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Scanning electron microscopic studies on the tear fracture of polyethylene filled natural rubber vulcanizate

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Tear failure of natural rubber (NR) filled with high density polyethylene (HDPE) was studied by scanning electron microscopy (SEM). The tear strength of NR was increased by the addition of HDPE. It was found that HDPE forms physical links with NR. The retention of tear strength by ageing attains an optimum value with HDPE loading.

1. Introduction

The service life of rubber products depends on their resistance to various types of failure modes, an important one of which is tear. Many theories have been proposed to describe the tear fracture of filled and unfilled rubber vulcanizates [1–5].

Thermoplastic filled elastomers have the advantage of good processing properties like lower die swell, better finish of extruded and calendered products and also higher green strength. Over the last two decades, several patents have appeared where thermoplastic semicrystalline materials have been blended with vulcanizable rubbers to obtain composites with improved properties [6–9]. This paper examined the mechanism of tear fracture in natural rubber vulcanizates filled with high density polyethylene. The effect of heat ageing on the tear strength of these vulcanizates has also been studied. Scanning electron microscopy (SEM) has been successfully used by

TABLE I Formulations of the mixes

Ingredients	Mix 1	Mix 2	Mix 3	Mix 4
[1]Natural rubber	100.00	100.00	100.00	100.00
Zinc oxide	5.00	5.00	5.00	5.00
Stearic acid	2.00	2.00	2.00	2.00
Sulphur	2.50	2.50	2.50	2.50
[2]Vulkacit CZ	1.00	1.00	1.00	1.00
[3]HDPE	0.00	10.00	30.00	50.00
Tear strength ($kN\,m^{-1}$)	36.5	35.9	41.4	50.8

[1]ISNR-5, supplied by Rubber Research Institute of India, Kottayam, India.
[2]N-cyclohexyl-2-benzothiazyl sulphenamide, supplied by Bayer (India) Limited, Bombay, India.
[3]High Density Polyethylene – HOSTALEN GA 7260, obtained from Polyolefins Industries Limited, Bombay, India. Melting point 128–132° C; Density $0.960\,g\,cm^{-3}$; Melt Flow Index (DIN 53735) – 16.

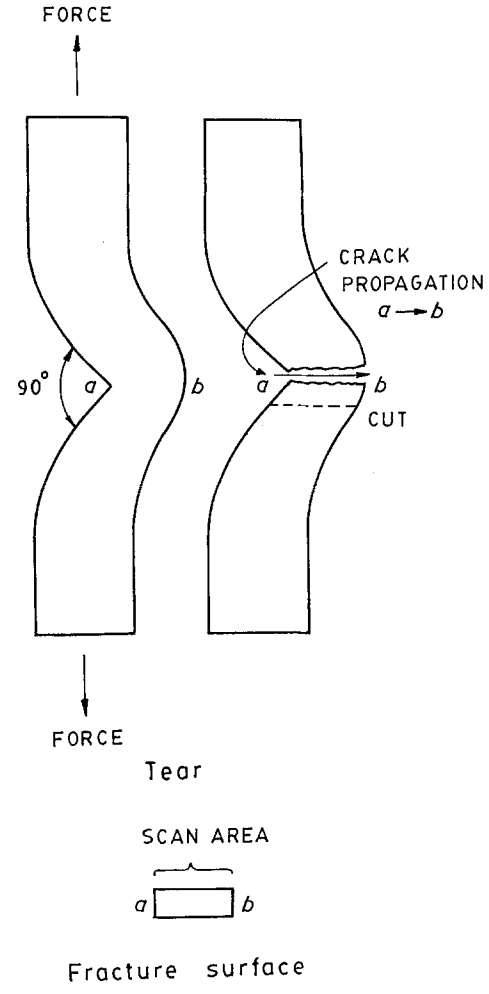

Figure 1 Tear test specimen.

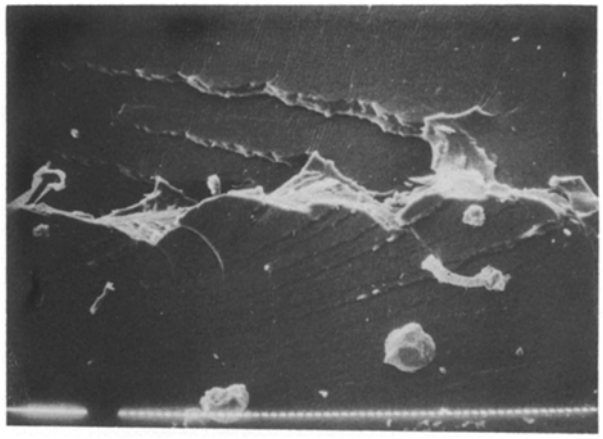

Figure 2 Tear fractograph of unfilled NR vulcanizate (100×).

