

Rubber Abrasion Resistance

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1. Introduction

Abrasion resistance is the ability of a material to resist mechanical action such as rubbing, scraping, or erosion that tends progressively to remove material from its surface. When a product has abrasion resistance, it will resist erosion caused by scraping, rubbing, and other types of mechanical wear. This allows the material to retain its integrity and hold its form. This can be important when the form of a material is critical to its function, as seen when moving parts are carefully machined for maximum efficiency. Abrasion resistant materials can be used for both moving and fixed parts in settings where wearing could become an issue.

The substances usually called "rubber" immediately brings to mind materials that are highly flexible and will snap back to their original shape after being stretched. In fact, there are three structural requirements for a given substance to be a rubber (i) rubber is made up of a polymer chain, liner or branched; (ii) the chain is flexible; and (iii) the chain is longer than a certain threshold length. Because the rubber is compliant and tough, it can easily absorb and survive a single strike of large deformation. However when used in contact with moving parts, a process of micro-tearing can occur on the rubber surface around the sharp asperities, gradually removing the material and finally terminating the functional life of the rubber. In many applications, abrasive wear is the major failure mode of rubbers. In normal materials, a rough surface is made smooth by repeated friction or abrasion with harder materials. Rubber hardly ever slides on other rubber like materials but on tracks grossly dissimilar from it in surface texture, chemical constitution and elastic behavior, however, when the smooth surface is abraded, periodic parallel ridged patterns, looking like a wind-wrought pattern on sand, are formed on the rubber surface. These typical patterns are held through all processes of rubber abrasion, on the surface of tires, conveyor belts, printing rolls and shoes for example, which are thus regarded as the essential basis of rubber abrasion.

Abrasion process involves removal of small particles ($1\text{-}5 \mu\text{m}$) leaving behind pits in the surface and then followed by removal of large particles ($> 5 \mu\text{m}$) (El-Tayeb & Nasir, 2007). Detachment of small particles plays an important role in initiating the abrasion (Muhr & Roberts, 1992) and this is related to either a structural unit or localized stresses in the rubber. Since abrasion is clearly a manifestation of mechanical failure, Shallamach (Schallamach, 1557/58, 1968) used tearing energy to describe the rubber wear mechanisms, and Ratner et al. (Ratner et al., 1967) has established an equation in which the wear loss is related to macroscopic mechanical properties such as tensile strength, elongation at break, hardness etc. Thomas (Thomas, 1958, 1974) proposed the problem of abrasion is presented using fracture mechanics which treats fatigue and tensile failure as crack growth processes from

small flaws. Crack growth can be influenced by the presence of oxygen or ozone. The nature of the vulcanizing system affects strength: crosslinks probably rupture and reform under stress. Other suggested factors responsible for particle detachment are internal subsurface failure due to flaws in the rubber such as dirt or voids (Gent, 1989) or interfacial adhesion at high speed rolling (Roberts, 1988). According to Pandey et al. (Pandey et al., 2003), there is no distinction between wear and abrasion, although other researcher (Schallamach, 1957/58) defined abrasion as that produced by laboratory machine on a rubber piece and wear as something that happens to tires or other rubber products. Thus, for rubber, "abrasion" covers all mechanisms, whereas the word "abrasion" for other materials refers in particular to scoring by hard, sharp particles. In the absence of transient effects such as clogging of the abrasive or evolution of an abrasion pattern it is found that the quantity of rubber abraded is proportional to the distance of sliding between rubber and counterpart. However, wear of tires and abrasion on certain laboratory abrasion machines (e.g. the Akron abrader) brings into play gross properties of tire or test piece which affect the rate of wear just as much as does the abrasion resistance of the compound. However, Muhr and Roberts (Muhr & Roberts, 1992) proposed that abrasion reserves for processes where the amount of sliding is controlled, and that wear applies to the many practical situations for which the amount of sliding is as significant a variable as the attrition per unit sliding distance.

Schallamach (Schallamach, 1957/58, 1968) defines abrasion of rubber as a purely mechanical failure produced frictionally by the asperities of the track and this process creates periodic structures often called "abrasion pattern", a series of parallel ridges perpendicular to the sliding direction created on the surface of rubber during abrasive wear. He proposed the mechanism of rubber abrasion from a fracture mechanics point of view, relating the rate of wear to the crack growth resistance of the rubber. Although the concept of crack growth plays a very important role in abrasion, particularly in the growth of a single ridge, when we consider that the essential subject of rubber abrasion is in the formation of the periodic surface pattern consisting of very many cracks, moreover abrasive wear is a consequence of friction, in other words, it is impossible for any abrasive transfer of material to occur without friction phenomena. As is well known, an abrasion pattern is formed at the initial stage of abrasion and grows in ridge spacing and ridge height, whose geometric feature remains constant in appearance once it has grown up to the critical size. The abrasion pattern moves very slowly along in the sliding direction in a manner that the crack at the root of the pattern wedge is deepened somewhat and the protruding flap is torn off.

When rubber is slid over another abrasive surface, contact of abrasive grits (asperities) occurs. Upon application of a normal load, the extremely low tensile modulus of rubber ensures extensive deformation to establish a conformal contact with the counter part. This causes the real area of contact to become comparable to the apparent area of contact. Owing to the curved and entangled structure of chains of molecules in rubber, they can undergo considerable lateral deformation without fracture by stretching and twisting of chains. Gent (Gent, 1989) proposed a hypothetical mechanism for creating subsurface cracks during frictional sliding as part of the process of abrasive wear of rubber. It consists of the unbounded elastic expansion of microscopic precursor voids until they burst open as cracks, under the action of internal pressure or of a triaxial tension in the surrounding rubber. This conjecture accounts for enhanced resistance to abrasion for compounds reinforced with carbon black, in terms of increased stiffness without much loss of extensibility, and for the

