STUDIES ON IN SITU PRECIPITATED SILICA FILLED RUBBER COMPOSITES

WITH SPECIAL REFERENCE TO NR, NBR AND SBR

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By

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Certificate

This is to certify that the thesis entitled **"Studies on in situ precipitated silica filled rubber composites with special reference to NR, NBR and SBR"** which is being submitted by Mrs. Maya K.S in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi - 22 is a record of the bonafide research work carried out by her under my guidance and supervision, in the Department of Polymer Science and Rubber Technology, Kochi - 22 and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.

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DECLARATION

I hereby declare that the work presented in this thesis entitled **"Studies on in situ precipitated silica filled rubber composites with special reference to NR, NBR and SBR"** is based on the original research work carried out by me under the guidance and supervision of Dr.Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 22 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

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PREFACE

Precipitated silica is promising non-black filler for rubber vulcanizates. It can be used to replace carbon black partly in tyres to reduce the rolling resistance of tyres and hence to bring down the fuel consumption. However, silica is not compatible with the commonly used olefinic hydrocarbon rubbers and hence mixing and homogeneous distribution of silica in rubber is difficult. Coupling agents are often necessary for proper binding of rubber and silica. Coupling agents facilitates filler incorporation and enhances the properties of the final product. The coupling agents also improve the processing behaviour by reducing the specific surface energy and the solubility parameter of the silica. However, these improvements are accompanied by other problems like ethanol formation, higher processing temperature and higher cost of the product. So alternative methods or materials for overcoming the problems associated with the silica reinforcement of rubbers are therefore a current research priority.

In this study a novel route for precipitating silica particles in rubber latex i.e. *in situ precipitation*, followed by coagulation of the latex to get rubber, containing silica is investigated. Properties of the composites prepared with the in situ precipitated silica are compared with the composites of conventional silica.

Contents of the thesis

The thesis is divided in to eight chapters.

A comprehensive introduction and review of literature pertaining to reinforcement of rubber, covering, reinforcement with particulate fillers, silica, reinforcing effects, mechanism of reinforcement, effect of silica reinforcement on processing and compounding aspects of silica with rubber are presented in Chapter 1. The scope and objectives of the study are also presented in this Chapter.

The specifications of the materials and details of the experimental techniques used in this study are given in Chapter 2.

A novel route for in situ precipitation of silica particles in concentrated natural rubber latex and analysis of the physical, chemical, thermal and morphological characteristics of in situ precipitated silica in comparison with commercial nano silica, VN3 are discussed in Chapter 3.

The studies on the vulcanizates of natural rubber filled with in situ precipitated silica and comparison of their properties with composites filled with other silica are presented in Chapter 4. Preparation and properties of composites containing both carbon black and in situ precipitated silica are also reported along with the in situ precipitation in field latex.

The effect of the use of epoxidised natural rubber as a reinforcement modifier for in situ precipitated silica based natural rubber composites is evaluated in Chapter 5. Comparison of the properties of the same with those of conventional silica based composites with and without Si 69 is also given in this chapter.

The possibility of in situ precipitation of silica in nitrile rubber latex and the properties of the composites filled with in situ precipitated silica are evaluated in Chapter 6. The mechanical properties of the vulcanizates containing this silica are compared with reference compounds prepared from conventional silica.

In situ precipitation of silica in Styrene butadiene rubber latex and the comparison of the mechanical properties of the in situ precipitated silica based Styrene butadiene rubber composites with vulcanizates prepared from conventional silica are given in Chapter 7.

The summary and conclusions of the study are presented in Chapter 8

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Chapter 1

INTRODUCTION

Rubber technology is passing through a major paradigmatic change due to the replacement of carbon black by silica. Silica filled tyres have the great advantage of reduced rolling resistance and as a consequence, reduced fuel consumption. The importance of this development is far reaching in the light of our limited resources of fossil fuels and aggravating environmental problems. A 2% reduction in the rolling resistance can give a fuel saving of about 3 to 4%. This environmental and economical incentive of silica technology is large enough to overcome the higher production cost due to the difficulty in incorporating silica in rubber and the need for coupling agents. However, if the incorporation of silica is made easier and the need for coupling agents can be dispensed with, silica technology will take a quantum leap in the years to come. This study has been undertaken with the objective of explaining methods that make silica incorporation easier and absolutely more efficient, without any coupling agents whatsoever or as an alternative, adopting cost effective alternatives.

Rubbers in general are seldom used in their pristine form. They are "too weak to fulfil practical requirements because of lack of hardness, strength properties and wear resistance. So they are used with a number of other components called compounding ingredients, which improve the processability, 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 characterised by their reinforcing effects, which ranges from inactive, semi active to very active fillers. The designation 'active` or 'reinforcing` refers to the influence of the filler on compound viscosity and failure properties such as tensile strength, abrasion and tear resistance. Structure as well as the surface properties of the filler is the main characteristics that determine the reinforcing effect. Active fillers are characterised by a large relative surface area and a high structure, both properties resulting in a strong interparticle 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. Figure 1.1 illustrates the influence of the addition of increasing amounts of reinforcing fillers on various properties of an elastomer.[1]

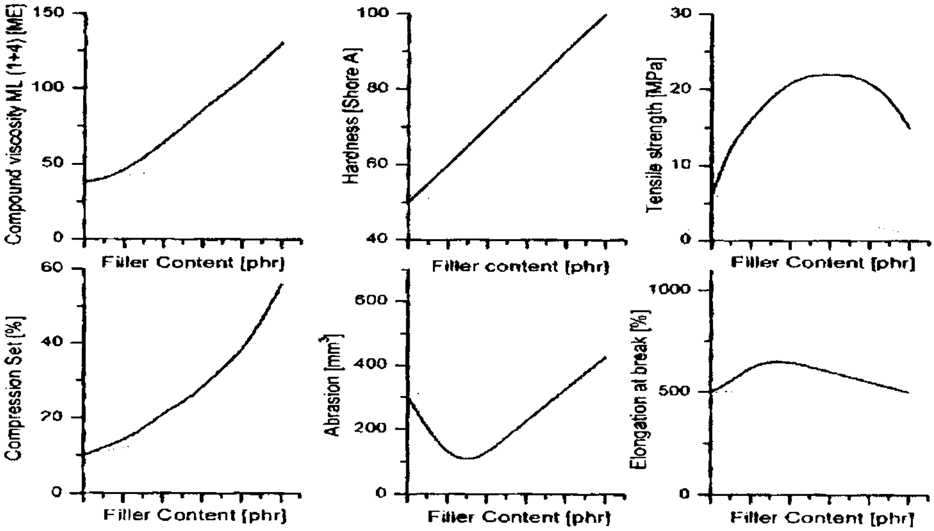


Figure 1.1. The influence of reinforcing fillers on the properties of an elastomer. — active fillers ...... non-active fillers

1.1 Reinforcement of rubber with particulate fillers

Another classification of fillers on the basis of its physical nature groups them in to continuous (fibre, filament or tape) and discontinuous in form (whisker, flakes or particle). Silica is generally a 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-crystallising rubbers.[2] 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.

Particle size

The reinforcement effect is mainly influenced by the size of the filler particles, the most important property that influences reinforcement.[3] The principal requirement for rubber reinforcement is sufficiently small domain size, less than about 1μm. Sufficiently small filler can give good reinforcement, even when matrix/domain bonding is poor (e.g. graphitised or fluorinated carbon black).[4,5] However, if domain size is greater than about a micron, reinforcement is absent or minimum, regardless of domain shape and strength of bonding between the matrix and domain.

Surface area

The most important single factor, which determines the degree of reinforcement is the development of a large polymer-filler interface. It can be provided only by particle of colloidal dimensions. Spherical particles of 1μm in diameter have a specific surface area of $6 m^2/cm^3$. This constitutes approximately the lower limit for significant reinforcement. The upper limit of useful specific surface area is of the order of 300-400 m^2/cm^3 and it is decided on the basis of considerations of dispensability and processability of the unvulcanized mix and serious loss of rubbery characteristics of the composite.[2] The surface area of particulate solid is related to its particle size.

If all the particles are considered as spheres of the same size, the surface area As, per gram of a filler can be calculated from the equation

$$As = 6/d\rho \qquad \text{.........................} \; 1.1$$

where d is the diameter and ρ the density of the filler particle. In reality particles have a distribution of size and are usually far from being spherical. Different fillers of the same particle size may not impart the same reinforcement, e.g., carbon black and silica. The shape of particle also may be different for different fillers, viz; spheroidal, cubic/prismatic, tubular, flaky or elongated. Non-spherical particles can impart better reinforcement.[6,7]

Specific surface activity / chemical composition

The specific surface activity denotes the chemical composition of the filler surface. The nature of the filler surface may be varying in a chemical sense, having different chemical groups, e.g., hydroxyl or metal oxide in white fillers and carbonyl, quinone, lactone etc in carbon black.[7] In a physical sense they may be different in adsorptive capacity and in energy of adsorption, e.g., polar rubbers showing dipole interaction with filler surface groups.

Chemical surface groups on fillers play an important role in their effect on rate of cure, with many vulcanizing systems. Physical adsorption activity of the filler surface is of greater importance than its chemical nature. Carbon black, which loses the active sites on heat treatment, exhibits poor mechanical properties. Strong chemical bonding between filler and polymer does not lead to desirable vulcanizate strength properties, but causes high moduli.

Structure /aggregation

The term `Structure' refers to the aggregation of primary particles resulting in deviation from the spherical shape leading to lower packing density and higher void volume. Aggregates can be of different shape such as (a) spherical (b) ellipsoidal (c) linear and (d) branched.[8] High structure carbon exhibits high oil absorption. In the case of inorganic or mineral fillers, differences in particle geometry depending on the crystal form of each mineral can be observed. Crystals with almost identical dimensions in the three directions will result in isometric particles. Higher anisometry as in the case of platelets, rod shape etc, when used in rubber results in high modulus.

Filler aggregates in elastomer matrix have a tendency to form agglomerates, especially at high loading, leading to chain like filler structure or cluster, generally termed as `secondary structure' or filler network. Such a network has a significant effect on the properties of filled rubber. Tables 1.1 and 1.2 show the various effects of filler particle size and structure on rubber compound processing and vulcanizates properties.[9]

Table 1.1. Effect of particle size and structure on processing characteristics

Processing properties	Decreasing particle size	Increasing structure
Loading capacity	Decreases	Decreases
Incorporation time	Increases	Increases
Oil extension potential	Little	Increases
Dispensability	Decreases	Increases
Mill bagging	Increases	Increases
Viscosity	Increases	Increases
Scorch time	Decreases	Decreases
Extrusion shrinkage	Decreases	Decreases
Extrusion smoothness	Increases	Increases
Extrusion rate	Increases	Little effect

For effective reinforcement, specific surface activity and structure are necessary. High structure without surface activity does not result in high reinforcement.[7]

Table 1.2. Effect of particle size and structure on vulcanizates properties

Vulcanizate properties	**Decreasing particle size**	**Increasing structure**
Rate of cure	Decreases	Little effect
Tensile strength	Increases	Decreases
Modulus	Decreases	Increases
Hardness	Increases	Increases
Elongation	Decreases to a minimum and then Increases	Decreases
Abrasion resistance	Increases	Increases
Tear resistance	Increases	Little effect
Cut growth resistance	Increases	Decreases
Flex resistance	Increases	Decreases
Resilience	Decreases	Little effect
Heat build-up	Increases	Increases slightly
Compression set	Little effect	Little effect
Electrical conductivity	Increases	Little effect

Porosity

Porosity is a characteristic property of carbon black and can be seen with many particulate fillers. Filler porosity can affect the valcanizate properties. However, its effect on reinforcement is secondary. In most cases the pores are too small for the polymers to enter although some smaller molecules in the compound may do so. In the case of carbon black, porosity results in higher viscosity and higher electrical conductivity.[7]

1.2 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.[2]

Carbon black

In 1904, S.C.Mote, working for the India rubber, Gutta Percha discovered the reinforcing effect of Carbon black.[10] 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. [2,3,7]

Carbon black is characterized based on its surface area, particle size, structure and tinting strength. Surface area is usually determined by iodine adsorption, nitrogen adsorption or cetyl trimethyl ammonium bromide (CTAB) adsorption. Structure refers to the bulkiness of the carbon black aggregate. Bulkiness is associated with large average number of particles per aggregate. Structure is measured by dibutyl phthalate (DBP) absorption (ASTM D-2414) method. Tinting strength is a measure of the amount of carbon per aggregate and is measured by optical means.[11,12,13] Elastomer reinforcement of carbon black is dependent on these properties. Dispersion of carbon black in the elastomer also influences the extent of reinforcement. A typical range of specifications of the four different carbon blacks is given in Table 1.3.[14]

Table 1.3. Specifications of different carbon blacks

Characteristics	Lamp	Channel	Furnace	Thermal
Average particle size (nm)	100-150	1-3	14-80	240-320
Surface area (N_2) (m^2/g)	20-95	100-1125	27-145	7-11
Oil absorption (ml/g)	1.05-1.65	1.0-6.0	0.67-1.5	0.32-0.47
Volatile matter (%)	0.4-0.9	3.5-16.0	0.3-2.8	0.1-1.0
Ash (%)	0-0.16	0-0.1	0.1-1.0	0.2-0.5
Sulphur (ppm)	-	0-0.1	0.5-1.5	10
pH	3-7	3-6	5.0-9.5	7-9

Table 1.4. Properties of furnace blacks

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

Carbon blacks have reactive organic groups on the surface that cause affinity to rubber.[15] Incorporation of carbon black into rubber gives enhanced modulus, improved fatigue and abrasion resistance and better overall technological properties. Details of a range of furnace blacks generally used for rubber reinforcement are given in Table 1.4.[14] The reinforcing action of filler - elastomer systems has been extensively studied for carbon black in hydrocarbon rubber and a mechanism of reinforcement has been developed by Boer.[16]

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

a. Fillers used to reduce cost

b. Semi- reinforcing filler

c. 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.[2, 7,17] 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.[18]

1.3 Silica

Silica is a crystalline compound occurring abundantly as quartz, sand and many other minerals and is used to manufacture a variety of materials, especially glass and concrete. Natural silica is non-reinforcing and has been used as a filler, only to reduce the cost. The synthetic ones are reinforcing and nowadays have particle sizes as small as the carbon black besides an extremely reactive surface.[19] Important natural varieties are silica (amorphous), silica (crystalline), silica diatomaceous (fossil origin) and silica (microcrystalline). Types of synthetic silica are precipitated, pyrogenic, aerogels and hydrogels. Of these varieties, precipitated silica and pyrogenic (fumed) silica are being used for elastomer reinforcement.

Production and Characterization of silica

Acidification of alkali silicate solutions under controlled conditions produces precipitated silica.[20]

$Na_2SiO_3 + HCl \rightarrow 2NaCl + H_2O + SiO_2$

Colloidal pyrogenic silica is produced by reaction of silicon tetrachloride at high temperatures with water.

$SiCl_4 + 2\,H_2O \rightarrow SiO_2 + 4HCl$

The reaction products are quenched immediately after coming out of the burner. Pyrogenic silica is too active and expensive.[15] Precipitated silica is silicon dioxide containing about 10-14% water, with particle size in the range 1-40 nm. They are reinforcing fillers giving composites of high tensile strength, tear resistance, abrasion resistance and hardness. It is being used in the manufacture of translucent and coloured products, shoe soling, tyres and other mechanical rubber goods. Fumed or pyrogenic silica is silicon dioxide containing less than 2% combined water. These silicas are highly reinforcing fillers of very small particle size, giving high tensile strength, tear resistance and abrasion resistance particularly to silicone rubbers.[7]

Characterization of silica filler is also based on particle size and specific surface area. Surface area measurement is usually done by nitrogen adsorption (BET) method. Also pH, chemical composition and oil absorption are specified. The smallest physically observable primary particle for precipitated silica is about 15-20 µm and for fumed silica it is about 15 µm in size. The surface forces of the small primary particles are so high that many particles agglomerate to form the so-called secondary particles. Usually the shear forces generated during rubber mixing are not sufficient enough to disperse primary filler particles in the rubber.[15]

The secondary particles of silica fillers form further agglomerates. They form chain-like structures, the so-called tertiary structures. Though the tertiary structures are also relatively stable, they get more or less shattered by the shear forces during mixing.[15] The higher the shear force, the better the dispersion.

Chemistry of silica

Silicon dioxide is commonly called silica. In silicon dioxide, silicon atom uses d orbitals for bonding and hence SiO_2 exists as infinite three-dimensional structures and it is a high melting solid.[22] Silica which is amorphous, contains about 4% water and can be represented as $SiO_2.nH_2O$. It consists of silicon and oxygen arranged in a tetrahedral structure with particle size usually ranging from 1-30 nm and the surface area from 20-300 m^2/g. Surface silanol concentration (silanol groups - Si-O-H) influences the degree of hydration. Water content can affect processing and vulcanization.[2] Absorbed water can decrease cure time, tensile strength and also abrasion resistance.[21] Silanol types fall into three categories - isolated, geminal (two-OH groups on the same silicon atom) and vicinal (-OH on adjacent silicon atoms).

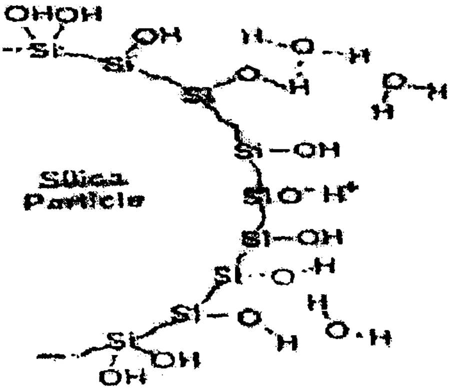


Figure I. 2. Adsorptive nature of silica filler

Isolated hydroxyls exist predominantly on dehydrated silicas, pyrogenic silica and to a lesser extent on precipitated silica. Vicinal hydroxyls are stronger adsorption sites and hence, have stronger reinforcement effect than the isolated hydroxyls. The hydroxyl groups on the surface of the silica control surface acidity. This intrinsic acidity can influence vulcanization. These sites affect the rubber filler interaction. A general silica structure is depicted in Figure I. 2.

The polar hydroxyl groups on the silica surface lead to the adsorption of foreign substances. So moisture is absorbed by silica. The higher moisture content increases the dispersion time of silica into the rubber. The filler also adsorbs organic compounds, particularly basic ones, e.g., diphenyl guanidine (DPG) and diortho tolyl guanidine (DOTG). Therefore, a larger amount of the same has to be added to compensate for the loss due to adsorption by silica. Accelerator adsorption by the filler will be lower, if it already contains water.

Silica properties and surface characteristics

The primary filler characteristics influencing elastomer reinforcement are:

- Surface chemistry, structure and relative surface area
- Particle size and particle size distribution
- Structure of the filler aggregates, agglomerates and primary particles

The rubber-filler interface formed during mixing is primarily responsible for the level of properties such as abrasion resistance, tensile strength and tear propagation. The structure of the filler network influences the viscoelastic properties like elasticity, loss modulus and hysteresis.

Surface chemistry

The surface chemical groups play an important role in their reinforcing ability for elastomers.[15] The surface of silica is covered by a layer of acidic silanol groups and different siloxane groups called geminal, vicinal, clustered and isolated groups.[22,23] The functional groups are randomly distributed over the whole surface,[24] in contrast to carbon black, where the functional groups are preferably located on the edges of the crystallites. The silanol groups on the surface of different silica particles interact with each other, resulting in strong agglomerates due to the hydrogen bonds between the silanol groups.[25,26] The moieties on the silica surface also interact with basic accelerators, resulting in reduced curing rates and lower crosslink densities. [27,28] They can react with other chemical compounds such as stearic acid, polyalcohols and amines. These compounds compete with the coupling agent for adsorption sites on the filler surface, reduce the concentration of free surface silanol groups and thus the silanization efficiency.[29]

The silica surface has a tendency to adsorb moisture due to the hydrophilic character of the filler. This adversely influences the curing reaction and hence the properties of the final product. However, certain moisture content is required for the silanization reaction, as hydrolysis of the ethoxy groups of the coupling agent is a precondition for the secondary reaction to take place.[30,31,32]

The average size of silica aggregates in a rubber matrix depends on the surface concentration of the silanol groups. A higher number of silanol groups per unit surface area results in an increase of aggregate size, leading to a higher concentration of occluded rubber.[33] The relative surface area has an ambivalent influence on processing and properties of a rubber compound: On one hand it has a negative influence on the processing behaviour, as a larger surface area results in a higher compound viscosity and compound additives like accelerators are inactivated on the filler surface to a higher degree. On the other hand, a higher surface area has a positive influence on filler dispersion.[34]

Surface energy

The energy distribution of the silica surface is inhomogeneous due to the distribution of silanol and siloxane groups and impurities.[35] The surface energy γ_s of fillers is comprised of a dispersive and a specific component, γ_s^d and γ_s^{sp} respectively.[36,37]

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \qquad \dots\dots\dots\dots \quad 1.2$$

The dispersive component, based for example on London forces, is responsible for the rubber-filler interaction.[22] Rubber-filler interaction depends on the surface energies of the two. It is the two components of the surface energy of the filler, which describes its distribution in the rubber γ_s^d is high for carbon black, while γ_s^{sp} is high for silica. This implies that the former can disperse easily in rubber, the latter leads to high filler-filler interaction, which in turn will lead to filler agglomeration and therefore poor dispersion in the rubber matrix. This component is rather low in the case of silica, thus resulting in a low reinforcing effect, expressed by very low concentrations of bound rubber and a low modulus at medium and large strain amplitudes.[38] However, polymer chains are entrapped in voids of the silica agglomerates and aggregates: occluded rubber.[26] The dispersive component is influenced by the degree of hydration of the silica. Increasing water contents are reducing the dispersive component even further.[39] The specific component characterizes the interaction between the filler particles, and examples of these forces are dipole-dipole forces, induced dipole forces or hydrogen bonds. The contribution of the specific forces to the surface energy is higher for silica compared to carbon black.[37] The balance of the dispersive and specific surface forces results in the unfavourable situation, that the filler-filler interaction is high and the interaction with the polymer is low for silica, with the consequence, that viscosity as well as Payne effect are high.[40] These effects can be reduced by using coupling agents, silanes for example, together with the silica filler.

Silica-polymer interaction

One of the models for the adsorption of polymers on the surface of carbon black is based on the uncoiling of the polymeric chains and multiple adsorption of these chains onto the surface of the filler. The released adsorption enthalpy is partly changing the chain conformation entropy, enabling the chains to abandon their coiled conformation and to take the form of trains. With several contacts per polymer chain the bonding strength of a polymer molecule is in the range of a chemisorptive interaction.

The intensity of wetting of the filler by a polymer depends on the difference of the solubility parameters.[41] The surface concentration of adsorbed trains is inversely proportional to the difference of the solubility-parameters between the polymer and the filler.[42] The solubility parameters for some polymers and fillers are given in Table 1.5.[40] For the silica-polymer system the difference of the solubility parameters is significant, with the effect that the two materials are difficult to blend. When a coupling agent is used, a hydrophobic shell is formed around the filler particle and the solubility parameter of the filler is reduced, the difference in the solubility parameters decreases and the compatibility of the two materials increases.

Table 1.5. The solubility parameters of common compounding ingredients

Material	Hildebrand Solubility parameter
FKM, silicones	7 - 7.5
PE, EPM, EPDM	8
NR, BR,IR	8 - 8.5
SBR, low molecular weight resins	8.5 - 9
CR, CSM, some NBR	9 - 9.5
Typical lubricants and process aids	8.5 - 9.5
PVC, ECO, ACM, some NBR	9.5 - 10
Carbon black	12 - 15
Clay, whiting, talk	13-14
Silica (untreated)	14-18

1.4 Silica - surface modification

The surface of silica is less complex than carbon black. Wagner[21] has made an extensive review on different aspects of silica and silicates. The imperfections in the lattice structure leave free silanol groups on the surface. The number of silanols, their distribution and also the conformation of the surface siloxanes depend on the method of preparation and thermal treatment. The distribution and also the close proximity of the hydroxyl groups have an influence on the adsorption and reinforcing properties.[43]

Various modifications have been done to improve the reinforcing ability of the silica, which include heat treatment, polymer grafting on silica surface and chemical modification. Heat treatment is the simplest way of modifying the silica surface. The surface hydroxyl groups remain constant up to a temperature of 300°C. At this temperature the adsorbed water molecules are removed and then thermal condensation begins. At temperatures beyond 600-700°C, only 1.5 -OH per nm^2 is left over.[44] Linger et al[45,46] have used Inverse Gas Chromatography (IGC) for characterizing the heat treated silica surface. At infinite dilution, IGC is an ideal tool to characterize the changes in the surface of the silica due to heat treatment.

To improve the performance properties of rubber compounds silica surface was modified using copolymers of isoprene with vinyl acetate, acrylonitrile, 4-methoxy styrene, 4-chloro styrene and methyl methacrylate.[47] Surface modification of silica so as to increase the silica – rubber bonding is a method used for the better reinforcement.[48] Surface-modified silica nanoparticles are used for the reinforcement of PMMA[49] Silica surface modification by grafting of alkyl chains through esterification has been reported by several workers. Esterification of silica surface by methanol, ethanol and butanol was reported.[50,51,52] Donnet et al [53,54,55] have reported the characterization of alkyl grafted silica surface using IGC. Grafting of methyl and hexadecyl chains on the surface of silica has been found to decrease the thermodynamic parameters. Esterification results in the reduction of the dispersive component γ_s^d of the surface energy. By esterification, the surface heterogeneity of the unmodified silica reduces and hence the filler- filler inter-aggregation diminishes. Silica surface was modified with primary boron-amine groups and its behaviour has been studied under different reaction conditions by M.Rosario et al.[56]

Silanes are used to modify the silica surface by chemical reaction with the silanol groups. Varieties of silanes are being used by the polymer industry for improving the interfacial adhesion or bonding of silica with the polymers. Plueddmann[57] gives a detailed account of the use of silanes, in bonding thermoplastic polymers to mineral surfaces. A series of silane coupling agents are available with general formula $YRSiX_3$, in which Y is the organofunctional radical, R represents the alkyl group and X the silico functional group such as chloro, alkoxy or acetoxy which on hydrolysis get attached to the silica surface groups. Silanes generally are of three categories viz; Monofunctional silanes, bifunctional silanes and non-sulphur bearing silanes.[58]

Examples of few commercially important monosilanes are

1. PTES - Propyl triethoxy silane
2. ETES- Ethyl triethoxy silane
3. OTES- Octyl triethoxy silane
4. HDTES - Hexa decyl triethoxy silane

Hydrophobation through silanization of silica with a monofunctional silane reduces the filler network, thereby makes the silica more compatible with the rubber matrix. The extent of network reduction depends not only on the degree of hydrophobation(amount of silane) but also on the kind of silane. Alkyl chain length is a factor in determining the reduction of filler network.

Bifunctional silanes are used as coupling agent, which chemically binds silica with rubber. The silicofunctional group reacts with the filler surface groups and the organofunctional group with the rubber resulting in rubber-silica bonding, thus results in improved reinforcement. Several silanes with appropriate functionality such as alkoxyl silyl groups have been successfully used as coupling agents.[59,60] Some of the bifunctional silanes of commercial importance are the following.

1. TESPT - Bis (triethoxy silylpropyl) tetrasulphide (Si 69)
2. TESPD - Bis (triethoxy silylpropyl) disulphide
3. TESPM- Bis (triethoxy silylpropyl) monosulphide
4. MTMO-Mercapto propyl trimethoxy silane (A 189)
5. Bis (triethoxysilyl ethyl tolylene) polysulphide (Y 9194)

1.5 Silica-silane reaction

The silane, by co-reacting with the polymers, modifies the polymer morphology at the interface between the filler and the polymer. The formation of a hydrophobic shell around the silica particle by the silica-silane reaction prevents the formation of a filler-filler network due to the reduction of the specific surface energy.[61]

Prior to the chemical reaction of the silane with the silanol groups on the silica surface, the silane molecule has to make contact with the silica surface by adsorption.[62,63] Then the chemical reaction of silica with an alkoxysilyl moiety of the coupling agent takes place in a two-step, endothermic reaction.[64] The primary step is the reaction of alkoxy groups with silanol groups on the filler surface.[29] Two possible mechanisms are reported: Direct reaction of the silanol groups with the alkoxy groups of the coupling-agent, and hydrolysis of the alkoxy groups followed by a condensation reaction with the silanol groups.[65,66] The fact that the rate of silanization is influenced by the moisture content, is an indication that a hydrolysis step is involved. The reaction follows a pseudo-first order kinetic law.[29,67] Figure 1.3 shows the mechanism of the primary reaction.

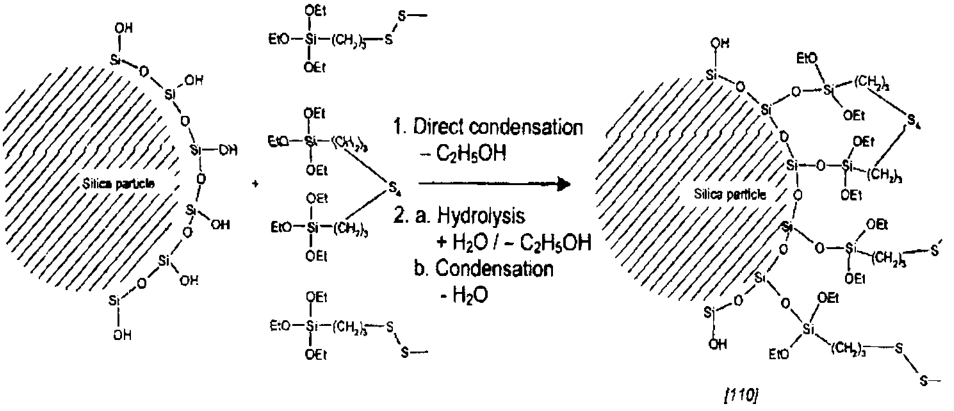


Figure 1.3. The primary reaction of silica with a silane

The secondary reaction (Figure 1.4) is a condensation reaction between adjacent molecules of the coupling agent on the filler surface or between alkoxy groups of the coupling agent and silanol groups of the silica. It is generally accepted that a hydrolysis step is involved in the reaction. In comparison to the primary reaction this step is slower with a factor of approximately 10. The energy of activation for both reactions, the primary and the secondary, is within the range of 30 to 50 kJ/mol. This value is rather low,. indicating that the temperature dependence of the reaction rate is not very strong. The rates of both reactions are influenced by the acidity of the matrix and the reaction is acid as well as alkaline catalysed. The reaction rate is reduced by steric hindrance and an electron donating effect of the leaving group.[68] Not all ethoxy groups react during the silanization reaction: The reaction results in two silane-silica bonds per silyl group, with one hydrolysed ethoxy group remaining.[69] But as the secondary reaction has only a slight influence on the properties of the compound, the incomplete reaction does not negatively influence the final quality of the material.[29]

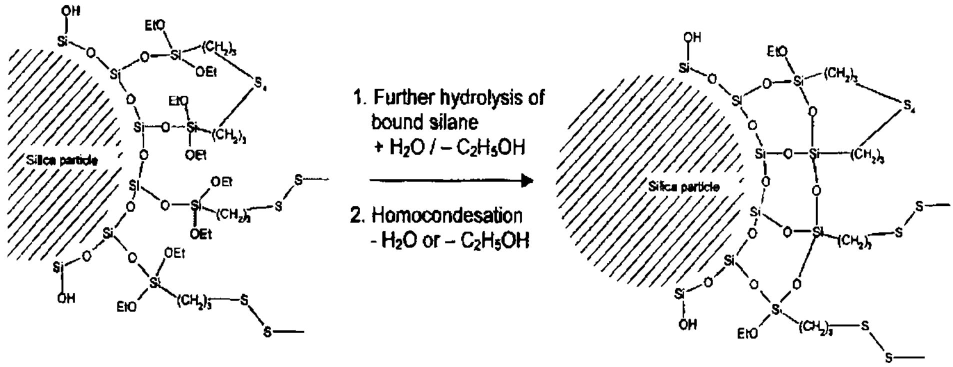


Figure 1.4. The secondary reaction of silica with a silane

The coupling agents need a moiety enabling them to react with the polymer during vulcanization in order to be reinforcing. This is shown in experiments with coupling agents, which can react with the filler but not with the polymer: The reinforcing effect is reduced, as the formation of bound rubber is impossible.[70] In general, the moiety reacting with the polymer is a sulphur group, either a poly- or disulfidic group or a blocked sulphur group. Other functional groups used to link the coupling agents to the polymer are double bonds, which have to be activated by the addition of an active sulphur-compound or by the generation of a radical moiety in order to have a simultaneous crosslinking of the polymer and the coupling agent with comparable reaction rates during curing.

The polysulfidic moieties of the silanes are unstable, and the cleavage of the sulphur groups results in active sulphur moieties, very probably radicals, which react with the polymer under formation of a filler-silane-polymer bond.[71,72,73] Gorl et al studied the reaction mechanism of the silane-polymer reaction with model compounds and they proposed a mechanism, in which an intermediate polysulfide is formed by the reaction of the silane, which is already bound to the silica, with an accelerator containing a disulfidic moiety. This polysulfide substitutes the allylic hydrogen atom on the polymer chain, and the accelerator part is released. Finally a chemical bond is formed between the polymer chains and the filler.[74,75,76] Figure 1.5 shows a general reaction scheme for the formation of the filler-polymer bond.

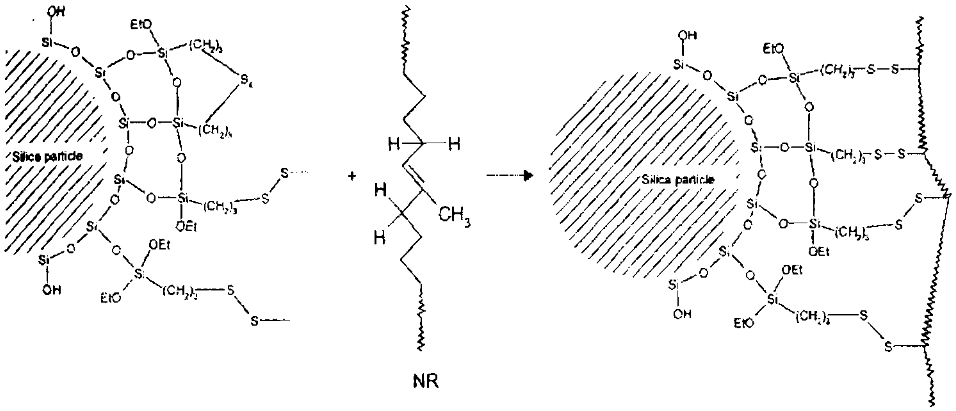


Figure 1.5. General reaction scheme of a polysulfidic silane with an unsaturated polymer.

1.6 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 a lower bound rubber content.[77] However, the combination of silica with a coupling agent has a higher reinforcing effect and different dynamic mechanical properties compared to carbon black.[78] 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.[22]

1.7 Reinforcing effects - mechanism of reinforcement

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.[79] 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. Figure 1.6 illustrates the strain-dependence of the Payne effect and the strain-independent contributions to the shear modulus for carbon black and silica filled compounds [80].

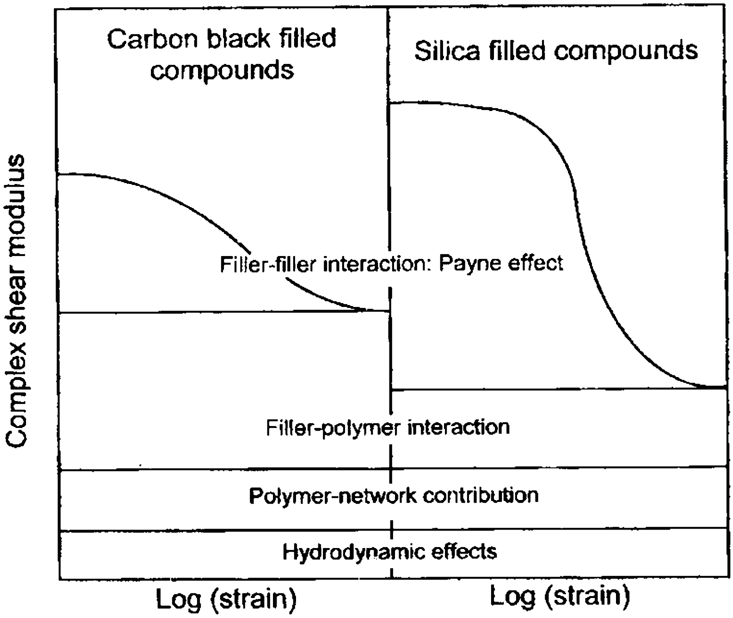


Figure1.6. Effects contributing to the complex shear modulus

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

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.[81] In a polymeric matrix this effect is also measured as an increase of the modulus. The phenomenon was modelled by *Einstein* almost a century ago, and he described the viscosity increase by rigid spherical particles dispersed in a liquid by the following equation.[82,83]

$$\eta_f = \eta_o(1+2.5\Phi) \qquad \ldots\ldots\ldots\ldots \quad 1.3$$

In this equation, η_f is the viscosity of the fluid containing the particles, η_o is the viscosity of the pure fluid and Φ is the volume fraction of the particles. Einstein made the following assumptions for his model:

- Perfect wettability of the spheres
- Uniform spherical particles
- No interaction between the particles

Especially the last two requirements are rarely met in filler-polymer systems. This discrepancy between Einstein's theory and practical experience was taken into consideration by an additional term, introduced by Guth and Gold.[84]

$$\eta_f = \eta_o(1+2.5\Phi+14.1\Phi^2) \qquad \ldots\ldots\ldots\ldots \quad 1.4$$

The term Guth and Gold added, is again a function of the filler volume fraction Φ to the power of two, emphasizing the influence of the filler concentration.

In the case of an elastic matrix, the viscosities of the material can be replaced by the shear moduli, as shown by Smallwood.[85]

$$G_f = G_o(1+2.5\Phi+14.1\Phi^2) \qquad \ldots\ldots\ldots\ldots \quad 1.5$$

The addition of the filler increases the shear modulus of the pure elastomer G_o and results in a shear modulus Gf for the filled compound.

The same correlation holds for the Young's modulus E. A correction for the non-spherical shape of the filler particles, a shape factor fs, was added by Guth, resulting in the following equation.[86]

$$G_f = G_o\,(1+0.67\,fs.\Phi+11.62\,fs^2.\Phi^2) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.6$$

The shape factor f_s represents the ratio of the longest dimension to the shortest dimension of the particle. The modulus as calculated by Equations 1.5 and 1.6 are independent of the applied strain.

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 behaviour 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.[87,88,89]

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 k_B.

$$G_o = \upsilon.k_B.T \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.7$$

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. Figure 1.6 shows the key difference between carbon black and silica. The Payne-effect is stronger for silica, as a consequence of the strong interparticle forces between the filler particles.[90,91]

1.8 Effect of silica reinforcement on processing and properties

Processing of silica compounds

The addition of silica to the elastomer results in a strong increase of the viscosity. Silanol groups, responsible for the strong interparticle forces, cover the silica surface. Silica particles tend to agglomerate, they are difficult to disperse and re-agglomerate after mixing.[22] One of the effects of reagglomeration is the reduction of processability during storage. The viscosity of a compound increases during storage, with an increasing rate at higher temperatures. The viscosity increase follows a second order kinetic law, suggesting that the process is based either on coalescence of filler-bound rubber entities or re-agglomeration of filler particles. The tendency of re-agglomeration is influenced by the water content of the silica. A higher water content results in a lower rate of viscosity increase during storage due to a shielding effect of the water molecules on the surface of the silica, which reduces the interparticle forces.[92]

Hewitt reported that compound viscosity is directly related to the surface area of silica.[93] Highly developed filler networks of silica can give rise to compounds of high viscosities. The difference between types of filler became less pronounced as the average filler particle size is increased.[94] At about 20 nm size silica produces significantly higher viscosity than carbon black of comparable size.[95] Viscosity modification studies of rubbers filled with smaller particle size silica was reported by Dunnom.[96,97] Use of silane coupling agent in silica filled rubbers is an effective means of reducing viscosity of the compounds.[98]

Cure behaviour

Surface groups on fillers have a prominent role in the cure behaviour. Generally they tend to accelerate or retard cure. Silica contains substantial amounts of combined oxygen in the form of silanol (Si-OH) and siloxane (Si-0-Si), which retard sulphur vulcanisation.[98] The silanol groups can interact with curatives through hydrogen bonding. Effect of these interactions can affect compound properties such as viscosity, scorch time, cure rate and cure efficiency and also the vulcanizate properties. Retardation of vulcanization was earlier attributed to the adsorption of curatives by the silica surface.[99] Later studies claim that retardation is due to a deactivation mechanism involving interaction of the filler with the zinc-accelerator-sulphur complex.[100] Addition of activators such as triethanolamine (TEA), diethylene glycol (DEG) and polyethylene glycol are used to reduce the adverse effects of silanol groups.[98] Effect of filler loading on cure time of natural rubber and epoxidised natural rubber and styrene butadiene rubber were studied[101] and found that cure time increases with filler content.

Vulcanizate properties

Tensile strength, tear strength and modulus at high elongation were found to be improved by the incorporation of low particle size fillers.

Strong rubber-filler bonding, which permits bridging of infinite number of rubber chain through the filler, is the main reason for improvement of the physical properties of vulcanizates. Development of high strength is on account of the ability of the rubber to dissipate strain energy near the tip of the growing crack by viscoelastic processes. The dispersed filler particles, in addition to providing energy dissipation, also serve to deflect or arrest growing cracks, thereby delaying the onset of catastrophic failure. The improvements in mechanical properties were related to the secondary structure of the fillers.[102] Tensile stress strain measurements were found to be very effective for characterising the silica filled compounds.[103] Hysterisis loss of natural rubber and Styrene butadiene rubber vulcanizates having variation in loading of silica, clay, resin and curatives were studied over a wide range of temperatures and strain rates and reported that hysteresis increased with filler loading.[104] Influence of silica on the irradiation ageing of silicone rubbers were studied by Stevenson and found that irradiation induces further cross linking at the surface of the nano particles.[105]

Two other important properties that get modified by reinforcement are wear and abrasion. Wear rate is related to filler surface area and structure. Colloidal silica, even when compounded with bonding agents, does not equal carbon black in wear reinforcing capability.[106] For off the road tires, blends of silica and carbon black provide improved cut growth resistance.[107]

Swelling behaviour

Rubber, when it is in the unvulcanized form gets dissolved in a good solvent, but when it is a vulcanized or crosslinked sample it can only swell. Swelling of rubber in a solvent is affected by incorporation of filler.[103] The percentage swelling decreases with increase of filler content.

In the case of a reinforcing filler, strong rubber-filler interaction will have some effect on the apparent crosslink density of the system. Ratio of the restriction of swelling of the filled rubber vulcanizate to that of the gum rubber is used as a means for evaluating the reinforcing ability of a filler in rubber. Kraus developed the following expression relating volume fraction of filled rubber in the swollen gel, Vr_f and volume fraction of gum or unfilled system in swollen gel, Vr_o as,[108]

$$Vr_o / Vr_f = 1 - (m\phi / 1-\phi) \qquad \text{.........................} \quad 1.8$$

where $m = 3C\,(1-Vr_o) + Vr - 1$, ϕ is the volume fraction of the filler and `C' the characteristic parameter of the filler related to the rubber-filler interaction.[109] Cunneen-Russell equation (Eq.1.9), which is based on vulcanizate swelling parameters, is also used for reinforcement characterization.[110]

$$Vr_o / Vr_f = ae^{-z} + b \qquad \text{.............................} \quad 1.9$$

where Vr_o and V_{rf} are the volume fractions of the rubber in the unfilled and filled wlcanizates respectively after swelling in a solvent to equilibrium, z is the weight fraction of filler in the polymer and a and b are two constants which depend on the filler activity. High value of `a' and low value of `b' indicates polymer-filler attachment. $Vr_o / Vr_f < 1$ indicates reinforcement.

