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Rupture of Rubber. V. Cut Growth in Natural Rubber Vulcanizates

A. G. THOMAS, *British Rubber Producers' Research Association, Welwyn Garden City, Herts, England*

Nick, a small cut

1. INTRODUCTION

It has been noted in Part I of this series[1] (referred to hereafter as I), that if a nicked specimen of a natural rubber vulcanizate is slowly stretched, tearing occurs at the tip for quite small applied forces. In the initial stages, this tearing continues only as long as the deformation of the specimen is being increased, and virtually ceases if the deformation is held constant. This tearing is essentially time independent, and is termed "static" cut growth. If, however, the deformation is continued until the cut has grown by a few hundredths of a millimeter the growth becomes time dependent and catastrophic tearing takes place, the cut suddenly increasing in length by perhaps a millimeter or so.

If a nicked specimen is alternately stretched and relaxed to the unstrained state, the cut gradually grows even though the applied force is less than that required to produce catastrophic tearing. This phenomenon is termed "dynamic" cut growth. Fatigue crack growth

This behavior can be compared to that of gum GR-S vulcanizates described in Part III,[3] where static cut growth of the above type does not occur, a dead load on a test piece producing a more or less steady rate of cut growth.

In the present paper, measurements on natural rubber gum vulcanizates only are described, and the numerical results expressed in terms of the theory developed in previous papers (Parts I,[1] II,[2] and III[3]).

It has been shown in I and II that the tear behavior of differently shaped test pieces cut from thin sheets of thickness t may be correlated by means of the concept of the energy for tearing. This is defined as the value of T

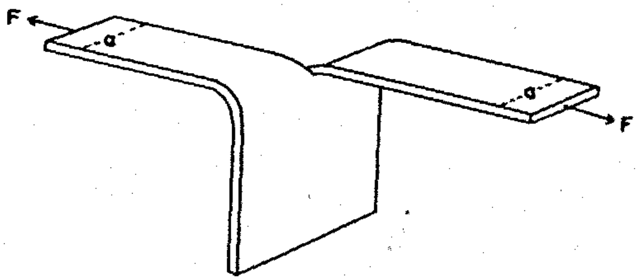

Fig. 1. Simple extension tear test piece.

Here T is the energy release rate, and Tc is the fracture energy

[$= (1/t)(\partial W/\partial c)_l$] at the instant of tear, and is denoted by T_c. In the definition of T, W is the total elastic energy stored in the test piece, c the length of the cut, and the subscript l indicates that the differentiation is to be carried out at constant displacement of those parts of the boundary that are not force-free. It was also shown that a convenient and direct method of obtaining T_c is by the use of the "simple extension" tear test piece described in I and shown in Figure 1, and this has been used for most of the experiments. Under most conditions, T for this test piece is nearly independent of the cut length, width of the test piece, and modulus of the rubber; T is very nearly equal to $2F/t$ where F is the force applied to the arms. In the cases where the use of the above approximate relation between T and F introduces an appreciable error, the exact theory given in I was used.

2. STATIC CUT GROWTH

A simple extension tear test piece was prepared with the tip of the cut formed by a razor blade, placed in a tensometer, and the tip of the cut observed through a low power microscope. On extending the test piece it could be seen that tearing was occurring at the tip. The freshly torn surface could be distinguished from the original under suitable illumination by means of the slight angle they made with one another. The freshly torn surface appeared to be in the form of a shallow arrow-head. If the specimen was viewed in a direction perpendicular to the plane of the sheet, the appearance of the tip was somewhat as shown in Fig. 2. This is reminiscent of the effect noted by Busse[4] when a cut is made in a sheet of highly stretched gum rubber, and suggests that this characteristic formation is due to the fact that at the tip the rubber is highly extended and thus crystalline and very hysteretic. That hysteresis plays an important part is suggested by the observation that, on relaxing the test piece, the characteristic formation disappeared when a sufficiently low strain was reached. On restretching, further cut growth took place at the new tip in a very similar manner to that which it would have followed if the whole incision had been made with a razor blade. A slight difference was noticeable, however, in that when cut growth occurred the initially smooth tip became somewhat rougher and on relaxing and restretching the new tip was not quite so well defined. This roughening, which continued with successive cycles, will be discussed later.

Hysteresis

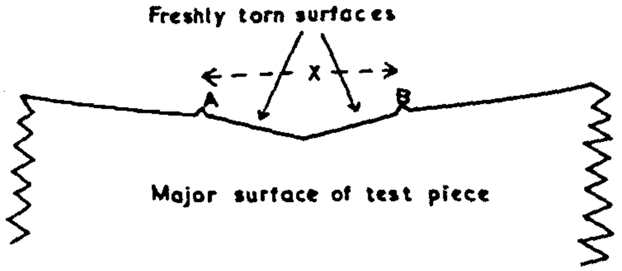

Fig. 2. Tip of cut during static cut growth.

