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Microscopic studies on the mechanisms of wear of NR, SBR and HNBR vulcanizates under different conditions

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Microscopic investigations, undertaken to understand the mechanism of wear of natural rubber (NR), styrene–butadiene rubber (SBR) and hydrogenated nitrile rubber (HNBR) vulcanizates abraded against hard rock, a knurled aluminium disc and a silicone carbide abrader under different conditions, are reported. The wear of NR and SBR vulcanizates against hard rock at low normal load (6 kPa) takes place by a fatigue wear mechanism and it switches over to frictional wear at high normal load (above 18 kPa). In HNBR vulcanizates the wear takes place by an abrasive wear mechanism. Ridges are observed on worn surface of swollen NR and SBR vulcanizates at low normal load, but at higher normal load the wear takes place by catastrophic fracture and extensive plough marks along the direction of abrasion are observed. The wear of NR and SBR vulcanizates proceeds by frictional wear, even at elevated temperatures. In HNBR vulcanizates, the mechanism changes from abrasive wear at 25 °C to frictional wear above 50 °C. Above 50 °C, ridges are observed and the spacing between adjacent ridges increases with rise of temperature.

1. Introduction

Wear is one of the most important properties of tyres and other rubber products. A scientific understanding of the mechanism of wear is still lacking, because wear is a complex phenomenon and its mechanism depends on many parameters like the physical and mechanical properties of mating surfaces, temperature, pressure, humidity and the velocity at which the wear takes place. Sometimes it is further complicated by mechano-chemical, thermomechanical and oxidative degradation.

Many workers [1–7] have proposed different mechanisms to explain their observations. The most common mechanism of wear with rubber is elastic or frictional wear, or pattern abrasion [1], where the abraded surface is characterized by ridges perpendicular to the direction of abrasion. Schallamach [2] explained the mechanism of ridge formation by proposing that the saw-teeth bend back, protecting the rear side and leaving the underneath exposed for further abrasion until the tongue is torn off. Champ *et al.* [3] and Thomas [4] suggested that wear was caused by cumulative growth of cracks. Later Gent and Pulford [5] concluded that the mechanism of wear appeared to be a competitive process between a fracture mechanism and chemical deterioration. The severity of competition depends on the fracture resistance of the polymer, the frictional force, the temperature and the presence of free-radical stabilizers.

The abrasion of a rigid surface against a sharp abrader is reported to proceed by an abrasive or plastic wear [6] mechanism. The sharp asperities on the abrader remove particles by microcutting, and the worn surface bears scratches along the direction of abrasion. This type of wear is not as severe as frictional wear.

At low frictional force with abrasion against a rough and blunt abrader, the asperities impose manifold deformation on the rubber surface causing fatigue failure of the surface layer [7]. This type of wear is known as fatigue wear and the worn surface will not bear any visible ridges except pitting marks. Fatigue wear is less intensive and the presence of anti-oxidants improves the fatigue wear [8].

Russian workers [9] have reported another mechanism known as wear by roll formation. This type of wear is observed during the abrasion of highly elastic material, having poor tear resistance, against a smooth surface. The high frictional force shears a projection on the rubber surface, causing it to tear and roll the tongue along the direction of abrasion. Since the material has a poor tear resistance, in the subsequent movement the accumulated shred is separated off to form a roll. This wear by roll formation is also as severe as frictional wear.

Though many mechanisms have been proposed, the available knowledge does not predict that a rubber product under specified conditions should undergo abrasion by any particular mechanism. Hence the microscopic study of worn surfaces becomes vital to understand the mechanism of wear for further improvement.

