Mechanisms of Rubber Abrasion

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Synopsis

Rates of wear have been determined for several elastomer materials, using a razor-blade abrading apparatus based on one described by Champ, Southern, and Thomas. Measurements have been carried out at different levels of frictional power input, corresponding to different severities of wear, at both ambient temperature and at 100°C, and both in air and in an inert atmosphere. It is concluded that wear occurs as a result of two processes: local mechanical rupture (tearing) and general decomposition of the molecular network to a low-molecular-weight material (smearing). Marked differences were shown by different elastomers. Carbon-black-filled natural rubber, SBR (styrene–butadiene copolymer) and EPR (ethylene–propylene copolymer) were particularly susceptible to decomposition and smearing, but for natural rubber and SBR the decomposition process was not observed in an inert atmosphere. It is attributed to molecular rupture under frictional forces followed by stabilization of the newly formed polymeric radicals by reaction with oxygen, if present, or with other polymer molecules, or with other macroradicals. *Cis*-polybutadiene and *trans*-polypentenamer did not appear to undergo smearing to a significant degree. The reactive radicals formed in these materials by molecular rupture are assumed to undergo rapid addition to other molecules so that the network structure is maintained. Rates of wear have been found to increase with the applied frictional force raised to a power n. The value of n was between 2.5 and 3.5 for unfilled materials at ambient temperature, in agreement with Champ, Southern, and Thomas, who pointed out a general correlation with mechanical fatigue. Filled materials were found to be less sensitive to the frictional force, whether wear took place by tearing or by smearing, having values of the index n of 1.5–1.8. Several observations suggest that wear, even in the absence of smearing, is not fully correlated with mechanical fatigue: the markedly lower wear rates for carbon-black-filled materials, the anomalous rankings of unfilled materials, and the relatively small effects of raising the test temperature to 100°C. It is concluded that abrasive wear by small-scale tearing is not accounted for solely by the crack growth properties of the material but involves other failure processes as well.

INTRODUCTION

The practical importance of the wear of rubbery materials does not need elaboration. Unfortunately, however, a detailed scientific understanding of abrasion has not yet been achieved. Tire tread materials, for example, have been developed on an empirical basis up to the present time. Although this procedure has been remarkably successful, there is no way of knowing which directions will prove valuable for further improvements or on what basis to choose new polymers, fillers, crosslinking agents, etc., without expensive and protracted service tests. There is thus a clear need for understanding the mechanism or mechanisms of abrasive wear in order to be able to specify relevant test methods and to design rubber formulations in a rational way.

Abrasion of rubber in a constant direction leads to the formation of a characteristic surface pattern, shown schematically in Figure 1. It consists of a series of parallel ridges lying perpendicular to the sliding direction.[1] Wear is con-

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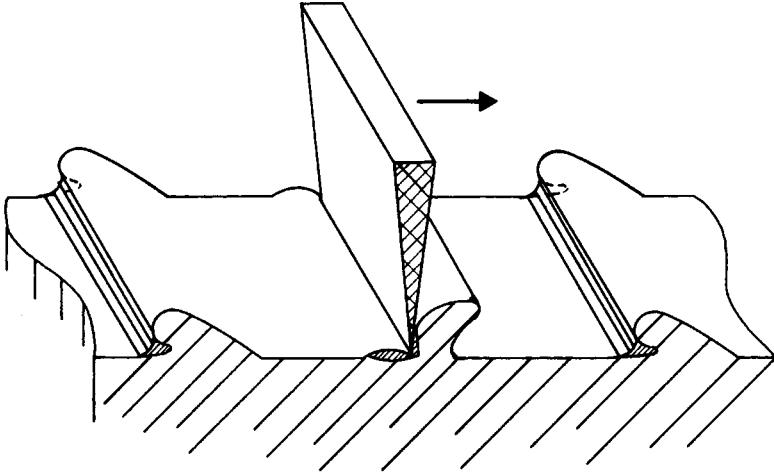
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Fig. 1. Sketch of surface wear pattern, in cross section, showing regions at the base of the ridges where wear is concentrated.

centrated at the leading edges of these ridges, causing them to move slowly backwards, i.e., in the same direction as the abrader, as wear proceeds. The coarseness of the wear pattern is related to the rate of wear, increasing with frictional load and with the compliance of the rubber.[2]

Recently, Champ, Southern, and Thomas[3] and Thomas[4] have suggested that abrasive wear (at least, under particularly simple abrasion conditions) is due to cumulative growth of cracks by tearing under repetitive loading, as in mechanical fatigue processes.[5] They have shown that the dependence of the rate of abrasion upon the magnitude of the frictional force is broadly similar to the dependence
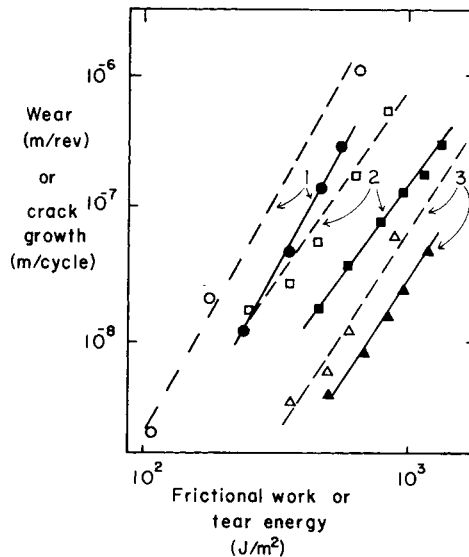

Fig. 2. Rates of wear (filled-in points) plotted against frictional energy input and rates of tear propagation (open points) plotted against tear energy input for three rubbery materials: (1) isom- erized NR; (2) SBR; (3) ABR (data taken from Ref. 3).

of the rate of crack growth upon the magnitude of an intermittently-applied tearing force. Indeed, for several unfilled elastomers the two relations were found to be in good numerical agreement; a typical comparison is shown in Figure 2.