Dynamic mechanical properties

The tire performance is related to the dynamic mechanical properties of the material. Rolling resistance, for example, is related to the hysteresis. When energy is brought into the material, it is partly dissipated into the tire material as heat and partly stored elastically. The energy input into a viscoelastic material can be modelled at sinusoidal shear deformation, $\gamma(t)$ of an angular frequency, ω. The shear stress response σ (t) is also sinusoidal, but out of phase with the strain.

$\gamma\ (t) = \gamma_0\ \sin\ (\omega t)$ 1.10

$\gamma\ (t) = \sigma_0 \sin(\omega t + \delta) = (\sigma_0 \cos\delta)\sin\omega t + (\sigma_0 \sin\delta)\cos\omega t$ ...... 1.11.

where γ_0 is the maximum strain amplitude, σ_0 is the shear response at maximum strain, t is the time and δ is the phase angle. The shear stress signal can be separated into two contributions, one in phase with the strain and the other 90° out of phase with the strain. The two components can be described by defining two moduli:

$G' = (\sigma_0 / \gamma_0)\cos\delta$ 1.12

$G'' = (\sigma_0 / \gamma_0)\sin\delta$ 1.13

where G' is the component in phase and G" is the component out of phase with the oscillatory strain. The correlation between strain and stress is expressed by combining Equations 1.11 to 1.13

$\sigma(t) = \gamma_0\ [G'\sin\omega t + G''\cos\omega t]$ 1.14

The two components are the real and the imaginary part of the shear modulusG*, when written in a complex form:

$G^* = G' + iG''$ 1.15

Where G' is the storage or elastic modulus and G" is the loss or viscous modulus. Using these two moduli, the phase angle is defined as follows:

$G''/G' = \tan\delta$ 1.16

Both moduli depend on frequency as well as on temperature. Figure 1.7 shows the frequency-dependence of the storage and loss modulus.[113]

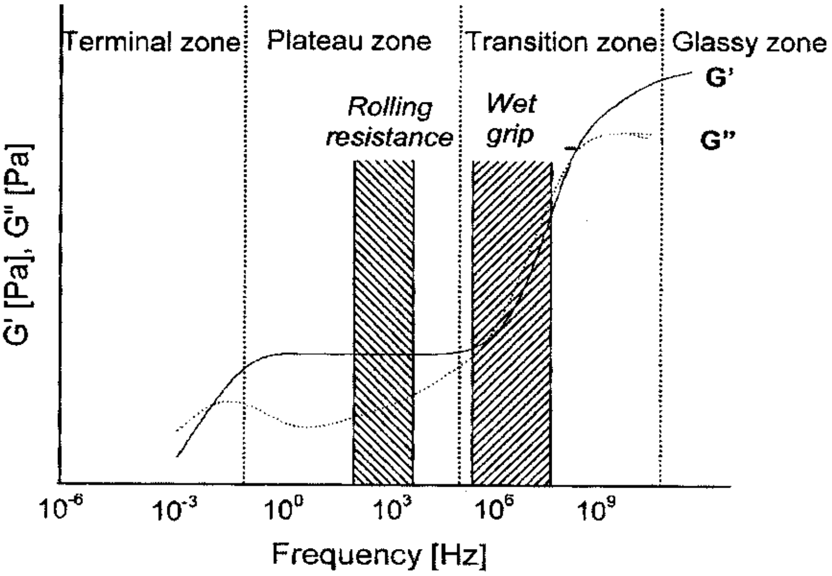


Figure 1.7. The frequency-dependence of the storage and loss modulus.

The dependence of the modulus on frequency is a result of chain and segment motion in the material. At low frequencies, in the terminal zone, the time scales of one cycle of stress application and the enforced chain movements are equal. The polymer chains can follow the applied strain without delay and without loss of energy. With increasing frequencies of the applied strain, entanglements are no longer able to follow the applied strain, they act as temporary cross-links and the material shows elasticity. All other movements are still taking place within the time scale of the load cycle. This region of a constant storage modulus and a minimum in loss modulus is called the rubber plateau. With further increasing frequency the material comes into a transition zone between the rubbery state and the glassy state, which is characterized by a strongly decreasing mobility of the molecules relative to the frequency, with the consequence that both moduli strongly increase. Finally the material enters the glassy state. The material has a high modulus, the result of the rigidity of the polymer chains at these high frequencies. The molecules are not flexible enough to follow the applied strain, only small local chain movements occur. In the transition zones energy dissipation is high, with a maximum of the loss modulus.[111]

The frequency region of rolling resistance and wet skid are indicated in Figure 1.7. Rolling resistance is a characteristic of the rolling tire, and the angular frequency of a rolling tire is within the rubbery zone. Wet skid is a high frequency phenomenon, in the transition zone between the rubbery and the glassy state, typically in the megahertz region. The position of wet skid on the frequency scale shows, that the glass transition temperature has a strong influence on this property of a tire. Materials with a high glass transition temperature are preferred, as their wet skid resistance is high.[112,113]

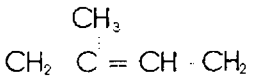
1.9 Compounding of silica with rubber

Compounding of rubber with precipitated silica is quite different from compounding with carbon black. Carbon black is the ideal filler for reinforcing hydrocarbon rubbers. Since both are hydrophobic substances, mixing and reinforcement problems do not usually arise when these two are mixed. Precipitated silica, which is of mineral origin, is one of the most promising alternatives to carbon black. However, due to the difference in surface energy, when silica is mixed with the commonly used non-polar olefinic hydrocarbon rubbers, leads to mixing and reinforcement problems. Another major problem is that silica-to-silica interaction is high, resulting in the formation of large aggregates ultimately impeding the compound flow character. In the case of both carbon black and silica with lower surface area (bigger particle size), viscosity is lower and dynamic properties are better.[114] Fine particle silica could reinforce rubber, but silica filled compounds exhibits higher viscosity and slower cure.

To reduce the viscosity some softeners are used effectively. Natural softeners like vegetable oils and hydrogenated rosin are effective in reducing viscosity, though its mechanism is not fully understood. Petroleum based aromatic resins are effective in giving smooth extrusion, better tensile strength, tear strength and abrasion resistance. Considerable reduction in viscosity is obtained only with additives that de-agglomerate the silica. Additives such as soluble zinc compounds (eg. zinc octoate), hexamethylene tetramine (HMT), magnesium Oxide etc. are reported to reduce compound stiffness. Activators such as Diethylene glycol (DEG), polyethylene glycol (PEG) and triethanolamine (TEA) are used in compounding, which reduces cure time, compression set and heat buildup and enhances the tensile strength.

1.10 Natural rubber and its reinforcement

Natural rubber (NR) is cis 1,4 polyisoprene, the structure of which is given below, is the only natural product in the rubber family. It has been identified in about 2000 plant species, but only the species *Hevea brasiliensis* is of any commercial significance. From the tree the rubber is collected in the form of latex by tapping. Rubber is separated from the latex by coagulation usually by acidification. The resultant coagulum is then processed into different marketable forms of NR such as sheet rubber, technically specified rubber and crepe rubber. Most of the natural rubber based products are made from any of these forms. Also certain products are made from concentrated latex.



$$CH_2 \ \overset{CH_3}{C} = CH - CH_2$$

The molecular weight of polymer ranges from 200,000 to 600,000 with a relatively broad molecular weight distribution.[115] Rubber separated from latex contains more than 90% of the hydrocarbon, cis-1, 4- polyisoprene in admixture with naturally occurring resins, proteins, sugars etc. Most of the latex rubber products can be made from NR latex and dry natural rubber. Apart from the conventional rubber products, NR finds a few specialized applications. Natural rubber is a versatile and adaptable material which has been successfully used for transport and engineering applications such automobile tyres, aero tyres, off-shore and aerospace industries, civil engineering, railways, vibration engineering etc. Though natural rubber exhibits very good strength even without reinforcement by filler, excepting a few latex products, most of the rubber products require reinforcement.[116] Natural rubber was reinforced with the unique composition of Jordanian silica sand at different loadings (10, 30, 50 and 75 phr) and different particle sizes (10, 25, 45 and 75μm) found that they are superior especially for hardness, tensile strength, compression set properties and density.[117] The discovery of reinforcement of natural rubber by particulate fillers is almost a century old. The literature available on this is immensely huge. Nowadays research works are on the challenges, modifications and behaviour related to this topic. Influence of polymer-filler interactions on retraction behaviours of natural rubber vulcanizates reinforced with silica and carbon black[118] is an example. Recently Varkey et al have reported the feasibility of using epoxidised natural rubber as a reinforcement modifier for silica filled rubbers.[119]

1.11 Silica reinforcement of synthetic rubbers

Nitrile Rubber (NBR)

Nitrile rubber (NBR) is a copolymer of acrylonitrile and butadiene and it is a polar rubber. NBR has good resistance to a wide variety of oils and solvents and hence is widely used products like oil seals, pipe protectors, blow out preventors etc.[15] Nitrile rubbers are manufactured by emulsion co-polymerisation of butadiene with acrylonitrile. Major properties of NBR depend on the acrylonitrile content (ACN) and usually vary from 20-50% by weight. Commercially available nitrile rubbers differ from one another in three respects: acrylonitrile content, polymerization temperature and Mooney viscosity. NBR has high viscosity that can be reduced by mastication.

Nitrile rubber in the unfilled form has very low tensile strength. Carbon black and non-black fillers are used for reinforcement. Studies conducted by Wang et al[120] using model compounds revealed that aromatic hydrocarbons exhibit stronger interaction with silica surface than olefins, which may be attributed to the high electron density associated with the conjugated π bond system. They have also found that nitriles exhibited the highest interaction with silica probably through the hydrogen bond interaction between the -CN group and silanol groups. Based on their study they have proposed the order of interaction of elastomers with silica as NBR> SBR> NR > BR> High vinyl-BR> EPR> IIR. Thus as the polarity of the elastomer increases, the silica-polymer interaction also increases and consequently the filler networking gets reduced. Silica or clays are used where non-black compounds are required, but compression set performance is not so good as a black reinforced compound, unless silane-treated silica is used.

Styrene butadiene rubber (SBR)

SBR is a non-polar synthetic rubber that is the most commonly used general-purpose synthetic rubber. They are produced by the co-polymerisation of butadiene and styrene under controlled conditions of reactions using different techniques of polymerisation. Different reaction conditions give different products. Depending on the method of manufacture SBR is divided into emulsion, solution, cold or hot etc. The products vary in chemical nature also since the butadiene polymerise in three different ways namely cis-1, 4, trans-1, 4 and vinyl.

The physical properties of SBR are much inferior to those of NR. Similarly its green strength is also inferior. But the extrusion properties of SBR are superior to those of NR and its stocks have fewer tendencies to scorch in processing. The unsaturation in SBR is less than that of NR and the double bonds are less active chemically than the double bonds of NR. Hence, SBR shows a slower curing than NR and more accelerators or more active accelerator system is required.

The gum vulcanizates of SBR are generally weak and it is essential to use reinforcing fillers to produce products of high strength. Many studies were done on the silica reinforcement of SBR. Sung-Seen Choi studied filler-polymer interactions in SBR compounds.[121] Effect of filler loading on cure time and swelling behaviour was studied in NR/ SBR blends and found that cure time increases with filler loading.[101] A quantitative morphological analysis of silica field SBR systems has been performed using AFM and SAXS measurements.[122] Effect of filler content on the mechanical properties was studied and results showed that the properties improved with filler loading. Study of the non-linear visco-elastic behaviour of silica filled SBR systems showed that the Payne effect is observed in SBR compounds.[123] The rubber filler interactions were found to be affecting the deformation behaviour of SBR-silica compounds.[124] The degree of chain scission was closely related to the mechanical energy applied to the vulcanizates. Reinforcing effect of silica on the properties of styrene butadiene rubber-reclaim rubber blend system was studied by sol-gel technique and conventional method.[125] Silica incorporation by conventional mechanical mixing in the absence of

TESPT showed a much higher tensile properties than that of the silica incorporated by the in situ sol-gel reaction of tetraethoxy silane both in presence and absence of TESPT. The effect of oleyl amine on processing and physical properties of SBR compounds filled with silane-silica particles has been evaluated.[126]

1.12 Scope and objectives of the work

The present work aims at finding an alternative and efficient method for the incorporation of silica in the rubber matrix. Conventionally, a silica-reinforced rubber is prepared by mechanical mixing and compression moulding along with silane coupling agents. Since silica is hydrophilic and rubber is hydrophobic, the mixing of silica and rubber will not give a uniform distribution causing difficulties like high initial viscosity. Silica has a number of hydroxyl groups, which result in filler-filler particle agglomeration and reagglomeration. These difficulties and the problems like ethanol formation and reduced scorch sensitivity related to the use of silane-coupling agents could be absolutely avoided if the silica is prepared in the rubber matrix itself. Further, to achieve excellent reinforcements it is important to generate very fine silica particles and to disperse them well in the rubbery matrix.

This study proposes to look at silica incorporation from a totally different angle: in situ precipitation of silica in rubber latex. The specific objectives of the study can be summarised as follows.

1. To examine the salient features of latex stage precipitation of silica in natural rubber.
2. To study the characterisation of silica obtained by burning off the rubber.

3. To study the characterisation of silica filled natural rubber vulcanizates.
4. To study the effect of Epoxidised Natural Rubber as coupling agent for in situ precipitation.
5. To study the silica precipitation in NBR and SBR lattices.
6. To compare the properties of the composites filled with commercial silica and in situ precipitated silica.

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Chapter 2

EXPERIMENTAL TECHNIQUES AND MATERIALS USED

The specifications of the materials and details of the experimental techniques used in this study are given in this chapter.

2.1 Materials

2.1.1 Rubbers: Natural rubber

The natural rubber used in this study was ISNR-5 of Mooney viscosity (ML 1+4,100°C) 85, obtained from the Rubber Research Institute of India, Kottayam. The Bureau of Indian Standards specifications for the grade of rubber are given in Table 2.1.[1]

Table 2.1. BIS specifications of ISNR- 5

SI. No	Parameters	Limit
1	Dirt content, % by mass, max	0.05
2	Volatile matter, % by mass, max	0.8
3	Nitrogen, % by mass, max	0.6
4	Ash, % by mass, max	0.6
5	Initial plasticity, Po, Min	30
6	Plasticity retention index (PRI), min	60

Rubber from the same lot has been used for the experiment since it is known that the molecular weight, molecular weight distribution and non-rubber constituents of natural rubber are affected by clonal variation, season, use of yield stimulants and method of preparation.[2]

Natural rubber latex: High ammonia type 60% centrifuged natural rubber latex conforming to the specifications of the Bureau of Indian Standards (BIS 5430-1981) was used in the study. The properties of the latex used are given below.

Table 2.2. Specifications of NR latex

Dry rubber content, % by mass	60.040
Total solids content, % by mass	61.050
Coagulum content, % by mass	0.030
Sludge content, % by mass	0.007
Alkalinity as ammonia, % by mass	0.730
KOH number	0.496

Epoxidised natural rubber (ENR) latex

Epoxidised natural rubber, ENR 50 containing 50 mole percent of oxirane rings, prepared in the pilot plant facility of the Rubber Research Institute of India is used in the study. DRC - 20%

Acrylonitrile butadiene rubber (NBR)

Nitrile Rubber, NBR 553 M of medium acrylonitrile content (33% by weight) a product of Gujarat Apar Polymers Ltd., India was used for the study.NBR latex: NBR latex - NLX 523 supplied by Apar industries ltd Gujarat was used in the study. The specifications of the material are given in Table 2.3.

Table 2.3. Specifications of NBR latex

Total solids content	48 - 52%
pH	8.5 - 10
Brookefield Viscosity	100 CPs
Surface tension	36 - 43 at 100°C

Styrene Butadiene Rubber (SBR)

Styrene Butadiene Rubber used was Synaprene 1502 grade, obtained from Synthesis and Chemicals Ltd., Barely, U.P., India. The Mooney viscosity (ML 1+4,100°C) was 52. The specifications are given below:

Table 2.4. Specifications of SBR

Volatile matter, % by mass	0.23
Ash, % by mass	0.24
Organic acid, %	5.53
Soap	Traces
Bound styrene, % by mass	24.00

SBR latex : SBR latex Encord 204, supplied by Jubilant Organosys Ltd. Gujarat, having the following specifications is used for the study

Table 2.5. Specifications of SBR latex

Total solids content (%)	50
pH	11.35
Brookefield viscosity (CPs)	29
Surface tension (dynes / cm)	54.4
Specific gravity	0.96 - 1.00

2.1.2 Fillers: The fillers used are silica and carbon black

Silica: Two grades of silica were used.

Ultrasil VN3: Precipitated nano silica, a product of Degussa AG, Germany. Specifications of the same are given below.[3]

Table 2.6. Specifications of VN3

Specific surface area (N_2), m^2/g	175
Heating loss, %	5.5
pH	6.2
Tapped Density, g/l	220
SiO2, content %	98
Appearance	white powder

Commercial silica: Precipitated silica of commercial grade supplied by Minar Chemicals, Kochi. It had the following specifications.

Table 2.7. Specifications of Commercial silica

pH (5% aqueous solution)	6.3
Density (g/cc)	2.03
SiO_2 content (%)	90
Loss of heating (%)	2.5 %

Carbon black

High Abrasion Furnace Black (N330), a product of M/s. Philips Carbon Chemicals Ltd, Kochi was used. It had the following specifications

Table 2.8. Specifications of carbon black

Appearance	Black granules
DBP absorption (cc/100g)	102
Pour Density (Kg/m3)	376
Iodine adsorption number	82
Loss on heating (%)	2.5

2.1.3 Coupling Agent

The coupling agent used was Si 69, a product of Degussa AG, Germany. Chemically the product is bis (triethoxysilyl propyl) tetrasulphide. The specifications of the product are given below.[4]

Table 2.9. Specifications of Si 69

Sulphur content, %	22.7
Volatiles, %	<4.0
Average molecular weight, g/mol	532
Density, g/cm^3	2.5
Appearance	clear yellow liquid

2.1.4 Other chemicals

Toluene and MEK used in the present investigation were of analytical grade. Sodium silicate, Ammonium chloride and acetic acid used were of commercial grade. Zinc oxide (activator), Stearic acid (co-activator), N-Cyclohexyl benzthiazyl sulphenamide (accelerator), Tetra Methyl Thiuram disulphide (accelerator), Diethylene glycol (activator) Sulphur (crosslinking agent), Naphthenic oil and Aromatic oil (process oils) used were of commercial rubber grade.

2.2 Experimental methods

2.2.1 Characterisation techniques

Mooney viscosity

Mooney viscosity of silica masterbatches was determined using a Shimadzu Mooney Viscometer, model SMV 202.

ICP- AES analysis

The purity of the ignited silica was tested with Inductively Coupled Plasma Atomic Emission Spectroscopy. The analysis was conducted with an ICP AES of Thermo Electron Corporation model IRIS INTREPID 11 XSP.

Infrared Spectroscopy

The IR spectra of the coagulum with and without silica were recorded with Fourier Transform Infrared Spectroscope, Bruker, Tensor 27 model.

2.2.2 Thermal analysis

Thermo Gravimetric Analysis

The thermograms of natural rubber, silica master batches and composites are recorded with a Thermo Gravimetric Analyzer Q-50, TA instruments. It is 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 a ultra sensitive microbalance. Air and nitrogen were used as purge gases

Differential Scanning Colorimetric analysis

The Differential Scanning Colorimetry of natural rubber before and after the silica incorporation is recorded with a Differential Scanning Colorimeter Q - 100, TA instruments. The energy changes associated with transitions were recorded in a temperature range of -60 to 100 °C. Samples of known weight encapsulated in standard aluminium pans placed in the sample holder were subjected to the analysis.

2.2.3 USAXS Analysis

The ignited silica and the coagulum containing silica were studied with Ultra Small Angle X-ray Scattering (USAXS) analysis. . USAXS helps to study the structure of mass fractal aggregates over several orders of magnitude of the length scale.[5] The scattering intensity **I** (cm^{-1}) is plotted as a function of corresponding scattering vector q (A^{-1}). The USAXS data were obtained from the UNICAT 33-ID beam line at the Advanced Photon Source, Argonne National Laboratory, US.

2.2.4 Bound rubber content

The fraction of the bound rubber that occurred in the master batches was determined by the following procedure.[6] Specimen of 1mm thickness and 1cm diameter was cut from the master batches and put into a previously weighed cage made by stainless steel wire gauze of 280 mesh. The cage was soaked in the solvent for 72 hours. The cage was taken out after 72h and air-dried. The bound rubber content R_B was calculated using the equation [7]

$$R_B = W_{fg} - W\,[m_f / (m_f + m_p)] / W\,[m_p / (m_f + m_p)] * 100 \ldots\ldots \quad 2.1$$

Where W_{fg} = weight of filler and gel, W = weight of specimen, m_f = weight of filler in the compound, m_p = weight of polymer.

2.2.5 Vulcanisation

Mixing and homogenisation of the rubber compound

The compounding was done on a laboratory size two roll-mixing mill (16x33cm) at a friction ratio of 1:1.25 for natural rubber 1:1.1 for styrene butadiene rubber and nitrile rubber as per ASTM D 3182-89. A nip gap of 0.2mm was set and the temperature maintained at 70±5°C. For mastication of rubber, the elastomer was passed through the rolls. After the nerve had disappeared, the compounding ingredients were added as per procedure given in ASTM D 3184-89 (2001). After the complete mixing, the stock was sheeted out at a nip gap of 3mm. Mixing time and temperature were controlled during the process.

Cure characteristics

Cure characteristics of the mixes were determined as per ASTM D 2084–1995 using Rubber Process Analyser (RPA 2000-Alpha Technologies). It uses two directly heated, opposed biconical dies that are designed to achieve a constant shear gradient over the entire sample chamber. The sample of approximately 5g was placed in the lower die that is oscillated through a small deformation angle (0.2°) at a frequency of 50cpm. The torque transducer on the upper die senses the force being transmitted through the rubber. The torque is plotted as a function of time and the curve is called a cure graph. The important data that could be taken from the torque-time curve are minimum torque (M_L), Maximum torque (M_H), Scorch time (T_{10}), Optimum cure (T_{90}) and cure rate index. Optimum cure time corresponds to the time to achieve 90 percent of the cure calculated using the Equation 2.2[8]

Optimum cure = $0.9 (M_H - M_L) + M_L$ 2.2

Cure rate index was calculated from the cure graph using Equation 2.3.

Cure rate index = $100/ t_{90} - t_2$ 2.3

where t_{90} and t_2 are the times corresponding to the optimum cure and two units above minimum torque respectively.

Moulding

Vulcanisation of various test samples was carried out in an electrically heated hydraulic press having 45 cm x 45 cm platen at 150 /160°C at a pressure of 200 kg/cm ^{2} on the mould up to optimum cure times. Moulded samples were conditioned for 24h. before testing.

2.2.6 Physical testing

Modulus, tensile strength and elongation at break (stress - strain properties)

These tests were carried out according to ASTM D 412-1998, using dumbbell specimens. Test specimens were punched out from the moulded sheets using the c-type die, along the mill grain direction. The measurements were carried out at a crosshead speed of 500mm per minute on a Shimadzu

Model AG1 Universal Testing Machine according to ASTM standards, D 412-68 and D 624-54 respectively.

Tear resistance

Tear resistance of the samples was tested as per as ASTM D 624-1998, using un-nicked 90° angle test specimens that were punched out from the moulded sheets, along the mill grain direction. The measurements were carried out at a crosshead speed of 500mm per minute on a Shimadzu Model AG1 Universal Testing Machine according to ASTM standards, D 412-68 and D 624-54 respectively. The tear strength was reported in N/mm.

Hardness

The testing was done as per ASTM D 2240-1997 using Shore A type Durometer.[8] Readings were taken after 15 seconds of the indentation when firm contact has been established with the specimens.

Rebound resilience

Basore Resilometer as per ASTM D2632–01 is used to measure rebound resilience. The sample was held in position by suction. It was conditioned by striking with the indentor six times. The test was carried out at 28+1 °C. Rebound resilience was calculated using Equation 2.4.

$$\text{Rebound resilience (\%)} = \frac{(1-\cos\theta_2)^*}{(1-\cos\theta_1)}100 \tag{2.4}$$

where θ_1 and θ_2 are the initial and rebound angles respectively. In all the tests θ_1 was 45°.

Abrasion resistance

The abrasion resistance of the samples were studied with a DIN Abrader (DIN 53516). Moulded samples of 6±0.2mm diameter and 12mm thickness were prepared as per ASTM D 3183 and abrasion loss was measured as per ASTM D5963-04. Abrasion loss was calculated using the equation

Abrasion loss = (loss of wt./sp.gr.)

Compression set

The samples (1.25 cm thick and 2.8 cm diameter) in duplicate compressed to a constant deflection (25%) were kept in an air oven at 70 °C for 22h (ASTM D 395-1998 method B)[8]. The samples were taken out, cooled to room temperature for half an hour and the final thickness measured. The compression set was calculated using Equation 2.5.

$$\text{Compression set } (\%) = \frac{t_0 - t_1}{t_0 - t_s} 100 \qquad \text{..........................} \quad 2.5$$

where t_o and t_1 are the initial and final thickness of the specimen and t_s is the thickness of the spacer bar used.

Heat build up

The Goodrich flexometer conforming to ASTM D 623-1999 was used for measuring heat build-up[8]. A cylindrical sample of 2.5 cm in height and 1.9 cm in diameter was used for the test. The oven temperature was maintained at 50 °C. The sample preconditioned in the oven for 20 minutes was subjected to a flexing stroke of 4.45 mm under a load of 10.9 kg. The temperature rise (4T °C) at the end of 20 minutes was taken as the heat build-up.

Flex cracking

Flex cracking was determined using a De Mattia flexing machine according to ASTM D 430-1995.[8] Standard specimens 15 cm x 2.5 cm x 0.6 cm having a semicircular groove moulded transversely in the centre of the strip were used. Samples fixed on the machine were subjected to flexing at a frequency of 300 cycles per minute. The number of cycles required to produce different levels of cracking was noted.

Rheological properties

The flow properties of the rubber-filler mixes were studied by conducting frequency sweep studies in an instrument REOLOGICA instrument AB. Samples for testing were consequently prepared by die cutting 46mm diameter disks out of around 2mm thick sheets of materials. The frequencies were varied up to 100Hz and the viscosity was measured at temperature 100 °C.

2.2.7 Thermal ageing studies

Tests were carried out as per ASTM D 573-1999.[8] Specimens of vulcanized rubber were exposed to the deteriorating influence of air at specified elevated temperature in an air oven, for known periods of time, after which their physical properties determined. These were compared with the properties determined on the original specimens and the changes noted.

2.2.8 Transmission Electron Microscopy (TEM)

The TEM imaging was carried out for the silica mixes of NR with different concentrations of silica using a Transmission Electron Microscope CM-200 of Philips Technology.

2.2.9 Scanning electron microscopy (SEM)

In SEM, the electron beam incident on the specimen surface causes various phenomena of which the emission of secondary electrons is used for the surface analysis. Emitted electron strikes the collector and the resulting current is amplified and used to modulate the brightness of the cathode ray tube. There is a one- to- one correspondence between the number of secondary electrons collected from any particular point on the specimen surface and the brightness of the analogous point on the screen and thus an image of the surface is progressively built up on the screen.

Scanning electron microscopic studies of the various silica filled samples were carried out in order to find out the variations in filler dispersion. The microscopic examinations were carried out on the freshly cut surface in a Hitachi SE Microscope (model H 6010). The sample surface was gold coated prior to the examination.

2.2.10 Strain sweep studies

The strain sweep measurements on unvulcanized samples and vulcanizates were conducted to study the rubber-filler interaction. Rubber Process Analyzer (RPA 2000 - Alpha Technologies) is a purposely-modified commercial dynamic rheometer.[9] Such instrument was modified for capturing strain and torque signals, through appropriate software. Filled rubber materials (vulcanized) exhibit strong non-linear viscoelastic behaviour, the well-known Payne effect, i.e. the reduction of elastic modulus with increasing strain amplitude.[10] RPA can do strain sweep tests in which the variation of storage modulus (G′), loss modulus (G″) and complex modulus (G*) with the change in strain amplitude are measured. With respect to its measuring principle, the RPA cavity must be loaded with a volume excess of test material. In agreement with ASTM 5289, the manufacturers recommends to load samples of about 5.0g i.e. 4.4 cm^3 for a standard filled rubber compound with a specific gravity of 1.14g/cc. Samples for RPA testing were consequently prepared by die cutting 46mm diameter disks out of around 2mm thick sheets of materials. The testing temperature was selected as 100°C; a temperature below the curing temperature and the shear strain was varied from 0.5% to 100% keeping the frequency of measurements at 0.5Hz.

For strain sweep measurements of cured compounds, uncured material is used as the test sample that is cured to its optimum cure time in the RPA cavity and then the strain sweep tests were carried out at 50°C in a two-stage programme.

2.2.11 Swelling studies

Contribution to the reinforcement effect arises from molecular interaction between the rubber and the filler. This interaction leads to an increase in the effective degree of crosslinking and can be evaluated by equilibrium swelling. The equilibrium swelling analysis of rubber vulcanizate is known to indicate the number of effective network chains per unit volume of rubber. For a filled vulcanizate it should reflect not only the effect of chemical linkages but also the density of polymer-filler attachments.

Circular specimens of diameter 20 mm. were punched out from the vulcanized sheets. Thicknesses and diameters of the specimens were measured by means of a screw gauge and vernier calipers respectively. Specimens of known weight were immersed in the solvents and automobile fuels and oils in diffusion test bottles and kept at room temperature. Samples were removed from the bottles at periodic intervals and the wet surfaces were quickly dried using tissue paper and the weights of the specimen after swelling were determined at regular intervals until no further increase in solvent uptake was detected.

Degree of swelling usually is expressed as V_r and is defined as V_r = Volume of rubber / Volume of swollen rubber-solvent gel. V_r is dependent on the swelling power of the solvent (high swelling power means low V_r) and the crosslink density. Higher crosslink density results in restraint on the network, which results in lower swelling. Vr of the unfilled vulcanizate is usually denoted as Vo and that of the filled vulcanizate as V_{rf}.

Vrf = Volume of rubber (filled) / Volume of swollen rubber-solvent gel (filled) where the numerator refers to total volume minus the filler volume and the denominator refers to the total swollen volume minus the filler volume. Volume fraction measurements could also be used for calculating the crosslink density using Flory- Rehner equation.[11]

$$\text{Crosslink density} = \frac{[\ln(1-V_r)+V_r+\chi V_r^2]}{2\rho V_s(V_r)1/3}$$

Where Vs = molar volume of the solvent

χ = rubber - solvent interaction parameter

2.2.12 Air permeability

The air permeability of the samples were tested by conducting the Manometric gas Permeability Testing in a Lyssy Manometric Gas Permeability Tester, L 100-2402. Vulcanised sheets of ≈ 2mm were used for the study.

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Chapter 3

IN SITU PRECIPITATION OF SILICA IN NATURAL RUBBER LATEX

3.1. Introduction

Commercial applications of elastomers often require the use of particulate fillers such as carbon black and silica.[1,2] For the composite to be effective there must be a strong interaction between the matrix and the reinforcing phase and this can be achieved using a filler with large surface area-to-volume ratio. Optimally this means using small fillers with a large aspect ratio. Recently particles with nanoscale dimensions have become the subject of extensive research. But the key issues for the nano particles, which ultimately determine their usefulness as fillers, are their effective dispersion in the matrix and the nature of the interface with the matrix.[3,4]

Precipitated silica is one of the promising non-black fillers for rubber. It improves mechanical properties and the material properties of elastomers. However, the mixing of silica with the commonly used olefinic hydrocarbon rubbers is a challenge as these materials are not very compatible in various aspects.

- Surface energy: The surface free energy has two parts. The dispersive part and specific part.[5,6] Silica has low dispersive part and high specific part.[7] As a result of low dispersive part the interaction between the filler and the polymer is weak and results in a low reinforcing effect. On the other hand the specific part is high,[8] so that the interaction between filler particles is very strong and the viscosity of silica compounds is high. So during mixing rubber with silica, the interparticle forces need to be overcome and a link between the silica particles and the polymer has to be established.

- Solubility: Good mixing is obtained when there is an intensive contact between filler surface and polymer matrix (wettability).[9] The wettability is determined by the difference of the solubility parameters of the two components.[10] This is quite significant in the case of silica and non-polar rubber.[11]
- Structure of filler: Silica has a high surface area and a high percentage of void volume within the filler particle. As the direct interaction between the filler and the polymer is rather low, polymer chains can be connected to the filler only by physical process. The polymer is trapped in the voids of the filler structure resulting in occluded rubber.[12] During mixing the structure of the filler has to be broken in order to increase the interaction between filler and polymer, releasing a part of the occluded rubber. The filler should not be broken to the level of primary particles.[13]

These shortcomings can be overcome by the application of coupling agents such as silanes, titanates and zirconates. Of these coupling agents silanes are widely used. Several silanes with appropriate functionality, such as alkoxyl silyl groups, have been successfully used as coupling agents. They provide a bond between the filler and the polymer by forming a chemical link. The application of a coupling agent greatly improves the processing behaviour by reducing the specific surface energy and the solubility parameter of the silica. This facilitates filler incorporation and also enhances the properties of the final product by increasing the dispersive component.[14,15,16] The application of coupling agents results in the formation of interpenetrating filler-polymer and polymer-polymer networks. This special network structure gives silica filled rubber its special characteristics in terms of dynamic properties for considering the important final product tyre, low rolling resistance and good wet grip.

However, these improvements are accompanied by other problems:

- Ethanol formation: When silane is mixed with silica a chemical reaction takes place in two steps. The hydrolysis of alkoxy silyl group followed by the condensation of the silanol groups.[17,18] The reaction is an endothermic one and usually carried out at a temperature of 150 - 160°C.[19] Ethanol is produced in this reaction and it competes with silane for adsorption and reaction sites on the silica surface, resulting in a reduction of silanization efficiency. Another problem with the ethanol is that the condensation of ethanol in the internal mixer wall causes slipping of the compound and reduces the mixing efficiency. So the removal of ethanol from the mixing site is very essential.
- Processing temperature: The reaction between silane and silanol is usually carried out at 150-160°C. So the processing should be done initially at this temperature range. But this temperature increases the scorch sensitivity due to the sulphur present in the silane-coupling agents. Lower range of temperature reduces the rate of silanization.
- Cost: The silanes are costly materials. So their application increases the cost of the product.

In order to achieve excellent reinforcement, it is important to incorporate very fine silica particles and to disperse them well in the rubbery matrix. Recently the sol-gel technique, which can generate in situ reinforcing particles, has been widely applied for the synthesis of hybrid organic - inorganic materials.[20] This process, which consists of hydrolysis and condensation of an alkoxy silane such as tetra ethoxy silane (TEOS), is expected to yield small and well-dispersed particles within the polymer matrix. The structure and morphology of the filler depends on the reaction conditions and essentially on the nature of the catalyst. A representative procedure is a method in which water and a catalyst are impregnated in to rubber swollen in TEOS and silica synthesis in rubber matrix is carried out. In situ precipitation of silica was done in Poly dimethyl siloxane (PDMS) by swelling PDMS in TEOS for different periods and then hydrolysing the TEOS by immersing the swollen mass in 2 wt % Diethylamine.[21]

In another procedure, the sol-gel reaction is carried out by the addition of alcohol, water, TEOS, and a catalyst to the rubber swollen in organic solvents such as THF.[22] Reinforcement of natural rubber has been done by applying the two procedures and a good dispersion of the silica is obtained.[23] MaTejka et al reinforced rubbery cross-linked epoxide with in situ formed silica-siloxane structures.[24] The increase in modulus by two orders of magnitude was achieved. Green composites with different amount of in situ nano silica particles were prepared by a sol-gel reaction of tetra ethoxy silane in natural rubber.[25] Shinzo et al reviewed the use of sol-gel process on general-purpose grade rubbers in the absence of silane coupling agents.[22] Mark et al carried out the sol-gel synthesis of silica in silicone rubber matrix using TEOS as a silica precursor and ethylamine as a catalyst.[26,27] Silica-gel nanowire/Na$^+$-montmorillonite (Na$^+$-MMT) nanocomposites were prepared by the *in situ* sol-gel process of tetraethyl orthosilicate (TEOS) in the presence of Na$^+$-MMT and ammonia as catalyst.[28]

However, these procedures are not conventional because of the use of a large amount of organic solvent and a long reaction time. Silica reinforcement of Synthetic diene rubbers by sol-gel process in the latex was conducted and found to produce drastic changes in the tensile strength.[29] Styrene butadiene and nitrile rubbers were reinforced with silica produced by sol-gel process of Tetra ethoxy silane in the latex. The sol-gel reaction was carried out with mixture of latex, TEOS, water and a catalyst (ammonia). The latex containing in situ silica was dried to get the rubber containing silica and compounding was carried out on a two-roll mill. Kohjiya et al conducted the sol-gel reaction of Tetra ethoxy silane in natural rubber latex.[30] In this chapter we propose a novel route for precipitating silica particles in situ in concentrated natural rubber latex followed by coagulation of the latex to get rubber containing silica. In situ precipitation of silica was carried out using sodium silicate and ammonium chloride. Analysis of the physical, chemical, thermal and morphological characteristics of in situ precipitated silica are also carried out.

3.2 Experimental

Materials: Natural Rubber Latex of dry rubber content (DRC) 60% was supplied by Njavallil Latex, Kochi, India. Sodium silicate 60% concentrate and other chemicals used were of commercial grade.

In situ precipitation

Natural rubber latex was filtered and stabilized with non-ionic stabilizer vulcastab VL, mixed with required amount of sodium silicate, stirred for one hour and then kept overnight. A saturated solution of ammonium chloride was added drop wise with constant stirring to precipitate silica. Latex containing silica was coagulated as crumbs by the addition of 2% acetic acid. The crumbs were washed with water till the washings were neutral and free from chloride, pressed to remove water and dried in an air oven at 70°C for 48hrs.

The precipitation of silica was repeated at different concentrations using different quantities of sodium silicate and ammonium chloride. The amount of silica in the sample was experimentally determined out by igniting the rubber in a known weight of the sample in a muffle furnace.

The precipitation was also repeated with different concentrations of the latex. Latex was diluted with water to different concentrations and precipitation of silica was done as above.

Characterization of silica filled coagulum

Ignition of coagulum

Rubber sample containing in situ precipitated silica was ignited in a muffle furnace at 550°C for 3 hours. Photographs were taken before and after ignition. For comparison, the procedure was repeated with VN3. Latex was mixed well with a dispersion of VN3, coagulated and dried to get the coagulum containing VN3 of the same concentration as that of the in situ precipitated silica. A piece of the dry coagulum was then ignited under similar procedure and photographs were taken before and after ignition.

Action of solvent on coagulum

Rubber coagulum containing the same concentration of latex precipitated silica, conventional silica and VN3 silica were immersed in toluene for 24 hours to study their solubility behaviour.

Bound rubber content

The bound rubber content of the rubber coagulum samples, containing different concentrations of precipitated silica, were found out by swelling the samples in toluene following the procedure given by Kazumasa et al.[29] Bound rubber contents (R_B) were calculated using the equation[31]

$$R_B = W_{fg} - W\,[m_f / (m_f + m_p)] / W\,[m_p / (m_f + m_p)] * 100 \quad \ldots\ldots\ldots 3.1$$

where W_{fg} = weight of filler and gel, W = weight of specimen, m_f = weight of filler in the compound and m_p = weight of polymer.

FTIR studies

The IR spectra of the coagulum with and without silica were recorded with Fourier Transform Infrared Spectroscope.

Thermal analysis

The thermograms of natural rubber before and after the silica incorporation were recorded. The Differential Scanning Colorimetry of natural rubber before and after the silica incorporation is recorded with a Differential Scanning Colorimeter.

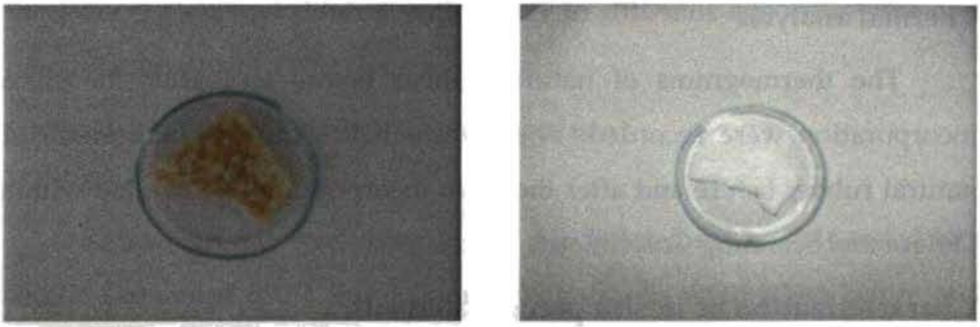
Characterization of in situ precipitated silica

The purity of the ignited silica was tested with Inductively Coupled Plasma Atomic Emission Spectroscopy. Physical constants were also measured. Scanning electron microscopic (SEM) studies of the silica samples prepared under different conditions were carried out in order to find the nature of the silica surfaces. The microscopic examinations were also carried out with Transmission Electron Microscopy (TEM). The ignited silica and the coagulum containing silica were studied with Ultra Small Angle X-ray Scattering (USAXS) analysis.

3.3 Results and discussion

3.3.1 Characterization of Coagulum

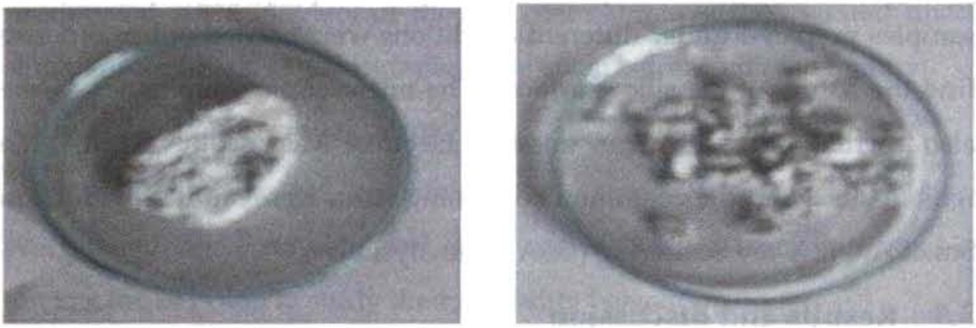
Ignition of the coagulum: The Figure 3.1a shows the photographs of rubber sample containing in situ precipitated silica before and after ignition and Figure 3.1b shows the photographs of rubber sample containing VN3 silica before and after ignition. During ignition the rubber particles were burnt off leaving only silica. Figure 3.1a shows that the original shape of the sample containing in situ precipitated silica is retained exactly during the ignition. This indicates that there exists a uniform distribution of filler in the in situ precipitated silica containing sample. This was not observed with VN3 sample. It is clear from the Figure 3.1b that the sample crumpled on ignition indicating that there is no uniform distribution of filler in the samples containing VN3.



In situ precipitated silica sample before ignition

In situ precipitated silica after ignition

Figure 3.1a. The in situ silica-incorporated latex coagulum before and after ignition



VN3 silica sample before ignition

VN3 silica sample after ignition

Figure 3.1b. The VN3 silica-incorporated latex coagulum before and after ignition

The in situ precipitation of silica may be represented by the chemical reaction

$$Na_2SiO_3 + NH_4Cl \rightarrow 2\,NaCl + H_2SiO_3 + NH_3\uparrow \qquad .. \qquad 1.1$$
$$H_2SiO_3 \rightarrow SiO_2 + H_2O.$$

The ammonia evolved during the precipitation was absorbed in a known excess of standard acid. The unreacted acid was then estimated by titrating with standard alkali. From the titre values the amount of ammonia evolved was calculated and that was in agreement with the expected theoretical value. This confirmed the occurrence of the reaction.

