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# Fatigue of Rubber at Low Strains

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## Synopsis

The fatigue failure of natural rubber vulcanizates undergoing repeated low tensile deformations has been investigated. It is found that below a critical deformation the life is greatly influenced by the ozone concentration in the test atmosphere. This result was anticipated theoretically from previous studies of cut growth behavior, and the theory enables the combined effects of the two cut growth mechanisms—mechanico-oxidative rupture and ozone scission—to be taken into account in predicting fatigue life.

## Introduction

Previous publications[1,2] have shown that the fatigue failure of rubber undergoing repeated deformations, in the absence of heat build-up, is due to cut growth from small flaws which are initially present in the material. Utilizing the concept of tearing energy, these papers dealt with fatigue at moderate and high tensile deformations, the test pieces being relaxed to zero strain on each cycle. Under these conditions the cut growth is attributable to mechanico-oxidative rupture of the polymer chains.

In the present paper, extension of this approach to lower deformations is considered. For strains below the mechanical fatigue limit,[3] which corresponds to the minimum tearing energy $T_0$ required for mechanico-oxidative cut growth, ozone becomes the major factor determining fatigue life. By using the naturally occurring flaw size deduced from the previous measurements at high strains, the fatigue life at low tensile strains can be quantitatively predicted by assuming that the flaws will grow only by ozone cut growth until $T_0$ is reached.

## Theory

As in the previous studies, the concept of tearing energy[4] is used to assess the stress concentration at a flaw in a piece of rubber. The tearing energy $T$ is defined as the decrease in the total elastic strain energy of a test piece held at constant deformation due to unit area of cut growth. For a test piece deformed in simple extension, containing a cut of length $c$ in one edge, as in Figure 1,

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

where $W$ is the strain energy density in the bulk of the rubber (i.e., away

from the stress concentration at the cut) and $k$ a known, slowly varying, function of strain;[5] these variables are combined, for convenience, into the "strain energy" factor $X$, which can be determined as a function of strain from the stress–strain curve for a given vulcanizate.

When the cut growth behavior of a rubber is expressed in terms of $T$, it is found to be independent of the type of deformation or shape of test piece employed and thus represents an intrinsic property of the rubber. In experiments in which the test piece is subjected to repeated deformations, the rate of cut growth is referred to the tearing energy attained at the maximum strain of the deformation cycle.

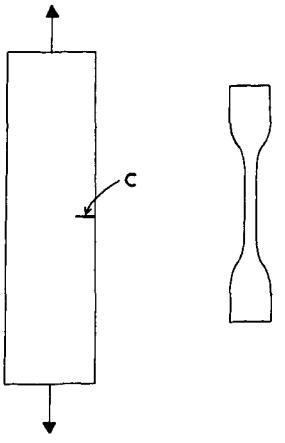


Fig. 1. Tensile strip test piece (left) used for cut growth measurements, and dumbbell test piece (right) used for fatigue tests.

Experimental observations indicate that for repeated deformations below a minimum tearing energy $T_0$, there is no cut growth due to mechanico-oxidative rupture, the sole cause of growth being ozone scission.[3,6] Furthermore, for the propagation of a single crack in natural rubber at room temperature, the rate of this ozone cut growth can readily be predicted from static test behavior by assuming that a crack will grow during the time the test piece is strained. Thus the cyclic rate $r$ of ozone cut growth is given by[6]

$$r = dc/dn = (F/f)\alpha q \tag{2}$$

where $n$ is the number of cycles, $F$ the time fraction of each cycle for which the test piece is strained, $f$ the frequency of cycling, $q$ the ozone concentration, and $\alpha$ the ozone cut growth constant for the rubber under static conditions (i.e., the rate of growth at unit ozone concentration).

It has been shown previously that for moderate and high tensile strains the fatigue failure of rubber can be quantitatively predicted by assuming that small, naturally occurring flaws, a few thousandths of a centimeter

long, are present in the material.[1,2] For flaws corresponding in size to an ideal cut of length $c_0$, the tearing energy at the commencement of a fatigue test is, from eq. (*1*),

$$T_i = Xc_0 \tag{3}$$

where $X$ is evaluated at the maximum strain of the cycle as in a cut growth test.