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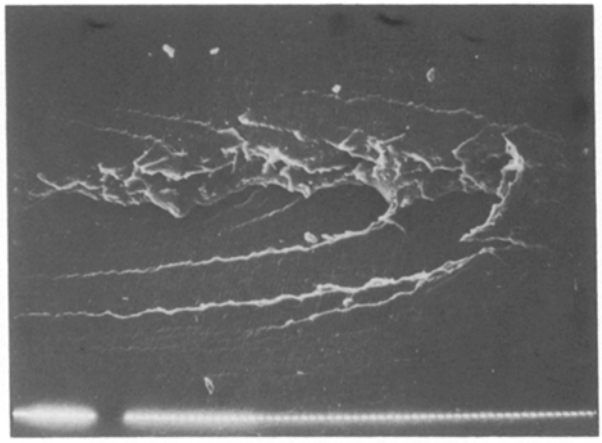

Figure 3 Tear fractograph of 10 phr HDPE filled NR vulcanizate (100 ×).

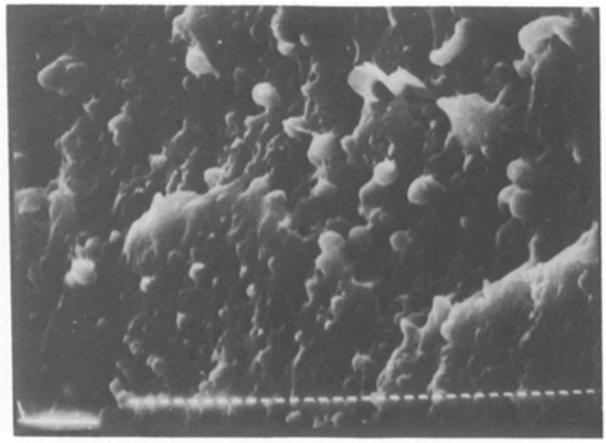

Figure 5 Tear fractograph of 30 phr HDPE filled NR vulcanizate, pitted matrix containing different shaped HDPE domains (1600 ×).

several authors for studying the fracture of thermoplastic–elastomer blends [10–12]. The fracture surfaces of high density polyethylene (HDPE) filled natural rubber (NR) vulcanizates have been studied with the help of SEM to gain an insight into the mechanism of failure.

2. Experimental details

Formulations of the mixes are given in Table I. The mixes were prepared by blending HDPE with NR at 150° C in a Brabender Plasticorder model PLE-330, using a cam type mixer with rotor speed of 60 r.p.m. The blending was accomplished by melting the HDPE in the mixer first and then adding the rubber strips and mixing for 4 min in the mixer at 150° C. This blend was then mixed with other compounding ingredients on a two-roll mixing mill. Vulcanization of the mixes up to optimum cure time, determined as the time to reach 90% of maximum rheometric torque (Monsanto Rheometer R-100), 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 tear testing were punched out from the vulcanized sheet along the grain direction. Tear testing of the samples was done according to ASTM designation D 624-48, using an unnicked 90° angle test piece. A line drawing of the test specimen is given in Fig. 1. The tear tests were carried out on the Instron Universal Testing model 1195 at 25° C and at 500 mm min^{-1} rate of separation of the grips.

The samples were heat aged at 100° C for various intervals of time in a cellular ageing oven in an atmosphere of air. After ageing, the samples were conditioned at room temperature for 16 h before the tear test was conducted. Fig. 1 also shows the direction in which force was applied during the tests and that in which the tear propagated.

After tear testing, the fracture surface was carefully cut out from one of the two pieces of failed test specimens 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 a Philips 500 model scanning electron microscope. The SEM scan area is also shown in Fig. 1.

Dynamic mechanical analysis of the vulcanizates were done on Rheovibron DDV-III-EP. The result is shown in Fig. 9.

3. Results and discussion

The tear strength of the vulcanizates is shown in Table I. With the incorporation of HDPE into the rubber matrix, the tear strength increases. Mix 2 shows no increase in tear strength whereas mixes 3 and 4 show considerable enhancement in tear strength.