When silica is formed in an aqueous medium, large number of hydroxyl groups present in silica led to inter molecular hydrogen bonds. So if the precipitation reaction is conducted in an aqueous medium, the silica formed will be in the form of large clusters. But when the same reaction is conducted in natural rubber latex, which is a colloid, the cations and anions of sodium silicate disperse in the latex due to the colloidal nature of the latex. The bulky polymer molecules prevent the clustering of the silica particles giving a uniform distribution. So upon precipitation of silica in the rubber latex a fine distribution of silica in rubber latex is obtained.

Action of solvent on coagulum

Figure 3.2 shows the result of solvent action on coagulum containing silica. A, B and C are the photographs of the coagulum of in situ precipitated silica, VN3 and conventional silica respectively before immersing in toluene. A′, B′ and C′ are the respective samples after immersing in toluene for 24hrs.

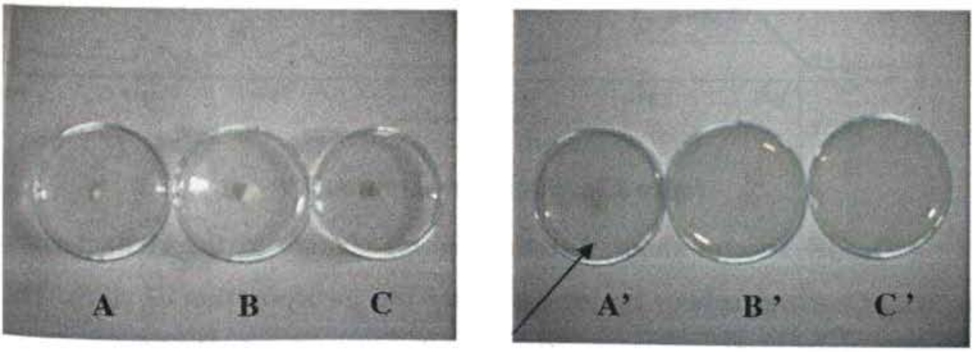


Figure 3.2. The result of the action of toluene on coagulum

It can be seen that the samples containing conventional silica and VN3 are dissolved completely in toluene. But the sample containing in-situ precipitated silica became a swollen mass. This clearly indicates that the filler-polymer interaction is present to a great extent in the sample containing in situ precipitated silica. This rubber-filler interaction holds the rubber preventing it from dissolution.

FTIR studies

FTIR spectrum of the natural rubber before and after the silica incorporation is given in the figures 3.3a and 3.3b respectively. IR spectroscopy is considered as the most important of the modern spectroscopic techniques that has found general acceptance in polymer structure analysis. IR spectrum of a compound is essentially the superposition of absorption bands of specific functional groups.[32]

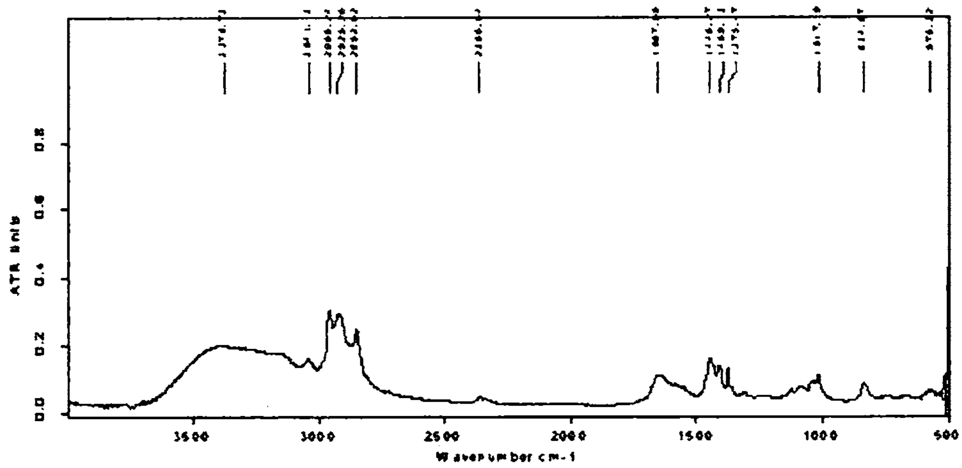


Figure 3.3a. IR spectrum of natural rubber

The IR spectra show that there is no change in the characteristic peaks of natural rubber before and after the incorporation of silica. The peaks remain unchanged indicating that there is only physical interactions between rubber and silica.

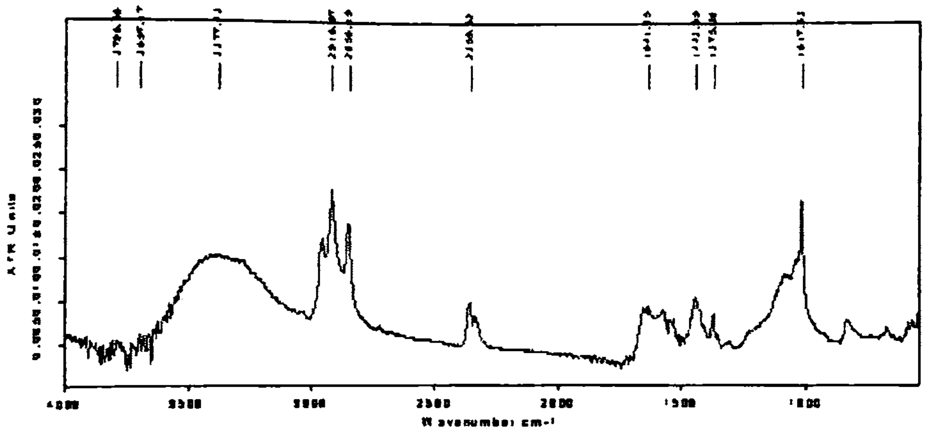


Fig 3.3b. IR spectrum of NR containing 20phr silica

A reduction in intensity of peaks except at 1017cm^{-1} is observed. The silica atmosphere might have reduced the stretching freedom of CH- groups. The increase in the frequency 1017cm^{-1} (R-OH bending frequency) may be due to some interaction of OH- of silica with the polymer chains of rubber.

Thermo Gravimetric Analysis

The thermograms of natural rubber before and after the silica incorporation are recorded. The figure 3.4 shows the thermograms of NR Gum, NR with 5phr precipitated silica and NR with 50phr precipitated silica.

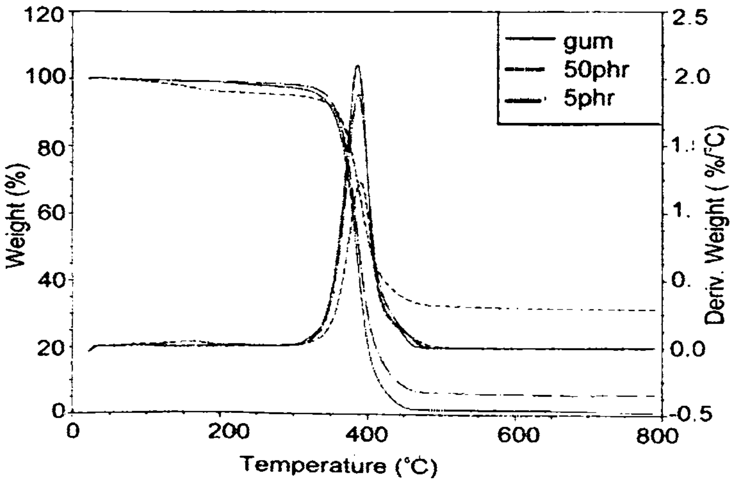


Figure 3.4. Thermograms of NR, 5phr and 50phr silica coagulums

There is no significant change in the thermograms due to incorporation of in situ silica. The changes in the initiation and maximum degradation temperatures are only proportional to the filler content. TGA values are given in the Table 3.1

Table 3.1. TGA values of the silica coagulums

Sample	Initiation temp. °C	Max.degg.temp. °C
GUM	164.30	386.31
5phr	232.46	387.25
50phr	245.66	391.2

Differential Scanning Colorimetry

The Differential Scanning Colorimetric study of the Gum rubber and the rubber containing in situ silica were done at low temperatures to study the change in glass transition temperature (Tg) during the silica incorporation. The DSC thermogram of natural rubber is given in Figure 3.5a and that of natural rubber containing precipitated silica is given in the Figure 3.5b. It is clear from the thermograms that there is no change in the glass transition temperature after the in situ precipitation, which indicates that the incorporation of silica by in situ precipitation will not affect the glass transition temperature of natural rubber.

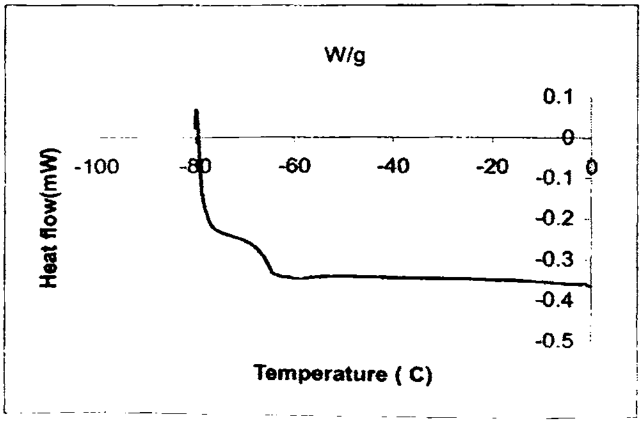


Figure 3.5a. DSC curve of natural rubber

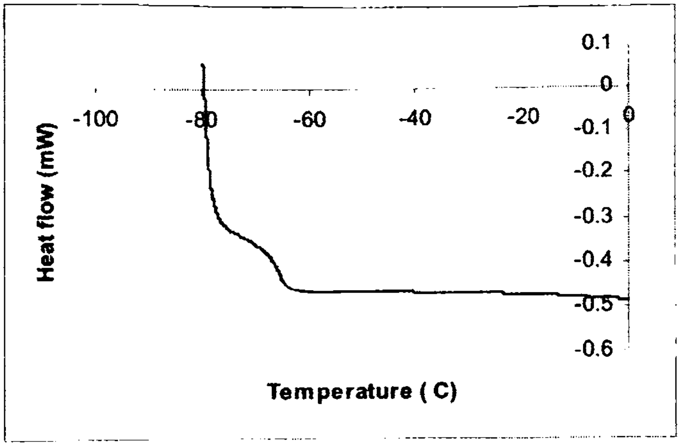


Figure 3.5b. DSC curve of natural rubber with 20phr silica

3.3.2 Characterisation of in situ precipitated silica

ICP - AES analysis

Results of ICP-AES analysis of precipitated silica are shown in the Table 3.2. Inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis is a highly successful multielemental analysis for testing the purity of the sample. ICP-AES operates on atomic emission spectroscopic technique and uses inductively coupled Argon plasma as the heating source.

Table 3.2. ICP – AES analysis of silica

Component	Concentration
Sodium	0.30
Aluminium	Nil
Iron	Nil
Calcium	nil

It is clear from the Table 3.2 that the silica precipitation and incorporation have achieved high purity. The only impurity present in the silica is the sodium at a negligible level. It is in good agreement with the chemical reaction4.1 of silica precipitation. According to the precipitation reaction the only expected impurity was the by-product sodium chloride.

Physical constants of silica

Table 3.3 gives the physical parameters of in situ precipitated silica and VN3 (reported).

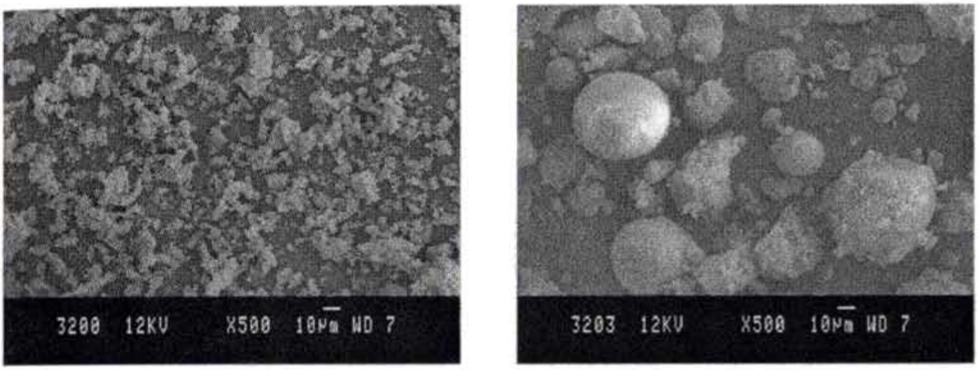
Table 3.3. Physical constants of in situ silica and VN3

Property	VN3	In situ precipitated silica
Heat loss, %	5.5	3.2
pH	6.2	6.8
Tapped density, g/l	220	105
Specific surface area (N_2), m^2/g	175	234
Appearance	White powder	White powder

One of the most important physical constants, which determine the degree of reinforcement of a filler, is the surface area of that filler. The reason is that the surface area of the filler helps in the development of a polymer-filler interface. A high degree of polymer-filler interaction can be provided by particles of colloidal dimensions with large surface area. The larger the surface area of the filler, the higher will be the reinforcing property. It is clear from the Table 3.3 that the surface area of precipitated silica is much higher than that of VN3. The heat loss is less than that of VN3, indicating a low moisture content. The low value of tapped density is also an indication of reduced size. All these physical constants support the fact that in situ precipitated silica is having a higher reinforcing capacity than the commercial nano silica VN3.

Scanning Electron Microscopic studies

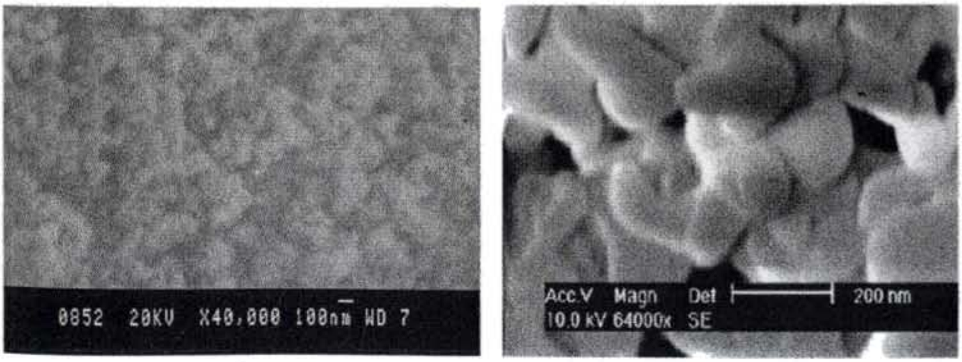
Figure 3.6 shows the SEM micrographs of precipitated silica obtained from igniting the dry coagulum and commercially available nano silica VN3. Scanning electron microscopy is widely used to study the morphology of ultra small particles. The morphology of the in situ precipitated silica powder is analysed in comparison with the commercial nano silica VN3.



In situ precipitated silica **VN3**

Figure 3.6. Scanning electron micrographs of silica

These pictures show that VN3 particles are large spherical in shape while the precipitated silica particles are smaller particles with uniform morphology and is having a structure more viable to interactions with the polymer. The SEM pictures of the silicas at higher magnification are given in the Figure 3.7.



VN3 **In situ precipitated silica**

Figure 3.7. The SEM pictures of VN3 and in situ precipitated silica at a higher magnification

It shows that the in situ precipitated silica comprises particles of very small size fused at ends to form a honey comb structure, indicating an irregular shaped mass. Non-spherical particles can impart better reinforcement.[33,34] Hence the morphology of precipitated silica also predicts better reinforcement than VN3.

Silica from mixes of different silica content

Figures 3.8a to 3.8f show the SEM micrographs of precipitated silica prepared from the dry coagulum of latex containing 1, 5, 10, 20, 30 and 50phr silica respectively.

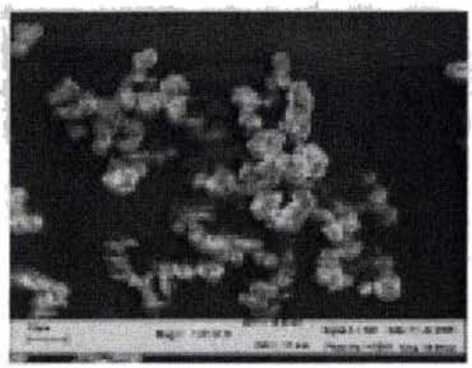


Figure 3.8a. SEM of 1phr silica

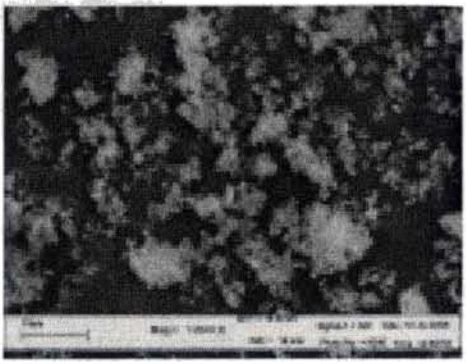


Figure 3.8b. SEM of 5phr silica

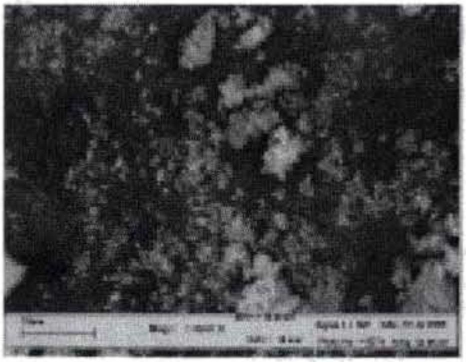


Figure 3.8c. 10phr silica

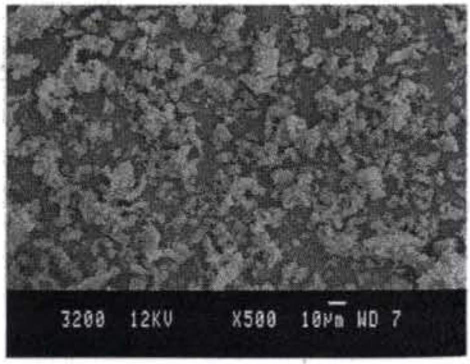


Figure 3.8d. 20phr silica

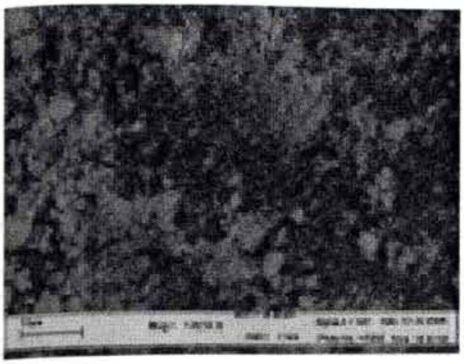


Figure 3.8e. 30phr silica

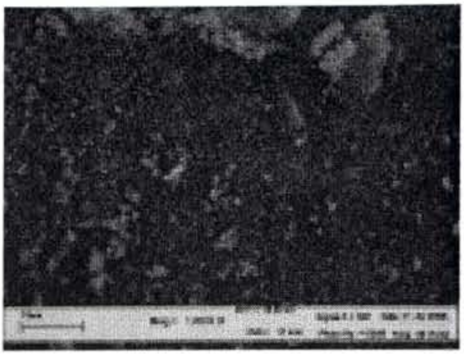


Figure 3.8f. 50phr silica

At low concentrations the particles are found as larger particles as in the case of VN3. The SEM photographs show that the density of particle distribution increases with rise in concentration. At concentrations above 20phr, the particles are formed as agglomerates and the degree of agglomeration varies positively with concentration of silica. Uniform distribution of particles with minimum clustering is observed for 20phr silica. Based on the morphology studies of the silica, 20phr silica is selected as an optimum concentration for in situ precipitation. Figures 3.9a, 3.9b, 3.9c and 3.9d show the SEM micrographs of 20phr silica prepared from the latex under different dilutions, say 60%, 40%, 20% and 10% respectively.

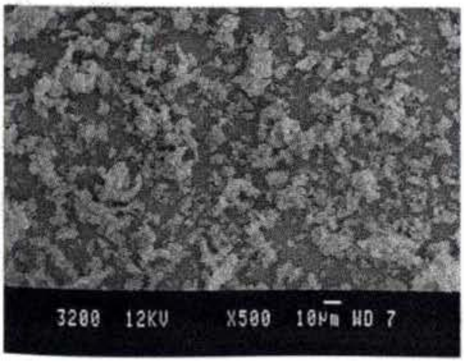


Figure 3.9a. Silica precipitated from 60% latex

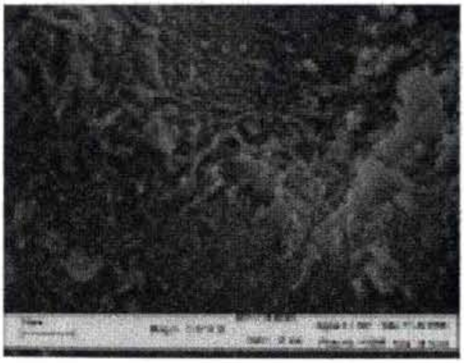


Figure 3.9b Silica precipitated from 40% latex

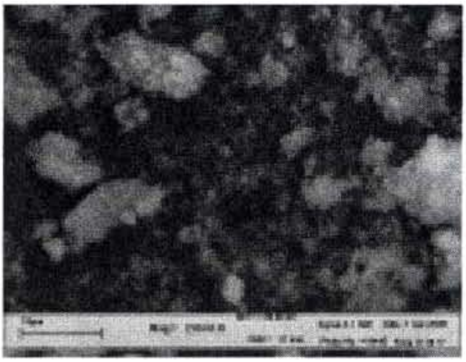


Figure 3.9c. Silica precipitated from 20%latex

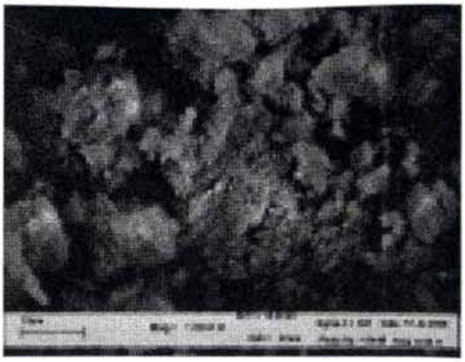


Figure 3.9d. Silica precipitated from 10% latex

It is clear from the photographs that the dilution affects the particle size and distribution. As the dilution of the latex increases i.e. the concentration of the latex decreases, the agglomeration of the silica particles increase and form large sized particles. The particle size increases as latex gets more diluted. This is because of the decrease in the density of the polymer matrix in which the reaction is conducted. As the dilution increases the bulky rubber molecules are pulled apart by water molecules, facilitating of easy mixing of the ionic reactants namely sodium silicate and ammonium chloride. The dilution with water helps the agglomeration of silica particles through hydrogen bonds also.

3.3.3 USAXS analysis

Ultra Small Angle X-ray Scattering analysis (USAXS) of precipitated silica and the coagulum containing silica is shown in the Figure 3.10. The scattering intensity I (cm^{-1}) is plotted as a function of corresponding scattering vector q (A^{-1}).

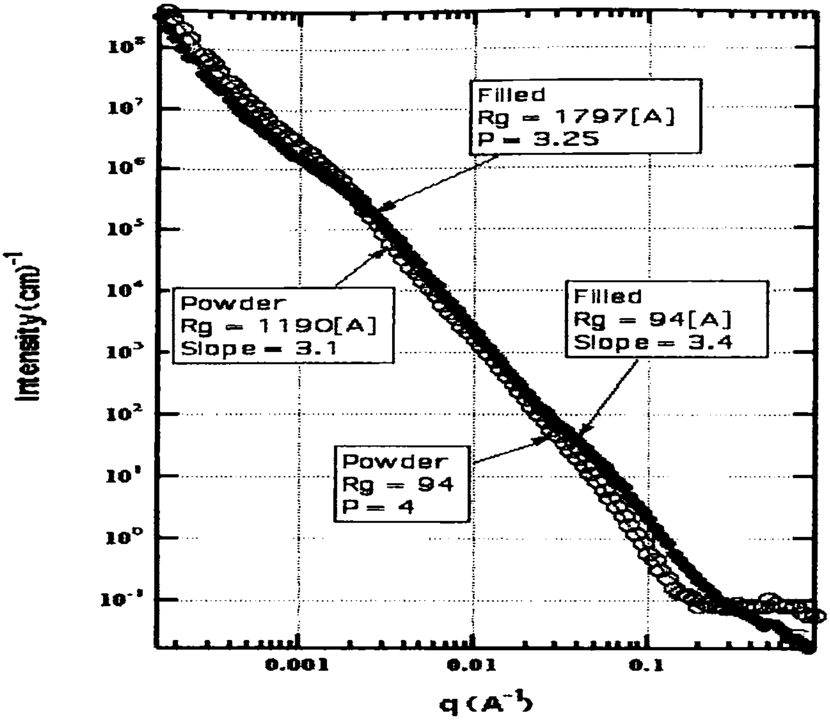


Figure 3.10. Comparison of USAXS data of silica in coagulum and in the ignited state.

USAXS helps to study the structure of mass fractal aggregates over several orders of magnitude of the length scale.[35] The angular dependence of the scattering vector is determined by the size of the particles and their tendency to aggregate.[36] The Figure shows that there is very little modification of the silica when incorporated into the rubber. The curves are quite featureless, but do show two length scales (94 Ã... and ~ 1500Ã...), which is typical of aggregated silica. The length scales do not change measurably, although there is extra scattering at high q (length scales < 100 Ã...) in the rubber. There could be some modification of the surface of the filler or, more likely, some contribution from voids or other artefacts of the dispersion process. So it is clear that there is very little modification of the silica, when it is present as dispersed in the rubber matrix.

3.3.4 Transmission Electron Microscopic (TEM) studies.

Figure 3.11a, b and c show the TEM photographs of rubber coagulum containing 5phr, 20phr and 50phr silica respectively.

Figure 3.11a. TEM photograph of sample with 5phr silica

The dark lines and areas are silica layers and aggregates and the light areas are the rubber matrix. The Figures show that the silica is present not only as individual particles but also in the form of aggregates with voids for holding the rubber. The thickness of the silica varies from 10nm to 100nm. As the concentration of silica increases in the rubber matrix the distribution of the silica improves. It is clear from the TEM of sample with 20phr silica (Figure 3.11b). The average particle size is calculated by measuring the diameter of the particle manually from the print. The average particle size was calculated using the following equation

$$\text{Average particle size} = \Sigma n_i D_i / \Sigma n_i \quad \text{..........} \quad 3.2$$

where n_i is the number of particles of diameter D_i. The particle size was found to be reduced to <50nm at 20phr concentration. The number of aggregates is also found to be reduced, indicating the presence of better distribution of silica in the rubber matrix.

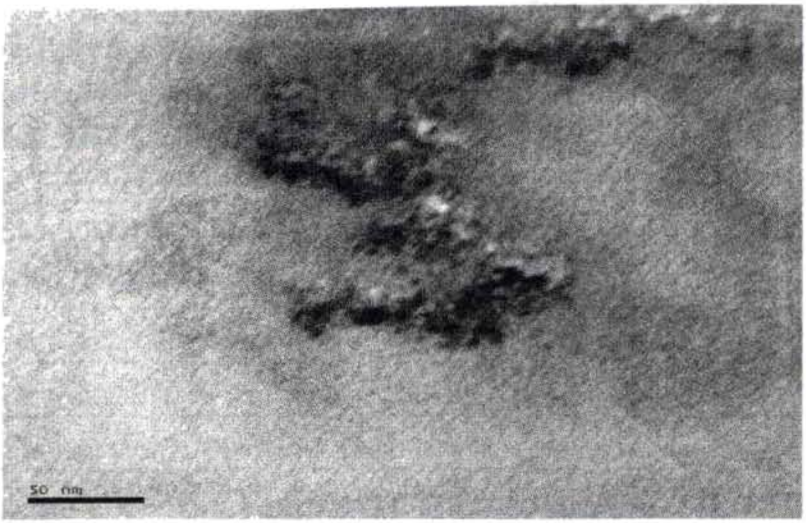


Figure 3.11b. TEM photograph of sample with 20phr silica

It is clear from the Figure 3.11c that at 50phr the silica agglomerates are having a hair like structure of thickness <20nm and the silica fibrils agglomerate and it leavesfrom the rubber surfaces.

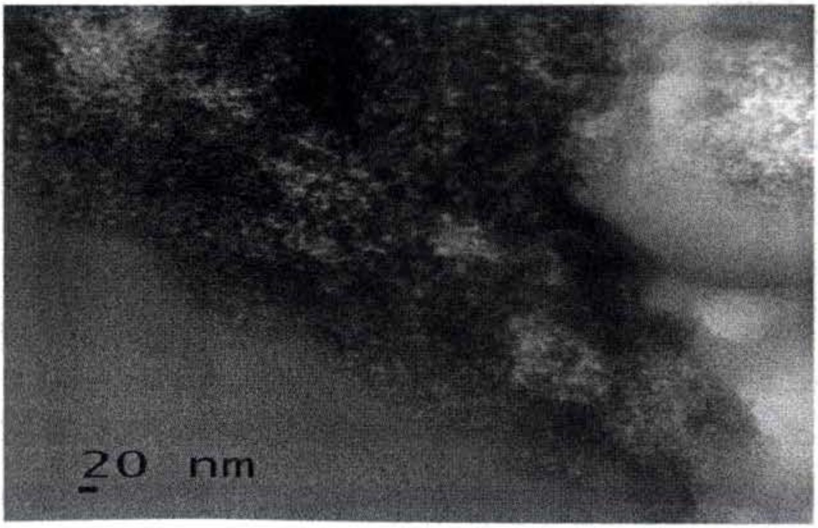


Figure 3.11c. TEM photograph of sample with 50phr silica

3.3.5 The bound rubber content and Rubber- filler interaction

The bound rubber content of the rubber samples with different concentrations of in situ silica is given in the table 3.4.

Table 3.4. The bound rubber content of silica filled samples

Concentration of silica (phr)	Bound rubber content (%)
1	5.120
2	5.260
3	9.835
5	12.86
10	39.24
15	63.45
20	82.41
25	82.78
30	83.86
40	83.37

The bound rubber content increases as the concentration rises and above 20phr, the change is less. It attains almost a limiting value at 20phr. It has been generally accepted that bound rubber provides valuable information regarding rubber-filler interaction. Several reviews have been published on this topic.[37] The mechanism of formation of bound rubber is not very clear.[38,34] Whether bound rubber can be taken as a measure of the surface activity of filler is also not well established.[39]

It is reported that bound rubber content assessment is an indirect method to study the elastomer–filler interactions.[40] The bound rubber content depends on characteristics of filler such as surface area, structure or morphology and surface activity. An increased rubber filler interaction increases the bound rubber content. So the limiting value of bound rubber at 20phr may be due to the uniform filling of silica in the matrix at 20phr as shown by the TEM analysis. Above 20phr or at higher concentrations the silica leaves the rubber surface as clusters and hence their interaction with the rubber do not show any improvement and this resultsin good agreement with that of TEM analysis.

3.4 Conclusions

Silica can be incorporated in natural rubber by the in situ precipitation technique. Silica with uniform morphology and lower particle size can be prepared by in situ precipitation technique. In situ precipitated silica is superior to the commercial nano silica VN3 in its physical characteristics. Morphological studies revealed that in situ precipitated silica has lower particle size with a honeycomb structure. The particle size of in situ precipitated silica is found to be less than 20nm when it is prepared at a concentration of 20phr. The high bound rubber content shows high polymer- filler interaction.

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Chapter 4

STUDIES ON IN SITU PRECIPITATED SILICA FILLED NATURAL RUBBER COMPOSITES*

4.1 Introduction

In the contemporary times it has become increasingly necessary and vital to develop eco-friendly materials in order to keep our environment on earth clean, safe and beautiful. One of the ways to produce eco-friendly materials is to use natural products, because many natural products are least irritant for nature than artificial ones in general. In this respect Natural Rubber (NR) is an eco-friendly material. Thus NR has been utilized in this study.

Carbon black is the ideal filler for reinforcing non-polar hydrocarbon rubbers like NR.[1] Since both are hydrophobic in nature, mixing is comparatively easy and the reinforcement problems do not usually arise when those two are mixed. Precipitated silica, which is of mineral origin, is one of the most promising alternatives to carbon black, as silica reduces the rolling resistance and hence fuel consumption.[2] Now-aday's people are thinking of green tyres i.e. eco friendly tyres. Green tyres, are thus called because the silica/silane technology enables the production of high-performance tyres with low rolling resistance. Lower rolling resistance results in better fuel economy and lower impact on the environment. So silica is achieving grater importance in tyre technology. The importance of this development is emphasized by the contemporary situation of limited reserves of non-regenerative energy and

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* A part of this Chapter has been published in Rubber world, 2005, 232(5), 16.

environmental hazards. The fuel saving capacity of such a tyre is 3% to 4% compared to a tyre having treads made from compounds with carbon black, corresponding to a reduction of the rolling resistance of 2%.[3]

The main problem with silica is the difficulty in incorporation. Silica is hydrophilic and rubber is hydrophobic in nature. So the conventional mixing procedure will not give uniform distribution. The rubber silica interaction can be improved by using silane coupling agents. Bis (3-triethoxy silyl propyl) tetrasulphide (TESPT or Si 69) is the most widely used one for improving silica-rubber bonding.[4] Compared to non-polar rubbers like NR and SBR, silica produces greater reinforcement in polar elastomers such as NBR, CR etc.[5] Silica exhibits better rubber filler binding in polydimethyl siloxane due to the interaction between silanol and siloxane groups.[6] Natural rubber modified with N- (3-Triethoxy silyl propyl) carbamoyl azoformate, exhibit increased silica reinforcement.[7,8] The effect of nitrile rubber on properties of silica - filled natural rubber compounds was studied by Hexiang Yan et al and reported improvement in the reinforcing capacity of silica due to the polar nature of Nitrile rubber, which enables a coupling effect.[9] Natural rubber, reinforced with the unique composition of Jordanian silica sand at different loadings (10,30,50 and 75phr) and different particle sizes (10,25,45 and 75μm) was found to be superior especially for hardness, tensile strength, and compression set properties and density.[10] Recently in situ precipitation of silica in the latex is tried as a method to prepare nano sized silica in the latex medium. The sol-gel reaction of Tetra ethoxy silane was conducted in natural rubber latex to produce nano sized and well-distributed silica particles and composites were prepared with that latex.[11] These composites showed superior mechanical properties. So novel methods for incorporating silica, to prepare composites are current research topics.

In this chapter the application of the novel route for precipitating silica in natural rubber latex by the method of polymer-mediated precipitation to prepare vulcanizates of superior properties is reported. This chapter is divided in to three parts. Part I deals with mechanical properties of the vulcanizates prepared using concentrated NR latex. In part II properties of composites prepared from an optimum concentration of silica mix are compared with those of composites with VN3 and conventional silica. Part III deals with the in situ precipitation of silica in field latex.

PART -I

In situ precipitated silica filled composites from centrifuged latex.

Precipitation of silica in natural rubber latex showed that the silica formed is having a reduced size and non spherical shape. Both properties are important requirements for rubber reinforcement. So composites of NR were prepared with silica incorporated by this novel method.

4.2 Experimental

Materials: Natural rubber latexes were supplied by Njavallil Latex, Kochi, India. Natural rubber, ISNR-5 was obtained from Rubber Research Institute of India. Kottayam, India and other chemicals used were of commercial grade.

Preparation of silica mixes

Centrifuged latex was filtered and stabilized with non-ionic stabilizer vulcastab VL. The stabilized latex was mixed with required amounts of sodium silicate and stirred for one hour. After keeping the mixture for 24 hours the silica was precipitated by the drop wise addition of saturated solution of ammonium chloride with constant stirring. Latex was coagulated as crumbs by the addition of 2% acetic acid. The crumbs were washed with water till the washings were neutral, pressed to remove water and dried in an air oven at 70°C for 48hrs. The precipitation was repeated with varying amounts sodium silicate to prepare silica rubber mixes of different concentrations as shown in the Table 4.1

Table 4.1. In situ precipitated silica filled coagulum samples prepared from concentrated latex

Name of the sample	Silica content (theoretical) in the dried coagulum (phr)
M-1	1
M-2	2
M-3	3
M-4	4
M-5	5
M-10	10
M-15	15
M-20	20
M-25	25
M-30	30
M-40	40
M-50	50

Determination of silica content in the sample

The silica content of the dried coagulum samples was determined by igniting a known weight of the sample in a previously weighed silica crucible in a muffle furnace. The temperature of the furnace was kept at 550°C for five hours time. The rubber content in the sample was burnt off leaving the silica in the crucible, which was cooled in a desiccator and weighed. From the weight of the ash the loading of silica and the loss of the silica was calculated.

Moisture content

The sample was equilibrated under room temperature (27°C), the equilibrium being approached from the dry side, and accurate weight of the sample was taken (w_1). The sample was then dried to constant weight in an air oven at 100°C and the moisture regain was calculated on the basis of oven dry weight (w_2).

$$\% \text{ Moisture content} = (w_1 - w_2)\, 100 \,/\, w_1 \quad \ldots\ldots\ldots\ldots \quad 4.1$$

Preparation of the composites

Table 4.2. Base compound formulation

Ingredients	Amount (phr)
Natural Rubber	100
ZnO	5
Stearic acid	2
Diethylene glycol	1
CBS	0.6
TMTD	0.2
Sulphur	2.5

Table 4.2 shows the base formulation for the preparation of composites. Compounds were prepared from silica mixes of different concentrations. The formulation of the compounds is given in the Table 4.3.

Table 4.3. Compounds from silica mixes of different concentrations of silica*

Compound name	Weight of Silica mix (g)	Silica content (phr)
INS -1A	M-1 (101)	1
INS -2A	M-2 (102)	2
INS -3A	M-3 (103)	3
INS -4A	M-4 (104)	4
INS -5A	M-5 (105)	5
INS -10A	M-10 (110)	10
INS -15A	M-15 (115)	15
INS -20A	M-20 (120)	20
INS -25A	M-25 (125)	25
INS -30A	M-30 (130)	30
INS -40A	M-40 (140)	40

*Mixes also contains the ingredients ZnO 5, Stearic acid 2, DEG 1, CBS 0.6, TMTD 0.2 and S 2.5

Composites with carbon

In situ precipitated silica masterbatch M-20 was mixed with carbon black and the formulation of the compounds are given in the Table 4.4. Compounds were prepared by mill mixing on a laboratory size (16 x 33cm) two-roll mill at a friction ratio of 1:1.25 as per ASTM D 3184-89 (2001).

Table 4.4. Compound formulations for composites with carbon black.

Component (phr)	B-1	B-2	B-3	B-4
NR	50	100	75	100
M-20	60	-	30	-
ZnO	5	5	5	5
Stearic acid	2	2	2	2
Comm. silica	-	10	-	5
DEG	1	1	1	1
Naphthenic oil	2	2	1	1
HAF black	40	40	50	50
Aromatic oil	8	8	8.5	8.5
CBS	0.95	0.95	0.95	0.95
HS	1	1	1	1
Sulphur	2.5	2.5	2.2	2.2

After complete mixing of the ingredients the stock was passed six times through tight nip and finally sheeted out at a fixed nip gap. The samples were kept overnight for maturation.

Testing

The cure characteristics of all mixes were determined using Rubber Processing Analyzer RPA 2000, Alpha Technologies, USA, as per ASTM standard, D 2084-01. Subsequently, the rubber compounds were vulcanized up to the optimum cure time at 150°C in an electrically heated hydraulic press. The mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 hr prior to physical testing.

Physical properties such as modulus, tensile strength, elongation at break, tear strength, hardness, abrasion loss, heat build-up, compression set, flex resistance and resilience were studied as per the respective ASTM Standards.

Reinforcing capacity of composites

Reduced stress

Reinforcing capacity of the composites were analysed as reduced stress (σ^*). It is reported that when silicone rubber was reinforced with in situ silica by sol-gel process an increase of the reduced stress was observed[12] and that is demonstrated as due to the inclusion of in situ silica in the rubber matrix.

Reduced stress can be calculated with the equation[13]

$$[\sigma^*] = \sigma / (\alpha - \alpha^{-2}) \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad 4.2$$

where σ is the stress and α is the strain.

4.3 Results and discussion

4.3.1 Characterization of the silica mix

Silica content during the precipitation in concentrated latex

The silica content of the dry rubber samples containing in situ precipitated silica is given in Table 4.5. The loading of silica is found to fall with increase in concentration of silica. It means that a small quantity of silica is lost during the in situ precipitation. It is clear from the Table 4.5 that the effluent loss of silica is less (less than 1%) up to 20phr silica, but above 20phr the loss of silica during incorporation increases abruptly. This may be due to the poor distribution of silica above 20phr. The distribution of silica attains an optimum value at 20phr. This has been confirmed from the SEM pictures (Figure 3.8a to 3.8f) of the ignited silica given in the Chapter 3. The increase in the % loss of silica at higher concentration makes the accurate filling of silica difficult. Calculated quantities should be added in excess to compensate for this loss.

Table 4.5. Silica content during the precipitation in concentrated latex

Sample name	Weight of silica expected (phr)	Silica content experimentally found (phr)
M-1	1.002	1.002
M-2	2.004	2.001
M-3	3.007	3.002
M-4	4.009	4.000
M-5	5.012	5.003
M-10	10.024	10.015
M-15	15.036	15.013
M-20	20.048	19.992
M-25	25.060	24.254
M-30	30.072	28.017
M-40	40.096	36.524
M-50	50.120	42.258

The percentage moisture content of all samples was found to be less than 0.01%.

Bound rubber content

The action of solvent on silica master batches showed that even at a very low concentration of silica (1phr), the sample did not dissolve completely in the solvent. Instead it showed a gel formation. This indicates that the filler polymer interaction is present to a great extent in the sample containing in-situ precipitated silica. The bound rubber content values of the silica masterbatches has been given in table 3.4.

The change of bound rubber content with the silica content of the masterbatches is graphically represented in the Figure 4.1. It is clear from the graph that as the concentration is increased the bound rubber content also increased and attained a maximum value for 20phr silica concentration. Above 20phr the bound rubber content shows only a small marginal increase. The change of the bound rubber fraction reflects the change of the interface interaction.[14,15,16] This can be explained on the basis that the fine distribution of nano silica in the rubber matrix attains its maximum value at this concentration and above that there is the chance of particle agglomeration. Or in other words the rubber can hold 20phr silica with maximum distribution. This also explains the increase in loss of silica at higher concentrations.

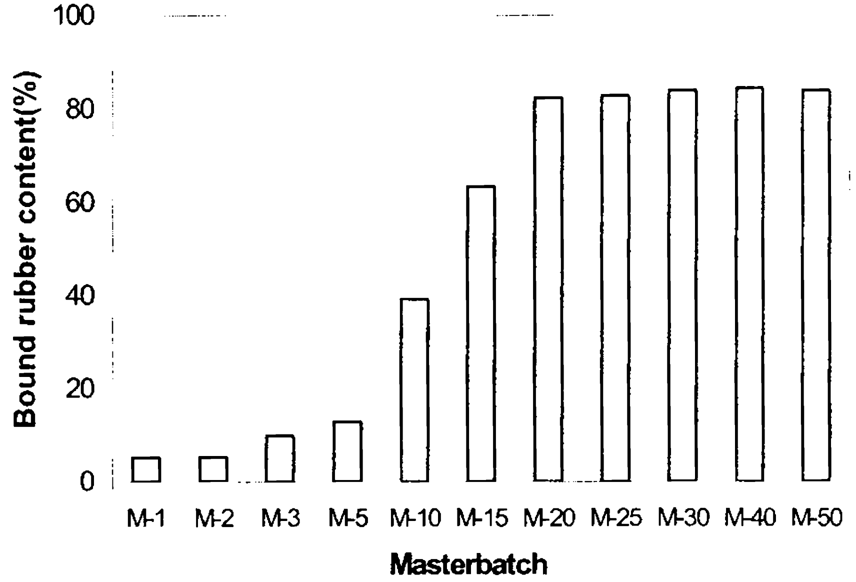


Figure 4.1. The variation of bound rubber with silica content

4.3.2 Properties of composites

Tensile properties

The tensile properties of the composites prepared from the silica mixes of different compositions are given in the Figures 4.2a to 4.2d. The graphs show that properties like tensile strength, modulus at 300% elongation, elongation at break (EB) and tear strength of the composites increase with the rise of in situ precipitated silica content.