We now consider a fatigue test at a strain below the mechanical fatigue limit, where $T_i$ is less than $T_0$, and tentatively assume that eq. (2) is applicable even though many cracks may develop. From eqs. (1) and (2), the number of cycles for which the cracks will grow purely by ozone (i.e., until the tearing energy reaches $T_0$) is given by

$$N_z = \int_{T_i}^{T_0} (1/Xr)dT = (T_0 - T_i)/Xr$$

To obtain the fatigue life $N$ we must add to $N_z$ the number of cycles $N_0$ required for a crack to grow from $T_0$ to the catastrophic tearing energy $T_c$[4] at which the test piece will rupture, i.e.

$$N = N_z + N_0 = [(T_0 - T_i)/Xr] + N_0 \tag{4}$$

$N_0$ can be determined by using both the ozone and the mechanico-oxidative cut growth characteristics of the rubber. The latter characteristic depends markedly on the polymer and vulcanizate used,[7] but in general, for $T \geqslant T_0$, we can put $dc/dn = \phi(T)$ and obtain, from eq. (1),

$$N_0 = (1/X) \int_{T_0}^{T_c} [1/\phi(T)]dT \tag{5}$$

The forms of $\phi(T)$ for two natural rubber vulcanizates are given in the Appendix. For the simplest case (vulcanizate B), substitution into eq. (5) yields

$$N_0 \simeq (1/XA) \ln (AT_c/r)$$

where $A$ is the mechanico-oxidative cut growth constant of the vulcanizate [see eq. (8) of the Appendix]. An equivalent expression, involving an additional term, is obtained for vulcanizate A. It may be noted from eqs. (3), (4), and (5) that, in general, the theory predicts a linear relationship between the fatigue life $N$ and $1/X$ for strains below the fatigue limit.

In the previous measurements it was shown that the magnitude of $T_c$ has very little effect on the fatigue life at high strains.[1,2] At low strains the effect of $T_c$ is even less, and furthermore if $T_i \ll T_0$, $N_0$ may be very small in comparison to $N_z$.* In this case the whole of the mechanico-oxidative region may be neglected and $T_0$ considered as the failure point.

* The ratio $N_0:N_z$ depends also on the ozone concentration and frequency.

## Experimental

Standard dumbbell test pieces (Fig. 1; B.S. 903, type C or D), die-stamped from sheets of vulcanized rubber about 1 mm. thick, were used for the fatigue experiments, because parallel-sided strips would have failed prematurely at the grips. Each test piece was repeatedly deformed to a fixed maximum extended length at a frequency of about 100 cycles/min., the deformation being relaxed through zero on each cycle. Ultimately, failure occurred in the central parallel-sided section of the test piece, where the rubber was deformed in simple extension, and the number of cycles to failure (the fatigue life) was recorded. The maximum strain of the deformation cycle was measured by means of gauge marks on the central section of each dumbbell. This measurement was repeated at intervals during the course of each test to enable the set occurring in the rubber to be taken into account.

The theory relates the fatigue life to the maximum strain energy density of the cycle. The latter was determined, as a function of strain, by numerical integration of the stress–strain curve for each vulcanizate.

The time fraction of each cycle $F$ for which a test piece was strained was measured from a suitable rotating part of the testing machine used. For the majority of the tests $F$ was kept constant at $0.50 \pm 0.05$. Fatigue experiments were carried out in three atmospheres: in the laboratory, outdoors on the laboratory roof, and in an ozone chamber. Ozone concentrations were determined by using a commercial instrument (Hampden Ozomat, Hampden Test Equipment Ltd., Rugby). The concentrations in the laboratory and outdoor atmospheres were found to be subject to considerable short-term fluctuations, but the average values, which are used in applying the theory, are in good agreement with independent estimates from the ozone cracking of natural rubber under static deformation.[6]

Two natural rubber gum vulcanizates were used for the experiments described in the present paper. The mix formulations and vulcanization conditions were as follows: vulcanizate A: natural rubber (RSS1) 100, zinc oxide 5, stearic acid 2, sulfur 2.5, *n*-cyclohexyl benzthiazyl sulfenamide 0.6, phenyl-$\beta$-naphthylamine 1.0; cure 40 min. at 140°C.; vulcanizate B: natural rubber (pale crepe) 100, zinc oxide 0.5, stearic acid 0.5, zinc stearate 1.5, sulfur 2, blend of MBT and a dithiocarbamate (Vulcafor DHC) 0.375, phenol condensation product (Nonox EX) 1.0; cure 10 min. at 140°C.

