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Cut-growth behaviour of EPDM–bromobutyl rubber blends under repeated stressing

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Cut-growth behaviour of ethylene–propylene–diene rubber (EPDM), bromobutyl rubber (BIIR) and their blends under dynamic loading has been studied over a range of temperatures. The crack-growth resistance increases with the increase of BIIR content in the gum and filled blends. The 30:70 EPDM:BIIR blend, however, gives the best fatigue resistance because of morphology and strain energy density factors. Failure surfaces have been examined both by photography and electron microscopic techniques. The crack always propagates from the precut. The rate of crack propagation is faster for EPDM gum samples. The blends show fracture features intermediate between those of fractured BIIR and EPDM rubbers. Straight flow lines, cracks and fatigue striations (10 to 15 μm distance between two consecutive striations) are observed for gum samples. The flow lines are increased and the cracks are reduced for filled samples. The fractography of the crack front at the precut and that away from it are similar. At a higher temperature (100° C), there is a reduction of fatigue life for the blends and pure rubbers. Many cracks are observed on the fracture surface of gum and filled samples.

1. Introduction

EPDM–bromobutyl rubber blends are used for high-temperature conveyor belt application, mainly for carrying hot coal. It has been observed that coal damages the surface of the cover compound and cracks propagate from these flaws.

Although the fatigue behaviour of single rubbers has been investigated in some detail [1], relatively little attention has been paid to rubber blends. A notable review was published by Beatty [2]. Growth of a crack in rubber under repeated stressing has been reported by Thomas [3], Gent *et al.* [4] and Bhowmick *et al.* [5] on various rubbers, but the fundamental mechanism is still not clear concerning the various processes involved in fatigue. Recently an investigation of the mechanism of growth of a crack under tensile loading has been reported [6]. The present study is an extension of that programme.

We have previously reported various properties of a heat-resistant conveyor belt cover compound based on EPDM–bromobutyl rubber blends [7, 8]. In this paper, our observations on crack-growth behaviour in EPDM, BIIR and their blends over a range of compositions and temperatures are highlighted. Both filled and unfilled rubbers at various precuts have been used. In addition, the nature of crack propagation has been investigated with the help of photography and scanning electron microscopy.

2. Experimental details

2.1. Raw materials

The elastomers used were EPDM (Royalene 521, Mooney viscosity ML_4 at 100°C 45, supplied by Uniroyal Chemical, Naugatuck, USA) and bromobutyl rubber (BIIR) (Polysar Bromobutyl X2, Mooney viscosity ML_4 at 100° C 37.5, supplied by Andrew Yule and Co. (P) Ltd, Kalyani, Nadia). Carbon black (N330, supplied by Phillips Carbon Black Limited, Durgapur, Burdwan) was used as filler.

2.2. Mixing procedure

Mixing was done in a laboratory-size two-roll mixing mill. At first the initial high torque value (56 Nm at (62 $\pm$ 2)° C and 25 r.p.m. rotor speed) of EPDM was brought down to that of BIIR (25 Nm under the same conditions). The low-viscosity EPDM was used in the final mix. For the preparation of the unfilled blends, all the ingredients were mixed in EPDM phase followed by the addition of the required amount of BIIR. The mixing was continued for homogenization of the blends. All the ingredients except the filler were mixed in EPDM phase in the case of filled blends. Up to 50% filler was incorporated in each phase. The final mix was done by mixing together EPDM-black-ingredients mix and BIIR-black mix. The formulations of the mixes are given in Table I.

2.3. Sample preparation and determination of cut growth during flexing

Cut growth during flexing was determined in De Mattia Flexing Machine according to ASTM D430-73 method. The machine operated at a constant speed under load at 300 $\pm$ 1 flexing c.p.m. The samples were prepared in an electrically heated hydraulic press at 150° C. Initially a vertical precut was given at exactly the middle point and along the length of the groove. Cut length was varied for both unfilled and filled rubbers. Generally, 0.5 and 1.0 mm cuts were used for

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TABLE I Mix formulations (p.h.r.)

Mix no.	EI	EB73	EB55	EB37	BI	EOC	EBC73	EBC55	EBC37	BOC
EPDM (Royalene 521)*	100	70	50	30	–	100	70	50	30	–
BIIR (Polysar Bromobutyl X2)†	–	30	50	70	100	–	30	50	70	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1	1
Antioxidant 2246‡	1	1	1	1	1	1	1	1	1	1
Paraffin wax	–	–	–	–	–	2	2	2	2	2
Carbon black (N330)§	–	–	–	–	–	50	50	50	50	50
Paraffinic oil	–	–	–	–	–	10	10	10	10	10
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MBTS¶	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD¶	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Optimum cure time at 150° C (min)	38	17.5	28	12.5	15	18	18	30	20.5	12

*Supplied by Uniroyal Chemical, Naugatuck, USA.
†Supplied by Andrew Yule and Co. (P) Ltd, Kalyani, Nadia, India.
‡Supplied by Bayer (I) Ltd, Calcutta, India.
§Supplied by Phillips Carbon Black Limited, Durgapur, India.
¶Supplied by IEL Limited, Rishra, India.

unfilled rubber and 1.0 and 3.15 mm cuts were used for filled rubber. Cut growth was determined at four different temperatures (25, 50, 70 and 100° C).

