

The Attack of Ozone on Stretched Rubber Vulcanizates. II. Conditions for Cut Growth

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INTRODUCTION

In Part I¹ an experimental study was reported of the factors determining the rate of propagation of a cut through a stretched rubber sheet under the action of an atmosphere containing ozone. It was remarked that no growth took place from a small razor cut made in one edge of the test piece unless a critical value of the applied tensile stress was exceeded. The value was quite small, of the order of 100 g./cm.² for a soft natural rubber vulcanizate.

In the present part an examination is reported of the conditions necessary for a crack to form or, being present, to grow.

EXPERIMENTAL METHOD

The experimental arrangement for producing a steady flow of ozonized oxygen through the test chamber has been described previously.¹ The concentration used in the present work was generally 1.15 mg. of ozone/l. The test pieces consisted of rubber strips 1.5 cm. wide and 7 cm. long, of various thicknesses in the range 0.02 to 0.2 cm. They were cut from vulcanized rubber sheets for which the mix formulations and vulcanization conditions were given in Table I of Part I.¹

Each test-piece was suspended by a clamp from the roof of the test chamber, and weights were added to a light lower clamp placing the central region of the test piece in simple extension. The whole of the test piece, except for the region under observation, was coated with a silicone stopcock grease to prevent ozone attack. The applied weight was varied to determine the minimum value at which cracks appeared in the exposed region or at which a cut initially present grew a detectable amount during a fixed period of exposure. The period was chosen so that growth at a rate one-twentieth of that obtaining under moderately large stresses could be detected. For the natural rubber vulcanizate A, for example, which exhibited

a rate of cut propagation of about 0.2 mm./min. at adequately large applied stresses, the observations were continued for 15 min. With the low power microscope employed, growth of a cut by 0.1 mm. could be detected.

It was found, however, that an intermediate rate of cut growth was never observed. Either the cut did not grow by a visible amount, even in exposure times of more than one hour, or the rate of growth was the constant value found for a wide range of stresses above the critical level.

The threshold stress necessary for cut growth to occur might arise from some physical barrier initially present at the cut tip, due to oxidative degradation of the surface layer, for example. The observed critical stress would then be that necessary to disrupt the protecting layer and allow the attack of ozone on the underlying rubber. In order to examine this possibility a test piece with a small razor cut in the center of one edge was prepared and placed in the test chamber with a tensile stress applied of 0.096 kg./cm.², somewhat greater than the critical value. After the cut had grown by about 2 mm. the applied stress was reduced abruptly to 0.046 kg./cm.² (below the critical amount). The cut was found to stop immediately. It appears therefore that the critical stress does not arise merely from the presence of a protecting film initially present at the cut tip.

EFFECT OF TEST CONDITIONS

Effect of Length of Razor Cut on Critical Stress

The critical applied tensile stress was determined for test pieces of a soft natural rubber vulcanizate A. It was found to be largely independent of the test-piece thickness, but to depend markedly on the length of the razor cut, as shown in Figure 1, where the measured values are plotted against the initial cut length.

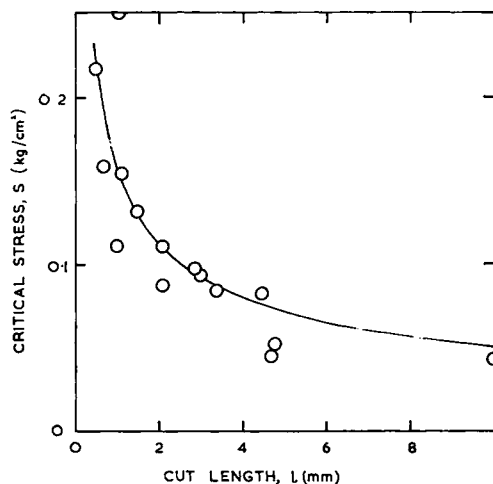


Fig. 1. Relation between the minimum applied stress S for cut growth and the cut length l . The full curve is of the form given in eq. (2).

