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Scanning electron microscopy studies on tensile rupture of rubber

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Tensile rupture of natural rubber (NR) and styrene-butadiene rubber (SBR), vulcanized by sulphur and peroxide systems, both with and without fillers, has been studied by scanning electron microscopy (SEM). NR gum fracture surfaces show evidence of strain-induced crystallization, which is absent in SBR. The fracture surfaces of filler-reinforced NR and SBR vulcanizates are characterized by their roughness and by the presence of short and curved tear lines. Increase of cross-link density changes the fracture mode. Peroxide-cured SBR undergoes brittle fracture, whereas sulphur-cured SBR shows a smooth surface with a few straight tear lines.

1. Introduction

In our earlier communications [1–5] we reported on SEM studies of failure of rubbers under different modes of fracture. We report here in detail the continuing research on tensile rupture characteristics of rubbers studied by SEM. We have studied: (a) two different rubbers, namely NR and SBR; (b) the effect of type and extent of cross-linking and (c) the effect of filler.

Theories of tensile rupture have been described previously by Greensmith [6], Thomas [7], Smith [8] and Gent [9]. These authors correlated strength with tearing energy or work to break per unit volume. However, the nature of the fracture surface under tensile rupture was not fully explored in those studies. The present study attempts to reveal the nature of the fracture surface formed in different types of vulcanizates.

2. Experimental

Formulations of the mixes and their optimum cure times, determined as the time taken to reach 90 per cent of maximum torque from Monsanto Rheometer R-100, are given in Table I. Mixing was done in a 6 in. × 13 in. two-roll laboratory mill and vulcanization to optimum cure was carried out in a hydraulic press having electrically heated platens. Tensile testing of the vulcanizates was done at room temperature (30° C) according to ASTM designation D412-51T using dumb-bell shaped specimens, which were punched out from the vulcanized sheets along the grain direction. The testing was done in a Zwick tensile testing machine and the rate of separation of grips was 50 cm min^{-1}. Fracture surfaces were then carefully cut from the failed test pieces without touching the surfaces. These specimens were stored in desiccator and then sputter-coated with gold within 24 h of testing. The SEM observations were made using ISI-60 (Figs 2, 3 and 6 to 15) and Philips 500 (Figs 4 and 5) scanning electron microscopes. The tilt was adjusted at 0° and the orientation of the photographs was kept the same in all cases. Figure 1 shows details of the test specimen and scan area.

V_r, the volume fraction of rubber in swollen vulcanizate is an index of cross-link density. It was determined after swelling of the vulcanizate in benzene at 35° C for 48 h, using the relation [10],

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

where T is the original weight of the sample, D is the de-swollen weight, F is the fraction of insoluble components and A_0 is the weight of the absorbed solvent, corrected for the swelling increment.

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TABLE I Formulations of the mixes

Mix	A	B	C	D	E	F	G	H	I
Natural rubber*	100	100	100	100	100	100	–	–	–
Styrene-butadiene rubber†	–	–	–	–	–	–	100	100	100
Zinc oxide	–	5	5	–	5	5	–	5	5
Stearic acid	–	2	2	–	2	2	–	2	2
HAF black (N-330)	–	–	–	50	50	–	–	–	50
China clay	–	–	–	–	–	50	–	–	–
Naphthenic oil	–	–	–	5	5	5	–	–	5
CBS‡	–	0.8	1.5	–	0.8	0.8	–	0.8	0.8
Sulphur	–	2.0	4.0	–	2.0	2.0	–	2.0	2.0
Dicumyl peroxide	2.0	–	–	2.0	–	–	2.0	–	–
Optimum cure time (min) §	17.5	12.0	9.5	24.0	8.5	12.5	25.0	33.0	19.5

* Crumb rubber, ISNR-5, obtained from the Rubber Research Institute of India, Kottayam.

† SBR-1502 as supplied by Synthetics and Chemicals Ltd., Bareilly.

‡ N-Cyclohexylbenzothiazyl sulphenamide, (Accicure HBS), obtained from Alkali and Chemical Corporation of India Ltd., Rishra.

§ Obtained from Monsanto Rheometer, R-100, at 150° C.