lack of correlation of abrasion resistance with other measures of strength. It should be noted that it is specific to soft, extensible materials, and thus it also accounts for marked differences in the nature of the wear process in rubbery materials compared to plastics and metals. Only rubbery materials appear to abrade away by a linking up of microcracks at right angles to the sliding direction to produce characteristic wear ridges known as the Schallamach abrasion pattern. Three mechanisms of generating a sufficiently large inflation pressure or triaxial tension are discussed. The most probable one seems to be thermal decomposition of rubber, generating volatile decomposition products a microscale blowout process. This would be aggravated by a simultaneous softening of the rubber on heating. Although strictly conjectural, it would be helpful to know whether the character of wear changes when abrasion is carried out under a large superimposed hydrostatic pressure. Sliding contact generates a shear stress along the surface of rubber and extensive shear stress along the stress axis is found to occur owing to the nature of elastomer (Chandrasekaran & Batchelor, 1997). When the shear stress exceeds the cohesive strength of the chain, fracture occurs by propagation of crack along the root of the contact area. The sudden release of deformation energy in the form of fracture in the contact area surface results in recovery of rubber to original coiled and entangled state. The visco-elastic nature of rubber limits the rate of recovery which results in shear wave propagation along the surface of rubber during sliding. Fukahori and Yamazaki (Fukahori & Yamazaki, 1994) proposed a new concept to understand the mechanism of formation of the periodic patterns characteristic in rubber abrasion. They showed that the driving force to generate the periodic surface patterns, and thus rubber abrasion consist of two kinds of periodic motion, stick-slip oscillation and the microvibration generated during frictional sliding of rubber. The stick-slip oscillation is the driving force to propagate cracks, then abrasion patterns and the microvibration with the natural frequency of the rubber induced in the slip phase of the stick-slip oscillation is another driving force for the initiation of the cracks. Although initial cracks originate in the slip region of the rubber surface, the propagation of the cracks is strongly excited in the stick region. Accordingly, the initial size of the abrasion pattern, pattern spacing, equals the distance determined by the natural period of the rubber and the sliding velocity while the constant pattern spacing after the critical number of frictional slidings agrees with the distance given by the period of the stick-slip oscillation and the sliding velocity. Consequently, during rubber abrasion, two driving forces produce bimodal size distribution of abraded particles, small particles of the order of ten micrometres by microvibrations and large ones of the order of a few hundred micrometres by the stick-slip motions. Sliding of rubber with high frictional forces does not necessarily entail abrasion (as it does for metal-metal contacts). Rather, abrasion of rubber results from mechanical failure due to excessively high local frictional stresses which are most likely to occur on rough tracks.

In spite of its practical importance, abrasion is perhaps the least understood phenomena amongst the various types of failures of rubber, as it is difficult to predict the abrasion behaviour from other rubber properties (Pandey et al., 2003). It is influenced by the hysteresis properties of the vulcanizates, magnitude of the frictional force and the resistance of rubber to rupture. The abrasion is a combination of mechanical, mechanochemical and thermochemical processes. The formation of an abrasion pattern depends on several factors such as crack growth process (Uchiyama and Ishino, 1992), mechanical properties of the rubber, and on the chemical, ageing and thermal conductivity properties of the composite. It depends on the modulus of elastomer, the abrasion pattern may be characterized by either

ridges at the right angles to the rubbing direction if the modulus of elastomer is sufficiently low or score lines parallel to the rubbing direction if the modulus of elastomer is sufficiently high (Evstratov et al., 1967). There are a number of ways to make a material resistant to abrasion. One option is to utilize a special coating which creates a hardened layer over the material and resists friction. Some materials are also naturally extremely hard, and are ideal for settings in which abrasion resistance will be desirable. Other materials can be specifically formulated for increased hardness, as seen in plastics facilities which manufacture abrasion resistant plastics with the use of chemicals which harden and strengthen the plastic. The properties of a vulcanized rubber can be significantly influenced by details of the compounding. Practical materials will have, in addition to the base polymer, fillers, anti-degradants, crosslinking agents, accelerators etc. All of these can have an influence on the physical and chemical stability of the finished material.

2. Rubber use

2.1 Compounding

The rubber industry began when Charles Goodyear developed the first useful rubber compound: natural rubber plus sulfur. The concept of mixing materials into rubber to improve performance is still primary importance today. Without compounding, few rubbers would be of any commercial value. Any given rubber application will have a long list of necessary criteria in addition to cost, encompassing appearance, processing, mechanical, electrical, chemical, and thermal properties. Developing such compounds requires a broad knowledge of material science and chemistry combined with experience. The use of designed experiments can greatly facilitate selecting the optimum compound formulation.

The major components in a compound are rubber, vulcanizing agents, fillers, plasticizers, and antidegradants.

2.2 Rubber

Rubber is polymeric material endowed with the properties of flexibility and extensibility: with the application of force, the molecules straighten out in the direction in which they are being pulled; on release from being extended, they spontaneously recover their normal, random arrangements. Rubbers include natural rubber, a naturally occurring substance obtained from the exudations of certain tropical plants, and synthetic rubbers, artificially derived from petrochemical products. Among the most important synthetics are styrene-butadiene, polybutadiene, and polyisoprene (commonly classified as the "general purpose"), as well as ethylene-propylene rubber (often referred to as "specialty rubber"). The prices of these synthetics have been historically in the range of natural rubber prices and their markets have, although to varying degrees, overlapped those of natural rubber. Synthetic rubbers are materials with distinctive chemical structures, whereas the emphasis with natural rubber lies on different types and grades within one single broad category.

2.2.1 Natural rubber

Natural rubber (polymer designation cis-1-4 polyisoprene, empirical formula $(C_5H_8)_n$) obtained from the sap (latex) of several rubber-yielding plants (e.g. Hevea Brasiliensis and

Parthenia argentatum) by coagulation with chemicals, drying, electrical coagulation, and other processes is the prototype of all elastomers. Latex extracted in the form of latex from the bark of the Hevea tree is a polydispersed colloidal system of rubber particles in an aqueous phase. With Hevea latex, the dry rubber content varies between approximately 28-40%, although it may rise to 45-50% after a long period of non-tapping (notice that, for statistical purposes, figures for natural rubber may include the dry rubber content of latex). The rubber produced from latex contains, besides the hydrocarbon, relatively small quantities of protein, carbohydrates, resin-like substances, mineral salts, and fatty acids.

The natural rubber polymer is nearly 100% cis-1,4 polyisoprene with M_w ranging from 1 to 2.5×10^6 . Due to its high structural regularity, natural rubber tends to crystallize spontaneously at low temperatures or when it is stretched. Low temperature crystallization causes stiffening, but is easily reversed by warming. The strain-induced crystallization gives natural rubber products outstanding resilience, flexibility, and tear and tensile strength, as well as low heat build-up and abrasion. However, a drawback is natural rubber moderate environmental resistance to factors such as oxidation and ozone; so too for its scarce resistance to chemicals, including gasoline, kerosene, hydraulic fluids, degreasers, synthetic lubricants, and solvents. In addition, latex contains proteins that can cause severe allergic response in a small percentage of the population and among medical professionals following extensive exposure. The largest use of natural rubber is in the tires. Over 70 percent of its manufacture consumption is in this area. The next largest use is as latex in dipped goods, adhesives, rubber thread, and foam. These uses account for approximately another 10 percent. The remainder is used in a variety such as convey or belts, hoses, gaskets, footwear, and antivibration devices such as engine mounts.

