Effect of Flaw Size on Tensile Rupture and Morphology of Fracture Surface of Synthetic Rubbers with Special Reference to Rocket Insulator Compound

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Synopsis

Studies on tensile strength of polybutadiene (BR) and ethylene-propylene diene rubber (EPDM) having a wide range of flaw sizes have been carried out under both normal and aging conditions. A similar study has been done for a solid propellant rocket insulator compound, based on EPDM. The morphology of tensile fracture surface has also been reported in each case in order to understand the mechanism of rupture. Unlike NR, EPDM, and BR gum vulcanizates, both unaged and aged, show no critical cut length (l_c). l_c may be defined as the cut length at which the strength decreases abruptly (sometimes there is a drop of a factor of 3 or more, at l_c). However, the insulator compound, based on EPDM, exhibits a definite l_c in the region of 1.5–1.7 mm. This arises because of anisotropic effect of asbestos fibers. Scanning electron microscopic studies show that the mechanisms of rupture of EPDM and BR gum vulcanizates are similar throughout the whole range of precuts. It occurs through a tearing process originated from the given precut at the center of the samples. A quantitative relation between tensile strength and distance between crack lines/tear lines has also been found. Though insulator compound shows a definite l_c, similar fracture surface has been observed over the entire range of flaw sizes.

INTRODUCTION

Tensile rupture of rubber starts from small flaws, which act as stress raisers. These flaws are introduced due to presence of inhomogeneities in the mix, improper mixing, and molding imperfections. The role of flaw sizes on the tensile strength of unaged and aged natural rubber (NR) has been reported.[1-3] A critical cut length, at which tensile strength falls abruptly, is observed for NR. On aging, the critical cut length increases and the slope of the sharp fall of tensile strength at the critical cut length reduces with time of aging. On prolonged aging, the critical cut length for NR disappears.[3]

It has been suggested that a change in mechanism of tensile rupture from a crack growth process, below l_c to a tearing phenomena, above l_c, takes place.[2] In a tearing process, the naturally occurring flaws can initiate failure before rubber molecules crystallize under extension, and the process is catastrophic. In a crack growth process, failure is retarded by crystallization and other factors. Scanning electron microscopy study of the fracture surfaces supports this view.[3] The mechanism of tearing of synthetic rubbers over a range of flaw sizes is not well documented. Only a preliminary study, without details about the mechanistic aspects, is reported for polychloroprene and nitrile rubber.[4] Hence, the purpose of this study is to investigate systematically the fracture

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mechanism in low strength synthetic rubber like ethylene–propylene diene rubber (EPDM) and polybutadiene (BR). Both aged and unaged compounds have been chosen for the study. A practical solid propellant rocket insulator compound, based on EPDM, has also been included in this present study.

The solid propellant insulator compound contains cork, asbestos and iron oxide (Fe_2O_3) as fillers. Due to poor interaction between rubber and the filler,[5] big holes have been observed on the fracture surface. These holes are not observed on the aged sample and the strength properties increase. So it would be interesting to study the effect of flaw sizes as well as aging on tensile rupture of the insulator compound.

EXPERIMENTAL

Formulation of the mixes is given in Table I. The mixes were prepared on a laboratory mill. Vulcanization was carried out at 150°C at the optimum cure time in an electrically heated press. The optimum cure time was calculated from the rheometer trace, which shows marching modulus. The tangents were drawn on the curves, and the meeting point was joined to the median of the straight line drawn, joining the points at which tangents were drawn. The straight line cuts the rheometer trace at a point. The time corresponding to this point is the optimum cure time. Moldings were quickly cooled in water at the end of the curing cycle.

Determination of Tensile Strength

Tensile strength was measured in an Instron machine (1195 Model) according to ASTM D412-80 using dumbbell specimens at 22°C. Oxidative aging of the vulcanizates was carried out in a Blue M aging oven at 150°C.

TABLE I
Mix Formulations (phr)

Mix no.	A	B_{As}	C_{Fe}	D_C	P	R (insulator)
EPDM (Nordel 1040)[a]	100	100	100	100	—	100
Polybutadiene (BR)[b]	—	—	—	—	100	—
Crystex sulfur[b]	1.5	1.5	1.5	1.5	—	1.5
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	1	1	1	2	1
Iron oxide (Fe_2O_3)	—	—	10	—	—	10
Ordinary sulfur	—	—	—	—	2	—
MBT[c]	1.5	1.5	1.5	1.5	—	1.5
TMTD[c]	1	1	1	1	—	1
CBS[c]	—	—	—	—	1	—
Asbestos[a]	—	10	—	—	—	10
Oil[b]	—	—	—	—	—	10
Cork[a]	—	—	—	50	—	50
Optimum cure time at 150°C (min)	24.0	10.5	11.0	10.0	35.0	10.0

[a]Supplied by V.S.S.C., Trivandrum.
[b]Supplied by Dunlop (India) Ltd.
[c]Supplied by IEL Ltd., Rishra.

