NATURAL RUBBER LATEX CARBON BLACK MASTERBATCH IN COMPARISON WITH CONVENTIONAL DRY MIX IN TYRE FORMULATIONS

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The Rubber Research Institute of India
Rubber Board, Ministry of Commerce and industry, Govt. of India

RT/ RES /PROJ / M.Tech / CUSAT 28th May 2018

CERTIFICATE

This is to certify that the thesis entitled "Natural Rubber Latex Carbon Black Masterbatch in Comparison with Conventional Dry Mix in Tyre Formulations" being submitted by Rajiv S., to the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, for the award of M.Tech in Polymer Technology, is a record of bona fide research work carried out by him. He has worked on this research topic from 10th August 2016 to 30th April 2017 under my supervision. The results included in this report have not been submitted for award of any other degree.

The research topic and the data given in this thesis being a subject matter for patenting, this should not be published as an open document without the consent of Rubber Research Institute of India.

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DECLERATION

I do hereby declare that the project work entitled ***"Natural rubber latex carbon black masterbatch in comparison with conventional dry mix in tyre formulations"*** *was carried out by me under the supervision of* ***Dr. JACOB K VARKEY, Principal scientist, Rubber Technology Division, RRII, Kottayam, Kerala,*** *during the period* ***10th August 2016 to 30th April 2017*** *as a partial fulfillment of the requirements for the award of the degree of* ***Master of Technology in Polymer Technology.*** *The contents of thesis have not been submitted and will not be submitted to any other institution or university for the award of any degree or diploma.*

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CERTIFICATE

This is to certify that the thesis entitled **"Natural rubber latex Carbon black masterbatch in comparison with conventional dry mix in tyre formulations"** being submitted by **Rajiv. S,** to the Department of Polymer Science and Rubber Technology, CUSAT for the award of Degree of **M.Tech** in **Polymer Technology,** is a record of bonafide research work carried out by him. He has worked on his research topic from **10th August 2016** to **30th April 2017** under my supervision. This results included in this report have not been submitted for award of any other degree.

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AIM AND SCOPE

Filler incorporation causes a considerable change in the dynamic properties of rubber, for both modulus and hysteresis. Though carbon black is usually dispersed in natural rubber by the conventional mill mixing technique, there are accompanying issues such as air pollution and higher energy consumption. In the case of silica it is extremely difficult to disperse the filler aggregates using a mixing mill without the aid of other additives like coupling agents. For carbon black, preparation of latex-carbon black master batch by the addition of carbon black as a slurry has been suggested as one of the methods to avoid some of these problems. To be economically viable, fresh NR latex needs to be used and it is essential to ensure that both latex and the carbon black slurry coagulate simultaneously to avoid loss of filler during coagulation. In most of the earlier cases reported, natural rubber latex is pretreated or various modifications are performed like cleavage of amide linkages, hydrolysis of proteins by enzymes, addition of monomer units etc., to prepare the master batch. Further these processes make use of different types of processing oils, and techniques like high flow rate of slurry and mixing under turbulent conditions for coagulation of the latex containing the filler slurry.

The exists a need for a very simplified and economic process for the production of master batches that gives vulcanizates with comparable or superior mechanical properties compared to mixes prepared by conventional mill mixing process.

OBJECTIVE

The objective is to develop a process for the preparation of filler incorporated natural rubber latex master batch by utilizing a quick coagulation process of latex, assisted by surfactants that give vulcanizates having superior cure characteristics and mechanical properties compared to mixes prepared by conventional mill mixing process.

SUMMARY OF THE PROCESS

The present finding relates to a process for preparing single or dual filler incorporated natural rubber master batch. The fillers used in the present invention are carbon black and silica. The individual filler dispersions are prepared and mixed with latex in presence of suitable surfactants. Then the latex-filler mixture is coagulated by the addition of acid to form coagulum. The coagulum is dewatered and dried to obtain filler incorporated natural rubber master batch. The mixed filler master batch is converted to a rubber compound by mixing with curatives and other necessary ingredients in a internal mixer and processed further in the conventional method.

MAIN OBSERVATION

The mechanical properties of the vulcanizates obtained from the latex stage and dry rubber incorporated mixes are evaluated using conventional formulations. Mixed filler containing master batch prepared by the new process shows good cure characteristics as compared to the dry rubber incorporated mix. The mechanical properties like tensile strength, modulus, tear strength, abrasion resistance and hardness are superior of the vulcanizates prepared by the new process. The heat buildup values are considerably low for the latex filler master batch. The improvement in mechanical properties shown by the silica/carbon black master batches over the conventional mill mixed compounds can be attributed to better filler dispersion and higher level of vulcanization.

CHAPTER-I

INTRODUCTION

CHAPTER-1

1. INTRODUCTION

Natural rubber latex is a colloid, the dispersed phase being predominantly rubber and the dispersion medium water. Fresh latex has a specific gravity of 0.96 to 0.98 and a pH in the range of 6.5 to 7.0. In addition to rubber and water, latex contains small quantities of proteins, resins including fats, fatty acids, other lipids, sterol and sterol esters, carbohydrates and mineral matter. Fresh latex is composed of rubber (30-40%), proteins (1-1.5%), resins (1.5-3%), mineral matter (0.7-0.9%), carbohydrates (0.8-1%) and water (55-60%) [1-4].

The size of the rubber particles range from 0.02 to 3.0 μm and their shape is mostly spherical. The particles are strongly protected by a film of adsorbed proteins and phospholipids [5-7]. The other particles in latex comprise lutoids and Frey-Wyssling particles. The lutoids are subcellular membrane bound bodies ranging in size from 2 to 5 μm, containing a fluid serum known as B-serum, which is a destabilizer for rubber particles. Frey-Wyssling particles are spherical, larger in size and are yellow coloured. Methyl-l-inositol (quebrachitol), sucrose and glucose are the major carbohydrates in latex. About 20% of the available proteins in latex is adsorbed on the rubber particles, an equal quantity is found in the B-serum and the remainder in the latex serum. The adsorbed proteins and phospholipids impart a negative charge on the rubber particles thereby improving the stability of the colloid [8-11]. The lipids associated with rubber and non-rubber particles play a key role in the stability and colloidal behavior of latex. Latex also contains amino acid nucleotides and low molecular weight thiols. The nucleotides are co-factors and intermediates in the biosynthesis of rubber.

1.1. History of Rubber

Rubber was known to the indigenous peoples of the Americas long before the arrival of European explorers. The first scientific study of rubber was undertaken by Charles de la Condamine, when he encountered it during his trip to Peru in 1735.

The first use for rubber was an eraser. It was Magellan, a descendent of the famous Portuguese navigator, who suggested this use. In England, Priestley popularized it to the extent that it became known as India rubber.

In 1815, Hancock had invented a rubber mattress and through an association with Macintosh he produced the famous waterproof coat known as the "Macintosh". Furthermore, he discovered how to cut, roll and press rubber on an industrial scale. He also noted the importance of heat during the pressing process, and built a machine for this purpose. Finally, in 1842, Hancock came into possession of vulcanized rubber produced by Goodyear.

In 1845, R.W. Thomson invented the pneumatic tire, the inner tube and even the textured tread. In 1850 rubber toys were being made, as well as solid and hollow balls for golf and tennis.

South America remained the main source of the limited amounts of latex rubber that were used during much of the 19th century. In 1876, Henry Wickham gathered thousands of Para rubber tree seeds from Brazil, and these were germinated in Kew Gardens, England. The seedlings were then sent to India, Ceylon (Sri Lanka), Indonesia, Singapore and British Malaya. Malaya (now Malaysia) was later to become the biggest producer of rubber. In the early 1900s, the Congo Free State in Africa was also a significant source of natural rubber latex, mostly gathered by forced labour. Liberia and Nigeria also started production of rubber.

In India, commercial cultivation of natural rubber was introduced by the British planters, although the experimental efforts to grow rubber on a commercial scale in India were initiated as early as 1873 at the Botanical Gardens, Calcutta. The first commercial ***Hevea*** plantations in India were established at ***Thattekadu*** in Kerala in 1902. In the 19th and early 20th century, it was often called "India rubber." In 2010, India's natural rubber consumption stood at 978 thousand tons per year, with production at 893 thousand tons; the rest was imported with an import duty of 20% [12].

1.2. LATEX

Hevea brasiliensis is the most important commercial source of natural rubber and more than 97% of natural rubber is produced from this tree. This tree is popularly called rubber tree. The main crop from ***Hevea brasiliensis*** **is** a white or slightly yellowish liquid known as latex. It is obtained from the bark of the tree by the process known as tapping. It is a process of controlled wounding of the plant in which a thin layer of bark is removed. Tapping opens the latex vessels in the regions of wound and latex flows out from the tree, which is channelled into a container, attached to it [13].

1.2.1 Composition of Latex

Latex is a white or slightly yellowish liquid with a specific gravity in the range of 0.96 to 0.98 and having variable viscosity. Field latex is a negatively charged colloidal dispersion of rubber particles suspended in an aqueous serum. The size of rubber particles ranges from 0.025 to 0.3 microns (1 micron $=10^{-4}$cm). These rubber particles are surrounded by a layer of proteins and phospholipids. Latex contains a variety of other non- rubber constituents also. The proportion of these constituents varies according to season, soil, atmospheric conditions, clone, and stimulation practices, tapping systems, etc. in general the composition of latex as follows:

Table 1.1: Composition of latex

Constituents	Percentage
Rubber	30-40%
Protein	2-2.5%
Resin	1-2%
Sugar	1-1.5%
Ash	0.7-0.9%
Water	55-60%

Fresh latex as it comes out from the tree is slightly alkaline or neutral. It becomes acidic rapidly due to bacterial action. The formation of organic acids neutralizes the negative charge on rubber particles and the latex is gradually thickens and gets coagulated on keeping. Therefore fresh latex cannot be kept for along without coagulation [13].

1.2.2. Processing of Latex

The latex that flows out from the rubber tree on tapping is channelled in to a container attached to it. The container can be coconut shells or glazed earthen ware. Generally coconut shells are used. The spouts and buckets are made of galvanized iron. The latex flow will continue for about 3hours and after that it would stop [13].

Latex has to be collected from the field as soon as possible after stoppage flow of latex. Latex collected in the cups is transferred in to clean buckets. Around 80% of crop from plantation is in the form of latex. The latex which gets dried up on the tapping panel (tree lace) and the collection cups (shell scrap) also part of the crop and are collected by the tapper in a basket just before tapping. The latex spilt and /or overflowed on the ground, when gets dried up, also collected as scrap (earth scrap) one in a month or so. Normally, 15 to25% of the total crop constitute tree lace, shells crap, and earth scrap, together called field coagulum rubbers.

The different forms of crop are highly susceptible o degradation due to bacterial contamination on keeping. Therefore it is essential to process them into forms that allow safe storage.

1.2.3 Anticoagulants

An anticoagulant is a chemical added to latex to prevent pre-coagulation before it is processed. A few drops of anticoagulants are previously added into coconut shells during tapping and rest amount is added into the collection buckets when it is half full. Anticoagulants are never added into empty buckets. Anticoagulants generally used are ammonia, sodium sulphite, and formalin. Of these ammonia is recommended, when the latex is to be processed as preserved latex or latex concentrates. For sheet processing anticoagulants are used only if essential and sodium sulphite is preferred [13].

1.2.4 Preservation

To keep latex for longer period's bacterial activity should be suppressed so as to prevent coagulation. This can be accomplished by addition of preservatives. Field latex preserved with suitable preservatives is termed as preserved field latex.

Why preservation is necessary?

Natural rubber latex is a colloidal dispersion of rubber particles in an aqueous serum. The presence of non- rubber constituents like proteins, carbohydrates etc. in latex make it a suitable medium for growth of microorganisms. Because of proliferation of microorganisms, organic acids are produced and these decrease the stability of latex and eventually coagulate it. This is called spontaneous coagulation that takes place within a period of 6-12 hours. Hence if latex is to be kept for longer periods, bacterial activity should be suppressed. This can be accomplished by addition of preservatives. This preservative should be added as soon as after tapping as possible [13].

1.2.4.1. Preservatives

A preservative is a chemical or mixture of chemicals which when added to latex can prevent bacterial action in it and at the same time stabilizes it. Ammonia is the most popular latex preservative. Usually field latex is preserved with 1% ammonia. A low ammonia system (LATZ) consisting of TMTD and zinc oxide (0.025%each) along with 0.35% ammonia is also popular.

1.2.4.2. Attributes of a preservative

- It should destroy or inactivate microorganisms.
- It should preserve against spontaneous coagulation.
- It should not be harmful to people.
- It should not have adverse reaction on rubber or containers of latex.
- It should be cheap, readily available and convenient to handle.
- It should deactivate or remove traces of metal ions present in latex.

- It should increase the colloidal stability of latex. This can be achieved by increasing the P^H of latex, and hence the preservative should preferably be an alkali.

1.2.4.3. Importance of ammonia as a preservative

Ammonia is the most popular latex preservative. Ammonia at a concentration of 1% by weight on latex is added for field latex and 0.7% by weight on latex is added for concentrated latex. This treatment preserves latex and maintains it in a stable colloidal condition almost indefinitely. Ammonia is a bactericide and being an alkali increases the P^H of latex. Ammonia reacts with magnesium and phosphate ions present in latex to form magnesium ammonium phosphate.

$$Mg^{++}+NH_3+HPO_4 \rightarrow Mg\,NH_4PO_4$$

This precipitate settles as sludge together with any sand dirt particles which may be present in latex. Copper ions in latex are also deactivated by ammonia by complex formation [13].

1.2.4.4. Ammonia as a preservative

Ammonia has been used as a standard preservative for latex since 1853. Preservative systems used even today have some proportion of ammonia in it.

Ammonia keeps VFA number of latex low while increasing the stability on storage. It complexes with metal ions like Zn &Mg and inhibits bacterial growth. Ammonia is not a harmful chemical and it has no effect on rubber molecules. It has the added advantage of easy de-ammoniation without adding chemicals.

However, it has the disadvantages of strong odour, Causing environmental pollution and also the slight tendency to discolour the rubber produced.

It can also interfere with latex processes such as reaction with ZnO in compounding and with sodium silicafluoride. Addition of ammonia in small quantities to increase the P^H from 6.5 to 8 will favour multiplication of bacteria. Hence for long preservation, ammonia should be added at 1% for field latex and it for 0.65% for concentrated latex.

1.2.4.5. Low ammonia preservative systems

In order to overcome the dis-advantage of ammonia, other chemicals have been successfully used in conjunction with ammonia. These other chemicals are called secondary preservatives and such systems are called **"Low ammonia preservative system"**. Though sodium pentachlorophenate, ZDC and boric acid are used as secondary preservatives, the latest and most widely used low ammonia system is tetramethyl thiuram disulphide (TMTD) and ZnO. Latex with low ammonia content (0.3%) preserved with TMTD& ZnO is referred to as LATZ latex.

1.3. Concentration of latex

The process of latex concentration involves the removal of a substantial quantity of serum from field latex and thus making latex richer in rubber content. Concentration of latex is necessary because of four reasons:

1. Economy in transportation.
2. Preference for high DRC by the consuming industry.
3. Better uniformity in quality.
4. Higher degree of purity.

Various processes have been proposed for concentrating latex. Out of these, four have emerged as of special importance.

- Creaming
- Evaporation
- Centrifugation
- Electro decantation

But only creaming and centrifugation are the commonly used method for the concentration of latex.

1.3.1. Centrifugation

Centrifugation is the most popular method and widely used technique for the manufacture of concentrated latex. This is because of the quality of concentrate is excellent for use in the manufacture of any type of latex product. About 90% of the NR latex concentrate used in industrially is produced by centrifugation. In centrifuging, centrifugal force replaces gravitational force which brings about separation of rubber particles in creaming [13].

Centrifuging involves the separation of preserved field latex into two fractions, one containing the concentrated latex of more than 60% dry rubber and the other containing 4-6% dry rubber, using a centrifuging machine. The rotating bowl of the centrifuge is fed continuously with preserved latex which results in the continuous collection of concentrated latex that is drawn out through an outlet at the center and the serum (skim latex) near the circumference from where it is withdrawn through another outlet.

1.3.2. Creaming

Rubber latex is a dispersion of rubber particles in an aqueous serum. In any dispersion, the dispersed particles or cream are sediment under the influence of gravity called creaming. Rubber particles being lighter than serum tend to cream up.

The processing of latex into creamed concentrates involves the mixing of a creaming agent such as ammonium alginate or cooked turmeric seed powder with properly preserved field latex and allowing the latex to separate into two layers, an upper layer of concentrated latex and lower layer of serum containing very little rubber. The two layers are removed, leaving the latex concentrate of 50-55% DRC which is tested, packed and marketed. Though, this method is very slow compared to centrifugal method, it is still employed by small scale rubber good manufactures for producing latex concentrate because of low investment [13].

1.3.3. Evaporation

Evaporation methods yield a concentrate having properties altogether different from those of centrifugally concentrated latex. This is primarily due to the fact that in evaporation the only constituent removed from latex is water in addition certain non-volatile stabilizers must be used. Since all of natural constituents of latex are retained. Such concentrates are referred to as whole latex and the rubber obtained from the concentrate as whole latex rubber. Latex is evaporated by action heat, with or without the assistance of vacuum, hot air currents over the evaporation surface, agitation or other means of hastening the removal of water.