The SEM fractographs of the torn surfaces of the vulcanizates are shown in Figs 2 to 8. Fig. 2 of

Figure 4 Tear fractograph of 30 phr HDPE filled NR vulcanizate (100 ×).

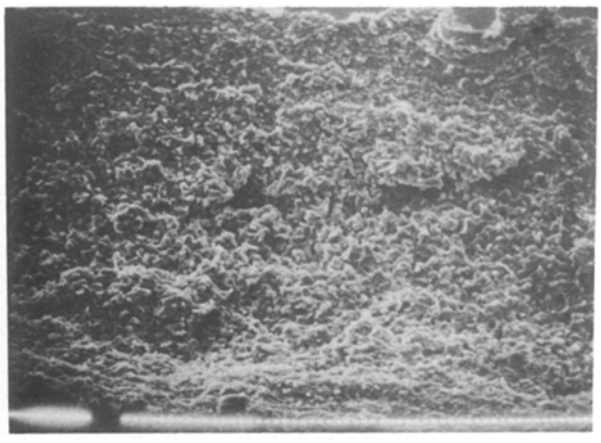

Figure 6 Tear fractograph of 50 phr HDPE filled NR vulcanizate, uniformly rough surface (100 ×).

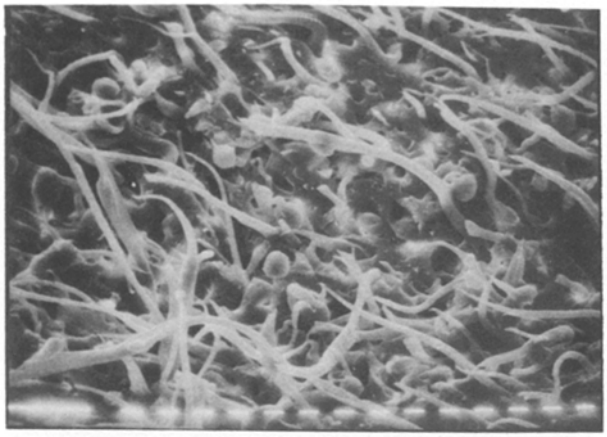

Figure 7 Tear fractograph of 50 phr HDPE filled NR vulcanizate, fibrils are seen at this tear initiation region (400×).

mix 1 shows a broad parabolic tear line which propagates by a stick-slip process. The fracture passes through several planes and is accompanied by subsidiary tear lines. This branching of the main fracture path indicates tear deviation and is characteristic of high strength vulcanizates. The tear fractograph of mix 2 is very similar to that of the unfilled one. In this case also the tear propagates in different layers via a stick–slip mechanism (Fig. 3). Many tear lines can be seen branching off from the main fracture path.

The fractograph of mix 3, Fig. 4, shows a change from the previous ones. This shows a rough surface with no parabolic tear lines; several straight, short tear lines in different layers are evident. At a higher magnification (Fig. 5), this fracture surface shows spherical and few irregularly shaped domains attached to a rough pitted matrix. These domains correspond to polyethylene which is dispersed in the rubber matrix.

Fig. 6 of mix 4 is entirely different from all the others. It is similar to the tear fracture surface of the 70NR–30HDPE thermoplastic elastomer blend and no tear lines can be seen on the rough surface [12].

At a higher magnification, the SEM fractograph of mix 4, Fig. 7, shows the polyethylene elongated into fibrils. Spherical domains of polyethylene can be seen along the sides of cavities created as a result of their displacement. A noticeable feature in this case is that the fibrils are observed only at the beginning of the fracture path. Fig. 8 shows the region towards the end of the fracture path (*b* in Fig. 1). The fibrils are conspicuous by their absence *vis a vis* Fig. 7. Elongated and spherical particles of PE are however, still observed.

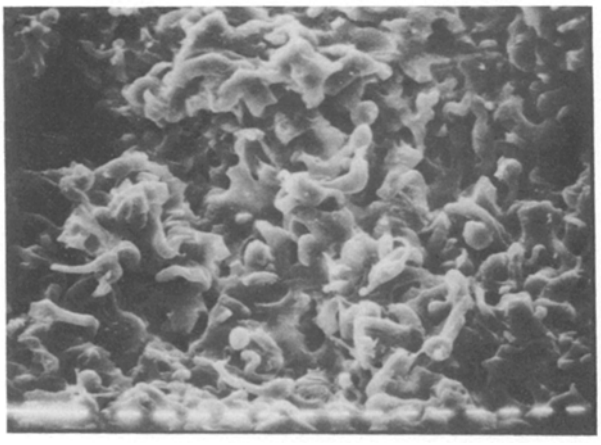

Figure 8 Tear fractograph of 50 phr HDPE filled NR vulcanizate, tear propagation region (400×).

