. The slope is still $2/3$, but the filled results follow straight lines displaced from the gum results except at low temperatures. For the same value of U_B the hysteresis increases with the concentration of the filler. This additional loss of energy arises because the filler particles are inextensible, and the overall strain of the sample is less than the actual strain in the rubber phase. Mullins and Tobin¹⁴ suggested that in filled rubbers the modulus of the rubber phase is increased by a factor X , which takes account of both the disturbance of the strain distribution and the absence of deformation in that fraction of material composed of filler. They considered the relation

$$X = \sigma/E_0\epsilon = E/E_0 = 1 + 2.5c + 14.1c^2 \quad (4)$$

where ϵ is the strain produced by the stress σ , E_0 is the modulus of the rubber without filler, and c is the volume concentration of the filler. This expression is identical with the relationship derived by Guth and Simha^{15,16} and Gold¹⁷ for small spherical particles in an elastic medium. Applying the X factor to the abscissa in Figure 3 brought the failure points into rea-

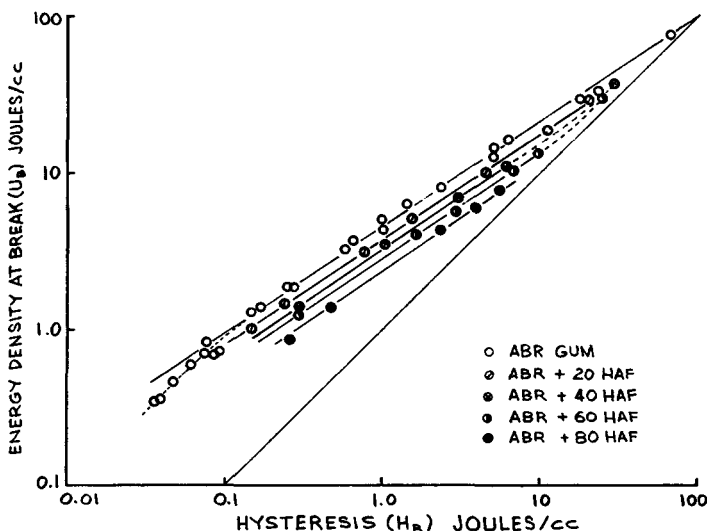


Fig. 3. Energy density at break as a function of hysteresis at break for unfilled and filler-loaded ABR vulcanizates.

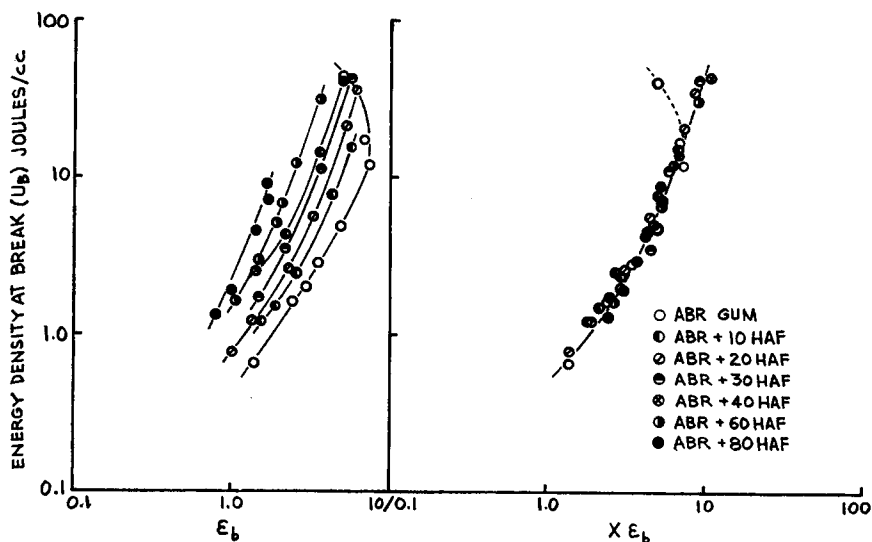


Fig. 4. Energy density at break as a function of (a) strain at break, ϵ_b and (b) $X\epsilon_b$.

reasonable coincidence with the results from the unfilled rubber. Thus the general expression for filled and unfilled rubbers at break becomes

$$U_B = K(H/X)^{2/3} \quad (5)$$

In terms of hysteresis ratio this becomes

$$U_B = K^3(h/X)^2 \quad (6)$$

However, the shift calculated from eq. (4) tended to overcorrect slightly the data from ABR containing different concentrations of HAF carbon black.

