Lecture No. (9)

Selection and Properties of Rubber Additives

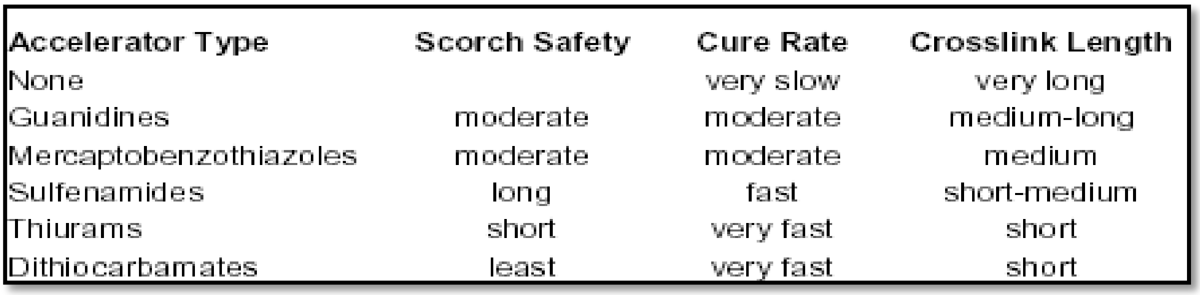
1- Accelerators

The vulcanization reaction can be modified in various desirable ways, one way using accelerators. When alone sulfur is used in the rubber vulcanization process, the rate of vulcanization was extremely slow to form polysulfide links, cross-linking is quite inefficient and requires curing times of about (3 to 5) hours. While when addition of accelerator with sulfur that leads to reduce the cure time between (2-5) min, increase the sulfur crosslinking efficiency and cure rate is fast. These additions affect by both type and quality of the rubber and accelerator, the type of accelerator is much too important than the level of accelerator in controlling of vulcanization reaction. The choice of accelerator will effect on the vulcanization safety, vulcanization activity, cure rate, curing time, crosslink length and crosslink density which form in rubber. While, when increased the levels of accelerator lead to increase the cross-linking density.

Generally, the acceleration was discovered in (1906) that observation significantly decreased in vulcanization times, when addition of aniline ($C_6H_5NH_2$) to rubber-sulfur or rubber-zinc oxide systems. In most cases the vulcanization processes include using two different types of accelerators, because they can be activated each other, but if we use two same types of accelerators, these materials are combined and then cure characteristics are approximately average of them.

The accelerators which have the large application and it product in greatest volume are the thiazoles (C_3H_3NS), and sulfonamides. They have the fast cure rate, good vulcanization safety and high vulcanization activity. Generally properties and effect of the accelerators are shown in Table (1). Almost all accelerators require use of inorganic and organic activators to develop their full effectiveness.

Table (1): Accelerators Proper



Accelerator Type	Scorch Safety	Cure Rate	Crosslink Length
None		very slow	very long
Guanidines	moderate	moderate	medium-long
Mercaptobenzothiazoles	moderate	moderate	medium
Sulfenamides	long	fast	short-medium
Thiurams	short	very fast	short
Dithiocarbamates	least	very fast	short

2- Activators

The main purpose of activator in rubber is support the vulcanization reaction, especially in the rubber-sulfur curing systems. The activators are materials that added during the vulcanization process, to improve acceleration activate, permit the vulcanization system to realize its full cross-links and leads to increase the speed of sulfur vulcanization rate more rapidly than crosslinking by sulfur acceleration alone.

The inorganic activators include zinc oxide, magnesium oxide, and carboxylic oxide, while the organic activators include (stearic (fatty), palmitic, carboxylic) acids and zinc salts. The efficiency of the polysulfide cross-links during rubber vulcanization can be controlled by the complex rubber compounding formed from rubber, sulfur, activators (zinc oxide and stearic acid), and accelerators. These materials represent constitutes of vulcanization system for the rubber compounding.

Zinc oxide reacts with stearic acid to form zinc stearate and create soluble zinc ions that activate reaction in the elastomer to formation polysulfide crosslink.

3- Anti-degradents

Rubber compounds can be degraded by reactions especially with oxygen, ozone, light, metal ions and heat. Because of the oxygen and ozone can react with elastomers and alteration network structure by causing chains splitting. Also many applications involve light colored products, which must not be darken with age or when exposure to light. Anti-degradents include (anti-oxidants and anti-ozonants) can be chemically or physically function, to protect rubber against of oxygen and ozone attack, by inhibits the action of these components. Also play main importance role to maintain the properties of rubber products at service conditions.

Chemical protectants function is capable of reacting with the degradant to prevent degradation of the rubber. The most common types are aromatic amines, phenolics, and phosphites. Physical protectants function is capable it of migrating to the rubber surface and providing barrier to degradants attack. The most commonly used is crystalline waxes, which are mixtures of alkanes and hydrocarbons. The rate of migrating is important and depends on the compatibility level with the elastomer.

Also, antioxidant and antiozonants are called resistors, which used to reduce aging processes of rubber vulcanized by decrease the deterioration of rubber products.