We have developed some suitable compounds for tank track pads based on natural rubber (NR),

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styrene–butadiene rubber (SBR) and hydrogenated nitrile rubber (HNBR). The track pads failed because of excessive wear, chipping and subsequent chunking of large pieces of rubber [10]. The severity of failure depended on the nature of the terrain. Computer modelling of track pads indicated that the surface temperature of pads during service would exceed 100 °C [11]. At high temperature, the viscoelastic energy dissipation is reduced and hence the polymer network becomes weak and the strength reaches its threshold limit [12]. In order to understand the influence of terrain on the wear of tank track pads, the abrasion of NR, SBR and HNBR compounds against various rocks was studied under laboratory conditions [13]. Also, the abrasion resistance of the track pad compounds against a silicon carbide abrader and a knurled metal disc under swollen conditions [14] and at elevated temperatures [15] (when viscoelastic energy dissipation is minimum) was studied.

In this paper we report our microscopic investigations on the mechanisms of wear of NR, SBR and HNBR vulcanizates against a rock surface. Also reported are the mechanisms of wear under swollen conditions and at elevated temperature against a knurled aluminium disc and silicon carbide abraders.

2. Experimental procedure

2.1. Materials and testing procedure

NR (RMA IX) and SBR (synaprene 1502) were obtained from Dunlop (India) Ltd, Sahaganj. HNBR (Zetpol 1020, acrylonitrile content 44%, iodine number 25 g/100 g) was supplied by Nippon Zeon Co. Ltd, Japan. Other materials like zinc oxide, stearic acid, sulphur etc. were chemically pure and rubber grade. The details of formulations, mixing, moulding and testing were given in our earlier reports [13–15]. NR and SBR vulcanizates were swollen in toluene and HNBR in DMF, till the swelling reached equilibrium conditions. A modified Du Pont abrader was used to study the abrasion against a rock surface. The abrasion of swollen compounds against a silicon carbide abrader and a knurled aluminium disc was carried out using the same equipment. An environmental chamber with temperature controller was attached to the same equipment to carry out abrasion at elevated temperatures against a silicon carbide abrader.

2.2. Microscopic studies

Microscopic studies of the worn surface of swollen vulcanizates, immediately after testing, were carried out using an optical microscope (Leitz Metallux 3, Ernst Leitz Wetzlar Gmbh, Germany). A scanning electron microscope (SEM) (Cam Scan Series 2, UK) was used to investigate the mechanism of wear of swollen samples. The worn surfaces were sputter-coated with gold and SEM photographs were taken within 48 h of testing.

3. Results and discussion

3.1. Mechanism of abrasion against rock

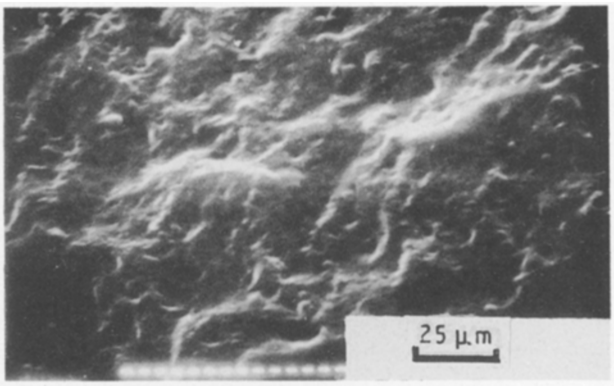

Figure 1 Dimples and pitting marks on abraded surface of filled (50 phr SAF) NR vulcanizate at 6 kPa normal load.

The surface of NR abraded against hard rock (granite rock having surface roughness 5–10 μm) at low normal load (6 kPa) is shown in Fig. 1. The abraded surface is smooth. The presence of dimples and pitting marks indicates that abrasion has taken place by a fatigue wear mechanism. At higher normal load (above 18 kPa) ridges perpendicular to the direction of abrasion are observed. The spacing between adjacent ridges increases with normal load as shown in Figs 2 and 3. Also the worn surface is tacky and the debris is oily as shown in Fig. 4. The above observations could be explained as follows: during abrasion, shear stress acting at the sliding interface causes mechanical fracture on the rubber surface only when the stress exceeds a critical value F_{crit}. The shear stress is generated due to frictional force F and F is a product of the coefficient of friction μ and normal load P [16], i.e.

