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A REVIEW PAPER ON VULCANIZATION OF RUBBER AND IT'S PROPERTIES

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ABSTRACT

Natural rubber is composed of long polymer molecules and is sticky in nature. It is obtained from trees in the form of latex. Elasticity as well as tensile strength of natural rubber is low. So, vulcanization is done to enhance the properties of natural rubber. Generally Sulphur along with additives is added to rubber and heated up. This will increase the properties of rubber. Vulcanized rubber gets application in various industries and products such as conveyor belts, pulleys, tires, vehicle mats, etc. This paper appraises the data regarding the process of vulcanization which improves desirable properties of rubber.

Keywords: Natural Rubber, Vulcanization, Rubber.

I. INTRODUCTION

Natural rubber is a polymer and is obtained directly from trees in the form of latex. Latex is milky white liquid, sticky in nature and is the polymer cis-1, 4-polyisoprene which comprises of one third water and one third rubber particles. Natural rubber is a polymer of isoprene (2-methylbuta-1, 3-diene) with the chemical formula (C₅H₈)_n.

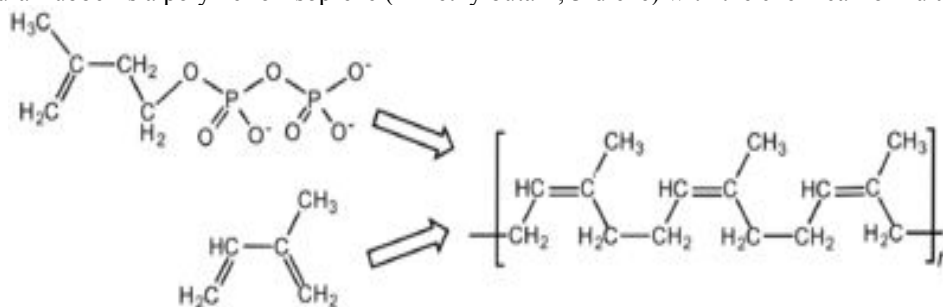


Fig. 1. Chemical Structure of Cis-Polyisoprene

The Natural rubber which is in the form of latex is sticky, soft, and thermoplastic. It has low tensile strength and low elasticity. It is a mixture of polymeric chains with varying lengths. Most importantly, there is no cross linking. As a result, the material did not find any significant application. However, these properties are changed by a process known as vulcanization.

Vulcanization is a chemical process in which natural rubber or related polymers are converted into more durable materials via the addition of accelerators (generally sulphur). These additives modify the polymer by forming cross-links between individual polymer chains. Vulcanized rubber is elastic & less sticky not alike raw rubber, doesn't harden or soften much with cold weather except at very high temperatures. In addition, it is highly resistant to abrasion. The cross linking improves its tensile strength. Vulcanized rubber is ten times stronger as well as more rigid than natural rubber.

The process of vulcanization of rubber is invented accidentally by an American inventor named Charles Goodyear in 1839 when he dropped some rubber containing sulphur onto a hot stove. He noticed that sulphur was not fully dissolved or dispersed in the rubber but combined chemically in the form of cross links. During the process of vulcanization, when we add sulphur with rubber, the C-H bonds get broken and replaced by C-S bond. There occurs cross linking of chains with each other which creates a three dimensional network of rubber. Each cross-link is made up of a chain of about 8 sulphur atoms between two long chains of polyisoprene. Now a

days, extenders usually carbon black or zinc oxide is added during vulcanization in order to further improve the properties of rubber, in addition to sulphur. The Process of vulcanization is carried out at about 140°–180° C temperature.

II. PROCESS

Polyisoprene or natural rubber and styrene-butadiene are the main polymers used for vulcanization. Styrene-butadiene is a polymer used for manufacturing of tires of most passenger cars. Mostly a separate “cure package” is required for each vulcanization process of rubber depending upon its application. "Cure sites" are allylic hydrogen atoms. Carbon-carbon double bonds and carbon- hydrogen bonds are adjacent to each other. A Sulphur atom linked with chain of another polymer replaces these carbon- hydrogen bonds during the vulcanization process. Properties of vulcanized rubber depend upon the number of sulphur atoms in the crosslink. Rubber with higher number of sulphur atoms present in crosslink exhibits less heat resistance but good dynamic properties which are crucial for flexing movement of rubber say side-wall of a running tire. Rubbers with short crosslink's give better heat resistance.

III. VULCANIZATION METHODS

There are various methods exists for vulcanisation of rubber. The most economical method uses increased temperature and pressure for vulcanization of tire rubber. Generally, for passenger tire vulcanization, 170 °C temperature is employed. The process is known as compression molding. Hot air vulcanization or microwave heated vulcanization which are both continuous processes are used to make door profiles for automobile vehicles. Commonly used curing systems are:

1. Sulphur systems
2. Metallic oxides
3. Peroxides
4. Urethane cross linkers
5. Acetoxysilane

Vulcanization with sulphur

Vulcanization with sulphur is the most commonly used method for vulcanizing. However, synthetic polyolefin's does not get vulcanized by sulphur as it is a slow vulcanization agent. Even, Vulcanization with large amount of sulphur at high temperatures and long heating periods provides unsatisfactory crosslinking efficiency. Vulcanization cannot be achieved only with sulphur alone because sulphur reacts with rubber very slowly and forms bonds in the form of cyclic structure and not in the form of sulphur cross-links. So vulcanization additives are used. The accelerators and activators are catalysts. Vulcanization of rubber with sulphur will occur only in the presence of catalysts i.e. accelerators and activators and antidegradants. Zinc oxide and stearic acid are some activators used in the process of vulcanization of rubber with sulphur.

