

Fillers for rubber compounds

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Bachelor thesis
2005



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I would like to thank my bachelor thesis supervisor Ing. Michal Černý for professional guidance, recommendations and remarks, which he offered me during elaborating bachelor thesis.

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SUMMARY

This work deals with the basic characteristics of fillers such as particle size, particle shape, surface area and surface activity and their influence on mechanical properties of rubber compounds. From practical view, white (mineral) fillers and carbon blacks are shared. Differences between their reinforcing effects are not given by chemical composition, but especially by particle size, their shape and surface activity.

From broad range of fillers, there are described carbon black, kaolin clay and silica, the most used fillers for rubber compounds.

RESUMÉ

Tato práce se zabývá studiem základních charakteristik plniv, jako je velikost částice, tvar částice, povrch a povrchová aktivita, a jejich vlivem na mechanické vlastnosti kaučukové směsi. Z praktického hlediska rozlišujeme bílá (minerální) plniva a saze. Rozdíly mezi jejich ztužujícími účinky nejsou dány chemickým složením, ale zejména velikostí, tvarem a povrchovou aktivitou částic.

Ze široké škály plniv jsou zde popsány saze, kaolin a silika, nejvíce používaná plniva pro kaučukové směsi.

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INTRODUCTION

Filled rubber compounds are complex polymer systems that exhibit a number of singular properties markedly different from those of unfilled, molten polymers. In addition to usual hydrodynamics (or volume fraction) effects, reinforcing fillers such as carbon blacks or high-structured silica, impart modification in flow properties whose origin assigned to strong interactions arising between the elastomer and the filler particle. Most usage of elastomers would be impossible without the reinforcing character of certain fillers, such as carbon blacks and structured silica. With an implicit reference to tire technology, reinforcement is usually defined as the “improvement in abrasion, tear, cutting and rupture resistance, in stiffness and hardness of vulcanized compounds through the incorporation of finely divided (minerals) particles”. Quite a large variety of powdered minerals can be compounded with elastomers but not all have reinforcing capabilities, and essentially classes of powdered minerals have been found to offer significant reinforcing effects: carbon black and high-structured silica.

Filler morphology such as particle size, structure, and, essentially, surface characteristics have a large influence on the physical performance of the elastomeric material. Most important, however, are the surface characteristics and the chemically active sites, which determine the interaction between the filler and the polymer chains. This interaction is the key parameter in rubber reinforcement, and a better characterization of this interfacial interaction is essential for understanding the mechanism of rubber reinforcement. Such interaction which leads to an adsorption of the network chains onto the particle surfaces, can result from physical interaction arising from Van der Waals forces between the surface and the polymer or from chemical interaction, which can be met directly by chemisorption of elastomer on active sites or indirectly by means of coupling agents used in the case of a filler having poor adhesive qualities for a polymer.

Carbon black reinforcement became a subject of scientific interests only in the 1940s, thanks to the development of suitable investigation tools and the growing use of synthetic rubber in demanding applications, namely automotive and truck tires. Silica reinforcement started to be considered in the 1980s when the benefit of surface treatment with silanes was recognized, with the need for lower rolling resistance tire being an important driving force in recent research efforts [1, 2].

1 RUBBER

1.1 History of rubber

The name rubber was given to a mass of Caoutchouc* in 1700 A.D. by Joseph Priestly, an English clergyman, because it would rub out pencil marks. In a strict sense rubber refers to a vegetable hydrocarbon of the chemical form $(C_5H_8)_n$ and for practical purposes it may be defined as a material that is capable of being stretched or distorted to a considerable extent, then retracting quickly to nearly its original dimension upon release of tension. Technically, this quality is more correctly covered by the word "Elastomer".

Rubber as it first appeared on the scene was used by the Maya Indians in South America. Cuts were made in rubber trees and the oozing latex was collected. The Indians would immerse their feet into the latex and upon removing they found a thin coating covering them. This process was repeated several times until the coating was thick enough to be used as a protective and waterproof boot and the Indians could cross the roughest terrain without damage to their feet. These same Indians, being athletic in nature, had developed a game that was made possible by the use of a ball formed from the tree latex. The ball was elastic and bounced very well.

In 1870, with dire threat to his life, Sir Henry Wickham took seedlings of the rubber trees from Brazil to London from where they were transferred and set up in plantations in Malaya. The seedlings flourished as did the tree rubber industry in Malaya. This interesting same tree latex was later used to coat cloth or other forms of material and then dried to give waterproof clothing or elastic and waterproof containers. These products at first proved to be very poor due to the lack of resistance to heat, becoming soft and tacky, or when cold, becoming hard and brittle. Due to such a poor temperature span the articles were practically useless. Many investigators were experimenting with methods to overcome these inherent problems, but it was Charles Goodyear's breakthrough in 1839 that isolated major obstacles when he performed the first successful vulcanization of rubber. Later in 1841 he produced a few yards of rubber-coated cloth heated in an iron trough. By the year 1850 several stable rubber companies were in existence and now rubber is one of our major industries [5, 9].

* Caoutchouc is the French derivation of the Maya Indians' name of Cachuc which means "weeping wood".

1.2 Basic characteristics of rubber

Rubber is water repellent and resistant to alkalies and weak acids. Rubber's elasticity, toughness, impermeability, adhesiveness, and electrical resistance make it useful as an adhesive, a coating composition, a fiber, a molding compound, and an electrical insulator. In general, synthetic rubber has the following advantages over natural rubber: better aging and weathering, more resistance to oil, solvents, oxygen, ozone, and certain chemicals, and resilience over a wider temperature range. The advantages of natural rubber are less buildup of heat from flexing and greater resistance to tearing when hot.

Compounds, which show rubber properties at normal temperature, are called elastomers. Elastomer is an amorphous, cross-linked high polymer above its T_g which will stretch rapidly under tension, reaching high elongations (500 to 1000%) with low damping. It has high tensile strength and high modulus when fully stretched. On the release of stress, it will retract rapidly, exhibiting the phenomenon of snap or rebound, to recover its original dimensions. Elastomers and synthetic rubbers are unlike thermoplastics in that they can be repeatedly softened and hardened by heating and cooling without substantial change in properties [8, 10, 12].

1.3 Types of rubber

Natural Rubber (NR) is the prototype of all elastomers. It is extracted in the form of latex from the bark of the Hevea tree. The rubber is collected from the latex in a series of steps involving preservation, concentration, coagulation, dewatering, drying, cleaning, and blending. Because of its natural derivation, it is sold in a variety of grades based on purity (color and presence of extraneous matter), viscosity, viscosity stability, oxidation resistance, and rate of cure. 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 high tensile strength and resistance to cutting, tearing, and abrasion.

Synthetic rubber (SR), which is derived from petroleum, coal, oil, natural gas and acetylene, has over a dozen major classes. They differ by type of monomer, their copolymerization ratio, polymerization method and conditions, type of used accelerator, emulsifier or stabilizer. Many of them are copolymers i.e. polymers consisting of more than one monomer. By changing the composition it is possible to achieve specific properties desired for special applications. The earliest synthetic rubbers were the styrene-butadiene copolymers, Buna S and SBR, whose properties are closest to those of natural rubber. SBR is the most commonly used elastomer because of its low cost and good properties; it is used mainly for tires. Approximately 70% of the rubber consumed is synthetic [3, 12, 13].

1.4 Rubber compound

Today there are a wide variety of rubber polymers, each with its own set of characteristic attributes, and each offered with modifications designed to enhance one or more of those attributes. In most cases, nevertheless, the elastomer by itself lacks one or more property necessary to produce a saleable product. A number of materials must be added to make it commercially useful. A compound is the intimate admixture of a polymer or polymers with other ingredients such as fillers, plasticizers, catalysts and colorants - prepared for further manufacturing. The compounding of rubber products starts with the choice of elastomer, filler (reinforcing or extending), crosslinking chemicals, and various additives which, when mixed together, will provide a compound with the desired properties and performance. Mixing is followed by forming operations such as milling, extrusion, and calendering. Particle dispersion has a basic influence on rubber properties and quality [2-4].

2 FILLERS

Filler is a relatively inert material added to a basic resin or adhesive to alter its physical, mechanical, thermal, or electrical properties or to reduce cost. Particulate additives are inert substances consisting of generally small particles that do not markedly improve the tensile strength of a product, whereas reinforcements are fibrous and do significantly improve the tensile strength. The most commonly used general purpose fillers are clays, silicates, talcs, carbonates, asbestos fines and paper. Fillers also act as pigments, e.g., carbon black, chalk and titanium dioxide; while graphite, molybdenum disulfide and PTFE impart lubricity. Magnetic properties can be obtained by incorporating magnetic mineral fillers such as barium sulfate. Other metallic fillers such as lead or its oxides are used to increase specific gravity. Powdered aluminum imparts higher thermal and electrical conductivity, as do other powdered metals such as copper, lead and bronze [8, 11].

