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The Mechanical Fatigue Limit for Rubber

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Synopsis

Investigations of the dynamic cut growth behavior of vulcanized rubbers indicate that there is a minimum tearing energy at which mechanical rupture of chains occurs. The limiting value is characteristic of each vulcanizate, but is in the region of 0.05 kg./cm. The mechanical fatigue limit, below which the number of cycles to failure increases rapidly, is accurately predicted from this critical tearing energy. Characteristics of cut growth at low tearing energies, and effects of polymer, vulcanizing system, oxygen, and fillers on the critical tearing energy and fatigue limit are discussed.

INTRODUCTION

Previous publications[1,2] have shown that, in the absence of heat build-up, fatigue failure of rubber strips undergoing repeated extensions is due to the growth of small flaws which are initially present in the rubber. These papers dealt with fairly high extensions, the flaw or cut growth being due to mechanical rupture of chains, considerably enhanced by oxygen.[3,4]

The present paper is concerned with cut growth and fatigue at small deformations, akin to those which are met with by many rubber components in practice. Although the duration of some experiments at these small deformations was quite long, no significant effects of aging were found (Appendix I). Experimental procedure is described below. As before, the rate of cut growth is related to the tearing energy—the elastic energy dissipated by cut propagation.

The experiments suggest that there is a minimum tearing energy T_0 at which "mechanico-oxidative" cut growth can occur. At tearing energies less than T_0 cut growth is attributable solely to chemical attack by ozone and is normally very much slower than mechanico-oxidative cut growth. Corresponding to T_0 it is found that there is a critical strain in fatigue tests below which the number of cycles to failure increases rapidly. This critical strain thus constitutes a mechanical fatigue limit for rubber, which is analogous to the fatigue limit found in metals.

Determinations of the critical tearing energy and mechanical fatigue limit for various vulcanizates and polymers are discussed, together with other features of cut growth at low tearing energies.

EXPERIMENTAL PROCEDURE

Cut growth measurements were carried out on thin strips of rubber normally 2.5 cm. wide, approximately 1 mm. thick, and of length at least four times the width (Fig. 1). A small cut, about 0.5 mm. in length, was inserted in one edge of each test piece, as nearly as possible perpendicular to both the major and minor surfaces. The test piece was then deformed in simple extension by repeated cycling to a fixed maximum extended length. As in the previous studies,[1,2] the tests were carried out in the laboratory at a frequency of 100–130 cycles/min., the test pieces being relaxed to zero strain on each cycle. Readings of cut length c in the unstrained state (Fig. 1) were made after a suitable number of cycles n enabling the cut growth rate dc/dn to be determined. (In practice the test piece was slightly strained to facilitate observation.) For this type of test piece the tearing energy is given by[5]

$$T = 2kWc \tag{1}$$

where W is the strain energy per unit volume in the bulk of the test piece and k a slowly varying function of strain.[6]

The strain energy density was determined as a function of strain by numerical integration of the stress–strain curve, enabling tearing energy to be determined from the measured values of cut length and strain and the known value of k.[6] Cut growth rate is referred to the tearing energy at the maximum strain of the cycle. (A detailed description of the determination of cut growth rate and tearing energy was given elsewhere.[1])

To avoid failure at the clamps, dumbbell test pieces were used for fatigue measurements, strain being measured on the central parallel-sided section

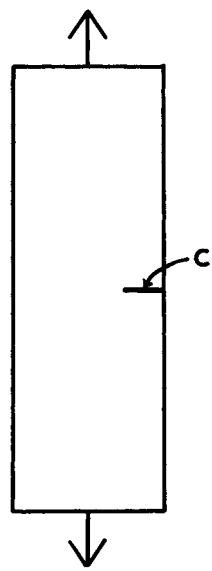

Fig. 1. Tensile cut growth test piece.

TABLE I

	Vulcanizate								
	A	B	C	D	E	F	G	H	J
Components, parts by weight									
cis-Polyisoprene (natural rubber RSS1)	100	100	—	—	—	—	—	—	—
Butadiene/styrene copolymer, 28% bound styrene (SBR Polysar S)	—	—	100	—	—	—	—	—	—
trans-Polyisoprene, 60% *trans* (isomerized natural rubber)	—	—	—	100	—	—	—	—	—
cis-Polyisoprene (synthetic, Shell Isoprene)	—	—	—	—	100	—	—	—	—
Polychloroprene (Neoprene WRT)	—	—	—	—	—	100	—	—	—
Butadiene/acrylonitrile copolymer (Hycar 1002)	—	—	—	—	—	—	100	—	—
Polyisobutylene (Polysar Butyl 400)	—	—	—	—	—	—	—	100	—
cis-Polybutadiene (Phillips Cis-4)	—	—	—	—	—	—	—	—	100
Zinc oxide	5	0.5	5	5	3.5	5	3	5	3.5
Zinc stearate	—	1.5	—	—	—	—	—	—	—
Stearic acid	2	0.5	2	2	2.5	0.5	0.5	1	2.5
Sulfur	2.5	2.0	1.75	2.5	2.5	—	1.5	2	2.0
Magnesium oxide	—	—	—	—	—	2	—	—	—
N-Cyclohexyl-2-benzthiazyl sulfenamide (CBS)	0.6	—	1.0	0.4	0.6	—	—	—	0.6
2-Mercaptobenzthiazole (MBT)	—	—	—	—	—	—	—	1	—
Dibenzthiazyl disulfide (MBTS)	—	—	—	—	—	—	1	—	—
Blend of MBT and a dithiocarbamate (Vulcafor DHC)	—	0.375	—	—	—	—	—	—	—
Tetramethylthiuram disulfide (TMTD)	—	—	—	—	—	—	—	1	—
2-Mercaptoimidazoline (NA-22)	—	—	—	—	—	0.35	—	—	—
Phenyl-β-naphthylamine (PBN)	1.0	—	1.0	—	—	2	—	—	—
90% PBN plus 10% diphenyl *p*-phenylene-diamine (Nonox HFN)	—	—	—	—	1.0	—	—	—	1.0
Phenol condenation product (Nonox EX)	—	1.0	—	—	—	—	—	—	—
Vulcanization conditions									
Time, min.	40	10	50	40	40	20	30	20	40
Temperature, °C.	140	140	140	140	140	153	155	150	140
Properties Young's modulus, kg./cm.^{2}	20	10	16	25	17	16	20	11	20
Tensile strength, kg./cm.^{2}	275	260	27	15	230	130	36	18	27