2.2.2 Polyisoprene

Synthetic polyisoprene is designed to be similar to natural rubber in structure and properties. Although it still demonstrates lower green strength, slower cure rates, lower hot tear, and lower aged properties than its natural counterpart, synthetic polyisoprene exceeds the natural types in consistency of product, cure rate, processing, and purity. In addition, it is superior in mixing, extrusion, molding, and calendering processes. The lithium based polymers were found to produce up to 94 percent cis, which still was not high enough to provide the properties of natural rubber. Polymers made with the coordination catalysts have cis contents of up to 98 percent, providing products that can more closely serve as replacements for natural rubber than the lithium-based polymers. In comparison with natural rubber, they offer the advantage of a more highly pure rubber (no non-rubber material) and excellent uniformity. A high trans-1,4 structure was produced by Polysar, and is now being produced by Kuraray. A Li-IR with increased 3,4 structure can be prepared by adding polar modifiers to the alkyl lithium catalyst system. However, since the higher cis-1,4 configuration most closely mirrors the properties of natural rubber and is the most important commercially. Currently synthetic polyisoprene is being used in a wide variety of industries in applications requiring low water swell, high gum tensile strength, good resilience, high hot tensile, and good tack. Gum compounds based on synthetic polyisoprene are being used in rubber bands, cut thread, baby bottle nipples, and extruded hose. Carbon black loaded compounds find use in tires, motor mounts, pipe gaskets, shock absorber bushings and many other molded and mechanical goods. Mineral filled systems

find applications in footwear, sponge, and sporting goods. In addition, recent concerns about allergic reactions to proteins present in natural rubber have prompted increased usage of the more pure synthetic polyisoprene in some applications.

2.2.3 Styrene-butadiene rubber

The largest-volume synthetic rubber consumed is styrene-butadiene rubber (SBR) produced by both emulsion (E-SBR) and solution (S-SBR). In 2003, SBR solid rubber accounted for 4 percent of all synthetic rubber. If SBR latex and carboxylated SBR latex are included, its share increases to 55 percent. The major application of solid SBR is in the automotive and tire industry, accounting for approximately 70 percent of the use. Therefore, SBR has been tightly tied to the tire business.

Most of the E-SBR contains about 24% by weight of styrene and it is a random copolymer with butadiene. Some specific grades contain as much as 40-46% styrene, and are much stiffer. The polymerization is by free radical initiator and there is a finite probability of chain-transfer reaction, which generates long branches.

Emulsion polymerization is carried out either hot, at about 25-50°C, or cold, at about 5-25°C, depending upon the initiating system used. SBR made in emulsion usually contains about 24% styrene randomly dispersed with butadiene in the polymer chains. At high temperature polymerization, many long-braches and gels were formed. The rubber was stiff and difficult to mill, mix, or calender than natural rubber, deficient in building tack, and having relatively poor inherent physical properties. Processability and physical properties were found to be greatly improved by the addition of process oil and reinforcing pigments. Polymerization at a lower temperature became possible, giving less branches and gels. "Cold" SBR generally has a higher average molecular weight and narrower molecular weight distribution. It thereby offers better abrasion and wear resistance plus greater tensile and modulus than "hot" SBR. Since higher molecular weight can make cold SBR more difficult to process, it is commonly offered in oil-extended form. S-SBR comes in two distinctly different subgroups, one made by an anionic initiator and the other by free radical initiators. SBR made in solution contains about the same amount of styrene, but both random and block copolymers can be made. Solution SBR can be tailored in polymer structure and properties to a much greater degree than their emulsion counterparts. The random copolymers offer narrower molecular weight distribution, low chain branching, and lighter color than emulsion SBR. They are comparable in tensile, modulus, and elongation, but offer lower heat buildup, better flex, and higher resilience. Certain grades of solution SBR even address the polymer's characteristic lack of building tack, although it is still inferior to that of natural rubber. The processing of SBR compounds in general is similar to that of natural rubber in the procedures and additives used. SBR is typically compounded with better abrasion, crack initiation, and heat resistance than natural rubber. SBR extrusions are smoother and maintain their shape better than those of natural rubber. SBR was originally developed as a general purpose elastomer and it still retains this distinction. It is the largest volume and most widely used elastomer worldwide. Its single largest application is in passenger car tires particularly in tread compounds for superior traction and tread wear. Substantial quantities are also used in footwear, foamed products, wire and cable jacketing, belting, hoses, and mechanical goods.

2.2.4 Polybutadiene rubber

Polybutadiene rubber (BR) was originally made by emulsion polymerization, generally with poor results. It was difficult to process and did not extrude well. This rubber became commercially successful only after it was made by solution polymerization using stereospecific Ziegler-Natta catalysts. This provided a polymer with greater than 90% cis-1,4-polybutadiene configuration. This structure hardens at much lower temperatures (with T_g of -100°C) than natural rubber and most other commercial rubbers. This gives better low temperature flexibility and higher resilience at ambient temperatures than most rubbers. Greater resilience means less heat buildup under continuous dynamic deformation as well. This high-cis BR was also found to possess superior abrasion resistance and a great tolerance for high levels of extender oil and carbon black. High-cis BR was originally blended with natural rubber simply to improve the latter's processing properties, but it was found that the BR conferred many of its desirable properties to the blend. The same was found to be true in blends with SBR.

The 1,3-butadiene monomer can polymerize in three isomeric forms: by cis 1,4 addition, trans 1,4 addition, and 1,2 addition leaving a pendant vinyl group. By selection of catalyst and control of processing conditions, polybutadiene is now sold with various distributions of each isomer within the polymer chain, and with varying levels of chain linearity, molecular weight and molecular weight distribution. Each combination of chemical properties is designed to enhance one or more of BR's primary attributes.

The major use of polybutadiene (cis-1,4-BR) having a very low glass transition temperature in the region -75°C to -100°C is in tires, with over 70 percent of the polymer produced used by the tire industry, primarily in blends with SBR or natural rubber to improve hysteresis (resistance to heat buildup), abrasion resistance, and cut growth resistance of tire treads. The type of BR used depends on which properties are most important to the particular compound. High-cis and medium-cis BR have excellent abrasion resistance, low rolling resistance, but poor wet traction. High-vinyl BR offer good wet traction and low rolling resistance, but poor abrasion resistance. Medium-vinyl BRs balance reasonable wet traction with good abrasion resistance and low rolling resistance. Polybutadiene is also used for improved durability and abrasion and flex crack resistance in tire chaffer, sidewalls and carcasses, as well as in rubber blends for belting. High- and medium-cis BRs are also used in the manufacture of high impact polystyrene. Three to twelve percent BR is grafted onto the styrene chain as it polymerizes, conferring high impact strength to the resultant polymer.