The tensile stress S_t at the tip of a sharp cut may be calculated by means of classical elasticity theory² in terms of the applied tensile stress S , the cut length l , and its effective radius r at the tip:

$$S_t = S[1 + 2(l/r)^{1/2}] \quad (1)$$

If it is assumed that a cut will propagate under the action of ozone when the tensile stress at the tip exceeds a characteristic value S_t , the relation between the stress in the bulk S necessary for cut propagation and the cut length l should be given by eq. (1). When l is many times the tip radius r , as seems probable for the razor cuts considered, eq. (1) becomes

$$S = S_t^{1/2} / 2l^{1/2} \quad (2)$$

The solid curve in Figure 1 is of this form, and is seen to describe the results with fair success in view of the limited experimental accuracy and the approximations in the theory. The quantity $S_t^{1/2}$ was chosen to give agreement with the experimental results, the value obtained in this way being 0.10 kg./cm.^{3/2}. Microscopic examination suggested that r had a value of 10^{-3} cm. or even smaller, corresponding to a value for S_t of 3.2 kg./cm.² or greater.

From the measured stress-strain relation in simple extension for the vulcanizate employed, the corresponding critical extension at the tip of the cut is 28% or more. This is probably too large for the classical treatment based on infinitesimal strains to apply accurately, and hence the predictions of eq. (2) might be expected to be quantitative

in error, the calculated values of S_t and the critical extension at the tip being particularly uncertain. However, the theoretical predictions are seen to be qualitatively in accord with experiment, and it therefore appears that the basic assumption—that a characteristic critical tensile stress is necessary at the crack tip for growth to occur—is correct. The value required appears to be relatively large, as the measurements reported below confirm.

Effect of Surface Finish

Measurements were made of the applied tensile stress necessary to cause a crack to appear in a small region at one edge of the test piece which was greased to prevent ozone attack at sites other than the one under observation. When the test piece was prepared by cutting with scissors from a vulcanized rubber sheet, the critical stress was irreproducible, varying between 0.45 and 0.90 kg./cm.². When the test piece was molded so that the exposed edge had been formed against a machined metal surface, a more reproducible value of about 0.85 kg./cm.² was obtained.

Although these values are considerably higher than the critical stresses observed for test pieces containing razor cuts (Fig. 1), it is probable that irregularities still exist in the exposed surfaces so that the values observed are not measures of the local critical tensile stress S_t . In an attempt to improve the surface smoothness, fresh test pieces were prepared by cutting from sheets molded between clean glass plates. A small circular area was left ungreased in the center of one major surface instead of at one edge as in the previous measurements, and the critical values of the applied stress determined. They were found to average 1.50 kg./cm.².

Even the glass-molded surfaces are likely to contain some flaws, as discussed below. It appears therefore that the critical stress S_t for cut propagation is greater than 1.5 kg./cm.². This conclusion is in general accord with that deduced from the measurements on test pieces containing razor cuts.

Effect of Size of Exposed Area

Using test pieces cut from a peroxide-vulcanized natural rubber sheet molded between clean glass plates, measurements were made of the applied tensile stress necessary for cracks to appear in a small, roughly circular region left ungreased in the center of one major surface. The values obtained

for the critical applied stress are given in Table I for various diameters of the exposed area.

TABLE I
Effect of Size of Exposed Area

Diameter of exposed area, mm.	Observed cracking stress, kg./cm. ²
7.75	0.8
3.65	0.8
2.70	1.2
1.35	2.4
0.68	>2.6

They are seen to increase as the size of the exposed area is reduced, until at the smallest diameter the protecting grease film failed, and cracks formed elsewhere in the test piece. It seems probable that there is a distribution of surface irregularities, deep flaws being sparsely distributed and hence not likely to occur within small exposed areas.