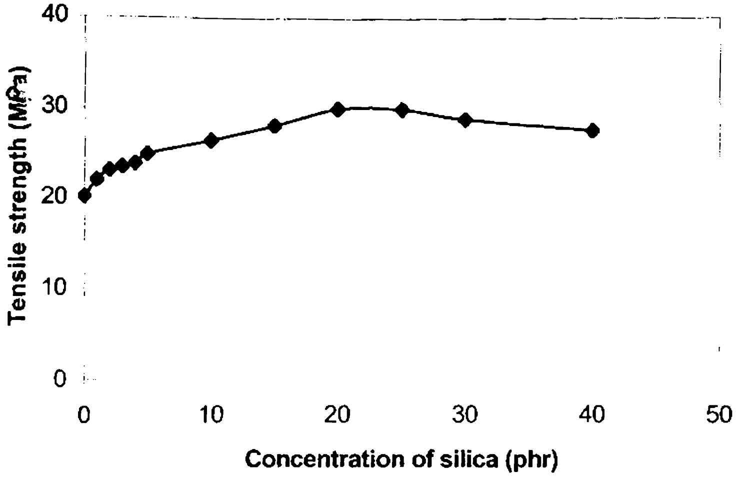


Figure 4.2a. Variation of tensile strength with concentration of silica

Tensile stress-strain measurements have been one of the standard methods for characterising rubber vulcanizates.[17] The tensile strength increases gradually with the increase in silica content. It attains a maximum at a concentration of 20phr and above that it does not show any increase but shows a small decrease. This decrease again confirms the change in particle size of silica at concentrations above 20phr. The variation of the tensile modulus is given in the Figure 4.2b.

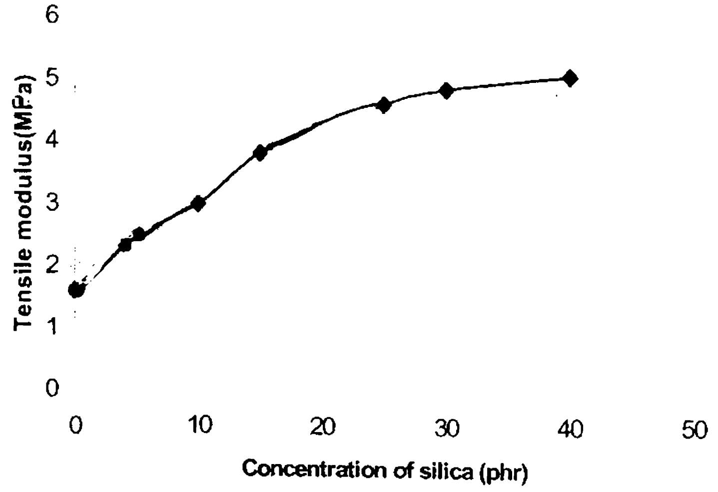


Figure 4.2b. Variation of tensile modulus with concentration of silica

Modulus showed a small increase even after 20phr. But the increase is not proportionate. Fig. 4.2c shows the variation of tear strength with silica content. Tear strength increases proportionally with increase in silica up to 20 phr. Above 20 phr it shows very small change Fig. 4.2d shows that elongation at break gradually decreased with silica incorporation.

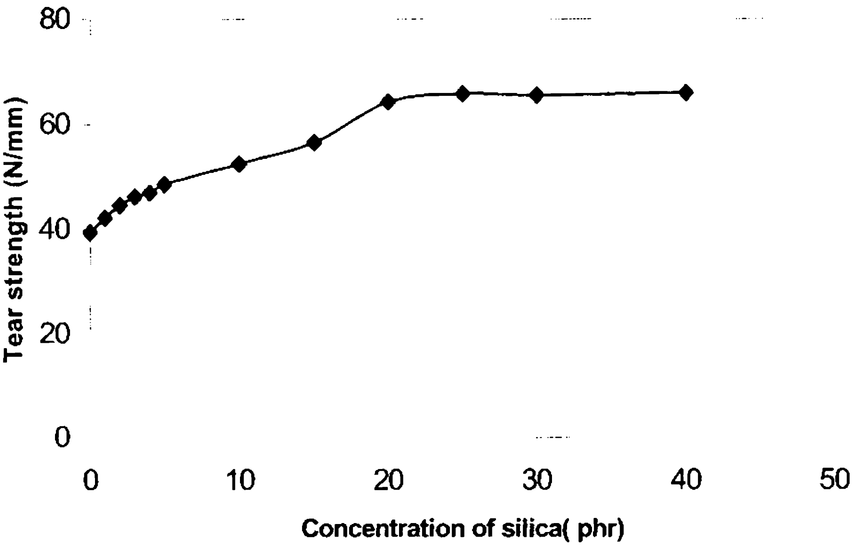


Figure 4.2c. Variation of tear strength with concentration of silica

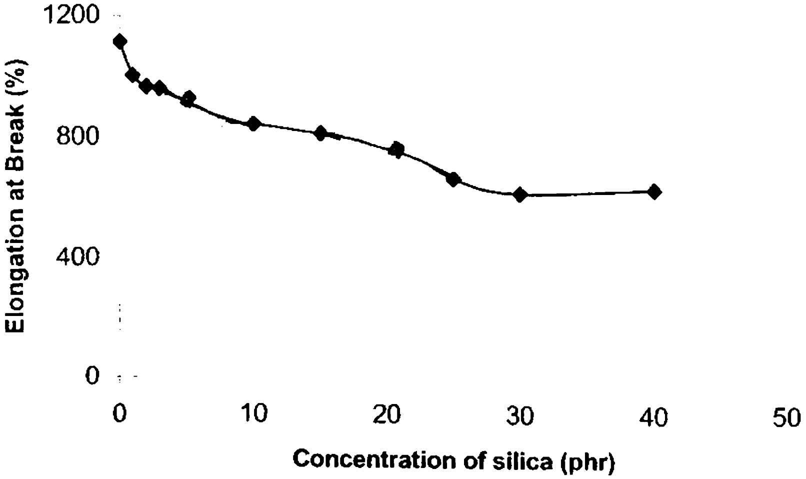


Figure 4.2d. Variation of Elongation at break with concentration of silica.

Reduced stress

Reduced stress (σ^*) values for all the composites were plotted as a function of silica content and are shown in the Figure 4.3

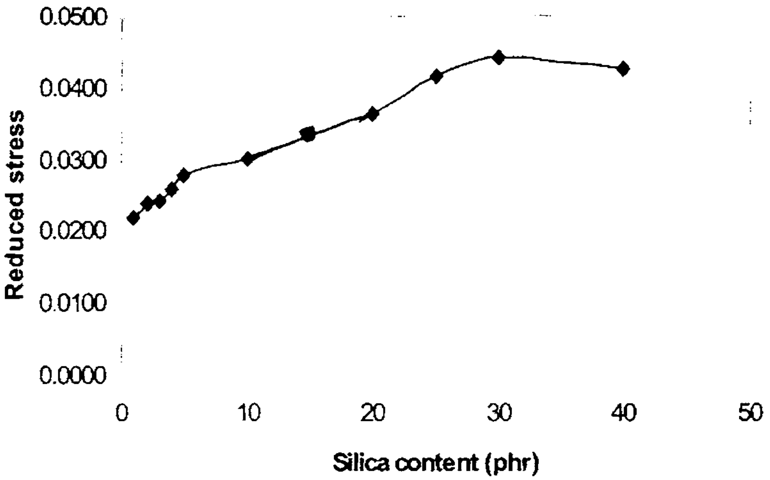


Figure 4.3. Variation of reduced stress with silica content

It is clear from the Figure 4.3 that the reduced stress values increased with increase in concentration of silica. The increase in the reduced stress values shows the improvement in the reinforcing capacity of the in situ silica. The reinforcement effect is mainly influenced by the size of the filler particles, the most important property that influences reinforcement.[18] The principal requirement for rubber reinforcement is sufficiently small domain size, less than about 1 µm. Sufficiently small filler can give good reinforcement, even when matrix/domain bonding is poor. This again supports the fact that the silica particles formed in the rubber matrix by in situ precipitation have sufficiently reduced size to give better reinforcement property.

Properties like Hardness, Resilience and Abrasion loss

Figures 4.4a, 4.4b and 4.4c show respectively the variation of hardness, resilience and abrasion loss of the composites with silica content.

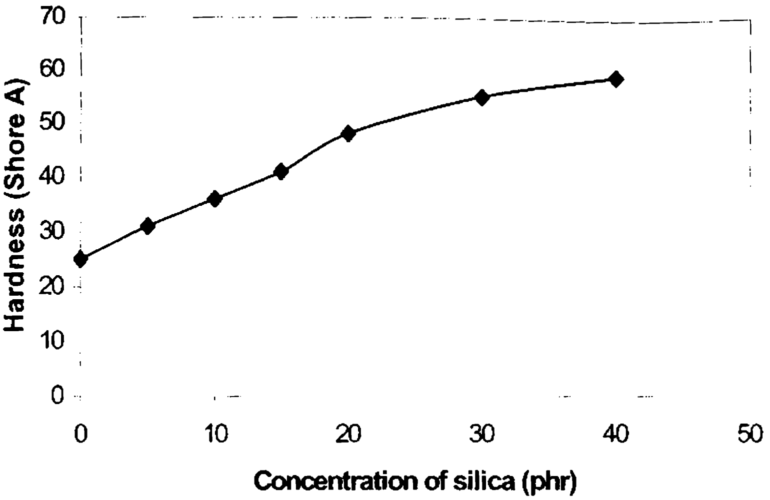


Figure 4.4a Variation of hardness with concentration of silica.

Hardness, a measure of low strain elastic modulus, was found to be increasing as the silica content increases. Resilience, a measure of the elastic component, was found to decline with increase in silica content.

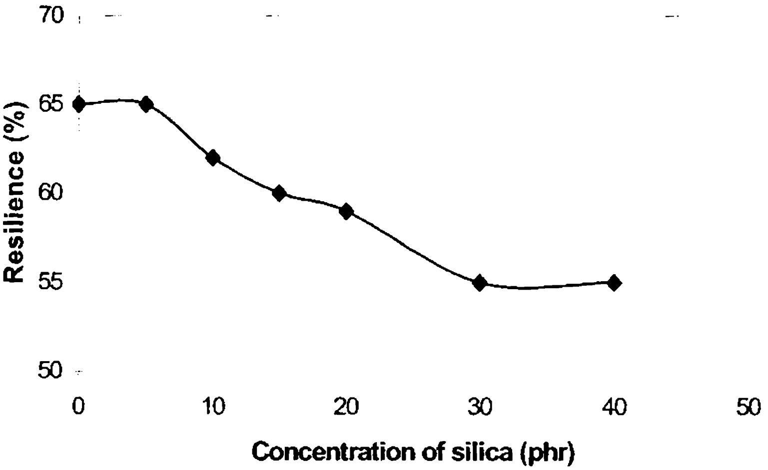


Figure 4.4b. Variation of resilience with concentration of silica.

Abrasion resistance (reciprocal of abrasion loss), a measure of reinforcement was found to improve with the in situ silica content. The improvement is significant up to a concentration of 20phr. Above 20phr the abrasion resistance shows only a marginal improvement. The improvements in mechanical properties were related to the secondary structure of the fillers.[19] Filler aggregates in elastomer matrix have a tendency to form agglomerates, especially at high loading, leading to chain like filler structure or cluster, generally termed as `secondary structure' or filler network. Such a network has a significant effect on the properties of filled rubber.[20] High structure increases abrasion resistance and hardness.

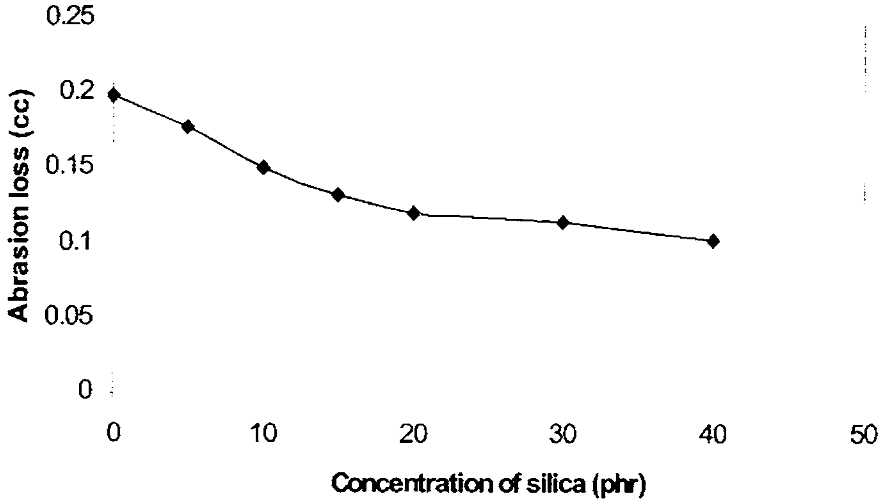


Figure 4.4c. Variation of abrasion loss with concentration of silica.

On evaluating all the above properties, 20phr is selected as the optimum concentration of in situ precipitated silica filled composite that can give better reinforcement.

4.3.3 Properties of composites with carbon black

Properties of composites with in situ precipitated silica and carbon black are given in the Table 4.6. Recently in tyre applications carbon black is partly replaced by silica. So to study the nature mixing of carbon black with in situ precipitated silica, composites were prepared with in situ precipitated silica masterbatch and carbon black as per the formulation given in the Table 4.4 by mill mixing on a two-roll mill.

Table 4.6. Properties of composites with silica and carbon black

Property	B-1	B-2	B-3	B-4
Tenslile strength MPa	28.02	28.83	30.4	29.7
Modulus (300%) MPa	7.23	6.94	9.01	8.52
Elongation at break	790	860	714	820
Tear strength N/mm	92	87	85	82
Hardness shore A	62	63	62	63
Resilience %	46	50	48	50
Abrasion loss cc	0.101	0.122	0.110	0.134
Compression set %	26.02	25.45	25.19	25.04
Heat build up °C	35	33	32	31

In one set of compounds (B-1, B-2), 10phr of silica was mixed with 40phr carbon black. In the other set (B-3, B-4) 5phr of silica was mixed with 50phr carbon (1&3 - in situ, 2&4 - conventional). Tensile properties are comparatively better for composites containing in situ silica while hardness showed equivalent values. Resilience values of the in situ precipitated silica containing composites are slightly lower and hence values of heat build up are slightly higher. Abrasion resistance as well as compression set showed comparable values. These results show that in situ precipitated silica mixes can be used in tyre tread compounds partly replacing carbon black. For off the road tyres, blends of silica and carbon black provide improved cut growth resistance.[21] It also reveals that rubber is not fully occluded in the rubber silica mix.

PART II

Comparison of the properties of the *In Situ* precipitated Silica with that of commercial silica

Based on the loading capacity of silica, bound rubber content, tensile properties and other technological properties, the optimum concentration of silica by in situ precipitation may be considered as 20phr. It has good loading of silica during precipitation and has the maximum value of bound rubber content. The reinforcing properties like tensile strength, tear strength and abrasion resistance showed that the concentration of silica that can give better properties is 20phr. So 20phr is selected as the optimum concentration of the masterbatch for preparing compounds of lower concentration, by mixing suitable amount of M-20 with dry rubber. For comparison of properties, composites of similar concentrations were prepared from conventional silica and commercial nano silica, VN3.

4.4 Experimental

Mooney viscosity and moisture absorption

The Mooney viscosity of the masterbatch is measured for M-20 and compared with that of ISNR-5 and masterbatch containing 20phr commercial silica, COM-20. The moisture absorption of the masterbatch was studied for a period of 30days

Preparation of composites

Formulation of the composites are given in the Table 4.7, 4.8, 4.9 and 4.10

Table 4.7. Composites of lower concentrations from M-20*

Compound name	Masterbatch M-20 (phr)	NR (phr)	Silica concentration (phr)
INS-1B	6	95	1
INS -2B	12	90	2
INS -3B	18	85	3
INS -4B	24	80	4
INS -5B	30	75	5
INS -10B	60	50	10
INS -15B	90	25	15

*Mixes also contains the ingredients ZnO 5, Stearic acid 2, DEG 1, CBS 0.6, TMTD 0.2 and S 2.5

Table 4.8. Compounds with conventional silica*

Sample name	COM -1	COM - 2	COM -3	COM -4	COM -5	COM -10	COM -15
NR phr	100	100	100	100	100	100	100
Silica phr	1	2	3	4	5	10	15

*Mixes also contains the ingredients ZnO 5, Stearic acid 2, DEG 1, CBS 0.6, TMTD 0.2 and S 2.5

Table 4.9. Compounds with commercial nano silica VN3

Sample name	VN3 -1	VN3 -2	VN3 -3	VN3 -4	VN3 -5	VN3 -10	VN 3 -15
NR phr	100	100	100	100	100	100	100
VN3 phr	1	2	3	4	5	10	15

*Mixes also contains the ingredients ZnO 5, Stearic acid 2, DEG 1, CBS 0.6, TMTD 0.2 and S 2.5

Table 4.10. Formulation of mixes with 20phr silica.

Sample name	NR	M-20	VN3	Com. silica
F-1	-	120	-	-
F-2	100	-	20	-
F-3	100	-	-	20

*Mixes also contains the ingredients ZnO 5, Stearic acid 2, DEG 1, Naphthenic oil 4, HS 1, CBS 0.6, TMTD 0.2 and S 2.5

After complete mixing the stock was passed six times through tight nip and finally sheeted out at a fixed nip gap. The samples were kept overnight for maturation. Optimum cure time was determined using Rubber Process Analyzer (RPA 2000- Alpha Technologies). Blanks cut from unvulcanized sheets were vulcanized at a temperature of 150±2°C and at a pressure of 200kgcm^{-2} in an electrically heated hydraulic press, up to their respective optimum cure times.

Physical properties

Physical properties such as modulus, tensile strength, elongation at break, tear strength, hardness, heat build-up, compression set, flex resistance and ageing resistance were studied as per the respective ASTM Standards. Swelling studies and Scanning Electron Microscopic studies were used to evaluate the internal cross links and distribution of silica respectively.

Reinforcing index

Reinforcing index (RI) gives an empirical relation between reinforcing capacity and filler content.

Reinforcing index RI = (N/N_0) (100/silica content) 4.3

where N and N_0 are the nominal values of the mechanical property measurements for the sample filled with and without silica respectively.[22]

Studies on rubber filler interactions

The strain sweep measurements on unvulcanized samples and vulcanizates were conducted to study the rubber-filler interactions. Filled rubber materials need special instruments for rheology. Rubber Process Analyzer (RPA 2000-Alpha Technologies) is a purposely-modified commercial dynamic rheometer.[23] The variation of complex modulus with strain was studied for all the compounds before and after curing.

Ageing studies

Thermal, radiation and ozone

Thermal ageing was carried out at a temperature of 100^{0}C for 24hrs, 48hrs, 72hrs and 160hrs as per ASTM D 573-1999. For radiation ageing the samples were irradiated with gamma rays from ^{60}Co source at a dose rate of 0.3413 Mrad/hr in a gamma chamber. Tensile testing before and after irradiation and thermal ageing were carried out according to ASTM D 412-68 and D 628-54 standards. Ozone resistance was determined according to ASTM D 518 method B. Samples were exposed to ozonised air in an ozone chamber (MAST Model 700-1) for 36 hrs. The concentration of ozone was maintained at 50 pphm and the inside temperature at 40°C. The ozone cracks developed on the samples were analyzed by optical microscopy.

Swelling studies

Swelling studies of the composites were conducted in toluene to find their cross-link densities using Flory-Rehner equation.[24] Swelling of the samples were done in diesel and lubricating oil to find the swelling index.

$$\text{Swelling index} = \frac{w_2 - w_1}{w_1} \times 100 \qquad \text{.....................................4.4}$$

where w_1 = weight of the sample, w_2 = weight of the swollen sample

TGA of Composites

Thermo gravimetric analysis of the composites was done to study the thermal stability of the composites with different silica.

4.5. Results and discussion

4.5.1 Mooney viscosity and the moisture absorption of masterbatch

Mooney viscosity and moisture absorption values of the masterbatch M-20 is measured and compared with that of ISNR-5 and masterbatch containing 20phr commercial silica, COM-20. The values are given in the Table 4.11.

Table 4.11. Comparison of moisture absorption and Mooney viscosity

Sample	Moisture absorption(%)in 30 days	Mooney viscosity, ML (1+4) @ 100°C
NR Gum	0.112	72
INS-20	0.266	120
COM-20	0.364	95

Water content can affect processing and vulcanization.[2] Absorbed water can decrease cure time, tensile strength and also abrasion resistance.[3] So absorption of moisture by the masterbatches should be as low as possible. Moisture absorption of the in situ silica masterbatch M-20 is low when compared to that of the coagulum containing commercial silica. Mooney viscosity of the masterbatch is an important parameter in processing. High Mooney is not appreciable for a masterbatch. But the Mooney viscosity of the in situ silica master batch is very high. This high Mooney viscosity is due to the close packing of small sized silica in the rubber matrix. So to reduce the Mooney viscosity, naphthenic oil emulsion was added in varying amounts to the latex before the silica precipitation. The Mooney viscosity of the dry coagulum containing varying amounts of oil is given in the Table 4.12. The addition of oil has reduced the viscosity and 6phr oil is considered as an optimum concentration.

Table 4.12. Variation of Mooney viscosity with the addition of oil

Amount of Oil (phr)	Mooney Viscosity, ML (1+4) 100°C
0	120
2	105
4	94
6	75
8	54

The concentration of the oil in the coagulum prepared with 6phr oil was estimated by solvent extraction and found to be 4.2phr. So in comparative studies, 4.2phr oil was added in all formulations with conventional silica.

4.5.2 Tensile properties

The tensile properties of the three types of composites are given in the Figures 4.5a to Figure 4.5d.

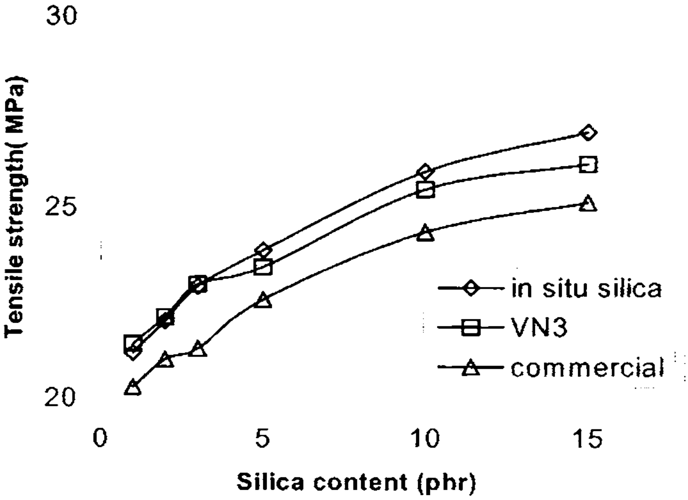


Figure 4.5a. Tensile strength of composites

Figure 4.5a shows the variation of the tensile strength of silica-reinforced composites of the three types. The nature and trend of the graphs are similar but the tensile strength values of in situ silica composites are more superior to that of commercial silica composites. They are equal to that of VN3 filled composites at lower concentrations of 1,2 and 3phr silica content and showed more improved values at higher concentrations. This is due to the improved distribution of in situ silica in the rubber matrix. Similar to the tensile strength, tensile modulus and tear strength showed more improved values for the in situ silica composites as indicated in Figures 4.5b and 4.5c. The results suggest that in situ precipitation of silica gives a better reinforcement compared to conventional silica and to the level of VN3. This may be due to the improved distribution of silica particles in the rubber matrix. It is also reported that non-spherical particles can impart better reinforcement.[25,26]

The previous study (Chapter 3) has showed that in situ precipitated silica has a non spherical structure with more voids. So the structure along with the distribution provides good rubber filler interactions. Strong rubber-filler bonding that permits bridging of infinite number of rubber chain through the filler is the main reason for improvement of the physical properties of vulcanizates. Development of high strength is on account of the ability of the rubber to dissipate strain energy near the tip of the growing crack by viscoelastic processes.[26] The dispersed filler particles in addition to providing energy dissipation, also serve to deflect or arrest growing cracks, thereby delaying the onset of catastrophic failure.

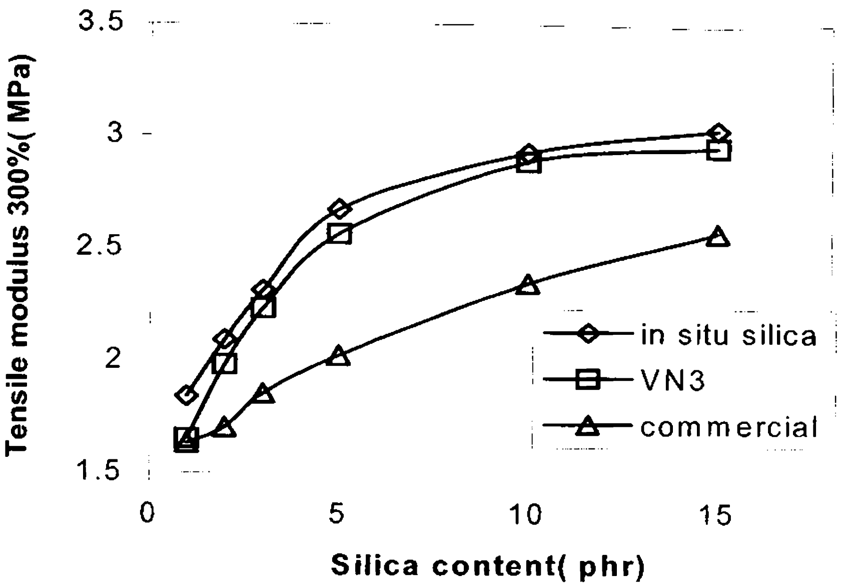


Figure 4.5b. Tensile modulus of composites

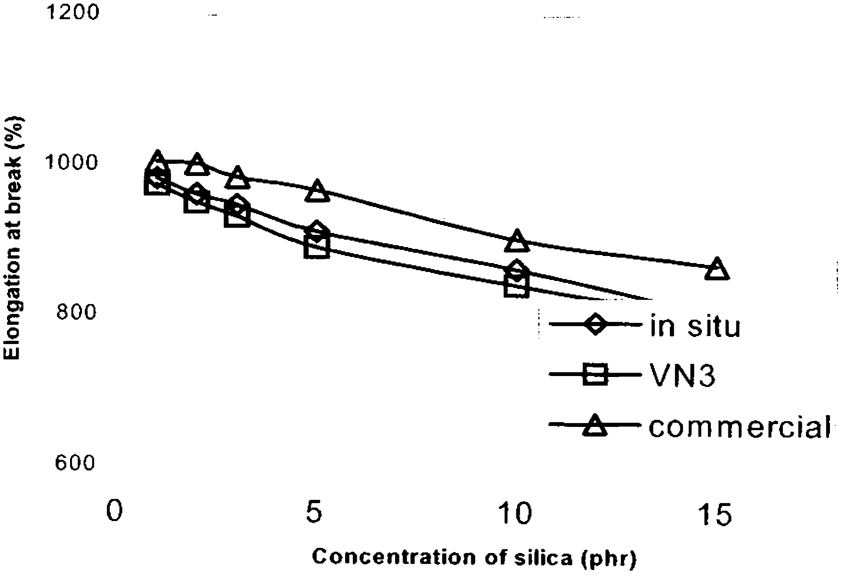


Figure 4.5c. Elongation at Break of composites

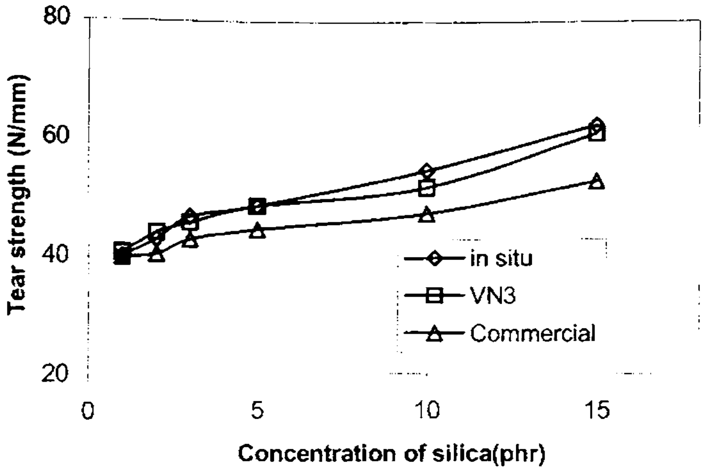


Figure 4.5d. Tear strength of composites

Reinforcing index

Reinforcing index values of all the three sets of composites with respect to tensile strength are given in the Table 4.13. The values of in situ silica composites are comparable with that of VN3 filled composites and are superior to those of conventional silica filled composites. This shows that in situ silica filled composites have reinforcing capacity equivalent to that of VN3 filled composites.

Table 4.13. Reinforcing index values of the composites filled with in situ precipitated silica, VN3 and commercial silica

Silica content phr	Reinforcing Index		
	In situ	VN3	Commercial
1	106.158	106.349	100.744
2	54.637	54.910	52.157
3	37.929	38.012	35.234
5	23.690	23.254	22.410
10	12.867	12.633	12.083
15	8.918	8.644	8.313

4.5.3 Rubber-filler interactions by strain sweep studies

Strain sweep tests for uncured compounds

The complex modulus (G*) values obtained for the uncured compounds are plotted and shown in the figures 4.6a, b and c.

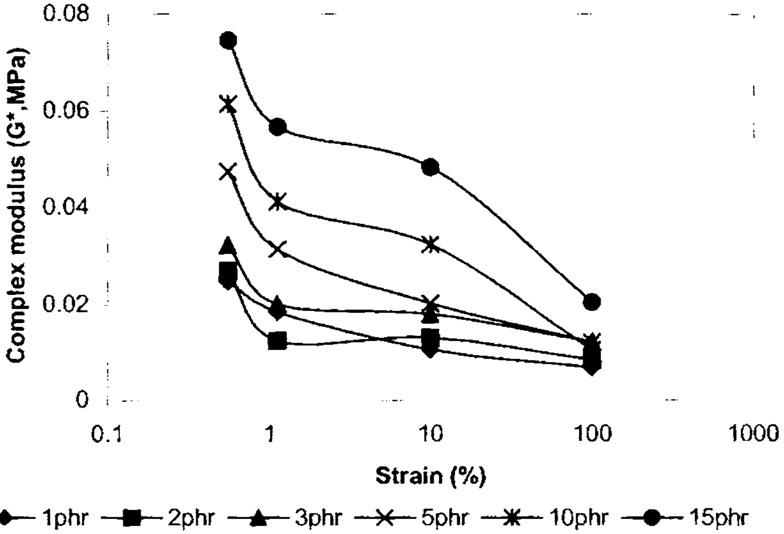


Figure 4.6a. Complex modulus versus strain for the latex precipitated silica

The elastic modulus of a filled rubber is experimentally, strongly dependent on the deformation and decreases substantially at higher strains. This phenomenon is known as the Payne effect[27] and is attributed to the presence and breakdown of the filler network during deformation. But investigations performed with both experimental and theoretical approaches showed that the decrease in G* with the amplitude of deformation (strain) has been attributed to the destruction - reformation of a percolating network of filler that can also involve polymer bonded to the filler[28] i.e. polymer filler links also. The complex modulus values at low strains (<15%) are a measure of the filler polymer interactions.[29] The limiting values at high strains are due to polymer networks and hydrodynamic effect. Polymer networks are the same for a fixed mass of rubber. But the hydrodynamic effect varies with the filler content and nature of the silica. The theoretical meaning of hydrodynamic effect is given by the modified form of Guth and Gold equation.[30,31]

The addition of the filler increases the shear modulus of the pure elastomer, G_o and results in a shear modulus, G_f for the filled compound.

$$G_f = G_o\,(1+0.67\,f_s.\Phi+11.62\,f_s^2.\Phi^2) \qquad \ldots\ldots\ldots\ldots \qquad 4.5$$

where Φ is the volume fraction of the particles and the shape factor f_s represents the ratio of the longest dimension to the shortest dimension of the particle. The modulus as calculated by Equations 4.5 is independent of the applied strain.[16]

Figure 4.6a shows that the complex modulus values at low strains gradually decrease with increase in silica content, indicating an increase in filler networks that involve filler - filler and filler - polymer interactions. The regular increase also supports the uniform distribution of newly formed silica in rubber matrix.

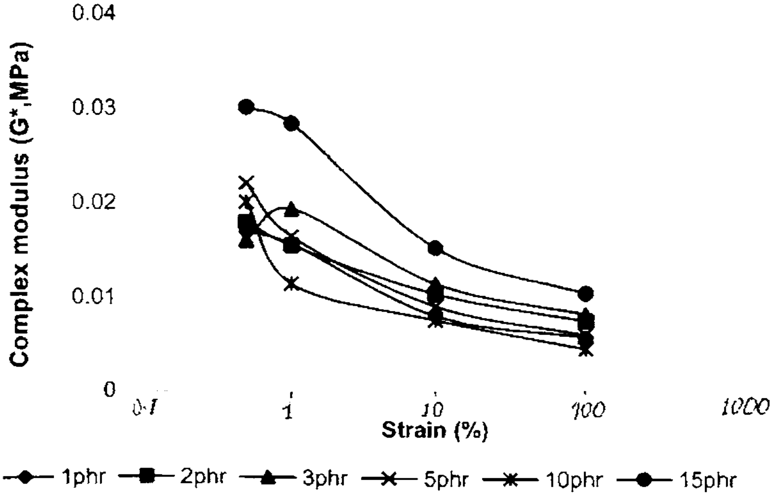


Figure 4.6b. Complex modulus versus % strain for the VN3 silica

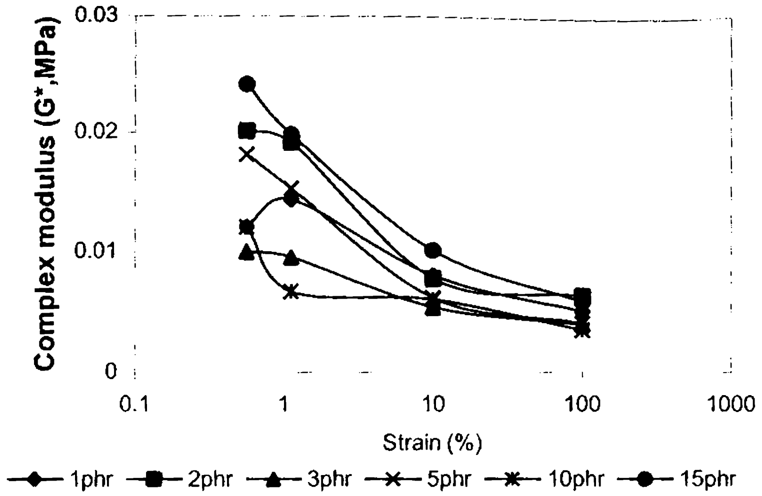


Figure 4.6c. Complex modulus versus % strain for the commercial silica

The Figure 4.6b and 4.6c shows that the complex modulus at low strains are comparatively low for the composites with VN3 and conventional silica. The values do not show a regular increase indicating a non uniform distribution.

Strain sweep test for cured compounds

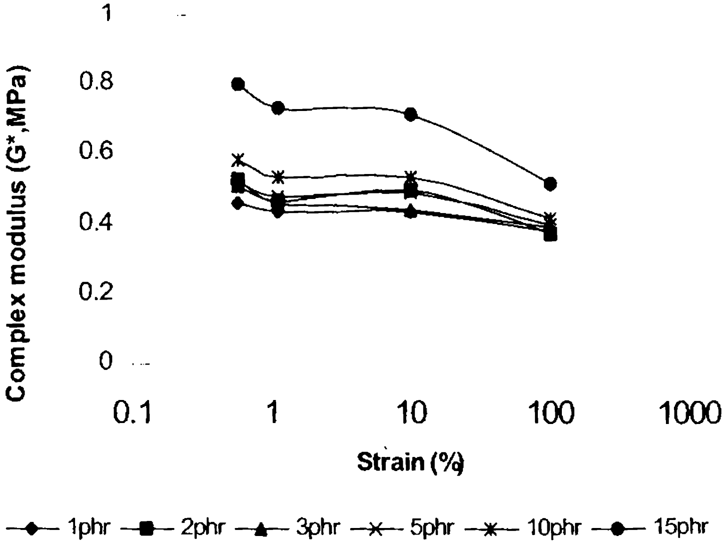


Figure 4.7a. Complex modulus versus % strain for the latex precipitated silica after curing.

The complex modulus values obtained for the cured complexes are plotted in the Figures 4.7a, b and c.

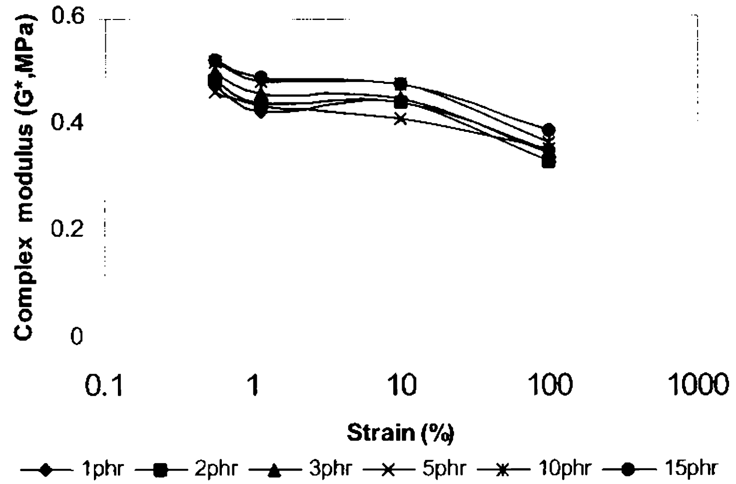


Figure 4.7b. Complex modulus versus % strain for the VN3 silica after curing.

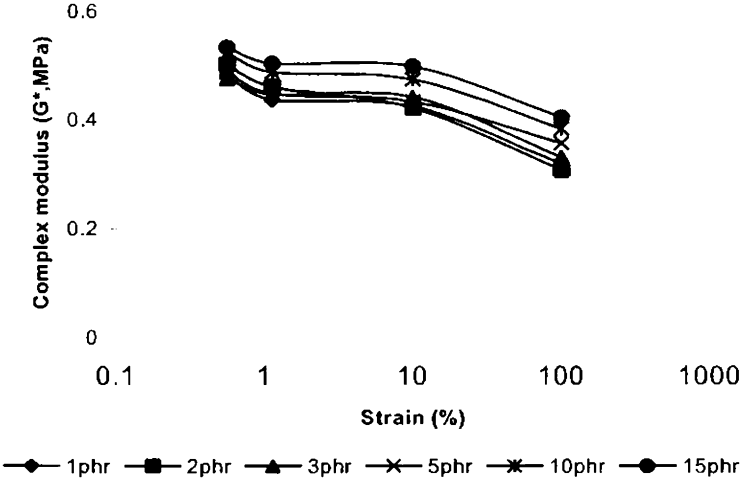


Figure 4.7c. Complex modulus versus % strain for the commercial silica after curing

The strain sweep studies after curing showed similar trend as that of the uncured compounds. The figures show that the modulus values are strain independent and a drop in the modulus occurred at low strains. Since the compounds are cured the modulus values are high but the behaviour is the same as that of the uncured compounds. Values at low strains increased gradually with the increase in concentration of in situ silica. No such increase is observed with VN3 and commercial silica. For in situ precipitated silica the limiting values are higher than that of VN3 and commercial silica. The higher values of modulus at low strains indicate the improved rubber filler interaction. The increased value at high strains reflects the higher values of hydrodynamic effect, which is dependent on the particle size and shape. [22]

4.5.4 Comparison of properties of in situ silica filled composites with commercial silica filled composites at the optimum concentration

Composites with 20-M showed maximum improvement in properties like bound rubber, tensile properties and rubber filler interactions. So composites with other commercially available silica were prepared at the same concentration and their properties were compared.

Cure characteristics

The cure characteristics of the mixes are given in the Table 4.14.

Table 4.14. Cure characteristics of the mixes

Property	F-1	F-2	F-3
Min. Torque, dNm	0.078	0.045	0.108
Max. Torque, dNm	4.154	3.962	3.321
Scorch time (ts_2), min	3.01	2.76	2.74
Opt. cure time (t_{90}), min	4.42	4.32	5.63
Cure rate index ($100/t_{90}-ts_2$)	63.69	64.11	34.60
Δ torque, dNm	4.076	3.917	3.091

The in situ precipitated silica filled composites exhibited higher rate and extent of cure over that of conventional silica and comparable results with that of VN3. Generally the polar nature of silica surface adsorbs a part of the curatives and or silica - zinc ion interaction leads to slowing down of the curing reaction.[4] This will result in an increased cure time and a reduced cure rate index. But the cure characteristics of in situ precipitated silica compounds indicate an improvement in these values.

Scorch safety has increased and cure time was found to be lower for in situ precipitated silica compounds. This might have resulted from the improved rubber filler interaction. This in turn may have reduced the chances of interaction of the silanol groups with either the accelerator or other compounding ingredients, thus making its availability for curing. The improved rheometric torque also supports it.

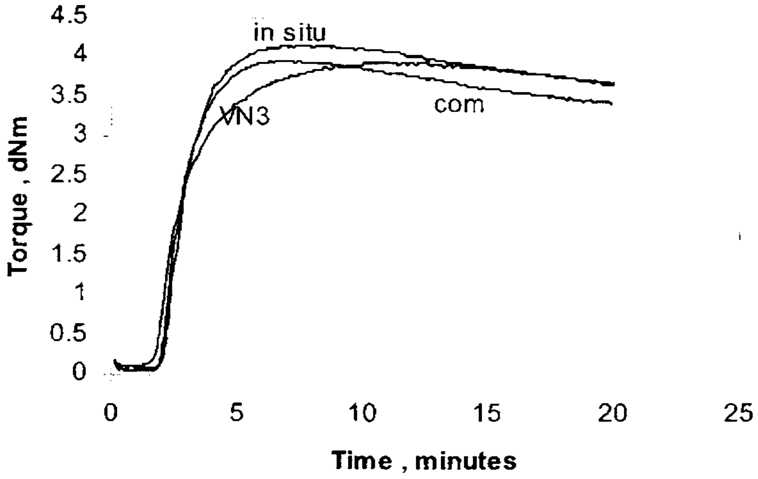


Figure 4.8. Cure graphs for the composites

The cure graphs of the three types of silica are showed in the Figure 4.8. The maximum torque is a measure of cross link density and stiffness in the rubber.[32] In general, for all the mixes the torque initially decreases, then increases and finally levels off. The initial decrease in torque to a minimum value is due to the softening of the rubber matrix, while the increase in torque is due to the cross linking of rubber. The leveling off is an indication of the completion of curing. It is found that the in situ precipitated silica increases the torque values. This increase is due to the presence of silica - rubber crosslink that imparts more restriction to deformation.

Tensile properties

Tensile properties of composites with in situ silica (F-1), VN3 (F-2), and commercial silica (F-3) are given in the Figure 4.9. The tensile properties of in situ silica composites are better than that of commercial silica and VN3 composites.