Vulcanization with metallic oxides

Metallic oxides are used for vulcanization of neoprene or polychloroprene instead of sulphur. Different type of accelerator is used because of various processing factors. Ethylene thiourea (ETU) is the most important accelerator used along metallic oxides. Ethylene thiourea (ETU) has been classified as reprotoxic and is the most important accelerator used along metallic oxides. Magnesium oxide (MgO), zinc oxide (ZnO), and lead oxide (PbO) are examples of metal oxides.

Vulcanization with peroxides

Peroxides are used as curing agent for the vulcanisation of rubber especially saturated which do not contain any reactive group. However, it is relevant to both natural rubber and saturated rubber. Peroxide produce radicals which are responsible for the formation of C-to-C linkages with adjacent polymer chains and does not enter into the polymer chains. Examples are dialkyl peroxide, zinc peroxide, benzoyl peroxide, 2,4-chlorobenzoyl peroxide & 2,5-bis(t-butylperoxy)-2,5-dimethylhexane. Radical transfer from the peroxide to the polymer chain gets oxidized in the presence of oxygen, so this process is not to be done in the presence of hot air.

Vulcanization with Urethane cross-linkers

Urethane cross linker is the newest vulcanizing agent discovered at the *Malaysian Rubber producers Research Association (MRPRA)* in England by a scientist and developed by Hughson Chemicals, Lord Corporation, in the United States. It is made available for sale under the trade name Novor 924 by Durham chemicals. It is free-flowing powder, dustless, expensive, 75% active ingredient and 25% naphthenic oil. It is used for vulcanization of natural rubber as well as styrene butadiene rubber. Resistance to reversion and ageing of natural compounds is improved by vulcanization with urethane cross linkers. This technique is fresh and hence its functions are not fully determined. ZDMC a catalyst and calcium oxide a drying agent are used along with urethane cross-linker to increase the formation of pendant groups and to absorb moisture from rubber compound respectively.

IV. ADDITIVES

The process of vulcanization of rubber with any curing system not only involves vulcanizing agent but also requires some kind of additives for effective and sufficient results. Accelerators, activators, inhibitors, antidegradants, reinforcing fillers, softeners, extenders and tackifiers all are termed as additives. The functions of all these terms are discussed below:

Accelerator: Sulphur is a slow vulcanization agent. It reacts very slowly and form cyclic structure bonds. Accelerators are added to increase the efficiency of sulphur crosslinking as well as rate of reaction. Guanidines, thiazoles, dithiocarbamates, xanthates and thiurams are five major categories of accelerators. Guanidines are combined with other accelerators when used as Guanidines gives the lowest rate of vulcanization.

Activators: Activators are used along with accelerators. The accelerators and activators are catalysts. Activators are metal oxides or salts of fatty acids. Zinc oxide and stearic acid are few examples of activators which are used in the process of vulcanization. Activators create ions that activate intermediate reaction involved in crosslink formation.

Inhibitors: A sufficient vulcanization process can be obtained by using an appropriate accelerator. But sometimes when these measures go wrong or do not give sufficient reaction, Inhibitors are used. Inhibitors delay the time of the completion of cure and prevent premature vulcanization.

Antidegradants: Antidegradants are used to inhibit the actions of degradants such as oxygen and ozone which can alter the network structure when react with elastomers. The function of Antioxidants can be chemically or physically. Chemical protectants react directly with degradants whereas physical protectants migrate to the surface to provide a barrier to any reaction or action by degradants. Amines, phenolics and phosphites are commonly used chemical protectants. Various waxes have been used as physical protectants.

Reinforcing fillers: Reinforcing fillers have its ability to change the viscosity of a compound and to improve the vulcanize properties which are tensile strength, abrasion resistance and tear resistance. It also increases stress values and hardness and decreases rebound and elongation at break. Carbon black and silica are most effective fillers for reinforcing rubber.

Softeners: To ease the process of mixing of rubber compounds, softeners are used to provide lot of energy for the process. Mineral oils are most important softener. Animal and vegetable oils are also some examples of softener.

Extenders: Extenders are added to stiffen rubber composition as well as to reduce cost. Oil extension of rubber is widely used in tyre treads which permits the use of elastomers with higher filler levels and higher molecular weight. Other examples of extenders are clay, calcium carbonate and ground coal. Oil levels of 30-40 phr are typical.

Tackifiers: Tackifiers are added to improve the ability of two materials to resist separation under pressure which is known as tack. In natural rubber, tackifiers are added to prevent tack degradation in the range of 1 to 10 phr. In Styrene-butadiene rubber, tackifiers increase initial tack as well as prevent tack degradation. Following are the types of tackifiers:

- a) Alkyl-modified phenol-formaldehyde resins
- b) Coumarone-indene resins obtained from coal coke oven lights consist of indene, coumarone, styrene and other hydrocarbons.
- c) Chemical mixtures of abietic acids known as rosin derivatives
- d) Terpene oligomers
- e) Aliphatic petroleum resins

V. CONCLUSION

This review paper concludes that physical as well as mechanical properties of natural rubber or styrene butadiene rubber are improved by the process of vulcanisation. Sulphur is commonly used for the process of vulcanisation. Apart from sulphur there are many other vulcanizing agents exist. These vulcanizing agents require additives for efficient reaction and desired results. The mechanical properties of vulcanized rubber are increased i.e. its tensile strength, elasticity, hardenability, wear, and life span. There are also many new technologies invented and possibly can be invented for further improvement of vulcanized rubber as well reducing its effect directly or indirectly on the environment.

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