$$F = \mu P. \qquad (1)$$

So at normal load, the frictional force is less than F_{crit} and hence asperities on the rough abrader surface impose repeated deformation resulting in fatigue failure of the surface layer of rubber. At higher normal load $F > F_{\text{crit}}$, the stress concentration at the tips of the asperities causes elastic deformation and fracture on the rubber surface, and hence the abrasion takes place by a frictional wear mechanism. At high normal load, mechanical shearing in the presence of oxygen degrades the debris and the abrading surface (like the cold mastication of raw rubber). This explains the observed oily debris and the tackiness of the worn surface. On the worn surface of HNBR compounds only scratch marks along the direction of abrasion, but no ridges, are observed. This indicates that abrasion has taken place by an abrasive or plastic wear mechanism, and this is explained in Section 3.3.

Schallamach [17] explained the formation of ridges on the worn surface of NR compounds and related the ridge spacing S to the normal load P and modulus E of rubber by the relation

$$S = \text{Const.} \left(\frac{P}{E} r d^2\right)^{1/3} \qquad (2)$$

where r is the radius of curvature of the abrasive grain at the point of contact and d the size of the grain. For a given abrader and rubber compound r, d and E can be considered as constant, so Equation 2 could be written

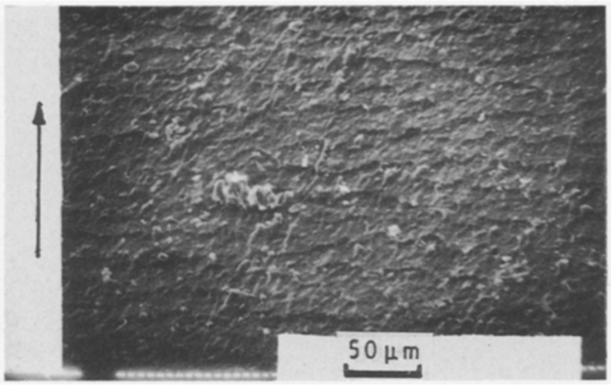

Figure 2 Ridges on abraded surface of filled (50 phr SAF) NR vulcanizate at 25 kPa normal load.

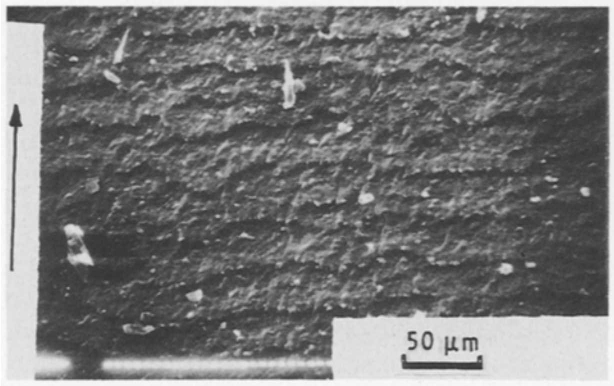

Figure 3 Ridges on abraded surface of filled (50 phr SAF) NR vulcanizate at 44 kPa normal load.

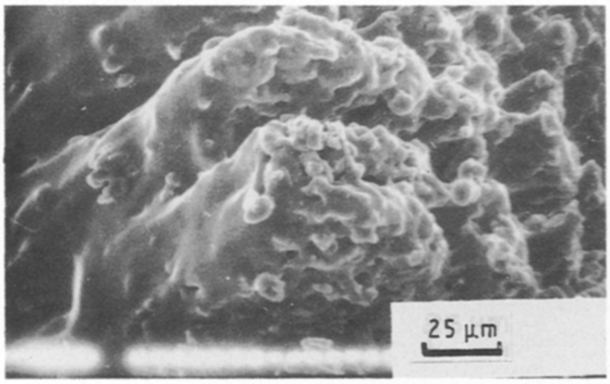

Figure 4 Oily debris of filled NR vulcanizate.

as

$$S = \text{Const. } P^{1/3} \qquad (3)$$

This equation explains clearly that the ridge spacing increases with normal load.

