JOURNAL OF MATERIALS SCIENCE 22 (1987) 4299–4306

Effect of ageing on critical cut length and morphology of fracture surface in tensile rupture of natural rubber

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Variation of tensile strength with flaw sizes has been studied both for unaged and aged natural rubber (NR) gum vulcanizates (aged up to 150° C). A precut of varying lengths is given at the centre of the tensile specimens. The morphology of the fracture surfaces has also been reported. A critical cut length is observed for NR vulcanizates. There is an increase in the critical cut length (l_c) on ageing. The sharp fall of tensile strength at the critical cut length, however, gradually diminishes. On prolonged ageing, no critical cut length is observed. A mathematical model has been made to explain the behaviour of the critical cut length of NR with ageing time/temperature. Scanning electron microscopic studies support the prediction of Thomas, that there is a change in the mechanism of rupture above the l_c. Below the l_c, it is a cut growth process and fracture is originated from natural flaws/nicks and proceeds towards the precut at the centre. However, for samples with precut greater than the l_c, the fracture is mainly a tearing phenomena initiating from the given precut. A quantative correlation between the tensile strength and the distance between crack lines/tear lines has been found.

1. Introduction

It is well known that improper cutting of sample edges, moulding imperfections, dirt particles and inhomogeneities in the mixes, are deleterious to the strength properties of rubber, because these act as stress raisers and cause initiation of failure of rubber at these points. The effect of flaw size on the tensile rupture of natural rubber (NR) has been described by Thomas [1]. He observed a critical cut length (l_c) of NR above which there is a drastic fall in tensile properties. Hamed [2] reported the effect of crosslink density on the critical cut length of NR. Similarly, a critical temperature, above which the tensile strength abruptly falls, has been reported for natural rubber [3, 4, 5]. There is no systematic study, however, on the effect of ageing on critical cut length of rubbers. In our earlier communications we have observed that there are modifications of the main chains and networks during ageing [6, 7].

In the present study, influence of ageing in air on critical cut length of NR gum vulcanizate has been reported. An attempt has been made to formulate these changes mathematically, so as to predict the behaviour of a range of ageing times and temperatures. To understand the mechanism of tearing, a morphological investigation of the fractured surface has been made with the help of scanning electron microscope (SEM).

2. Experimental

Formulation of the natural rubber mix is given in Appendix 1. The mix was prepared on a laboratory mill and vulcanization was carried out at 150° C at the optimum cure time in an electrically heated press (see Appendix). Mouldings were quickly cooled in water at the end of the curing cycle.

2.1. Determination of tensile strength before and after ageing

The tensile strength of NR vulcanizates before and after ageing was measured in a Zwick machine 1445 (Zwick GmbH, Germany) according to ASTM D412-80 using dumbell specimens at 22° C. Oxidative ageing of vulcanizates was carried out in a Blue M (Blue M Electric Co., USA) ageing oven at different temperatures (up to 150° C).

2.2. Application of cut of various sizes

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

2.3. Microscopic study

Fracture surfaces of tensile specimens were observed with the help of SEM. The samples were sputter coated with gold and were examined within 48 h after fracture. A surface examined under SEM has been shown in Fig. 2.

3. Results and discussion

3.1. Variation of tensile strength with flaw size

Figs 3, 4 and 5 show the variation of tensile strength with flaw sizes for unaged and aged NR gum

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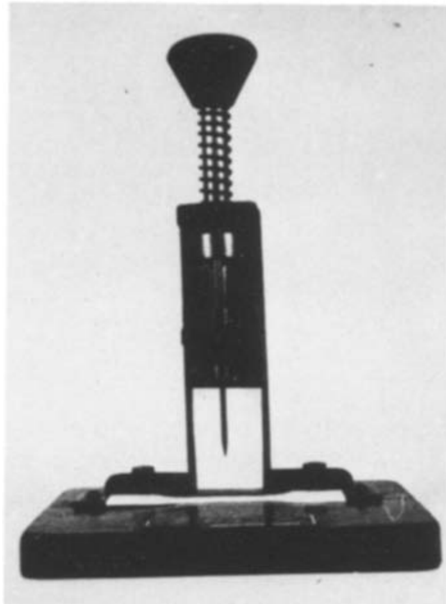

Figure 1 Shape of the jig.

