Role of Ozone in Dynamic Cut Growth of Rubber

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Synopsis

The effect of ozone on the growth of cuts in rubber strips subjected to repeated tensile deformations has been investigated. At tearing energies below a critical value ozone accounts for all the cut growth, and in this region the rate of growth is substantially independent of tearing energy. At higher tearing energies, cut growth also occurs due to mechanico-oxidative rupture, the rate of this type of growth increasing rapidly with increasing tearing energy so that the effects of ozone are normally slight. For vulcanizates of natural rubber and SBR unprotected by antiozonant, the characteristics of dynamic ozone cut growth can be deduced from static measurements. If a natural rubber test piece is not allowed to relax to zero strain on each cycle, the effects of ozone are important over a wider range of tearing energy.

INTRODUCTION

In a previous paper,[1] we showed that the rate of growth of a cut in a rubber strip subjected to repeated deformation decreases markedly below a critical value of tearing energy (the elastic energy dissipated by the cut growth). This value, denoted T_0, depends on the type of polymer and vulcanization system, but is in the region of 0.05 kg./cm. In the earlier paper[1] cut growth at tearing energies less than T_0 was attributed solely to ozone. Evidence supporting this statement is given in the present paper, and in view of the potential importance of ozone in fatigue at low strains[1] the characteristics of dynamic cut growth at very low tearing energies are considered in more detail.

EXPERIMENTAL PROCEDURE

The technique employed in cut growth measurements, which has been described in detail previously,[1-3] is only outlined here. The test piece is a parallel-sided strip of rubber, about 1 mm. thick, with a cut inserted in one edge perpendicular to both major and minor surfaces (Fig. 1). It is deformed in simple extension, either by repeated cycling to a fixed maximum extended length (dynamic tests), or by being held under constant load or at constant extended length (static tests). The test piece is normally relaxed to zero strain on each cycle during dynamic tests.

Measurement of the cut length c (Fig. 1), at suitable intervals of the number of cycles n or time t, enables the cut growth rate dc/dn or dc/dt

respectively, to be calculated. This is related to the tearing energy T, which for this test piece is given by[4]

$$T = 2kWc \qquad (1)$$

where c is the cut length, W the strain energy density in the body of the test piece (i.e., away from the cut), and k a slowly varying function of strain.[5] W is determined as a function of strain from the stress–strain curve for each vulcanizate. In dynamic tests, dc/dn is referred to the tearing energy pertaining at the maximum strain of the cycle.

When cut growth is due to ozone, subsidiary cracks form in the major test piece surfaces near the cut tip. This makes measurement more difficult and may increase the rate of growth.[6] Uncertainty in measurement due to the presence of surface cracks was small compared with the differences in rate between mechanico-oxidative and ozone cut growth.[1]

In dynamic ozone cut growth measurements the time fraction of cycle for which a test piece is strained affects the rate of growth. This was determined from some suitable rotating part of the various testing machines used.

Details of the compounds used are given in Table I.

TABLE I

	Vulcanizate A	Vulcanizate B	Vulcanizate C
Natural rubber (RSS1)	100	100	—
SBR (Polysar S)	—	—	100
Zinc oxide	5	0.5	5
Zinc stearate	—	1.5	—
Stearic acid	2	0.5	2
Sulfur	2.5	2.0	1.75
N-Cyclohexyl-2-benzthiazyl sulfen-amide (CBS)	0.6	—	1.0
Blend of MBT and a dithiocarbamate (Vulcafor DHC)	—	0.375	—
Phenyl-β-naphthylamine (PBN)	1.0	—	1.0
Phenol condensation product (Nonox EX)	—	1.0	—
Vulcanization time, min.	40	10	50
Vulcanization temperature, °C.	140	140	140

CHARACTERISTICS OF STATIC CUT GROWTH DUE TO OZONE

The influence of ozone on the growth of a single cut in a test piece held under constant load has been investigated by Braden and Gent.[6,7] Their test pieces, of the type shown in Figure 1, were deformed in simple extension, the surfaces being coated with silicone grease to prevent formation of subsidiary cracks.