## Experimental Results and Discussion

Fatigue results for vulcanizates A and B, at deformations below and above the mechanical fatigue limit, are compared to the theory in Figures 2–4 and Table I. The theoretical fatigue lives were calculated from the cut growth constants and naturally occurring flow sizes given in the Appendix for the experimental conditions stated on the legends by using eq. (4) for the low strain region and a similar treatment to that given previously for higher strains.

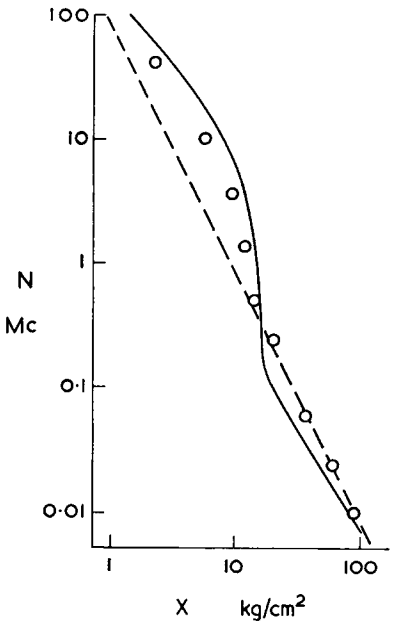


Fig. 2. Fatigue life $N$ vs. strain-energy factor $X$ for vulcanizate A in the laboratory atmosphere ($q \sim 0.3$ pphm by volume, $f = 116$ cycles/min., $F$ unknown): (O) averaged experimental results; (——) full theoretical relationship (assuming $F = 0.5$); (— —) square-law relationship.

Figure 2 shows averaged values of earlier fatigue results for vulcanizate A obtained in the laboratory atmosphere.[1] At the time that these experiments were carried out, the significance of ozone in low strain fatigue was not realized; consequently, the strained fraction of cycle $F$ was not recorded. A value of $F = 0.5$ was assumed in applying the low strain theory, which is in agreement with experiment to within a factor of two for lives up to 40 Mc.

The broken line in Figure 2 is the theoretical relationship deduced previously[1] from eq. (7) of the Appendix. This predicts that $N$ should vary as $X^{-2}$ and is only strictly applicable at high strains. As can be seen, however, not only does this relationship give a good fit to the results at high strains but also it is quite a reasonable approximation down to very low strains. The latter agreement is fortuitous, as these results depend on the ozone concentration as is shown for vulcanizate B in Figure 3.

Although the mechanical cut growth behavior of vulcanizate B does not predict $N$ to be proportional to $X^{-2}$, this type of relationship is again quite a good fit to the results obtained in the laboratory atmosphere. However, the experiments on the laboratory roof, where the ozone concentration is approximately 10 times greater, show a marked reduction in the fatigue life at small deformations, and a corresponding departure from the simple square-law relationship. This result, which illustrates the