2.1 Characteristics of fillers

The characteristics, which determine the properties filler will impart to a rubber compound, are particle size, particle shape, surface area and surface activity. Surface activity relates to the compatibility of the filler with a specific elastomer and the ability of the elastomer to adhere to the filler [4, 12].

1) Particle size

If the size of the filler particle greatly exceeds the polymer interchain distance, it introduces an area of localized stress. This can contribute to elastomer chain rupture on flexing or stretching.

Fillers with particle size greater than 10,000 nm (10 μm) are therefore generally avoided because they can reduce performance rather than reinforce or extend. Fillers with particle sizes between 1,000 and 10,000 nm (1 to 10 μm) are used primarily as diluents and usually have no significant affect, positive or negative, on rubber properties. Semi-reinforcing fillers, which range from 100 to 1000 nm (0.1 to 1 μm), improve strength and modulus properties. The truly reinforcing fillers, which range from 10 nm to 100 nm (0.01 to 0.1 μm) significantly, improve rubber properties (Fig. 1).

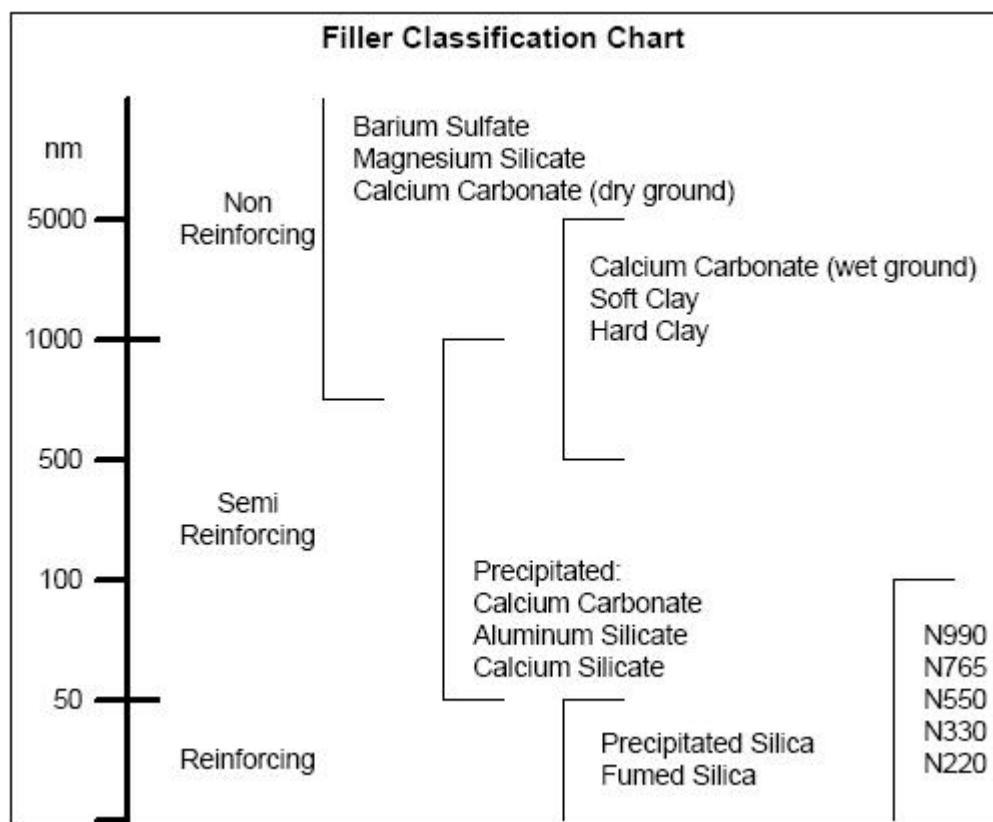


Fig. 1 Classification of fillers according to average particle size

Methods of determination:

• Oil absorption

The test, using an absorptometer, measures the quantity of DBP required to change the consistency of the filler from a free-flowing powder to a coherent paste. The results are expressed as milliliters of DBP per 100 grams of filler. The structure or the DBP absorbed is a function of the void volume of the aggregates and describes the degree to which the filler particles have fused together to form aggregates [11].

2) Particle shape

A particle's shape plays a significant role in its ability to intercept stress applied to the elastomer composite. In general, anisometric particles - those having a significant difference in length vs. width - are more effective as reinforcements than isometric particles - those similar in length and width. The basic particle shape characteristics of fillers are shown in Fig. 2 with their typical aspect ratios, the measure of their anisometry.

For needle and fiber shaped fillers, aspect ratio is the ratio of length to diameter. For kaolin clay and other platy minerals, it is the ratio of the diameter of a circle with the same area as the face of the plate to the thickness of the plate. Isometric fillers that are approximately round, cubic or blocky in shape, are considered low aspect ratio. Low means less than about 5:1 aspect ratio. Platy, acicular (needle-shaped) and fibrous fillers are considered high aspect ratio.

Aspect ratio is not applied to carbon black and precipitated silica. The primary particles of these fillers are essentially spherical, but these spheres aggregate in such a way that the functional carbon black and precipitated silica filler “particles” are chains or bundles with various degrees of branching. The anisometry of these fillers is described in terms of “structure”, which incorporates aggregate shape, density and size. The higher structure offers the greater reinforcement potential.

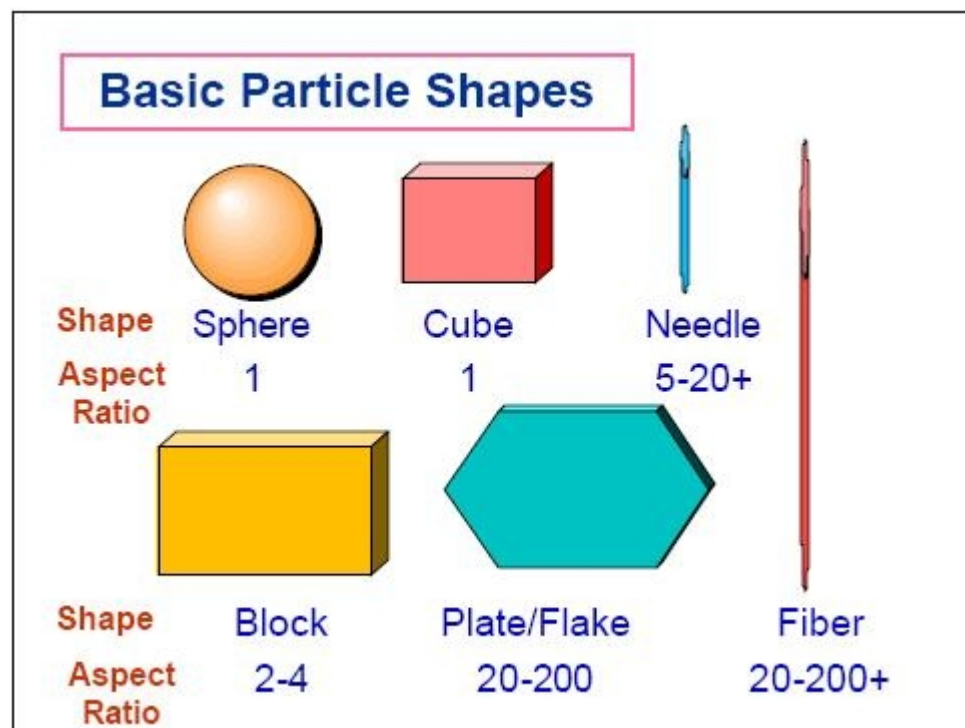


Fig. 2 The basic particle shapes with their typical aspect ratios

3) Particle surface area

Filler must make intimate contact with the elastomer chains if it is going to contribute to reinforcement of the rubber-filler composite. Fillers that have a high surface area have more contact area available, and therefore have a higher potential to reinforce the rubber chains. The shape of the particle is also important. Particles with a planar shape have more surfaces available for contacting the rubber than spherical particles with an equivalent average particle diameter.

Clays have planar-shaped particles that align with the rubber chains during mixing and processing, and thus contribute more reinforcement than spherical-shaped calcium carbonate particles of similar average particle size. Carbon black and precipitated silica chains and bundles are considerably smaller than the particles of clay. They thus have more surface area per unit weight available to make contact with the polymer. Rubber grade carbon blacks vary from 6-250 m²/g. Most reinforcing precipitated silicas range from 125-200 m²/g; typical hard clay ranges from 20-25 m²/g.

Methods of determination:

- **BET method**

It comes from the initials Brunauer, Emmett and Teller, the men who invented a straight-forward method to determine the effective surface of solid materials with complicated shapes, such as porous powders, by using adsorbed nitrogen molecules as rulers. The observation of the so-called adsorption and desorption isotherms is used to determine the amount of nitrogen molecules adsorbed to a surface. Knowing the size of a molecule, one can then calculate the entire effective surface.