The amount of cut growth which has occurred on application of a given force can be estimated by measuring the width of the torn rubber at the tip, the distance AB $(= x)$ of Figure 2. As the rubber just around the tip is presumably stretched to about its limiting extension ratio, λ_b, the distance the cut has grown, Δc, referred to the unstrained state, is given approximately by

Limiting stretch

$$\Delta c = x/2\lambda_b \tag{2.1}$$

The measurement of x is facilitated by applying a small amount of a suitable powder, e.g., carbon black, to the inside of the tip of the cut before stretching takes place. If the tip is then viewed throughout its thickness as the test piece is extended, the freshly torn surface can be seen as a pale area in a dark surround and x estimated by an eyepiece scale in the microscope. The corresponding T values can be found from the applied force, F. In this way static cut growth curves were obtained for rubbers A and B, prepared from the mixes in the Appendix.

Conventional tensile rupture tests were made to find λ_b, and also stress-strain measurements to determine the elastic constants C_1 and C_2 as described by Gumbrell, Mullins, and Rivlin.[5] Table I shows the results.

TABLE I

Mix	λ_b	C_1, kg./cm.^{2}	C_2, kg./cm.^{2}
A	8.3	1.24	1.16
B	7.6	2.34	1.12

From eq. (2.1), Δc can be calculated, giving the cut growth curves shown in Figure 3.

It was found empirically that Δc was approximately proportional to T^2 except at the highest T values approaching T_c, where in any case Δc was becoming time dependent. Figure 4 shows the plot of Δc *vs.* T^2 for rubbers A and B. Assuming proportionality,

$$T^2 = G_s \Delta c \tag{2.2}$$

R-curve

The values of the constant G_s were found to be 1.6 and 2.7×10^{16} c.g.s. units, respectively, for the two rubbers.

3. DYNAMIC CUT GROWTH

Experiments have been done with the simple extension tear test piece using the apparatus shown diagrammatically in Figure 5. This consists of a rocking arm A driven by a crank C; A carries a rod R which can be slid along and clamped where required. The test pieces P, usually four in number, are attached to this rod by means of calibrated spiral springs S and tension adjusters B, and clamped at their lower ends.

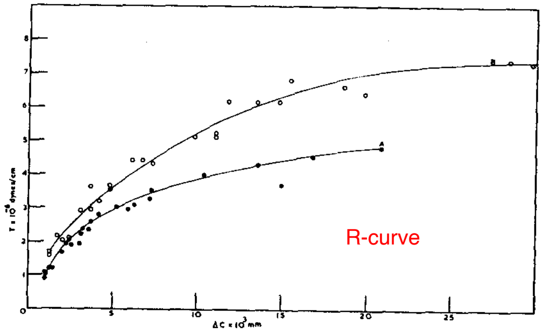

Fig. 3. Static cut growth curves.

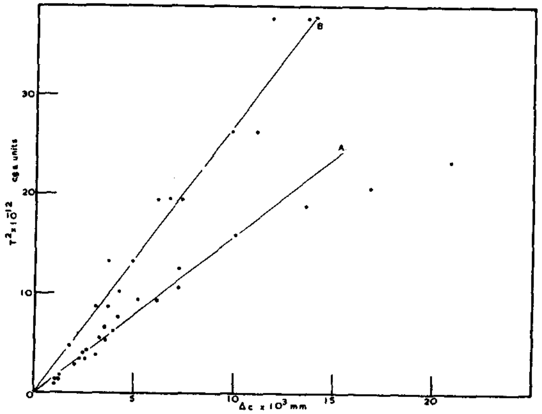

Fig. 4. Plot of T^2 vs. Δc for static cut growth.

The amplitude of oscillation could be varied by moving the rod *R* and by altering the throw of the crank *C*. It was in general arranged so that the test pieces were completely relaxed for a portion of the cycle. The maximum forces were found from the maximum extensions of the springs. As cycling proceeded and the cuts grew, these maximum extensions of course decreased, but at intervals the springs were restored to their original maximum extensions by means of the tension adjusters. The amount of cut growth between successive adjustments was small (<1 mm.), and the use of soft springs made errors from this source negligible compared with the spread in the results as a whole.

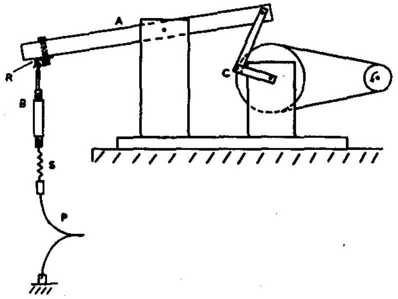

Fig. 5. Dynamic cut growth machine for simple extension tear test pieces.

