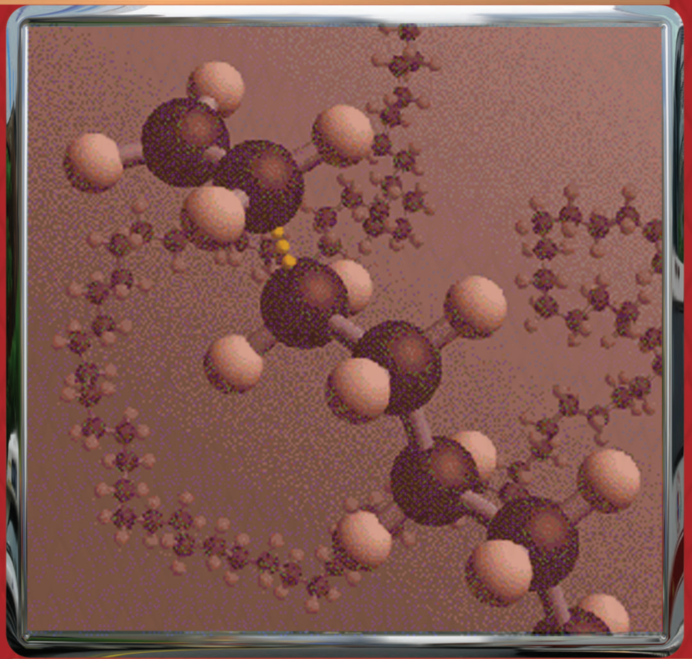
Ph.D Thesis

Studies on the use of nano zinc oxide and modified silica in NR, CR and SBR



P.M.SABURA BEGUM

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July 2009

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Studies on the use of nano zinc oxide and modified silica in NR, CR and SBR

Thesis submitted to the
Cochin University of Science and Technology
In partial fulfillment of the requirements
for the award of the degree of
Doctor of philosophy
in
Chemistry
Under the faculty of Science

By

P.M.SABURA BEGUM

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July 2009

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Dedicated to
my parents

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Certificate

This is to certify that the thesis entitled "**Studies on the use of nano zinc oxide and modified silica in NR, CR and SBR**", submitted by Mrs. P.M. Sabura begum in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy of Cochin University of Science and Technology, Kochi -22 is a record of the bonafide research work carried out by her under our supervision and guidance, in the Department of Applied Chemistry and Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-22 and no part of the work reported in the thesis has been presented for the award of any other degree.

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Declaration

I hereby declare that the thesis entitled "**Studies on the use of nano zinc oxide and modified silica in NR, CR and SBR**" submitted for the award of the degree of Doctor of Philosophy of Cochin University of Science and Technology is based on the original work done by me under the guidance of Dr. K. K. Mohammed Yusuff, Professor, Department of Applied Chemistry, and Dr. Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-682 022 and this work has not been included in any other thesis submitted previously for the award of any other degree.

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27 July 2009

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Preface

Nanotechnology is now recognized as one of the most promising areas of technological development in the 21st century. In materials research, the development of polymer nanocomposites is rapidly emerging as a multidisciplinary research area which can broaden the applications of polymers to the great benefit of many different industries. Polymer nanocomposites are polymers that have been reinforced with small quantities of nano-sized particles which have high aspect ratios. In contrast to conventional composites, where the reinforcing filler size is of the order of microns, polymer nanocomposites are exemplified by reinforcing fillers of the order of few nanometers. The large surface area in this nanosize filler can introduce dramatic improvement in properties.

Contents of the thesis

The main objective of the study was to upgrade the performance of rubber products (1) by reducing amounts of zinc oxide and (2) by modifying silica for easy incorporation in rubber. The thesis is divided into nine chapters.

A comprehensive introduction and review of literature pertaining to composites, nanoparticles and the various ingredients added during rubber compounding 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.

Preparation and characterization of nano zinc oxides (ZnO(p) and ZnO(s)) are presented in Chapter 3.

The use of nano zinc oxide in natural rubber compounds and their vulcanizates is given in Chapter 4.

Use of zinc oxides (ZnO(p) and ZnO(s)) in typical polar synthetic rubber (polychloroprene) compounds and their vulcanizates is given in Chapter 5.

The use of prepared zinc oxides as activator in a typical non polar synthetic rubber (styrene butadiene rubber) is presented in Chapter 6.

Modification of precipitated silica surface with antioxidants (derivatives of p-phenylenediamines) and the effect of the use of modified silica in comparison to unmodified silica in natural rubber, polychloroprene and styrene butadiene rubber compounds and their vulcanizates are presented in Chapter 7.

Preparation and characterization of mesoporous silica and rice husk silica from low cost silica source are presented in Chapter 8. The use of modified mesoporous silica and modified rice husk silica in natural rubber compounds and their vulcanizates in comparison to the unmodified form is also presented in this chapter.

The summary and conclusions of the study are presented in Chapter 9.

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Chapter I

Introduction

1.1 Composites

Composite materials are well known to mankind since pre-historic times and used for many applications. But with the development of polymers and polymer science, the concept and technology have undergone a sea change in the understanding of the basics like the role of matrix and reinforcement, bonding mechanism, morphological features, environmental effects etc.

Polymer composites due to their light weight, chemical and corrosion resistance and heterogeneous nature provide unlimited possibilities. Their unique flexibility in design and tailoring and other characteristics such as ease of manufacturing, high specific strength, stiffness, corrosion resistance, durability, adaptability and cost effectiveness have attracted the attention of engineers, material scientists and technologists. They have become materials of the 21st century to meet the requirements of space, missile, marine and medical aid technologies. Various additives are incorporated to these materials to modify their properties in the processing stage. Fillers constitute the largest bulk of these additives, especially in the case of rubber products. The introduction of mineral fillers, which are finely dispersed in rubber, induces substantial changes in their physicochemical and mechanical properties, which are caused by the mobility of the macromolecules in the boundary layers, the orienting behaviour of the filler surface and by different types of filler-polymer interactions.

1.1.1 Definition and importance of composites

Composites are combination of two materials, in which one of the materials, called the reinforcing phase, is in the form of fibres, sheets or particles and is embedded in the other materials called the matrix phase. The reinforcing material and the matrix material can be metal, ceramic or polymer. Typically, reinforcing materials are strong with low densities, while the matrix is usually a ductile or tough material. If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve combination of desirable properties not available in any single conventional material.[1]

Designers of structures have been quick to capitalize on the high strength-to-weight or modulus-to-weight ratios of composites. But there are other advantages as well as some disadvantages. The advantages include: weight reduction (high strength- or stiffness- to weight ratio), tailoring properties (strength of stiffness can be tailored to be in the load direction), redundant load paths (fiber to fiber), longer life (no corrosion), and lower manufacturing costs, inherent damping and increased (or decreased) thermal or electric conductivity. The disadvantages include: high cost of raw materials and fabrication, possible weakness of transverse properties, weak matrix and low toughness, environmental degradation of matrix, difficulty in attaching and problems associated with analysis. Proper design and material selection can avoid many of the disadvantages.

Over recent decades, many new composites have been developed, some with very valuable properties. By choosing an appropriate combination of reinforcement and matrix material, manufacturers can produce properties that exactly fit the requirements for a particular structure for a particular purpose.

Individual polymer can not provide all the superior properties like strength, low thermal coefficients, resistance to shock loads, resistance to thermal or chemical degradation etc. Fillers have important roles in modifying properties of various polymers. Mineral fillers, metals and fibers have been added to rubbers, thermoplastics, thermosets etc to form composites. The effect of fillers on properties of the composites depends on their concentration, their particle size and shape as well on their interaction with matrix.

1.1.2 Classification of composites

Composites can be classified in different ways

I Depending on the matrix system

- a. Polymer matrix composites (PMC)
- b. Ceramic matrix composites (CMC)
- c. Metal matrix composites (MMC)
- d. Rubber matrix composites (RMC).

II Depending on the occurence of composites

- a. Natural composites – (e.g., jute, silk, wood, bamboo)
- b. Man made composites – (e.g., glass reinforced fibre)

III Depending on the size of constituents

- a. Macrocomposites- consisting of macrosized particle like galvanized steel, helicopter blades etc.
- b. Microcomposites - comprising of metallic alloys, reinforced plastics etc.
- c. Nanocomposite – polymers having particles in the nano-size range.

IV Depending on structural components

a. Fibrous composites (composed of fibrous filler in matrix)
b. Laminar composites (composed of layers of materials)
c. Particulate composite (composed of particulate fillers in matrix)
d. Skeletal composites (composed of continuous skeletal matrix filled with a second matrix)

1.2 Nanomaterials

Nanomaterials serve as a bridge between the molecular and condensed phase.[2-3] The thousands of substances that are solids under normal temperatures and pressures can be subdivided into metals, ceramics, semiconductors, composites and polymers. These can be further subdivided into biomaterials, catalytic materials, coatings, glasses and magnetic and electronic materials. All of these solid substances, with their widely variable properties taken on another subset of new properties when produced in nanoparticle form.

1.2.1 Classification of nanomaterials[4]

***Cluster*:** A collection of units of up to about 50 units.

***Colloid*:** A stable liquid phase containing particles in the 1-1000nm range.

***Nanoparticle*:** A solid particle in the 1-100nm range that could be nanocrystalline, an aggregate of crystallites or a single crystallite.

***Nanocrystal*:** A solid particle that is single crystal in the nanometer size range.

***Nanostructured or nanoscale material*:** Any solid material that has a nanometer dimension; three dimension–particles; two dimension-thin films; one dimension-thin wire. Metals, semiconductors, ceramics belong to this class.

Nanophase material: They are same as nanostructured material.

Quantum dot: A particle that exhibits a size quantization effect in at least one dimension.

1.2.2 Preparation of nanomaterials

There are two general ways available to produce nanomaterials. The first way is to start with bulk material and then break it into smaller pieces using mechanical, chemical or other form of energy (top-down). An opposite approach is to synthesize the material from atomic or molecular species via chemical reactions and allow the precursor particles to grow in size (bottom-up). Both approaches can be done in either gas, liquid, super critical fluids, solid states or in vacuum.[5-9] Most of the manufacturers are interested in the ability to control: a) particle size b) particle shape c) size distribution d) particle composition e) degree of particle agglomeration.[10-12]

Process used for bottom–up manufacturing[13]

Methods to produce nanoparticles from atoms are chemical processes based on transformations in solution. (e.g., sol-gel processing, chemical vapour deposition (CVD), plasma or flame spraying synthesis, laser pyrolysis,[14] atomic or molecular condensation. These chemical processes rely on the availability of appropriate "metal-organic" molecules as precursors. Sol–gel processing differs from other chemical processes due to its relatively low processing temperature. This makes the sol–gel process cost effective and versatile. In spraying processes, the flow of reactants (gas, liquid in form of aerosols or mixtures of both) is introduced to high-energy flame produced by plasma spraying equipments or carbon dioxide laser. The reactants decompose and particles are formed in a flame by homogeneous nucleation and growth. Rapid cooling results in the formation of nanoscale particles.

Sol – gel process

The sol–gel technique is a long established industrial process for the generation of colloidal nanoparticles from liquid phase, which has been further developed in last years for the production of advanced nanomaterials and coatings.[15] Sol-gel processes are well adapted for oxide nanoparticles and composites nanopowder synthesis. The main advantages of sol-gel techniques for the preparation of materials are low temperature of processing, versatility and flexible rheology allowing easy shaping and embedding. They offer unique opportunities for access to organic-inorganic materials.[16-18] The most commonly used precursors of oxides are alkoxides, due to their commercial availability and to the high liability of the M-OR bond allowing facile *tailoring in-situ* during processing

Aerosol-based process

Aerosol-based process is a common method for the industrial production of nanoparticles. Aerosols can be defined as solid or liquid particles in a gas phase, where the particles can range from the size of molecules up to 100μm in size. Aerosols were used in industrial manufacturing long before the basic science and engineering of the aerosols were understood. For example, carbon black particles used in pigments and reinforced car tyres are produced by hydrocarbon combustion; titania pigment for use in paints and plastics is made by oxidation of titanium tetrachloride; fumed silica and titania are formed from respective tetra chloride by flame pyrolysis and optical fibers are manufactured by similar process.

Traditionally, spraying is used either to dry wet materials or to deposit coatings. Spraying of the precursor chemicals onto a heated surface or into the hot atmosphere results in precursor pyrolysis and formation of the particles. For example, a room temperature electro–spraying process was developed at Oxford University to produce nanoparticles of compound,, semiconductors and some metals. In particular, CdS nano particles were produced by generating aerosol micro-droplets containing Cd salt in the atmosphere containing hydrogen sulphide.

Chemical vapour deposition (CVD)

CVD consists in activating a chemical reaction between the substrate surface and a gaseous precursor. Activation can be achieved either with temperature (thermal CVD) or with a plasma[19] (PECVD: Plasma Enhanced Chemical Vapour Deposition). The main advantage is the nondirective aspect of this technology. Plasma allows decreasing significantly the process temperature compared to the thermal CVD process. CVD is widely used to produce carbon nanotube.

Atomic or molecular condensation

This method is used mainly for metal containing nanoparticles. A bulk material is heated in vacuum to produce a stream of vapourized and atomized matter, which is directed to a chamber containing either inert or reactive gas atmosphere. Rapid cooling of the metal atoms due to their collision with the gas molecules results in the condensation and formation of nanoparticles. If a reactive gas like oxygen is used, then metal oxide nanoparticles are produced.

Super critical fluid synthesis

Methods using supercritical fluids are also powerful for the synthesis of nanoparticles. For these methods, the properties of a super critical fluid (fluid forced into supercritical state by regulating its temperature and its pressure) are used to form nanoparticles by a rapid expansion of a supercritical solution. Supercritical fluid method is currently developed at the pilot scale in a continuous process.

Mechanical process

These include grinding, milling and mechanical alloying techniques. Provided that one can produce a coarse powder as a feed stock, these process utilize the age-old technique of physically pounding coarse powders into finer and finer ones, which is similar to the grinding flour mills. Today, the most common processes make use of either planetary or rotating ball mills. The advantages of these techniques are that they are simple and require low-cost equipment. However, there can be difficulties such as agglomeration of the powders, broad particle size distributions and contamination from the process equipment itself. Often there would be difficulty in getting the very fine particle sizes with viable yields. It is commonly used for inorganic materials and not for organic materials.

