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Scanning electron microscopy studies in abrasion of NR/BR blends under different test conditions

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The abrasion of NR/BR blend vulcanizates has been studied in three different testing machines and the abraded surfaces have been observed in a scanning electron microscope. The ranking of the unfilled blends obtained from Akron abrader is different from that obtained from Du Pont and DIN abraders, while in the case of the black-filled vulcanizates the same ranking can be obtained from all the three machines. Tensile and fatigue properties are believed to play major roles in determining abrasion loss in the Akron abrader, while the effect of friction is more pronounced in the other two machines. The slip angle of 20° and the deformation of the surface layer of rubber during abrasion accounts for the difference in the direction of the abrasion pattern observed in the case of Akron abrader. The carbon black-reinforced vulcanizates give rise to a fine abrasion pattern. Because of the continuous change in the direction of abrasion in DIN abrader, a well-defined pattern was not observed. The very low abrasion loss of 50/50 blend vulcanizates in Du Pont abrader is also evident from the nature of the abraded surface.

1. Introduction

Abrasion is an important factor leading to the failure of a number of rubber products including tyres. It is, perhaps, the least understood among the various types of fracture of rubber. A number of studies has been made by several authors in an attempt to understand the abrasion process in detail. Schallamach [1] was the first to study in detail the abrasion pattern on abraded rubber surfaces, which is believed to play a significant role in the abrasion process. Later studies by the same author [2–4] have given more information on the phenomenon. But the exact mechanism of formation of the abrasion pattern and the extent of its influence on abrasive wear are not clearly known. Reznikovskii and Brodskii [5–7] have described the different types of wear occurring during abrasion of elastic materials and attempted to find out the influence of non-mechanical factors on abrasion as well as the relation between mechanical properties of rubber and its abrasion resistance. A recent study by Southern and Thomas [8] describes the application of fracture mechanics to explain abrasion of rubber. According to these authors, the formation of the abrasion pattern is followed by crack growth which plays an important role in the abrasion process. Laboratory tests for abrasion resistance are used mainly to rank materials. Usually these tests are used to control manufacturing uniformity. Over the years a number of tests have been developed to test the abrasion resistance of rubbers [9]. None of these tests can predict precisely the behaviour of rubbers under actual service conditions and even the ranking obtained from one test method may not hold good in another. This shows the complex nature of abrasion of rubber and that the mechanism of abrasion under different test conditions is quite different.

The superior abrasion resistance of polybutadiene rubber (BR) is well known [10]. Blends of BR with natural rubber (NR), which combine

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TABLE I Formulations of the mixes

	Mix			
	A	B	C	D
Natural rubber*	75	75	50	50
Polybutadiene rubber†	25	25	50	50
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
HAF black (N 330)	–	50	–	50
Naphthenic oil	–	5	–	5
CBS‡	3.5	3.5	3.5	3.5
Sulphur	0.5	0.5	0.5	0.5

*Crumb rubber, ISNR-5, obtained from the Rubber Research Institute of India, Kottayam.
†Nipol BR 1220.
‡*N*-cyclohexyl benzothiazyl sulphenamide (Accicure HBS), obtained from the Alkali and Chemical Corporation of India Ltd, Rishra.

the superior abrasion resistance of the former with the excellent processing and physical properties of the latter, are now popularly used in areas such as tyre treads and conveyor belts. However, studies on the mechanism of abrasion of these blends, especially when tested under different conditions, have not been made. Recently, Bhowmick *et al.* [11] have studied the abraded surfaces of BR and styrene–butadiene rubber (SBR) using the scanning electron microscope (SEM) with a view to study the mechanism of wear of these rubbers. Of late, SEM has been used as a tool to study the fracture mechanism of rubber [12–17].

In the present work, we have made an attempt to study the abrasion of NR/BR blends, in different abrasion test machines, using SEM. The parameters studied include: (a) effect of test conditions, (b) effect of blend ratio, and (c) effect of reinforcing carbon black. The test conditions were varied by using three different testing machines; a Croydon–Akron abrader, a DIN abrader and a Du Pont abrader.