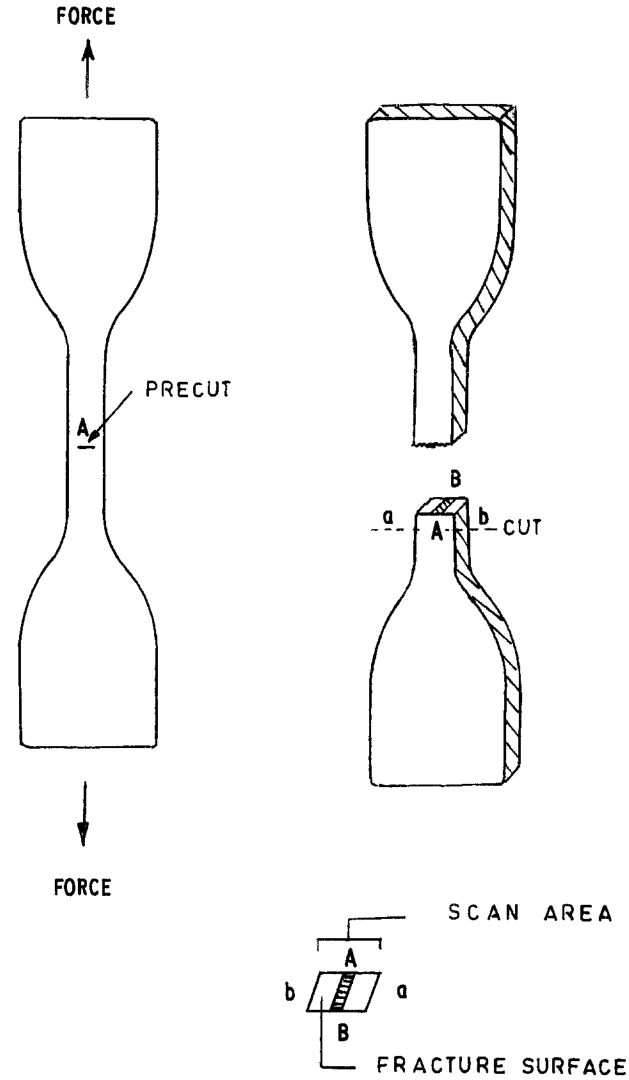

Figure 2 The tensile test specimen and the portion from where the surface has been cut for SEM. Cut has been given from A to B.

vulcanizates at different temperatures. In general, the tensile strength decreases with the increase in the size of the flaw (Zone I) as reported previously [1]. At the critical cut length (l_c), the tensile strength falls abruptly (Zone II). The value of l_c for unaged NR, is found to be in the range of 1.21 to 1.30 mm. A similar value has been reported previously [1, 8]. The critical cut length, however, increases with the time of ageing. For example, in the case of NR aged in air at 100° C for 32 h, the l_c is shifted to the range of 1.43 to 1.52 mm (an increase of about 20%). However, on extended ageing (for 45 h at 100° C), no critical cut length is observed (Fig. 3). Similarly, the critical cut length of samples aged at 120° C for 4 h is 1.36 to 1.44 mm (an increase of about 10%) (Fig. 4). No critical cut length is observed, however, for the vulcanizates, aged at still higher temperature, e.g. at 150° C even for 1 h time of ageing (Fig. 5). There is a gradual drop in tensile strength with cut length in this case.

The variation of critical cut length with ageing time at different temperatures is reported in Fig. 6. The critical cut length increases exponentially with ageing time.

It can be concluded from the above results that the ageing of rubber in air has two effects on the critical cut length; (1) the critical cut length increases with time of ageing, (2) the sharp fall of tensile strength at the critical cut length gradually diminishes on extensive ageing at any particular temperature. Ultimately no critical cut length is detectable at high temperature.

Ageing of rubber produces several changes, like (1) main chain breakage, (2) main chain modification, (3) crosslink formation, (4) crosslink destruction, (5) other reactions of network bound and extra network material to generate a complex structure.

The net result is reflected on the properties like modulus, tensile strength etc. The changes in network structure with the changes in time and temperature of ageing has been shown before [6]. Initially, there will be a reduction in the crosslink density and the polysulphidic crosslinks, which will reduce the modulus. This results in an increase in the l_c value. An increase in modulus reduces the critical cut length. Similar observation has been made by Thomas & Whittle [3]. However, on extensive ageing, main chain is modified and structurally complex network is formed. The tensile strength of vulcanizates reduces significantly and at sufficiently low breaking stress of the vulcanizates (8 MPa) (Figs 3, 4, 5), no strain crystallization is possible in the bulk of the test piece. This results in the disappearance of critical cut length in these samples.

3.2. Mathematical formulation

Let us denote the maximum and minimum strength (in MPa) by $\sigma_{T_{\max}}$ and $\sigma_{T_{\min}}$ respectively. It is found that $\sigma_{T_{\max}}$ and $\sigma_{T_{\min}}$ are varying systematically with ageing time and temperature (Fig. 7). The following empirical relations for the straight lines in Fig. 7 are found,

$$\sigma_{T_{\max}} = -m_{\max} t + 29.5 \quad (1)$$

$$\sigma_{T_{\min}} = -m_{\min} t + 14.6 \quad (2)$$

where, t is the time of ageing in hours and $m_{\max}$ and $m_{\min}$ are the slopes of the lines. $m_{\max}$ and $m_{\min}$ are functions of temperature of ageing and can be expressed as