2.4. Photography and microscopy studies

In order to understand the cut-growth mechanism during flexing, the fracture surfaces at room temperature (25° C) and at 100° C were studied using a scanning electron microscope. The samples were sputter coated with gold and were examined within 48 h of fracture.

For comparison of the nature of cut growth of different blends at different flexing cycles, photographs of different samples were taken (Rolleiflex camera). Both gum and filled blends were studied at room temperature (25° C) and at 100° C.

3. Results and discussion

3.1. Crack growth in gum rubber

Increment in cut length plotted against number of flexing cycles is shown in Fig. 1 for several rubber and rubber blends. It has been observed that with increase of bromobutyl content in the blends, the rate of crack growth decreases. This is valid for samples having either a small or a large cut length. When the precut length is larger, the crack-growth rate is little faster. The increased crack-growth resistance of 30:70 EPDM : BIIR blend may be explained on the basis of morphological consideration and strain energy density. 30/70 EPDM/BIIR blend forms an interpenetrating network morphology [9] and has the highest strain energy density ($2.0 \times 10^7\,J\,m^3$). It is interesting to see that the growth step, Δl, is a function of flexing cycle, and at higher flexing cycles the growth rate is higher due to increased energy input. A linear correlation exists at the initial stage between these two parameters for gum samples. It must be mentioned here that for both natural rubber and styrene butadiene rubber, such relations were established [1].

Fig. 2 shows the cut-growth behaviour of various

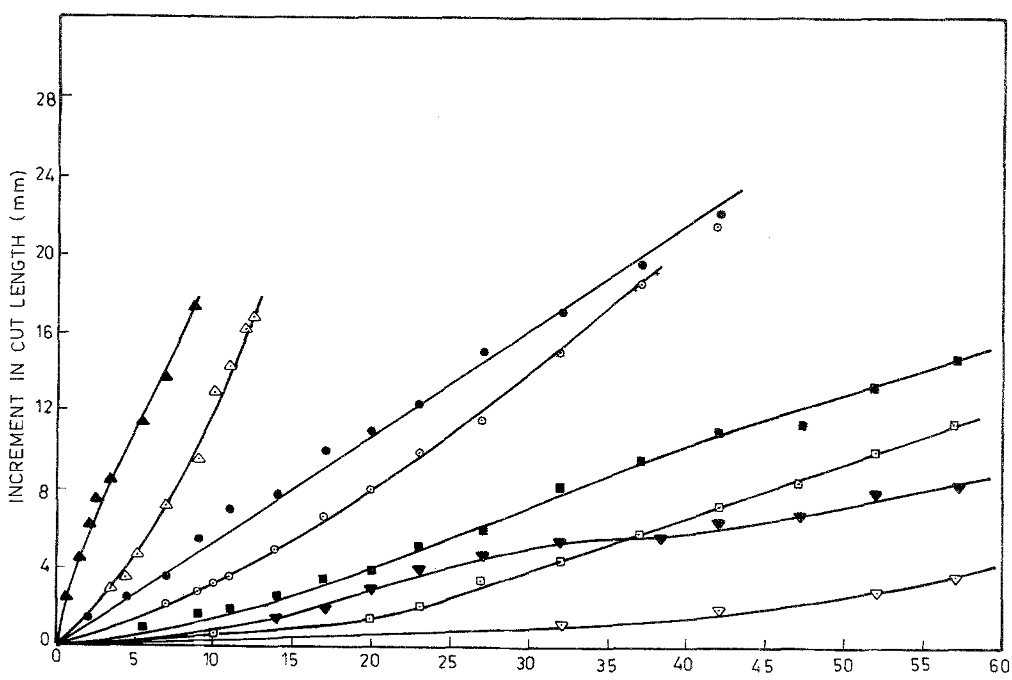

Figure 1 Plot of increment in cut length against flexing cycles of gum blend vulcanizates at room temperature (25° C). EPDM : BIIR and precut (mm): (△) 70 : 30, 0.50; (○) 50 : 50, 0.50; (▽) 30 : 70, 0.50; (□) 0 : 100, 0.50; (▲) 70 : 30, 1.0; (●) 50 : 50, 1.0; (▼) 30 : 70, 1.0; (■) 0 : 100, 1.0.