A- Anti-oxidants

In general, the reaction of oxygen with elastomers causes both chain scission that lead to elastomers become softens and sticky. Therefore, the finally network have high chain-end defects, reduced the strength and increase elongation of rubber.

A concentration of oxygen about (1 to 2%) is normally sufficient to cause severe deterioration in an elastomer. The principal mechanism of oxygen attack involves free radical reaction. The first step is the creation of macroradicals as a result of hydrogen abstraction from rubber chains. Oxidation continues by reaction of macroradicals with oxygen and finally formation of peroxy or oxy radicals and hydro-peroxides. The oxidation rate increases when sulfur content increases, temperature increases, exposure to ultraviolet light, stress applied, high quantity of oxygen absorbed, and presence some metal, such as copper, cobalt, and manganese.

Anti-oxidants are employed to protect large surface area of most rubber products especially (unsaturated elastomers) from degradation when contact with oxygen attack. Which design to scavenge and destroy oxy and peroxy free radicals.

Anti-oxidants have two types with different functions. The first type, called preventive antioxidants, that reacts with hydro-peroxides to form non-radical products. The second type, called chain-breaking antioxidants, destroys peroxy or oxy radicals. Additionally, non-staining antioxidants such as hindered phenols and amine derivatives must be used. These have good heat stability and effective against copper contamination, which cause rapid degradation of rubber.

B- Anti-ozonants

Ozone, when present in the atmosphere at only a few parts per hundred million, lead to readily break carbon-carbon double bonds in elastomers, therefore unsaturated elastomers as well as saturated when exposed to ozone, quickly increases of surface cracks especially when applied small stress. Anti-ozonant is used for the protection of rubber against ozone attack especially for use in warmer environment or high service temperatures. For example, para-phenylene diamines (PPDs) are effective in reducing ozone cracking in diene rubber (contain two carbon double bonds) and react directly with ozone, instead of reaction rubber with ozone.

4- Stabilizers

The naturally stabilizing system occurring in ammonia preserved latex is not adequate to face the conditions that happen during concentration, transportation and distribution process, but can't to withstand the more severe conditions that met during compounding and processing, therefore stability of rubber must ensure by the addition of more powerful agents called stabilizers.

Some degree of stabilization may be obtained by adding simple materials such as soap and proteins. The proteins are susceptible to bacteria and give high viscosity rubber, which finally may give products having low physical properties. Soaps are convenient to use but their behavior is not known and they have limited applications. While the synthetic stabilizers are now available and free from the limitations associated with soaps or proteins, which include anionic surface-active agents and non-ionic surface-active agents, which different in functioning method.

An anionic surface-active agent such as sodium salt, when present in sufficient quantity, leads to stabilizes rubber compounds against heat and mechanical action. This type is most effective and efficiency in alkaline medium, but loses its activity in the acids medium and when increasing the temperature.

While non-ionic surface active agent such as an ethylene oxide have remarkable stabilizing power to protect rubber compounds against the effects of mechanical action and salts, also it affords excellent protection to rubber compounds during storage at room temperature. This type is most effective and efficiency in acids medium, but loses its activity when heating at high temperature.

5- Plasticizers Agents (Processing Aids)

The plasticizers agents are one types of additives have lower viscosity and do not react chemically with rubber when it add, when it use lead to fabricated rubber compound with less energy, and increase melt stability so that increasing the processing rate. Also it is added to rubber compounding to aid in dispersing dry filler particles and pigment particles into rubber and function to modifying the physical properties, elongation, and impact strength, but decreasing the hardness and tensile strength of rubber compounds and rubber vulcanized, the effect of plasticizers on both mechanical property and processing rate as shown in Figure (1).