Braden and Gent found three well-defined characteristics of ozone cut growth: (1) a small stress, corresponding to a critical tearing energy T_z, is

necessary for cracks to grow at all, T_z being of the order of 10^{-4} kg./cm. for vulcanizates unprotected by antiozonant; (*2*) above T_z cut length increases linearly with time, the rate of growth being independent of tearing energy; (*3*) for a number of polymers, including natural rubber and SBR, the rate of crack growth is similar, and proportional to the ozone concentration.
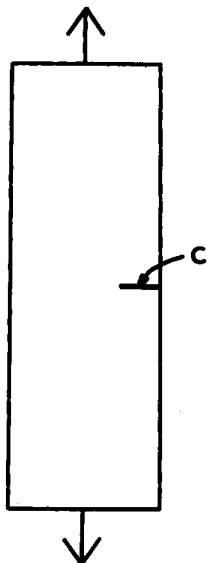

Fig. 1. Cut growth test piece.

From these results the rate of growth of a cut due to ozone under static conditions may be represented by

$$dc/dt = 0 \qquad\qquad T < T_z \qquad (2)$$

$$dc/dt = \alpha q \qquad\qquad T \geqslant T_z \qquad (3)$$

where α is a constant for a given vulcanizate and q the ozone concentration.

APPLICATION TO DYNAMIC CONDITIONS

Following the results of Braden and Gent we take the ozone cut growth occurring on each cycle in a dynamic test to be proportional to the ozone concentration and to the time for which the tearing energy is above T_z.

Under static conditions, T_z is very small for unprotected vulcanizates, and it appears to be even less under dynamic conditions (Fig. 2). Thus, with generally negligible error, we may take $T_z = 0$ and represent dynamic cut growth due to ozone by

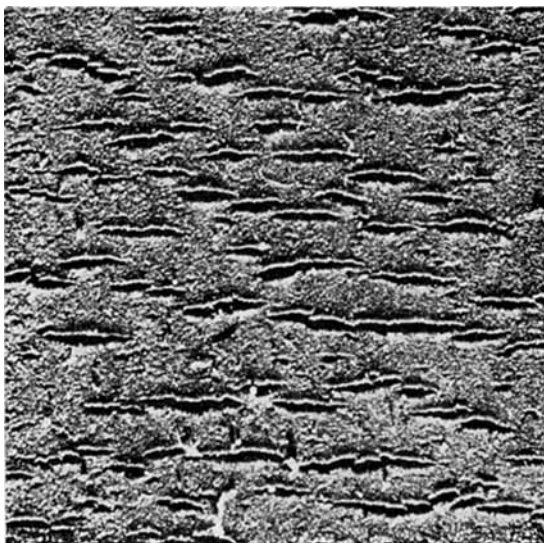$$dc/dn = (F/f)dc/dt = (F/f)\alpha q \qquad (4)$$

Fig. 2. Ozone cracks in the surface of a test piece of vulcanizate A cycled to 0.8% tensile strain, indicating a critical tearing energy $T_z < 10^{-5}$ kg./cm. Under static conditions the critical strain for test pieces cut from the same sheet of this vulcanizate is about 4% ($T_z > 10^{-4}$ kg./cm.).

where F is the time fraction of each cycle for which the test piece is strained, f the frequency of cycling, and α can be determined from static measurements by using eq. (3).

According to eq. (4), the dynamic ozone cut growth rate should be independent of tearing energy and inversely proportional to frequency. This contrasts with mechanico-oxidative cut growth, where the rate is markedly dependent on tearing-energy and substantially independent of frequency (except at frequencies below 30-cycles/min. for a noncrystallizing rubber).[1-3] The validity of eq. (4) is examined in the next three sections.

EXPERIMENTS IN THE LABORATORY

Dynamic Experiments

Results of dynamic cut growth experiments at a frequency of 100–130 cycles/min. on vulcanizates of natural rubber (A and B) and SBR (C) were given previously.[1] The low tearing energy region of these cut growth characteristics is shown again in Figure 3. For this region the fitted curves (given by eqs. (2) and (3) of the previous paper[1]) are of the form

