

INFLUENCE OF STYRENE CONTENT ON SBR
HARDNING
(IN THE PRESENCE OF HEAT AND UV)

By

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DECLARATION

"I certify that this dissertation does not incorporate without acknowledgement any material property submitted for the degree or diploma in any university and to the best of my knowledge and belief It does not contain any material previously published or written or orally communicated by another person except where due reference is made in the text "

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**AFFECTIONATELY
DEDICATED
TO
MY EVER LOVING
PARENTS, SISTORS
AND
BROTHERS.**

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ABSTRACT

Rubber is a group of industrial material like metals, fibres, wood, plastic, glass etc. 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 the recent years at the rate of about 4% per annum. Out of this about 1/3 is man made synthetic rubber mainly produced from petroleum fractions. Total rubber consumption in India in 1990 were approximately 460,000 tons and the ratio of NR: SR consumption is about 70:30.

The resilience and elasticity are factors that distinguish different types of rubbers. Many of its modern applications rubber is not used alone but reinforced with textiles, metals etc. contributions of rubber in the field of engineering, space research, medical sciences, family planning etc is vital.

According to my research, my raw materials are Styrene butadiene rubber (SBR), Poly butadiene (BR), & High styrene resin (piolite/HSR). HSR is a powder form rubber. In order to prepare rubber blends I have mixed 2 raw materials among them. Then above samples divided into 2 series. I have exposed to sunlight & heat treatment. Then I was determined the Mooney viscosity of samples according to the number of days 0, 3, 7, 10, 14, 21, 30...etc. SBR, BR and HSR are synthetic rubbers that are been used in tire industry. They are used at various composition mixtures.

This work involves study of viscosity properties of several blends of rubber that was prepared by mixing SBR and HSR at different proportions with BR. The viscosity properties of the blend was determined using Mooney viscometer and in the presence of heat and UV radiation.

SBR, BR blends showed sensitivity towards heat and HSR: BR blends showed sensitivity towards UV radiation.

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Chapter 1

INTRODUCTION

Rubber is the most fascinating material known to the mankind on account of its range of applications in every day life defense civilian purposes and its behavior under the most diverse conditions of applications. Natural rubber is obtained from the latex bearing plants. *Hevea brasiliensis* is the main plant, which produces the remarkable latex since this erases the pencil mark therefore it, is known as rubber.

Natural rubber accounts almost 30% of elastomers used in the world rubber industry today.(Chandra & Mishra 1981) The 3 or 4 south East Asian countries as per demand of the world rubber industries produce the major amount of the natural rubber.

Due to the increasing consumption of natural rubber and to improving the rubber properties researchers synthesized the rubber, which is mainly produced from petroleum fractions.(Chandra & Mishra 1981) Most of the synthetic rubbers, which are used widely, available in the latex form. Styrene butadiene copolymer with 25% of styrene and total solid content up to 60% are supplied by several producers. Up to 50% solid contents the chloroprene nitrile and butyl rubber lattices with air and solvent resistance and are available to replace the natural rubber.(Chandra & Mishra 1981) The advantage of synthetic rubber lattices is taken in to the glove and bonded fabric design to with stand dry cleaning. The fire retardant property of CR is also exploited.

The synthetic rubber established usages and were not earlier in competition with natural rubber because they met application, which the latex could not meet. In the series of development of oil resistant the copolymer of butadiene and acrylonitrile were also produced.

Not only had adequate properties to be developed in the vulcanized product, but also it was expected that the raw polymer would be capable of being handled by the same process as natural rubber. (Chandra & Mishra 1981) It is of interest and significance that the four types of rubbers available after 2nd world war were

having this feature. The raw rubbers were millable and mixable in rubber machinery and reinforcing fillers, softners.

In 1940 the low gas permeability rubber produced by the mixing isobutalene with small percent of isoprene. This rubber was kept in special class of that time. Its good resistance to ozone, oxidation and chemicals has led to its adoption for a number of applications as a replacement of natural rubber. **(Chandra & Mishra 1981)**

With the invention of catalyst the natural rubber like products was obtained and the poly butadiene and poly isoprene were obtained through solution process. These two rubbers have made a considerable impact on general-purpose rubber market and have established themselves in tyre compounds. Poly butadiene rubber (BR) is mixed with oil extended grade because BR is capable of co accepting large amounts of oil and carbon black.the road hold in quality of BR restricts its use unblended but it confers improved wear resistance and cracking resistance.

OBJECTIVES

My major objectives are,

- To find out the heat sensitive compound and **UV** sensitive compound in **HSR** and **SBR** rubber mixture.
- Study the variation of Mooney viscosity of synthetic **SBR** rubber blends with various ratios of styrene and Polybutadiene (**BR**).
- Study the affection of styrene content on hardening of **SBR** (Styrene butadiene rubber) in the presence of heat and **UV** (sunlight).

2.1. INTRODUCTION TO THE LOADSTAR (Pvt) Ltd.

Loadstar (Pvt) Ltd is a one of the member in **Jinasena** group of companies. **Jinasena** group of companies was stated in **1905**. First manager of the company was **Mr. Jinasena**. Now company have 15 members & the head office of the group of companies is situated at No.04, Hunupitiya Road, and Colombo-02.

Loadstar (Pvt) Ltd was started in **1984**. It has 65% of shares from **Jinasena** & other 35% of shares from Belgium sol ideal company. The factories of **Loadstar (Pvt) Ltd** are situated at Ekala, Kotugoda, & Midigama. The oldest factory of company is Ekala tyre division (**ETD**) started at 1984. They are produced black & white solid tyres & Rims. Second factory is Kotugoda tyre division (**KTD**) started at **1992**. They are produced Black & white solid tyres & pneumatic tyres. Midigama tyre division (**MTD**) is youngest member of **Loadstar (Pvt) Ltd**. This factory was stated in **1999**. They are produced solid tyres, Pneumatic tyres & Rubber tracks. But Midigama tyre division dose not complete their constructions. Main work shops, steel band section, Bead wire section, IT unit, Project office, Main stores & one of the administration offices are situated at Jenasene Industrial park, Ekala.

Loadstar (Pvt) Ltd becomes main industrial solid tyre supplier in the world. They are complete 20% of world industrial solid tyre requirement. They are exporting their product to America, Europe, Asia, Australia and Africa. 45% of products are export to America, 40% of products are export to Europe, 10% of products are export to Asia & others are export to other countries.

Loadstar (Pvt) Ltd is complete 5% of international pneumatic tyre requirement. They are exporting their product to America, Europe, Asia, Australia and Africa. 49% of products are export to America, 44% of products are export to Europe, 4% of products are export to Asia & Australia others 3% are export to Africa.

Loadstar (Pvt) Ltd has a steel rim production factory. They supply the complete wheel & rims to the original equipment manufactures. New product of **Lodestar (Pvt) Ltd** is rubber tracks for backhoe etc. It is produced by **MTD**.

Total production capacity of their factories is 155 Tonus per day. Complete production capacities of **ETD, KTD & MTD** are 50, 60 & 45 Tonus for each factory. Central mixing plant has a 100 Tons capacity.

Loadstar (Pvt) Ltd has 4500 workers. There are 110 qualified engineers and 60 managers.

Loadstar (Pvt) Ltd buys a rim factory from Japan. It was one of the main Japanese rim & split wheel producer. Midigama factory has robotics machines. Those machines assemble and transport to the Sri Lanka. Then these are fixed in new factory in Sri Lanka. It was situated at Ekala industrial park.

Loadstar (Pvt) Ltd principally engaged in the manufacturing and marketing of industrial solid tyres, pneumatic tyres, rims, split wheels & rubber tracks. All of their products are exported to international market. They got **ISO 9002** quality standard in 1998 from London Loid Company. Now they aiming to achieve **ISO 14000** strandeds.

2.2. TIRE RUBBER INDUSTRY.

The tire industry has kept pace with the technological development that have taken place else where in the world initially the tires were manufactured with cotton fabric as the reinforcing material they switched over the rayon fabric during sixties and to nylon fabric during seventies.

Today the cotton fabric has been completely eliminated and rayon is also on the way out. Initially tires were made only from natural rubber. Now they are using synthetic rubbers to varying content. The use of various improved types of carbon black and rubber chemicals and new reinforcing material like precipitated silica are also introduced to achieve higher durability and higher performance of tires. The overall performance of tires has also increased with the adoption of technological innovations the entire production of tires in cross ply tires whereas advanced countries. Have switched over to radial tires. Many of tire companies have been planning to switch over to radial tires but this may take little more time.

Although considerable technological developments and innovations have been inducted to improve the quality of tires, the industry still depends on the foreign technology. Almost all the major units have an ongoing foreign technological collaboration.

