

A TECHNICAL REVIEW ON RUBBER

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Abstract

Rubbers are elastomeric materials, whose dimensions can be greatly changed when stressed and which return to their original dimensions when the deforming stress is removed. It is the most fascinating material known to mankind on account of its range of applications in everyday life, defence, civilian purposes and its behaviour under the most diverse conditions of applications. In this review paper, history of rubber is discussed in detail to know about their origin. The general characteristics and physical properties of natural rubber and synthetic rubber are explained in this technical review. A comparative approach is handled and both the types of rubber are distinguished. Besides, rubber physics is precisely discussed in order to understand their physical characteristics. Various rubber processing methods are described in this paper. The science and practice of rubber mixing during processing is discussed. In this article, fact sheets of rubber are provided in the form of tables for quick reference and to review easily. Finally, the applications of rubber and rubber products in engineering are discussed elaborately.

Key words: Rubber history, Natural rubber, Synthetic rubber, Vulcanization, Rubber physics, Rubber mixing, Rubber processing.

I. INTRODUCTION

Rubber is a collective term for macromolecular substances of natural origin known as natural rubber or synthetic origin known as synthetic rubber. It is capable of recovering from large deformations quickly¹. The term rubber was originally used only for the natural product that is obtained from a thick milky fluid called as latex that oozes from certain plants when they are cut. Most latex comes from the Para rubber tree that grows in South America, and Sri Lanka. Prior to Second World War, this material was important in the manufacture of many products, and sources of supply were considered to be valuable. Natural rubber is the oldest commercial elastomer and it is made from the processed sap of a tropical tree. In its crude form, it is an excellent adhesive and different types of cements can be made by dissolving it in suitable solvents. Its use as an engineering material dates from 1839, when Charles Goodyear discovered that it could be vulcanized by the addition of about 30% sulphur followed by heating to a suitable temperature^{2,3}. The cross linking of the molecules restricts the movement of the molecular chains and imparts strength.

Rubber is an indispensable product to the modern society like steel, wood and mortar. Rubber products are used at home, at work, at play and even when we travel. Automobiles, trains, aircraft, and manufacturing industries rely on it for variety of purpose. So, it is rightly said that rubber in the modern world is omnipotent. It is a yellowish, elastic, amorphous material obtained from the latex or milky sap of various tropical plants like the rubber tree. This latex is vulcanized, pigmented, finished and modified into various products like electric insulation cables, elastic bands, belts, tires, hoses, gaskets and

containers. So, the applications of rubber are wide spread. Rubber processing methods include many of the same processes as used in plastics³. Among these are various molding processes for products such as tires. Extrusion is used for tube moldings, and hose. Calendaring is used to make sheet products and to coat fabrics and metal with powder.

II. HISTORY

Rubber is also known by its scientific name "Caoutchouc" or "India rubber". The indigenous people of the Americas had known and used rubber long before the arrival of European explorers. Rubber makers in ancient Mesoamerica were almost 3,500 years ahead of Charles Goodyear and his vulcanized rubber^{1,4}. The ancient Mayan people used latex to make rubber balls which were used in an important ritual game. This game was called Tlachtlic, a cross between football and basketball, but had religious significance. This was recorded in the Popul Vuh, a Mayan religious document. In 1525, a person called Padre d'Anghieria reported that he had seen Mexican tribes people playing with elastic balls. An eraser was considered to be the first use for rubber. This was suggested by Magellan, a descendent of the famous Portuguese navigator. It was popularized in England by someone called Priestley and it became known as India Rubber^{4, 5}. The Portuguese meaning of rubber was borracha and this was originated from making jars replacing the leather borrachas that the Portuguese used to ship wine. In 1735, the first scientific study of rubber was undertaken by Charles de la Condamine. According to him, rubber could be used to produce flexible tubes. Since then, there were many craftsmen who become involved with rubber. In 1820, Nadier, a British industrialist

produced rubber threads and attempted to use them in clothing accessories. This was the time when America was seized by rubber fever, and there was the waterproof footwear used by the indigenous people which became a success. Snow boots and waterproof fabrics were produced in New England^{6, 7}.

In 1832, the Rosburg factory was set up, and unfortunately did not do well as cold weather affected goods produced from non-vulcanized natural rubber, leaving them brittle and thereby discouraging consumers. Charles Goodyear discovered the process of vulcanization accidentally in 1840⁸. Till 1839, rubber was subject to the change in weather conditions. The rubber was hot and sticky during hot weather. It became cold and brittle during cold weather. Goodyear discovered the process of vulcanization when a mixture of rubber, lead and sulfur were accidentally dropped onto a hot stove. This resulted in a product which wasn't affected by weather, and which came back to its original form if stretched. The process was refined and thereby the uses for rubber materials increased. This new vulcanized rubber was resistant to water and chemical interactions and did not conduct electricity, and hence suitable for a variety of products⁹.

Today more than 75% of rubber in production is a synthetic product made from crude oil. During World War II, the United States could not supply rubber worldwide, and they stepped up the production of synthetic rubber for use in the war effort. There are about 20 grades of synthetic rubber and ultimately it is the intended end use which determines selection. Natural rubber is just one kind. Because, the rubber plant only thrives in hot, damp regions near the equator. Today, ninety percent of rubber production is by the Southeast Asian countries like Malaysia, Thailand, and Indonesia^{9, 10}. However, Indonesia's production has dropped in recent years and new rubber plantations were started in Africa to take up the slack. Rubber belongs to a class, made up of a number of materials that have the unique property of high elasticity. Natural rubber is an elastic hydrocarbon polymer that naturally occurs as a milky colloidal suspension, or latex, in the sap of some plants. The entropy model of rubber was developed in 1934 by Werner Kuhn. The scientific name for the rubber tree is *Hevea brasiliensis*. The major commercial source of natural rubber latex is the Para rubber tree (*Hevea brasiliensis*: Family: Euphorbiaceae). This is largely because it responds to wounding by producing more latex¹¹.