1.3.4. Electro decantation

The electro decantation process is based on the phenomenon of stratification resulting from electro dialysis of latex. The latex is placed in a cell having walls constructed of permeable diaphragms such as cellophane. On either side of the cell are electrodes in a conducting medium, as in conventional electro dialysis cell. When a potential is imposed across the cell the latex particles move toward the diaphragms nearest the anode. If the potential is correctly adjusted, the particle is not coagulated at the diaphragm, but because of its density tends to move upward along the membrane wall. Frequent reversal of current prevents accumulation at the diaphragm and eventual coagulation. For maximum efficiency several factors must be controlled including potential gradient, frequency of current reversal, charge on particles, are of membranes etc. [13]

1.3.5. Three types of concentrated lattices are marketed:

A) Type HA: Centrifuged natural rubber latex preserved with ammonia only or formaldehyde followed by ammonia with an alkalinity of at least 0.6 percent.

B) Type MA: Centrifuged natural rubber latex preserved with ammonia and other preservatives as agreed to between the purchaser and the supplier with an alkalinity above 0.32 percent but lower than 0.6 percent.

C) Type LA: Centrifuged natural rubber latex preserved with ammonia and other preservatives as agreed to between the purchaser and the supplier, with an alkalinity of not more than 0.3 percent.

Table: 1.2. The chemical requirements for the three types of concentrated latex

SL. No	Characteristics	Requirement		
		Type HA	**Type MA**	**Type LA**
1	Dry rubber content, % by mass (min).	60.0	60.0	60.0
2	Non-rubber solids, % by mass (max)	2.0	2.0	2.0
3	Coagulum content, % by mass of latex (Max.)	0.05	0.05	0.05
4	Sludge content, % by mass (max)	0.10	0.10	0.10
5	Alkalinity if ammonia, %by mass of latex	0.6 min.	>0.3 but<0.6	0.3 max
6	KOH number (max.)	1.0	1.0	1.0
7	Mechanical stability (Min. in sec)	475	475	475
8	Volatile fatty acid number (Max.)	0.15	0.15	0.15
9	Copper content, ppm of total solids (Max)	8	8	8
10	Manganese content, ppm of total solids (Max.)	8	8	8

1.4. Marketable forms of Natural Rubber

The important forms, in which the crop can be processed and marketed, are

1. Sheet rubber.
2. Crepe rubber.
3. Block rubber (Technically specified rubber).
4. Preserved field latex.
5. Latex concentrates.

The crop collected in the form of latex can be processed in to any of the above forms. But crop collected as field coagulum can be processed only into crepe or block rubber. [13]

1.4.1. Sheet Rubbers

Latex is coagulated in suitable containers into thin slabs and sheeted through a set of smooth rollers followed by a grooved set, and dried to obtain sheet rubber. Depending upon the drying method, sheet rubbers are classified in to two; 1. Ribbed smoked sheets and 2. Air dried sheets (Pale amber unsmoked sheets). A major quantity of rubber in India (about 73%) is marketed in the sheet from at present, as it is the oldest and simplest method of processing latex into marketable form. [11]

1.4.2. Crepe Rubbers

When coagulated latex or any form of field coagulum (tree lace, shell scrap, and earth scrap) is passed several times through a minimum of three mills with heavy rolls, a crinkly lace-like rubber will be obtained. This lace like when air-dried is called crepe rubber. There are different types of crepe rubber depending upon the type of starting materials. They are:

1. Pale latex crepe.
2. Sole crepe.
3. Estate brown crepe.
4. Remilled crepe.
5. Smoked blanket crepe.
6. Flat bark crepe.

1.4.3. Technically Specified Rubbers (TSR)

The main drawbacks in the processing and marketing of the crop as RSS or as crepe rubber are the following:

1. Multiplicity of grades, posing problems the consumers to choose.
2. Inadequacy of the visual grading in indicating the technical quality.
3. Poor presentation of rubber in large bareback bales prone to contamination.
4. Requirements of more processing operations for manufacture of rubber goods.
5. Non availability of technical information on quality of rubber.

These difficulties are reduced in TSR and new methods of processing and presentation were developed to market natural rubber in compact medium sized blocks wrapped in PE and graded adopting technical standards. These are called TSR block rubber. [13]

1.5. Properties of Natural rubber

Natural rubber molecule is a linear, unsaturated, long chain aliphatic hydrocarbon polymer identified chemically as cis-1,4 polyisoprene. As in the case of other high polymers, natural rubber too is formed of molecules of different sizes with the weight average molecular weight ranging from 100,000 to about 10 million. A random blend of natural rubber shows a weight average molecular weight of $3\text{-}5\times10^5$. High molecular weight results in high viscosities. The Mooney Viscosities of fresh dry natural rubber is in the range of 55 to 90. During storage the viscosity of natural rubber increases from 70 to 100 Mooney units depending on the length of the storage period. The natural storage hardening is believed to be due to crosslinking reaction between aldehyde groups present in the rubber molecule with the amino groups of free amino acids and proteins [14, 15]. The aldehyde groups can be deactivated and storage hardening reaction can be inhibited by treating the rubber with 0.15% hydroxylamine salt. This is the technique used for the production of viscosity stabilized rubber grades, also known as constant viscosity (CV) rubbers.

Because of the high structural regularity, natural rubber crystallizes spontaneously when stored at low temperatures, or when it is stretched. Unstrained sample shows a maximum rate of crystallization at about -26^{0}C. Maximum degree of crystallinity attained is about 25-30%. The un-stretched raw rubber shows a crystalline melting point (T_m) of +25^{0}C [16, 17]. The strain induced crystallization behavior gives natural rubber high tensile strength even in pure gum or vulcanizates filled with non-reinforcing fillers. Glass transition temperature of natural rubber is higher than that of cis-1,4 polybutadiene. The density of natural rubber is about 0.913g per cc., and its bulk density is about 0.85 g per cc. The rubber hydrocarbon content of raw natural rubber is about 94%. The presence of small quantities of non-rubber constituents such as proteins, fats, fatty acids, carbohydrates and mineral matter in natural rubber influences its physical and chemical properties.

A small percentage of rubber undergoes crosslinking even when present within the latex vessels of the tree. This is evident from the 5-10% gel content (microgel) in freshly prepared natural rubber. The gel content increases during storage and it is known as the macrogel. The macrogel is responsible for increased viscosity of natural rubber during storage. The macrogel breaks down almost completely during mastication of the rubber, and dissolves completely in aliphatic and aromatic solvents, chlorinated hydrocarbons, tetrahydrofuran and carbon disulphide. Coagulated and dried natural rubber is highly elastic at ambient temperature. On subjecting the dry rubber to intensive mechanical shearing it becomes progressively more plastic. This process is known as mastication. Masticated rubber is capable of flow, and therefore it can be shaped.

The efficiency of mastication is temperature dependent and is minimum at about 100^{0}C [18]. Staudinger and Boundy [19] suggested that mastication involves the rupture of the rubber molecules due to the shearing forces. Efficiency of mastication can be improved by the addition of small quantities of chemicals known as peptizing agents (e.g. Zinc pentachlorothiophenate).

The high molecular weight and the polymer chain entanglements make the dissolution of natural rubber in solvents difficult. The chemical reactivity of natural rubber is influenced by the presence of double bond in its molecular backbone. The presence of methyl group in the cis-1,4-polyisoperene further enhances the reactivity of the double bond. Thus natural rubber is more reactive than polybutadiene, and poly styrene butadiene rubber to a number of chemicals, including the vulcanization chemicals.

Some physical properties of natural rubber are given in the table 1.3

Density	0.92
Refractive index (20^0 C)	1.52
Coefficient of cubical expansion	0.00062^0 C
Cohesive energy density	63.7 cal/c.c
Heat of combustion	10,700 cal/g
Thermal conductivity	0.00032cal./sec/cm^2/^{0} C
Dielectric constant	2.37
Power factor (1,000 cycles)	0.15-0.2
Volume resistivity	10 raise to 15 ohms/c.c
Dielectric strength	1,000 volts/ mil

Distributions of natural rubber by products usage are given in table 1.4

PRODUCT	PERCENT
Tries and tries products	68.0
Mechanical goods	13.5
Latex products	9.5
Footwear	5.5
Adhesives	1.0
Miscellaneous	2.5

Table: 1.5. Physical and chemical requirements for natural rubber

SL No	Requirements	ISNR Grades					
		3CV	**3L**	**5**	**10**	**20**	**50**
1	Dirt content % by mass (Max).	0.03	0.03	0.05	0.1	0.2	0.5
2	Volatile matter % by mass (Max).	0.80	0.80	0.80	0.80	0.80	0.80
3	Ash content % by mass (Max).	0.50	0.50	0.60	0.75	1.0	1.5
4	Nitrogen % by mass (Max).	0.60	0.60	0.60	0.60	0.60	0.60
5	Initial plasticity (Min).	40+5	30	30	30	30	30
6	Plasticity Retention Index (Min).	60	60	60	50	40	30
7	Color Lovibond Scale (Max).		6.0	-	-	-	-

1.6. OTHER FORMS OF NATURAL RUBBER

1.6.1. Oil Extended Natural Rubber:

Natural rubber can be extended by suitable type petroleum oils like naphthenic oils or aromatic oils to produce viscosity rubber. Oil extension can be done by latex master batch or dry mixing method. In latex master batch method, latex known DRC is mixed with calculated amount of oil emulsion, the mix coagulated and processed to give block rubber. In dry mixing process dried crumbs are soaked in oil for definite period when the rubber absorbs oil. Normally 20-40 Phr oil is mixed with NR for making OENR.

1.6.2. Deprotenized Natural Rubber:

It is a purified form of rubber with low nitrogen content. It is prepared by treating latex with a proteolytic enzyme that hydrolyses most of the protein. The nitrogen and ash content of DPNR are 0.1% or less. It shows low stress creep, low relaxation and highly reproducible modulus in vulcanizates and is thus suitable for use in engineering components.

1.6.3. Superior Processing Rubber:

It consists of an intimate blend of vulcanized and unvulcanized rubber prepared at the latex stage. The first step is to vulcanizates natural rubber latex by addition suitable chemicals and heating the mix for a definite period at particular temperature. The vulcanized latex is blended in the required proportion with field latex and then coagulated. The coagulum is processed into sheet, crepe or block.

1.6.4. Expoxidised Natural Rubber

The double bonds of NR can be oxidized under suitable conditions to produce expoxidised natural rubber. NR dissolved in benzene or NR latex can be reacted with organic peracids to yield ENR. The extent of epoxidation can be controlled by varying the conditions of reaction. It shows good oil resistance and air impermeability compared to NR. It finds application in adhesive formulation, surface coatings, production of oil resistant goods etc.

1.6.5. Thermoplastic Natural Rubber

It can be prepared by blending NR and polypropylene or polyethylene. Mixing is done at 18^0C or higher and in the presence of cross linking agents. The application included footwear, sports goods, car body protection slips, etc.

1.6.6. Chlorinated Natural Rubber

It is produced by passing chlorine through NR solution 75^0C in presence of catalyst for about 8 hour. Its main application is in anti-corrosive paints and adhesives.

1.6.7. Liquid Natural Rubber

It is prepared by depolymerizing natural rubber either in latex form or in dry form. Depolymerization can be effected by a combination of thermal, mechanical and chemical energies. Its main application is in the production of grinding wheels, where it acts as binder for abrasive powder. It can also be used as a reactive plasticizer for rubber compounding and for further chemical modifications.

1.7. Manufacture of rubber products

Rubber has such remarkable and desirable properties that it is being put to many engineering applications like bearings, springs, and seals in addition to the manufacture of bulk products like tyres, tubes, belts hoses etc. Loads could be safely supported and misalignments accommodated by its ready elastic deformability. Resilience of rubber could be used to advantage in the production of efficient seals. In applications requiring exposure to adverse conditions like high temperature, exposure to oils, fuel solvents, ozone and other corrosive environments synthetic rubbers are preferred over natural rubber.

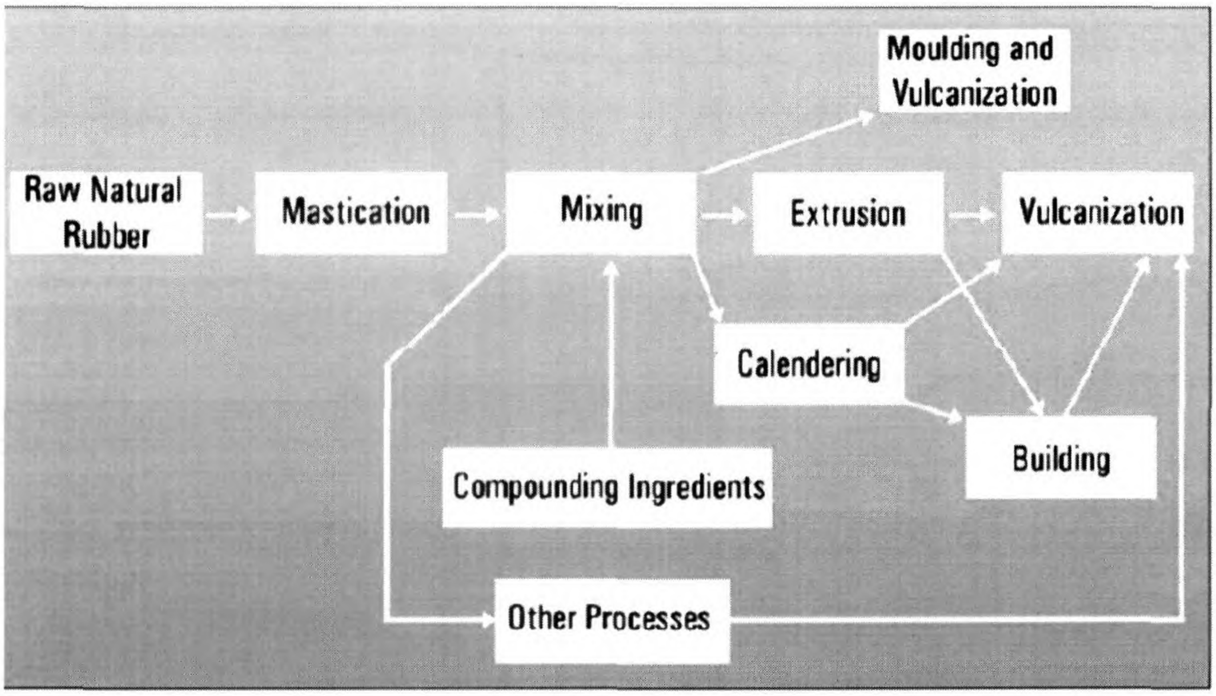


Figure: 1.1.Basic steps in the manufacture of rubber products

A simplified flow diagram, which shows the basic steps in the manufacture of products from natural rubber, is shown in figure [20]. Starting with the raw rubber, the first step is usually mastication to soften the rubber by mechanical working and heat. The next step is the mixing or compounding of the softened raw rubber. This is also done in an open two roll mill or in an internal mixer. A wide variety of substances are frequently mixed with natural rubber. To develop a rubber compound the various ingredients to be used are compiled into recipe. A recipe contains a number of components apart from the base rubber, each having a specific function during processing vulcanization, or during service of the product. They are vulcanizing agents, accelerators, activators, fillers, processing aids, anti- degradants, and a number of special ingredients. The processing aids are generally liquids or resinous materials, which mix intimately with rubber and are used as softeners to permit incorporation of fillers, and to modify the flow behavior of the rubber.

Fillers are classified into two groups: reinforcing and non-reinforcing. Reinforcing fillers are used for enhancement of properties like tear strength, abrasion resistance, and tensile strength. Examples of reinforcing fillers are carbon black, precipitated silica, and silicates. Non-reinforcing fillers are incorporated primarily to cheapen and stiffen the final product. Vulcanizing agents are substances which are added in order that cross-linking may occur subsequently. When the compounded rubber is heated to an appropriate temperature. Sulphur is the principal vulcanizing agent for natural rubber. Accelerators and activators are essential ingredients in the compound to achieve economic rates of vulcanizations. A wide variety of organic accelerators are available today. The most widely used vulcanization activators are combinations of a metal oxide (e.g. Zinc oxide) and a higher fatty acid (e.g. Stearic acid). Anti-degradants are added in rubber compounds in order to increase the ability of the vulcanized products to resists the various deteriorative influences like oxygen, ozone, sunlight, etc., to which it may be subjected to during service.

1.8. Reinforcing fillers

Reinforcement of a rubber vulcanizate results in increase of tensile strength, improved tear strength and abrasion resistance as compared to the gum vulcanizate of the same rubber. The degree of reinforcement depends to a large extent on the molecular, chemical and rheological characteristics of the elastomer, filler characteristics, and the mixing process. The surface area of the filler particles together with the loading determines the effective contact between the filler and the polymer. For a significant reinforcement the filler particles must have high specific surface area [21-23]. Carbon black, silica and recently nanoclay too have attained great significance as reinforcing fillers in rubber industry. These fillers are popular for tyres due to the requirement of durability, fuel efficiency and improved safety [24-25]. The level of dispersion of fillers in a rubber matrix is a very important parameter that decides the mechanical and dynamic mechanical properties of a large variety of rubber products [26-27]. The mixing of filler and dry rubber includes stages like incorporation, distribution and dispersion. The mixing of dry rubber and reinforcing fillers is an energy intensive and environmentally harmful operation. The production of natural rubber-latex-reinforcing filler master batch by the addition of suitable filler dispersion to the latex is a technique to avoid these problems [28].

