SILICA FILLED NATURAL RUBBER COMPOSITES THROUGH LATEX / SILICA MASTERBATCH TECHNIQUE

Submitted for the Partial Fulfillment of the Requirements for the award of the
Degree of M. Tech Polymer Science and Technology

By

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November 2014

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RUBBER RESEARCH INSTITUTE OF INDIA

Kottayam, India.

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भारतीय रबड़ गवेषण संस्थान
रबड़ बोर्ड, वाणिज्य एवं उद्योग मंत्रालय, भारत सरकार

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

Ref: RT/Res/ Proj/1 5/11/14

CERTIFICATE*

This is to certify that Ms. Chinnu M. Paul has carried out her project work on *"Silica Filled Natural Rubber Composites through Latex / Silica Masterbatch Technique"* under my supervision for the partial fulfillment of the award of M. Tech. Polymer Science and Technology from School of Chemical Sciences, Mahatma Gandhi University, Kottayam. Ms Chinnu has worked on this topic from 21st November 2013 to 5th November 2014. The present work or any part thereof has not been submitted for the 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*The research topic and the data given in this thesis being a subject matter for patenting, this should not be published as an open document without the consent of Rubber Research Institute of India.

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CERTIFICATE

This is to certify that Ms. Chinnu M. Paul carried out her M. Tech. project work on ***"Silica Filled Natural Rubber Composites through Latex / Silica Masterbatch Technique"*** at Rubber Technology Division, RRII, Kottayam, for the partial fulfillment of the award of M. Tech. Polymer Science and Technology from School of Chemical Sciences, Mahatma Gandhi University, Kottayam.

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Acknowledgement

I am grateful to Dr. James Jacob, Director of Research, Dr. Rosamma Alex, Deputy Director, Rubber Technology Division, Rubber Research Institute of India, Kottayam for allowing me to do the project at RRII and also providing me the necessary facilities for completion of the work. Also I thank almighty god for his blessings, which helped me in completing this dissertation. I would like to express my deep felt gratitude to Dr. Suresh Mathew , Director of School of chemical science ,, M G University Kottayam for the valuable help and encouragement..

I would like to express my deep felt gratitude to Dr. Sabu Thomas, Director of Centre for Nano Science and Technology,, M G University Kottayam for the valuable help and encouragement given for doing this work at RRII, Kottayam..

I express my deep sense of gratitude to Dr.Jacob K. Varkey, Principal Scientist, Rubber Technology Division, Rubber Research Institute of India, Kottayam for his inspiring guidance and valuable suggestions as well as his ceaseless encouragement through out the course of work.

I express my sincere gratitude to all scientists and staff of RT division especially to Dr. Benny george, Mr.Joy Joseph, Mr. K.N. Madhusoodanan , Mr. S.N. Sajeev, Dr.Manoj Kurian Mr.C.Madheswaran, Mrs. Susamma Joseph, Treasa Cherian ,Valsa George, Dr. Geetha for their assistance at various stages of this project. I would also acknowledge with thanks the service rendered by the RRII library

I convey my gratefulness for the prayers and encouragement of my parents and friends during the entire course of the work.

Chinnu M. Paul

Declaration

I hereby declare that the project work entitled "***Silica Filled Natural Rubber Composites through Latex / Silica Masterbatch Technique***" was carried out by me under the supervision of Dr. Jacob K. Varkey, Principal Scientist, Rubber Technology Division, RRII, Kottayam -686009, Kerala, during the period 21st November 2013 to 5th November 2014 as a partial fulfillment of the award of the degree of M. Tech Polymer Science and Technology. The contents of the thesis have not been submitted and will not be submitted to any other Institute or University for the award of any degree or diploma.

Chinnu M. Paul

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CHAPTER -1

INTRODUCTION

INTRODUCTION

Rubber technology is passing through a major paradigmatic change due to the replacement of carbon black by silica. Silica is now one of the most commonly used reinforcing fillers, since it enhances the performance of highly technical rubber products, especially tires and mechanical rubber goods. It not only improves tear strength and abrasion resistance but also reduces rolling resistance in tires when compared to the traditional carbon black [1–3].

However, a major drawback of using silica is difficulties in processing that come from the polarity difference between silica and rubber. Conventional mixing of rubber with silica is a time and energy consuming process, where silica aggregates are dispersed throughout the rubber matrix. Therefore, several attempts have been made to develop methods to enhance the dispersion of silica in the rubber. These include the addition of dispersing agents, such as silane and glycol derivatives, and in-situ generated silica Nanoparticles prepared by a sol–gel method with silane precursor [2–5]. Furthermore, the addition of silane coupling agent into the rubber compound containing silica synthesized from the sol–gel technique to enhance Rubber–Filler interaction has been reported [6]. Although, improvement of the mechanical properties of rubber vulcanizates is observed, the sol–gel technique is relatively expensive and rather complicated for manufacturing. Utilization of silica/rubber masterbatch is another means to achieve good dispersion of silica in the rubber, thus resulting in better mechanical properties of the vulcanizates.

Additionally, the loss of silica and its contamination in the workplace are also prevented during conventional mixing. Both solid and latex forms of the rubber used for preparing silica/rubber masterbatch prior to compounding have been reported [7–9]. Although, the wet masterbatch method gives relatively low dust exposure and consumes lower compounding energy, the addition of as-received silica into the latex leads to poor silica distribution. This is because silica has a tendency to associate with the aqueous medium and form agglomerates. This results in an obvious reduction in the mechanical properties of vulcanizates. Therefore, it is necessary to prepare a well-dispersed silica suspension before adding into the latex.

In this work the silica dispersion was prepared by mixing silica in water in the presence of soap. After obtaining the well-dispersed silica suspension, it was added into NR latex for preparing the silica/ NR master batches which were finally dried and utilized for compounding by the conventional method. Cure characteristics, mechanical and dynamic properties of NR vulcanizates reinforced by silica were investigated and compared.

1. 1 NATURAL RUBBER

1.1.1 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% [10].

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 channeled into a container, attached to it [11].

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 neutralises 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 [11].

1.3 Processing of Latex

The latex that flows out from the rubber tree on tapping is channeled 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 [11].

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) once in a month or so. Normally, 15 to25% of the total crop constitute tree lace, shell scrap and earth scrap, together called field coagulum rubbers.

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

1.4 Anticoagulants

An anticoagulant is a chemical added to latex to prevent pre-coagulation before it is processed. A few drops of anti coagulants are previously added into coconut shells during tapping and rest amount is added into the collection buckets when it is half full. Anti coagulants are never added into empty buckets. Anti coagulants 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 [11].

1.5Marketable Forms of Natural Rubber

The important forms, in which the crop can be processed and marketed, are (1) sheet rubbers, (2) crepe rubbers, (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 colleted as field coagulum can be processed only into crepe or block rubber [11].

1.5.1 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; ribbed smoked sheets and air dried sheets (Pale Amber Un smoked Sheets). A major quantity of rubber in India (About 73%) is marketed in the sheet form at present, as it is the oldest and simplest method of processing latex into marketable form [11].

1.5.2 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

1.5.3 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 to 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 [11].

1.5.4 Preserved Field Latex

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.

1.6 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 micro organisms. Because of proliferation of micro organisms, 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 [11].

1.7 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.

1.7.1 Attributes of a preservative

- It should destroy or inactivate micro organisms.
- 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.

1.7.2 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 [11].

1.8 Latex Concentrates

About 12% of the world's NR processed in the form of latex concentrates. Concentration of latex increases the rubber content in the latex to 60% or more from an initial value of about 30 to 40% in the field latex.

1.8.1 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.

1.8.1.1 Centrifugation

Centrifuging 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 industrially is produced by centrifugation. In centrifuging, centrifugal force replaces gravitational force which brings about separation of rubber particles in creaming [11].

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 centre and the serum (Skim Latex) near the circumference from where it is withdrawn through another outlet.

1.8.1.2 Creaming

Rubber latex is a dispersion of rubber particles in an aqueous serum. In any dispersion, the dispersed particles are cream or 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% dry rubber content (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 [11].

1.8.1.3 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 of 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.

1.8.1.4 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 [11].

1.9 Other forms of natural rubber

- Oil extended natural rubber
- Deproteinized natural rubber
- Skim rubber
- Superior processing rubber
- Epoxidised natural rubber
- Thermoplastic natural rubber

1.10 Filler Reinforcement of Rubber

Elastomers in general are not used in their pure form. So they are used with a number of other components called compounding ingredients, which improve the processibility, performance properties and life of the final product. Fillers are used to enhance the performance related properties of rubbers. The fillers used in rubber compounding are characterized by their reinforcing effect, which ranges from inactive over semi-active to very active fillers. The designation 'active' or 'reinforcing' refers to the influence of the filler on compound viscosity and mechanical properties such as tensile strength, abrasion and tear resistance. Structure as well as surface properties of the filler are the main characteristics which determine the reinforcing effect. Active fillers are characterized by a large relative surface area and a high structure; both properties resulting in a strong inter particle forces, which negatively influence the processing behaviour due to agglomeration of filler particles during mixing and storage of the compound. The use of reinforcing fillers gives the material unique properties: a combination of high elasticity with high strength [12].

1.11 Reinforcing Effects

A condition for filler reinforcement is the interaction between the filler particles and the polymer. These interactions can be strong, for example in the case of covalent bonds between functional groups on the filler surface and the polymer, or weak as in the case of physical attractive forces. When carbon black is blended with a polymer, the level of physical interaction is high [13]. In contrast to this, the interaction between silica particles and the polymer is very weak, and only by the use of a coupling agent a bond is formed between the filler and the polymer.

Besides the interaction between the polymer and the filler, an interaction between filler particles occurs, predominantly above a critical concentration threshold, the percolation threshold: The properties of the material change drastically, because a filler-filler network is established. This results for example in an over proportional increase of electrical conductivity of a carbon black filled compound. But even at lower concentrations, the filler-filler interactions influence the material characteristics, as expressed by the Payne effect. [14]

The main contributions to the complex shear modulus are the hydrodynamic effect, the polymer network, the filler-polymer and the filler-filler interaction.

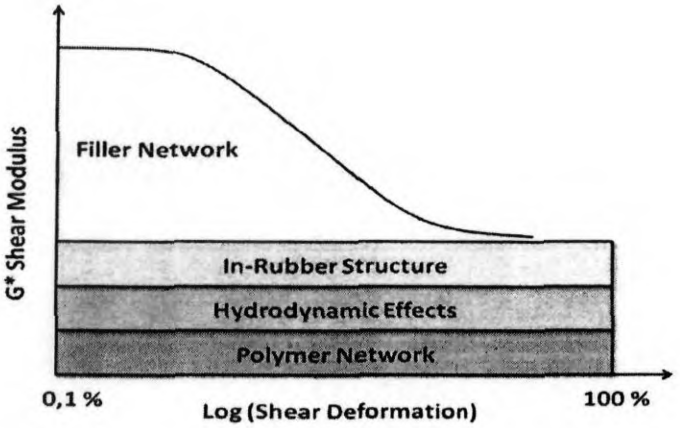


Fig 1.1 Effects contributing to the complex shear modulus

1.11.1. Hydrodynamic effect

The addition of particles to a viscous fluid results in an increase of the viscosity of the fluid, commonly designated as the hydrodynamic effect. [15] In a polymeric matrix this effect is also measured as an increase of the modulus. The addition of the filler increases the shear modulus of the pure elastomer and results in a shear modulus for the filled compound.

1.11.2. Filler-polymer interaction

The filler-polymer related effects are determined by the special structure of the filler in the rubber matrix and its interaction with the polymer. The occluded rubber contributes to this effect: Polymer chains are trapped in the voids of the filler agglomerates and aggregates; they are immobilized and shielded from deformation. They do not contribute to the elastic behavior of the matrix, as their properties resemble the properties of the rigid filler particles rather than the properties of the elastic and flexible free polymer chains. Occluded rubber increases the effective filler loading and thus the strain independent contribution to the modulus. The filler-polymer interaction can be attributed to physical interactions, for example Van Der Waals forces, or chemical reactions as in the case of a silica-coupling agent system. [16-19]

1.11.3. Polymer network contribution

The polymer network formed during vulcanization is the third strain-independent contribution to the modulus: The modulus is proportional to the concentration of elastically active network chains υ and the absolute temperature T, with the proportionality constant being the Boltzmann constant kB:

$$G_0 = \upsilon . k_B . T$$

1.11.4. Filler-filler interaction: Payne effect

The strain-dependent contribution to the modulus is caused by filler-filler interactions. This effect was first brought into focus by Payne, and he interpreted the sigmoidal decrease of the storage modulus versus the double strain amplitude in logarithmic scale from a limiting zero-amplitude value to a high amplitude plateau as the result of the breakage of physical bonds between filler particles, for example Van Der Waals or London forces. This effect is largely reversible once the strain is released and is independent of the type of polymer, but is dependent on the type of filler. The Payne-effect is stronger for silica, as a consequence of the strong inter particle forces between the filler particles. [19-22]

1.12 Reinforcement of rubber with particulate fillers

Another classification of fillers on the basis of its physical nature groups them in to continuous (Fiber, Filament or Tape) and discontinuous in form (Whisker Flakes or particle). Silica is generally particulate filler. Particulate fillers reinforce the vulcanised rubbers. The elastomers reinforced with particulate fillers can maintain almost the same flexibility as that of the unfilled. The improvement in modulus and other physical properties achieved for elastomeric vulcanizates through particulate fillers is more pronounced with non-crystallizing rubbers [23]. The interaction of particulate fillers is dependent on a number of factors. The primary filler characteristics influencing elastomer reinforcement are particle size, surface area, specific surface activity/chemical composition and structure/ porosity.

1.13 Particulate Fillers

Particulate fillers used in rubber industry in general can be classified as "Black" and "Non black", depending on their origin, the former being mostly produced from petroleum feed stock and the latter from mineral sources. The most important particulate fillers being used in rubber industry are carbon black and silica. Silicates, clays, whiting (Calcium Carbonate) and other mineral fillers are used extensively where a high degree of reinforcement is not essential [23].

1.13.1 Carbon black

In 1904, S.C.Mote, working for the India rubber, Gutta Percha discovered the reinforcing effect of Carbon black [24]. It is a colloidal form of elemental carbon. It owes its reinforcing character to its colloidal morphology (The Size and Shape of the Ultimate Units) and to its surface properties. The particles of carbon black are not discrete but are fused clusters of individual particles. Carbon blacks are prepared by incomplete combustion of hydrocarbons or by thermal cracking. Carbon blacks are classified into furnace blacks, channel blacks, thermal blacks, lamp black and acetylene black depending on their method of manufacture. The major types of rubber reinforcing carbon blacks are manufactured by the furnace process. The predominant purpose of furnace type carbon blacks in elastomers is the reinforcement they impart to the vulcanizates [23, 25, 26].