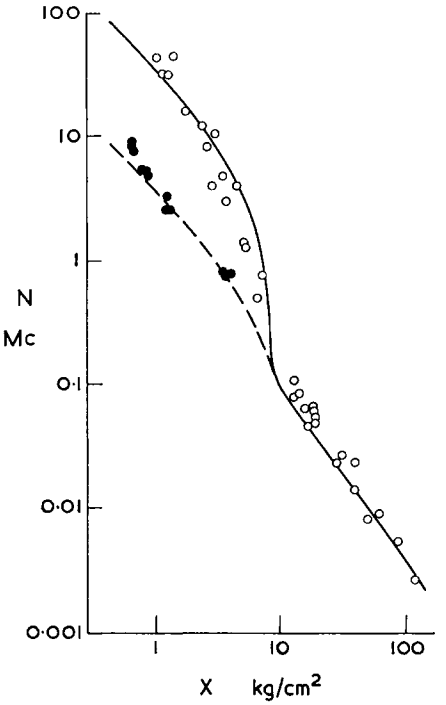


Fig. 3. Fatigue life $N$ vs. strain energy factor $X$ for vulcanizate B in the laboratory atmosphere ($q \sim 0.3$ pphm, $f = 116$ cycles/min., $F = 0.50 \pm 0.05$), and outdoors on the laboratory roof ($q$ increased to $\sim$3.5 pphm, $f$ and $F$ the same): (O) experimental results, laboratory: (●) experimental results, roof; (— —) calculated relationships, laboratory; (— —) calculated relationships, roof.

importance of the ozone concentration in low strain fatigue measurements, is predicted substantially correctly by the present theory.

To check that the effects observed outdoors were due to the increase in ozone concentration, and not to some other atmospheric degradation process, further experiments were carried out on vulcanizate B in an ozone chamber at a concentration some 25 times that in the laboratory atmosphere. The experiments were at strains below and above the mechanical fatigue limit (ca. 80% tensile strain for vulcanizate B), and the results are compared to those obtained in the laboratory atmosphere in Table I. The increased ozone concentration causes a very marked reduction in the fatigue life at 40% strain (approximately twentyfold) but virtually no change at 150% strain. Both effects are substantially in accord with the theory.

The results in Table I also emphasize the significance of the fatigue limit in determining the relative contributions of ozone and mechanico-oxidative cut growth to fatigue failure. In Figure 4 experimental and calculated fatigue lives for vulcanizate B below the fatigue limit are plotted against strain on linear scales. In the laboratory atmosphere the fatigue limit is

TABLE I

Comparison of Fatigue Lives for Vulcanizate B in the Laboratory Atmosphere and in an Ozone Chamber at Strains below and above the Mechanical Fatigue Limit[a]

| Nominal maximum strain, % | Calculated | | | Observed | | |
|---|---|---|---|---|---|---|
| | $N_L$, Mc.[b] | $N_c$, Mc.[c] | $N_L/N_c$ | $N_L$, Mc.[b] | $N_c$, Mc.[c] | $N_L/N_c$ |
| 40 | 10.4 | 0.64 | 16.3 | 8.8 | 0.45 | 19.5 |
| 150 | 0.0378 | 0.0370 | 1.02 | 0.0575 | 0.0525 | 1.09 |

[a] For vulcanizate B the mechanical fatigue limit corresponds to about 80% tensile strain. Each result given is the mean of 4 tests.

[b] $N_L$ = fatigue life in the laboratory atmosphere ($q \sim 0.3$ pphm, $F = 0.50 \pm 0.05$, = 116 cycles/min.).

[c] $N_c$ = fatigue life in the ozone chamber ($q = 8$ pphm, $F = 0.50 \pm 0.05$, $f = 100$ cycles/min.).

characterized by a sharp increase in life to values of a million cycles or more. Outdoors, the higher ozone concentration makes this increase less sharp.

The work described in this paper strongly suggests that ozone cracking is the major factor in fatigue at strains below the mechanical fatigue limit. For the natural rubber vulcanizates used it appears that the contribution of ozone to dynamic cut growth, and hence to fatigue failure, can be calculated from the growth rate of a single crack under static conditions. Of the two tearing energy constants, the catastrophic value $T_c$, which is the usual measure of the tear strength of a rubber, has a negligible in-

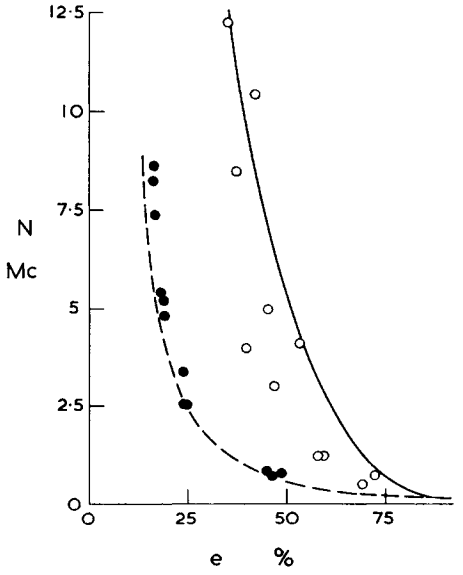


Fig. 4. Fatigue life $N$ vs. maximum strain $e$ for vulcanizate B at strains below the mechanical fatigue limit (ca. 80%). Experimental conditions and key as in Fig. 3.