Using templates to form nanoparticles

Any materials containing regular nano-sized pores or voids can be used as a template to form nanoparticles. Examples of such templates include porous alumina, zeolites, diblock co-polymers, dendrimers, proteins and other molecules. The template does not have to be a 3D object. Artificial templates can be created on a plane surface or on a gas-liquid interface by forming self-assembled mono layers.

1.3 Polymer matrices - Elastomers

Different types of polymers are used as matrices in composites. Elastomers are one of the most interesting materials on account of its range of applications. These polymers have unique properties of deformation and elastic recovery after vulcanization with sulphur or other cross linking agent, which in effect change the polymer from thermoplastic to thermosetting. Natural rubber (NR) is a commonly used rubber and has been used for the production of different products.

Rubbers are broadly classified into natural and synthetic. Synthetic rubbers are further classified into two categories namely general purpose rubbers - like SBR , BR etc. which are intended for the manufacture of tyres and general mechanical products and special purpose rubbers -NBR, CR etc which have special properties and are in consequence intended for specialized applications.

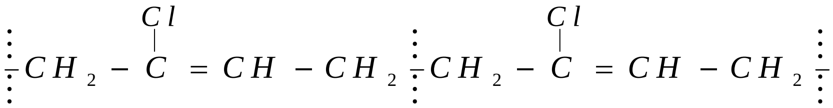
1.3.1 Natural rubber (NR)

Natural rubber is made up of 1, 4 isoprene units arranged in a highly stereo regular manner. The molecular weight of the polymer ranges from 10^5 to 10^6 and it varies widely.[20] Due to the high structural regularity, NR tends to crystallize on stretching. This strain induced crystallization gives high tensile strength for its gum vulcanizates. NR is preferred in many areas of application because of its superior building tack, green strength, better processibility, high resilience and excellent dynamic properties. Natural rubber is a versatile and adaptable material which has been successfully used for transport and engineering applications such as automobile tyres, aerotyres, off-shore and aerospace industries, civil engineering, railways, vibration engineering etc. Though natural rubber exhibits very good strength even without reinforcement by fillers, excepting a few latex products, most of the rubber products require reinforcement.[21] 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) are superior especially for hardness, tensile strength, compression set properties and density.[22] 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 work on the challenges, modifications and behaviour are being carried out to a greater extent. Influence of polymer-filler interactions on retraction behaviours of natural rubber vulcanizates reinforced with silica and carbon black[23] has been studied. Recently, Varkey et al. have reported the feasibility of using epoxidised natural rubber as a reinforcement modifier for silica filled rubbers.[24]

1.3.2 Chloroprene rubber (CR)

Polychloroprene (Neoprene) comes under special purpose rubbers. This rubber is used in specific applications which require solvent resistance, fire resistance and thermal resistance.

The structural formula of CR is as follows



$$\vdots\, CH_2 - \overset{\overset{Cl}{|}}{C} = CH - CH_2 \,\vdots\, CH_2 - \overset{\overset{Cl}{|}}{C} = CH - CH_2 \,\vdots$$

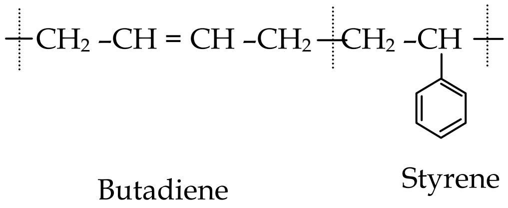
Chloroprene unit

CR is a polar rubber because it contains one chlorine atom for every four carbon atoms in the chain of homopolymers. Therefore, CR has a better resistance to swelling in mineral, animal and vegetable oils and fats when compared to hydrocarbon rubbers except NBR. The chlorine atoms also impart to CR a better flame, weather and ozone resistance than that normally encountered with diene rubbers. These properties are particularly enhanced in copolymers of chloroprene and dichlorobutadiene because of the higher chlorine content in the copolymer. The tendency to crystallize depends primarily on CR type. CR grades with little or moderate tendency towards crystallization are used in many different technical rubber goods which are resistant to flame, oils and fats, weathering and ozone. These rubber goods include mouldings, extrusions, seals, hoses, profiles, rolls, belts, V-belts,[25] bearings, linings, rubberized fabrics, shoe soling and many applications in the construction industry (e.g., window and construction profiles, roofing membranes and cable jackets). For the latter application, the CR grades with a moderate crystallizability are often preferred. Strongly crystallizable CR grades are commonly used for the production of contact adhesives.[26]

The polymers are prepared by emulsion polymerization using free-radical polymerization. Unlike other elastomers, chloroprene is not vulcanized with sulfur or peroxides. Its general physical properties are enhanced by compounding it with metallic oxides such as zinc oxide and magnesium oxide.

1.3.3 Styrene butadiene rubber (SBR)

Styrene butadiene rubber is a non-polar synthetic rubber that is the most commonly used general-purpose synthetic rubber. It is produced by the copolymerization of butadiene and styrene under controlled conditions of reactions using different techniques of polymerization.[27] Different reaction conditions give different products. Emulsion grade SBR is divided into two categories, cold and hot. SBR is also produced by solution process and is called solution SBR. The products vary in chemical nature also, as butadiene polymerizes in three different ways, namely, cis-1,4, trans-1,4 and vinyl. SBR can be considered as a general purpose rubber, since it is used in many applications and especially in tire components. Besides NR, it constitutes the most important rubber.[28] The structural formula of SBR is as follows.



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 lesser tendency for scorching. 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.

Styrene butadiene rubber (SBR), the widely used and easily available synthetic rubber, has unique place among elastomers. This is because practically all automotive tires use SBR, especially in the tread, due to its wear advantage over natural rubber treads.

1.4 Compounding ingredients

In most of the rubber formulations there are many ingredients, which are meant for specific purposes. Developments of rubber formulations that are environmentally safe, factory-processible, cost-competitive with other compounds in the same applications and are able to provide satisfactory properties and service life are getting much importance. These requirements put considerable demands on the compounder, who must have extensive knowledge of materials having these properties in elastomer products. Generally in rubber compounding, we can classify the materials based on their functions. These include vulcanizing or cross linking agents, accelerators, activators retarders, process aids, softeners and plasticizers, fillers and other miscellaneous materials.

The cross linking efficiency of some vulcanizing agents in natural rubber was assessed by Lorenz and Parks.[29-30] It is generally assumed that the presence of filler might affect the efficiency of the curing agent. The filler-curing agent interaction might influence the rate of cross linking which give vulcanization rates in filled stocks different from those in gum stocks. Pal et al.[31-32] have studied the effect of reinforcing black, silica and clay on vulcanization.

1.4.1 Zinc oxide

Zinc oxide is one of the basic components of rubber compounds. It acts as an activator of rubber cross linking by sulphur or sulphur donors. It increases the amount of bound sulphur as well as the efficiency of crosslink system. Borros and Agullo[33] made an investigation on the effect of sulphenamide accelerating system on natural rubber vulcanizations and on the active role of zinc oxide and the olefinic chain in NR. Recently Kruger and McGill have published papers on the interactions between the components of the cross linking systems.[34-35]

Importance of ZnO[36]

Perhaps the most common use of zinc is for healing and protecting the skin. Zinc oxide has been used for generations to soothe diaper rash and relieve itching. Zinc oxide is a natural sunscreen to protect chopped lips and skin from the sun's UV rays. Zinc sulfate can be taken orally to effectively treat acne, while it also comes in a topical form to improve healing of wounds caused by surgical incision, burns or other skin irritations. Zinc alleviates sun burns and blisters and can also be used as an anti-inflammatory.

In rubber

The rubber industry, in its development over the past one hundred years, has utilized an increasing number of the many optical, physical and chemical properties of ZnO. ZnO proved the most effective activator to speed up the rate of cure with the new accelerators. Heavy-duty pneumatic tyres carry high loadings of ZnO for heat conductivity as well as reinforcement since heat build-up is critical at their higher operating speeds compared with their solid-rubber counterparts.

a. Activation

In the curing process for natural rubber and most types of synthetic rubbers, the chemical reactivity of ZnO is utilized to activate the organic accelerator.

The unreacted portion of the ZnO remains available as a basic reserve to neutralize the sulphur–bearing acidic decomposition products formed during vulcanization. Adequate level of ZnO contributes markedly to chemical reinforcement; scorch control, and resistance to heat ageing and compression fatigue.

b. Acceleration

Zinc oxide serves as the accelerator with some types of elastomer and the cross linking, which it induces, takes several forms. With some systems, ZnO is an effective co-accelerator in the vulcanization process.

c. Biochemical activity

ZnO is useful in the preservation of plantation latex as it reacts with the enzyme responsible for the decomposition. The oxide is also a fungistat, inhibiting the growth of such fungi as mold and mildew.

d. Heat stabilization

ZnO similarly retards devulcanization of many types of rubber compounds operating at elevated temperatures.

e. Latex gelation

In the production of latex foam rubber products, ZnO is particularly effective in gelation of the foam with sufficient stability.

f. Light stabilization

ZnO is outstanding among white pigments and extenders for its absorption of ultraviolet rays. Thus, it serves as an effective stabilizer of white and tinted rubber compounds under prolonged exposure to the destructive rays of the sun.

g. Pigmentation

Through its high brightness, refractive index, and optimum particle size, ZnO provides a high degree of whiteness and tinting strength for such rubber products as tyre sidewalls, sheeting and surgical gloves.

h. Reinforcement

ZnO provides reinforcement in natural rubber, and in some synthetic elastomers such as polysulfides and chloroprene. The degree of reinforcement appears to depend upon the combination of the particle size of the oxide, the finest size being the most effective, and the reactivity of the oxide with the rubber.

Under such service condition involving rapid flexing or compression, ZnO also provides heat conduction to more rapidly dissipate the heat and thereby provides lower operating temperatures. In addition, it imparts heat stabilization by reacting with acidic decomposition products.

i. Rubber- metal bonding

In the bonding of rubber to brass, ZnO reacts with copper oxide on the brass surface to form a tightly adhering zinc-copper salt.

j. Tack retention

One of the unique properties of ZnO is its ability to retain over many months of shelf-storage the tack of uncured rubber compounds for adhesive tapes.

In plastics

Zinc compounds can provide a variety of properties in the plastics field. Heat resistance and mechanical strength are imparted to acrylic composites by ZnO. ZnO contributes to the formation and cure of epoxide resin. Addition of ZnO to epoxy resins cured with aliphatic polyamines imparts higher tensile strength and water resistance. ZnO imparts fire-resistant properties to nylon fibers and mouldings. ZnO is also useful in the preparation of nylon polymers and in increasing their resistance. The formation of polyesters in the presence of ZnO imparts higher viscosity and other improvements. ZnO reacts with unsaturated polyesters to form higher viscosity and a thixotropic body. The dye ability of polyester fibres is improved by ZnO. ZnO mixtures stabilize polyethylene against ageing and ultraviolet radiation. ZnO increases the transparency of poly(chlorofluro-ethylene) moulding resin. Polyolefins are improved in colour, tensile strength, and vulcanization properties by addition of ZnO. Thermal stabilization of PVC is effected by ZnO. Antistatic, fungistatic and emulsion stability are additional properties imparted to vinyl polymers by ZnO.

Applications in development for ZnO-stabilized polypropylene and high-density polyethylene include safety helmets, stadium seating, insulation, pallets, bags, fiber and filament, agricultural and recreational equipment.

Ceramics

The properties imparted by ZnO to some of the newer applications are as electronic glass, low-melting glass for metal-to-glass seals, thermistors for use as lighting arresters and as devitrified glasses of low thermal expansion.

ZnO imparts a unique combination of properties when used in glass. ZnO reduces the coefficient of thermal expansion, imparts high brilliance and luster and high stability against deformation under stress. As a replacement flux for the more soluble constituents, it provides a viscosity curve of lower slope. The specific heat is decreased and the conductivity increased by the substitution of ZnO for BaO and PbO.

Pharmaceutical industry

ZnO is mainly used in zinc soap, ointment, dental inlays, food powders etc. ZnO forms an indispensable element of the production process of this industry.

Cosmetics

The optical and biochemical properties of ZnO and its derivatives impart special features to a variety of cosmetic preparations for care of the hair and skin. In powders and creams it protects the skin by absorbing the ultraviolet sunburn rays; in burn ointments it aids healing.

Simple salts of zinc provide astringent and skin conditioning properties to creams, while more complex salts furnish fungistatic properties which contribute to the effectiveness of deodorants, soaps and antidandruff preparations.

Adhesives, mastics, sealants

ZnO has long been a major constituent of surgical and industrial tapes based on natural or synthetic rubber as it is outstanding in retention of tack during shelf-ageing.

Neoprene adhesives are improved by the addition of both phenolic resins and zinc compounds (including ZnO). The reaction products impart special properties such as high heat resistance, high bond strength, improved peel and shear–stress resistance, and stability to settling of neoprene solution adhesives.

Paints

Zinc oxide in organic coatings provides a broad spectrum of properties: optical, chemical, biochemical and physical. Over the past century the paint industry, in its constant development of improved products, has utilized various aspects of those properties to high degree.

Manufacturers discovered that they could produce coatings of brushing consistency and good suspension properties by incorporation of ZnO into their pastes. Painters noted that they furnished better hiding power, whiteness, cleaner tints, tint retention and durability as well as nondarkening in the presence of sulfur fumes. French-process ZnO has been proved superior to American-process type in fungus resistance and less sulphide staining.

Metal – protective coatings

Zinc metal powder (zinc dust) and zinc compounds have long been utilized for their anticorrosive properties in metal-protective coatings, and today they are the basis of such important especially metal primers as zinc chromate primers.

Zinc dust-ZnO paints are especially useful as primers for new or weathered galvanized iron. Such surfaces are difficult to protect because their reactivity with organic coatings leads to brittleness and lack of adhesion. Zinc dust- ZnO paints however, retain their flexibility and adherence on such surfaces for many years. These paints also provide excellent protection to steel structures under normal atmospheric conditions, as well as to steel surfaces in such under-water conditions as dam faces and the interior of fresh water tanks.

Fire retardants

ZnO and its derivatives were used extensively in fire retardants for the military in World War II and those zinc compounds have since been the subject of extensive research and development for preparation of fire-retardant compositions for a variety of substances. Solutions for fireproofing textiles contain ZnO, boric acid, and ammonia in various proportions. It deposits water-insoluble zinc borate on the fibers.

Ferrites

ZnO continues as an essential ingredient in the "soft" type of ferromagnetic materials for television, radio, and tele-communication applications. In these fields ferrites based on magnetite, nickel oxide and ZnO are used as elements in many types of electronic devices.