The anomaly in filled rubbers at low temperatures, referred to earlier, arises when the hysteresis exhibited by the gum rubber is such that

$$H_B/U_B \geq 1/X$$

for under these conditions an amplification of hysteresis in the gum rubber by a factor X would produce the unlikely situation of

$$H_B/U_B > 1$$

This points to the elastic interaction correction's being too large at low temperatures when the moduli of the filler and rubber phases approach parity.¹⁸

It is informative to plot U_B as a function of the strain to break ϵ_b for both the filled and unfilled rubbers (Fig. 4a). This is similar to the approach of Smith² and others,¹⁹ who plotted the real stress at break $\sigma_b(1 + \epsilon_b)$ as a function of ϵ_b , obtaining the so-called failure envelopes. The ultimate strain passes through a maximum at a temperature of approximately 21°C., and Smith and other investigators^{3,20} have shown that the maximum

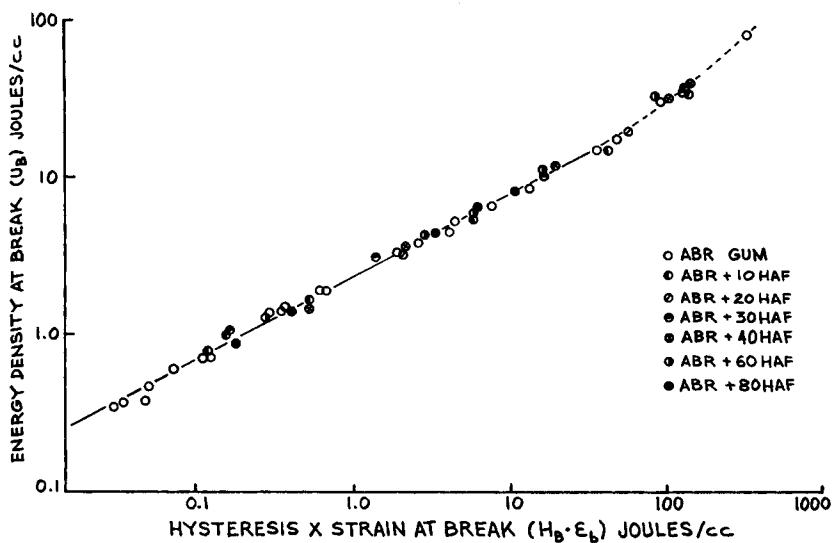


Fig. 5. Energy density at break as a function of the product of hysteresis and strain at break.

ultimate strain ratio $\lambda_{b(\max)} = 1 + \epsilon_{b(\max)} \approx N^{1/2}$, where N is the statistical number of freely rotating segments in a rubber chain between crosslinks, and $N^{1/2}$ is the apparent maximum extensibility of an ideal rubber network.

By applying the X factor to the strain axis in Figure 4a the data for the filled rubbers coincide with the results from the unfilled rubber, for temperatures above that at which $\epsilon_{b(\max)}$ is observed (Fig. 4b). At lower temperatures the results do not coincide, and this is possibly a reflection of the anomaly previously referred to. Alternatively, it could reflect a reduction in the *effective* number of freely rotating segments (N) as the temperature is reduced.²¹ However, for the temperature range above 21°C. over which agreement is good the data in Figure 4b can be expressed as

$$U_B = A(\epsilon_b X)^2 \quad (7)$$

Combining eqs. (5) and (7) eliminates the X factor and its associated uncertainties, and the general expression for filled and unfilled results is

$$U_B = B(H_B \epsilon_b)^{1/2} \quad (8)$$

where B is a constant. The results plotted in this form are shown in Figure 5. This general expression, unlike eq. (5), is not a very sensitive criterion of failure, but it does emphasize that the strengths of filled and unfilled rubbers can be unified by considering hysteresis.