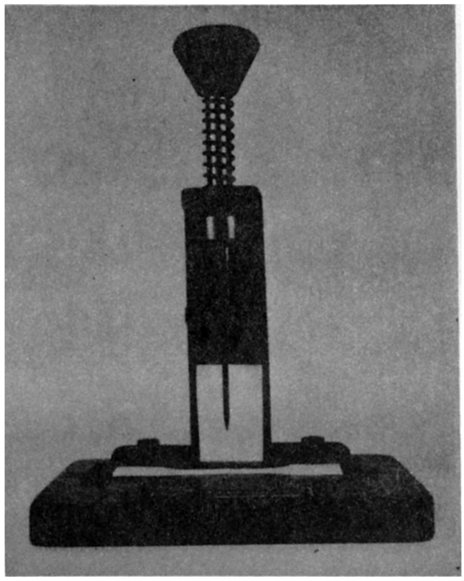
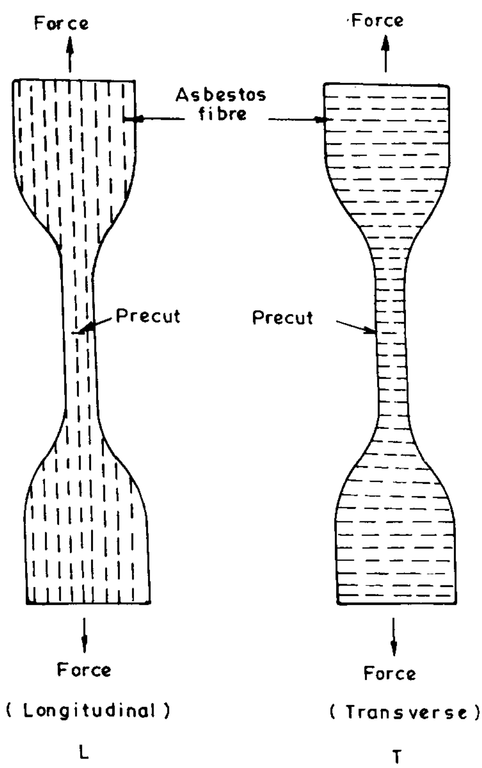
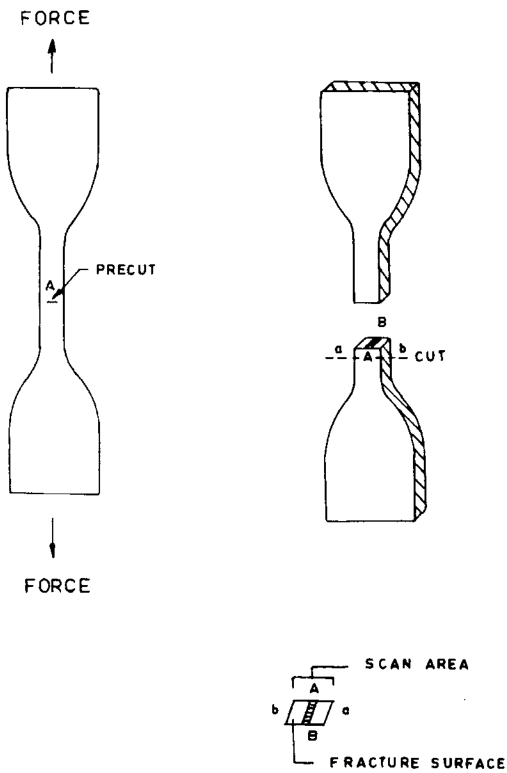


Fig. 1. Shape of the jig.



(a)

Fig. 2(a). Tensile test specimen with direction of asbestos fiber orientation.



(b)

Fig. 2(b). Tensile test specimen and the portion from where the surface has been cut for SEM. Cut has given from A to B. Length of ab = 4.05 mm; length of AB = 2.04 mm; width of AB = variable.

Application of Cut of Various Sizes

The dumbbell test specimens were held rigidly in a special jig (Fig. 1) while the prescribed chisel cuts were applied through the center of the test specimen and directed perpendicularly towards the applied tensile force [Figs. 2(a) and 2(b)]. Great care was taken to ensure cutter sharpness.

Microscopic Study

Fracture surface of tensile specimens was observed with the help of a scanning electron microscope. The samples were sputter-coated with gold and were examined within 48 h after fracture. The surface examined under scanning electron microscope has been shown in Figure 2(b).

RESULTS AND DISCUSSION

Studies on Mechanical Properties

Figure 3 shows the variation of tensile strength with given precuts for EPDM and BR gum compounds. In general, there is an exponential decrease

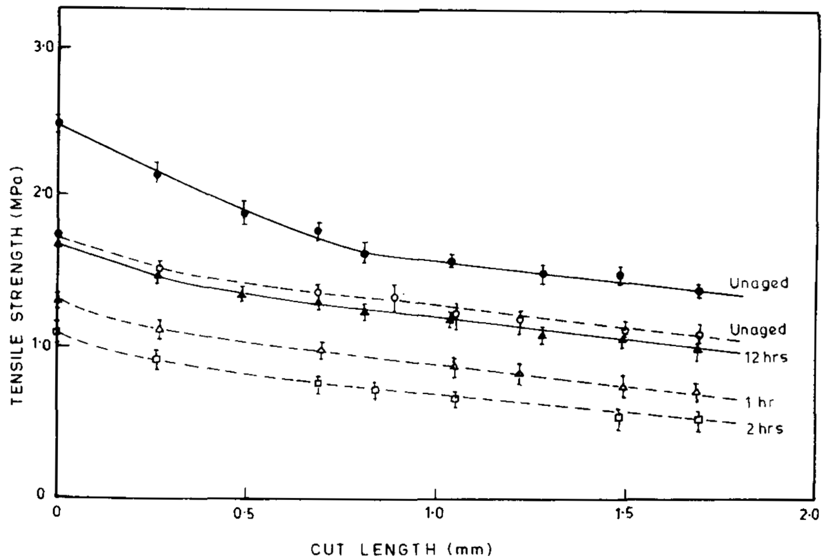


Fig. 3. Variation of tensile strength with given precut for EPDM and BR gum vulcanizates, aged at 150°C. (—) EPDM; (---) BR.

of tensile strength with given precut length. No critical cut length is found in this range. For the aged samples, also, the same trend is observed. So the fracture behavior of low strength rubbers like EPDM and BR compounds, both unaged and aged, is different from that of Natural Rubber.

The effect of fillers, like cork, asbestos, and Fe_2O_3, on tensile strength of EPDM vulcanizates, has been reported before by us.[5] The tensile strength of EPDM vulcanizates, filled with individual filler like cork and asbestos, at different flaw sizes, is shown in Figure 4. The results show that cork filled EPDM sample shows no critical cut length phenomena. Similar behavior is observed with nonreinforcing Fe_2O_3-filled compound. Reinforcing asbestos, unlike the other two fillers, because of its fibrous characteristics, shows orientation properties. The strength of asbestos-filled EPDM vulcanizate without any precut along the longitudinal direction is slightly higher than that along the transverse direction. Along the grain direction, it shows a definite critical cut length near 1.4–1.5 mm cut length (Fig. 4). The appearance of critical cut length might be due to the deviation of tear path by the asbestos fiber.

Figure 5 shows the variation of elongation at break (ϵ_b) for insulator compound with the length of precuts. For the unaged sample, ϵ_b falls with cut length exponentially. ϵ_b along the transverse direction also shows a similar variation. On aging, however, ϵ_b decreases, and the nature of the variation of ϵ_b with cut length is linear (Fig. 5).