- **Iodine number [mg/g]**

The amount of iodine adsorbed from an aqueous solution as a measure for the specific surface area. Generally, it is in agreement with nitrogen surface area. The presence of volatiles, surface porosity or extractable will influence the iodine adsorption number [11].

4) Particle surface activity

A filler can offer high surface area, high aspect ratio and small particle size, but still provide relatively poor reinforcement if it has low specific surface activity. The specific activity of the filler surface per cm^2 of filler-elastomer interface is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Nonpolar fillers are best suited to nonpolar elastomers; polar fillers work best in polar elastomers. Beyond this general chemical compatibility is the potential for reaction between the elastomer and active sites on the filler surfaces.

Carbon black particles have carboxyl, lactone, quinone, and other organic functional groups which promote a high affinity of rubber to filler. The non-black fillers generally offer less affinity and less surface activity toward the common elastomers. This can be compensated to a greater or lesser extent by certain surface treatments. Kaolin clay and all of the non-black, non-carbonate reinforcing or semireinforcing fillers have one feature in common. The clays, silicas, and silicates all have surface silica (SiO_2) groups which have hydrolyzed to silanols ($-\text{SiOH}$). These silanol groups behave as acids ($-\text{SiO}-\text{H}^+$) and are chemically active. The higher surface area fillers have more silanols available and are thus more reactive.

2.2 Fillers effects

The principal characteristics of rubber fillers – particle size, shape, surface area and surface activity – are interdependent in improving rubber properties. In considering fillers of adequately small particle size to provide some level of reinforcement, the general influence of each of the other three filler characteristics on rubber properties can be generalized as follows [4, 12]:

1) Increasing surface area (decreasing particle size): higher Mooney viscosity, tensile strength, abrasion resistance, tear resistance, and hysteresis; lower resilience.

2) Increasing surface activity (including surface treatment): higher abrasion resistance, chemical adsorption or reaction, modulus (at elongation $>300\%$), and hysteresis (except for silane treated clay, as we'll see).

3) Increasing aspect ratio: higher Mooney viscosity, modulus (at elongation <300%), and hysteresis; lower resilience and extrusion shrinkage; longer incorporation time.

Modulus/Tensile strength

The primary filler effects in rubber can be related to tensile properties: in simplest terms, the ability of the filler-rubber composite to respond to stretching forces. The force required to stretch a defined specimen of rubber to a given percent elongation is measured as modulus. Most often, modulus is reported at 300% elongation (four times original length).

The introduction of filler into the vulcanizate provides additional resistance to elongation. A filler with low surface activity will increase resistance to elongation by the viscous drag its surface provides to the polymer trying to stretch and slide around it. Higher surface area, greater aspect ratio, and higher loading (the latter two effectively increasing the surface area exposed to the elastomer) will all increase the modulus. Fillers with strong chain attachments, via active sites or coupling agents, provide the most resistance to the chain extension and separation required for elongation and ultimate rupture. The effect of filler particles on the ability of the compound to stretch is shown in Fig. 3.

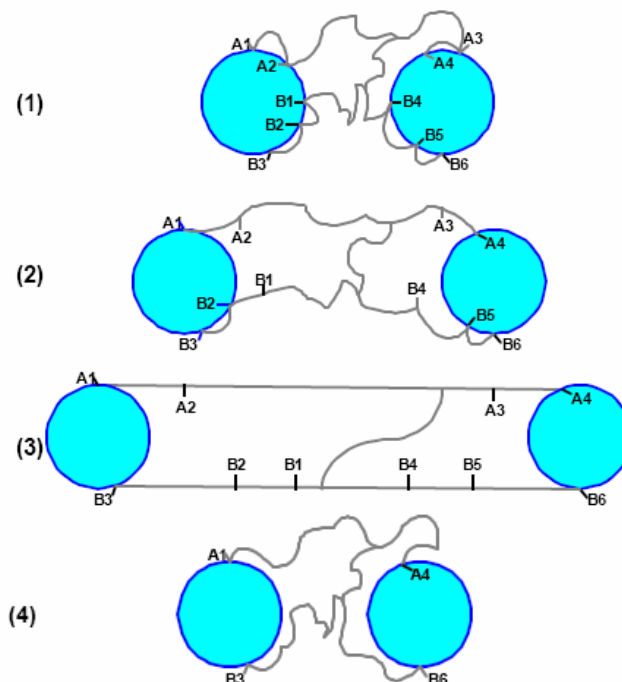


Fig. 3 Effect of interaction between filler and polymer chain by stretching

Before stretching, as in step 1, the polymer chains are in random configuration. Chains A and B have multiple points of attachment to the filler particles, corresponding to the particle's active sites. On elongation, resistance is supplied as the energy required detaching the chain segments from these active sites, as in steps 2 and 3. The amount of energy required to attain maximum elongation, and then required to cleave chain-chain and chain-filler attachments, accounts for the tensile strength of a filled system of this type.

After the elongating force has been removed, the elastomer chains return to their preferred random orientation, as in step 4, except that now they have the minimum number of points of attachment to the filler as a consequence of having been extended in Step 3. Less force would now be required to return these chains to ultimate extension, because the intermediate points of attachment that existed in Steps 1 and 2 have been eliminated. This explains the phenomenon known as **stress softening**. With repeated stress-relaxation cycling, a decrease in modulus from the initial maximum is obtained. Stress softening is a temporary effect. After a period without strain, the rubber will recover to near its original modulus, as the active filler sites again attach to polymer segments. A percentage of the original modulus is permanently lost, however, due to irrecoverable chain and bond cleavage.

Hardness/Flexural Strength

The analogous resistance to elastomer chain deformation accounts for the increase in rubber hardness obtained in proportion to filler loading, surface area, structure activity/surface treatment, and structural anisometry. Hardness is typically measured as resistance to surface indentation under specific conditions, so the force is supplied as a point of compression rather than an area of tension. Similar filler particle dynamics apply, nevertheless. Flexural strength is likewise related as a measure of a sample's resistance to deformation (flex) under a compressive force. With a force supplied to an end-supported test sample, the upper surface is under compression and the lower surface is in tension (elongation). Both compression and elongation are effectively resisted in proportion to the durability of the filler-elastomer bond. High structure or anisometric fillers provide greater resistance to compression because this force is generally perpendicular to their more rigid planar or elongate dimension.

Impact Strength

Impact strength or impact resistance is the measure of a hard rubber's resistance to fracture under sudden impact or force. The impact force is one of compression on one side of the rubber and tension on the other, so that fracture is a result of failure similar to that occurring when a tensile sample is elongated to break.

Tear Strength/Flex Resistance

Tear strength and flex resistance are essentially a measure of resistance to crack or slit propagation. Both typically measure the growth of a crack under tension, although flex testing, with multiple flexing cycles, introduces the additional factor of heat generation and fatigue. Large or poorly bound fillers will act as flaws and initiate or propagate cracks under test conditions. Small particles size, high surface area, and high surface activity allow the filler particles to act as barriers to the propagation of microcracks, and provide the higher tensile strength required to resist failure.

Resilience

Resilience is essentially a measure of rubber elasticity – the characteristic ability to quickly return to original shape following deformation. Unfilled elastomers are at their

peak resilience because there is no obstacle to elastomer chain extension and contraction (return to randomness). The introduction of filler creates such an obstacle in proportion to the strength of the particle-polymer interaction. Resilience is therefore generally in inverse proportion to filler loading and reinforcement.

Hysteresis

If resilience is considered the ratio of energy release on recovery to the energy impressed on deformation, hysteresis can be viewed as a measure of the amount of impressed energy that is absorbed. An unfilled (elastic) elastomer will convert most of the energy of deformation into the mechanical energy used in returning to the original shape. The degree to which input energy is converted to heat, due to friction from polymer chains sliding past each other, is a function of polymer chain morphology. All fillers tend to increase the hysteresis of rubbers, the most reinforcing fillers generally producing the largest increases. This is due to the energy consumed in polymer-filler friction and in dislodging polymer segments from active filler surfaces. This is heat energy which would otherwise have a mechanical manifestation as elastic rebound. In short, hysteresis is inversely related to resilience.

Abrasion Resistance

Abrasion resistance is a function of filler structure, particle size, and surface activity (filler-elastomer adhesion). At equivalent loadings, large particles will be more easily dislodged from the rubber surface than finer particles. Finer particle sizes also provide more uniform distribution and more particles per unit surface area. Loss of a larger particle will expose more of the relatively soft surrounding elastomer matrix to wear. The effect is acute on the edge of the depression left by the dislodged filler particle. This is the area most susceptible to elongation, crack initiation and ultimate loss. For a fine filler, the better the rubber-particle bond – a function of surface area and surface activity or coupling agent treatment – the more difficult it will be to dislodge. Abrasion resistance under dynamic conditions is also affected by compound hysteresis which, in turn, is a function of filler selection.