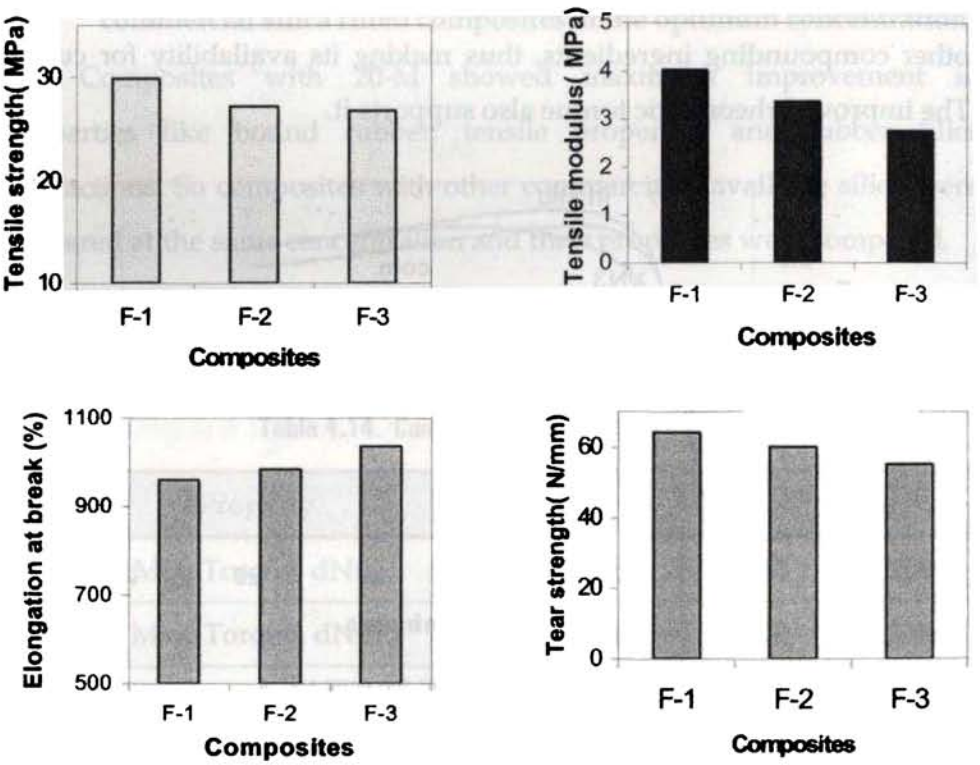
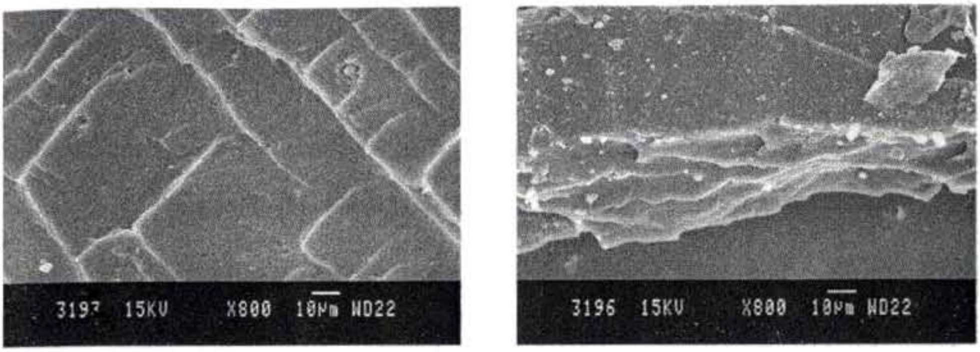


Figure 4.9. Tensile properties of composites

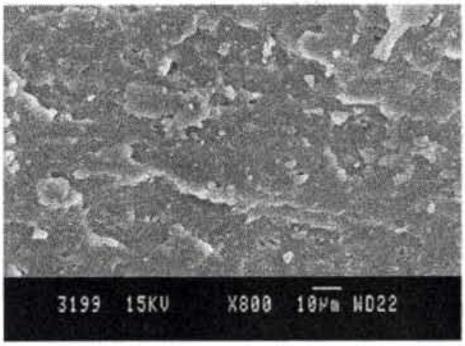
Fig.4.9 indicates that in situ precipitated silica has better reinforcement than VN3 at 20phr. This improvement is due to the fine distribution of silica particles in the rubber matrix and reduction in the size of the filler particles during in situ precipitation, which has resulted in an improved rubber filler interaction.

Scanning Electron Microscopy

Scanning electron microscopy can be used as a tool to characterise the filler distribution in the rubber matrix. SEM photographs of the cut surfaces of the three composites with in situ precipitated silica, VN3 and commercial silica are given in the Figure 4.10.



In situ precipitated **VN3**



Conventional

Figure 4.10 SEM photographs of the tear fractured surfaces of rubber compounds containing in situ precipitated silica , VN3 and conventional silica

In the tear fracture surfaces of rubber vulcanizates free silica particles are not seen in the vulcanizate containing in-situ precipitated silica, which indicates that a fine distribution of filler due to the improved filler-polymer interaction is present in this sample to a great extent. Tear lines are also more prominent in the in situ silica composites giving additional support to the increased reinforcement.

Ageing studies

Thermal ageing

The retention of properties on thermal ageing is given in the table 4.15. The graphical representations of the variation of properties are given in the Figure 4.11a, b and c. During thermal ageing, cross-link formation or cross-link breakage can take place or an existing cross-link may break and a stable linkage can be formed. It is observed that there is an initial increase in the tensile modulus after 24 hrs of ageing and after that there is a decline. The increase in modulus is due to the agglomeration of filler particles at higher temperature or due to increased cross links.

Table 4.15. Retention of properties on thermal ageing

Sample	Property	Retention of properties (%)			
		24 h	48 h	72 h	120 h
F1	Tensile strength	99	94	81	66
F2		98	90	79	55
F3		94	91	80	54
F1	Tensile modulus 300%	101	91	89	85
F2		103	92	89	76
F3		105	82	83	83
F1	Elongation at break	95	93	85	74
F2		97	93	87	73
F3		95	90	87	72
F1	Tear strength	100	95	89	71
F2		100	93	80	67
F3		93	84	73	65

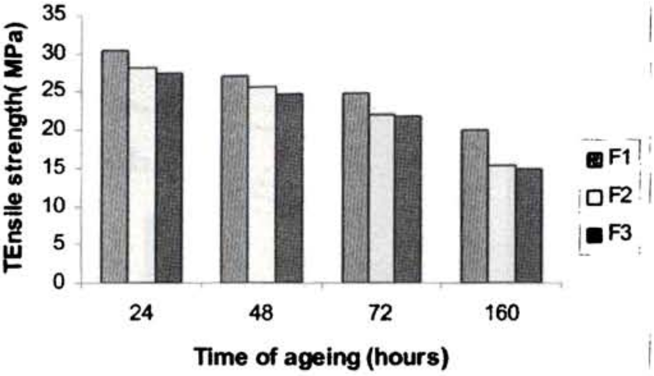


Figure 4.11a. Variation of tensile strength with thermal ageing

Tensile strength showed a gradual decrease, while tear strength showed no change after 24hours of ageing for in situ silica and VN3 samples. But a gradual decline after 24 hours was observed for both samples. Elongation at break showed a reduction even with 24 hours of heating. Modulus enhancement on ageing may be due to additional crosslinking during ageing. It can be seen from the figures that the composites with the in situ precipitated silica showed a better resistance to thermal degradation. This may be due to the increased rubber filler interactions, which lead to an increased occlusion of rubber molecules in the voids of in situ silica.

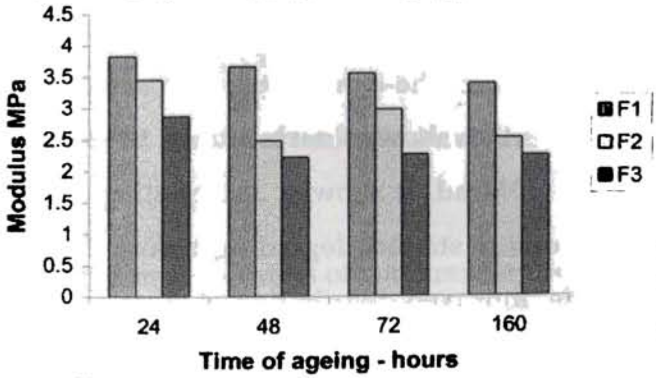


Figure 4.11b. Variation of tensile modulus with thermal ageing

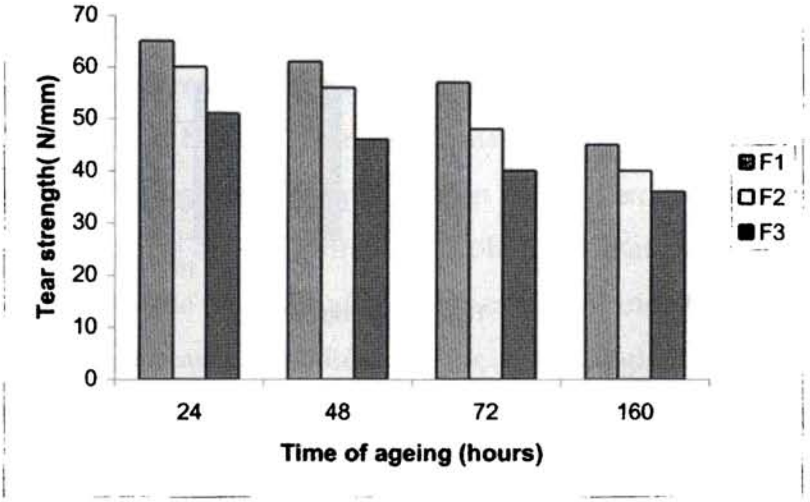


Figure 4.11c. Variation of tear strength with thermal ageing

Radiation ageing

The effects of radiation on polymeric materials and their blends and composites have been reported by researchers.[33,34] The mechanical properties of the polymers changed considerably under the influence of high-energy radiations. This may be due to the cross-linking or by the degradation of polymer chain. Mechanical properties such as tensile strength, modulus, elongation etc; are reduced by chain degradation, while cross-linking enhance these properties. Fig. 4.12a and 4.12b show the effect of radiation on the composites. The sample containing latex stage precipitated silica showed a resistance to degradation up to a radiation doze of 2.5Mrad. It showed a degrading tendency only after 2.5 Mrad, while others started degrading before that. This resistance may be due to the improved distribution of silica in rubber matrix that holds the rubber together.

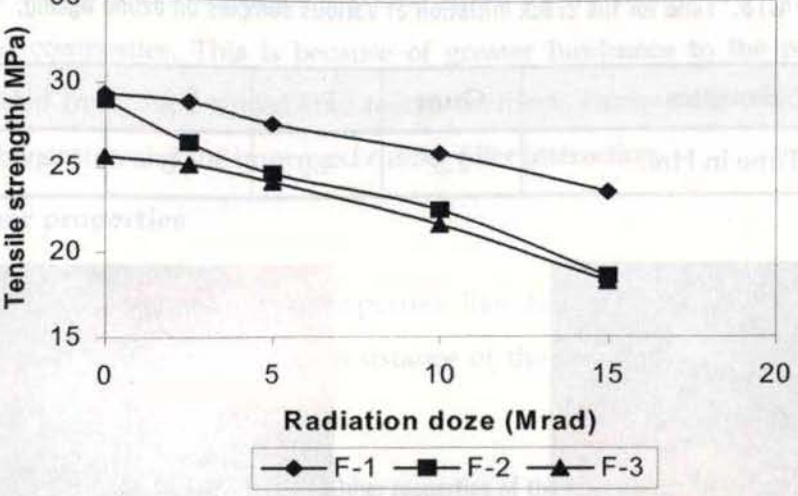


Figure 4.12a. Variation of tensile strength with radiation doze

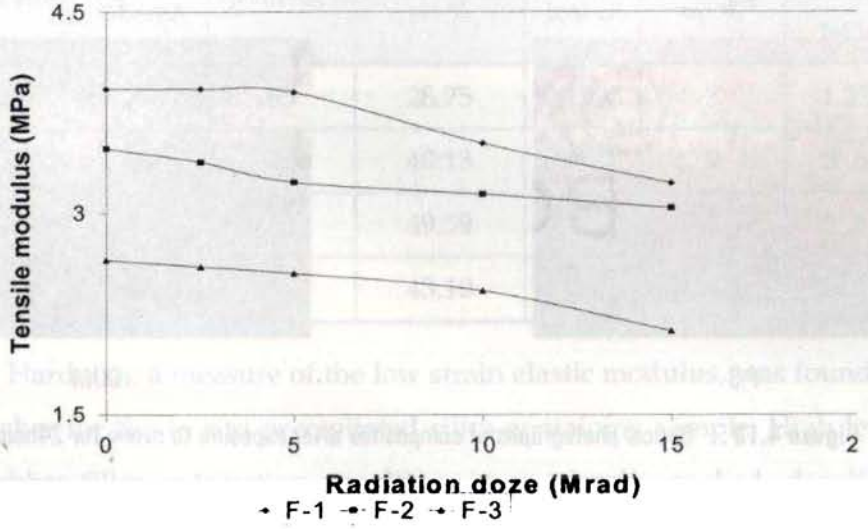


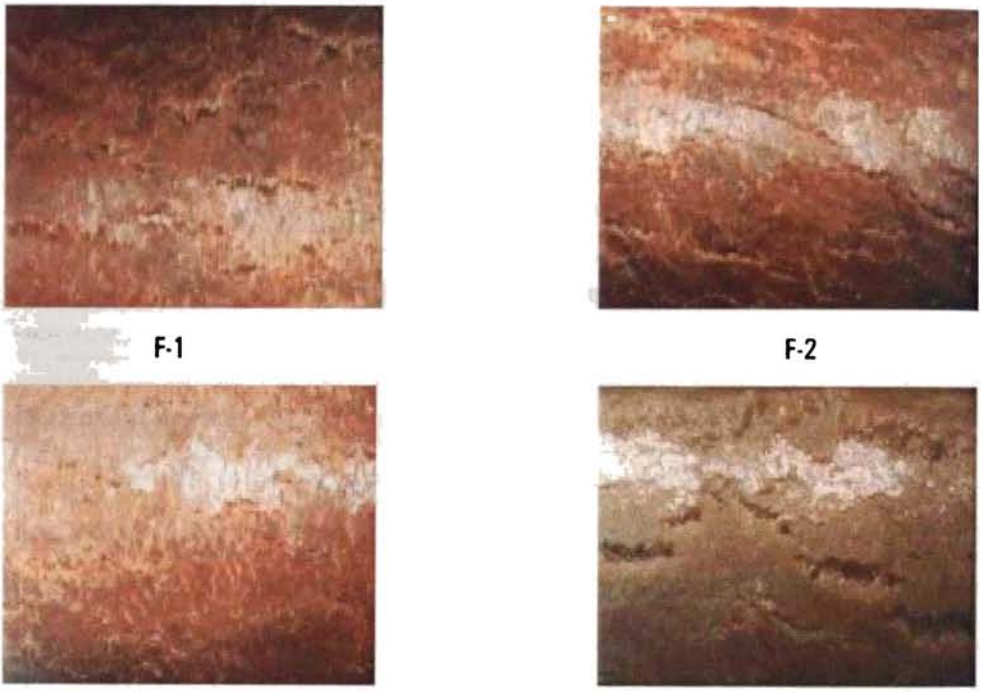
Figure 4.12b. Variation of tensile modulus with radiation doze

Ozone ageing

The time for the crack initiation of various samples on ozone ageing is given in the Table 4.16 and the Figure 4.13 shows the photographs of composites after exposure to ozone for 24 hours.

Table 4.16. Time for the crack initiation of various samples on ozone ageing.

Samples	Gum	F-1	F-2	F-3
Time in Hrs.	2.5	4.0	4.0	4.0



F-1

F-2

F-3

GUM

Figure 4.13 . Optical photographs of composites after exposure to ozone for 24hours.

Unsaturated elastomers, especially those containing active double bonds in the main chain, are severely attacked by ozone resulting in deep cracks in a direction perpendicular to the applied stress. Protection against ozone attack can be achieved by the use of antiozonants. Several studies have been reported on the protection of rubber against ozone attack.[35,36] Table 4.16 shows that all composites containing silica cracked in 4 hours irrespective of the nature of the silica. The photographs in Figure 4.13 showed that the intensity of crack is low for composite containing in situ precipitated silica.

This shows better resistance to ozone attack for the in situ precipitated silica filled composites. This is because of greater hindrance to the progress of fracture front experienced due to the uniform distribution of silica in the rubber matrix and the improved rubber filler interaction.

Other properties

Other technological properties like hardness, resilience, abrasion loss, heat build up and flex resistance of the composites are given in the Table 4.17

Table 4.17. Other properties of the composites

Composite	Hardness ShoreA	Resilienc%	Compression set %	Abrasion loss cc	heat build up °C	Flex resistance lakh
GUM	25	65	28.75	0.1995	3	1.32
F-1	48	56	40.13	0.1218	9	3 .5
F-2	45	60	49.59	0.1223	7	3 .6
F-3	41	60	43.10	0.1330	10	3 .1

Hardness, a measure of the low strain elastic modulus, was found to be higher for the in situ precipitated silica-containing sample. High level of rubber–filler interaction resulting in a closely packed densified composite might have raised the low strain modulus. Higher composite packing due to rubber - filler bonding and higher crosslink density may be the reason for this behaviour. In situ precipitation has improved the abrasion resistance also. Improved abrasion resistance is considered as a measure of enhanced filler reinforcement. Compression set and resilience are found to be comparatively low for in situ precipitated silica composite. Resilience is a measure of the elastic component and decreased with in situ precipitation. Changes in compression set, heat build up and resilience are attributed to the lower elasticity of in situ precipitated silica filled sample. Dematia flex testing is an important measure of the flex resistance, especially for tyre applications. The number of flex cycles required for crack initiation was noted and it is comparatively high for in situ precipitated silica filled sample, indicating that the in situ precipitated silica filled composite is suitable for tyre applications.

Swelling studies

Swelling resistance in oils

The swelling resistance of the silica filled composites in different oils was studied by swelling a cut sample in oil for constant weight. The swelling index is given in the table 4.18.

Table 4.18. The swelling index values of composites

Composite	Swelling index %	
	Diesel	Lubricating oil
GUM	346.0	39.9
F-1	150.6	23.3
F-2	157.4	26.1
F-3	178.9	31.3

Swelling values of in situ silica composites are found to be much less than that of the composites with commercial silica and the values are comparable with that of VN3. Reduced swelling index values also support the improved rubber filler interactions.

Swelling in toluene

Table 4.19 shows the crosslink density of composites prepared from different types of silica. It is found that the crosslink density of in situ precipitated silica filled composite (F1) is higher than that of VN3 (F2) and commercial silica (F3). The swelling of rubber in a solvent is affected by incorporation of filler. In the case of reinforcing filler, strong rubber- filler interaction will have some effect on the apparent crosslink density of the system. Ratio of the restriction of swelling of the filled rubber vulcanizate to that of the gum rubber is used as a means for evaluating the reinforcing ability of a filler in rubber. The high value of crosslink density confirms the presence of improved rubber-filler interaction in composites containing in situ precipitated silica.

Table 4.19. Crosslink density of composites

Composite	Crosslink density 10^{-5} mole/g
GUM	2.148
F-1	5.357
F-2	5.213
F-3	4.479

Air permeability

The air permeability values of the composites are given in the Table 4.20.

Table 4.20. Air permeability of composites

Composite	Air Permeability (ml/mm^2. day)
F-1	208.07
F-2	203.30
F-3	234.30

The air permeability values show a reduction of 11% for the composites filled with in situ silica and 13% for composites filled with VN3 when compared with that of the conventional silica. This reduction of air permeability is due to the improved distribution of silica in rubber matrix giving a more efficient filling than the filling of conventional silica.

TGA studies of the composites

The thermograms of the composites F1, F2 and F3 are given in the Figure 4.14. It can be seen that the stability of the composite is retained even with in situ precipitation. The initiation of degradation is found delayed for in situ precipitated silica composite. This indicates that NR is more stabilised by in situ precipitation. It is clear from Table 4.21 that the temperature of complete degradation has improved with in situ precipitation, while maximum degradation temperatures do not show any change. Similarly the rate of degradation also showed no change.

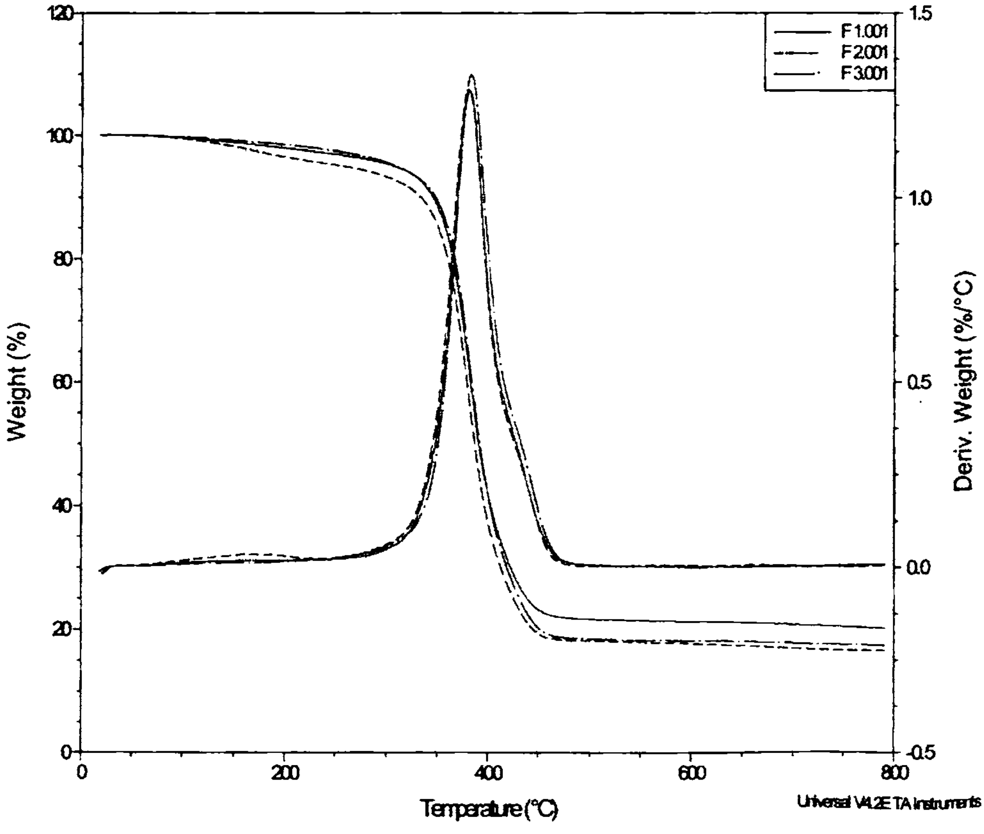


Figure 4.14. Thermograms of the composites

Table 4.21. Thermo gravimetric values of composites

Sample	Initiation temp. °C	Max.deg g.temp. °C	Rate at max. degg.%/°C	Completion temp. °C	50% degg. Temp. °C
F-1	283.5	381.26	1.28	492.3	391.0
F-2	247.1	380.46	1.29	483.2	386.6
F-3	248.9	383.34	1.33	489.3	381.1

PART-III

In Situ precipitated silica filled composites from field latex

In view of the fact that encouraging results were obtained in the application of in situ precipitation in concentrated NR latex to prepare composites, this method was tried in the Field latex also.

4.6 Experimental

Preparation of silica mixes

Table 4.22 gives the details of the different silica mixes prepared from Field latex. The formulation of the composites prepared from those mixes are given in the Table 4.23.

Table 4.22. In situ silica filled coagulum samples prepared from field latex

Sample name	Concentration of silica (phr)	Conc. of CMC added in the latex (phr)
M-5C	5	-
M-10C	10	-
M-20C	20	-
M-25C	25	-
M-20D	20	1
M-20E	20	2
M-20F	20	3

Table 4.23. Formulation of compounds with in situ precipitated silica in the field latex*

Name of composite	Masterbatch (phr)
INS-5C	M-5C (105)
INS-10C	M-10C (110)
INS-20C	M-20C (120)
INS-25C	M-25C (125)
INS-20D	M-20D (120)
INS-20E	M-20E (120)
INS-20F	M-20F (120)

*Mixes also contains the ingredients ZnO 5,Stearic acid 2, DEG 1,CBS 0.6, TMTD 0.2 and S 2.5

After complete mixing the stock was passed six times through tight nip and finally sheeted out at a fixed nip gap. The samples were kept overnight for maturation. Optimum cure time was determined using Rubber Process Analyzer (RPA 2000- Alpha Technologies). Blanks cut from unvulcanized sheets were vulcanized at a temperature of 150±2° C and at a pressure of 200kgcm^{-2} in an electrically heated hydraulic press, to their respective optimum cure times.

Testing

The silica content and bound rubber content of the in situ silica filled dry rubber samples were found. Properties like tensile properties, hardness, resilience, abrasion loss and compression set measurements were done as per the respective ASTM standards. Crosslink densities were calculated by studying the swelling of the composite in toluene. SEM photographs of the silica and tear fracture surfaces of the composites were taken to study the morphology of the silica.

4.7 Results and discussion

4.7.1 In situ precipitated silica from field latex

The silica content and bound rubber content of the silica mixes prepared from field latex are given in the Table 4.24. The loading of silica is more than 99% up to a silica concentration of 20phr. But the bound rubber content values were very low compared to the samples of similar silica concentration prepared from concentrated latex. The change of the bound rubber fraction reflects the change of the interface interaction.[37,38]

Tensile properties of the composites prepared with the above silica mixes, as per the formulation given in the table 4.23, were measured and the tensile strength values are given in the Table 4.25. The tensile strength values also showed a decrease when compared to that of composites prepared from concentrated latex.

One of the main differences between the field latex and concentrated latex is in the viscosity. The Brookefield viscosity of Field latex is only 31, while that of concentrated latex is 75. So the viscosity of the field latex is increased by adding a viscosity modifier, carboxy methyl cellulose (CMC). The change in viscosity with the addition of CMC is given in the Table 4.26. Viscosity of the latex increased with the increase in concentration of CMC. Addition of 2phr CMC changed the viscosity of field latex from 31 to 77. A graphical representation of the variation of the viscosity with the CMC content is given in the Figure 4.15. So in situ precipitation of 20phr silica was done in field latex, with varying amounts of CMC. The loading of silica and bound rubber content of the mixes were improved during the addition of CMC. The values are given in the Table 4.24. The change in bound rubber content with the addition of CMC is given in the Figure 4.16. Similarly composites prepared with CMC showed improved tensile properties (Table 4.25).

Table 4.24. Loss of silica and bound rubber content during the precipitation in field latex

Masterbatch	Composition of latex	Concentration of Silica phr	Loss of silica on loading %	Bound rubber content %
M-5C	Field	5	0.159	5.628
M-10C	Field	10	0.241	13.114
M-20C	Field	20	0.314	32.414
M-25C	Field	25	2.417	34.047
M-20D	Field +1phr CMC	20	0.328	64.105
M-20E	Field + 2hr CMC	20	0.264	82.161
M-20F	Field + 3hr CMC	20	0.281	81.453

Table 4.25. Tensile properties of the composites

Composite	Tensile strength MPa	Modulus (300%) MPa	Tear strength N/mm	EB %
INS-5C	20.22	1.68	40.04	1026
INS-10C	23.04	2.02	42.71	989
INS-20C	25.14	2.81	47.15	942
INS-25C	24.72	2.78	49.64	904
INS-20D	26.94	3.49	60.54	814
INS-20E	28.92	4.01	61.72	797
INS-20F	28.74	3.97	64.16	789

Table 4.26. Viscosity of latex and latex mixes

Latex	Brookefield viscosity (cP)
Concentrated latex (CL)	75
Field latex (FL)	31
Field latex with 1phr CMC (FL1CMC)	50
Field latex with 2hr CMC (FL2CMC)	77
Field latex with 3hr CMC (FL3CMC)	119

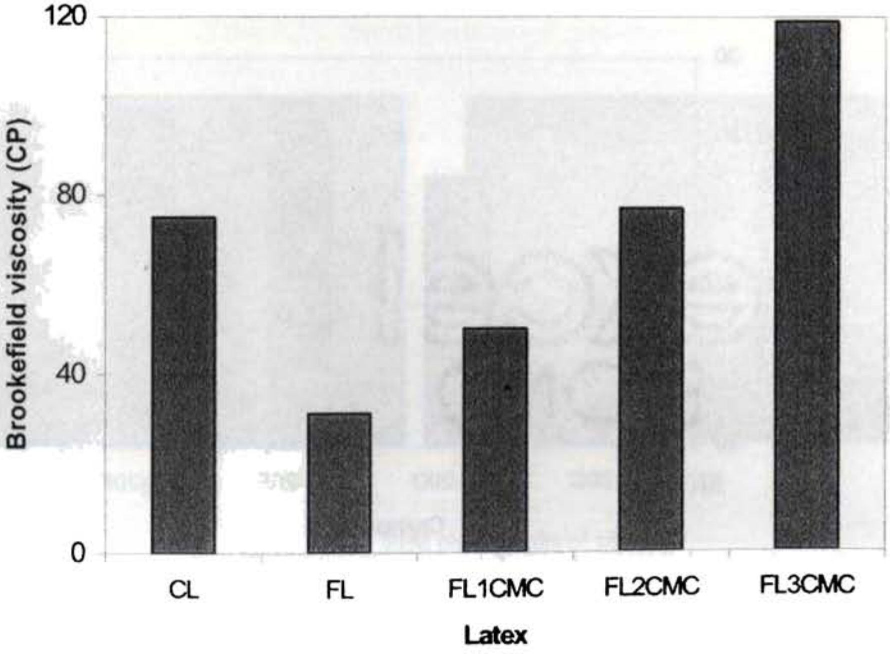


Figure 4.15 Brookefield viscosity of latex mixes

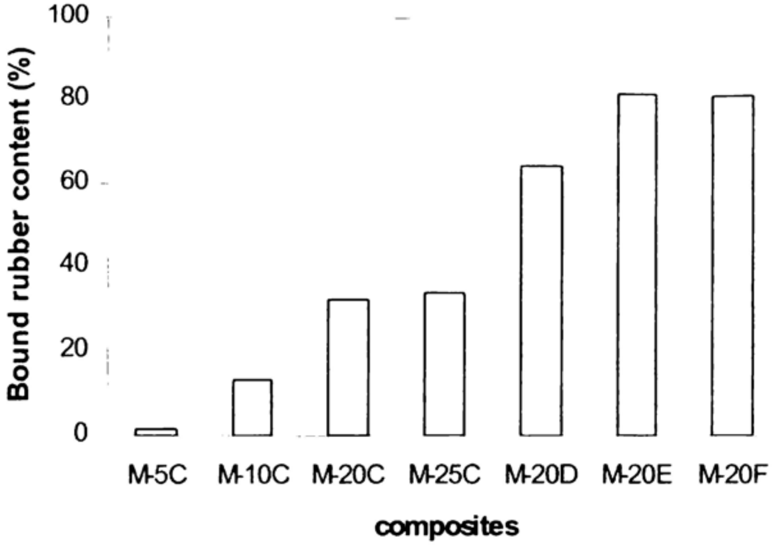


Figure 4.16. Bound rubber content of silica mixes from field latex

To highlight the effect of concentration of CMC present in the latex, the tensile strength values of the composites are given in the Figure 4.17

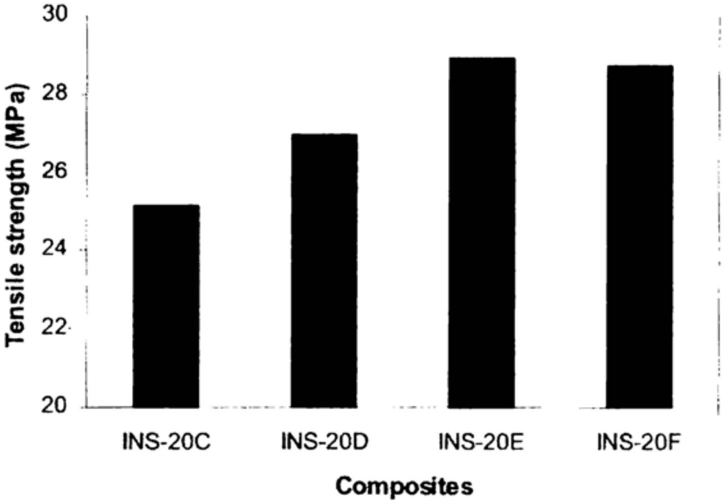
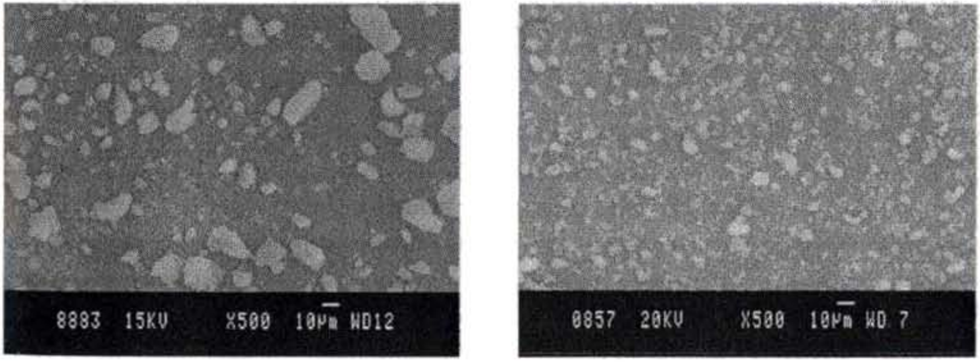


Figure 4.17. Tensile strength of composites

From the Figure 4.17 it is clear that tensile strength increased with the addition of CMC. The tensile value reached a maximum at 2phr CMC and then it show. a small decrease. Similarly the tensile modulus, elongation at break and tear strength increased with the concentration of CMC up to 2phr and then decreased [illegible] above 2phr. When the viscosity of the polymer matrix is too low the chance of agglomeration is present and hence a decrease in reinforcement. When the viscosity is too high that might have affected the uniform distribution of sodium silicate i.e. the migration of ions in the colloidal medium might have hindered by the polymer molecules. The results support the fact that the viscosity of the latex has an effect on the in situ precipitation of silica in rubber latex. A very low viscosity and a very high viscosity reduced the quality and the distribution of silica in the rubber matrix.

4.7.2 SEM Studies

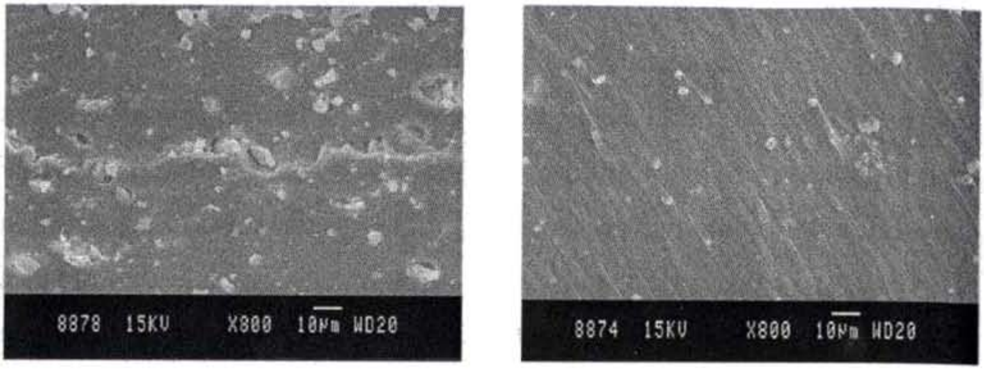
The SEM photographs of the ignited silica obtained from the M-20C and M-20E are given in the Figure 4.18. They show that with the increase in viscosity of the latex there is a reduction in the agglomeration of silica particles.



M-20C M-20E

Figure 4.18. SEM photographs of silica

The SEM photographs of the tear fracture surface of the composites prepared from M-20C and M-20E are given in the Figure 4.20. The tear lines are more visible in the composite INS-20E, indicating a better reinforcement. Similarly the loose silica particles are less in INS-20E. These micrographs give a firm support for the greater reinforcement of silica when it is precipitated in presence of CMC.



INS-20C **INS-20E**

Figure 4.19. SEM photographs of tear fracture surfaces

So in situ precipitation of silica can be applied to field latex by mixing it with 2phr CMC.

4.7.3 Physical properties of the composites

Other properties like hardness, abrasion resistance and swelling index in oils show improved values for composites prepared with CMC and are shown in Table 4.27 and 4.28. The values are comparable or better than that of composite prepared from concentrated latex (F-1)

Table 4.27. Other properties of composites with field latex

Composite	Hardness Shore A	Abrasion loss cc	Resilience %	Compression set %
GUM	32	0.1995	65	35.78
INS-20C	42	0.1315	60	40.34
F-1	48	0.1218	56	40.13
INS-20E	51	0.1208	58	40.81

Table 4.28 . Swelling index (%)of the composites in different oils

Composite	Diesel oil	Transformer oil
GUM	346	214
INS-20C	168	116
F-1	150	102
INS-20E	151	106

Crosslink density

The swelling studies of the composites prepared from field latex were done in the solvent toluene to calculate the crosslink density and the values were compared with the Crosslink density of the composite prepared from concentrated latex. Table 4.51 gives the crosslink density values of the composites. The crosslink density of composite prepared with 2phr CMC is higher than that of the composite prepared from concentrated latex.

Table 4.29. Crosslink densities of composites

Composite	Crosslink density x10^{-5} mole / l
GUM	2.148
INS-20C	3.790
F-1	5.357
INS-20E	5.854

4.8 Conclusions

The study shows that silica can be incorporated in NR latex by in situ precipitation procedure to prepare rubber composites. Mixing of in situ precipitated silica mix with carbon black showed that composites can be prepared with carbon black partly replaced by in situ precipitated silica.

The vulcanizates prepared by this novel technique show superior mechanical properties compared to those prepared from VN3 and conventional silica. The latex precipitated silica is found to have better rubber- filler interaction compared to commercial silica. Silica of any desired concentration can be incorporated in to the dry rubber by mill mixing of silica masterbatch with dry rubber or directly from the in situ precipitation of silica at the desired concentration in the latex. Swelling index values and crosslink density showed that the rubber filler interaction is more in the in situ precipitated silica compounds. Similarly properties like ageing resistance and permeability showed improved values. This method is simple and cost reducing.

In situ precipitation of silica can be done in field latex also by mixing with CMC to prepare composites of superior qualities.

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Chapter 5

EPOXIDISED NATURAL RUBBER AS A COUPLING AGENT FOR IN SITU PRECIPITATED SILICA FILLED NR COMPOSITES

5.1 Introduction

The mixing of silica with commonly used olefinic hydrocarbon rubbers like NR, SBR, BR, etc is a challenge as these materials are not very compatible in various aspects. Such shortcomings can be overcome by the use of coupling agents such as silanes, titanates and zirconates. Of these coupling agents silanes are widely used.[1] Several silanes with appropriate functionality, such as alkoxyl silyl groups, have been successfully used as coupling agents.[2] They provide a bond between the filler and the polymer by forming a chemical link. This facilitates filler incorporation and also enhances the properties of the final product by increasing the dispersive component.[3,4] The application of a coupling agent greatly improves the processing behaviour by reducing the specific surface energy and the solubility parameters of the silica. However, these improvements are accompanied by other problems like

- Ethanol formation
- Higher processing temperature and
- Higher cost of the product.

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So viable alternative methods or materials for overcoming the problems associated with the silica reinforcements of rubbers are therefore a current research priority. Surface modification of silica, so as to increase the silica-rubber bonding, is a method used for the better reinforcement.[5,6,7] Various modifications have been done to improve the reinforcing ability of the silica, which include heat treatment, polymer grafting on silica surface and chemical modification. Esterification of silica surface by methanol, ethanol and butanol is also reported.[8,9,10] In all these works silica surface is made hydrophobic and then incorporated in the rubber matrix. Varkey et al have reported the feasibility of using epoxidised natural rubber as a reinforcement modifier for silica filled rubbers.[11] Use of epoxidized rubber seed oil as a coupling agent and a plasticizer in silica-filled natural rubber compounds, was studied by Reethamma et al.[12] The study revealed that the epoxidised rubber seed oil caused the hydrophobation of silica, which increased its degree of dispersion and the formation of chemical bonds with the rubber, thereby, ensuring strong polymer-filler interactions.

Epoxidised Natural rubber is a modified form of natural rubber with inherent reinforcement with silica. Unlike NR, epoxidised natural rubber (ENR) can be reinforced with silica without silane coupling agent.[13] ENR (50 mol%) is found to have high interaction with the silanol groups of silica.[14] In ENR the epoxy groups are randomly distributed along the hydrocarbon chain backbones, giving increased polarity and it frequently facilitates reinforcement by silica without the need of a coupling agent. Nanoclay reinforcement of ENR is also reported.[15,16] It has been reported that by using ENR as a component together with silica, it is possible to achieve improvement in mechanical properties with respect to similar NR compounds.[17] Epoxidised natural rubber in small proportions is used as a reinforcement modifier for silica-filled nitrile rubber (NBR).[18] Two cure systems were used: *N*-cyclohexyl- 2-benzthiazyl sulfenamide (CBS) alone and in combination with diphenyl guanidine (DPG). Chemical interaction or chemical crosslink between epoxy group and silanol groups has been proposed to explain the unusual reinforcement.[19]

This chapter explains the effect of the use of ENR as a reinforcement modifier for in situ precipitated silica based natural rubber compounds and compares the same with that of silane modified silica based compounds. The vulcanizates prepared by this technique are compared with those prepared from conventional silica.

5.2 Experimental

Materials: Natural Rubber Latex of 60% dry rubber content (DRC) was supplied by Njavallil Latex, Kochi, India. Natural Rubber of grade ISNR-5 and ENR 50mol % latex of DRC 20% were obtained from the Rubber Research Institute of India, Kottayam, India. Sodium silicate and other chemicals used were of commercial grade.

Preparation of in situ silica masterbatches

Natural rubber latex was filtered and stabilized with non-ionic stabilizer vulcastab VL, mixed with required amount of ENR latex and stirred for 10 minutes. The required amount of sodium silicate was added and stirred for 1hour and a saturated solution of ammonium chloride was added drop wise with constant stirring to precipitate silica. The latex was coagulated as crumbs by the addition of 2% acetic acid. The crumbs were washed with water until the washings were neutral, pressed to remove water and dried in an air oven at 70°C for 48hrs. Two masterbatches with 20phr and 40phr silica were prepared with and without ENR. The details of the masterbatches are given in the table 5.1.

Table 5.1. Composition of silica master batches

Sample name	NR (phr)	ENR (phr)	In situ silica content (phr)
M-20-1	100	0	19.92
M-20-2	100	4	19.95
M-40-1	100	0	39.81
M-40-2	100	8	39.86

Characterisation of the coagulum

The fraction of bound rubber in the masterbatches was determined by the procedure suggested by Kazumasa Toshikai et al.[20] Mooney viscosity and moisture absorption of the silica masterbatches were also measured.

Preparation of the composite

The rubber with in situ precipitated silica was kept as the master batch and compounds were prepared by mill mixing. Different quantities were added to get the desired concentrations of silica in NR. Mixing was done in a laboratory size (16 x 33cm) two-roll mill at a friction ratio of 1:1.25 as per ASTM D 3182 (1982). The compounding formulation used in the present study is given in Table 5.2.

Table 5.2. Formulation for the preparation of silica – filled NR compounds (phr)

sample code	NR	Master batch	Commercial Silica	Si 69
GUM	100	0	0	0
INS-1	0	120(M-20-1)	0	0
COM-1	100	0	20	0
CA-1	100	0	20	3
ENR-1	0	124(M-20-2)	0	0
INS-2	0	140(M-40-1)	0	0
COM-2	100	0	40	0
CA-2	100	0	40	6
ENR-2	0	148(M-40-2)	0	0

Base formulation: ZnO 5, Stearic acid 2, DEG 1, Naphthenic oil 3/6 CBS 0.6, TMTD 0.2, Sulphur 2.5

Testing

The cure characteristics of the mixes were determined using Rubber Processing Analyser RPA 2000 supplied by Alpha Technologies, USA, as per ASTM standard, D 2084-01. Subsequently, the rubber compounds were vulcanized up to the optimum cure time at 150°C in an electrically heated hydraulic press. The mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 hr, prior to physical testing.