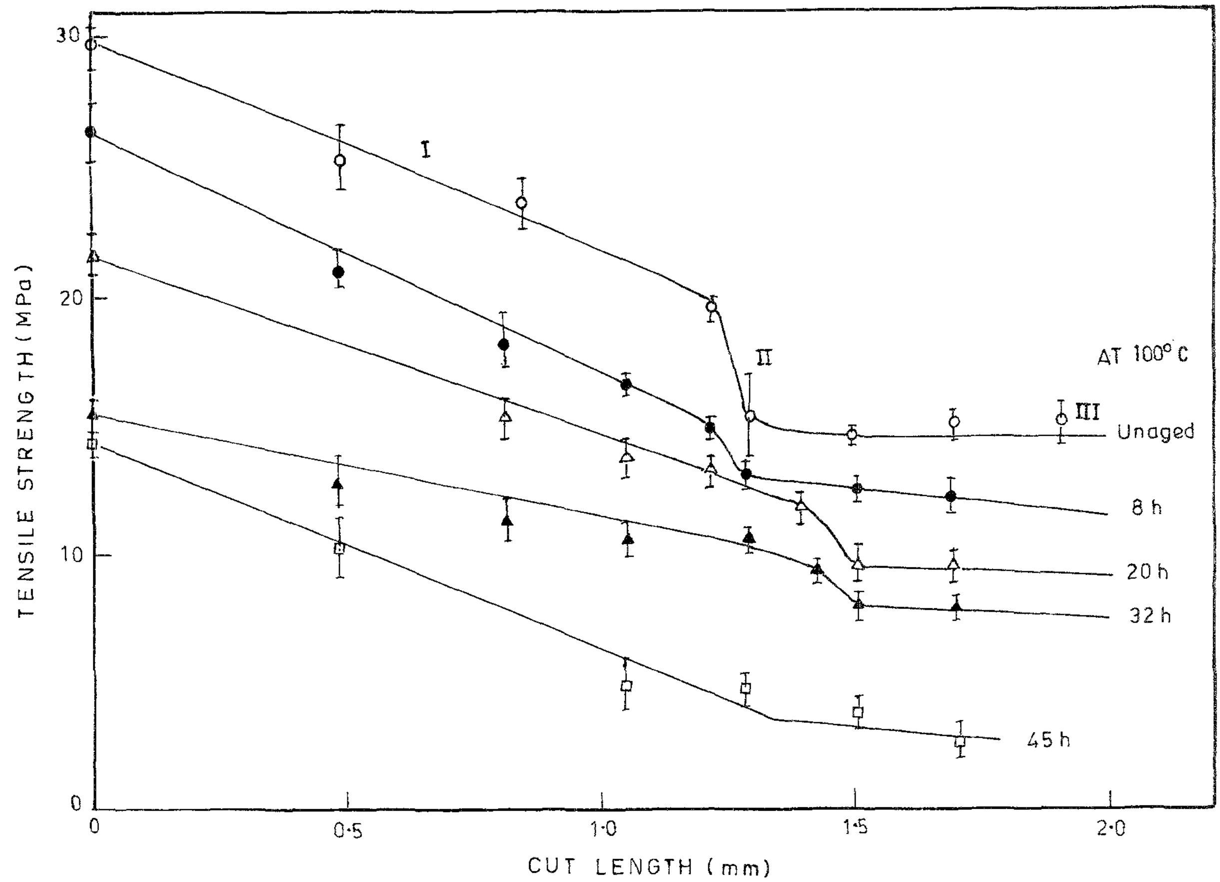

Figure 3 Variation of tensile strength with given precuts for NR gum vulcanizate aged at 100°C in air.

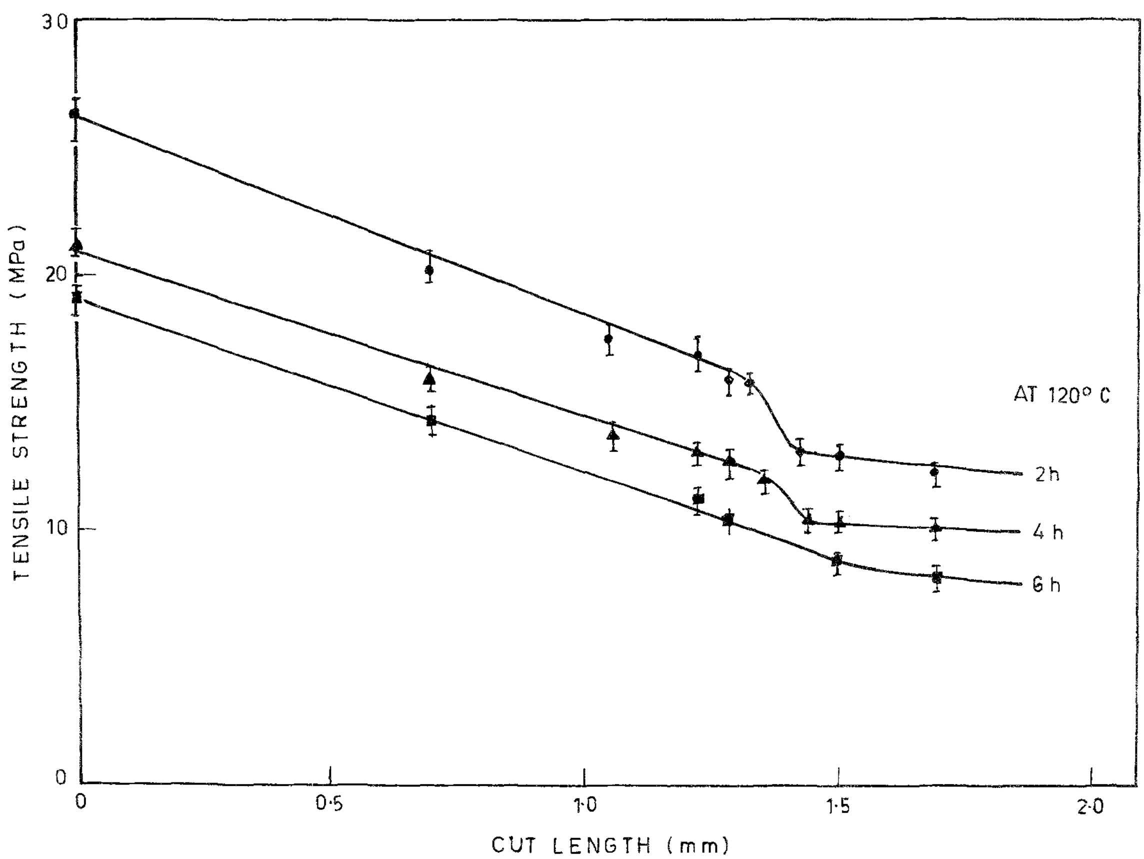

Figure 4 Variation of tensile strength with given precuts for NR gum vulcanizate aged at 120°C in air.