2.3 Types of fillers

Fillers, which improve some technical important properties – especially destruction properties as tensile strength, structural strength and abrasion resistance – are called activated fillers, reinforcing fillers or reinforcements. Addition of reinforcing fillers also improves energy required to rubber rupture and its quantity is considered as simple standard of reinforcement. Size of energy required to rubber rupture is area under tensile line. Reinforcement of rubber can be viewed as modification viscoelastic and destruction properties of rubber through fillers with aim obtain one or several desired properties without seriously defect on deformation reversibility. Some properties improvement is generally following by declining others. In general, as activated filler can be identified ever filler, which modify certain properties on required value – e.g. compound hardness or stiffness.

From practical view fillers can be shared as carbon black and mineral fillers (silicates, carbonates and oxides). Differences between effects of fillers are given not by chemical structure but especially by particle size, particle shape and particle activity.

3 CARBON BLACK

3.1 Structure

Carbon black is essentially elemental carbon in the form of fine amorphous particles. Each particle is composed of randomly oriented microcrystalline layered arrays of condensed carbon rings. Because of their random orientation, many arrays expose open layer edges with unsatisfied carbon bonds at the particle surface. This in turn provides the sites for chemical activity.

Individual round carbon black particles do not exist as discrete entities but form aggregates, which may be clumps or chains of various sizes and configurations when particles collide and fuse together in the combustion zone of the reactor. Several of those aggregates may be held together by weak forces to form agglomerates (Fig. 4). These agglomerates will break down during mixing into rubber, so the aggregates are the smallest ultimate dispersible unit of carbon black. The functional carbon black “particle”, therefore, is actually the aggregate. Average particle size and aggregate configuration (structure) are the major determinants of the utility of a given carbon black in a specific rubber compound. The major differences between commercial grades result from control of these averages.

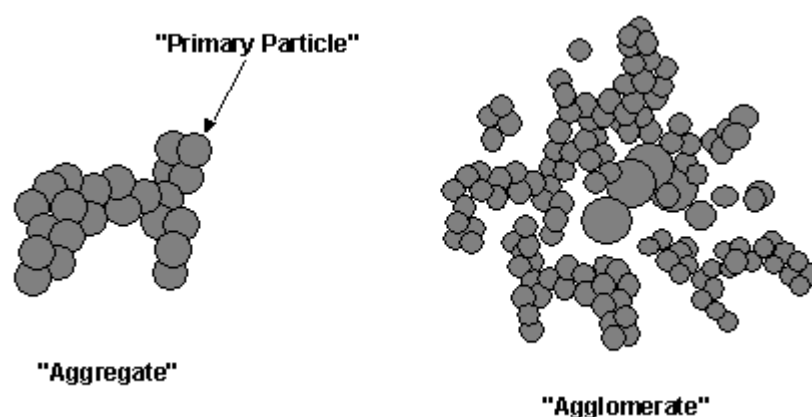


Fig. 4 Particles of carbon black

3.2 Surface chemistry

Carbon black particles have carboxyl, lactone, quinone, and other organic functional groups which promote a high affinity of rubber to filler (Fig 5). This, together with the high surface area of the black, means that there will be intimate elastomer-black contact. The black also has a limited number of chemically active sites (less than 5% of total surface) which arise from broken carbon-carbon bonds as a consequence of the methods used to manufacture the black. The close contact of elastomer and carbon black will allow these active sites to chemically react with elastomer chains. The carbon black particle effectively becomes a crosslink.

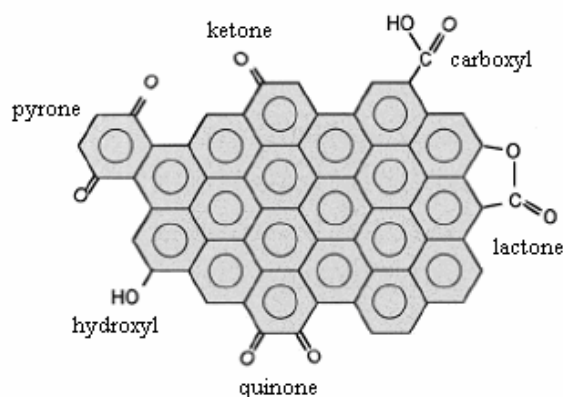


Fig. 5 Surface chemistry of carbon black

3.3 Types of blacks

Prior to World War II, the predominant reinforcing black was made from small flames of natural gas impinging on iron channels. The deposit scraped from these channels was known as **channel blacks**. The finest particle size used for rubber, about 24 nm average, was Hard Processing Channel (HPC) because it produced the stiffest stocks. Larger particle sizes were available as Medium Processing Channel (MPC) at 26 nm average and Easy Processing Channel (EPC) at 29 nm averages. Channel blacks are no longer used in rubber because of their high cost and the availability of suitable alternatives.

Furnace blacks began displacing channel blacks for rubber reinforcing in the early 1940s. Furnace blacks were at first, as early as the 1920s, made by burning natural gas in large horizontal furnaces, yielding a relatively coarse (60 to 80 nm average) semi-reinforcing product. Synthetic rubber development during World War II, particularly the

reinforcement requirements of the otherwise unusable SBR, promoted the production of finer grades. Ultimately, natural gas was abandoned as a feedstock in favor of residual aromatic petroleum oils. This liberated carbon black manufacture from proximity to natural gas sources and allowed location of plants more convenient to the consuming industries. Oil furnace blacks today account for about 95% of the carbon black used in rubber.

The thermal process, introduced in 1922, makes the largest particle size and lowest structure blacks. **Thermal blacks** are made in a large cylindrical furnace by the thermal decomposition of natural gas in the absence of flame or air. Thermal blacks range from 100 to 500 nm average and are generally used as low cost functional extender fillers. Because of their relatively large size and low structure they can be used at higher loadings and provide better resilience and lower hysteresis than the more reinforcing furnace blacks. The production of thermal blacks requires a sufficiently long reaction time that they are largely graphitized in this way. Thermal blacks consequently provide characteristically low surface activity and reinforcement potential [4].

3.4 Manufacture of carbon black

Carbon black is essentially an elemental carbon in a form different from diamond, cokes, charcoal and graphite and is manufactured by the incomplete combustion of a heavy aromatic feedstock in a hot flame of (preheated) air and natural gas. Most rubber blacks today are produced using the Oil Furnace process, in which feedstock is injected into a hot gas flame zone in an enclosed reactor (Fig. 6).

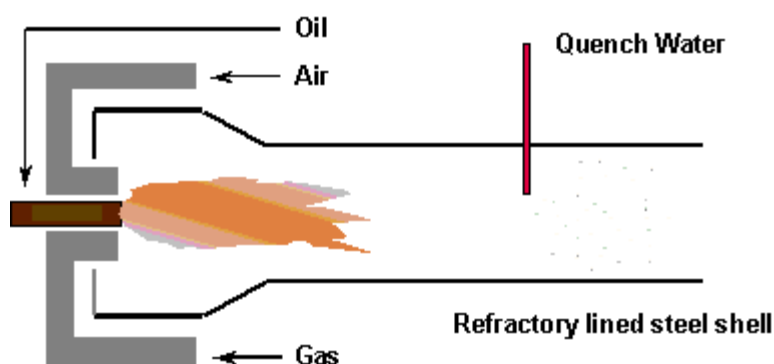


Fig. 6 A simplified schematic picture of the Oil Furnace reactor

A broad range of carbon black types can be made by controlled manipulation of the reactor conditions. The carbon black formation reaction in the furnace is controlled by

steam or water spray. The carbon black particles produced are conveyed through the reactor, cooled and continuously collected via filters (Fig. 7) [6, 17].

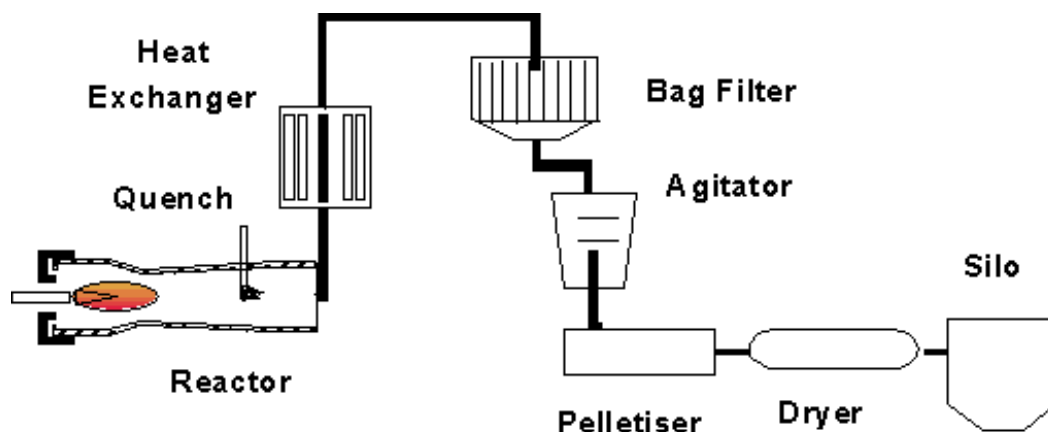


Fig. 7 A simplified schematic picture of the carbon black overall process

3.5 Carbon black characteristics

Carbon black is the predominant reinforcing filler used in rubber compounds, and the improvement in rubber properties is a function of the fundamental physical and chemical characteristics of carbon black. The most important fundamental physical and chemical properties are aggregate size and shape (structure), particle size, surface activity, and porosity. These properties are distributional in nature and this distribution in properties has an impact on in rubber performance. Other non-fundamental properties include the physical form and residue. The physical form of carbon black (beads or powder) can affect the handling and mixing characteristics of carbon black and, hence, rubber properties. The ultimate degree of dispersion is also a function of the mixing procedures and equipment used [7, 16].

