A Review on Sulfur Vulcanization Of natural rubber Coating & Lamination Textiles: Processes and their application

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ABSTRACT

Natural rubber is sticky in nature and it is compounding of long polymer molecules. In the foam of latex it is obtained from trees. Various characteristics like Tensile strength and density of natural rubber is very low. So vulcanization is done is done to improve the properties of natural rubber. Many additives are added to rubber mostly with sulfer and heated up for vulcanization. Due to this properties of sufer are increased. Various industries and products used vulcanized rubber its many application such as gloves, raincoat, mats, vehicle cover bags etc. This paper array the data which improves the desirable properties of rubber, rigidity the process of vulcanization. Rubber has the properties of flexibility, strength and elasticity. Vulcanization is the process whereby the polymer chains of the rubbers are cross-linked, making use of the double bond present. Sulphur is the most common cross-linking substance. A variety of other compounds are added to give the final rubber product the required properties.

1. INTRODUCTION

Rubber is a widely used material having properties of flexibility, strength and elasticity. The basic raw input, either natural rubber or synthetic rubber, is imported from New Zealand in latex or solid form, and treated into many different products. The raw rubbers, composed essentially of long polymer chains, are combined together with “crosslinks” in a process called vulcanization to give the final material its characteristic properties. [1]

Natural rubber (NR): Natural rubber latex is obtained principally from rubber-producing trees of the species Hevea brasiliensis, which grow in tropical regions. Natural rubber is an elastic hydrocarbon polymer. It is naturally occurs as a milky colloidal suspension, or latex, in the sap of some plants. Natural latex is obtained from plants. Natural rubber latex may be tapped off from part of plants, such as bark, roots, leaves, stems, tubers and fruits. [2] Natural rubber is also categorized as a radiation crosslinking type of polymer as it contains a double bond. Due to these properties, it would be expected that natural rubber attains higher TS than styrene butadiene rubber (SBR). Elastomer blends are used for many purpose such as lowering the compound cost, the complex shaped product may be easily fabricated during production. Styrene butadiene rubber (SBR) / Natural rubber (NR) are a special performing blend which is suitable for variety of applications from race car tires to footwear applications. [3]
For many products like tires, hoses and belts the preformed parts have to be assembled to the shape of the final product. The product is then treated at a temperature of 140 - 200 °C to receive its requested final properties. Through the curing is the crosslinking process, the rubber compound characteristics are changed from a plastic to an elastic state. In some instances, the curing is done online at the same time as the forming of the product i.e. for extruded products like sealing profiles and cables. [4]

**History**

Rubber is also known by its scientific name “caouthonc” or “India rubber”. The ancient people used latex to make rubber bolls which were used in important ritual name. In 1525 a person is called padre “angheieria” reported that he had seen mexiean tribes people playing with elastic balls. An eraser was considered to be first use of rubber. In 1775 the first scientific study of rubber was undertaken by Charles de la condamine. According to Charles rubber could be used as flexible tubes. Today more than 75% of rubber is production is synthetic product made from crude oil. The major commercial source of natural rubber latex is the pera rubber tree (Hevea brasiliensis). [5]

**Background**

For every industry to survive in present and future, they have to be a component of the development in new textile products. There are many areas in which development is in progress like

1. Medical textiles
2. Protective textiles
3. Defense textiles etc. [6]

**Compounding and Processing of Rubber**

For coating of rubber & fabric, it has to be properly processed. The steps involved are as follows:

1. Milling
2. Compounding
3. Coating by calendaring
4. Preparing dough and spread coating

**NR-Latex Properties:**

1. Whitish fluid, Density = 0.975-0.980
2. PH = 6.5-7.0
3. Surface free energy = 40-45 ergs/cm2
4. Rubber particles = 35 % by weight
5. Aqueous phase = 55 % by weight
6. Lutoid phase = 10 % by weight
7. Rubber phase = 25 –35 % by weight (typical = 33 %). [8]

**Properties of vulcanized natural rubber**

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<tr>
<td>Elongation</td>
<td>750-850%</td>
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<tr>
<td>Density</td>
<td>0.93gm/cc</td>
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<td>Recommended operating temperature</td>
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**2. VULCANIZATION**

**Vulcanization:** Conventional cross-linking process of rubber is known as vulcanization of rubber, the vulcanized rubber can be considered in its cross-linking state as a huge molecule. The material becomes less elastic than before vulcanization, possesses reasonable tensile strength and is insoluble in organic solvents but only swells.