Chemical degradation processes leading to liquidlike wear products have been observed under other, milder wear conditions.[6] Oxygen in the atmosphere plays a role in this process, but several questions still remain unanswered. For instance, what is the mechanism of this degradation process? And what is the connection, if any, between it and the process of cumulative tearing?

Measurements have now been carried out of the rates of abrasion for a number of filled and unfilled elastomers using basically the same experimental methods as Champ, Southern, and Thomas, but using a somewhat wider range of experimental conditions. In view of the possible importance of temperature effects, some measurements were made with the test wheel warmed to 100°C. Also, because of clear signs of chemical decomposition of the rubber at the surface of some test wheels during wear measurements, some measurements were carried out with the test wheel and blade abrader surrounded by an inert (nitrogen) atmosphere. The results are presented here under two general headings: (i) the nature of the wear process for different elastomers and mix formulations and (ii) the rates of wear observed under various test conditions. Some observations by scanning electron microscopy of the morphology of the abraded surfaces and of particles of debris are also described.

EXPERIMENTAL

Solid cylindrical rubber wheels were prepared from a number of different mix formulations, given in the Appendix. The wheels were generally 63.5 mm in external diameter, 25.4 mm in internal diameter, and 25.4 mm wide. They were cemented to aluminum hubs and abraded by rotating them against a stationary razor blade ("Schick Plus Platinum") pressed into the wheel surface in a radial direction while the wheel was rotated at 3–30 rev/min. A sketch of the wear apparatus is shown in Figure 3. It is based on the test arrangement described
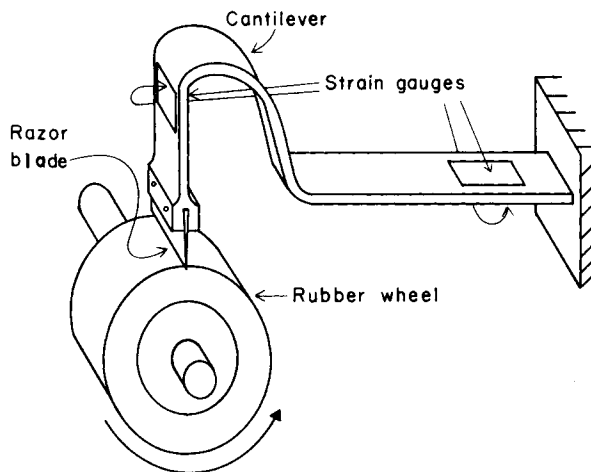

Fig. 3. Sketch of blade abrader.

by Champ, Southern, and Thomas[3] and Thomas,[4] and employed by them to study the wear of several unfilled elastomers.

The razor blade abrader was held in a clamp at the end of a stiff cantilever beam, to which strain gauges were cemented. These gauges were so placed that independent measurements of the normal force N pressing the blade into the rubber surface and the transverse (frictional) force F were obtained simultaneously from flexure of different parts of the cantilever beam, as shown in Figure 2. It was thus possible to measure the effective sliding frictional coefficient μ at the same time as the rate of wear, although irregular fluctuations in both N and F prevented accurate determination of μ.

Measurements of wear were carried out with the frictional force F maintained approximately constant during the entire experiment. This was accomplished by adjusting the position of the cantilever support from time to time, by means of a micrometer screw. Wear measurements were carried out in this way for values of F ranging from 200 to 1600 N/m wheel width. The frictional work expended therefore ranged from 200 to 1600 J/m^2 wheel surface.

Unless otherwise indicated, all of the experiments were carried out at room temperature, $23 \pm 3°C$, and with the wheel rotating at 10 rev/min corresponding to a sliding speed of 33 mm/s. Under these conditions no significant temperature rise of the wheel surface was noted, even though up to about 2 calories of frictional work were expended per revolution.

The weight loss due to rubber being abraded away was measured after steady-state wear conditions were attained. This took hundreds, and sometimes thousands, of revolutions of the test wheel. The surface of the wheel gradually adopted a characteristic roughened texture, coarser at high frictional forces and finer at low ones, while the rate of wear approached a constant value, characteristic of the particular test conditions employed. With a new razor blade, the rate of wear was initially abnormally high, but within a hundred revolutions or less this effect disappeared and the abrading power of the blade did not change subsequently during many thousands of revolutions. This initial effect is attributed to a lubricant film on new blades that was rapidly removed under the test conditions.

The measured loss in weight of the wheel per revolution was converted into a volume loss using the known density of the rubber compound (1000–1500 kg/m^3). Then, by reference to the surface area of the test wheel, about 5×10^{-3} m^2, the volume loss per revolution was converted into a reduction in radial thickness per revolution, and this quantity, denoted A, has been employed to characterize the rate of wear of the rubber.

A weight loss of 1 mg/wheel revolution corresponds to a reduction in radial thickness of about 200 nm/rev. The rates of wear observed ranged from less than 0.02 to 4.0 mg/rev, i.e., A ranged from less than 4 to 800 nm. For comparison, a normal automobile tire which loses about 5 mm in height of tread in, say, 30,000 km, suffers an average rate of wear of only about 0.5 nm/rev, while a typical aircraft tire may wear at a hundred times this rate.

Following Champ, Southern, and Thomas, adhesive tape (3M Co. Highland Brand No. 6200) was generally employed to remove particles of rubber which tended to cling to the surface of the wheel. This cleaning procedure was replaced by frequent brushing for other experiments, particularly those carried out in a nitrogen atmosphere or at high temperatures, when cleaning with tape proved to be impractical.