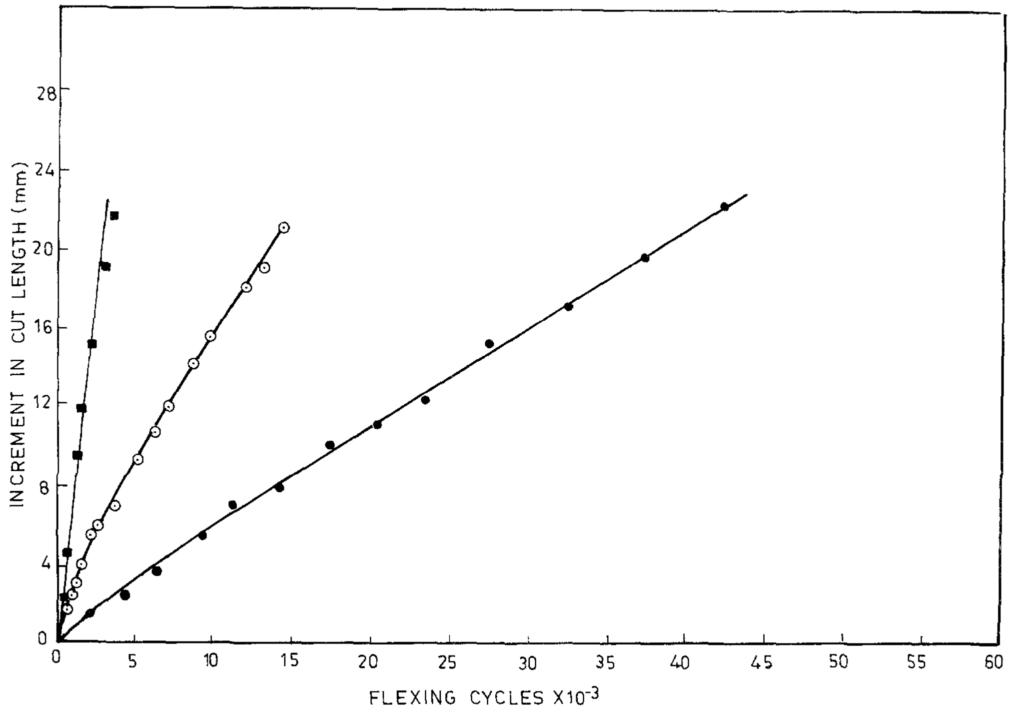

Figure 2 Plot of increment in cut length against flexing cycles of 50/50 EPDM/BIIR blend at different temperatures and at a precut of 1.0 mm. (●) 25° C, (○) 50° C, (■) 70° C.

rubbers over a range of temperatures. For simplicity, only 50/50 EPDM/BIIR blend with a precut of 1 mm is shown. With the increase in testing temperature, the crack-growth rate becomes faster, as observed from the slope of Δl against flexing cycle curves (Fig. 2); this is true for all rubbers and their blends (Fig. 3). This is caused by a reduction of viscoelastic effect with temperature and the crack has little resistance to propagation.

3.2. Crack growth in filled rubber

The addition of carbon black increases the resistance to cut growth, especially for EPDM rubber. As shown in Fig. 4, 70/30 to EPDM/BIIR blend shows the maximum resistance to cut growth. Increase of temperature has the same effect as reported above (Fig. 5). The increment in cut length, however, varies exponentially with flexing cycle for all the blends. This may be due to a complicated fracture mechanism in the case of carbon black-filled samples.

3.3. Photographic observation of the growth of a crack

The growth of a crack in various samples was observed at regular time intervals using a photographic technique. The gum EPDM samples tear more easily than gum BIIR samples. At 600 cycles the EPDM sample fails, while BIIR sample shows a cut growth of 12% from the original value. The blends show intermediate behaviour. The higher the content of BIIR, the higher is the resistance to cut growth (Fig. 6). With the addition of filler, the cut-growth resistance