The number of cycles to failure, or fatigue life, was determined as a function of the maximum strain of the cycle, the frequency again being within the range 100–130 cycles/min.

In determining strain, and hence strain energy density, allowance was made for set occurring during the course of both cut growth and fatigue measurements.

Details of vulcanizates used are given in Table I.

CUT GROWTH AT LOW TEARING ENERGIES

Natural Rubber

In the previous study[1] the cut growth rate of a natural rubber vulcanizate (A) was shown experimentally to be approximately proportional to the square of the tearing energy for tearing energies ranging from about 0.1 to 10 kg./cm.* The experimental points showed some deviation from a

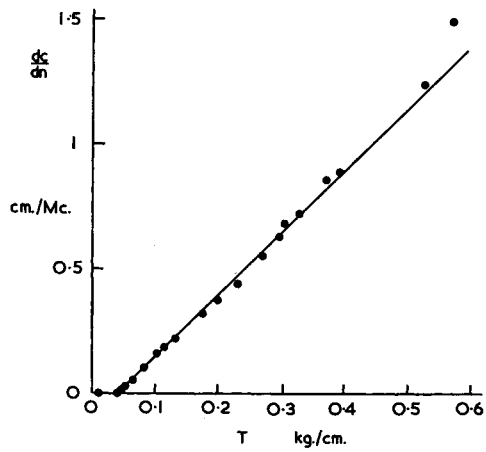

Fig. 2. Cut growth rate dc/dn vs. tearing energy T for a natural rubber gum vulcanizate (A) having a Young's modulus of 20 kg./cm.^{2} (linear scales).

square law toward each end of this range. At the upper end the deviation was attributed to proximity to the catastrophic tearing energy T_c, at which the cut growth rate approaches infinity,[5] and we will show that the deviation at the lower end is due to a change in the dependence of cut growth rate on tearing energy. Results for vulcanizate A at low tearing energies are shown in Figure 2, where cut growth rate dc/dn is plotted against tearing energy T on linear scales.

Two features of Figure 2 are noteworthy. Firstly, dc/dn varies substantially linearly with T below about 0.5 kg./cm., and secondly this linear relationship intercepts the T axis at a finite value of about 0.04 kg./cm. A positive intercept on the T axis occurs for all rubbers ex-

* Surface energies of kg. cm./cm.^{2} are abbreviated throughout to kg./cm.

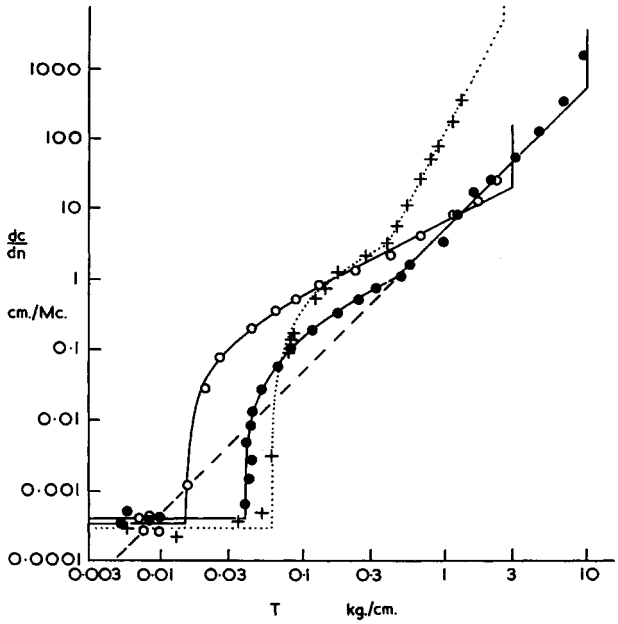

Fig. 3. Full cut growth characteristics (logarithmic scales): (●) vulcanizate A; (○) vulcanizate B; (+) vulcanizate C (SBR). The lines represent eqs. (2)–(6). Values of the constants are given in Table II.

amined; it is denoted by T_0. Some cut growth does, in fact, occur at tearing energies below T_0. As will be discussed in a later paper,[7] it is solely attributable to ozone, and the rates of growth r are substantially independent of tearing energy. We therefore interpret T_0 as the minimum tearing energy at which mechanico-oxidative cut growth occurs.