Numerous electronic instruments for the consumer market utilize ferrites to impart specific functions. In portable and car radios, the antenna cores are ferrites designed to provide highly selective tuning. Television picture tubes constitute a major market for ferrites, particularly for use in fly back transformers and deflection yokes. In the communications area, ferrites are extensively used in the filter inductors of telephone circuit to permit precise inductance adjustment for the purpose of separating channels. Magnetic tape for recorders is improved by use of a magnetite precipitated in the presence of ZnO.

Thermoelements

ZnO plays an important role in semiconductor ceramic elements for operation at elevated temperatures or high voltages. Such thermoelements can be produced to cover a broad range of thermal and electrical properties. Varistors are composed of semiconductor ZnO modified by other oxides. Developed for use as lightning arrestors and high-voltage surge arrestors in electric transmission lines, they are based on a unique electronic property of semiconductor ZnO, nonlinear resistance. ZnO varistors have high-temperature stability and resistance to humidity, electrical load and current shocks.

Portland cement

The beneficial effects of ZnO additions to Portland cement have long been known. They are retardation of setting and hardening (to reduce the rate of heat evolution), improvement in whiteness and final strength.

1.4.2. Classification of fillers

Among the various compounding ingredients, fillers become one of the most important components in the manufacture of rubber products, with consumption second to rubber. Fillers are widely used to enhance the performance of rubbers and other polymeric materials. In certain cases they lower the cost of production of the final products. They influence almost all properties, including density, hardness, tensile strength, impact strength, chemical resistance, heat distortion temperature, processability and even the appearance of the final products.

Filler may either be active or inactive according to the mutual interaction between filler and polymer. This classification is rather arbitrary since it is based on the difference in chemical composition and characteristics of filler-particle surfaces, particle shape, size and treatment of surfaces by coupling agents. The filler activity is controlled by the mutual adhesion of the polymer and filler; it corresponds to the physicochemical character of the polymer-filler interface, which determines the extent of sorption process on the solid surface as well as the type of polymer-filler bonds. The results of many studies describing the different aspects of filler-polymer interaction are available in the literature.[37-38]

Today there are hundreds of commercial fillers providing a performance range from non-reinforcing to highly reinforcing; giving the rubber compounder a wide choice of cost benefit option. Fillers used in rubber compounds are generally classified into black and non-black fillers.

1.4.2a. Carbon blacks

The primary purpose of using carbon black with rubber is to reinforce it. Incorporation of carbon black into rubber gives enhanced modulus, improved fatigue and abrasion resistance and better overall performance. Five types of carbon blacks, based on manufacturing method, are used in rubber compounds, which are

1. Lamp black
2. Channel black
3. Thermal black
4. Acetylene black
5. Furnace black

The acetylene carbon is a coarse, very high-structure black, produced from acetylene gas in an exothermic reaction. Its principal use in the rubber industry has been that of a conducting carbon. Thermal blacks are made by the thermal decomposition of natural gas and are of two types medium thermal (MT) and fine thermal (FT). Today the channel process furnishes two grades of carbon blacks differing essentially in fineness, they are easy processing channel (EPC) and medium processing channel (MPC). The most popular blacks are those made by the oil furnace process. The furnace process produces a series of carbon blacks such as general-purpose furnace (GPF), fast extrusion furnace (FEF), high abrasion furnace (HAF), super abrasion furnace (SAF) etc.

As surface area of the black particle increases, the viscosity of the uncured stock increases, mixing takes longer and the smoothness of the extrusion increases. In the vulcanizate, abrasion resistance, tear strength, cut growth and flex resistance increase along with tensile strength and modulus. Increasing structure decreases tensile strength but increases modulus, hardness and abrasion resistance. In the ASTM D 1765 classification for carbon blacks about 42 commercial blacks were recognized.

1.4.2b. Non-black fillers

Non-black reinforcing fillers for rubber include hydrated silica, calcium silicate, zinc oxide, the fine particle size precipitated calcium carbonate etc. The use of coupling agent is more relevant with these non-black fillers.[39-42] Reinforcement by silica and silicates has been reviewed by Wagner.[43] 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.[44-46] 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.[47]

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.[48] 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.[49]

$$Na_2SiO_3 + HCl \rightarrow 2NaCl + H_2O + SiO_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots 1.1$$

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

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.2$$

The reaction products are quenched immediately after coming out of the burner. Pyrogenic silica is too active and expensive.[50] 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 colored products, shoe soling, tyres and other mechanical rubber goods. Fumed or pyrogenic silica is silicon dioxide containing less than 2% combined water. These silica particles are highly reinforcing fillers of very small particle size, giving high tensile strength, tear resistance and abrasion resistance particularly to silicon rubbers.[45]

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 15-20μm and for fumed silica it is about 15μm 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 is not sufficient enough to disperse primary filler particles in the rubber.[51]

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.[50] The higher the shear forces, the better the dispersion.

Reinforcement by fillers

Reinforcement is the enhancement of tensile strength, modulus, abrasion and tear resistance obtained by adding a material like fillers. Active fillers called reinforcing fillers, interact with polymer molecules through Van der Waals forces, chemisorption forces and eventually covalent forces. It is possible to create chemical bonds with the surface of the filler particles using coupling agents. Reinforcing agents are substances having shape and structures such as short fibrous forms or powdery form, and are impregnated with polymers and the moulded product thus obtained possess remarkable mechanical properties. Interaction between carbon black and polymer are one of the most important mechanisms of carbon black reinforcement, often measured as bound rubber.[51] Bellander et al. studied the influence of pressure and temperature on bound rubber for carbon black-polybutadiene composites and concluded that elevated pressure and temperature increased the amount of bound rubber. The reinforcement of elastomers by particulate fillers, to a large extent depends on polymer properties, filler characteristics and processing methods.[52] The various filler characteristics that influence the elastometer reinforcement are as follows.

Surface area

The total surface area of the filler is the most important parameter that influences the reinforcement. Particle size naturally is directly related to surface area by simple geometric considerations, in the absence of porosity. Other factors like shape of particle, size distribution and pattern of particle packing etc, affect the total surface area of a given quantity of filler. In reality there is always a distribution of sizes that can be averaged in various ways[53] and particles are usually far from round.[54]

Porosity

Frequently particles are porous. In particular the presence of microspores, of diameters below 0.5 nm, excludes part of the particle surface from direct interaction with the larger elastomers molecules or segments, thereby influencing reinforcement. Carbon black particles with pores and cracks have surface area greater than blacks of similar size without such features. This leads to an increased number of particles per unit weight. Thus porous blacks gives decreased resilience and increased electrical conductivity when compared with equal weight loadings of non-porous blacks.

Wolff studied the chemical aspects of rubber reinforcement by fillers.[55] Bound rubber is regarded to be the result of rubber-to-filler interaction and is therefore often taken as a measure of surface activity of the filler, which is also a function of specific surface area.[56-58]

Morphology of aggregates

While elementary filler particles may be spherical, such particles have often coalesced into larger, irregular shaped aggregates. Moreover, such aggregates are most frequency united into larger agglomerates by attractive forces of the Van der Waals types. The extent of aggregation and agglomeration has a marked influence on the reinforcing properties of fillers. By comparing the reinforcing action of fillers in the same surface area range, the morphology is the major factor determining reinforcement. Highly structured aggregates typically have branches that form voids between them, where polymer can be occluded, which results in higher effective loading of the carbon black in an elastomeric compound. Skeletonisation method has been used for the first quantitative and direct measurement of branching in carbon black aggregates.[59]

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.[60] 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. 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.[61]

Hewitt reported that compound viscosity is directly related to the surface area of silica.[62] 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.[63] At about 20 nm size silica produces significantly higher viscosity than carbon black of comparable size.[64] Viscosity modification studies of rubbers filled with smaller particle size silica was reported by Dunnom.[65-66] Use of silane coupling agent in silica filled rubbers is an effective means of reducing viscosity of the compounds.[67]

Polymer-filler interaction

The reinforcement of elastomers by fillers is the physical expression of the microscopic balance at the rubber-filler interface and the interactions between the filler particles making up a filler network. The rubber-filler interface formed during the mixing process is primarily responsible for properties such as abrasion resistance, tensile stress at break, tear propagation resistance etc. The dispersion of the fillers depends on both the particle size and the structure of the primary aggregates and agglomerates.[68-70] During mixing, fracture of filler aggregates takes place.[71] Continued mixing decreases the number of inter-aggregate contacts and increases the average distance of separation of the aggregate from each other. Electron microscopic studies have shown the break down of aggregates to two third of their original size, with the extent of break down increasing with increased structure and increased polymer-filler interaction.[72]

The effects of interaction between the rubber and filler on the adhesion characteristics of elastomer compositions were studied by Kiselev and Vnukova.[73] When filler is introduced, adhesion interactions between the elastomer and the filler increase with decreasing size of the filler particles. The surface interaction between fillers and rubber molecules or network segments involves a range of bond energies from relatively weak Van der Waals force to very strong chemical bonds. In all cases, physical adsorption undoubtedly occurs to varying degrees depending on particular surface and molecular segments. 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.[74-76]

1.4.3 Mesoporous silica

Precipitated silica particles have been utilized successfully as rubber reinforcing fillers instead of carbon black.[77-81] The development of new mesoporous silica particles with properties different than that of the precipitated silica particles, specially their high BET surface area and their organized pore structures with pore sizes between 1.5-10 nm, make them potential materials in rubber reinforcing. It is well known that mesoporous silica materials are synthesized by synergistic self assembly between surfactant and silica species to form mesoscopically ordered composites.[82-83] Generally two types of surfactants are used for the formation of mesoporous silica materials. Ionic surfactants such as alkyltrimethylammonium bromide[84] and nonionic surfactants such as alkylamine[85] and poly(ethylene oxide) -type copolymers.[86] The ionic surfactants interact electrostatically with inorganic species, whereas the nonionic surfactants result in the formation of mesocomposites through hydrogen bond or Van der Waals interaction. The nonionic surfactants give commercially important advantages compared with the ionic surfactants. They are easily removable, non-toxic, biodegradable and relatively inexpensive. Pinnavaia et al.[87] have reported the synthesis of MSU-X mesoporous materials with several nonionic surfactants. These materials are composed of worm-like channels, which are disorderedly arrayed. Stucky et al.[88] have reported the synthesis of SBA mesoporous silica materials, which have well-ordered channel and cage structures, using amphiphilic di and triblock copolymers as the structure directing agents at or below the isoelectric point (pH≤3). However these synthetic procedures using non-ionic surfactants are not as commercially viable as they might be due to the use of tetraethylortho silicate (TEOS) as a silica source.

Applications of mesoporous silica

Mesoscopically ordered mesoporous silica materials have attracted a wide interest since their discovery in the early 1990's due to their diverse potential application areas; including catalysis, filtration and chromatography. As the purely siliceous mesoporous materials have been shown to be biocompatible, or sometimes even bioactive, there is an increasing interest in this class of materials for applications in the field of bioceramics especially as bone substitute materials. Furthermore, the highly organized porous silica matrix could be used as a potential controlled drug release system. Another attractive advantage is that amorphous silica is degradable in an aqueous solution, and thus problems related to the removal of the material after use can be avoided.

Andersson et al.[89] describe the use of calcined mesoporous silica materials as pharmaceutical carrier systems for controlled drug release. The drug release abilities were investigated on a series of MCM-41 and SBA materials. Ibuprofen, a common non-steroidal anti-inflammatory pharmaceutical, was used as a model drug due to its size and possibility to interact with silanol groups in the pore walls of the siliceous materials. The major factor contributing to the release of a drug from a porous ceramic matrix, such as the mesoporous silica matrix, is the pore size. This was especially seen for the materials exhibiting a 2D hexagonal structure with cylindrical pores, where the release rate is increased in the order of μ SBA-3 < mSBA-3 < MCM-41.

Defect free siliceous mesoporous molecular sieve with composition of SiO_2 are electrically neutral and this leads to a lack of strong intrinsic surface acidity. Numerous attempts were made to incorporate transition metal atoms as well as main group elements into mesoporous silica. Substitution of trivalent cations such as B^{+3}, Ga^{+3}, Al^{+3} and Fe^{+3} [90-96] for silica in the wall of mesoporous silica, results a negative frame work charge, which can be compensated by protons providing catalytically active acid sites. The number of acid sites and strength is related to the amount and nature of the incorporated metal. These materials are used in acid catalyzed reaction and the main applications are in petroleum refining process.[97-98] The Ti, V and Cr containing MCM-48 molecular sieves are active catalysts for oxidative double bond cleavage of methyl methacrylate pyruvate and benzaldehyde as the dominant respective products.[99-101] Zr MCM-41 has been found to be active towards the dehydration of isopropyl alcohol.[102] A few reports describe the synthesis and characterization of mesoporous silica modified by metals like Mn[103] or Mo[104], which have been found to be catalytically active in the hydroxylation of phenol, 1-naphthol and oxidation of aniline with aqueous H_2O_2.

Besides variable pore diameters and large surface areas, mesoporous materials contain different types of silanol groups, i.e., external surface, internal surface and interstitial silanol groups. The interstitial silanol groups are not accessible in chemistry, but the other two groups can be functionalized by introducing functional organic groups. The silanol groups present at the surface of the walls are suitable for chemical bonding of organic ligands or anchoring inorganic species.[105-106] For example Ti, V, Zr or Mo grafted MCM-48 were used as a catalyst for the oxidation of bulky 2,6-di-tertbutyl phenol (2,6-DTBP) using hydrogen peroxide.[107] Mesoporous materials anchored with $AlCl_3$, $SnCl_2$, $Zn(O_2CMe)_2$ or $Mn(O_2CMe)_2$ have high stability and catalytic activity along with ion-exchange capacity.[108]

It has been reported that Co and Mo incorporated Al-MCM-41 shows higher hydrogenation and hydrocracking activities than Co-Mo/Al_2O_3 catalysts.[109]

Mesoporous silica particles exhibits certain specific properties as very fine size and good dispersion of the particles besides of its high surface area and porosity can give rise to strong interaction with styrene butadiene rubber as long as their degree of hydration before been processed is low.[110]

1.4.4 Rice husk silica

Rice has been one of the most important agricultural products of India since ancient time. It was cultivated not only for domestic consumption but also for export. Consequently several million tons of rice husks, which can be considered as agricultural waste, are obtained every year. It was found that when rice husk is burnt, the resulting black ash contains silica. However, this silica from rice husk carries too many impurities and exhibits some inferior properties. As a result, researches have been carried out to convert this rice husk into high purity amorphous silica.[111-112] It is common to use silica as reinforcing filler owing to the fact that silica is non-black filler, that has the highest reinforcing capacity. The presence of silica in rice husk has been known since 1938.[113] Silica is in hydrated amorphous form, either opal or silica gel. Rice husk on burning gives ash containing 90% silica, which is highly reactive due to its ultra fine size and high surface area.[114-116] Silica in these cases is at a nanoscale and scientists in India and abroad has been successful in harnessing this nanosized silica to manufacture silicon carbide that has hardness next only to diamond.[117] Silica is widely used in electronics, ceramics, and polymer material industries. Because the silicon atoms in the rice husk have been naturally and uniformly dispersed by molecular units, silica powder with very fine particle size and very high purity and surface area can be prepared under controlled conditions. The ash contains >90%

silica by mass with minor amounts of metallic elements. Extensive research has been carried out in order to explore the possibility of using silica from rice husk.

