

Lecture No. (13)

**None-Sulfur
Vulcanization**

Sulfur Blooming Process

Two forms of sulfur are used in vulcanization process includes: soluble sulfur (crystals, rings sulfur), and insoluble sulfur (amorphous, sulfur). The blooming process which refers to migrates of sulfur to the surface of rubber compound and crystallizes there. Blooming can occur when large amounts of soluble sulfur are used at high mixing temperature the solubility of (S8) is high and enabling large amounts to dissolve.

When is reached to the solubility limit or solubility decreases at cooling this mixture, lead to excess sulfur blooms to the surface. Sulfur bloom reduces the viscosity of a rubber compound, and considers a necessary property to make a composite structure such as a tire. Usually, in the rubber compounds that containing high levels of insoluble sulfur, insoluble sulfur is used to prevent sulfur blooming process, Insoluble sulfur does not bloom because it disperses in rubber as discrete particles, which cannot readily diffuse through the rubber. However, above 120°C, insoluble sulfur transforms into soluble sulfur. Thus, mixing temperatures must be kept below (120 °C) to take advantage of the bloom resistance of insoluble sulfur.

Non-Sulfur Based Curing Systems by (Free-Radical Interlinking)

The saturated elastomers materials that backbones (haven't double carbon bond), cannot be crosslinked with sulfur and so require alternate curing agents such as peroxides are used in general cases, also the metal oxides and di-functional compounds are used in special cases. However, sulfur interlinking is still the first curing agent that choice for rubber vulcanization.

Therefore, when vulcanization (interlinking) of rubber with other than sulfur can be carried out by free-radical reactions, that do not require the presence of C=C bonds in the rubber chain. Free radicals are formed by irradiation with ultraviolet light, by electron beam, by nuclear radiation, or by thermal decomposition of unstable additives. In each case, hydrogen atom is broken away from the elastomer molecule chain, and remove to generate a highly reactive carbon atom (the free

radical), that will react with another carbon atom to form a stable C–C bond (crosslinking), between elastomer molecular chains.

1- Peroxides

The peroxides are one type of curing agent that most widely used as alternative to sulfur for elastomers vulcanization. Unlike sulfur vulcanization, carbon-carbon double bonds are not required for peroxide curing. Thus, the peroxides may be used to crosslink saturated elastomers, for examples (ethylene-propylene rubber, chlorinated polyethylene rubber, chlorosulfonated polyethylene rubber, and silicone rubber). Also, the peroxides are used with unsaturated elastomers.

Peroxides cure take place by the thermal decomposition into oxy and peroxy free radicals, which abstract hydrogen atoms from the saturated elastomer to generate elastomer chain radicals. The rate of cross-linking is directly proportional to the rate of decomposition of the peroxide. Therefore, the cure rates and curing temperatures depend on the stability of the peroxide.

Although the peroxides give the carbon-carbon crosslinks are more thermally stable than carbon-sulfur crosslinks, but they provide generally poor tensile and tear strength. Also peroxides are readily crosslinks elastomers and incompatible with many of the antioxidants that used in rubber. Finally, the peroxides cannot be used with butyl rubber because they cause chain scission and depolymerization.

2- Metal Oxides

Some elastomers materials can be crosslinked by using metal oxides as curing agents, which includes (ZnO, MgO and Pb₂O₃). Generally, mixtures of (ZnO and MgO) are used because ZnO alone is too scorchy and MgO alone is inefficient. Also metal oxides that usually contain (zinc oxide and lead oxide) for improved water resistance. Generally, the metal oxides are used as cross-linking agents for halogenated elastomers such as polychloroprene rubber, butyl rubber, and chlorosulfonated polyethylene rubber. The metal oxide abstracts the halogen from adjacent elastomer chains to form an oxygen crosslink plus the metal chloride salt.

3- Di-functional Compounds

Certain di-functional compounds are used to crosslink elastomers chains by free-radical reacting to bridge elastomer chains. For example, diamines (e.g., hexamethylene diamine carbamate), isocyanates and urethane are used as crosslinks for fluoroelastomers.

Factors of Rubber Vulcanization

When curing of elastomer material, the type of crosslinks that created depends on:

- 1) Sulfur level.
- 2) Accelerator type.
- 3) Accelerator to sulfur ratio.
- 4) Curing time.

Generally, high accelerator to sulfur ratio and longer curing time lead to increase the number of monosulfidic linkages more than of polysulfidic linkages. Vulcanizates containing particularity monosulfidic crosslinks have better heat stability (less scission), resilience resistance, and promote better thermal and aging characteristics than those with polysulfidic crosslinks. This is attributed to greater stability of C-S bonds compared to S-S bonds. On the other hand, compounds containing a high proportion of polysulfidic crosslinks possess greater tensile strength, fatigue resistance and provide better molecular flexibility compared with monosulfidic crosslinks.

Influence of Crosslink Length

The length of the sulfide crosslinks is formed during the vulcanization process affect strongly on the rubber properties. The choice of accelerator type will influence on the crosslinks length, but this can be further controlled by detect the accelerator to sulfur ratio. At increasing this ratio gradually lead to shorter crosslinks. The use of a cure system designed to form short crosslinks is referred to as efficient vulcanization (EV). The thiuram accelerators, particularly the (disulfides) are commonly used for this purpose.

Influence of Crosslink Density

Mechanical properties of an elastomer material depend strongly on the crosslinks density. The fracture properties such as (tear strength and tensile strength), modulus of elasticity and hardness increase with increasing crosslink density, and the elastomer material becomes more elastic. To understand this behavior, it is first to consider fracture in an uncrosslinked elastomer, and then discuss changes in the fracture mechanism of elastomer as crosslinks are introduced.

When uncrosslinked elastomer is exposing to low stress, the molecules chains may readily slide past one another and disentangle. And the ductile fracture occurs without breaking chemical bonds. The effect of a few crosslinks is lead to creating branched molecules. It is more difficult for these branched molecules to disentangle, finally the strength of elastomer increases. But when crosslinking is increased, the strong three dimensional network forms, then, cannot be fractured without breaking chemical bonds to create crack that is very difficult. Thus, the strength of elastomer increases to maximum value.

When uncrosslinked elastomer is deformed by an external force, part of the input energy is stored in molecules chains and it is available as a driving force for crack growth and fracture. The remainder of the energy is dissipated through molecular motions as heat, and unavailable to break chains. At high crosslink levels, the molecules chain motions become restricted and the three dimensional networks is incapable of dissipating much energy, the result is brittle fracture. Therefore, the crosslink level must be high enough to prevent ductile failure, but low enough to avoid brittle failure. Both types of cross-linking are important in elastomers materials.