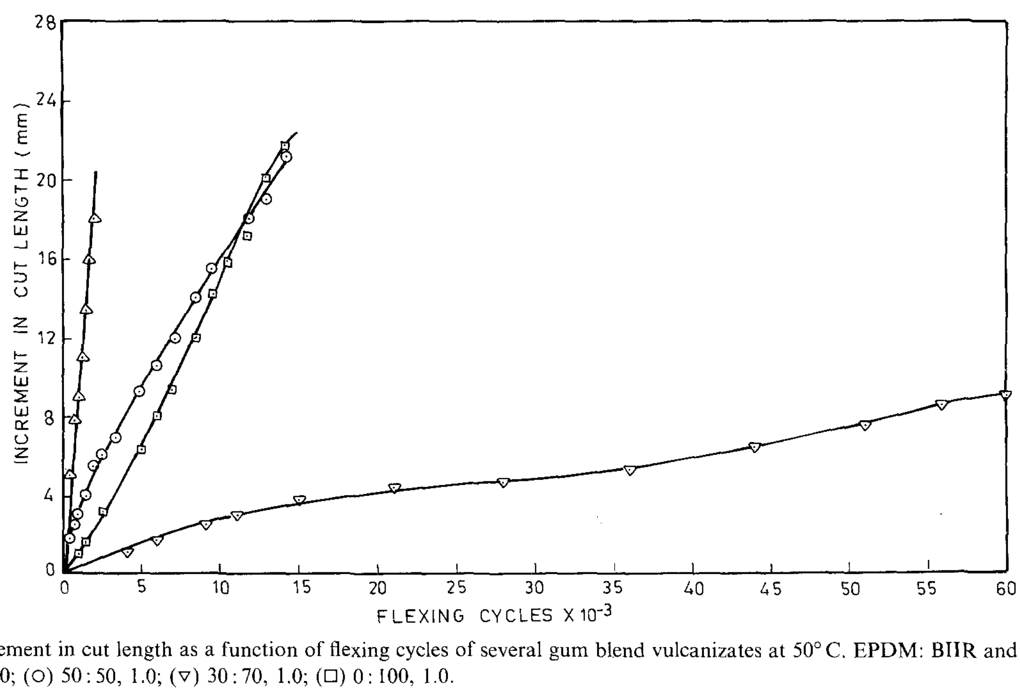

Figure 3 Increment in cut length as a function of flexing cycles of several gum blend vulcanizates at 50° C. EPDM: BIIR and precut (mm): (△) 70:30, 1.0; (○) 50:50, 1.0; (▽) 30:70, 1.0; (□) 0:100, 1.0.

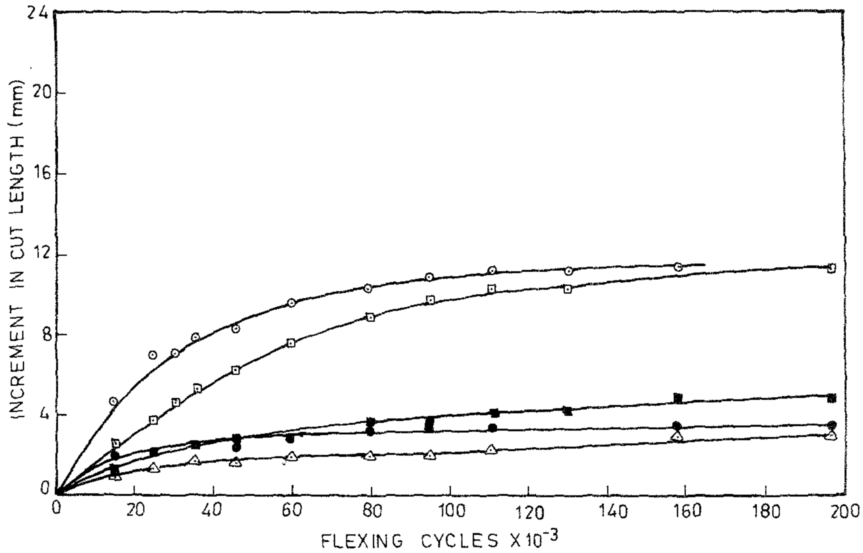

Figure 4 Plot of increment in cut length against flexing cycles of several filled blend vulcanizates at room temperature (25° C). EPDM: BIIR and precut (mm): (○) 100:0, 3.15; (△) 70:30, 3.15; (■) 50:50, 3.15; (●) 30:70, 3.15; (□) 0:100, 3.15.

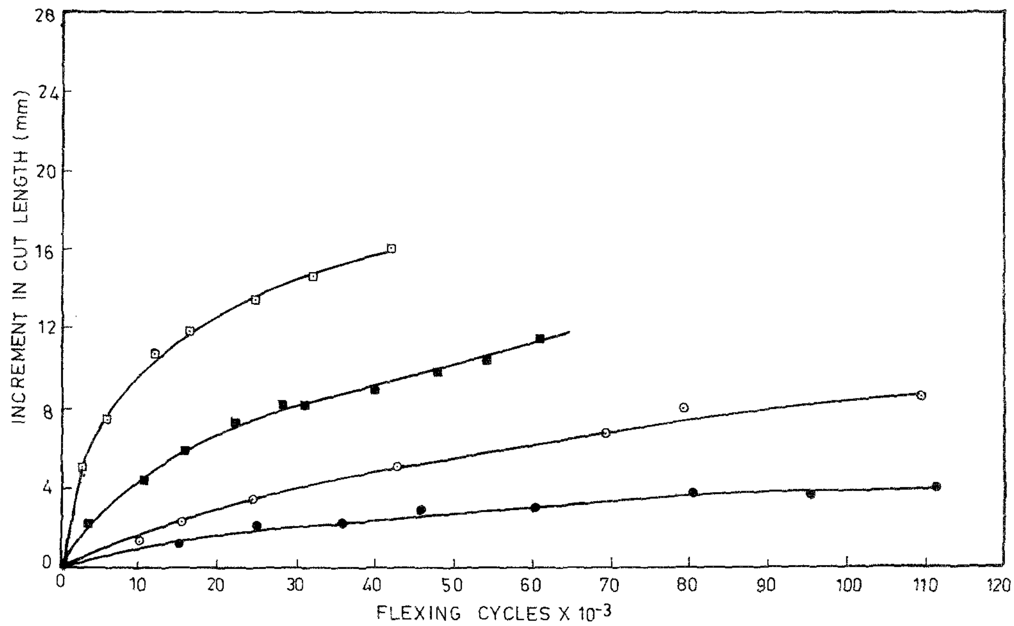

Figure 5 Plot of increment in cut length as a function of flexing cycles of 50/50 EPDM/BIIR filled gum vulcanizate at different temperatures and at 3.15 mm precut. (●) 25° C, (○) 50° C, (■) 70° C, (□) 100° C.

increases and the filled EPDM and BIIR samples show similar behaviour. Fig. 7 demonstrates this for pure rubbers and blends. Here also the blends show maximum resistance. This may be because of filler distribution. It is expected that filler will distribute more in the EPDM phase because of enhanced rubber–filler interaction [9]. At flexing higher temperatures, the cut-growth rate, in general, increases.