1.9. Carbon black

In rubber industry carbon black is the most commonly used reinforcing filler. Its application plays a major role in elastomers, plastics, paints and inks. The beneficial effects in rubber applications include increase in strength- related parameters (tensile strength, tear, and cut growth resistance), abrasion resistance, stiffness (hardness and modulus), energy absorption characteristics, and tyre traction [29, 30]. Well known detrimental side effects are increased hysteresis properties and poor fatigue resistance as the stiffness of the polymer-back mixture increases. About 90% of the worldwide production of carbon black is used by the rubber industry. Most of the reinforcing blacks are manufactured by oil furnace process. Complete combustion of natural gas generates a very hot zone in the furnace [31]. An aromatic hydrocarbon feed stock continuously fed into the zone as a mist without air is thermally cracked in less than a microsecond to obtain carbon black nuclei (figure). The combustion of feed stock produces individual carbon particles that are still in a liquid state. They collide in the gas stream and from grape like clusters or aggregates [32]. Quenching determines the final aggregates configuration. Bag filters separate carbon black from the combustion gas to yield a fluffy black with a bulk density of about 30 kg/m^3. The palletizing processing increases the bulk density to 300-640 kg/m^3 foe ease of handling, economical transportation and safety [33].

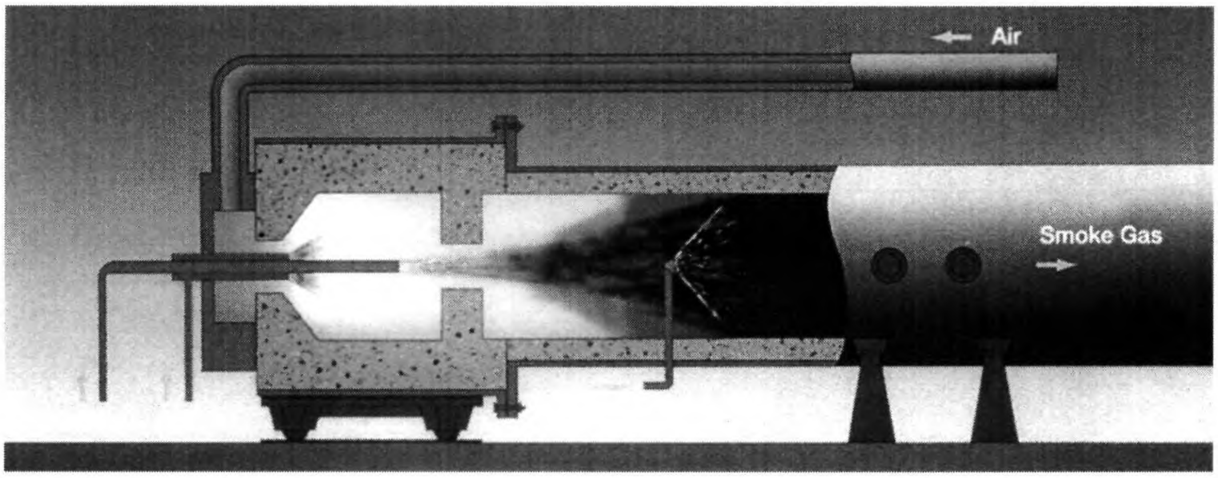


Figure: 1.2.Furnace process for the production of carbon black

Black with various structures can be obtained in a furnace process through the combination of feed stock and operating conditions such as, flow rate, gas rate, air rate, quench position [34]. Compared to other types of carbon blacks furnace black has low oxygen content, neutral surface, and minimum retardation of cure in rubber compounds [35]. Practically all the blacks used by the rubber industry today are supplied in pellet form for ease of handling. Pellet hardness could affect carbon black dispersion in rubber. Pellets that are too hard will not break up during mixing of the rubber with the compounding ingredients causing a dispersion problem. Pellets that are too soft tend to break up during shipping and handling resulting in finer particles that are difficult to disperse [36, 37].

Although carbon black is mainly composed of carbon, they also contain small amounts of chemically combined functional groups such as carboxyl, phenol, quinone, and lactone that react with rubber molecules [38]. The functional groups play a major role in the interaction between carbon black and the polymer. The oxygen content in the functional groups on the carbon black surface, reduce the P^H that could significantly retard cure rate when mixed in the rubber compound [39, 40]. Other materials found on carbon black are small amount of sulphur, ash, moisture [41-43].

Carbon black is classified in several ways. One way is to classify carbon black in accordance to their levels of abrasion resistance as super abrasion furnace (SAF), intermediate super abrasion furnace (ISAF), and high abrasion furnace (HAF). Extrusion rate is another way to classify carbon black, where fast extrusion furnace (FEF), and general purpose furnace black (GPF), are in that category. These are other classifications, but basically they all depend on their manufacturing process, structure and surface area. The American Society for Testing and Materials (ASTM) has designated numbers for rubber grade carbon blacks [44-47].

A carbon black contains a number of primary particles, also called nodules or nodes. A high structure black may consist of as many as 200 primary particles, while a low structure black may contain as low as 20 or 30. The aggregate is the primary reinforcing unit of the carbon black and is not easily broken down into smaller units. The aggregates are formed by collision of semi-solid primary particles in the high temperature environment of the furnace. The aggregates in-turn combines readily with neighboring aggregates to form agglomerates as secondary structure. The final pellet-form that is produced to facilitate handling and to reduce dust is a condensed form consisting of many agglomerates.

1.9.1. Primary properties of carbon black

The properties of carbon black that determine its behavior in a rubber vulcanizate are specific surface area, structure, size and surface activity. The surface area is one of the main parameters used to characterize carbon black grades. Usually surface area measurements include molecular adsorption and this phenomenon is influenced by the surface activity and surface energy of carbon black, which is inhomogeneous across the surface, due to the turbostratic crystalline structure of graphitic layers mixed with amorphous carbon. The most widely accepted and commonly used measurement technique for surface area is the Brunauer, Emmet and Teller (BET) method (ASTM D3037 and D4820). Other commonly used and widely accepted methods are the surface area determination using cetyl trimethyl ammonium bromide (CTAB, ASTM D3765) and the iodine adsorption method (ASTM D1510).

The iodine adsorption number is expressed in grams of iodine adsorbed per kilogram (g/kg) of carbon black and is not the true surface area. However the concentration of the iodine solution has been adjusted so that the values are generally in good agreement with the nitrogen surface area for nonporous and non-oxidized carbon blacks. Surface impurities such as residual oil or oil used for beading depress the iodine number. The presence of high levels of surface oxygen functionality will also cause a severe reduction in the iodine number. The oxygen groups on the surface of the carbon black actually react with the potassium iodide in the test solution, thereby causing release of free iodine which makes the surface area to appear lower. But for routine production control or quality assurance testing of known grades, the iodine test is widely used. Structure is defined as the degree of aggregate irregularity or bulkiness of the carbon black. In general, high structure is associated with a large average number of primary particles per aggregate. This parameter characterizes the empty space between randomly packed primary particles in aggregates. In the test: ASTM D2414-08 (Oil absorption method) a moderately viscous liquid, di-butyl phthalate (DBP) is gradually added to dry carbon black in an internal mixer capable of measuring the torque as the mixing blades turn. An appreciable torque is not developed until the voids in the interstices between primary particles in the aggregates and agglomerates are filled with DBP. The rise to a predetermined torque is taken as the endpoint. The DBP absorption value is expressed as the number of grams of DBP absorbed per 100 grams of carbon black.

It is believed that surface activity plays a key role in the reinforcing capabilities of carbon black. Surface activity includes the surface roughness of small length scales, lower than the primary particle diameter, and the energy site distribution in relation to the primary particle microstructure and the specific reactivity of adsorption sites with a polymer.

1.9.2. Properties of furnace blacks

Carbon black is characterized based on its surface area, particle size, structure and tinting strength. Surface area is usually determined by iodine adsorption, nitrogen adsorption or cetyl trimethyl ammonium bromide (CTAB) adsorption. Structure refers to the bulkiness of the carbon black aggregate. Bulkiness is associated with large average number of particles per aggregate. Structure is measured by dibutyl phthalate (DBP) adsorption (ASTM D-214) method. Tinting strength is a measure of the amount of carbon per aggregate and is measured by optical means [48-51]. Elastomer reinforcement of carbon black is dependent on these properties. Dispersion of carbon black in the elastomer also influences the extent of reinforcement. A typical range of specifications of the four different carbon blacks are given in Table.

Table: 1.6.Specifications of different carbon blacks

Characteristics	**Lamp**	**Channel**	**Furnace**	**Thermal**
Average particle size (nm)	100-150	1-3	14-80	240-320
Surface area (N_2) (m^2/g)	20-95	100-112.5	27-145	7-11
Oil absorption (ml/g)	1.05-1.65	1.0-6.0	0.67-1.55	0.32-0.47
Volatile matter (%)	0.4-0.9	3.5-16.0	0.3-2.8	0.1-1.0
Ash (%)	0-0.16	0-0.1	0.1-1.0	0.2-0.5
Sulphur, ppm	-	0-0.1	0.5-1.5	10
pH	3-7	3-6	5.0-9.5	7-9

Black					
Type	**ASTM**	**Name**	**Surface area (m^2/g)**	**Average particle size (nm)**	**DBP absortion (Cm^3/g)**
N110	SAF	Super abrasion furnace	140	20-25	1.13
N220	ISAF	Intermediate super abrasion furnace	120	24-33	1.14
N330	HAF	High abrasion furnace	80	28-36	1.02
N550	FEF	Fast extrusion furnace	45	39-55	1.21
N660	GPF	General purpose furnace	37	50-60	0.91
N774	SRF	Semi-reinforcing furnace	28	70-96	0.70

1.9.3. Incorporation of carbon black into rubber

Carbon black is incorporated into rubber by shear forces experienced in an open mill or an internal mixer. In a mixing a batch of rubber, a number of elementary steps are involved [52-55]. The steps are shown in fig. These steps are believed to be subdivision, incorporation, dispersion, distribution, and viscosity reduction. Subdivision results in the breaking of larger lumps, or agglomerates to smaller ones, suitable for incorporation, into the rubber. Incorporation of carbon black filler particles into rubber to forms a coherent mass. During incorporation, encapsulation and wetting take place as the polymer breaks into small pieces and seals in the carbon black. Without incorporation the ingredients are tumbled around in the mixer with little energy being spent while practically no mixing takes place.

Dispersion involves reduction of the size of agglomerates to their ultimate size: i.e., changing their physical state, while at the same time distributing the primary aggregates formed. This is of special importance when adding carbon black. This phase is also called dispersive or intensive mixing. Distribution involves the homogenization of the mix by distributing the carbon black particles within the polymer matrix. This phase is also called simple mixing or extensive mixing. As the mixing proceeds viscosity reduction by mechano-chemical breakdown of the polymer occurs transforming it into a more easily deformable and less elastic mass. This process may be improved by the addition of rubber process oil.

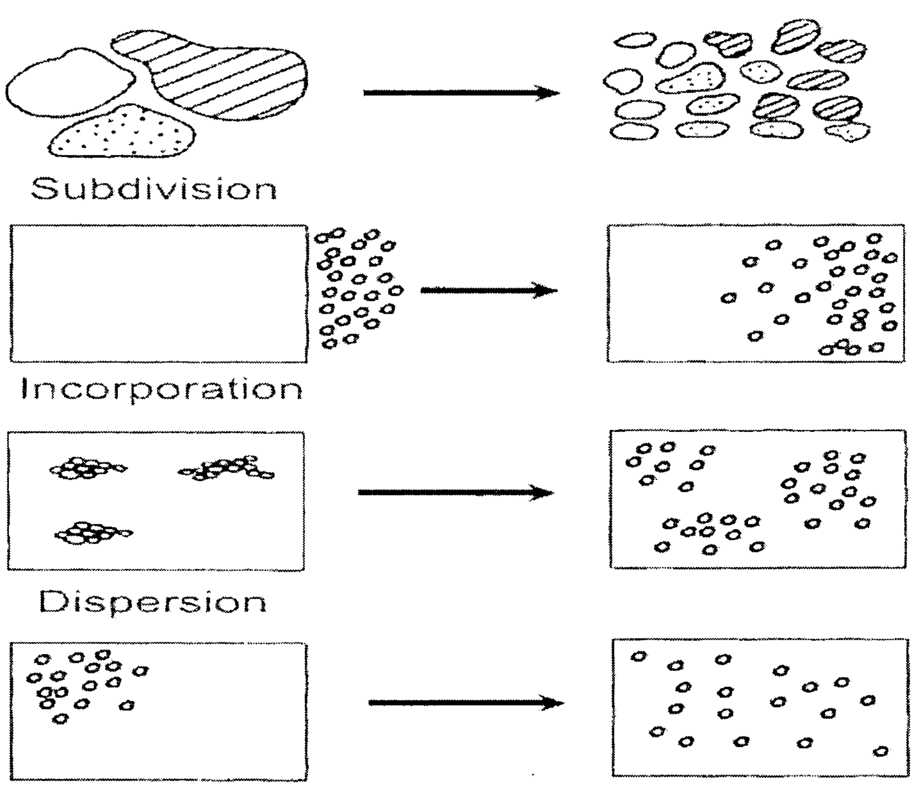


Figure: 1.3.Various stages of rubber mixing [56].

1.10. Silica

Various forms of silica are commercially available. The important natural forms include silica (amorphous), silica (crystalline), silica diatomaceous (fossil origin) and microcrystalline silica. The important types of synthetic silica are precipitated, fumed (pyrogenic), aerogels, and hydrogels. The types of silica used for rubber reinforcement are precipitated, and fumed [57].

Precipitated silica is produced by acidification of alkali silicate solution under controlled conditions. Fumed silica is manufactured by the flame hydrolysis of silicon tetrachloride [58].

$$SiCl_4 + 2\,H_2O \rightarrow SiO_2 + 4HCl \text{ ---------------------------- } (1.5)$$

Precipitated silica is silicon dioxide containing about 10-14% water with particle size in the range 1-40 nm. They are reinforcing fillers giving high tensile strength, tear strength, abrasion resistance and hardness. Fumed silica is silicon dioxide containing less than 1.5% of adsorbed water [59]. High surface area of the filler results in a high level of reinforcement. Silica surface area values are higher than those of blacks of comparable particle size. Efficient reinforcing action, however, requires the presence of surface functional group (surface activity) which provide a substantial bond of filler to elastomer. In contrast to the organic nature of the black surface, the silica surface is inorganic and saturated with silanol (SiOH). These silanols are the reason for the hydrophilic reactivity of precipitated silica.

Silica without coupling agent is less reinforcing than carbon black. Coupling agent acts as a connecting bridge between the silica and the rubber thereby enhancing the rubber reinforcement aspect of silica. Coupling agents are composed of a silane moiety which is capable of reacting with silica surface and also a part capable of reacting with rubber, particularly with sulfur vulcanizable rubber containing carbon-carbon double bonds [60]. Some of coupling agents of commercial importance are TESPT (bis (triethoxy silypropyl) tetrasulphide), TESPD (bis (triethoxy silypropyl disulphide), TESPM (bis (triethoxy silypropyl) monosulphide) and MTMO (mercapto propyl trimethoxy silane (A189)) [61, 62]. The main advantage of silica combined with a coupling agent over carbon black are improved tear resistance, abrasion resistance, heat resistance flex stability, hardness, modulus, tack and resilience[63,64]. The replacement of carbon black by silica fillers with the selection of a proper coupling agent in tyre and reduced fuel consumption of the vehicle, while keeping the wet traction and abrasion resistance on the same level. This environmental and economic incentive of silica technology is enough to overcome the higher production costs due to the difficult processing behavior and the higher raw material costs of these tyres [65, 66].

1.11. Non-black fillers

Non -black fillers include a range of inorganic materials with a variety of particle shapes and sizes. It is available in a broad range of sizes from about 10 to 0.015 microns. These fillers can broadly be classified as:

- Fillers used to reduce cost
- Semi- reinforcing filler
- Reinforcing filler

Earlier non-black fillers used were mainly naturally occurring minerals or by - products of manufacturing such as clay, whiting, barytes, zinc oxide, zinc sulphide, blanc-fixe, mica, asbestos, kieselguhr, magnesium carbonate, iron oxide, litharge etc. They were used in rubber to reduce tack, increase hardness, improve durability and reduce cost, [67, 68, 69].other important non-black fillers being used in the elastomer industry are aluminium hydrate, aluminium oxide and titanium dioxide.

The need for more reinforcing non-black fillers in many rubber applications led to the introduction of calcium carbonate, calcium silicates, hydrated silica and fumed silica between 1940 and 1960. These were characterized by very small particle size much smaller than the natural products and similar to the reinforcing carbon blacks. Since then a lot of developments and refinements in hydrated silica and fumed silica have taken place resulting in a number of grades for specific applications [70].

1.12. Reinforcement mechanism

Addition of fillers to rubber has a strong impact on its static and dynamic behavior. Surface interaction between fillers and rubber molecules involves a range of bond energies from relatively weak to very strong. In general, physical adsorption of polymers on filler surface occurs to varying degrees depending on the filler surface and the nature of polymer segments. In the case of carbon black, the level of physical interaction is high [71]. Although chemical interaction between carbon black and rubber is taking place, it occurs only to a minor extent and is not a necessary condition for reinforcement. Filler, above a critical concentration in rubber matrix, can cause filler-filler interaction, extent of which is determined by both physical or chemical interaction and the distance between filler aggregates in the rubber compound.

When rigid spherical particles are dispersed into a fluid, an increase in viscosity takes places in the case of liquids or a modulus enhancements in the case of polymers, which is known to be due to the hydrodynamic effect [72].