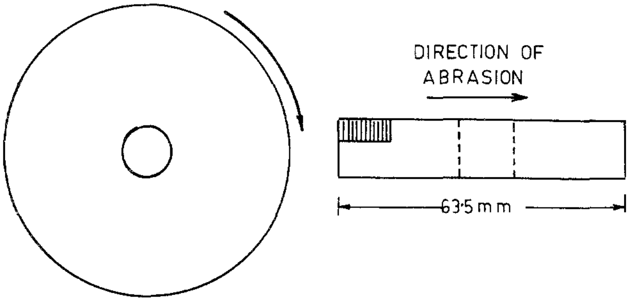
2. Experimental procedure

The formulations of the mixes are given in Table I. As the rubber industry uses efficient vulcanizing (EV) systems in many instances, we have chosen a typical EV system for this study. The mixes were prepared in a two-roll laboratory mixing mill. The blending of the rubbers were done at the same level of viscosity and subsequently the other ingredients were added to the blend. The optimum cure times of the mixes were determined using a Monsanto Rheometer, R-100. Vulcanization was carried out at 150° C, in a hydraulic press having electrically heated platens. For the vulcanization of test specimens for abrasion and compression set tests, an extra cure time of 5 min, and for that of the heat build-up test specimens an extra cure time of 10 min, were given to ensure optimum level of cure in the inner sections of the specimens. The other test specimens were vulcanized up to the optimum cure times. The physical properties of the vulcanizates were determined following ASTM test methods [18].

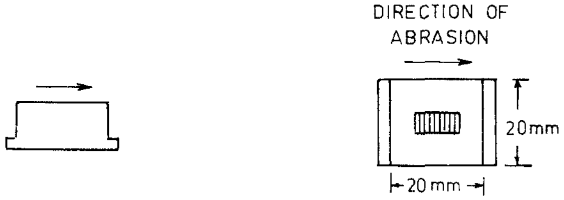
The abrasion tests were carried out using three different test machines: (1) the Croydon–Akron abrasion tester, (2) the Du Pont abrader, and (3) the DIN abrader. The details of test conditions are summarized in Table II. In the Akron abrader the contour of the circular test specimen, mounted on a motor-driven spindle, is brought into contact

TABLE II Test conditions in different abraders

	Akron	DIN	Du Pont
1 Nature of abrasive action	Discontinuous	Discontinuous	Continuous
2 Temperature of test (° C)	30	30	30
3 Test specimen	Circular in shape, 1.37 cm thick, 6.35 cm o.d., with a central hole of 1.27 cm diameter	Cylindrical in shape with 1.6 cm diameter	2 cm square, 1 cm thick with provision for easy insertion of the specimen in the clamp
4 Abrasive	Aluminium oxide wheel, Grade A, 36-PS-V, 15 cm diameter, 2.54 cm thick	Emery cloth no. 60	Silicon carbide paper, grain size 325
5 Slip angle (deg)	20	0	0
6 Normal load (kg)	4.5	1.0	3.62
7 Speed of testing	Specimen rotates at 250 rpm; corresponding speed of the abrasive wheel 104 rpm	Drum rotates at 40 rpm	Abrasive disc rotates at 40 rpm
8 Sliding velocity (cm sec^{-1})	83	26	27



(a) AKRON



(b) DU PONT

(c) DIN

Figure 1 Shape and size of the test specimens and the direction of abrasion. The shaded area is the portion of the abraded surface removed for SEM observations.

with the periphery of an abrasive wheel, which is mounted on another spindle. Rotation of the specimen causes the abrasive wheel to rotate and the two are held together under a force of 4.5 kg. The axis of the specimen and the axis of the abrasive wheel are at an angle of 20°, which causes a rubbing action. The abrasion resistance of the specimen is calculated from its weight loss after a specified number of revolutions of the abrasive wheel. During the test, the abrasive wheel was cleaned manually with a brush and the specimen surface was continuously cleaned with a circular brush which was running in contact with the specimen. In the Du Pont machine two test pieces, each having 2 cm square surfaces, are simultaneously held against an abrasive paper disc rotating at a speed of 40 rpm. The two are held together under a load of 3.62 kg and the abrasive paper disc used was a silicon carbide type having a grain size of 325. The specimens were abraded for 10 min and the abrasion loss was calculated in terms of volume loss. During the test the abrasive surface was continuously cleaned with a compressed air jet. The DIN abrader differs from the other two in that the direction of abrasion changes continuously. This is achieved by rotating the specimen on its own axis while undergoing abrasion. The cylindrical specimen, 16 mm diameter, is brought into contact with the abrasive surface (emery cloth no. 60 mounted on a drum) under a normal load of 1.0 kg. The specimen is made to travel from one end of the drum to the other. The drum rotates at a speed of 40 rpm so that by the time the specimen reaches the other end of the drum, it traverses a distance of 40 m. The abrasion is calculated in volume loss per 40 m run.