Carbon black is characterized based on its surface area, particle size, and structure and tinting strength. Elastomer reinforcement of carbon black is dependent on these properties. Dispersion of carbon black in the elastomer also influences the extent of reinforcement. Carbon blacks have reactive organic groups on the surface that cause affinity to rubber [27]. Incorporation of carbon black into rubber gives enhanced modulus, improved fatigue and abrasion resistance and better overall technological properties.

1.13.2 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, [23, 26, 28]. 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 [29].

1.14 Silica as reinforcing filler

From the non-black fillers silica provides the highest reinforcement to rubber products which is ascribed to the small particle size of the silica. Silica is an amorphous material, consisting of silicon and oxygen atoms connected in a non-regular 3D network of Si-O-Si bonds with silanol groups (Si-OH) present inside and on the surface (Figure 1.2) [31, 32].

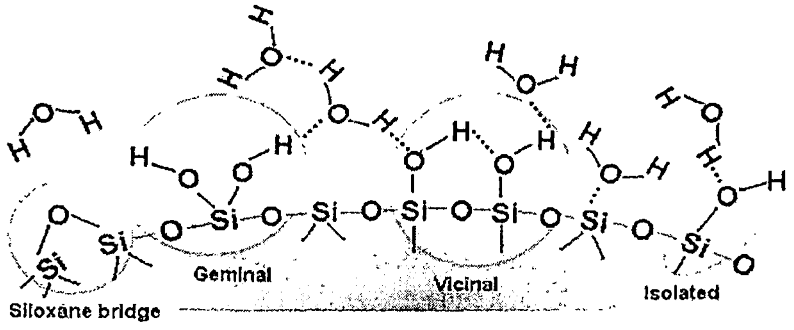


Fig 1.2 Siloxane and silonal groups present on a silica surface.

Three different types of silanol groups can be distinguished on the silica surface: i) isolated silanol that has only one hydroxyl group, ii) vicinal that contains hydroxyl group's close enough to develop hydrogen interactions and iii) germinal silanol where two hydroxyl groups are linked to one silicon atom. The silanol groups are directly responsible for the high polarity of the silica and the strong affinity to absorb water on its surface (~6 % for precipitated silica) [33]. The silanol groups have a strong tendency to form hydrogen bonds with the silanol groups from the neighboring particles, resulting in aggregates with various sizes. Three structures of silica at different length scales are distinguished, such as primary particles (10 - 50 nm), aggregates (primary particles fused together via hydrogen bonding: 100 - 500 nm) and agglomerates (aggregates are held together with van der Waals forces: > 1 μm) (Figure 1.3) [32, 34, 35].

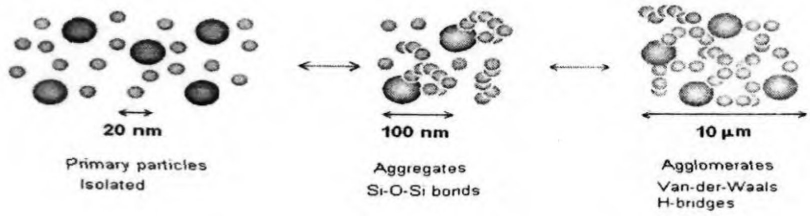


Fig 1.3 The Characteristic Structure of silica

The silica surface covered with a large number of silanol and siloxane groups can be characterized by the surface energy. The surface free energy of filler particles such as silica can be quantified using inverse gas chromatography (IGC). The surface free energy of a solid or filler γ_s, can be represented as [45]:

$$\gamma_s = \gamma_s^d + \gamma_s^{sp}$$

Where γ_s^d is the dispersive component

γ_s^{sp} is the specific component of the surface free energy.

Specific interactions measure the filler- filler interaction which include hydrogen bonding, polar and acid-base interactions. The dispersive interactions between rubber and filler are non- specific interactions like van der waals interactions.

In comparison with carbon black, the surface energies of silica are characterised by lower dispersive component γ_s^d , and a higher specific component γ_s^{sp} [46, 47]. The low γ_s^d of silica would result in lower filler to rubber interaction, whilst high γ_s^{sp} of silica leads to strong agglomeration of silica in rubber matrix. In contrast, the high γ_s^d of carbon black gives strong filler to rubber interaction.

There are two types of commercially available silica: precipitated and fumed. The precipitated silica is prepared by the reaction of sodium silicate and sulphuric acid under alkaline conditions and the fumed silica is prepared by oxidation of silicon tetrachloride vapour at high temperatures(~1000 ^{0}C) [30,32]. The physical properties of these two amorphous silica grades are determined by the production route and the reaction parameters (Table 1.2). In the rubber industry the precipitated silica is the preferred type of silica used because of the lower price and better mixing with the rubber material. The more expensive fumed silica has very low bulk density (very fluffy white powder) due to which is mainly used in silicon rubber.

Table1.2. Physical properties of amorphous silica [36]

Property	Type of silica	
	precipitated	fumed
Surface area [m2/g]	60-300	50-400
Moisture [%]	<6	<1.5
Silanol groups [nm-2]	8-10	2-4
Primary particle size [nm]	10-50	7-50

Silica is also used in shoe soles for improving the resistance to wear and tearing. It is also used to improve the tear strength and heat aging resistance in a wide variety of manufactured rubber goods, including conveyor and power transmission belts, hoses, motor and dock mounts, bumper pads and rubber rolls. Nowadays, the application of rubber depends on finding the optimum balance between type and amount of filler needed for achieving maximum improvement in mechanical properties [37, 38].

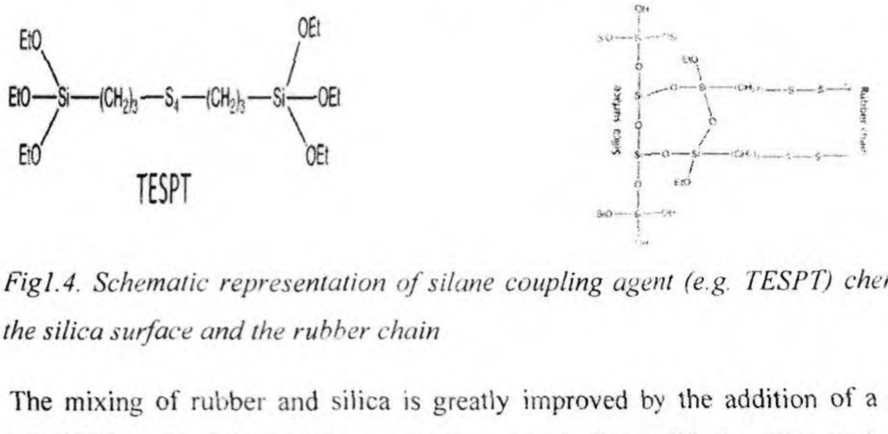


Fig1.4. Schematic representation of silane coupling agent (e.g. TESPT) chemically bridges the silica surface and the rubber chain

The mixing of rubber and silica is greatly improved by the addition of a coupling agent [40,41].The role of the coupling agent is to chemically modify the silica surface by forming a hydrophobic layer, which allows easier breakage of the agglomerates into smaller aggregates during the mixing stage and their better dispersion in the rubber matrix. Additionally, coupling agents (bis (triethoxysilylpropyl) tetrasulphide - TESPT) have the ability to chemically bridge the silica surface and the rubber chains by forming sulphur bonds with the rubber and Si-O-Si bonds with the silica surface (Figure 1.4). Silica in combination with a coupling agent is superior when compared to carbon black because it provides a stronger reinforcing effect which allows the use of lower filler content in the rubber without any negative consequences on the mechanical properties.

There have been numerous efforts to improve silica dispersion, for example by varying the chemistry and content of the coupling agents, improving the mixer rotor design, [39] ultrasound pre-treatment of the silica particles and different methods for chemical modification [42-44] of the silica surface, but dispersion still remains a serious issue not only for rubber materials but also for thermoplastics.

1.15 Silica versus Carbon Black

Silica compared to carbon black is characterized by weaker filler-polymer interactions and stronger filler-filler interactions. This results in a higher compound viscosity, a higher modulus at low strain amplitudes, a lower modulus at high strain amplitudes and lower bound rubber content [49]. However, the combination of silica with a coupling agent has a higher reinforcing effect and different dynamic mechanical properties compared to carbon black [50]. The main influence on the mechanical properties when replacing carbon black by silica combined with a coupling agent is found for:

- Tear, abrasion and heat resistance
- Flex stability
- Hardness, stiffness and modulus
- Tack
- Heat build up
- Resilience

The stronger reinforcing effect of silica compared to carbon black allows the reduction of the filler content without any negative influence on the property profile, but with an additional positive effect on elasticity due to the higher ratio of elastic component to damping filler. This results in an additional reduction of the rolling resistance

The stability of the covalent silica-polymer network results in a lower rate of breaking and reformation of the silica-polymer bonds compared to the carbon black-polymer network during a deformation cycle, resulting in a decrease of the loss modulus. A low value of the loss modulus together with a high value of the storage modulus results in a low value of the phase angle. As both, loss modulus and storage modulus, depend on deformation, the phase angle is also influenced by the applied strain: It increases with increasing deformation [48].

1.16 Silane coupling agents

An organo functional silane [51, 53] is a unique chemical that has vast applications. Due to its unique combination of organic activity and silicon reactivity, it is used in application such as coatings, adhesives, sealants, elastomer, electronic materials, fiber glass, and foundry sand binders as well as in many other advanced and innovative technologies. A bi functional organo silane coupling agent through the organo functional and silicon functional moiety is able to chemically bond a polymer matrix to inorganic substrate such as silica. The bi functional organo silane coupling agent serves two functions:

- For coupling with hydrophilic silica surface
- For coupling with the hydrophobic polymer or rubber

Coupling agent act as a connecting bring between silica and rubber and improves the reinforcement of silica in rubber. The chemical structure of a organo silane coupling agent is simply describes as: [51, 52, 53-56]

$$X_3\text{-Si-}(CH_2)\text{-Y}$$

Structure of bi functional silane coupling agent

Where x is a silicon functional group or hydrolysable group which reacts with inorganic surfaces. The group may be halides, alkoxides or acryloxy.

Some examples of this group include:

$$-OCH_3, -OC_2H_5, -OC_2H_4OCH_3$$

Y is the organo functional group that provides bonding with a polymer matrix which can consists of an amino, methacrylate, epoxy, mercapto, glycidoxy, chloropropyl group.

Some examples of this group include:

$$-SH, -NH_2, -Cl, -CH{=}CH_2, -OC({=}O)\text{-}C(CH_3){=}CH_2, -N{=}C{=}O, \text{etc}$$

Stable $(CH_2)_n$ carbon atoms are attaching the Y organo functional group with the central silicon atom.

Organo-functional silane coupling agents chemically bond to organic polymers *via* different methods as follows [53]:

- Reaction with terminal or pendent groups;
- -this reaction can occur for isocyanato, hydroxyl and amine end blocked polymers as well as polymers with residual activated unsaturation.
- Grafting to reactive sites on backbones;
- -this method involves the free radical grafting with unsaturated silanes.
- Addition or condensation polymerization
- -this method includes the incorporation within sulphur crosslinked rubber, free radical – cured acrylates/ methacrylates, thermo set epoxy resins, phenolic resins, and thermoset acrylic resins.
- Formation of interpenetrating polymer networks.
- -silanes are used to form interpenetrating polymer networks.

The hydrolysable groups on silicon are able to react through hydrolysis and condensation. Alkoxy silane groups of silane coupling agents may react directly with a silanol group on siliceous surface [56], although a catalyst is recommended to accelerate the condensation.

Organo functional silanes used for sulphur cured rubber compounds can be categorized into the following types: [51]

Di - and polysulphide silanes : $[(RO)_3\text{-}Si\text{-}(CH_2)_3\text{-}S]_2\text{-}S_x$

Mercaptosilanes : $(RO)_3\text{-}Si\text{-}(CH_2)_3\text{-}SH$

Blocked mercaptosilanes : $(RO)_3\text{-}Si\text{-}(CH_2)_3\text{-}S\text{-}B$

Where $R = CH_3$ or C_2H_5; $B=CN$ or $C_7H_{15}C=O$; $x= 0\text{-}8$

Coupling agents may be pre –mixed, or pre- reacted with the silica filler or added to the rubber mix during the rubber and silica mixing stage. If the coupling agent and silica are added separately to the rubber mix during mixing, it is considered that the coupling agent then combines *in situ* with the silica [57].

To date, the common and effectively used coupling agents in rubber systems are bis (tri ethoxy silyl propyl) tetra sulphide (TESPT) [58] and bis (tri ethoxy silyl propyl) disulphide (TESPTD) [51].The structure of TESPT or often called Si 69 is shown below. TESPT is a silane with different sulphur ranks, ranging from S_1 to S_6 and average sulphur ranks around

3.83. During mixing of silica filled rubber compound, the silane coupling agent reacts with silica resulting in hydrophobation of the silica surface. This hydrophobation reduces the silica- silica network and makes the polar silica surface more compatible with the non-polar rubber.

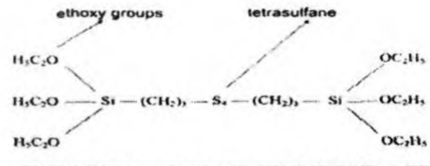


Fig1.5. Bis (tri ethoxy silyl propyl) tetra sulphide (TESPT)

The effect of silane coating on surface free energy of silica has been accessed with IGC [47]. With silane modification, the surface chemistry of silica changes and both the dispersive and specific components of the silica free energy are reduced. This results in lower interaction between the silica particles and gives better dispersion of silica in the rubber matrix. The lower dispersive component of surface energy of silane modified silica is compensated by introducing covalent linkages during vulcanisation when bi functional silanes are employed.

The reaction mechanism between silica, silane coupling agent and rubber has been extensively reviewed [34, 39, 40, 59]. The triethoxysilyl group of TESPT reacts with the silanol groups of silica during compounding with loss of ethanol, while the rubber reactive group of silane (tetrasulphane) has strong tendency to form rubber-to-filler bonds during curing of rubber compounds. The primary and secondary reaction of TESPT and silica as well as the reaction of TESPT and rubber are shown in figures 1.6, 1.7, 1.8 respectively.