$$dc/dn = r \qquad\qquad\qquad T \leqslant T_0 \qquad (5)$$

$$dc/dn = A(T - T_0) + r \qquad\qquad T > T_0 \qquad (6)$$

where r, T_0, and A are constants for each vulcanizate which are given in Table II.
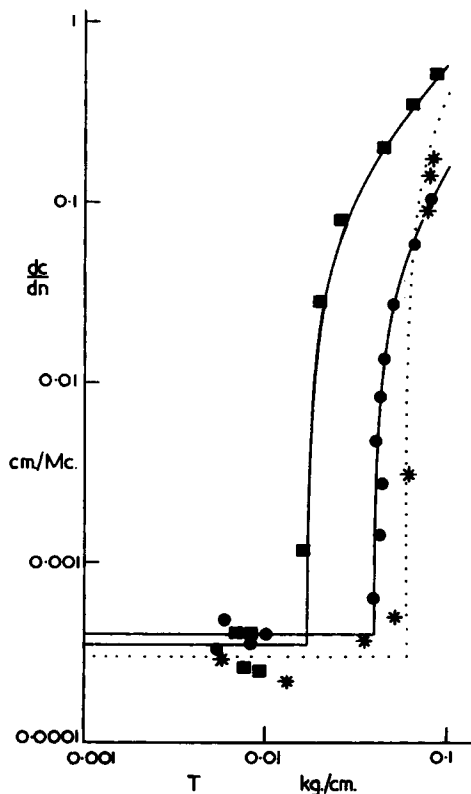
Fig. 3. Dynamic cut growth characteristics at low tearing energies. Cyclic cut growth rate dc/dn vs. tearing energy T: (————●————) vulcanizate A; (————■————) vulcanizate B; (. . .*. . .) vulcanizate C (SBR). The lines represent eqs. (5) and (6) for the values of the constants given in Table II.

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
F	0.50	0.43	0.34
α, cm.sec.$^{-1}$/mg. O_3 l.$^{-1}$	2.0×10^{-4}	3.4×10^{-4}	3.8×10^{-4}

Immediately above the tearing energy T_0 the rate of growth increases rapidly; we have attributed this[1] to the commencement of mechanico-oxidative cut growth (represented by the factor $A(T - T_0)$ in eq. (6)). We are now concerned with the region of tearing energy below T_0. In this region eq. (5), which represents the dynamic results, is consistent with eq. (4) derived from the characteristics of static ozone attack, provided

$$dc/dt = fr/F \qquad (7)$$

Static Experiments

To check eq. (7), static cut growth measurements were carried out concurrently with the dynamic tests, the test pieces being held either at constant extended length, or under constant load, instead of being cycled. It is known that in strain-crystallizing natural rubber, mechanico-oxidative cut growth does not occur under static conditions unless the tearing energy is very close to the catastrophic rupture value T_c.[4] At lower tearing energies the only known cause of static cut growth is ozone. For non-crystallizing SBR, static cut growth occurs at tearing energies well below T_c, the rate of growth being approximately proportional to T^4 as in dynamic tests.[3] In view of this behavior, static tests on natural rubber were carried out at tearing energies both above and below T_0, but those on SBR were restricted to tearing energies below the dynamic T_0 value.

Comparison of Static and Dynamic Results

Results from both types of experiment are plotted in Figure 4 as dc/dt versus tearing energy T. For the dynamic tests dc/dt values were calculated by using eq. (7) and measured values of F and f. Variations in F were small, all experiments having a value within the range 0.3–0.55. Mean values for each vulcanizate are given in Table II. With the exception of three tests on vulcanizate C carried out at 130 cycles/min., the frequency in dynamic tests was 100 cycles/min. The small differences in F and f account for the slight variation in r in Table II. On a time basis the rate of growth is a little higher for the SBR vulcanizate (C) than for the natural rubber vulcanizates (A and B).
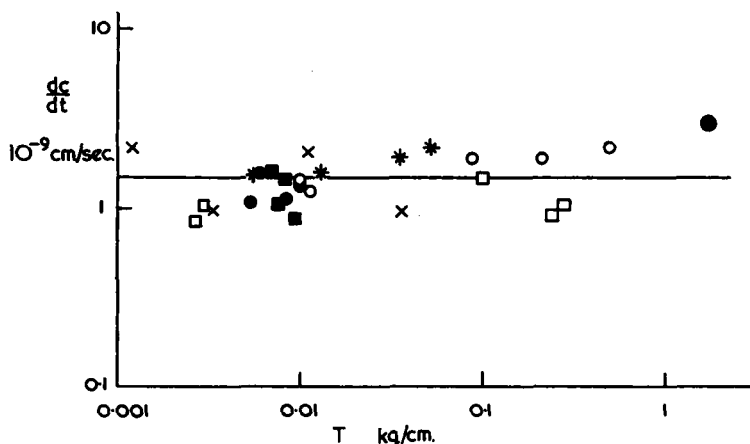

Fig. 4. Comparison of static and dynamic cut growth tests in the laboratory. Cut growth rate dc/dt vs. tearing energy T: (O) static tests, vulcanizate A; (□) static tests, vulcanizate B; (×) static tests, vulcanizate C; (●) dynamic tests (100–130 cycles/min.), vulcanizate A; (■) dynamic tests, vulcanizate B; (*) dynamic tests, vulcanizate C; (◉) nonrelaxing experiment on vulcanizate A (130 cycles/min.).