1.4.5 Antioxidants

Natural and synthetic polymers deteriorate on ageing in varying degrees as a result of the combination of a number of factors such as heat, light, oxygen and ozone. Thermal and light initiated oxidation in polymers proceeds by a free radical chain mechanism involving the formation of hydroperoxides, which can be summarized as below.

Initiation

$$\underset{(Polymer)}{R_H} \xrightarrow[\text{Conditions}]{\text{under oxidative}} R^\bullet + H^\bullet \qquad \text{……………………………(1.3)}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad \text{……………………………(1.4)}$$

Propagation

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \qquad \text{…………………………… (1.5)}$$

$$ROOH \rightarrow RO^\bullet + {}^\bullet OH \qquad \text{…………………………… (1.6)}$$

$$ROOH + RH \rightarrow RO^\bullet + R^\bullet + H_2O \qquad \text{…………………………… (1.7)}$$

Termination

$$ROO^\bullet + RO^\bullet \rightarrow \text{Inert products} \qquad \text{……..……………...(1.8)}$$

Impurities such as a low concentration of certain transition metal ions can greatly accelerate initiation through reduction and oxidation of hydroperoxides.

$$\mathrm{M}^+ + \mathrm{ROOH} \rightarrow \mathrm{M}^{++} + RO^\bullet + OH^- \qquad \text{…………………… (1.9)}$$

$$\mathrm{M}^{++} + \mathrm{ROOH} \rightarrow \mathrm{M}^+ + RO\dot{O} + H^+ \qquad \text{..………………… (1.10)}$$

The external manifestations of these reactions cause changes in physico-chemical properties and include decrease in strength and elongation at break, change in resistivity and colour etc. Thus the degradative processes impair the useful properties of polymers. Oxidative degradation of polymers can be retarded by appropriate antioxidants.[118-124]

Degradation by ozone

The unsaturation in diene based elastomers accounts for their high sensitivity to ozone attack. Ozone causes surface cracking of stressed or flexed vulcanized rubbers as a result of chain scission and formation of polymeric peroxide.

Inhibitors

Two broad groups of additives are used commercially to inhibit ozonolysis of unsaturated elastomers. One group includes relatively unreactive film forming waxes while the other group reacts with ozone, i.e., antiozonants. Wax protection alone is inadequate for products, such as tyres that flex in service causing film to break. In general the most effective class of antiozonant is N-N′disubstituted p-phenylenediamines, and continues to enjoy widespread growth, especially for tyre applications.[125]

Essentially three theories of antiozonant action have been developed.

1. The antiozonant blooms to the surface of the rubber compound and reacts preferentially with the incident ozone.
2. The antiozonant blooms to the surface of the rubber and forms a protective film on the surface.
3. The antiozonant reacts with intermediates formed in the ozonation of rubber preventing chain scission or recombining severed rubber chains.[126-128]

Antiozonant efficiency should therefore be dependent on the rate of diffusion of fresh antiozonant to the surface, rate of reaction of antiozonant with O_3 and the initial concentration of the antiozonant in the rubber phase.[129] Products of the ozonation of aromatic amines and diamines include oximes, hydroxylamines, nitroso and nitro compounds.[130-133]

Service requirement placed on many finished rubber products demand improved polymer stabilization. The effectiveness of antioxidants depends on two factors.

(a) Intrinsic activity of the antioxidant

This is the fundamental ability of the antioxidant and its transformation products to interfere with and retard the radical chain oxidation process, which in turn depend on the chemical structure of the antioxidant.

(b) Permanence of the antioxidant in the polymer

The concentration of the antioxidant in a polymer decreases during long term use, as a consequence of two process (1) chemical loss of antioxidant, (2) physical loss of antioxidant from the polymer.[134-138]

1.5 Scope and objectives of the work

The main objective of this study has been to develop more environment friendly, coloured and cheaper rubber products: (i) by reducing the amount of zinc oxide and (ii) by making the incorporation of silica easier. Release of zinc from rubber products occurs during disposal, recycling and also during service life. In view of the upcoming legislations and ecolabelling requirements for vehicle tyres, for instance, it can be stated that it is desirable to keep the ZnO content in rubber compounds as low as possible, not only from environmental considerations but also from economical reasons. The concern for a clean environment has gripped all development more than ever before. Rubber technology has also to adopt safer, cleaner and greener ways.

Since silica is hydrophilic and rubber is hydrophobic, uniformly distributing silica in rubber is extremely difficult and poses problems like high initial viscosity. Silica has a number of hydroxyl groups, which results in filler-filler particle agglomeration and reagglomeration. Incorporation of silica in rubber is quite difficult compared to that of carbon black. Carbon black and hydrocarbon rubbers are hydrophobic materials and the incorporation of carbon black in rubber is easy. To overcome this difficulty, it is proposed to modify silica surface with antioxidants.

The specific objectives of the work are

1. To prepare nano zinc oxide by precipitation method and by solid-state pyrolytic method [ZnO(p) and ZnO(s)].
2. To characterize the prepared zinc oxides using X-ray diffraction (XRD), transmission electron microscopy (TEM), BET adsorption and infrared spectroscopy.
3. To use this nano zinc oxide in rubber compounding and to compare the cure characteristics and mechanical properties of three typical rubbers: natural rubber, polychloroprene, styrene butadiene rubber compounds using low dosage of zinc oxides [ZnO(p) and ZnO(s)] with those of compounds containing conventional zinc oxide.
4. To prepare modified precipitated silica and compare the properties of modified silica filled natural rubber, polychloroprene and styrene butadiene composites with those of unmodified silica filled natural rubber, polychloroprene and styrene butadiene composite.
5. To prepare mesoporous silica and rice husk silica from low cost silica source (rice husk) and to characterize these silica particles using X-ray

diffraction (XRD), transmission electron microscopy (TEM), BET adsorption and infrared spectroscopy.

6. To compare the mechanical properties of modified mesoporous silica and rice husk silica filled natural rubber composites with those of unmodified mesoporous silica and rice husk silica filled natural rubber composites.

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Chapter 2

Experimental Techniques and Materials used

Contents

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 the study was ISNR-5 of Mooney viscosity ML (1+4) at 100°C equal to 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

Sl. 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

In a particular experiment, rubber from the same lot has been used. This is because the molecular weight distribution and non-rubber constituents of natural rubber are affected by clonal, seasonal variation and method of preparation etc.[2]

Chloroprene rubber

Chloroprene rubber (CR) with a Mooney viscosity ML (1+4), at 100°C of 47 and specifications given in Table 2.2 was supplied by Toyo Soda Mfg Co. Ltd, Tokyo.

Table 2.2 Specifications of CR

Sl. No.	Parameters	Limit
1.	Viscosity	Very low
2.	Crystallization resistance	poor
3.	Peptizable	poor
4.	Extendable	good
5.	Stability	excellent

Styrene butadiene rubber (SBR)

Styrene butadiene rubber used was SBR 1502 grade, obtained from JSR Company, Japan. The Mooney viscosity (ML 1+4, 100°C) was 52. The specifications are given below.

Table 2.3 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

2.1.2 Compounding ingredients

Fillers: The fillers used were silica and carbon black.

Commercial silica:

Precipitated silica of commercial grade was supplied by Minar chemicals, Kochi. It had the following specifications.

Table 2.4 Specifications of commercial silica

pH (5% aqueous Solution)	6.3
Density (g/cc)	2.03
SiO_2 content (%5)	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 2.5 Specifications of carbon black

Appearance	Black granules
DBP absorption (cc/100g)	102
Pour Density (kg/m^3)	376
Iodine adsorption number	82
Loss on heating (%)	2.5

Zinc oxide (activator)

Zinc oxide supplied by M/S Meta Zinc Ltd; Bombay, had the following specifications.

Specific gravity (g/cm^3) 5.5

Zinc oxide content (% by mass) 98.0

Stearic acid (co–activator)

Stearic acid was supplied by Godrej Soaps (Pvt.) Ltd, Bombay and the specifications are given below.

Melting Point	65°C
Acid number	200

Accelerators

(a) N-cyclohexyl-2-benzothiazyl sulphenamide

CBS used in this study was santacure CBS supplied by NOCIL Ltd, Mumbai with specific gravity 1.27 (g/cm^3)

(b) Tetramethylthiuram disulphide

Tetramethylthiuram disulphide (TMTD) supplied by NOCIL Ltd, Mumbai, had the following specifications.

Melting Point	138°C
Specific gravity (g/cm^3)	1.3

Process oils

a) Aromatic Oil

Aromatic oil was supplied by Hindustan Organic Chemicals, Cochin. It had the following specifications.

Specific gravity (g/cm^3)	0.98
Aniline point (° C)	43.00
Viscosity gravity constant	0.96

b) Naphthenic Oil

Naphthenic oil was supplied by M/S Hindustan Petroleum Ltd; Mumbai, India.

c) Diethylene glycol (DEG)

Diethylene glycol was supplied by S.D fine chemicals Ltd, Mumbai.

Antioxidants

a) Vulkanox HS

Commercial antioxidant vulkanox HS (1,2-dihydro-2,2,4-trimethyl quinoline, polymerized) was obtained from Bayer India Ltd. It had a specific gravity of 1.1.

b) Para-phenylenediamine derivatives

IPPD [N-isopropyl-N′-phenyl-p-phenylenediamine], 6PPD [N-(1,3-dimethyl buty1)–N′-pheny1-p-phenylenediamine], DPPD [N,N′-diphenyl-p-phenylenediamine] were obtained from NOCIL Ltd. Thane, India.

Sulphur (cross linking agent)

Sulphur was supplied by M/S Standard chemicals Co Pvt. Ltd, Madras. It had the following specifications.

Specific gravity (g/cm^3)	2.05
Ash (%)	0.10
Solubility in CS_2 (% by mass)	98

2.2 Experimental

2.2.1 Vulcanization

Mixing and homogenization on a mixing mill

Mixes were prepared on a laboratory size two roll mixing mill (6 x 12 inch) as per ASTM D 3182–89. The mixing was carried out at a friction ratio of 1:1.25. The mill opening was set at 0.2 mm and the elastomer was passed through the rolls twice without banding. This was then banded on the slow roll with mill opening at 1.4 mm and was increased to 1.9 mm as the band became smooth. The temperature of the rolls was maintained at 70±5 °C. The compounding ingredients were added as per procedure given in ASTM D 3184–89 and ASTM D 3182–89 in the following order: activator, filler, accelerator and curing agents. Before the addition of accelerator and sulphur, the batch was thoroughly cooled.

After mixing all the ingredients, homogenization of the compound was carried out by passing the rolled stock end wise six times at a mill opening of 0.8 mm. The mill was opened to give a minimum stock thickness of 6 mm and the stock was passed through the rolls four times folding it back on itself each time.

Mixing of the compounds using brabender plasticorder

Brabender plasticorder has been widely used for measuring processability of polymer. The heart of the torque rheometer is a jacketed mixing chamber whose volume is approximately 40 cc for the model used (PL 3S). Mixing and shearing of the material in the mixing chamber is done by horizontal rotors with protrusions. The resistance put up by the test material against rotating rotors in the mixing chamber is indicated with the help of a dynamometer balance. The dynamometer is attached to a mechanical measuring system, which records the torque. A dc thyrister controlled drive is used for speed control of the rotors (0 to 150 rpm). The temperature can be varied up to 300°C. A thermocouple with a recorder is used for temperature measurements. Different type of rotors can be employed depending upon the nature of the polymer used. The rotors can be easily mounted using the simple fastening and coupling system. 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 5 g was placed in the lower die that is oscillated through a small deformation angle (0-2°) at a frequency of 50 cpm. The torque transducer on the upper die senses the forces 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 time (T_{90}) and cure rate index. Cure rate index was calculated from the cure graph using the equation 2.1.

Cure rate index = $100/\ t_{90} - ts_2$ ……………….. 2.1

Where t_{90} and ts_2 are the times corresponding to the optimum cure and two units above minimum torque respectively.

Moulding

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

2.2.2 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 molded sheets using the C-type die, along the mill grain direction. The measurements were carried out at a cross head speed of 500 mm/min on a Shimadzu Model AGI Universal Testing Machine according to ASTM standards, D 412–68 and D 624–54 respectively.

Tear strength

Tear resistance of the samples was tested as per 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 a crosshead speed of 500 mm per minute on a Shimadzu Model AGI 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.[3] Readings were taken after 15 seconds of the indentation when firm contact has been established with the specimens.

Abrasion resistance

The abrasion resistances of the samples were studied with a DIN Abrader (DIN 53516). Moulded samples of 6 ± 0.2 mm diameter and 12 mm thickness were prepared as per ASTM D 3183 and abrasion loss was measured as per ASTM D 5963–04. Abrasion loss was calculated using the equation 2.2.

Abrasion loss = (loss of wt. /sp.gr.) ……..……… 2.2

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 22 hrs (ASTM D 395-1998 method B).[4] The samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated using equation 2.3.

$$\text{Compression set (\%)} = \frac{t_o - t_1}{t_o - t_s} \times 100 \qquad \text{.......................2.3}$$

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.[5] A cylindrical sample of 2.5 cm height and 1.9cm 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 (ΔT°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.[5] Standard specimens 15 cm × 2.5 cm × 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.

2.2.3 Thermal ageing studies

Tests were carried out as per ASTM D 573–1999.[5] Test specimens were exposed to oxygen atmosphere at specified elevated temperature in an air oven, for known periods of time, after which their physical properties were determined and were compared with the properties of the samples.