Figure 6 shows the variation of tensile strength with cut length for insulator compound. The critical cut length for the insulator compound appears in the region of 1.5–1.7 mm. On aging, there is a steady increase of tensile strength because of increased rubber to filler interaction, as explained by a Kraus plot and SEM study.[5] The range of the critical cut length remains, however, the same. The sharp fall of tensile strength at the critical cut length increases

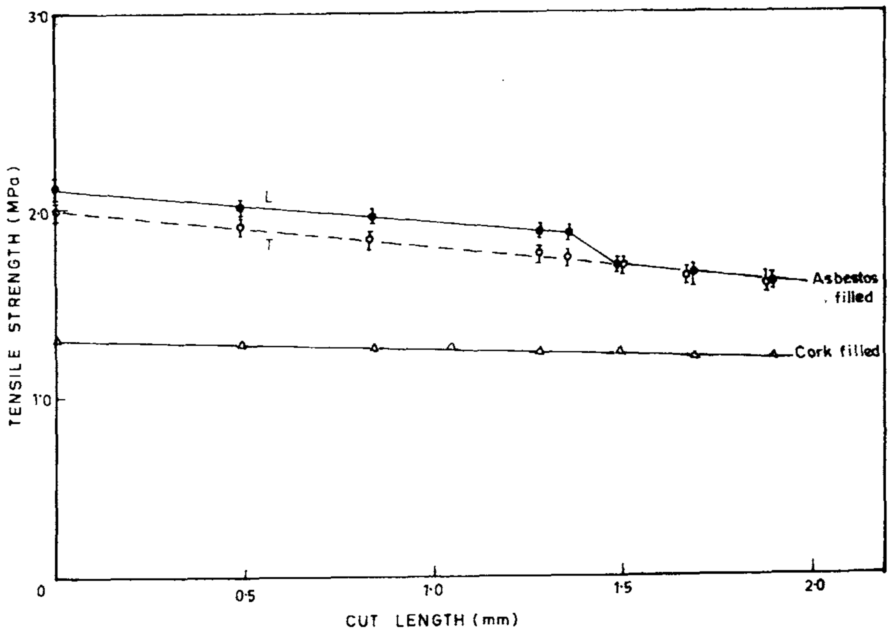


Fig. 4. Variation of tensile strength with given precut for asbestos fiber- and cork-filled EPDM vulcanizates: L = longitudinal, T = transverse.

with aging time, as shown in Figure 6. On aging, the bonding between rubber to filler increases, which reduces inherent flaws inside the matrix. This results in a large increase in tensile strength. It is clear from our previous discussion that both anisotropy in strength properties and critical cut length arise due to the presence of asbestos as one of the fillers.

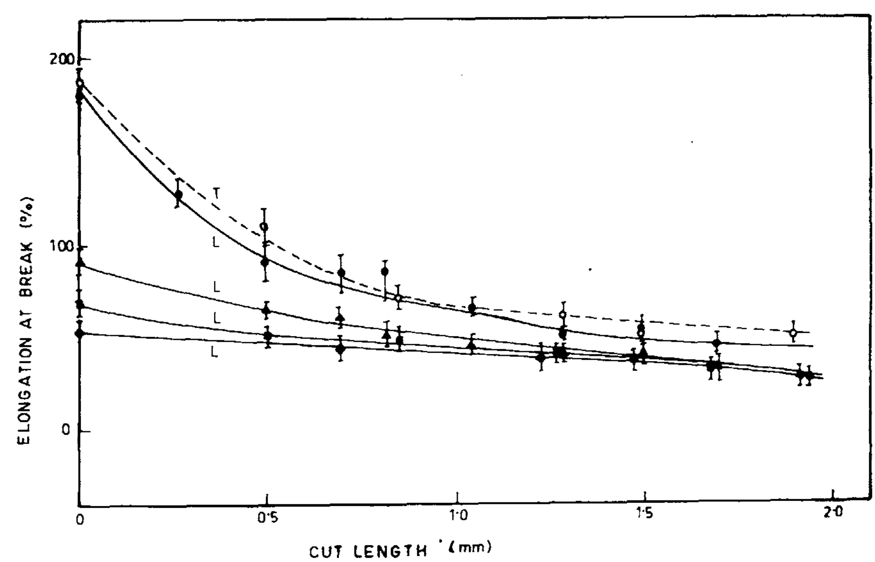


Fig. 5. Variation of elongation at break (ϵ_b) with given precut for insulator compound R. (-●-) unaged (L = longitudinal); (-▲-) aged for 12 h at 150°C; (-○-) unaged (T = transverse); (-■-) aged for 24 h at 150°C; (-◆-) aged for 48 h at 150°C.

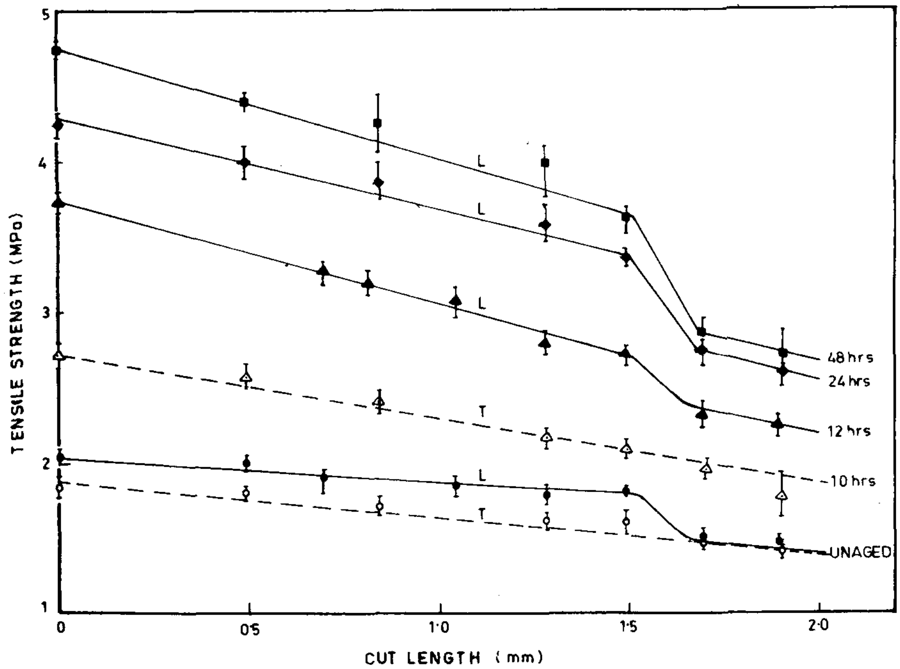


Fig. 6. Variation of tensile strength with given precut for insulator compound R, aged at 150°C: L = longitudinal; T = transverse.