The agreement between the results from static and dynamic tests is remarkably good. The rate of growth in dynamic tests is very similar for natural rubber and SBR vulcanizates and is substantially constant for a tenfold variation in tearing energy. These features are consistent with all the cut growth being due to ozone; they contrast with behavior at higher tearing energies, where the rate of mechanico-oxidative cut growth varies markedly with tearing energy and in general has very different values for these polymers.[1-3]

Nonrelaxing Experiment

Cadwell, Merrill, Sloman, and Yost have shown that the fatigue life of natural rubber is greatly increased if a test piece is not allowed to return to zero strain on each cycle.[8] The result of a dynamic cut growth test on vulcanizate A under these nonrelaxing conditions is shown in Figure 4. The minimum tearing energy on each cycle was approximately $1/3$ of the maximum, both values being well above T_0. As before, dc/dt was calculated by using eq. (7), f and F in this case being 130 cycles/min. and 1, respectively.

The rate of growth is about 10^4 times slower than would have occurred in a relaxing (zero minimum strain) test at the same maximum tearing energy, but is very similar to the rate observed in relaxing tests below T_0, suggesting that ozone is again the cause of crack growth. Thus it appears that mechanico-oxidative cut growth may be suppressed by not allowing the minimum tearing energy to fall to zero; a large increase in fatigue life would then be expected due to the very slow rate of the residual ozone cut growth.

It is interesting to make a quantitative comparison with the fatigue results of Cadwell et al.,[8] who tested a vulcanizate of similar hardness indoors in simple extension. For example, at 300% maximum extension they found a fatigue life of 1.7 kcycles for a test piece relaxed to zero strain on each cycle. To reproduce the ratio ($1/3$) of minimum to maximum tearing energy employed in the cut growth test described above requires a minimum strain of about 150% for 300% maximum strain. Interpolating Cadwell's results indicates a fatigue life of about 15 Mcycles under the latter conditions. Thus the ratio of the fatigue lives in the two cases is about 10^4, which correlates very closely with the inverse ratio of the cut growth rates measured in our tests.

Laboratroy Ozone Concentration

Using a similar technique to that employed by Braden and Gent,[6] the rate of cut growth of vulcanizates A, B, and C at an ozone concentration of 1 mg./l. was found to be within the range 2–4 $\times$ 10^{-4} cm./sec. under static conditions (Table II). From these results an estimate can be made of the ozone concentration in the laboratory by using eq. (3), i.e., by taking the rate of cut growth to be proportional to ozone concentration.

The results in Figure 4, where $dc/dt \simeq 1.5 \times 10^{-9}$ cm./sec., indicate a laboratory concentration of about 5×10^{-6} mg./l., or 0.25 parts per hundred million by volume (pphm) at 20°C. (approximate laboratory temperature). This is about one-tenth of chemical measurements of the outdoor ozone concentration at ground level in Great Britain,[9,10] and is not implausible in view of the readiness with which ozone is destroyed by matter.

EXPERIMENTS ON THE LABORATORY ROOF

Following the calculation of the proceeding section, if dynamic cut growth at tearing energies below T_0 is due solely to ozone, the rate of growth outdoors should be 10 times faster than in the laboratory. To check this, cut growth experiments were carried out on vulcanizates A and B on the laboratory roof. As an additional check the frequency of the dynamic tests was reduced to 1 cycle/min.—a change calculated to have no effect on time dependent growth but reduce cyclic dependent growth in a given time by a factor of 100.

Average results from static and dynamic tests are shown in Figure 5, eq. (4) being used to calculate dc/dt from the dynamic cut growth rate dc/dn, using the measured F values which were in the range 0.27–0.37. The rates of growth from both types of test are again in good agreement and, as anticipated, are some 10 times faster than in the laboratory.

