Lecture No. (7)

Rubber Fillers
Introduction of Rubber Fillers

Rubbers in general are seldom used in their only form because of they are too weak to fulfill practical requirements for many applications such as lack of hardness, strength properties and wear resistance, but when addition of particulate fillers the strength could be increased by 10 times. The elastomeric materials can be modified when using the additives such as fillers, pigments, stabilizers, plasticizers, accelerators, etc.

The fillers are used with other components called compounding ingredients. The use of fillers in rubber products is nearly as old as the use of rubber itself, because of most rubber applications is modified by incorporation the rubber with particulate fillers such as improve the processability, performance, properties and life of the final rubber product, reduce cost, and impart its color.

The selection any type of fillers that used in rubber is depended on the required property of the end rubber product. The first used of fillers in the early of 20th century, prior to World War I, which was used for color of rubber products.

Sources of Rubber Fillers

Almost every selected material has been added to rubber in order to cheapen and improve their properties. The major particulate fillers used in the rubber industry general can be classified as (black) and (non-black), depending on their original, which mostly produced from petroleum and mineral sources.

1- Non-Black Fillers

A wide range of non-black fillers, such as precipitated silica, fumed silica, alumina, clays, cellulose, magnesium carbonates and whitening fillers (calcium carbonate), in the past the rubber reinforcement with different types of clay minerals as fillers.

2- Black Fillers.

The most important particulate fillers have been used in rubber industry are carbon black and silica as conventional reinforcing fillers to enhance the mechanical properties of various rubbers. In general, the carbon black would be
used as black filler reinforce of rubber to enhance tensile strength and exhibits higher modulus of elasticity than silica reinforced only. While the silica including the highly dispersible in the rubber. The carbon black is the most widely used as reinforcing filler in elastomers, due to the physical, chemical or mechanical characteristics and performances it gives to original rubbers. About 5 million tons of carbon black is globally consumed each year, while only 250,000 tons of the silica, used each year.

**Reinforcement Fillers of Rubber Types**
1- Non-reinforcing or degrading fillers.
2- Semi-reinforcing or extending fillers.
3- Reinforcing fillers.

The term (reinforcement) refers to an improvement in the performance of the rubber compounding when it is using. Reinforcing filler is a particulate material that is able to increase the tensile strength, tear resistance and abrasion resistance of natural or synthetic rubber. Semi-reinforcing filler is a particulate material that is able to moderately improve the tensile strength and tear strength, but does not improve the abrasion resistance. Non reinforcing filler is unable to provide any increase on these properties and it function only as a diluent.

**Carbon Black Fillers**

Carbon black (CB) is the general term used to describe a commercial powder form of carbon. Carbon black is a fluffy powder has extreme fineness, chemical stability, and have high surface area about (6-15) m²/gm. When, the carbon black incorporation with rubber gives improved tensile strength, modulus of elasticity, fatigue resistance, and abrasion resistance, but due to its_polluting nature, black color of the rubber compounding and dependence on oil feedstock for the synthesis caused to look at for (white reinforcing) materials.

Carbon black is prepared by incomplete combustion or by thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions, and prepared by incomplete burning of natural gas on the carbon surface. Carbon blacks
can also be produced by thermal decomposition of hydrocarbons in the absence of oxygen.

The carbon black is composed essentially from three colloidal particles morphological forms existing in rubber compounding includes (primary particle, aggregate, and agglomerate). The sizes of these morphological forms have the following order: particle < aggregate < agglomerate. Single carbon black particles typically have their particle size ranges (15 to 300) nm, they are the fewest using in rubber industry. While, the aggregates do not break during rubber compounding and have their particle size ranges (85 to 500) nm, the carbon black particles are most widely used as aggregate. The commonly used carbon black to rubber compounding as agglomerate, consists of a group of aggregates and have their particle size ranges (1-100) µm. Which it require large amount of energy to break down during rubber compounding due to high cohesive forces among carbon black particles, as shown in Figure (1).