The full extent of the cut growth characteristic for vulcanizate A is shown more clearly in Figure 3, where dc/dn is plotted against T on logarithmic scales. Above a cut growth rate of 0.01 cm./Mcycle, the points represent averages of 6–10 experimental results; at lower rates individual points are shown, since fewer results were obtained here owing to the very long time scales involved.* The full line represents an empirical approximation to the results. It has the form

$$dc/dn = r \qquad T \leqslant T_0 \qquad (2)$$

$$dc/dn = A(T - T_0) + r \qquad T_0 \leqslant T \leqslant T_t \qquad (3)$$

$$dc/dn = BT^2 \qquad T_t \leqslant T < T_c \qquad (4)$$

$$dc/dn = \infty \qquad T = T_c \qquad (5)$$

* For example, for the results obtained at a cut growth rate of about 4×10^{-4} cm./Mcycle, 6 months continuous running at 100 cycles/min. was necessary to obtain an increase in cut length of 0.1 mm. No significant effects of aging were found, even for these long-term tests (Appendix I).

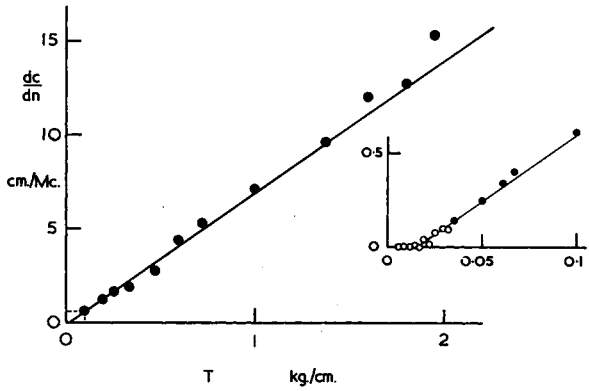

Fig. 4. Cut growth rate dc/dn vs. tearing energy T for a natural rubber gum vulcanizate (B) having a Young's modulus of 10 kg./cm.^{2} (linear scales). The inset shows the region close to T_0 (enlarged scales): (●) average points; (O) individual points.

where r, A, and B are rate of growth constants, T_0 is the minimum tearing energy for mechanico-oxidative cut growth, T_t is a transition tearing energy at which the dependence of cut growth rate on T changes from linear to square law, and T_c is the catastrophic tearing energy at which rupture occurs virtually instantaneously.[5] Experimental values of the constants for vulcanizate A are given in Table II.

TABLE II
Cut Growth and Tearing Energy Constants

	Vulcanizate A	Vulcanizate B	Vulcanizate C
r, cm. Mcycle^{-1}	4×10^{-4}	3.5×10^{-4}	3×10^{-4}
T_0, kg. cm.$^{-1}$	0 04	0.017	0.06
A, cm. Mcycle^{-1}/kg. cm.$^{-1}$	2.5	7	10
T_t, kg. cm.$^{-1}$	0.45	—	0.4
B, cm. Mcycle^{-1}/kg.^{2} cm.$^{-2}$	5	—	—
D, cm. Mcycle^{-1}/kg.^{4} cm.$^{-4}$	—	—	130
T_c, kg. cm.$^{-1}$	10	3	2.5

Above T_t (0.45 kg./cm.) the full line, represented by eqs. (4) and (5), and experimental points are those given in Figure 5 of an earlier paper. The broken line in Figure 3 of the earlier study represents the extension of this square law relationship to tearing energies below T_t. However a better approximation in the region from T_0 to T_t is given by the full line based on the linear relationship of eq. (3). Many more tests have now been carried out enabling better averages to be obtained, and the points in this region differ slightly from but include the results given previously.[1] The scatter of the individual results corresponds, at most, to a factor of about 2 in rate of growth throughout the whole of the tearing energy range, except at tearing energies close to T_0 where dc/dn varies very rapidly with T. Scatter

of this magnitude appears to be inherent in the cut growth (and hence fatigue) properties of natural rubber, but is very small compared with the overall variation in cut growth rate of about ten million.

The very rapid increase in rate as the tearing energy exceeds T_0 (Fig. 3) indicates that a major contribution to cut growth has commenced. The contribution of ozone cut growth r to the total growth rapidly becomes negligible once T_0 is exceeded (Fig. 3).

Although the cut growth rate for vulcanizate A varies substantially linearly with T at low tearing energies (Fig. 2) it is evident from Figure 3 that a square law is a fairly good approximation, even at low tearing energies. However, investigation of other natural rubber vulcanizates has shown that a square law does not hold in general. For example the cut growth rate of vulcanizate B varies linearly with T up to the vicinity of the catastrophic tearing energy T_c (Fig. 4). The results are replotted on logarithmic scales in Figure 3. The cut growth characteristic can again be described by eqs. (2)–(5), except that eq. (4) is no longer required, since for practical purposes the upper tearing energy limit for eq. (3) becomes T_c instead of T_t. Values of the constants are given in Table II.

As in the case of vulcanizate A, the experimental results for vulcanizate B indicate a tearing energy T_0 (smaller in magnitude than that of vulcanizate A) below which mechanico-oxidative cut growth does not occur.