The shape and size of the test specimens are shown in Fig. 1. The direction of abrasion is also marked in the case of the Akron and Du Pont abraders. In the case of the DIN abrader, the direction changes continuously. The specimens for SEM study were carefully cut from the abraded surfaces (after 500 revolutions in the case of Akron, after 10 min abrasion in Du Pont and after 1 run of 40 m in DIN) and were gold-shadowed in a sputter coater within 72 h of testing. The SEM observations were made using a Philips 500 model scanning electron microscope within a week of coating. The specimens were stored in a desiccator both before and after gold coating until the SEM

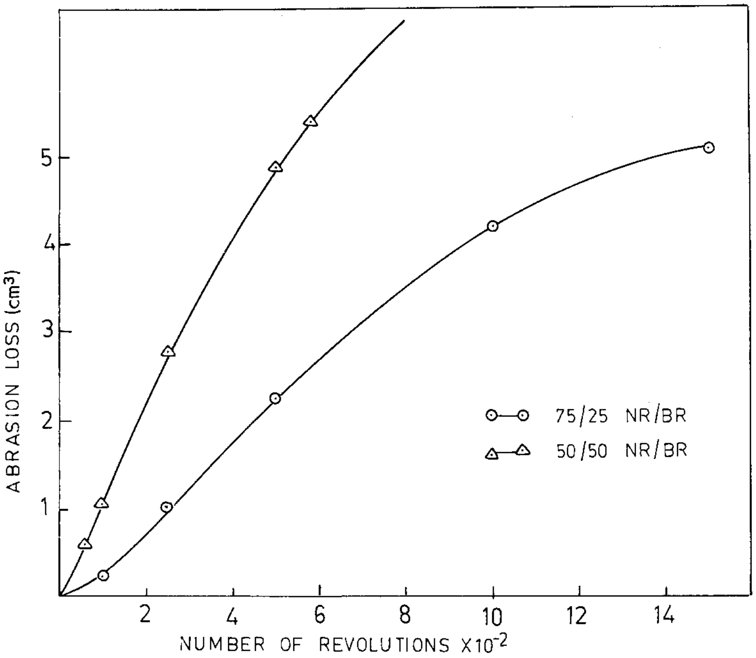


Figure 2 Abrasion loss of the unfilled vulcanizates as a function of the number of revolutions in the Akron abrader.

observations were made. From our preliminary experiments we found that storage of fracture surfaces of rubber up to a period of 1 week before gold coating and up to a period of 1 month after gold coating, does not alter the fracture surface topography as observed in SEM.

3. Results and discussion

3.1. Akron abrader

Figs. 2 and 3 show the plots of abrasion loss of the unfilled and filled vulcanizates against the number of revolutions in the Akron abrader. The unfilled 75/25 NR/BR blend shows a slow rate of abrasion