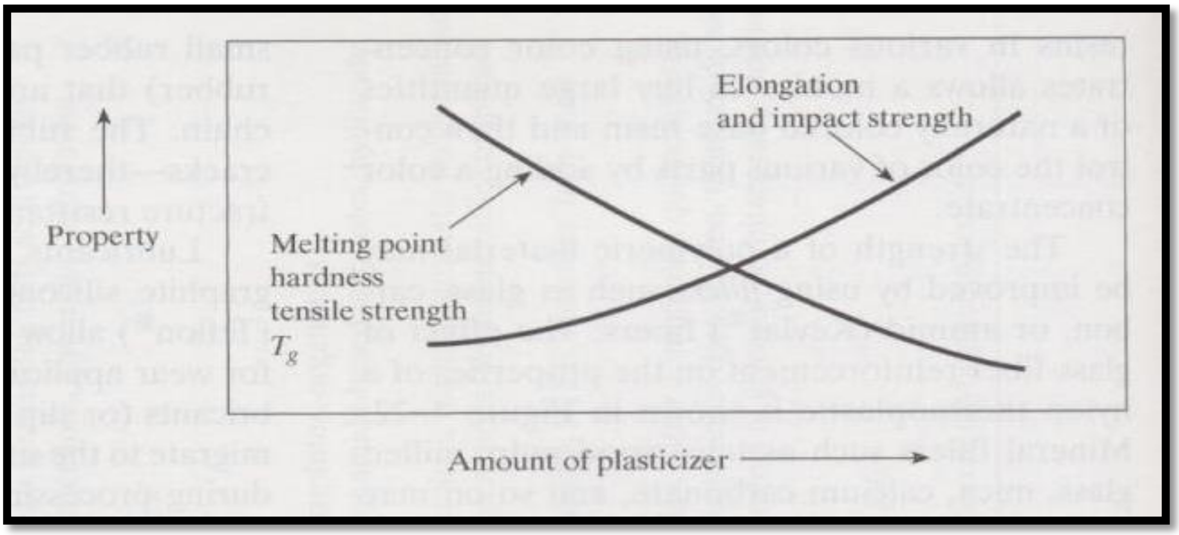


Figure (1): Effect of Plasticizer on the Properties of Rubber Materials.

There are two types of plasticizers agents include chemical plasticizers and physical plasticizers. Chemical plasticizers typically added about (1 to 3 pphr) to NR such as sulfonic acids and penta chloro phenol. The excess chemical plasticizers must be avoided, because it results in reduced strength of rubber vulcanized.

Physical plasticizers include (oils, fatty acids, esters and liquid polymers), which function is softening rubber compounds by decreasing entanglements force and internal friction, also may be improvement the flexibility at low temperature. Physical plasticizers should have good compatibility, which can become a problem at low temperatures, because a poorly compatible plasticizer at low temperatures.

In some rubber applications like toy balloons, plasticizers are added to rubber to soften them so that they may be easily inflated. In this case the plasticizers agents call (blowing agents), the most common used of blowing agents are liquid paraffin, paraffin wax, and stearic acids.

6- Wetting Agents

The wetting agents can act as same as the processing aids by reducing surface tension and allowing the rubber to better wet the surfaces of pigment particles, also it is allowing easier dispersion of filler particles into rubber.

Sometimes the addition of a wetting agent to rubber compounds is necessary for successful saturation of filler fibers in the rubber, for examples sulfonated oils (wetting agent) have been effective in complete penetration of rubber between textile fibers without any danger of destabilizing the rubber.

7- Flame Retarders

The desired level of safety from flame can be obtained by use of flame retarders with accelerators. The traditional retarders are benzoic acid and salicylic acid, which interfere with the activity of the accelerators. These acids lead to retard the flame time but slow the curing rate. The widespread use of sulfenamide accelerators as new type of retarder which leads to improve these accelerators, and give superior flame safety and scorch safety for rubber without reducing curing rate.

8- Extenders

Limits amount of extender can be added to rubber compositions to reduce cost, decrease physical properties of rubber, lead to stiffen the rubber compositions, also have little effect on the rubber strength or diminish the strength of rubber and permits use of elastomers with higher molecular weight. Oil is widely used to extension of rubber, especially in tire with levels about (30 to 40 pphr). The other types of extenders are particulate solids with primary particle sizes greater than (1 µm), such as clay, calcium carbonate and ground coal.

9- Tackifiers

Tack is the ability of two materials to resist separation after being in contact for a short time under light or pressure affect. Tackifiers are a class of resins that added to elastomers about (1 to 10 pphr), it have softening points between (50 to 150 °C) and often have limited compatibility with the elastomer the (NR, SBR and NR/SBR blends) have high compatibility, they are less compatible than a plasticizer, but more compatible than filler, this is dependent on chemical composition and molecular weight of rubber. Tackifiers typically added to rubber, in order to improve initial tack and prevent tack degradation that occur after stock it.

10- Thickening Agents

Thickening may be accomplished with either colloidal thickeners or solution thickeners, small particle size of colloidal thickeners such as silica will thicken rubber when added to it. Solutions thickeners which include: protein, starch, glue, gelatin, casein, sodium poly acrylates and poly (vinyl methyl ether).

11- Dispersing Agents

The selection and amount of dispersing agent is determined by the requisite physical properties of rubber products. The functions of these agents are wet the powders, reduce the foamy and prevent re-aggregation of particles. The concentration of dispersing agents rarely exceeds (2%), except in special conditions.

The most common use of dispersing agents include (gelatin, protein, glue or soap), possesses all the requisite properties and it is necessary to use for mixtures that contains two or more of dispersing agents, deionized water and small amount of bactericide about (0.01%) sodium trichlorophenat. The mixed ingredients are dispersed by ball milling at least 48 hr. The mixed ingredients dispersion has excellent storage stability against re-aggregation and settling of particles in rubber.

12- Emulsifying Agents

An emulsion is defined as systems that contain two liquids in which one liquid is colloidal dispersed in another. The emulsions use for rubber latex should be containing (oil-in-water) type in which water is the continuous phase.

Various synthetic emulsifying agents are available in the market, such as soaps that have been used to be quite satisfactory of emulsion for the rubber compounds. In this method, the cationic part of the soap (ammonia, KOH or amine) is dissolved in water and the anionic part of the soap (stearic acid) is dissolved in the other liquid to be emulsified.