In the rubber industry so many chemicals, rubbers and additives are added to compounding rubbers. They are

- ❖ Rubbers (natural and synthetic)
- ❖ Accelerators
- ❖ Fillers
- ❖ Lubricants
- ❖ Vulcanizing agents
- ❖ Reinforcing agents
- ❖ Antioxidants
- ❖ Activators
- ❖ Retarders

2.3.NATURAL RUBBER.

The widespread development and use of natural rubber although is quite new, but there is an evidence that this was known long back.

Christopher Columbus was acknowledged to have discovered rubber in 1493-96. He observed that the natives of Haiti playing with a ball made by smoke-drying the latex of a tree called Catchu or weeping woods. Besides this, the natives also used the latex to make waterproof clothing & footwear.

Early in 19th century it was felt in Europe & America that a flexible, elastic, tough & water proof material like rubber should have wide spread use. Attempts by Mackintosh Hancock of UK and Charles Good Year of USA were not very successful. Until in 1839 when GoodYear discovered the process of heating rubber with sulphur. This process greatly increases the elasticity, strength and is no longer affected by weather/temperature changes.

2.3.1 RUBBER PLANTATION

The principal rubber-producing tree is the species *Hevea brasilliensis*, an indigenous tree of Brazil. But with the demand of rubber increased by leaps and bound it was felt in the last quarter of 19th century that Brazil would be unable to meet would demand.

In 1873, Sir Joseph Hooker brought some seedlings from Amazon, Brazil and planted the same in Kew gardens, London. Another attempt by Sir Henry Wikham led to the success of spreading the cultivation to far east. Vast plantation has gradually grown up in Sri Lanka, India, Malayasia, Indonesia & other places.

2.3.2 NATURAL RUBBER PRODUCTION

Natural rubber is obtained from *Hevea brasilliensis* by tapping tree. The milky white exudes called latex is preserved with ammonia and for dry rubber usage the preservation is done by Na₂So₄ or formaldehyde.

The field latex thus preserved is brought to the factory, where the latex is strained through a 60-80-mesh sieve to remove the dirt and foreign matters. It is then diluted to 15-20% of concentration by adding water depending on whether pale crepe or smoked sheet is to be produced. The latex coagulation is done by acetic acid or formic acid. The coagulum contains 80% of water, is brought to sheeting battery consisting of a series of twin rollers 4 or 5 equipped with water sprays. Passage through the rollers reduces the water content of the coagulum to less than 40%.

There are several types of natural rubbers,

1. Crepe rubber
2. White and pale crepe
3. Ribbed smoked sheet (RSS)
4. Technically classified rubber (TCR)
5. All dried sheets
6. Superior processing rubber

2.3.2.1 CREPE RUBBER

Several pairs of rollers heavily mill the wet strip, the thickness of the strip being ultimately reduced in to a thin lace like sheet. These thin sheets are plied up to the desired thickness allowed to dry and packed.

2.3.2.2 WHITE AND PALE CREPE

The natural color of crepe is pale yellow, mainly owing to its content of β -Carotene. To produce the palest crepe, the latex coagulation is done by fractionally. Initially about 30% of latex is coagulated with acetic acid and the coagulation of the remainder portion is done by bleaching the latex with Xylyl mercaptan (0.05% max) to get pale color, prior to coagulation.

2.3.2.3 RIBBED SMOKED SHEET

If smoked sheet is to be produced, the battery of the roller is similar to that for crepe, but the milling is not so heavy. The final pair of rollers is engraved to impart the Diamond or ribbed pattern. The sheets are then hung and allowed to drip for several hours and finally smoked by burning wood. The smoke not only guards the rubber under bacteriological work, but also protects the rubber from oxidation by air.

2.3.2.4. TECHNICALLY CLASSIFIED RUBBER

The rate of cure of NR is sensitive test mixes are affected significantly by the pH at which coagulation occurs and to lesser degree to the dilution of latex prior to coagulation. By control these variables, the natural rubber in addition to its regular market grade, can be classified on the rate of its vulcanisation. This grade is called the technically classified rubber (TCR) and bears a red or yellow or blue circle depending on the cure rate which are slow, medium & fast respectively.

2.3.2.5 ALL DRIED SHEET (ADS)

This is a light colored sheet prepared in the same way as Ribbed smoked sheet but dried in hot air without smoke. The sheet surface is sometimes treated with p-nitrophenol solution to prevent mould.

2.3.2.6. SUPERIOR PROCESSING RUBBER

Superior processing rubbers are made by mixing 20% by weight of vulcanized latex with 80% by weight of unvulcanised latex, coagulating the mixture and processing the coagulum in the normal manner. SP smoked sheet, SP crepe, SP Air dried Sheet are available.

The advantages of SP rubbers are improved processing properties and fewer watermarks in open steam vulcanisation.

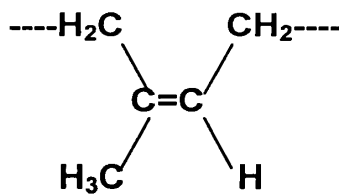
SPECIAL TYPES OF NR

A few other special types of NR are:

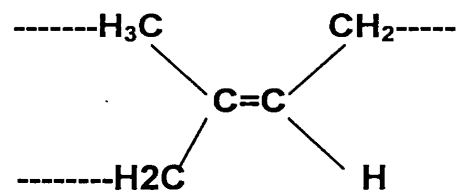
- I) Oil Extended Natural Rubber (OENR).
- II) Partially purified crepe
- III) Rubber Powders
- IV) Skim Rubber.
- V) Softened Rubber

NATURAL RUBBER: STRUCTURE

NR is polymer of isoprene (C_5H_8), which may have 4 different isomeric structures viz.



(Cis 1,4)



(Trans 1,4)

Natural rubber is made of a minimum of 96% cis (1,4) polyisoprene structure. The term 'cis' & 'trans' refer to the particular carbon atoms in each unit, which are attached to the adjacent unit. Since the C=C double bond is considered to prevent rotation, thus trans (1,4) structure where the propagating $-\text{CH}_2-$ ridge are at opposite side of the double bond which would result in a rigid and non flexible structure. While in the cis (1,4) structure, the $-\text{CH}_2-$ are on the same side and hence NR itself is highly stereo regular and stretching leads to crystallinity which ultimately leads to high gum strength of the same. Natural rubber is vulcanized with sulphur compound or by 'S' donor accelerators because of the presence of reactive of reactive double bond in each repetitive unit.

2.4.SYNTHETIC RUBBER ITS DEVELOPMENT.

Shortage of natural rubber has repeatedly been the major spur for the development of synthetic rubber. In World War I, Germany developed methyl rubber, which is of very limited success. However, it was not until 1930's that bulk production of synthetic rubbers had begun both in the USA & in Germany. In Germany two synthetic rubbers were developed, one is copolymer of styrene and butadiene for general purpose while the co polymers of butadiene with acrylonitrile for special purpose. In USA polychloroprene was developed which was considered to be a purpose rubber.

2.5. TYPES OF SYNTHETIC RUBBERS.

Synthetic rubbers are generally two types,

1. **General-purpose rubbers:** These are class of rubbers that find applications in areas where NR is used like tires, tubes, beltings etc. these include SBR, Polybutadiene & Polyisoprene. Special
2. **Special purpose synthetic rubbers:** on the other hand find specific applications because of their own special properties e.g. Nitrile rubber for resistance, EPDM for ozone and weathering resistance, Butyl for low permeability to air, acid and out standing heat resistance.

2.5.1 MANUFACTURING PROCESS.

Two commonly known processes generally manufacture the synthetic rubbers

1. Emulsion polymerization.
2. Solution polymerization

In the emulsion polymerization process the reactant monomers are taken in water by the addition of an emulsifier and then polymerized and in solution polymerization processes, the monomers are kept in solution in a suitable hydro carbon solvent.

2.6. STYRENE BUTADIENE RUBBER (SBR).

The most common general-purpose rubber is SBR. It is a copolymer of styrene and butadiene (normally in the proportion of 25% styrene & 77% butadiene). It is produced by mainly by emulsion process, although solution SBR also available. Polymerization in emulsion process is carried out under pressure to yield hot SBR at 50°C and cold SBR at 5°C.

Cold SBR has narrower molecular weight distribution, is more crystalline in structure leading to higher mechanical, abrasion, cut growth resistance and hence is preferred in many industrial products including tires. Hot SBR is somewhat easier to breakdown by milling, develop less heat during mixing, easier to process, and is faster curing. Hot SBR is having high ozone resistance.

2.6.1 TYPES OF SBR

SBR divides in to the following types and the ASTM designation for them is internationally used.