![Figure (1): Morphological of Carbon Black Particles.](image)

Carbon blacks are classified into furnace blacks, channel blacks, thermal blacks and lamp black depending up on their method of manufacturing. The major types of carbon blacks as filler reinforcement of rubber are manufactured by the furnace process, over 95 % of all carbon black produced today by this process. Table (1) shows carbon blacks by ASTM classification, the old classification and size ranges. Carbon black is used principally as reinforcing filler of rubber, black pigment of tires and electrically conductive for other application.
Table (1): Classification and Size Average of Carbon Blacks.

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

The primary filler factors influence on the elastomer reinforcement are particle size, particle dispersion, particle shape, structure, surface area, surface activity and surface chemistry, these properties represented the basic properties of carbon black, and have a large effect on properties of rubber compounding when they are mixed with rubber such as blackness, porosity and dispersibility.

**Silica Fillers**

Silicon dioxide (SiO₂) is commonly referred to silica, which is formed by strong covalent bonds, and four oxygen atoms are arranged at the corners around central of tetrahedron silicon atom, as shown in Figure (2).

![Figure (2): Crystal Structure of Silica Atom.](image)

There are two types of silica are precipitated silica and fumed silica with different manufacturing methods. Precipitated silica is manufactured by acid precipitation from silicate solution, silicate solution product by reactions of sodium silicate with acid or alkaline earth metal salts, it has average particle size (10 to 100) nm and water contains is (10-14%), While fumed silica is produced at a high
temperature by a reaction of silicon tetrachloride with water vapor, it has average particle size (7-15) nm.

Silica is important filler in the rubber industry although of silica is not quite reactive with rubber as carbon black. In the recent years, rubber tires filled with silica to reducing rolling resistance and increasing hardness, therefore the largest application of silica is tire products.

The silica usually exists as aggregates and agglomerates, when exits hydrogen on the silica surface, that causes a serious problems in rubber compounding, such as poor dispersion of silica. This problem could be solved by adding silane coupling agents into rubber to modification of silica particles surface and increase the interaction between the silica and rubber. However, the curing time of rubber with silica is longer than with carbon black, thus the production time is extended but reduced in productivity.

**Alumina Fillers**

Aluminum oxide (Al₂O₃), is commonly referred to alumina, which is most widely used as engineering ceramics. It has strong ionic interatomic bonding, which gives rising to its desirable characteristics such as hardness, high stiffness, good wear resistant, high abrasion resistance, high compressive strength, good thermal conductivity. It also has extreme temperatures resistance, high corrosive and environmental resistance.

The purity of alumina filler ranges (94-99.9%), with excellent size and shape, so that it has a very wide range of applications such as wear pads, seal, or any rubber applications, which require abrasion resistance and dimension stability at high temperature.

**Cellulose Fillers**

Cellulose is the most available natural polymer, which represented the main component for all plants such as cotton and trees, because of it has high mechanical properties. The cellulose structure consists of large linear polymer chains with
many hydroxyl groups, and has low amorphous and highly crystalline compact structures, strong intermolecular and hydrogen bonding among cellulose chains.

Cellulose can be used in the many applications such as coatings, packing and papers, because of its biodegradability, biocompatibility, available in nature and low cost. Also, when using cellulose fiber as a filler reinforcement of rubber, give rubber product have high strength, high stiffness, and insoluble in water, that used for many applications such as ropes, hose, belt, mats and insulation, but have not been used for tire applications.

**Clay Fillers**

Clay is represent the cheap filler and largest volume of non-black filler that used in the rubber industry, and has poor reinforcing capability because of its large particle size and low surface activity. Clay minerals are widely used in rubber compounding to reduce rubber compound cost while providing good reinforcing, and improving physical or processing properties.

The main clay mineral is kaolin and derivative that produced by chemical and heat treatment. Kaolin clay is typically used rubber filler that classified as either hard clay or soft clay in relation to their particle size and stiffening that affect in rubber. Hard clay will have a median particle size (250 to 500) nm, and when it reinforces rubber imparts high tensile modulus, tensile strength, stiffness, and abrasion resistance to rubber compounds. Soft clay has a median particle size (1000 to 2000) nm, when it reinforces rubber impart low physical properties and when it is produced rubber compounding where high loadings and faster extrusion rates are more important than strength.

Several clays particles can be treated with silane coupling agents before added to rubber, in order to improve the adhesive bond between clay particles and rubber, increased tensile modulus, tensile strength and improve the performance of rubber compounding.