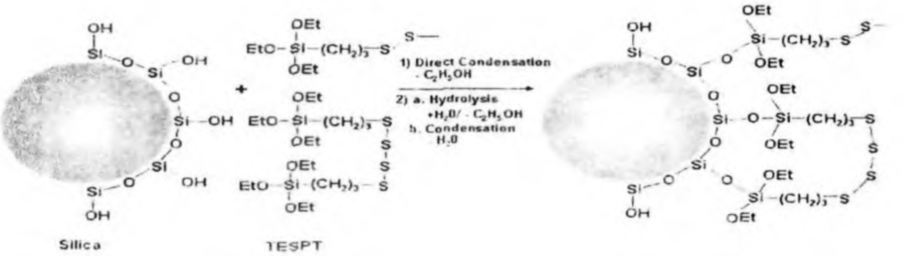
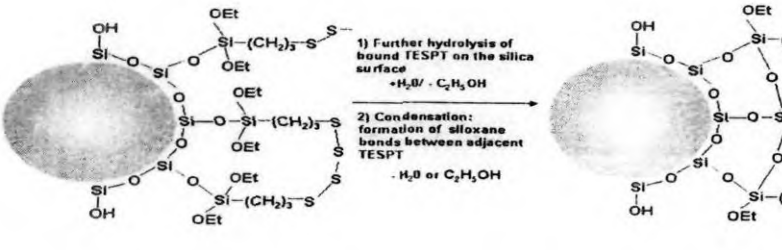
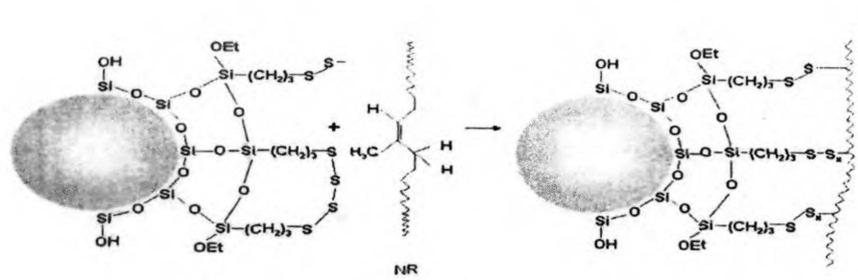


Fig1. 6: primary reaction of silica and TESPT



Figl.7: secondary reaction of silica and TESPT



Figl. 8: General scheme of the reaction of polysulphidic silane with rubber.

The reactivity of silane coupling agent is generally influenced by the hydrolysable group of silane. By comparing the methoxy, ethoxy, propoxy and butoxy derivatives, the rate of silanisation decreases in the order [60] of:

$$CH_3O^- > C_2H_5O^- > C_3H_7O^- > C_4H_9O^-$$

The reaction rate with propoxy and butoxy groups is too slow to acceptable. The methoxy group reacts too rapidly, and it is not used as a silanisation agent for toxicological reasons as it evolves methanol. Thus, the ethoxy group is preferred as a silanisation agent which reacts quickly enough and when precautions are taken, it is toxicologically harmless.

TESPT has been proven as a curing agent and the carrier of the crosslinking reaction is the tetra sulphidic group [61]. With rubber, TESPT reacts as a sulphur donor which builds up rubber –to- rubber bonds. Nonetheless, the reaction of TESPT in silica filled rubber compounds results in the immobilized tetra sulphidic group of the silane modified silica, which leads to the formation of filler-to- rubber bonds.

1.17 Dry blending challenges

Silica and carbon black have been commonly used as reinforcing agents and/ or fillers in rubber and thermoplastic polymers. A number of techniques have been developed to incorporate such reinforcing agents and fillers into the polymer compositions, including both wet and dry blending processes. The incorporation of such silica and carbon black as reinforcing agents and/or fillers is far more complex than might other wise appear. One problem in wet blending of silica with lattices of such polymers arises from the fact that the hydrophilic silica has a tendency to associate with the aqueous phase and not blend uniformly with the hydrophobic polymer. Use cannot be made of the hydrophobic fumed silica's because these have been treated to eliminate most of the hydrophilic, reactive sites and consequently cannot be dispersible in water. The relatively high cost of the hydrophobic fumed silica's also prohibits their use in many dry blending applications [62].

Perhaps the most commonly employed practice, used commercially, is the technique of dry blending either silica, carbon black or both of them into rubber and thermo plastic polymers in a high-shear milling operation. That practice has many limitations. Notable among them include the tendency of the filler particles to agglomerate to each other, resulting in non-uniform dispersion of the filler throughout the polymer constituting the continuous phase. Physical properties of the cured rubber compound are not their best. Another problem commonly experienced in such high-shear milling operations is the tendency of the polymers to degrade during milling. Milling necessitates the use of higher molecular weight polymers, which sometimes require the incorporation of various types of processing aids to facilitate mixing and dispersion of the filler particles into the polymer constituting the continuous phase. The cost associated with the use of such processing aids also increases the manufacturing cost of the polymeric compound or article. The use of processing aids has the further disadvantage in that such processing aids may have a negative effect on the cure or end use of the polymer. Also Processes for incorporating silica into rubber using the dry mixing process have been effective, but are time-consuming and energy intensive. And, in addition, dry blending techniques add additional processing costs, in part due to the accompanied excessive equipment wear by the abrasive fillers [62].

To improve dispersion of the silica during dry mixing, it has been proposed that such compounding operations employ silica which has been treated with an organo silane coupling agent having dual functionality. Representative of such coupling agents are those well known compounds that include either an organic group such as an amino alkyl or a mercapto alkyl group bonded directly to the silicon atom along with a readily hydrolyzable group, such as an alkoxy group as represented by a methoxy group or an ethoxy group likewise bonded directly to the silicon atom. In those systems, it is generally recognized that the alkoxy group hydrolyzes in the presence of moisture typically found on the surface of the silica to form the corresponding silanol which reacts with or condenses in the presence of the silica surface to bond the silicon atom to the silica surface. The organic groups likewise attached to the silicon atom are thus available for chemical reaction with the polymer matrix during vulcanization. As a result, the polymer matrix may become chemically bonded by means of the coupling agent to the silica surface during cure or vulcanization of the polymer. Problems associated with the use of such silanes during compounding include the release of volatile organic compounds (VOC) due to the hydrolysis of readily hydrolysable groups, unpleasant odour due to the presence of mercapto or sulphur containing organic groups, and premature curing, and/or scorching [63].

The mixing process requires a great deal of time and capital, operating and maintenance expense. Longer mixing time greatly reduces the efficiency of the mixing operation further, ethanol from the silane must be removed in the mixing step or in a downstream processing step. Rubber mixing facilities are not designed to function as chemical plants, and extra equipment must be installed to either isolate or to burn the alcohol so as to meet environmental standards [64].

1.18 Wet master batch process

Mixing filler with rubber is one of the most critical processes in rubber compounding. Along with physical changes of the materials, the primary functions of mixing are incorporation, dispersion and distribution of the filler and other ingredients in the polymers. Traditionally, this is achieved using batch mixing of fillers and solid rubber blocks or pellets, referred to as dry mixing. The final dispersion quality of the filler in the polymer is a critical parameter in controlling the performance of rubber products, including mechanical failure properties, dynamic properties, electrical properties. The degree of filler dispersion is determined by the filler morphology, aggregate- aggregate interactions and shear stress applied during mixing [65].

Filler incorporation causes 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 [66].

It has long been considered desirable to incorporate silica fillers into rubber by means of a technique known as latex master batching. Ideally, such a technique involves the mixing of an aqueous dispersion of silica with latex of the particular rubber content to be employed with the co- precipitation thereafter of a homogeneous blend of rubber and silica [67].

Such a direct technique has heretofore been very difficult because carefully controlled amounts of additional components have had to be added to the silica or the latex in order to assure efficient co precipitation. Without such additional components, the dispersed silica is known to exhibit a tendency to remain in suspension during the coagulation step thereby causing precipitation of essentially pure rubber instead of a silica-rubber mixture [67].

1.19 Review on Rubber- Silica Wet Master batching

US patent application 2009003659 discloses a method for producing a rubber-filler composite, comprising a dispersion step of irradiating filler slurry containing filler with high amplitude ultrasonic waves having amplitude of 80 μ m or more to finely disperse the filler in the slurry, and a mixing step of mixing the dispersion-treated filler slurry with concentrated natural rubber latex. The dispersion-treated filler slurry and the concentrated natural rubber latex are mixed in the mixing step while conducting irradiation with high amplitude ultrasonic waves having amplitude of 80 pm or more. The filler used is carbon black [68].

US patent application 20080262123 discloses a method for the production carbon black master batches .pre vulcanized latex is firstly diluted to dry rubber content (DRC) of 10 to 15%. The pre vulcanized latex can be either natural latex or synthetic latex. Carbon black is then added to the diluted pre vulcanized latex with vigorous stirring. The final product mix is treated with a small quantity of formic acid to ensure total coagulation and rubber coating of the carbon black powder [69].

US2009/0088496a1 patent discloses a process for the preparation of master batch wherein a rubber-filler composite is disclosed. The rubber-filler composite is obtained by jetting field latex of natural rubber in a form of a high speed flow having a flow rate of 500 m/sec or more into a mixing chamber while supplying a filler slurry containing a filler to the mixing chamber, thereby separating and removing protein in the field latex from a rubber component and at the same time, mixing the field latex and the filler slurry [70].

US 6841606 patent discloses a process where in natural rubber master batch is prepared by mixing natural rubber latex having its amide linkages cleaved and an aqueous slurry having a filler dispersed in water. The process includes Step 1 of cleaving amide linkages in a natural rubber latex; and step 2 for mixing the latex having its amide linkages cleaved with an aqueous slurry having been dispersed with at least one filler selected from the group consisting of carbon black, silica and an inorganic filler [71].

US Pat. No. 7,786,208 patent discloses a method for producing a modified natural rubber master batch, which comprises the step of mixing modified natural rubber latex with fillers. The rubber latex is modified by the addition of a Polar group-containing monomer. Further the modified rubber latex is mixed with a slurry solution formed by previously dispersing at least one filler selected from the group consisting of carbon black, silica and an inorganic compound [72].

US Pat. No. 7,960,466 patent discloses a process of mixing natural rubber latex with a slurry containing water and a carbon black dispersed therein. The natural rubber latex used preferably has been treated in a cleavage step of cleaving amide bonds in the natural rubber latex. A surfactant is preferably used to enhance the stability of the latex. The master batch may further contain various additives such as filler including silica or an inorganic filler, a surfactant, a vulcanizing agent, an anti-aging agent, a colorant, and a dispersant as required in addition to the carbon black [73].

Patent application CN 103203810 A, discloses a continuous manufacturing method for rubber masterbatch, the rubber masterbatch prepared by using the continuous manufacturing method and a rubber product. The manufacturing method comprises the following steps: 1) adding a filling material into a rubber solution, carrying out stirring so as to form a rubber/filling material/solvent mixture and subjecting the rubber/filling material/solvent mixture to further fine dispersion and refined dispersion so as to improve the dispersion degree of the filling material in the rubber solution; 2) subjecting rubber and the filling material in the rubber/filling material/solvent mixture having undergone refined dispersion in step 1) to hetero-coagulation so as to obtain a mixture of a rubber/filling material compound and a solvent; and 3) removing the solvent and drying the mixture so as to obtain the rubber/filling material masterbatch. The invention further provides the masterbatch prepared by using the manufacturing method and the rubber product prepared from the masterbatch. Compared with a conventional wet rubber compounding technology, the invention has the following advantages: there are no special requirements on rubber and the filling material, the prepared masterbatch has a wide application scope, and dispersity of the filling material in a rubber compound is accordingly improved [74].

Patent application CN 102924758 A discloses a method of producing an elastomer composite. The method includes A) combining a first fluid comprising elastomer latex with a second fluid comprising particulate filler; B) causing the elastomer latex to coagulate, thereby forming masterbatch crumb; C) bringing the masterbatch crumb to a water content of about 1 weight percent to about 20 weight percent, thereby forming a dewatered coagulum; D) removing water from the dewatered coagulum by subjecting the dewatered coagulum to mechanical energy, thereby causing the dewatered coagulum to heat as a result of friction, while allowing the dewatered coagulum to achieve a temperature of about 130 deg. C to about 190 deg. C, wherein water content is reduced to about 0.5 % to about 3 % and wherein substantially all of the decrease in water content is accomplished by evaporation, thereby producing a masticated masterbatch; and E) subjecting the masticated masterbatch to at least an additional 0.3 MJ/kg of mechanical energy while further reducing the water content [75].

US patent application 20130203915 A1 (also published as WO 2014031941 A1) discloses a method for a compatibilized silica for incorporation into natural and synthetic polymers in latex form using precipitated or fumed silica with at least two organosilicon coupling compounds in an aqueous suspension. Polymer-silica reinforced masterbatches are prepared by addition of the compatibilized silica slurry using the formed compatibilized silica [76].

US patent 20060205867 A1 (also published as EP 1652873 A1) discloses a method for producing a rubber master batch capable of producing a rubber master batch having an excellent homogeneity without a special equipment, and more particularly to a method for producing a rubber master batch comprising a step of mixing a rubber solution with a slurry solution of a filler previously dispersed into a liquid, characterized in that a static mixer or a high shear mixer comprising a rotor and a stator portion is used in the mixing of the rubber solution and the slurry solution [77].

US patent application 20140011922 A1 (also published as WO 2012085135 A1)Discloses a process for preparing a masterbatch in the liquid phase, which is based on one or more diene elastomer lattices and on one or more fillers comprising the following successive steps: producing a stable and homogeneous aqueous dispersion (C), by mixing, of one or more diene elastomer latices (A) with one or more stable aqueous dispersions (B) of one or more fillers; homogenization of the aqueous dispersion (C); coagulation within the aqueous dispersion (C) of said diene elastomer latex or latices with the filler or fillers via provision of mechanical energy; recovery of the coagulum; drying of the recovered coagulum in order to obtain the masterbatch [78].

US patent 5763388 A discloses A process for the incorporation of silica into a polymer in latex in which a silica is treated with an organo silicon compound coupling agent in aqueous suspension to form a compatibilized silica and then contacting a polymer latex with the compatibilized silica whereby the silica becomes substantially uniformly distributed throughout the latex and can be recovered when the latex is coagulated to yield little residual silica in the liquid residue from the latex. Also described is a process for preparing the compatibilized silica [79].

US patent application 20140083598 A9 Discloses a process for making silica-filled rubber masterbatch using silica hydrophobated with a trimethoxy silane coupling agent that is soluble in an alcohol-water solution containing at least about 70 wt % water. One embodiment uses a mixture of trimethoxy silanes, one or more of which react with rubber to bond the silica to the rubber, and one or more of which do not react with rubber, but do hydrophobate the silica. Hydrophobated silica is mixed with latex polymer and incorporated into rubber during coagulation of the latex, which is preferably coagulated with calcium chloride. The present invention further provides a process for making the trimethoxy silane coupling agents. Preferred trimethoxy silane coupling agents include bis-(3-trimethoxysilylpropyl)-disulfide and bis-(3-trimethoxysilylpropyl)-tetrasulfide. Rubber products, particularly tires, compounded with the inventive silica masterbatch can be processed for a long time before scorching because the silica masterbatch provides a long scorch time [80].