3.4. SEM studies of crack growth around a flaw

3.4.1. Gum compounds

It has been demonstrated that the fracture in fatigue starts from the given cut, whether small or large. In order to understand the mechanism of crack growth and surface morphology around the crack and at the crack front, SEM studies have been undertaken.

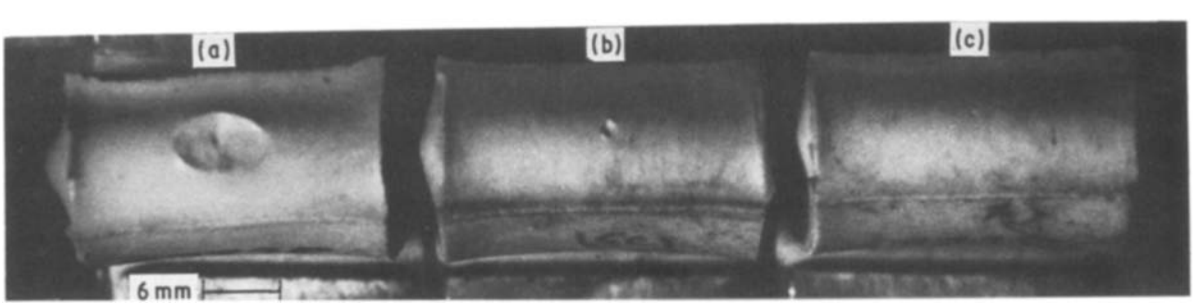

Figure 6 Photograph of the nature of cut growth of gum blend vulcanizates at 25° C and at 0.6 kilocycles, precut = 0.50 mm. (a) 70/30 EPDM/BIIR blend, (b) 50/50 EPDM/BIIR blend, (c) 30/70 EPDM/BIIR blend.

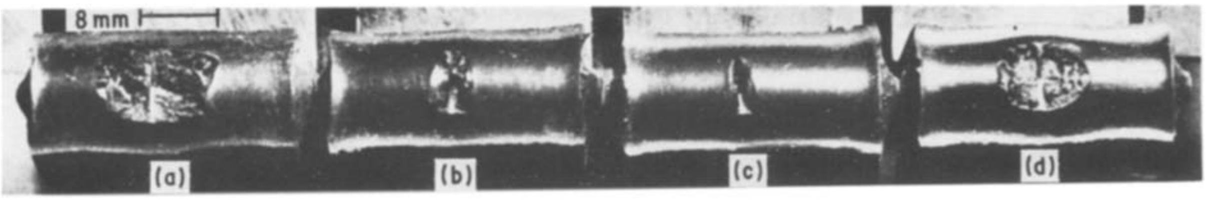

Figure 7 Photograph of the nature of cut growth of filled blend vulcanizates at 25° C and at 100 kilocycles, precut = 3.15 mm. (a) 100/0 EPDM/BIIR blend, (b) 70/30 EPDM/BIIR blend, (c) 30/70 EPDM/BIIR blend, (d) 0/100 EPDM/BIIR blend.

Fig. 8 shows the fatigue fractured surface of unfilled EPDM rubber. The flow lines and cracks radiate outwards from the flaw. The flow lines are at an angle of 60 to 80° to the cut. In between the flow lines, fatigue striations are observed. Fig. 9 shows such striations at higher magnification. The distance between two successive striations is ~ 10 to 15 μm. The surface that is further away from the crack shows shorter flow lines; but other features are almost the same. It must be noted here that the surface is not sufficiently deformed to form dimples. Dimples and striations have been observed in the fatigue fracture surface of natural rubbers [10]. However, in the case of bromobutyl rubber, such dimples are formed. Fig. 10 shows the general fractured surface and Fig. 11 shows the dimples. The flow lines are much shorter here and deformed. All the flow lines originate from the given cut. The formation of dimples may be assumed to be the result of deformed flow lines.

The samples containing EPDM and BIIR show intermediate features. There are shear flows and cracks on the surface (Fig. 12). It is also interesting to note that the flow lines are observable on the tensile fractured surface of samples containing a cut (Fig. 13). In fatigue, because of repeated stressing at lower critical forces, the number of lines appearing on the fractured surface is greater. A few samples were taken at intermediate cycles (before complete failure of the test specimen) to observe the morphology of the crack front. Fig. 14 shows the morphology of the crack front for blend vulcanizate at 18 × 10^3 cycles (failure life, 50 k.c.s.). The features are almost the same. The distance between striations is ~ 10 to 15 μm; the flow lines and crack lines become more random than those near the cut.