3.2. Mechanism of abrasion of swollen vulcanizates

The abrader surface of swollen NR and SBR vulcanizates at low normal load (6 kPa) shows ridges perpendicular to the direction of abrasion (Fig. 5). The ridge spacing is around 50 times higher than the same observed on unswollen samples. At higher normal load (44 kPa) extensive plough marks along the direction of abrasion are observed (Fig. 6). The worn surface bears both ridges and plough marks at intermediate normal load (18 kPa) as shown in Fig. 7. HNBR does not show any ridges, but the same compound swollen in DMF shows ridges at all normal loads (18–44 kPa) as shown in Fig. 8.

The above observations indicate that even at lower normal load $F > F_{\text{crit}}$ (since F_{crit} under swollen conditions is reduced) the stress at the tip of asperities is just enough to cause elastic deformation and tears on the swollen rubber surface. However, at higher normal load the projections on the rough abrader surface penetrate into the swollen rubber. Since the tear resistance under swollen conditions is much reduced [18], when sliding occurs, these projections tear off the rubber surface catastrophically. Hence plough marks along the direction of abrasion are observed. At intermediate load, the stress concentration on some of the sharp projections on the abrader surface is adequate to cause catastrophic fracture. Hence a combination of ridges and plough marks is observed. The mechanisms of wear of swollen samples abraded against a knurled aluminium disc at different normal loads are the same as those observed against a rough surface. The ridge spacing is high compared to that of unswollen samples as the modulus in Equation 2 is reduced drastically on swelling [12].

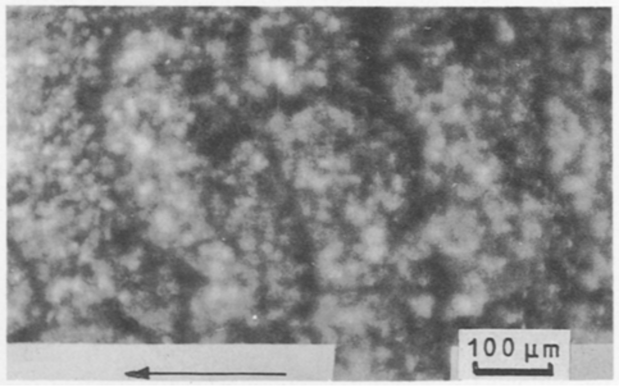

Figure 5 Ridges on worn surface of filled (50 phr HAF) swollen NR vulcanizate at 6 kPa normal load.

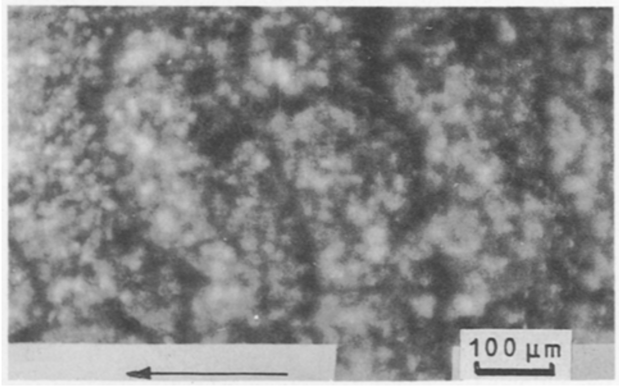

Figure 6 Plough marks on abraded surface of filled (50 phr HAF) swollen NR vulcanizate at 44 kPa normal load.