Depth of Surface Flaws

It is possible to calculate by means of eq. (2) the depth of a razor cut which would require a critical stress for propagation of the order of that observed for test pieces with molded surfaces, i.e., 1–2 kg./cm.². The value obtained is 0.5×10^{-3} to 2×10^{-3} cm.

It does not seem improbable that flaws of this order of magnitude exist in molded surfaces. They might arise, for example, from the presence of particles of foreign matter in the rubber, apart from imperfections in the mold surface.

Number of Cracks Formed

Test pieces having one vertical edge left ungreased were exposed in the test chamber with varying applied stresses. Cracks formed at several points on the edge and grew across the test piece at a uniform rate. In Figure 2 the number of cracks formed per unit length of the exposed edge are plotted against the applied tensile stress for test pieces stamped out with a die from sheets of the soft natural rubber vulcanizate A. The experimental results are represented by open circles.

If it is assumed that many flaws exist in the die-cut edge, each of length l and tip radius r , the stress at the tip of each is given by classical elasticity theory³ in the form

$$S_t = S[1 + 2(d/\pi r \tanh \pi l/d)^{1/2}] \quad (3)$$

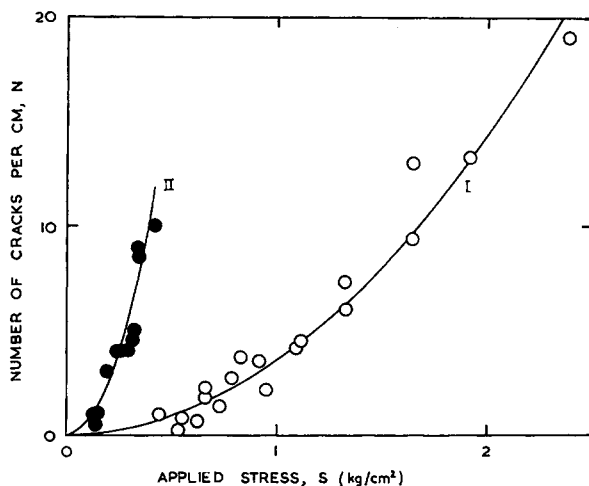


Fig. 2. Relations between the number N of cracks formed per unit length of an exposed edge and the applied tensile stress S : (I) when the edge is formed by die-cutting; (II) when the edge contains numerous small razor cuts. The full curves are of the form given in eq. (4).

where S is the applied tensile stress and d is the distance between adjacent flaws. Crack growth will occur when the stress at the tip of each crack exceeds the critical value S_t . The maximum value of the quantity $\tanh \pi l/d$ is unity, and hence the minimum possible crack separation d is

$$d = (\pi r/4)(S_t - S)^2/S^2$$

As the applied stress S is considerably smaller than the value S_t necessary at the crack tip to cause propagation, this relation may be simplified to yield

$$N = 1/d = 4S^2/\pi S_t^2 r \quad (4)$$

where N is the maximum possible number of cracks which may occur per unit length.

Curve I of Figure 2 is of the form given in eq. (4) and is seen to describe the experimental results with fair success. The quantity $S_t^2 r$ was chosen to give the most satisfactory agreement; the value obtained in this way for $S_t^2 r$ was $0.59 \text{ kg./cm.}^{3/2}$.

The parameter governing the density of cracks $S_t^2 r$ is similar to that governing the effect of initial cut length on the observed critical stress [eq. (2)]. Measurements were therefore made of the number of cuts which grew from a test-piece edge which had many small razor cuts made in it, at about 1 mm. spacings. The observed number of cuts per unit length of the exposed edge which grew on exposure to ozone is plotted in Figure 2 against the applied stress, the experimental points being represented by filled-in circles. Curve II is of the form given in

eq. (4); it is seen to describe the results satisfactorily.