ρ_r and ρ_s are the densities of rubber and solvent respectively ($\rho_r = 0.92\,\mathrm{g\,ml^{-1}}$ for NR and $0.94\,\mathrm{g\,ml^{-1}}$ for SBR, $\rho_s = 0.875\,\mathrm{g\,ml^{-1}}$ for benzene).

3. Results and discussion

The tensile strengths of the different vulcanizates are given in Table II. Fig. 2 is the SEM fractograph of the peroxide-cured NR vulcanizate. Long thin tear lines are observed on the surface. A large number of bright spots are also seen on the surface, which act as nucleii for microfolds emanating radially as seen in Fig. 3. We believe that these spots are characteristic of a strain-crystallized matrix undergoing rupture at high strain. The fracture surface of the sulphur-cured NR gum vulcanizate (Mix B) shows a rough zone near one end of the surface (Fig. 4). The surface also shows a number of bright spots, which act as nucleii for microfolds (Fig. 5). Similar observations were reported by us earlier [2]. The cross-link density of Vulcanizate C is high as indicated by V_r in Table II, and the fracture mode changes appreciably. Fig. 6 is the SEM fractograph of the tensile fracture surface in the case of Vulcanizate C. Fig. 6 shows folding on the surface and a random distribution of tear lines. The sample breaks at a much lower elongation, even before the occurrence of strain-induced crystallization. Therefore the bright spots, which were seen in the other NR gum vulcanizates, are much less apparent in this case. Expectedly, the strength is also poor (Table II).

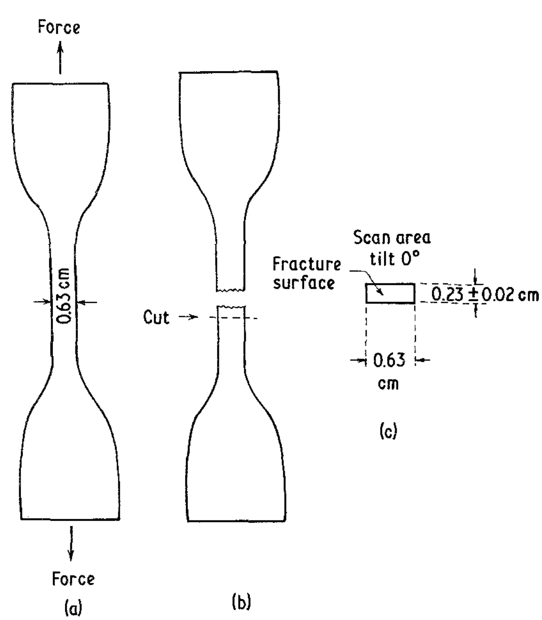

Figure 1 (a) Original test specimen (thickness 0.23 ± 0.02 cm). (b) Failed specimen. (c) Fracture surface and scan area.

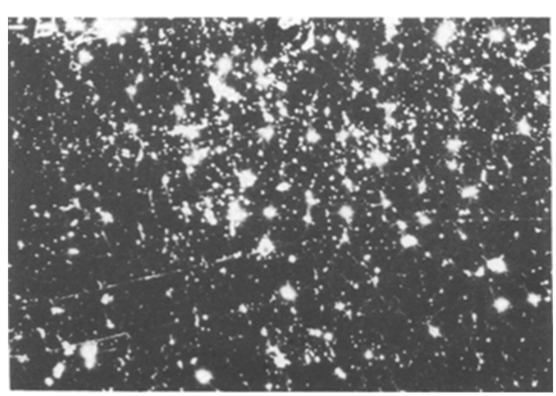

Figure 2 General surface, peroxide-cured NR (× 51).