2.2.4 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.[3] 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 in elastic modulus with increasing strain amplitude.[6] 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 an excess volume of test material. In agreement with ASTM 5289, the manufacturers recommend to load samples of about 5.0g i.e. 4.4cm^3 for a standard filled rubber compound with a specific gravity of 1.14 g/cc. Samples for RPA testing were consequently prepared by die cutting 46 mm 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 0.5 Hz.

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 as a two–stage programme.

2.2.5 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 cross linking 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. Specimens of known weight were immersed in the solvents in different 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.

The volume fraction of rubber, V_r, in the swollen network was then calculated by the following equation 2.4 .[7, 8]

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_o\rho_s^{-1}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.4)$$

Where,

T = the weight of the test specimen

D = the weight of the deswollen test specimen

F = the weight fraction of insoluble components

A_o = the weight of the absorbed solvent corrected for the swelling increment

ρ_r = density of the rubber

ρ_s = density of the solvent

Knowing the value of $V_{r,}$ the total chemical crosslink density $\frac{1}{2}$Mc was calculated using Flory-Rehner equation.[9, 10]

$$\text{Cross link density} = \frac{[\ell n(1-V_r)+V_r+\chi V_r^{\,2]}}{2\rho Vs(V_r)^{1/3/}}$$

Where Vs = molar volume of the solvent

χ = rubber – solvent interaction parameter

2.2.6 Bound rubber content

Bound rubber is the rubber that is trapped by the filler aggregates after mixing. The rubber chain are attracted either physically or chemically to form a rubber shell on the surface of the silica particles. The rubber fraction of an uncured compound is amount of rubber that is not extracted when it is exposed to a good solvent.

The mixture samples were cut in small pieces and put over a stainless steel sieve (40 µm meshes), then extracted with toluene for 4 days and finally dried for one day at 80°C. Contents of bound rubber were determined from the weights of the samples before and after the extraction.

The BRC is calculated from the weight of the residue after extraction (b), the weight of the initial mixture (m), and the amount of silica present in the initial mixture (a), determined by calcination at 600° C.

$$\text{BRC \%} = [(b-a) / (m-a)] \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 2.5$$

The BRC can be related to the amount of rubber in the mixture before the extraction and was calculated using the equation 2.5.[11]

2.2.7 Ozone resistance

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 12 hrs. The concentration of ozone was maintained at 50 pphm at 20% strain and the inside temperature at 40°C. The ozone cracks developed on the samples were observed by a lens and the photographs were taken.

2.2.8 Thermogravimetric analysis

The thermograms of natural rubber, silica composites are recorded with a thermogravimetric 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 an ultra sensitive microbalance. Air and nitrogen were used as purge gases.

2.2.9 Differential scanning calorimetry

Differential scanning calorimetry (DSC Q 100, TA instruments) equipped with a RCS cooling system was employed to study the crystallization characteristics of the nanocomposites. Heat flow, i.e., heat absorption or heat emission, per unit volume, is measured for the sample and the result is compared with that of thermally inert reference. Indium was used for temperature calibration. The sample weight was around 5mg.

2.2.10 Characterization techniques

Transmission Electron Microscope

The morphology and particle size of zinc oxide and mesoporous silica were observed using transmission electron microscope (TEM). The transmission electron microscope (TEM) images were taken on a JEOL GEM 3010 transmission electron microscope operating at 300 KV.

X–ray powder diffraction studies

X–ray powder diffraction (XRD) was used to characterize the zinc oxide and silica powders. Bruker, D8 advance rotaflex diffraction meter using CuK α radiation and λ = 1.5406 A° was used.

Surface area

Surface area of nanoparticles was measured using BET method. Surface area analysis was done using Micromeritics BJH surface analyzer tristar 3000. Measurements were carried out under nitrogen adsorption at liquid nitrogen temperature

Infrared Absorption Spectra

Infrared absorption spectra were collected using Thermo Avtar 370 spectrometer.

Small angle XRD

Small angle XRD is generally used to probe the mesopore structural ordering of the material and to determine the phase structure of the developed material. Powder XRD of mesoporous silica was taken on a Rigaku D/max–C system with Ni filtered CuK α radiation (λ -1.5406A) within the 2θ range 0 – 6 at a speed of 1°/ minute.

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Chapter 3

Preparation and characterization of zinc oxide

Contents

3.1 Introduction

Nanocrystalline materials may be considered as the challenge of this age. Intensive investigations were stimulated for several applications for these new classes of materials. Zinc oxides of particle size in nanometer range have been paid more attention for their unique properties. They are widely used for solar energy conversion, non-linear optics, catalysis, varistors, pigments, gas sensors, cosmetics etc.[1-10] As a wide band gap semiconductor, ZnO has been widely studied in varistors, transparent conductors, transparent U.V. protection films, chemical sensors and so on.[11-14]

Zinc oxide in combination with stearic acid is used as activator for sulphur-vulcanization of elastomers. In addition to its role as an activator, there are also evidences that the inclusion of ZnO in the compound brings also other benefits such as reduction in heat build–up, improvement of abrasion resistance and heat resistance of the vulcanizates and their resistance to dynamic loading[15] helps to dissipate local heat concentrations in rubber products. Zinc oxide is a necessary ingredient in rubber compounds for bonding rubber to the reinforcing steel cord etc.

Besides improving the properties of vulcanized rubbers, ZnO also assists in the processing of uncured rubbers. ZnO is added to rubber formulation to reduce shrinkage of moulded rubber products and maintain the cleanliness of moulds. Although zinc is generally considered as one of the least harmful among heavy metals, there is an increased concern about its environmental effects.[16] Diffuse emissions of zinc from rubber products, such as the wear of tyres may enter into the environment. In view of the upcoming legislation and ecolabelling requirements for tyres for instance, it can be stated that it is desirable to keep the ZnO content in rubber compounds as low as possible, not only for environmental but also for economical reasons.[17-18]

The efficiency of ZnO during vulcanization can be enhanced by the maximization of the contact between the ZnO particles and the accelerators in the compound. This contact is dependent on the size of the particles, their shape and the specific surface area. Zinc oxides of particle size in nanometer range have been paid more attention for their unique properties. Various methods have been employed for the synthesis of nano ZnO which include precipitation from an alcoholic solution of zinc acetyl acetonate by alkali, hydrolysis of zinc acetate in polyol medium and a modified sol-gel procedure where in an alkylzinc reacts with tert-butyl alcohol to form alkylzinc alkoxide, which then reacts with aqueous ethanol.[19-21] Despite recent advances, commercial exploitation of ZnO nanoparticles is currently limited by the high synthesis costs. In this chapter, we describe the preparation and characterization of nano zinc oxide by precipitation[22] and solid state pyrolytic method[23] which is simple, rapid and low cost.

3.2 Experimental

3.2.1 Materials

Zinc sulfate, ammonium bicarbonate, zinc acetate and sodium bicarbonate were supplied by Sd. fine chem. Ltd., Mumbai, India

3.2.2 Method I- Precipitation method

Zinc sulfate (1.5 mol/l) and ammonium bicarbonate (2.5 mol/l) were prepared in distilled water and 100 ml $ZnSO_4$ solution was added to 126ml NH_4HCO_3 solution while stirring and the reaction mixture was kept at 45°C. The slurry of basic zinc carbonate (BZC) in the form of a white precipitate was obtained. It was then filtered, washed and dried. Finally zinc oxide nanoparticle was prepared by calcining the precipitate at 500°C for 1 hour.

In this process, the reaction of Zn ions and ammonium acid carbonate proceeds according to the equation 3.1.

$$5ZnSO_4 + 10NH_4HCO_3 \rightleftharpoons Zn_5(OH)_6(CO_3)_{2\,(S)} + 5\,(NH_4)_2SO_4 + 8CO_2\uparrow + 2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3.1)$$

The complex formed decomposes upon calcining to ZnO according to the equation 3.2.

$$Zn_5(OH)_6(CO_3)_2 \rightleftharpoons 5ZnO + 2CO_2\uparrow + 3H_2O\uparrow \qquad \ldots\ldots\ldots\ldots\ (3.2)$$

3.2.3 Method II– Solid-state pyrolytic method:

$Zn(CH_3COO)_2.2H_2O$ (2.2g, 10mmol) and NaHCO3 (2g, 23.8mmol) are mixed at room temperature. The mixture is pyrolysed at 300°C for 3 hours. The $Zn(CH_3COO)_2.2H_2O$ is changed into ZnO nanoparticles, while the $NaHCO_3$ is changed into CH_3COONa and eventually washed away with deionized water. Consequently, white ZnO nanoparticles are obtained through the thermal decomposition process.

3.3 Characterization of ZnO

Bulk density (ASTM D 1895)

Bulk density is defined as the weight per unit volume of a material. It is primarily used for powders or pellets. The test can provide a gross measure of particle size and dispersion, which can affect material flow consistency and reflect packaging quantity.

Procedure

The small end of the funnel was closed with hand or a suitable flat strip and pour 115 ± 5 cm^3 samples into the funnel. The bottom of the funnel was opened quickly and the material was allowed to flow freely into the cup. If caking occurs in the funnel, the material may be loosened with a glass rod. After the material has passed through the funnel immediately scrap off the excess on the top of the cup with a straight edge without shaking the cup.

Bulk density= M/V where, M is mass of the sample and V is the volume of the container.

Purity of zinc oxide[24]

Weighed accurately about 1.5g of the material and 2.5g of ammonium chloride. Dissolved in 50 ml of standard hydrochloric acid (1N) and titrated the excess of acid with standard sodium hydroxide solution (1N) using methyl orange as indicator. Carried out a blank determination without using the material. Purity of zinc oxide is calculated using equation 3.3.

Zinc oxide, percent by mass = 4.07 (B-A) /(M) ………………………. (3.3)

Where, B = Volume in ml of standard sodium hydroxide solution used in the blank determination.

A = Volume in ml of standard sodium hydroxide solution used in the titration with the material

M = mass in gm of the material taken for the test

Energy dispersive X-ray spectrometry

The chemical stoichiometry of ZnO nanoparticle is investigated with EDX, (EDS, HITACHI, and S-2400).

Transmission Electron Microscopy (TEM)

The morphology and particle size of zinc oxide were observed using transmission electron microscope (TEM). The transmission electron microscope (TEM) images were taken on a JEOL GEM 3010 Transmission Electron Microscope operating at 300kv.

XRD

X-ray powder diffraction (XRD) was used to characterize the zinc oxide powders. Particle size of the samples was determined using X-ray diffraction technique. XRD patterns were collected using Bruker, D8 advance rotaflex diffraction meter using CuK radiation and $\lambda = 1.5406A^\circ$. Crystallite size is calculated using Scherrer equation 3.4.

$$CS = 0.9\lambda \Big/ \beta \cos\theta \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.4$$

Where, CS is the crystallite size, β is full width at half maximum (FWHM) of an hkl peak at θ value.[25]

Surface area

Surface area of the zinc oxide nanoparticles and conventional zinc oxide were measured using BET method. Surface area analysis was done using Micromeritics BJH surface analyzer tristar 3000. Measurements were carried out by nitrogen adsorption at liquid nitrogen temperature.

Fourier transform infrared spectroscopy

Fourier transform infrared spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm^{-1}. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are the indication of the band structures and structural geometry of the molecule. FTIR spectra were taken using Thermo Avtar 370 spectrometer.

Thermogravimetric analysis

Thermogravimetric analyzer (TGA, Q-50, and TA Instruments) was used to study the thermal stability of ZnO. Approximately 5 mg of the samples were heated at the rate of 20°C/min to 800°C.

Differential scanning calorimetric analysis

The differential scanning calorimetry of natural rubber with ZnO is recorded with a differential scanning calorimeter 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.

3.4. Results and discussion

ZnO Characterization

3.4.1 Bulk density

The different types of ZnO prepared in the laboratory are characterized by determining the bulk density. Determination of the bulk density of the sample is the primary identification. The bulk density of the prepared samples is shown in Table 3.1.

Table 3.1 Bulk densities of ZnO

Sample name	Bulk density (g/cm$^{3)}$
ZnO(c)	0.538
ZnO(p)	0.655
ZnO(s)	0.596

From the bulk density results, it is seen that ZnO prepared in the laboratory has high values when compared with those of the conventional ZnO. This may be due to reduction in particle size and difference in structure. It is observed that particle size is lower for ZnO(p) and ZnO(s) than that of ZnO(c).

3.4.2 Purity of zinc oxide

Purity of ZnO are shown in Table 3.2.

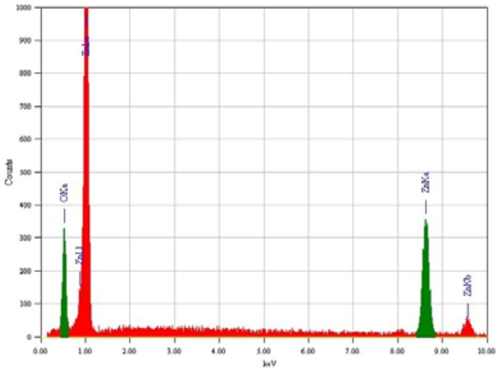
Table 3.2: Purity of zinc oxide

Sample	Purity of ZnO (%)
ZnO(p)	99.8
ZnO(s)	99.9
ZnO(c)	99.8

The purity of nano zinc oxide prepared from precipitation and solid state pyrolytic method is not less than 99.0 percent. This indicates the high purity of prepared nano zinc oxide and conventional zinc oxide.

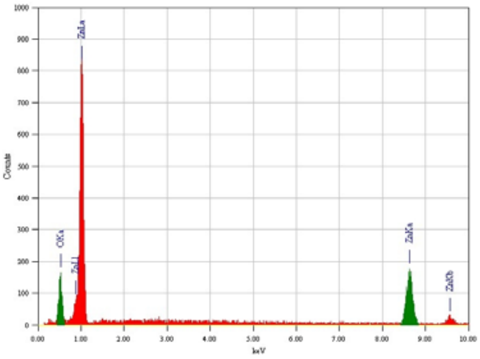
3.4.3. Energy dispersive X-ray spectrometry

The chemical stoichiometry of ZnO nanoparticle was investigated with EDX (Figure 3.1 a, b), which affirmed an atomic ratio of Zn: O ≅ 1:1.