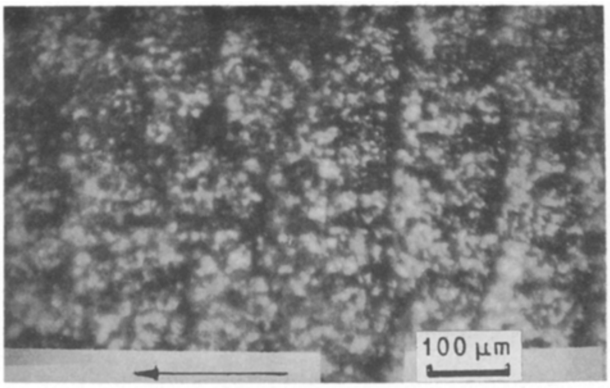

Figure 7 Ridges and plough marks on abraded surface of filled (50 phr HAF) swollen NR vulcanizate at 18 kPa normal load.

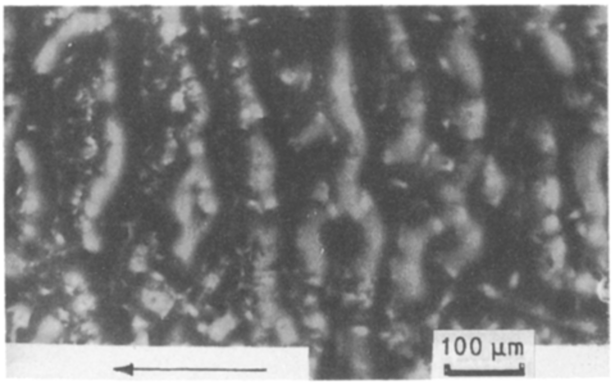

Figure 8 Ridges on abraded surface of filled (50 phr HAF) swollen HNBR vulcanizate at 44 kPa normal load.

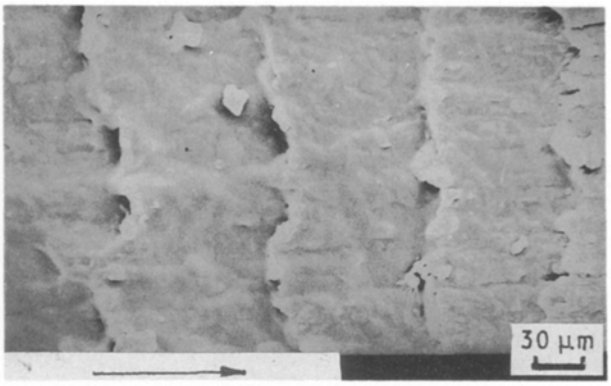

Figure 9 Ridges on abraded surface of filled (30 phr SAF) SBR vulcanizate at 100 °C.

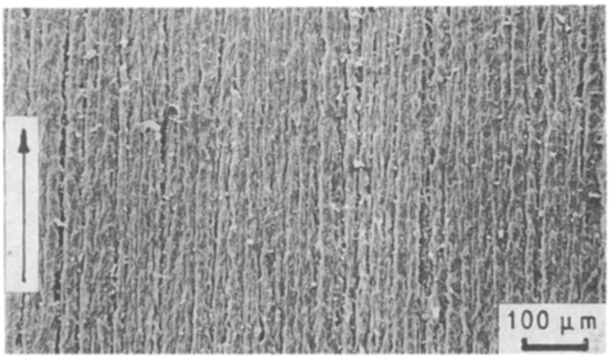

Figure 10 Scratches on abraded surface of filled (50 phr SAF) HNBR vulcanizate at 25 °C.

The high T_g of HNBR may bring the surface in contact with the abrader into a glassy region at the frequency of deformation taking place during abrasion. Hence only the sharp microasperities remove rubber by micro-cutting, leaving the others to slide over the glassy surface with little loss of energy. On swelling, T_g is shifted to lower temperature (T_g for the unswollen compound is -3 °C and the same for the swollen compound is -60 °C at 10 Hz as determined from DMTA). Hence, patterns are observed with the swollen HNBR vulcanizates. HNBR may have adequate fracture resistance even under swollen conditions to resist catastrophic fracture by the projections on the abrader, and hence ridges are observed at all normal loads (6–44 kPa). The mechanism of wear thus changes from abrasive wear to frictional wear upon swelling the vulcanizates.