According to Payne the enhancement of mechanical properties due to the presence of a filler in rubber compounds can be attributed to the additive effects of polymer network, hydrodynamic effect, in rubber structure and the filler-filler interaction. The dynamic modulus, G*, of a reinforced rubber hence depends both on strain independent parameters such as crosslinking of the matrix, hydrodynamic effect, filler to rubber interaction (in-rubber structure) and the strain dependent filler-filler interaction. The phenomena of stress softening of a filled rubber with strain known as **"Payne effect"** arises from filler-filler interaction [73, 74]. A comparison of the reinforcement behavior due to the above 4 factors of carbon black and silica is given in figure.

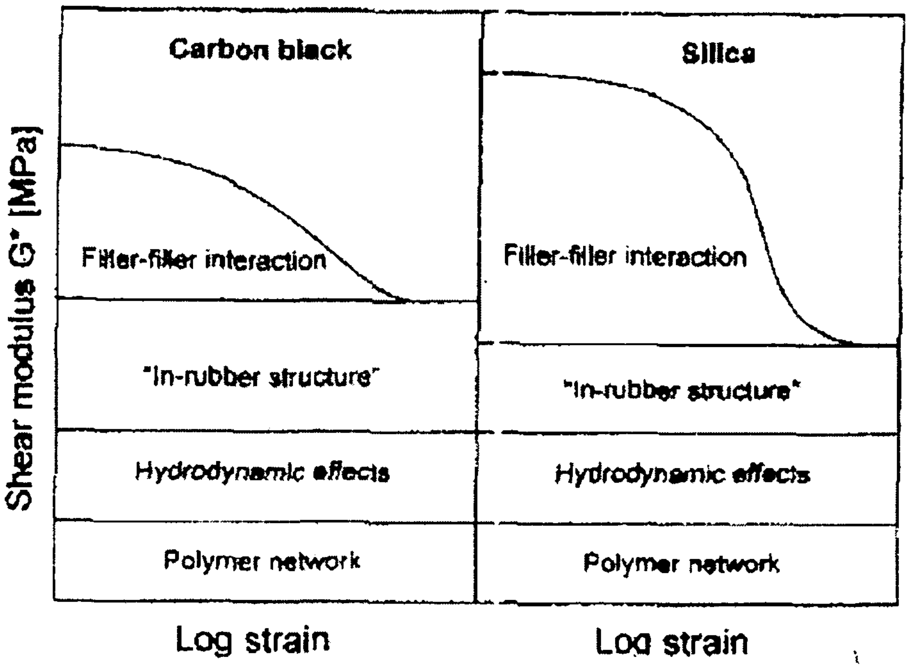


Fig: 1.4.Payne effect- carbon black, silica comparison

a) Polymer network

The first component of the 'additive factor' of reinforcement is the strain independent polymer network which results from the proportionality of the modulus (Go) to that of the cross link density and can be represented using equation 1.2 as

$$G_o = vkT$$

Where v = number of moles of elastically effective network chains per unit volume as a result of vulcanization.

K = Boltzmann constant

T = Temperature (K)

b) Hydrodynamic effect

When rigid spherical particles are dispersed into a fluid, whether it be a liquid or an elastomer, an increase in viscosity takes place in the case of the liquid or of the modulus in the case of a polymer. This is generally designated as hydrodynamic effect. The viscosity or modulus increase due to filler addition in liquids and elastomers respectively due to hydrodynamic effect can be represented by the equation proposed by the Guth-Gold [75] and smallwood [76].

Guth-Gold equation (equation 1.3) for viscosity [75]

$$\eta = \eta_0 (1+2.5\phi + 14.1\phi^2) \qquad \text{Eq.1.3}$$

Where η and η_0 are the viscosities of the filled and unfilled system, ϕ is the volume fraction of the filler.

Smallwood [76] showed that for an elastic material filled with rigid spherical particles the equation for modulus enhancement can be represented as in equation 1.4

$$G = G_0 (1+2.5\phi + 14.1\phi^2) \qquad \text{Eq.1.4}$$

Where G and G_0 are the shear moduli of the filled and unfilled system respectively and ϕ is the volume fraction of the filler. The value of G_0 is obtained from equation 1.2. The shear modulus can also be replaced by tension elasticity modulus without much change of the equation.

For nonspherical particles, Guth introduced a shape factor, f (the ratio of the longest dimension of the particle to the shortest) and proposed the following equation [77].

$$G = G_0 (1+0.67 f\phi + 1.62 f^2\phi^2) \qquad \text{Eq.1.5}$$

The equations were derived on the assumption that the medium wets the filler particles, but does not chemically react with the filler surface. The modulus as given in equation 1.4 and 1.5 is independent of applied strain.

c) In-rubber structure

The in-rubber structure can be understood as a combination of the structure of the filler in the in-rubber state and the extent of filler-polymer interaction. The in-rubber structure is, amongst others a measure for the occluded rubber, which is shielded from deformation and therefore increases the effective filler content leading to a strain independent contribution to the modulus. The filler-polymer interaction can be attributed to physical (Van der walls) as well as chemical linkages or both. In the case of silica-coupling agent system, this interaction is formed by chemical linkages [78-81].

d) Filler-filler interaction

Elastic modulus of a filled rubber is strongly dependent on deformation and decreases substantially at higher strains **('Payne effect')**. This is attributed to the presence and breakdown of the filler network during dynamic deformation. The sigmoidal decline of the storage modulus at zero amplitude (G_0') to a high amplitude plateau (G_∞') was interpreted by Payne as due to the breakage of physical (London and Van der walls) bonds between filler particles. It was also noted that the value G_0' is mostly recoverable upon return to smaller amplitudes and showed that the phenomenon is independent of the polymer, provided enough time is allowed for recovery. When using silica as reinforcing filler, a high level of elastic modulus and the drop of elastic modulus at higher strain amplitudes prove the existence of a stable filler network formed by silica as is represented in Fig.1.2 [74, 81-84].

1.13. Rubber ingredients

A rubber compound is obtained by mixing a base polymer or crude mixture with a series of additives. The choice of the base polymer and the additives is closely linked to the type of properties to be achieved. The resulting product is a non -vulcanized compound. The quantity of additives used varies for 20 to 130 percent as a percentage on the weight. The most common additives are:

Fillers

There are two types of fillers, reinforcing and non- reinforcing fillers. Carbon black is commonly used as reinforcing filler. This is also the reason why most rubbers are black. Calcium carbonate is an example of non- reinforcing filler.

Plasticizers

Besides fillers, plasticizers play the biggest quantitative role in building a rubber compound. The reasons for the use of plasticizer are: improvement of flow of the rubber during processing, improved filler dispersion, influence on the physical properties of the vulcanizate at low temperatures. Mineral Oils and paraffin's are widely used as a plasticizer.

Vulcanization chemicals

Vulcanization is the conversion of rubber molecules into a network by formation of crosslinks. Vulcanizing agents are necessary for the crosslink formation. These vulcanizing agent are mostly sulfur or peroxide and sometimes other special vulcanizing agents or high energy radiation. Since the vulcanization is the process of converting the gum- elastic raw material into the rubber-elastic end product, the ultimate properties like hardness and elasticity depend on the course of the vulcanization.

Accelerators

Accelerating agents increase the rate of the cross linking reaction and lower the sulfur content necessary to achieve optimum vulcanizate properties.

Activators

Like Zinc-oxide and stearic acid. They activate the vulcanization process and help the accelerators to achieve their full potential.

Anti-degrading agents

These agents increase the resistance to attacks of ozone, UV light and oxygen.

Process aids

Chemicals that improve the processability

Pigments

Organic and inorganic pigments are used to colour rubber compounds. The colour pigments are also considered inactive fillers.

1.14. Reviews on wet master batch

CS patent application **201410632796** discloses the field of rubber processing, and relates to a preparation method for a white carbon black/NR (Natural rubber) master batch for a belted layer of a tire. The preparation method comprises the following steps: adding white carbon black, water, a dispersant and a stabilizer into a reactor, and performing stirring at a high speed to prepare high-dispersity white carbon black slurry; adding the white carbon black slurry into a natural latex solution, mixing the white carbon black slurry and the natural latex solution with stirring at the high speed, and performing acid coagulation, washing and drying to obtain the white carbon black/NR master batch. According to the preparation method, a process is simple; a wet process is adopted, and white carbon black is subjected to silanization-free treatment, so that time for mixing a great amount of white carbon black is shortened, energy consumption is lowered, the dispersity and uniformity of white carbon black in rubber are improved, damage caused by mechanical shearing and high-temperature thermal oxidation to rubber molecules in a dry method is avoided, and the steel wire bonding property and tear resistance of a sizing material adopting a resorcinol-formaldehyde donor-white carbon black bonding system can be remarkably improved; the prepared white carbon black/NR master batch can be applied to the belted layer of the tire [85].

US patent Application **8716366 B2** this invention relates to a process for preparing tri-filler incorporated natural rubber master batch. The fillers used in the present invention are carbon black, silica and nano-clay (modified montmorillonite clay, Cloisite 93 A). The process of preparing fillers incorporated master batch involves preparation of the individual filler dispersions by mixing each filler with surfactants. Further fresh rubber latex is soap sensitized by mixing it with surfactant. The filler dispersions are added to the soap sensitized rubber latex slowly under stirring to form the master mix. Then the master mix is coagulated by the addition of acid to form coagulum. The coagulum is dewatered and dried to obtain filler incorporated natural rubber master batch [86].

US patent Application **9012535 B2** this invention is to provide a production method of a natural rubber master batch including a step of mixing a natural rubber latex and an aqueous slurry having carbon black dispersed in water, wherein a mixing amount of the carbon black is from 10 to 100 parts by mass based on 100 parts by mass of a natural rubber component; and the carbon black is satisfied with the relationships expressed by (1) 120<CTAB adsorption specific surface area<160, (2) 50<24M4DBP<100, and (3) 75<toluene discoloration transmittance<95. Also, the present invention is to provide a natural rubber master batch obtained by the subject production method. Furthermore, the present invention is to provide a rubber composition using the foregoing natural rubber master batch and a tire using the subject rubber composition [87].

US patent Application **7960466 B2** this invention provides a natural rubber master batch effective in achieving a tread rubber composition which is suitable for heavy-duty tries for rough roads and which is effective in greatly enhancing the abrasion resistance of the tries without impairing the low heat build -up of the tries, a method of producing the natural rubber master batch, a rubber composition prepared using the natural rubber master batch, and a tire. In a mixing step of mixing a natural rubber latex with a slurry containing water and a carbon black dispersed therein, 10 to 100 weight parts of the carbon black is mixed with 100 weight parts of a natural rubber component in the natural rubber latex. The carbon black satisfies the following conditions: (1) N_2SA is 120 to 180 m^2/g; (2) the relationship between 24M4DBP and N_2SA is represented by the inequality $15 \leqq 24M4DBP - 0.375 N_2SA \leqq 38$; and (3) the Dst of aggregates of the carbon black is represented by the inequality $Dst \leqq 65$ nm and the ratio ($\Delta D50/Dst$) of the

ΔD50 of the carbon black aggregates to the Dst thereof is represented by the inequality $\Delta D50/Dst \leqq 0.70$ [88].

WO patent Application 2009072413 **A1** Disclosed is a method for producing a natural rubber master batch, which comprises a step for mixing a natural rubber latex with an aqueous dispersion slurry in which a carbon black is dispersed. In this method, 10-100 parts by mass of the carbon black is mixed per 100 parts by mass of the natural rubber component, and the carbon black satisfies the following conditions: (1) 120 < CTAB adsorption specific surface area < 160; (2) 50 < 24 M4DBP < 100; and (3) 75 < toluene coloring transmittance < 95. Also disclosed are a natural rubber master batch obtained by such a production method, a rubber composition using such a natural rubber master batch, and a tire using rubber composition [89].

WO patent Application **2006068078 A1** Disclosed is a method for producing a natural rubber master batch having a mixing step of mixing a natural rubber latex and a slurry prepared in advance by dispersing carbon black in water, wherein carbon black is mixed in an amount in the range of 10 to 100 parts by weight relative to 100 parts by weight of the natural rubber component in the natural rubber latex, and wherein, with respect to the carbon black, (1) it has an N_2SA of 120 to 180 m^2/g; (2) the relationship between 24M4DBP and N_2SA is represented by $15 \leq 24M4DBP - 0.375\ N_2SA \leq 38$, (3) aggregates of the carbon black have a Dst represented by $Dst \leq 65$ nm and have a ratio of ΔD50 to Dst (ΔD50/Dst) satisfying the relationship represented by $\Delta D50/Dst \leq 0.70$; a natural rubber master batch produced by the above method; and a natural rubber composition and a tire using said master batch. The above natural rubber master batch can provide a rubber composition for a tread being markedly improved in abrasion resistance, which is especially suitable to a heavy –duty for use on a rough road, without detriment to its low heat build-up property [90].

EP patent Application **1283219** this invention relates to a natural rubber master batch, a production method thereof, and a natural rubber composition. More specifically, the present invention relates to a natural rubber composition having improved processability, reinforcing property and abrasion resistance, a natural rubber master batch suitable for producing the natural rubber composition, and a production method of the natural rubber master batch [91].

EP patent Application 1834985 **B1** this invention relates to natural rubber master batches and methods for producing the natural rubber master batches. This present invention particularly relates to a natural rubber master batch effective in achieving a tread rubber composition which is suitable for heavy duty-tires for rough roads and which is effective in greatly enhancing the abrasion resistance of the tires and relates to a method of producing the natural rubber master batch. Furthermore, the present invention relates to a rubber composition prepared using the natural rubber master batch and tire sand particularly relates to a heavy -duty tire for rough roads [92].

1.15. Scope of the present work

Fillers when added to polymer systems are known to cause a considerable change in dynamic properties. This phenomenon has been investigated in- depth, especially in relation to rubber products. The level of dispersion of fillers like carbon black, silica in a rubber matrix is an important issue in a large variety of rubber products. Though carbon black could be easily dispersed in natural rubber by conventional mill mixing, there are issues like air pollution, material loss and high energy consumption. In the case of fillers such as silica it is extremely difficult to disperse these highly aggregate fillers in natural rubber using a mixing mill. Preparation of latex- carbon black and silica master batch by the addition of filler dispersion slurry has been suggested as one of the methods to avoid some of these problems.

A simple method for production of natural rubber latex- carbon black/ silica master batches with enhances mechanical properties is described. The main steps involved in the process are the preparation of filler dispersion, addition of the dispersions to the fresh natural rubber latex under stirring, coagulation of the mixture by the addition of acid, dewatering of the coagulum, and drying to obtain filler incorporated natural rubber (NR). The mechanical properties of the vulcanizates obtained from the latex stage and dry rubber incorporated mixes were evaluated and the filler interaction characteristics were studied. The master batch prepared by the new process showed a higher level of vulcanization as compared to the dry rubber mix. The mechanical properties like tensile strength, modulus, tear strength, abrasion resistance and hardness were superior for the vulcanizates prepared by the new method. The heat build-up values were considerably low for the latex filler master batches.

CHAPTER-II

EXPERIMENTAL TECHNIQUES AND MATERIALS USED

CHAPTER-II

2. EXPERIMENTAL TECHNIQUES AND MATERIALS USED

The materials used for the study and the experimental procedures are given in this chapter.

2.1. Materials

2.1.1. Polymer

- **Fresh natural rubber latex**

Fresh natural rubber latex used in the investigation was collected from the plantation of the RRII, Kottayam.

Composition of fresh latex used is given in Table. 2.1

Table 2.1: composition of latex

Constituents	Percentage
Rubber	30-40%
Protein	2-2.5%
Resin	1-2%
Sugar	1-1.5%
Ash	0.7-0.9%
Water	55-60%

2.1.2. Preservatives

A preservative is a chemical or mixture of chemicals which when added to latex can prevent bacterial action in it and at the same time stabilizes it. Ammonia is the most popular latex preservative. Usually field latex is preserved with 1% ammonia. A low ammonia system

(LATZ) consisting of TMTD and zinc oxide (0.013% each) along with 0.30% ammonia is also popular.

Preparation of LATZ system (10 liters)

The following ingredients in the given quantity were taken and stirred well prior to addition to latex to the require system.

Ammonia solution: 120 ml

TMTD : 1.3 g

ZnO : 1.3 g

Water : 400 ml

Ammonium laurate

(Soap) : 25 ml

2.1.3. Fillers

- **Carbon Black**

The carbon black used was Intermediate super abrasion furnace black (ISAF) N220 grade.

- **Precipitated Silica**

Precipitated silica used was Ultrasil VN3 of DEGUSSA, INDIA.

2.1.4. Other Chemicals

- **Ammonium laurate**

20 % ammonium laurate was prepared in the laboratory.

- **Zinc oxide**

Zinc oxide (ZnO) used in the study for crosslinking activator.

- **Stearic acid**

Stearic acid used in the study for crosslinking activator.

- **Sulphur**

Sulphur used in the study for crosslinking agent.

- **Other compounding ingredients**

The materials such as antioxidants, rubber process oils and accelerators used in this study were rubber chemical grade.

- **Surfactants**

S1, S2 and S3 were prepared in the laboratory.

2.2. Experimental Method

2.2.1. Dry rubber content (DRC) of latex

After the addition of LATZ system, the latex is stirred well prior to collection of samples for determining DRC.