The value used for the quantity $S_c r^{1/2}$ in obtaining curve II was 0.135 kg./cm.^{3/2}, in reasonable agreement with the value of 0.10 kg./cm.^{3/2} obtained previously from the observed relation between critical stress and initial length of a razor cut. The hypothesis that a critical stress condition at the flaw tip governs the onset of crack growth in an ozone atmosphere is thus seen to be capable of predicting the bulk stress required to make cuts of different lengths grow, and the number of cuts which grow out of many initial ones, in terms of a single parameter. In a later section this parameter is considered from a different viewpoint, as a measure of the energy necessary for crack growth.

It has frequently been observed that the number of cracks formed per unit area of an exposed surface increases as the applied stress is increased. Such measurements are, however, not readily compared with those reported above, of the number of cracks formed per unit length, although they are qualitatively in agreement.

EXPERIMENTAL RESULTS

Test Conditions

In order to compare the values of critical stress for various rubbers, test pieces were prepared with a razor cut about 2 mm. long in the center of one vertical edge and the applied stress necessary for growth determined. It is possible that the effective radius of the tip of a razor cut is somewhat different for rubbers of very different properties, and measurements were therefore also made of the applied stress necessary to cause cracks to appear in a small, ungreased, circular region, about 3 mm. in diameter, in the center of a glass-molded surface. The two methods of measurement are denoted by method 1 and method 2, respectively.

To obtain relatively uniform razor cuts for the Method 1 measurements, a procedure similar to that described by Buist and Kennedy⁴ was adopted. The test piece was secured between flat metal plates and the edge of the razor blade passed through a narrow slot in them.

The critical stress was found to be greater for a test piece exposed repeatedly under gradually increasing load than for one without previous exposure. It seems likely that ozone attack occurs at tensile stresses below the critical amount, but is restricted to the surface regions. Such attack would

render the tips of the initial cuts or flaws less sharp and hence necessitate a higher stress for growth.

In the measurements described below, a new test piece was exposed at each load, the values being decreased until crack growth did not occur. The critical stress values obtained for vulcanizate A were, therefore, only about one half of those determined previously.

Effect of Vulcanizate Stiffness

Values were obtained by Method 2 of the critical applied stress S_2 for dicumyl peroxide (DCP) vulcanizates of natural rubber and a conventional sulfur vulcanizate A. The results are given in Table II together with the values of Young's modulus E for each vulcanizate determined by measurements of the load-extension relations for small extensions, and the extension e_2 corresponding to the observed critical stress S_2 .

TABLE II
Critical Conditions for Crack Formation in Natural Rubber
Vulcanizates

Vulcanizate	Young's modulus E , kg./cm. ²	S_2 , kg./ cm. ²	e_2 , %	$W \times 10^{-4}$, ergs/ cm. ³
1½% DCP	4.5	0.80	21.0	8.3
3% DCP	9.6	1.35	15.0	10.5
6% DCP	14.3	1.45	10.5	8.1
Sulfur vulcanizate A	15.0	1.50	10.4	8.1

The experimental measurements of critical stress were somewhat inaccurate. Moreover, the different vulcanization systems employed may well affect the type and number of surface flaws and hence the applied stress necessary to produce a critical condition at the flaw tips. Within these limitations, however, it appears that neither the critical stress nor the extension is independent of vulcanizate stiffness. To a first approximation, the stored elastic energy W appeared to be constant, the values obtained from the areas under the stress-extension curves up to the critical point being given in the last column of Table II. This observation is discussed in a later section.

The critical stress was also determined for a vulcanizate similar to A, but containing in addition 45 parts by weight of carbon black (Philblack O) per hundred parts of rubber. The value obtained was 3.8 kg./cm.², considerably larger than that for the soft, unfilled vulcanizates. If, however, a similar

value of the stored elastic energy is required, a substantially higher value of critical stress would be expected for such a stiff rubber. It was found from the experimentally-determined stress-extension relation that a value of the stored elastic energy similar to those listed in Table II obtained at an applied stress of 3.0 kg./cm.^2 , in fair agreement with the observed critical stress. To a first approximation, therefore, it appears that the higher critical stress observed for the filled vulcanizate is merely a reflection of its enhanced stiffness.