Extrapolating, as before, from static measurements at a high ozone concentration, the average rate of growth of about 2×10^{-8} cm./sec. indicates an ozone concentration in the region of 7×10^{-5} mg./l. or 3.5 pphm, which is consistent with chemical measurements.[9,10]
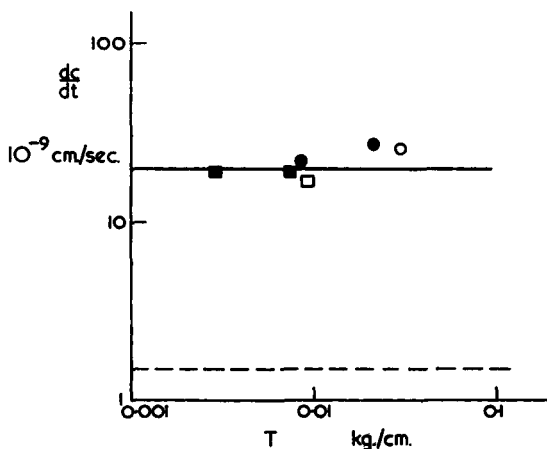

Fig. 5. Cut growth rate dc/dt vs. tearing energy T for static and dynamic tests on the laboratory roof: (O) static tests, vulcanizate A; (□) static tests, vulcanizate B; (●) dynamic tests (1 cycle/min.), vulcanizate A; (■) dynamic tests, vulcanizate B; (– – –) mean of results obtained in the laboratory.

EXPERIMENTS IN AN OZONE CHAMBER

In the previous paper[1] we showed that, corresponding to the critical tearing energy T_0, there exists a mechanical fatigue limit for rubber. Consequently ozone is likely to be a major factor in determining the fatigue life of many rubber components. An ozone chamber was therefore used to enable the characteristics of dynamic ozone cut growth to be further investigated under more controlled conditions and in more detail than was practicable in the laboratory or outdoors.

Ozone was generated from oxygen at a high concentration of about 1 mg./l. by using a mercury discharge lamp. The ozonized oxygen was then diluted with a measured quantity of air and passed through the chamber. The latter was approximately cubic, about 1 m. in side, and the throughput was kept constant at 1000 l./min., so that the gas inside was completely changed once per minute.

The ozone concentration in the chamber was measured by using a commercial instrument (Hampden Ozomat, Hampden Test Equipment Ltd., Rugby) based on a device developed for studies of atmospheric ozone concentrations.[10] The concentration measured in this way was lower than the nominal value calculated from the high ozone concentration input, presumably due to destruction of ozone by the apparatus in the chamber, or on dilution.[11] The concentration was varied by changing the quantity of ozone generated by the discharge lamp.

Dynamic cut growth tests were carried out in the chamber at 100 cycles/min. on test pieces of vulcanizate A. The results are compared to the theoretical relationship given by eq. (4), using the value of α deduced from static high ozone concentration measurements (Table II).

Dependence of Rate of Growth on Tearing Energy

These experiments were carried out at an ozone concentration of 7.5 pphm (1.5×10^{-4} mg./l.). Various tearing energies were obtained by
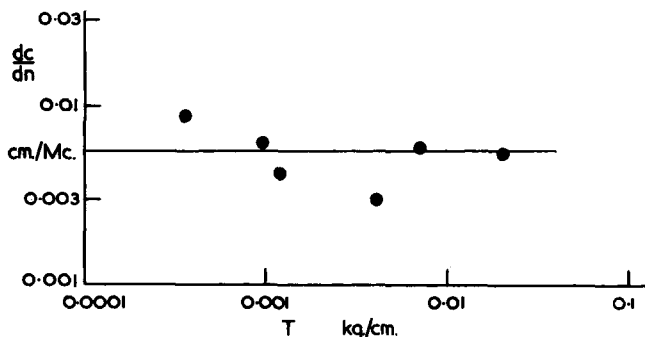

Fig. 6. Dynamic cut growth results for vulcanizate A at tearing energies below T_0 in the ozone chamber. Cut growth rate dc/dn vs. tearing energy T. Ozone concentration $q = 1.5 \times 10^{-4}$ mg./l. = 7.5 pphm, $F = 0.31 \pm 0.06$, $f = 100$ cycles/min. The line represents eq. (4) using α from Table II.

altering both the maximum strain (and hence strain energy) and the length of the inserted cut, the strained fraction of cycle F being set initially within the range 0.35–0.40. During the course of the experiments F decreased, and the range widened to 0.25–0.37 due to differential set. The effect of this variation in F is small, however, in comparison to the scatter. The set was taken into account in calculating strain energy and hence tearing energy.