The vulcanization of rubber is done by heating rubber and sulfur in the presence of accelerators produced by reacting mercapto-aryl-thiazoles, their alkaline salts and the like, with dinitrochlorbenzene. The Mercapto-aryl-thiazoles are vulcanization accelerators. It has now been found that on reacting mercapto-aryl-thiazoles, such for example as the potassium salt of mercapto-benzo thiazole with dinitrochlorbenzol there formed an important class of compounds which may be used alone as a vulcanization accelerator or a mixed accelerator. Such delayed action on the part of vulcanization accelerators is of particular importance, as it prevents partial curing of the rubber taking place during the milling operations or at other times prior to the actual vulcanization process. [9]
The discovery of vulcanization

During the first half of the 19th century, several attempts had been made in Germany, Great Britain and the USA to improve the properties of rubber so that it was stable in shape, dry and flexible instead of being soft and sticky.

It was the American, Charles Nelson Goodyear, who in 1839 after many years of unsuccessful attempts and great personal sacrifice discovered that if you mixed a small amount of sulfur into the rubber and heated it then it obtained the desired properties.

Vulcanization is a process in which rubber, by a change of its chemical structure, Charles Nelson Goodyear using cross-linking, is transformed to an elastic state. [10]

The discovery of sulfur vulcanization of rubber by Goodyear and independently by Hancock more than 150 years ago was the creator of one of the important classes of engineering materials. A vigorous research effort resumes today to develop a fundamental understanding of this complex chemical process. Although the starting work by Goodyear and Hancock was concerned with the addition of sulfur to natural rubber, various accelerators, activators and retarders have been consequently employed in order to better control the various aspects of the rate and degree of the vulcanization process. More recently, mixed accelerator systems like thiuram-sulfenamides have been made to allow additional control over the vulcanization process. It is not surprising that the cure chemistry is complicated for these complex mixtures of elastomer, sulfur, accelerators, activators, and retarders. Notwithstanding the significant research in studying the vulcanization process, a fundamental understanding is far from complete as clearly stated by two pioneers in the field: “Perhaps nowhere in chemistry is there encountered a field which even in its literature alone shows so many uncertainties and (possibly only apparent) contradictions as that of the vulcanization of rubber.” [11]

PROCESS

Polyisoprene or natural rubber and styrene-butadiene are the main polymers used for vulcanization. Styrenebutadiene 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. [12-13]

Vulcanization with sulphur

Vulcanization with sulphur is the most commonly used method for vulcanizing. However, synthetic polyolefin’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 anti degradants. Zinc oxide and stearic acid are some activators used in the process of vulcanization of rubber with sulphur. [14]

Vulcanizing Agents:

Sulfur: Sulfur is the universal vulcanizing agent for all diene lattices. Fine particle size Rubber grade sulfur powder is used. Sulfur dosage 0.3 to 2.5 phr on dry basis in the form of 50% dispersion in water. The dosage of sulfur depends on the rate and state of cure desired and the amounts of other compounding ingredients used. For the best heat resistant vulcanizes the sulfur dosages are kept at minimum and consistent with the ‘modulus’ requirements. [15]

Radiation vulcanization of rubber:

In radiation vulcanization process, the molecular chains are linked with each other at higher reactive sites by chemical crosslink to form a three dimensional network structure. These reactive sites are the free radicals that are formed in the polymer chains. Their high reactivity is attributed to the occurrence of unpaired electrons in these species and hence their high tendency to react with other free radicals in their neighborhood leading to crosslinking. [16]

Room-Temperature-Vulcanizing (RTV) Elastomers

RTV Application Methods: When the RTV is used as 100 percent solids as a sealant or adhesive, it is applied via extrusion using a pump system with a follower plate and an extrusion head at the point of use. When the RTV is used as a coating, it is diluted with solvent and sprayed. Airless spraying is preferred.
Curing RTVs

- RTV elastomers do not cure under a nitrogen blanket. Because the RTV reacts with moisture in the air, the surface cures first. Consequently, for proper cure, thick sections (>5 mm) should be avoided. Cure time for a 1-mm layer is approximately 1 hour at room temperature.
- The coating cures faster at higher temperatures and humidity. Small amounts of acetic acid byproduct are emitted during cure; consequently, ventilation is necessary. Post-cure at high temperature improves coating properties. [17]

2.4 Additives

Various chemicals and fillers accelerators and cross linking agent are added to rubber facilitate process and vulcanization. The properties of and product can be significant altered by proper choice and significantly altered by proper choice and amount of the comingling ingredients to meet the diverse end use requirements.