STRUCTURE / AGGREGATE SIZE: Carbon blacks do not exist as primary particles. Primary particles fuse to form aggregates, which may contain a large number of particles. The shape and degree of branching of the aggregates is referred to as structure. The structure level of a carbon ultimately determines its effects on several important in-rubber

properties. Increasing carbon black structure increases modulus, hardness, electrical conductivity, and improves dispersibility of carbon black, but increases compound viscosity.

PARTICLE SIZE is the fundamental property that has a significant effect on rubber properties. Finer particles lead to increased reinforcement, increased abrasion resistance, and improved tensile strength. However, to disperse finer particle size requires increased mixing time and energy. Particle size distribution can only be accurately measured using a transmission electron microscope. Typical particle sizes range from around 8 nanometers for furnace blacks up to around 300 nanometers for thermal blacks. Surface area is utilized in the industry as an indicator of the fineness level of the carbon black and, therefore, of the particle size.

SURFACE ACTIVITY (or surface chemistry) is a function of the manufacturing process and the heat history of a carbon black. While difficult to measure directly, surface chemistry manifests itself through its effects on such in-rubber properties as abrasion resistance, tensile strength, hysteresis, and modulus. The effect of surface activity on cure characteristics will depend strongly on the cure system in use.

POROSITY is a fundamental property of carbon black that can be controlled during the process of production. It can affect the measurement of surface area providing a total surface area (NSA) larger than the external value (STSA). Increasing the porosity reduces the density of the aggregates. This allows a rubber compounder to increase carbon black loading while maintaining compound specific gravity. This leads to an increase in compound modulus and electrical conductivity for a fixed loading.

PHYSICAL FORM has an impact on the handling and mixing characteristics of carbon black. The most common physical form of rubber carbon black is beads (pellets). In addition, Columbian also produces powdered and oil-beaded carbon blacks.

3.6 Classification of carbon black

Until 1968, carbon black nomenclature was informal and based on a variety of characteristics, including level of abrasion resistance, level of reinforcement, vulcanizate

modulus, processing properties, general usefulness, particles size, and electrical conductivity. In 1968, the ASTM Committee on Carbon Black established a common nomenclature system consisting of a prefix followed by a three digit number. The prefix is either N, for normal curing, or S for slow curing. At the time, rubber grade channel blacks, which are slow curing, were still used. They have since been discontinued; all current rubber grade blacks carry the N prefix. The first of the three digits indicates a range of average particle size in nanometers. The second and third digits are assigned by the ASTM Committee to new products as they are developed. In general, lower structure blacks are assigned lower numbers and higher structure blacks, higher numbers, although there are some exceptions. Figure 8 shows the series of carbon blacks used today by ASTM classification, the old letter classification and size ranges [4].

Carbon blacks		
ASTM Series Classification	Old Classification	Size Avg (nm)
N100	SAF (Super Abrasion Furnace)	11 – 19
N200	ISAF (Intermediate Abrasion Furnace)	20 – 25
N300	HAF (High Abrasion Furnace)	26 - 30
N400	FF (Fine Furnace)	31 – 39
N500	FEF (Fast Extruding Furnace)	40 – 48
N600	GPF (General Purpose Furnace)	49 - 60
N700	SRF (Semi-Reinforcing Furnace)	61 – 100
N800	FT (Fine Thermal)	101 – 200
N900	MT (Medium Thermal)	201 – 500

Fig. 8 Classification of carbon blacks

3.7 Usage

Traditionally, black has been used as a reinforcing agent in tires. Today, the uses of carbon black have expanded to include acting as a pigmenting, UV stabilizing and conductive agent in a variety of common and specialty products, including:

- **Plastics:** Carbon blacks are now widely used for plastic masterbatch applications, such as conductive packaging, films, fibers, moldings, pipes and semi-conductive cable compounds.
- **Toners and Printing Inks:** Carbon blacks enhance formulations and deliver broad flexibility in meeting specific color requirements.
- **Coatings:** Carbon blacks provide pigmentation, conductivity and UV protection for a number of coating applications including marine, aerospace and industrial.
- **Tires and Industrial Rubber Products:** Carbon black is used in tire innerliners, carcasses, sidewalls and treads, as well as in industrial rubber products, like belts, hoses and gaskets.

4 SILICATES

4.1 Structure

Kaolin clay and related platy silicates (talc, mica, pyrophyllite) can be considered inorganic polymers based on two basic “monomer” structures - the silica tetrahedron and the alumina or magnesia octahedron (Fig. 9). These minerals contain a continuous octahedral layer with the joined octahedra tilted on a triangular side. This layer is bound on one side (as in kaolin) or both sides (as in talc, mica and pyrophyllite) by a continuous silica layer.

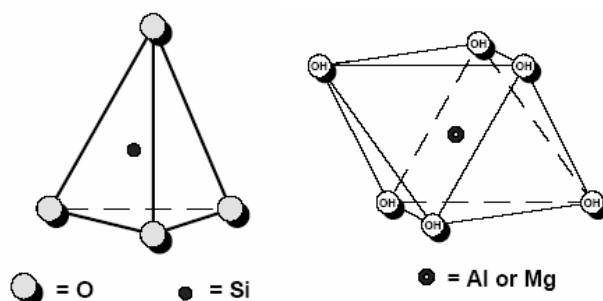


Fig. 9 Basic structures of silicates

The continuous silica layer is composed of tetrahedra with three shared oxygens and fourth (apical) oxygen pointed in the same direction. This forms a layer of linked rings with hexagonal openings, as illustrated here in Fig. 10.

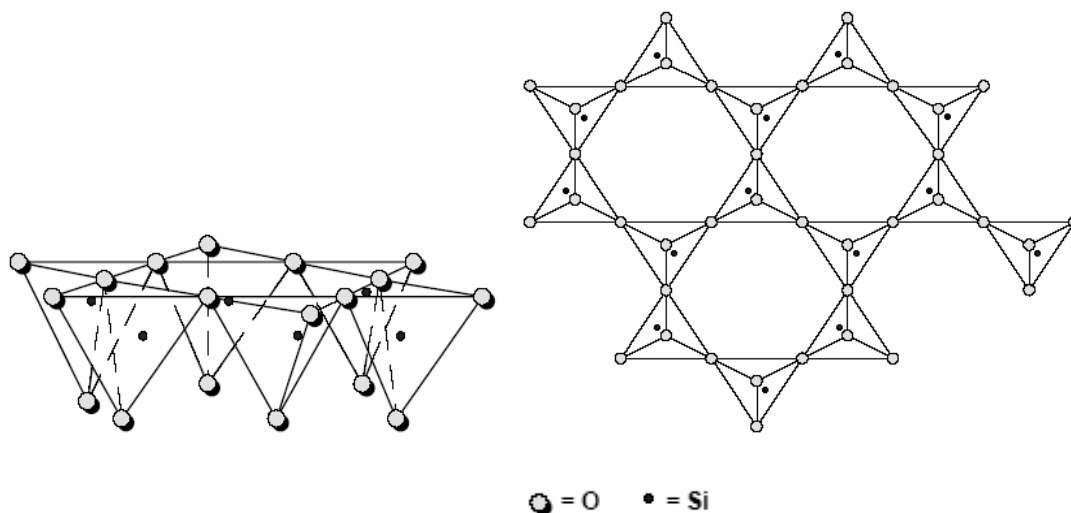


Fig. 10 Silica rings

4.2 Surface chemistry

Kaolin clay and all of the non-black, non-carbonate reinforcing or semireinforcing fillers have one feature in common. The clays, silicas, and silicates all have surface silica (SiO_2) groups which have hydrolyzed to silanols ($-\text{SiOH}$). These silanol groups behave as acids ($-\text{SiO}-\text{H}^+$) and are chemically active (Fig. 11). The higher surface area fillers have more silanols available and are thus more reactive.

