

# Scanning electron microscopy studies on tear fracture of natural rubber

N. M. Mathew and S. K. De

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India  
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Tear fracture surfaces of peroxide- and sulphur-cured natural rubber vulcanizates, both unfilled and filled, have been studied using scanning electron microscope. Peroxide-cured unfilled vulcanizate shows stick-slip tear whereas the HAF black-filled vulcanizate gives rise to a layered fracture surface. Tear branching, observed in the unfilled sulphur-cured vulcanizate changes to a high level of tear deviation resulting in a rough surface, with the addition of HAF black. FT black improves tear resistance only slightly and the fracture surface appears comparatively smooth. The low level of polymer-filler interaction in clay filled vulcanizates causes the filler agglomerates to come out of the matrix during the test thus decreasing tear resistance and giving rise to a pitted surface.

**Keywords** Tear; scanning electron microscopy; natural rubber; crosslinking system; polymer-filler interaction

## INTRODUCTION

The service life of rubber products depends on their resistance to various types of fracture among which, an important one is tear. Theories have been proposed in the past to describe the tear fracture of rubber vulcanizates<sup>1-5</sup>, but little is known about the damaged zone, where deformation and fracture take place. Recently scanning electron microscopy (SEM) has been used as a tool to study the characteristics of the fracture surfaces of rubber vulcanizates<sup>6-11</sup>. These studies are expected to throw more light on the mechanism of rubber fracture. In this note we report our SEM studies on tear fracture of natural rubber vulcanizates. The parameters studied are, (a) effect of the crosslinking system and (b) the effect of filler.

## EXPERIMENTAL

Formulations of the mixes are given in Table 1. The mixes were prepared on a 6" × 13" two-roll laboratory mill. Vulcanization of the mixes up to optimum cure times, determined from time to reach 90% of maximum rheometric torques, was carried out in a hydraulic press having electrically heated platens, at 150°C. On removal from the mould, the vulcanizates were quickly cooled in

water. Specimens for tensile and tear testing were punched out from the vulcanized sheets along the grain direction. Tensile testing was done as per ASTM designation D412-51T using dumb-bell specimens. Tear resistance of the samples were tested according to ASTM designation D 628-48 using the unnicked, 90° angle test piece, a line drawing of which is given in Figure 1. Both tensile and tear tests were done in a Zwick tensile testing machine at 30°C and at a rate of separation of the grips of 50 cm per minute.  $V_r$ , the volume fraction of rubber, after swelling in benzene at  $35 \pm 1^\circ\text{C}$  for 48 h, was determined using the relation<sup>12</sup>,

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

where  $T$  is the sample weight,  $D$  is the deswollen weight,  $F$  the weight fraction of the insoluble components and  $A_0$  the weight of the absorbed solvent, corrected for the swelling increment,  $\rho_r$  and  $\rho_s$  are the densities of rubber and solvent respectively, ( $\rho_r = 0.92 \text{ g ml}^{-1}$  for NR and  $\rho_s = 0.875 \text{ g ml}^{-1}$  for benzene). Optimum cure times of the mixes,  $V_r$  values and physical properties of the vulcanizates are furnished in Table 2.

Figure 1 indicates the direction in which force was applied in the tear tests and that in which tear

Table 1 Formulations of the mixes

Mix	A	B	C	D	E	F
Natural rubber <sup>a</sup>	100	100	100	100	100	100
Zinc oxide	—	—	5	5	5	5
Stearic acid	—	—	2	2	2	2
HAF black (N-330)	—	50	—	50	—	—
FT black (N-880)	—	—	—	—	50	—
China clay	—	—	—	—	—	50
Naphthenic oil	—	5	—	5	5	5
CBS <sup>b</sup>	—	—	0.8	0.8	0.8	0.8
Sulphur	—	—	2	2	2	2
Dicumyl peroxide	2	2	—	—	—	—

<sup>a</sup> Crumb rubber, ISNR-5, obtained from Rubber Research Institute of India, Kottayam

<sup>b</sup> *N*-cyclohexylbenzothizyl sulphenamide (Accicure HBS), obtained from Alkali and Chemical Corporation of India Ltd., Rishra