Effect of Vulcanization System Employed

Measurements were made of the critical stress for dicumyl peroxide (DCP), tetramethylthiuram disulfide (TMT), and conventional sulfur vulcanizates. No significant difference was found between the critical stress values determined by Method 2 for the peroxide and the conventional vulcanizate A (1.50 and 1.45 kg./cm.^2) respectively. A markedly lower value (0.38 kg./cm.^2) was obtained for the TMT vulcanizate, however. It was noted that the glass-molded surface for this test piece was not as smooth in appearance, due to the presence of a "bloomed" material, and the low critical stress is considered to arise from the presence of flaws associated with this inferior surface finish. The value of critical stress determined by Method 1 when a razor cut is made in the test piece was found to be similar to that for the DCP vulcanizate and somewhat larger than that for the conventional sulfur vulcanizate A.

In Part I the presence of extractable materials in DCP and TMT vulcanizates was shown to reduce the rate of cut growth considerably. The measurements reported above suggest that the effect of these materials on the critical stress required for crack growth is relatively slight.

Effect of Polymer

The critical stress values were determined by the two experimental methods for vulcanizates of a number of polymers. The results are given in Table III.

The values obtained by Method 1 for the butyl rubber vulcanizate D are seen to be considerably larger than those for A, B, and C. However, the initial razor cuts appeared to be of a somewhat different character in this material and they may well have been less sharp. The results by Method 2 are comparable for the four materials.

The polychloroprene vulcanizate E exhibited a considerably higher critical stress in both experimental arrangements. It was, however, appreciably stiffer than the other materials. The values of Young's modulus E determined from the measured stress-extension relations at small extensions are given in Table III and also the values of the applied stress S_2' at which the stored elastic energy was found to be $8.2 \times 10^4 \text{ ergs/cm.}^3$, the critical value obtained previously for a series of natural rubber vulcanizates. The values obtained for S_2' are seen to be in reasonable accord with the experimental values of the critical stress S_c .

It is concluded, therefore, that, to a first approximation, the critical condition is similar for all the polymers, i.e., that the stored elastic energy in the bulk rubber should have a characteristic value of about 10^5 ergs/cm.^3 for attack to take place on a glass-molded surface. A razor cut 2 mm. in length appears to constitute a "flaw" of differing severity in different polymers. The corresponding values of the critical stored energy range between 10^2 and 10^3 ergs/cm.^3 .

Measurements were also made of the critical stress for vulcanizates containing 25 parts by weight of an ester plasticizer, diethylhexyl adipate,

TABLE III
Critical Stress Values for Vulcanizates of Various Polymers at 20 and 50°C.

Polymer	Mix reference	E_r , kg./cm. ²	S_1 , kg./cm. ²		S_2 , kg./cm. ²		S_2' , kg./cm. ²
			20°C.	50°C.	20°C.	50°C.	
Natural rubber	A	15.0	0.065	0.055	1.23	1.18	1.50
Butadiene-styrene copolymer (75/25) (Polysar S)	B	12.5	0.064	0.045	1.06	—	1.35
Butadiene-acrylonitrile copolymer (60/40) (Polysar Krynac 801)	C	13.2	0.070	0.068	0.97	1.13	1.40
Butyl rubber (Polysar Butyl 400)	D	7.4	0.12	0.23	0.91	0.68	1.02
Polychloroprene (Neoprene GN)	E	25.0	0.21	—	2.30	—	2.00

per hundred parts of polymer. The values obtained by both Method 1 and Method 2 were generally similar to those for the unplasticized vulcanizates given in Table III. It appears, therefore, that the critical conditions for ozone attack are largely independent of the segmental mobility of the polymer molecules, in marked contrast to the rates of cut growth.¹

Effect of Test Temperature and Concentration of Ozone

A limited number of measurements were made of the critical stress at a temperature of 50°C. for both plasticized and unplasticized vulcanizates, the results for the latter being included in Table III. They were similar to the values obtained at 20°C. and suggest that the critical conditions do not depend markedly on temperature.