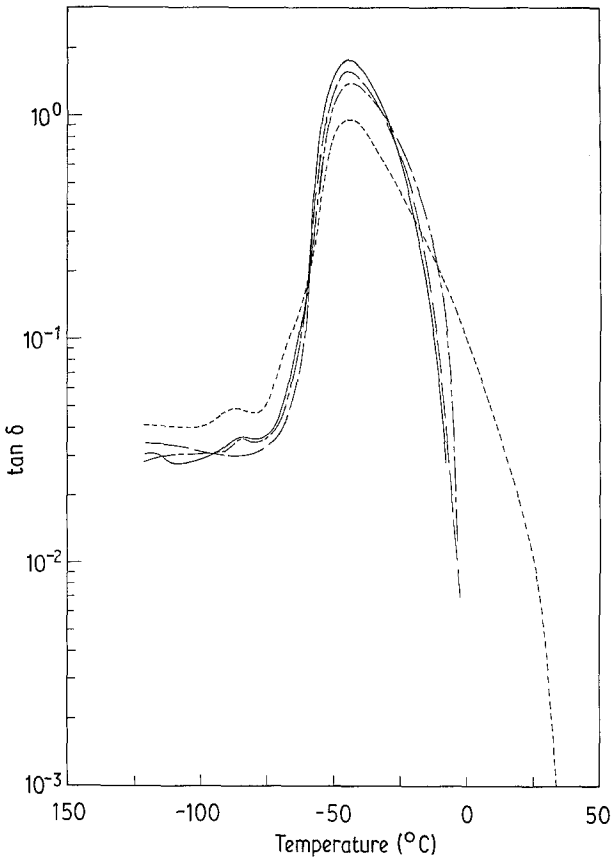

Figure 9 Tan δ plotted against temperature for different filled NR vulcanizate obtained from dynamic mechanical analysis (—— 0 phr HDPE, – – – 10 phr HDPE, -·-·-· 30 phr HDPE, - - - - - 50 phr HDPE).

Fig. 8 shows the propagation region of tear. Due to the high speed of tear propagation, rubber acts as a high modulus material and this may be the reason for the absence of fibrillar structure in the fracture propagation region.

The dynamic mechanical analysis of the different

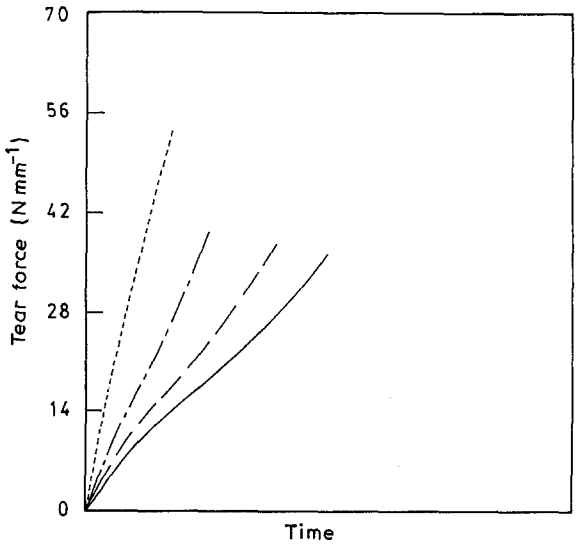

Figure 10 Tear force plotted against time for different filled NR vulcanizate (—— 0 phr HDPE, – – – 10 phr HDPE, -·-·- 30 phr HDPE, - - - - - - 50 phr HDPE).