Measurements of wear rate were carried out in a nitrogen atmosphere by enclosing both the blade abrasion apparatus and a balance for repeated weighings of the test wheel inside a laboratory glove box (Model 50004, Labconco Corp.) into which nitrogen was flushed continuously. The volume of the glove box was approximately 300 L and the rate of flow of nitrogen was approximately 10 L/min. Using the relationship given by Schallamach,[6] for the concentration C of oxygen after a time t at a nitrogen flow rate R into a volume V:

$$\ln(C/C_0) = -Rt/V,$$

the oxygen concentration would be expected to fall to 2.7% after 1 h and 0.4% after 2 h. After 2 h the concentration of oxygen was indeed found to be less than 0.5%, the minimum amount measurable accurately with the oxygen analyzer employed (Fyrite Oxygen Gas Analyzer, 0–7%, Model CVE, Bacharach Instrument Co.). Measurements of wear rate were started under these conditions, i.e., after 2 h of nitrogen flushing. However, significant changes in the character of wear debris were first noted when the oxygen concentration fell to about 0.1%, about 1 h later.

RESULTS AND DISCUSSION

Character of the Wear Process

Different modes of wear could be recognized by the physical characteristics of the product.

Particulate Wear

In this case, fine or coarse particles of rubber were produced by a tearing process. They could be readily removed from the wheel with tape or by brushing, and, in some instances, were swept away by the blade itself in the form of a fine spray of rubber particles. A photomicrograph of a wear particle from material B is shown in Figure 4.

Close examination of the worn surface and the debris with a scanning electron microscope revealed that the tearing process actually took place on two levels. A basic wear process led to the detachment of small particles, 1–5 μm in dimension. This process resulted eventually in the formation of the characteristic pattern of ridges (Fig. 1) by cumulative wear concentrated at the leading edges of the ridges. The ridges folded over and protected the downstream parts of the surface from further wear, as described by Schallamach.[1] The tips of the abrasion pattern ridges were periodically torn away, probably as a result of repeated straining (mechanical fatigue) as proposed by Champ, Southern, and Thomas[3] and Thomas.[4] The latter process created larger particles of debris, up to several hundred μm in size in especially severe cases. A bimodal size distribution of abraded particles has been reported previously for tires worn under normal service conditions.[7,8] It seems to be a characteristic feature of abrasion by repeated sliding in one direction.

Although the small-scale process produces an insignificant fraction of the total weight of debris, nevertheless, it seems to be the primary mode of wear. It leads to the formation of the characteristic abrasion ridge pattern and also to the erosion of the ridge tips that culminates in their tearing away as large particles.
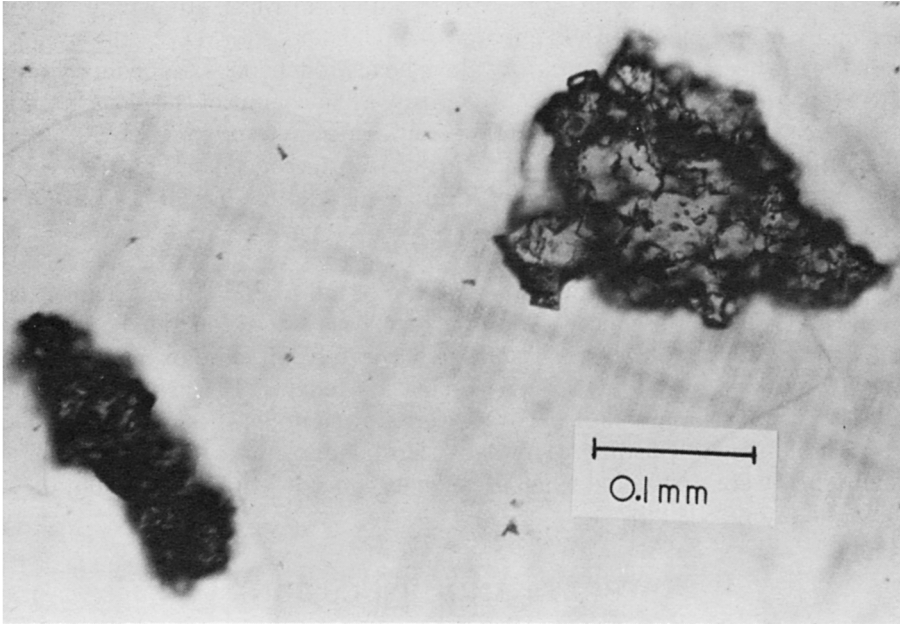
Fig. 4. Wear debris from unfilled SBR material B: $F = 0.8 \text{ kJ/m}^2$.

The latter process is responsible for most of the wear, but it appears to be merely a consequence of the primary small-scale wear step.

Because the ridges are larger and more widely spaced for larger frictional
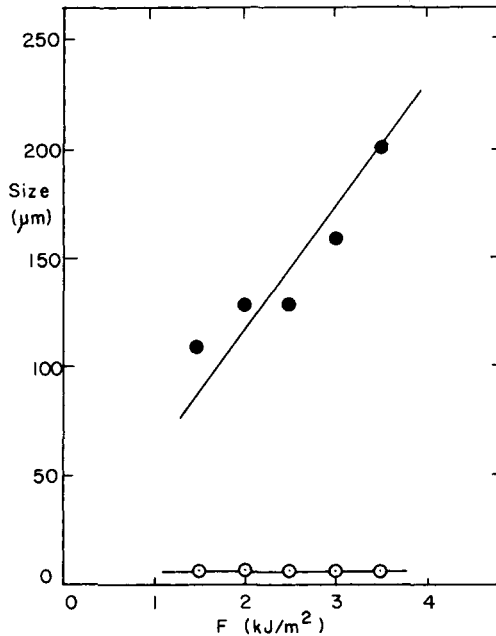