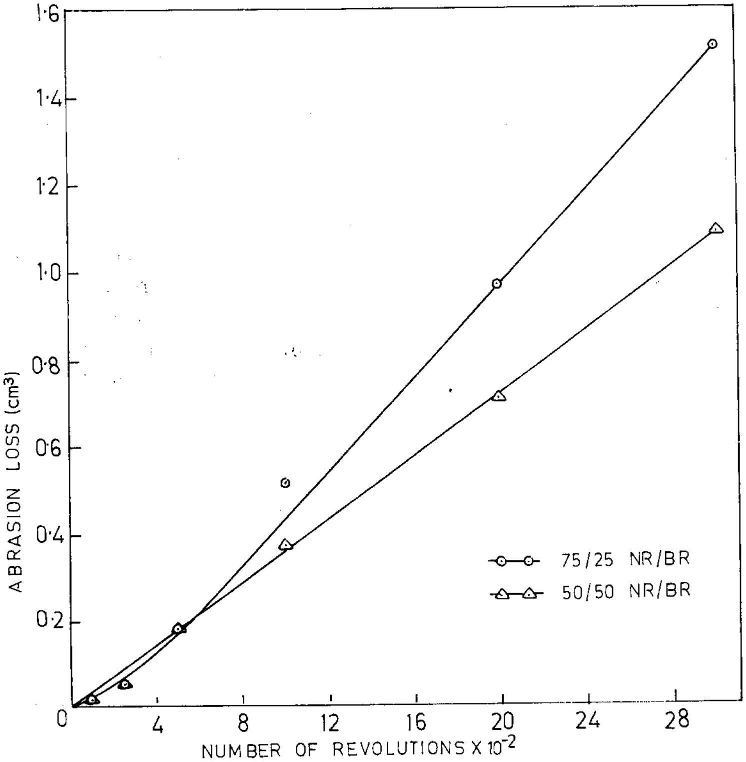


Figure 3 Abrasion loss of the filled vulcanizates as a function of the number of revolutions in the Akron abrader.

TABLE III Physical properties of the mixes

	Mix			
	A	B	C	D
Optimum cure time at 150° C (min)*	18	10	22	11
300% modulus (MPa)	1.5	9.7	1.6	10.1
Tensile strength (MPa)	14.1	22.1	6.2	19.4
Elongation at break (%)	690	510	550	440
Tear resistance (kN m^{-1})	19.7	53.7	18.0	43.1
Hardness, shore A	40	64	44	66
Resilience (%)	77	53	83	58
Heat build-up, ΔT (° C)	9.0	33.3	9.0	33.8
Permanent set (%)	0.6	2.8	0.8	2.1
Compression set (%)	18	28	13	22
Flexing resistance (kilocycles to failure)	> 130	22	10	30
Cut growth resistance (kilocycles)	19	10	1.5	3.0

*Obtained from Monsanto Rheometer, R-100.

initially which increases and again slows down as the abrasion is continued. However, the unfilled 50/50 NR/BR blend shows a different behaviour, exhibiting a rapid rate of abrasion right from the beginning. It may be assumed that abrasion in the Akron abrader is governed by the tensile and fatigue properties. From Table III it is seen that tensile strength, flexing resistance and crack-growth resistance are higher for the 75/25 NR/BR blend. Southern and Thomas [8] have shown that crack growth plays an important role in abrasion. The initial slow rate of abrasion observed in the case of the 75/25 NR/BR blend is believed to be caused by the delay in the formation of the abrasion pattern. Schallamach [1] found earlier that the rate of abrasion is slow until the abrasion pattern is well developed and from then onwards the rate increases rapidly. The decrease in the rate of abrasion as the abrasion is continued for a longer time, can be attributed to smearing, as reported by Schallamach [19]. Smearing is caused by the thermo-oxidative degradation of the surface layer of the rubber accelerated by high mechanical action and results in a sticky surface layer.

Figs. 4 and 5 are scanning electron micrographs (SEMs) of the abraded surfaces of the unfilled 75/25 NR/BR blend vulcanizates. Fig. 4 shows a coarse abrasion pattern. The ridges are large but are wide apart. It is interesting to note that, contrary to earlier reports, the ridges here are not perpendicular to the direction of abrasion. This is caused by two factors: the slip angle of 20° and the deformation of the sample in the contact area. In the case of soft unfilled vulcanizates, the deformation is so large that the direction of abrasion is believed to be turned almost by 90°. Thus the actual direction of abrasion in those samples is more or less across the circumference of the speci-

Figure 4 Coarse abrasion pattern (Akron abrader, mix A, × 21).

