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Effects of particle size and structure of carbon blacks on the abrasion of filled elastomer compounds

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Abstract The effects of the particle size and structure of various carbon blacks on friction and abrasion behavior of filled natural rubber (NR), styrene–butadiene rubber (SBR) and polybutadiene (BR) compounds were investigated using a modified blade abrader. The effect of particle size and structure on abrasion resistance should be considered for the optimum design of desired wear properties. Characteristic parameters were introduced from the particle size and the structure of carbon blacks, with a linear relationship between the Young's modulus and these characteristic parameters. The frictional coefficient depended not only on the particle size, but also on the structure of carbon black. The rates of abrasion were decreased with increasing surface area and developing structure of carbon blacks. Abrasion rates of the compounds were found to be proportional to a power *n* of the applied frictional work input. It was also observed that BR compounds caused much slower wear than NR and SBR compounds. The worn surfaces of the rubber compounds filled with carbon black having smaller particle size and a more developed structure showed narrower spaced ridges and better abrasion resistance. It means that smaller particle size and better structure development of carbon black resulted in improved abrasion resistance.

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Introduction

Reinforcement by fillers, especially carbon black, is one of the most important aspects of elastomer technology [1]. Reinforcement of elastomers is characterized by the increase in modulus and improvement of fracture properties such as tensile strength, tear and abrasion resistance [2, 3]. The most common filler used for reinforcing or strengthening elastomer is carbon black. The properties of the rubber compounds and vulcanizates filled with carbon black depend on the nature and the concentration of the carbon black. The nature of carbon black is determined by its particle size or specific surface area, geometrical arrangement of the carbon black unit (the so-called structure) and the surface nature. Particle size is the primary determinant of surface area for most carbon blacks. The surface area is inversely proportional to the particle size for non-porous carbon blacks [4]. The most widely accepted methods for surface area determination are those based on adsorption of a gas, especially nitrogen [1] and CTAB-absorption. The morphology investigations of carbon black have shown conclusively that the structure originates from fusion of primary particles into more or less randomly coiled primary aggregates [5]. The structure is measured by absorption of dibutylphthalate (DBP). The properties of rubber compounds are affected not only by the filler content but also by its structure and particle size. Carbon black is an additive with a decisive effect on the abrasion resistance.

The practical importance of the abrasion of rubber materials does not need elaboration. Rubber abrasion consists of the removal of particles of rubber by frictional forces [6]. It is suggested that the abrasion of rubber occurs by a competition between two quite different processes [7, 8]. One is the removal of microscopic particles from the rubber surface by mechanical rupture and the other is chemical deterioration of rubber in the surface region, initiated by mechanical stress and promoted by oxygen in the atmosphere. Chemical deterioration of rubber is due to both thermal and oxidative effects. It was proposed that the occurrence of smearing seems to depend on the chemical nature of the elastomer [7]. Abrasion of rubber in a constant direction leads to the formation of a characteristic surface pattern, a series of parallel ridges lying perpendicular to the sliding direction. The ridges folded over and protected the downstream parts of the surface from further wear [7]. It is commonly observed that abraded particles are bimodal in size [9]. Although the small particles formed by intrinsic abrasion are far more numerous, the large particles formed by pattern abrasion account for most of the rubber lost, typically more than 90% [7, 9]. It is also suggested that abrasion of rubber is a viscoelastic process and abrasive wear is due to cumulative growth of cracks by tearing under repetitive loading, as in mechanical fatigue processes [10]. However, some features of the mechanism of rubber abrasion are too complicated and still unclear. The effects of particle size and structure of carbon black on abrasion resistance of rubber compounds should be considered for the optimum design of desired abrasion properties.

In this study, a modified blade abrader [11, 12] was constructed to abrade the flat surface of a filled rubber disk by rotating it against a stationary knife-blade scraper at constant frictional torque. One advantage of this device is that a larger surface area is abraded, relative to the volume of the sample, with the great sensitivity of measurement. The effects of the particle size and structure of various carbon blacks on abrasion rates of filled rubbers were investigated for better understanding of the reinforcement phenomenon. The friction and the wear behavior were examined and also the relation with the characteristic parameter, introduced from the particle size and the structure of carbon black, was studied.

Experimental

Materials

The rubbers used in this experiment were natural rubber (NR, SMR CV60), styrene–butadiene rubber (SBR, 23.5% bound styrene, KOSYN-1500S, Kumho petrochemical Co., Ltd.) and butadiene rubber (BR, *cis*-1,4-solution BR, Kumho petrochemical Co., Ltd.). The other compounding ingredients were sulfur, zinc oxide (ZnO), stearic acid (Hanil Chemical), and *N*-*t*-butyl-2-benzothiazole sulfonamide (TBBS, Monsanto Inc.). The recipes used are given in Table 1. The used carbon blacks were N103, N121, N220, N326, N330, N351, N358, N550, N660 and N990. Figure 1 shows N_2 adsorption and DBP absorption of 10 types of carbon blacks.