Fig. 5. Size of particulate wear debris from an unfilled polybutadiene material H: (○) mean effective diameters of the small particles; (●) mean effective diameters of the larger particles.

forces,[2] the size of the larger debris particles was found to increase with the applied frictional force, substantially in proportion (Fig. 5). The size of the smaller primary particles remained constant, however. Other attempts to change the scale of the primary wear process by altering the intrinsic strength of the rubber in several ways were also unsuccessful. These included: changes in the elastomer employed and in the mix formulation, increasing the degree of crosslinking by a factor of about 5, increasing the test temperature to 100°C, and changing the sharpness of the blade abrader from a new razor blade edge to a blunted edge, having a tip diameter of about 0.5 mm. Apparently, the scale of the primary wear process, 1–5 μm, is a basic feature of sliding contact between elastomers and rigid substrates. It may represent a structural feature of the elastomeric state.

Oily Debris

Boonstra, Heckman, and Kabaya have reported previously that a typical tire tread material was transformed under relatively mild wear conditions into a sticky, apparently degraded, material in the surface regions.[9] It was found that certain rubber compounds wore in this way, and produced sticky, oily wear debris; for example, carbon-black-filled compounds of SBR, NR, and EPR. An example is shown in Figure 6. Carbon-black-filled compounds of PB and TPR, on the other hand, produced only dry, particulate debris with no signs of chemical deterioration. Indeed, the latter compounds appeared to wear by the same tearing processes as unfilled compounds of NR and SBR, i.e., as described in the preceding section.

The decomposition process could, in principle, be ascribed to several mechanisms: thermal decomposition due to local heating during sliding; oxidative
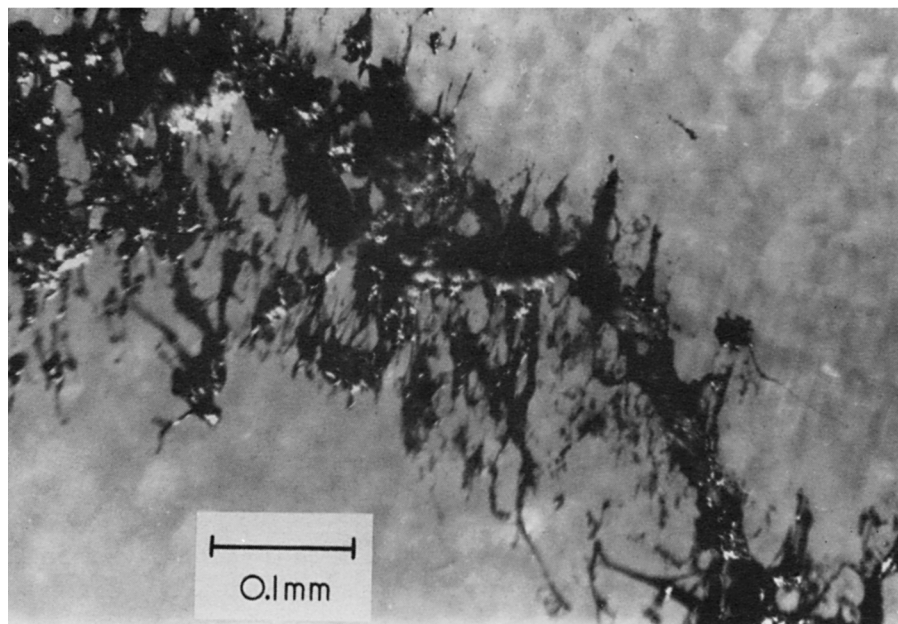

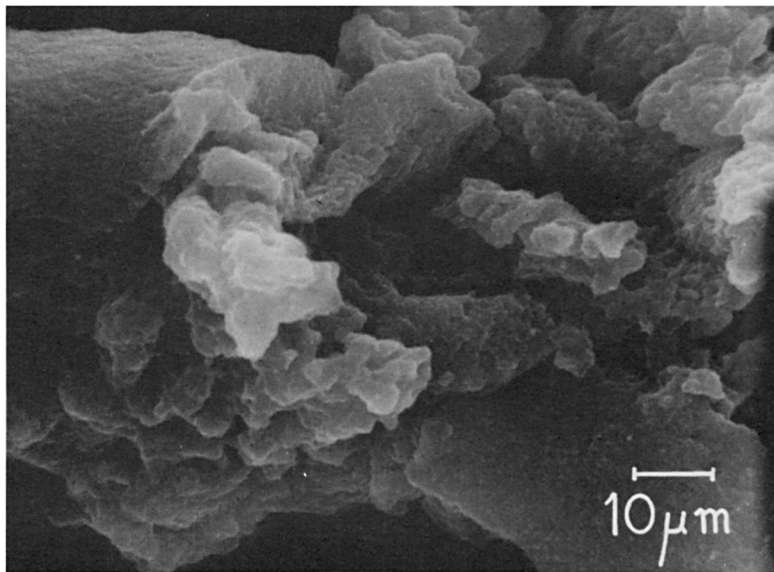Fig. 6. Wear debris from carbon-black-filled SBR material C: $F = 1.2$ kJ/m^2.

Fig. 7. Particle of wear debris from carbon-black-filled NR, material F, worn under nitrogen: F = 1.6 kJ/m^2.

deterioration, possibly accelerated by local heating; and mechanical rupture of macromolecules to form reactive radical species. Several features point to the latter as the principal cause of decomposition. Experiments in a nitrogen atmosphere and *in vacuo* completely changed the mode of wear of carbon-black-filled NR.[6,10,11] The debris changed to a dry powder, exactly like that from carbon-black-filled PB worn in air (Figs. 7 and 8). This proves that frictional heating alone was not responsible for the observed decomposition. Secondly, even in an inert atmosphere, sticky, oily debris was formed in the presence of a free-radical trapping substance, thiophenol. Evidently, oxygen is not essential for decomposition. Instead, the process resembles mastication of rubber on a mill, in which macroradicals are formed by molecular fracture and then react with atmospheric oxygen, if present, or with other substances, or with each other, depending upon their intrinsic reactivity and environment.[12] Chemical analysis of rubber surfaces worn in air has shown that oxygen-containing species are formed during both particulate and oily wear,[13] as would be expected from the ready reaction of macroradicals with oxygen.