Hypoallergenic rubber can be made from Guayule. Early experiments in the development of synthetic rubber also led to the invention of Silly Putty. Natural rubber is

often vulcanized, a process by which the rubber is heated and sulfur, peroxide or bisphenol are added to improve resilience and elasticity, and to prevent it from perishing. It has greatly improved the durability and utility of rubber from 1830. The successful development of vulcanization is most closely associated with Charles Goodyear. Carbon black is often used as an additive in rubber to improve its strength, especially in vehicle tires. Early rubber technologists were found among the Aztecs and Mayas of South America, who used rubber for shoe soles, coated fabrics, and play balls, well over 2000 years ago. An MRPRA (Malaysian Rubber Producers Research Association) article mentions that the Aztec King, Montezuma was paid tribute by the lowland tribes in the form of 16,000 rubber balls, and that ball counts have been excavated in snake town in the south western United States dating back to AD 600-900^{4, 10, 11}.

Subramaniam, in the late Maurice Morton's book rubber technology³ attributes Christopher Columbus as the first European to discover natural rubber, in the early 1490s, when he found natives in Haiti playing ball with an extract from a tree. The book goes on to describe how, by the 18th century, uses for natural rubber were well established in Europe, where the English Chemist J.B. Priestly gave its name since it rubbed out pencil marks. Stern mentions the Scotsman Macintosh who in 1823 used the solvent naphtha to dissolve rubber and applied the resulting solution to textiles in order to produce rainproof clothing⁴. Rubber at that time was supplied in hard blocks. He notes that Thomas Hancock in London in 1830 used what can be described as the first internal mixing machine, which mechanically worked the rubber, making it softer and therefore more easily processable. He mentions that Hancock moved on to two roll mills and that it took a hundred years before the internal mixer reappeared, becoming a key element in the industry. Buist says that Hancock's internal mixer was invented in 1820, and mentions that Hancock called it as a pickle as Buist puts it to confuse his competitors⁵. He also mentions that Hancock's Company, James Lyne Hancock Ltd, in London was the first British Rubber Company, founded in 1820. Rubber products, up to the 19th century, had a major flaw, because, they were sticky on hot days, and very stiff when cold. This problem was solved by a major discovery attributed to Charles Goodyear of Woburn, Massachusetts, USA in 1839^{4, 6}.

Duerden writes that Goodyear accidentally visited the rubber good store of the Roxbury Company in New York, USA, around 1832⁶. He comments that, in his search to modify rubber to make it more useful, "Goodyear purchased the claim of combining sulphur with India rubber" from Nanthaniel Hayward. Goodyear was then

awarded a contract from the US Government to manufacture mail bags. These bags were made from rubber containing sulphur and white lead. Before long, the mail bags started to decompose. Instead of leading him to riches, Duerden mentions that it brought Goodyear and his large family to poverty. By chance, he heated the raw rubber-sulphur-lead combination, and found that the material charred like leather, and vulcanized leather. The resulting composition was a much stronger material and no longer sticky at higher temperatures. Duerden writes that Goodyear took out a US patent for this momentous discovery in 1841 but that he profited little from it. Later in 1843, Hancock was also combining sulphur with rubber and using heat. Stern states that an artist friend of Hancock coined the term Vulcanization for this process, after Vulcan, the God of fire in Greek word⁷. The words vulcanize, cure, and cross-linking will be used synonymously. At this time went on, the quantity of rubber consuming continuously increased. Suzuki mentions that the native people of the Amazon were ruthlessly exploited, and that a rubber tapper could be killed, simply for not bringing the required quantity of rubber from the surrounding trees⁸. White describes how, in 1876, seeds were taken out of Brazil and grown into seedlings at Kew gardens in England⁹. They were then shipped to the Far East. In 1889, John Dunlop in England invented the first commercially successful pneumatic tire, which was at that time used for bicycles¹⁰. Dunlop produced his first vehicle pneumatic tire in 1906¹¹.

An interesting observation by Stern is that in 1904 in England, it was found that a powder called carbon black, blended into rubber, and significantly increased a number of its mechanical properties¹². It seems surprising that this major discovery was then "left on the shelf" for about 8 years. By 1910, the motor car truly arrived and both the use and price of natural rubber exploded. Kuzma notes that the Russians in 1910 prepared such a rubber, known chemically as polybutadiene¹³. In the 1930s, the German began commercial production of synthetic rubber called Buna-S¹⁴,¹⁵. A priest synthesized a chemical building block which led to the discovery of a rubber by DuPont who marketed it as Duprene, in 1931, then changed the name to Neoprene¹⁶. Bryant points out that in 1934 production of an oil resistant rubber called Buna-N was started in Germany, the name later changed in 1937 to Perbunan¹⁷. Its given name is nitrile rubber (NBR, Nitrile Butadiene Rubber). It seems to be a fairly straight forward wood. The French call it as Caoutchoue recognizing its historically South American native origin. The word derives from a South American Indian word, meaning 'weeping wood'¹⁸,¹⁹. Blow makes comments similar to these, about the word 'rubbers' have several meanings²⁰. He suggests that the vulcanized material be called

"elastomer". ASTM Standard D 1566-98 defines "elastomer" as a term often used for rubber and polymers that have the properties similar to those of rubber.

III. GENERAL CHARACTERISTIC FEATURES AND PROPERTIES OF RUBBER

Rubber can be compounded to provide a wide range of characteristics, ranging from soft and gummy to extremely hard. When additional strength is required, textile cords or fabrics can be coated with rubber. The fibers carry the load and the rubber serves as a matrix to join the cords while isolating them from one another to prevent chafing. For severe service, steel wires can be used as the load bearing medium. Vehicle tires and heavy duty conveyor belts are examples of this technology^{1,24}.