US patent application 20120264875 A1 Discloses a method for preparing a masterbatch of natural rubber and silica, comprising the following successive steps of: doping the silica with magnesium, preparing at least one dispersion of the thus-doped silica in water, bringing into contact and mixing a natural field-rubber latex and the aqueous dispersion of doped silica in order to obtain a coagulum, recovering the coagulum, and drying the recovered coagulum in order to obtain the masterbatch [81].

Patent CN101084258 B Discloses a method for producing a modified natural rubber masterbatch, which comprises the step of mixing a modified natural rubber latex, which is formed by adding a polar group-containing monomer to a natural rubber latex to graft-polymerize the polar group-containing monomer onto a natural rubber molecule in the natural rubber latex, with a slurry solution formed by previously dispersing a filler into water, and a modified natural rubber masterbatch produced by the method and capable of highly improving a low loss factor, a wear resistance and fracture characteristics of a rubber composition [82].

Patent application No. WO 2013108436 A1 Provides method for producing a rubber wet masterbatch, wherein the method at least includes: a solidifying step in which a filler-containing rubber coagula is produced by mixing a slurry solution including a filler and a dispersing solvent with a rubber latex solution followed by solidifying the mixture; a dehydrating step in which a rubber wet masterbatch is produced by dehydrating the filler-containing rubber coagula by heating at 100°C to 180°C using a first single screw extruder; and a drying and plasticizing step in which a rubber wet masterbatch having a further reduced water content is produced by plasticizing the rubber wet masterbatch by heating at 120°C to 180°C using a second single screw extruder [83].

US patent 8716366 B2 discloses 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 [84].

1.20 Scope of the present work

Natural rubber is a versatile polymer, which forms the base material for the manufacture of variety of rubber products, of which tyre is one of the major one. At present annual production of natural rubber is about 11 million tones and about 5 to 6 million tones is consumed by the tyre industry alone. Carbon black and silica are the two important fillers being used for the reinforcement of majority of rubber products. Current production of carbon black is about 10 Million tons and approximately 7 million (70%) goes to the tyre sector (REF:Rubber Asia May 2013). Carbon black being a petroleum derived product, due to ecological reasons use of carbon black is to be limited and renewable materials are to be used. Research attempts are going on in this direction. Second largest filler being used by the rubber industry is silica, a mineral product and is more favoured than carbon black on ecological grounds, due to its mineral origin and also due to some technological advantages. Unlike carbon black, silica has the technological advantage of low heat build-up in tyres, which in turn is a measure of rolling resistance in tyres. Higher rolling resistance of tyres result in higher fuel consumption in vehicles. Silica while offering these advantages, also causes some technical disadvantage such as poor processability and lower reinforcement in hydrocarbon rubbers. Primary rubbers used in tyres are mostly hydrocarbon based, and hence results in poor reinforcements with silica. This could be overcome to a large extend with the use of silane coupling agents. However this alone is not a complete solution to the use of silica in hydrocarbon rubbers.

In this study we use latex –filler wet master batching technique to improve the dispersion of silica in natural rubber. This method is simple and cheaper technique with some additional advantages like relatively low environment pollution, lesser energy for compounding compared to the conventional mixing. Because of the increasing demand for natural rubber and silica as eco-friendly materials for preparation of rubber goods, this method has an emerging future in rubber industry.

CHAPTER -2

EXPERIMENTAL TECHNIQUES AND MATERIALS USED

EXPERIMENTAL TECHNIQUES AND MATERIALS USED

The details of the material used and the experimental techniques adopted in the present investigation are described in this chapter

2.1 MATERIALS USED

2.1.1 Natural rubber Latex [11, 85]

Latex used in the study was fresh NR latex obtained from the Rubber Research Institute of India, Kottayam

2.1.2 Natural rubber

The natural rubber (NR) used was the technically specified rubber as obtained from the Rubber Research Institute of India, Kottayam. This rubber conforms to the Bureau of Indian standard (BIS) specification for ISNR-3L grade natural rubber. The BIS specification for ISNR-3L is given in Table 2.1.

Table 2.1 Specification of ISNR-3L grade natural rubber

Parameter	**Limit**
Dirt content % (max)	0.03
Volatile Matter %(max)	0.80
Nitrogen content %(max)	0.6
Ash content %(max)	0.50
Initial plasticity %(max)	30.0
Plasticity Retension Index	60.0

2.1.3 Filler-Silica [86]

The reinforcing filler used for the experiment is 'Ultrasil VN3' type silica, a product of Degauss an A.G, Germany. It is having specific surface area $175m^{2/}/g$, tapped density of 220g/l, SiO_2 content of 98%, moisture content of about 5.5% by weight and P^H of 6.2.

2.1.4 Coupling agent

Coupling agents most frequently used in silica compounding. Viz; bis [3-tri ethoxy-silylpropyl] tetra sulphide is used for the present experiment .The material used is 'Si-69', a 'Degussa' product.

2.1.5 Sulphur

Commercial rubber industry grade

2.1.6 Zinc oxide

Commercial rubber industry grade

2.1.7 Stearic acid

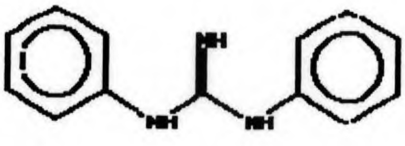
Commercial rubber industry grade

2.1.8 Accelerators

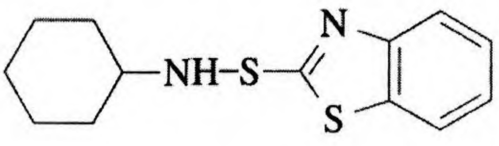
Higher cross linking efficiency could be achieved by the use of activators and accelerators in a vulcanization process with sulphur.

In this experiment, two type of accelerators were used viz; N-cyclohexyl benzothiazole-2 sulphenamide (CBS) and N, N Biphenyl guanidine (DPG). In carbon black filled system usually primary accelerator alone used. In the present study CBS was used as the primary accelerator, along with DPG as secondary accelerator.

CBS is a yellowish powder with a faint smell, soluble in acetone, benzene, and ethanol, chloroform etc. Owing to its low melting point it is very well dispersed in rubber. It is a fast and high modulus accelerator with a delayed action. During the processing, it is safe at temperature 135^0c and it is very active.



N, N Biphenyl guanidine (DPG)



N-cyclohexyl-2-benzothiazole sulfonamide

DPG is a white grayish powder soluble in acetone, benzene, ethanol etc., readily dispersible in rubber, having good storage ability. It is used as a secondary accelerator for vulcanization of silica filled rubbers.

2.1.9 Antioxidant

Rubbers are affected by aging process when in service resulting in lowering in physical properties. Antioxidants are added to slowdown and improve the aging behaviour and to enhance the service life.

In the present experiment [N-(1, 3 dimethyl butyl)-N' Phenyl-p-phenylene diamine] a Merchem product under the trade name 'Mernox 6c' was used as an antioxidant.

2.1.10 Process oil

Process oils used for the experiment are naphthenic oil and vegetable oil based plasticizer.

2.1.10.1 Naphthenic oil

Naphthenic are a class of hydrocarbons also referred to as 'cyclo paraffins'. Though their structure is similar to the aromatic ring, these are single bonded thus having a stable structure. Several such hydrocarbon rings may be linked indicating a variety of available grades their unique color stability, solubility and good thermal stability makes them ideal for molded articles. A typical specification is given in Table 2 2

Table 2.2 Specifications of Naphthenic Oil

Item	Specification	Test Method
Density at 20 °C kg/m³	885-900	ASTM D-1298
Flash Point °C	190Min	ASTM D-92
Pour Point °C	-15Max	ASTM D97
Aniline Point °C	90Min	ASTM D611
Viscosity-Gravity constant	0.820-0.850	ASTM D-2501
Refractive Index at 20°C	1.48-1.50	ASTM D-1747
UV Absorbance at 260nm	0.4max	ASTM D-2008

2.1.10.2 Vegetable oil based plasticizer

Laboratory grade

2.2 Latex Testing

2.2.1 Dry Rubber Content

About 10-15 g of the sample latex is accurately weighed by the difference method into a100ml beaker from a Stoppard 50ml conical flask. The latex is coagulated with sufficient quantity of 2% acetic acid / 1% formic acid (using 1% HCOOH 3ml/gm of latex heating about 5-15min to coagulate) 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 a oven at about 70°c for 16 hrs. The dried rubber obtained is cooled in a desicater and weighed in a balance.

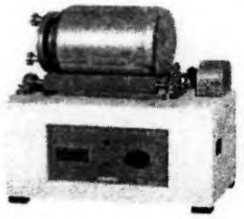
DRC (%) = Wt. of dry coagulum/Wt. of latex ×100

2.3 Preparation of silica dispersion

25% silica dispersion was prepared using 'Ultrasil VN3', precipitated silica and fatty acid soap as dispersing agent and water. Silica, water and soap are mixed and milled using a ball mill for 24h at room temperature.

2.4 Ball milling

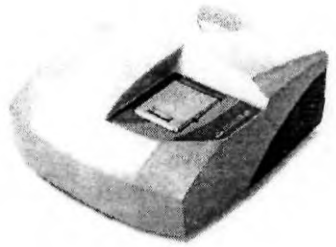
The container is rotated about its cylindrical axis in a horizontal plane at such a speed that the charge is tumbled. In ball mill the grinding charge consists of unglazed porcelain balls, their size being governed by the diameter of the container. A small laboratory mill may use balls of 1.2–1.5 cm 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.



Ball Mill

2.5 Particle Size Determination

Particle size distribution is a property unique to powders and is an important physical property for determining the behavior and nature of powders. For this reason, particle size distribution must be measured when handling powders. The particle size of filler dispersions prepared are determined using a particle size analyzer model Nano sizer (Malvern, Worcestershire, UK), based on the dynamic light scattering technique.

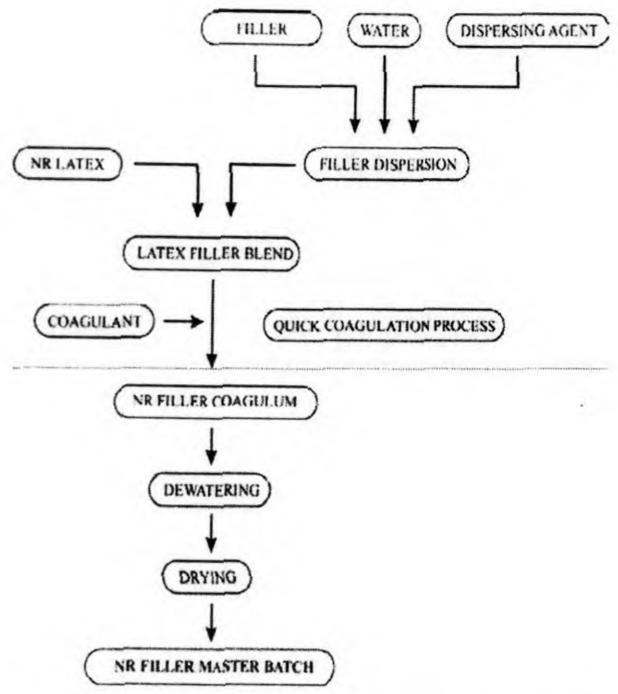


Particle size analyzer

2.6 Preparation of silica –NR masterbatch

Latex - Silica, 'Masterbatch' is made by adding silica, in the form of dispersion, to latex. The resultant rubber- silica mixture is coagulated and dried. The silica dispersion was prepared by soap sensitized mixing of silica in water. The dispersion was added slowly into the field latex under stirring and coagulated by addition of acid to produce Latex - Silica, 'Masterbatch'. The coagulum was washed well to remove acid and rolled to a thin film, dried in an air oven at 70°c. 0.8% $H_2SO_4$was used to coagulate the mixture. 23 master batches were prepared with different filler loading. The actual amounts of silica in the masterbatches were determined by using a Thermo Gravimetric Analyzer (TGA 60, Shimadu Instrument, Japan) and also by Ash Test.

Master batches containing similar silica content were mixed in a laboratory model two roll mill and the actual amounts of silica in the final master batches were determined by ash test. The final master batches contains 40.9, 46.4, 151.2, 76, 58.2 parts of silica per 100 parts of rubber respectively. The batches containing 151.2 and 76 parts silica per 100 parts rubber were mixed with latex grade rubber (ISNR 3L) using a laboratory model two roll mill to get a final master batch with 50 and 55 parts of silica per 100 parts of rubber . Ash test results of these two batches after mixing with raw rubber (ISNR 3L) showed that it contains 50.8 and 53.3 parts of silica per 100 parts of rubber respectively.



Schematic Diagram of Preparation of NR/Silica Masterbatch

2.7 Silica content estimation

2.7.1 Ash Content (IS: Part 1)-1972(No: 3)

The ash of raw rubber contains varying proportion of oxides, carbonates and phosphates of Na, K, Mg, Ca, and other trace elements. The ash represents the amount of mineral matter present in the rubber. Weigh accurately 5g of test portion wrapped filter paper and place in a crucible, previously dried and weighed. Keep crucible with its contents in a muffle furnace and heat to 550°c. when ashing is complete, cool the crucible in desiccators and weigh.

Ash content (%) = Wt. of ash /Wt. of sample x100

2.7.2 Thermogravimetric Analysis (ASTM D 6370)

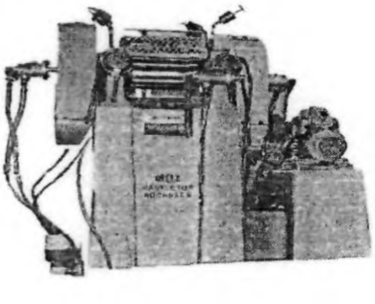
Thermogravimetric analysis (TGA) of the master batch samples was carried out using a thermogravimetric analyzer (TGA 60 from Shimadzu Instrument, Japan) in accordance with - ASTM D 6370 Standard Test Method for Rubber Compositional Analysis by Thermogravimetry (TGA). It is a computer-controlled instrument that permits the measurement of the weight changes in the sample material as a function of temperature. The sample placed in a temperature programmed furnace is subjected to temperatures in the ranges 30°C to 800°C with a heating rate of 10°C/ minute and the corresponding weight changes were noted with the help of an ultra sensitive microbalance. Air and nitrogen were used as purge gases

TGA

2.8 Compounding machinery used

2.8.1 Two roll open mixing mill [87]

Laboratory Two roll mill used in the present experiment was of DAVID BRIDGE & CO LTD., Castleton Rochdale, England. The two roll mixing mill consists of two rolls, revolving at different speeds and in opposite directions. The back roll is driven from the gear box or back shaft and the front roll through roll and gears. The rolls are made of chilled cast steel, cored to allow circulation of water for efficient cooling. Another important feature of the mill is the friction ratio. i.e.; the relative surface speed at which the two rolls revolve. The ratio used for the present work is 1.1.2



Two-roll Mill

2.8.2 Hakkae Rheocord 90

The Haake Rheocord 90 is a versatile computer controlled instrument that is capable of mixing and extruding. It consists of two main components, the Computer Processing Unit (CPU) and the Measuring Drive Unit (MDU). The CPU controls and records all the information during the run of the experiment. The MDU measures the torque, temperatures, rotor speed and totalized torque, which are then recorded by the CPU. The mixer, a Rheomix 610, has the capability to mix at temperatures up to 450°C using twin screws. It contains three heated zones controlled by the MDU.