DEPENDENCE OF U_B ON TEMPERATURE

The earlier sections have described the dependence of energy density at break on hysteresis as the temperature is changed. It is also useful to ex-

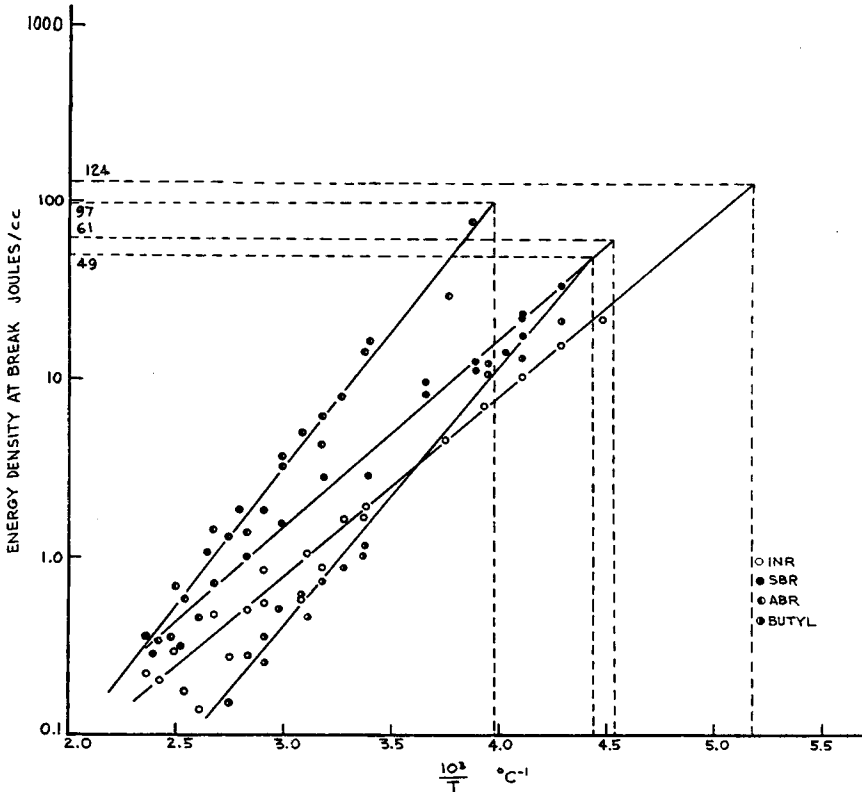


Fig. 6. Energy density at break as a function of reciprocal absolute temperature for INR, SBR, ABR, and butyl rubber.

amine how the energy density at break varies with temperature. If $\log U_B$ is plotted as a function of reciprocal absolute temperature (Fig. 6) the following general expression can be derived:

$$U_B = K' \exp \{C/T\} \tag{9}$$

where C is the slope of the plot. The temperature at which $U_B = U_{B(max)}$ is found to be the glass transition temperature T_g of the individual rubber, $U_{B(max)}$ being the upper boundary condition to eqs. (1) and (2). This is clearly shown in Figure 6. Hence

$$U_{B(max)} = K' \exp \{C/T_g\} \tag{10}$$

and combining eqs. (9) and (10) gives the following expression:

$$U_B = U_{B(max)} \exp \{C(1/T - 1/T_g)\} \tag{11}$$

If eq. (11) is considered analogous to the Vant Hoff isochore, then the constant C (the gradient of the plot) may be expressed as δ/R , where δ is an apparent activation energy and R is the gas constant. Equations (9)