Styrene–Butadiene Rubber

We showed experimentally in an earlier study[2] that for a noncrystallizing styrene–butadiene(SBR) vulcanizate (C) the cut growth rate was approximately proportional to T^4 for moderate and high tearing energies. SBR thus differs from natural rubber, for which dc/dn is proportional to T or T^2 at these tearing energies. However, investigation of vulcanizate C at

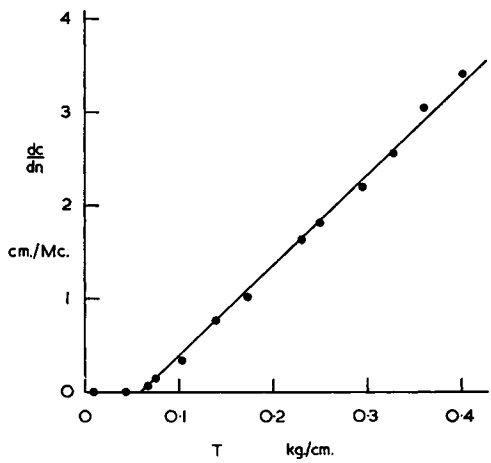

Fig. 5. Cut growth rate dc/dn vs. tearing energy T for SBR gum vulcanizate C (linear scales).

lower tearing energies has shown that, similarly to natural rubber, a T_0 value exists immediately above which the cut growth rate varies approximately linearly with T. Results from this region for vulcanizate C are shown in Figure 5 on linear scales, and the full cut growth characteristic is shown in Figure 3 on logarithmic scales. The intercept in Figure 5 represents a T_0 value of 0.06 kg./cm., which is similar to but somewhat higher than the values for the natural rubber vulcanizates A and B. Cut growth below T_0 is again characteristic of ozone. The line for SBR in Figure 3 is described by eqs. (2), (3), and (5) together with eq. (6).

$$dc/dn = DT^4 \qquad T_t \leqslant T < T_c \qquad (6)$$

which replaces eq. (4). Values of the constants for vulcanizate C are given in Table II.

THE MECHANICAL FATIGUE LIMIT

Theoretical

In the preceding section we have shown that a large increase in cut growth rate occurs once the tearing energy reaches a critical value (T_0) for each vulcanizate. Corresponding to this, a rapid increase in fatigue life is to be expected when the tearing energy at the commencement of a fatigue test, T_t, falls below T_0. In the previous studies[1,2] it was shown that fatigue of vulcanizates of natural rubber and SBR, at moderate and high strains, could be explained by assuming that flaws of a characteristic size c_0 were initially present in the rubber. From this assumption and eq. (1) we have for simple extension

$$T_t = 2kWc_0 \qquad (7)$$

As we have taken T_0 to be the minimum tearing energy at which mechanico-oxidative cut growth can occur, then the strain e_0, at which $T_t = T_0$, represents the mechanical fatigue limit. (At strains less than e_0, initially cut growth will occur only due to ozone.) If we let $(2kW)_0$ be the value of 2kW at tensile strain e_0, then from eq. (7), the mechanical fatigue limit is defined by

$$(2kW)_0 = T_0/c_0 \qquad (8)$$

Since the relationship between strain e and $2kW$ may be derived from the stress–strain curve for a vulcanizate, e_0 can be obtained from c_0 and T_0, c_0 being determined as previously[1,2] and T_0 from cut growth tests.

Determination of T_0

T_0 can be determined in several ways. Firstly, as we have shown earlier (Figs. 2,4,5), for some vulcanizates the dc/dn versus T plot is essentially linear for a range of tearing energy above T_0. Thus an estimate of T_0 may be made by extrapolation to zero cut growth rate, although the

scatter inherent in cut growth results makes it desirable to work at very low cut growth rates (close to T_0) to obtain a good approximation. Ideally, the cut should start off at a tearing energy below T_0 and grow by ozone until T_0 is reached, when a very rapid increase in rate of growth occurs, but unfortunately this method is protracted owing to the very slow rate of ozone growth. However some determinations have been made in this way from tests which started at tearing energies close to but below T_0.

A compromise between the above methods is to proceed gradually to lower tearing energies in testing a vulcanizate. Proximity to T_0 is indicated by the commencement of a marked drop in cut growth rate. T_0 may then be bracketed by carrying out a test, or tests, at a lower tearing energy, at which only very slow ozone growth occurs.

In determining T_0 care must be taken to avoid anomalous effects due to initial growth from a razor cut (Appendix II).

Direct Experimental Determination of the Mechanical Fatigue Limit

The predicted sharp increase in fatigue life at a critical value of strain does in fact occur for all vulcanizates examined. Typical results are shown in Figure 6, where fatigue life is plotted against strain. The experimental results are approximated by straight lines on either side of the critical strain, the intersection of the lines being taken as the mechanical fatigue limit, e_0. (The lines do not represent the quantitative dependence of fatigue life on deformation in this region which will be discussed in a later paper.[8])

EXPERIMENTAL RESULTS FOR T_0 AND THE MECHANICAL FATIGUE LIMIT

Values of T_0, c_0, and the fatigue limit have been determined for vulcanizates of various polymers. Effects of oxygen, antioxidants, vulcanizing system, modulus, and fillers in natural rubber, and of type of polymer are described and discussed below.

In cut growth measurements scatter of the order of $\pm 30\%$ in tearing energy for a given rate of growth occurs for all vulcanizates. A similar scatter appears to exist in T_0. The results, in general, represent good average values; less certain results are indicated by circa, although it is unlikely, even in these cases, that the average value will lie outside the $\pm 30\%$ limits. Corresponding variability occurs in fatigue tests.