Rubber exhibits unique physical and chemical properties. Rubber's stress-strain behavior exhibits the Mullins effect, the Payne effect and is often modeled as hyperelastic. Owing to the presence of a double bond in each and every repeat unit, natural rubber is sensitive to ozone cracking. The properties of natural rubber make it an elastomer and a thermoplastic material. It should be noted that as the rubber is vulcanized it will turn into a thermoset²¹.

When rubber is stretched, the loose pieces of rope are taut and thus no longer able to oscillate. Their kinetic energy is given off as excess heat. Therefore, the entropy decreases when going from the relaxed to the stretched state, and it increases during relaxation^{21,22}.

This change in entropy can also be explained by the fact that a tight section of chain can fold in fewer ways than a loose section of chain, at a given temperature. Relaxation of a stretched rubber band is thus driven by an increase in entropy, and the force experienced is not electrostatic, rather it is a result of the thermal energy of the material being converted to kinetic energy.

Rubber relaxation is an endothermic event, and for this reason, the force exerted by a stretched piece of rubber increases with temperature. The material undergoes adiabatic cooling during contraction. This property of rubber can easily be verified by holding a stretched rubber band to your lips and relaxing it. Stretching of a rubber band is equivalent to the compression of an ideal gas, and relaxation is equivalent to its expansion²².

A compressed gas also exhibits elastic properties, for instance inside an inflated car tire. The fact that stretching is equivalent to compression may seem somewhat counter intuitive, but it makes sense if rubber is viewed as a one dimensional gas. Stretching reduces the space available to each section of chain.

IV. PHYSICS OF RUBBER

Rubber is composed of long chains of randomly oriented molecules. These long chains are subjected to entanglement and cross linking. The entanglement has a significant impact on the viscoelastic properties such as stress relaxation.

When a rubber is exposed to stress or strain energy, internal rearrangements such as rotation and extension of the polymer chains occur²³. These changes occur as a function of the energy applied, duration and rate of application, as well as the temperature at which the energy is applied. A rubber's response to an applied energy can be elastic energy storage or viscous energy dissipation.

For sealing elastomers, the elastic component response is an important one. An applied stress induces a corresponding strain which creates contact stress or sealing force. As the polymer chains rearrange to reduce this internal energy, or stored force, a loss of sealing force occurs and it is shown below (Figure 1)²⁴.

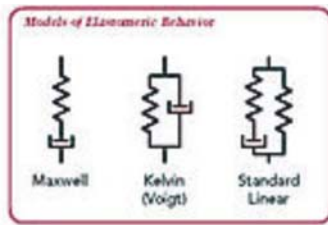


Fig. 1. Models of elastomeric behavior

Rubber products are cured at high temperature and pressure. The addition of curatives and accelerators forms cross links between the polymer chains. The network of cross links largely determines the physical properties like tensile strength, compression strength, and elongation.

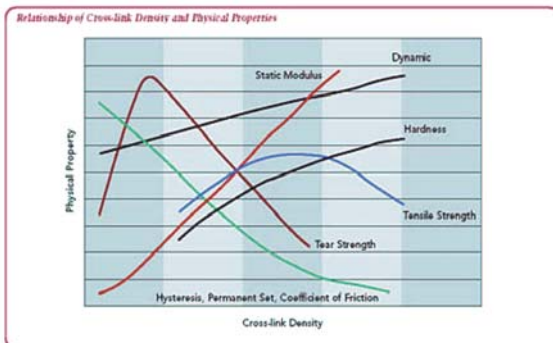


Fig. 2. Physical property and Cross link density Relationship of Rubber

Fillers play a large role in rubber technology. Carbon black and silica fillers can serve to improve the hardness, abrasion resistance, tensile properties and tear strength.

Non-black fillers such as titanium dioxide and barium sulfate can offer pigmenting properties for part identification, as well as improved stability in strong oxidizing environments²⁴.

However, the viscoelastic response and hysteresis losses are greatly enhanced by the use of fillers. The physical properties of an elastomer vary with the test conditions especially due the change in temperature. (Figure 2)³⁰ shown below explains the relationship of physical property and cross link density.

V. NATURAL RUBBER

A. Introduction

Natural rubber is produced commercially from the latex of the *Hevea brasiliensis* tree. The source of natural rubber is a milky liquid known as latex which is a suspension containing very small particles of rubber. The liquid latex is collected from the trees and taken to a processing center where the fluid latex is diluted to 15% rubber content and coagulated with formic acid²⁵. The coagulated material is then compressed through rollers to remove water and to produce a sheet material. The sheets are either dried with currents of hot air or by the heat of a smoke fire. The rolled sheets and other types of raw rubber are usually milled between heavy rolls in which the mechanical shearing action breaks up some of the longer polymer chains and reduces their average molecular weight. Natural rubber production in 1980 accounted for about 30 percent of the total world's rubber market²⁶. Natural rubber is mainly cis-1, 4 polyisoprene mixed with small amounts of proteins, lipids, inorganic salts, and numerous other components. Cis-1, 4 Polyisoprene is a long chain polymer, having an average molecular weight of about 500000 gm/mol. The polymer chains of natural rubber are long, entangled, and coiled at room temperature, which are in a state of continued agitation.