TABLE II Properties of the vulcanizates

Vulcanizate	A	B	C	D	E	F	G	H	I
300% modulus (MPa)	0.2	0.8	1.9	9.9	12.7	2.1	–	1.7	10.9
Tensile strength (MPa)	11.8	23.1	3.6	13.8	22.4	20.2	0.3	2.3	20.6
Elongation at break (%)	700	800	360	400	450	615	40	330	460
V_r	0.173	0.210	0.275	0.184	0.241	0.212	0.223	0.176	0.225

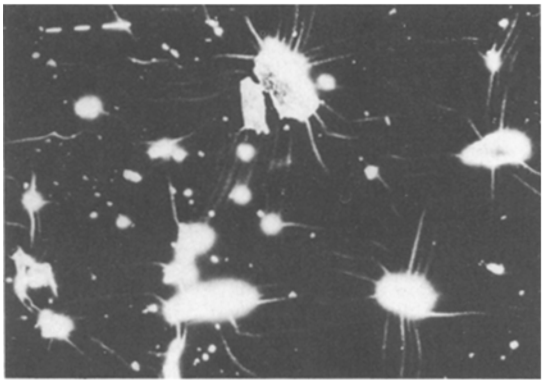

Figure 3 Nucleation of microfolds, peroxide-cured NR (× 370).

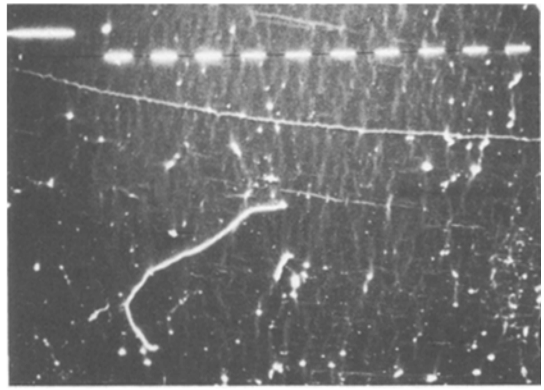

Figure 5 General surface, sulphur-cured NR (× 45).

Introduction of HAF black changes the fracture mode in both peroxide and sulphur-cured vulcanizates. A fractograph of the peroxide-cured vulcanizate containing HAF black (Mix D) is shown in Fig. 7. It shows a number of curved tear lines. The fracture surface of the HAF black-filled sulphur-cured vulcanizate (Mix E) shows a larger number of shorter curved tear lines (Fig. 8). The surface also shows improperly dispersed filler agglomerates, which nucleates fracture through the formation of cracks (Fig. 9). Addition of china clay into the conventional sulphur-cured NR mix changes the fracture mode remarkably, as seen in Fig. 10. The surface is rough and a few fissures are visible on the surface, but no tear line. The small pits which appear on the surface result from the removal of loosely bound clay agglomerates from the matrix during fracture. As indicated by V_r values (Table II), the extent of polymer–filler interaction in this vulcanizate is less compared to HAF black-filled vulcanizate. A similar phenomenon has been observed by us during tear fracture of clay-filled NR vulcanizate [11]. As natural rubber vulcanizates exhibit strain-induced crystallization, their tensile strengths are high even without reinforcement. Addition of fillers does not enhance tensile strength appreciably. However, the fracture surfaces of the filled vulcanizates are very different from those of the

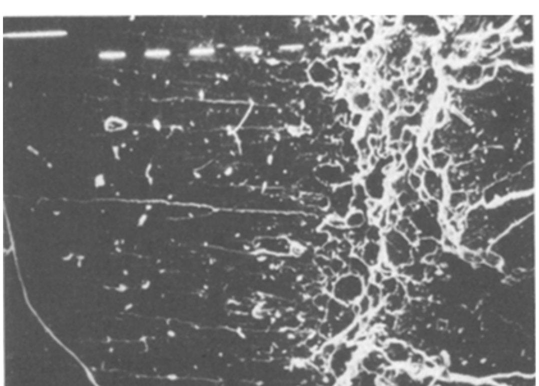

Figure 4 Rough zone, sulphur-cured NR (× 45).

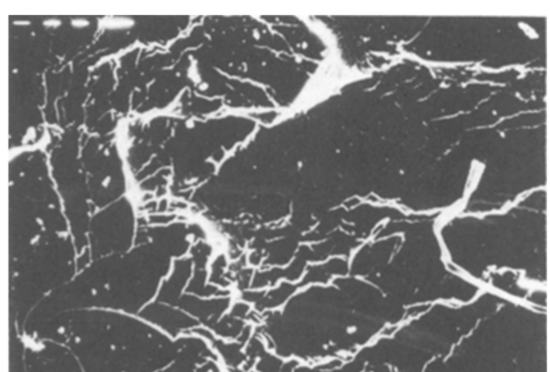

Figure 6 General surface, sulphur-cured NR, highly crosslinked (× 42).