Correlation between Cut Growth and Fatigue for Various Polymers

Values of the mechanical fatigue limit calculated from T_0 and c_0 by using eq. (8), and determined directly from fatigue measurements are compared in Table III for gum vulcanizates of a number of polymers. The results from the two methods are in good agreement for all the polymers, thus constituting further evidence for the intimate connection between cut growth and fatigue. The critical tearing energy tends to be somewhat

TABLE III
Mechanical Fatigue Limit for Various Polymers: Comparison of Theory and Experiment

Polymer	Vulcanizate	Approximate Young's modulus, kg. cm.$^{-2}$	Critical tearing energy T_0, kg. cm.$^{-1}$	Initial flaw size c_0, 10^{-3} cm.	Mechanical fatigue limit e_0, %	
					Theoretical	Experimental
Natural rubber	A	20	0.04	2.5	82	75
SBR	C	16	0.06	5.5	75	70–90
Isomerized natural rubber (60% *trans*)	D	25	ca. 0.07	3.5[a]	—	ca. 75
Synthetic isoprene	E	17	0.07	4.5	85	ca. 80
Polychloroprene[b]	F	16	ca. 0.07	4.5	ca. 95	ca. 90
Butadiene–acrylonitrile	G	20	<0.1	4	<100	ca. 65
Butyl rubber	H	11	0.02–0.06	5	50–100	85
Butadiene	J	20				95

[a] Owing to the weakness of this vulcanizate it was not possible to estimate c_0 in the normal way. The value given is that required to correlate T_0 with the experimental estimate of e_0.

[b] The results for polychloroprene showed more variation than usual, apparently due to anisotropy of the sheet.

higher for the synthetic polymers than for natural rubber, but this is offset by the fact that the flaw size is also higher for the synthetic polymers. Consequently the fatigue limits all lie within the range 65–95%.

Crystallization appears to have little effect on T_0, in marked contrast to its effects on macroscopic properties such as tensile strength (Table I). For example, the T_0 value is higher for the SBR vulcanizate (C) in which strain-induced crystallization does not occur, than for the strain-crystallizing natural rubber vulcanizate (A). Isomerization of natural rubber increases its T_0 value, but theoretical considerations[9] suggest that this is due to increased length of the monomer unit, rather than to loss of crystallization. Unfortunately the improvement in T_0 with 60% *trans*-polyisoprene is obtained at the expense of severe weakening of other elastic properties.

Consistent with the proposal that cut growth below T_0 is due solely to ozone, the ozone-resistant polymers show a greater increase in fatigue life on passing through the fatigue limit. This is illustrated in Table IV, where the fatigue lives of natural rubber and polychloroprene are compared at strains 10% above and below the fatigue limit.

TABLE IV
Change in Fatigue Life on Passing through the Mechanical Fatigue Limit

Polymer	Vulcanizate	Mechanical fatigue limit e_0, %	Fatigue life at a strain, Mcycles	
			$e_0 + 10\%$	$e_0 - 10\%$
Natural rubber	A	75	0.3	3
Polychloroprene	F	90	0.3	>9

Effect of Antioxidants and Oxygen

Many authors have shown that oxidation plays an important part in fatigue at moderate and high strains, substantial increases in life being obtained by the addition of suitable antioxidants,[10–14] although these increases are not as large as are obtained *in vacuo*.[3] Similar considerations appear to apply to T_0 and the fatigue limit, as is shown in Table V, where results for natural rubber vulcanizates A and A′ are given. Vulcanizate A′ has the same composition as vulcanizate A, except that the one part of antioxidant PBN (phenyl-β-naphthylamine) is omitted. This antioxidant increases the critical tearing energy measured in cut growth tests by about 50% for this vulcanizate. A corresponding effect is observed in fatigue tests where, although the elastic properties of the vulcanizates are identical, the upturn in the life versus strain plot occurs at about 52% for vulcanizate A′, and at 75% for vulcanizate A (Fig. 6).

Cut growth tests on vulcanizate A′ *in vacuo* indicate a critical tearing energy which is appreciably higher than that of vulcanizate A at atmospheric pressure (Table V). Experiments on the effects of oxidation at

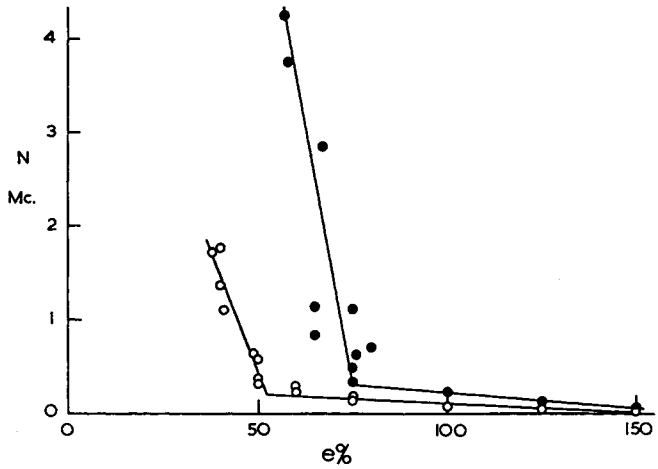

Fig. 6. Tensile fatigue life N vs. strain e showing the mechanical fatigue limit e_0: (●) natural rubber gum vulcanizate A (with antioxidant), $e_0 = 75\%$; (○) natural rubber gum vulcanizate A′ (without antioxidant), $e_0 = 52\%$.

TABLE V
Effect of Antioxidant and Oxygen Pressure

Vulcanizate	Pressure, mm. Hg.	T_0, kg. cm.$^{-1}$	c_0, 10^{-3} cm.	e_0, % Theoretical	e_0, % Experimental
A′	Atmospheric	0.027	2.5	63	52
A	"	0.04	2.5	82	75
A′	10^{-6}	ca. 0.06			

higher tearing energies[15] show that PBN is one of the most effective of the known antioxidants in cut growth. Thus it appears that the fatigue limit is diminished by the presence of oxygen, an effect which can be offset to some extent, but at present not wholly, by inclusion of an antioxidant in the rubber.