Part B Scanning Electron Microscopy (SEM) Study

SEM study of fracture surface of rubbers over a wide range of precuts has been done to understand the mechanism of tensile rupture. It has been postulated by Thomas and Whittle[2] that a change in the mechanism of tearing occurs at the critical cut length from a retarded crack growth process to a catastrophic tear process above l_c for NR. We have given evidence to similar mechanisms with the help of morphology of fracture surface of NR.[3] Morphology of fracture surface of low strength synthetic rubbers like EPDM and BR (both unaged and aged) with given precuts is reported here to study the mechanism of tearing. A similar study has been done for the insulator compound.

In Figure 7, the nomenclature of different terms to be used in the subsequent discussion is given.

BR Gum Vulcanizate

Figure 8 shows the tensile fractograph of the unaged BR gum vulcanizate without any precut. The fracture surface is quite rough. The cracks and the tear lines originate from the edge of the samples. The distance between two successive tear lines and two adjacent crack lines at the initiation zone of fracture is measured. The distance between tear lines (D_T) is found to be ~ 80 μm and that of crack lines (D_C) is ~ 80–200 μm. Figure 9 shows the nature of cracks. Both the cracks and the tear lines are parabolic in nature. A multitude of them indicates that fracture starts from many different centers. They move at the same speed but at different times. The straight radial lines

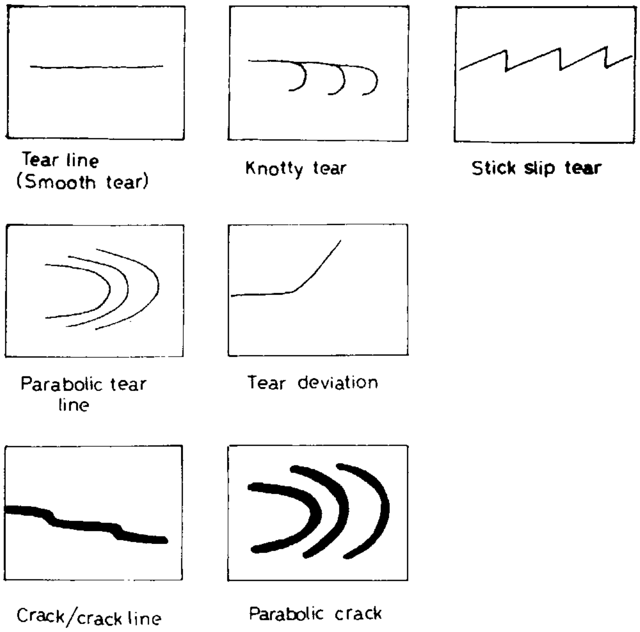


Fig. 7. Nomenclature of different terms used in morphology of fracture surface. The difference between a crack line and a tear line is that a crack line will be sufficiently deep on a microscopic scale and will divide the materials into two or more pieces, whereas a tear line indicates the flow of the material and is always a few μm above the fracture surface. Smooth surface is defined as the surface which has no microscopic features, i.e., absence of tear lines, crack/crack lines, surface rugosity, etc.

are orthogonal to expanding circular crack fronts.[6] On aging, the fracture surface changes. There are fewer tear lines and more cracks (Fig. 10).

Figure 11 shows the general fracture surface of the unaged samples with precut of 0.69 mm. The zone *AB* represents the precut given through the sample from upper side to bottom (Fig. 2). A number of cracks originate from precut at the center of the samples. The parabolic nature of the cracks is

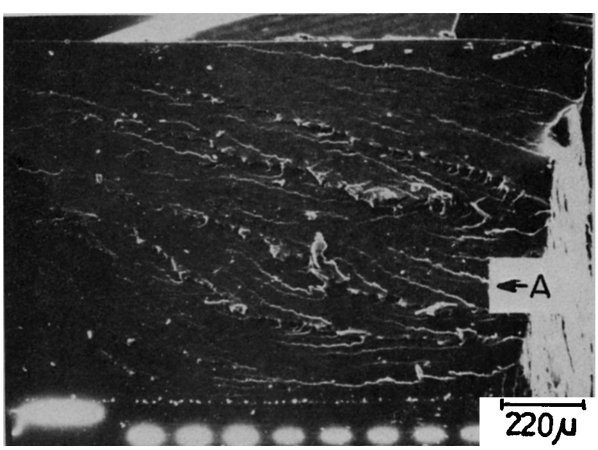


Fig. 8. SEM photograph of tensile fracture surface for unaged BR gum vulcanizate without precut. A = edge of the samples. Arrow mark shows direction of fracture.

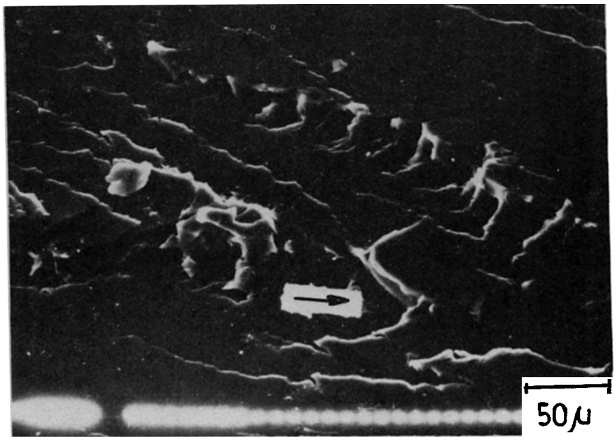


Fig. 9. Magnified version of the crack in Figure 8. Arrow mark shows the parabolic nature of cracks and tear lines.