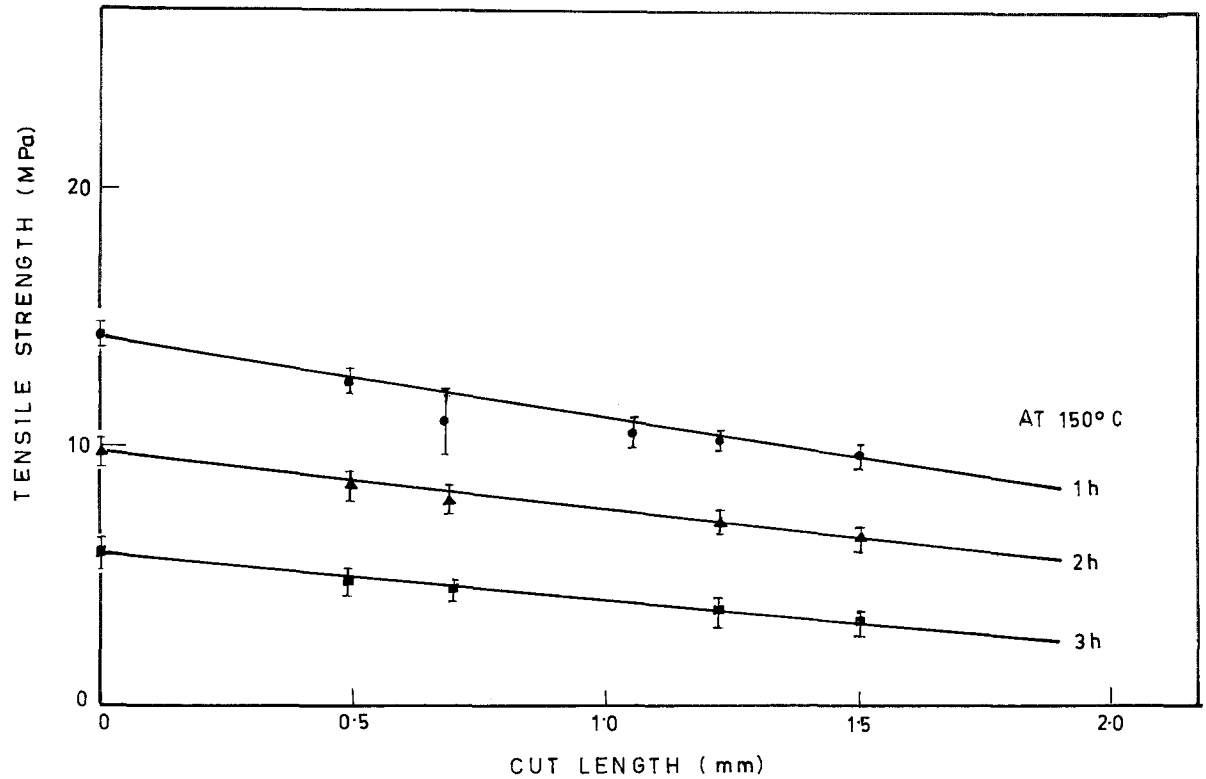

Figure 5 Variation of tensile strength with given precuts for NR gum vulcanizate aged at 150° C in air.

follows,

$$m_{\max} = 5.63 \times 10^{11}\, e^{-10425/T} \quad (3)$$

$$m_{\min} = 4.42 \times 10^{11}\, e^{-10550/T} \quad (4)$$

The values of $m_{\max}$ and $m_{\min}$ in the above equations has been found out from the tensile strength measurement on samples aged at various times and temperatures.

From Figs 3 and 4, it is evident that the slope of zone II decreases with increasing ageing time and the value is approximately 55 for unaged sample. It steadily decreases with time of ageing and temperature (Fig. 7).

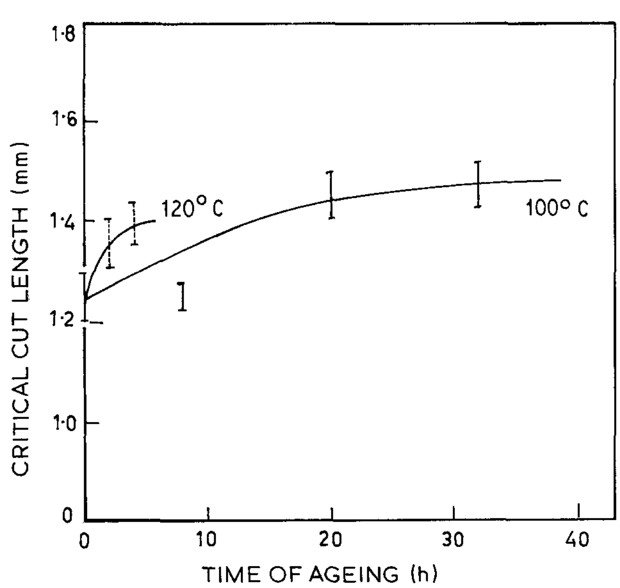

Figure 6 Variation of critical cut length of NR gum vulcanizate with time of ageing at different temperatures.

When the slope approaches 6 ± 3, as that of zone I, no critical cut length is observed. The variation of slope (n) of the curve at the critical cut length with time of ageing can be expressed as follows,

$$n = -at + 54 \quad (5)$$

Once again, "a" is a function of temperature,

$$a = 1.796 \times 10^{18}\, e^{-15610/T} \quad (6)$$

Using the above equations, one can predict quantitatively, the behaviour of NR during ageing and the time required for disappearance of the critical cut length at any ageing temperature.