In our earlier paper [6], a relationship was established between the distance between crack lines/flow lines and tensile strength of vulcanizates. However, in the

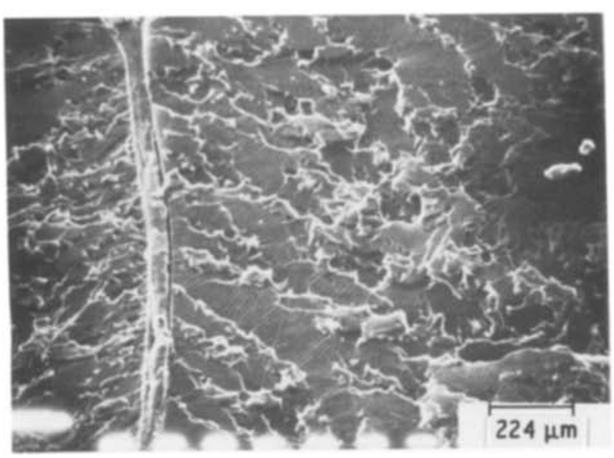

Figure 8 Scanning electron micrograph of the fatigue fracture surface of EPDM gum vulcanizate around the precut (0.50 mm). Testing temperature 25° C.

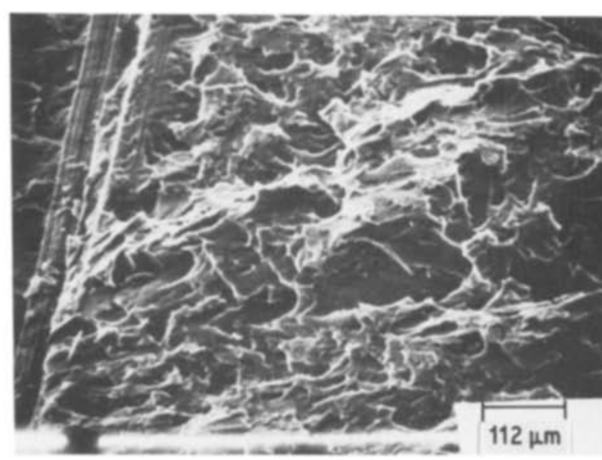

Figure 10 Scanning electron micrograph of the flexed fracture surface of bromobutyl gum vulcanizate around the precut (0.50 mm) at a testing temperature of 25° C.

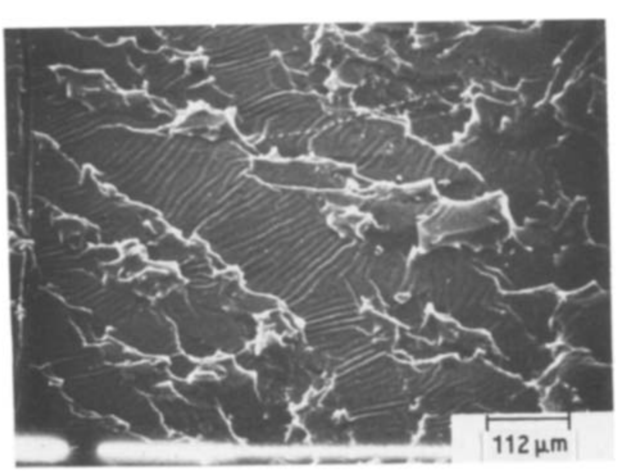

Figure 9 Magnified version of the right-hand portion of the precut in Fig. 8.

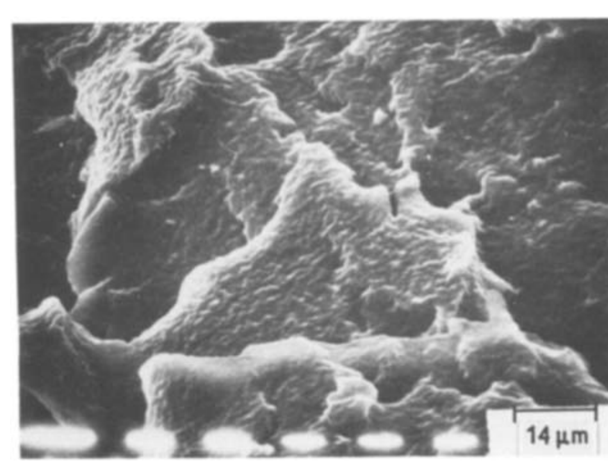

Figure 11 Dimples on the fracture surface at higher magnification.

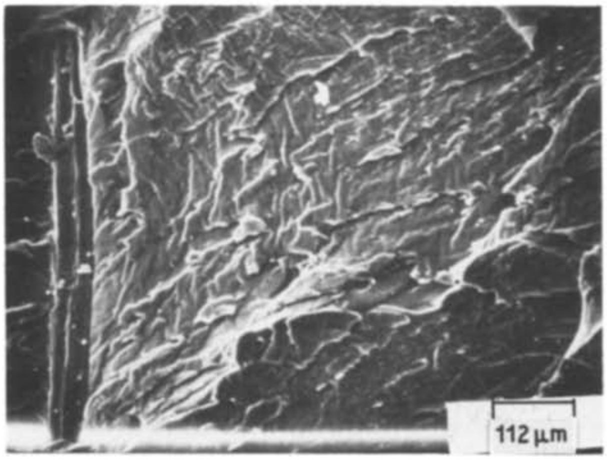

Figure 12 Scanning electron micrograph of the fracture surface of a 50/50 EPDM/BIIR gum blend vulcanizate around the precut (0.50 mm) at 25° C.