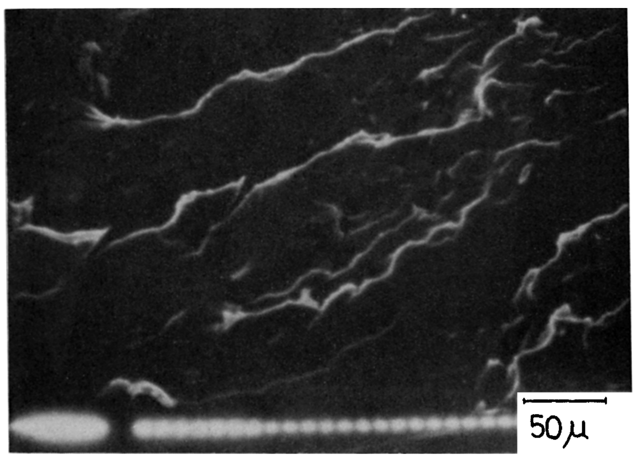


Fig. 10. SEM photograph of tensile fracture surface for BR gum vulcanizate aged at 150°C for 1 h.

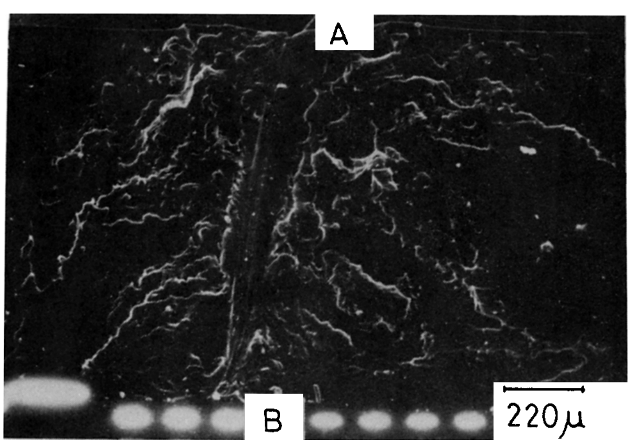


Fig. 11. SEM photograph of tensile fracture surface of unaged BR gum vulcanizate with precut of 0.69 mm.

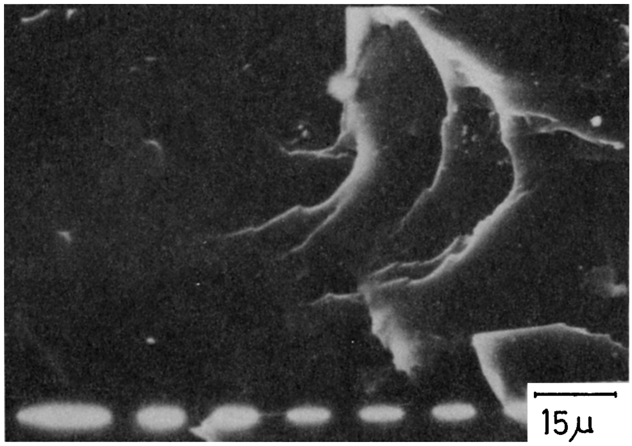


Fig. 12. Magnified version of the crack in Figure 11.

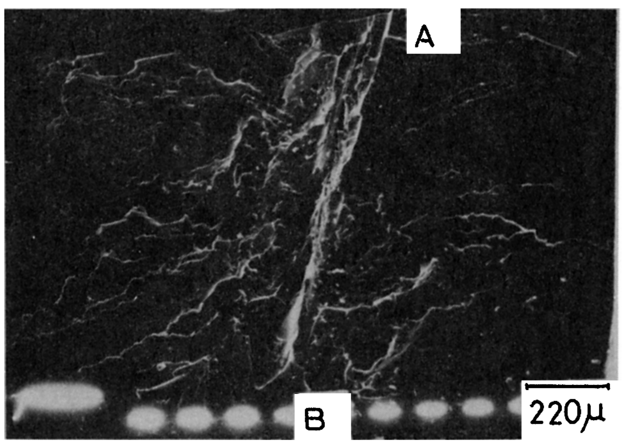


Fig. 13. SEM photograph of tensile fracture surface of unaged BR gum vulcanizate with precut of 1.49 mm.

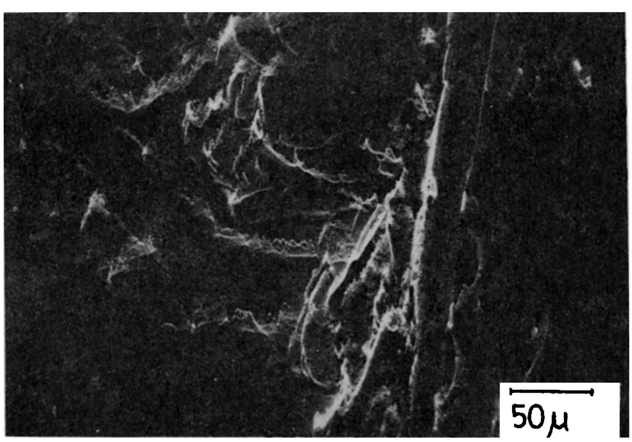


Fig. 14. SEM photograph (with image of the *y–z* component) of tensile fracture surface of BR gum vulcanizate with precut of 0.69 mm, aged at 150°C for 1 h.

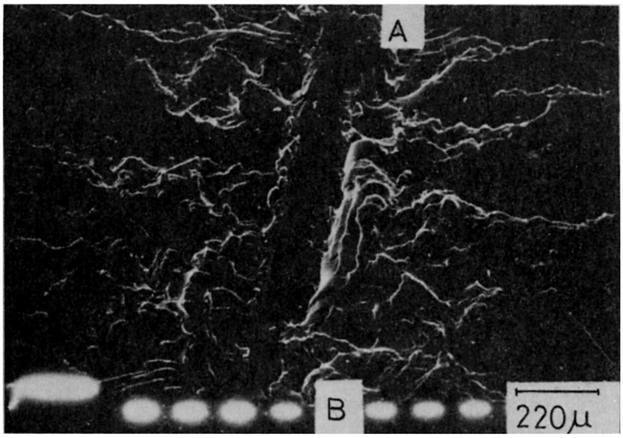


Fig. 15. SEM photograph of tensile fracture surface of BR gum vulcanizate with precut of 0.83 mm, aged at 150°C for 1 h.

observed (shown in Fig. 12). On increasing length of precut (up to 1.69 mm), the same type of fracture surface with more cracks is obtained (Fig. 13). So it can be concluded that the same mechanism of tensile rupture operates over the whole range of flaw sizes for BR gum vulcanizate. The tearing starts from the precut given at the center. The mechanism of rupture of NR, however, changes at the l_c, and the mechanisms above and below l_c are different.[3] This is the reason why no critical cut length is observed for BR gum vulcanizates (Fig. 3).