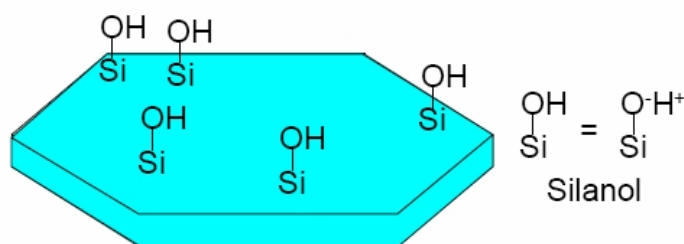


Fig. 11 Surface silica groups

Silanols show similarities to carboxylic acid groups in their reactions with amines, alcohols, and metal ions. While water adsorbed on the surface of filler particles will reduce silanol reactivity, hot compounding volatilizes some of this, leaving a reactive surface. Some of the reactions with silanols can have a significant effect on the properties of the rubber compound, especially where the chemical involved is an important part of the cure system. Most of the accelerators used in sulfur cure systems contain an amine group. Strong adsorption or reaction with filler particles can decrease the amount of accelerator available for vulcanization reactions. This can give slower cure rates and a reduced state of cure. Similar effects can result from the reaction of zinc ions with filler particles.

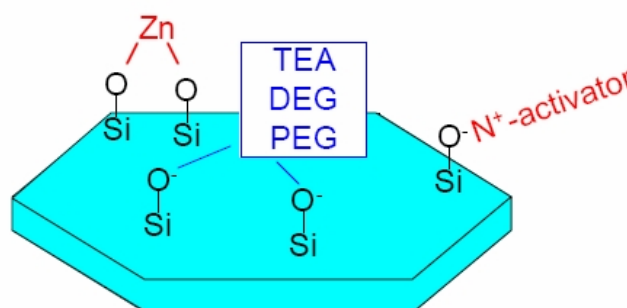


Fig. 12 Reactivity of silanols groups and its reduction

The adsorption or reaction of accelerators by hard clay usually requires about 15-25% increase in acceleration. These negative effects on the cure system can be reduced or completely avoided, however, by adding other chemicals that will tie up the silanol groups and reduce their activity (Fig. 12). Triethanolamine (TEA), diethylene glycol (DEG) and high molecular weight polyethylene glycol (PEG) typically serve this function. These are mixed into the compound prior to the addition of the accelerators [4, 12].

4.3 Kaolin clay

4.3.1 Structure

The prototypical clay mineral is the aluminum silicate, kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Its structure (Fig. 13) is composed of an octahedral alumina layer joined to a tetrahedral silica layer via shared apical oxygens.

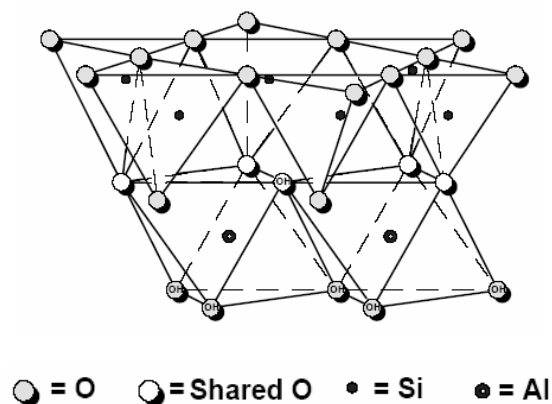


Fig. 13 Structure of kaolinite

The continuous sheet structure produces thin particles which are often found in nature as overlapping flakes. These are informally called “books” because of their resemblance under magnification to stacks of paper (Fig. 14). Kaolin books are bound via hydrogen bonding of the octahedral layer hydroxyl face of one flake to the tetrahedral layer oxygen face of the adjacent flake. Separation of books into individual clay flakes is therefore difficult [4, 12].

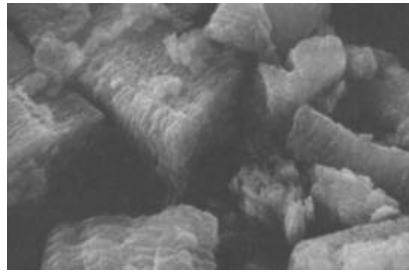


Fig. 14 Kaolin books

4.3.2 Kaolin types

Kaolin clays are classified in various ways, with terminology specific to certain industries. We'll preface the descriptions of the clays commonly used in the Rubber Industry, with a brief review of several clay aliases.

- **Primary or residual kaolin clay** occurs in the deposit where it formed. It contains only 40-50% particles under 2 μm . The world's major source is Cornwall, England.
- **Secondary or sedimentary kaolin clay** has been eroded and transported from its site of formation and deposited at a distant location.

Rubber filler clays are classified as either "hard" or "soft" in relation to their particle size and stiffening affect in rubber.

- **Soft clay** has a median particle size of approximately 1000 to 2000 nm and is used where high loadings (for economy) and faster extrusion rates are more important than strength.
- **Hard clay** will have a median particle size of approximately 250 to 500 nm, and will impart high modulus, high tensile strength, stiffness, and good abrasion resistance to rubber compounds [4, 12].

4.3.3 Production of kaolin

Water-washed kaolin has been slurried in water and centrifuged or hydrocycloned to remove impurities and produce specific particle size fractions. The refined slurry is either dewatered (to reduce soluble impurities) and dried, or concentrated to 70% solids and sold in slurry form to the Paint and Paper Industries. Water-washed clays are often treated to improve brightness. This includes chemical bleaching and/or high-intensity magnetic separation to remove iron and titanium impurities. Although most of the clay used in rubber is airfloat, some water-washed clay is used because its lower level of impurities provides better color and less die wear with rubber extrusions.

Airfloat clay is dry-ground kaolin that has been air separated to minimize impurities and control the particle size distribution. About 80% of the kaolin used in the Rubber Industry is airfloat hard clay.

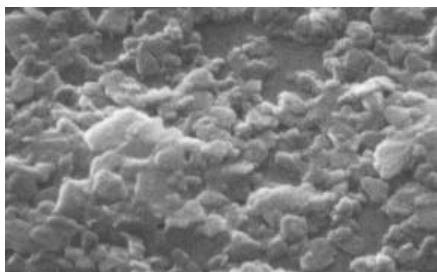


Fig. 15 Airfloat clay

To produce **delaminated clay**, the coarse clay fraction from water washing is attrition milled to break down the kaolinite stacks into thin, wide individual plates. This improves brightness and opacity. Delaminated clay is the highest aspect ratio form of clay available, and it is used for high stiffness and low die swell, as demonstrated in this natural rubber compound.

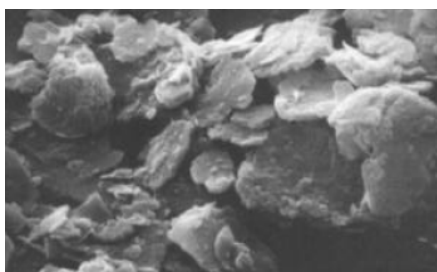


Fig. 16 Delaminated clay

Calcined clay is usually waterwashed soft clay calcined to partially remove surface hydroxyl groups. Calcining increases brightness and opacity, as well as oil absorption and hardness (i.e. abrasivity or abrasion resistance). The partial or complete removal of surface hydroxyls provides a corresponding decrease in surface activity, and thus reinforcement. Calcined clay is commonly used in wire and cable coverings because it provides excellent dielectric and water resistance properties.

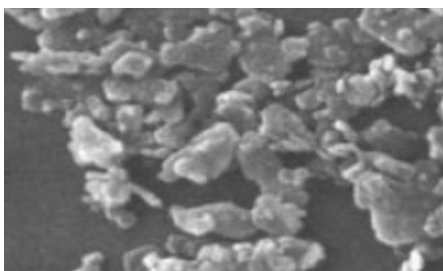


Fig. 17 Calcined clay

Surface-treated clay is processed kaolin that has been surface modified (e.g., with silanes) to improve compatibility with and performance in elastomer matrices.

Silane treated hard clays provide better reinforcement than untreated clay, and in some applications can rival furnace blacks. The combination of platy shape and chemical reactivity enable the silane treated kaolins to impart a unique blend of properties to elastomers. These include high modulus, low hysteresis, good abrasion resistance, low viscosity, low set, and resistance to heat and oxidative aging. The unusual combination of high modulus and low hysteresis, in particular, have earned them a place alone or as a partial carbon black replacement in products requiring good dynamic properties, such as transmission and V belts, and non-tread tire components.

Aminosilane and mercaptosilane treated clay are compared here to an untreated hard clay in a synthetic polyisoprene compound. The improvements in modulus, tear strength, compression set and the reduction in elongation with the treated clays are all indicative of the improved elastomer-clay bonding. The ultimate tensile strength is not significantly affected since the rupture strength of the polymer-polymer linkages remains unchanged [4, 12].