The critical stress was also determined by Method 2 for the natural rubber vulcanizate A at a concentration of ozone of 0.23 mg./l. i.e., about one fifth of that normally employed. The value obtained, 1.13 kg./cm.², is closely comparable to that found at the normal ozone concentration, namely, 1.23 kg./cm.², and it appears that the critical condition does not vary markedly with ozone concentration.

CHARACTERISTIC ENERGY FOR CRACK PROPAGATION

The stored elastic energy W in the bulk rubber is related to the energy T available for cut propagation at the tip of a cut of length l by the relationship⁵:

$$T = 2KIW \quad (5)$$

where K is a numerical quantity having a value⁵ of about 2. The observation in preceding sections that the stored energy W is substantially constant for a number of natural rubber vulcanizates and for vulcanizates of a number of polymers thus indicates that a characteristic energy T is required at the flaw tip for growth to occur in an atmosphere of ozone. A similar characteristic energy criterion has been proposed by Griffith⁶ to account for the observed strength of glass, and has been shown by Rivlin and Thomas⁵ to govern the tearing of rubber.

The eq. (5) may be transformed to yield the dependence of the critical bulk stress S upon the crack length l , in the form

$$S = (TE/Kl)^{1/2} \quad (6)$$

where E is Young's modulus for the rubber, the extensions of the bulk rubber being assumed sufficiently small for a linear stress extension relation to apply. An equivalent relation is given in eq. (2) and has been shown to predict the form of the observed dependence of the critical stress upon the length of an initial razor cut.

The values of the critical stress S for vulcanizates of natural rubber A and of a butadiene-styrene copolymer B were found to be about 65 g./cm.² for test pieces with an initial razor cut of 2 mm. length. The corresponding values of T may be calculated from eq. (6) by use of the measured values of Young's modulus E . The values obtained in this way are about 120 ergs/cm.². In contrast, the characteristic energies for tearing similar vulcanizates are much higher,⁷ of the order of 10⁶ ergs/cm.².

Somewhat greater values of critical stress, and hence T , obtain for the other polymers, where it seems likely that the initial razor cuts are less sharp. Indeed, the present value of about 120 ergs/cm.² is only realized with carefully controlled incisions, and significantly lower values were never obtained. It appears therefore that the characteristic energy for ozone attack is extremely low in comparison with that for tear propagation, but somewhat larger than would be expected as a measure of twice the surface energy of the newly formed surfaces, when a value of about 50 ergs/cm.² would be anticipated.⁸ The discrepancy might arise from slight adhesion of the newly formed surfaces.

GENERAL CONCLUSIONS

(1) It has been found that a cut in the edge of a stretched sheet of rubber will not grow in an atmosphere of ozone unless the applied tensile stress exceeds a well-defined critical value. Moreover, if the stress is subsequently reduced below the critical amount, the cut stops. The critical stress appears therefore to be a property of the rubber rather than of a barrier layer at the surface.

(2) The critical stress for ozone attack is found to depend on the cut length in nicked test pieces and on the surface smoothness of unnicked test pieces, in accordance with a proposed criterion for crack growth to occur, that the stress at the tip of the cut or surface flaw should exceed a characteristic value. The same criterion is shown to account for the observed number of cracks which form per unit length of an exposed edge as a function of the applied stress.

(3) The critical stress values for various natural rubber vulcanizates suggest that a constant stored elastic energy is the appropriate criterion when rubbers of different stiffness are considered.

(4) The critical stored energy appears to be similar for vulcanizates of natural rubber, a butadiene-styrene copolymer (75/25 Polysar S), a butadiene-acrylonitrile copolymer (60/40 Polysar Krynac 801), butyl rubber (Polysar Butyl 400) and polychloroprene (Neoprene GN). It also appears to be largely unchanged by plasticization, by a temperature change from 20 to 50°C., and by a considerable reduction in the concentration of ozone.