Typically ingredients of rubber formulations are as follow:
1. Raw rubber
2. Cross-linking agent
3. Accelerators
4. Accelerators activators
5. Antidegradants
6. Fillers reinforcing diluents
7. Processing aids
8. Pigment and dyes
9. Special additives for flam retardants fungicides [18]

Additives improve properties of coating polymers such as:
- Softeners imparting better flexibility and softness,
- Cross-linking agents and binders improve the bond between the textile material and the coated polymer
- Antimicrobial agents (Sanitized),
- Light fastness agents (Tinuvin),
- Various pigments for dyeing the polymer coating (pigments). [19]

3 COATING OF TEXTILES

Those textiles which are coated on the surface from both sides with cellular and homogeneous structure coating are coated textile. Coating is termed as the application of coating compounds on one or both sides of woven, knitted or non-woven fabrics. Lamination is different from coating in the way that in lamination the polymer materials which cannot be easily formulated in paste can be converted into film first and then applied to textiles by different laminating processes.

Coating polymeric materials to textiles exhibits different functional and aesthetic properties such as soil-resistant, water repellent and conductor etc. There are different methods of coating and this classification is done on the basis of equipment used, metering method and the form of coating material. [20]

Types of Coating Methods

There are several processes for the application of coating to the textile material depending upon the requirement of end product. Some of these processes are described below:
There are several factors on which selection of coating method depends. [21]

Principle of knife coating

The knife unit consists of blade holder and blade liner. The coating material is applied to doctor blade and the distance between blade and fabric is set by holder. As the fabric moves, the material also moves under the fixed doctor blade which exerts shear force on paste causing it to flow. This shear force depends on working speed, blade profile and the tilt angle of doctor blade. The angle can be adjusted by doctor blade holder. The coating paste quantity depends upon the distance between doctor blade and fabric and also on tilt angle. By increasing the angle, the amount of paste applied can be reduced. The thickness of paste depends upon. [22]

1. Doctor blade speed
2. Blade tilt angle
3. Doctor blade distance
4. Substrate tension
5. Paste viscosity
Direct Coating
The simplest coating procedure is the direct method, also termed as ‘floating knife’ In this the fabric is stretched flat to form an even uniform surface and is transported under a stationary doctor blade. As the fiber moves forward, it is scrapped by the knife and the polymer resin compound is spread evenly over the surface.

Uses: Waterproof protective clothing fabric, tarpaulins, automotive car seat fabrics and light weight material for inflatable. [23]

Foamed and Crushed Foam Coating
This method is used to apply polymer to woven fabrics and knitted fabrics and also to fabric produced from spun yarn. The no. of fabrics which can be coated can be increased in this as well as penetration of resin into the fabric is also reduced, which produce much softer handles and better drape than direct coating.

Uses: This technique is used for apparel goods, floor coverings, wall coverings, black-out curtains and curtain linings and filter materials. [20-24]

Transfer Coating
The principle of transfer coating is first to spread the polymer on to release paper to form a film and then to laminate this film to the fabric. The procedure include the processes like Lay the fabric on top of the coating, then nip together, the solvent is evaporated and the two layers to be cross-linked together.

Uses: The main uses are the transfer coated polyurethane fabrics are in up-market and the waterproof protective clothing. Other application includes upholstery, luggage, footwear, gloves and waterproof mattress covers. Woven velvet automotive seat fabric is processed in above way to lock in the pile. Carpets and other articles are also processed using back licking techniques. [20-25]

Hot Melt Extrusion Coating
This method is used for thermoplastic polymers such as polyurethane, polyolefin and PVC, which are applied by feeding granules of the material into the nip between moving heated rollers. Generally two types of design are used; the Zimmer machine, which has two melt rollers, the Bema machine, which has three. This method can apply resin to fabric at a faster rate than that can be achieved by transfer coating or direct coating.

Uses: It is used to produce light weight coverings or tarpaulins. [20-26]

Calendar Coating
Calenders are mainly used to produce unsupported films of PVC and rubbers from compounded polymer ‘dough’. Calenders consist of a number of massive rollers that rotate to crush the ‘dough’ and smooth it into films of proper thickness. The thickness of the film is decided by the gap separation of the rollers. [27]

Rotary Screen Coating
This technique which put on compound to a fabric by forcing it between a cylindrical screen, it is used primarily for textile printing. The technique can also be utilised for coating polymer onto fabric with add-ons. It is used to apply foamed coatings or for foam processing of fabric finishes instead of padding. [28]

Properties of coated textile materials
Properties of coated textile materials primarily depend on their application. As it is not possible to use the classic textile for technical purposes, excellent properties are acquired by combination with other substances that are coated in the form of paste or laminated to material. By means of the value-added material, Nano products and modern technology the use of textile materials has been enhanced several times. [29]

Characteristics of latex coated fabric
The coating techniques used was single dip, single dip-pad, double dip, and double dip-pad. The NR latex-coated and uncoated fabrics were evaluated for their areal densities. Thickness, tensile properties, tearing strength, puncture resistance and yarn pull-out strength.