- ❖ 1000 series (1000-1099)
- ❖ 1100 series (1100-1199)
- ❖ 1500 series (1500-1599)
- ❖ 1600 series (1600-1699)
- ❖ 1700 series (1700-1799)
- ❖ 1800 series (1800-1899)
- ❖ 1900 series (1900-1999)
- ❖ 2000 series
- ❖ 2100 series.

2.6.2 PROCESSING OF SBR

SBR is produced in the same way as that of natural rubber. The difference are summarized below

- (a) Mill mastication should be performed at a lower temp and normally a larger quantity of processing oil is required. The nip gap should be tight and this may require some reduction in batch weight.
- (b) SBR is less effected b peptiser.

- (c) SBR stocks have less tendency to scorching.
- (d) SBR having less unsaturation compared to other diene rubbers requires less sulphur. It is slower curing than NR and hence require more accelerators.
- (e) SBR containing some fatty acids requires less stearic acid for activation.
- (f) In general compounding, the same types of ingredients are added to SBR like NR and their mixing & processing are also very close.

2.6.3 TECHNOLOGICAL PROPERTIES OF SBR

The great draw back of SBR with respect to NR its very poor gum strength of unloaded vulcanisates.

Property	SBR	Natural rubber
Tensile strength, psi	300-400	3000
Elongation at break	500-600	750-800
Modulus at 300% elong, psi	300-400	400-600
Hardness (IRHD)	45-50	40

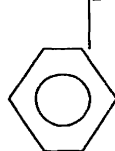
2.6.4 APPLICATIONS OF SBR

The main applications of SBR are in

- a) Scooter and passenger car types.
- b) Beltings
- c) Wire and cables.
- d) Mechanical goods.

2.6.5 THE STRUCTURE OF SBR

The chemical structure of SBR is as follows:



SBR made by emulsion process usually contain 25% styrene randomly dispersed with 75% butadiene in the polymer chain. In emulsion SBR, the structure of butadiene is 18% cis, 65% trans & 17% vinyl. SBR mad in solution contains about the same amount of styrene but both random and block copolymers are made. They have lower trans, lower vinyl & higher cis content than emulsion SBR. This difference mainly causes a linear crystalline structure of solution SBR with higher mechanical properties than emulsion SBR.

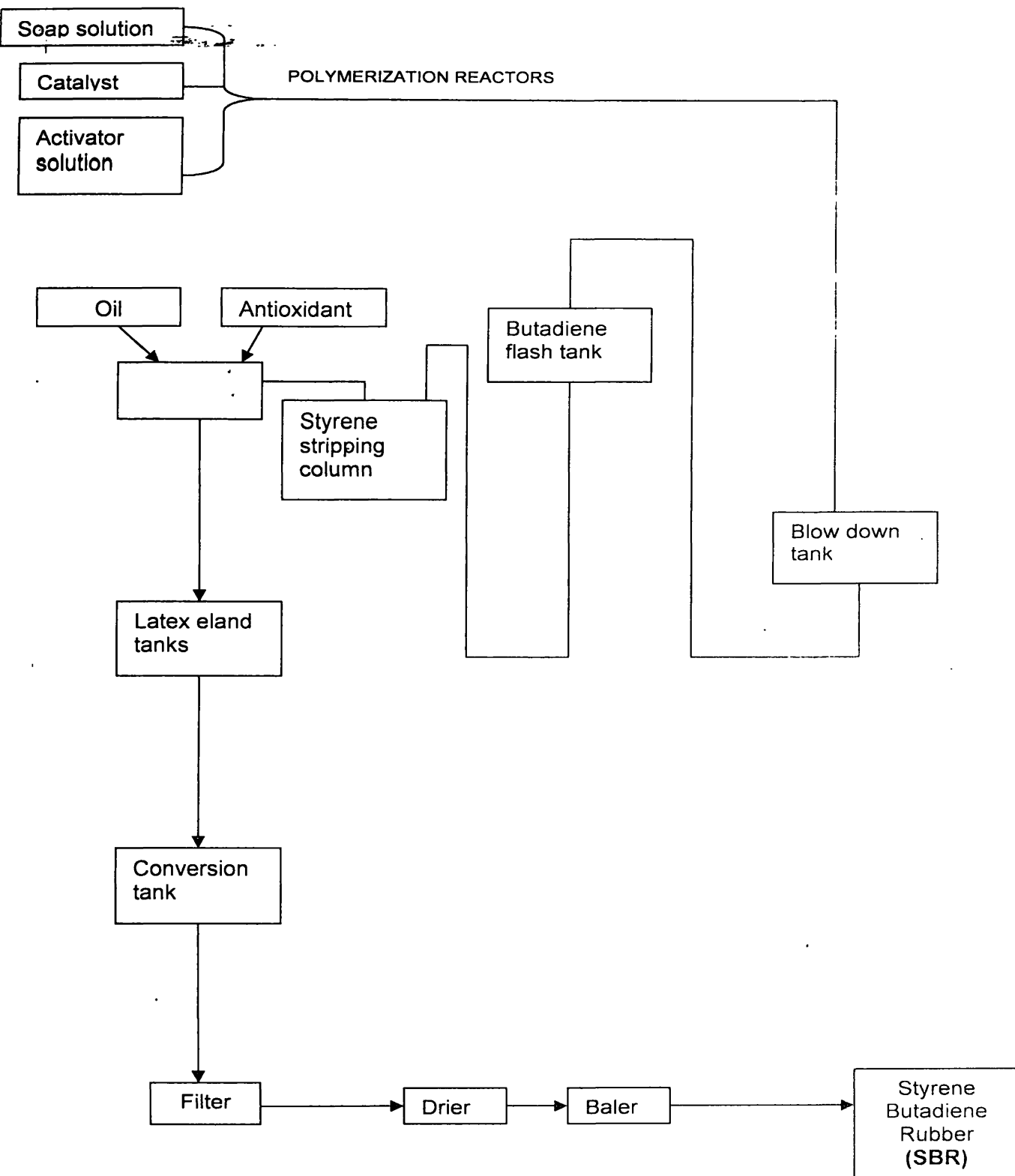


Figure 2.2. The production of SBR.

2.7.POLY BUTADIENE

Polybutadiene is homopolymer of 1,4 Butadiene and is produced by mainly solution process and to some extent by emulsion process by addition polymerization technique.

It is commercially available as a high cis (97%) 1,4 Polybutadiene or low cis (40%) content polymer in normal or oil extended form.

Polybutadiene is very poor in processing characteristics, low track, does not band in mill, weak in form resulting in high cold flow. Hence it is invariably used in blends with natural rubber or SBR.

A few plus & minus of points of polybutadiene are summarized below.

Advantage	Disadvantage
Higher resilience, hence dynamic Properties are good	Poor tack-resulting difficulty in building up of material
Higher resistance to flex cracking	Low tear strength-resulting in chunking out of portion in large tires
Higher abrasion resistance	Low skid resistance-specially in wet surface Causing problems with tire slipping
Low Tg, better low temperature properties.	Poor mill banding-hence used in blends.
High order of acceptance of oil & black	

The cure characteristic of polybutadiene is more in line with natural rubber. The compound design and suitable blending with NR & SBR have made this rubber used extensively.

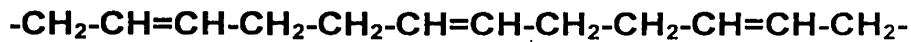
2.7.1 APPLICATIONS OF POLYBUTADIENE

The main applications of polybutadiene are, in

1. Tires (treads & sidewalls)
2. Beltings
3. Play balls & footwear

2.7.2 THE STRUCTURE OF POLYBUTADIENE (BR)

The structure of cis (1,4) polybutadiene is given below



Since the $-\text{CH}_2-$ bridges are on the same side of the same of double bond, this structure would lead to a linear, stereo regular, crystalline polymer.

2.8.HIGHSTYRENE RESIN (HSR)/PLIOLITE

This is a copolymer with Butadiene and Styrene. This rubber is commercially available as a white powder form like granules. The styrene content is 85% and butadiene (BR) content is 15%. This is used for rubber modification (SBR, EVA, NR, BR, CR, EPDM) High styrene content to give thermo plasticity. Butadiene to give flexibility & possibility to cross-link.

2.8.1 PROPERTIES OF HIGH STYRENE RESIN.

Gives high hardness & modulus with good flex & cut growth resistance at low specific gravities.

Cost effectiveness & technical alternative to high loadings of mineral fillers & SBR master batches.

Improves processing smooth calendared sheets and extrusions/improved moulding properties.