B. Vulcanization

The tensile strength of natural rubber is increased by a process called as 'vulcanization'. It is a chemical process by which polymer molecules are joined together by cross linking into larger molecules to restrict molecular movement. In 1839, Charles Goodyear discovered this process for rubber by using sulphur and basic lead carbonate. The word Vulcan indicates the roman god of fire. He found that when a mixture of natural rubber, sulphur, and lead carbonate was heated, the rubber changed from a thermoplastic state to an elastomeric material²⁷. Although, even today the reaction of sulphur

with rubber is complex and not completely understood. Rubber and sulphur react very slowly even at elevated temperatures. To shorten the curing time at elevated temperatures, accelerator chemicals are usually compounded with rubber along with other additives such as fillers, plasticizers, and antioxidants. Usually, vulcanized soft rubbers contain about 3 weight % sulphur and are heated in the 100 to 200 degree C range for vulcanizing or curing. If the sulphur content is increased, the cross linking that occurs will also increase, producing harder and less flexible material. A fully rigid structure of hard rubber can be produced with about 45% sulphur. The use of fillers can lower the cost of the rubber product also strengthen the material. Carbon black is commonly used as a filler for rubber, the finer the particle size of the carbon black, the higher the tensile strength is. It also increases the tear and abrasion resistance of the rubber. Silica such as calcium silicate and chemically altered clay are used as fillers for reinforcing rubber²⁸. Some of the properties of vulcanized natural rubber: cis-polyisoprene is shown below (Table 1)¹.

Table 1. Properties of vulcanized natural rubber: Cis-Polyisoprene¹

Tensile strength	2.50 to 3.50 ksi
Elongation	750 to 850 %
Density	0.93 gm/cc
Recommended operating temperature	-50 to 82 degree C

Natural rubber compounds are outstanding for their flexibility, good electrical insulation, low internal friction, and resistance to most inorganic acids, salts, and alkalis. However, they have poor resistance to petroleum products, such as oil, gasoline, and Naptha. In addition, they lose their strength at elevated temperatures, so it is advisable that they not be used at temperatures above 80 degree C. They also deteriorate fairly rapidly in direct sunlight unless specially compounded. It has good resistance to abrasion and fatigue, and it has high frictional properties, but it has low resistance to oil, heat, ozone, and sunlight. Typical applications are tires, seals, shoe heels, couplings, and engine mounts. Natural rubber is a vital agricultural product or commodity which is used in the manufacture of a wide range of products. Rubber plays a major role in the socio-economic fabric of many developing countries. Products made from natural rubber, like tyres, engineering components and latex products are very essential to modern life. It is available in many grades.

C. Properties of Natural Rubber

Natural rubber combines high strength with outstanding resistance to fatigue. It has an excellent green strength and tack which means that it has the ability to stick to itself and to other materials which makes it easier to fabricate. It has moderate resistance to environmental damage by heat, light and ozone which are one of its drawbacks.

The natural rubber has an excellent adhesion to brass-plated steel cord, which is ideal in rubber tyres. It has low hysteresis which leads to low heat generation, and this in turn maintains new tyre service integrity and extends retreadability. The natural rubber has low rolling resistance with enhanced fuel economy. It has high resistance to cutting, chipping and tearing.

D. Reasons for Natural Rubber Usage

Natural rubber forms an excellent barrier to water. This is possibly the best barrier against pathogens, and so latex is used in surgery as surgical and medical examination gloves. It is an excellent spring material. Natural rubber latex is also used in catheters, balloons, medical tubes, elastic thread, and also in some adhesives. Other than rayon, it is the sole raw material, which is used by the automotive industry. Rubber wood is a bye product of natural rubber. It is a source of charcoal for local cooking.

E. Natural Rubber as a Tyre Material

The technical strengths of natural rubber matches well and best suitable to be used as an efficient tyre material. These have been succinctly summarized below by Baker²⁸.

- High green strength, tack and cohesive properties: These are essential for maintaining green tyre uniformity and stability during building and shaping operations.
- Excellent adhesion to brass-plated steel cord.
- Low hysteresis which imparts low heat generation, which in turn maintains new tyre service integrity and extends retreadability.
- Low rolling resistance with enhanced fuel economy.
- Excellent snow and ice traction for winter tyres and all season treads.
- High resistance to cutting, chipping and tearing.

VI. SYNTHETIC RUBBER

A. Introduction

Synthetic rubber is a white, crumbly plastic mass which is processed and vulcanized in the same manner as natural rubber. In other words, synthetic rubber is an

artificially produced material having properties similar to natural rubber. Most synthetic rubbers are obtained by polymerization or polycondensation of unsaturated monomers. There are wide varieties of synthetic rubbers, reflecting various applications due to the chemical and mechanical properties they have²⁹. Co-polymerization of different monomers leads to the material properties to be varied across a wide range. Though, World War II became the force for the emergence of synthetic rubber on a large-scale basis when governments began building plants to balance natural rubber shortages. Also, there were other reasons as well after the war which led to the development of an alternative or substitute for natural rubber.

B. Necessity for Synthetic Rubber Production

Synthetic rubbers were first created in the early 1930s and were subsequently developed because of the uncertainty of the supply of natural rubber. This first rubbery synthetic was derived from acetylene gas and was a long chain molecule called polychloroprene, better known as neoprene. Synthetic rubbers in 1980 accounted for about 70 % of the total world's supply of rubber materials. Some of the important synthetic rubbers are styrene-butadiene, nitrile rubbers, and the polychloroprenes. Synthetic rubbers are further developed than natural rubbers. Examples are synthetic natural rubber, butyl, styrene butadiene, polybutadiene, and ethylene propylene. Some of the important factors are listed below.

- Rising prices for natural rubber on the world market in response to the general state of the economy
- Political events which cut customers off from the suppliers of raw materials
- Long transport distances
- Regional constraints with respect to establishing rubber plantations
- The increase in global demand for rubber.

C. Applications of synthetic rubber

Like natural rubber, synthetic rubbers have a varied range of applications and are mentioned below.

