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NON-BLACK FILLERS FOR ELASTOMERS

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ABSTRACT
Almost all rubber products utilize fillers as reinforcing agents. Functional fillers transfer applied stress from the elastomer matrix to the strong and stiff mineral. 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. The non-black fillers for elastomers are calcium carbonate, kaolin clay, precipitated silica, talc, barite, amorphous silica, diatomite, etc.. This papers deals with three most widely used types of non-black fillers: calcium carbonate, kaolin clay and precipitated silica.
Keywords: fillers, elastomers, calcium carbonate, kaolin clay, precipitated silica

1. INTRODUCTION

A filler is, in the most general term, a finely divided solid that is used to augment weight or size or fill space. Although the original purpose is to lower the cost of the products, prime importance is nowdays attached to the selective functional fillers that are able to modify the mechanical, electrical and/or optical properties of a material in which it is dispersed. From the inception of the elastomer industry, the importance of fillers in providing durability and performance has been recognized. Carbon black is the major reinforcing filler for tires and many other rubber and plastic products. However, carbon black impose a restriction on the color of the vulcanized products. On the other hand, non-black fillers offer the possibility that any color can be mixed in and be seen in the products. Non-black fillers can be used to impart a number of desirable properties to rubber compounds, including:

- increased tear strength;
- increased adhesion to fibers or adjoining compounds;
- lower hysteresis;
- increased resistance to abrasion;
- lower or higher coefficient of friction;
- chemical compatibility or chemical resistance;
- lower cost, [1]

The non-black fillers for rubber are calcium carbonate, kaolin clay, precipitated silica, talc, barite, amorphous silica, diatomite, etc. Of these, the three most widely used, by volume and by functionality, are calcium carbonate, kaolin clay and precipitated silica, [1].

2. AN OVEVIEW OF THE MOST IMPORTANT TYPES OF NON-BLACK FILLERS

2.1. Calcium carbonate

Calcium carbonates for rubber are divided into two general groups. The first is ground natural limestone (wet or dry), with particle sizes of 700-5000 nm. The second is precipitated calcium carbonate with the average particle size range down to 40 nm,[2]

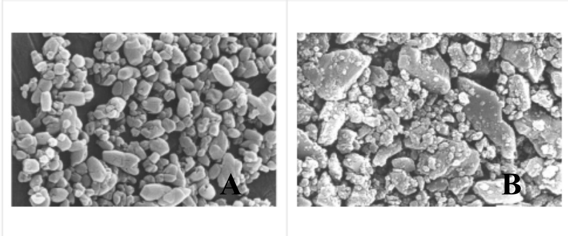

Figure 1. SEM image of dry ground calcium carbonate (A) and precipitated calcium carbonate (B), [3]

The ground natural calcium carbonates have particles with low aspect ratio and low surface area. Their disadvantage is also relatively poor polymer-filler adhesion, and as a consequence the elastomer compound has poor abrasion and tear resistance. However, because of their low cost, and because they can be used at very high loadings with little loss of compound softness, elongation or resilience, they are widely used, [2].

Table 1. Physico-mechanical properties of typical ground calcium carbonate, [2]

Property	Value
Specific gravity (g/cm^3)	2,65
Oil absorption (ml/100g)	35
Particle size (μm)	3,25
Surface area (m^2/g)	3,6

Precipitated calcium carbonates have much higher surface area. Precipitated products are produced by controlled carbonization of a dilute solution of calcium hydroxide. With various reaction concentrations, time and temperature it is possible to obtain different crystal forms (calcite or aragonite), and different crystal shapes. For use in rubber, usually only the finer products below 0.1 μm are considered. The ultrafine products, with particles smaller than 100 nm, can provide surface areas equivalent to the hard clays, [2].

2.2. Kaolin clay

Kaolin clay is a platy aluminosilicate. Its continuous sheet structure produces thin particles which exist in nature as overlapping flakes. Kaolin crystals are bound via hydrogen bonding of the octahedral layer hydroxyl face of one plate to the tetrahedral layer oxygen face of the adjacent plate. Separation into individual clay plates is therefore difficult, but can be accomplished by mechanical means to produce delaminated kaolin,[1]. The various types of kaolin clay fillers are shown in figure 2.