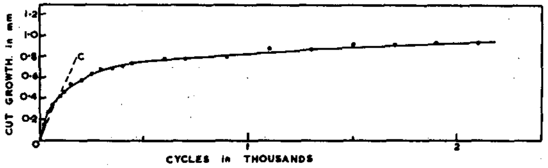

Fig. 6. Dynamic cut growth curve.

The cut growth was found by measuring with a microscope the distance of the tip from marks made on the test piece. The observation of the tip was made easier by slightly separating the arms and holding the test piece flat with a microscope slide.

The initial cut in the test pieces, which were 1–2 mm. thick, was always formed by a razor blade. A typical cut growth curve is shown in Figure 6 for the early stages of cut growth. Vulcanizate A was used and the maximum force was equivalent to a value of *T* of 1.96 × 10⁶ dynes/cm. It can be seen that the initial rapid rate of cut growth gradually slows down and finally, after a few thousand cycles, becomes substantially constant apart from irregular fluctuations. This decrease in rate is accompanied by a visible roughening of the tip of the cut.

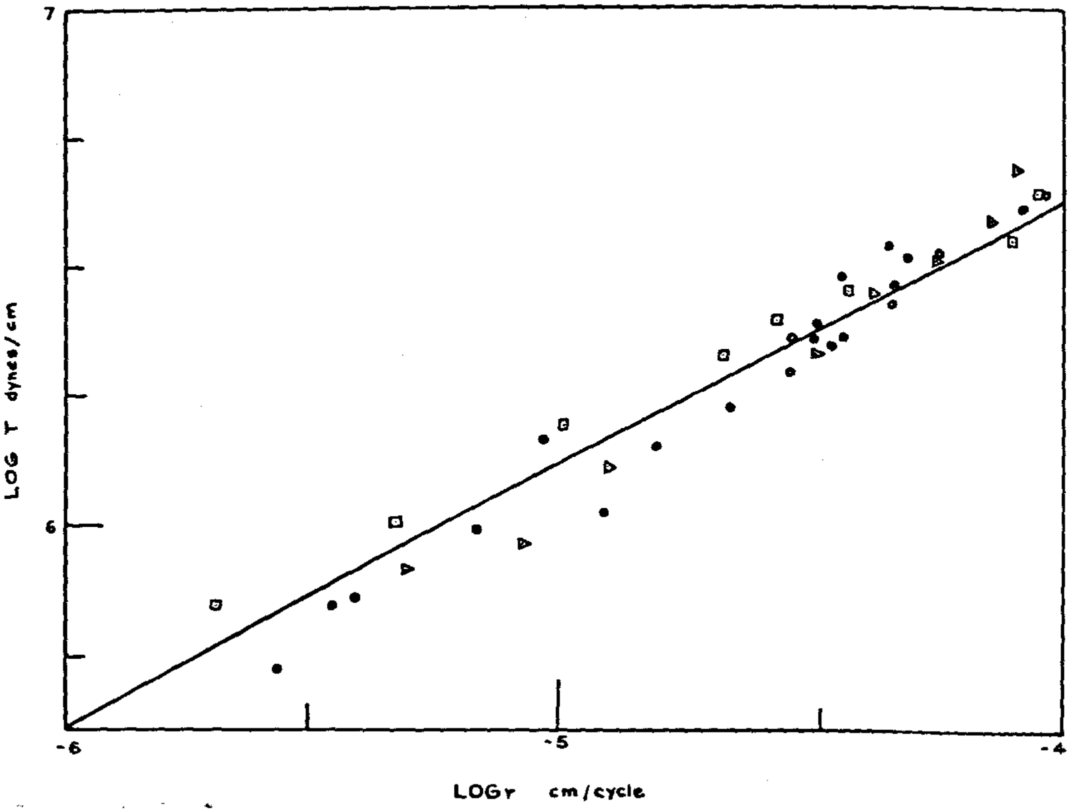

Fig. 7. Relation between rate of cut growth and T for dynamic cut growth. Mix C (●); Mix D (⊡); Mix E (○); Mix F (△).

It is of interest to compare the rate of cut growth which would be expected from the static cut growth results for this rubber, assuming that the static cut growth value of Δc occurs for each cycle. The broken straight line in Figure 6 gives the result, which is seen to correspond to a much faster rate of growth than the final value found in the dynamic measurements, but is consistent in order of magnitude with the initial rate found. The ratio of the initial to the final rate is about 10. The initial stage of the dynamic cut growth curve is not very reproducible, the cut attaining its final rate after very variable distances of travel.