Radicals formed in PB by main-chain rupture are known to react with the polymer itself, leading to further crosslinking rather than to decomposition. On the other hand, the resonance-stabilized radicals formed in SBR and NR react with oxygen (if present) and the initial chain fracture is rendered permanent in this way. In the first case (PB), the presence or absence of oxygen had little effect on the type of wear. In the other (NR and SBR), wear in an inert atmosphere resembled that for PB, yielding a fine, dry, particulate debris, but in oxygen the product was a sticky, tarry material.

Carbon-black-filled EPR was found to produce oily wear debris both in air and in nitrogen. Internal reactions of the radicals formed in EPR (for example,
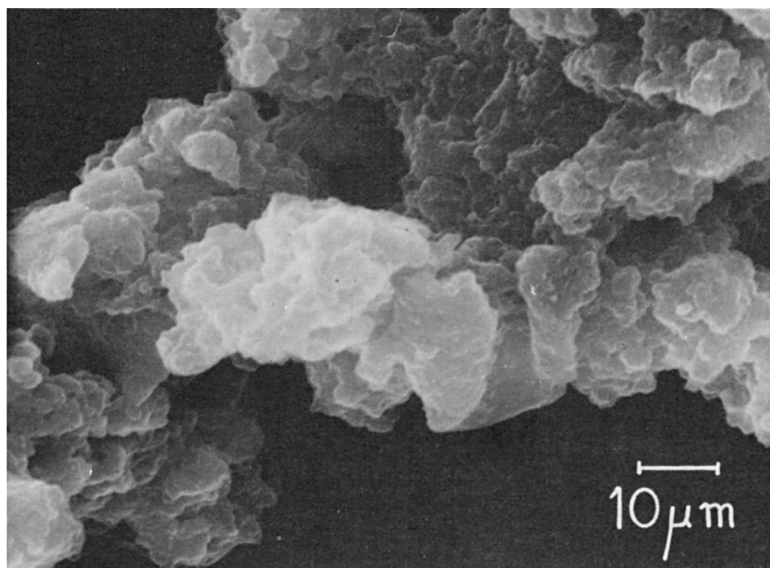
Fig. 8. Particle of wear debris from carbon-black filled PB, material E, worn in air: $F = 1.6$ kJ/m^2.

H abstraction from neighboring molecules) apparently leads to consummation of molecular rupture and the formation of oily debris even in the absence of oxygen.   EPR materials are well known to crosslink inefficiently by free-radical reactions alone.[14,15]

Competitive Wear Processes

Thus, the abrasion of rubber is governed by a competition between two quite different processes: removal of microscopic particles from the rubber surface by fracture and mechanochemical decomposition of the rubber.   Presumably the dominant process depends on the relative susceptibility of the material. Incorporation of carbon black in the mix formulation increases the stiffness and strength of rubber and thereby suppresses tearing failures, so that mechano-chemical attack then becomes the principal mode of wear in materials, like NR and SBR, that are susceptible to decomposition by this mechanism.

The presence of the oily product appeared to decrease further wear, even when the frictional force was maintained constant.   Apparently it acted as a viscous protective film, alleviating the local concentrations of tearing force that are presumably responsible for the detachment of wear particles.   However, when the wear fragments were strongly adhering but not liquidlike, they accumulated into large particles of debris, and the beneficial effect of a protective film was lost.   Debris of this type was found to be produced in the abrasion of a 75/25 blend of natural rubber and cis-polybutadiene.   Apparently, the PB fraction prevented complete decomposition of the elastomer blend to a tarry liquid, while the NR fraction became strongly adhesive as it underwent molecular rupture, so that the wear debris formed large adhering rolls, as shown in Figure 9.
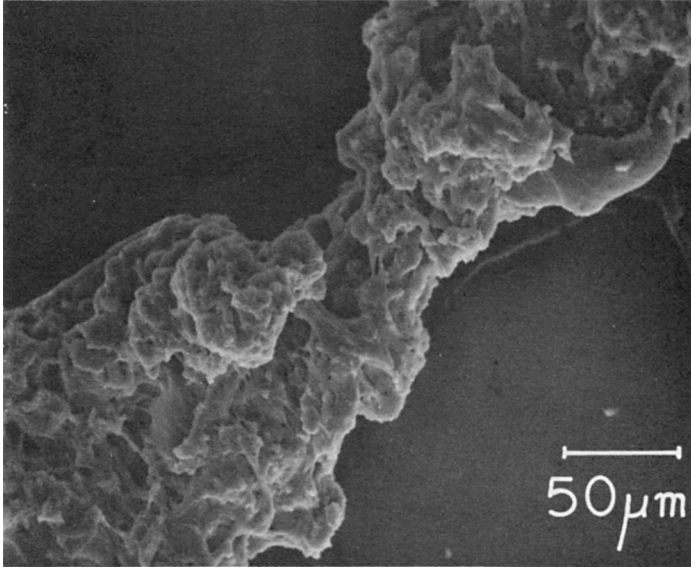
Fig. 9. Wear debris from a 75/25 blend of natural rubber and *cis*-polybutadiene, material G: $F = 1.6$ kJ/m^2.