4.3.4 Usage

The principal use of kaolin in coatings is as a TiO_2 extender. Partially calcined grades generally provide the best extension, durability, and dry hide. Water-washed and delaminated clays are used in water-based coatings to control gloss, film integrity, durability, scrub resistance, covering power, suspension ability, flow, and leveling. The largest single use of kaolin in plastics is as calcined kaolin in PVC wire insulation to improve electrical resistivity. Calcined kaolin is also used in agricultural polyethylene films to improve IR absorption characteristics, and in engineering resins, both untreated and silane-treated, for improved physical properties and heat deflection. Airfloat and water-washed kaolins are used in thermosets to provide a smooth surface finish, reduced cracking, warping and crazing, and to obscure fiber reinforcement patterns. Delaminated clays improve thermoplastic physical properties, including enhanced impact resistance when surface-treated. Kaolin for rubber is principally airfloat hard clay. Water-washed and delaminated clays are used for better color, physical properties, and abrasion resistance. Calcined and surface-treated clays are used for improved electrical properties and ease of extrusion. High brightness, low abrasion water-washed kaolins are used as paper fillers. Kaolin is the preferred filler in acid pH papers. Partially calcined and delaminated grades act as TiO_2 extenders. Kaolins add brightness, gloss, smoothness, and ink receptivity to paper coatings. Fine particle size airfloat kaolins are used as pitch control agents. In adhesives and sealants, kaolin is used to control flow, penetration, and adhesion on application, as well as adhesive strength, tear strength, tensile strength and elongation after cure [4, 10, 18].

4.4 Silica

4.4.1 Structure

Silica is the name given to a group of minerals composed of silicon and oxygen, the two most abundant elements in the earth's crust. Silica is found commonly in the crystalline state and rarely in an amorphous state. It is composed of one atom of silicon and two atoms of oxygen resulting in the chemical formula SiO_2 .

Silica exists in ten different crystalline forms or polymorphs, quartz being by far the most common. Quartz is the second most common mineral on the earth's surface and it is found in almost every type of rock, i.e. igneous, metamorphic and sedimentary [15, 19].

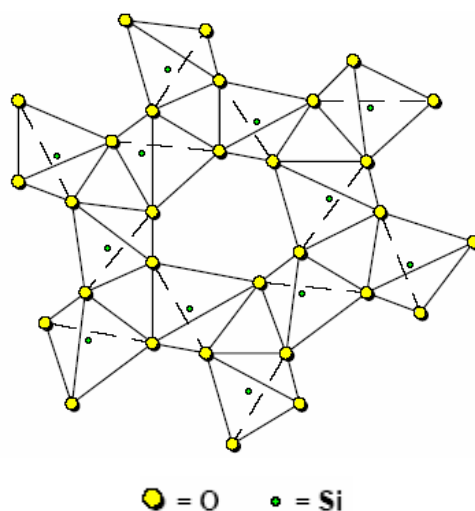


Fig. 18 Structure of quartz

4.4.2 Silica types

Ground silica, also known as ground quartz and silica flour, is produced by grinding high-purity quartz, quartzite, sandstone, or silica sand to finer than 200 mesh. Air separation is used as required to remove kaolin, mica, feldspar, or calcite impurities. Silica sand recovered as a byproduct during the flotation of other minerals is also used as a source. Ground silica for filler uses typically assays $>99\%$ SiO_2 and offers high brightness, low moisture, chemical inertness, relatively low surface area, and the low liquid absorption that allows high loading levels. Because of its hardness and the creation of sharp, angular particles upon grinding, most ground silica is too abrasive for use in certain plastics compounding machinery.

Novaculite is microcrystalline quartz that is milled to low-moisture, high-purity ($>99\%$ SiO_2), plate-like or disc-like particles. Brightness is generally lower than for other forms of ground silica, but particle shape, lower binder demand, lower abrasivity, and availability in a range of particle size distributions (to as small as 2 micrometers average) has earned novaculite a place in filler applications, particularly in paint.

Tripoli is a general term for a friable or powdery rock composed substantially of microcrystalline quartz. Commercial tripoli is ground mainly for use as an abrasive agent in buffing and polishing compounds, since particle edges tend to be less sharp than for most other forms of ground silica.

Silica sand can be broadly defined as natural quartz sand that is - 4 mesh and + 200 mesh. Silica sand has more rounded grains than are obtained by grinding high-silica rocks to an equivalent size range, although grain angularity varies from source to source. Products are commonly named for their intended use – e.g., glass sand, foundry sand, blasting sand, and hydraulic fracturing sand. Each term indicates compliance with requirements for minimum SiO₂, maximum chemical impurities, particle size distribution, and grain shape for that application. Most uses require at least 95% SiO₂ and have limits on the Al₂O₃ and Fe₂O₃ content.

Precipitated silica is made by the controlled neutralization of a sodium silicate solution under alkaline conditions using either sulfuric or carbonic acid (as CO₂ + HCl). This is carried out in a heated stirred reactor. The rate and order of addition of reactants, reactant concentration, and reaction temperature are varied to manipulate particle size and particle structure. Precipitation produces low-solids slurry of amorphous silica particles within the byproduct salt solution. The discrete primary silica particles that initially form fuse into aggregates, which in turn form loose agglomerates. The precipitate is filtered, washed, and dried (usually spray dried) to a neutral pH product. The dry silica is milled to reduce average agglomerate size and is then frequently compacted to balance bulk density, freedom from dustiness, and dispersibility. The particle size conventionally reported is that of primary particles (10 to 30 nanometers), although it is the aggregates (30 to 150 nanometers) that are the actual functional particles. BET surface area is therefore frequently preferred for classifying the various grades.

Precipitated silicas are also classified according to structure, which is a function of the manipulation of primary particle size and aggregate water pore volume during manufacture. For convenience, structure has been related to oil absorption, with five structure levels designated. These range from VLS (very low structure) at less than 75ml/100g to VHS (very high structure) at greater than 200ml/100g. In elastomer compounding, which uses approximately 75% of the precipitated silica produced, the silica is commonly treated with silane coupling agents *in situ* to promote better matrix

compatibility and improved compound properties. Silica grades pretreated with silane are also available.

Silica gel is made by reaction a sodium silicate solution with sulfuric acid under acid conditions. Silica properties are manipulated by controlling the reaction rate, order of reactant addition, reactant concentration, reaction temperature, and mixing conditions. The silicate-acid reaction first forms a hydrosol, which is aged to a transparent rigid gel. This gel is broken into small lumps, washed to remove residual salts, and dried. When the water is removed slowly, the colloidal silica structure contracts. Then dry silica xerogel results. When the water is removed quickly, the colloidal silica structure is preserved. Dry silica aerogel with lower density and higher pore volume results. Aerogels are neutral in pH, while xerogels are usually processed to produce an acid pH (4 to 5) in water. The dried xerogel or aerogel is milled to a controlled particle size distribution, with the average particle size measurement reflecting aggregate rather than primary particles. Surface-treated grades are available for improved organic matrix compatibility. Major applications for silica gel depend on its small particle size for rheology control and its porosity for low particle density and high liquid absorption.

Fumed silica is prepared by the hydrolysis of silicon tetrachloride in a flame of hydrogen and oxygen. Particle size and surface area are controlled by varying the ratio of the three reactants. The primary silica particles are round and 7 to 40 nanometers. These primary particles collide and fuse into branched or chain-like clusters. These aggregates, the functional particles, average about 1 micrometer, and in turn form agglomerates. In aqueous dispersions fumed silica provides a pH of approximately 4. The very low bulk density of the agglomerates is increased by compaction with vacuumdeaeration before packaging. Fumed silica is sold in a hydrophilic form as produced and in a hydrophobic form with silane surface treatment [4, 14].

4.4.3 Usage

To a large extent natural and synthetic silicas have little in common other than their gross chemistry. Applications reflect this. The United States produces about 25 million metric tons of silica annually under the general description “industrial sand and gravel”. Of this total about 40% is glass sand, 20% is foundry sand, 7% is abrasive sand, 6% is hydraulic fracturing sand, and 6% is gravel. Specialty silica, consisting of ground natural

and synthetic silicas, accounts for 2 to 4% of total silica output. For silica sand the major use is as an inexpensive source of SiO_2 . This encompasses the production of nearly all types of glass, plus ferrosilicon, silicon metal, silicon carbide, and metallurgical fluxes. Each of these applications has its own requirements for particle size distribution, minimum SiO_2 , and maximum Fe and Al, as well as control over other chemical and mineralogical impurities. Other major silica sand uses have similar requirements, plus additional specifications on particle shape. Fracturing sand, for example, must penetrate and maintain openings through which oil or gas can flow to a well. It must consist of well-rounded grains to allow ease of placement and maximum permeability. Fractured angular grains with sharp edges are obviously preferred for most abrasive sand uses. The major uses of specialty silicas are in ceramics, coatings, rubber, plastics, adhesives, and sealants [10].