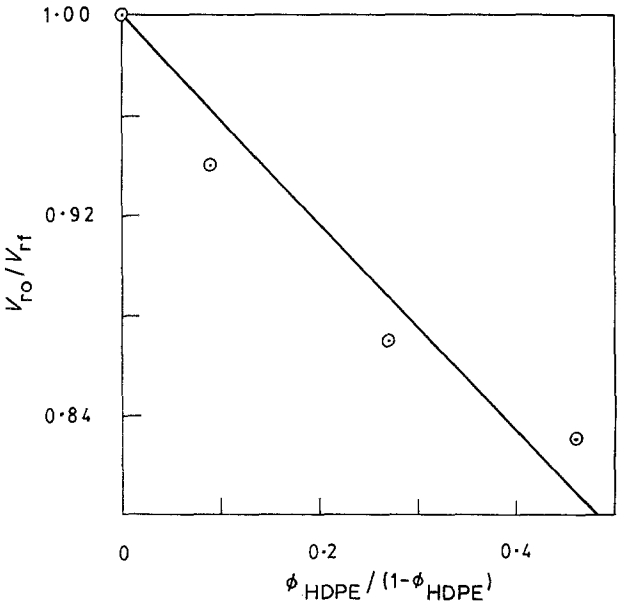

Figure 11 Plot showing the restriction of swelling of NR vulcanizate due to the presence of HDPE.

mixes carried out is shown in Fig. 9. It is clear that all the different mixes have shown a glass transition temperature coinciding with that of the unfilled mix. This indicates that NR and HDPE are incompatible [13]. The tear curves (tear force plotted against time) of the different vulcanizates are given in Fig. 10. It can be seen beyond 30 phr HDPE loading, the initial modulus of the samples increases drastically. The nature of the curve in the initial region changes from that of pure rubber to that of pure thermoplastic as HDPE loading increases. This implies that the initial modulus is controlled by the HDPE content in the mix.

The method of differential swelling [14, 15] has been used to see, if any, the interaction between HDPE and NR. Fig. 11 is obtained by using the equation

$$\frac{V_{ro}}{V_{rf}} = 1 - M_0 \frac{\phi_{HDPE}}{1 - \phi_{HDPE}}$$

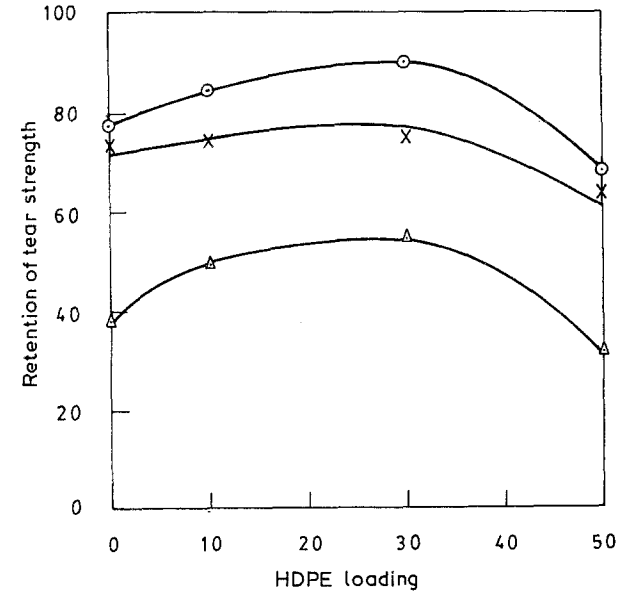

Figure 12 Plot of retention of tear strength against HDPE loading (⊙ 12 h aged, × 24 h aged, △ 48 h aged).

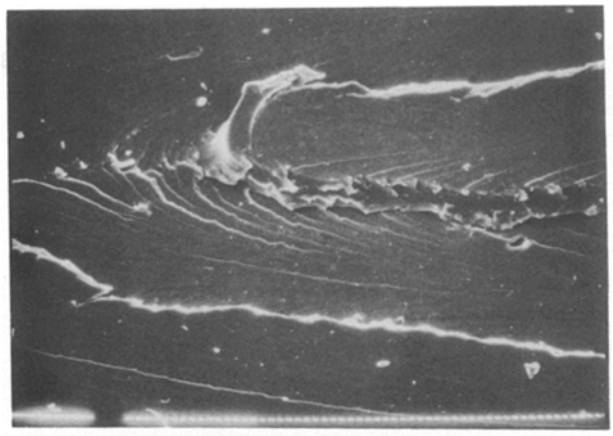

Figure 13 Test fractograph of unfilled NR vulcanizate after 1 day ageing at 100° C (100 ×).

where V_{ro} is the volume fraction of NR in the swollen state when no HDPE present, V_{rf} the volume fraction of NR phase in the swollen filled vulcanizate, ϕ_{HDPE} the volume fraction of the HDPE phase in the unswollen vulcanizate and M a parameter depending on the V_{ro} and the swelling restriction.