Physical properties, such as modulus, tensile strength, elongation at break, tear strength, hardness, heat build-up, compression set, flex resistance and ageing resistance, were studied as per the respective ASTM Standards. Swelling studies and Scanning Electron Microscopic studies were used to study the internal cross links and distribution of silica respectively. Strain sweep studies on uncured and cured samples were done to study the rubber filler interactions. The strain sweep measurements on unvulcanized samples and vulcanizates were conducted to study the rubber-filler interaction. The study was done in Rubber Process Analyzer (RPA 2000-Alpha Technologies).[21] The testing temperature was selected as 100°C; a temperature below the curing temperature and the shear strain was varied from 0.5% to 100% keeping the frequency of measurements at 0.5Hz.

For strain sweep measurements of cured compounds, uncured material was used as the test sample, which is cured to its optimum cure time in the RPA cavity and then the strain sweep tests were carried out in a two-stage programme. The equilibrium swelling studies of the compounds were carried out in toluene and crosslink densities were calculated.

5.3 Results and discussion

5.3.1 Distribution of silica

The SEM photographs of the silica precipitated in the presence of ENR latex is given in the Figure 5.1. The Figure 5.2 gives the SEM photograph of the silica precipitated from NR latex alone.

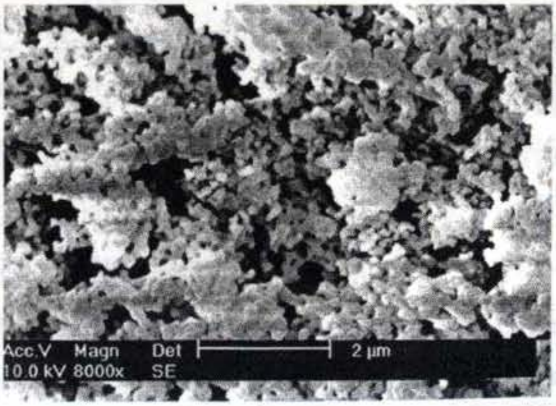


Figure 5.1. SEM photograph of the precipitated silica from NR-ENR latex mix

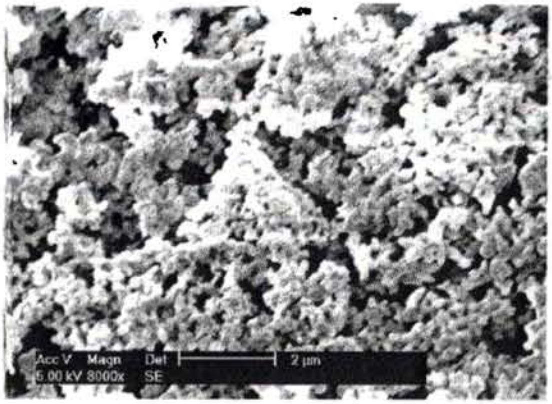
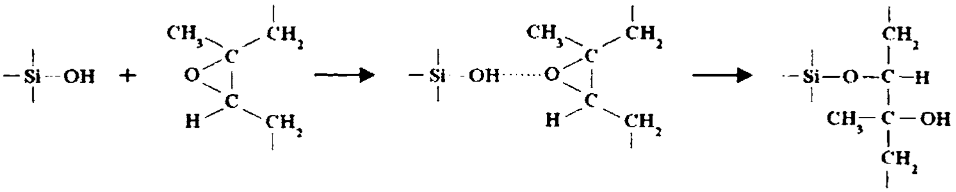


Figure 5.2. SEM photograph of the precipitated silica from NR latex

From the Figures 5.1 and 5.2 it is clear that the particles of in situ precipitated silica from NR-ENR latex mix are more uniformly distributed compared to that of silica prepared from NR latex alone. Silica from NR latex alone has more clusters than that prepared from NR-ENR silica mix. This may be due to the presence of ENR, which has an inherent capacity to link[14] with the silica particles, preventing them from clustering. In the in situ precipitation method, silica is prepared from sodium silicate in the latex medium after the uniform distribution of sodium silicate in the latex, giving a fine distribution of silica in rubber latex. The polymer matrix prevents the agglomeration of silica and provides a better distribution for the silica particles. When the precipitation is conducted in the NR-ENR latex mix, the silica particles are well exposed to the ENR molecules since the latter in the rubber matrix is in the colloidal form. This will facilitate the interaction of silica with ENR.

Coupling effect of ENR

The coupling effect of ENR can be explained on the basis of the chemical interaction between the epoxy groups and silanol groups[19], i.e. the polar part of ENR would have coupled with hydroxyl group in the silica through dipole-dipole interaction. Under acidic conditions, the epoxy groups are likely to open as a di-ol moiety which can form inter molecular hydrogen bond with the silanol groups of silica.[22] The remaining hydrocarbon part is in contact with the rubber matrix, thus acting as a coupling agent. The scheme of interaction is reported as given below.[22]



5.3.2 Characterisation of the coagulum

Bound rubber content

The bound rubber content of the silica mixes is shown in the Table 5.3. The high values (80 to 88%) of bound rubber content shown by the mixes are due to the increased filler polymer interaction. The bound rubber content depends on characteristics of filler such as surface area, structure or morphology and surface activity. It is reported that the physical structure and surface chemistry of filler and the property of the rubber affect formation of bound rubber.[23]

Table 5. 3. Bound rubber content of silica master batches

Sample name	Bound rubber content (%)
M-20-1	80.13
M-20-2	84.92
M-40-1	85.22
M-40-2	87.95

It is clear from the table that for the same concentration of silica, the bound rubber content tends to increase in the presence of ENR. This may be due to a preferential adsorption of ENR over the silica surface through the epoxy-silanol interaction and/or by hydrogen bonding. The polar surface groups on silica interact with ENR resulting in an increased rubber filler interaction. Thus ENR modified silica would have well dispersed in the rubber matrix, giving the possibility of better rubber filler binding. This again confirms that ENR has some coupling effect between silica and rubber.

Mooney viscosity and moisture absorption

The Mooney viscosity and % of moisture absorption of the different masterbatches measured after 30days are given in the Table 5.4.

Table 5.4 The Mooney viscosity and moisture absorption of masterbatches

Masterbatch	Mooney viscosity ML(1+4)100°C	Moisture absorption % in 30 days
NR-Gum	72	0.112
M-20-1	120	0.226
M-20-2	62	0.261
M-40-1	135	0.758
M-40-2	74	0.736

Silica absorbs moisture and silica filled rubbers show increased initial processing viscosity.[24] So Mooney viscosity and moisture absorption are significant for silica master batches. Mooney viscosity of 20phr in situ precipitated silica filled rubber is 120 and it is observed in the earlier studies that it can be reduced to 75 by adding 6phr Naphthenic oil during precipitation. Present study shows that Mooney viscosity falls in the presence of ENR also. From the Table 5.4, it can be seen that the Mooney viscosity is reduced to 62, when the precipitation was conducted in the presence of 4phr ENR. It follows that ENR acts as a plastisizer also. This behaviour is also observed for 40phr silica samples. The value is reduced from 135 to 74, when the precipitation was conducted with 8phr ENR. This behaviour reveals that the presence of ENR increases the filler polymer interactions.

The moisture absorption values of all samples are less than 1% and the %moisture absorption is not affected considerably. So these masterbatches were used for preparing composites

Crosslink densities

Table 5.5 shows the crosslink densities of the different composites. The additional cross-links can be confirmed by equilibrium swelling studies. The crosslink density of ENR -1 and ENR -2 are comparatively high, clearly indicating the presence of increased cross-links.

Table 5.5 Crosslink densities of the composites

Sample	COM 1	CA 1	INS 1	ENR 1	COM 2	CA 2	INS 2	ENR 2
Crosslink density x 10^{-5}	4.74	5.53	6.65	6.85	7.43	8.21	9.22	9.54

5.3.3 Comparison of the properties of the composites

Tensile properties

The tensile properties of the composites are shown in the Figures 5.3 to 5.6.

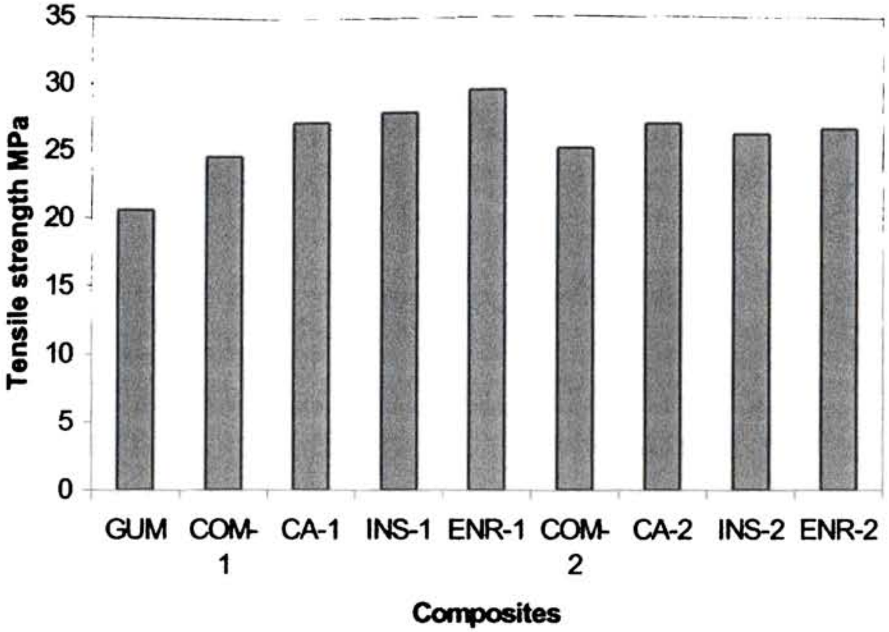


Figure 5.3. Tensile strength of composites

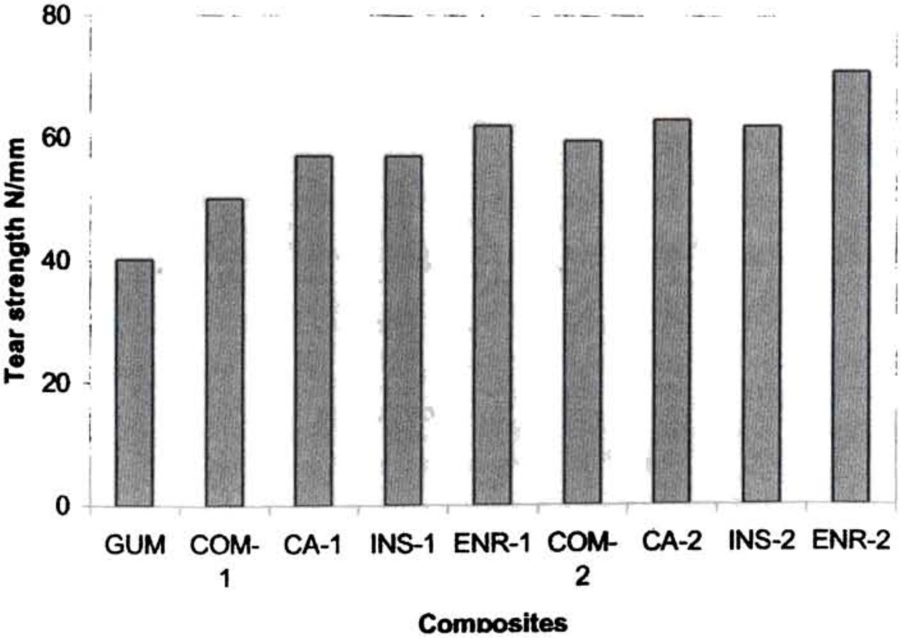


Figure 5.4. Tear strength of composites

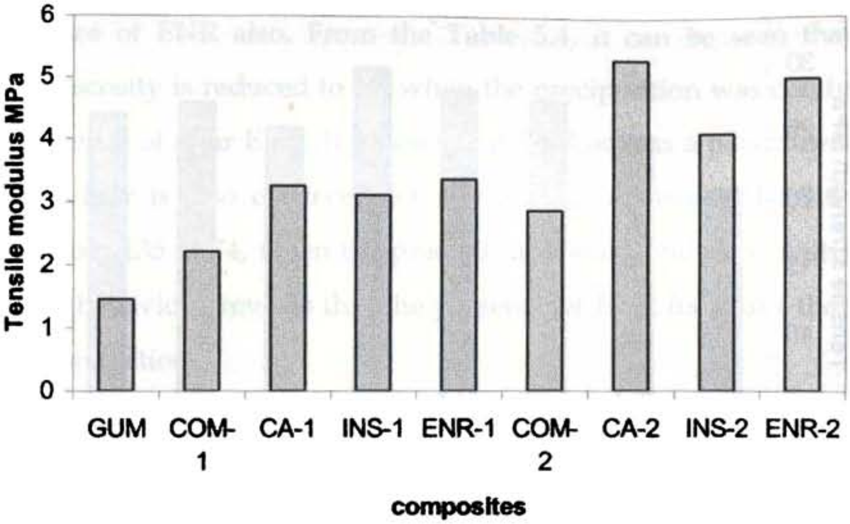


Figure 5.5. Tensile modulus of composites

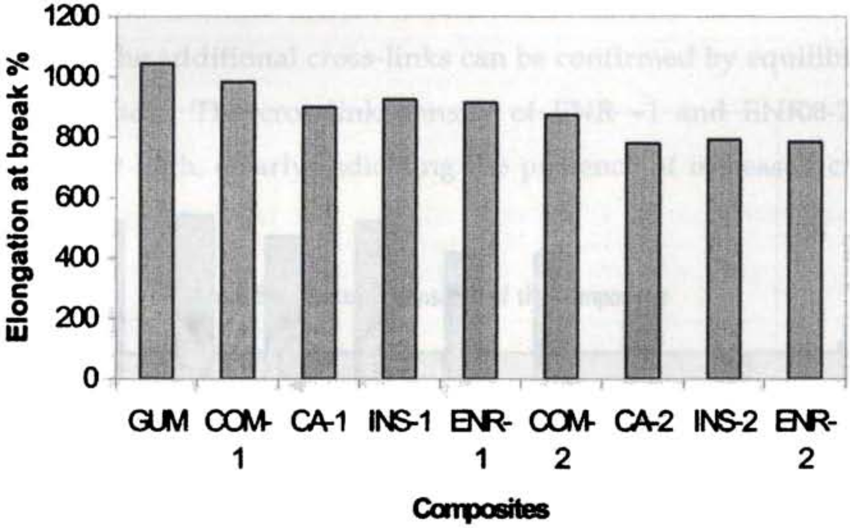


Figure 5.6. Elongation at break of composites

Figure 5.3 shows the tensile strength of different vulcanizates. It is interesting to note that composite containing in situ precipitated silica and composite with silane coupling agent show almost similar values of tensile strength. It follows that application of silane coupling agent can be replaced by latex stage precipitation of silica. Addition of ENR to the latex stage precipitation of silica shows further improvement in the tensile strength. Strength variations with ENR might have resulted from the changes in the crosslink density. Tensile strength decreases, when the filler concentration is 40phr. This effect is well known[25] and can be attributed to poor wetting of the reinforcement particles at filler contents above the optimum composition. Similarly tear strength values showed the same trend for 20phr (Fig.5.4). But the tear strength increased with increase in concentration of filler and the presence of ENR has improved the tear strength values. This again confirms the coupling effect of ENR. Figure 5.5 shows the tensile modulus of different composites. The presence of a coupling agent increases the tensile modulus. With 20phr silica, the tensile modulus was in the order COM < INS < CA < ENR. But for 40phr silica, the order of tensile modulus is COM < INS < ENR < CA. It means that at higher concentrations of silica in situ precipitation is inferior to the application of silane coupling agent. Figure 5.6 shows the elongation at break of the composites. As the reinforcing capacity increases, generally the EB % decreases. But the in situ precipitated silica containing samples showed a little higher values of elongation at break (Fig.5.6). The increase in the elongation at break is due to the inclusion of filler particles in the intermolecular space in the rubber matrix.

Reinforcing index

Reinforcing Index (RI) values of the composites are given in the Figure 5.7.

Reinforcing index was calculated using the equation RI = (N/N_o) (100/silica content) where N and N_o are the nominal values of the mechanical property (tensile strength) measurements for the sample filled with and without silica respectively.[26]

The values indicate that for the same concentration of silica, composite with ENR showed maximum reinforcing index. The values are decreasing at higher concentrations of silica content, as a consequence of dilution effect.

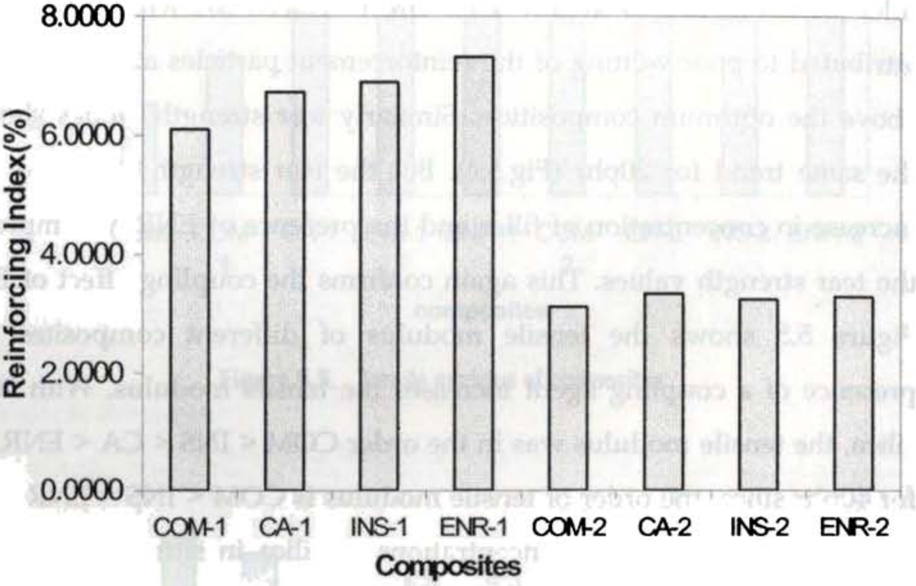


Figure 5.7. Reinforcing Index values of the composites

Other technological properties of the composites

Other technological properties like abrasion loss, hardness and resilience are given in the Table5.6. Hardness of the samples depends on composition of the filler. They do not vary much with the type of filler. But abrasion loss values vary considerably with the type of filler incorporation. At both concentrations 20phr and 40phr, in situ silica with ENR showed remarkably reduced abrasion loss. This is due to the strong adhesion of silica particles on rubber chains. Resilience, a measure of the elastic component, decreases with in situ precipitation and in the presence of ENR it shows no further change.

Table 5.6. Other technological properties of the composites

Sample	Resilience(%)	Hardness (Shore A)	Abrasion loss (cc)
COM-1	65	45	0.1320
CA-1	60	49	0.1251
INS-1	58	48	0.1254
ENR-1	58	48	0.1224
COM-2	60	58	0.1170
CA-2	54	60	0.1159
INS-2	55	59	0.1156
ENR-2	53	59	0.1152

5.3.4 SEM studies

The Scanning electron microscopic photographs of the tear fracture surfaces of vulcanizates with ENR and Si 69 are shown in figures 5.8 and 5.9 respectively.

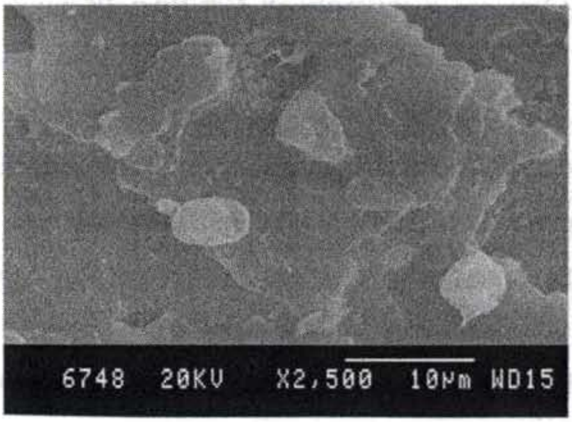


Figure 5.8. SEM photographs of composites with ENR

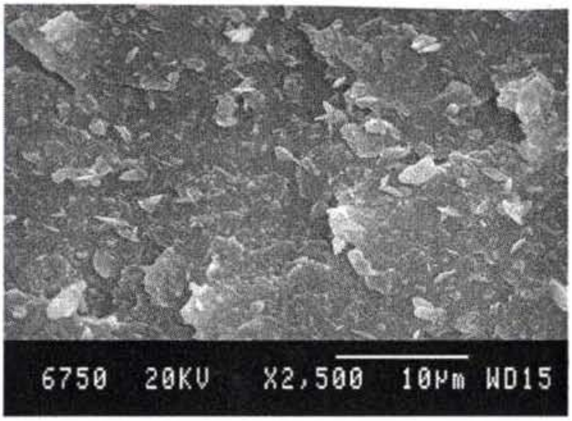


Figure 5.9. SEM photographs of composites with Si 69

The tear lines are more visible in the sample with ENR (Figure 5.8) indicating a uniform distribution and improved binding of silica in rubber. This morphological evidence gives more firm support to the coupling effect of ENR.

5.3.5 Strain sweep studies

The variation of complex modulus (G^*) with strain for all the composites before curing are plotted and shown in the figures 5.10 and 5.11. The Figures 5.12 and 5.13 show the variation of complex modulus (G^*) with strain for cured compounds. The complex modulus values at low strains (<15%) are a measure of the filler polymer interactioin.[27,28] These graphs make it clear that the compounds with ENR have comparatively high complex modulus values at low strains for both cured and uncured compounds, compared to the compounds with Si 69. It follows that presence of ENR improves filler polymer interaction. All samples in each set have the same composition of filler and rubber. So the high values of G^* are only due to filler cross-links, either filler-filler or filler polymer. Findings on mechanical properties of the composites explained earlier shows that the cross-links are of filler-polymer.

The presence of additional cross-links has been confirmed by equilibrium swelling studies (Table5.5). So the high G* values of composites with ENR may be considered as an indication of improved rubber filler interaction.

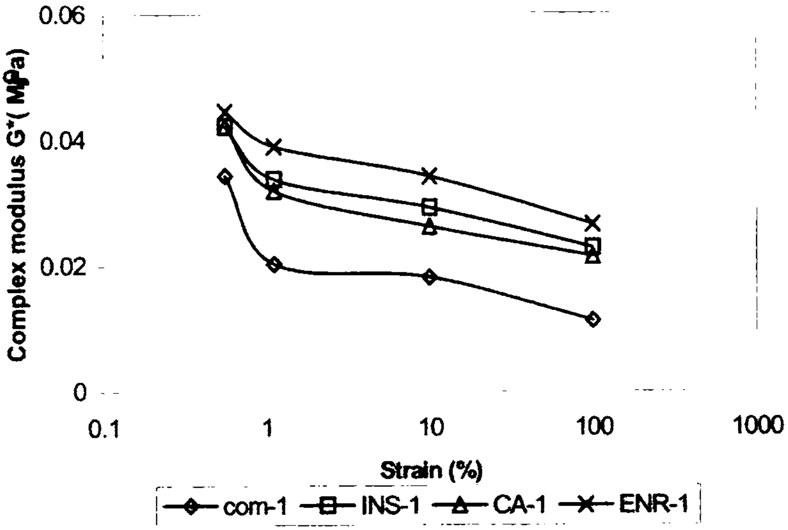


Figure 5.10. Variation of complex modulus with strain for uncured compounds (20phr)

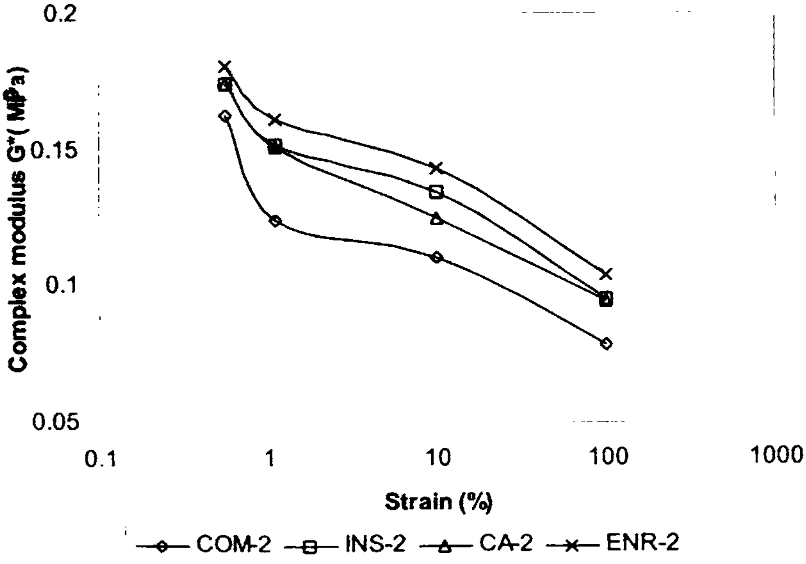


Figure 5.11 Variation of complex modulus with strain for uncured compounds (40phr)

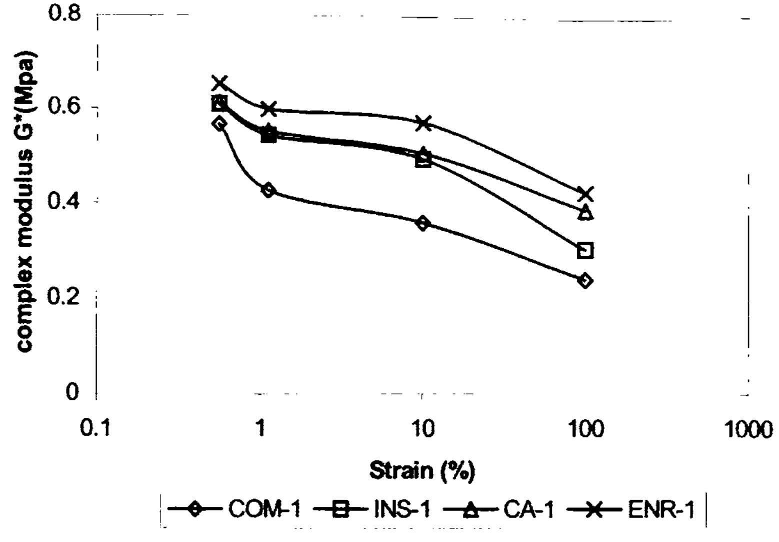


Figure 5.12. Variation of complex modulus with strain for cured compounds (20phr)

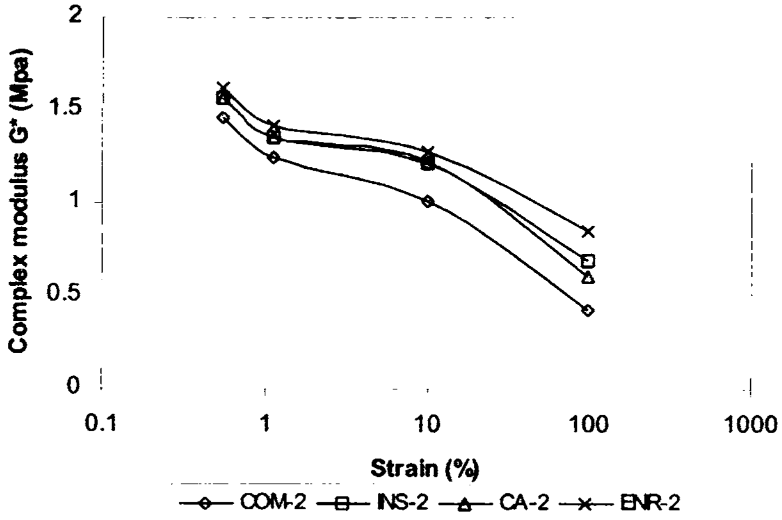


Figure 5.13. Variation of complex modulus with strain for cured compounds (40phr)

5.3.6 Flow properties

The complex viscosity of the composites is measured as a function of shear frequency using the frequency sweep studies. The variation of complex viscosity of the composites with shear frequency is given in the

Figure 5.14. A sharp decrease in viscosity is observed at low frequencies and the behaviour was similar for all composites. All samples exhibited pseudoplastic behaviour, that is the viscosity decreased with shear rate.

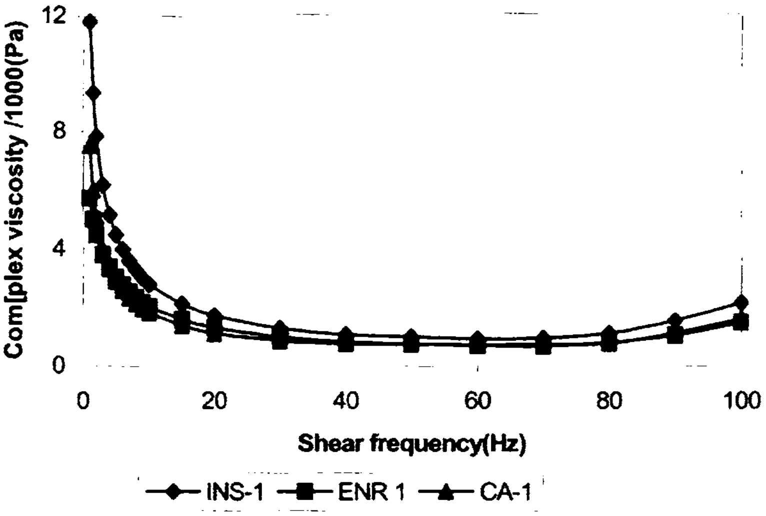


Figure 5.14. Variation of viscosity with shear frequency

The addition of silica to the elastomer results in a strong increase of the viscosity. Silanol groups, responsible for the strong interparticle forces, cover the silica surface. So silica particles tend to agglomerate and they are difficult to disperse and re-agglomerate after mixing.[21] Silica filled rubbers generally exhibit high viscosity and therefore their processability is poor as compared to the black filled rubbers.[1] Time and temperature of storage enhances the viscosity of the silica filled composites, which is attributed to the filler networks or bound rubber.[29] Processing of most of the rubbers is in the non - Newtonian flow regime.[30] Processability of composites can be characterized by rheological means. The rheological properties of polymers in the presence of filler depend largely on polymer filler interaction. [31,32]

The Figure reveals that the viscocity of INS-I is comparatively high at all frequencies. But the viscocities of both ENR-1 and CA-1 are similar at all frequencies. It means that presence of ENR has reduced the processing viscocity of in situ silica. This result again confirms the coupling action of ENR.

5.3.7 TGA studies

The thermograms of the composites are given in the Figure 5.15 and TGA values are given in the Table 5.7. Thermo gravimetric analysis of the samples was done to study the change in thermal stability of the composites with different silica. It can be seen that the stability of the composite is retained even with in situ precipitation in the latex mix. The initiation of degradation is higher for in situ precipitated silica composite with ENR. Maximum degradation temperature was also found improved with in situ precipitation while temperature of complete degradation does not show any change and the rate at maximum degradation showed a decrease.

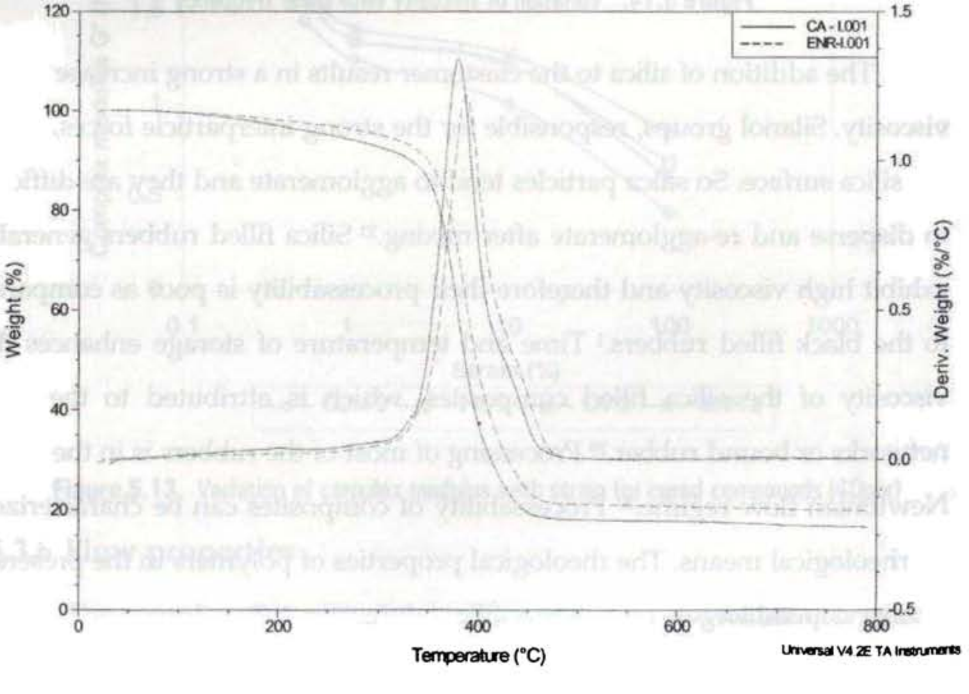


Figure 5.15. Thermograms of the composites

Table 5.7. Thermogravimetric values of composites

Sample	Initiation temp. °C	Max.degg.temp. °C	Rate at max. degg.%/°C	Completion temp. °C	50% degg. Temp. °C
CA_1	240.07	379.74	1.339	488.29	387.16
ENR-1	244.13	387.56	1.218	488.29	398.23

5.4 Conclusions

In this chapter evaluation of ENR as a reinforcement modifier in latex stage precipitated silica filled NR was made in comparison with silane modified silica filled NR.

Presence of ENR increased the distribution of silica in the rubber matrix. Preparation of masterbatches with in situ silica coupled with ENR showed a significant reduction in the Mooney viscosity. This makes the processing of the silica mix easier. It is observed that in situ precipitation of silica gives reinforcement equivalent to that of using Si 69. In situ precipitation in presence of ENR showed further improvement in the mechanical properties, indicating that ENR has a coupling effect in silica filled rubber composites. Composites prepared with ENR showed higher rubber filler interactions. ENR is found to act as a coupling agent for in situ silica and give improved technological properties, when compared with Si 69.

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Chapter 6

IN SITU PRECIPITATION OF SILICA IN NITRILE RUBBER

6.1 Introduction

Synthetic rubbers are more uniform in quality and compounds are more consistent in both processing and product properties[1]. Natural rubber crystallises on stretching giving a high tensile strength to the gum vulcanizates. On the other hand gum vulcanizates of synthetic rubbers like SBR, NBR etc are generally weak and it is essential to use reinforcing fillers to produce products of high strength. There are polar and non-polar synthetic rubbers. Acrylo nitrile Butadiene rubber, known as nitrile rubber (NBR), is a polar rubber and is generally considered as a special purpose rubber being used for applications requiring oil and solvent resistance. Presence of acrylo nitrile (ACN) makes it polar and provides special features to the polymer.[2] The properties of NBR vulcanizates also mainly depend on the ACN content. As the ACN content increases the oil resistance, the cure rate and heat resistance increase while resistance to permanent set decreases. High viscosity and low die swell are also observed.

NBR shows no self-reinforcing effect, as it cannot undergo crystallisation on stretching. So gum vulcanizates have very low tensile strength.[3] When used in combination with reinforcing fillers, vulcanizates with excellent properties are obtained.[4] Carbon black and silica are the common fillers used for reinforcement of NBR. Being a polar rubber the distribution of silica is much easier and the reinforcement with silica is better than that of non-polar rubbers like

NR or SBR.[5] Butadiene copolymerised with vinyl pyridine show improved reinforcement by silica, due to the interaction between silanol and pyridine groups.[6] However, for achieving optimum reinforcement, silane-coupling agents are being used.[7] Attempts have also been made to improve the silica reinforcement of NBR by functionalising it with pendant epoxy groups.[8] A study on the effects of interactions between nitrile rubber and silica on the development of agglomerates by silica particles and of bound rubber in silica filled NBR composites was done by Nozomu Suzuki et al.[9]

In the conventional mixing of silica with rubber, due to the fluffy nature of silica there is the chance of fly loss and hence environmental pollution and health problems. These problems can be overcome by the method of in situ precipitation of silica in latex. The reinforcement of synthetic rubbers by silica is reported by conducting sol gel reaction in the latex using Tetra ethoxy silane TEOS.[10] The particle size and reinforcing behaviour of silica were greatly influenced by the amount of TEOS and [(H2O)/(TEOS)] ratio.

It has been observed that in situ precipitation of silica in natural rubber latex improved the mechanical properties and rubber filler interactions.[11] The present study examines the possibility of in situ precipitation of silica in NBR latex and compares the mechanical properties of the composites filled with in situ precipitated silica and conventional silica. In situ precipitation of silica was carried out in NBR latex using sodium silicate and ammonium chloride. The silica filled latex is coagulated, dried and kept as masterbatch. Compounds with silica composition varying from 1phr to 15 phr were prepared and vulcanised up to the optimum cure time. The mechanical properties of the vulcanizates are compared with reference compounds prepared from NBR and conventional silica.

6.2 Experimental

Materials: NBR latex - NLX 523 of dry rubber content (DRC) 50% and Nitrile Rubber NBR 553 M of medium Acrylo nitrile content (33% by weight) supplied by Apar Industries Ltd, Gujarat were used in the study. Sodium silicate and other chemicals used were of commercial grade.

Preparation of in situ silica masterbatches

NBR latex was filtered and stabilized with non-ionic stabilizer vulcastab VL. Required amount of sodium silicate was added and stirred for one hour and a saturated solution of ammonium chloride was added drop wise with constant stirring to precipitate silica. The latex was coagulated as crumbs by the addition of 2% hydrochloric acid. The crumbs were washed with water until the washings were neutral, pressed to remove water and dried in an air oven at 70°C for 48hrs. Silica mixes of different concentrations were prepared by adding calculated quantities of sodium silicate and ammonium chloride. The names of the mixes with their silica content are given in the Table 6.1

Table 6.1. Silica mixes of different composition

Name of silica mix	Concentration of silica (phr)
M-1	1
M-5	5
M-10	10
M-15	15
M-20	20
M-30	30

Characterisation of silica masterbatches

Silica incorporation during in situ precipitation

The silica content of the dried coagulum samples was obtained by igniting a known weight of a sample in a previously weighed silica crucible in a muffle furnace. The temperature of the furnace was kept at 550°C for five hours. The rubber content in the sample was burnt off leaving silica in the crucible, which is cooled in a dessicator and weighed. From the weight of the silica the loading of silica is calculated.

Bound rubber content

The fraction of the bound rubber that occurred in the silica mixes (master batches) was determined by keeping the samples in Methyl Ethyl Ketone (MEK) for 72 hours following the procedure given by Kazumasa et al.[10] The bound rubber content R_B was calculated using the equation[12]

$$R_B = W_{fg} - W\,[m_f / (m_f + m_p)] \;/\; W\,[m_p / (m_f + m_p)] * 100$$

where W_{fg} = weight of filler and gel, W = weight of specimen, m_f = weight of filler in the compound and m_p = weight of polymer.

Preparation of the composites

The base formulation for the preparation of NBR composites is given in the Table 6.2. Composites were prepared with dry coagulum samples of silica concentration ranging from 1phr to 30phr as per the formulation given in the Table 6.3.

Table 6.2. Base formulation for NBR compounds

Ingredient	Concentration (phr)
NBR	100
Sulphur	1.5
ZnO	4.5
Stearic acid	1.75
DEG	1
HS	1
CBS	1.0
TMTD	0.5

Composites of lower concentrations were also prepared from in situ precipitated silica filled rubber sample M-15, keeping it as a masterbatch and mixing it with dry NBR on a two roll mill. The compounding formulation is given in Table 6.4. Different quantities of M-15 were added to get the desired concentrations of silica in NBR. Composites of similar concentrations were prepared with conventional silica for comparison of properties. Mixing was done on a laboratory size (16 x 33cm) two-roll mill at a friction ratio of 1:1.25 as per ASTM D 3182 (1982). After complete mixing the stock was passed six times through tight nip and finally sheeted out at a fixed nip gap. The samples were kept overnight for maturation. Optimum cure time was determined using Rubber Process Analyser (RPA 2000- Alpha Technologies) and vulcanised at a temperature of 150 ± 2°C and at a pressure of 200kgcm^{-2} in an electrically heated hydraulic press, up to their respective optimum cure times.

Table 6.3 Formulation for the preparation of silica – filled NBR compounds from silica mixes of different concentrations*

Name of compound	Weight of silica mix (g)	Silica Content (phr)
INS-1A’	M-1 (101)	1
INS-2A’	M-2 (102)	2
INS-3A’	M-3 (103)	3
INS-5A’	M-5 (105)	5
INS-10A’	M-10 (110)	10
INS-15A’	M-15 (115)	15
INS-20A’	M-20 (120)	20
INS-30A’	M-30 (130)	30

*Base formulation: Sulphur 1.5, ZnO 4.5, Stearic acid 1.75, DEG 1, HS 1, CBS 1.0, TMTD 0.5.

Table 6.4. Formulation for the preparation of silica – filled NBR compounds from silica masterbatch (15phr)*

Name of the compound	NBR (phr)	Masterbatch (phr)	Commercial silica (phr)
INS-1	93.5	7.5	0
COM-1	100	0	1
INS-2	87	15	0
COM-2	100	0	2
INS-3	80.5	22.5	0
COM-3	100	0	3
INS-5	67.5	37.5	0
COM-5	100	0	5
INS-10	35	75	0
COM-10	100	0	10
INS-15	0	115	0
COM-15	100	0	15

*Base formulation: Sulphur 1.5, ZnO 4.5, Stearic acid 1.75, DEG 1, HS 1, CBS 1.0, TMTD 0.5.

Composites containing carbon black were prepared to study the mixing behavior of in situ precipitated silica with carbon black. The formulation of the compounds are given in Table 6.5

Table 6. 5. Compounding formulation for composites with carbon black. *

Ingredient	C-1	C-2	C-3	C-4
M-15	115	Nil	115	Nil
NBR	Nil	100	Nil	100
Silica	Nil	15	Nil	15
HAF	15	15	20	20

*Base formulation: Sulphur 1.5, ZnO 4.5, Stearic acid 1.75, DEG 1, DOP 5, CBS 1.0, TMTD 0.5.

Testing of the composites

The cure characteristics of the mixes were determined using Rubber Processing Analyser RPA 2000 supplied by Alpha Technologies, USA, as per ASTM standard, D 2084-01. Subsequently, the rubber compounds were vulcanized up to the optimum cure time at 150°C. The mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 h. prior to physical testing.

Physical properties such as modulus, tensile strength, elongation at break, tear strength, hardness, heat build-up, compression set, flex resistance and ageing resistance were studied as per the relevant ASTM Standards. Swelling studies and Scanning Electron Microscopic studies were used to study the crosslink density and distribution of silica respectively.

Rubber filler interaction studies

The strain sweep measurements on unvulcanized samples and vulcanizates were conducted to study the rubber-filler interactions using

Rubber Process Analyzer (RPA 2000 - Alpha Technologies) by capturing strain and torque signals, with appropriate software. For unvulcanized samples the testing temperature was selected as 100°C; a temperature below the curing temperature and the shear strain was varied from 0.5% to 100% keeping the frequency of measurements at 0.5Hz. For strain sweep measurements of cured compounds, uncured material is used as the test sample that is cured to its optimum cure time in the RPA cavity and then the strain sweep tests were carried out at 50°C in a two-stage programme.

Swelling studies

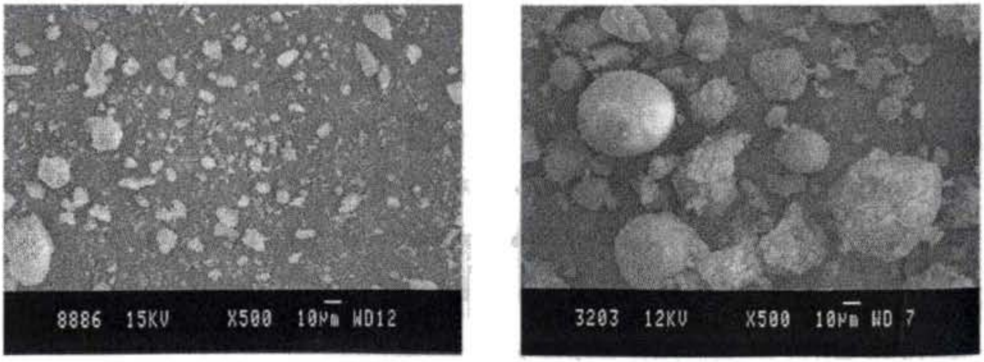
Swelling in oils: The swelling resistance of the samples in different oils was studied by keeping the sample of known size in oil for 24 hours. The swelling index (%) i.e. the weight of solvent absorbed per one gram of the rubber was calculated for the composites.