- Applied in the tyre industry to manufacture car, aircraft and bicycle tires
- Used to manufacture drive belts
- To produce hoses.
- To manufacture medical equipments

- To make seals
- To apply as floor coverings
- To process conveyor belts
- To manufacture molded parts.

D. Properties of Synthetic Rubber

Different varieties of synthetic rubber are available, and each having their unique properties. Some of the common properties of synthetic rubber are as listed below.

- Better abrasion resistance
- Good elasticity
- Better heat and aging resistance
- Used as an electrical insulation material
- Flexible at low temperatures
- Flame retardant
- Resistant to grease and oil

VII. NATURAL RUBBER VS SYNTHETIC RUBBER - A COMPARISON

Natural rubbers have better resistance to heat, gasoline, chemicals, and can withstand high temperatures. Examples of synthetic rubbers that are resistant to oil are neoprene, nitrile, urethane, and silicones. Synthetic rubbers are applied to process tyres, shock absorbers, seals, and belts³⁰.

Styrene-butadiene rubber (SBR) is an important synthetic rubber and also the most widely used one. Actually, it is a butadiene-styrene copolymer. After polymerization, it contains 20% to 23% styrene. SBR rubber is lower in cost than natural rubber and so utilized in many rubber applications.

Nitrile rubbers are copolymers of butadiene and acrylonitrile with the proportions ranging from 55% to 82% butadiene and 18% to 45% acrylonitrile. These rubbers are more costly than ordinary rubbers, so these copolymers are limited to special applications such as fuel hoses and gaskets where high resistance to oils and solvents is required.

The polychloroprene or neoprene rubbers are similar to isoprene. They also have fair fuel and oil resistance and increased strength over that of ordinary rubbers. However, they do have poorer low temperature flexibility and are higher in cost. As a result, neoprenes are used in specialty applications such as wire and cable covering, industrial hoses and belts, and automotive seals and diaphragms.

Silicone rubbers or Silicones have the highest useful temperature range up to 315 degree C, but such other properties as strength and resistance to wear and oils are generally inferior to those in other elastomers. Typical applications of silicone rubbers are sealants, gaskets, thermal insulation high temperature electrical switches, electrical insulation, auto-ignition cable, spark-plug boots, and electronic apparatus. Fact sheets on rubber are summarized below in Table 2,3,4 & 5 respectively.

Table 2. List of Industrial Rubber Products

Anti Vibration mountings	Automobile rubber products	Calendered rubber products
Extruded rubber products	Medical rubber products	Metal bonded components
Rubber adhesives	Rubber ball	Rubber bands
Rubber beading	Rubber bearing	Rubber belt
Rubber lining	Rubber buckets	Rubber magnets
Rubber bullets	Rubber molded products	Rubber cable
Rubber pads	Rubber coating	Rubber rollers
Rubber duct	Rubber stopper	Rubber expansion joints
Rubber suit	Rubber flooring	Rubber track
Rubber footwear	Rubber valve	Rubber gloves
Rubber injection parts	Rubber sealants	Rubber matting

Table 3. List of different types of synthetic rubbers

Acrylic rubber	Isoprene rubber	Silicone rubber
Butadiene rubber	Nitrile rubber	Styrene butadiene rubber
Butyl rubber	Perfluoroelastomer rubber	Neoprene rubber
Chlorosulfonated polyethylene/ Hypalon	Polychloroprene rubber	Polysulfide rubber
Ethylene propylene diene monomer	Fluoroelastomers/Viton	Polychloroprene or polyneoprene rubber

Table 4. List of Industries where Rubber is Used

Agricultural industry	Defence industry	Printing and paper industry
Aerospace / aviation industry	Medical industry	Textile industry
Automobile industry	Mining industry	Petroleum industry
Chemical industry	Construction industry	Power generation industry

Table 5. Abbreviation of Representative Commercial Rubbers

Type of the rubber	Abbreviation
Natural Rubbers	NR
Styrene-butadiene copolymer	SBR
Styrene-isoprene-butadiene terpolymer	SIBR
Polyisoprene	IR
Acrylonitrile-butadiene copolymer	NBR
Polychloroprene	CR
Ethylene Propylene copolymer	EPM
Ethylene-propylene-diene terpolymer	EPDM
Polyisobutylene	IIR
Poly ethyl acrylate	ACM
Chlorosulphonated polyethylene	CSM
Polydimethylsiloxane	MQ
Vinylidene fluoride polymer	FKM
Tetrafluoro ethylene-propylene	TFEP
Tetrafluoro ethylene-perfluoromethyl vinyl ether	FFKM
Fluorosilicone	FQ
Epichlorohydrin rubber	CO
Epichlorohydrin-ethylene oxide	ECO
Polysulphide	T
Polyurethane	U
Chlorinated polyethylene	CPE
Ethylene Vinyl acetate polymer	EVA

Vulcanized rubber has numerous applications. Resistance to abrasion makes softer kinds of rubber valuable for the treads of vehicle tires and conveyor belts, and makes hard rubber valuable for pump housings and piping used in the handling of abrasive sludge.

The flexibility of rubber is often used in hose, tires, and rollers for a wide variety of devices ranging from domestic clothes wringers to printing presses. Its elasticity makes it suitable for various kinds of shock absorbers and for specialized machinery mountings designed to reduce vibration. Being relatively impermeable to gases, rubber is useful in the manufacture of articles such as air hoses, balloons, balls, and cushions.

The resistance of rubber to water and to the action of most fluid chemicals has led to its use in rainwear, diving gear, and chemical and medicinal tubing, and as a lining for storage tanks, processing equipment, and railroad tank cars. Because of their electrical resistance, soft rubber goods are used as insulation and for protective gloves, shoes, and blankets; hard rubber is used for articles such as telephone housings, parts for radio sets, meters, and

other electrical instruments. The coefficient of friction of rubber, which is high on dry surfaces and low on wet surfaces, leads to the use of rubber both for power-transmission belting and for water-lubricated bearings in deep-well pumps.