Preparation of vulcanizates

The carbon black filled rubber compounds were mixed using a Banbury mixer (Farrel). The rubber was mixed with zinc oxide, stearic acid, sulfur, TBBS and carbon black in a Banbury mixer, according to ASTM Standards given in Table 1. To improve the mixing quality, a two-roll mill (Farrel) was used for 5 min at 50 °C. The roll speed was maintained at 8 rpm.

The compression molding of disks and slabs was performed with an electrically heated compression molding press (Dake). According to the cure curve, the cure time was determined on the basis of the maximum torque. An Oscillatory Disk Rheometer (Benz) was used to obtain the torque–time curves according to ASTM Standard D2084. The used cure time and temperatures were 45 min at 150 °C for NR, 60 min at 145 °C for SBR and 45 min at 145 °C for BR.

Tensile test

A Universal Tensile Tester (Shimadzu Autograph AGS-550D) was used for the tensile measurements of the rubber compounds according to ASTM Standard D412. All tests were performed at room temperature with a crosshead speed of 100 mm/min.

Abrasion test

A schematic diagram of the blade abrader used in this study is shown in Fig. 2. A sharp steel blade was pressed against the flat surface of a rubber disk to measure the abrasion rate. Figure 3 shows a schematic of a rubber disk. A cylindrical disk of rubber was vulcanized and bonded to an aluminum backing plate. The flat surface of a rubber disk

Table 1 Recipes for NR, SBR and BR compounds

Rubber	Sulfur	TBBS	ZnO	Stearic acid	Carbon black	ASTM
NR	2.5	0.6	5.0	2.0	50	D3192
SBR	1.75	1.0	3.0	1.0	50	D3191
BR	1.5	0.9	3.0	2.0	50	D3189

Unit: phr

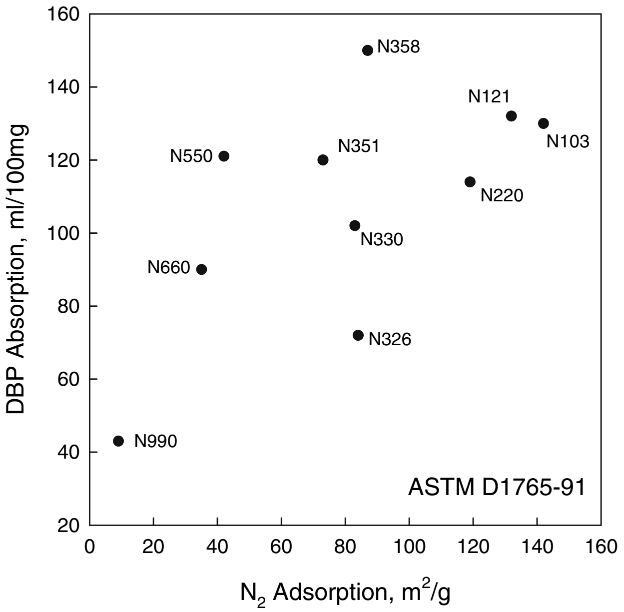


Fig. 1 N_2 adsorption versus DBP absorption of 10 types of carbon blacks

was abraded by rotating it against a stationary knife-blade scraper at constant frictional torque. The rotating speed was 10 rpm. The rate of abrasion can be characterized by the loss in thickness of the wheel per revolution [11, 12]. A steel blade was mounted on the shaft and could be advanced horizontally to press against the rubber disk. The shaft was made in part of a steel tube to which strain gauges were attached to allow the measurement of torque and normal force acting on the blade. The abrasion rates (W_R) of various carbon black filled rubber compounds were measured over wide ranges of frictional work input (W_f) at ambient temperature. The rate of abrasion is determined by the average loss in weight per revolution of the disk and examined as a function of the amount of work expended in frictional sliding per unit area of surface and per revolution [11, 12]. The torque (M) is regarded as being due to two equal frictional forces (F) acting at the mean radius of the disk ($r_m = (r_o + r_i)/2$) on each half of the knife blade, where r_o and r_i are the outer and inner radii of the disk, 18.6 and 5.9 mm for the present disk. Thus,

$$F = M/2r_m \tag{1}$$

The work (W_f) done against friction per unit area and per revolution was obtained by