In the subsequent experiments the dynamic rate of cut growth is taken to be that finally attained, when there is no further consistent decrease in the rate. In practice, this means that the cut growth curve for the first few thousand cycles is ignored in fitting the final slope to the line.

Experiments have been done on rubbers C, D, E, and F, with the results shown in Figure 7. The C_1 and C_2 values are given in Table II.

TABLE II

Mix	C_1, kg./cm.^{2}	C_2, kg./cm.^{2}
C	1.46	1.20
D	1.58	1.24
E	1.70	1.31
F	1.80	1.36

Figure 7 shows that the rates of cut growth of these rubbers are not significantly different. Rubbers D and E are nominally identical, except that D contains antioxidant.

In Section 2, it was found empirically that the amount of static cut growth Δc was approximately proportional to T^2. This suggests that a corresponding relation may hold for dynamic cut growth. The full line in Figure 7 is drawn with a slope of 2, and it can be seen that it is consistent with the results except possibly at the highest values of T. Thus we have the relation

$$T^2 = G_d r \tag{3.1}$$

where r is the rate of cut growth in centimeters per cycle, and G_d a dynamic cut growth constant for these rubbers having the value 1.7×10^{17} c.g.s. units.

The cut growth per cycle is not very sensitive to the period of cycling at about the period used. No significant difference in rate was observed when the period was increased from 1.5 to 4.2 seconds, and the bulk of the measurements were carried out using the shorter period. The fastest speed of cycling which can be used with the present apparatus is limited by the oscillations of the test pieces and the attached clamps and springs.

4. VALIDITY OF THE RUPTURE CRITERION WHEN APPLIED TO CUT GROWTH

In I and II a theoretical treatment was given of two types of tear test piece, "simple extension" and "pure shear," on the basis of the criterion of rupture then proposed. It was shown experimentally in I that, for a given rubber, tearing occurred at the same value of T in test pieces of different shape, in particular the two above-mentioned types. In the case of cut growth it may be expected by analogy that equivalent values of T will similarly produce the same rate of cut growth. Experiments have been done to test this conclusion by comparing the behavior of the simple extension and pure shear test pieces.

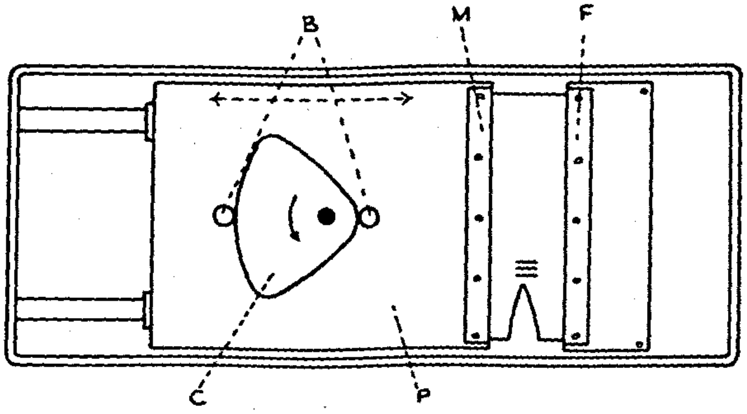

Fig. 8. Dynamic cut growth machine for pure shear tear test pieces.

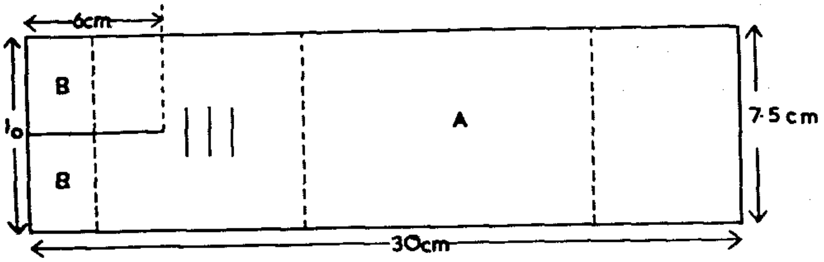

Fig. 9. Pure shear tear test piece.