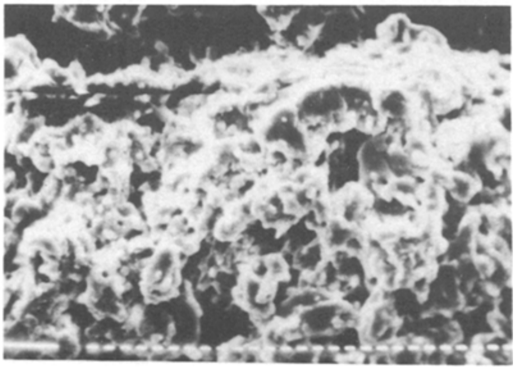


Figure 5 Magnified image of the ridge (Akron abrader, mix A, × 170).

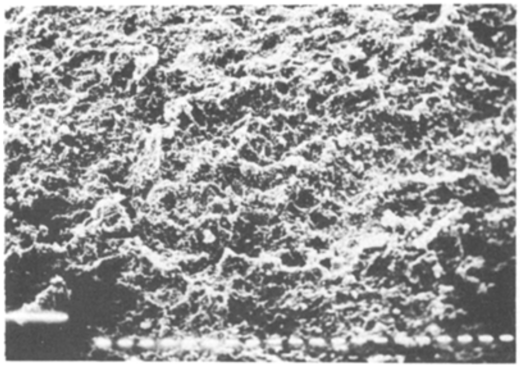


Figure 6 Ridge-free surface (Akron abrader, mix B, × 21).

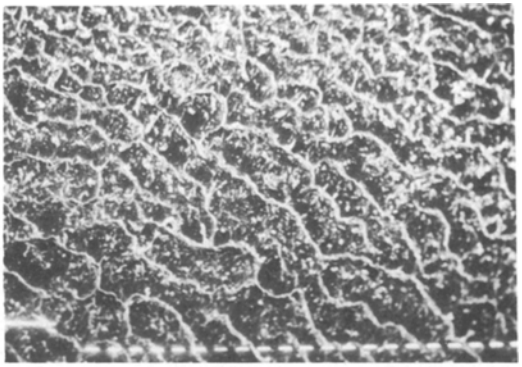


Figure 8 Pattern forming an angle with the direction of abrasion (Akron abrader, mix C, × 21).

men, giving rise to a pattern with ridges running along the circumference. Therefore, the contradiction regarding the direction of the abrasion pattern, as mentioned above, is only an apparent one. Fig. 5 is a magnified image of one of the ridges. The intense mechanical action on the ridges produces folding on the surface which is clearly seen in Fig. 5. When the proportion of BR is increased as in 50/50 NR/BR blend, the unfilled vulcanizate shows much higher abrasion loss as is evident from Fig. 1.

Figs. 6 and 7 are SEMs of the abraded surface of the unfilled 50/50 NR/BR blend vulcanizate. The abrasion pattern which was observed in the case of the 75/25 NR/BR blend is not prominent in this case. Although ridges are formed during abrasion, the strength of the matix is so poor that the ridges are torn off soon after their formation, thereby giving rise to an apparently ridge-free surface. From Fig. 7 it appears that material from the surface has been chipped off by the hard asperities on the abrasive surface.

Addition of reinforcing carbon black makes the matrix stronger, as is evident from Table III. Abrasion resistance is markedly improved. Fig. 3 shows that the 75/25 NR/BR blend shows slightly lower abrasion loss initially but as the abrasion is continued it registers a higher loss than the 50/50 NR/BR blend. The tensile strengths of these vulcanizates are more or less the same. However, the fatigue resistance of the filled 75/25 NR/BR blend is less than that of the 50/50 NR/BR blend. This might account for the slightly higher abrasion loss of the 75/25 NR/BR blend, when the abrasion is continued for a longer period.

Fig. 8 is an SEM of the abraded surface of the black-filled 75/25 NR/BR blend. Here the ridges are much closer and they are formed at an angle of about 45° to the circumferance of the specimen. The difference in the direction of the ridges in the unfilled and filled vulcanizates may be due to the difference in the extent of deformation that the specimen surface undergoes when it slides against the abrasive wheel.

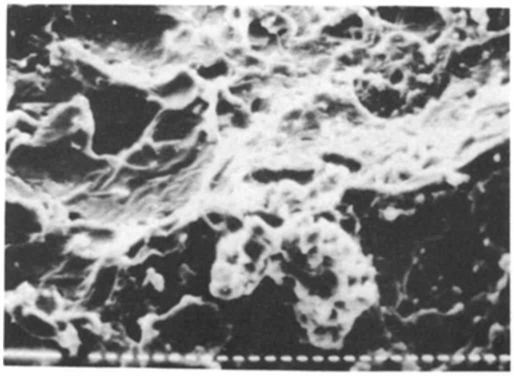


Figure 7 Material removal from the surface (Akron abrader, mix B, × 170).