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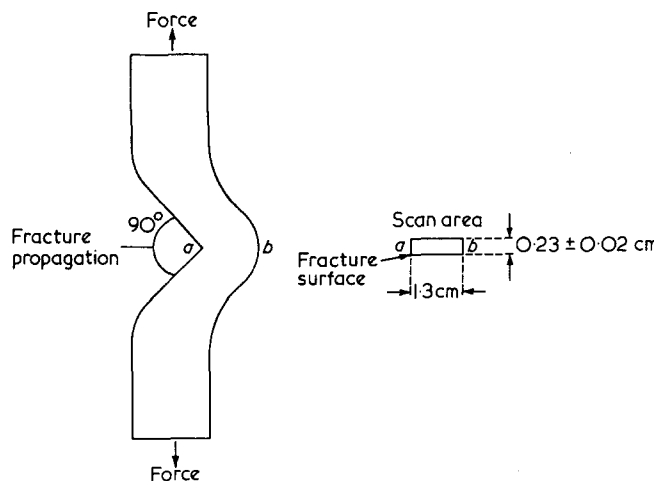


Figure 1 Tear test specimen showing direction of stress, tear and scan

propagation occurred. After tear testing, the fracture surface was carefully cut out from one of the two pieces of the failed test specimen without touching the surface. The specimens were stored in a desiccator to avoid contamination and then sputter coated with gold within 24 h of testing. SEM observations were made using ISI-60 model scanning electron microscope. The scan area is also shown in Figure 1. All the photographs were taken in the same direction.

## RESULTS AND DISCUSSION

From Table 2 it can be seen that the tear resistance of natural rubber vulcanizates is very much dependent on the crosslinking system. As expected, the peroxide-cured vulcanizates (mixes A and B) show low tear resistance both in unfilled and in filled systems. The sulphur vulcanizing system gives appreciable tear resistance even in the unfilled mix (mix C). Addition of HAF black to this system (mix D) enhances its tear resistance remarkably. FT black is only semi-reinforcing and china clay is non-reinforcing as shown by their effect on tear resistance (mixes E and F). Stress dissipation near the tip of a growing crack by viscoelastic processes is essential to the development of high strength. In the case of sulphur-cured vulcanizates, stress dissipation is possible through the slippage of sulphur crosslinks. In peroxide-cured vulcanizates, however, crosslink slippage is prevented as the crosslinks are of carbon-carbon type and, therefore, stress dissipation is minimized. Addition of reinforcing black induces additional mechanisms by which strain energy is dissipated. Mechanical energy dissipation through increased hysteresis resulting from the inclusion of particles in a viscoelastic medium has been studied by Radok and Tai<sup>13</sup>. Any loss of segmental mobility in the polymer matrix resulting from interaction with the filler, further increases hysteresis. Motions of filler particles, chain slippage or breakage and dewetting at high strains also accentuate hysteretic behaviour. In addition to causing increased energy dissipation, dispersed particles may serve to deflect or arrest growing cracks, thereby further delaying failure<sup>14</sup>.

The low level of interaction between clay and rubber, as reported earlier by Mukhopadyay and De<sup>15</sup>, causes the formation of loose agglomerates in the matrix, which act as stress raisers and provide an easy path for the tear to follow, thereby causing premature failure. This accounts for the low tear resistance of the clay filled mix. The SEM observations discussed later in this report support some of these explanations. Failure to enhance the tear resistance of peroxide-cured NR vulcanizate by HAF black may be due to the dominant effect of the crosslink type, as discussed earlier, which is not influenced even by the reinforcing filler.

Figure 2a, which is the SEM photograph of the tear fracture surface of the peroxide-cured unfilled vulcanizate, shows one tear path on the surface. From the Figure it is apparent that the tear propagates in a stick-slip manner. A similar mode of fracture was described by Glucklich and Landel<sup>16</sup>. De and coworkers<sup>17</sup> also made similar observations in their SEM studies on failure of carboxylated nitrile rubber. One end of the fracture surface is shown in Figure 2b, which shows microfolds on the surface. Addition of HAF black to the same system changes the fracture pattern (Figure 2c), though it does not enhance the tear resistance. The surface is rough and has a layered structure. Separation of the matrix near the filler agglomerates is also seen in this photomicrograph.