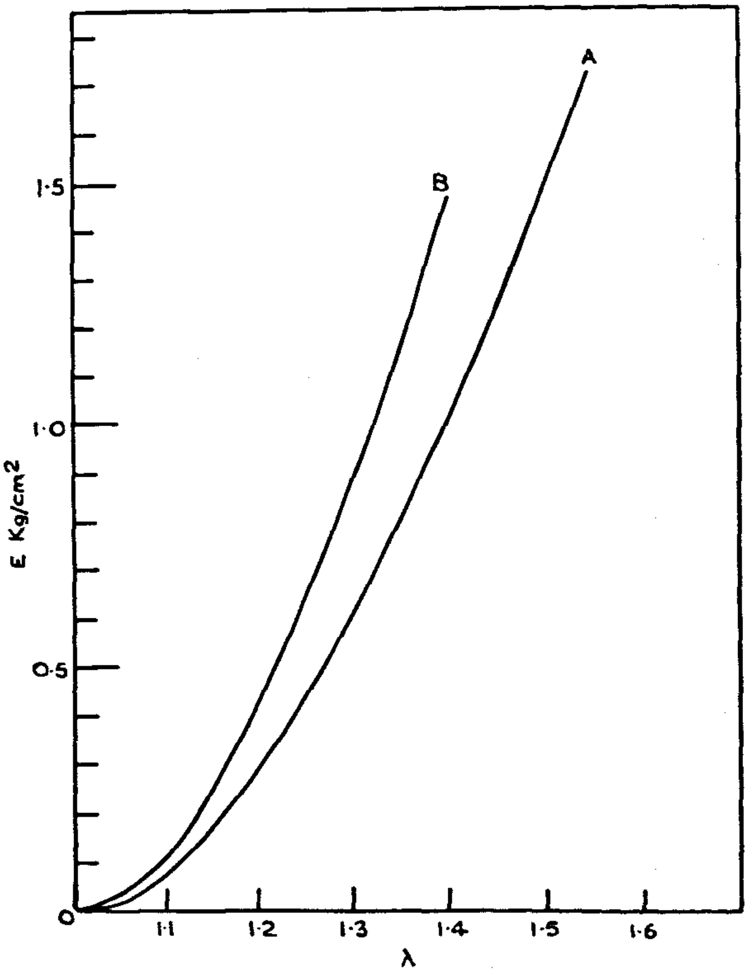

Fig. 10. Stored energy/unit volume in pure shear.

The apparatus used to stretch and relax the pure shear test piece is shown diagrammatically in Figure 8. The cam *C* rotates, driving the platform *P* to and fro, maintaining contact continuously with the ball bearings *B*. A clamp *M* is attached to this moving platform opposite a similar fixed one *F*. These clamps are about 30 cm. long and the test piece is stretched between them. The position of clamp *F* can be varied so that the test piece is unstrained for part of the cycle and is then stretched to a suitable maximum strain. The amplitude of motion of the clamp *M* is about 5 cm. As the test pieces used were thin (0.1 cm.) compared with their length (6 cm.), any buckling that occurred when the clamps approached each other produced only negligibly small strains. The period of cycling was 1.9 seconds.