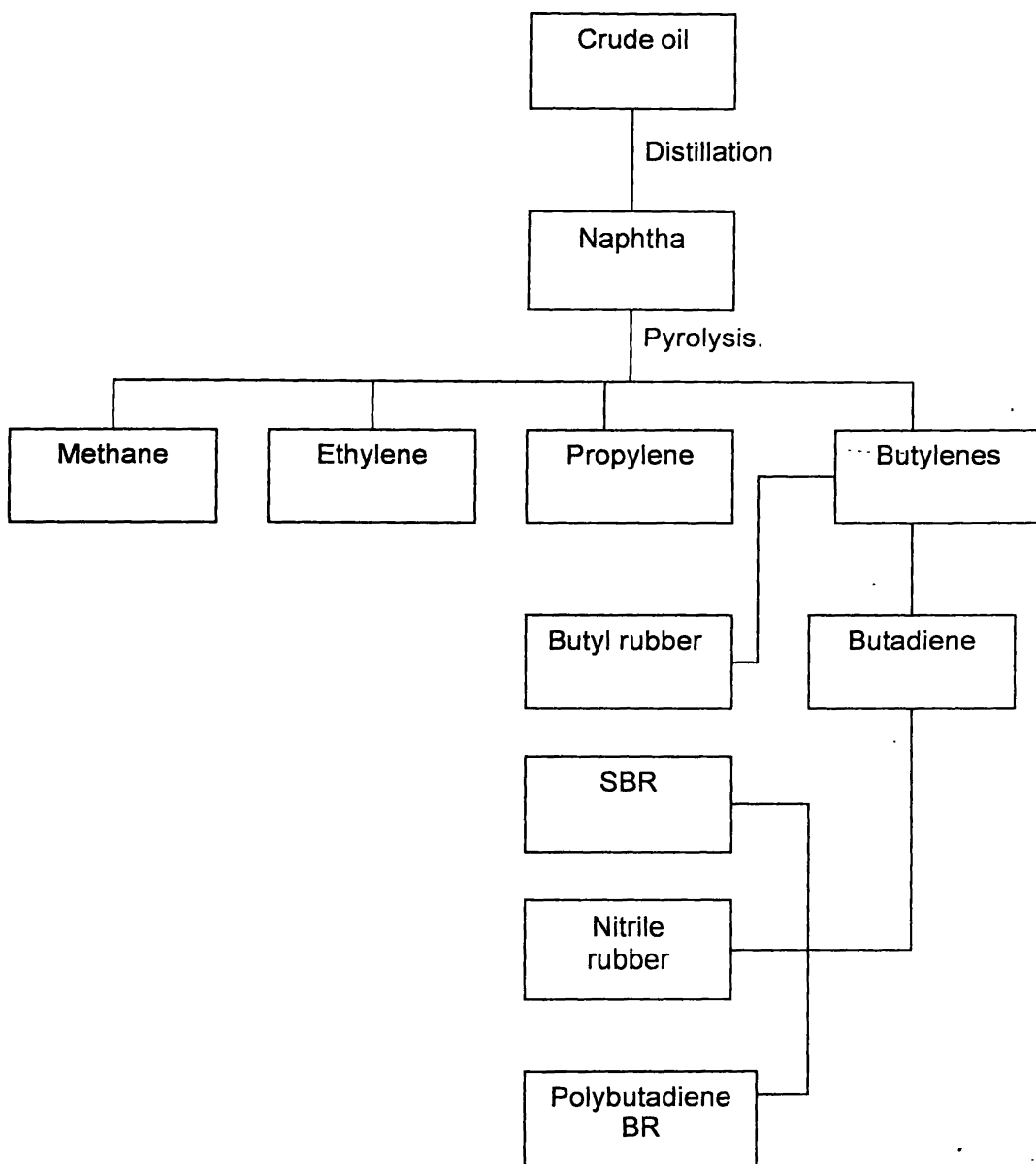


Figure 2.3. The production of BR

2.9.FILLERS AND OTHER CHEMICALS.

2.9.1 CARBON BLACK

Carbon blacks are added to rubber to develop physical strength properties and are therefore commonly known as reinforcing agents although the phenomenon of carbon black reinforcement of rubber was discovered about 50 years ago the nature of mechanism is still a subject of considerable debate. The modification of an elastomer by carbon black reinforcement and vulcanization generates a unique three-dimensional viscoelastic net work that transforms the soft elastomer in to a strong elastic product.

Available carbon blacks have a range of physical and chemical attributes (particle size, surface area, structure, surface activity) and can change elastomer properties to different degrees. A rubber compo under must select the right polymer, the right carbon black grade/loading lead combination,. And the right vulcanization system to give a rubber compound with the desired properties at the lowest possible cost. Carbon blacks are classified as follows. N220, N375, N330,,N550,N660.

2.9.2 NON-BLACK FILLERS.

Non black have always been an important part of the rubber industry. Initially they were considered as filler but now they are playing an important role in rubber products alongside carbon black.

The early non carbon black fillers were mainly naturally occurring minerals or by products of manufacturing such as clay, whiting, ZnO, zinc-sulphide, mica, asbestos, magnesium carbonate, iron oxide.etc.They were added to natural rubber or reduce tack increase hardness, improve durability and reduce cost. As the demand of rubber products increased specially tires the need for more reinforcing non-black fillers led to introduction between 1940 and 1960, of CaCO_3 calcium silicates hydrates silica and fumed silica. Further reinforcements in hydrated and fumed silica in the last two decades have produced a number of grades for specific types of performance.

CaCO₃ (both natural and precipitated) and silica (both hydrated & fumed) are the principal non-black fillers these days.

These non-black fillers have a broad spectrum of performance characteristics from reinforcing. But economical to highly reinforcing and these properties are related to average particle size of the filler which ranges from 10 microns (whittlings) down to 0.01 micron (fumed silica).

There are other miscellaneous non-black fillers like talc, Magnesium carbonate Aluminium tri hydrate etc. and they find minor usage in rubber industry. Talc is used mainly for dusting rubber in mould lubricants and reinforcing fillers.

Examples for other fillers: Clay, Calcium Carbonate, Calcium sulphate.

2.10.VULCANIZING AGENTS

With the exception of thermoplastics elastomers, these materials are necessary for vulcanization, since without the chemicals cross linking reactions involving these agents no improvements in the physical properties of the rubber mixes can occur. The type of cross linking agents required will vary with the type of rubber used. They can be grouped in two categories.

- I) **Sulphur and related elements:** the most common agent is sulphur, as it enters into reactions with the majority of the unsaturated rubbers to produce vulcanizates. In addition two other elements in the same periodic family, namely Se, Te are capable of producing vulcanization.
- II) **Non sulphur vulcanization:** most non sulphur vulcanization agents belong to one of three groups namely,
 - a) Metal oxides, ZnO
 - b) Difunctional compounds, epoxy resins
 - c) Peroxides.

2.11.ACCELERATORS

In combination with vulcanization agents, these materials reduce the vulcanization time (cure time) by increasing the rate of vulcanization. In most cases, the physical properties of the products are also improved.

Reduction in the time required for vulcanization is generally accomplished by changes in the amounts and/or types of accelerators used. E.g. for accelerators are given below.

- MBT (mercaptobenzothiazole)
- MBTS (benzothiazole disulphide)
- CBS (N-cyclohexyl-2-benzothiazole sulphenamide)
- MOR (2(4-morpholinylmercapto) benzothiazole)
- TMTD
- TMTM

2.12.ANTIOXIDENTS.

Rubbers are affected by natural or accelerated ageing process. Therefore it is necessary to add materials that are capable of retarding this type of deterioration.

The loss in physical properties, associated with ageing process, is normally caused by chain scission, cross linking or some of chemical alteration of the polymer chains. Consequently the age resistors used must be capable of reacting with the agents causing ageing (ozone, oxygen, prooxidants, heat, light, & radiation) to prevent or slow the polymer break down to improve the ageing qualities, and to extend the service life of the product involved. Styrenated phenols are non staining and non-discoloring antioxidants finding applications in white & transparent vulcanizates. Phenol- β -naphthyleamine is a general purpose heat resistant and anti flex-cracking antioxidants. It belongs to staining type of antioxidants and is recommended for black or dark colored rubber goods only. Examples for antioxidants are, IPPD, Zinc diethyl lithic carbonate.

2.13.LUBRICANTS

These materials have a technology to migrate to the surface of the plastic melt during the processing, reducing, friction and providing a release layer between the plastic and the mould. The most widely used release agents are metallic stearates, followed by waxes, fatty acids, amides, and fatty acid esters. E.g. ; stearic acid, zinc stearate, wax

2.13.1 WAXES

The properties and performance of petroleum-derived sunolite waxes used to protect vulcanized rubber from degradation by ozone in ambient air are described in the companies' product guide.

2.14.ACTIVATORS.

ZnO: natural rubber, synthetic rubber, latex activator, rein forcer, inorganic color add directly, readily disperses gives excellent processing low heat build up develops good stiffness at reinforcing levels.