The SEM fractograph of the sulphur-cured unfilled NR vulcanizate (mix C) is shown in Figure 2d. The surface shows a large number of broad tear lines which propagate

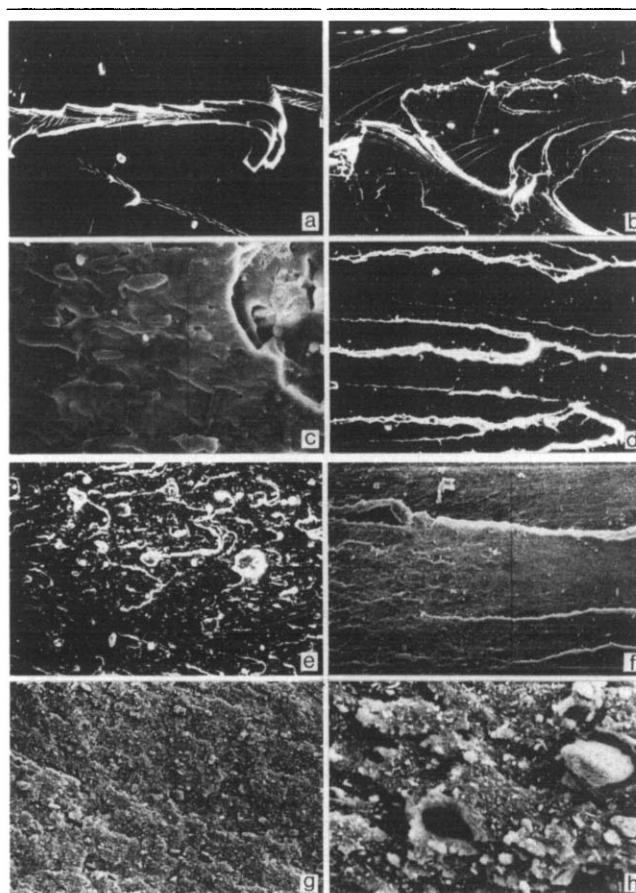


Figure 2 (a) Stick-slip process (116X) [Mix A]; (b) microfolds on the surface (48X) [Mix A]; (c) layered structure (174X) [Mix B]; (d) branching of tear lines (64X) [Mix C]; (e) rough surface with rounded tear lines (87X) [Mix D]; (f) smooth tear lines (76X) [Mix E]; (g) general surface (97X) [Mix F]; (h) formation of pits on the surface (480X) [Mix F]

Table 2 Characterization of the mixes

Mix	A	B	C	D	E	F
Optimum cure time (min) <sup>a</sup>	17.5	24.0	12.0	8.5	8.5	12.5
$V_r$	0.1726	0.1835	0.2096	0.2410	0.1976	0.2120
300% Modulus (MPa)	0.2	9.9	0.8	12.7	2.5	2.1
Tensile strength (MPa)	11.8	13.8	23.1	22.4	21.7	20.2
Elongation at break (%)	700	400	800	450	630	615
Tear resistance ( $\text{kN m}^{-1}$ )	13.8	13.7	27.6	86.4	42.5	22.4

<sup>a</sup> Obtained from Monsanto Rheometer R-100 at 150°C

by the stick-slip process. There is appreciable branching of the tear lines, which indicates tear deviation. This accounts for the higher tear resistance of the sulphur-cured mix as compared to the peroxide-cured one. The addition of HAF black to the same system changes the fracture mode remarkably as seen from *Figure 2e*, which is the SEM fractograph of vulcanizate of mix D. The high tear resistance of this mix can be correlated to the roughness of the surface and to the appearance of a large number of short but rounded tear lines which are distributed at random. Reinforcing HAF black provides improved wetting and adhesion characteristics and prevents tear from proceeding straight.

Addition of FT black improves tear resistance only slightly. The fracture pattern as given in *Figure 2f* is different from that obtained with HAF black. The surface is smoother with a few long but straight tear lines. *Figure 2g* is the SEM fractograph of the clay-filled vulcanizate. The surface does not show any tear line. The poor bonding between clay agglomerates and rubber causes the former to come out of the matrix. This results in the formation of a large number of pits on the surface and thus makes the surface appear rough. *Figure 2h* is the same surface under higher magnification, where the formation of pits on the surface as a result of clay agglomerates coming out of the matrix is clearly seen. As pointed out earlier, such loose agglomerates in the matrix act as stress raisers and provide an easy path for the tear to follow, thereby reducing the overall strength of the vulcanizate. The low level of polymer-filler interaction in the case of FT black- and clay-filled mixes is also evident from their  $V_r$  values, which are lower than that of the HAF black-filled sulphur-cured mix. Since the actual crosslink density of vulcanizates is not much influenced by the presence of fillers, changes in  $V_r$  may be taken as a measure of

polymer-filler interaction<sup>18,19</sup>. The increase in  $V_r$  on addition of HAF black is much less with the DCP curing system. If this indicates less interaction between rubber and filler, this could account for the lack of reinforcement as discussed earlier.

Further investigations are required to understand clearly the mechanism of tear and our work in this area is continuing.

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