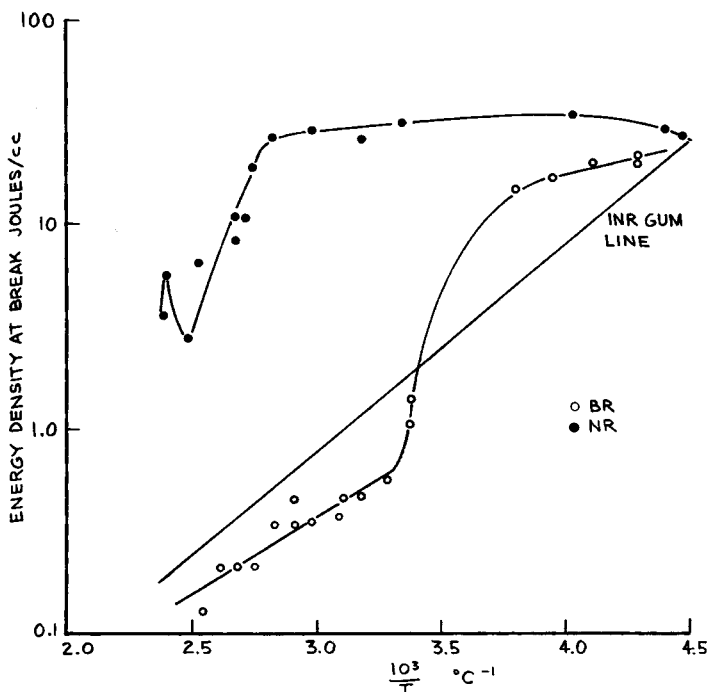


Fig. 7. Energy density at break as a function of reciprocal absolute temperature for NR and BR.

and (11) do not describe the results from either NR or BR (Fig. 7), showing that these expressions are more sensitive to the effects of crystallization than eq. (1).

The values of $U_{B(\max)}$ and δ/R for the different rubbers, together with their respective glass transition temperatures, are presented in Table II.

TABLE II

Rubber	$U_{B(\max)}$, joules/cm. ³	δ/R , joules-°C./cm. ³	T_g , °C.
SBR	61	5.7×10^2	-53
ABR	97	8.3×10^2	-22
BR	88	—	—
Butyl	49	8.3×10^2	-48
INR	124	5.5×10^2	-80

Because $U_{B(\max)}$ appears to represent the maximum energy a rubber can withstand before failure, it is likely that it reflects the cohesive forces between the molecules. In fact, as far as can be ascertained, the values listed in Table II rank in the same order as the cohesive-energy densities of the rubbers.

LIMITS TO THE FAILURE EQUATION

A failure criterion in terms of energy density and energy loss at break has been derived for several rubbers and applies over a wide range of temperature. As the temperature is lowered, the hysteresis ratio and energy density at break exhibited by the rubber increase, and the energy density approaches a maximum $U_{B(\max)}$. This apparently occurs at the glass-transition temperature and when the rubber is completely hysteretic. As the temperature is raised, the energy density at break and the hysteresis ratio decrease, and the highest practical test temperature gives values of U_B of approximately 0.15 joules/cm.³.

At this temperature the rubber is almost elastic, the hysteresis ratio being only 0.05. It is interesting to compare this lowest measured value of energy density, $U_{B(\min)}$, with theoretical values calculated from molecular bond strengths, assuming the rubbers to be elastic.

Theoretical Calculation of $U_{B(\min)}$

Method 1. Using a solution obtained by Inglis,²² Griffith^{23,24} calculated the change in elastically stored energy for the case of an elliptical hole in a deformed metal plate, the deformation stress acting normal to the major axis of the ellipse. He calculated the critical stress on the plate σ_b required to extend the hole, in terms of the crack length, $2c$, to be

$$\sigma_b = (2\gamma E/\pi c)^{1/2} \quad (12)$$

where E is Young's modulus of the metal and γ is the energy required to produce unit area of new surface by the growth of the hole. This solution for elastic materials can be applied to rubbers at high temperatures, when they exhibit very little hysteresis. However, it is first necessary to obtain a value for γ . The concentration of molecular chains in a rubber is approximately 1 chain per 20 Å.², giving 5×10^{14} chains cm.⁻², and the dissociation energy of a single carbon bond is approximately 80 kcal./mole. The number of moles represented by 5×10^{14} chains cm.⁻² is $(5 \times 10^{14})/N$ where N is Avogadro's number.

Thus the energy required to form 1 cm.² of new surface (γ) is approximately 2.8×10^3 ergs.