The dynamic cut growth rate dc/dn is plotted against T in Figure 6. Each point represents the mean result for a single test. Although there is considerable scatter, the rate is substantially constant for variation in tearing energy of more than a factor of 50, in agreement with eq. (4). The average rate of growth of 0.055 cm./Mcycle correlates closely with the full line calculated from eq. (4) by using $F = 0.31$, $f = 100$ cycles/min., $q = 1.5 \times 10^{-4}$ mg./l. and the value of α given in Table II.

Dependence of Rate of Growth on Ozone Concentration

For this investigation the strained fraction of cycle and tearing energy were, as closely as possible, kept constant, F being within the range 0.31–0.34 and T lying between 0.004 and 0.008 kg./cm. The results of dynamic
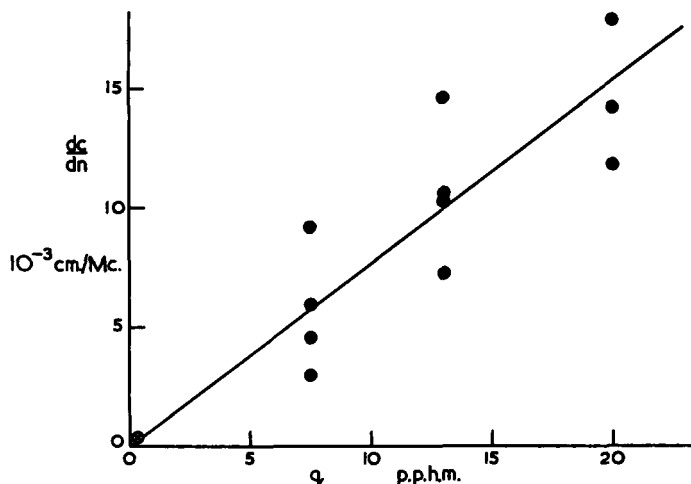

Fig. 7. Variation of cut growth rate dc/dn with ozone concentration q for vulcanizate A at a tearing energy below T_0: (●) results obtained in the ozone chamber ($F = 0.31$–0.34); (⊗) mean of laboratory results ($F = 0.5$). Frequency $f = 100$ cycles/min.; $0.004 < T < 0.008$ kg./cm. The line represents eq. (4) using $F = 0.32$ and α from Table II.

cut growth tests carried out in the chamber at different ozone concentrations are shown in Figure 7. The mean of previous measurements at 100 cycles/min. for vulcanizate A in the laboratory is also plotted, the ozone concentration deduced from static measurements being used. The results bracket the straight line calculated from eq. (4) and, within the

limits of the rather large experimental scatter, are consistent with the rate being proportional to the ozone concentration q.

Dependence of Rate of Growth on Strained Fraction of Cycle

These measurements were carried out at an ozone concentration of 7.5 pphm, the tearing energy being kept approximately constant within the range 0.005–0.008 kg./cm.

The scatter involved in crack growth measurements is of the same order as the variation which can readily be obtained in F with the approximately sinusoidal movement we employed, so that the results are not very definitive (Fig. 8). However, they are in reasonable agreement with the line calculated from eq. (4), the dynamic rate of growth showing the expected tendency to increase with F.
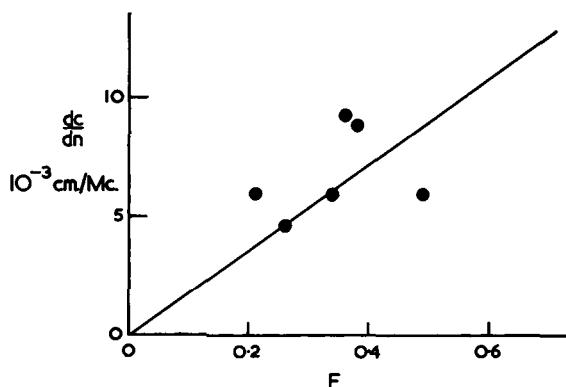

Fig. 8. Dependence of cyclic cut growth rate dc/dn on strained fraction of cycle F for vulcanizate A at a tearing energy below T_0. Ozone concentration $q = 7.5$ pphm; frequency $f = 100$ cycles/min.; $0.005 < T < 0.008$ kg./cm. The line represents eq. (4) using α from Table II.