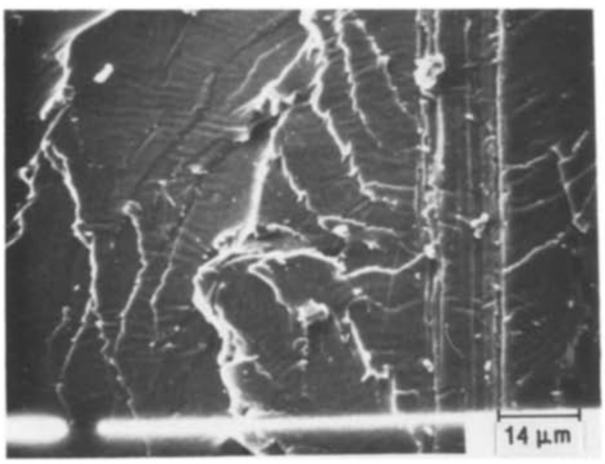

Figure 13 Scanning electron micrograph of the tensile fractured surface of 50/50 EPDM/BIIR gum blend vulcanizate around the precut (1.0 mm).

present study we are not able to put forward such a correlation. All the above samples were tested at room temperature.

At testing higher temperatures (say 100° C), the general features remain unchanged, the crack lines are more numerous and deformation is slight giving plate-like features (Fig. 15). The strength properties are also low at higher temperatures.

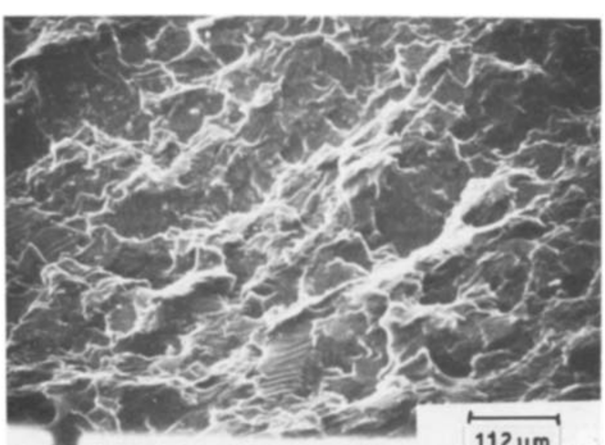

Figure 14 Scanning electron micrograph of the fracture surface fatigued up to 18×10^3 cycles of a 50/50 EPDM/BIIR gum blend vulcanizate (initial precut 0.50 mm and temperature of testing 25° C).

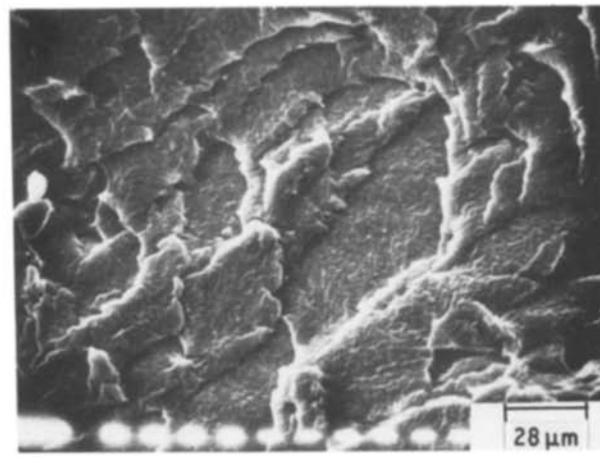

Figure 15 Scanning electron micrograph of the fracture surface of a 50/50 EPDM/BIIR gum blend vulcanizate (initial precut of 0.50 mm) at a testing temperature of 100° C.

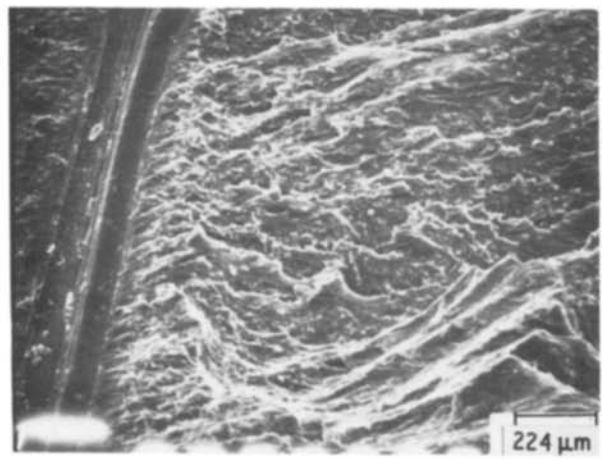

Figure 16 Scanning electron micrograph of the flex-fractured surface of filled EPDM vulcanizate around the precut (1.0 mm) at 25° C testing temperature.