Other significant uses of rubber are door and window profiles, hoses, belts, matting, flooring and dampeners for the automotive industry. Significant tonnage of rubber is used as adhesives in many manufacturing industries and products, although the two most noticeable are the paper and the carpet industry. Rubber is also commonly used to make rubber bands and pencil erasers.

VIII. INTRODUCTION TO THE SCIENCE OF RUBBER MIXING PRACTICE AND PRODUCTION OF SYNTHETIC RUBBER

Manufacturing rubber products requires the use of many additives. Mixing of rubber involves several additives, such as reinforcing fillers, non-reinforcing fillers, oils, vulcanization chemicals, stabilizers, and so on. Therefore, mixing is a very important step in rubber processing.

The commercial rubbers are those confined within the cost performance window and there are other rubbers which may be synthesized, if needs arise. Some rubbers are used to perform mechanical functions only and others are used because of additional special features³⁰. Such features may be the outdoor and chemical stability, oil resistance, and high temperature stability.

Mixing of rubber is often preceded by kneading the gum rubber to soften it, a process called "Mastication". NR, in general, has a very high MW and hence mastication is used to bring its molecular weight down to a more easily processable range. Synthetic rubber can be produced in different ways.

One common process is shown below in the Fig. 3 and it is self explanatory.

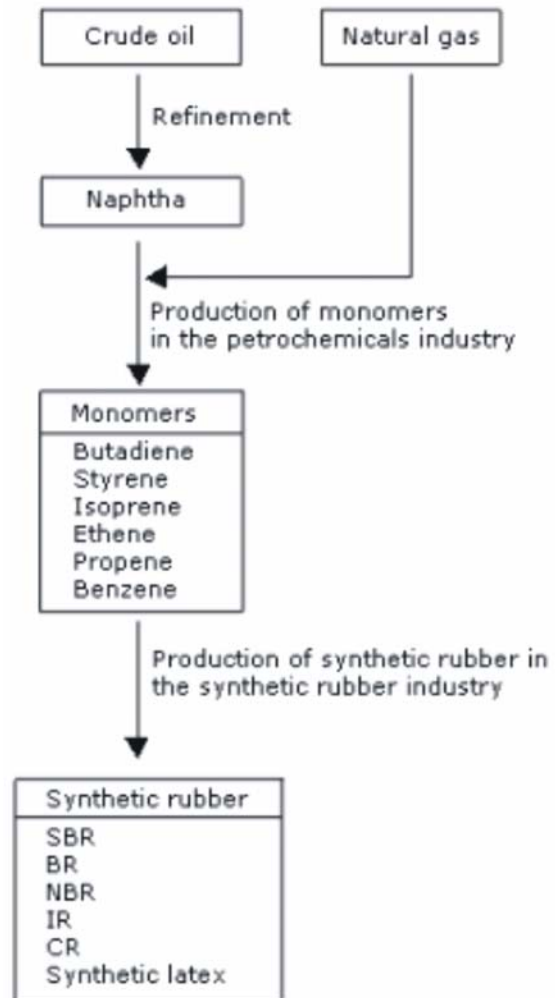


Fig. 3. Production of Synthetic rubber

IX. RUBBER PROCESSING METHODS

The fabrication of rubber products from latex concentrate and from dry rubber is completely different, although both involve shaping, vulcanization and some of the shaping processes are common to both materials. In general, the latex and dry rubber industries are totally distinct^{29, 30}. This section refers entirely to dry rubber processing. Fabrication of rubber products demands three main processes:

- Mixing
- Shaping
- Vulcanization.

A. Mixing

The mixing process is usually performed in heavy internal mixers, capable of processing 200 kg batch weight in two minutes. This process has two functions: firstly, to soften the rubber, often known as mastication and, secondly, to admix the rubber with the compounding ingredients, which may include fillers, vulcanizing agents, protective agents and blends with other synthetic rubbers. This technique is known as compounding. After mixing, the compounded rubber becomes plastic and is now ready to be shaped. This is done in a variety of ways and is frequently combined with vulcanization in which the rubber undergoes a chemical reaction at a high temperature, becoming converted from the plastic state into a strong, highly elastic material.

B. Shaping

The most common process is by moulding under pressure in a heated mould in which vulcanization occurs. There are three important variants of the process: compression, transfer and injection moulding. Other important shaping techniques include extrusion and calendaring. Bonding of rubber to metal or thermoplastic or glass fabric normally takes place as part of the moulding process. The metal component will require pretreatment to clean it and the application of a bonding agent.

C. Compression Moulding

A blank of appropriate weight is shaped in a steel mould within a heated press. The majority of rubber articles are made by this process. It has the following advantages.

- Cheap
- Rapid
- Capable of long or short runs
- Gives a fair degree of precision if care is taken

High rates of production are possible in multi-daylight presses in which down-time is reduced to a minimum by using alternately each of two separate sets of moulds, mechanically handled.

D. Transfer Moulding

A slug of rubber compound is put into the upper cavity of the transfer mould. When placed in the press, the rubber is squeezed through a small aperture to fill the second cavity, having the required shape, in which the rubber is vulcanized. This method is used for precision work which justifies the high mould cost and relatively

slow throughput. Short runs are feasible and the method is particularly useful for components having metal inserts such as engineering components.

E. Injection Moulding

This is a semi continuous process in which rubber is extruded from a heated barrel of a screw or ram machine through a nozzle. The work of extrusion produces a further rise of temperature, before the rubber is forced into a heated mould where the rubber is vulcanized. Because the rubber reaches the mould at a high temperature, vulcanization times are short and thick articles are homogeneously vulcanized. The high capital cost is justified by the use of the machine for long runs of articles of good quality, particularly those which are difficult to mould by compression moulding.