Stearic acid: Used for natural rubber, synthetic rubber, latex activator, plasticiser, softener, gives acid type activation improves processing acids, filler and pigment dispersion. Add directly.

2.15.RETARDERS

P V I:

PVI is a pre vulcanizing inhubuter for natural and synthetic rubber. It is used will all sulfonamide or thiazole accelerators to control processing safety with mineral changes in curing characteristics or vulcanizate properties. It improves green stock storage stability & can be used to recover stocks. Useful in such applications as faster extrusion hotter processing and single stage mixing.

2.16.REINFORCING AGENTS.

- Carbon blacks
- Fast extrusion furnace (FEF)
- Super reinforcing furnace (SRF)
- High abrasion furnace (HAF)

2.17. TIRE PRODUCTION.

A tire is an integral component of a vehicle and is the intermediary between the vehicle and the road. Further one would expect from a tire-high millage, resistance to cut and damages, no failure and constant performance, number of re trading savings in fuel consumption etc.

Tyre technology is a vast complex combination of science, technology/engineering and art: bringing together a verity of disciplines. The science of tires involves knowledge of area in composite structures and geometry. These concepts have been used to derive mathematical models of tire mechanics.

The chemistry and technology of component materials involves areas of specialty such as tire rein forcing systems. Adhesives theories and applications and rubber and matrix technology. The properties of tire materials and their relationship determine the integrity of tire. The construction and composite configurations must be designed to fulfill dynamic tire behavior requirements

Fundamentally a tire along with stipulated rim fitment forms a toroidal pressure vessel (carcass) capable of supporting load. At a quantified degree of deformation. The deflection degree of deformation of the tire complements the vehicle suspension.

Mechanics of pneumatic tire are tire design are apparently seem to be dealing same aspects of tire technology. But infact they are entirely different subjects.

Mechanics deals with answering questions what makes tire to fulfill its functions whereas design deals with how to maintenance such a tires.

2.17.1 FUNCTIONS OF PNEUMATIC TIRE.

- a) Load carrying capacity.
- b) Cushioning and enveloping
- c) Transmit driving and braking torque.
- d) Produce cornering force.
- e) Produce lateral stability/dimensional stability
- f) Provide cushioning & floatation
- g) Resist abrasion
- h) Provide steering force/response
- i) Low rolling resistance
- j) Minimum noise and road vibration
- k) Durable and safe

2.17.2 COMPONENTS OF TIRE TECHNOLOGY.

The different disciplines essential for satisfying the expectations and function of tire can be grouped as below,

- 1) Technologies to materials: a) rubber its compounding and vulcanization
b) Textiles c) other raw materials e.g. chemicals, fillers, bead wire etc. d) bonding rubber / rubber, rubber / textiles, rubber / steel, rubber / glass, fiber etc.
- 2) Tire design: (pattern design, tire geometry, structural design)
- 3) Manufacturing technology: (mixing textile processing, calendaring, extrusion, tyre building, vulcanization, inspection etc.
- 4) Quality control: (raw material intermediate steps, process, components finished products)
- 5) Product evaluation methods / controls.
- 6) Application engineering.

2.17.3 BASIC TIRE TYPES

- Cross ply
- Radial ply
- Bias belted

2.17.4 TIRE DESIGNATION.

A tire is designated by its size “ply rating” pattern and code besides the manufacturer’s name, serial numbers, load place, etc. these are marked on the side wall of the tire.

2.17.5 TIRE DESIGN

A tire is a hard / rubber composite. The tire composite is in the form of a network of cord structures arranged in a parallel configuration and embedded in a rubber matrix.

The composite materials approach to the analysis of pneumatic tire is based on the finite element technique a finite three-dimensional element is considered as a laminated composite structure. Each of the laminates are considered separately in terms of cord and matrix (rubber) components. The property of lamina is combined with the geometry of the laminate structure to describe the character of the finite element.

2.17.6 DESIGN.

Like any other design & construction work, tire design is also starts with the understanding of certain parameters.

1. Tire of service: the refers to requirements expected of the tire in service.
2. Tire size required: for most conventional tire sizes, the basic dimensions of section with and height, skid depth, rim with, and profile have been established for load capacity by industry experience with various service conditions.

2.17.7 DESIGNING OF MOULD CAVITY.

Based on selected tire size, standards and vehicle parameters, tire dimension are decided. Then the growth of the reinforcing material e.g. Rayon, Nylon, Steel, etc. is taken in to consideration.

On setting the above basic parameters, the designer has to finalize tread pattern, under and side wall areas.

A TREAD PATTERN: A tire operators best in-service for which its tread pattern has been designed these are generally classified as:

- ❖ **Rib pattern:** Used mainly on front / driven axle because of steering response.
- ❖ **Lug pattern:** Used mostly on rear / driven axle for heavy haulage and long distance operation.
- ❖ **Semi lug pattern:** generally used on front axle, but as well as on rear axle.
- ❖ **Mud and snow pattern:** Used on rough roads.

Other terminologies like hiway, crosslug, cross-country etc. are also frequently used for tread pattern.

Tread life is proportional to its depth up to an optimum limit. Beyond this increasing of tread depth brings life to a plateau level.

2.17.9 CARCASS DESIGN

Carcass or casing is the backbone of the tire. A tire is fabric rubber composite and its strength entirely depends upon this composite matrix of rubber and reinforcing material extended from bead to bead and turned around them reinforcing materials are selected for each components of carcass (plies, breakers, chafer etc.). To achieve optimum reinforcement for-intended service performance.

Commonly used reinforcing materials are Rayon, Nylon, Polyester and steel. Nylon as reinforcing material is predominant and preferred for bigger size tires because of its advantages over rayon.

Strength of the casing or carcass depends on the material number of cords in unit area (per 10 cm or per inch) and number of plies. Higher number of cords per unit area results in higher tire plunger impact values / strength whereas lower no of cords give better separation resistance because o sufficient compound insulation. Breakers are also of lower cord number to improve adhesion to tread. Maximum number of cords per unit area is restricted by heat build up and minimum number is by fatigue and strength failure. Also cord construction plays an important role in design of carcass.

2.17.10 BEADS.

Bead is the part of the tire which holds the tire on the rim under high inflation pressure and dynamic flexing. It is important to calculate the bead strength critically as any failure can be hazardous. Bead is composite of rubber and high tensile steel wires, which applied together to form a bundle.

2.17.11 TIRE CONTROL STANDARDS

After calculating and deciding all design parameters, finally a control standard for a particular design has to be laid down. A control standard contains all details like rubber gauges, pattern depth, crown angle, ply turn up heights, material under bead, bead core construction, etc. it is necessary to check these parameters under routine check to maintain quality and uniformity of a tire.