Hakke Rheocord 90

2.9 SILANE MIXING

Calculated quantity of silane was mixed with NR/Silica master batch using a laboratory sized two roll mill and heat treatment was done in a Haake Rheocord 90 at 140°C at an rpm of 100. The mixer chamber temperature was set at 130°C and the fill factor selected was 0.7. NR/ Silica masterbatch was mixed silane for 5min. The mix was then taken out and rolled through a laboratory rubber mixing mill at 2.0 mm nip setting to form a sheet.

2.10 COMPOUNDING

The Rubber – silica masterbatch sheets obtained from the blending process were compounded in a laboratory model two roll mixing mill (David Bridge, England) of size 15x30 cm as per the formulations given in Table 2.3

Table2.3. Compound Formulation

Ingredients	Compound No.									
	1	2	3	4	5	6	7	8	9	10
Natural rubber	100	100	100	100	100	100	100	100	100	100
Silica	40.9	46.4	50.8	53.3	58.2	40.9	46.4	50.8	53.3	58.2
Silane	2.45	2.78	3.05	3.20	3.49	2.45	2.78	3.05	3.20	3.49
Naphthenic oil	5	5	5	5	5	-	-	-	-	-
Vegetable oil based plasticizer	-	-	-	-	-	5	5	5	5	5
Zinc oxide	4	4	4	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2	2	2
Mernox 6C	2	2	2	2	2	2	2	2	2	2
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
DPG	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	2	2	2	2	2	2	2	2	2	2

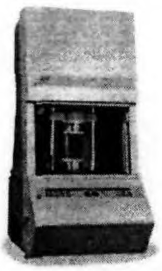
2.11 Compound testing equipments

2.11.1 Determination of cure characteristics (ASTMD 5289-06) [85]

Cure time is the time for the torque to reach a given percentage of full cure. The cure characteristics of the compounds were determined using RPA 2000 (type of moving die rheometer) at 150 °C according to ASTM D 5289 procedure. In rheometer test, the rubber compound placed in the test cavity of the equipment is subjected to an oscillatory strain by the lower die at a specified speed. The test is performed while the specimen is confined in a heat chamber at the curing temperature under pressure. The stiffness of the sample proceeds and reaches maximum and remains same. The force required to stretch the rubber (stress) is directly proportional to the stiffness of the rubber. The optimum cure time corresponds to the time to achieve 90% of the cure. It was calculated from the equation, optimum cure time (**t_{90}**)

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

where, MH = maximum torque, ML = minimum torque



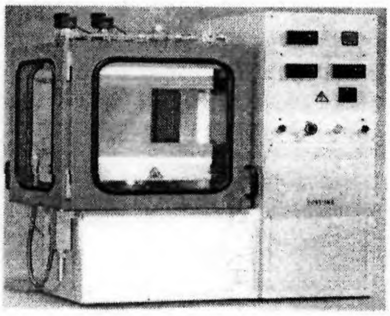
RPA 2000

2.12 Molding of test samples

2.12.1 Hydraulic press (ASTM D-3182) [87]

Test samples for physical testing were prepared by compression moulding method using a hydraulic press according to ASTM D3182. The press shall be capable of exerting a pressure of not less than 3.5 M pa (500 Psi) on the total cross sectional area of the cavities of the mould during the entire period of vulcanization. There are two heated plates. The lower platen moves under hydraulic pressure. Molding operations include cleaning the mold surfaces, preheating the mold initially to curing the compound, pressure application, curing and stripping. Hydraulic press used for the present experiment was Fontijne presses manufactured by M/s Fontijne, Netherland, Model no.TP.600.

The sheeted out compounds were compression moulded using the hydraulic press at 150°c and the molding pressure was 1600 psi. These compounds were cured to its optimum cure time. Test samples for Tensile / Tear properties, Compression set, Heat build-up, DIN Abrasion loss, De-mattia flex crack were moulded as per the respective ASTM standards.



Hydraulic Press

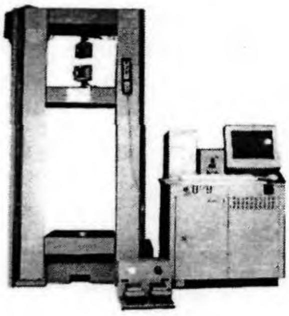
2.13 Determination of vulcanizate properties:

2.13.1Tensile Properties (Modulus, Tensile Strength and Elongation at Break (ASTM D412-87) [88, 89]

Tensile strength is defined as the force per unit area of the original cross-sectional area, which is applied at the time of rupture of a test specimen. It is expressed in pounds force per square inch, kilograms force per square centi meter, or mega Pascals. Tensile strength is an important characteristic as a tool for compound development, manufacturing control and determination of susceptibility to deterioration by oil, heat, weather, and other environmental factors. It is not necessarily an indication of quality, but is often used as such. It is true that the low range of tensile strength values is indicative of low quality compounds and the high range indicative of high quality.

Ultimate elongation or elongation at break is another property measured in conjunction with tensile strength. Elongation, or strain, is defined as the extension between benchmarks produced by a tensile force applied to a specimen. It is expressed as a percentage of the original distance between the benchmarks. Ultimate elongation is the elongation at the moment of rupture. Like tensile strength, elongation is used as a tool for quality control and determination of resistance to environmental effects.

Tensile stress, more commonly called modulus, is the stress required to produce a certain strain, or elongation. Modulus values can be taken at any elongation of the stress/strain curve. In rubber testing, modulus is usually reported as 100% modulus, 300% modulus, meaning the stress at 100%, 300%, elongation.



UTM

Tensile properties were determined according to the ASTM 412-80 test method, using dumb-bell shaped test pieces. The test pieces were punched out from the moulded sheets using C-type die, along the mill grain direction of the vulcanised sheets. The thickness of the narrow portion of the specimen was measured using a dial gauge. The test were carried out in a Zwick Universal Testing Machine (UTM) model 1474 at (25 ± 2)0c and a cross head speed of 500 mm per minute. The modulus at 100, 200 and 300% elongation and tensile strength were recorded. Ultimate tensile strength and ultimate elongation result from pulling dumbbell specimen to rupture.

2.13.2 Tear Strength (ASTM D624-02) [88, 90]

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 centi meter (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. Samples were punched out from the sheets parallel to the grain direction. This test was also carried out using the 'Zwick UTM'. The test sample was mounted on the testing machine. Steadily increasing force was applied at 500 ± 50 mm/min and at $(25 \pm 2)^0$c until the test piece was completely ruptured. The tear strength values are reported in N/mm. The maximum force required to initiate or propagate tear is recorded as force per unit thickness. Tear strength is frequently used to indicate relative toughness of different compounds. However, it is difficult to correlate with end-use performance

2.13.3 Hardness (ASTM D-2240) [88, 91]

Hardness, as applied to rubber products, is the relative resistance of the surface to indentation under specified conditions. Hardness of rubber usually measured with a small spring-loaded hardness gauge known as a durometer (ASTM D-2240). The durometer may be hand held or mounted on a stand. The measurement is made by pressing the indentor against the sample and reading the scale, which is calibrated in arbitrary units ranging from 0(soft) to 10(hard). 'Type A' durometer is used for most soft rubber products; there is also a 'Type D' durometer for hard rubber and plastic-like materials.

Durometer-Shore "A"

The hardness of the samples were measured as per ASTM D-2240 standards using a shore A type Durometer, which employed a calibrated spring to provide the indenting force. Since the hardness reading decreased with time after firm contact between the indenter and the sample, the readings were taken immediately after the establishment of firm contact.

2.13.4 Abrasion Resistance (DIN 53516)[88, 92]

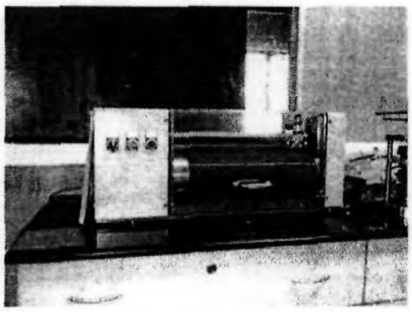
Abrasion resistance is defined as the resistance of a rubber composition to wearing away by contact with a moving abrasive surface. It is usually reported as an Abrasion Resistance Index, which is a ratio of the abrasion resistance of the test compound compared to that of a reference standard measured under the same test conditions.

Abrasion resistance is measured under defined conditions of load, speed and type of abrasive surface. The standard laboratory tests generally cannot be used to predict service life, because factors affecting abrasion are complex and vary greatly from application to application. Nevertheless, abrasion resistance tests are useful in making quality control checks on rubber products intended for rough service.

Abrasion resistances of the samples were measured using a DIN abrader (As per DIN 53516). It consists of a drum on to which a standard abrasion paper is fixed .The drum rotated at a speed of 40 ± 1 rpm and the total abrasion length is 42m. Sample having a diameter of 16 ± 0.2 mm and thickness of 6-10 mm is kept on rotating sample holder with a 10 N load applied over the sample. Initially a pre-run was given for the test sample for a definite distance and it was weighed. The weight after the final run was also noted. The difference in the weight is the abrasion loss. It is expressed as the volume of test piece getting abraded away by its travel through 42 meters on a standard abrasive surface. The abrasion loss is calculated as follows.

$$\mathbf{V = \Delta W / \rho \quad \times 1000}$$

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



Din Abrader

2.13.5 Compression set (ASTM D395 B)[88, 93]

Compression set under constant deflection was tested using a compression device of three plates between the parallel faces of which the specimen may be compressed. Steel spacers, were placed on each side of the specimen to control their deformation while compressed.

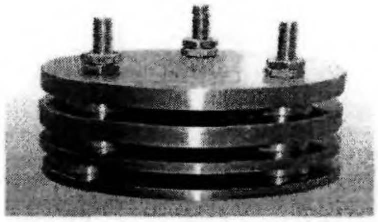
Samples were placed in the compression device after measuring the original thickness (to). The bolts were tightened so that the plates are drawn together uniformly until they are in contact with the spacers. The extent of compression employed was about 25%. The assembled device was then placed in an oven at 70°C for 22 hrs. The pieces were removed and the thicknesses (t_1) were measured after cooling for 30 min.

Compression set was calculated using the following formula.

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

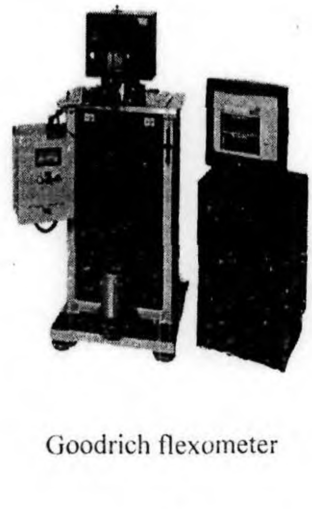
Where

t_0 = the original thickness, t_1=compressed thickness, t_s = spacer thickness



2.13.6 Heat build-up (ASTM D 623-67) [88, 94]

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°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 4.45 mm. 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.



Goodrich flexometer

2.13.7 Flex crack resistance: ASTM D 413-95

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 energy density) at a point in the material. The second approach 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 vulcanizates was measured using De-Mattia flexing machine Model 'de-mattia flexon' check. The machine operated at a constant speed under load at 300 ± 1flexing 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 centre of the groove by a piercing tool of 2 mm width. The flexing is such that the specimen is bent almost double at the groove then straightened out without extension. Crack growth is measured at regular intervals with the point being the number of cycles required to extend the crack to 20 mm. The test was conducted at room temperature and was reported as the increment in cut length in milli meter. Crack initiation and crack failure also tested using 'de-mattia flexon' check.

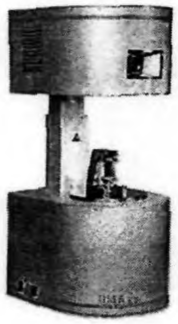
Gibitre Flexometer

2.13.8 Payne Effect (Difference in Storage Modulus G' at Small Strains and at High Strains):

The filler-filler interaction was first measured by Payne and is termed as 'Payne effect'. The Payne effect is the drop of the shear modulus (G') with increasing strain amplitude. It corresponds to a gel-sol transition of the filler network at moderate strain and a breakdown of remaining sub-clusters at large strain. Measurements were done using a Rubber Process Analyzer 'RPA 2000' from Alpha Technologies.

2.13.9 Dynamic mechanical analysis

.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 analyser. Dynamic Mechanical analysis of prepared samples are done using DMA model01dB DMA 50N of metrvib, France.



DMA

CHAPTER -3

RESULTS AND DISSCUSSION

RESULTS AND DISSCUSSION

3.1 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric studies showed that the various Rubber-silica master batches prepared contains 40.9, 46.4, 150, 76, 58.2 silica respectively. One typical TGA graph is given below.