Element	Element %	Atomic %
O	19.66	24.21
Zn	80.34	75.79
Total	100.00	100.00

Figure 3.1 a: .EDX patterns of ZnO(p) nanoparticles



Element	Element %	Atomic %
O	19.66	24.57
Zn	80.34	75.43
Total	100.00	100.00

Figure 3.1.b: EDX patterns of ZnO(s) nanoparticles

3.4.4 Transmission electron microscopy studies

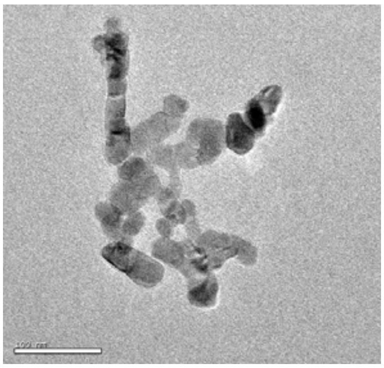


Figure3.2a Tem image of ZnO nanoparticles: precipitation method

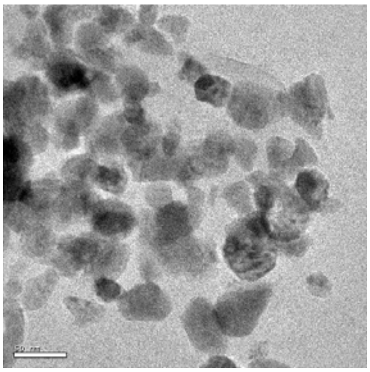


Figure3.2b Tem image of ZnO nanoparticles: solid- state pyrolytic method

Figure 3.2a and Figure 3.2b show TEM images of zinc oxide prepared by precipitation method and solid state pyrolytic method. It shows that ZnO particle size prepared by precipitation method is having an average particle size of 20 nm and that prepared by pyrolytic technique have an average particle size of 30 nm.

3.4.5. X–ray powder diffraction studies

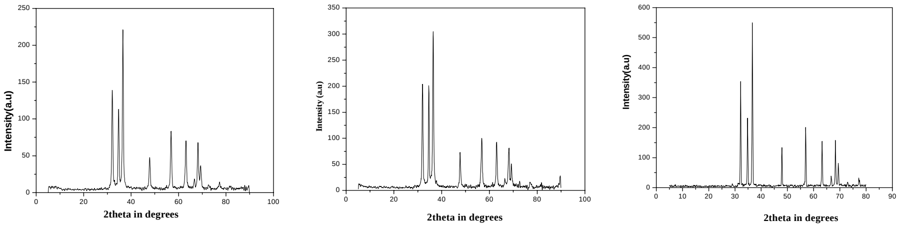


Figure.3.3 XRD patterns of ZnO prepared by (a) method 1 (b) method 2 (c) Conventional ZnO

Figure 3.3 shows the XRD patterns of ZnO samples. It is very clear from the above figures that the major reflections between 30° and 40° (2θ values) indicate more crystalline regions in the zinc oxide sample. Also the less intense peaks at 48°, 57°, 63° and 70° (2θ values) indicate the high crystallinity of ZnO samples. The detailed analysis of the XRD and the assignments of various reflections are given in the Table 3.3.

Table 3.3 Analysis of XRD and the assignments of various reflections of ZnO

Sample	d (Obs)	FWHM	Crystallite size (nm)
ZnO(p)	2.455	0.471	19.36
ZnO(s)	2.463	0.444	20.52
ZnO(c)	2.451	0.236	38.66

Crystallite size of the ZnO samples was calculated using Scherrer's formula.[25] The crystallite size for zinc oxide prepared from method 1 and 2 ranges from 15 nm–30 nm and the crystallite size for conventional zinc oxide range from 40 nm to 60 nm.

3.4.6. Surface area

Table 3.4 Surface area of zinc oxide

Sl. No.	Samples	Surface area (m^2g^{-1})
1	Conventional zinc oxide	4
2	Zinc oxide from method 1	34
3	Zinc oxide from method 2	12

Table 3.4 shows the surface area for conventional zinc oxide and zinc oxide nanoparticle prepared from method 1 and 2 respectively. The surface area is found to be about 8 times high for ZnO from precipitation method and about 3 times high for ZnO from pyrolysis method compared to conventional zinc oxide.

3.4.7. Fourier transform infrared spectroscopy

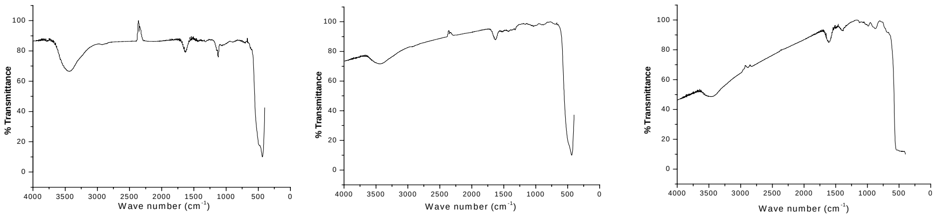


Figure.3.4 FTIR spectrum of ZnO sample prepared by (a) method 1 (b) method 2 (c) Conventional ZnO

Figure **3.4** shows the IR spectra of ZnO samples. The peak at 450 cm^{-1} shows the distinct stretching vibration of zinc oxide.

3.4.8. Thermogravimetric analysis

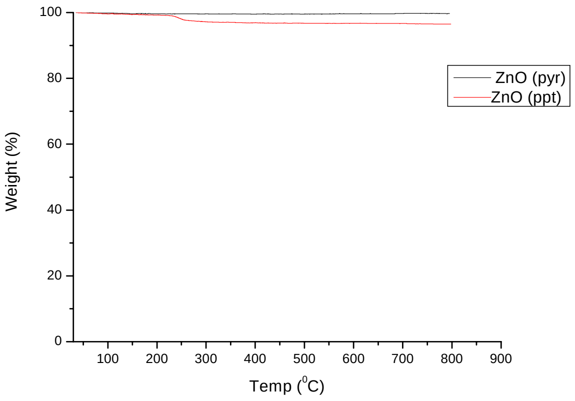
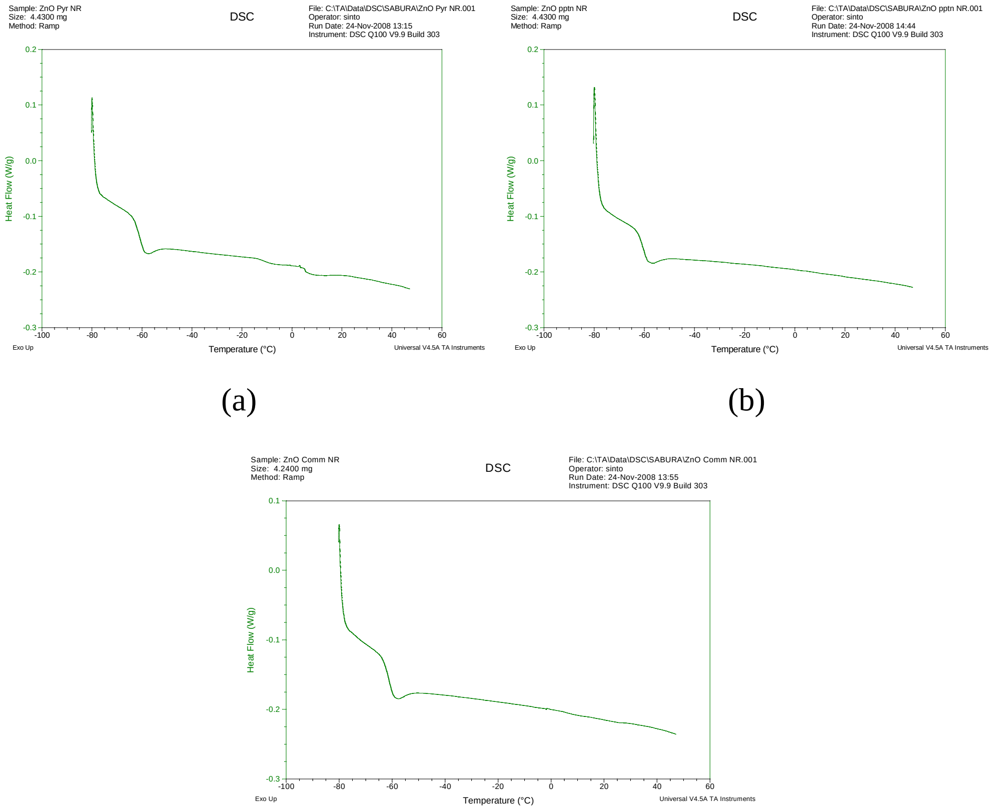


Figure 3.5 Thermogravimetric analysis of zinc oxides **(a)** ZnO(p) **(b)** ZnO(s)

From the figure it is seen that TGA curve for the nano ZnO from pyrolytic method shows the absence of any actual loss in weight. This indicates the thermal stability and high purity of nano ZnO(s). The TGA curve for the nano ZnO from precipitation method shows a very small decrease in weight percentage at around 190°C-250°C. As reported by Morishige et al.[26] the peaks at around 250°C may be caused by the decomposition of the condensation dehydration of the hydroxyls.

3.4.9 Differential scanning calorimetry



(a) (b)

(c)

Figure 3.6 DSC thermogram of natural rubber with (a) ZnO(p) (b) ZnO(s) and (c) ZnO(c)

The differential scanning calorimetric study of the natural rubber with prepared nano zinc oxides and with conventional ZnO were done at low temperatures to study the change in glass transition temperature (Tg) during the zinc oxide incorporation. The DSC thermogram of natural rubber with ZnO(p), ZnO(s) and ZnO(c) are shown in the figure 3.6(a),(b),(c) respectively. It is clear from the thermograms that there is no change in the glass transition temperature after the ZnO incorporation, which indicates that the incorporation of zinc oxides will not affect the glass transition temperature of natural rubber.

3.5 Conclusions

1. Nano zinc oxides could be successfully prepared by precipitation and pyrolytic methods and their yield is high.
2. Bulk density of prepared zinc oxides is greater than that of conventional zinc oxide.
3. Surface area of prepared zinc oxides is greater than that of conventional zinc oxide.
4. Zinc oxides prepared in the laboratory are highly pure.

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Chapter 4

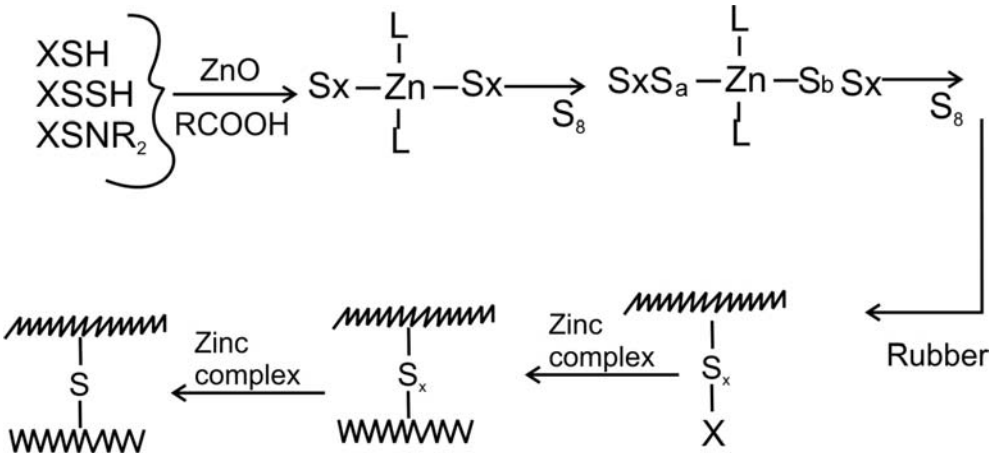
Use of nano zinc oxide in natural rubber

Contents

4.1 Introduction

Natural rubber (NR) is a high molecular weight polymer of isoprene (2-methyl-1,3-butadiene). It is the oldest known rubber and the most versatile one for fabrication of rubber products. The high and reversible deformability of natural rubber is of great industrial importance. However, its initial modulus and durability are low and an additional reinforcement is required for practical applications. Carbon black and precipitated silica have been extensively used for this purpose. In addition, $CaCO_3$, ZnO, MgO, talc, mica etc. have also been used.

Zinc oxide is added to rubber compounds as an activator to activate sulfur vulcanization and there by reduce the vulcanization time. Besides its effect on the curing process, ZnO has many beneficial effects on the physical properties of rubber.[1] Furthermore, ZnO assists in the processing of uncured rubber.[2] ZnO is a dense material that tends to compact and disperse with difficulty. Therefore, it is distributed in the form of crystal particles in rubber mixes.[3] Nieuwenhuizen in his thesis proposed a mechanism in which the ZnO surface function both as a reactant and as a catalytic reaction template, activating and bringing together reactants.[4] Molecules of accelerators, sulphur and fatty acids diffuse through the rubber matrix and are adsorbed onto ZnO with the formation of intermediate complexes.[5,6] Fatty acids are generally regarded as indispensable activators in conjunction with zinc oxide. The function of fatty acid activators such as stearic acid , is to solubilize the zinc oxide, a secondary effect is an increase in the amount of zinc sulphide produced.[7] The zinc salts of fatty acids, which are a type of surfactant , also solubilize insoluble accelerators to form the actual catalyst. A general scheme of accelerated sulfur vulcanization that demonstrates the role of zinc oxides in conjunction with fatty acids is shown in scheme I.[8,9]



Scheme I: Role of ZnO and fatty acid in accelerated sulfur vulcanization

X= Accelerator residue. L = ligand

Duchacek[10] noted that increasing zinc oxide concentration increased the rate and extent of cross linking up to a certain zinc oxide concentration, this concentration is believed to be the minimum level of zinc oxide needed for complete conversion of accelerator to the zinc-accelerator sulfur complex. It was also noted that the optimum zinc oxide content to minimize reversion was slightly greater than this minimum. Coran[11] also noted that the induction time had a dependence on the zinc oxide concentration in excess of that required for formation of the accelerator-zinc complex. This suggests that zinc oxide exerts an influence beyond inclusion in the accelerator complex. The efficiency of ZnO during vulcanization can be enhanced by the maximization of the contact between the ZnO particles and the accelerators in the compound. This contact is dependant on the size of the particle, their shape and the specific surface area.

In some rubbers such as natural rubber (NR) and ethylene-propylene diene rubber (EPDM), there is evidence that a considerable amount of ZnO is consumed and transformed into ZnS.[12-14] The zinc content in rubber products has come under increased scrutiny due to environmental concerns. The trend in rubber industry is, therefore, to reduce the zinc content in rubber products.

This chapter describes the use of nano ZnO samples prepared in the laboratory in dry NR and the mechanical properties of the vulcanizates are evaluated with reference to the vulcanizates prepared using conventional ZnO.