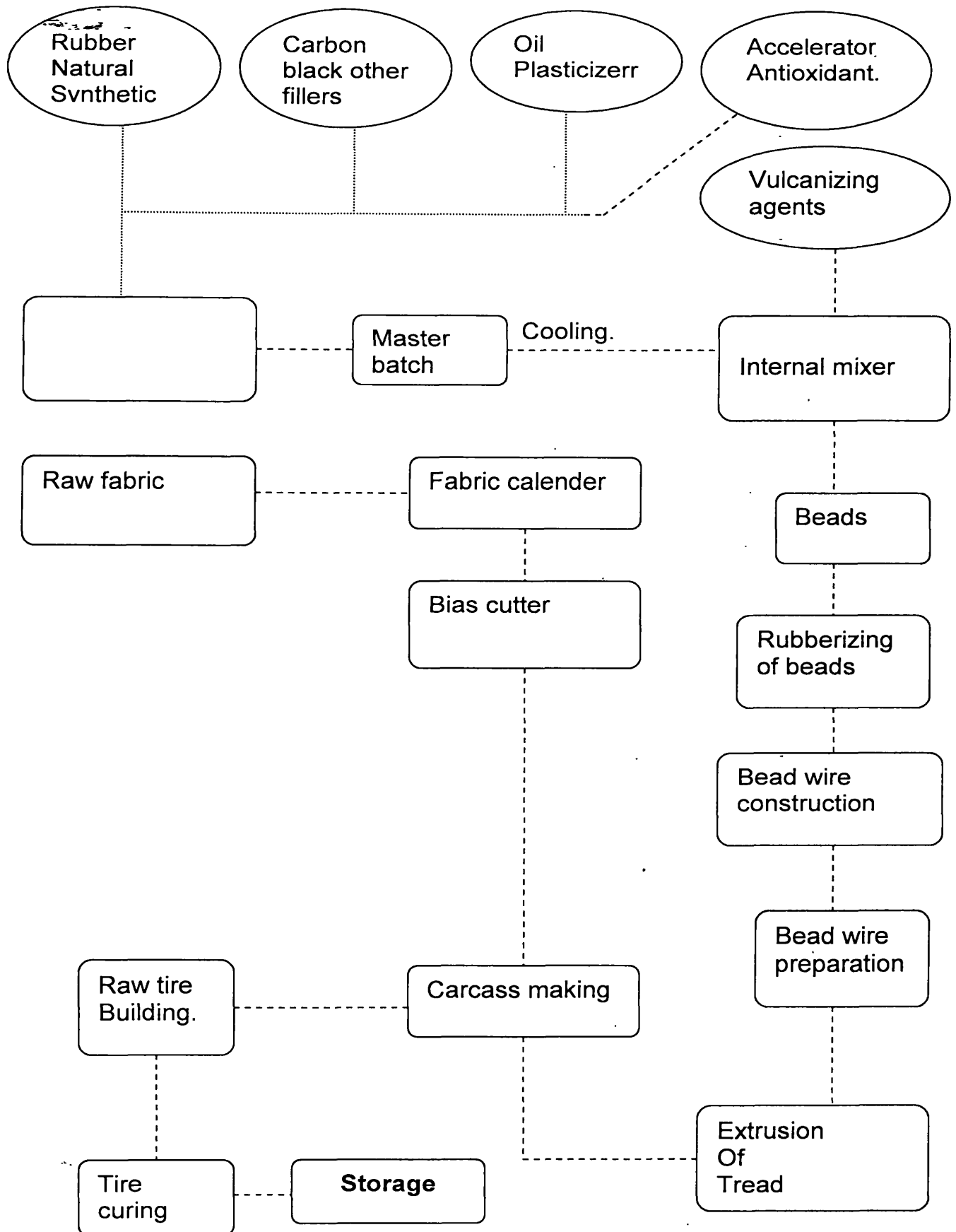


Figure 2.1. Pneumatic tire manufacturing process.

2.18 MANUFACTURE OF TIRE.

A brief description of tire production sequence is briefly described below:

Steps of tire manufacturing are as follows:

1. Compounding of rubber and processing.
 - a) Mastication of rubbers
 - b) Mixing of rubber and ingredients.
 - c) Extrusion.
2. Fabric (tire cord) processing
 - a) Dipping and processing
 - b) Calendering / rubberizing the treated fabric.
3. Bias cutting of calendered fabric.
4. Bead construction / building.
5. Tire building.
6. tire curing.

2.19 MAIN PARTS OF THE TIRE.

- ❖ Tread.
- ❖ Sidewall.
- ❖ Carcass.
- ❖ Rim lines.
- ❖ Bead wires.
- ❖ Chafer.

2.20.ROLE OF EACH PART.

2.20.1 TREAD:

The tread is an external rubber layer protecting the carcass from wear and external damage caused by the road surface. It is the part that directly contacts the road and generates the frictional resistance, which transmits the vehicle's driving, breaking and cornering forces to the road. The tread pattern, which consists of grooves moulded into the tread surface. Is designed to help the tire transmit these forces to the road more effectively.

2.20.2 SIDEWALL:

The sidewalls are rubber layers, which cover the sides of the tire and continuously flex under the loads applied during travel and protect the carcass from external damage.

The sidewalls bear the manufacturer's name, tire size and other information's.

2.20.3 CARCASS (CASING):

The carcass is the framework of the tire. It must be strong enough to hold high-pressure air, yet flexible enough to absorb load changes and impact. It consists of plies (layers) of tire cords (sheets of parallel strands of a strong material) bonded together with rubber. The cords in bus and truck tires are generally made of nylon or steel, while in passenger car tires polyester, rayon or nylon cords are used.

CHAPTER 3

MATERIALS AND METODS

My raw materials are given below,

1. Styrene butadiene (SBR).
2. High styrene resin. (HSR)
3. Polybutadiene. (BR)

METHOD

Proportions of mixing raw materials are given below.

Table 3.1.test samples (batches).

Sample no (Batch no)	Sample weight Of HSR (grams)	Contained styrene (Grams)	Contained Butadiene (Grams)	Added weight of BR (grams)	Ratio of Styrene: Butadiene
1	470.6	400	70.6	529.4	2:3
2	411.8	350	61.8	588.2	7:13
3	352.9	300	52.9	347.1	3:7
Sample no (Batch no)	Sample weight of SBR (grams)	Contained styrene (Grams)	Contained Butadiene (Grams)	Added weight of BR (grams)	
4	1000	250	750	0	1:3
5	800	200	600	200	1:4
6	400	100	300	600	1:9
7	0	0	1000	0	0:1

According to the above table SBR was mixed with BR and High styrene resin with BR. According to the table, sample no 1 to 3 was prepared by adding High styrene resin with BR and sample no 4 to 7 was prepared by adding SBR with BR. The 4th sample was used SBR 1500 series raw rubber only. Sample 7 was pure BR only. All the above 7 samples are divided in to two parts as sheets. One part was exposed to sunlight and the other part was put in to an electric oven. The rubber was blended without adding any chemicals or any other additives. To blend above samples laboratory small-scale two roll mill was used. The milling time for above all the samples were 5 minutes. All the samples were prepared under same conditions (temperature and other conditions) sunlight was used as the UV source. An electric oven at 70° C was used as the heat source.

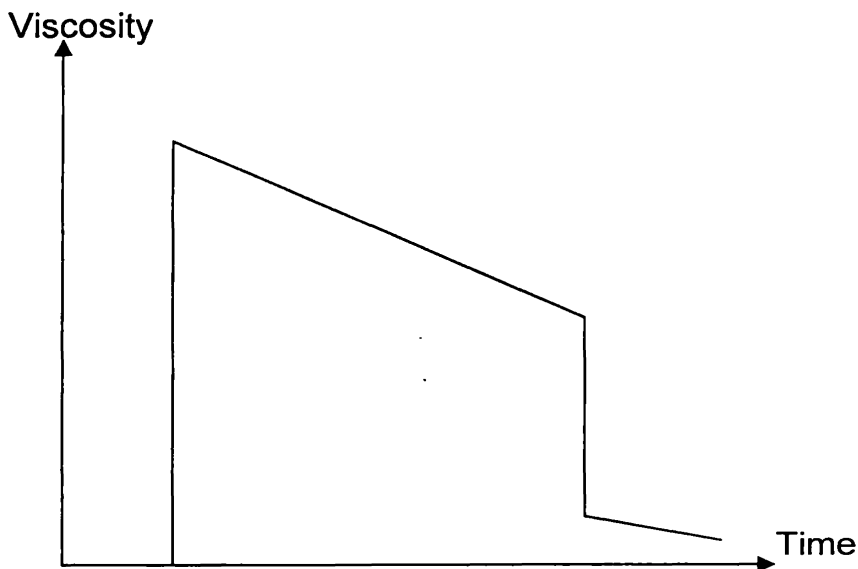
The Mooney viscosity readings of the samples that were treated with UV and heat was obtained.

The Mooney viscosity was determined by using a small sample portion from samples 1 to 7 and that determining up to 30 days.

3.3 TESTING MOONEY VISCOSITY

An idea about cure time. Is essential when performing this experiment. The rubber portion was masticated it on two roll mill for about 6 times and when mills were very close to each other two square rubber samples were cut out. Heat the upper and lower platens to 100° C were heated and two rubber samples were on the rotor, topside and bottom side. Once the rubber samples were placed on the rotor the instrument and platens were closed. The instrument was preheat for one minute before starting the motor.the reading was determine after 4 minutes.

A sketch diagram of Mooney viscosity graph is given below.



3.3.1 MOONEY VISCOSITY.

These tests are helpful in predicting processing characteristics where correlation between viscosity values & molecular mass is present. Viscoelastic characteristics can be correlated with stress relaxation. It can be also predict the rate of cure and incipient cure time during very early stages of vulcanization.

A Mooney viscometer is the most common equipment used for these tests by the rubber processing units. The instrument consists of a motor driven disk within a die cavity formed by two-die closure force. Two rotors are used.

Large one with 1.5 inch, diameter smaller one of 1.2-inch dia. The test consists of determining the torque necessary to rotate the disk in the chamber filled with rubber. A number proportional to this torque is taken as an index of the viscosity of the rubber where $8.3 \pm 0.02 \text{ Nm}$, $8.3 \pm 0.02 \text{ Nm}$ equals 100 Mooney units (MU). The rotor is driven at 2rpm. Generally Mooney viscosity, stress relaxation and delta Mooney tests are carried out at 100°C & Mooney scorch at 125°C or 135°C . Mooney viscosity is usually expressed as $50\text{ML}1+4@100^\circ\text{C}$, where 50 is the viscosity in MUL, L indicates the large (standard) rotor 1 is the preheating time, 4 is the test time and 100°C is the test temperature other parameters which can be calculated by a Mooney viscometer are scorch time, cure index, optimum cure time, delta Mooney etc.