The approximate dimensions of the test pieces, shown in Figure 9, were

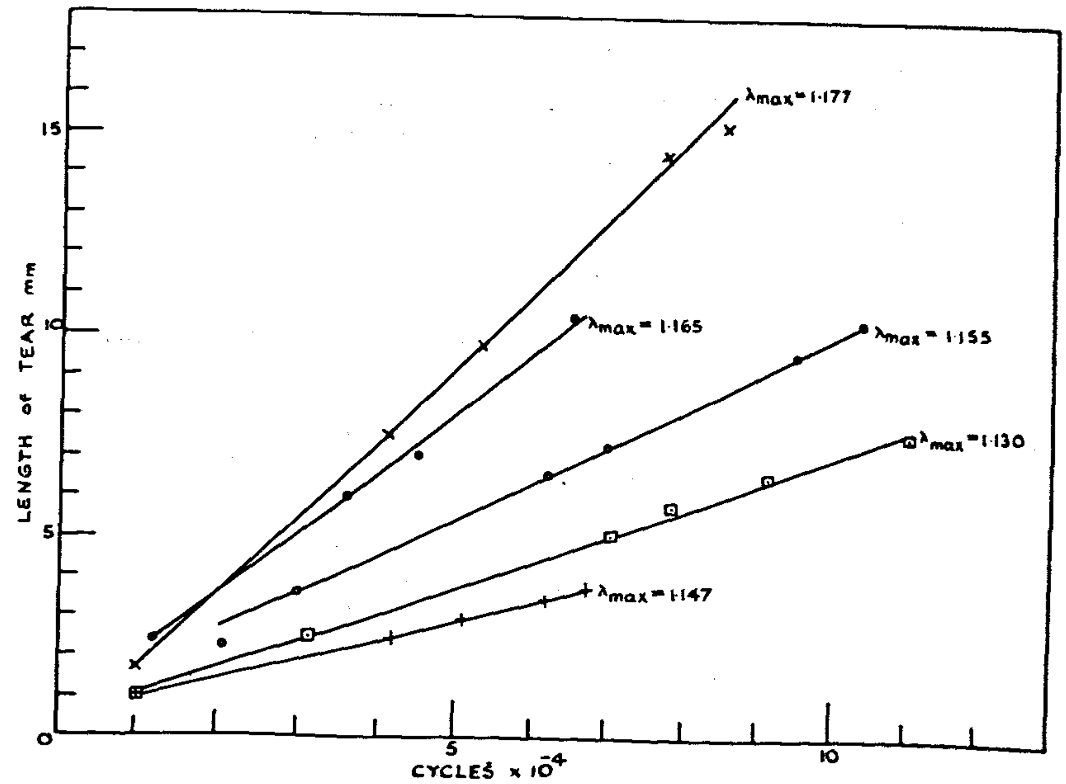

Fig. 11. Dynamic cut growth curves for pure shear tear test piece.

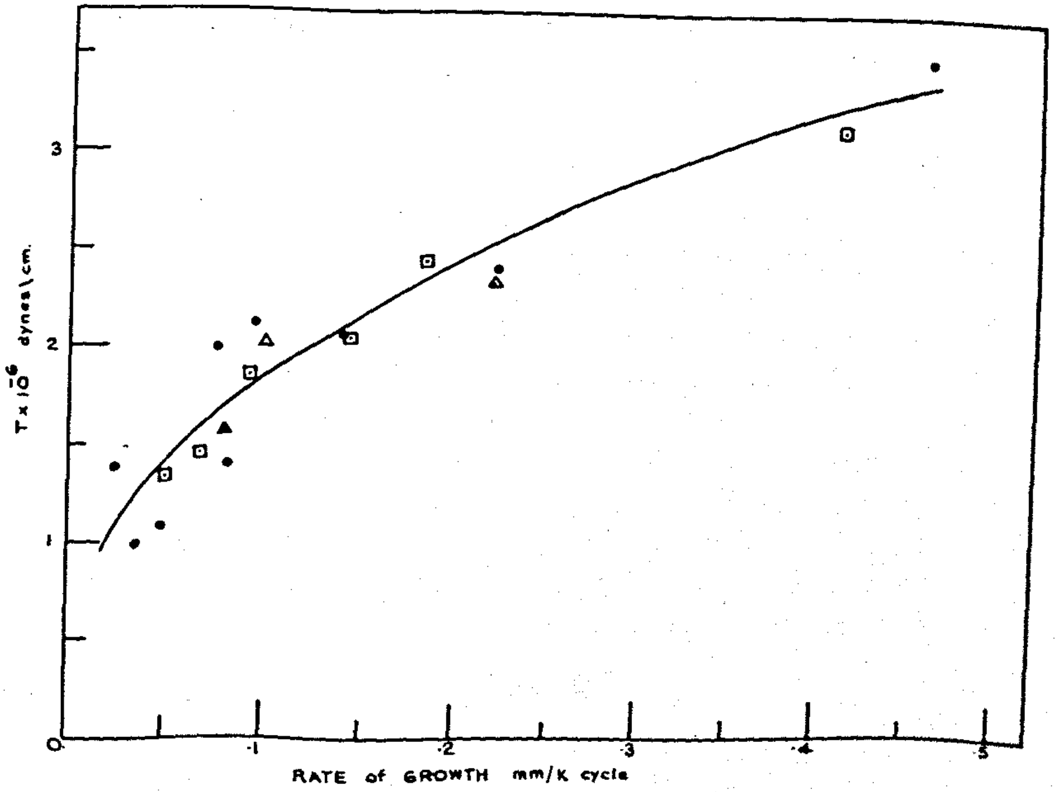

Fig. 12. Comparison of rates of cut growth for simple extension and pure shear tear test pieces. Simple extension: Mix A (O); Mix B (●). Pure shear: Mix A (△); Mix B (⊡).

chosen so as to meet the requirements stated in I; viz., there was a region *A* substantially in pure shear and regions *B* which were substantially unstrained.

Two vulcanizates, A and B, were used. Their stress-strain properties in pure shear were first determined by the method of Rivlin and Saunders.[6] The stored energy per unit volume E was then calculated as a function of the extension ratio λ_s by graphical integration under the stress-strain curve, giving Figure 10.

From I, T for this test piece is given by

$$T = El_0 \tag{4.1}$$

where l_0 is the unstrained length. The maximum value of λ_s was measured and hence, from Figure 10, E was found.

Test pieces were cycled on the machine, and the distance of the tip of the cut from marks on the rubber, as indicated in Figure 9, was measured at intervals. After a conditioning period of a few thousand cycles the cut growth curve was substantially linear, as was also found with the simple extension test pieces. Figure 11 shows some typical results.