Effect of Vulcanizing System and Modulus

The nature of the crosslink produced in natural rubber vulcanizates can be varied by using different curing systems. We have investigated three systems: (*1*) accelerated sulfur vulcanizates in which polysulfidic crosslinks containing many sulfur atoms are produced, (*2*) vulcanizates cured with the use of tetramethylthiuram disulfide (TMTD) in the absence of elemental sulfur, where the crosslinks mainly consist of one sulfur atom, and (*3*) dicumyl peroxide vulcanizates, where the crosslinks formed are direct carbon-carbon linkages between adjacent chains in the network.

The results shown in Table VI compare the fatigue limits determined from cut growth and measured directly from fatigue tests for gum vul-

TABLE VI
Comparison of Theoretical and Experimental Values of e_0 for Natural Rubber Gum Vulcanizates

Curing system	Young's modulus, kg. cm.$^{-2}$	T_0, kg. cm.$^{-1}$	c_0, cm. $\times$ 10^{-3}	e_0, % Theoretical	e_0, % Experimental
Accelerated sulfur (A′)	20	0.027	2.5	63	52
TMTD sulfurless	27	0.022	2.5	51	48
Dicumyl peroxide	12	ca. 0.02	2.5	ca. 65	<95

canizates of each curing system. The two methods give good agreement for all three vulcanizing systems, although there are differences in T_0 and the fatigue limit on going from one system to another.

In view of the good correlation between T_0 and e_0, further investigation of the effect of vulcanizing system and modulus was limited to determination of the critical tearing energy, T_0. A range of Young's moduli was obtained for gum vulcanizates of each curing system by varying the quantity of curing ingredients. The results for vulcanizates containing no added antioxidant* are shown in Table VII.

TABLE VII
Effect of Vulcanizing System and Modulus on T_0 for Natural Rubber Vulcanizates

Approximate Young's modulus kg. cm.$^{-2}$	T_0 for various curing systems, kg. cm.$^{-1}$		
	Accelerated sulfur	TMTD sulfurless	Dicumyl peroxide
10	0.017	0.015	ca. 0.015
14	0.022	0.015	—
20	0.027	0.015	ca. 0.02
27	ca. 0.05	0.022	<0.03

For the accelerated sulfur vulcanizates, T_0 increases approximately proportionally to Young's modulus, but for the other curing systems the increase is very slight, T_0 being almost independent of modulus. Thus, while the critical tearing energy is very similar for all three curing systems at low moduli, it is substantially higher for the accelerated sulfur vulcanizates at high moduli. The superiority of the latter may be due to the labile nature of polysulfidic crosslinks, which are able to break and reform in the

* Subsidiary experiments on extracted test pieces of these vulcanizates at higher tearing energies gave cut growth results indistinguishable from those for unextracted test pieces, although, for both types of test piece, considerable reduction in rate of growth was found *in vacuo*. Thus any "natural" antioxidant present in the rubber, or antioxidant formed during cure, appears to have no significant effect in cut growth. In particular, this applies to zinc dimethyldithiocarbamate formed in the TMTD sulfurless vulcanizates, which is effective against oxidative aging.

strained state, thus relieving the stress concentration and necessitating a higher externally applied force or energy to cause chain rupture.

For all the natural rubber gum vulcanizates which have been examined, we have found the effective initial flaw size c_0 to be close to 2.5×10^{-3} cm. Using this value the mechanical fatigue limit e_0 can be calculated from the data of Table VII, eq. (8), and the stress–strain properties of the vulcanizates. For the accelerated sulfur vulcanizates the fatigue limit is approximately constant but for the other curing systems it decreases with increasing modulus, since T_0 increases less rapidly than the modulus.

Effect of Fillers

Fillers are generally classified into two groups: reinforcing and nonreinforcing. The cut growth and fatigue properties of vulcanizate A′ with added lampblack (nonreinforcing) and HAF black (reinforcing) have been investigated in some detail. The stress–strain properties of black-filled vulcanizates were evaluated after a period of precycling, during which occurred most of the irreversible softening (Mullins' effect), due to breakdown of structure.

Results for loadings of 50 parts of black per hundred rubber by weight (pphr) are shown in Table VIII. The fillers have little effect on T_0, but the fatigue limit e_0 is reduced, since the moduli of the black-filled rubbers are much higher. However, the critical stress, S_0, corresponding to e_0, is increased by the addition of fillers, again primarily due to change in modulus (Table VIII). HAF black reduces the rate of cut growth considerably at tearing energies above T_0, but in fatigue this improvement is cancelled out by the larger flaw size (approximately 5×10^{-3} cm.) which addition of this filler appears to create.

TABLE VIII
Effect of Fillers

Filler	Parts per hundred rubber (by weight)	T_0, kg. cm.$^{-1}$	c_0, 10^{-3} cm.	e_0, % Theoretical	e_0, % Experimental	S_0, experimental kg. cm.$^{-2}$
None (A′)	0	0.027	2.5	63	52	5.5
Lampblack	50	0.025	2.5	34	ca. 33	ca. 9
HAF black	50	0.031	5	25	28	8.5

Approximate determinations of T_0 have been made for a wide range of black and other fillers, each added to vulcanizate A′ in a volume loading equivalent to 50 pphr (by weight) of black. All the critical tearing energies are found to lie within a range of ±30% of the value for the control (A′). There appears to be a tendency for reinforcing fillers to increase T_0, and for nonreinforcing fillers to reduce T_0, but, as in Table VIII, these effects

are very slight. Increasing the HAF black loading to 100 pphr also has little effect, T_0 again being about 0.03 kg./cm. for this vulcanizate.