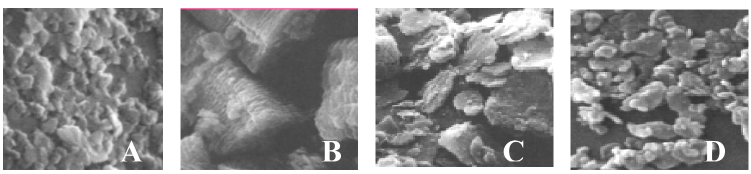

Figure 2. SEM image of varius types of kaolin clay fillers,[3]

There are for basic processes for producing kaolin clay for rubber reinforcement from the mined form:

- Air-floated clay in which the ore is milled to break up lumps and air classified. It is the least expensive form of clay and has moderate reinforcement, Fig 2.A.
- Water washed clay involves gravity separation of impurities, bleaching and magnetic separation to improve color properties and centrifuging to produce the desired particle size range. Water washed clay has higher reinforcement with the ability to control pH, color and particle size, Fig 2.B

- Delaminated kaolin (figure 10) uses chemical and/or mechanical means to break apart the platelet structure of the clay, which further increases the available surface area and reinforcement properties, Fig 2.C.
- Calcined (figure 11) is heated to 1,000 [degrees] C, which produces a very white, high surface area mineral with an inert surface, Fig 2.D,[1]

Clay is a widely used filler for rubber compounds of all types, including components of tires such as fiber adhesive compounds, and the entire range of non-tire rubber applications where good reinforcement, moderate cost and good processability are desired,[1]

2.3. Amorphous silica

Many processes exist to produce amorphous precipitated silica, and the majority of these processes start with creating an aqueous solution of silica, followed by steps of hydrolysis and condensation. An alternative method to produce silica particles is by flame synthesis which includes combustion of either a liquid or vapor containing silica molecules. The reinforcement potential of silica is greatly influenced by its structure. Precipitated silica consists of a three-dimensional network of coagulated primary silica particles. The standard practice in the elastomer industry is to classify the structure of these fillers in terms of primary particles, aggregates, and agglomerates, figure 3.

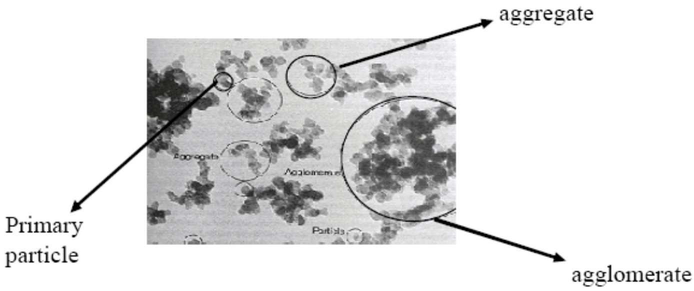

Figure 3. TEM picture of silica (primary particles, aggregates and agglomerates)[3]

At the smallest size is the ‘primary particle’. The primary particles are joined together with other particles of similar size to make up a larger aggregate structure. A third structure is used to describe the clustering or clumping together of the aggregates to form a still larger structure known as agglomerates, [4]. Agglomerates are described as being made up of weakly bonded aggregates, forming a structure that has a size from the µm to mm size scale, [5]. According to the standards that are defining quality of SiO_2 fillers in the rubber industry, values of main characteristics are given in table 2.

Table 2. Physico-mechanical properties of precipitated silica, [4]

Property	Value
Specific gravity (g/cm3)	2,1
Oil absorption (ml/100g)	min. 200
Particle (primary) size (µm)	0,005-0,08
Surface area (m^2/g)	125 - 200

Active silicas are used in the production of various types of rubber, such as tires, rubber parts of shoes, rubber parts of technical products, artificial leather, some types of plastics, etc. Compared to carbon black, the traditional filler for rubber, silica improves some mechanical properties and also gives the possibility of neutral colored rubber, [4]

3. CONCLUSION

All mineral fillers are usually white or light colored so there is an obvious benefit that non-black mineral fillers can be used to make light colored products. The characteristics of filler which determine the properties of elastomer compound are: particle size, particle shape, surface area and surface activity. Filler must make intimate contact with the elastomer chains in order to reinforce the elastomer compound. Therefore, fillers that have a smaller particles have more contact area available and a higher reinforcement potential. The shape of particles also influences a reinforcement ability of a filler. A planar particles have more surfaces available for contacting the elastomer matrix than spherical particles with similar particle size. Clays have planar-shaped particles that produce greater reinforcement effect than spherical-shaped calcium carbonate. For this reason, it provides very little reinforcement or strength enhancement to the rubber. Calcium carbonate is added to lower cost, improve processing, and impart light color. Kaolin clay is extensively added to mechanical goods to lower cost and provide some reinforcement. Precipitated silica chains and bundles are considerably smaller than the particles of clay an calcium carbonate. They thus have more surface area available to make strong connection with the elastomer. Finally, it must be emphasized that a filler may have high surface area and high aspect ratio, but still provide relatively poor reinforcement if it has low specific surface activity, which is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer.

4. REFERENCES

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