Simple extension tear test pieces were also tested as previously described. The range of the maximum values of T was about the same in the two sets of measurements; Figure 12 summarizes the results on both test pieces. There seems to be no significant difference in their behavior within the usual rather large spread in the results. Thus the rupture criterion proposed in I appears to apply to cut growth as well as catastrophic tearing, and in principle enables the rate of cut growth in one type of test piece to be calculated from measurements on another.

5. THE ROUGHNESS OF THE TIP OF THE CUT

It has been mentioned above that during cycling the tip becomes considerably rougher. The marked decrease in rate of the cut growth which is frequently observed in the initial stages of growth from a razor cut appears to be associated with the development of this roughness, so this phenomenon may be of considerable importance.

In II it was suggested that roughness or unevenness of the tip could act as if it produced a finite radius of curvature, making the strain concentration less acute. The observed roughness was of the same order of magnitude as the effective diameter d of the tip, the latter being deduced from the measured T_c value and the work to break per unit volume in simple extension E_b, using the relation

$$T_c \simeq d \times E_b \tag{5.1}$$

Equation (5.1) enables the effective diameter of the tip of a cycled test piece to be estimated from T_c, calculated from the force required to tear it catastrophically, and E_b. Thus a quantitative measure of the roughening which occurs may be obtained.

Table III gives results obtained on cycled test pieces of vulcanizate B, for which E_b was 5.0×10^8 ergs/cc. For a pest piece with its tip formed by a razor cut, T_c was 8.2×10^6 dynes/cm., which gives a value of d of 0.016

cm. Also shown are the average rates of cut growth after the conditioning period which the test pieces were giving when they were being cycled.

The values of T_c for the cycled test pieces are erratic, but the following points may be noted: (i) these values of T_c, and hence d, are on the average about three times larger than those of the uncycled (razor cut) test pieces; (ii) comparing test pieces cycled to similar maximum values of T, there is a tendency for those test pieces which gave lower cut growth rates to give

TABLE III

T at which cycling took place × 10^{-6} dynes/cm.	Rate of cut growth, mm./kc.	T_c for cycled test pieces × 10^{-6} dynes/cm.	T_c/E_b for cycled test pieces, cm.
2.10	0.12	25.8	0.052
2.17	0.084	21.2	0.042
2.13	0.140	17.4	0.035
2.11	0.040	40.5	0.021
1.94	0.09	21.8	0.044
1.88	0.04	42.3	0.085
1.94	0.08	17.9	0.038
2.02	0.10	27.8	0.056
1.37	0.015	35.0	0.070
1.26	0.018	22.5	0.045
1.39	0.038	18.0	0.036
1.50	0.030	22.5	0.045
0.98	0.018	25.1	0.050
1.01	0.040	19.5	0.039
1.03	0.030	31.8	0.064
1.01	0.040	16.2	0.032

TABLE IV

Mix	T, dynes/cm. × 10^{-6}	T_c, dynes/cm. × 10^{-6} (cut formed by cycling at T)
D	0.70	23.28
	1.02	17.26
	1.54	19.61
	2.11	23.12
	2.48	21.05
	2.81	28.2
	3.53	32.4
	4.36	38.2
E	0.72	16.1
	2.32	20.7
	3.32	22.6
	4.15	24.1
F	0.82	10.9
	0.92	12.3
	1.29	17.8

higher values of T_c. This last point is not invariably borne out, as might be expected in view of the unevenness of the cut growth curve and the difficulty of determining the rate of cut growth just before the removal of the test pieces for tearing. The values of T_c predict d to be of the order of 0.03 to 0.08 cm. This is consistent with the observed roughnesses, which are quite pronounced, and suggests that this aspect of tear behavior is governed by fairly large-scale effects.

Table IV shows results for vulcanizates D, E, and F. The values of T_c for the cycled test pieces are shown for various maximum values of T attained during cycling. These results cover a wider range of T than those of Table III and, although again some readings are erratic, there is a general trend for T_c to increase with T.

6. DISCUSSION

It has been found that the amount of static cut growth Δc occurring at the tip of a razor cut in a test piece is given approximately by equation (2.2)

$$T^2 = G_s \Delta c$$

where G_s is a constant. An analogous relation (3.1)

$$T^2 = G_d r$$

holds for dynamic cut growth, with r the amount of cut growth/cycle. This similarity in the dependence of the cut growth on T in the two cases suggests that the basic mechanism is identical. The constants G_s and G_d differ by a factor of about 10, and this appears to be associated with the different shape of the tip of the cut in the two cases. In the dynamic measurements the cut became very rough, effectively increasing the radius of curvature and presumably reducing the stress concentration. This is also indicated by the increased value of T_c for a cycled specimen, equivalent to a two to fivefold increase in radius of curvature.