4.2 Experimental

Materials:

Natural rubber used in this study was ISNR- 5 of Mooney viscosity (ML 1+4,100^{0}C) 85. Conventional zinc oxide (ZnO(c)), zinc oxide samples prepared in the laboratory (ZnO(p), ZnO(s)), stearic acid, high abrasion furnace black, aromatic oil, antioxidantHS, N-cyclohexylbenzothiazyl sulphenamide (CBS), tetramethylthiuram disulphide (TMTD), sulphur were also used in this investigation.

Preparation of composites

The base formulation for the preparation of NR compounds is given in Table 4.1.

Table 4.1 Base formulation for NR compounds

Ingredient (phr)	N-1	N-2	N-3	N-4	N-5	N-6	N-7	N-8	N-9	N-10
NR	100	100	100	100	100	100	100	100	100	100
ZnO(c)	5	-	-	2	5	-	-	2	-	
ZnO(p)	-	2	-	-	-	2	-		1	-
ZnO(s)	-	-	2	-	-	-	2	-		1
Stearic acid	2	2	2	2	2	2	2	2	2	2
HAF	-	-	-	-	40	40	40	40	40	40
Aromatic oil	-	-	-	-	8.0	8.0	8.0	8.0	8.0	8.0
HS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
TMTD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Compounds were prepared by mill mixing on a laboratory size (16 x 33 cm) two-roll mill at a friction ratio of 1:1.25 as per ASTM D 3184-89. After mixing all the ingredients, the stock was passed six times through tight nip gap and finally sheeted out a fixed nip gap. The samples were kept for 24 hrs for maturation.

Testing

The cure characteristics of all mixes were determined on a Rubber Process Analyzer, RPA 2000, Alpha technologies, USA, as per ASTM 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 hrs prior to physical testing.

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

4.3 Results and discussion

4.3.1 Cure characteristics

Torque values of gum and filled compounds with ZnO(c), ZnO(p), and ZnO(s) are shown in Table 4.2.

Table 4.2 Torque values of NR compounds

Property	N-1	N-2	N-3	N-4	N-5	N-6	N-7	N-8	N-9	N-10
Min Torque dNm	0.02	0.03	0.03	-0.04	0.11	0.06	0.12	0.02	-0.04	0.02
Max Torque dNm	2.64	2.79	2.70	2.44	6.14	6.19	6.19	4.01	3.85	4.32
ΔTorque dNm	2.62	2.76	2.67	2.48	6.03	6.13	6.07	3.99	3.89	4.30

The torque values of filled and gum compounds with 2phr ZnO(p), ZnO(s) are comparable to that containing 5phr ZnO(c) compounds. The torque values of filled compounds with 2phr ZnO(p), ZnO(s) are higher than that compounds with 1phr ZnO(p), ZnO(s) and 2phr ZnO(c). So compounds with 2phr ZnO(p), ZnO(s) show higher cross linking compared to compounds with 1phr ZnO(p), ZnO(s). Compared to the torque values of filled and gum compounds of 2phr and 5phr conventional ZnO, it is found that 5phr conventional ZnO compound show high torque values compared to compound with 2phr conventional ZnO.

After evaluating the torque values, 2phr ZnO(p) and 2phr ZnO(s) and 5phr ZnO(c) are selected as the optimum dosage in filled and gum compounds.

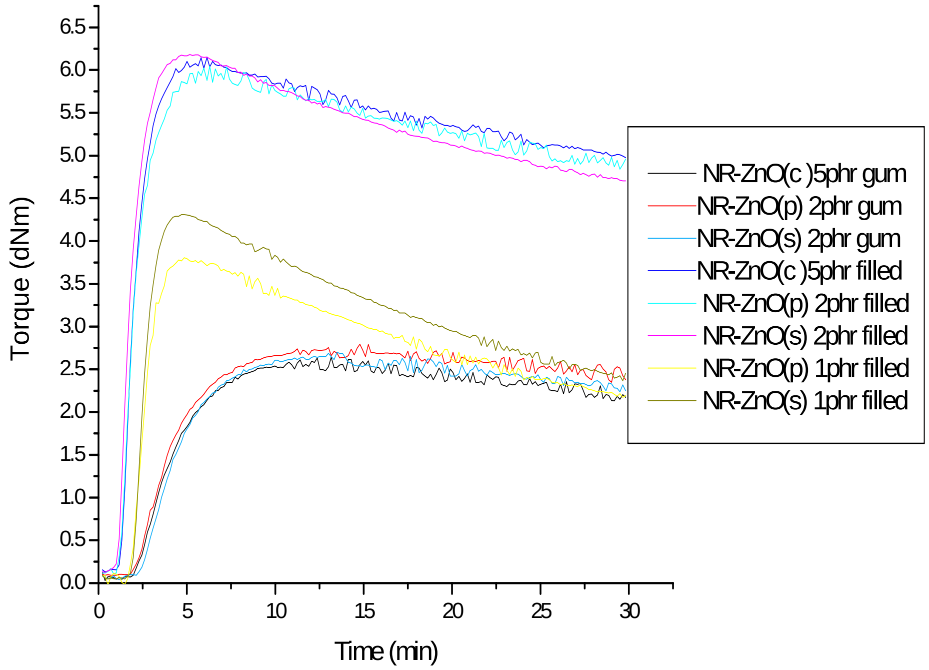


Figure 4.1 Cure graph of natural rubber compounds

Table 4.3 Cure behaviour of gum and filled compounds

Property	N-1	N-2	N-3	N-4	N-5	N-6	N-7	N-8	N-9	N-10
Scorch time (t_{s2}),min	5.22	5.74	5.63	4.33	2.54	2.56	2.59	2.44	2.44	1.78
Optimum cure time (t_{90}), min	7.89	7.79	7.68	7.27	4.94	4.48	4.46	5.46	5.06	4.84
Cure rate index (100/-t_{90}-t_{s2})	37.45	48.78	48.78	34.01	41.66	52.08	53.47	33.11	38.16	32.67

Cure behavior of gum and filled compounds are given in the Table 4.3 and figure 4.1. Comparing the cure characteristics of filled and gum compounds, compounds with 2phr ZnO(p) and ZnO(s) exhibited higher rate and extent of cure over that of 5phr and 2phr of conventional ZnO compounds. This indicates ZnO(p) and ZnO(s) with larger surface area developed the full potential of the accelerator, there by making vulcanization faster. Scorch safety has increased, and cure time was found to be lower for ZnO(p) and ZnO(s) compounds compared to conventional ZnO compounds. Compounds with 2phr ZnO(p) and ZnO(s) show faster curing compared to compounds containing 1phr ZnO(p) and ZnO(s).

4.3.2 Properties of gum composites

Tensile properties

Table 4.4 Tensile properties of gum vulcanizates

Compound	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus at300% elongation (MPa)	Tear strength (N/mm)
N-1	23.02	1735	1.17	38
N-2	22.94	1591	1.46	40
N-3	23.06	1656	1.25	40
N-4	20.80	1899	1.04	33

Tensile properties of gum vulcanizates with ZnO(c), ZnO(p) and ZnO(s) are shown in Table 4.4. Gum vulcanizate with 2phr conventional ZnO has relatively low tensile properties compared to vulcanizates with 5phr conventional ZnO, 2phr ZnO(p) and ZnO(s). Modulus and tear strength values for vulcanizates with 2phr ZnO(p) and ZnO(s) are slightly greater than vulcanizate with 5phr ZnO(c). Elongation at break is decreased for N-2 and N-3 vulcanizates compared to N-1 vulcanizate. Tensile strength values for N-2 and N-3 vulcanizates are comparable with N-1 vulcanizate. These values show that the reinforcement effect of ZnO(p) and ZnO(s) are influenced by the larger surface area of activator. Small size of particles can give good reinforcement and this supports the good accelerating effect of ZnO(p) and ZnO(s) compared to conventional zinc oxide.

Other technological properties

Other technological properties like hardness, compression set values and abrasion loss for gum vulcanizates are given in Table 4.5.

Table 4.5 Technological properties of gum vulcanizates

Property	N-1	N-2	N-3	N-4
Hardness(Shore A)	45	45	46	40
Compression set (%)	42.57	41.05	37.03	49.25
Abrasion loss (cc/hr)	5.26	4.75	4.48	5.80

Hardness, compression set and abrasion resistance for N-1, N-2, and N-3 vulcanizates are superior compared to N-4 vulcanizate. It is clear from the table that the hardness and compression set values of N-2 and N-3 vulcanizates are comparable with N-1 vulcanizate. The abrasion loss values for N-2 and N-3 vulcanizates are lesser than N-1 vulcanizate. This indicates that low dosage of ZnO(p) and ZnO(s) are enough to get the same strength as that with higher dosage of conventional ZnO.

4.3.3 Properties of filled composites

Tensile properties

Table 4.6 Tensile properties of filled vulcanizates

Compound	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus at 300% elongation (MPa)	Tear strength (N/mm)
N-5	31.04	893	6.32	105
N-6	32.26	826	7.76	107
N-7	31.48	849	6.41	104
N-8	26.03	946	4.75	80

Table 4.6 shows the tensile properties of filled NR vulcanizates. Filled vulcanizate with 2phr conventional ZnO (N-8) has low tensile properties compared to vulcanizate with 5phr conventional ZnO (N-5). Tensile strength, tear strength, tensile modulus values for vulcanizates with 2phr ZnO(p) (N-6) and ZnO(s) (N-7) are comparable to that of vulcanizate with 5phr conventional ZnO (N-5). Elongation at break values are decreased for ZnO(p) and ZnO(s) vulcanizates. As the reinforcing capacity increases, generally the EB % decreases. The accelerating effect is mainly influenced by the size of the particles. The results suggest that small particle size and larger surface area of ZnO(p) and ZnO(s) give better accelerating effect compared to conventional zinc oxide.

Other technological properties

Table 4.7 Technological properties of filled vulcanizates

Property	N-5	N-6	N-7	N-8
Hardness (Shore A)	66	66	65	53
Compression set (%)	39.31	40.15	33.82	46.92
Abrasion loss (cm^3/hr)	3.71	3.50	3.23	4.54
Heat build-up (ΔT)°C	4.4	3.4	3.2	4.8
Flex resistance (k cycles)	34.80	46.28	52.28	28.31

Properties like hardness, compression set, abrasion loss, heat build-up and flex resistance of the filled vulcanizates are given in Table 4.7. Hardness, compression set, abrasion loss, heat build-up and flex resistance for N-5, N-6 and N-7 vulcanizates are superior compared to N-8 vulcanizate.

Hardness, a measure of low strain elastic modulus was found to be equal for N-5, N-6 and N-7 vulcanizates. Compression set and abrasion loss of ZnO(p) and ZnO(s) vulcanizates were also found to be comparable with ZnO(c) vulcanizates. This indicates low dosage of ZnO(p) and ZnO(s) with smaller particle size is having good reinforcement as that with higher dosage of ZnO(c).

Heat build-up values for N-6 and N-7 vulcanizates are lower compared to N-5 vulcanizate. In vulcanizates of high elasticity, the loss of energy is small and the heat build-up during dynamic stress is small. Demattia 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 N-6 and N-7 vulcanizates, indicating that these vulcanizates with 2phr ZnO(p) and ZnO(s) are suitable for tyre applications. The better flex crack resistance may be due to the stronger cross links between the chains.

Reinforcing index

Reinforcing index values of vulcanizates with respect to tensile strength are given in the Table 4.8.

Table 4.8 Reinforcing index values of vulcanizates

Composite	Reinforcing index (%)
N–5	3.37
N-6	3.51
N-7	3.41
N-8	3.12

Reinforcing index was calculated using the equation. RI = (N/No) (100/m_{filler}) where N and No are the nominal values of the mechanical property (tensile strength) measurements for the sample filled with and without filler respectively.[15] Reinforcing index value for N-8 is lesser than N-5, N-6 and N-7 vulcanizates. The reinforcing index values of N-6 and N-7 vulcanizates with lower dosage of ZnO(p) and ZnO(s) are comparable with N-5 vulcanizate with higher dosage of ZnO(c).

4.3.4 Swelling studies

Swelling studies in toluene

Table 4.9 shows the crosslink density of the filled vulcanizates.

Table 4.9 Crosslink density of NR vulcanizates

Vulcanizates	Crosslink density × 10^{-5} mol/g
N-5	4.62
N-6	5.40
N-7	4.89

Crosslink densities were calculated using Flory-Rehner equation.[16] It is found that the crosslink densities of N-6 and N-7 vulcanizates are slightly higher than that of N-5 vulcanizate. The high value of crosslink density confirms the presence of higher crosslink in vulcanizates with ZnO(p) and ZnO(s) compared to vulcanizate with conventional ZnO.

Swelling resistance in other solvents

The swelling resistance of the gum and filled vulcanizates were studied by swelling a cut sample in various solvents for constant weight. The swelling index is given in the Table 4.10. The swelling index values of all filled vulcanizates are lesser than that of all gum vulcanizates. When the forces that hold the macromolecules together are increased through cross links, the high polymer will not dissolve any longer, but will swell to a smaller or larger extent. With increasing cross linking, swelling becomes less. The swelling index values of ZnO(p) and ZnO(s) composites are comparable to that of conventional zinc oxide composites.

Table 4.10 Swelling index of gum and filled composites

Vulcanizates	Cyclohexane	Petrol	Diesel
N – 1	308	237	210
N – 2	307	237	210
N – 3	307	235	220
N – 5	152	116	113
N – 6	150	116	115
N– 7	151	115	115

4.3.5 Thermal ageing studies

Thermal ageing was carried out at a temperature of 100°C for 24, 48, 96 and 120 hrs as per ASTM D 573–1999. Variation of tensile strength and tear strength after ageing at 100°C for various periods are shown in figure 4.2 and 4.3. After ageing for specified periods, a moderate enhancement of tensile strength is observed for ZnO(p) and ZnO(s) composites. But there is gradual reduction in tear strength for ZnO(p) and ZnO(s) composites.