At high temperatures the stress-strain curves of rubber approximate to straight lines, and this eq. (12) can be rewritten in terms of work done, or energy density to break, U_B :

$$U_B = \sigma_b \epsilon_b / 2 = \gamma / \pi c \quad (13)$$

For NR it has been calculated²⁵ that the cut length c is 2.5×10^{-3} cm. and thus

$$U_B = 3.6 \times 10^5 \text{ ergs/cm.}^3 = 0.036 \text{ joules/cm.}^3$$

and for SBR with $C = 5.5 \times 10^{-3}$ cm.

$$U_B = 0.016 \text{ joules/cm.}^3$$

Method 2. Another method of calculating the energy at break for a highly elastic rubber is to use the expression derived by Lake and Thomas²⁶ for the tearing energy T_0 :

$$T_0 = (2/3\pi)^{1/2} \cdot (\gamma\rho Uln^{1/2}/m) \quad (14)$$

where, for a typical vulcanizate NR, ρ = the density = 1 g. cm.⁻³, γ^2 = the ratio of the lengths of the statistical link and the monomer unit = 2.25, U = the energy required to break one monomer in a single chain, 4–15 $\times 10^{-12}$ ergs, l = the length of a monomer unit = 5×10^{-8} cm., n = the statistical number of monomer units between crosslinks = 100, m = the mass of a monomer unit = 10^{-22} g. Thus T_0 = 1.4×10^4 to 5.2×10^4 ergs, depending on which value of U is used.

The dependence of T_0 on flaw size C has been shown to be²⁵

$$T_0 = 2\pi U_B C \quad (15)$$

for tensile tests.

Assuming T_0 values shown above and values for C , as in method 1,

$$U_B \text{ for NR} = 0.09 - 0.33 \text{ joules/cm.}^3$$

$$U_B \text{ for SBR} = 0.041 - 0.152 \text{ joules/cm.}^3$$

These calculated values of U_B are very similar to the lowest measured values obtained at high temperatures and reflect the high elasticity of the network prevailing under these conditions, but the calculations do not take account of the configurational energies associated with the energy barriers impeding free rotation of segments of the backbone chain. At high temperatures these energy barriers are relatively low, but their relative size increases with decreasing temperature and must first be overcome, before a chain or network between crosslinks is fully extended. Furthermore, the molecular mobility of the chain segments depends, not only on the intrinsic flexibility of each chain segment, but also on the interaction between adjacent chains. Again, at high temperatures or high swelling ratios these interactions are very small, but they become very large near the glass transition temperature of the rubber.

By taking account of this lower limit, $U_{B(\min)}$, eq. (11) can be rewritten as

$$U_B = U_D + U_{B(\min)} = U_{B(\max)} \exp \{ \delta/R(1/T - 1/T_g) \} \quad (16)$$

where U_D is the energy of deformation and becomes negligible at temperatures approximately 200°C. above the glass transition temperature T_g .

CONCLUSIONS

This paper describes a unique expression relating the energy density at break, U_B , to the hysteresis at break, H_B . This criterion of failure is strain-sensitive and is applicable to all the amorphous rubbers examined over temperatures ranging from the temperature of vulcanization to near

the glass transition temperature. For strongly crystallizing NR the criterion is limited to the extremes of this temperature range.

By plotting U_B as a function of absolute temperature it is apparent that the experimental data extrapolate to two limits: an upper limit, occurring at the glass transition temperature, when the rubber is completely hysterical, and a lower limit at high temperatures, when the rubber is elastic. The upper limit is thought to reflect the cohesive-energy density of the rubber; the lower limit can be calculated from bond dissociation energies and inherent flaw size, assuming the absence of energy loss mechanisms.

The presence of fillers in the amorphous rubber vulcanizates merely modifies the failure equations by a hydrodynamic factor. However, if U_B is expressed as a function of hysteresis and extension at break, the filled and unfilled rubbers yield coincident curves without the necessity of recourse to hydrodynamic or other corrections.