3.4.2. Filled vulcanizates

Fracture surfaces of filled vulcanizates are shown in Figs 16 to 19. The number of flow lines is increased to a large extent. The flow lines in EPDM propagate at ~ 90° to the given cut (Fig. 16), whereas those in BIIR fractured surface seem to be almost parallel to the cut (Fig. 18). The blends again show intermediate behaviour (Fig. 19). Here, the dimple surfaces are observed without fatigue striations. Rubber balling

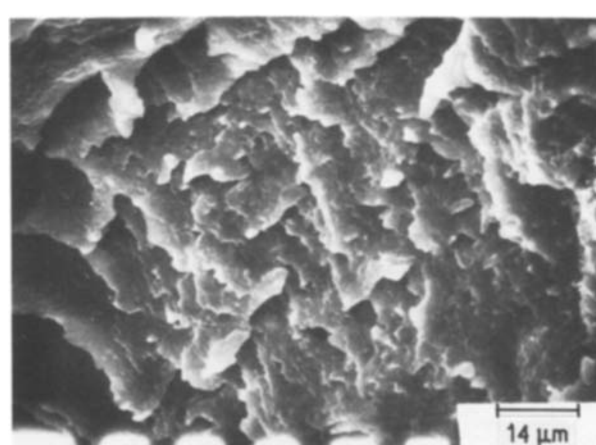

Figure 17 Flow of the filled EPDM matrix at higher magnification (initial precut 3.15 mm, testing temperature 25° C).

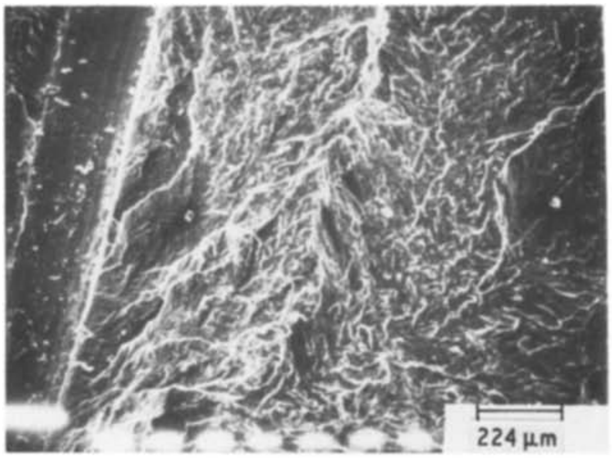

Figure 18 Scanning electron micrograph of the flex-fractured surface of filled bromobutyl vulcanizate around the precut (1.0 mm) at 25° C.

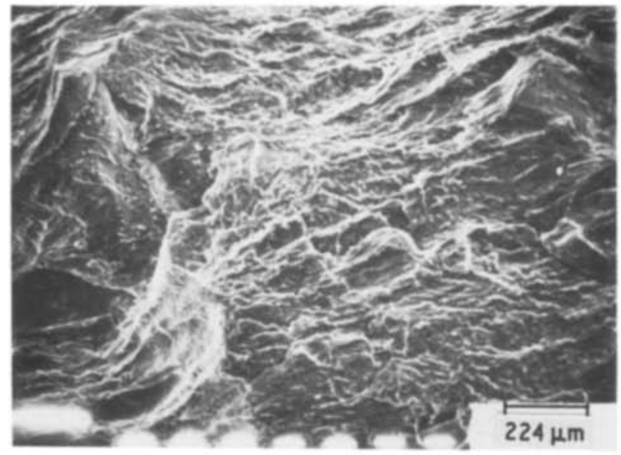

Figure 19 Scanning electron micrograph of the side of the precut (1.0 mm) of the flex-fractured surface of a filled 50/50 EPDM/BIIR vulcanizate at 25° C.

observed on NR fractured surfaces [11] are absent here and the mechanism seems to be very similar to that in gum vulcanizate. Because of the high strain energy density and a higher critical fracture energy compared to gum compounds, the fatigue strength is higher. At higher testing temperatures long crack lines and flow lines are observed.

4. Conclusion

Studies on cut-growth behaviour of EPDM and bromobutyl rubber under repeated stressing have been reported. The crack-growth resistance increases with the incorporation of bromobutyl rubber in the gum and filled rubber blends. 30:70 EPDM:BIIR shows the highest fatigue properties. Photographic observation of the increment in cut length also supports the result.

SEM studies demonstrate that the failure starts from the precut and that crack propagation is faster in EPDM gum rubber with straight flow lines, cracks and fatigue striations than that in BIIR rubber. The blends show an intermediate fracture surface. The distance between two consecutive striations is about 10 to 15 μm. On addition of the filler, the strength of EPDM rubber increases considerably, and a large number of flow lines and few cracks are observed. The crack front at the intermediate cycle is found to have the same fracture surface morphology as that near the given precut. Dimple formation is the result of deformation of flow lines. On increasing the testing temperature, fatigue strength is reduced and many cracks and plate-like features are observed on the surface.

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