fluence on fatigue life, whereas the mechanical cut growth limit $T_0$, which has only been identified quite recently, is of major importance.

Taken in conjunction with the previously developed high-strain theory, the fatigue life of a rubber in simple extension can now be predicted accurately for lives from about 1 kc. to approaching 100 Mc.

## APPENDIX

### Cut Growth Equations for Natural Rubber Vulcanizates

Equations (6)–(8) have been found empirically to give a good fit to the experimental results.[3] $dc/dn$ is the cyclic rate of cut growth, expressed as a function of the tearing energy $T$. $A$ and $B$ are mechanico-oxidative cut growth constants, and $r$ the ozone rate of growth defined by eq. (2) of the theory. $T_0$ is the limiting tearing energy for the commencement of mechanico-oxidative cut growth, and $T_c$ that for catastrophic rupture.

TABLE II

| | Vulcanizate A | Vulcanizate B |
|---|---|---|
| $\alpha$, cm. sec.$^{-1}$/pphm | $4.0 \times 10^{-9}$ | $6.8 \times 10^{-9}$ |
| $T_0$, kg. cm.$^{-1}$ | 0.04 | 0.017 |
| $A$, cm. Mc.$^{-1}$/kg. cm.$^{-1}$ | 2.5 | 7 |
| $T_t$, kg. cm.$^{-1}$ | 0.45 | — |
| $B$, cm. Mc.$^{-1}$/kg.$^2$ cm.$^{-2}$ | 5 | — |
| $T_c$, kg. cm.$^{-1}$ | 10 | 3 |
| $c_0$, cm. | $2.5 \times 10^{-3}$ | $2.0 \times 10^{-3}$ |

For vulcanizate A, the transition tearing energy $T_t$ represents the point at which the cut growth rate changes from a linear to a square-law dependence on $T$.

Vulcanizate A:

$$dc/dn = A(T - T_0) + r \qquad T_0 < T \leqslant T_t \tag{6}$$

$$dc/dn = BT^2 \qquad T_t < T < T_c \tag{7}$$

Vulcanizate B:

$$dc/dn = A(T - T_0) + r \qquad T_0 < T < T_c \tag{8}$$

Values of the constants for vulcanizates A and B, together with the naturally occurring flaw size $c_0$, are given in Table II.

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## Résumé

On a étudié la cassure à la fatigue de vulcanisats de caoutchoucs naturels subissant des déformations à la tension répétées. On a trouvé qu'en dessous d'une déformation critique, la durée de vie est fortement influencée par la concentration en ozone de l'atmosphère d'essai. Ce résultat avait été anticipé théoriquement au départ d'études antérieures sur le comportement d'accroissement d'une coupure, et la théorie permet de tenir compte des effets combinés des deux mécanismes de croissance de coupure, mécanique-oxydatif et scission à l'ozone en vue due pourvoir prédire la durée à la fatigue.

## Zusammenfassung

Das Ermüdungsverhalten von Naturkautschukvulkanisaten bei wiederholten Deformationen unter niedriger Zugbeanspruchung wurde untersucht. Unterhalb einer kritischen Deformation wurde die Lebensdauer stark durch die Ozonkonzentration in der Testatmosphäre beeinflusst. Dieses Ergebnis war aus früehren Untersuchungen des Verhaltens des Schnittwachstums theoretisch abgeleitet worden, und die Theorie ermöglicht eine Berücksichtigung des gemeinsamen Einflusses der beiden Schnittwachstumsmechanismen —mechanisch-oxydative Spannung und Ozonspaltung—bei der Voraussage der Ermüdungslebensdauer.

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