The negative slope of the curve implies that there is an interaction between the two polymer phases. However, dynamic mechanical analysis has shown that the two polymers are incompatible. Hence it may be concluded that this apparent interaction is due to the structure and shape of the HDPE domains present in the rubber matrix. This is also supported by the presence of fibre like formation and different shaped domains of HDPE seen on the fracture surfaces of the filled vulcanizates.

After ageing for different periods at 100° C, the tear strength of the vulcanizates decreases. From Fig. 12, it can be seen that as the plastic content in the matrix increases the retention of tear strength first increases and then decreases. Thus mix 4 exhibits the lowest tear strength retention after 48 h of ageing. An insight into the mechanism of failure can be obtained from the SEM studies of the fracture surfaces of the aged samples.

Fig. 13, the SEM fractograph of mix 1 after ageing for 24 h shows a steady fracture path in addition to the parabolic tear line progressing in a stick–slip manner.

Figure 14 Tear fractograph of 30 phr HDPE filled NR vulcanizate aged for 1 day at 100° C (100 ×).

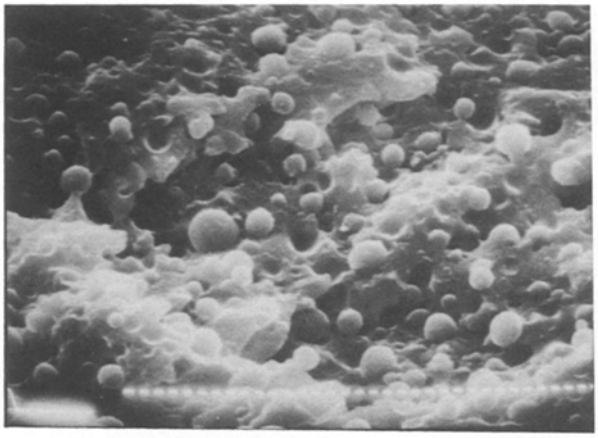

Figure 15 Magnified view of the tear fractograph for 30 phr HDPE filled NR vulcanizate after ageing for 1 day at 100° C (1600 ×).

Several secondary tear lines can be seen branching off from the main parabolic tear line. These changes in the fracture surface of the aged sample compared with that of unaged samples reflects the reduction in the tear strength.

Figs 14 and 15 are the SEM fractographs of mix 3. At the lower magnification (Fig. 14), no significant feature is visible. However, at a high magnification (Fig. 15), spherical domains of polyethylene can be clearly seen. A large number of rounded cavities also can be seen on the fracture surfaces. The smooth round particles of HDPE denote poor adhesion between NR and HDPE. They are dislodged from the cavities because the rubber matrix became brittle by the ageing. Clearly, there is a qualitative change in fracture surface of the mix 3 *vis a vis* Fig. 5 of the unaged sample, where no such cavities and globules of PE are evident, Fig. 16 of mix 4 shows a similar trend. In this case, in addition to spherical domains of PE, elongated lumps of PE and large holes also can be seen on the fracture surface. No signs of adhesion between PE and NR are in evidence. It can be concluded that as a result of heat ageing, the strength of the NR matrix drops and the HDPE in the matrix act as stress raisers and provided an easy path for the tear to follow. Due to the ageing, the rubber matrix underwent brittle failure [16].

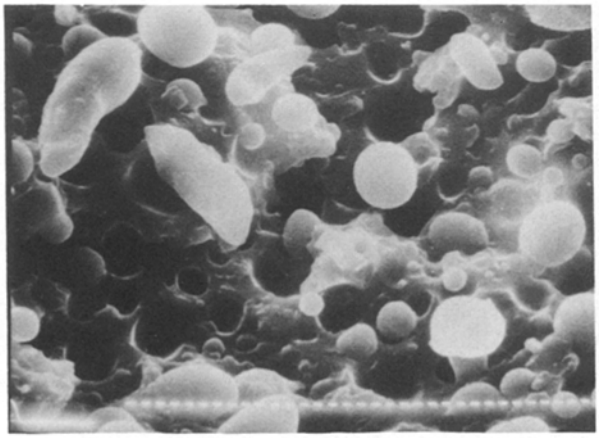

Figure 16 Tear fractograph of 50 phr HDPE filled NR vulcanizate after ageing at 100° C for one day (1600 ×).

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