About 10-15g of the sample latex is accurately weighed by the difference method into 100ml beaker from a stoppered 50 ml of conical flask. The latex is coagulated with sufficient quantity of 2% formic acid and heated on a water bath until a clear serum is obtained. The coagulum is thoroughly washed rolled to a thin film of around 2mm and placed in an oven at about 70^0C for 16 Hrs. The dried rubber obtained is cooled in a desiccator and weighed in a balance.

$$\text{DRC (\%)} = \frac{\text{Wt .of dry Coagulum} \times 100}{\text{Wt. of latex}}$$

2.3. Preparation of fillers dispersion with surfactants

- **Surfactants**: S1, S2, S3 and S were used in these studies.

- **Preparation of filler dispersion slurry**

ISAF black, silica, water and surfactants are mixed and using a ball mill for 24 hrs at room temperature.

2.3.1. Ball milling

The container is rotated about its cylindrical axis in a horizontal plane at such a speed that the charge is tumbled. In ball mill the grinding charge consists of unglazed porcelain or glass balls, their size being governed by the diameter of the container. A small laboratory mill may use balls of 1.2–1.5 cm diameter. Larger mills require balls of an average diameter of about 2.5 cm. The rate of grinding by the mill is related to the diameter of the container. If the mill rotates too rapidly, centrifugal force will cause the charge to adhere to the container walls and no grinding results. Large mills must rotate more slowly than small ones and the following table of optimum speeds assists the operator in arranging the milling operation. Slower speeds may be used but the time of milling will be extended since the grinding is achieved by a definite number of rotations of the mill.

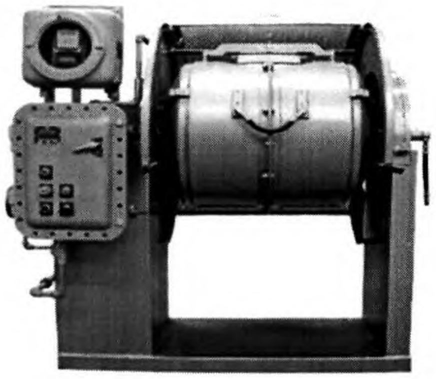


Fig: 2.1. Ball mill.

2.4. Preparation for carbon black, silica –NR master batch

NR latex carbon black and silica master batch is made by adding carbon black and silica in the form of dispersion, to latex. The resultant rubber –fillers dispersion mixture is coagulated, dried. The fillers dispersion is prepared by surfactants sensitized mixing of fillers with water. The dispersion was added slowly into field latex under stirring and coagulated by addition of acid to produce latex carbon black silica master batch. The coagulum is washed well to remove acid and rolled to a thin sheet, dried in an air oven at 70^0C.

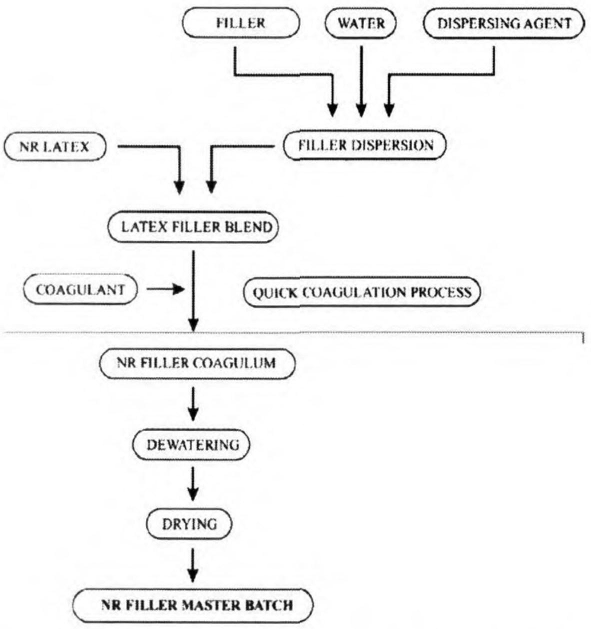


Figure: 2.2. Schematic Diagram of Preparation of NR/ Carbon black -Silica master batch

2.5. Rubber compounding process

Compounding is the operation of bringing together all the ingredients required to mix a batch of rubber compound. Each component has a different mix of ingredients according to the properties required for that component. Rubber compounding is generally carried out on open mills or internal mixers.

2.5.1. Two Roll Mill

The two roll mill in Fig. consists of two horizontal, parallel, heavy metal rolls which can be jacketed with steam and water to control temperature. These rolls turn towards each other with a pre-set, adjustable gap or nip to allow the rubber to pass through to achieve high- shear mixing. The back roll usually turns at a faster surface speed than the front roll; this difference increases the shear forces. The difference in roll speeds is called the ***friction ratio***. The rubber generally forms a "band" around the front roll. Mill mixing is the oldest method of rubber mixing, dating back to the very beginning of the rubber industry; however, it is a relatively slow method and its batch size is limited. Internal mixers overcome these problems.

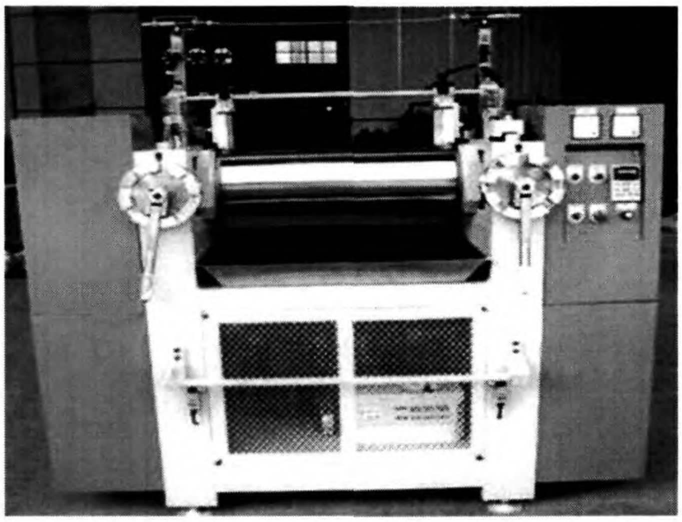


Figure: 2.3. Small size laboratory open mixing two roll mill.

2.5.2. Internal mixers

Internal mixers were first developed by **Fernley H. Banbury** in 1916. Today, these internal mixers are commonly used because they are much more productive than two rolls. Internal mixers consists of two rotors or blades turning toward each other in an enclosed metal cavity. These rotors can be either tangential or intermeshing in arrangement. The cavity is open to a loading chute through which rubber, fillers, and various chemicals are placed. Upon completion of the mix cycle, the mixed rubber stock is discharged through a door in the bottom of the mixer.

Mixing time is determined by the shape and size of the rotors, rotor speed, and horsepower of the motor turning them. The rotors generally turn at a high friction ratio. Some internal mixers can handle batches in excess of 1000 pounds (greater than 455kg), and in some cases, can completely mix a compound in less than two minutes. Of course, with so much energy being absorbed by the rubber stock, the batch temperature can rise well above 120^0 C (250^0 F) before it is dumbed and cooled. The temperature rise that results from viscous heating of the rubber compound often means the compounds must pass through the internal mixer more than once to disperse fillers and other compounding ingredients. Batches are usually dumped from an internal mixer onto a mill where they may be further worked while being cooled. Sometimes, additional compounding ingredients, such as curatives, are added at this point.

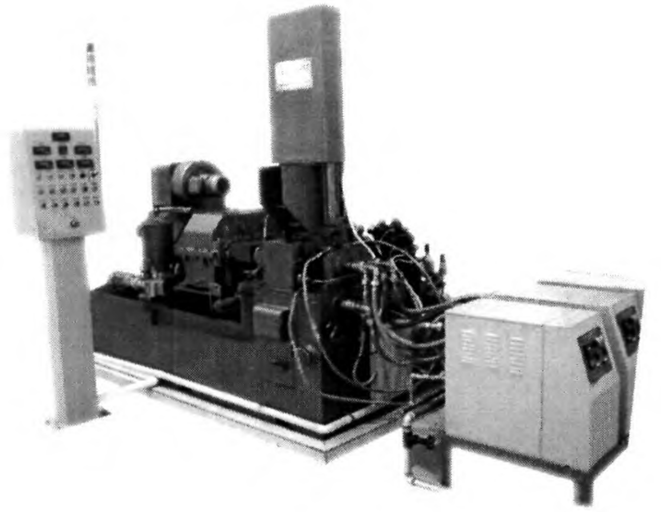


Figure: 2.4.Laboratory internal mixer.

2.6. Sample preparation for test and Evaluation

2.6.1. Cure characteristics (ASTM D 5289) [93]

From each compounded master batch samples are drawn for Rheometer study. Minimum 12 hours maturation time is given for all the samples. The cure characteristics of the compounds are determined using RPA 2000 (type of moving die rheometer) at 150 °C according to ASTM D 5289 procedure. The optimum cure time corresponds to the time to achieve 90% of the cure represented by the maximum torque attained. It was calculated from the equation optimum cure time.

$$t_{90} = \{(MH - ML) + ML\}\ 90/100$$

where,

MH = maximum torque

ML = minimum torque

Figure: 2.5. Rubber Process Analyzer (RPA-2000).

2.7. Preparation of testing samples

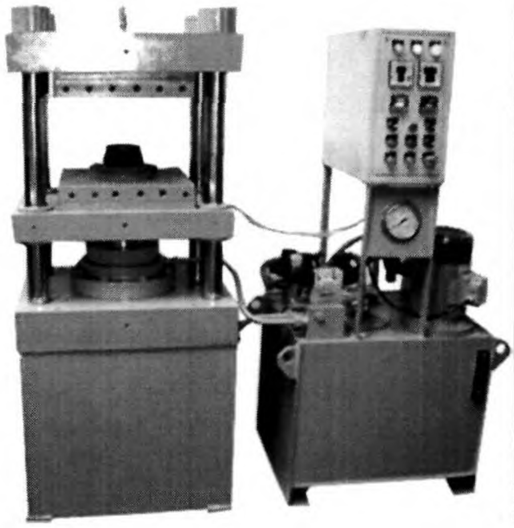
The test specimens for the physical property determination were prepared by vulcanizing the blanks cut from un-vulcanized rubber compound sheets marked with mill direction, at a temperature of 150^{0}C by compression molding in an electrically heated hydraulic press. The molded samples after curing were quickly cooled and stored for 24 h before tests.

2.8. Mechanical properties

2.8.1. Stress- Strain Properties (ASTM D412) [94]

For the test described below five specimens per sample were tested for each property and mean values are reported.

The stress-strain properties were determined according to ASTM D412 (2006), Test Method A using dumbbell specimens on a Universal Testing Machine All the tests were carried out at ambient temperature. Samples were punched out from compression molded sheets along the mixing mill direction using a dumb-bell die. A thickness gauge was used to measure the thickness of the narrow portion. The sample was held tight by the two grips, the upper grip of which was fixed. The gauge length between the jaws at the start of each test was adjusted to 30 mm and the rate of separation of the power activated upper grip were fixed at 500 mm/min. The tensile strength, elongation at break and modulus were tested.



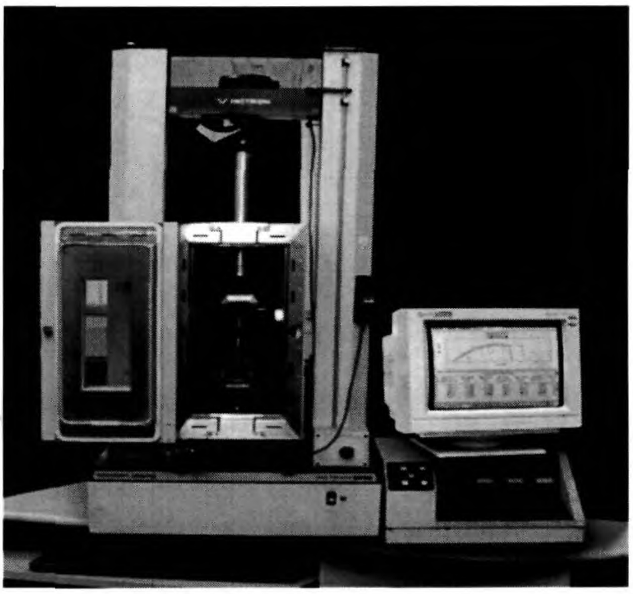


Figure: 2.6.Hydraulic press **Figure: 2.7.Universal Testing Machine- (Instron)**

2.8.2. Tear Strength (ASTM D624-02) [95]

Tear strength or tear resistance of rubber is defined as the maximum force required to tear a test specimen in a direction normal to (perpendicular to) the direction of the stress. Tear strength is expressed as force per unit of specimen thickness-pounds force per inch (1bf/in), kilograms force per centimeter (kgf /cm), or kilo Newton's per meter (KN/m) or N/mm.

The tear resistance of the sample was tested as per ASTM D-624 test method, using un-nicked 90^0 angle test specimen. This test was also carried out using the 'Zwick UTM'.

2.9. Specific gravity (ASTM D1817) [96]

This property is fully defined by the composition of the material. The specific gravity is the mass per unit volume and is measured by weighing the sample in air and in water.

Specific gravity = weight in air/ (weight in air-weight in water)

Standards: ISO 2871, ASTM D1817.

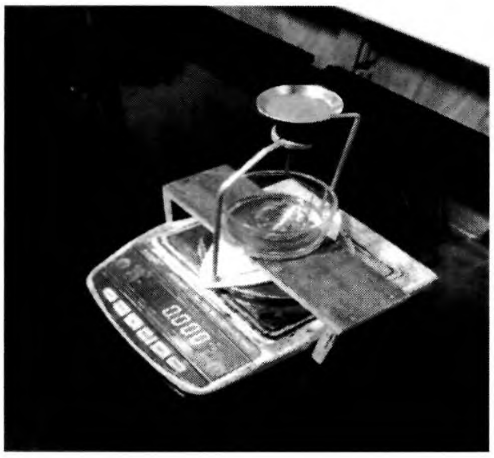


Figure: 2.8. Specific gravity balance.

2.10. Hardness (ASTM D2240) [97]

Durometer hardness testing measures the hardness of rubber elastomer and plastic materials. The most widely used hardness measuring instrument is called the Durometer. It measures hardness values in points that range from 0 to 100. 0 points represent a very soft material, while 100 points represents a very hard material. Rubber elastomers are measured using the Shore Type-A scale.

Test procedure:

- Test specimens are placed on a hard flat surface.

- The indentor of the Durometer gauge is pressed into the specimen making sure that it is parallel to the specimen surface.
- The hardness value is read within one second of firm contact with the specimen.

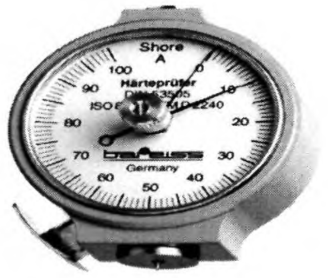


Figure: 2.9.Hardness tester Shore-A Durometer

2.11. Compression set (ASTM D 395 [98]

Compression set Testing measures the ability of rubber to return to its original thickness after prolonged compressive stresses at a given temperature and deflection. As a rubber material is compressed over time; it loses its ability to return to its original thickness. Compression set results for a material are expressed as a percentage.

ASTM D395 describes two types of compression set tests:

- Method A, compression set under constant load
- Method B, compression set at constant deflection of 25%.

For rubber, performs compression testing using method B.

Test Procedure

- ➢ The thickness of the original specimen is measured and record.
- ➢ The specimen in then placed between the plates of the compression set assembly.

- The specimen is compressed to 75% of its original height. Spacers are used to ensure that the compression force is accurately maintained.
- The loaded compression set assembly is placed in an oven at a specified temperature for the suggested periods of 22 hours at 70^0 C.
- The specimen is removed from the oven and conditioned for 30 minutes on a wooden plank.
- The final thickness of the specimen is then measured.
- Compression set is expressed as a percentage of the original deflection and is calculated using the following formula:

$$\textbf{Compression set} = (t_0 - t_1) / (t_0 - t_s) \times 100$$

Where; t_0 = the original thickness, t_1=compressed thickness, t_s = spacer thickness.

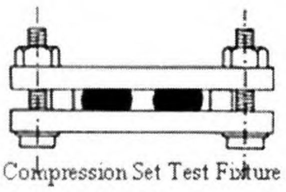


Figure: 2.10. Compression set apparatus

2.12. Abrasion resistance (ASTM D5963) [99]

Abrasion resistance is an importance factor for many rubber products, such as tires, conveyor belts, power transmission belts, hoses, footwear and floor covering.

The abrasion resistance is measured by moving a test piece across the surface of an abrasive sheet mounted to a revolving drum, and is expressed as volume loss in cubic millimeters or abrasion resistance index in percent.