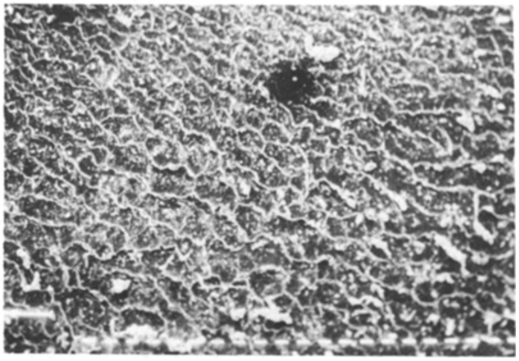


Figure 9 Finer abrasion pattern (Akron abrader, mix D, × 21).

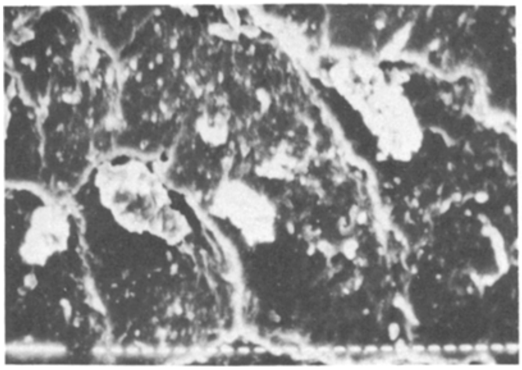


Figure 10 Material removal (Akron abrader, mix D, × 170).

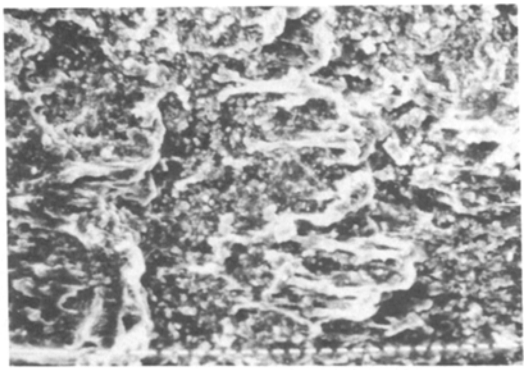


Figure 12 Deformed ridges (DIN abrader, mix A, × 170).

Figs. 9 and 10 are SEMs for the black-filled 50/50 NR/BR blend. Fig. 9 shows a pattern which is almost identical to that obtained in the case of the 75/25 NR/BR blend. Fig. 10 shows material being removed from the ridges.

3.2. DIN abrader

In the DIN abrader the results obtained are different from those from the Akron abrader. This is especially true in the case of the unfilled vulcanizates. The abrasion loss of the 50/50 NR/BR blend is almost a half that of the 75/25 NR/BR blend (Table IV). Under testing conditions in the DIN abrader, the coefficient of friction is believed to play a major role in determining abrasion loss. Grosch and Schallamach [20] have reported that the coefficient of friction of BR is lower than that of NR and that carbon black reduces it still further. The coefficient of friction of NR/BR blends may be assumed to decrease with increase in the proportion of BR. This might account for the lower abrasion loss of the 50/50 blend in the DIN abrader. The SEMs in the case of the unfilled 75/25 NR/BR blend vulcanizates (Figs. 11 and 12) are different from those obtained from the same vulcanizate tested in the Akron abrader. The ridges are not continuous and do not form a well-defined pattern of abrasion during the test. Deformation of the ridges is clearly seen in Fig. 12. The abrasion pattern is still less defined in the case of the unfilled 50/50 NR/BR blend, as shown in Figs. 13 and 14. Ridges are not observed at all. Here, material removal is found to occur in small lumps. Two such lumps are magnified and shown in Fig. 14. The structure of the lumps is very similar to that of the ridges found in samples obtained from the Akron abrader. As expected, the reinforcing black-filled vulcanizates show lower abrasion loss, the 50/50 NR/BR blend being better than the 75/25 NR/BR blend. The abraded surface of the 75/25 NR/BR blend vulcanizate does not exhibit any clear patterning, although a few coarse ridges are seen (Fig. 15). However, a more or less well-defined pattern is formed in the case of the