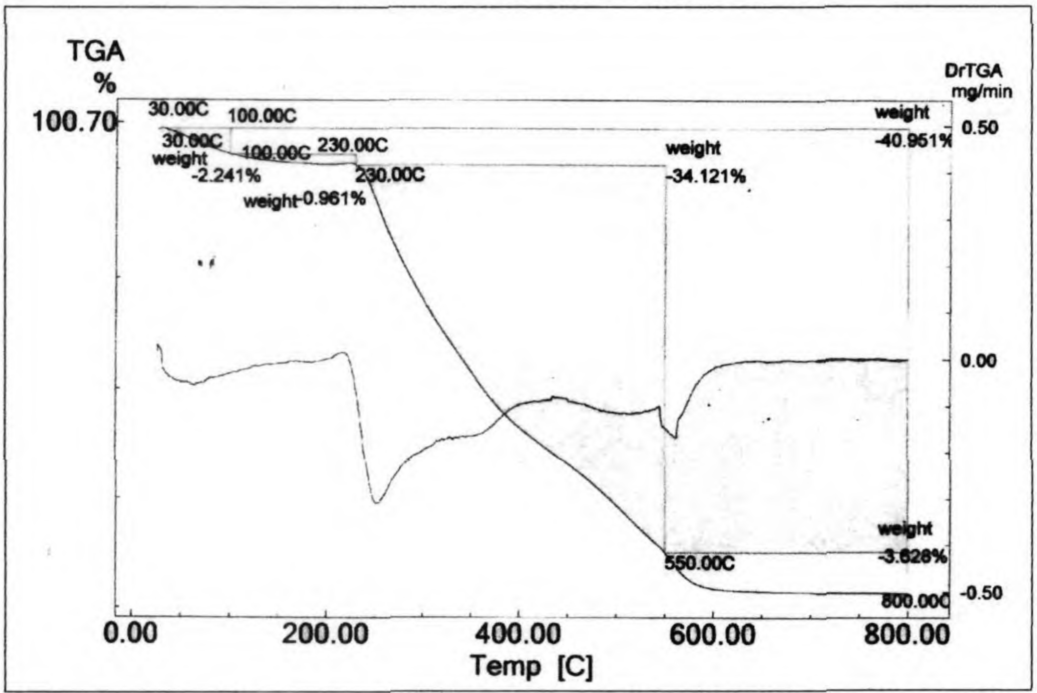


Fig 3.1 TGA of Masterbatch

3.2 Ash test

Ash test results are shows that the various master batches prepared contains 40.9, 46.4, 150, 76, 58.2 silica respectively. The 3rdbatch with 150 parts silica per 100 rubber and 4th batch with 76 parts silica per hundred rubber are then diluted to 50 and 55 parts of silica respectively by blending with required quantity of ISNR-3L, the final silica content of these samples were found to contain 50.8 and 53.3 parts of silica per 100 rubber respectively.

3.3 Particle Size Analysis

Particle size of silica dispersions were measured and are given in Table 3.1. and in Fig.3.22

Table 3.1 Particle Size of Dispersions

Mixing condition	Size (d.nm)			% intensity		
	1st peak	2nd peak	3rd peak	1st peak	2nd peak	3rd peak
24 hour ball milling	441.7	132.6	-	63.1	36.9	-

3.4. Cure characteristics

The cure characteristics of the compounds were studied using RPA 2000. Cure time, scorch time, minimum torque and maximum torque values are recorded for this test. Cure characteristics of silica filled NR compounds with various plasticizers, are given in Table 3.2, Figures 3.2 and 3.3.

Table 3.2 Cure characteristics

Property	Compound number									
	1	2	3	4	5	6	7	8	9	10
Maximum torque, (M_H)dN.m	16.96	17.71	14.21	17.47	21.34	15.57	16.48	15.68	16.25	18.28
Minimum torque, (M_L)dN.m	0.73	0.72	0.15	0.86	0.90	0.49	0.66	0.23	0.88	0.65
M_H-M_L	16.23	16.99	14.07	16.61	20.44	15.07	15.82	15.46	15.36	17.66
Scorch time, ts_2,min.	1.70	1.67	1.80	1.31	2.43	2.28	2.42	2.43	1.75	2.74
Optimum cure, t_{90}, time(min.)	4.21	4.23	4.34	4.53	5.86	5.78	5.90	5.59	5.01	6.70
Optimum cure,t_{95}, time(min.)	5.19	5.17	5.00	5.54	7.015	7.33	7.34	6.49	6.12	8.18

Minimum rheometric torque is indirectly proportional to the Mooney Viscosity of the compounds and Maximum torque value in the torque in the RPA is associated with the modulus of the vulcanizates. In the case of naphthenic oil based compounds Maximum torque (M_H) values are in the order compound 5 > compound 2 > compound 4 >compound 1 >compound 3. At the same time for the vegetable oil based plasticizer containing compounds, the corresponding values are in the order compound 10 > compound 7 > compound 9 > compound 8 > compound 6. In the case of naphthenic oil based compounds, Minimum torque (M_L) values are in the order compound 5 > compound 4>compound 1 > compound 2 > compound 3. At the same time vegetable oil based compounds are in the order of compound 9 > compound 7 > compound 10 > compound 8 > compound 6. Minimum torque values, an indication of processability shows that vegetable oil plasticized compounds are better in this regard.

In both plasticizer cases, Optimum Cure time (t_{90}) values increases with filler loading. Two exceptional cases in compounds 3,4,8,9 are likely to be due to the experimental error (These batches were prepared by diluting the masterbatches with ISNR-3L and this may have resulted in improper filler distribution). Optimum Cure time (t_{95}) values of naphthenic oil based compounds are in the order of compound 5 > compound 4 > compound 1 > compound 2 > compound 3. Cure time values of vegetable oil based compounds are in the order of compound 10 > compound 7 > compound 6 > compound 8 > compound 9.

Scorch time is the premature vulcanization and it is a measure of shelf life of the compounds. Scorch time values of naphthenic oil based compounds are in the order of compound 5 > compound 3 > compound 1 > compound 2 > compound 4. Scorch time values of vegetable oil based compounds are in the order of compound 10 > compound 8> compound 7 > compound 6 >compound 9. Naphthenic oil based compounds show lower scorch values when compared to vegetable oil plasticized compounds.

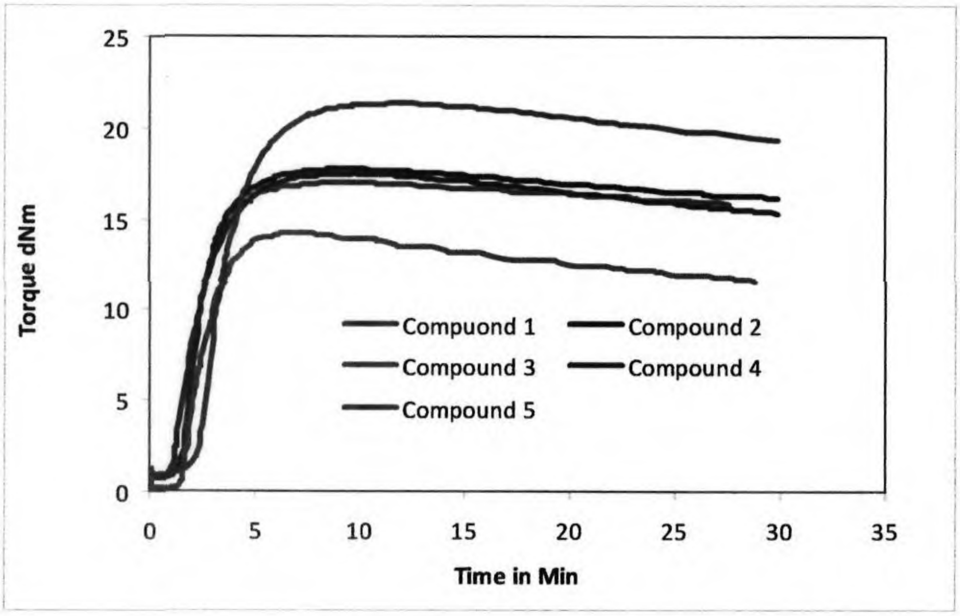


Fig. 3.2 Cure curve of Samples 1-5

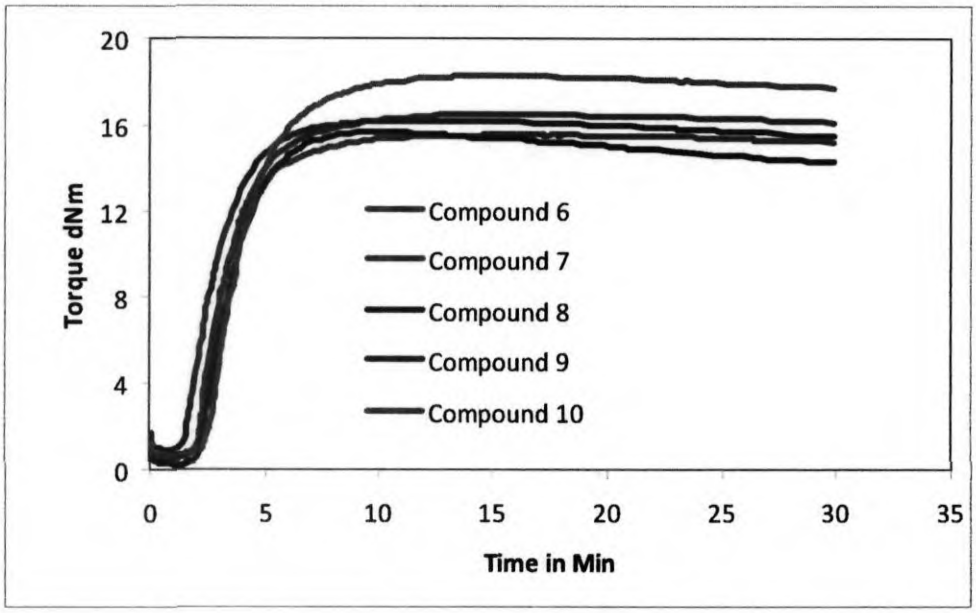


Fig.3.3. Cure curve of Samples6-10

3.5. Tensile properties

In cross linked rubbers reinforcing fillers can enhance its mechanical properties Viz, modulus, tensile strength etc. Tensile properties of the experimental vulcanizates are given in Table 3.3. Variations in Tensile Strength and Elongation at break are plotted in Figures 3.4, and 3.5.

Table 3.3 Tensile properties

Properties	**Compound number**									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Tensile Strength (N/mm^2)	29.5	28.5	7	24.6	27.5	27.5	27.5	8.1	24.5	28
100% modulus (N/mm^2)	2.65	2.9	3	3.14	3.40	2.3	2.55	3.4	2.95	3.3
200% modulus (N/ mm^2)	6.5	7.4	5	6.8	8.3	5.7	6.5	5.7	6.6	8.4
300% modulus (N/ mm^2)	11.6	13.1	-	11.4	14.3	10.5	11.7	-	10.9	14.5
Elongation at break (%)	640	600	285	595	510	650	650	290	650	545

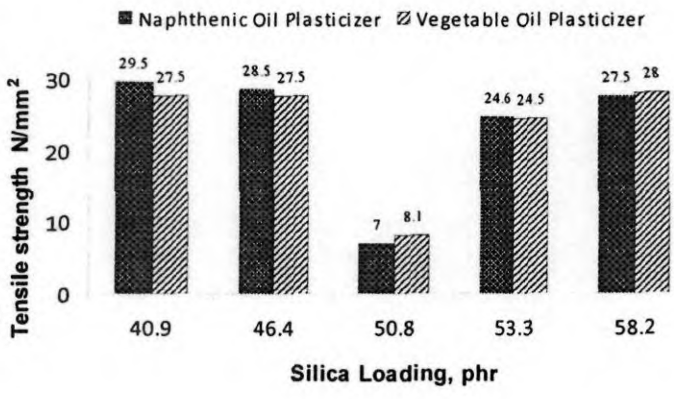


Fig.3.4. Tensile Strength of Samples

It can be observed that in silane modified silica filled NR based compounds, tensile strength values were in the range 26.6 to 30 N/mm^2 .Comparing the first 5 batches, the tensile strength was in the order of compound 1 > compound 2 > compound 5> compound 4 > compound 3 and for the next 5 batches was in the order of compound 10 > compound 6 = compound 7 > compound 9 > compound 8.

In the case of first 5 batches, the plasticizer used is naphthenic oil and the tensile strength of master batches decreases with filler loading and in the case of next 5 batches with vegetable oil based plasticizer, the tensile strength of master batches increases with filler loading with two exceptional results in both cases at 50.8 and 53.8 phr loading of silica. These two batches were made by diluting master batches contain very high loading of silica, which might have resulted in poor dispersion of silica and hence erratic results. On comparison of the results of the master batches with two different plasticizer, the batches with vegetable oil plasticizer exhibited almost consistent result.

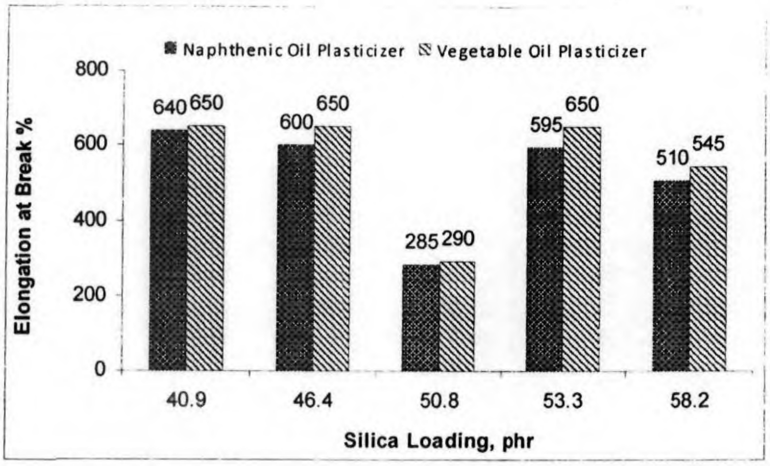


Fig. 3.5 Elongation at break of Samples

In the case of first five master batches Elongation at break (EB) was in the order compound 1 > compound 2 > compound 4 > compound 5 > compound 3. In the case of vegetable oil based plasticizer used master batches the EB was in the order of compound 6 = compound 7 = compound 9 > compound 10 > compound 8 .In the naphthenic oil based first 5 batches, Elongation at break decreases with increase in silica loading and in next 5 batches Elongation at break shows almost similar result.

Modulus variations of various composites are shown in Figures 3.6 and 3.7. In the case of first five master batches, modulus at 100% was found to increase with increase in silica loading. Corresponding 200% modulus values were in the order of compound 3 < compound 1 < compound 4 < compound 2 < compound 5 and 300% modulus values were in the order compound 4 < compound 1 < compound 2 < compound 5.

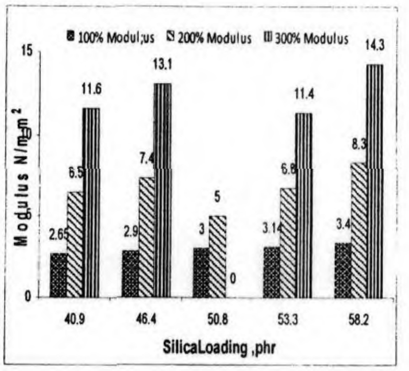


Fig.3.6 Modulus of Samples 1-5

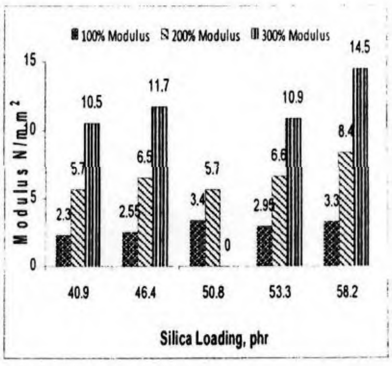


Fig. 3.7 Modulus of Samples 6-1

For the last five batches modulus at 100% was in the order of compound 6 < compound7 < compound 9 < compound 10 < compound 8 .Corresponding 200% modulus values were in the order of compound 6 = compound 8 < compound 7 < compound 9 < compound 10 and 300% modulus values were in the order compound 6 < compound 9 < compound 7< compound 10.