Abrasion resistances of the samples were measured using a DIN abrader (As per DIN 53516). The abrasion loss is calculated as follows.

$$V = \Delta W / \rho \times 1000$$

Where ΔW is the weight loss, ρ -specific gravity and V-abrasion loss

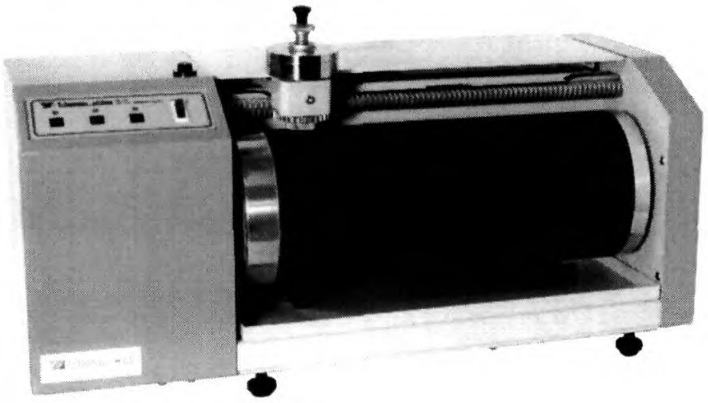


Figure: 2.11. Din abrasion tester

2.13. Heat build-up (ASTM D623-67) [100]

Heat build-up of the samples were measured as per ASTM standards. Cylindrical test specimen with diameter of 17.8±0.1 mm and height of 25±0.5 mm were used. The test piece was subjected to rapidly oscillating compressive stresses in Goodrich flexometer at 1800 cycles per min, at an initial chamber temperature of 50^{o}C. A constant initial compressive load was applied to the specimen through a level having high inertia and imposing on the specimen and an additional high frequency cyclic compression of definite amplitude. The stroke given was 4.45mm. The increase in temperature at the base of the test specimen was measured with a thermocouple which provided indication of the heat generated in flexing the specimen.

Figure: 2.12. Goodrich Flexometer

2.14. Flex crack resistance (ASTM D413-95) [101]

Failure in rubber articles mainly happens due to fatigue, which includes repeated loads smaller than the strain at break. Two approaches to determine the fatigue life of rubber have been established: The crack nucleation approach and the crack growth approach. The first one is based on the assumption that fatigue life depends on the history of a certain quantity (stress, strain or strain engery density) at a point in the material. The second apporach deals with fatigue crack growth from pre existing flaws and estimates total fatigue life from fatigue crack growth (FCG) curves.

Resistance to flex crack of the vulcanizate was measured using De-Mattia flexing machine model 'de-mattia flexon' check. The machine operated at a constant speed under load at 300±1 flexing cycles per minute. The sample was 6" long, 1"wide and 0.25" thick with a groove moulded across the width with grain direction perpendicular to the length of the specimen. The samples were held in a special jig and a chisel cut was being applied exactly at the center of the groove by a piercing tool of 2mm width. The flexing is such that the specimen is bent almost double at the groove then straightened out without extension. Crack growth is measures at regular intervals with the point being the number of cycles required to extend the crack to 12mm. The test was conducted at room temperature and was reported as the increment in cut length in millimeter. Crack initiation and crack failure also tested using 'de-mattia flexon' check.

Figure: 2.13. De-Mattia flexing machine

2.15. Thermo gravimetric Analysis (ASTM D6370) [102]

Thermo gravimetric analysis (TGA) of the master batch samples was carried out using a thermo gravimetric analyzer (TGA 60 from Shimadzu Instrument, Japan) in accordance with ASTM D6370 standard test method for compositional analysis by thermogravimetry (TGA). It is a computer-controlled instrument that permits the measurement of the weight changes in the sample material as function of temperature. The sample placed in a temperature programmed furnace is subjected to temperatures in the ranges 30^0C to 800^0C with a heating rate of 10^0 C per minute and the corresponding weight changes were noted with the help of an ultrasensitive microbalance. Air and nitrogen were used as purge gases.

Figure: 2.14. Thermo Gravimetric Analyzer (TGA)

The test has to be performed firstly under nitrogen to decompose the organic matter and then under oxygen to burn the carbon content. The following experimental procedure has to be used.

- Place a small piece (40mg) of the sample into the alumina crucible.
- Apply nitrogen flow rate ($60cm^3.min^{-1}$)
- Heat to 50^0 C and allow the instrument to equilibrate for a minimum of 2 minutes.
- Heat from 50^0 C to 350^0 C at 20^0 C per minute.
- Stabilize at 350^0 C during 15 minutes.
- Heat from 350^0 C to 600^0 C at 20^0 C per minute and cool to 400^0 C at 20^0 C per minute.
- Change the nitrogen gas to air ($60cm^3 .min^{-1}$) and heat from 400^0 C to 800^0 C at 20^0 C per minute.

2.16. Dynamic Mechanical Analyzer (DMA)

Dynamic mechanical analysis is a high- precision technique used for measuring materials visco-elastic properties. It consists of applying sinusoidal stress to a specimen and measuring the resultant force transmitted by the specimen, by means of a dynamic mechanical analyzer. Dynamic Mechanical analysis of prepared samples are done using DMA model 01 dB DMA 50N of metrvib, France.

Figure: 2.15. Dynamic mechanical analyzer (DMA); Figure: 2.16. DMA- Testing specimen cutter

CHAPTER-III

CARBON BLACK/ SILICA MASTER BATCHES FROM PRESERVED NATURAL RUBBER LATEX

CHAPTER-III

3. CARBON BLACK/ SILICA MASTER BATCHES WITH SURFACTANTS FROM PRESERVED NATURAL RUBBER LATEX

3.1. OBJECTIVE

The objective is to develop a process for the preparation of filler incorporated natural rubber latex master batch by utilizing a quick coagulation process of latex, assisted by surfactants that give vulcanizates having superior cure characteristics and mechanical properties compared to mixes prepared by conventional mill mixing process.

3.2. Preparation of NR- Carbon black and silica master batch using with soap solution

3.2.1. DRC determination

Preserved natural rubber latex of dry rubber content DRC-32.00 % was used in the investigation.

3.2.2. Preparation for filler dispersion slurry

5% Filer dispersion slurry of carbon black and precipitated silica was prepared by using a ball milling technique rotating at high speed for about 24 hours and finally added 20% soap solution and mix it well into that slurry dispersion.

This dispersion slurry was added slowly in to fresh natural rubber latex under stirring and coagulated to produce carbon black master batch. This coagulum was pressed mechanically to effect uniform coagulation of latex – carbon black slurry. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet master batch and dried in an air oven maintained at 70^0 C to get the latex filler master batch.

Table: 3.1. Formulation for NR-CB- Silica master batch with soap solution

Ingredients	Amount
LATZ latex (0.3%)	250 g
ISAF black	45 g
Precipitated silica	5 g
Alkaline solution	3.5 ml
Soap solution	2 ml
Water	948 ml

3.3. Preparation of NR- Carbon black and silica master batch using with surfactants SI and S2

3.3.1. Preparation for filler dispersion slurry

5% Filer dispersion slurry of carbon black and precipitated silica was prepared by using a ball milling technique rotating at high speed for about 24 hours in presence of surfactants S1 and S2.

This dispersion slurry was added slowly in to fresh natural rubber latex under stirring and coagulated to produce carbon black master batch. This coagulum was pressed mechanically to effect uniform coagulation of latex – carbon black slurry. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet master batch and dried in an air oven maintained at 70^0 C to get the latex filler master batch.

The preparation of master batches with S1 and S2 were separately and dried at 70^0 C in air oven and finally labeled.

Table: 3.2. Formulation for NR-CB- Silica master batches with surfactants: S1and S2

Ingredients	Surfactant S1	Surfactant S2
LATZ latex (0.3%)	250 g	250 g
ISAF black	45 g	45 g
Precipitated silica	5 g	5 g
Alkaline solution	3.5 ml	3.5 ml
Surfactants	12 ml	18 ml
Water	938 ml	932 ml

3.3.2. Compounding for carbon black/ silica master batch with soap solution and surfactants by two roll mill

Table: 3.3.Formulation for compounding of NR- CB- Silica master batch with soap solution

Ingredients	Phr (g)	Amount (g)
Master batch	150	450
Zno	5	15
Stearic acid	1.5	4.5
Mernox 6C	2.0	6.0
Naphthenic oil	5.0	15.0
CBS	1.5	4.5
Sulphur	1.5	4.5

The formulations employed for the study are shown in Table 1. The compounding of NR was done on open two roll mill.

The same formulation and procedure followed to prepare the compounding of remaining two master batches (S1 and S2).

3.4. Preparation of Control specimen (Dry- mix)

About 2 liters of LATZ latex is added in clean rectangular tray. Then sufficient quantity of water and formic acid are added to produce coagulated latex. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet raw rubber and dried in an air oven maintained at 70^0 C to get the dried raw natural rubber.

3.4.1. Compounding for control specimen

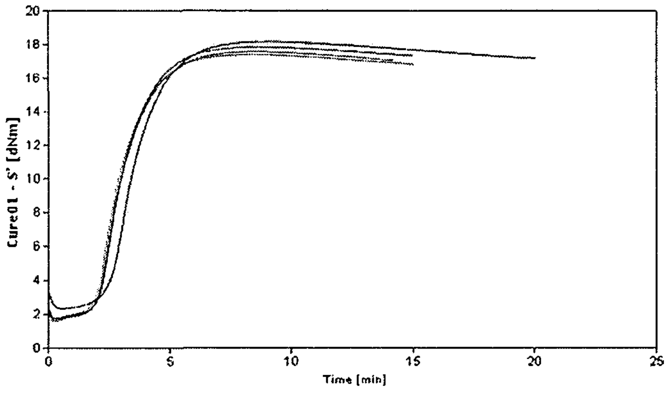
Table: 3.4.Formulation for compounding of control specimen

Ingredients	Phr (g)	Amount (g)
Natural rubber	100	300
ISAF black	45	135
Precipitated silica	5.0	15
ZnO	5.0	15
Stearic acid	1.5	4.5
Mernox 6C	2.0	6.0
Napthenic oil	5.0	15
CBS	1.5	4.5
Sulphur	1.5	4.5

The formulations employed for the study are shown in Table 2. The compounding of NR was done on a two roll open mill.

3.5. Cure characteristics

Cure characteristics were obtained by using Rubber processing analyzer at temperature of 150^0 C. The resulting values are given below:



1. Cure characteristics graph

Table: 3.5. Results for cure characteristics

Sample	Ts_2(mint)	T_c90(mint)	T_c95(mint)	MH(dn-m)	ML(dn-m)	MH-ML
Control (Black)	2.62	5.29	6.01	18.178	2.316	15.862
S (Blue)	2.21	4.78	5.50	17.864	1.718	15.922
S1 (Red)	2.15	4.80	5.51	17.576	1.573	16.003
S2 (Green)	2.09	4.67	5.38	17.407	1.728	15.679

3.6. Preparation of Test Specimen

The test specimens for the physical property determination were prepared by vulcanizing the blanks cut from un-vulcanized rubber compound sheets marked with mill direction, at a temperature of 150^0C by compression molding in an electrically heated hydraulic press. The molded samples after curing were quickly cooled and stored for 24 h before tests.

3.7. Mechanical properties

In general the vulcanizates prepared from the latex based master batches shows higher modulus, tensile strength, hardness, tear strength, poor compression set, slightly higher heat buildups, more abrasion losses than the vulcanizate prepared from the control dry rubber based vulcanizate.

Table: 3.6. Mechanical properties of master batches and control specimen

Parameters	**S**	**S1**	**S2**	**Control**
Tensile strength (Mpa)	24.888	23.886	24.19	24.43
Elongation at break in (%)	696	674	755	699
Modulus @100% (MPa)	1.948	2.084	1.908	1.876
Modulus @200% (MPa)	4.340	4.434	3.980	3.992
Modulus @300% (MPa)	8.218	8.116	7.244	7.166
Tear strength in N/mm	114	135	130	114
Hardness (Shore A)	62	62	61	59
Compression Set in (%)	39	47	40	38
Heat buildup, $\Delta T(^0C)$	21	20	22	17
Abrasion loss (mm^3)	110	115	114	104

3.8. Cut growth resistance

The Cut growth resistance of the vulcanizates were determined using De Mattia flexing machine. The resulting values are given below:

Table: 3.7. Cut- growth results for master batches and control specimen

Samples	Control	S1	S2	S
1.Cut growth develop up to 12.5mm (No. of counts)	16757	22023	139007	123486
2. Cut growth develop up to 12.5mm (No. of counts)	20139	231588	151539	257193

Latex based master batches shows more resistance from the dry rubber based control specimen.

3.9. Flexing Resistance

The flex resistances of the vulcanizates were determined using De Mattia felxing machine as per ASTM D 813-95. The resulting values are given below:

Table: 3.8. Flexing resistance results for master batches and control specimen

Samples	Control	S1	S2	S
Initial crack observation (No. of counts)	49007	126476	126476	126476
Final crack observation (No. of counts)	143978	554960	557613	668130

Latex based master batches shows more flexing resistance from the dry rubber based control specimen.

CHAPTER-IV

CARBON BLACK/SILICA MASTER BATCH WITH S2 SURFACTANT FROM PRESERVED FIELD LATEX

CHAPTER-IV

4. CARBON BLACK/SILICA MASTER BATCH WITH S2 SURFACTANT FROM FRESH LATEX

4.1. DRC determination

Preserved natural rubber latex of dry rubber content (DRC) 39.00% was used in the investigation.

4.2. Preparation for filler dispersion slurry

5% Filer dispersion slurry of carbon black and precipitated silica was prepared by using a ball milling technique rotating at high speed for about 24 hours in the presence of S2 surfactant.

This dispersion slurry was added slowly in to fresh natural rubber latex under stirring and coagulated to produce carbon black master batch. This coagulum was pressed mechanically to effect uniform coagulation of latex – carbon black slurry. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet master batch and dried in an air oven maintained at 70^0 C to get the latex filler master batch.

Table: 4.1. Formulation for NR- CB-Silica master batch with surfactants-S2

Ingredients	Amount
LATZ latex (0.3%)	205 g
ISAF black	45 g
Precipitated silica	5 g
Alkaline solution	3.5 ml
Surfactant S2	18 ml
Water	932

4.2.1. Preparation of compounding for NR- Carbon black and silica master batch with surfactant S2 solution

Table: 4.2.Formulation for compounding of NR- CB- Silica master batch with S2 surfactant

Ingredients	Phr (g)	Amount (g)
Master batch	150	450
ISAF black	3	9
Precipitated silica	3	9
ZnO	4.5	13.5
Stearic acid	3	9
TMQ	1	3
6 PPD	2.75	8.25
TBBS	1.6	4.8
Sulphur	1.2	3.6

The formulations employed for this study are shown in Table 1. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Master batch
15	ISAF+Silica+ZnO+Stearic acid+TMQ+6PPD
120	Dump

Curing agent and accelerator were added at the end of before mixing done on to open two roll mill.

4.3. Preparation of control specimen

About 2 liters of LATZ latex is added in clean rectangular tray. Then sufficient quantity of water and formic acid are added to produce coagulated latex. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet raw rubber and dried in an air oven maintained at 70^0 C to get the dried raw natural rubber.

4.3.1. Preparation of compounding for dry rubber (control specimen)

Table: 4.3.Formulation for compounding of control specimen

Ingredients	Phr (g)	Amount (g)
Natural rubber	100	500.00
ISAF black	48	240.00
Precipitated silica	8	40.00
ZnO	4.5	22.5
Stearic acid	3.0	15.0
TMQ	1.0	5.00
6 PPD	2.75	13.75
TBBS	1.6	8.00
Sulphur	1.2	6.00

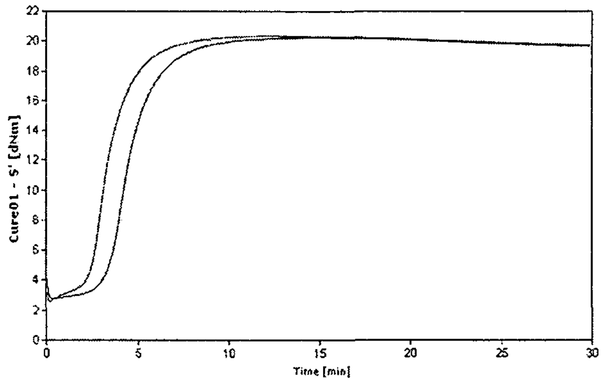
The formulations employed for this study are shown in Table 2. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Rubber
60	120 g ISAF+20 g of VN_3
120	120 g ISAF+20 g of VN_3
180	ZnO+Stearic acid+TMQ+6 PPD
240	Sweeping
300	Dump

Curing agent and accelerator were added at the end of before mixing done on to open two roll mill.

4.4. Cure characteristics

Cure characteristics were obtained by using Rubber processing analyzer at temperature of 150^0 C. The resulting values are given below:



2. Cure characteristics graph

Table: 4.4. Results for cure characteristics

Sample	Ts_2(mint)	T_c90(mint)	T_c95(mint)	MH(dn-m)	ML(dn-m)	MH-ML
Control (Black)	3.37	6.84	8.00	20.226	2.756	17.470
S2 (Blue)	2.40	5.50	6.62	20.334	2.588	17.746

4.5. Preparation of Test Specimen

The test specimens for the physical property determination were prepared by vulcanizing the blanks cut from un-vulcanized rubber compound sheets marked with mill direction, at a temperature of 150^0C by compression molding in an electrically heated hydraulic press. The molded samples after curing were quickly cooled and stored for 24 h before tests.

4.6. Mechanical properties

In general the vulcanizate prepared from the latex based master batches shows higher tensile strength, higher tear strength, modulus, hardness, poor compression set, slightly higher heat buildups, more abrasion losses than the vulcanizate prepared from the control dry rubber based vulcanizate.