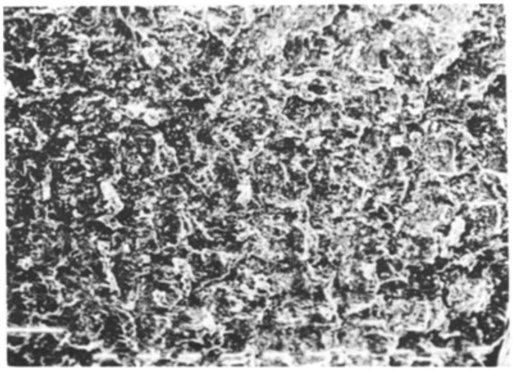


Figure 11 Discontinuous ridges (DIN abrader, mix A, × 42).

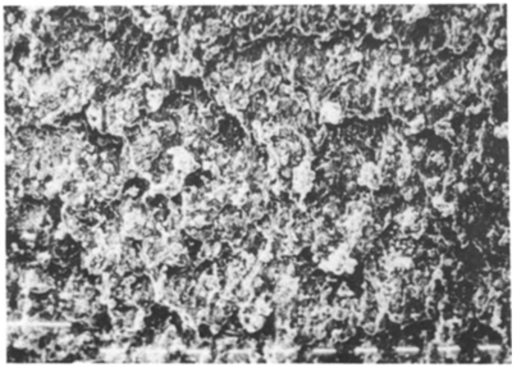


Figure 13 Ridge-free surface (DIN abrader, mix B, × 42).

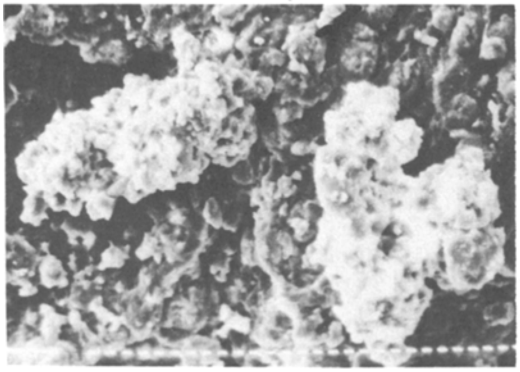


Figure 14 Lumps of abraded rubber (DIN abrader, mix B, × 170).

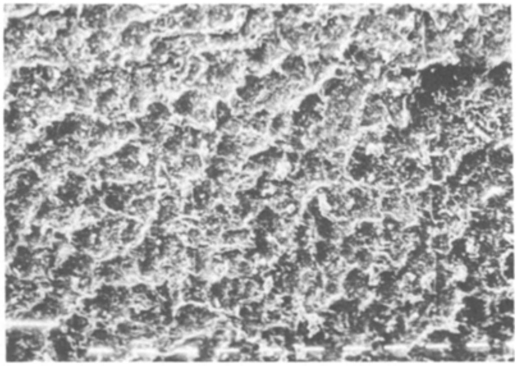


Figure 16 Discontinuous ridges (DIN abrader, mix D, × 42).

50/50 NR/BR blend (Fig. 16). Here the ridges are not continuous as in the case of the Akron abrader.

3.3. Du Pont abrader

Results obtained from the Du Pont abrader are more or less similar to those obtained from the DIN abrader, except that the unfilled 50/50 NR/BR blend vulcanizate shows a remarkably low abrasion loss (Table IV). Here also it is believed that the coefficient of friction plays a major role in determining the abrasion loss. It may be noted here that the abrasive surface used in the Du Pont abrader (silicon carbide paper, grain size 325) was quite fine as compared to those in the other two machines. But unlike in those machines, the abrasive action in the present case is continuous and in the same direction.

Figs. 17 and 18 show the abraded surfaces of the unfilled 75/25 NR/BR vulcanizate. A pattern of ridges formed at right angles to the direction of rotation is clearly visible. Unlike in the case of the Akron abrader, the ridges here are finer. Material removal from the ridge is shown in Fig. 18.