EFFECT OF OZONE ON DYNAMIC CUT GROWTH AT TEARING ENERGIES ABOVE T_0

In tests at 100 cycles/min. in the laboratory, the rate of cut growth increases by several orders of magnitude once the tearing energy exceeds T_0 (Fig. 3). In the previous paper[1] this was attributed to the commencement of mechanico-oxidative cut growth.

At tearing energies below T_0, increasing the ozone concentration from the very low level in the laboratory (ca. 0.3 pphm) to 20 pphm increases the cut growth rate in dynamic tests by a factor of about 50. However at tearing energies above T_0 this increase in ozone concentration would be expected to have little or no effect, since the mechanico-oxidative cut growth occurring would still be much greater than the ozone cut growth. To verify this, tests were carried out in the ozone chamber at 100 cycles/min. on vulcanizate A at an ozone concentration of 20 pphm.
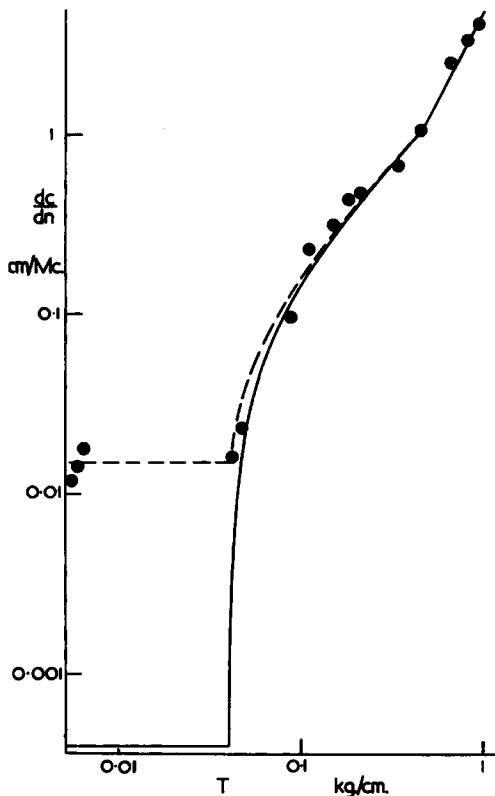
Fig. 9. Contrast between the effects of ozone on dynamic cut growth at tearing energies below and above T_0: (———) laboratory results from Fig. 3 ($q = 0.25$ pphm; $F = 0.50$); (--●--) experimental results and theoretical relationship in the ozone chamber ($q = 20$ pphm; $F = 0.32$). Vulcanizate A; frequency $f = 100$ cycles/min.

The results are compared to those obtained previously[1] in the laboratory atmosphere (solid line) in Figure 9. Consistent with our interpretation,[1] the magnitude of T_0 is not significantly affected by increasing the ozone concentration. The theoretical relationship for 20 pphm is given by the broken line which represents eqs. (5) and (6), with r calculated from eq. (4), using the values of f and q given above, α, T_0, and A from Table II, and the experimental F of 0.32. Above T_0 the difference in rate of growth at the two ozone concentrations rapidly becomes negligible, in accordance with theory.

GENERAL DISCUSSION

In the previous paper[1] we identified two mechanisms responsible for cut growth: mechanico-oxidative rupture and ozone scission. At tearing energies below a critical value (T_0) the extremely slow rate of growth in vulcanizates of natural rubber and SBR tested at 100 cycles/min. in the

laboratory, corresponds to cleavage of one polymer chain every 100–1000 cycles. Even at the very low laboratory ozone concentration (ca. 0.3 pphm), the ozone present is sufficient to cause all the growth observed in these dynamic tests. Furthermore, the dynamic growth is characteristic of ozone in being substantially independent of tearing energy. Once T_0 is exceeded, the growth per cycle becomes markedly dependent on tearing energy and rapidly increases to the order of molecular dimensions, indicating that the stress at the tip of the cut is now sufficient to cause mechanical rupture of at least one chain each time the deformation is imposed.[1] This evidence suggests very strongly that dynamic cut growth at tearing energies below T_0 is due solely to ozone.