$$W_f = M/\left(r_o^2 - r_i^2\right) \tag{2}$$

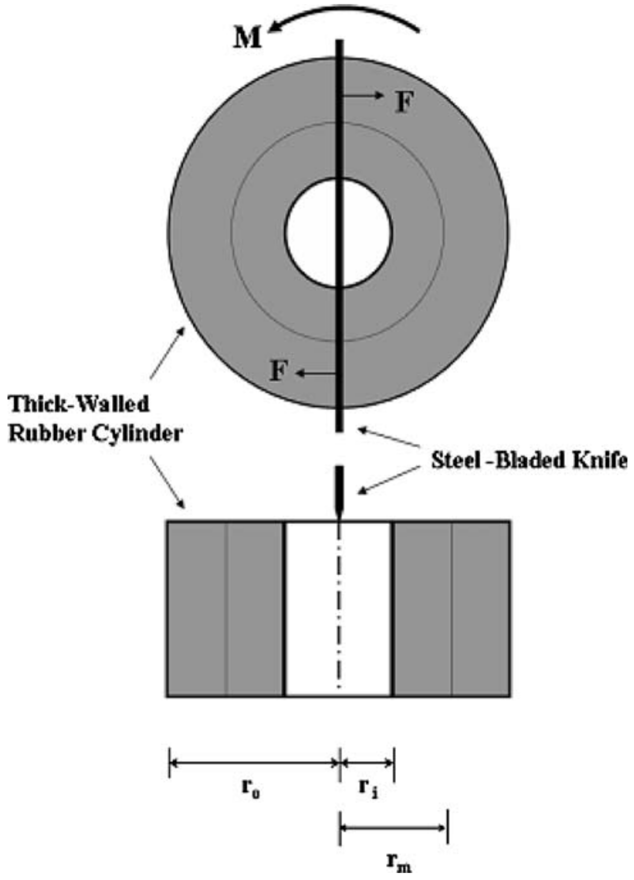
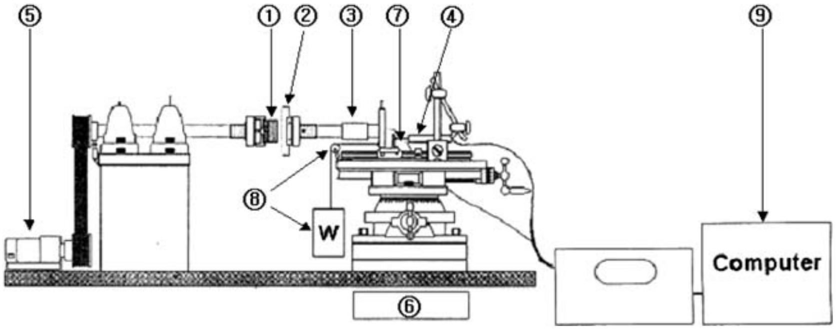


Fig. 3 A schematic of an abrasion test sample

Fig. 2 A schematic drawing showing a friction and abrasion tester for rubbery materials. 1, Rubber specimen; 2, knife blade; 3, strain gauges for measuring frictional torque; 4, potentiometer; 5, electric motor; 6, power regulator; 7, frictionless linear slider; 8, normal load application system; 9, strain amplifier and personal computer



The experimentally determined relationships [7] between abrasion rate (W_R) and frictional work (W_f) can thus be represented by the general result

$$W_R = k \cdot W_f^n \tag{3}$$

where the coefficient k and exponent n are characteristics of the particular material. The rates of wear depended strongly upon the frictional force exerted by the blade. A friction coefficient is described as

$$\mu = \frac{2F}{N} \tag{4}$$

where N is the normal force exerted to the sample. The normal forces applied in this study were 9.8, 19.6, 29.4 and 39.2 N to determine the rate of abrasion. With a new razor blade, initially the rate of wear was 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. It was reported that the sharpness of a knife-blade has little effect on rate of abrasion [13].

Results and discussion

Effects of carbon black on the Young's modulus

When carbon black is incorporated, its influence on the properties of the compound or the vulcanizate depends on its morphological parameters, such as the particle size and the surface area, as well as on the surface chemistry and the degree of dispersion of the carbon black in the rubber. The effect of carbon black on modulus is attributed to immobilization of part of the rubber by the carbon black, thus leading to an increase in the effective volume fraction of filler. This concept has been used by several authors [3, 5, 14, 15] to account for the effect of carbon black structure on viscoelastic properties. The volume of immobilized rubber can be calculated directly from viscoelastic measurements in rubber [16]. The effective volume fraction (V) of carbon black in rubber can also be determined from the DBP absorption value [15].

$$V = \Phi\left(\frac{1 + 0.081 \cdot \mathrm{CDBP}}{1.59}\right) \tag{5}$$

where Φ is the volume fraction of carbon black in a filled rubber compound and *CDBP* is the 24M4 (compressed carbon black) version of the DBP absorption value, as a basis for primary structure–property correlations. The 24M4 version is independent of the mechanical history of the carbon black experience during manufacturing [3]. Figure 4 shows the Young's modulus of carbon black filled rubbers as a function of the effective volume fraction. The modulus of filled rubber was considerably higher than those of gum compound. It was also seen that the transition from loose filler particles to a network at $V > 0.3$. The theoretical descriptions for the modulus enhancement by carbon black have been attempted. However, the modulus is higher than the theoretical expectation due to immobilized rubber or filler networking [14]. Because of the interaction between rubber and carbon black, the rubber molecules can be adsorbed on to the filler surface either chemically or physically. This is related to the restriction of the segmental movement of polymer molecules. The viscoelastic properties of the rubber, such as the viscosity of the uncured compounds and the hardness and modulus of the vulcanizates, are dominated by the carbon black structure and also by the surface area [5]. However, the effective volume fraction of carbon black is calculated just from the structure. Therefore, a characteristic parameter (Ψ), obtained from the surface area and the structure of carbon black, is introduced in this study,

$$\Psi = \sqrt{N_2^2 + \mathrm{CDBP}^2} \tag{6}$$

where N_2 is the nitrogen adsorption on the surface of carbon black. Figure 5 shows the Young's moduli of carbon black filled rubbers as a function of the characteristic parameters of various types of carbon blacks. The Young's modulus increased with increasing the characteristic parameter of carbon black. It shows a