F. Extrusion

During extrusion, compounded rubber is passed from a short screw extruder through a die of an appropriate shape. Vulcanization is a separate process, and can be performed in a variety of ways: (i) batchwise in a steam or air autoclave, or (ii) continuously in steam or hot air, or (iii) in a bath containing a eutectic mixture of molten metal salts or in a fluidized bed. Simple or complex sections, either solid or sponge, may be extruded. Extrusion is used for the manufacture of hose, weatherstrip seals for automobiles and cables. Parts of tyres are also extruded, notably the sidewalls.

G. Calendaring

In the calendaring process, rubber is passed through a three or four roll calendar either to produce a sheet of controlled thickness or to force the rubber into close contact with a textile or metal cord. Calendaring is frequently followed by a building process, e.g. sheet may be built up into a rubber roller or the rubberized textile may be built up into a carcass for a tyre or conveyor belt. Vulcanization is then performed in heated presses or in autoclaves.

X. APPLICATION OF RUBBER AND RUBBER PRODUCTS IN ENGINEERING

A. Introduction

Rubber is a group of industrial material like metals, fibres, wood, plastics, and glass on which the world of modern technology depends. The world consumption of rubber is in the order of about 16 million tons per annum and has been increasing in recent years at the rate of about 4% per annum. Out of this, about one third is manmade synthetic rubber mainly produced from petroleum fractions. The unique and versatile properties of rubber have made it highly indispensable for the modern

way of life. It has high resilience and elasticity. Contribution of rubber in the field of engineering, space research, and medical sciences is vital. Various reinforcing materials in rubber are high tenacity rayon, nylon-6, nylon-66, polyester, steel, fibre glass, and aramids. Kevlar in rubber has come into existence and being used to meet the specific requirements of a special rubber composite product. Tyre is a composite material consisting of cords embedded in the rubber matrix. The overall length, and ability to bear load by the tyre depend strongly upon the nature of cord²³. EPDM, a terpolymer of ethylene, propylene and a non-conjugated diene, is a weather resistant rubber possessing exceptionally good weather resistance. It is often called as crackless rubber. The inherent properties of EPDM Rubber are characterized by ozone resistance, weather resistance, heat resistance, oxidation resistance, polar fluids resistance, water resistance, aqueous solutions resistance, low temperature flexibility, high resilience, excellent electrical properties, and radiation resistant^{24, 25}.

B. Rubber as an engineering material

Rubber has several properties which make it useful as an engineering material. It has large deformability. Some rubbers can be stretched 10 times without rupture and regain almost the original shape after the removal of the stress. This constitutes both an advantage as well as a disadvantage depending upon the same requirement. It has low modulus, that is, low stresses produce deformation or change in shape^{26, 27}. This property enables rubber to absorb shocks and to be used for cushioning and sealing. Because rubber regains its original shape after larger deformation, it can store energy more than most of the materials. When rubber is subjected to cyclic, alternating loading, as in automobile tyres which are cyclically stressed when the automobile is moving, not all the energy is recovered. This results in some hysteresis loss of energy which appears as heat energy and the rubber gets heated. This shortens the life of the rubber. This loss of energy enables rubber to reduce vibration²⁸. It is a bad conductor of electricity. Soft rubber is used as an insulator, and hard rubber or ebonite is used as a high grade dielectric material. It is impermeable to water and to a large degree to gases. Natural rubber is superior to synthetic rubber in mechanical properties, but is inferior in resistance to solvents and oils. Presently used artificial rubbers are listed below.

- Buna S. (SBR, GRS) Rubber
- Buna N (GR-A and GR-N) Rubber
- Butyl Rubber (GR-1)

- Neoprene (GR-M)
- Thiokol (GR-P)
- Silicone Rubber
- Polyurethane Rubber

Buna S. (SBR, GRS) Rubber: It is a copolymer of butadiene, and styrene. It is also called GR-S (Government Rubber Styrene) or SBR. Buna S Rubber can be combined with natural rubber, thus combining the useful properties of both, and it is used for the manufacture of tyres belting, shoe soles, coated fabrics, floor tiles, tank lining, and carpet backing. This rubber has lower strength and flexibility than the natural rubber.

Buna N (GR-A and GR-N): It is a copolymer of butadiene, and acrylonitrile. It has good resistance to abrasion, aging, and to low temperatures. This rubber is vulcanized with sulphur and is used for hose, conveyer belts, tank linings, and for high altitude aircraft. It is also used in matching adhesives, oil resistant foams and automotive parts.

Butyl Rubber (GR-I): This type of rubber contains 98% of isobutylene, which polymerizes to give a saturated polymer. It is cheaper than other artificial rubbers. Another advantage of this rubber is that it is impermeable to gases, here it is satisfactory for making cycle and automobile tubes. It is also resistant to aging, ozone, acids, or alkalis. It's other uses one for hose, tank linings, and electrical insulation.

Neoprene (GR-M): It is a polymer of chloroprene. It has very useful properties and resembles natural rubber, but it is more expensive than rubbers. It has very good resistance to aging, and oils and it is used for hose, wire insulation and belts.

Thiokol (GR-P): Several types of rubbers of this group are made by copolymerization of organic dichlorides, like ethylene dichloride, with inorganic polysulphides like Sodium Sulphide. These rubbers neither resemble natural rubber in structure nor in properties they have very good resistance to solvents and can withstand cold, but not heat. They are cheap and can easily shaped, but have an unpleasant smell. Vulcanizing of Thiokol using sulphur is not done since it does not yield the hardened rubber. It is done using active metal oxides like Zinc Oxide.