CHAPTER 4
RESULTS.

Table .4.1.
Final Mooney viscosity variation readings (MU) in the presence of heat

Day	batch 1	batch 2	batch 3	batch 4	batch 5	batch 6	batch 7
0	53,98	52,72	54,61	48,83	48,15	45,01	44,35
3	57,72	56,29	29,98	53,65	52,25	39,8	42,2
6	56,88	56,1	55,57	65,03	65,49	49,35	44,38
10	99,82	66,25	110,97	79,28	84,9	81,57	43,46
14	113,77	97,61	126,64	96,84	92,12	96,74	43,83
21	153,1	122,51	125,14	114	105,6	109,99	44,07
30	163,8	129,98	157,18	151,56	135,97	138,43	45,37

Table.4.2.
Final Mooney viscosity variation readings (MU) in the presence of sun light (uv)

Day	batch 1	batch 2	batch 3	batch 4	batch 5	batch 6	batch 7
0	53,98	52,72	54,61	48,83	48,15	45,01	44,35
3	41,74	54,59	54,73	53,84	53,83	59,81	59,27
6	64,01	57,48	55,11	58,44	58,87	65,77	83,54
10	57,79	57,81	55,64	70,17	62,8	69,19	106,82
14	59,72	57,61	55,89	71,66	67,2	106,51	130,79
21	59,18	58,53	55,96	75,05	82,39	113,09	167,03
30	58,5	57,1	58,74	96,33	94,54	138,66	170,61

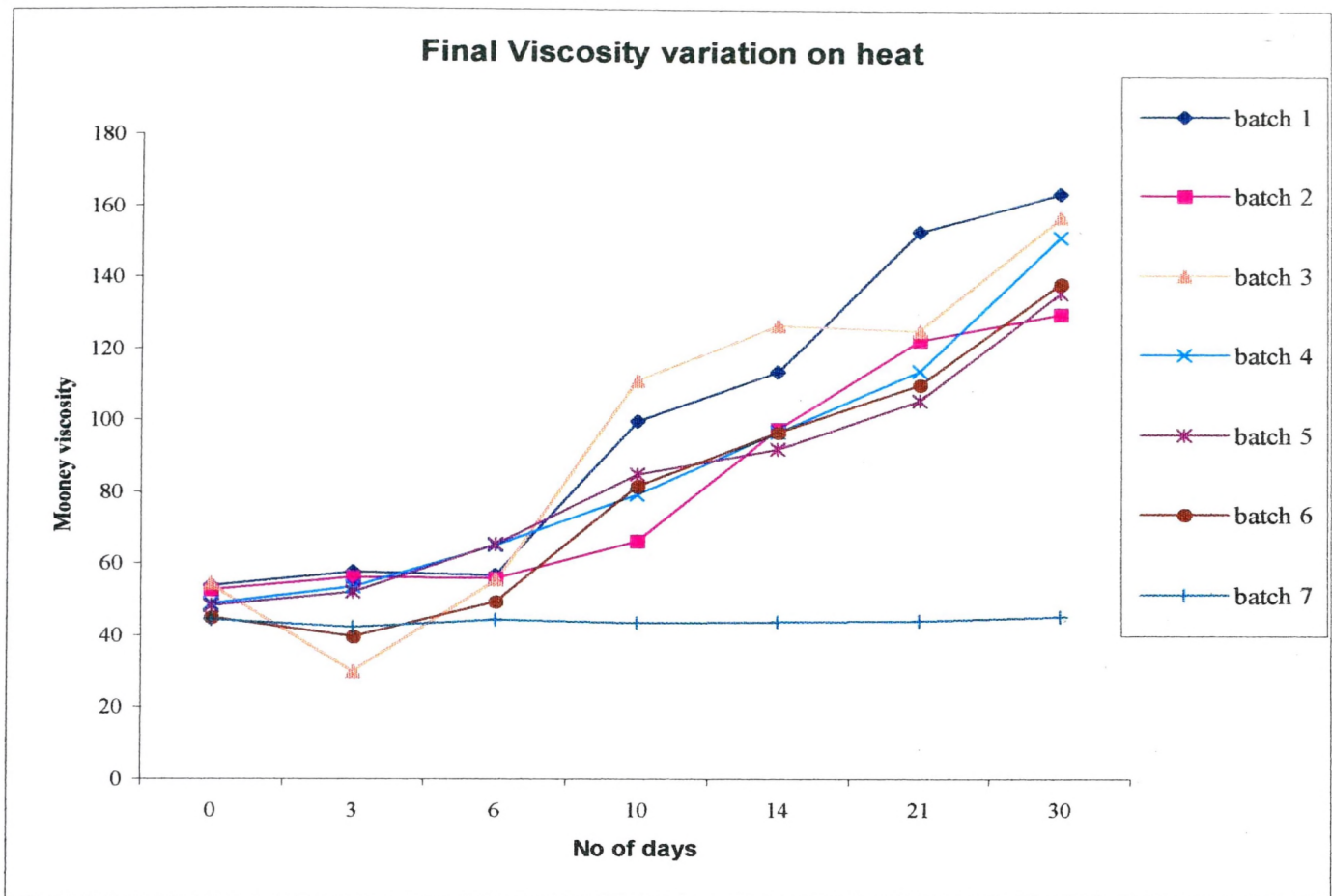


Figure 4.1. The graph of final viscosity variation Vs no of days in the presence of heat.

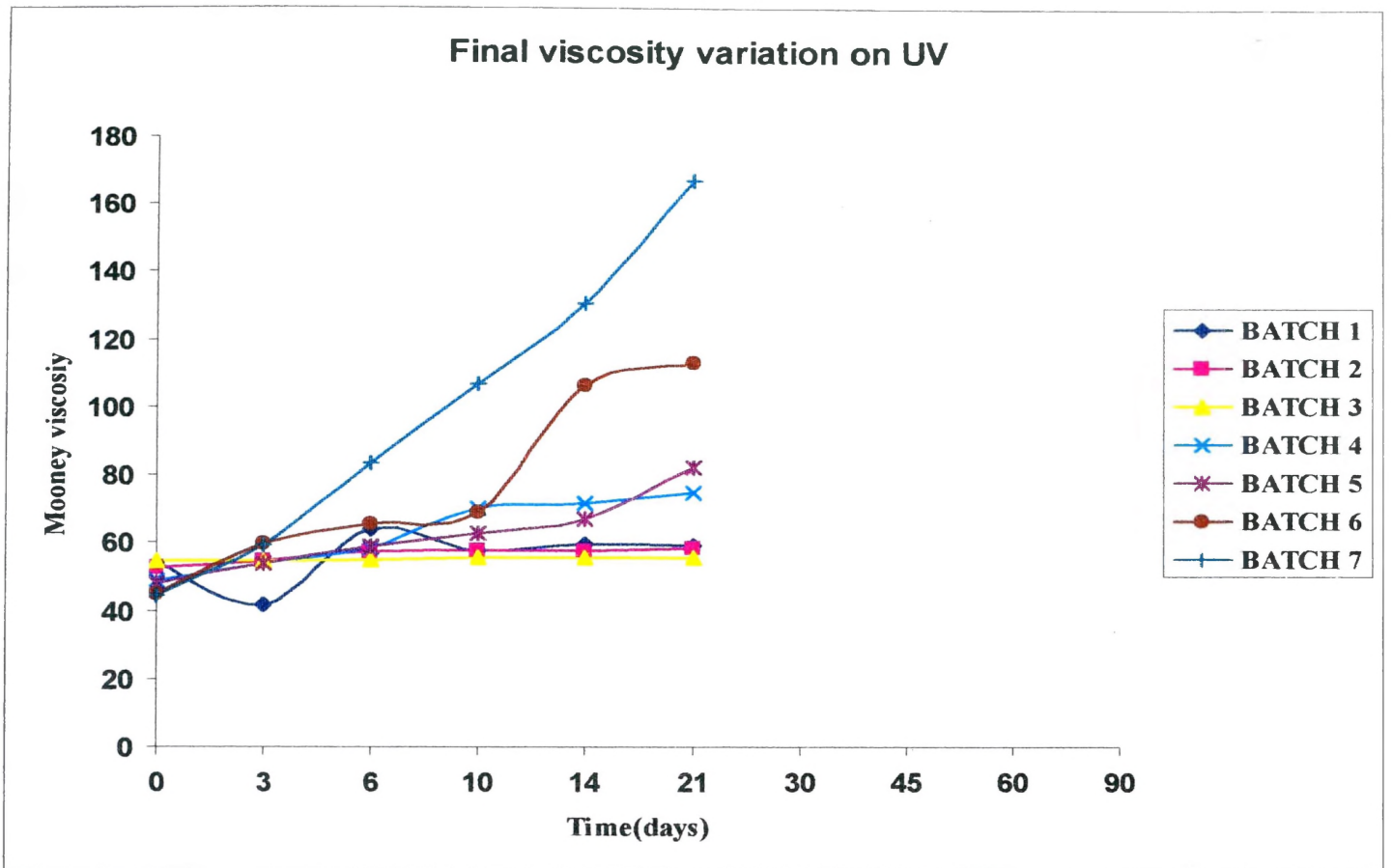


Figure 4.2. The graph of final viscosity variation Vs no of days in the presence of sunlight (UV).