(5) The measurements are shown to be in accord with the criterion that the propagation of a cut in an ozone atmosphere requires a characteristic energy T at the tip of the initial cut or surface flaw. For an initial sharp razor cut, the value of T obtained is of the order of 100 ergs/cm.², only about twice as large as that expected from the energy of formation of the new surfaces.

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Synopsis

Experimental measurements are described of the conditions necessary for crack growth in an atmosphere containing ozone. It is proposed that a characteristic value of the tensile stress at the tip of an initial cut or surface flaw is required for growth to occur. This criterion is shown to predict the observed dependence of the applied stress required for crack growth on the length of an initial cut and on the surface smoothness of uncut test pieces. The number of cracks formed in an exposed edge is also shown to be

in accordance with the proposed criterion. For vulcanizates of differing stiffness, the appropriate criterion is found to be the stored elastic energy. The critical value is shown to be similar for a number of different polymers, and largely unchanged by plasticization, a change in temperature from 20°C. to 50°C., and alteration in the concentration of ozone. For initial flaws consisting of sharp razor cuts, the energy required for cut propagation is found to be about 60 ergs/cm.² of newly formed surface.

Résumé

Les mesures expérimentales des conditions nécessaires à la croissance d'une fissure dans une atmosphère d'ozone ont été décrites. On a proposé l'existence d'une valeur caractéristique de la tension d'élongation à l'extrémité d'une coupure initiale ou d'une crevasse de la surface permettant la croissance du phénomène de coupure. Ce critère permet de prévoir la dépendance de la croissance d'une fissure en fonction de la tension appliquée à la longueur de la coupure initiale et à l'uniformité de la surface non coupée des échantillons témoins. Le nombre de crevasses formées sur une arête exposée est également en accord avec le critère précité. Dans le cas de vulcanisats de rigidité variable, l'énergie élastique interne s'est avérée être le critère approprié. La valeur critique est identique pour une série de polymères différents; l'adjonction de plastifiants, la variation de la température de 20 à 50°C et la modification de la concentration en ozone sont sans effet sur cette valeur. Dans le cas de fissures initiales provoquées dans une surface nouvellement formée par des coupures à l'aide d'un rasoir acéré, l'énergie requise à la propagation de ces coupures s'élève environ à 60 ergs/cm.².

Zusammenfassung

Es werden Experimente zur Messung der für das Wachsen eines Risses in einer ozonhaltigen Atmosphäre notwendigen Bedingungen beschrieben. Es wird die Annahme vorgeschlagen, dass zum Eintritt des Wachstums ein charakteristischer Wert der Zugspannung an der Spitze eines primären Schnittes oder Oberflächenrisses erforderlich ist. Dieses Kriterium liefert, wie gezeigt wird, die beobachtete Abhängigkeit der zum Wachstum eines Risses erforderlichen, angewendeten Spannung von der Länge des primären Schnittes und von der Glätte der Oberfläche der Testprobe vor dem Schnitt. Ebenso wird gezeigt, dass die Anzahl der an einer beanspruchten Kante gebildeten Risse in Übereinstimmung mit dem vorgeschlagenen Kriterium steht. Bei Vulkanisaten mit verschiedener Steifigkeit wird festgestellt, dass die gespeicherte elastische Energie das geeignete Kriterium ist. Für eine Anzahl verschiedener Polymerer wird das Auftreten eines ähnlichen kritischen Wertes nachgewiesen, der auch durch Weichmachung, Temperaturänderung von 20 auf 50°C und Änderung der Ozonkonzentration keine grösseren Änderungen erfährt. Es wird gefunden, dass bei Primärrissen in Gestalt von scharfen Rasiermesserschnitten die zum Schnittwachstum erforderliche Energie etwa 60 erg/cm² neugebildeter Oberfläche beträgt.

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