3.3. SEM studies

SEM studies of the fracture surfaces over a range of cut lengths have been done to understand the mechanism of tearing. It has been pointed out by Thomas [1] that a change in the mechanism of tearing occurs at the critical cut length from a crack growth process to an essentially tear process above the l_c. The kind of fracture surface generated by these two mechanisms is not known however. The fracture surfaces of both unaged and aged samples have been reported here. The fracture surfaces of NR under different modes of fracture have been published before [9, 10].

3.3.1. Unaged sample without precut

Fig. 8 shows the tensile fractograph of the NR vulcanizate without any precut. The surface shows a rough zone where the tear lines initiate, followed by a comparatively smooth region. Naturally occurring flaws and nicks at the edge in the test specimen cause stress concentration and failure starts from these

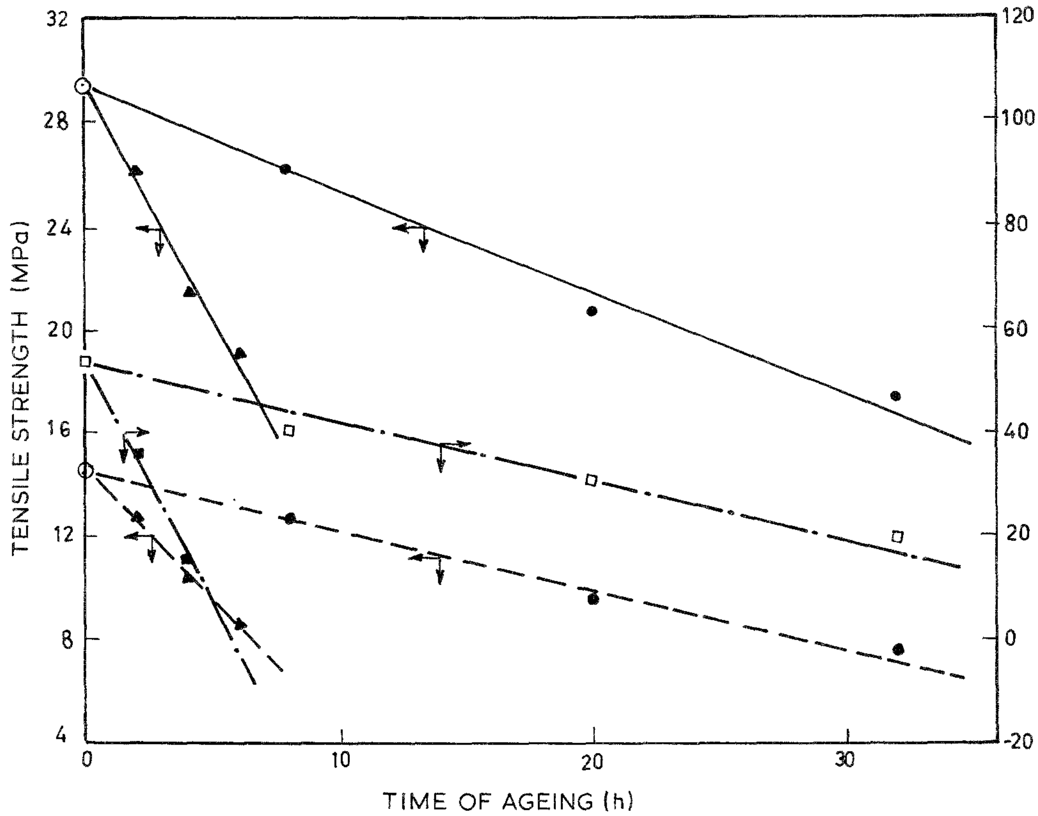

Figure 7 Plot of $\sigma_{T_{max}}$, $\sigma_{T_{min}}$ and slope of zone II (n) in Fig. 3 for NR gum vulcanizate against time of ageing at different temperatures. For $\sigma_{T_{max}}$: (—●—) at 100° C, (—▲—) at 120° C; For n: (–·–□–·–) at 100° C, (–·–■–·–) at 120° C; For $\sigma_{T_{min}}$: (– – –●– – –) at 100° C, (– – –▲– – –) at 120° C.

points. Gent and Lindley [11] suggested that high stress concentration near the flaws would be adequate enough to produce cavitation in a rubber of conventional modulus and this may be the cause of the roughness developed around the tip. Once the failure starts, it proceeds through a catastrophic tearing giving rise to a comparatively smooth surface with some tear lines. The distance between the two successive tear lines measured from the magnified image is $\sim 10\,\mu$m.

3.3.2. Aged sample without precut

On ageing for 1 h at 150° C, however, low tensile strength results. Smooth zone with less number of tear lines is observed (Fig. 9). The distance between two tear lines is found to be almost the same i.e., $\sim 10\,\mu$m. On further ageing at 150° C for 3 h, fracture surface becomes smoother. Only few tear lines at large distance ($\sim 30\,\mu$m) are noticed (Fig. 10).