Polybutadiene made by emulsion polymerization with a free radical initiator is used as the rubber component of an impact modifier in plastics, in particular high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene resin (ABS). In the HIPS application the rubber is dissolved in the styrene monomer, which is then polymerized via a free-radical mechanism. A complex series of phase changes occurs, resulting in small rubber particles containing even smaller polystyrene particles being incorporated into a polystyrene matrix. The rubber is added to increase impact strength. Because of the unique morphology that is formed, low levels of rubber (typically around 7%) provide rubbery particles having a volume fraction of 30-40 percent. This morphology leads to high impact at very low rubber levels, providing good stiffness and hardness.

There is also a fairly large market for high cis BR in solid core golf balls. In this application, the polymer is compounded with zinc acrylate and the mixture is cured with peroxide. This produces an ionically cross-linked compound that has outstanding resilience. The covers are also ionomers with superior cut resistance. In the last few years the golf ball market has been shifting away from the traditional wound ball to these new solid core balls that use polybutadiene.

2.2.5 Nitrile rubber

Acrylonitrile butadiene rubber (NBR) is made as an emulsion with a free radical initiator. Polymers are made with an acrylonitrile (AN) content of, for example, 28, 33 or 40 weight percent, depending upon the required oil resistance. It also has good elongation properties as well as adequate resilience, tensile and compression set. The major applications for this material are in areas requiring oil and solvent resistance. As the acrylonitrile content increases in the polymer chain, the properties change predictably. The glass transition temperature increases approximately 1.5°C for each percent increase in acrylonitrile. Properties such as hysteresis loss, resilience, and low-temperature flexibility will correspondingly change. The oil resistance increases with increased acrylonitrile content, as does the compatibility with polar plastics such as PVC. The major market for nitrile rubber is in the automotive area because of its solvent and oil resistance. Major end uses are for hoses, fuel lines, O-rings, gaskets, and seals. In blends with polyvinyl chloride (PVC) and acrylonitrile butadiene styrene (ABS), nitrile rubber acts as an impact modifier. Some nitrile rubber is sold in latex form for the production of grease-resistant tapes, gasketing material, and abrasive papers. Latex also is used to produce solvent resistant gloves.

Hydrogenated NBR (HNBR) is produced by first making an emulsion-polymerized NBR using standard technique. Almost all the butadiene units become saturated to produce an ethylene-butadiene-acrylonitrile terpolymer. These "post-polymerization" reactions are very expensive so HNBR usually command a premium price. HNBR is usually cured with peroxides, similar to ethylene-propylene rubber, because it has no unsaturation for a conventional sulfur cure system. HNBR has many uses in the oil-field, including down hole packers and blow-out preventers, because of its outstanding oil resistance and thermal stability. For the same reasons, it has also found uses in various automotive seals, O-rings, timing belts, and gaskets. Resistance to gasoline and aging make HNBR ideal for fuel-line hose, fuel-pump and fuel injection components, diaphragms, as well as emission-control systems. HNBR is the best selection to achieve to the highest abrasion and heat resistance. Service temperature of this rubber is up to 160°C and it's used in temperatures up to 200°C for short times and its abrasion resistance and wet traction is very good. But price of HNBR is high and it isn't an economy rubber for general applications.

2.2.6 Ethylene-propylene rubber

Ethylene-propylene rubber continues to be one of the most widely used and fastest growing synthetic rubber having both specialty and general purpose applications. Polymerization and catalyst technologies in use today provide the ability to design polymers to meet specific and demanding application and processing needs. Versatility in polymer design and performance has resulted in broad usage in automotive weather-stripping and seals, glass-

run channel, radiator, garden and appliance hose, tubing, belts, electrical insulation, roofing membrane, rubber mechanical goods, plastic impact modification, thermoplastic vulcanizates and motor oil additive applications. Ethylene-propylene rubber are valuable for their excellent resistance to heat, oxidation, ozone and weather aging due to their stable, saturated polymer backbone structure. Properly pigmented black and non-black compounds are color stable. As non-polar rubber, they have good electrical resistivity, as well as resistance to polar solvents, such as water, acids, alkalies, phosphate esters and many ketones and alcohols. Amorphous or low crystalline grades have excellent low temperature flexibility with glass transition points of about minus 60°C. Ethylene-propylene rubber uses the same chemical building blocks or monomers as polyethylene (PE) and polypropylene (PP) thermoplastic polymers. These ethylene (C2) and propylene (C3) monomers are combined in a random manner to produce rubbery and stable polymers. There are two general types of polymers based on ethylene and propylene: ethylene-propylene rubber (EPM) and ethylene-propylene terpolymer (EPDM). EPM accounts for approximately 20 percent of the polyolefin rubber produced. Comprising a totally saturated polymer, these materials require free-radical sources to cross-link. EPDM was developed to overcome this cure limitation. For EPDM a small amount (less than 15%) of a nonconjugated diene is terpolymerized into the polymer. One of the olefinic groups is incorporated into the chain, leaving its other unsaturated site free for vulcanization or polymer modification chemistry. This ensures that the polymer backbone remains saturated, with corresponding stability, while still providing the reactive side group necessary for conventional cure systems. The nonconjugated dienes used commercially are ethylidene norbornene, 1,4 hexadiene, and dicyclopentadiene. Each diene incorporates with a different tendency for introducing long chain branching (LCB) or polymer side chains that influence processing and rates of vulcanization by sulfur or peroxide cures.

2.3 Vulcanizing agents

Vulcanization is a chemical process for converting rubber or related polymers into more durable materials via the addition of sulfur or other equivalent vulcanizing agent. The function of vulcanizing agent is to modify the polymer by forming crosslinks (bridges) between individual polymer chains; the most common ones are the sulfur type for unsaturated rubber and peroxides for saturated polymers. Uncured natural rubber is sticky, deforms easily when warm, and is brittle when cold. In this state, it is a poor material when a high level of elasticity is required. Vulcanized material is less sticky and has superior mechanical properties. A vast array of products is made with vulcanized rubber including tires, shoe soles, hoses, and hockey pucks. The main polymers subjected to vulcanization are polyisoprene (natural rubber) and styrene-butadiene rubber, which are used for most passenger tires. Chemicals called accelerators may be added to control the cure rate in the sulfur system; these materials generally are complex organic chemicals containing sulfur and nitrogen atoms. Stearic acid and zinc oxide usually are added to activate these accelerators. Metal oxides are used to cure halogenated polymers such as polychloroprene or chlorosulfonated polyethylene.