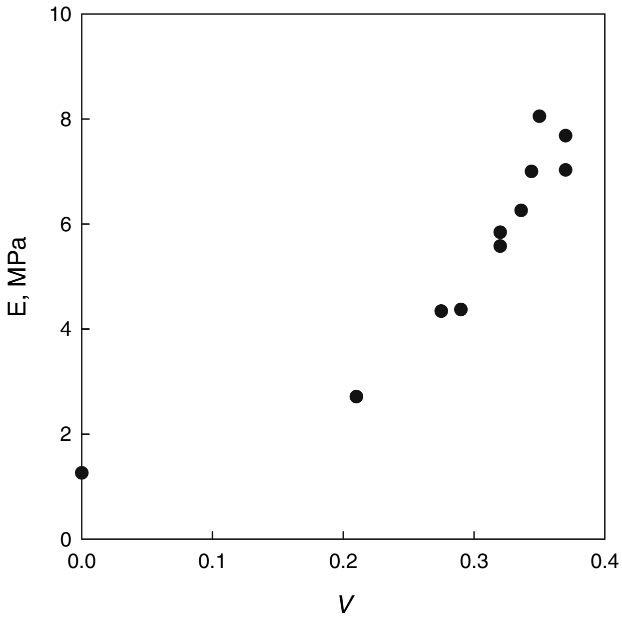


Fig. 4 Young's modulus as a function of the effective volume fraction (V) for carbon black filled NR compound

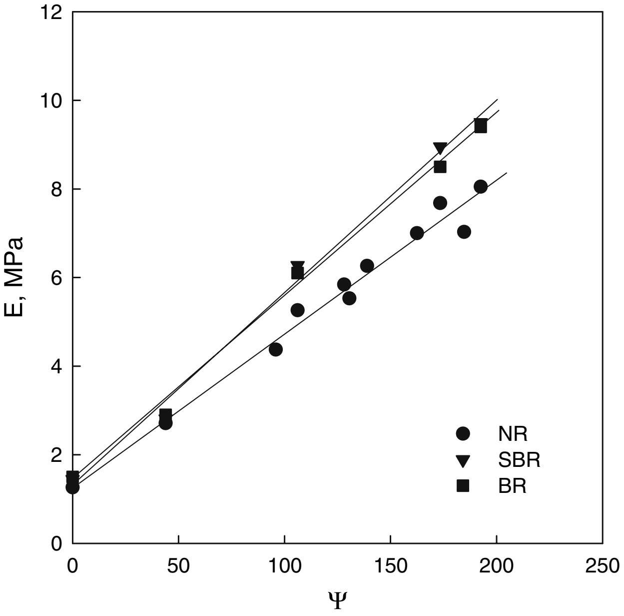


Fig. 5 Young's modulus as a function of Ψ for NR, SBR and BR compounds mixed with various types of carbon blacks

linear relationship between the Young's modulus and the characteristic parameter of carbon blacks.

$$E = A + B\Psi \tag{7}$$

where A and B are constant. The values were A = 1.26, B = 0.035 for NR, 1.30, 0.044 for SBR, and 1.38, 0.042 for BR, respectively. It was observed from the slope that SBR and BR were more sensitive to carbon black loading than NR. The smaller the particle size and the more developed structure of carbon black, the greater reinforcing effect on the Young's modulus.

Effects of carbon black on abrasion properties

The particle size of carbon black has a great effect on the physical properties of filled rubber compounds. For investigation of the particle size effects on abrasion resistance, the carbon blacks used in this study were arranged in order by particle size, N103 < N351 < N550 < N990. The particle size was inversely proportional to the surface area. N103 has the smallest particle size and was expected to give the best reinforcing effect to the rubber compound. Figure 6 shows the frictional coefficients as a function of the normal force for SBR compounds filled with various sizes of carbon blacks. The frictional coefficient increased with decreasing the particle size of the carbon black and decreased with increasing applied normal force. Also, the structure of the filler has a significant effect on the frictional coefficient of filled rubber. Figure 7 shows the frictional coefficient as a function of the normal force for SBR compounds filled with carbon blacks having different structures. It showed that the structure dominates the frictional coefficient. The frictional coefficient of the rubber compounds depend greatly on the particle size, but also on the structure. The particle size of the filler affects the interaction with elastomer, and the structure of the filler