3.3.3. Unaged sample with precut

Fig. 11 shows the general fracture surface of the unaged sample with precut of 0.49 mm (much less than l_c). The zone AB represents the precut given through the sample from upper side to the bottom (Fig. 2). Stress concentration occurs at the rough zone near the two edges of the samples and fracture initiates from these points. Some tear lines connecting the rough zone and the given precut indicates that after initiation

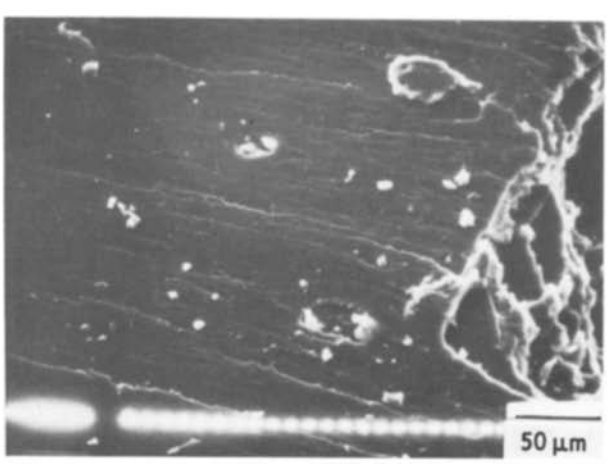

Figure 8 SEM photograph of tensile fracture surface for unaged NR gum vulcanizate without precut.

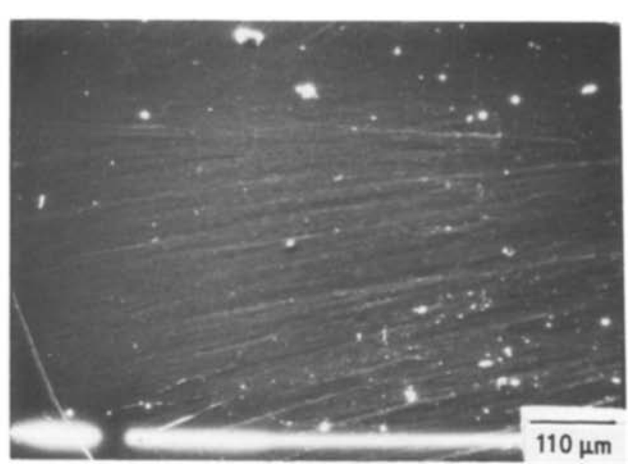

Figure 9 SEM photograph of tensile fracture surface for NR gum vulcanizate without precut, aged for 1 h at 150° C.

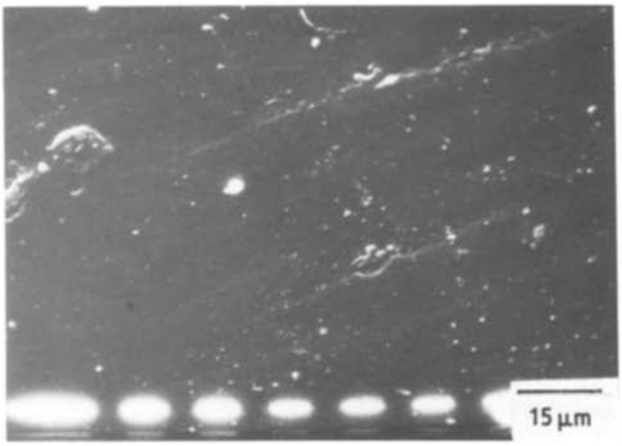

Figure 10 SEM photograph of tensile fracture surface for NR gum vulcanizate without precut, aged for 3 h at 150° C.

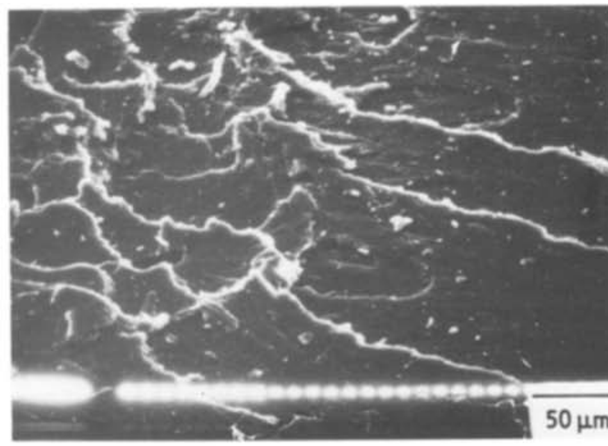

Figure 13 Magnified version of edge in Figure 11.

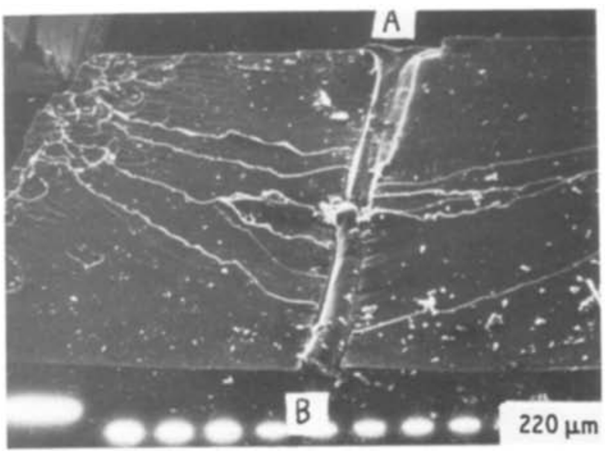

Figure 11 SEM photograph of tensile fracture surface for unaged NR gum vulcanizate with precut of 0.49 mm.