2.4 Fillers

Natural and synthetic rubbers, also called elastomers are rarely applied in their pure form. They are too weak to fulfill practical requirements because of lack of hardness, strength

properties and wear resistance. A rubber compound contains, on average, less than 5 kg of chemical additives per 100 kg of rubber, while filler loading is typically 10-15 times higher. Of the ingredients used to modify the properties of rubber products, the filler often plays a significant role. Most of the rubber fillers used today offer some functional benefit that contributes to the processability or utility of the rubber product. Styrene butadiene rubber, for example, has virtually no commercial use as an unfilled compound. Fillers are used in order to improve the properties of rubber compounds. The characteristics which determine the properties a filler will impart to a rubber compound are particle size, particle surface area, particle surface activity and particle shape. Surface activity relates to the compatibility of the filler with a specific rubber and the ability of the rubber to adhere to the filler. Rubber articles derive many of their mechanical properties from the admixture of these reinforcing (active) fillers at quantities of 30% up to as much as 300% relative to the rubber part. The introduction of carbon black as a reinforcing agent in 1904, lead to strongly increased tread wears resistance. Carbon black is in use as the most versatile reinforcing filler for rubber, complemented by silicas. In tire manufacturing silicas are more and more used nowadays, mainly to decrease the rolling resistance. The increased attitude of protecting the environment gives rise to a demand for tires combining a long service life with driving safety and low fuel consumption, achieved by this lower rolling resistance. However, the change from carbon black to silica is not at all obvious because of technical problems involved. In particular, the mixing of rubber with pure silicas is difficult, because of the polarity-difference between silica and rubber. Therefore, coupling agents are applied in order to bridge this polarity difference. Sometimes fillers are added to reduce cost, increase hardness, and color the compound. Generally they do not provide the dramatic improvement in properties seen with reinforcing agents, but they may have some reinforcing capability. Carbon black and silica are the most common reinforcing agents. These materials improve properties such as tensile strength and tear strength; also, they increase hardness, stiffness, and density and reduce cost. Almost all rubbers require reinforcement to obtain acceptable use properties. The size of the particles, how they may be interconnected (structure), and the chemical activity of the surface are all critical properties for reinforcing agents. In tire applications, new polymers are currently being developed which contain functional groups that directly interact with carbon black and silica, improving many properties. Typical fillers are clays, calcium carbonate, and titanium dioxide.

2.5 Plasticizers

These materials are added to reduce the hardness of the compound and can reduce the viscosity of the uncured compound to facilitate processes such as mixing and extruding. The most common materials are petroleum-based oils, esters, and fatty acids. Critical properties of these materials are their compatibility with the rubber and their viscosity. Failure to obtain sufficient compatibility will cause the plasticizer to diffuse out of the compound. The oils are classified as aromatic, naphthenic, or paraffinic according to their components. Aromatic oils will be more compatible with styrene-butadiene rubber than paraffinic oils, whereas the inverse will be true for butyl rubber. The aromatic oils are dark colored and thus cannot be used where color is critical, as in the white sidewall of a tire. The naphthenic and paraffinic oils can be colorless and are referred to as nonstaining.

2.6 Antidegradents

An antidegradant, this group of chemicals is an ingredient in rubber compounds to deter the aging of rubber products. The most important are the antioxidants, which trap free radicals and prevent chain scission and crosslinking. Antiozonants are added to prevent ozone attack on the rubber, which can lead to the formation and growth of cracks. Antiozonants function by diffusion of the material to the surface of the rubber, thereby providing a protective film. Certain antioxidants have this characteristic, and waxes also are used for this purpose.

2.7 Processing

A wide range of processes are used to convert a bale of rubber into a rubber product such as a tire. The first process generally will be compounding. Typical compounding ingredients were discussed previously. In many compounds more than one rubber may be needed to obtain the performance required. Uncured rubber can be considered as a very high viscosity liquid; it really is a viscoelastic material possessing both liquid and elastic properties. Mixing materials into rubber requires high shear, and the simplest method is a double roll mill in which the rubber is shear-mixed along with the other compounding ingredients in the bite of the mill. Large scale mixing is most commonly done with a high-shear internal mixer called a Banbury. This mixing is a batch process, although continuous internal mixers also are used. The compounded rubber stock will be further processed for use. The process could be injection or transfer molding into a hot mold where it is cured. Tire curing bladders are made in this fashion. Extrusion of the rubber stock is used to make hose or tire treads and sidewalls. Another common process is calendering, in which a fabric is passed through rolls where rubber is squeezed into the fabric to make fabric-reinforced rubber sheets for roofing membranes or body plies for tires. The actual construction of the final product can be quite complex. For example, a tire contains many different rubber components some of which are cord or fabric reinforced. All of the components must be assembled with high precision so that the final cured product can operate smoothly at high speeds and last over 50,000 miles.

3. Abrasion test

An abrasion test is a test used to measure the resistance of a material to wear stemming from sliding contact such as rubbing, grinding, or scraping against another material. Abrasion may be measured in a variety of ways, depending on the resistance test used and the information that is desired from the test (Dick, 2001). For example, where the amount of material lost is a concern regardless of whether the material fails, abrasion may be measured in terms of the percentage of material lost, either by mass or by volume, between the start and end of the test. Another measure sometimes used is the number of abrasion cycles a material withstands before failure. This would be more appropriate if information on how long the material or product will survive before outright failure is of primary interest. Abrasion tests try to accelerate the process by applying more cutting-like conditions; however, this approach may not simulate actual wear. It is also important to try to match the severity of the abrasion test to the severity of the product wear conditions. For example, the severity of test conditions imparted by most abraders is usually greater than what the

highway pavement may impart to a tire tread compound during normal driving. Wear resistance is an important rubber compound property related to the useful product life for tires, belts, shoe soles, rubber rolls, and sandblasting hose, among other products. A wide variety of different abrasion testers have been developed over the years in an attempt to correlate to these product wear properties. Several factors are typically considered in developing or selecting an appropriate abrasion test for the application at hand. The shape of the contact area is taken into consideration, as is the composition of the two surfaces making contact with one another. Speed of sliding contact between the two surfaces, the force with which they act on one another, and the duration of contact between them may also be considered. In addition to the materials themselves, the environment in which they are making contact also plays a role in selecting an appropriate abrasion test.