Appendix: Compounding Details

Gum vulcanizates						
Rubber	NR	INR	SBR	BR	ABR	Butyl
RSS (SMR5)	100					
Isomerized NR		100				
Polysar Krylene NS			100			
Cis 4				100		
Polysar Krynac 801					100	
Polysar Butyl 400						100
ZnO	3.5	3	3.5	3.5	3	5
Stearic Acid	2.5	1	2.5	2.5	0.5	1.5
PBN	1	1	1			
Nonox HFN				1	1	1
Sulfur	2.5	1.45	2	2	1.5	2
CBS	0.6	0.4	1.1	0.6		
TMT						1
MBTS					1.5	1.5
Time cure, 140°C., min.	40	35	60	60	60	
Time cure, 153°C., min.						40
Filled vulcanizates						
	ABR gum mix shown above with:					
	1	2	3	4	5	7
Diocetyl sebacate	1	2	3	4	5	7
HAF Black	10	20	30	40	60	80
Cured for 25 min. at 153°C.						

This work forms part of the program of research undertaken by the Natural Rubber Producers' Research Association, and the authors wish to thank R. Whittaker for experimental assistance.

References

1. T. L. Smith, *J. Polymer Sci. A*, **1**, 3597 (1963).
2. T. L. Smith, *J. Appl. Phys.*, **35**, 27 (1964).
3. T. L. Smith and J. E. Frederick, *J. Appl. Phys.*, **36**, 2996 (1965).
4. J. C. Halpin, *J. Appl. Phys.*, **35**, 3133 (1964).
5. J. C. Halpin and F. Bueche, *J. Appl. Phys.*, **35**, 3142 (1964).
6. R. F. Landel and R. F. Fedors, in *Fracture Processes in Polymeric Solids*, B. Rosen, Ed., Interscience, New York, 1964, Ch. IIIB.
7. K. A. Grosch and L. Mullins, *Rev. Gen. Caoutchouc*, **39**, 1781 (1962).
8. F. R. Eirich, in *High Speed Testing, Vol. V (Appl. Polymer Symp., No. 1)*, A. G. H. Dietz and F. R. Eirich, Eds., Interscience, New York, 1965, p. 271.
9. K. Grosch, J. A. C. Harwood, and A. R. Payne, *Nature*, **212**, 497 (1966).
10. K. A. Grosch, J. A. C. Harwood, and A. R. Payne, presented in *Inst. Phys. Phys. Soc. Conf. Ser.*, No. 1, p. 144.
11. K. A. Grosch, *J. Appl. Polymer Sci.*, **12**, 915 (1968).
12. A. Schallamach, D. B. Sellen, and H. W. Greensmith, *Brit. J. Appl. Phys.*, **16**, 241 (1965).
13. J. A. C. Harwood and A. R. Payne, *J. Appl. Polymer Sci.*, **11**, 1825 (1967).
14. L. Mullins and N. R. Tobin, *J. Appl. Polymer Sci.*, **9**, 2993 (1965).
15. E. Guth and R. Simha, *Kolloid-Z.*, **74**, 266 (1936).
16. E. Guth, *J. Appl. Phys.*, **16**, 20 (1945), and *2nd Rubber Technol. Conf. (London)*, 353 (1948).
17. O. Gold, Thesis, Vienna, 1937.
18. R. F. Landel, *Trans. Soc. Rheol.*, **2**, 53 (1958).
19. F. N. Kelley, in *High Speed Testing, Vol. V (Appl. Polymer Symp., No. 1)*, A. G. H. Dietz and F. R. Eirich, Eds., Interscience, New York, 1965, p. 274.
20. J. C. Halpin, *J. Appl. Phys.*, **36**, 2975 (1965).
21. J. A. C. Harwood and A. Schallamach, *J. Appl. Polymer Sci.*, **11**, 1835 (1967).
22. C. E. Inglis, *Trans. Inst. Naval Arch. London*, **55**, 219 (1913).
23. A. A. Griffith, *Phil. Trans. Roy. Soc. (London)*, **A221**, 163 (1921).
24. A. A. Griffith, *Proc. Intern. Congr. Appl. Mech. (Delft)*, 55 (1924).
25. G. J. Lake and P. B. Lindley, *J. Appl. Polymer Sci.*, **9**, 1233 (1965).
26. G. J. Lake and A. G. Thomas, *Kautschuku. Gummi*, **20**, 211 (1967).

Received July 21, 1967

Revised August 29, 1967