Rates of Wear

Effect of Frictional Force

As would be expected, the rates of wear depended strongly upon the frictional force exerted by the blade. At low levels of frictional force, the wear was light, the worn surface was relatively smooth, and the debris consisted of relatively small particles. At higher frictional forces, the wear was rapid, the surface was much rougher in texture, and the main wear particles were larger, frequently exceeding 100 μm in mean diameter (Fig. 7). Values of the steady-state rate of wear are given in Table I for unfilled materials under various frictional forces.

The experimentally measured rates of wear given in Table I are plotted in Figure 10 against the frictional work input per revolution of the wheel, using logarithmic scales for both axes. In this representation the results are described

TABLE I

Measured Rates of Wear, A, at Various Values of Frictional Work Input F for an Unfilled NR Material A, an Unfilled SBR Material B, an Unfilled PB Material H, and a Carbon-Black-Filled PB Material F

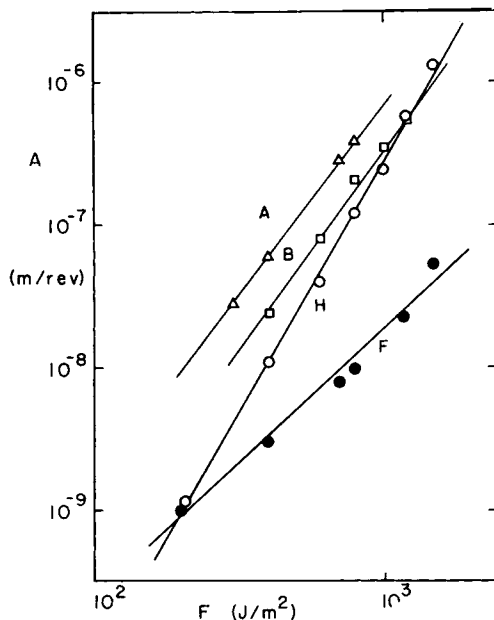| F (kJ/m^2)	A (nm/rev)			
	Material A	Material B	Material H	Material F
0.2			1	1
0.3	28		—	—
0.4	60	24	11	3
0.6	145	80	40	—
0.7	290	—	—	8
0.8	395	210	120	10
1.0		345	245	—
1.2		550	590	23
1.5			1350	53

Fig. 10. Rates of wear, A (m/rev), plotted against frictional work F (J/m^2): (A) unfilled NR; (B) unfilled SBR; (H) unfilled PB; (F) carbon-black-filled PB.

rather accurately by a linear relationship. This was also found to be the case for other materials, although, in the case of the filled SBR material C, oily debris was formed under most test conditions and the rates of wear were therefore less well defined.

The experimentally determined relationships between wear A and frictional work F can thus be represented by the general result

$$A \text{ (m/rev)} = k \ [F \ (\text{J/m}^2)]^n,$$

where the coefficient k and exponent n are characteristic of the particular material being examined. The values obtained are given in Table II. For the unfilled NR and SBR materials A and B, the exponent n was found to be about the same, 2.8 ± 0.2, and for the unfilled PB material H it was somewhat larger, about 3.5. In contrast, exponents for the filled materials C and E were considerably

TABLE II
Experimentally-Determined Relations between Rate of Wear, A, and Frictional Work F for
Various Materials at Room Temperature

Material	
A (unfilled NR)	A (m/rev) $= 5.9 \times 10^{-15}[F \ (\text{J/m}^2)]^{2.7}$
B (unfilled SBR)	A (m/rev) $= 7.0 \times 10^{-16}[F \ (\text{J/m}^2)]^{2.9}$
C (filled SBR)	A (m/rev) $= 2.0 \times 10^{-12}[F \ (\text{J/m}^2)]^{1.5}$
E (filled PB)	A (m/rev) $= 4.0 \times 10^{-14}[F \ (\text{J/m}^2)]^{1.9}$
H (unfilled PB)	A (m/rev) $= 9.0 \times 10^{-18}[F \ (\text{J/m}^2)]^{3.5}$
Results of Champ, Southern, and Thomas[3,4]	
Unfilled NR	A (m/rev) $= 1.1 \times 10^{-13}[F \ (\text{J/m}^2)]^{2.6}$
Unfilled SBR	A (m/rev) $= 2.0 \times 10^{-14}[F \ (\text{J/m}^2)]^{2.4}$
Unfilled PB	A (m/rev) $= 7.5 \times 10^{-16}[F \ (\text{J/m}^2)]^{3.0}$

smaller, 1.5–1.9, corresponding to a lesser dependence of the rate of wear upon the frictional force for these materials. Values of k and n have also been read from the experimental plots presented by Champ, Southern, and Thomas[3,4]; they are included in Table II for comparison with the present results. The linear relations obtained by Champ, Southern, and Thomas appear to be generally similar to the present ones, and the rates of wear at a given value of frictional force were similar in magnitude.

As discussed in connection with Figure 2, for unfilled elastomers the dependence of the rate of wear upon the frictional force is broadly similar to the dependence of the rate of crack growth upon the level of an intermittently applied force.[3,4] However, the rate of wear of the NR material A seems anomalously high. Natural rubber compounds are particularly resistant to crack growth, and yet the rates of wear are relatively high for this material.

A discrepancy in the opposite sense is shown by the carbon-black-filled materials. Whereas the addition of carbon black does not greatly increase the resistance to mechanical fatigue of rubber compounds, it causes a major reduction in the rates of abrasion, particularly under severe conditions. Thus, there are distinct anomalies in relating the rates of wear to the corresponding susceptibilities of materials to crack growth under intermittently applied forces, even though there are also some close parallels. It is conjectured that the wear process involves both a small-scale stepwise tearing process, analogous to crack growth under repeated stressing, and also direct fracture of the material on a single stress application. The latter process would be better correlated with the tensile strength of the material rather than with its resistance to small-scale crack growth.