The abrasion resistance is expressed as volume loss in cubic millimetres or abrasion resistance index in percent. For volume loss, a smaller number indicates better abrasion resistance, while for the abrasion resistance index; a smaller number denotes poorer abrasion resistance. Tested compounds are usually compared on a "volume loss" basis which is calculated from the weight loss and density of the compound. Abrasion test results are known to be variable; therefore, it is important to control and standardize the abradant used in the test. Also, it is a good idea to relate test results to a standard reference vulcanizates.

ASTM D394, the Dupont Abrasion Test Method, consists of a pair of rubber test pieces pressed against a disk of a specified abrasive paper which rotates whilst a pair of moulded test pieces is continuously pressed against it either with a constant force or with a force adjusted to give a constant torque on the arm holding the test pieces. Care should be taken with soft rubber compounds because "smearing" can occur, affecting test results.

ASTM D1630 describes the rotary-platform, double-head abrader is commonly referred to as the NBS Abrader used on rubber compounds for shoe soles and heels. The NBS abrader uses rotating drums with a specified abrasive paper around them onto which the test pieces are pressed by means of levers and weights, a specified standard reference compound to be used for the calculation of an abrasive index.

ASTM D2228 describes the Pico Abrader. This unique test works on the principle of abrading the rubber surface by rotating a rubber specimen against a pair of tungsten carbide knives. A special dusting power is fed to the test piece surface, which doubtless helps to avoid stickiness. This method specifies five standard rubbers and the result also expressed as an abrasion index. Force on the test piece and speed of rotation can be varied and, presumably, different abradant geometries could be used, although the distinctive feature of the Pico is the use of blunt metal knives in the presence of a powder.

ASTM D3389 refers to the Taber Abrader using a pair of abrasive wheels, a method not originally from the rubber industry. This very general method uses two abrasive wheels against the rubber test piece (disk) attached to a rotating platform. Although the degree of slip cannot be varied; however, the force on the test piece and the nature of the abradant are very readily varied and tests can be carried out in the presence of liquid or powder lubricants. When using the usual type of abrasive wheel, a refacing procedure is carried out before each material tested.

ISO 4649 refers to the DIN Abrader, based on the German Standard. The rubber test piece with a holder is traversed a rotating cylinder covered with a sheet of the abradant paper. By allowing the sample holder to move the test piece across the drum as it rotates, there is less chance of rubber buildup on the abradant paper. This method, used extensively in Europe, is very convenient and rapid and well suited to quality control the uniformity of a specific material. The achieved test results provide important parameters in respect to the wear of rubbers in practical use. The details of procedure and expression of results are something of a compromise, being a compilation of the German approach and the British approach. Two procedures are specified, using a rotating or non-rotating test piece respectively. In principle, the abrasion should be more uniform if the test piece is rotated during test. The standard abradant is specified in terms of weight loss of a standard rubber using a non-rotating test piece and has to be run in against a steel test piece before use. Results can either be expressed as a relative volume loss with the abradant normalized relative to a standard rubber or as an abrasion index relative to a standard rubber.

British Standard BS903: Part A9 still describes the Akron Abrader. The rubber test piece is a moulded wheel which is positioned against an abrasive cylinder under constant speeds and held against the abrasive wheel by a constant force. The Akron Abrader has the advantage of allowing variation in the degree of slip in the test by varying the angle of the test piece.

4. Effect of compounding ingredients on abrasion resistance

4.1 Rubber

In rubbery materials, when the smooth surface is abraded, periodic parallel ridged patterns are formed on the rubber surface. These typical patterns are held through all processes of rubber abrasion, on the surface of tires, conveyor belts, printing rolls and shoes for example, which are thus regarded as the essential basis of rubber abrasion. In the absence of any serious chemical decomposition the abrasion process initially results in the removal of small rubber particles just a few microns in size, leaving pits behind in the surface. With continued rubbing, larger pieces of rubber are removed. Although most weight loss is attributable to the larger pieces, it is thought that the detachment of the smaller particles initiates the abrasion process. The small particles have a characteristic size of 1-5 μm , but whether this relates to a structural unit in the rubber compound (Muhr & Roberts, 1992). Other suggestions are that mechanical rupture to produce the particles relates to flaws in the rubber, including dirt, or voids that cavitate leading to internal subsurface failure (Gent, 1989). A rolling experiment suggested that particle detachment might be linked to interfacial adhesion (Roberts, 1988). Schallamach (Schallamach, 1557/58, 1968) reported that rubber often develops a pattern of ridges perpendicular to the direction of abrasion. In the simplest case abrasion is produced by a line contact pulling a tongue of rubber from the ridge producing crack growth at the base of the tongue. Provided the surface configuration is in a steady state, the quantity of rubber abraded can be related quantitatively to the frictional force and the crack growth characteristic of the rubber. The abrasion of rubber results from mechanical failure due to excessively high local frictional stresses which are most likely to occur on rough tracks. Theories of abrasion thus require details of the local stresses, which together with the strength properties of the rubber may enable the rate of abrasion to be predicted. Gent and Pulford (Gent & Pulford, 1983) reported the reversal in the relative rates of wear of unfilled polybutadiene rubber comparing to those of unfilled natural rubber and

styrene butadiene rubbers as frictional force increased. Fukahori and Yamazaki (Fukahori & Yamazaki, 1994) investigated the mechanism of the formation of the periodic ridges in rubber abrasion by designing the razor blade abrader. They reported that the driving force to generate the periodic surface patterns, and thus rubber abrasion consists of two kinds of periodic motions, stick-slip oscillation and the microvibration generated during frictional sliding of rubber. The stick-slip oscillation is the driving force to propagate cracks, then abrasion patterns and the microvibration with the natural frequency of the rubber induced in the slip phase of the stick-slip oscillation is another driving force for the initiation of the cracks. Although initial cracks originate in the slip region of the rubber surface, the propagation of the cracks is strongly excited in the stick region. Champ et al. (Champ et al., 1974) proposed the mechanism of rubber abrasion from a fracture mechanics point of view, relating the rate of wear to the crack growth resistance of the rubber. Although the concept of crack growth plays a very important role in abrasion, particularly in the growth of a single ridge, when consider that the essential subject of rubber abrasion. Liang et al. (Liang et al., 2010) investigated the blade abrasion of four different rubber materials, unfilled natural rubber, unfilled styrene butadiene rubber, unfilled polybutadiene rubber and carbon black filled styrene-butadiene rubber. Each is abraded until the steady state abrasion pattern is developed on the surface of moulded rubber wheels. The steady state conditions are measured using the weight loss per revolution of the wheel. The abraded surface is cut to examine the typical asperity profile. Each profile is modeled using finite element analysis to calculate the stored energy release rate for each combination of material and test condition. The stored energy release rate when combined with an independent measure of the rate of crack growth measured using a fatigue crack growth test gives a reasonable prediction of the abrasion rate. They has shown that the low strength of the BR material results in much smaller asperities being formed under steady state abrasion which results in a much slower abrasion rate. Conversely the strongest material NR has the longest tongue on the asperity and this in turn generates much larger values for the tearing energy at the tip of the asperity and this contributes to its poor abrasion resistance. Hong et al. (Hong et al., 2007) observed that BR compounds caused much slower wear than NR and SBR compounds. Arayapranee and Rempel (Arayapranee & Rempel, 2009) studied the cure characteristics, mechanical properties before and after heat ageing, and abrasion and ozone resistances of hydrogenated natural rubber (HNR), providing an ethylene-propylene alternating copolymer, vulcanizate and compared with those of natural rubber (NR), ethylene propylene diene terpolymer (EPDM) and 50:50 NR/EPDM vulcanizates. They reported that the highest abrasion resistance of the NR vulcanizate could be attributed to high unsaturated structure, as evident from its highest tensile strength compared to other vulcanizates. The abrasion loss of 48% HNR is higher than that of the NR vulcanizate, due to a reduction in the number of the double bonds. This suggests that abrasion resistance is heavily dependent on the unsaturation content in the backbone chain.