Similar effects have been observed with the addition of black fillers to other gum stocks having different T_0 values. The filled stocks appear to retain closely the T_0 appropriate to their gum base.

GENERAL DISCUSSION

Two mechanisms responsible for the growth of cuts or flaws have been identified. These are mechanico-oxidative rupture and ozone scission. A large increase in cut growth rate, a hundredfold or more, occurs over a very narrow range of tearing energy immediately above a critical value (T_0) of about 0.05 kg./cm. for all vulcanizates examined. As the tearing energy exceeds T_0, the cut growth per cycle rapidly attains a value of a few angstroms, which is of the order of molecular dimensions and is compatible with rupture of one, or more, chains during each cycle. As will be shown elsewhere,[7] when the tearing energy is less than T_0, cut growth occurring is attributable solely to ozone. We have therefore postulated that this critical value represents the minimum tearing energy at which mechanico-oxidative cut growth can occur.

Once the tearing energy exceeds T_0, the contribution of ozone scission, which is substantially independent of tearing energy,[7] to the total cut growth is generally negligible. For many vulcanizates, mechanico-oxidative cut growth increases linearly with tearing energy immediately above T_0, although at high T values the form of the relationship varies markedly for different types of polymer and vulcanizate. Thus T_0 separates two distinct regions: one in which ozone scission is the prime mechanism and the other in which mechanico-oxidative cut growth predominates.

A physical interpretation of T_0 is that it is the minimum tearing energy at which the stress at the tip of a cut reaches the breaking value for the vulcanizate. Experiments *in vacuo* show that T_0 is primarily a mechanical property of vulcanized rubber, although its value is somewhat reduced by the presence of oxygen. We have not equated breaking stress with tensile strength, as the latter is itself a rupture measurement, which is influenced by the presence of small, naturally occurring flaws. The breaking stress of rubber at the tip of the cut will therefore be higher than the conventional measure of tensile strength and, in view of the extreme localization of the high stress region, may well approach the strength of the molecular bonds. Consistent with this interpretation, values of T_0 show much less variation for different polymers than bulk properties, such as tensile strength, which vary markedly. An approximate theoretical calculation for natural rubber, based on molecular considerations, yields a T_0 of the same order as determined experimentally.[9]

The relationship between cut growth rate and tearing energy represents the fundamental cut growth property of a rubber vulcanizate, which can, in principle, be applied to predict cut growth and hence fatigue for any type of component or mode of deformation. Thus corresponding to T_0 there will,

in general, be a minimum deformation (mechanical fatigue limit) below which fatigue will be governed mainly by ozone. In this paper we have considered the fatigue of thin strips of rubber deformed in simple extension to which the cut growth characteristics may be readily applied. Values of the tensile mechanical fatigue limit e_0, calculated theoretically from the critical tearing energy and naturally occurring flaw size, are found to be in good agreement with direct experimental observations for a wide range of polymers. For gum vulcanizates, e_0 is found to be about 75% strain for simple extension. Since the rate of ozone cut growth is very much slower than mechanico-oxidative cut growth, fatigue life increases rapidly for strains below the fatigue limit. It is consistent with the interpretation of e_0 that this increase is greater for ozone-resistant polymers.

Experiments on natural rubber indicate that the critical tearing energy and fatigue limit are increased by inclusion of antioxidants, although the increase is not as great as is obtained *in vacuo*. Thus, from the point of view of cut growth and fatigue, improvement upon the present known antioxidants would be beneficial. Vulcanizing system and modulus also affect the critical tearing energy for gum vulcanizates of natural rubber, a hard accelerated sulfur vulcanizate having the highest T_0 value. The reduction in fatigue limit caused by fillers is due mainly to the increased modulus of the rubber, T_0 values obtained being similar to that of the gum base for a wide range of fillers. Consequently, while e_0 is reduced, the stress corresponding to it is increased by incorporation of a filler. Although a reinforcing black filler (HAF) improves cut growth resistance it increases the naturally occurring flaw size to a greater extent, so that a nonreinforcing filler (lampblack) gives superior fatigue properties. It appears that better fatigue properties in a filled vulcanizate are to be obtained by using a stiff gum base with a minimum of filler, rather than a soft gum base with a larger amount of filler.

The tearing energy theory for rubber[5] was developed from Griffith's fracture criterion for glass.[16] It has also been applied to the rupture of hard plastics,[17] and a published relationship for crack growth in metals[18] is close to the form suggested by this energy balance approach. The success of the tearing energy theory in predicting fatigue of rubber suggests that it may be relevant to fatigue of other materials such as metals and plastics.

The existence of a mechanical fatigue limit for rubber is of considerable practical significance as many components operate below it. For these fatigue is primarily controlled by the chemical process of ozone attack, so that protection against ozone is a major factor in improving resistance to fatigue.

APPENDIX I

Effect of Aging

Oxidative aging can cause breakdown of chains or crosslinks substantially uniformly throughout a piece of rubber to an extent which increases with

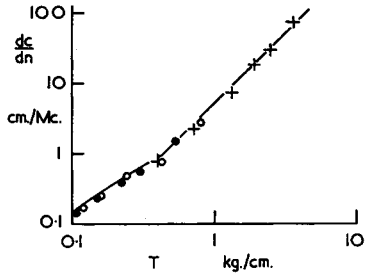

Fig. 7. Effect of aging on cut growth characteristics of vulcanizate A: (——) unaged results (from Fig. 3); (+) new sheet aged 7 days at 70°C.; (O) after 3 years shelf aging; (●) 3 years shelf aging plus 7 days at 70°C.

time. It is therefore distinct from the oxidative contribution to cut growth referred to previously. (The latter is localized at the tip of a flaw or cut, results from mechanical rupture, and is essentially cyclic rather than time dependent in nature.)