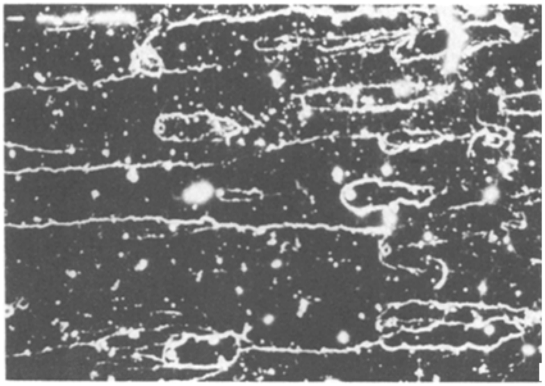

Figure 7 Straight and curved tear lines, peroxide-cured NR, HAF black-filled (× 51).

Figure 10 Pitted surface with fissures, sulphur-cured NR, clay-filled (× 83).

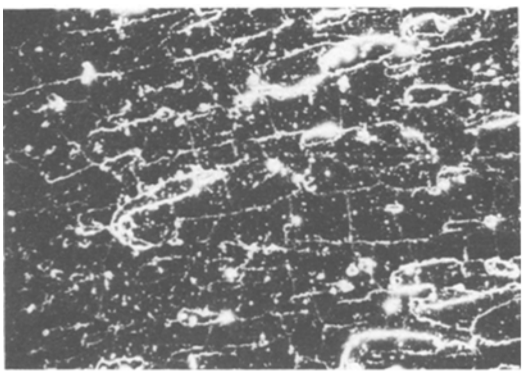

Figure 8 Rough surface with curved tear lines, sulphur-cured NR, HAF black-filled (× 51).

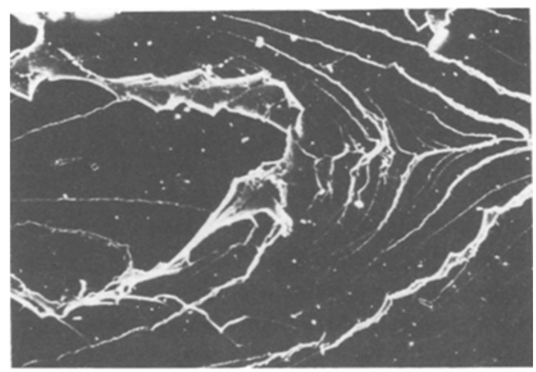

Figure 11 Slip lines, peroxide-cured SBR (× 51).

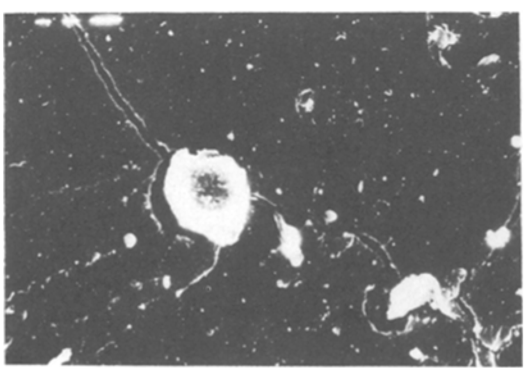

Figure 9 Filler agglomerates nucleating cracks, sulphur-cured NR, HAF black-filled (× 420).

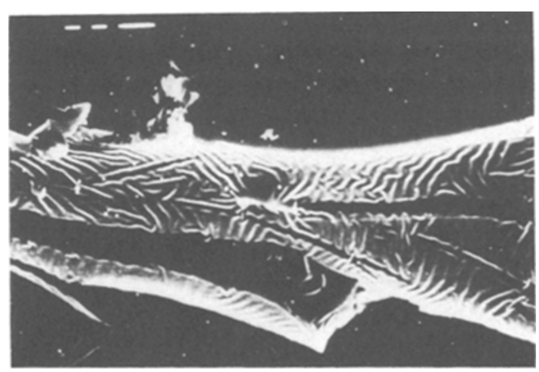

Figure 12 Details of the tear path, peroxide cured SBR (× 510).

unfilled ones. This shows that the mechanism of fracture is different in unfilled and filled NR vulcanizates and in filled vulcanizates the nature of the filler (reinforcing or non-reinforcing) changes the fracture mode.