Determination of crosslink density

Swelling of the vulcanised samples were done in MEK and crosslink densities were calculated using Flory-Rehner equation.[13]

6.3 Results and discussion

6.3.1 Characterization of in situ precipitated silica



In situ precipitated silica

VN3

Figure 6. 1. Scanning Electron Microscopic photographs of silica

Figure 6.1 shows the SEM photographs of silica obtained after igniting the dry coagulum in a furnace to a temperature 550°C for three hours and that of VN3. The SEM photographs show that the silica particles obtained from the latex are having a structure more viable to interactions with the polymer. SEM pictures also show that there is better-reduced particle size for in situ precipitated silica than the commercially available nano silica VN3. The small particle size provides a large surface area, which results in improved mechanical properties. The precipitation of silica was conducted after the uniform distribution of sodium silicate in the polar matrix of NBR latex, giving a fine distribution of silica in rubber latex. The polymer matrix prevents the agglomeration of silica and provides a reduced size for the silica particles.

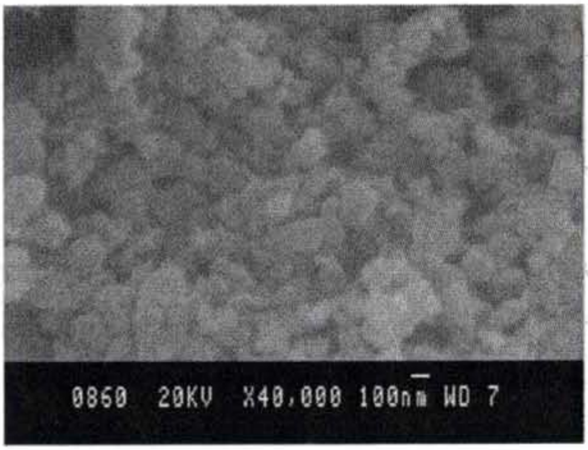


Figure 6. 2. Scanning Electron Microscopic photograph of in situ precipitated silica at a higher magnification

Figure 6.2 shows the SEM photograph of in situ silica at a higher magnification. An important thing is that, the silica particles are not fused as in the case of the silica precipitated from NR latex (Figure 3.7). Silica obtained from the NBR latex exists as individual particles. This may be due to the polar nature of the matrix NBR, which facilitates the easy distribution of sodium silicate in the colloidal matrix. So silica formed will have a reduced chance for agglomeration.

6.3.2 Characterisation of silica mix

IR spectroscopic analysis: FTIR spectra of NBR (Gum) and NBR containing 15phr silica (M-15) are given in the Figure 6.3. The analysis of the spectra shows that all the spectral bands of NBR are present in M-15 indicating that NBR is not chemically affected by the reaction leading to the precipitation of silica. But there is a reduction in the intensity of the peeks. This may be due to the reduction in the stretching freedom of the bonds due to the silica environment.

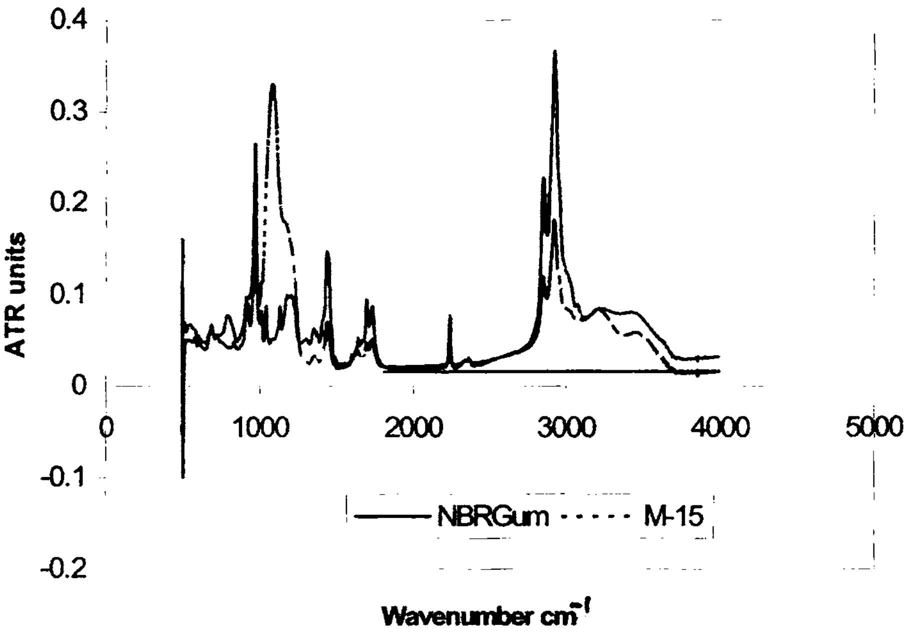
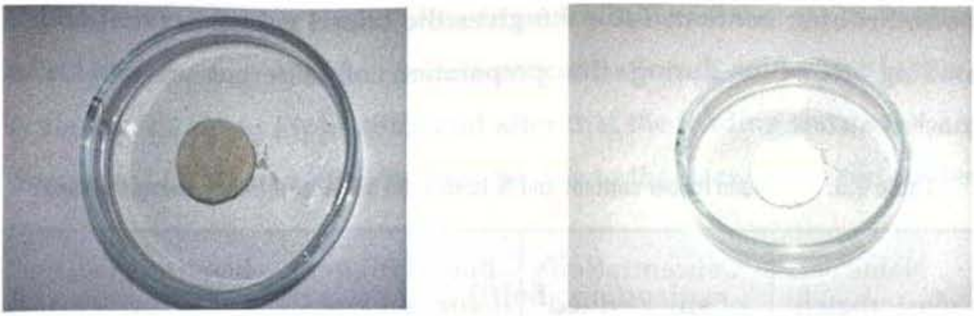


Figure 6.3. IR spectrum of NBR and in situ silica filled NBR

Ignition of the dry coagulum: Figure 6.4 shows the photographs of the sample containing in situ precipitated silica before and after ignition. It is interesting to note that the sample retained its original shape as that of the silica mix even after ignition.



Before ignition

After ignition

Figure 6.4. Photographs of sample containing in situ silica before and after ignition.

It is confirmed from the photographs that an improved uniform distribution of silica in the rubber matrix is present in the in situ silica sample. In the case of conventional silica, which is crumbled upon ashing there is no uniform distribution.

Effect of solvent on dry coagulum: Figure 6.5 shows the photograph of the sample containing in situ precipitated silica kept in Methyl Ethyl Ketone (MEK) for 24 hours. It can be seen that the sample became a swollen mass when it is immersed in MEK. It remained as a swollen mass and showed no tendency to dissolve completely. But the sample containing conventional silica dissolved completely in MEK. This shows that good filler-polymer interaction is present in the sample containing in situ precipitated silica.

Figure 6.5. Result of solvent action on coagulum containing in situ precipitated silica.

Bound rubber content: Table 6.6 gives the bound rubber content and % loading of silica during the preparation of different in situ silica masterbatches.

Table 6.6. The bound rubber content and % loading (of silica) of different masterbatches

Name of masterbatch	Concentration of silica added (phr)	Bound rubber content (%)	Loading of silica (%)
M-1	1	61.83	99.85
M-5	5	84.40	99.51
M-10	10	92.14	99.24
M-15	15	96.13	99.01
M-20	20	86.45	97.89
M-30	30	90.12	94.85

Table 6.6 shows that the bound rubber content increases with increase in concentration of in situ silica and approaches a maximum at a concentration of 15hr silica. Above that concentration the bound rubber content is not showing any fixed relation. Instead it shows variations. Bound rubber content assessment is an indirect method to study the elastomer-filler interactions.[14] The bound rubber content depends on characteristics of filler such as surface area, structure or morphology and surface activity. An increased rubber filler interaction increases the bound rubber content. The increase of bound rubber content up to 15 phr and then decrease indicates that rubber filler interaction is maximum for 15phr silica content and above that the filler-filler interaction is higher than that of polymer-filler interaction. This may be the reason why bound rubber content decreases after

15phrsilica content. It is also clear from the Table 6.6 that the % loading of silica decreases with increase in concentration of silica. The loading is above 99% up to 15phr silica and after that the loading shows a sharp decrease. This decrease is also may be due to the decrease in the rubber filler interactions.

6.3.3 Properties of in situ silica filled composites

Tensile properties

The tensile properties of in situ silica composites prepared from different concentrations of silica were studied and the values are given in the Figures 6.7 and 6.8. The tensile strength and tear strength showed a proportionate increase with increase in concentration of silica up to 15phr silica content. Above 15phr tensile strength showed a decrease while tear strength showed a very small increase. Tensile modulus and elongation at break showed a gradual increase with increase in silica content.

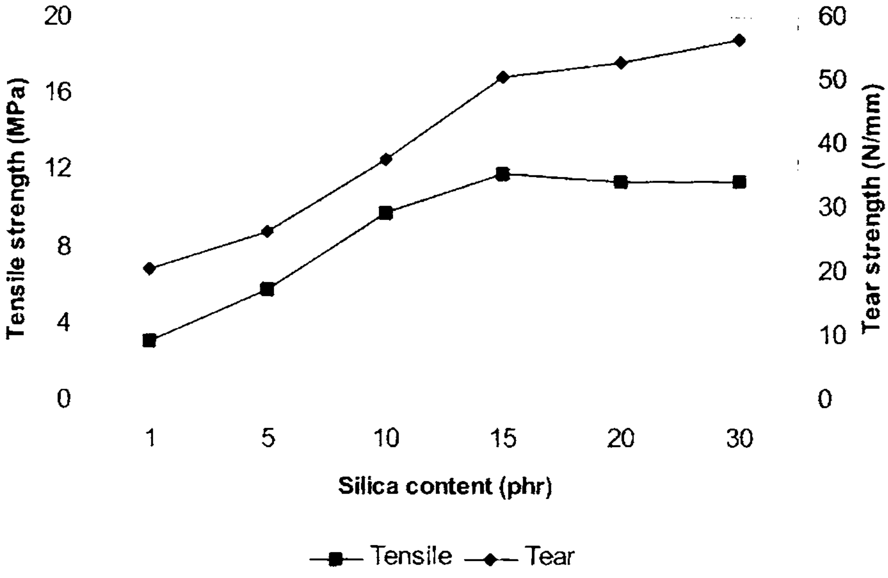


Figure 6.6. Variation of Tensile strength and Tear strength with silica content

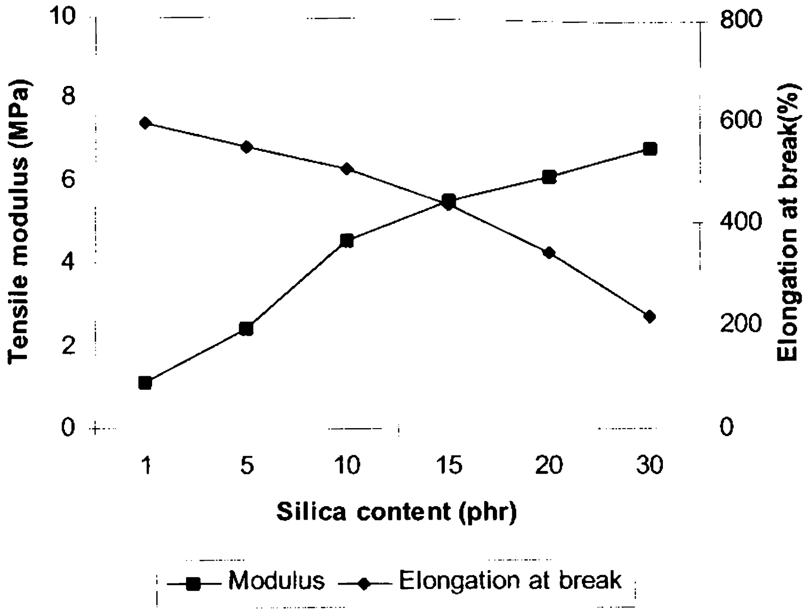


Figure 6.7. Variation of Tensile modulus and elongation at break with silica content

The increase in tensile properties with increase in silica content reveals the uniform distribution of in situ precipitated silica giving proportionate reinforcement. The decrease in tensile strength above 15phr indicates that there may be some agglomeration of particles resulting from the dilution effect.[15] Modulus gradually increased due to the inclusion of filler particles resulting from the hydrodynamic effect.[16] When rigid spherical particles are dispersed into a fluid, whether it be a liquid or an elastomer, an increase in viscosity takes place in the case of the liquid or of the modulus in the case of a polymeric matrix. Elongation at break gradually decreased with increase in silica concentration. Generally EB decreases with increase in filler content. In situ precipitation leads to an improved distribution of fillers in the matrix, which leads to decrease of elongation.

Reinforcing capacity

Reduced stress $[\sigma^*]$[17] of the composites is given in the Figure 6.8. Reduced stress values increased with increase in concentration of silica.

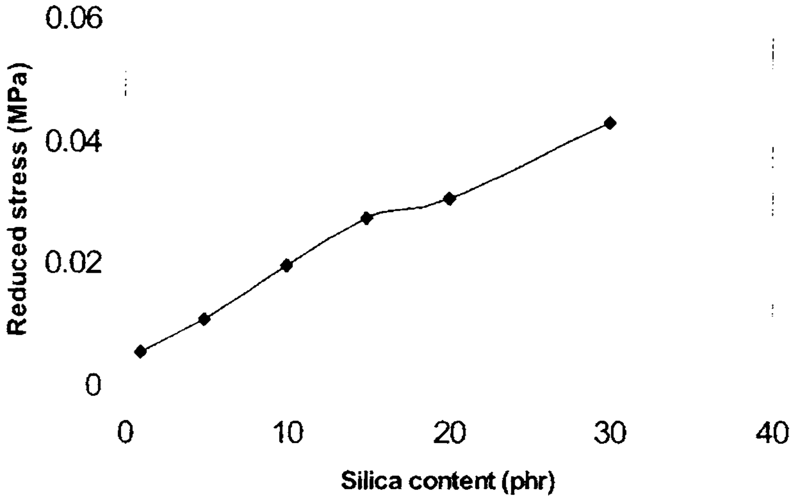


Figure 6.8. Reduced stress values of in situ precipitated silica

The improvement in the reduced stress values indicates that the reinforcing capacity increases with inclusion of in situ silica.

6.3.4 Comparison of properties of in situ silica filled and commercial silica filled composites

Based on the tensile properties, bound rubber content and % loading of silica, the optimum concentration of silica by in situ precipitation may be considered as 15phr. So M-15 is selected as the masterbatch and composites were prepared by mixing with dry NBR. Properties of these composites were compared with the composites prepared with commercial silica of the same concentration.

Tensile properties

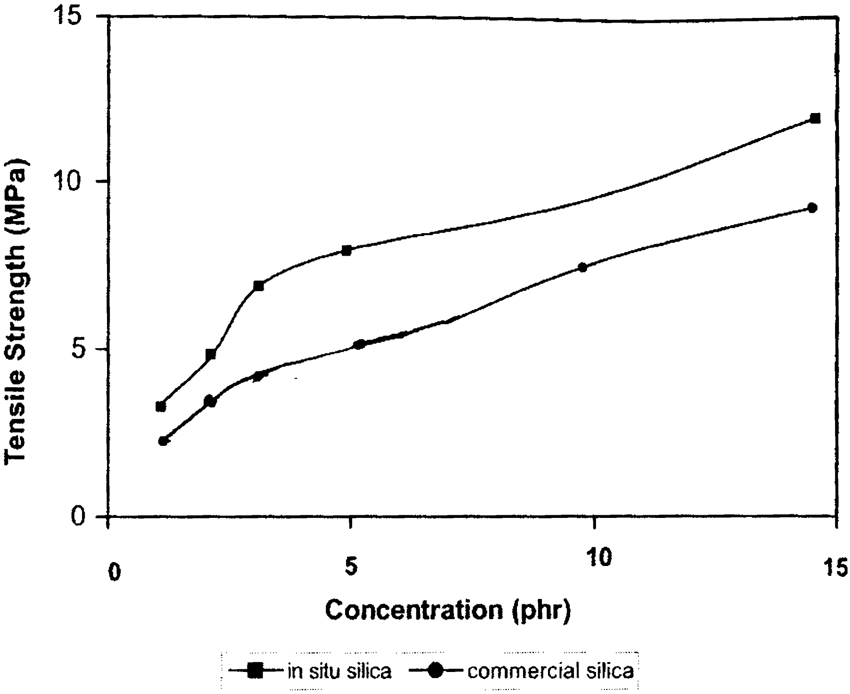


Figure 6.9. Tensile strength of composites

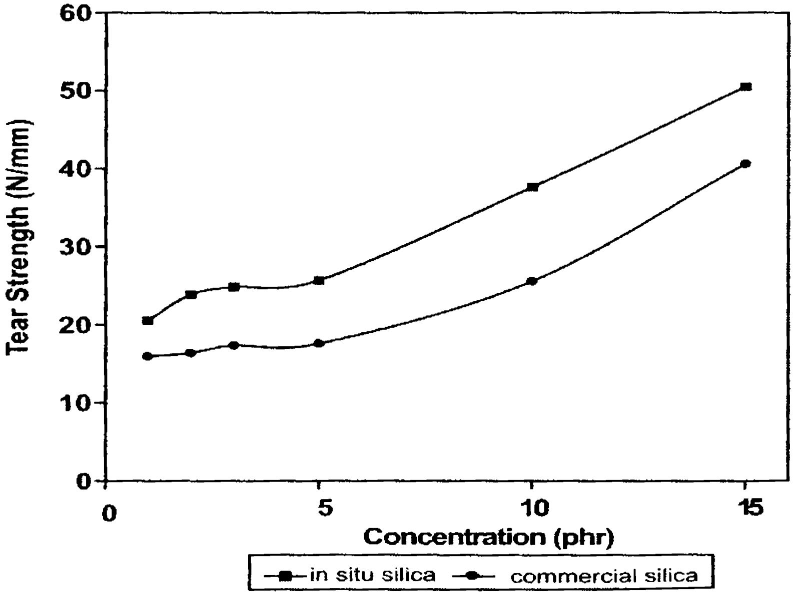


Figure 6.10. Tear strength of composites

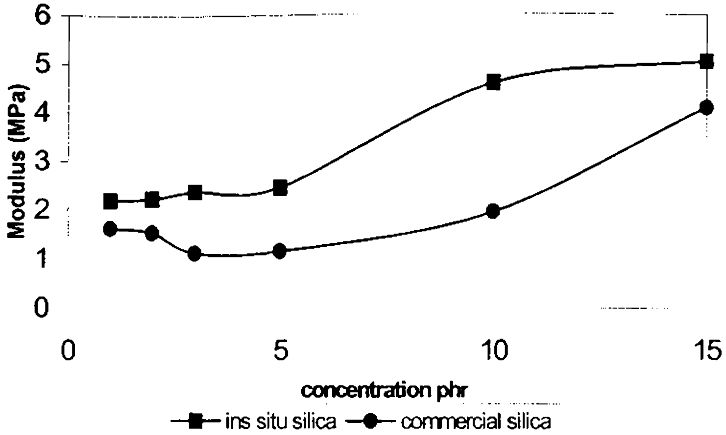


Figure 6.11. Tensile modulus of the composites

Figure 6.9 shows the tensile strength of vulcanizates containing varying amounts of in situ precipitated silica and conventional silica. The behaviour is similar. But there is considerable improvement of properties for in situ precipitated silica composites. Figure 6.10 shows the tear strength values of composites. As in the case of tensile strength, in situ silica samples showed considerable improvement in tear strength. This can be attributed to the better dispersion and improved filler rubber interaction.

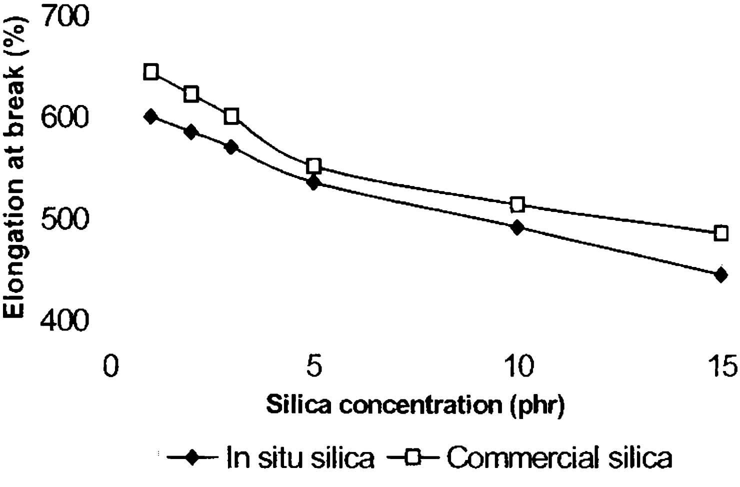


Figure 6.12. Elongation at break of composites

Figure 6.11 shows the tensile modulus values of the NBR composites with in situ silica and commercial silica. The tensile modulus values also show the similar behaviour indicating better reinforcement. Elongation at break of different composites show that the elongation at break is less for in situ silica composites, compared to commercial silica composites, as shown in Figure 6.12. Improved tensile strength and reduced elongation at break are considered as criteria for higher filler reinforcement.[18] The improvement in tensile properties for the in situ precipitated silica composites proves the better distribution of filler in the rubber matrix. NBR being a polar rubber the sodium silicate gets uniformly distributed in the rubber matrix. The finely distributed sodium silicate produces silica particles well distributed in the rubber matrix

Reinforcing index

Reinforcing index[19] values of the composites for tensile strength are given in the Table 6.7

Table 6.7. Reinforcing index values of composites

Silica content phr	Reinforcing index	
	In situ silica composite	Commercial silica composite
1	154.0909	102.2727
2	106.8182	51.8182
3	102.2727	61.6667
5	71.9091	41.0909
10	28.2121	22.3333
15	35.9091	27.8485

The values of in situ silica composites are compared with that of conventional silica filled composites. The value of in situ silica is higher than that of commercial silica at all concentrations. This shows that in situ silica filled composites have more reinforcing capacity than commercial silica filled composites. The use of reinforcing fillers gives the material unique properties: a combination of high elasticity with high strength.[20]

6.3.5 Comparison of properties at the optimum concentration

Cure characteristics of the composites

Table 6.8 gives the cure characteristics of the composites with an optimum concentration of 15phr silica. INS -15 has 15phr in situ silica and COM-15 has 15phr commercial silica. The in situ precipitated silica filled composites exhibit higher cure rate and extent of cure over that of conventional silica. Chemical surface groups on fillers play an important role in their effect on rate of cure, with many vulcanizing systems. Physical adsorption activity of the filler surface is of greater importance than its chemical nature. The polar nature of silica surface adsorbs a part of the curatives and silica-zinc ion interaction leads to slowing down of the curing reaction.[7]

Table 6.8. Cure characteristics of composites

Property	INS-15	COM-15
Min. Torque, dN.m	0.719	0.170
Max.Torque, dN.m	4.952	5.619
Scorch time (ts_2), min	2.58	2.32
Opt. Cure time (t_{90}), min	3.24	3.49
Cure rate index ($100/t_{90}-ts_2$)	104.16	85.47
Δ Torque (Max-Min), dNm	4.233	5.52

Incorporation of in situ precipitated silica in NBR improves the cure behaviour. The scorch time is increased and optimum cure time is reduced with in situ precipitated silica. This indicates that the adsorption of curatives by silica is reduced. The improvements noted in the cure behaviour of in situ precipitated silica might have resulted from the increased rubber filler interactions. Figure 6.13 gives the cure graphs of the composites.

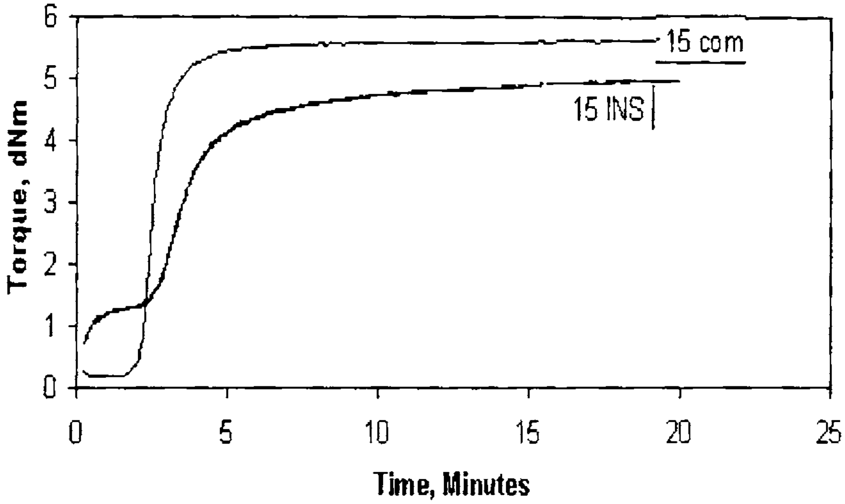


Figure 6.13. Cure graphs for the composites

Other technological properties

The technological properties like hardness, resilience, abrasion loss and air permeability were compared for the composites with 15phr silica and is given in the table 6.9 In situ precipitated silica composites showed better abrasion resistance. This is due to the strong adhesion of silica particles on rubber chains. Hardness also showed the same improvement while resilience decreased. The reduction in permeability shows that the filling of in situ precipitated silica is more efficient than the filling of commercial silica. J.B. Horn studied the effects of filler particle size and structure on vulcanizates properties and reported that as the particle size decreases abrasion resistance increases and resilience decreases[21] The above results therefore supports the fact that in situ silica has a reduced particle size compared to the conventional silica.

Table 6.9. Technological properties of composites

Sample name	INS- 15	COM -15
Hardness (shore A)	68	65
Resilience (%)	25	35
Abrasion loss (cc)	0.111	0.130
Heat buildup (°C)	43	38
Compression set (%)	33.24	35.18
Air permeability (ml/m^2.day)	92.25	107.38

Thermal ageing

Ageing resistance of the composites containing 15phr in situ precipitated silica and commercial silica were assessed by measuring the tensile properties after ageing to 72 hours and is given in the table 6.10. Retention of properties is comparatively high for in situ silica filled composite. During thermal ageing crosslink formation or crosslink breakage can take place or an existing crosslink may break and a stable linkage can be formed. All these reactions greatly influence the performance of the composites. Tear strength and tensile modulus also show a similar trend on ageing.

Table 6.10. After ageing properties

propertiies	INS-15	COM-15
Tensile strength (MPa)	9.26	7.02
Retention (%)	78.14	76.39
Modulous (MPa)	3.49	2.52
Retention (%)	69.52	62.22
Tear strength (MPa)	42.49	30.9
Retention (%)	84.15	76.07

Flow Behaviour

The rheological properties of polymers in the presence of filler depend largely on polymer filler interaction.[22,23] Processing of most of the rubbers is in the 'non-Newtonian' flow regime. Silica filled rubbers generally exhibit high viscosity and therefore their processability is poor compared to the black filled rubbers.[7] The variation of complex viscosity is measured as a function of frequency using the frequency sweep studies. A comparison of the plot of viscosity vs. shear frequency is given in the Figure 6.14.

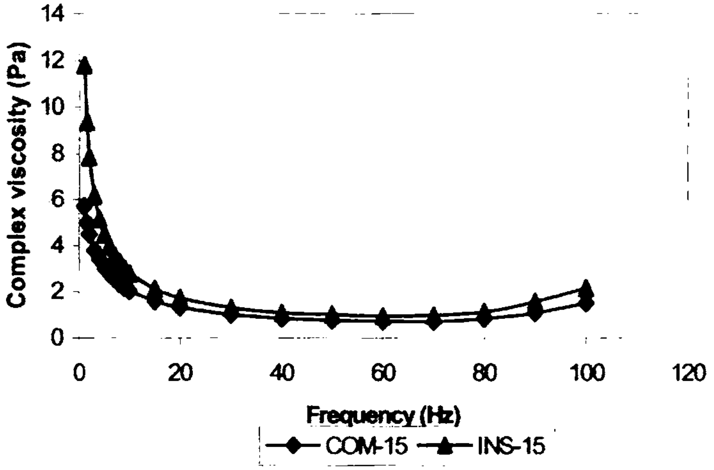


Figure 6.14. Comparison of the complex viscosity vs. shear frequency

At low frequencies the viscosity of in situ precipitated silica is very high compared to that of the commercial silica. The processing conditions usually involve high frequencies. As the frequency increases the viscosity decreases abruptly and the viscosity margin get reduced with commercial silica composites.

Swelling index in oils

Table 6.11 shows the swelling index of composites in different oils. It is clear from Table that the swelling index is minimum for composite prepared with in situ precipitated silica.

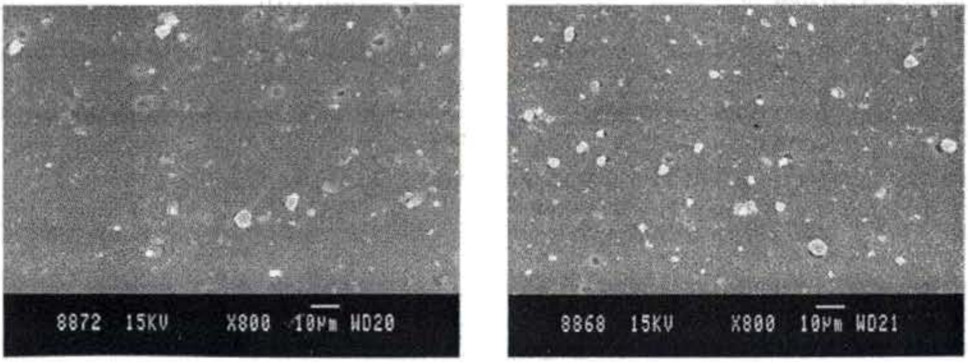
Several researchers have extensively studied the transport behaviour of various organic liquids in polymer composites[24,25] The phenomenon of transport of liquids through rubbers is controlled by the polymer structure, its cross link density, presence of fillers, penetrant size etc. So the reduced value of the in situ silica filled composite confirms the increased polymer filler interaction and uniform distribution of silica in the rubber matrix.

Table 6.11. Swelling index of composites in oils

Name of oil	Swelling index %		
	GUM	INS-15	COM-15
Diesel	9.21	6.52	8.07
Petrol	21.34	17.13	18.87
Naphthenic oil	1.35	1.01	1.44
Transformer oil	1.36	1.05	1.16
Lubricating oil	1.01	0.25	0.82

6.3.6 SEM photographs of the composites

Scanning electron microscopy can be used as a tool to characterise the filler distribution in the rubber matrix. SEM photographs of the tensile fractured surfaces the composites are shown in Figure 6.15



Precipitated silica

Commercial silica

Figure 6.15. SEM photographs of tensile fracture surfaces of composites

The SEM micrographs show that loose silica particles are more visible in commercial silica composites while the number of such free particles is found to be reduced in the in situ silica precipitated composites. This clearly supports the fine distribution of silica in rubber matrix.

6.3.7 Rubber filler interaction studies

The complex modulus G* of composites containing 15phr silica was measured before and after curing. The variation of G* with strain for uncured and cured samples are given in Figure 6.16 and Figure 6.17 respectively. The complex modulus at low strains is a measure of the filler polymer interaction.[26,27,28] The contribution to G* in unvulcanized filled compounds arise from the gum polymer, a hydrodynamic effect, filler networking and polymer-filler linkages.[29] The difference in G* values at very low and very high strains provide a means to exclude the contribution of the gum polymer and the hydrodynamic effect so that it gives a measure of the rubber-filler interaction.

From the Figures 6.16 and 6.17 it is clear that compounds with in situ precipitated silica are having comparatively high storage modulus values at low strains compared to the compounds with commercial silica indicating better rubber filler interaction.

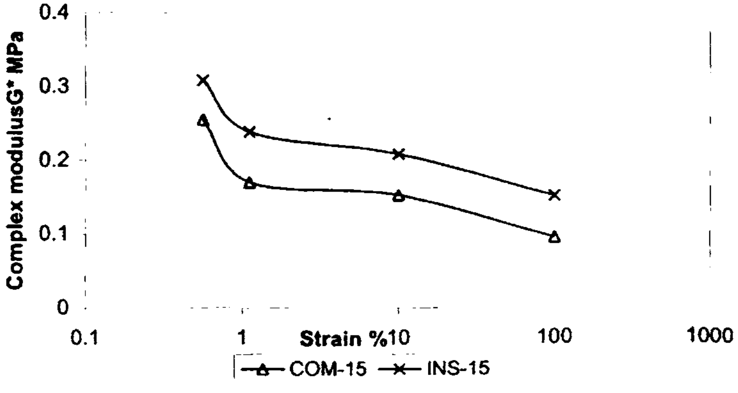


Figure 6.16. Strain sweep test for uncured composites

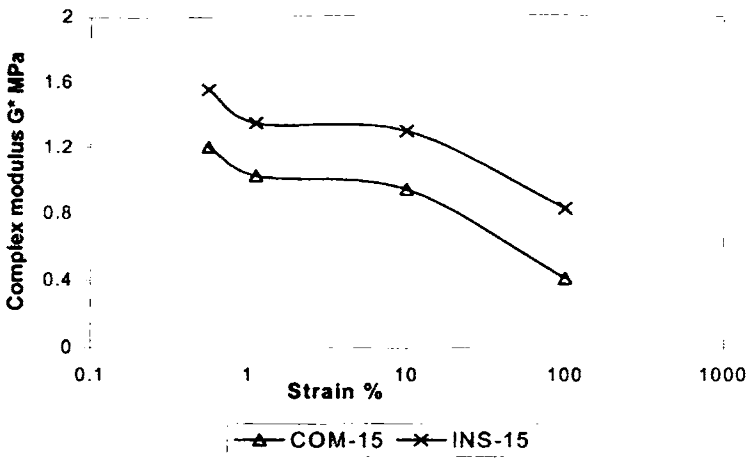


Figure 6.17. Strain sweep test for cured composites

At low strains the storage modulus of in situ precipitated silica composites are remarkably high for 15phr silica. The increase in modulus is due to the inclusion of rigid filler particles in the soft rubber matrix, hydrodynamic effect and additional contribution arise from the molecular interaction between the rubber and the filler leading to additional cross-links in to the polymer network structure. In the absence of polymer -filler interaction only hydrodynamic effect is expected. It is observed that the novel composite show superior modulus indicating higher load carrying capacity and filler- rubber interaction. The additional cross-links can also be confirmed by equilibrium swelling studies.

Crosslink densities

Figure 6.18 shows the crosslink density of silica composites with 15phr silica. It can be seen that the in situ precipitated silica composite has better value. The increased crosslink density of the in situ silica composites indicates a better adhesion between the rubber and silica particles.

Contribution of fillers to the reinforcement effect arises from molecular interaction between the rubber and the filler. This interaction leads to an increase in the effective degree of crosslinking and can be evaluated by equilibrium swelling. The equilibrium swelling analysis of rubber vulcanizate is known to indicate the number of effective network chains per unit volume of rubber. For a filled vulcanizate it should reflect not only the effect of chemical linkages but also the density of polymer-filler attachments.

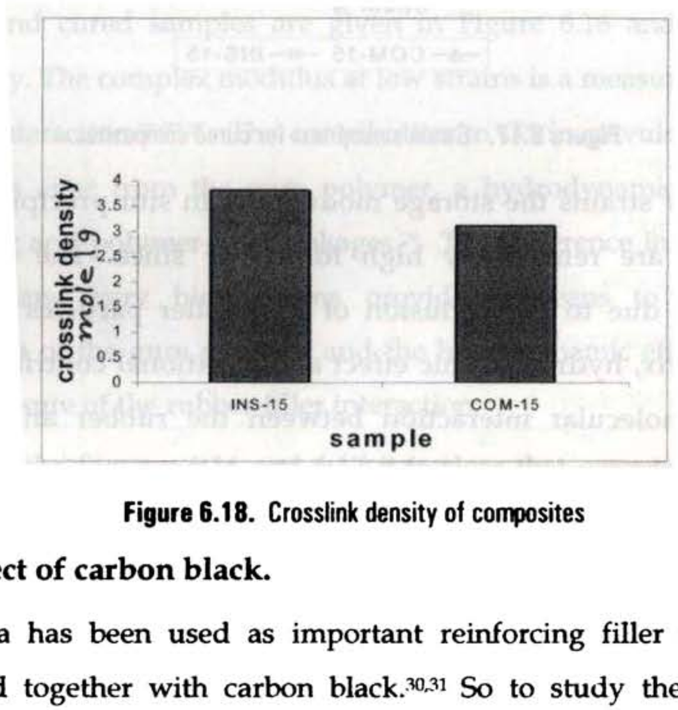


Figure 6.18. Crosslink density of composites

6.3.8 Effect of carbon black.

Silica has been used as important reinforcing filler in a rubber compound together with carbon black.[30,31] So to study the reinforcing capacity of in situ silica when it is combined with carbon black, composites were prepared by mixing suitable amount of the silica masterbatch M-15 with Carbon black and other compounding ingredients. Compounds of similar compositions were prepared with conventional silica and carbon black. Composites were prepared as per the formulation given in the Table 6.5 by varying the composition of silica and carbon black. In situ silica composites are C-1 & C-3 and conventional silica composites are C-2 & C-4.

Tensile properties of the composites before and after thermal ageing

The tensile properties of the composites are given in the Table 6.12 before and after thermal ageing. The values show that the addition of carbon increases the tensile strength, tensile modulus, elongation at break and tear strength. The values when compared with commercial silica composites showed a better reinforcement nature of the in situ silica.

Table 6.12. The tensile properties of the composites

Property	C-1	C-2	C-3	C-4
Tensile strength (MPa)	14.27	11.77	15.59	11.90
Tensile modulus (MPa)	7.8	4.2	9.1	5.7
Elongation at Break (%)	451	528	458	494
Tear strength (N/mm)	47	41	62	41
After 24hrs ageing				
Tensile strength (MPa)	14.33	9.83	16.79	11.35
Tensile modulus (MPa)	13.17	8.29	14.19	9.04
Elongation at Break (%)	269	325	275	328
Tear strength (N/mm)	47	40	63	44
After 48 hrs ageing				
Tensile strength (MPa)	14.19	8.98	15.76	10.41
Tensile modulus (MPa)	12.86	8.12	11.35	8.41
Elongation at Break (%)	274	294	248	298
Tear strength (N/mm)	47	40	61	42

The thermal ageing does not reduce the properties of the NBR composites. The same trend is observed for both in situ and commercial silica. Modulus showed a significant increase, may be due to the formation of cross-links on ageing.

6.4 Conclusions

The study shows that silica can be incorporated in NBR latex by precipitation process. The vulcanizates prepared by this novel technique show superior mechanical properties compared to those prepared from commercial silica's. The latex precipitated silica is found to have better rubber- filler interaction compared to commercial silica's. Silica of any desired concentration can be incorporated in to the dry rubber by mill mixing of silica masterbatch with dry rubber or directly from the in situ precipitation of silica at the desired concentration in the latex.

Mixing of in situ precipitated silica with carbon black also show comparable values of mechanical properties indicating that compounds can be prepared with carbon black partly replaced by silica.

Swelling index values and crosslink density showed that the rubber filler interaction is more in the in situ precipitated silica compounds. Similarly properties like ageing resistance and permeability showed improved values. The method is simple and cost reducing and fully effective in polar synthetic rubber like NBR.

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Chapter 7

IN SITU PRECIPITATION OF SILICA IN STYRENE BUTADIENE RUBBER

7.1 Introduction

It was observed that in situ precipitation of silica in polar synthetic rubber latex NBR has improved the rubber filler interactions and mechanical properties. So the same method was studied in non-polar synthetic rubber latex, Styrene Butadiene Rubber (SBR). SBR is the most commonly used general-purpose synthetic rubber which is a copolymer of styrene and butadiene, and the butadiene unit is composed of cis-1,4-, trans-1,4- and vinyl components. They are produced by the co-polymerization of styrene and butadiene under controlled conditions of reaction using different techniques of polymerization and the product varies with the method of polymerisation.

The unsaturation in SBR is less than that in NR and the double bonds are less active chemically than the double bonds of the isoprenoid unit in NR. The compounding of SBR is done in a way more or less similar to that of NR and other unsaturated hydrocarbon rubbers.[1] All types of SBR require less sulphur than NR for curing. On the other hand, SBR requires more accelerator because of lower unsaturation. Without reinforcing fillers such as carbon black or silica, the physical properties of SBR are much inferior to those of NR. Similarly its green strength is also inferior. Many studies are reported on the silica reinforcement of SBR, comparison with carbon black, rubber filler interactions, bound rubber content, hysteresis loss etc.[2,3] A study on the mechanical properties of silica filled SBR systems in relation to the secondary structure formed by silica particles in the systems, which was controlled by a surface chemistry of silica particles was carried out which revealed that the initial modulus of the filled rubber systems increased with the increase of the agglomerates.[4] But the incorporation of silica has the drawbacks, those are explained in the case of NR, in the case of SBR also. So the development of new techniques and materials that facilitate the incorporation of silica is a topic of current research. The use of sol-gel process on SBR to produce silica generated in situ is conducted and found that the sol-gel reactions of tetraethoxysilane (TEOS) in SBR produced in situ silica that has better dispersion due to its formation in place.[5] Reinforcing effect of silica on the properties of styrene butadiene rubber-reclaim rubber blend system was studied by sol-gel technique and conventional method.[6] Silica incorporation by conventional mechanical mixing in absence of TESPT showed a much higher tensile properties than that of silica incorporated by the in situ sol-gel reaction of tetra ethoxy silane both in presence and absence of TESPT. The effect of oleyl amine on processing and physical properties of SBR compounds filled with silane-silica particles has been evaluated.[7] A silica reinforcement of SBR latex by the sol-gel method of tetraethoxysilane was conducted and found that the particle size and reinforcing behaviour of silica were greatly influenced by the amount of TEOS and (H2O/TEOS). The diameter of the silica particles was less than 100 nm.[8]

In this chapter the in situ precipitation of silica in SBR latex and the mechanical properties of the vulcanizates prepared with in situ precipitated silica are reported. The mechanical properties of the vulcanizates are compared with reference compounds prepared from SBR and conventional silica.

7.2 Experimental

Materials : SBR latex Encord 204 of dry rubber contents 50% and dry SBR (1502) supplied by Jubilant Organosys Ltd. Gujarat were used in this study. Other chemicals used were of commercial grade.

In-situ precipitation of silica

Table 7.1. Silica mixes of different composition

Name of silica mix	Concentration of silica (phr)
M-1	1
M-5	5
M-10	10
M-15	15
M-20	20
M-25	25

SBR latex was filtered and stabilized with non-ionic stabilizer, vulcastab VL. Required amount of sodium silicate was added and stirred for 1hour and a saturated solution of ammonium chloride was added drop wise with constant stirring to precipitate silica. Latex was coagulated as crumbs by the addition dilute acetic acid. The crumbs were washed with water till the washings were neutral, pressed to remove water and dried in an air oven at 70° C for 48hrs. Silica mixes of different concentrations were prepared by adding calculated quantities of sodium silicate and ammonium chloride. The details of the mixes are given in the table 7.1

Characterization of the silica mixes

Silica content of the coagulum

The silica content of the dried coagulum samples was obtained by igniting a known weight of a sample in a previously weighed silica crucible in a muffle furnace. The temperature of the furnace was kept at 550^{0}C for 5 hours. The rubber content in the sample was burnt off leaving silica in the crucible which is cooled in a dessicator and weighed. From the weight of the silica the % loading of silica was calculated.