Finer (<0.025 micrometer) precipitated silica is the only fully reinforcing alternative to carbon black for general rubber compounding. Most of the precipitated silicas used in rubber are reinforcing grades rather than the coarser extending grades. Precipitated silica is used in compounds designed to be translucent or colored, and in general compounding to promote abrasion resistance, cut growth resistance, tear strength, elastomer-to-textile adhesion, and resistance to heat aging. It is often compounded with silane coupling agents to improve matrix compatibility. Because of its particular attributes, precipitated silica is used in radial ply passenger tires, off-road tires, and footwear. Fumed silica is the conventional reinforcing filler in silicone elastomers, although more recently it has been supplemented with precipitated silica and finely ground natural silica that extend its reinforcing properties at lower cost. Synthetic silicas have an index of refraction close to that of silicone rubber, so that transparent compounds can be formulated [4].

5 OTHER MINERAL FILLERS

Barite

Finely ground barite is used in rubber, where its weight, inertness, isometric particle shape, and low binder demand are advantageous. It has little effect on cure, hardness, stiffness, or aging. It is used in acid-resistant compounds, in white sidewalls for tires, and in floor mats. Blanc fixe (precipitated barium sulfate) fine enough to be semireinforcing is used to provide the same compound softness and resilience as barite but better tensile strength and tear resistance. Barite is used in PVC and polyurethane foam backings for carpeting and sheet flooring because of its ability to form dense coatings due to its high specific gravity and its ability to be used at high loadings.

Calcium carbonate

Calcium carbonates for rubber fall into two general classifications. The first is wet or dry ground natural limestone, spanning average particle sizes of 5000 nm down to about 700 nm. The second is precipitated calcium carbonate (PCC) with fine and ultrafine products extending the average size range down to 40 nm.

Ground natural products show low anisometry (specific shape depends on grinding process), low surface area and low surface activity. They are widely used in rubber, nevertheless, because of their low cost, and because they can be used at very high loadings with little loss of compound softness, elongation or resilience. This all follows from the relatively poor polymer- filler adhesion potential, as does poor abrasion and tear resistance. Dry ground limestone is probably the least expensive compounding material available and more can be loaded into rubber than any other filler. Wet ground limestone is somewhat more expensive, but offers better uniformity and finer particles size.

The ultrafine PCC products (<100 nm) can provide surface areas equivalent to the hard clays. Manipulation of manufacturing conditions allows the production of precipitated calcium carbonates of two distinct particle shapes. Precipitated calcites are essentially isometric particles, while precipitated aragonites are acicular. The natural aragonite form is found in oyster shells and pearls. Precipitated calcite is the form generally used in rubber compounding. The PCC provides superior tensile strength, tear resistance, resilience, abrasion resistance, and flex-crack resistance.

Stearate-treated versions of both the ground and precipitated calcium carbonates are available. The surface coating controls moisture absorption, improves dispersion and promotes better elastomer-particle contact, and protects the calcium carbonate from decomposition by acidic ingredients or compounding reaction products.

Diatomite

Diatomite used as a white filler is flux-calcined and then milled, screened, and air classified. In paint, its primary application, it is used to roughen the paint film to provide flatting and improved intercoat adhesion. It also improves film toughness and durability, and helps control vapor permeability for reduced blistering and peeling. Diatomite is used in mortars, grouts, plasters and stucco for improved plastic and cured properties. Natural and flux-calcined products are used in certain specialty papers as a lightweight bulking agent, as a drainage aid, as an opacity builder, and as a fiber dispersion aid. In polyolefin films fine-ground products are used as antiblocking agents by projecting through the film surface and providing mechanical separation of film layers. Diatomites are used as processing aids (absorbents) in high-oil, highly loaded rubber compounds and as both processing aids and semi-reinforcing fillers in mechanical goods.

Feldspar

In plastics, rubber, adhesives, and coatings, feldspar offers low vehicle demand, high dry brightness with low tint strength, and resistance to abrasion and chemical degradation. In coatings it also provides good film durability and high resistance to chalking and frosting.

Mica

Fine-ground and micronized mica is used in paint to improve suspension stability, to control film checking, chalking, shrinkage and blistering, to improve resistance to weathering, chemicals and water penetration, and to improve adhesion to most surfaces. Mica is considered the most effective mineral for reducing warpage and increasing stiffness and heat deflection temperature in plastics. Fine-ground and micronized grades are also used to improve electrical, thermal and insulating properties. Its largest single use is in polyolefins. Mica is used as an asbestos substitute in brake linings and gaskets, and as

a mold lubricant and release agent in the manufacture of tires and other molded rubber goods.

Nepheline Syenite

Nepheline syenite is a natural blend of about 25% nepheline and 75% feldspar. It offers low vehicle demand, high brightness with low tint strength, abrasion resistance and good film durability. It is more widely used than feldspar in coatings, due in part to the absence of crystalline silica. Nepheline syenite is also used as filler in plastics, rubber and adhesives because of its low vehicle demand, high dry brightness with low tint strength, and resistance to abrasion and chemical degradation.

Pyrophyllite

Coatings use fine-ground pyrophyllite products for low cost pigment extension. The product's platy components (pyrophyllite, kaolin, mica) promote good dispersion by inhibiting pigment settling, help film dry, and increase resistance to film cracking. Its high quartz content contributes to scrub resistance. Relatively coarse grades are used to impart mud-crack resistance to texture paints and block fillers, and checking/cracking/frosting resistance to exterior latex paints. Fine-ground pyrophyllite is also used in wallboard joint cements and in mastics to control rheology and provide reinforcement, and as a low cost alternative to kaolin and talc in rubber, plastics, adhesives and sealants applications that can accommodate its higher abrasivity.

Talc

Talc's principal use in coatings is for sheen control. It also contributes to TiO_2 extension, suspension stability, flatting, chemical resistance, leveling, film integrity and weatherability. Because it contains a variety of particle shapes and is lower in oil absorption, tremolitic talc provides easier dispersion, higher loading levels, less flatting and better dry hide than platy talc. It also provides better durability in exterior and traffic paints. Micronized platy talc is used for pitch adsorption in pulp and paper mills because of its low abrasion and its ability to preferentially wet oily materials in the presence of water. In paper and paper coatings, high purity, high brightness platy talc is used for TiO_2 extension and for improved gloss, opacity, brightness, and ink holdout. Platy talc is used to reinforce and/or fill both thermosets and thermoplastics, although principally the latter to

control melt flow, reduce creep in molded parts, increase molding cycles, increase heat deflection temperature and improve dimensional stability. Its single largest use is in polypropylene to increase both stiffness and resistance to high temperature creep. Talc is also used as a functional filler in adhesives and sealants, as a wicking preventer in automotive undercoatings, as a filler in carpet and textile backings and as a filler for rubber. Platy talc is used as a dusting agent for rubber.

Wollastonite

Wollastonite is used in coatings as an extender pigment, and to provide resistance to flash and early rust. Its acicular nature imparts film durability and superior scrub resistance. Fine ground and micronized grades provide smooth flow, water resistance, improved wet adhesion, and good gloss in epoxy powder coatings. Acicular grades impart mud-crack resistance to texture paints. Wollastonite is used as reinforcing filler in plastics because of its low oil and moisture absorption, high brightness and acicularity, and availability with a variety of surface treatments. High aspect ratio wollastonite is a lower cost alternative or complement to short-milled glass fibers for both thermoplastics and thermosets, and is used together with organic and metallic fibers in asbestos-free formulations for friction products such as clutches, brake linings and brake pistons. It is also used as an asbestos substitute in phenolic molding compounds and as a reinforcing filler in nylons, particularly high-impact and platable compounds. Wollastonite is white reinforcing filler in adhesives and sealants, where it can be used at high loadings. Powder and fine particle sized high aspect ratio grades are used as semireinforcing fillers in rubber [4, 10].

CONCLUSION

The main objective of this bachelor thesis was sharing the most used fillers, description of their basic characteristic and influence on mechanical properties of rubber compounds.

Filler morphology such as particle size, structure, and, essentially, surface characteristics have a large influence on the physical performance of the elastomeric material. Most important, however, are the surface characteristics and the chemically active sites, which determine the interaction between the filler and the polymer chains. This interaction is the key parameter in rubber reinforcement.

The filled rubber compounds found greatest exercise in automotive and truck tire manufacture. The benefits of carbon black have been known for more than a century as the best material to strengthen (reinforce) tire rubber compounds and to extend tread life. Recently, silica has become a popular reinforcing ingredient for rubber. Silica has the benefit of enhancing wet grip while also providing lower rolling resistance. The downside of silica is that its use requires an expensive coupling agent and longer mixing time. Due to economy and no requirement of coupling agents, carbon black will certainly be the main reinforcing agent for tire rubber compounds in the foreseeable future.

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