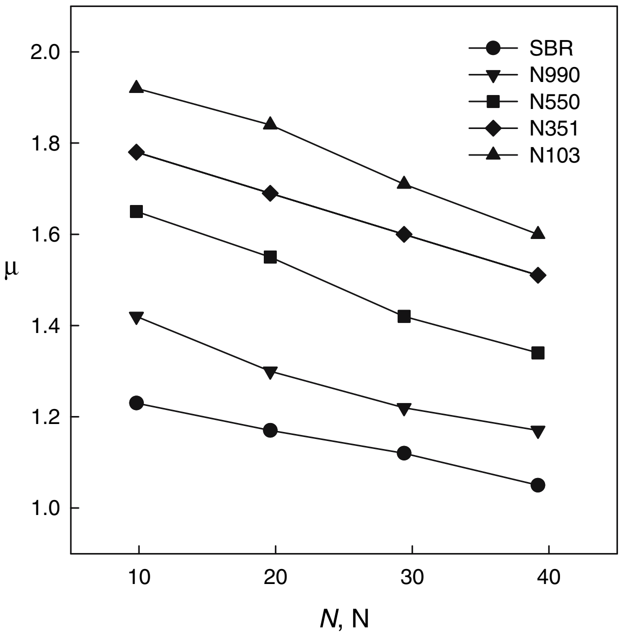


Fig. 6 Frictional coefficient as a function of the normal force for SBR compounds filled with various sizes of carbon blacks

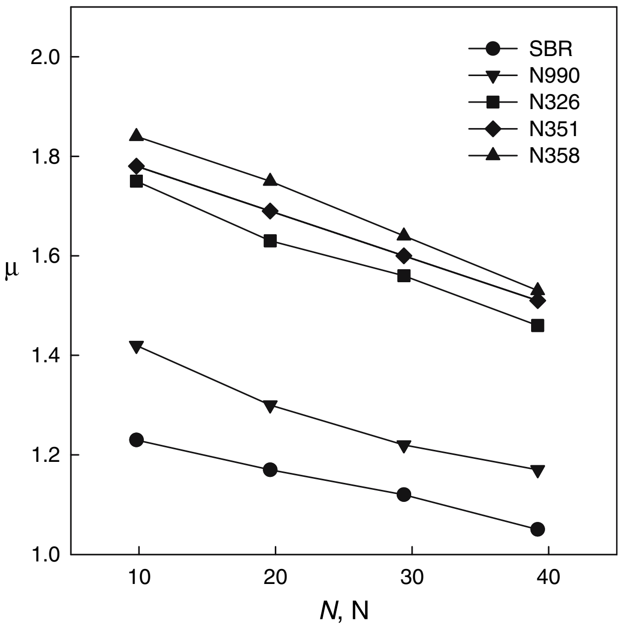


Fig. 7 Frictional coefficient as a function of the normal force for SBR compounds filled with various structures of carbon blacks

affects polymer movement under deformation [17]. It was reported that, in friction behavior of carbon black filled compounds, the filler broadens distribution of relaxation time and the true contact area is smaller than unfilled rubber because of their greater hardness [8].

The measured wear rates were plotted in Figs. 8 and 9 against the frictional work input for SBR compounds filled with various sizes and the structures of carbon blacks, using logarithmic scales for both axes. The filled compounds with carbon black were more resistant to abrasion. The rates of abrasion decreased with increasing the surface area and structure of carbon black. The particle size and the structure of carbon black has a significant effect on the wear rates and the worn surface pattern, and the effect of them on abrasion resistance should be considered for the optimum design of desired wear properties. The improvement in abrasion resistance is identified as a reinforcement effect of the carbon black addition to the rubber. The wear rates depend strongly upon the frictional force exerted by the blade. It shows that rates of abrasion of the compounds are found to be proportional to a power *n* of the applied frictional work input. The exponent is characteristic of the particular material being examined [7] and, for unfilled SBR in this study, it was found to be about 2.58. Exponents for the carbon black filled SBR were considerably smaller, 1.82–2.10 given in Table 2, corresponding to a lesser dependence of the rate of wear upon the frictional force. However, it was seen that the values of exponents were not greatly different for the various carbon black filled SBR compounds.

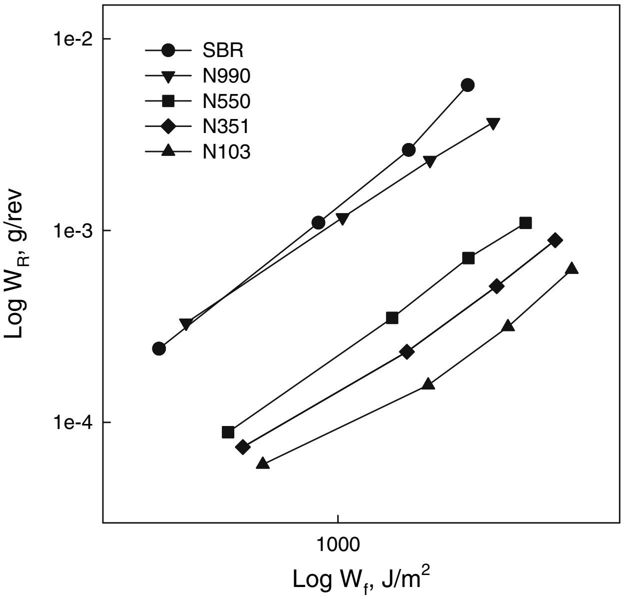


Fig. 8 Wear rates versus frictional work input for SBR compounds filled with various sizes of carbon blacks