3.6 Technological properties

Technological properties of the compounds are given in Table 3.4

3.6.1 Tear strength

Tear strength, is a critical measure of the filler reinforcement. The values of tear strength for the experimental composites are given in Table 3.4 and Figure 3.8.

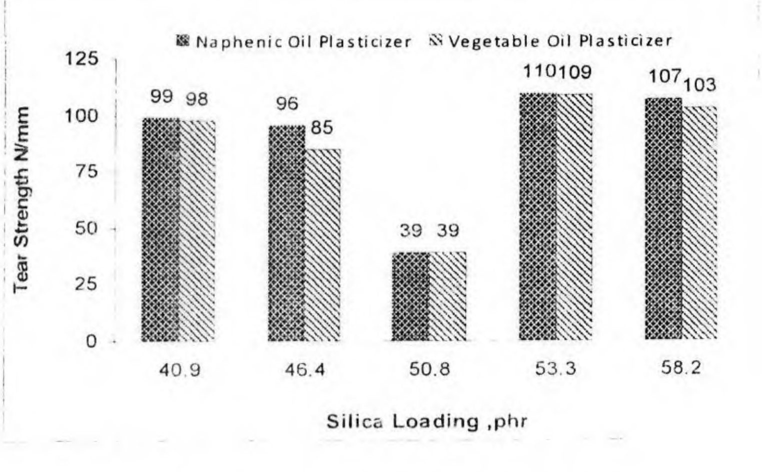


Fig. 3.8 Tear Strength of Samples

Various silica filled NR master batches using naphthenic oil as plasticizer shows tear strength in the order of compound 4 > compound 5 > compound 1 > compound 2 > compound 3 and master batches using vegetable oil based plasticizer shows tear strength in the order of compound 9 > compound 10 > compound 6 > compound 7 > compound 8. The results indicate that the physical and chemical nature of plasticizer has an effect on the distribution of silica in the matrix and consequently the properties. When compared, the batches with similar silica loading and with different plasticizer exhibit closer tear strength values.

3.6.2 Hardness

Hardness values (shore A) of the experimental composites are given in Table 3.4 and Figure 3.9. In general, Hardness values increases with increase in silica loading for both plasticizers and varies in the range of 60 to 71. Hardness values for naphthenic oil based compounds (from 1 to 5) are 60, 60.5, 65, 71 and 65 respectively and for vegetable oil based compounds (from 6 to 10) are 60, 62, 65, 67 and 65 respectively. When compared, the batches with different plasticizer and with similar silica content also have almost closer Hardness.

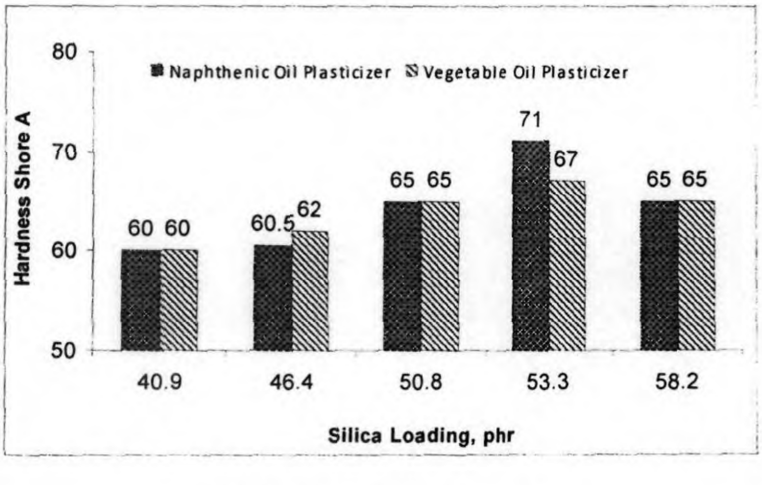


Fig. 3.9 Hardness of Samples

3.6.3 Heat-Build up

The values of heat build up for various composites are given in the Table 3.4 and Figure 3.10.

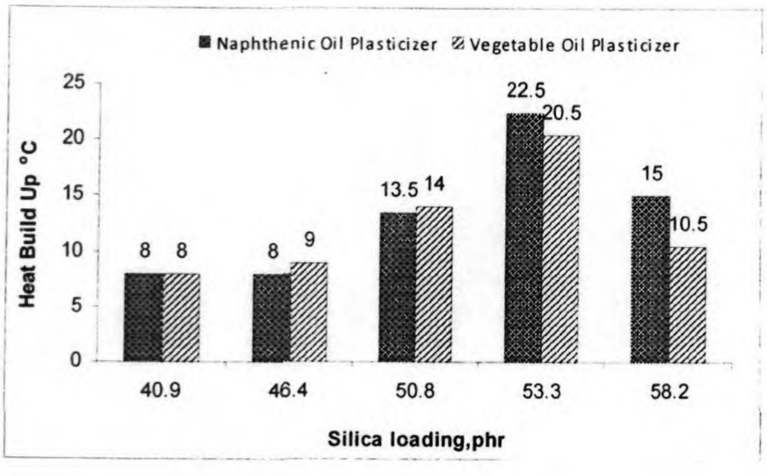


Fig. 3.10 Heat Bulid-up of Samples

For the experimental composites heat build up values vary in the range 8 to 22.5. Heat build-up values for naphthenic oil based compounds are in the order 8, 8, 13.5, 22.5, 15 respectively for samples 1 to 5 and for vegetable oil based are in the order 8, 9, 14, 20.5, 10.5 respectively for compounds 6 to 10 respectively. When compared, the batches with similar silica content and with different plasticizer exhibited closer heat build- up values.

3.6.4. Compression set

Compression set values of the experimental composites are given in Table 3.4 and Figure 3.11. Compression set values can be taken as a measure of the viscous and elastic component of the composites.

Variations in Compression set values with silica loading for the two plasticizers are in the range of 29.3 to 40.5 for first five compounds (naphthenic oil based) and for next five are in the range 23.5 to 33.3 (Vegetable oil based). Compression set values for naphthenic oil containing compounds from 1 to 5 are 32, 31.5, 37, 40.5, 29.3 respectively and for vegetable oil incorporated compounds from 6 to 10 are 23.6, 23.5, 33.3, 30.5, 24 respectively. Vegetable oil based plasticizer incorporated compounds exhibits lower set values than naphthenic oil incorporated systems. The batches 3, 4, 8 and 9 were made by diluting master batches containing high loading of silica and these samples exhibited comparatively high values which might have resulted from improper silica distribution in the matrix.

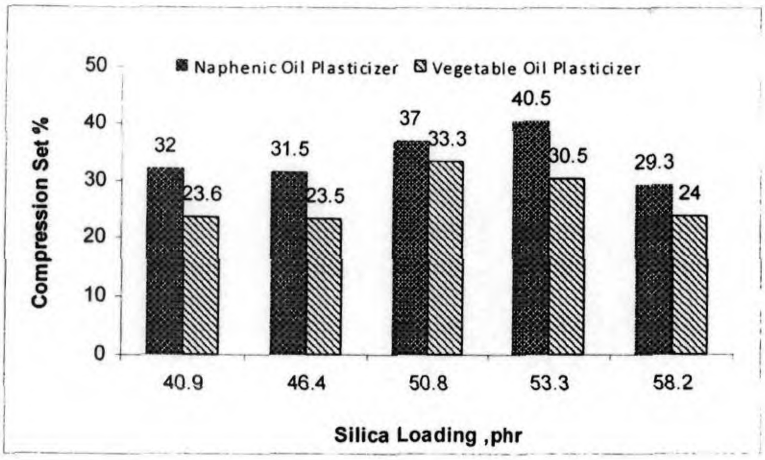


Fig. 3.11 Compression Set of Samples

Rubber composites being visco-elastic, compression set is caused by the viscous component. As the cross link density is more, the elastic component becomes higher and the viscous component becomes lower. From Table 3.2, it can be noted that the cross link density as indicated by the (M_H - M_L) is higher for compound 5 and hence might have resulted in lower compression set.

3.6.5. Abrasion resistance

Abrasion resistance test of rubber is a laboratory measure of the wear resistance of rubber products. In filler incorporated products, abrasion resistance is a measure of the extent of reinforcement which again is dependent on filler dispersion in the matrix. Higher the abrasion resistance better will be the reinforcement. Values of volume loss of samples on abrasion test carried out as per DIN 53516 are given in Table 3.4 and Figure 3.12.

Abrasion loss of first fives compounds increased with filler loading with two exceptional results in the case of 3rd and 4th compound. In the case of last five compounds the results in the range of 89.5-94.2 with two exceptional results in the 8th and 9th compounds. Samples with vegetable oil based plasticizer exhibited comparatively good abrasion resistance over naphthenic oil based.

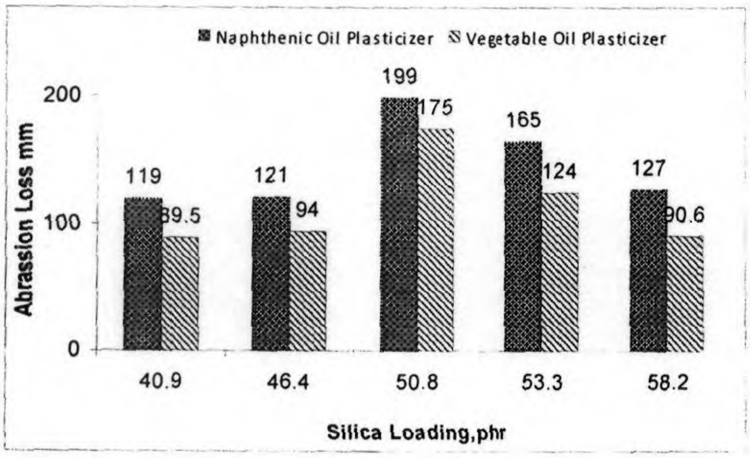


Fig. 3.12 Abrasion Loss of Samples

Table 3.4 Technological properties

Properties	Compound number									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Tear strength(N/mm)	99	96	39	110	107	98	85	39	109	103
Hardness, Shore A	60	60.5	65	71	65	60	62	65	67	65
Abrasion loss(mm^3)	119	121.1	199.3	165	127	89.5	94.2	175.4	124.2	90.6
Compression set (%)	32	31.5	37	40.5	29.3	23.6	23.5	33.3	30.5	24
Heat build up(°c)	8	8	13.5	22.5	15	8	9	14	20.5	10.5

3.7 Payne Effect of Compounds

RPA 2000 was used to study filler- filler interaction of the experimental compounds. Shear modulus (G') values were plotted against strain %. From the plot of G' vs strain percentage, the higher G' at lower strain exhibits higher filler-filler interaction in a rubber compound and the lower values denote lower filler-filler interaction. The reinforcing effect depends on several parameters such as filler particle size and its structure, surface energy and morphology; and volume fraction of filler. Lower filler-filler interaction and better filler-rubber interaction are desirable for lower hysteresis loss in rubber compounds. In this study, filler-filler interactions of two compounds with identical silica loading and with different plasticizers (Naphthenic oil and Vegetable oil based) were compared. Observations are given in Figures 3.13, 3.14, 3.15, 3.16, 3.17 and 3.18 respectively.

Values of G_0 - G_∞ , a measure of filler-filler interaction for different compounds are also compared in Table 3.5.

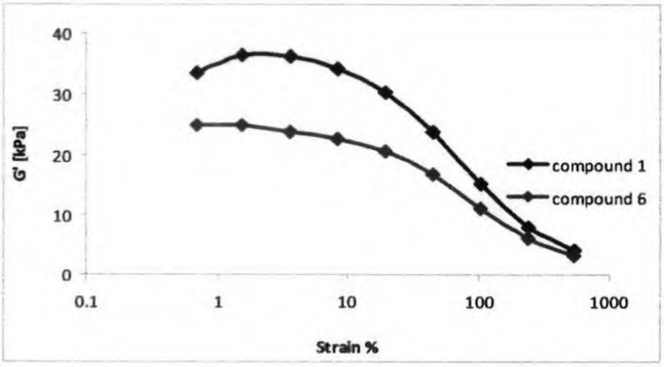


Fig. 3.13 Payne Effect of Compound 1 and 6

On comparison of compounds 1and 6 with 40.9 parts silica loading, the latter exhibited lower filler -filler interaction as can be observed from Fig.3.13.

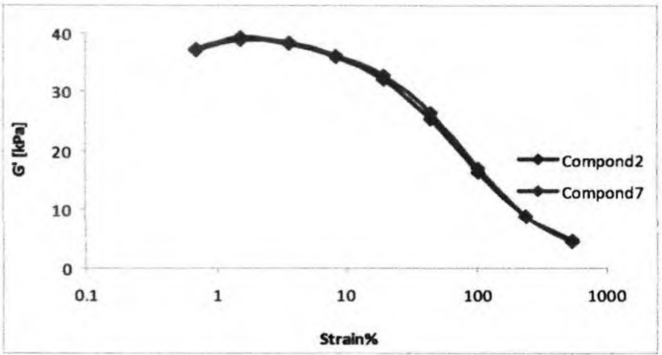


Fig. 3.14 Payne Effect of Compound 2 and 7

Comparison of Payne effect of compounds 2 and 7 with 46.4 parts silica loading is given in Fig. 3.14. It is observed that both the compounds exhibited almost similar level of filler- filler interaction.

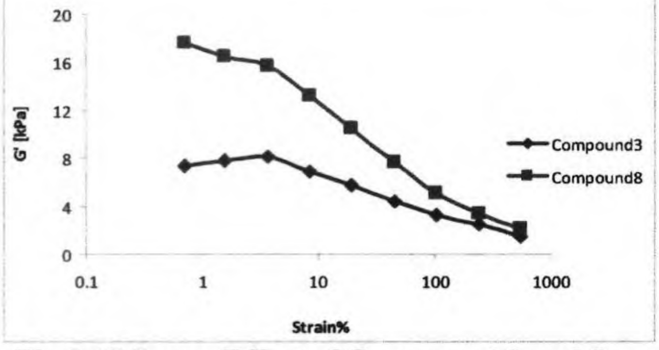


Fig.3.15 Payne Effect of Compound 3 and 8

Payne effect comparison of Compounds 3 and 8 with 50.8 parts silica loading is given in Fig.3.15. Compound 3 exhibited higher level of filler- filler interaction compared to 8.