3.3. Mechanism of abrasion at elevated temperatures

The abrader surface of NR and SBR compounds exhibits ridges or patterns perpendicular to the direction of abrasion at all temperatures (Fig. 9). The debris is oily and the worn surface is tacky due to mechanochemical degradation. The ridge spacing between adjacent ridges increases with rise of temperature. HNBR vulcanizates at 25 °C do not show ridges, but scratches along the direction of abrasion are observed as shown in Fig. 10. But ridges are observed above 50 °C and the ridge spacing increases with temperature as shown in Figs 11 and 12. The above observations indicate that NR and SBR, and HNBR above 50 °C, undergo abrasion by frictional wear or a pattern mechanism of wear. A detailed study indicates that the surface of HNBR in contact with microasperities on the abrader surface is brought to a leathery region at the high rate of deformation imposed by microasperities at 25 °C [15], and hence the wear takes place by an abrasive wear mechanism. When the temperature is increased, the modulus of rubber decreases [12] and hence the ridge spacing increases in accordance with Equation 2.

4. Conclusions

1. The abrasion of NR and SBR vulcanizates against hard rock at lower normal load takes place by a fatigue wear mechanism. At higher normal load the mechanism of wear changes to frictional wear and the abrader surface exhibits ridges perpendicular to the direction of abrasion.

2. In HNBR vulcanizates, the abrasion takes place by abrasive wear and the worn surface is characterized by scratches parallel to the direction of abrasion.

3. Ridges are observed on the worn surface of swollen NR and SBR vulcanizates at low normal load. At high normal load extensive plough marks are observed.

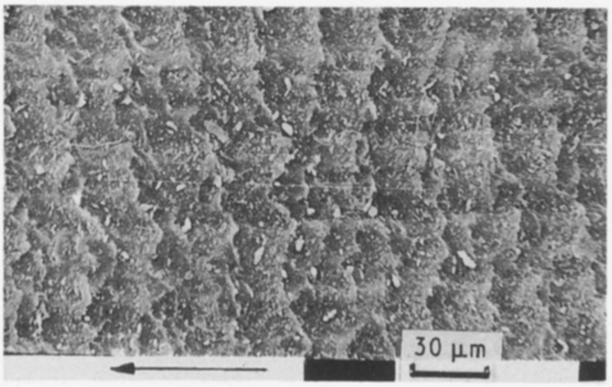

Figure 11 Ridges on abraded surface of filled (50 phr SAF) HNBR vulcanizate at 75 °C.

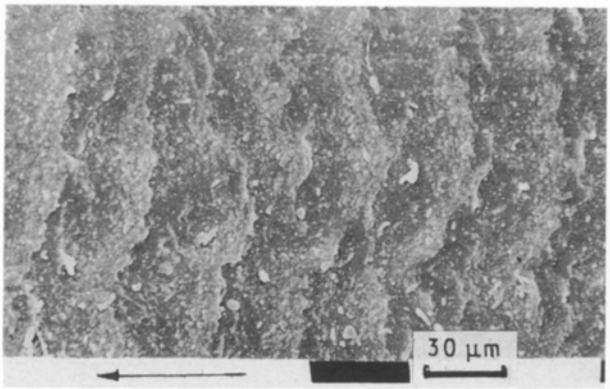

Figure 12 Ridges on abraded surface of filled (50 phr SAF) HNBR vulcanizate at 100 °C.

4. The worn surface of swollen HNBR vulcanizates shows ridges at all normal loads (6–44 kPa).

5. The abrasion in NR and SBR vulcanizates takes place, even at elevated temperatures, by a pattern formation mechanism.

6. No ridges except scratches are observed on the worn surface of HNBR at 25 °C, but the same compound above 50 °C exhibits ridges and the spacing between adjacent ridges increases with rise of temperature.

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