Effect of Temperature

Measurements have been carried out at room temperature (25°C) and also at 100°C in order to examine the effect of such a temperature change on the rates of wear. A thermostatted hot-air jacket was placed around the test wheel in order to achieve a steady ambient temperature of 100°C for the high temperature measurements. Because it was not feasible to clean the wheels by means of adhesive tape at 100°C, tests were also performed at 25°C without adhesive tape, so that the results would be fully comparable. The wear results at 25°C are therefore slightly different from those reported in the previous section, being generally somewhat smaller because the present cleaning procedure by intermittent brushing was less efficient.

Several materials were examined in this way: A, unfilled NR; B, unfilled SBR; C, carbon black filled SBR; D, carbon-black-filled TPPR (trans-polypentenamer); and G, carbon-black-filled NR/PB blend. The results are presented in Table III. They show a relatively small effect of temperature upon the rate of wear, ranging from hardly any effect for material D to an increase by a factor of about 2 for the SBR materials B and C. This relatively small effect of a large temperature rise does not seem to be consistent with a mechanical fatigue mechanism of abrasion as proposed by Champ, Southern, and Thomas, because the rate of growth of fatigue cracks is greatly increased by a temperature rise of this amount, by orders of magnitude for SBR materials.[16]

TABLE III
Measured Rates of Wear, A, at 25°C and 100°C for Various Materials

Temp (°C)	F (kJ/m²)	A (nm/rev)	μ	Type of wear[a]
A, unfilled NR				
25	0.4	60	1.40	I
100	0.4	32	1.00	I
25	0.6	150	1.44	I
100	0.6	190	1.18	I
B, unfilled SBR				
25	0.4	24	1.78	I
100	0.4	68	1.62	I
25	0.6	82	1.58	I
100	0.6	195	1.37	I
C, filled SBR				
25	0.8	16	2.05	II
100	0.8	22	1.35	II
25	1.6	80	2.10	II
100	1.6	240	1.50	II
D, filled TPPR				
25	0.8	16	1.80	I
100	0.8	18	1.35	I
25	1.6	44	2.0	I
100	1.6	44	1.4	I
E, filled PB				
25	0.8	10	1.60	I
25	1.6	62	1.50	I
F, filled NR				
25	1.6	22	1.65	II
G, filled NR/PB blend				
25	0.8	40	1.80	III
100	0.8	70	1.25	III
25	1.6	210	1.80	III

[a] I denotes dry particulate debris; II denotes formation of an oily coating; III denotes adhering rolls.

Effect of Composition

The rates of wear given in Tables I–III are strikingly different for the different materials. This is made clear by considering the rates of wear at a given frictional work input, say 1.6 kJ/m², at 25°C. Values for the unfilled materials A and B are obtained by extrapolation; the results are 1400 and 700 nm/rev, approximately. For the filled materials C and D the measured rates are 80 and 44 nm/rev, respectively. Thus, a range of over 30-fold is found in the rates of wear of different materials under similar wear conditions. To what degree these differences can be ascribed to differences in hardness, tensile strength, tear strength, and mechanical fatigue properties, or to differences in resistance to chemical changes, is discussed below. It should be pointed out here, however, that the frictional properties of the various materials are not greatly different. Values of the frictional coefficient μ given in Table III show the expected reduction with increase in temperature and increase with carbon black loading, but they are otherwise rather similar for the various materials.

The wear debris from materials A, B, D, and E were rather similar in character,

TABLE IV
Measured Rates of Wear, A, at 1.6 kJ/m^2 Frictional Work Input and Coefficients μ of Sliding
Friction in Air and Dry Nitrogen

	A (nm/rev)	μ	Type of wear[a]
E, filled PB			
Air	48	1.5	I
Nitrogen	52	2.2	I
F, filled NR			
Air	15	1.6	II
Nitrogen	90	2.7	I

[a] I denotes dry particulate debris; II denotes formation of an oily coating.

consisting of dry particulate matter. For materials C, F, and I, however, the debris showed clear indications of chemical decomposition, as discussed previously. These wear processes with the blade abrader seem to be quite consistent with the wear of actual tire treads in road testing. SBR-based treads have been observed to develop a liquidlike surface, while PB-based treads did not.[17]

The rates of wear for material F were greatly increased in a nitrogen atmosphere (Table IV), and the wear debris then took the form of dry particles rather than a partially decomposed oily coating. In contrast, material E, which formed dry particulate debris in both air and nitrogen, wore away at about the same rate in both atmospheres (Table IV). Thus, the cumulative tearing process does not appear to be strongly affected by the presence or absence of oxygen. On the other hand, the competing process of mechanochemical decomposition, to which materials C and F are particularly prone, is consummated by oxygen, acting as a radical acceptor. When the oily decomposition product forms, it seems to protect the underlying rubber from tearing and thus reduce the rate of wear.

Polybutadiene is an ideal material for assessing the purely mechanical effects of carbon black on the wear rate of rubber since it is inherently resistant to smearing. Measurements on filled and unfilled polybutadienes show a quantitative difference in the frictional load dependence of wear, despite the similarity in wear mechanism. The wear rate of material H, unfilled PB, is much more sensitive to frictional load, increasing approximately with the third power, whereas wear of the filled material E increases with the 1.5 power only (Fig. 10 and Table I). Thus carbon black does not reduce the wear rate of rubber to the same degree at different severities of abrasion. At high severities carbon black reduces the wear rate of PB substantially, a 25-fold reduction at 1.6 kJ/m^2 frictional work input, but this advantage is lost at low severities. Extrapolation of measured data suggest that the wear rate of filled PB will actually be greater than that of unfilled PB for frictional loads less than about 0.2 kJ/m^2.