On aging in air, a similar fracture mechanism is observed for BR. Figure 14 shows the tensile fracture surface (image in the y–z-plane) for BR gum vulcanizate, with precut of 0.69 mm, aged for 1 h at 150°C. It clearly shows that cracks develop around the given precut. A similar fracture is obtained for aged samples with higher precuts (Fig. 15).

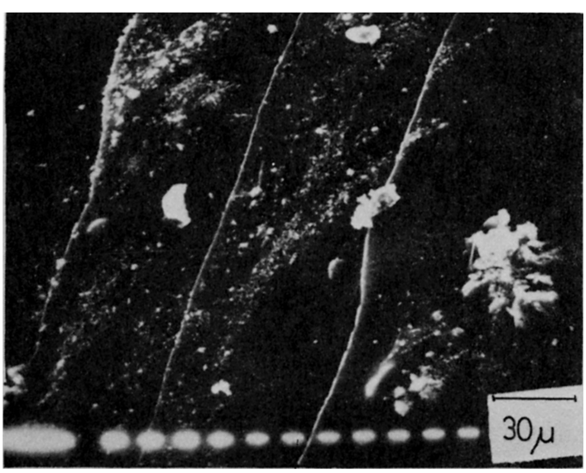


Fig. 16. SEM photograph of tensile fracture surface of unaged EPDM gum vulcanizate without precut.

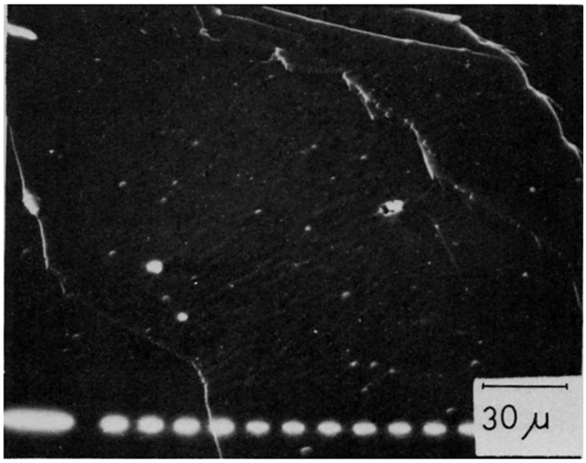


Fig. 17. SEM photograph of tensile fracture surface of EPDM gum vulcanizate without precut, aged at 150°C for 48 h.

EPDM Gum Vulcanizate

Figure 16 shows the tensile fracture surface of unaged EPDM gum vulcanizate without precut. Few tear lines are shown on the fracture surface. On aging, however, a smaller number of tear lines and randomly placed crack lines are observed on the fracture surface (Fig. 17).

For unaged samples of EPDM with precut of 0.69 mm, the tensile fracture surface shows the following features. Tear lines and cracks are found to originate from the given precut and proceed towards the edge as obtained for BR (Fig. 18). At the initiation zone, D_T is found to be ~ 80–120 μm and D_C is ~ 120–250 μm. A similar fracture surface is obtained for all unaged samples with higher precuts (Fig. 19). With increase in length of precut, the number of cracks/crack lines on the fracture surface increases. The nature of flow of the material around the given precut is shown in Figure 20. The fracture surface obtained for aged EPDM gum vulcanizate over a range of

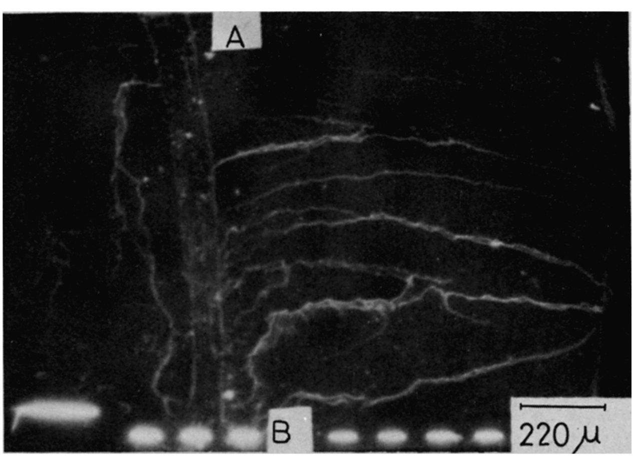


Fig. 18. SEM photograph of tensile fracture surface of unaged EPDM gum vulcanizate with precut of 0.69 mm.

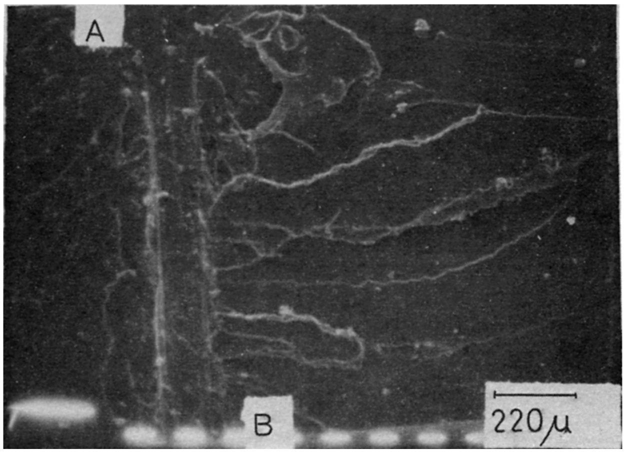


Fig. 19. SEM photograph of tensile fracture surface of unaged EPDM gum vulcanizate with precut of 1.04 mm.

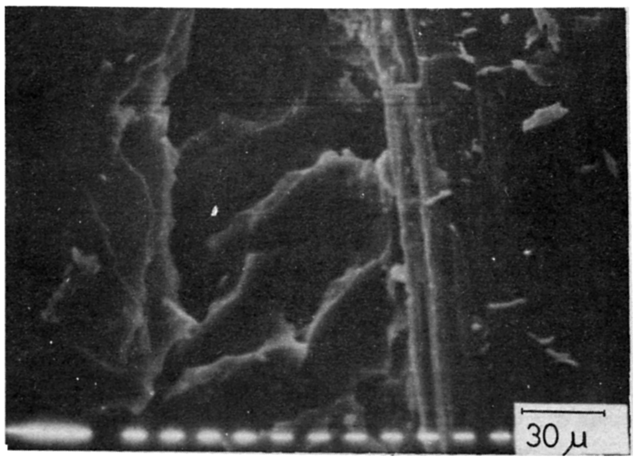


Fig. 20. Magnified version of cracks around the given precut in Figure 19.