1. It is waterproof
2. It has dry-cleaning properties
3. It is heat and light resistant [30-31]

4. RECENT DEVELOPMENT
These are all the conventional procedure of coating application and formulation but in modern era the requirements of human beings has been totally changed , so research is going on to accomplish human needs . Some of such
achievements are phase change coatings, conductive coating, anti-bacterial coating etc. After all introduction of Nanotechnology has changed the thinking. Some of those are discussed below. [20]

Phase Change Materials
Phase change materials have the ability to change their state within a definite temperature range. These types of materials absorb energy during the heating process as phase change takes place and release energy to environment in the phase change range during a reverse cooling process.

Working principle of PCM- the PCMs change phases in the temperature range which is just above and below human skin temperature are suitable for application in textiles. This property is useful for making protective textiles in all-season. Fiber, fabric and foam with PCMs could store the heat that body creates & then release it back to body, as it needs. [32]

Flame Retardancy
The advantages of the concept of encapsulated Flame Retardant agent is compatible with a polymeric matrix in order to give a everlasting FR effect and to be itself an efficient FR intumescent formulation for many materials. The reaction to fire of cotton fabrics coated by FR polyuria loaded with neat or microencapsulated DAHP was studied with the cone calorimeter acting as fire model. Both types of DAHP microcapsule present in the polyuria coatings on cotton fabric give an effectual FR effect, although the char developed with microcapsules is a little less heat resistant than that developed with the pure DAHP. Coatings containing microcapsules with poly-ester-polyurethane shells evolve the smallest quantity of smoke and CO. [33]

5. LAMINATION

A laminated fabric involves two or more layers; one is a textile fabric, bonded closely together by means of an added adhesive or by the properties of adhesion of one or more of the component layers. Generally the layer in a laminated fabric is a polymeric substance; however in some metalized fabrics, the metal is laminated using an adhesive or by use of an electric arc. Here the adhesive is applied as a thermo-fusible resin in the form of a dot coating that imparts greater flexibility and less stiffness to the laminate, factors important in subsequent molding applications. [34]

Lamination of fabrics with Nano pore coating
Laminated fabric with polyurethane coating with Nano pores is a multilayered compound material. Textile compound materials are comprised of two or more different materials with at least one textile layer (knitted fabric, woven fabric & nonwoven material). Nowadays the material with woven fabric on the front side and polyurethane with Nano pores on the back side is mostly used for military or police outerwear as well as for civil uses. This kind of composites are more durable and stronger, their body protection against meteorological effects (rain, wind, UV radiation), they did not drop their comfort (they are airy and have good sweat permeability), they are more resistant to load and abrasion, and they have less anisotropic properties compared to the classic fabrics. [35]

Lamination Faults
There some faults can be generally appears in the laminated products during the process. This fault can be removed or partially reduced by a proper m/c setting, controlling various parameters like heating, temperature, degree of adhesion limit etc.

Waterproof Coaster:
A waterproof coaster can be made by taking a piece of cotton’s cloth fabric and cut into a circle. The liquid latex is applied to both sides of the fabric and set the latex to the fabric as discussed in the process section. After the latex has dried, the coaster is tested by placing water on the coaster to see if it sheds water. [36]

Rubber soled shoes:
Polymer clothing had its infancy in 1868 when a type of canvas shoe with rubber soles was created. Because they made no noise when people wore them, they became forever known as "sneakers". [37]

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<th>Uses in industries:</th>
<th>Agriculture industry</th>
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<td>Aerospace aviation industry</td>
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This review paper determines that physical as well as mechanical characteristics of natural rubber or styrene butadiene rubber are improved by the process of vulcanisation. Sulphur is commonly used for the procedure 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.

The coating and lamination gives a powerful tool for the advancement of textile technology. It provides the opportunities to develop the special fabrics like water-proof resistant tarpaulins, coverings, large tents and architectural uses, back coating for upholstery including auto seats, Food, Medical applications, parachutes, Woven curtains, for heat-sensitive fabrics, automotive fabrics, disposable hospital apparel etc. the recent developments also enhanced the lamination and coating technique into state-of-art process of the future in textile field.

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