Table: 4.5. Results for mechanical properties of master batches and control specimen

Tests	Surfactant-S2	Control
Tensile strength in (Mpa)	24.02	23.81
Elongation at break in (%)	579	583
Modulus @100% (MPa)	2.14	2.73
Modulus @200% (MPa)	4.80	6.14
Modulus @300% (MPa)	11.00	10.67
Tear strength in N/mm	141	120
Hardness (Shore A)	69	63
Compression Set in (%)	37	33
Heat buildup $\Delta T(^0C)$	27	21
Abrasion loss(mm^3)	132	114

4.7. Cut growth Resistance

The Cut growth resistance of the vulcanisates were determined using De Mattia flexing machine. The resulting values are given below:

Table: 4.6. Cut- Growth results for master batch and control specimen

Samples	Control	S2
1.Cut growth develop up to12.5mm (No. of counts)	12818	136239
2. Cut growth develop up to12.5mm (No. of counts)	24582	68641

Latex based master batches shows more resistance from the dry rubber based control specimen.

4.8. Flexing Resistance

The flex resistances of the vulcanisates were determined using De Mattia flexing machine as per ASTM D 813-95. The resulting values are given below:

Table: 4.7. Flexing resistance results for master batch and control specimen

Samples	Control	S2
Initial crack observation (No. of counts)	44421	128279
Final crack observation (No. of counts)	132671	365608

Latex based master batches shows more flexing resistance from the dry rubber based control specimen.

CHAPTER-V

CARBON BLACK/SILICA MASTER BATCH WITH S3 SURFACTANT FROM FRESH LATEX

CHAPTER-V

5. CARBON BLACK/SILICA MASTER BATCH WITH S3 SURFACTANT FROM FRESH LATEX

5.1. DRC determination

Preserved natural rubber latex of dry rubber content (DRC) 35.00% was used in the investigation.

5.2. Preparation for filler dispersion slurry

5% Filer dispersion slurry of carbon black and precipitated silica was prepared by using a ball milling technique rotating at high speed for about 24 hours in the presence of S3 surfactant.

This dispersion slurry was added slowly in to fresh natural rubber latex under stirring and coagulated to produce carbon black master batch. This coagulum was pressed mechanically to effect uniform coagulation of latex – carbon black slurry. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet master batch and dried in an air oven maintained at 70^0 C to get the latex filler master batch.

Table: 5.1. Formulation for NR- CB-Silica master batch with surfactant-S3

Ingredients	Amount
LATZ latex (0.3%)	229 g
ISAF black	45 g
Precipitated silica	5 g
Alkaline solution	3.5 ml
Surfactant S3	11 ml
Water	939 ml

5.2.1. Preparation of compounding for NR- Carbon black and silica master batch with surfactant S3 solution

Table: 5.2. Formulation for compounding of NR- CB- Silica master batch with surfactant- S3

Ingredients	Phr (g)	Amount (g)
Master batch	150	450
ISAF black	3	9.0
Precipitated silica	3	9.0
ZnO	4.5	13.5
Stearic acid	3	9.0
TMQ	1	3.0
6 PPD	2.75	8.25
TBBS	1.6	4.8
Sulphur	1.2	3.6

The formulations employed for this study are shown in Table 1. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Master batch
15	ISAF+Silica+ZnO+Stearic acid+TMQ+6PPD
120	Dump

Curing agent and accelerator were added at the end of before mixing done on to open two roll mill.

5.3. Preparation of control specimen

About 2 liters of LATZ latex is added in clean rectangular tray. Then sufficient quantity of water and formic acid are added to produce coagulated latex. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet raw rubber and dried in an air oven maintained at 70^0 C to get the dried raw natural rubber.

5.31. Preparation of compounding for dry rubber (control specimen)

Table: 5.3. Formulation for compounding of control specimen

Ingredients	Phr (g)	Amount (g)
Natural rubber	100	500.00
ISAF black	48	240.00
Precipitated silica	8	40.00
ZnO	4.5	22.5
Stearic acid	3.0	15.0
TMQ	1.0	5.00
6 PPD	2.75	13.75
TBBS	1.6	8.00
Sulphur	1.2	6.00

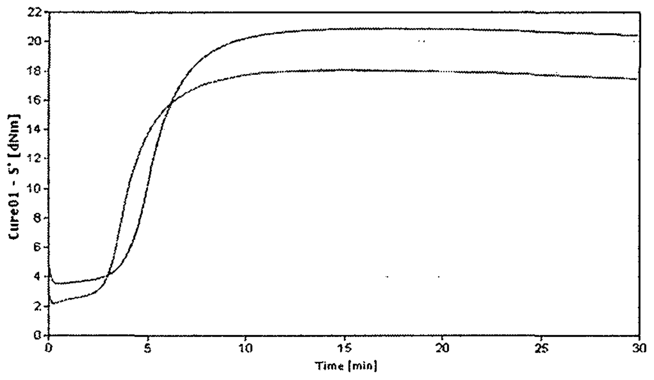
The formulations employed for this study are shown in Table 2. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Rubber
60	120 g ISAF+20 g of VN_3
120	120 g ISAF+20 g of VN_3
180	ZnO+Stearic acid+TMQ+6 PPD
240	Sweeping
300	Dump

Curing agent and accelerator were added at the end of before mixing done on to open two roll mill.

5.4. Cure characteristics

Cure characteristics were obtained by using Rubber processing analyzer at temperature of 150^0 C. The resulting values are given below:



3. Cure characteristics graph

Table: 5.4. Results for cure characteristics

Sample	Ts_2(mint)	T_c90(mint)	T_c95(mint)	MH(dn-m)	ML(dn-m)	MH-ML
Control (Black)	3.98	8.10	9.42	20.893	3.534	17.360
S3 (Blue)	3.03	6.97	8.40	18.092	2.195	15.897

5.5. Preparation of Test Specimen

The test specimens for the physical property determination were prepared by vulcanizing the blanks cut from un-vulcanized rubber compound sheets marked with mill direction, at a temperature of 150^0C by compression molding in an electrically heated hydraulic press. The molded samples after curing were quickly cooled and stored for 24 h before tests.

5.6. Mechanical properties

In general the vulcanizate prepared from the latex based master batches shows higher tensile strength, equal tear strength, lower modulus, hardness, poor compression set, slightly higher heat buildups, better abrasion resistance than the vulcanizate prepared from the control dry rubber based vulcanizate.

Table: 5.5. Results for mechanical properties of master batch and control specimen

Tests	S3	Control
Tensile strength in (Mpa)	26.48	26.45
Elongation at break in (%)	629	555
Modulus @100%	2.29	2.95
Modulus @200%	5.38	7.07
Modulus @300%	10.09	12.56
Tear strength in N/mm	121	121
Hardness (Shore A)	64	63
Compression Set in (%)	32	29
Heat buildup	21	22
Abrasion resistance	114	114

5.7. Cut growth Resistance

The Cut growth resistance of the vulcanisates were determined using De Mattia flexing machine. The resulting values are given below:

Table: 5.6. Cut- Growth results for master batch and control specimen

Samples	Control	S3
1.Cut growth develop up to 12.5mm (No. of counts)	18426	47253
2. Cut growth develop up to 12.5mm (No. of counts)	28712	69249

Latex based master batches shows more resistance from the dry rubber based control specimen.

5.8. Flexing Resistance

The flex resistances of the vulcanisates were determined using De Mattia flexing machine as per ASTM D 813-95. The resulting values are given below:

Table: 5.7. Flexing resistance results for master batch and control specimen

Samples	Control	S3
Initial crack observation (No. of counts)	36717	63405
Final crack observation (No. of counts)	75220	123653

Latex based master batches shows more flexing resistance from the dry rubber based control specimen.

CHAPTER-VI

CARBON BLACK/SILICA MASTER BATCHES WITH S2 AND S3 SURFACTANT FROM FRESH LATEX

CHAPTER-VI

6. CARBON BLACK/SILICA MASTER BATCHES WITH S2 AND S3 SURFACTANT FROM FRESH LATEX

6.1. DRC determination

Preserved natural rubber latex of dry rubber content (DRC) 34.00% was used in the investigation.

6.2. Preparation for filler dispersion slurry

5% Filer dispersion slurry of carbon black and precipitated silica was prepared by using a ball milling technique rotating at high speed for about 24 hours in presence of surfactants S2 and S3.

This dispersion slurry was added slowly in to fresh natural rubber latex under stirring and coagulated to produce carbon black master batch. This coagulum was pressed mechanically to effect uniform coagulation of latex – carbon black slurry. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet master batch and dried in an air oven maintained at 70^0 C to get the latex filler master batch.

The preparation of master batches with S2 and S3 were separately and dried at 70^0 C in air oven and finally labeled.

Table: 6.1. Formulation for NR-CB- Silica master batches with surfactants-S2and S3

Ingredients	Surfactant S2	Surfactant S3
LATZ latex (0.3%)	235 g	235 g
ISAF black	45 g	45 g
Precipitated silica	5 g	5 g
Alkaline solution	3.5 ml	3.5 ml
Surfactants	18 ml	11 ml
Water	932 ml	939 ml

6.2.1. Preparation of compounding for NR- Carbon black and silica master batch with SAL and SAS solution

Table: 6.2.Formulation for compounding of NR- CB- Silica master batch with S2 and S3 solution.

Ingredients	Phr	S2 Master batch Amount (g)	S3 Master Batch Amount(g)
Master batch	150	450	450
ISAF black	3.0	9.0	9.0
Precipitated silica	3.0	9.0	9.0
ZnO	4.5	13.5	13.5
Stearic acid	3	9.0	9.0
TMQ	1	3.0	3.0
6 PPD	2.75	8.25	8.25
TBBS	1.6	4.8	4.8
Sulphur	1.2	3.6	3.6

The formulations employed for the study are shown in Table 1. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Master batch
15	ISAF+Silica+ZnO+Stearic acid+TMQ+6PPD
120	Dump

Curing agent and accelerator were added at the end of before mixing done on open two roll mill.

6.3. Preparation of control specimen

About 2 liters of LATZ latex is added in clean rectangular tray. Then sufficient quantity of water and formic acid are added to produce coagulated latex. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet raw rubber and dried in an air oven maintained at 70^0 C to get the dried raw natural rubber.

6.3.1. Preparation of compounding for Control specimen

Table: 6.3.Formulation for compounding of control specimen

Ingredients	Phr (g)	Amount (g)
Natural rubber	100	500.00
ISAF black	48	240.00
Precipitated silica	8	40.00
ZnO	4.5	22.5
Stearic acid	3.0	15.0
TMQ	1.0	5.00
6 PPD	2.75	13.75
TBBS	1.6	8.00
Sulphur	1.2	6.00

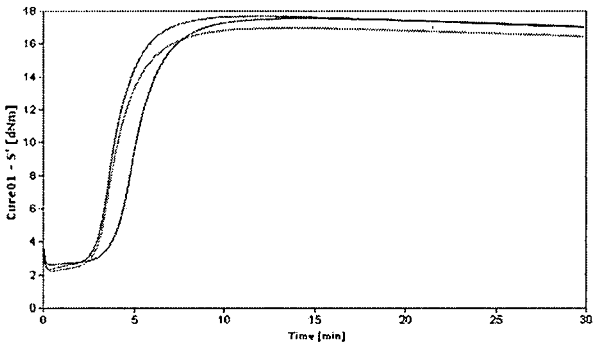
The formulations employed for the study are shown in Table 2. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Rubber
60	120 g ISAF+20 g of VN_3
120	120 g ISAF+20 g of VN_3
180	ZnO+Stearic acid+TMQ+6 PPD
240	Sweeping
300	Dump

Curing agent and accelerator were added at the end of before mixing done on open two roll mill.

6.4. Cure characteristics

Cure characteristics were obtained by using Rubber processing analyzer at temperature of 150^0 C. The resulting values are given below:



4. **Cure characteristics graph**

Table: 6.4. Results for cure characteristics

Sample	Ts_2(mint)	T_c90(mint)	T_c95(mint)	MH(dn-m)	ML(dn-m)	MH-ML
Control (Black)	4.03	7.41	8.48	17.564	2.615	14.949
S2 (Blue)	3.03	5.95	6.90	17.700	2.34	15.360
S3 (Green)	3.11	6.41	7.58	16.993	2.21	14.783

6.5. Preparation of Test Specimen

The test specimens for the physical property determination were prepared by vulcanizing the blanks cut from un-vulcanized rubber compound sheets marked with mill direction, at a temperature of 150^0C by compression molding in an electrically heated hydraulic press. The molded samples after curing were quickly cooled and stored for 24 h before tests.

6.6. Mechanical properties

In general the vulcanizate prepared from the latex based master batches shows higher tensile strength, equal tear strength, lower modulus, hardness, poor compression set, slightly higher heat buildups, little higher abrasion losses than the vulcanizate prepared from the control dry rubber based vulcanizate.

Table: 6.5. Results for mechanical properties of master batches and control specimen

Tests	S2	S3	Control
Tensile strength in (Mpa)	25.32	24.73	24.28
Elongation at break in (%)	548	538	526
Modulus @100%	2.72	2.38	2.65
Modulus @200%	6.48	6.03	6.55
Modulus @300%	12.01	11.7	11.90
Tear strength in N/mm	123	136	142
Hardness (Shore A)	66	65	63
Compression Set in (%)	38	39	34
Heat buildup	24	26	21
Abrasion resistance	116	116	114

6.7. Cut growth Resistance

The Cut growth resistance of the vulcanisates were determined using De Mattia flexing machine. The resulting values are given below:

Table: 6.6.Cut- Growth resistance results for master batches and control specimen

Samples	Control	S2	S3
1.Cut growth develop up to 12.5mm (No. of counts)	39684	178012	128729
2. Cut growth develop up to 12.5mm (No. of counts)	44201	217617	159468

Latex based master batches shows more cut growth resistance from the dry rubber based control specimen.

6.8. Flexing Resistance

The flex resistances of the vulcanisates were determined using De Mattia flexing machine as per ASTM D 813-95. The resulting values are given below:

Table: 6.7. Flexing resistance results for master batch and control specimen

Samples	Control	S2	S3
Initial crack observation (No. of counts)	23426	61126	44254
Final crack observation (No. of counts)	90763	241757	293846

Latex based master batches shows more flexing resistance from the dry rubber based control specimen.

6.9. Dynamic mechanical properties

Damping characteristics from 30 to 100^0 C for the vulcanizate prepared from the preserved field natural rubber latex based masterbatch and dry natural rubber based vulcanizate. For masterbatch vulcanizates there is a lowering of the tan delta peak height compared to the dry rubber vulcanizates indicating stiffening as a result of better polymer filler interaction of the masterbatch as compared to the dry rubber based vulcanizates.

It is observed that a lower tan delta at 60^0 C is obtained for the masterbatch compared to the control.

Table: 6.8. Results for Tan delta values at 60^0 C

Samples	Tan delta at 60^0 C
S2	0.1418
S3	0.1438
Control	0.1513

6.10. Filler dispersion characteristics

- **Dispersion grading by using disper grader**

The filler dispersion of the vulcanizate prepared from natural rubber latex based masterbatch and dry rubber based vulcanizate. The results show that better dispersion of the filler particles is shown by masterbatch vulcanizates and the dry rubber based vulcanizates is almost similar.

The details of the sample results given in table 6.9:

Sample name	Filler dispersion (X)	Agglomerate dispersion (Y)	% of filler dispersion
S2	8.48	9.68	97.24
S3	8.04	9.89	99.48
Control	8.23	9.9	99.18

CHAPTER-VII

CARBON BLACK/SILICA MASTER BATCHES WITH OUT SURFACTANT FROM FRESH LATEX

CHAPTER-VII

7. CARBON BLACK/SILICA MASTER BATCHES WITH OUT SURFACTANT FROM FRESH LATEX

7.1. DRC determination

Preserved natural rubber latex of dry rubber content (DRC) 38.30% was used in the investigation.

7.2. Preparation for filler dispersion slurry

5% Filer dispersion slurry of carbon black and precipitated silica was prepared by using a ball milling technique rotating at high speed for about 24 hours for without surfactant. This dispersion slurry was added slowly in to fresh natural rubber latex under stirring and coagulated by the addition of formic acid to produce carbon black master batch. This coagulum was pressed mechanically to effect uniform coagulation of latex – carbon black slurry. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet master batch and dried in an air oven maintained at 70^0 C to get the latex filler master batch.

Table: 7.1. Formulation for NR-CB- Silica master batch without surfactant

Ingredients	Amount
LATZ latex (0.3%) (09-02-17)	209 g
ISAF black	45 g
Precipitated silica	5 g
Alkaline solution	3.5 ml
Water	950 ml

7.2.1. Preparation of compounding for NR- Carbon black and silica master batch without surfactant by internal mixer

Table: 7.2.Formulation for compounding of NR- CB- Silica master batch without surfactant

Ingredients	Phr (g)	Amount (g)
Master batch	150	450
ISAF black	3	9
Precipitated silica	3	9
ZnO	4.5	13.5
Stearic acid	3	9
TMQ	1	3
6 PPD	2.75	8.25
TBBS	1.6	4.8
Sulphur	1.2	3.6

The formulations employed for the study are shown in Table 1. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Master batch
15	ISAF+ Silica+ ZnO+ Stearic acid+TMQ+6PPD
120	Dump

Curing agent and accelerator were added at the end of before mixing done on open two roll mill.

7.3. Preparation of control specimen

About 2 liters of LATZ latex is added in to clean rectangular tray. Then sufficient quantity of water and formic acid are added to produce coagulated latex. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet raw rubber and dried in an air oven maintained at 70^0 C to get the dried raw natural rubber.