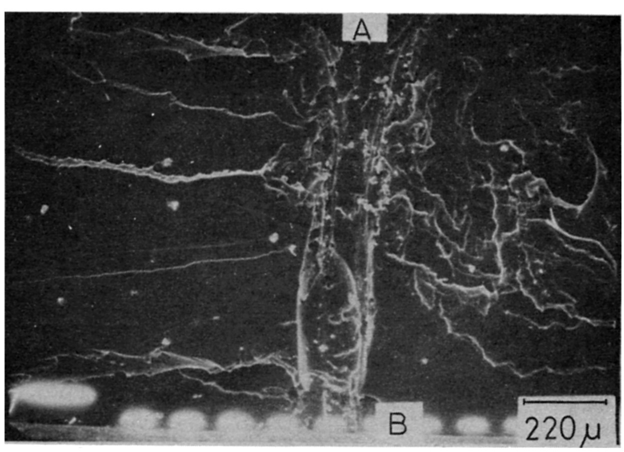


Fig. 21. SEM photograph of tensile fracture surface of EPDM gum vulcanizate with precut of 1.04 mm, aged at 150°C for 12 h.

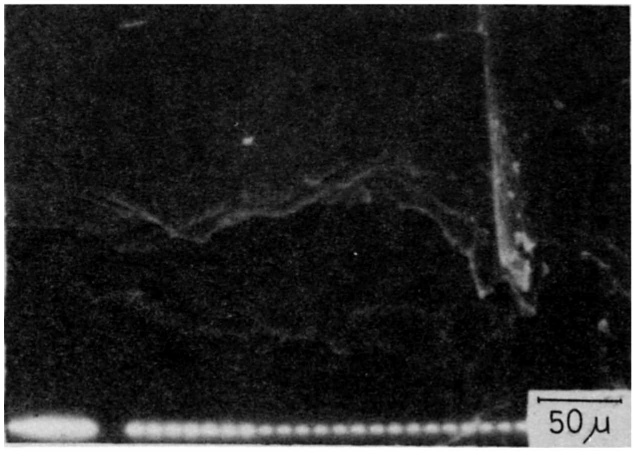


Fig. 22. Magnified version of the region around the crack in Figure 21.

precuts is similar to unaged sample (Fig. 21). The region around the crack is shown in Figure 22.

It is evident from the above discussion that for BR and EPDM gum vulcanizates without precut (both unaged and aged), the fracture initiates from the naturally occurring flaws/nicks at the edge. For the samples with given precut, however, tearing starts from the precut at the center. This mechanism holds good for tensile rupture of samples with entire range of precuts (up to 1.69 mm) and l_c phenomena do not arise.

Insulator Compound

In our previous discussion, it is clearly understood that the insulator compound, based on EPDM, shows a definite critical cut length. The mechanism of tensile rupture with precut below and above l_c is studied with the help of a scanning electron microscope.

Figures 23 and 24 show the tensile fractograph of insulator compound with precut of 0.49 mm (less than l_c) and 1.69 mm (greater than l_c), respectively. In general, in both cases, similar fracture surfaces are obtained. On aging also, the tensile fractograph of all the samples with a wide range of precuts are found to be similar.

Hence the critical cut length phenomena can arise due to the existence of either strain-induced crystallization common for natural rubber compound or anisotropic effect of the fiber in the fiber-filled matrix. In the former case, the morphology of fracture surface below and above l_c is different while, in the latter, it is similar.

Relation between Tensile Strength (σ_b) and Distance between Tear Lines (D_T) or Distance between Crack Lines (D_C)

The distances between crack lines (D_C) and between the tear lines (D_T) have been measured at the initiation zone of fracture. These are plotted against σ_b in Figure 25 for EPDM and BR gum vulcanizates. Both the rubbers behave similarly in the sense that σ_b increases with increase in the

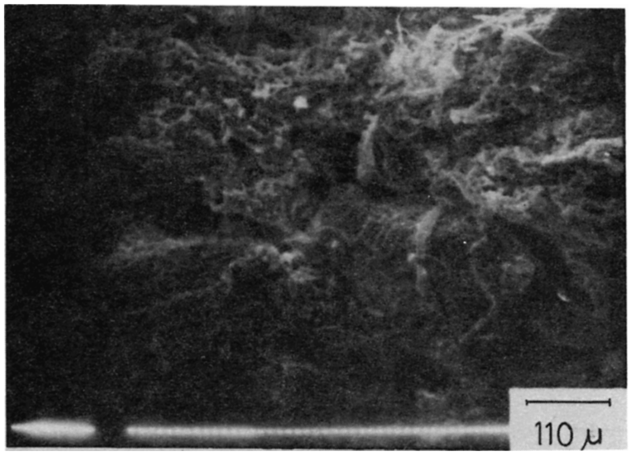


Fig. 23. SEM photograph of tensile fracture surface of unaged insulator compound R, with precut of 0.49 mm.

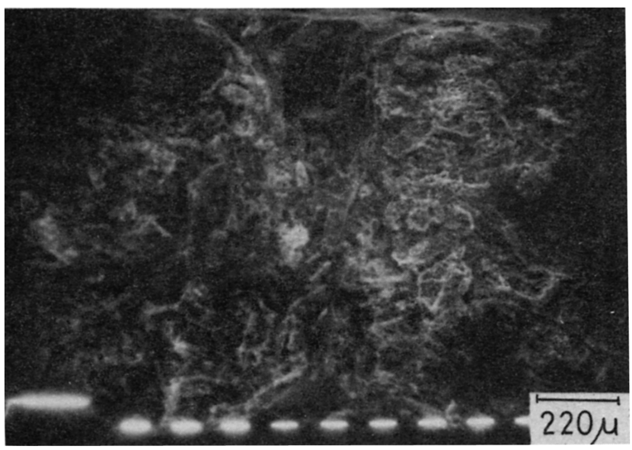


Fig. 24. SEM photograph of tensile fracture surface of unaged insulator compound R, with precut of 1.69 mm.