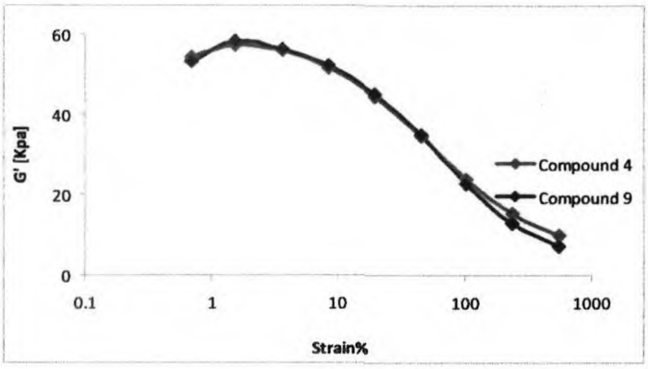


Fig 3.16 Payne Effect of Compound 4 and 9

On comparison of compounds 4 and 9 with 53.3 parts silica loading, for Payne effect is given in Fig. 3.16. Both of them gave almost similar nature in filler- filler interaction except that the G' value at higher strain for compound 9 is lower than that of compound 4 which may be due to comparatively lower filler-filler interaction

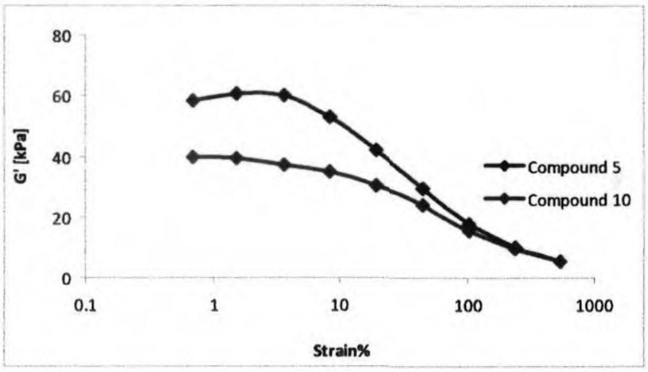


Fig. 3.17 Payne Effect of Compound 5 and 10

Table 3.5 Payne effect data

Property	Sample Number									
	1	2	3	4	5	6	7	8	9	10
G_0	33.50	37.12	7.34	54.38	58.11	24.78	37.24	17.59	53.18	39.90
G_∞	4.16	4.73	1.44	9.86	5.24	3.26	4.41	2.13	6.98	5.31
$G_0 - G_\infty$	29.34	32.39	5.9	51.12	52.87	21.52	32.83	15.46	46.2	34.59

On comparison of compounds 5 and 10 with 58.2 parts silica loading, compound 5 showed higher filler- filler interaction compared to compound 10.

From the Payne effect studies it is observed that vegetable oil based compounds can contribute to lower filler - filler interaction in silica filled natural rubber.

3.8 Demattia Flex Crack Resistance

Results of the study are given in Tables 3.6 and 3.7. Two approaches to determine the fatigue life of rubber have been established, viz: the crack nucleation approach and the crack growth approach. Crack initiation of all the samples was in the range of 120-145 kilo cycles and crack failure in the range 220 - > 400 kilo cycles, except 3and 8 (which are batches diluted with fresh rubber and hence might have resulted in improper dispersion).

Table 3.6 Demattia Crack Initiaion / Complete Failure analysis

Compound Number	1	2	3	4	5	6	7	8	9	10
Crack Initiation (kCys)	121.5	121.5	0.63	121.5	145	121.5	130	0.63	120	123
Complete Failure (kCys)	220	>400	70	>400	>400	>400	>400	70	230	>400

In crack growth study most of the samples required more than 26 kilocycles to crack to 12mm width from an initial 2mm crack width. For various samples, 12mm crack length is reached in a range of flexing cycles from 3 to > 300 kilocycles. Almost all samples in general exhibited better crack growth resistance except batches 3 and 8. Poor results of batches 3 and 8 might be due to poor silica distribution in the matrix.

Table 3.7Crack Growth resistance of Samples

Compound Number	1	2	3	4	5	6	7	8	9	10
No. of kilo Cycles used to crack 12mm	34	29	< 3	27	49	27	26	< 3	29	> 300

3.9. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was carried out using DMA model 01 dB DMA 50 N of Metravib, France, using temperature sweep mode from -90 to +100 °C. DMA of samples 1and 6 (40.9 phr silica with different plasticizer) are compared in Figure 3.18 and 3.19 respectively. DMA of samples 2 and 7 (46.4 phr silica with different plasticizer) are given in Figures 3.20 and 3.21 respectively.

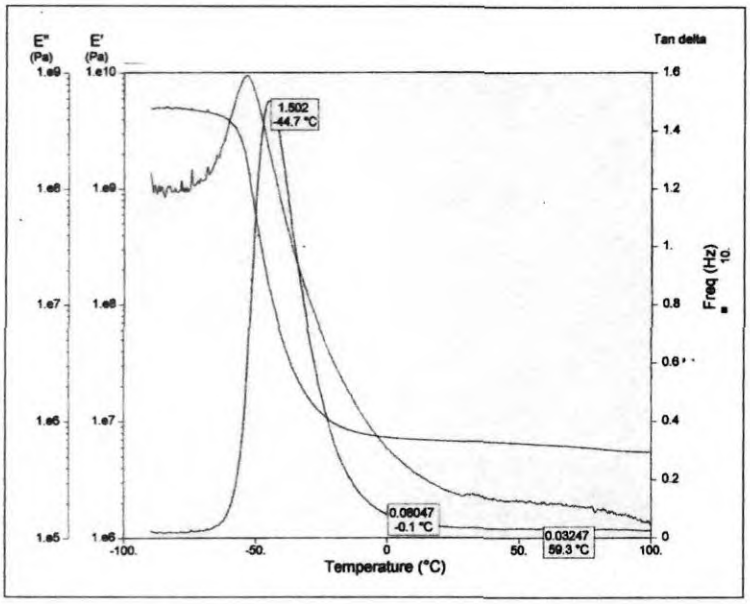


Fig.3.18. DMA Cure of Sample 1

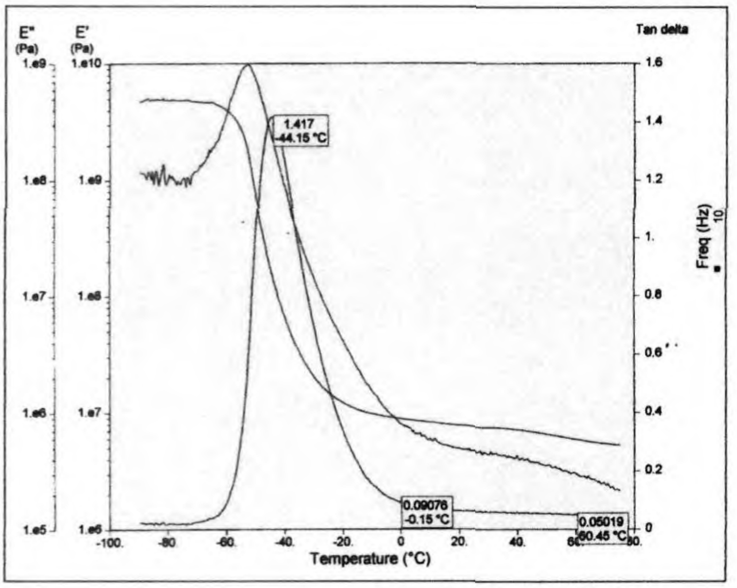


Fig.3.19. DMA Cure of Sample 6

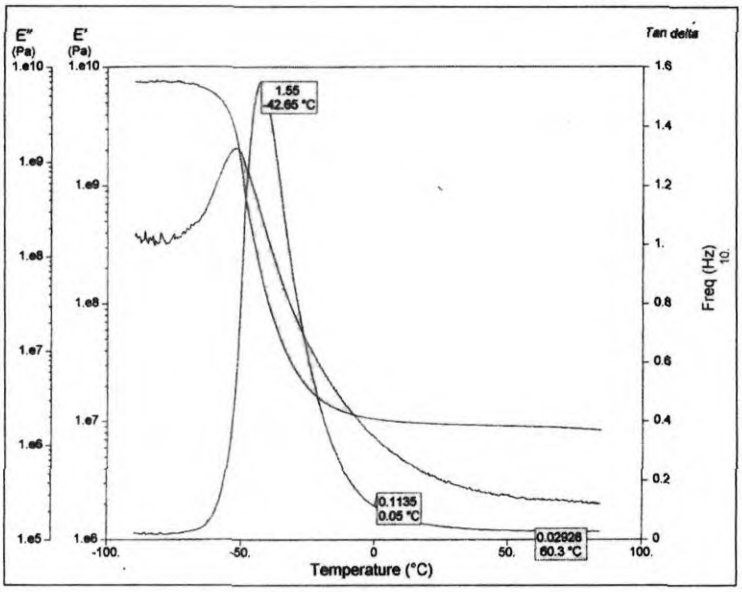


Fig.3.20. DMA Cure of Sample 2

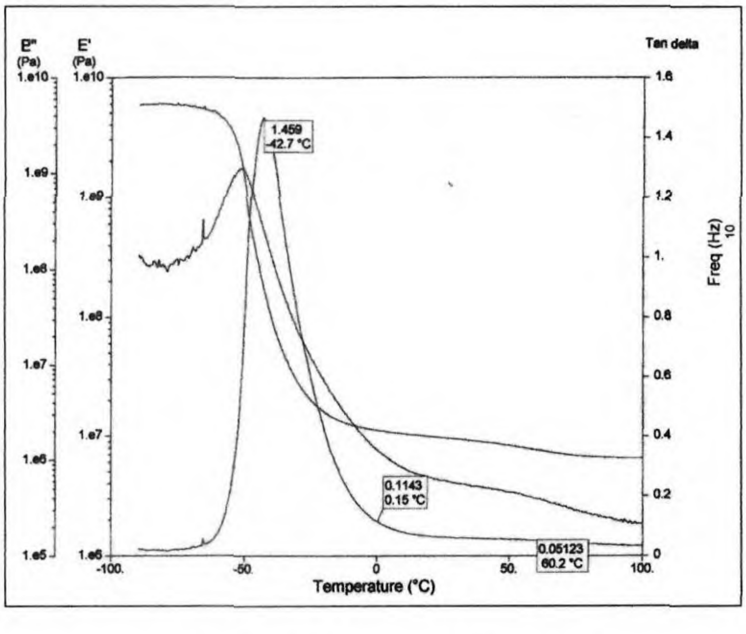


Fig.3.21. DMA Cure of Sample 7

On comparing the DMA graphs of samples 1 and 6, tan delta values indicates that filler - rubber interaction of sample 6 is better than compound 1(Lower tan delta peak value for sample 6). Similar is the case with samples 2 and 7.

Results indicate that samples 6 and 7 with vegetable oil based plasticizer exhibits better filler to rubber interaction than samples which contains naphthenic oil plasticizer.

CHAPTER 4

SUMMARY AND CONCLUSIONS

CHAPTER- 4

SUMMARY AND CONCLUSIONS

In silica filled rubber composites, effective dispersion of silica in the rubber matrix is important for achieving optimum properties in the ultimate product. Use of silanes and functionalisation of the polymers are some of the techniques being used for achieving this objective. In the present study silica filled rubber composites are prepared by wet master batching technique with different filler loading. Also in these composites two different plasticizers exhibited variations in processability, cure characteristics, tensile and technological properties.

The major conclusions drawn from this study are discussed in this chapter.

- Wet master batching of silica in natural rubber gave almost similar properties as that obtained by dry mixing.
- Properties of composites varied with filler loading
- Master batches with a definite filler concentration made directly from latex exhibited properties better than that made by blending masterbatch with fresh rubber to achieve same level of filler concentration.
- Choice of plasticizer is a critical parameter in deciding the ultimate properties of silica filled composites.
- Payne effect studies showed that masterbatches incorporated with vegetable oil based plasticizer resulted in lower filler –filler interaction.
- DMA analysis shows that plasticizer also plays a role in rubber-filler interaction.

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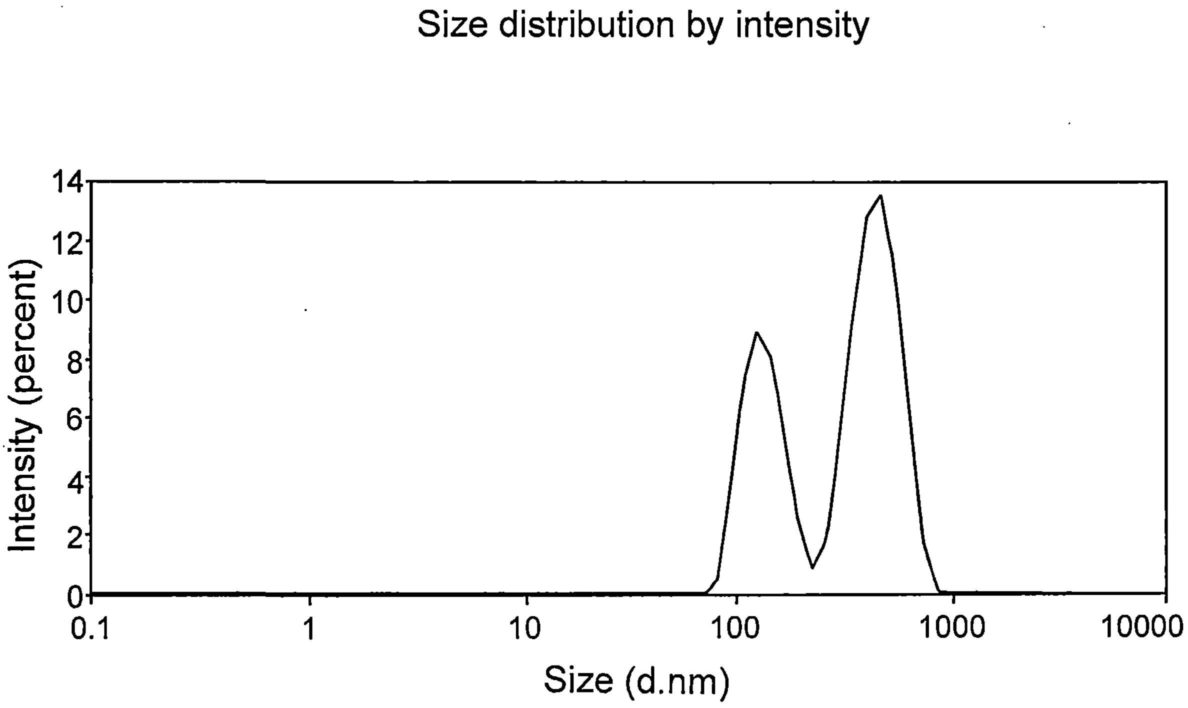
Size distribution by intensity
Intensity (percent)
0
2
4
6
8
10
12
14
0.1
1
10
100
1000
10000
Size (d.nm)

Figure 3.22