Silicone Rubber: Silicone rubbers are polymers composing alternate silicon and oxygen atoms in which the silicon atoms are joined to organic groups. They were developed in 1930s during searches for heat resistant electrical insulating materials. It has an outstanding

thermal stability and also water repellent. So, silicone rubbers are mainly used in making lubricants, electric blankets, protective coatings for fabrics, types for fighter crafts that could withstand high frictional heat and for making thermal impulsion for washing machines²².

C. Rubber in Automotive Applications

Approximately, 500 to 600 applications in the automobile involve the use of elastomers. Some crucial uses having safety implications are as follows:

- Tires
- Fuel hoses
- Brake hoses and cups
- Various fluid gaskets
- Engine and TBI gaskets
- Weather strips
- Windshield wiper blades
- Radiator hoses
- Electrical wiring insulation
- Flexible body panels
- Movable impellers or diaphragms for fluids or gas transfer
- Safety padding and air bags
- Conduits for liquids and gases

D. Application as Rubber Rolls

- Rubber covered rolls

In the broad field of rubber technology, the application of rubber to the surface of metal cores to make rubber-covered rolls generally referred to as rubber-covered rolls, is a highly specialized area comprised of unique methods, practices, and standards using a well balanced combination of the rigidity of metal core and the elasticity of rubber²⁹. Although rubber rolls may vary in importance, their versatility ensures that they are used almost in all sectors of industry for a wide variety of purposes and on almost all kinds of machines—from tiny rolls for making envelopes and movie film to giant rolls used in paper making.

One of the most extensive uses of rubber rolls is in the contact of liquids by pressing or squeezing, an exemplified in the manufacture of paper and in the processing of metals, textiles, and leather. Such typical devices as the press roll, the touch roll for paper making, the padding roll for textile applications, and the transferring roll for printing, all take advantage of the elasticity of rubber. Rubber rolls are used for many conveying purposes such as feed rolls, and guide rolls, and guide rolls of various kinds, as used in the paper (table rolls), steel (sink rolls, deflector rolls, tension rolls), textile (guide rolls, thinner rolls, and expendable rolls) and plastic industries. The properties of rubber that are important for such applications include elasticity, friction, abrasion resistance, and chemical resistance. In addition, resistance to solvents, and plasticizers as well as resistance to heat are desired in applications such as laminating, embossing, and coating (textiles, plastics, paper, and printing). The design of rubber rolls involves consideration of general factors such as the work place the working conditions, the desired performance, and the required durability.

- Industrial rolls

The characteristics and compounding of rubber rolls related to a few industrial applications are explained below one by one:

- Paper mill rolls

The chief function of paper mill rubber rolls is to remove water from the sheet of pulp that is being converted to paper. The general requirements of paper mill rolls are high mechanical stability an good dynamic property, uniform hardness, resistance to chemicals used in paper making, resistance to the temperature likely to be encountered, resistance to scratching and marking, and good grinding characteristics. Since paper mill rolls must be reformed occasionally, the ability to furnish a smooth, unblemished, or ground surface is important. Natural rubber is still the preferred polymer for paper mill roll covers³⁰. Blends of polybutadiene and natural rubbers also offer interesting opportunities. Some of the paper mill rolls are now being made with chloroprene rubber.

- Steel mill rolls

Rubber rolls used in steel mills, in continuous electrolytic tin plating machines, and in galvanizing plants are not crowned but are ground to a uniform diameter throughout. Most steel mill rolls are covered with polychloroprene rubber and some with natural rubber, NR, in the hardness range of 45 to 80 shores.

● Printing Rolls

The function of printing rolls is to apply ink to a selected and prepared surface at a conducted rate, and the quality of printing depending very much on the quality of the roll cover. The specific requirements for the rubber coverings of printing rolls depend on the printing processes (letter press, lithography, offset, photogravure printing, and duplication process). Offset printing uses an inking roll which transfers ink to the plate, and watering rolls, which supplies water to the nonprinting area of the plate, to repel ink. The following factors must be considered for such rolls. They are strength, resistance to oils and solvents, resistance to glaze, hardness, and dimensional accuracy.

● Tanning industry rolls

All tanning industry rolls require no staining cover compounds. Degraining, buffing, and splitting machine rolls are covered with natural rubber, whereas in fleshing and dehairing machines, rolls with nitrile rubber covering are used.

● Rolls for plastic industry

Rubber rolls with hardness of roughly 60 shores, made of natural, chloroprene, and nitrile rubbers are frequently used. It should have tear resistance and no tackiness. The rubber rolls employed for the calendaring of PVC consist of touch rolls (lamination rolls) embossing rolls and sand rolls, where properties such as heat resistance, plasticizer resistance and abrasion resistance are required^{29,30}. Butyl and EPDM rubbers are commonly employed as the covering material for touch rolls with hardness of 65 to 80 shores.

● Textile mill rolls

Textile mill rubber rolls are used in the textile industry for different purposes to withstand widely different conditions involved in designing, dyeing, mercerizing, and finishing. Coverings with natural rubber are used widely in the removal of water-soluble sizes and for rolls needed for bleaching purposes, mercerizing, dyeing, and finishing. Roll covers based on nitrile rubber are particularly suitable for use in desizing with fat dissolving soaps, mercerizing, special dyeing processes, and special type of finishing³⁰. The rubber covering is made in the range of 65 to 80 Shores A.

XI. DISCUSSIONS AND CONCLUSIONS

Various aspects on rubber are discussed in detail. An in-depth review on rubber history is conducted and the origin of rubber is identified. From this review, physical

characteristics of natural rubber and synthetic rubber are well understood. This has also provided information on the various methods of rubber processing. The facts sheets of rubber have helped to know about the commercial names of different types of rubber in industrial use. It is concluded that rubber is an effective and suitable elastomer for manufacturing engineering and metal working industries.

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