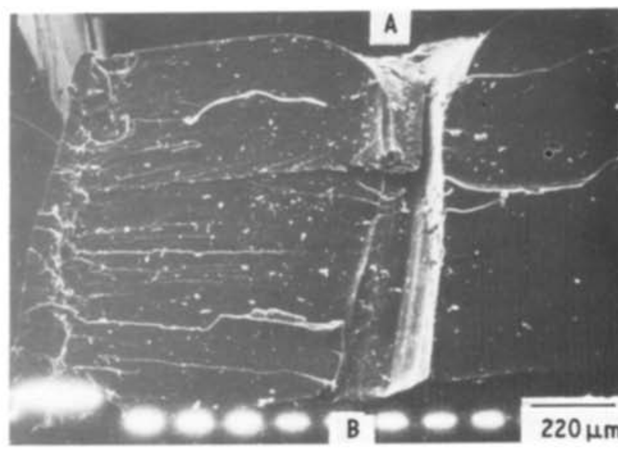

Figure 14 SEM photograph of tensile fracture surface for unaged NR gum vulcanizate at the critical cut length.

of fracture at the end, tearing proceeds towards the centre (precut). The nature of the tear lines are shown in Fig. 12. These are placed at a distance of 30 to 80 μm near the initiation of fracture. The rough zone near the edge of the sample is shown in Fig. 13. A similar type of fracture surface was observed for NR with other precuts less than the l_c.

Fig. 14 shows the general fracture surface of NR vulcanizate at the critical cut length (1.21 to 1.30 mm). Big cracks perpendicular to the precut have been noticed. In addition large number of tear lines generate from the rough zone near the edges. It is thought that the fracture may initiate from the centre or from the edges.

Above the critical cut length, there is no rough zone in the fractograph near the edges (Figs 15 and 16). So it is obvious that the fracture does not initiate from the edges. The applied precut is the source of fracture. In

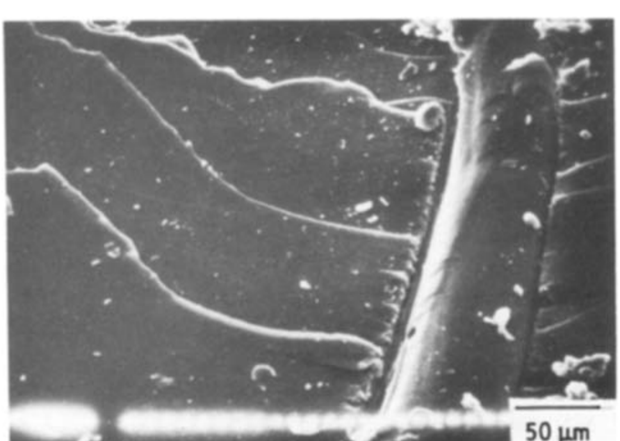

Figure 12 Magnified version of cut area of Figure 11.

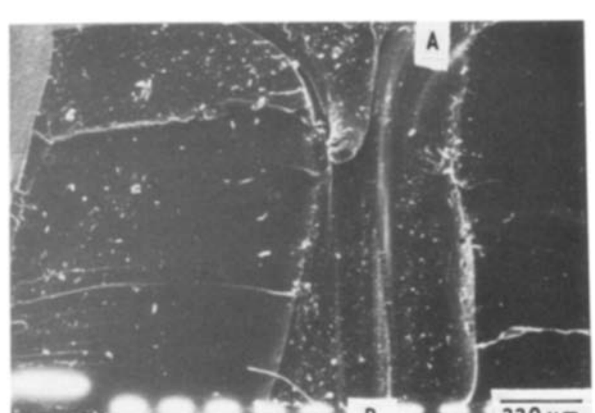

Figure 15 SEM photograph of tensile fracture surface of unaged NR gum vulcanizate with precut of 1.49 mm.

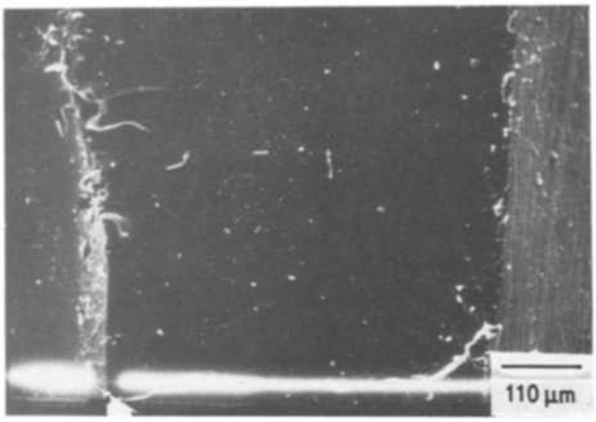

Figure 16 Magnified version of edge in Figure 15.

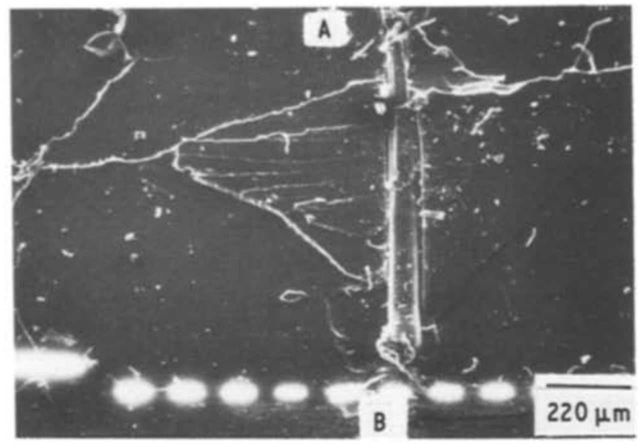

Figure 17 SEM photograph of tensile fracture surface of NR gum vulcanizate with precut (0.49 mm) aged 1 h at 150° C.

general, fracture surface of the samples with precut higher than the critical cut length, is smooth with few tear lines at a distance about 180 μm. So it can be concluded that the fracture of the sample with precut less than the l_c, occurs through a cut growth process originated from the rough zone at the two ends where stress concentration takes place due to presence of natural flaws and proceeds towards the centre where the precut is given. But, for the sample with precut above the l_c, tearing proceeds from the given precut.