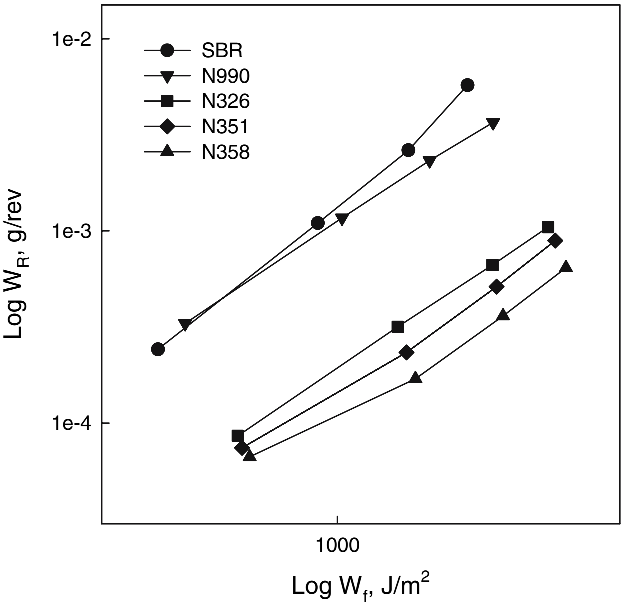


Fig. 9 Wear rates versus frictional work input for SBR compounds filled with various structures of carbon blacks

Figure 10 shows the comparison of frictional coefficients among NR, SBR and BR compounds mixed with N103. SBR compounds had higher values of frictional coefficients than NR and BR compounds. The differences in frictional coefficients could be dependent on differences in hardness. The wear rates of NR, SBR and BR compounds mixed with N103 is shown in Fig. 11 as a function of the frictional work input. It is seen that BR compounds caused much slower wear than NR and SBR compounds. Abrasion of rubber involves both tearing and general decomposition of the molecular network [7]. Incorporation of carbon black in the rubber compound increases the stiffness and strength of rubber and thereby suppresses tearing failures, so that mechanochemical attack then becomes the principal mode of wear in materials, like NR and SBR, that are susceptible to decomposition by this mechanism. Radicals formed in BR 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 radicals formed in SBR and NR react with oxygen, causing decomposition. Carbon black filled

Table 2 Exponent *n* values of filled SBR compounds

Carbon black	Exponent
Pure rubber	2.58
N990	2.02
N326	2.07
N550	2.10
N351	2.03
N358	1.82
N103	1.89

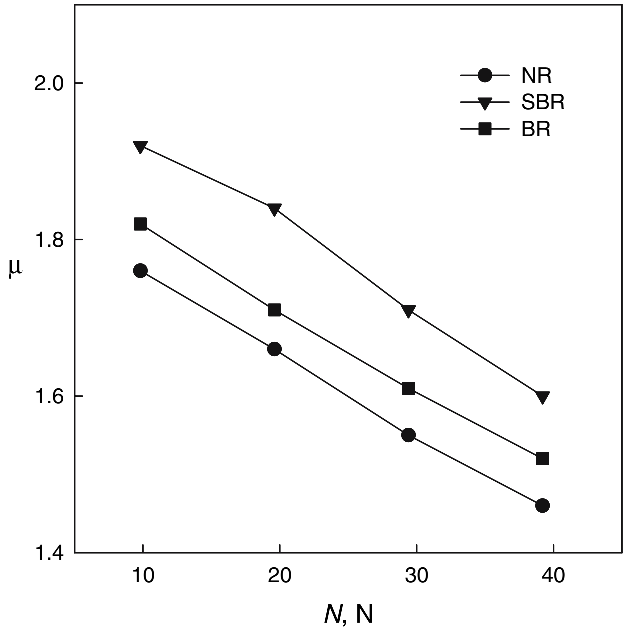


Fig. 10 Comparison of frictional coefficient among NR, SBR and BR compounds mixed with N103

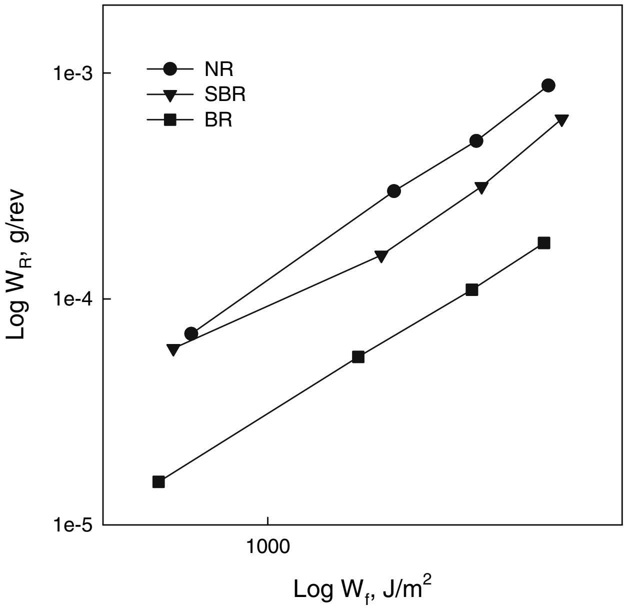


Fig. 11 Comparison of wear rates among NR, SBR and BR compounds mixed with N103

compounds of SBR and NR produced sticky, oily debris during abrasion in air, while carbon black filled BR compounds did not. Thus the occurrence of smearing seems to depend on the chemical nature of the rubber. This result could be an evidence for chemical deterioration. Figure 12 represents the rates of abrasion as a function of the characteristic parameters of carbon blacks in NR, SBR and BR compounds at a friction energy of 1,000 J/m^2/rev. The wear rates of filled BR compounds were much less sensitive to the characteristic parameters of carbon blacks. The abrasion rates were inversely proportional to the characteristic parameters. Therefore, it is concluded that smaller particle size and better structure development of carbon black resulted in improved abrasion resistance of the filled rubber compound.