Reversals in the relative rates of wear of the unfilled PB material H compared to the unfilled NR and SBR materials A and B are also suggested by the present data (Fig. 10) at different severities of wear. These materials are of similar hardness and wear away in the same manner, forming particulate debris, so that the reversal in ranking must be associated with the detailed way in which rubber is torn from the surface. It probably reflects differences in their strength and extensibility at high severities, compared to differences in the crack growth rates at low severities of wear.

CONCLUSIONS

Abrasion of elastomers, whether filled or unfilled, strain crystallizing or amorphous, appears to involve a competition between two different mechanisms. One is the removal of microscopic particles of rubber by a fracture process and the other is chemical deterioration of rubber in the surface region, initiated by mechanical stress and promoted by oxygen in the atmosphere.

When the fracture process dominates, as in unfilled NR, SBR, and PB and filled PB and TPPR, the rubber surface develops a fine texture on two scales. One is associated with the removal of particles a few microns in size. It occurs randomly over the surface and appears to be an inevitable feature of the fracture of rubber by friction. The other, on a coarser scale, is confined to the ridges of the abrasion pattern which determines the size of the debris and probably the rate of wear also. When mechanochemical degradation dominates wear, as in the filled NR and SBR materials worn in air, a sticky oily layer forms on the rubber surface, protecting it to some degree from further abrasion and leading to low wear rates.

These general features of rubber wear by a blade abrader are quite consistent with those observed in more complicated wearing situations, such as occur in actual tire use, and indicate that, despite its simplicity, this test method is of value for rating tread materials.

Rates of wear of elastomeric materials have been found to be proportional to a power n of the applied frictional force. The value of n depended upon the composition of the elastomer, ranging from about 1.5 for carbon-black-filled SBR to over 3 for an unfilled PB material. As a consequence of these different dependencies upon frictional force, reversals in the relative rates of wear of different elastomers were sometimes observed under different severities of wear.

A general parallel was evident between the observed rates of wear and rates of crack growth under repeatedly applied stresses (mechanical fatigue), as proposed by Champ, Southern, and Thomas[3] and Thomas.[4] However, this parallel failed to hold in many instances. For example, the rates of crack growth of NR materials are exceptionally low, especially under high stresses, but the rates of wear were found to be, if anything, somewhat higher than for other elastomers. The rates of crack growth for carbon-black-filled materials are not much lower than for unfilled materials and yet the rates of wear were greatly reduced. Finally, the rates of wear were found to be surprisingly insensitive to temperature, changing by a factor of about 3 at most between 25°C and 100°C, whereas much greater changes in rates of crack growth by mechanical fatigue are generally observed, by orders of magnitude for unfilled SBR.

Hence, it is concluded that the rates of stepwise tearing under repeatedly applied stresses do not fully account for the observed rates of wear. Instead, the rates of wear appear to depend upon the detailed mechanism by which debris is removed, involving partly mechanical fatigue and partly direct fracture under a single application of stress. In addition, for materials that are particularly resistant to fracture, mechanochemical processes take place in the surface layer and lead to decomposition or further crosslinking depending upon the chemical nature of the elastomer, its composition, and its environment.

APPENDIX

The mix formulations in parts by weight and vulcanization conditions used for preparing test wheels are given below:

A: Unfilled NR

Natural rubber (SMR-5L)	100
Zinc oxide	5
Stearic acid	2
Phenyl-2-naphthylamine	1
Santocure	0.6
Sulfur	2.5

Vulcanized for 50 min at 145°C

B: Unfilled SBR

SBR (Firestone FRS-1502)	100
Zinc oxide	5
Stearic acid	2
Phenyl-2-naphthylamine	1
Santocure	1
Sulfur	2

Vulcanized for 60 min at 150°C

C: Carbon-Black-Filled SBR

SBR (FRS-1502)	100
N330 carbon black (Cabot Corp., Vulcan 3)	54
Zinc oxide	5
Stearic acid	2
Phenyl-2-naphthylamine	1
Santocure	1
Sulfur	2

Vulcanized for 60 min at 150°C

D: Carbon-Black-Filled TPPR

Trans-polypentenamer	100
Pentachlorothiophenol (E.I. DuPont de Nemours and Co., RPA No. 6)	0.07
N330 carbon black (Cabot Corp., Vulcan 3)	50
Zinc oxide	5
Stearic acid	2
Phenyl-2-naphthylamine	2
Processing oil (Philrich HA5)	7.5
Sulfur	0.5
Sulfasan R	1.5
Santocure MOR	1

Vulcanized for 35 min at 145°C

E: Carbon-Black-Filled PB

Mix formulation as for D except for the use of *cis*-polybutadiene (Phillips Cis-4 1203) in place of *trans*-polypentenamer.

Vulcanized for 45 min at 145°C

F: Carbon-Black-Filled NR

Mix formulation as for D except for the use of natural rubber (SMR-5L) in place of *trans*-polypentenamer.

Vulcanized for 35 min at 145°C

G: Carbon-Black-Filled NR/PB Blend

Mix formulation as for D except for the use of:

Natural rubber (SMR-5L)   75 ⎱
⎰ 100
Cis-polybutadiene (Phillips Cis-4 1203) 25 ⎰

in place of *trans*-polypentenamer.

Vulcanized for 45 min at 150°C

H: Unfilled PB

Polybutadiene (Firestone Diene 35 NFA)   100
Dicumyl peroxide   0.05

Vulcanized for 120 min at 160°C

I: Carbon-Black-Filled EPR

Ethylene-propylene copolymer (Exxon Vistalon 404)   100
N330 carbon black (Cabot Corporation, Vulcan 3)   54
Dicumyl peroxide   2.7
Sulfur   0.32

Vulcanized for 30 min at 145°C,

then 70 min at 160°C

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