4.2 Fillers

Fillers increase the stiffness of rubber in various degrees depending on quantity and quality of the fillers. The properties of rubber compounds are affected not only by the filler content but also by its structure and particle size. Despite outstanding resilience and high tensile strength, natural rubber possesses poor abrasion resistance. Thus, blending with high abrasion resistance rubbers and/or reinforcing by inorganic fillers are generally used to

improve the abrasion resistance of NR and other rubbers. Carbon black and silica are two common fillers used to reinforce rubbers. However, high loadings of these fillers are required to obtain desirable properties. Incorporation of reinforcing fillers such as carbon black improves stiffness and strength of rubber (Tabsan et al., 2010). Hence, the abrasion resistance is improved by suppressing tearing of the rubber under the sliding contact (Gent & Pulford, 1983). Arayapranee et al. studied the effect of filler type and loading on the abrasion loss (Arayapranee et al., 2005). They found that the incorporation of silica and carbon black reduces the abrasion loss of the natural rubber materials notably, whereas rice husk ash shows no effect with filler loading. Reinforcing fillers, silica and carbon black, interact preferentially with the natural rubber phase, as shown by the higher reduction of abrasion loss in the compounds. This improvement is probably due to the greater surface area and better filler-rubber interfacial adhesion resulting in an improved abrasion resistance. Fine particles actually reflect their greater interface between the filler and the rubber matrix and, hence, provide a better abrasion resistance than the coarse ones. Similar results were also reported by (Sae-oui et al., 2002).

Filled compounds are found to be less sensitive to the frictional force, whether wear took place by tearing or by smearing (Gent & Pulford, 1983). Carbon black is an additive with a decisive effect on the abrasion resistance. Hong et al. (Hong et al., 2007) investigated the effects of the particle size and structure of various carbon blacks on friction and abrasion behavior of filled natural rubber, styrene-butadiene rubber and polybutadiene rubber 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. 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. Yang et al. (Yang et al., 1991) reported that the abrasive wear of rubbers is strongly affected by the filler particles dispersed in the rubber matrix. The fillers are incorporated usually for the purposes of mechanical reinforcement and improving the conductivity of the neat resins. It is found that rigid filler particles normally increase the abrasive wear loss of the filled silicone rubbers. The wear rates of the filled silicone rubbers increase slowly with filler concentration until a critical volume fraction is reached, at which point they increase very rapidly with increasing filler. The critical filler fraction should carry important information, as it apparently divides two wear regimes dominated by different mechanisms. The first regime, where the filler concentration is low, is dominated by the properties of the neat resin. The increase of wear rate due to the filler is gradual here. In the cases of effective filler reinforcement, a reduction of wear rate can occur. The second regime is dominated by the filler's detrimental effects where the wear rate increases very rapidly with filler concentration. The stress concentration introduced by the rigid particles effectively creates a 'damage zone' surrounding the particles, a location where micro-cavitation and debonding takes place. Cavitation appears to dominate in the composites of very small filler particles, while debonding dominates when larger particles are involved. In view of the importance of carbon blacks on tread wear, it is surprising that relatively little understanding of the phenomenon has been set out in print. Although for synthetic rubbers such as BR and SBR it may seem unnecessary to look further than the dramatic enhancement of strength properties imparted by the use of particular grades of black, for NR such enhancement is modest and additional mechanisms for the effect of blacks on tread

wear should be sought. In any case there is a consensus that high surface area, high surface activity and high structure promote tread wear resistance. Even so, the evidence that carbon black does not necessarily enhance the abrasion resistance of rubber under conditions of equal sliding suggests that the effect of carbon black on tread wear may in part be simply associated with stiffening, and hence reduced sliding, without weakening the compound as a high crosslink density would do. Arayapranee and Rempel (Arayapranee & Rempel, 2008) studied the effects of incorporation of three different fillers, i.e. rice husk ash (RHA), silica and calcium carbonate (CaCO_3), over a loading range of 0-60 phr on the abrasion loss of 75:25 natural rubber (NR)/ethylene propylene diene monomer (EPDM) blends. The incorporation of silica reduced the abrasion loss of the 75:25 NR/EPDM blends notably, whereas CaCO_3 showed a different trend in abrasion loss tending to increase it with an increase in CaCO_3 loading. However, RHA showed less of an effect with filler loading. At a similar filler loading, silica filled 75:25 NR/EPDM blends had the lowest abrasion loss followed by RHA and CaCO_3 filled 75:25 NR/EPDM blends.

4.3 Lubricants

Lubricants is widely used in the compounding of diene rubbers to improve the processability of the compounds and to impart the desired physicomechanical properties of rubber compounds and vulcanizates. The presence of a liquid can prevent moving surfaces from coming into intimate contact if viscous flow from the contact region is sufficiently sluggish. Lubricants, such as non-swelling fluids or dust, greatly reduce friction on smooth surface but the effect is smaller on rough surface. Changes in friction properties of rubber are possible by adding substantial amounts of standard lubricants, but this reduces strength, especially at high temperatures. Contrary, improvement in friction properties of rubbers based on blends NR and BR could be reached by introducing 0.5 wt% of K95 experimental lubricant (Jurkowska et al., 2006). Lubricant K95 added in a quantity of 0.5 wt% reduced the viscosity of rubber compound; it also improved compound flow in the mold. Mechanical properties of cured rubber not decrease while resistance to abrasion and fatigue increased. The influence of Lubricant K95 on reducing of the internal friction of rubbers is found.