3.3.4. Aged sample with precut

The mechanism of tearing of unaged and aged vulcanizates, showing the critical cut length phenomena, is almost similar i.e. the mechanism above the critical cut length is different from that below it. However, it is worth mentioning the fracture surfaces of rubber vulcanizates, showing no critical cut length.

Fig. 17 shows the general fracture surface of NR aged for 1 h at 150° C, with precut of 0.49 mm. In general, parabolic tear lines, originated from the given precut are observed on the surface. The fractograph of samples with higher precut also shows similar parabolic tear lines. Only difference is that the apex of the parabola moves towards the edge. Smooth surface has been obtained inside and outside the precut on ageing as compared to unaged samples. Cracks are also found on the fracture surface of aged sample.

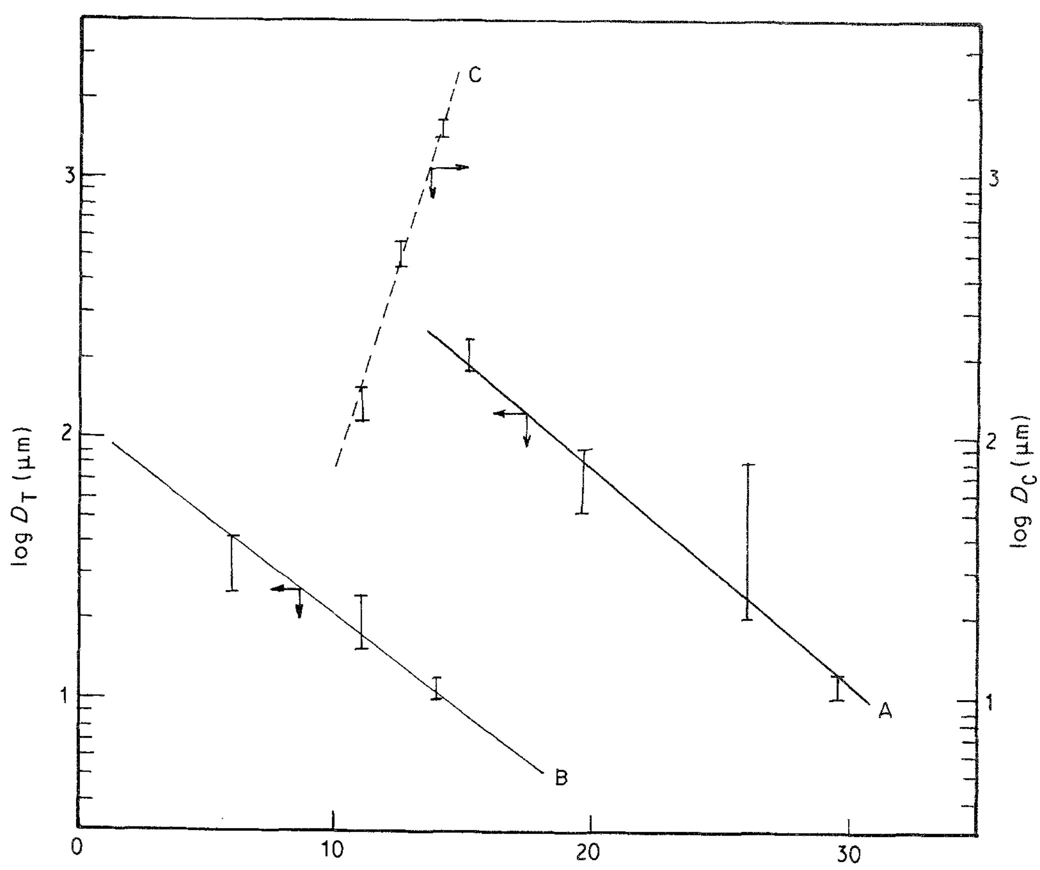

Figure 18 Plot of crack line distance (D_C) and tear line distance (D_T) against tensile strength (σ_b). (A) variation of D_T with σ_b for unaged NR gum vulcanizate, (B) variation of D_T with σ_b for NR gum vulcanizate aged at 150° C, (C) variation of D_C with σ_b for NR gum vulcanizate.

3.3.5. *Quantitative relation between σ_b and distance between tear lines or crack lines*

It has been observed from the previous discussion that the lower tensile strength results from the large number of crack lines on the fracture surface. Similarly, high strength can be associated with large number of tear lines. The distance between the tear lines (D_T) and the crack lines (D_C) has been measured. These are plotted against the tensile strength (σ_b) in Fig. 18. The straight lines could be described by the following empirical relations,

$$\log D_T = 3.52 - 0.079\,\sigma_b \text{ (unaged sample)} \quad (7)$$

$$\log D_T = 2.04 - 0.074\,\sigma_b \text{ (on ageing)} \quad (8)$$

$$\log D_C = -1.62 + 0.36\,\sigma_b \quad (9)$$

Appendix

Mix Formulation – NR, 100; Zno, 5; Stearic Acid, 2; Sulphur, 2.5; CBS, 0.8.

The compound was cured for 9 min at 150° C.

Acknowledgement

The authors are grateful to Indian Space Research Organisation, for funding. The authors thank Mr. Tapan K. Bhaumik for experimental assistance.

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Received 23 June 1986
and accepted 15 January 1987