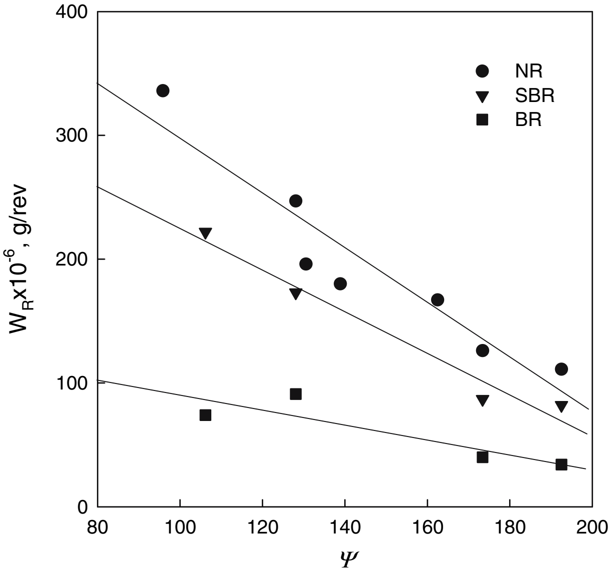


Fig. 12 Wear rates as a function of the characteristic parameters of carbon black filled NR, SBR and BR compounds at 1,000 J/m^2/rev

It is very important for the study of abrasion resistance to examine the worn surface of the rubber compounds. Abrasion of rubber in a constant direction leads to the formation of a characteristic surface pattern. Figure 13 shows the worn surface of the SBR compounds containing N358 at various frictional forces. 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. As abrasion proceeds, edges of abraded regions were bent over backwards by the frictional force and then protect the surface lying immediately behind them from further abrasion [11]. Abrasion becomes concentrated at the foot of ridges lying perpendicular to the sliding direction. The ridges were larger and more widely spaced by larger frictional forces. The worn surfaces of the SBR compounds containing various carbon blacks at a frictional force of 29.4 N are given in Fig. 14. The worn surfaces of N103 and N358 filled compounds showed narrower spaced ridges and better abrasion resistance because of the smaller particle size of N103 and the more developed structure of N358. The compounds with N550 having bigger particle size and N326 having lower developed structure showed worse abrasion resistance. Figure 15 shows the worn

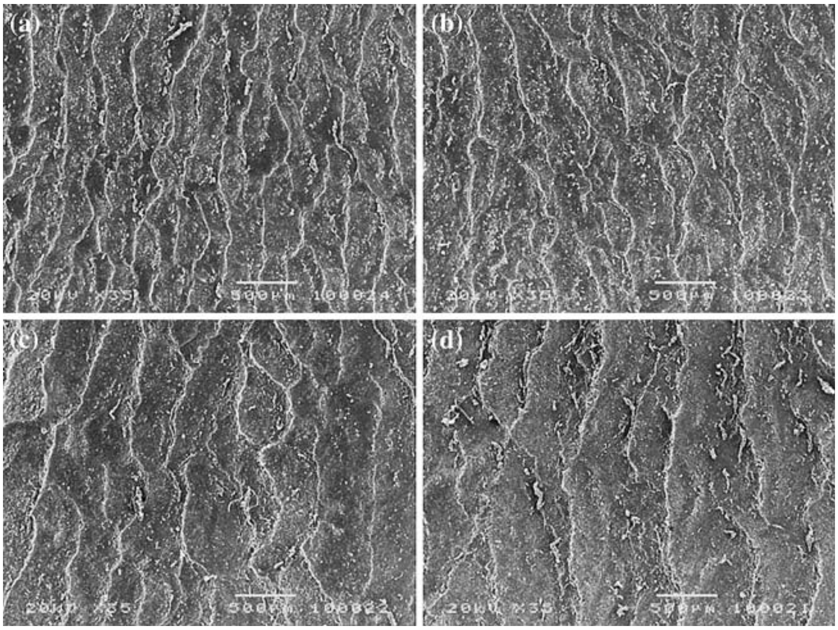


Fig. 13 Worn surfaces of the SBR compounds containing N358 at various frictional forces (**a**) 9.8 N, (**b**) 19.6 N, (**c**) 29.4 N and (**d**) 39.2 N

surfaces of NR, SBR and BR compounds. It was observed that the surfaces of NR and SBR compounds exhibited smearing. Smearing may be caused by decomposition due to thermal and oxidative effects [7]. The worn surface of BR compound showed different abrasion pattern.