In the case of SBR, the peroxide curing system makes the vulcanizate brittle with very low tensile strength and elongation at break. The fracture surface shows "slip lines", as seen from the fractograph (Fig. 11). This type of slip line has been described as characteristic of brittle fracture in the case of polymethylmethacrylate [12]. These slip

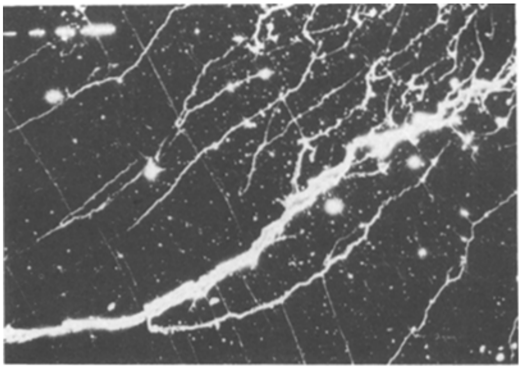

Figure 13 Smooth surface with tear lines, sulphur-cured SBR (X 44).

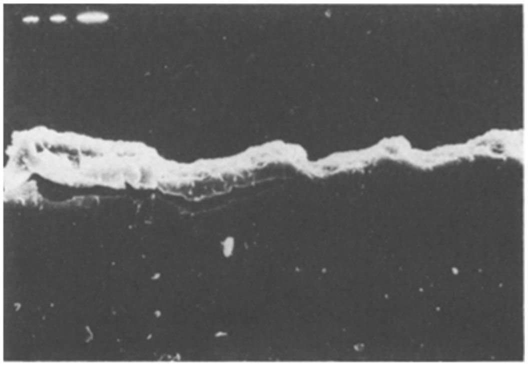

Figure 15 Crack along a tear line, sulphur-cured SBR, HAF black-filled (X 420).

lines are "hyperbolae" formed on the fracture surface at the junction of two advancing cracks, which start from two different centres at the same speed, but at different times [12]. Fig. 12 is a magnified image of the surface which shows microfolding on a portion of one of the tear paths. The sulphur-cured SBR gum vulcanizate shows a different type of fracture. The surface is smooth with a few tear lines (Fig. 13). Unlike in the case of NR, small bright spots, which are believed to be due to crystallites, are much less apparent in SBR. This again confirms the idea that these spots result from strain-induced crystallization, which cannot be realized in non-crystallizing copolymer rubbers such as SBR. With the addition of HAF black the strength of SBR increases remarkably. This improvement in strength is also reflected in the nature of the fracture surface, which is rough with curved tear lines (Fig. 14). Compared with the corresponding NR fracture suface, there are fewer tear lines, but they are larger. Fig. 15 is a magnified fractograph of the HAF black-filled SBR vulcanizate, which shows a crack along one of the tear lines. The high level of polymer–filler interaction in the case of HAF black-filled vulcanizates causes formation of regions of high strength in the composite and hence smooth propagation of fracture is hindered. This results in the occurrence of a rough fracture surface and curved tear lines and enhanced tensile strength of the vulcanizate.

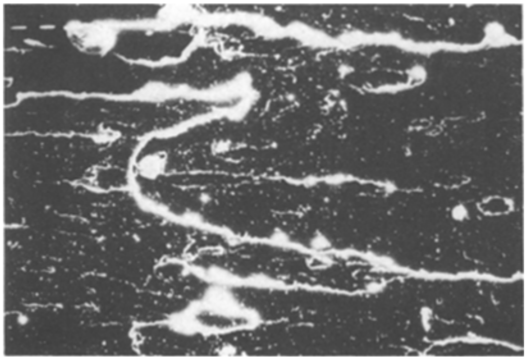

Figure 14 Curved tear lines, sulphur-cured SBR, HAF black-filled (X 111).

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