Bound rubber content

The fraction of the bound rubber that occurred in the master batches were determined by swelling the samples in toluene as per the procedure suggested by Kazumasa Yoshikai et al[8] and using the equation[9]

$$R_B = W_{fg} - W\,[m_f\ /\ (m_f + m_p)]\ /\ W\,[m_p/(m_f + m_p)]\ {*}100$$

where W_fg = weight of filler and gel, W = weight of specimen, m_f = weight of filler in the compound and m_p = weight of polymer.

Preparation of the composites

The base formulation for the preparation of composites is given in the table 7.2.

Table 7.2. Base formulation for SBR compounds

Ingredient	Concentration (phr)
SBR	100
ZnO	5
Stearic acid	2
DEG	1
Naphthenic oil	3-6
HS	1
CBS	0.6
TMTD	0.2
Sulphur	1.5

Composites were prepared with dry coagulum samples of silica concentration ranging from 1phr to 25phr. Composites of lower concentrations were also prepared from *in-situ* precipitated silica filled rubber sample M-15, keeping it as a masterbatch and mixing it with dry NBR on a two roll mill. Different quantities were added to get the desired concentrations of silica in SBR. The compounding formulation is given in Table 7.3 and 7.4

Table 7.3. Recipe for the preparation of silica – filled SBR compounds from silica mixes of different concentrations*

Name of compound	Weight of Silica mix (phr)	In situ Silica content (phr)
INS-1A	M-1 (101)	1
INS-2A	M-2 (102)	2
INS-3A	M-3 (103)	3
INS-5A	M-5 (105)	5
INS-10A	M-10 (110)	10
INS-15A	M-15 (115)	15
INS-20A	M-20 (120)	20
INS-25A	M-25 (125)	25

*Base formulation: ZnO 5, Stearic acid 2, DEG 1, Naphthenic oil 3-6, HS 1 CBS 0.6, TMTD 0.2, Sulphur 1.5

Table 7.4. Recipe for the preparation of silica – filled SBR compounds from silica masterbatch (15phr)*

Name of the compound	SBR(phr)	Masterbatch (phr)	Commercial silica (phr)
INS-1	93.5	7.5	0
COM-1	100	0	1
INS-2	87	15	0
COM-2	100	0	2
INS-3	80.5	22.5	0
COM-3	100	0	3
INS-5	67.5	37.5	0
COM-5	100	0	5
INS-10	35	75	0
COM-10	100	0	10
INS-15	0	115	0
COM-15	100	0	15

*Base formulation: ZnO 5, Stearic acid 2, DEG 1, Naphthenic oil 3-6, HS 1 CBS 0.6, TMTD 0.2, Sulphur 1.5

Testing of the composites

The cure characteristics of the mixes were determined using Rubber Processing Analyser RPA 2000 supplied by Alpha Technologies, USA, as per ASTM standard, D 2084-01. Subsequently, the rubber compounds were vulcanized up to the optimum cure time at 150 ^{0}C. The mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 h. prior to physical testing.

Physical properties such as modulus, tensile strength, elongation at break, tear strength, hardness, heat build-up, compression set, flex resistance and ageing resistance were studied as per the relevant ASTM Standards. Swelling studies and Scanning Electron Microscopic studies were used to study the crosslink density and distribution of silica respectively.

Rubber filler interaction studies

The strain sweep measurements on unvulcanized samples and vulcanizates were conducted to study the rubber-filler interaction. These were done using Rubber Process Analyser (RPA 2000- Alpha Technologies) at 100°C and 50°C respectively at 0.1Hz by varying the strain from 0.5 – 100%.

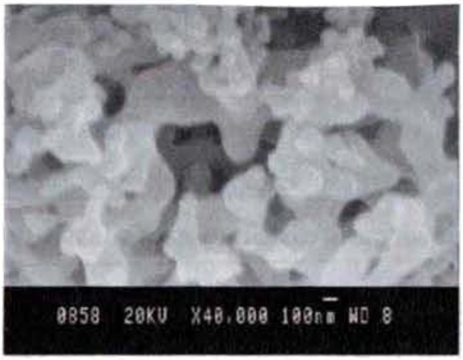
Crosslink density

The equilibrium swelling studies of the compounds were carried out in toluene and crosslink densities were calculated using Flory-Rehner equation.[10]

7.3 Results and discussion

7.3.1 Characterisation of in situ precipitated silica

The SEM picture of the silica obtained after igniting the rubber coagulum to a temperature 550°C for five hours is shown in the Figure 7.1. The Figure shows that precipitated silica is having a structure with more voids for interactions with the polymer. The precipitation of silica was conducted after the uniform distribution of sodium silicate in the rubber latex giving a fine distribution of silica in rubber latex. The polymer matrix prevents the agglomeration of silica and provides a uniform distribution and reduced size for the silica particles. It is clear from SEM pictures that in situ precipitated silica has a reduced particle size. The small particle size provides a large surface area, which can contribute to an improvement in the mechanical properties.



In situ Precipitated silica

Figure 7.1. Scanning Electron Microscopic photograph of silica

7.3.2 Characterisation of silica mix

Ignition of the dry coagulum : Figure 7.2 shows the photographs of the sample containing in situ precipitated silica before and after ignition. Heating of silica mix to a very high temperature of 550°C in a muffle furnace showed that the sample retained its original shape even after the burning off of rubber particles leaving the silica. This reveals that uniform distribution of silica is possible in non polar synthetic rubber medium also. The coagulum with VN3 crumbled on ignition , indicating that there is no uniform distribution.

Before ignition

After ignition

Figure 7.2. Photograph of sample containing in situ silica before and after ignition.

Silica content and bound rubber : The % loading of silica during the precipitation and bound rubber content of the silica mixes are given in the Table 7.5. As in the case of NR and NBR, SBR also showed a gradual decrease in the % loading of silica with increase in concentration of in situ silica. The loss of silica is negligible or less than 1% up to 15phr silica content and then it increases abruptly.

Table 7.5. % loading of silica and the bound rubber content of different masterbatches

Name of silica mix	% loading of silica	Bound rubber content (%)
M-1	99.88	52.48
M-5	99.84	74.13
M-10	99.56	85.23
M-15	99.15	92.26
M-20	96.86	92.54
M-25	89.75	91.22

Table 7.5 shows that the bound rubber content increases with increase in concentration of in situ silica and approaches a maximum at a concentration of 15hr silica. The bound rubber content values are high even at a concentration of 1phr.Variation of the bound rubber formation in SBR compounds filled with silica was studied by Sung Sen Choi and reported that the bound rubber content increases with increase in silica content ratio.[11] Bound rubber content assessment is an indirect method to study the elastomer-filler interactions.[12] The bound rubber content depends on characteristics of fillers such as surface area, structure or morphology and surface activity. It is reported that freshly formed filler surfaces have great adsorption capacity.[10] So the high value of bound

rubber is due to the newly formed silica surfaces which hold rubber by adsorption. The maximum value of bound rubber at 15phr indicates that 15phr silica has the maximum rubber filler interaction. Above 15phr the interaction decreases, may be due to agglomeration of silica particles. The decrease in % loading of silica with increase in concentration is a proof for this.

IR spectroscopic analysis: FTIR spectra of SBR (Gum) and SBR containing 15phr silica (M-15) are given in the Figure 7.3. The analysis of the spectra shows that all the spectral bands of SBR are present in M-15 also indicating that SBR is not chemically affected by the reaction leading to the precipitation of silica. No chemical bonds are formed between the silica and rubber but there is a reduction in the intensity of the peeks. This may be due to the reduction in the stretching freedom of the bonds due to the silica environment.

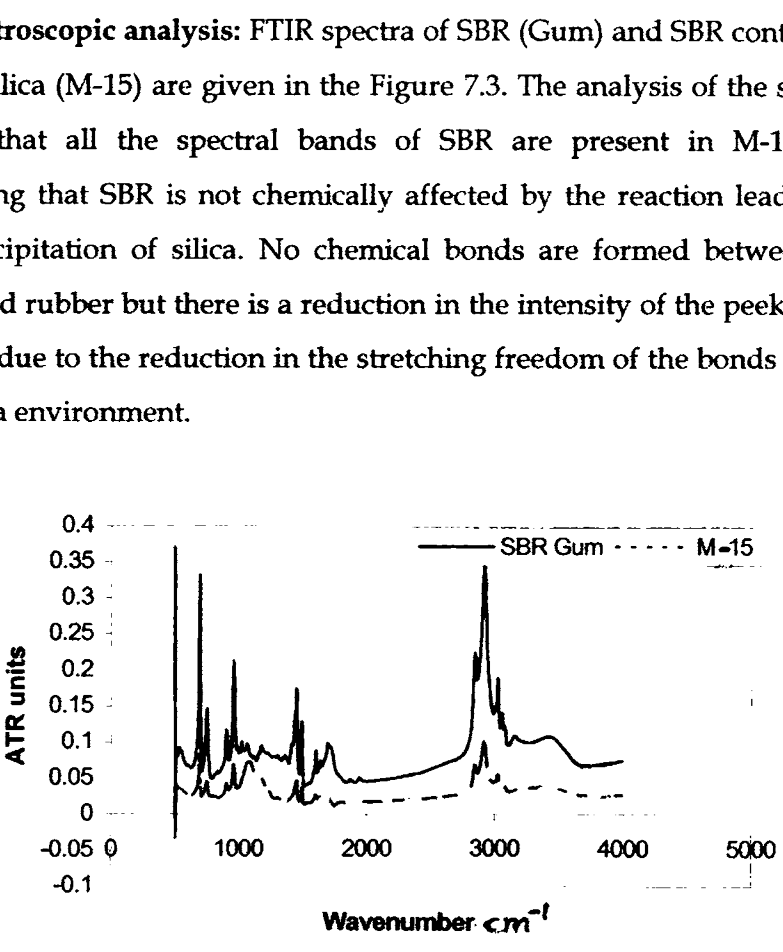


Figure 7.3. IR spectrum of SBR and in situ silica filled SBR

7.3.3 Properties of the composites

Tensile properties: The tensile properties of in situ silica composites prepared from silica mixes of different concentrations are given in the

Figures 7.4 and 7.5. The tensile strength showed a proportionate increase with increase in concentration of silica up to 15phr. At concentrations above 15phr tensile strength showed a small decrease. Tensile modulus at 300% elongation showed a gradual increase with increase in silica content.

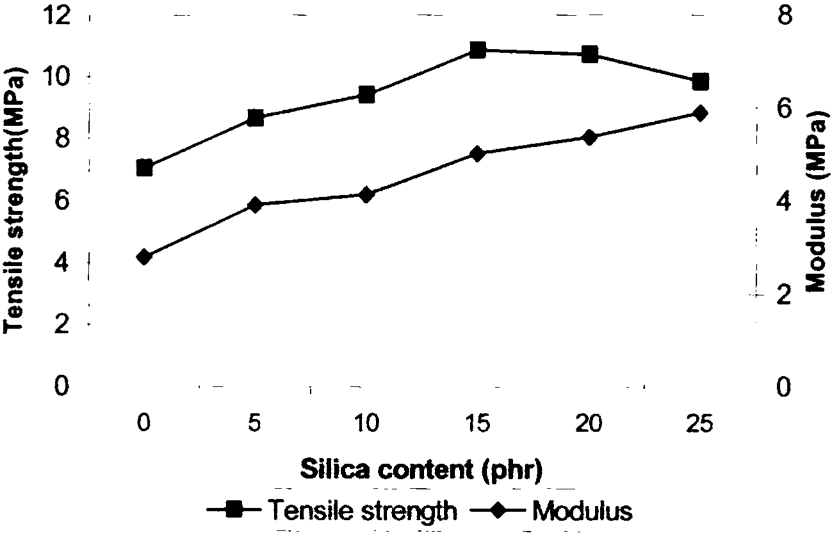


Figure 7.4. Variation of tensile strength and modulus with silica content

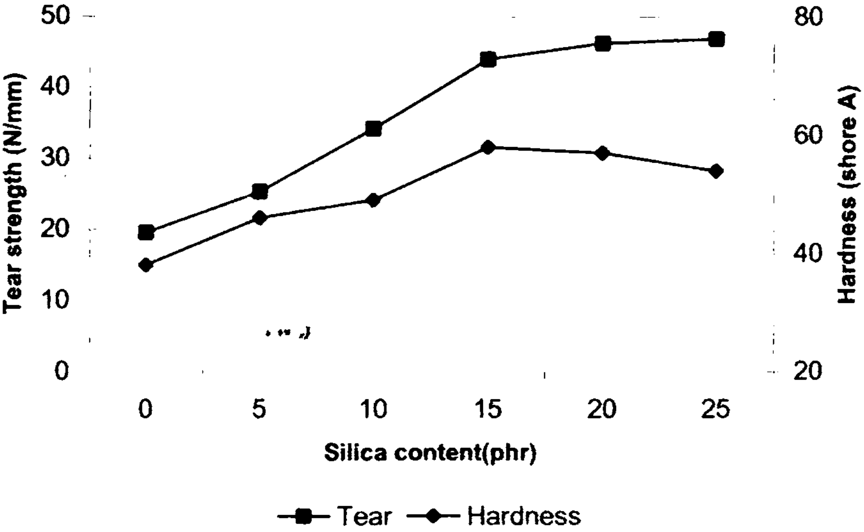


Figure 7.5. Variation of tear strength and hardness with silica content

The tear strength showed a proportionate increase with increase in silica up to 15phr. Above 15phr the increase is not proportional, may be due to a reduction in the rubber filler interaction. Hardness also increased proportionately with the increase in silica up to 15 phr and thereafter it showed a tendency to decline with increase in silica concentration. All these properties reveal that the reinforcing capacity is optimum for 15phr silica concentration.

Figures 7.6a to 7.6d give the comparison of the tensile properties of the two types of composites, namely composites with in situ precipitated silica and composites with conventional silica. From the observation of high bound rubber content, % loading of silica and improved tensile properties, 15phr silica was selected as an optimum concentration of silica for in situ precipitation. Keeping it as a masterbatch composites were prepared and their properties were compared with the composites prepared with conventional silica.

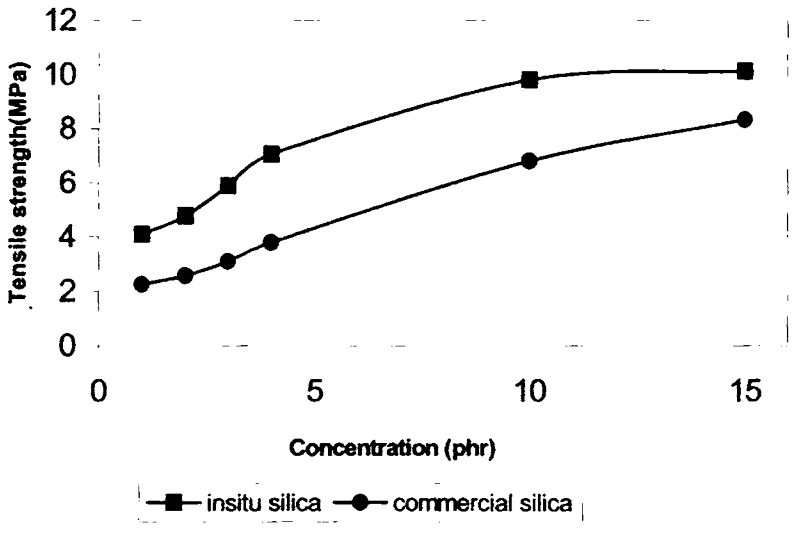


Figure 7.6 a. Comparison of tensile strength

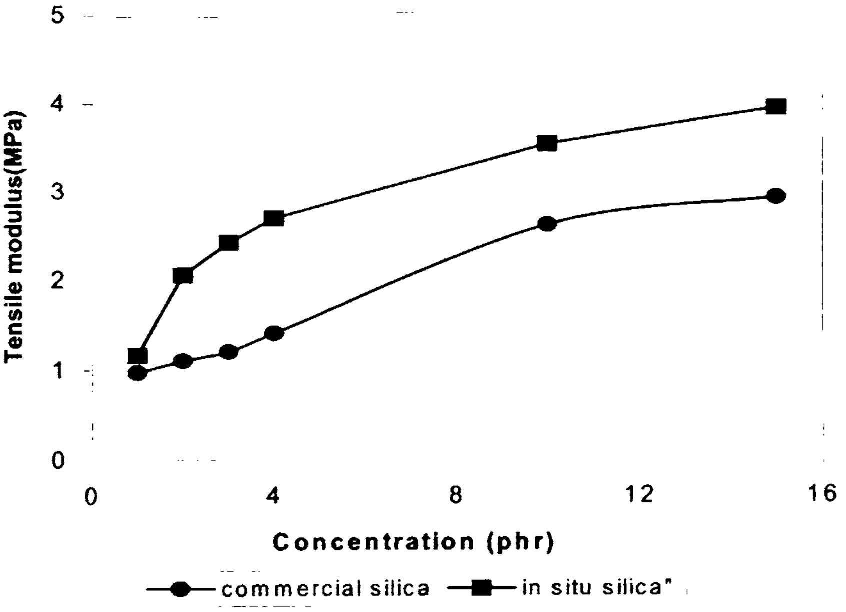


Figure 7.6 b Comparison of tensile modulus

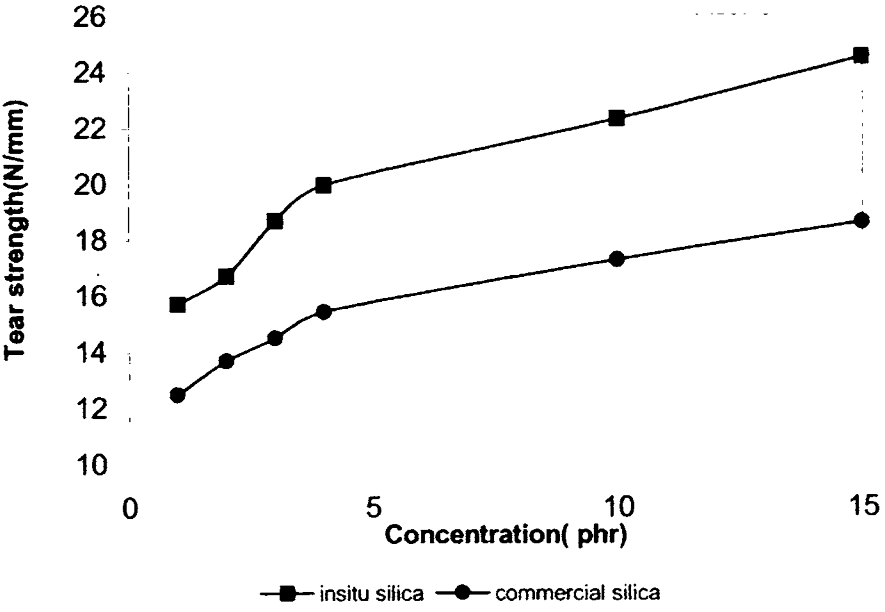


Figure 7.6 c. Comparison of tear strength

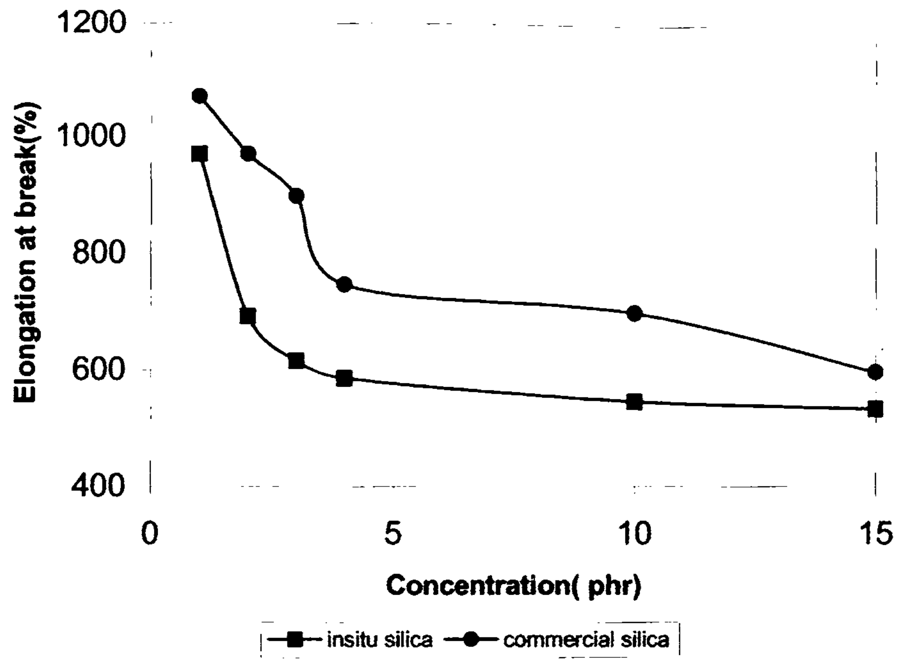


Figure 7.6 d. Comparison of elongation at break

The shapes of the curves are similar for both composites. But the values show significant improvement with in situ precipitation. The increase in tensile strength gradually decreases at higher loadings. This effect is well known[13] and can be attributed to poor wetting of the reinforcement particles at filler contents above the optimum. The tensile modulus of the composites at 1phr does not show considerable difference. But above 1phr the values showed an increase of nearly 100% and at higher concentrations i.e. at 15phr the values showed 80% improvement for in situ precipitated silica composites. As in the case of tensile strength, the tear strength of in situ silica samples shows nearly 80% improvement. The elongation at break (%) is found to be decreasing with filler content and this decrease is higher for in situ silica composites. This points to a better reinforcing action of in situ silica. This may be the result of more effective distribution and filler-rubber interaction in comparison with commercial silica.

Reinforcing index

Reinforcing index (RI) values of the composites with respect to tensile strength are given in the Table 7.6. The values of in situ silica composites are superior to those of conventional silica filled composites. At low concentrations the values show very high difference and as the concentration increases the difference also decreases. This shows that in situ silica filled composites have more reinforcing capacity compared to commercial silica composites.

Table 7.6. Reinforcing index values of composites

Silica content phr	Reinforcing index	
	In situ silica composite	Commercial silica composite
1	203	111
2	118	63
3	97	51
5	70	37
10	48	33
15	33	27

7.3.4 Comparison of technological properties

Comparison of other properties was carried out with composites of in situ precipitated silica and conventional silica at the optimum concentration. INS-15 represents composite containing 15phr in situ precipitated silica and COM-15 represents composite containing 15phr conventional silica

Cure characteristics

Table 7.7 gives the cure characteristics of the composites INS -15 and COM-15. The in situ precipitated silica filled composites exhibited higher cure rate and extent of cure over that of conventional silica.

Table 7.7. Cure characteristics of composites

Property	INS-15	COM-15
Min. Torque, dNm	0.434	0.160
Max.Torque, dNm	8.452	4.609
Scorch time (ts_2), min	3.98	3.84
Opt. Cure time (t_{90}), min	6.18	7.45
Cure rate index ($100/t_{90}-ts_2$)	45.45	27.05
Δ Torque (Max-Min), dNm	8.018	4.449

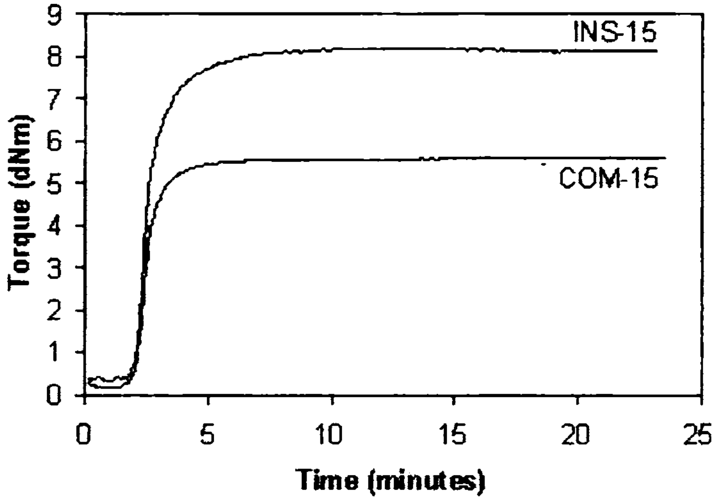


Figure 7.7. Cure graphs for the composites

The cure graphs for the composites are given in the Figure 7.7. Incorporation of in situ precipitated silica in SBR improves the cure behaviour. The scorch time showed only a marginal increase but the cure time reduced by one degree with in situ precipitated silica. The reduction in the cure time reveals that the adsorption of curatives on the silica surface is reduced with in situ precipitation. The minimum and the maximum torque values are higher for INS-15, and the rheometric torque, ΔTorque, of INS-15 is also higher compared to that of COM-15. The improvements noted in the cure behaviour of in situ precipitated silica might have resulted from the increased rubber filler interactions

Other technological properties

The properties like hardness, abrasion loss, resilience etc. are given in the table 7.8.

Table 7.8. Technological properties of composites

Sample name	Abrasion loss (cc)	Hardness (Shore A)	Resilience (%)	Compression set (%)	Heat buildup (°C)
COM-15	0.5590	57	38	37.35	21
INS-15	0.2012	63	10	37.78	21

From the Table 7.8 it can be seen that the abrasion loss is considerably low in INS-15 compared to COM-15. In situ precipitation reduces the abrasion loss by 64%. The abrasion resistance, which is the reciprocal of abrasion loss, has more than doubled with in situ precipitated silica. This is due to the strong adhesion of silica particles on rubber chains. Hardness, a measure of low strain elastic modulus, has increased with in situ precipitated silica whereas the resilience, a measure of the elastic component, decreased with in situ precipitation. Compression set and heat build up showed no change in their values.

Flow properties

Variation of complex viscosity of the composites INS-15 and COM-15 measured as a function of the shear frequency is given in the Figure 7.8. Processability of composites can be characterized by rheological means.

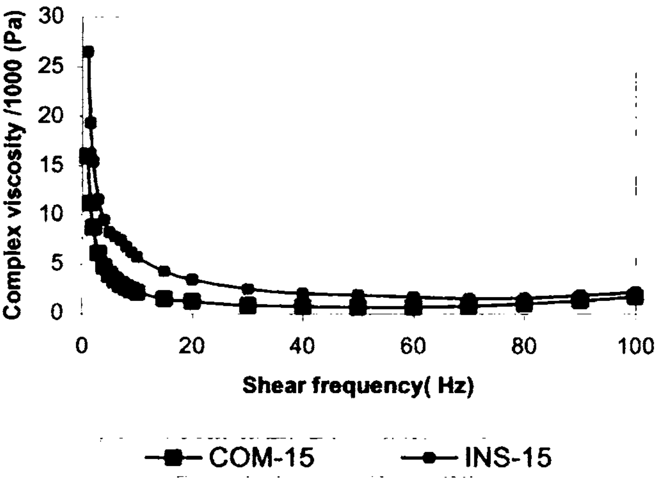
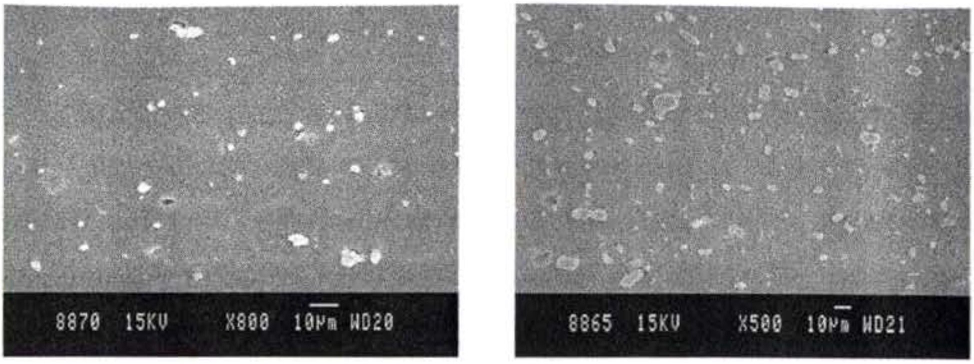


Figure 7.8. Variation of complex viscosity with the shear frequency

It can be seen from the figure that at low frequencies the viscosity of in situ precipitated silica is very high compared to that of the conventional silica. The processing conditions usually involve high frequencies. As the frequency increases the viscosity of INS-15 decreases abruptly and the viscosity margin between the two composites get reduced. It follows that there is no much difference in the processability of in situ silica filled and conventional silica filled composites.

7.3.5 SEM photographs of the composites

The Scanning electron microscopic photographs of the tensile fracture surfaces of vulcanizates with 15phr in situ precipitated silica and commercial silica are shown in Figure 7.9. The SEM micrographs show that more free silica particles are present in COM—15 compared to INS-15. For INS-15 the particles are visible at a high magnification (x 800). This indicates that a uniform distribution of particles with a reduced size and improved binding in *in situ* silica filled composites.



In situ precipitated silica composite **Commercial silica composite**

Figure 7.9. SEM pictures of tensile fracture surfaces

7.3.6 Rubber filler interactions

The storage modulus values at low strains (<15%) are a measure of the filler polymer interactions[14,15]. So the variation of storage modulus with strain was studied for the compounds with 1phr and 15phr silica before and after curing. The values obtained for the uncured compounds are plotted and shown in the Figure 7.10. The figure 7.11. shows the values obtained for cured compounds.

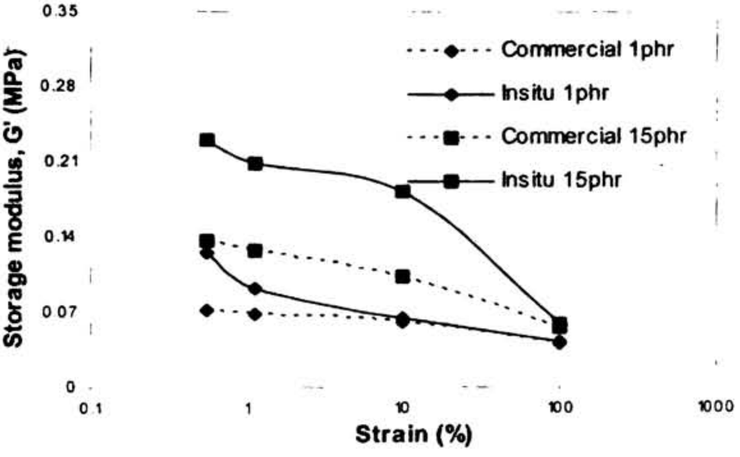


Figure 7.10. Variation of storage modulus with strain for uncured compounds

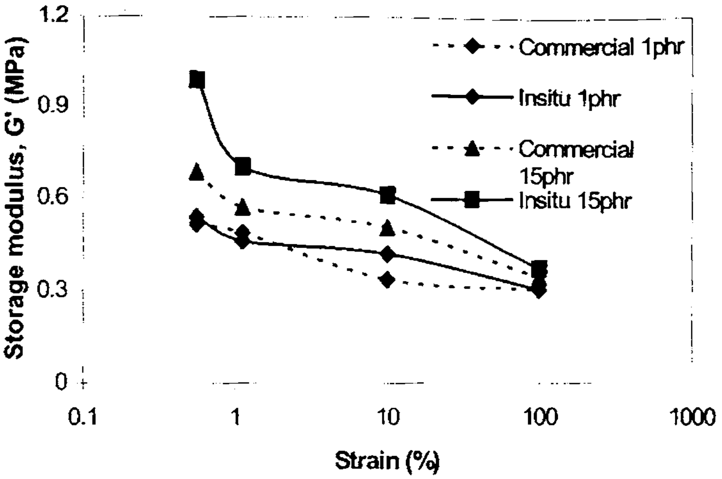


Figure 7.11. Variation of storage modulus with strain for cured compounds

From the graphs it is clear that compounds with in situ silica is having comparatively high storage modulus values at low strains for both cured and uncured compounds, compared to the compounds with commercial silica, indicating better rubber-filler interaction. The increase in modulus is due to the inclusion of rigid filler particles in the soft rubber matrix, hydrodynamic effect and additional contribution arise from the molecular interaction between the rubber and the filler leading to additional cross-links in to the polymer network structure. In the absence of polymer-filler interaction only hydrodynamic effect is expected. The additional cross-links can also be confirmed by equilibrium swelling studies.

Crosslink density

Swelling studies of the composites were done in toluene and the crosslink density of the composites are given in the Table 7.9

Table 7.9. Crosslink density of composites

Sample name	Crosslink density $*10^{-5}$
INS-15	7.2218
COM-15	5.2156

The crosslink density of in situ silica filled compound is higher than that of conventional silica compound. This clearly indicates the presence of increased cross-links.

6.4 Conclusions

In situ precipitation of silica can be successfully conducted in SBR latex. Latex stage precipitation helps easier incorporation of silica of reduced particle size with uniform distribution. In situ silica filled composites are found to give improved mechanical properties and rubber filler interactions when compared to conventional silica filled composites.

6.5 References

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Chapter 8

SUMMARY AND CONCLUSIONS

Commercial applications of rubbers require the use of particulate fillers such as carbon black, silica etc. Precipitated silica is one of the promising non-black fillers for rubbers in tyre applications, as it has the great advantage of reduced rolling resistance and as a consequence, reduced fuel consumption. Conventionally silica-reinforced rubber composites are prepared by mechanical mixing of rubber and silica with silane coupling agent, which provides a chemical link between silica and rubber. However, the mixing of silica with the commonly used olefinic hydrocarbon rubbers is a challenge as these materials are not very compatible in various aspects. So viable alternative methods or materials for overcoming the problems associated with the silica reinforcement of rubbers are therefore a current research priority.

A promising alternative method for the incorporation of silica in the rubber matrix is the goal of this thesis. The novel method involves precipitation of silica particles in rubber latex followed by coagulation of the latex to get silica filled rubber i.e. in situ precipitation of silica. Precipitation of silica was done by the reaction between sodium silicate and ammonium chloride in concentrated natural rubber latex. By varying the amount of sodium silicate and ammonium chloride, precipitation of different concentration of silica was carried out. Analysis of the silica filled rubber coagulum showed that silica is uniformly distributed in the rubber matrix and there exists a strong rubber filler interaction. Analysis of the physical, chemical, thermal and morphological characteristics of in situ precipitated silica are also carried out in comparison with commercial nano silica VN3. The results showed that in situ precipitated silica is superior to the commercial nano silica (VN3) in its physical characteristics. Morphological studies revealed that in situ precipitated silica has lower particle size with a honeycomb structure. USAXS Studies confirmed that the silica present in the rubber matrix has little modification with the silica obtained from the ignition of the silica filled coagulum. Analysis with TEM showed that the particle size of in situ precipitated silica is less than 20nm when it is prepared at a concentration of 20phr. It showed uniform distribution at about 20phr, which is confirmed by the bound rubber content. Since it is having a non spherical shape, it can contribute to improved rubber reinforcement. SEM and TEM studies revealed that the particle agglomeration increases with increase in concentration of silica and increase in dilution of the rubber matrix.

Natural rubber composites were prepared with the in situ precipitated silica-rubber mixes of different silica content. Tensile properties of these composites showed that the reinforcing capacity of in situ precipitated silica increases with silica content and decreases at higher concentrations. Bound rubber content, effluent loss of silica and tensile properties revealed that 20phr silica is an optimum concentration for the preparation of composites. Mixing of in situ precipitated silica with carbon black also showed comparable values of mechanical properties with conventional silica indicating that compounds can be prepared with carbon black partly replaced by silica. The vulcanizates prepared by this novel technique showed superior mechanical properties compared to those prepared from commercial silica's. Rubber filler interactions were studied by strain sweep measurements in Rubber Process Analyser. The latex precipitated silica is found to have better rubber- filler interaction compared to commercial silica's. It is also found that composites of any silica concentration can be prepared by mill mixing of silica master batch with dry rubber. Swelling index values and crosslink density showed that the rubber filler interaction is more in the in situ precipitated silica compounds. Similarly properties like ageing resistance and permeability showed improved values. In view of the fact that we got encouraging results in the application of in situ precipitated silica in concentrated NR latex to prepare composites, this method was tried in the field latex also. In situ precipitation of silica in field latex can give the same or better properties if the viscosity of the latex is increased. It is found that silica precipitated from latex mixed with Carboxy methyl cellulose showed superior properties.

Evaluation of Epoxidised natural rubber as a reinforcement modifier in latex stage precipitated silica filled NR was made in comparison with silane modified silica filled NR. ENR is a modified form of natural rubber with inherent reinforcement. Presence of ENR in the rubber matrix during precipitation of silica has improved the distribution of silica in the rubber matrix. Preparation of silica mixes with in situ silica coupled with ENR showed a significant reduction in the Mooney viscosity. This helps in the processing of the silica mix. The mechanical properties of the composites containing in situ precipitated silica were compared with that of conventional silica with and without Si 69. It is observed that in situ precipitation of silica gives reinforcement equivalent to that of using Si 69. In situ precipitation in presence of ENR showed further improvement in the mechanical properties indicating that ENR has a coupling effect in silica filled rubber composites. Composites prepared with ENR showed improved bound rubber content and rubber filler interactions. ENR is found to act as a coupling agent for in situ silica and give improved technological properties when compared with Si 69.

Gum vulcanizates of synthetic rubbers are generally weak and it is essential to use reinforcing fillers to produce products of high strength. Acrylo nitrile butadiene rubber that is called as Nitrile rubber (NBR) is selected as polar rubber and the possibility of in situ precipitation of silica in NBR latex was examined. The properties of the composites filled with in situ precipitated silica were compared with that of conventional silica. In situ precipitation of silica was carried out in NBR latex using sodium silicate and ammonium chloride. The silica filled latex is coagulated, dried and kept as masterbatch. Compounds with silica composition varying from 1phr to 15 phr were prepared and vulcanised up to the optimum cure time. The mechanical properties of the vulcanizates are compared with reference compounds prepared from block NBR and commercially available silica. The study showed that silica can be incorporated in NBR latex by precipitation procedure to prepare rubber compounds. The vulcanizates prepared by this novel technique show superior mechanical properties compared to those prepared from commercial silica's. The latex precipitated silica is found to have better rubber- filler interaction compared to commercial silica's. Silica of any desired concentration can be incorporated in to the dry rubber by mill mixing of silica masterbatch with dry rubber or directly from the in situ precipitation of silica at the desired concentration in the latex.

Mixing of in situ precipitated silica with carbon black also showed comparable values of mechanical properties, indicating that compounds can be prepared with carbon black partly replaced by silica. Swelling index values and crosslink density showed that the rubber filler interaction is more in the in situ precipitated silica compounds. Similarly properties like ageing resistance and permeability showed improved values. The method is simple and cost reducing and fully effective in polar synthetic rubber like NBR.

It was observed that in situ precipitation of silica in polar synthetic rubber latex NBR improved the mechanical properties and rubber filler interactions. So the same method was studied in non-polar synthetic rubber latex, Styrene butadiene rubber (SBR). SBR is the most commonly used general-purpose synthetic rubber. In situ precipitation of silica was tried in the SBR latex and analysis of the silica mix and silica obtained from the silica mix after ignition were carried out. Composites were prepared with the silica mixes and their properties were compared with that of conventional silica. The study showed that in situ precipitation of silica could be successfully conducted in SBR latex.

In situ silica filled composites are found to give improved mechanical properties and rubber filler interactions when compared with commercial silica filled composites. Latex stage precipitation helps easier incorporation of silica and gives improved mechanical properties and rubber filler interactions.

The incorporation of silica in the latex stage seems to be a very promising technique for both tyre and non-tyre applications.

LIST OF ABBREVIATIONS AND SYMBOLS

ACN : Acrylo Nitrile
ASTM : American Society for Testing and Materials
BET : Brunauer, Emmett and Teller
BIS : Bureau of Indian Standards
BR : Polybutadiene rubber
CBS : N-cyclohexyl-2-benzothiazyl sulphenamide
CMC : Carboxy methyl cellulose
CR : Chloroprene rubber
CRI : Cure rate index
cc : Cubic centimeter
CP : Centi Poise
DMA : Dynamic mechanical analysis
dNm : Deci Newton meter
DEG : Di Ethylene Glycol
DSC : Differential scanning calorimetry
DOP : Dioctyl Phthalate
ENR : Epoxidised Natural Rubber
EB : Elongation at Break
G' : Storage modulus
G'' : Loss modulus
G^* : Complex modulus
g : Gram
FTIR : Fourier transform infrared
Gum : Rubber compound without fibre/filler
HAF : High Abrasion Furnace
hrs : Hours
Hz : Hertz
ISNR : Indian Standard Natural Rubber
ICPAES : Inductively Coupled Plasma Atomic Emission Spectrometer
min : Minutes
mol : Mole
M_H : Maximum torque
M_L : Minimum torque
MPa : Mega Pascal
NaOH : Sodium hydroxide
NR : Natural rubber

NBR : Acrylonitrile butadiene rubber
N/mm : Newton/ Millimeter
nm : Nano metre
PDMS : Poly dimethyl siloxane
phr : Parts per hundred rubber
pphm : Parts per hundred million
Pa : Pascal
R_B : Bound rubber content
SBR : Styrene butadiene rubber
SEM : Scanning Electron Microscope
Si 69 : Bis- (triethoxy silyl propyl) tetrasulphide
SiO_2 : Silica
TEM : Transmission Electron Microscope
TESPT : Bis- (triethoxy silyl propyl) tetrasulphide
THF : Tetra hydro furan
TEOS : Tetra ethoxy silane
tan δ : Loss factor
T_g : Glass transition temperature
TMTD : Tetramethyl thiuram disulphide
TGA : Thermo gravimetric analysis
UTM : Universal testing machine
USAXS : Ultra small angle X ray scattering
VN3 : Precipitated Nano silica, Ultrasil VN3
V_f : Volume fraction of rubber in swollen sample
V_i : Volume fraction of rubber in unswollen sample
V_τ : Change in volume fraction of rubber due to swelling
% : Percentage
°C : Degree Celsius
μm : Micro meter
A : Angstrom
ZnO : Zinc Oxide

SCIENTIFIC PUBLICATIONS

A. International/National journals

1. A novel route in preparing silica reinforced Natural rubber composites: **Rubber world, 2005, 238(5), 16.**
2. Epoxidised Natural Rubber as a coupling agent in *in situ* precipitated silica - natural rubber composites: **Journal of Rubber Research, 2006, 9(4), 204.**
3. In situ silica filled Nitrile rubber composites: **Progresses in Rubber Plastics and Recycling Technology** (in press).
4. Preparation of in situ precipitated silica filled Styrene Butadiene rubber composites and its comparison with commercial silica composites. **Journal of Elastomers and Plastics** (Communicated).
5. Latex Stage precipitation of silica in Natural rubber. **Journal of Applied Polymer Science** (Communicated).

B. International/National Conference papers

1. **A novel route for the preparation of silica reinforced natural rubber nanocomposites.** Presented at a meeting of the Rubber Division, ACS, Columbus, OH, October 5-8, 2004, Paper no. 67.
2. **Nanosilica: precipitation and use in natural rubber.** Presented at the International Conference on biotechnology held at CUSAT on 28-31 December 2004.
3. **A novel route for the precipitation of silica in styrene-butadiene and nitrile rubber lattices.** Presented at the International Seminar, Rubber Expo 2004, held at Mumbai, March 28-31.

4. **Epoxidised natural rubber as a coupling agent in *in situ* precipitated silica natural rubber composites.** Presented at Science Congress 2006, held at Thiruvananthapuram, 29-31 January 2006.

5. **Preparation of in situ precipitated silica based natural rubber composites using epoxidised natural rubber as coupling agent.** Presented at "Polymer 2006" National conference held at IACS, Kolkatta jointly organized by SPSI Kolkatta Chapter and IACS, on February 10-13, 2006.

6. **Silica reinforcement of nitrile rubber by in situ precipitation in the latex.** Presented at the "National Symposium on Bio medical and Natural materials" organized by the Material Research Society of India held at University of Lucknow, Lucknow, February 13-15, 2006

7. **Studies on in situ silica filled natural rubber composites.** Presented at the International Conference ISNRM, held at PR of China, 11-13 October 2006.

8. **Preparation of in situ silica filled styrene butadiene rubber composites.** Presented at the Asia Rubber Expo 2006, held at Kochi, 23-25 November 2006.

9. **Studies on in situ silica filled nitrile rubber composites.** Presented at Science Congress 2007, held at Kannur, 29-31 January 2007.

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