Conclusion

In this study, a modified blade abrader was constructed and the effects of the particle size and the structure of various carbon blacks on friction and abrasion rates of filled NR, SBR and BR compounds were investigated. The characteristic parameter was introduced from the particle size and the structure of carbon black and the relation with the rate of abrasion was examined. There was a linear relationship between the Young's modulus and the characteristic parameter of carbon blacks. The smaller the particle size and the higher the structure of carbon black, the greater was the reinforcing effect on the Young's modulus. The frictional coefficient depends on the particle size, but also on the structure of carbon black. The rates of abrasion decreased with increasing the surface area and with developing the structure of carbon black. The wear rates depend

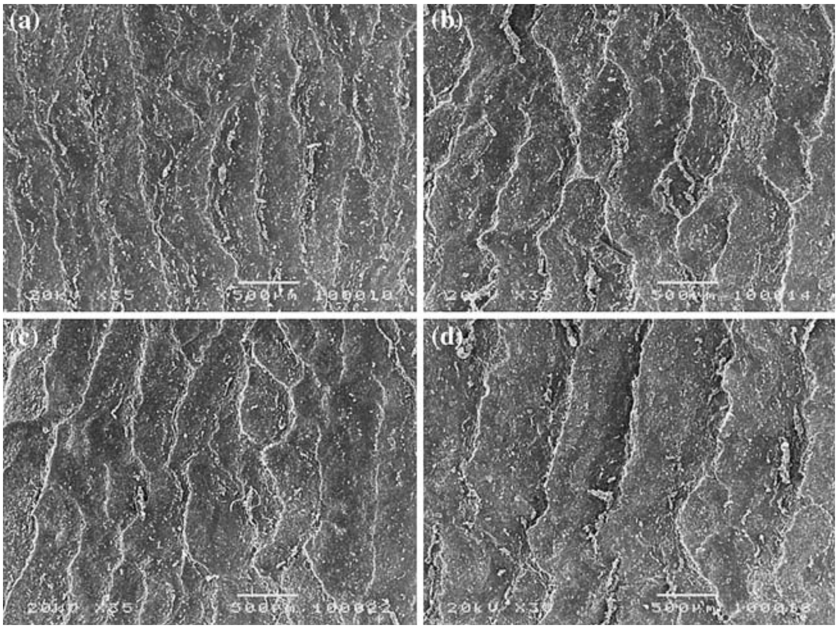


Fig. 14 Worn surfaces of the SBR compounds containing various carbon blacks at a frictional force of 29.4 N. (**a**) N103, (**b**) N550, (**c**) N358 and (**d**) N326

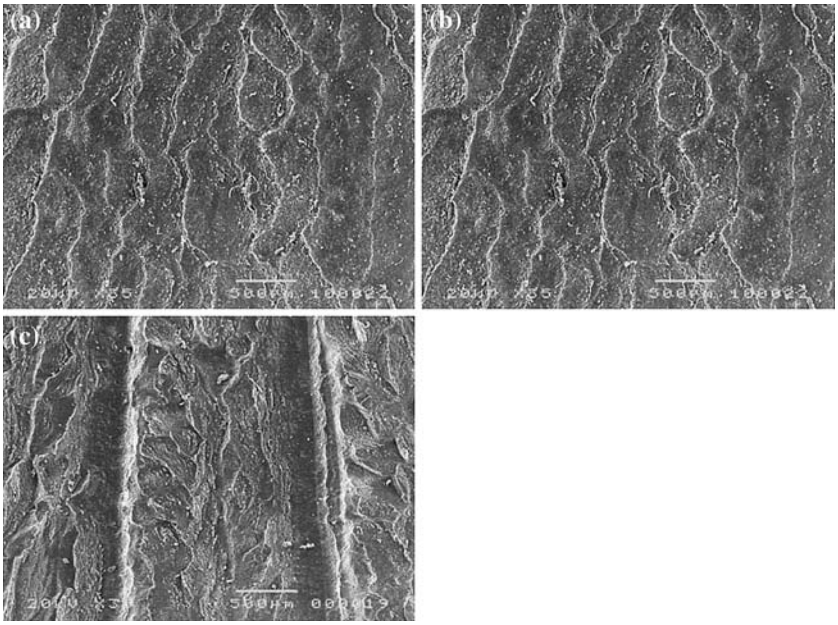


Fig. 15 Worn surfaces of the (**a**) NR, (**b**) SBR and (**c**) BR compounds containing N358 at a frictional force of 29.4 N

strongly upon the frictional force exerted by the blade. It was observed that rates of abrasion of the compounds were found to be proportional to a power *n* of the applied frictional work input. BR compounds caused much slower wear than NR and SBR compounds. Radicals formed in BR by main-chain rupture were known to react with the polymer itself, leading to further crosslinking rather than to decomposition. On the other hand, the radicals formed in SBR and NR react with oxygen, causing decomposition. The ridges of worn surfaces were larger and more widely spaced by larger frictional forces. The worn surfaces of the rubber compounds filled with smaller particle size and more developed structure of carbon black showed narrower spaced ridges and better abrasion resistance.

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