TABLE IV Abrasion loss of different vulcanizates as tested in different abraders

	Akron Abrasion loss after 500 revolutions (cm^3)	DIN Abrasion loss after 1 run of 40 m (cm^3)	Du Pont Abrasion loss after 10 min abrasion (cm^3)
75/25 NR/BR, unfilled (mix A)	2.24	0.89	0.57
50/50 NR/BR, unfilled (mix C)	4.84	0.49	0.10
75/25 NR/BR, black-filled (mix B)	0.17	0.12	0.16
50/50 NR/BR, black-filled (mix D)	0.17	0.06	0.06

Figure 15 Coarse ridges (DIN abrader, mix C, × 42).

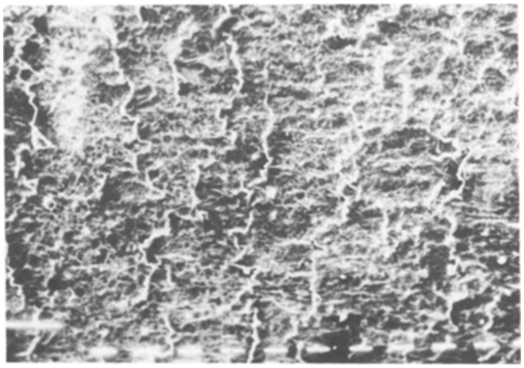


Figure 17 Ridges running perpendicular to the direction of abrasion (Du Pont abrader, mix A, × 42).

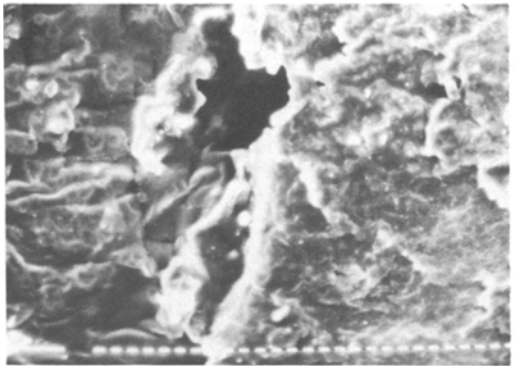


Figure 18 Material removal from the ridges (Du Pont abrader, mix A, × 170).

Figure 19 Scratch marks on the surface (Du Pont abrader, mix B, × 42).

Figure 20 Ball formation on the surface (Du Pont abrader, mix B, × 170).

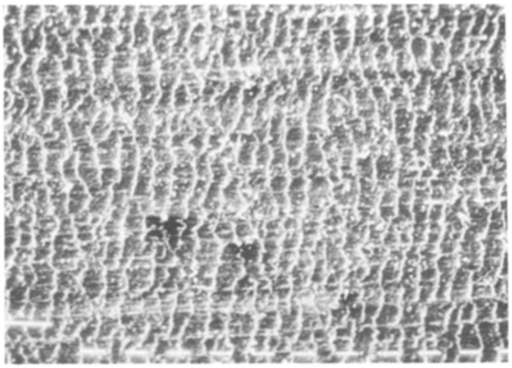


Figure 21 Fine pattern (Du Pont abrader, mix C, × 42).

Figure 22 Abrasion pattern in the early stages of formation (Du Pont abrader, mix D, × 42).

The abraded surfaces of the unfilled 50/50 NR/BR blend, as shown in Figs. 19 and 20 show a very different picture. Only some scratch marks are observed on the surface. Some sort of ball formation is observed possibly due to the continuous rubbing action, which is clearly shown in Fig. 20. As pointed out earlier, abrasion loss in this case is abnormally low. The abrasion loss in the case of black-filled blend vulcanizates, as expected, is low, but the difference between the unfilled and filled vulcanizates of the 50/50 NR/BR blend is not significant. The abraded surface of the black-filled 75/25 NR/BR blend, as shown in Fig. 21, shows a very fine and well-defined pattern with ridges running perpendicular to the direction of abrasion. But in the case of the black-filled 50/50 NR/BR blend, the pattern is not well developed, as shown in Fig. 22. There is, however, a definite tendency towards the formation of a pattern.

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