At low tearing energies, particularly below T_0, the rate of growth is so slow that cut growth tests may last for a considerable period of time. Stress–strain measurements carried out after some of these long-term tests showed little of the reduction in modulus which accompanies aging; indeed, slight stiffening often occurred. The rate of ozone crack growth is not particularly sensitive to modulus,[19] so that aging is unlikely to have had any significant effect on the rate of crack growth in the ozone region in our tests.

To find the effect of aging on mechanico-oxidative cut growth, tests were carried out on samples of vulcanizate A which had been (*1*) kept in the laboratory for about 3 years, and (*2*) artificially aged in an oven for 7 days at 70°C. The tests were carried out at moderate and high tearing energies so that they were of fairly short duration.

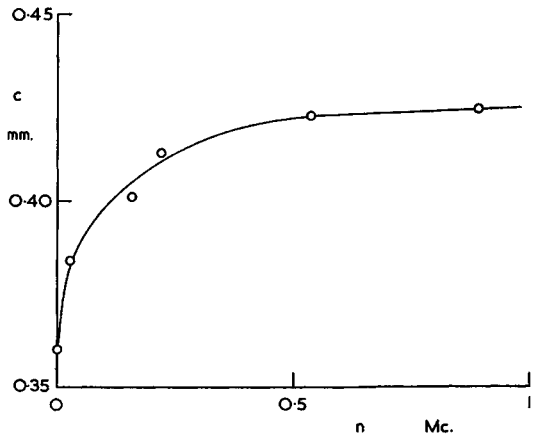

Fig. 8. Growth from a razor cut in the ozone region for vulcanizate C; cut length c vs. number of cycles from start of test n.

The results are shown in Figure 7. There is no significant difference between the results for the artificially and naturally aged test pieces and the previous results for unaged test pieces (indicated by the full line taken from Fig. 3). Studies of the effect of accelerated aging on tensile strength indicate that for natural rubber an increase of about 10°C. corresponds to a factor of about 2.3 in rate of aging.[20] Taking room temperature as 20°C., the rate of aging at 70°C. will be 2.3^5 or about 60 times faster; 7 days at 70°C. therefore corresponds to rather more than a year at room temperature. The duration of cut growth tests, even at very low tearing energies, was much less than the period of aging for the naturally aged test pieces, and less than the equivalent room temperature period for the artificially aged test pieces.

APPENDIX II

Effect of a Razor Cut

In tests which commence at a tearing energy just below T_0, growth sometime occurs at first from the razor cut, and subsequently stops after the cut has grown a short way (except for very slow ozone growth). A plot of cut length against number of cycles for a test in which this occurred is shown in Figure 8. A similar effect is observed in the initial growth from a razor cut in the mechanico-oxidative region,[1,2] and it is attributed to the very sharp tip occurring in a razor incision. As a sharp tip causes a higher stress concentration than a rough tip, the stress concentration at a razor incision can be considered as corresponding to a higher effective tearing energy than that of a natural or roughened tip. From previous observations on vulcanizate A the effective tearing energy for a razor cut appears to be about three times the measured tearing energy. Consequently, for a razor cut having a measured T value just below T_0, the effective tearing energy may well exceed T_0. As the cut grows, however, the tip roughens to its natural state, so that the effective tearing energy falls to the measured value, which may still be below T_0. Consistent with this interpretation, initial rapid growth has not been observed in tests starting well below T_0. Here the additional sharpness of a razor tip would not be expected to have any effect, since the effective tearing energy would not exceed T_0, and the ozone rate of growth is independent of T. In determining T_0 and rates of growth in the ozone region any initial rapid growth from a razor cut has been ignored.

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Résumé

Des recherches effectuées sur la croissance dynamique des coupure dans les caoutchoucs vulcanisés montrent qu'il y a une énergie minimum de déchirement pour laquelle les chaînes sont rompues mécaniquement. La valeur limite est caractéristique pour chaque vulcanisation, mais se situe aux environs de 0.05 kg/cm. La limite de fatigue mécanique, en dessous de laquelle le nombre de cycles de rupture augmente rapidement, est prévue d'une façon précise à partir de cette énergie de rupture critique. On discute les caractéristiques de croissance des ruptures aux faibles énergies de déchirement, de même que l'influence du polymère, du système de vulcanisation, de l'oxygène et des charges sur l'énergie critique de déchirement et sur la limite de fatigue.

Zusammenfassung

Die Untersuchung des dynamischen Risswachstumsverhalten von vulkanisiertem Kautschuk zeigt, dass eine minimale Reissenergie vorhanden ist, bei welcher ein mechanisches Reissen der Ketten eintritt. Der Grenzwert ist für jedes Vulkanisat charakteristisch, liegt aber jedenfalls im Bereich von 0,05 kg/cm. Die mechanische Ermüdungsgrenze, unterhalb welcher die Anzahl der zum Bruch führenden Benanspruchungen rasch ansteigt, lässt sich aus dieser kritischen Reissenergie genau voraussagen. Die Charakteristik des Risswachstums bei niedriger Reissenergie und der Einfluss des Polymeren, des Vulkanisationssystems, von Sauerstoff und Füllstoffen auf die kritische Reissenergie und die Ermüdungsgrenze werden diskutiert.

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