The ratios of the cut growth constants and the T_c values may be related by the following argument. If the roughened tip is assumed to consist of a number of small sharp tips, the value of T for one of these will be less than that for the tip as a whole by a factor of, say, α. The ratio of T_c for the cycled to that for the razor cut specimen will then be α. If cut growth takes place by the growth of one of these elementary sharp tips, then as the value of T is lower by the factor α, the rate of cut growth will be reduced by α^2 according to eq. (2.2), giving

$$\left[\frac{T_c\ [\text{cycled}]}{T_c\ [\text{razor cut}]}\right]^2 \simeq \frac{G_d}{G_s} \tag{6.1}$$

The uncertainty of the experimental data prevents any precise check of (6.1); however, it was noted in Section 3 that G_d was about 10 times G_s, and in Section 5 that the ratio of the T_c values was about 3 so that (6.1)is at least consistent with the data.

The experiments comparing dynamic cut growth in pure shear and simple extension tear test pieces are consistent with the tear criterion proposed in I and II. This implies that the roughness developed at the tip of the cut is independent of the overall shape of the test piece.

The dynamic cut growth measurements described in this paper have all been carried out with the test piece returning to zero stress each cycle. Some preliminary measurements with a finite minimum stress indicate that the rate of cut growth is greatly reduced, in keeping with previous work on fatigue life.[7] This is consistent with the view that the static cut growth is governed by a structure developed in the crystalline rubber around the tip as the cut grows. If the test piece is relaxed to zero stress, this structure will disappear with the crystallization and further cut growth will occur on the next cycle. If not, some of this structure will remain and will reduce the amount of cut growth on the next cycle.

My thanks are due to Dr. A. N. Gent for supervising some of the experimental work.

APPENDIX

	A	B	C	D	E	F
Rubber (S.S.)	100	100	100	100	100	100
Sulfur	3	3	2.5	2.5	2.5	2.5
Zinc oxide	5	5	5	5	5	5
Mercaptobenzothiazole	0.5	0.5	—	—	—	—
D.P.G.	—	1.0	—	—	—	—
Santocure	—	—	0.4	0.6	0.6	0.8
Stearic acid	1	1	2	2	2	2
Antioxidant	1	1	—	1	—	—
Vulcanization time (minutes at 140°C.)	45	6	30	30	30	30

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Synopsis

Cut growth in natural rubber gum vulcanizates has been studied using both steady and repeated loading. The results have been expressed in terms of the concept of the energy for tearing that has been put forward previously. With cut growth under repeated loading the tip, initially smooth, becomes rough and the rate of growth simultaneously decreases markedly to a final steady value. Some consequences of this roughening have been discussed. Measurements of cut growth under repeated loading have also been made using two different types of test piece. A rupture criterion, which has been previously proposed, predicts a definite relationship between the behavior of the two test pieces, and this has been confirmed experimentally.

Résumé

La croissance d'une déchirure dans des vulcanisats de caoutchouc naturel a été étudiée en opérant soit sous charge constante soit sous charge répétée. Les résultats ont été exprimés en termes d'énergie de déchirement qui a été proposée précédemment. Dans le cas de l'aggrandissement d'une déchirure sous charge répétée, l'encoche, initialement lisse, devient rugueuse et la vitesse d'accroissement décroît simultanément de façon marquée jusqu'à une valeur finale constante. Quelques conséquences de cette rugosité ont été discutées. Les mesures de croissance de la déchirure sous charge répétée ont été également effectuées en utilisant deux types différents de pièces témoins. Le critère de rupture, précédemment proposé, prédit une relation définie entre le comportement des deux pièces témoins, et ceci a été confirmé expérimentalement.

Zusammenfassung

Schneidewachstum in Gummivulkanisaten von natürlichem Kautschuk wurde durch sowohl beständige als auch wiederholte Ladung untersucht. Die Resultate wurden mittels der Auffassung von Reiss-Energie ausgedrückt, die früher gegeben wurde. Mit Schneidewachstum unter wiederholter Ladung wird die Spitze, die anfänglich glatt war, rauh, und die Wachstumsgeschwindigkeit nimmt gleichzeitig erheblich ab, bis sie einen beständigen Endwert erreicht. Einige Folgen dieses Rauhwerdens wurden diskutiert. Es wurden auch Messungen des Schneidewachstums unter wiederholter Ladung unter Verwendung von zwei verschiedenen Arten von Probestücken ausgeführt. Ein Reiss-Kriterium, welches früher vorgeschlagen wurde, sagt eine bestimmte Beziehung zwischen dem Verhalten der zwei Probestücke voraus, und dies wurde experimentell bestätigt.

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