Evstratov et al. (Evstratov et al., 1967) found that abrasion on a ribbed metal surface increases abruptly, by an order of magnitude or so, when the friction coefficient (μ) exceeds about 1.4. Abrasion patterns were observed for μ above the critical value, but not for lower values. It did not matter whether μ was an unlubricated value for the compound or was determined by the presence of a lubricant. The renowned abrasion resistance of cis-BR compounds may relate to this observation; such compounds have low dry friction and form only very fine abrasion patterns. In spite of their low strength, their abrasion resistance can be excellent. When a lubricant is applied, a much finer pattern develops and the rate of abrasion is much lower.

4.4 Antioxidants

Gent and Pulford (Gent & Pulford, 1983) determined rates of wear have been determined for several rubber materials, using a razor-blade abrading apparatus 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). The decomposition process could, in principle, be ascribed to several mechanisms: thermal decomposition due to local heating during sliding; oxidative deterioration, possibly accelerated by local heating; and mechanical rupture of macromolecules to form reactive radical species. The most plausible mechanism of smearing appears to be oxidative consummation of scissions produced by mechanical stress, in much the same way as occurs during cold mastication of natural rubber. They provided rather convincing evidence of mechanochemical degradation of certain rubbers during abrasion by a razor blade. The degradation of carbon black-filled natural rubber (NR), styrene-butadiene rubber (SBR), and ethylene-propylene rubber (EPM) to a sticky material during blade abrasion occurred only in the presence of oxygen or thiophenol, but not in a nitrogen atmosphere (just as for cold mastication). Polybutadiene rubber (BR) produced only dry debris during abrasion, consistent with the expectation that any free radicals of BR produced by main chain rupture would react with the polymer itself, leading to an increase in cross-linking rather than degradation. Carbon black-filled natural rubber, styrene-butadiene rubber, and ethylene-propylene rubber 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. Polybutadiene rubber produced only dry debris during abrasion. Radicals of BR produced by main chain rupture would react with the polymer itself, leading to an increase in cross-linking rather than degradation. 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. Filled materials were found to be less sensitive to the frictional force, whether wear took place by tearing or smearing, having values of the index n of 1.5-1.8. It is well known that for some conditions the surface of rubber becomes tacky during abrasion experiments, drum testing of tires and sometimes even for tires on the road. It has been suggested that either exudation of low molecular weight additives or degradation of the polymer to a material of low molecular weight could be responsible. Degradation might result from either thermal or mechanical stress, at high sliding speeds, such as skidding of a vehicle on locked wheels, frictional heating certainly causes degradation. However, the phenomenon of smearing is associated with conditions of mild abrasion, e.g. on smooth surfaces, and can occur even for low sliding speeds.

The most plausible mechanism of smearing appears to be oxidative consummation of scissions produced by mechanical stress, in much the same way as occurs during cold mastication of NR. Similar experimental observations to those of Gent and Pulford (Gent & Pulford, 1983) were previously obtained by Rudakov and Kuvshinski (Rudakov & Kuvshinski, 1967) for abrasion of NR and BR by a smooth indenter in air and in helium. They also gave a calculation suggesting that the rise in temperature of the rubber surface was quite inadequate to cause thermal degradation. However, this calculation ducks the possibility of local hotspots: the smaller the region of real contact, the higher is the calculated temperature rise, but we can only conjecture as to the size of the real contacts (Schallamach, 1967).

Schallamach (Schallamach, 1968) investigated the factors influencing smearing on the Akron laboratory abrader. He found that smearing could be prevented for NR tire tread

compounds by carrying out abrasion in nitrogen or obviated by feeding a dust (magnesia proved most effective) into the nip between test piece and abrasive wheel. He concluded that oxidative degradation (to which he attributed smearing) affects the rate of abrasion in two distinct ways. If smearing occurs, the rate of abrasion is reduced (presumably because the "smear" acts as a lubricant). When the abrasion of a rubber is low in air, owing to smearing, its abrasion in nitrogen can become greater than in air. However, in air the less grossly degraded rubber is mechanically weakened, so that if smearing is obviated by the use of a suitable dust, the rate of abrasion is greater in air than in nitrogen. He also showed that the susceptibility of the compound to oxidative degradation can be influenced by the choice of antioxidant and other formulation details. Pulford (Pulford, 1983) studied antioxidant effects during abrasion of NR tire tread compounds by a razor blade. He reported that all compounds exhibited smearing at sufficiently low friction loads, but antioxidants reduce the critical frictional force below which smearing occurs. He found that antioxidants reduce the rate of wear for conditions in which smearing occurs but have no effect at higher severities. He considered this to be evidence of two mechanisms of wear, namely degradation at low frictional force and fracture at high frictional force. However, antioxidants also protect against fatigue crack growth, but only at low tearing energies (Lake, 1983). Thus it may not be necessary to invoke an entirely different mechanism of abrasion when smearing occurs. Instead, smearing can be seen as a complication superimposed on the general fracture mechanism of abrasion. Antioxidants can be used to, at least, partially restore the abrasion and crack growth resistance.

5. Conclusions

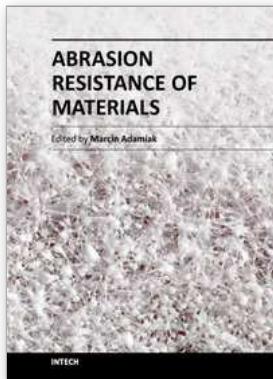
Abrasion resistance is the ability of a material to withstand mechanical action such as rubbing, scraping, or erosion that tends progressively to remove material from its surface. Such an ability helps to maintain the material's original appearance and structure. Numerous companies manufacture abrasion resistant products for a variety of applications, including products which can be custom fabricated to meet the needs of specific users. Abrasion resistant materials can be used for both moving and fixed parts. In vulcanized material or synthetic rubber compounds, a measure of abrasion resistance relative to a standard rubber compound under defined conditions. The properties of a vulcanized rubber can be significantly influenced by details of the compounding. Practical materials will have, in addition to the base polymer, fillers, antioxidants, crosslinking agents, accelerators etc. All of these can have an influence on the physical and chemical stability of the finished material. For example, rubber abrasion resistance can be related quantitatively to the frictional force and the crack growth characteristic of the rubber. Rigid filler particles normally increase the abrasive wear loss of the filled rubbers. A lubricant may cause a small decrease in frictional force but a dramatic decrease in abrasion. Antioxidants can be used to, at least, partially restore the abrasion and crack growth resistance because they are added to prevent ozone attack on the rubber, which can lead to the formation and growth of cracks.

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