number of tear lines and decreases with increase in the number of crack lines. The tear lines probably act as a stress distributor. An increase in the number of tear lines means, however, more flow on the matrix, which arises due to higher energy dissipation. It is well known that σ_b is related to energy dissipation. The higher the energy dissipation, the higher is the value of tensile strength. Hence, there is some indirect relation between energy dissipation and D_T. Similarly, when the number of crack lines are more, the tear has propagated more easily. Hence, there is a direct correlation between D_C and σ_b. The empirical relations between D_T/D_C and σ_b are as follows:

For EPDM gum vulcanizates:

$$\log D_C = 0.55 + 0.85\sigma_b \tag{1}$$

$$\log D_T = 5.85 - 2.30\sigma_b \tag{2}$$

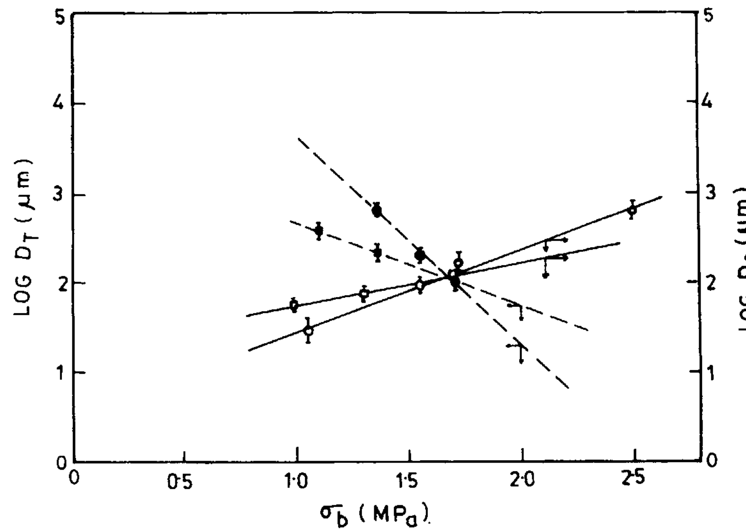


Fig. 25. Variation of D_T/D_C with σ_b. For EPDM gum vulcanizate (–○–) variation of D_C with σ_b; (–●–) variation of D_T with σ_b. For BR gum vulcanizate: (–□–) variation of D_C with σ_b; (–■–) variation of D_T with σ_b.

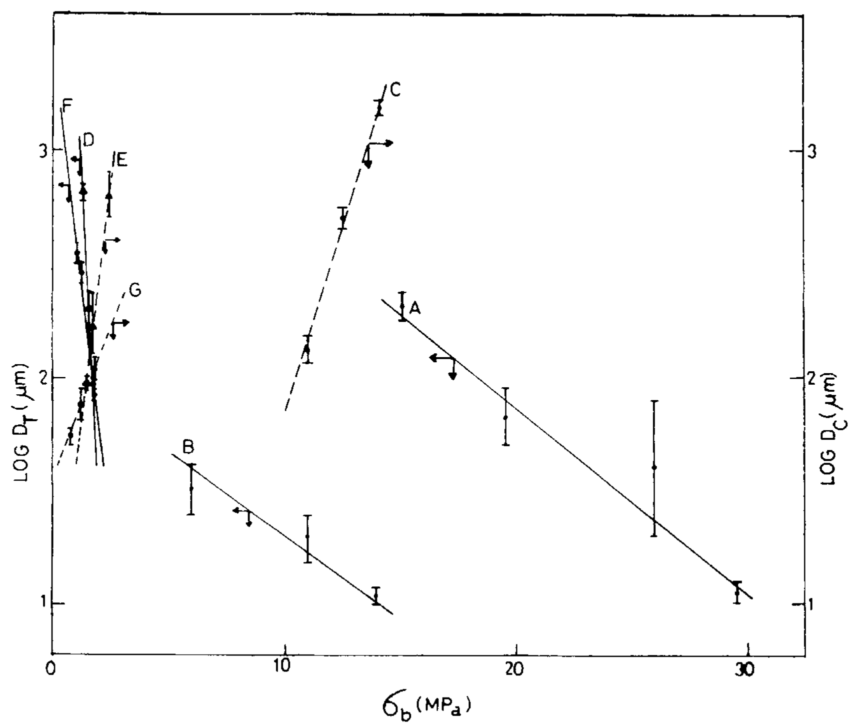


Fig. 26. Variation of D_T/D_C with σ_b. D_T: (*A*) NR (unaged); (*B*) NR (aged); (*D*) EPDM; (*F*) BR. D_C: (*C*) NR; (*E*) EPDM; (*G*) BR.

For BR gum vulcanizates:

$$\log D_C = 1.30 + 0.40\sigma_b \tag{3}$$

$$\log D_T = 3.50 - 1.05\sigma_b \tag{4}$$

Comparison of these features with NR has been shown in Figure 26. The slope of D_T vs. σ_b is stiffer for EPDM or BR, while that of D_C vs. σ_b for EPDM and NR are comparable. Further studies in this line are in progress in our laboratory.

CONCLUSION

Tensile strength of polybutadiene (BR), ethylene propylene diene (EPDM) rubber, and an insulator compound, having a wide range of flaw sizes, have been investigated under normal and aging conditions. The fracture surfaces have been analyzed with the help of a scanning electron microscope. Unaged and aged BR as well as EPDM gum vulcanizates show no critical cut length. However, the insulator compound shows a critical cut length in the region of 1.5–1.7 mm due to the anisotropic nature of asbestos fiber used in the formulations. It has been observed from SEM studies of the gum compounds of BR and EPDM that the mechanism of rupture is similar all through the cut length. It initiates from a given precut. A quantitive relation has been developed between the tensile strength (σ_b) and distance between crack lines (D_C) and tear lines (D_T) as follows: For EPDM gum vulcanizates,

$$\log D_C = 0.55 + 0.85\sigma_b$$

$$\log D_T = 5.85 - 2.30\sigma_b$$

For BR gum vulcanizates,

$$\log D_C = 1.30 + 0.40\sigma_b$$

$$\log D_T = 3.50 - 1.05\sigma_b$$

Fracture surfaces of the insulator compound are similar over the entire range of precuts, though it shows a critical cut length.

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