7.3.1. Preparation of compounding for Control specimen

Table: 7.3.Formulation for compounding of control specimen

Ingredients	Phr (g)	Amount (g)
Natural rubber	100	500.00
ISAF black	48	240.00
Precipitated silica	8	40.00
ZnO	4.5	22.5
Stearic acid	3.0	15.0
TMQ	1.0	5.00
6 PPD	2.75	13.75
TBBS	1.6	8.00
Sulphur	1.2	6.00

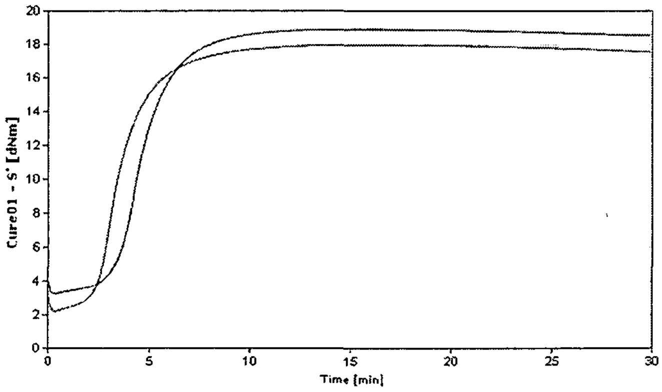
The formulations employed for the study are shown in Table 2. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Rubber
60	120 g ISAF+20 g of VN_3
120	120 g ISAF+20 g of VN_3
180	ZnO+ Stearic acid+TMQ+6 PPD
240	Sweeping
300	Dump

Curing agent and accelerator were added at the end of before mixing done on open two roll mill.

7.4. Cure characteristics

Cure characteristics were obtained by using Rubber processing analyzer at temperature of 150^0 C. The resulting values are given below:



5. Cure characteristics graph

Table: 7.4. Results for cure characteristics

Sample	**Ts_2(mint)**	**T_c90(mint)**	**T_c95(mint)**	**MH(dn-m)**	**ML(dn-m)**	**MH-ML**
Control (Black)	3.44	7.09	8.28	18.902	3.268	15.634
FLWOS (Blue)	2.55	6.18	7.64	17.977	2.208	15.769

7.5. Preparation of Test Specimen

The test specimens for the physical property determination were prepared by vulcanizing the blanks cut from un-vulcanized rubber compound sheets marked with mill direction, at a temperature of 150^{0}C by compression molding in an electrically heated hydraulic press. The molded samples after curing were quickly cooled and stored for 24 h before tests.

7.6. Mechanical properties

In general the vulcanizate prepared from the latex based master batches shows higher tensile strength, less tear strength, higher modulus, hardness, poor compression set, less low heat buildups, abrasion losses than the vulcanizate prepared from the control dry rubber based vulcanizate.

Table: 7.5. Results for mechanical properties of master batch and control specimen

Tests	FLWOS	Control
Tensile strength in (Mpa)	27.27	24.28
Elongation at break in (%)	523	526
Modulus @100%	3.02	2.65
Modulus @200%	6.83	6.55
Modulus @300%	12.92	11.90
Tear strength in N/mm	129	142
Hardness (Shore A)	63	63
Compression Set in (%)	37	34
Heat buildup	22	21
Abrasion resistance	114	114

7.7. Cut growth Resistance

The Cut growth resistance of the vulcanisates were determined using De Mattia flexing machine. The resulting values are given below:

Table: 7.6. Cut- Growth results for master batch and control specimen

Samples	FLWOS	Control
1.Cut growth develop up to12.5mm (No. of counts)	71489	39684
2. Cut growth develop up to 12.5mm (No. of counts)	86092	44201

Latex based master batches shows more cut growth resistance from the dry rubber based control specimen.

7.8. Flexing Resistance

The flex resistances of the vulcanisates were determined using De Mattia flexing machine as per ASTM D 813-95. The resulting values are given below:

Table: 7.7. Flexing resistance results for master batch and control specimen

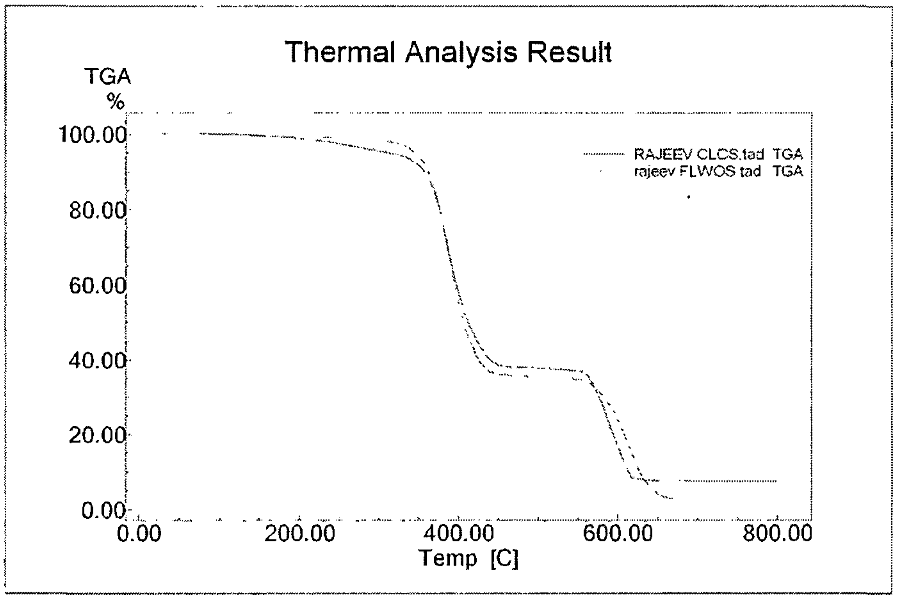
Samples	FLWOS	Control
Initial crack observation (No. of counts)	72486	23426
Final crack observation (No. of counts)	358011	90763

Latex based master batches shows more flexing resistance from the dry rubber based control specimen.

7.9. Thermogravimetric analysis (TGA)

This technique employs a thermo-balance (Sensitivity of 0.1 micrograms, accuracy ±1%), which continuously measures the change in sample weight with respect to temperature (at a controlled rate of heating or cooling) and time (in isothermal mode) in a specified environment. The observed weight loss in the polymer can be the result of volatile products formed by thermal degradation. The gravimetric estimation of moisture, volatile ingredients and inert or thermally stable additives in a polymer can be easily estimated by this technique. TGA of the fillers and composition were done from 30 to 800^0 C in nitrogen atmosphere at a heating rate of 20^0 C/min using TA instruments (TGA 60 from Shimadzu Instrument, Japan). The thermograms were obtained by plotting weight loss against temperature using TA instruments Universal analysis software.

The thermograms of the vulcanizates prepared from the preserved natural rubber latex based masterbatch and by dry rubber based vulcanizate are shown in fig7.1. The results are tabulated in table. The results show that the thermal stability of vulcanizates prepared from the preserved natural rubber latex masterbatch and dry rubber based vulcanizate is almost similar.



6. **Thermogravimetric analysis graph.**

Table: 7.8. Results of Weight loss of the masterbatches

Masterbatches	Weight Loss (%)			
	Volatile matter	Polymer	Filler	Ash
S	1.824	61.828	33.957	2.391
S1	2.006	60.947	31.153	5.894
S2	3.684	57.408	31.823	7.085
S3	1.150	63.537	31.765	3.548
FLWOS	1.481	63.950	30.673	3.896
Control	3.758	57.258	30.825	8.159

CHAPTER-VIII

CARBON BLACK/SILICA MASTER BATCHES WITH S3 SURFACTANT FROM CENTRIFUGING LATEX

CHAPTER-VIII

8. CARBON BLACK/SILICA MASTER BATCHES WITH S3 SURFACTANT FROM CENTRIFUGING LATEX

8.1. DRC determination

Preserved centrifuging natural rubber latex of dry rubber content (DRC) 60.00% was used in the investigation.

8.2. Preparation for filler dispersion slurry

5% Filer dispersion slurry of carbon black and precipitated silica was prepared by using a ball milling technique rotating at high speed for about 24 hours in presence of surfactants S3.

This dispersion slurry was added slowly in to centrifuged natural rubber latex under stirring and coagulated by the addition of formic acid to produce carbon black master batch. This coagulum was pressed mechanically to effect uniform coagulation of latex – carbon black slurry. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet master batch and dried in an air oven maintained at 70^0 C to get the latex filler master batch.

Table: 8.1. Formulation for centrifuged NR latex-CB- Silica master batch with S3 surfactant

Ingredients	Amount
Centrifuged latex	134 g
ISAF black	45 g
Precipitated silica	5 g
Alkaline solution	3.5 ml
S3 Surfactant	11 ml
Water	939 ml

8.2.1. Preparation of compounding for centrifuging latex- Carbon black and silica master batch with SAS solution by internal mixer

Table: 8.2.Formulation for compounding of centrifuging latex- C- silica master batch with SAS solution

Ingredients	Phr (g)	Amount (g)
Master batch	150	450
ISAF black	3	9
Precipitated silica	3	9
ZnO	4.5	13.5
Stearic acid	3	9
TMQ	1	3
6 PPD	2.75	8.25
TBBS	1.6	4.8
Sulphur	1.2	3.6

The formulations employed for the study are shown in Table 2. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Master batch
15	ISAF+ Silica+ ZnO+ Stearic acid+TMQ+6PPD
120	Dump

Curing agent and accelerator were added at the end of before mixing done on open two roll mill.

8.3. Preparation of dry rubber from centrifuging latex

About 1 liter of centrifuging latex is added in to clean rectangular tray. Then sufficient quantity of water and formic acid are added to produce coagulated latex. This coagulum was washed well to remove acid and passed through rubber roller to get crepe sheet of wet raw rubber and dried in an air oven maintained at 70^0 C to get the dried raw natural rubber.

8.3.1. Preparation of compounding for centrifuging latex dry mix by internal mixer

Table: 8.3.Formulation for compounding of centrifuging latex control specimen

Ingredients	Phr (g)	Amount (g)
Natural rubber	100	500.00
ISAF black	48	240.00
Precipitated silica	8	40.00
ZnO	4.5	22.5
Stearic acid	3.0	15.0
TMQ	1.0	5.00
6 PPD	2.75	13.75
TBBS	1.6	8.00
Sulphur	1.2	6.00

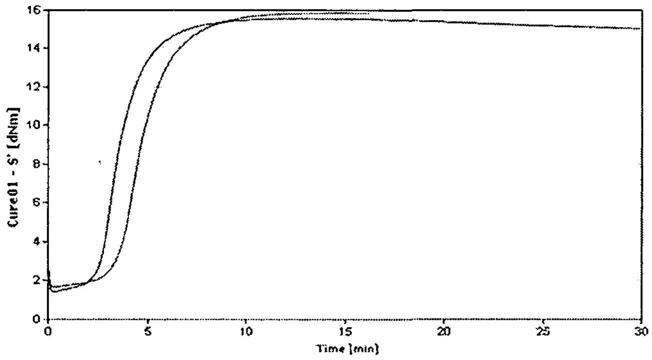
The formulations employed for the study are shown in Table 3. The compounding of NR was done on an internal mixer. For making compound the following mixing sequences are as follows:

Time (Seconds)	Ingredients
0	Rubber
60	120 g ISAF+20 g of VN_3
120	120 g ISAF+20 g of VN_3
180	ZnO+ Stearic acid+TMQ+6 PPD
240	Sweeping
300	Dump

Curing agent and accelerator were added at the end of before mixing done on open two roll mill.

8.4. Cure characteristics

Cure characteristics were obtained by using Rubber processing analyzer (RPA) at temperature of 150^0 C. The resulting values are given below:



7. **Cure characteristic graph**

Table: 8.4. Results for cure characteristics

Sample	Ts_2(mint)	T_c90(mint)	T_c95(mint)	MH(dn-m)	ML(dn-m)	MH-ML
CLSAS (Black)	3.52	5.59	6.67	15.560	1.428	14.132
CLCS (Blue)	4.03	7.07	8.20	15.882	1.670	14.212

8.5. Preparation of Test Specimen

The test specimens for the physical property determination were prepared by vulcanizing the blanks cut from un-vulcanized rubber compound sheets marked with mill direction, at a temperature of 150^0C by compression molding in an electrically heated hydraulic press. The molded samples after curing were quickly cooled and stored for 24 hrs before tests.

8.6. Mechanical properties

In general the vulcanizate prepared from the latex based master batches shows higher tensile strength, lower tear strength, higher modulus, higher hardness, higher compression sets, lower heat buildups, little higher abrasion losses than the vulcanizate prepared from the control dry rubber based vulcanizate.

Table: 8.5. Results for mechanical properties of master batch and control specimen

Tests	CLSAS	CLCS
Tensile strength in (Mpa)	26.10	25.29
Elongation at break in (%)	468	498
Modulus @100%	3.42	3.27
Modulus @200%	8.46	7.59
Modulus @300%	15.26	13.47
Tear strength in N/mm	112	117
Hardness(Shore A)	63	61
Compression Set in (%)	38.94	38.01
Heat buildup	22	22
Abrasion resistance	117	107

8.7. Cut growth Resistance

The Cut growth resistance of the vulcanisates were determined using De Mattia flexing machine. The resulting values are given below:

Table: 8.6. Cut- Growth results for master batch and control specimen

Samples	CLSAS	CLCS
1.Cut growth develop up to12.5mm (No. of counts)	98952	303354
2. Cut growth develop up to 12.5mm (No. of counts)	141637	237446

Latex based master batches shows less cut growth resistance from the dry rubber based control specimen.

8.8. Flexing Resistance

The flex resistances of the vulcanisates were determined using De Mattia flexing machine as per ASTM D 813-95. The resulting values are given below:

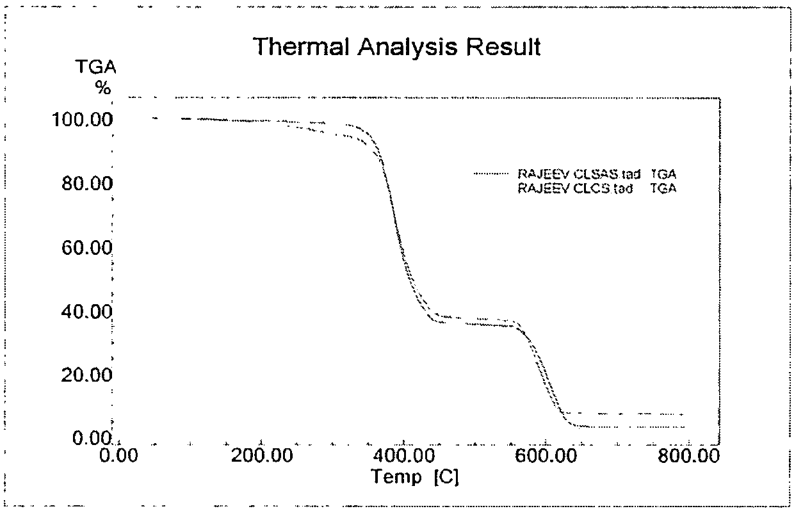
Table: 8.7. Flexing resistance results for master batch and control specimen

Samples	CLSAS	CLCS
Initial crack observation (No. of counts)	72486	83271
Final crack observation (No. of counts)	225750	541233

Latex based master batches shows less flexing resistance from the dry rubber based control specimen.

8.9. Thermogravimetric analysis (TGA)

The thermograms of the vulcanizates prepared from the preserved centrifuged natural rubber latex based master batch and dry rubber (Control specimen) based vulcanizate are shown in fig: 8.1. The results shows that the thermal stability of vulcanizates prepared from the preserved natural rubber latex based master batch and the dry rubber based vulcanizates is almost similar.



8. Thermogarvimetric analysis graph.

Table: 8.8. Results of weight loss of the masterbatches

Masterbatches	Weight Loss (%)			
	Volatile matter	Polymer	Filler	Ash
CLSAS	1.094	63.883	31.809	3.214
CLCS	1.092	62.285	29.949	6.674

8.10. Mooney Viscosity

The Mooney viscosity of the rubber samples were measured using Mooney viscosity (Mooney MV 2000 ALPHA Technologies, Akron, USA), which is designed for measuring the 'shearing viscosity' of polymers and compounds by a rotating disc in a cylindrical cavity set at 135^0 C as per ASTM D1646 (2007) (103). The results of samples were expressed as ML (1+4) at 135^0C.

The results for Mooney viscosities of masterbatches are given in table: 8.9.

Sample	**S3**	**FLWOS**	**Control**
Masterbatch raw rubber	63.20	155	78.1
Compounded masterbatch	43.5	35.60	33.30

CHAPTER-IX

CONCLUSIONS

CHAPTER-IX

CONCLUSIONS

In present study Natural rubber latex carbon black masterbatch were prepared by wet masterbatch technique used with different surfactants by the addition of acids. During this process, carbon black incorporation, dispersion, and distribution are completed in a very short period of time. It has been found that this wet masterbatch technique offers the following benefits over the conventional dry mixing:

- ✓ Simplified mixing procedure.
- ✓ Environment friendly operation
- ✓ Reduced mixing costs due to reduced mixing equipment, energy and labour;
- ✓ Elimination of free carbon black handling and reduced dust emission;
- ✓ Excellent dispersion of fillers;
- ✓ Improved vulcanizate Properties.

A modified coagulation process of natural rubber latex provides a method to produce fresh natural rubber latex / carbon black/ silica masterbatches with very good mechanical and dynamic properties. The filler masterbatch prepared by this method shows a higher level of vulcanization along with better filler dispersion compared to conventionally prepared mixes.

Cut-growth resistance and flex-fatigue life of the vulcanizates are significantly improved over their dry mixed vulcanizates.

This is a simpler and cheaper method of master batch preparation as compared to the conventional dry mixes.

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