DISCUSSION

To increase the Mooney viscosity, polymer chains should be cross linked or branched. (Gerald Scott 1979) increase in the viscosity is related to the physical hardening of polymer blends. Sometimes in this process chain scission also occurred.

in order to maintain the stability of Mooney viscosity of polymer blends, polymer chains shouldn't be cross linked, branched or and chain scission occurred. They blend should be stabilized.

In this research in the presence of UV (Sunlight) Mooney viscosity of pure BR was increased, this could be due to the polymer chains of pure BR were cross linked and branched, but in the presence of heat (70°C) Mooney viscosity of pure BR did not show a significant change, therefore we can assume presence of heat did not cross linked or branched the polymer chains.

In the presence of heat at 70°C, more styrene containing rubber blends (more than BR) showed an increase in Mooney viscosity than the others. Therefore we can assume the polymer chains were branched, cross linked or with chain scission happen occurred.

In the presence UV (sunlight), Mooney viscosity of polymer blends did not show a sunlight change therefore we can assume that the polymer chains were cross linked or branched or with chain scissions occurred. (There is no clear reaction with sunlight)

According to the above results, we can assume styrene is heat sensitive & BR (Polybutadiene) is photo (UV) sensitive.

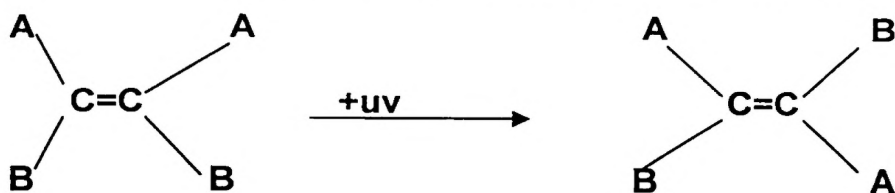
BR is going to photo oxidation, photo degradation and heat stabilized.

Styrene is going to thermal degradation & oxidation and UV stabilization.

3.4.1 Photo degradation and photo oxidation of -1, 4-polybutadiene.

Both isomers of -1,4-polybutadiene and isomerizes when irradiated by UV light(2537Å) in a vacuum. The mechanism of these reactions has been

distributed to π -electron excitation in the double bonds to an antibonding state in which free rotation and hence steric inter conversion can occur.

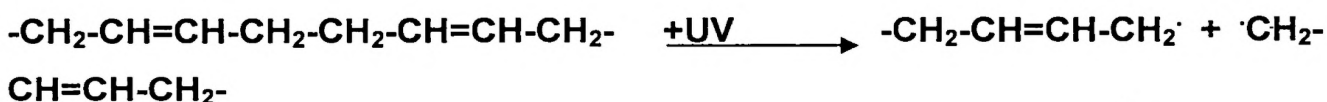


It has been proved that there is no migration of double bonds in the main chain during UV-radiation. of cis-1,4-polybutadiene containing $(-\text{CH}_2-\text{CD}=\text{CD}-\text{CH}_2-)$ units. Only, cis trans isomerisation was found during this reaction, a degree of unsaturation occurs. Which was interpreted by these authors as a chain cyclisation. The quantum yield of these process for light of different wave lengths are shown in the table. The weak link in a polybutadiene chain is the CH_2-CH_2 bond (c.55Kcal/mol). The bond strength is lower than that.

-1,4-photochemical changes in cis -1,4-polybutadiene after UV. (Gerald Scott 1979)

Chemical changes observed	Quantum yields		References
	1236 \circ A	2537 \circ A	
Cis/ trans formation	2.5×10^{-1}	3.6×10^{-2}	750,751
Loss of initial unsaturation	1.53×10^{-1}	6.1×10^{-2}	751

Normal c-c bond 183Kcal/mol. This is due to the resonance energy of 2 allyl radicals formed in chain scission:



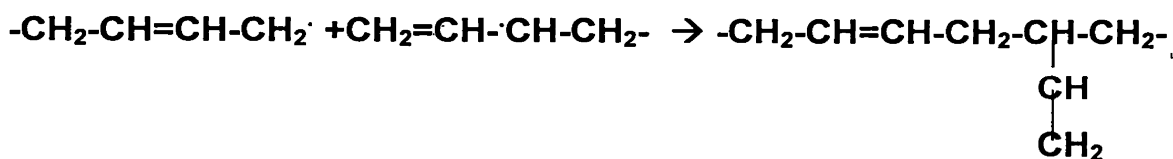
Scission of diene main chain may be accompanied by a shift to terminal vinyl groups.

Formation of cyclopropyl group may also occur by the following mechanism:

The e.s.r. spectra obtained during the UV-irradiation of cis -1,4-polybutadiene were interpreted as being due to radicals (4.3) & (4.4) formed by scission of the C-C bond between the methylene groups in reaction.

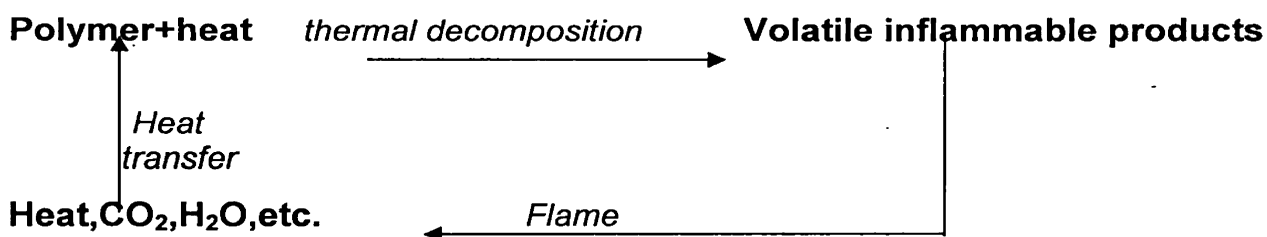
Some additional weak e.s.r. signals were attributed to radicals of alkyl type (4.5) and polyenyl radicals (4.6) formed by hydrogen abstraction.

Addition of radicals (4.3) will lead to the formation of vinyl side groups and loss of unsaturation in the main chain. (Gerald Scott 1979)



3.4.2 Thermal degradation.

In general, vinyl polymers are particularly susceptible either to thermal degradation, which can occur by chain scission involving the breakage of the backbone bonds to yield free radical segments or by nonchain scission involving the elimination of a small molecule from a constituent group and double bond formation.



3.4.3 Mechanism of UV stabilization.

The photo stabilization of polymers involves the retardation or elimination of photochemical processes in polymers and plastics. "ultraviolet absorbers" are additives to plastics and other polymer materials which prevent the photo degradation or photocrosslinking caused by uv, present in sunlight various kinds of artificial light sources. To date many reviews have been published which discuss the photo stabilization mechanisms and effects of photo stabilizers.

Photo stabilization can be obtained in many ways,

1. Screening of radiation.

2. Absorption of radiation.
3. Intersystem crossing.
4. Internal conversion.
5. Quenching process.

3.4.4 Thermal stabilization.

In the most practical sense, thermal stability means the ability of a material to maintain the required mechanical properties such as strength, toughness or elasticity at a given temperature. There are two principal factors to be considered, one physical and chemical.

The physical requirement of thermally stable polymer is that it has high melting or softening temperature. The “use temperature” of many polymers is limited not by breaking of chemical bonds but rather by changes in physical characteristics at elevated temperatures; that is although retaining their chemical structures, they become weak, soft and finally, fluid. Melting points polymers may be increased by the introduction of polar substituents (e.g. Cl, CN) or by hydrogen bonding groups such as amides. **(Gerald Scott 1979)**

CONCLUSIONS.

- Styrene is very heat sensitive less photosensitive.
- Butadiene is very photo sensitive and less heat sensitive.
- In the presence of UV (sunlight) Polybutadiene (BR) was cross linked and branched. When we increase the percent of styrene Mooney viscosity was decreased.
- In the presence of heat 70°C pure Polybutadiene (BR) was not clearly cross linked or branched, when we increase the percent of styrene Mooney viscosity was increased.

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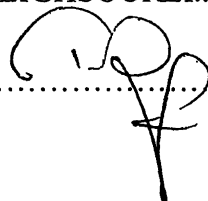
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