The above considerations apply to dynamic experiments in which the test piece is allowed to return to zero strain on each cycle. If the test piece is not relaxed, mechanico-oxidative cut growth in crystallizing natural rubber may be entirely suppressed at tearing energies far above the T_0 observed under relaxing conditions. Effectively, this means that T_0 may be increased by not allowing the test piece to relax. The reduction in cut growth rate obtained in this way is adequate to account for the greatly increased fatigue life of natural rubber under nonrelaxing conditions.[8]

The important role of ozone in dynamic cut growth at tearing energies below T_0 is confirmed by the proportionality of rate of growth to ozone concentration. In this region the characteristics of dynamic cut growth are given to a good approximation by eq. (4) for a vulcanizate unprotected by antiozonant (except for 1 part of PBN which, although normally classified as an antioxidant, reduces the rate of ozone crack growth by a factor of about 2). At higher tearing energies ozone has little or no effect on dynamic cut growth under our experimental conditions (100 cycles/min. and 20 pphm). These results are consistent with those of Gent,[12] who found little effect of ozone on fatigue life at a strain above the fatigue limit.[1] The effects of ozone will be more important at higher ozone concentrations or lower frequencies, but under normal atmospheric conditions are likely to be slight at tearing energies above T_0 when the frequency exceeds about 1 cycle/min.

Braden and Gent[7] have suggested that the critical tearing energy T_z required for ozone crack propagation in unprotected vulcanizates represents the surface energy of the newly formed surfaces. The extremely low value of T_z ($<10^{-5}$ kg./cm.) indicated by the results for vulcanizate A under dynamic conditions does not appear consistent with this simple interpretation, since it is much lower than is observed for this vulcanizate under static conditions and considerably less than would be expected from the surface energies of simple liquids.

Under static conditions, inclusion of an antiozonant in a rubber vulcanizate can be beneficial in two ways:[13] (1) by reducing the rate of crack growth, and (2) by increasing T_z.

Some antiozonants reduce the rate of crack growth but have little effect on the critical energy, so that T_z will be close to zero as for the vulcanizates

we have investigated. A vulcanizate containing antiozonant of this type should therefore obey eq. (4), with a lower value of α than the corresponding unprotected vulcanizate. Addition of other antiozonants can considerably increase the critical energy under static conditions,[13] but if the rubber is disturbed, this effect is greatly reduced, so that under dynamic conditions eq. (4) may also be applicable to vulcanizates containing this type of antiozonant.

In conclusion it must be emphasized that the experimental results and foregoing discussion apply to the growth of a single crack, so that the results must be applied with caution to situations in which many cracks develop. Application of these results to the tensile fatigue of rubber at low strains will be considered in a subsequent paper.

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Résumé

On a étudié l'influence de l'ozone sur la croissance des coupures dans des bandes de caoutchoucs soumises à des déformations de tension répétées. Aux énergies de rupture, situées en-dessous d'une valeur critique, l'ozone est responsable de toute la croissance des coupures, et dans cette région la vitesse de croissance est réellement indépendante de l'énergie de rupture. Pour des énergies de rupture plus élevées, il y a également croissance des coupures, due à une rupture mécanique–oxydante. La vitesse de ce type de croissance augmente rapidement avec l'augmentation de l'énergie de rupture de telle sorte que les effets de l'ozone sont normalement faibles. Pour les vulcanisats du caoutchouc naturel et du SBR non protégés par des antiozonisants, on peut déduire les caractéristiques de la croissance dynamique des coupures dues à l'ozone à partir de mesures statiques. Si on ne laisse pas l'échantillon de caoutchouc naturel retourner à une tension nulle à chaque cycle, les effets de l'ozone sont importants dans un domaine plus large de l'énergie de rupture.

Zusammenfassung

Der Einfluss von Ozon auf das Schnittwachstum in Kautschukstoffen, die einer wiederholten Zugdeformation unterworfen wurden, wurde untersucht. Bei Rissenergien unter-

halb eines kritischen Wertes kann das gesamte Schnittwachstum auf Ozon zurückgeführt werden und in diesem Bereich ist die Wachstumsgeschwindigkeit im wesentlichen von der Rissenergie unabhängig. Bei höheren Rissenergien tritt ein Schnittwachstum auch durch ein mechano–oxydatives Reissen ein; die Geschwindigkeit dieses Wachstumstyps nimmt mit steigender Rissenergie rasch zu, sodass normalerweise Ozon nur einen schwachen Einfluss hat. Bei Naturkautschuk- und SBR-Vulkanisaten ohne Antiozonanszusatz können die charakteristischen Grössen des dynamischen Ozonschnittwachstums aus statistischen Messungen abgeleitet werden. Wenn eine Naturkautschuktestprobe nicht in jedem Zyklus auf die Verformung 0 relaxieren kann, ist der Ozoneinfluss über einen weiteren Rissenergiebereich von Bedeutung.