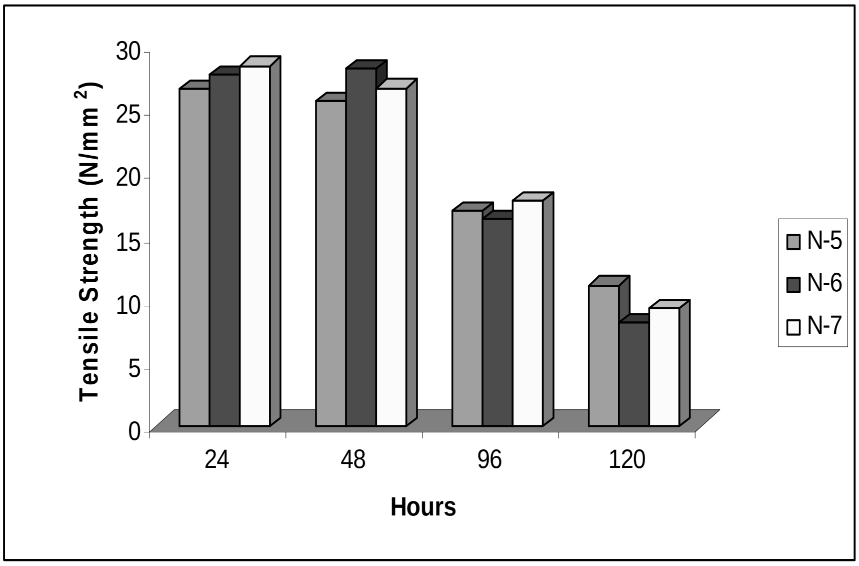


Figure 4.2 Variation of tensile strength after ageing at 100^0C for various periods

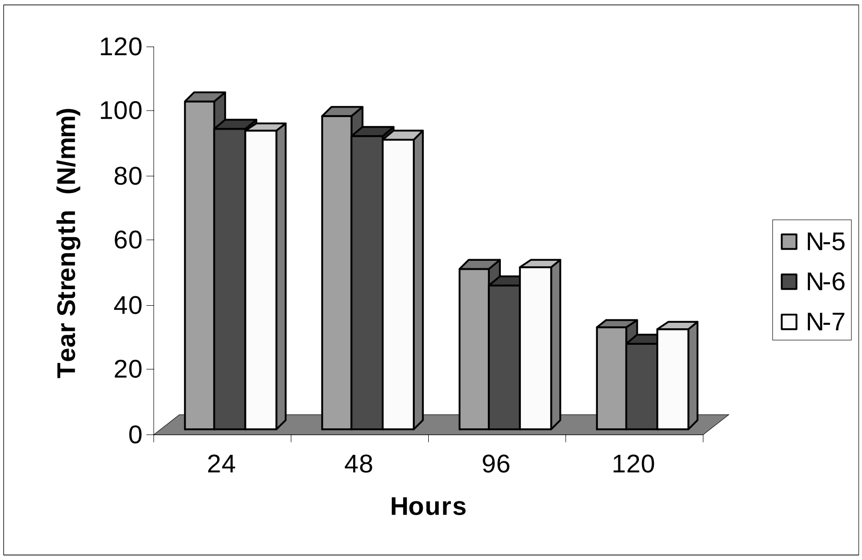


Figure 4.3 Variation of tear strength after ageing at 100^{0}C for various periods

4.3.6 Differential scanning calorimetric (DSC) studies

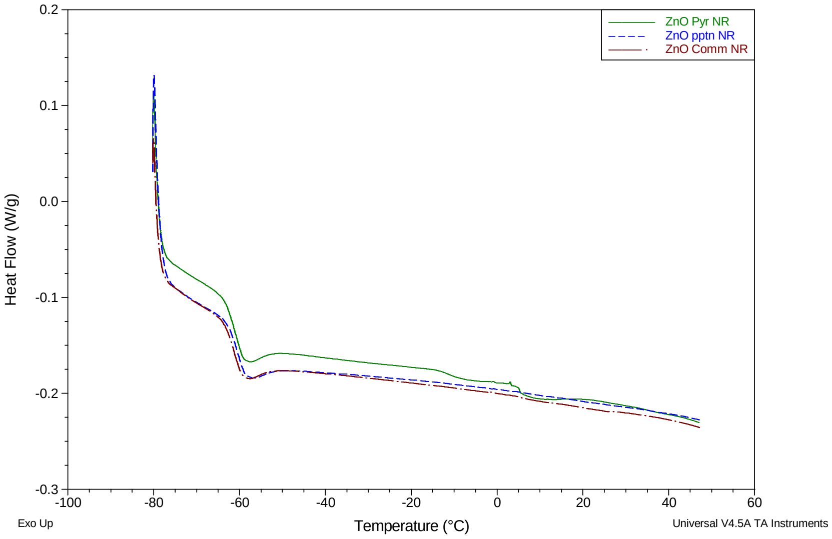


Figure 4.4 Differential scanning calorimetry of vulcanizates with ZnO(p), ZnO(s), ZnO(c)

Differential scanning calorimetry of vulcanizates with ZnO is given in Figure 4.4. The Tg value of vulcanizates with the above zinc oxides is approximately -61^{0}C. So the chain flexibility is not affected by the addition of prepared zinc oxides.

4.4 Conclusions

1. Cure characteristics, tensile properties and other technological properties are superior for vulcanizates with 5phr ZnO(c) compared to vulcanizates with 2phr ZnO(c).
2. Cure characteristics and physical properties are superior for vulcanizates with 2phr ZnO(p) and 2phr ZnO(s) compared to vulcanizates with 1phr ZnO(p) and ZnO(s).
3. Cure characteristics of compounds with 2phr ZnO(p) and ZnO(s) are superior to vulcanizate with 5phr ZnO(c).
4. The vulcanizates containing a lower dosage (2phr) of zinc oxide prepared in the laboratory (ZnO(p) &ZnO(s)) was found to have better mechanical properties than the vulcanizates containing (5phr) conventional zinc oxide.
5. Reinforcing index, heat build-up, flex resistance, crosslink density values are superior for vulcanizates with 2phr ZnO(p) and ZnO(s) compared to vulcanizates with 5phr ZnO(c).
6. Hardness, compression set, abrasion loss and swelling index values are comparable for vulcanizates with 2phr ZnO(p), 2phr ZnO(s) and 5phr ZnO(c).
7. The chain flexibility is not affected by the addition of prepared zinc oxides.

4.5 References

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Chapter 5

Use of nano zinc oxide in chloroprene rubber

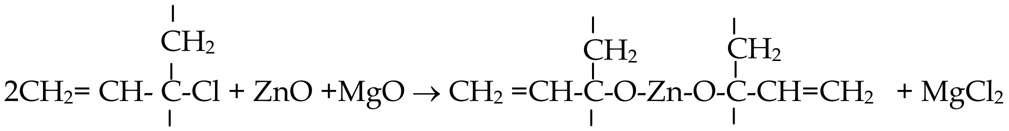
Contents

5.1 Introduction

Synthetic rubbers are more uniform in quality and compounds are more consistent in both processing and product properties.[1] There are polar and non-polar synthetic rubbers. Polychloroprene known as neoprene is a polar rubber and is generally considered as a special purpose rubber being used for applications requiring oil and solvent resistance.

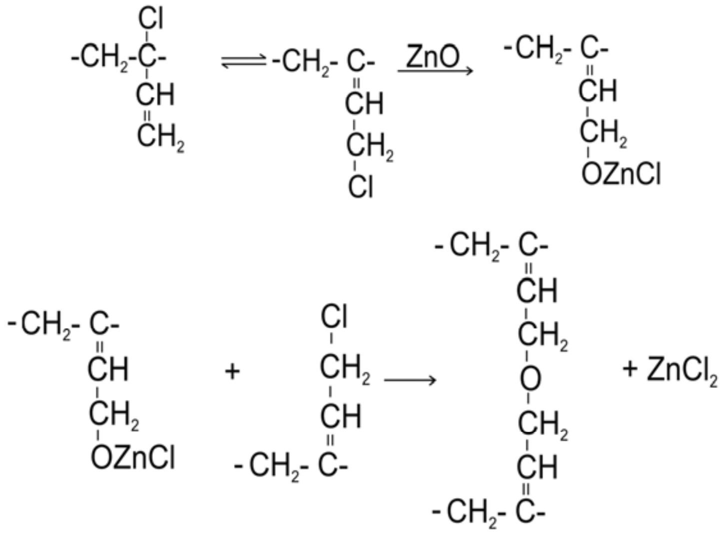
There has been a long standing commercial need for oil resistant elastomers.[2] For example, oil resistant materials are very important to the automotive industry since a variety of components may come in contact with a number of fluids. In the specific case of engine seals, it is important that they be able to withstand the fluids they are sealing without losing their ability to maintain the seal either by becoming too soft or too brittle.[3] Examining the specific reasons for the chemical resistance of polymers, it can be seen that polar side groups tend to provide resistance to swelling in hydrocarbon oils.[4] This induces slight electronegative charge on the electronegative atom with a slight positive around the carbon atom. The dipole moment produced tends to provide oil resistance. As the electronegativity of the side chain group increases on a polymer, so does its oil resistance to oil swelling. Polychloroprene is structurally similar to polyisoprene with a chlorine atom replacing methyl group attached to the back bone. This chlorine atom is more electronegative than the methyl group, and as such increases the resistance of the material.

Chloroprene rubbers are generally vulcanized using metal oxide.[5-6] The primary cross linking agent is zinc oxide which is used along with magnesium oxide. Lead oxides are sometime used when low water absorption is required. Two routes have been proposed for the curing. One requires the incorporation of zinc atoms into crosslink (scheme 5.1), the other leads to ether cross links (scheme 5.2).



$$2CH_2{=}\,CH-\overset{\overset{|}{CH_2}}{\underset{|}{C}}-Cl + ZnO + MgO \rightarrow CH_2{=}CH-\overset{\overset{|}{CH_2}}{\underset{|}{C}}-O-Zn-O-\overset{\overset{|}{CH_2}}{\underset{|}{C}}-CH{=}CH_2 \;\; + MgCl_2$$

Scheme 5.1 – Mechanism of cross linking in 1,2-polychloroprene involving incorporation of Zn atom



$ZnCl_2 + MgO \rightarrow ZnO + MgCl_2$

Scheme 5.2 – Mechanism of showing cross linking in 1,2–polychloroprene through the formation of ether cross links

Chloroprene is not characterized by one out standing property, but its balance of properties is unique among synthetic elastomers. It has good mechanical strength, high ozone and weather resistance, good ageing resistance, low flammability, good resistance to chemicals, good oil and fuel resistance and adhesion to many substrates. Vulcanization of polychloroprene can be accelerated using accelerator like ethylene thiourea (NA22).

It has been observed that study of nano zinc oxides (ZnO(p) and ZnO(s)) in natural rubber[7] improved the mechanical properties and reinforcement. The present study explains the use of ZnO(p) and ZnO(s) in chloroprene rubber in comparison to conventional ZnO. The cure characteristics, mechanical properties and ageing resistance are compared with reference compounds prepared from CR and conventional zinc oxide (ZnO(c)).

5.2 Experimental

Materials:

Neoprene–W manufactured by M/s Dupont, USA with Mooney viscosity (ML (1+4) 100°C) 47, light magnesium oxide, stearic acid, high abrasion furnace black, dioctyl phthalate (DOP), antioxidant HS, conventional ZnO, prepared zinc oxides (ZnO(p), ZnO(s)) and ethylene thiourea Na22.

Preparation of the composites

The base formulation for the preparation of composites is given in the Table 5.1.

Table 5.1 Formulations of gum and filled CR compounds

Ingredient phr	C -1	C - 2	C - 3	C-4	C - 5	C - 6	C- 7	C-8	C - 9	C-10
Neoprene-W	100	100	100	100	100	100	100	100	100	100
Light MgO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HAF	-	-	-	-	40	40	40	40	40	40
DOP	-	-	-	-	8	8	8	8	8	8
ZnO(c)	5	-	-	2	5	-	-	2	-	-
ZnO(p)	-	2	-	-	-	2	-	-	1	-
ZnO(s)	-	-	2	-	-	-	2	-	-	1
Na 22	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Mixing was done in a laboratory size (16 X 33 cm) two roll mill at a friction ratio of 1:1.25 as per ASTM D 3182 (1982).

Testing

The cure characteristics of the mixes were determined using Rubber Process Analyzer RPA 2000, as per ASTM standard, D 2084–01. Subsequently, the rubber compounds were vulcanized up to their 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 hrs, prior to physical testing.

Physical properties, such as modulus, tensile strength, elongation at break, tear strength, hardness, heat build–up, compression set, abrasion loss, flex resistance and ageing resistance were studied as per the respective ASTM standards. Swelling studies of the compounds were carried out in methyl ethyl ketone and crosslink densities were calculated.

5.3 Results and Discussion

5.3.1 Cure characteristics

Table 5.2 Torque values of gum and filled compounds

Property	C – 1	C – 2	C – 3	C-4	C – 5	C – 6	C – 7	C-8	C –9	C- 10
Min torque (dNm)	0.163	0.177	0.177	0.182	0.506	0.402	0.333	0.385	0.297	0.235
Max torque (dNm)	2.605	2.713	2.707	2.48	6.041	5.964	6.240	5.32	4.835	5.423
ΔTorque (dNm)	2.442	2.536	2.530	2.29	5.535	5.562	5.907	4.93	4.538	5.188

Torque values of gum and filled compounds with ZnO(c), ZnO(p) and ZnO(s) are shown in Table 5.2. Compared to the torque values of filled and gum CR compounds with 2phr and 5phr conventional ZnO, it is found that compound with 5phr conventional ZnO (C-1) shows better torque values than compound with 2phr conventional ZnO compound (C-4).

The torque values of filled and gum CR compounds, with 2phr ZnO(p) and 2phr ZnO(s) are equivalent with the torque values of compounds with 5phr ZnO(c). Comparing the torque values of C– 6, C– 7, C– 9 and C–10, the torque values of C-6 and C-7 compounds are better than the torque values of C-9 and C-10 compounds. So 2phr ZnO(p) and 2phr ZnO(s) are selected as the optimum dosage of compounds that can give better reinforcement compared to 1phr ZnO(p) and 1phr ZnO(s).

Table 5.3 Cure behaviour of gum and filled compounds

Property	C– 1	C– 2	C– 3	C-4	C- 5	C– 6	C-7	C-8	C-9	C-10
Scorch time (t_{s2}),min	12.96	12.67	12.96	14.60	4.02	4.53	4.36	4.03	3.98	3.58
Optimum cure time (t_{90}), min	17.53	17.04	17.26	19.80	19.29	19.70	19.60	22.41	20.31	21.12
Cure rate index ($100/t_{90}– t_{s2}$)	21.88	22.88	23.25	19.20	6.54	6.59	6.56	5.44	6.12	5.70

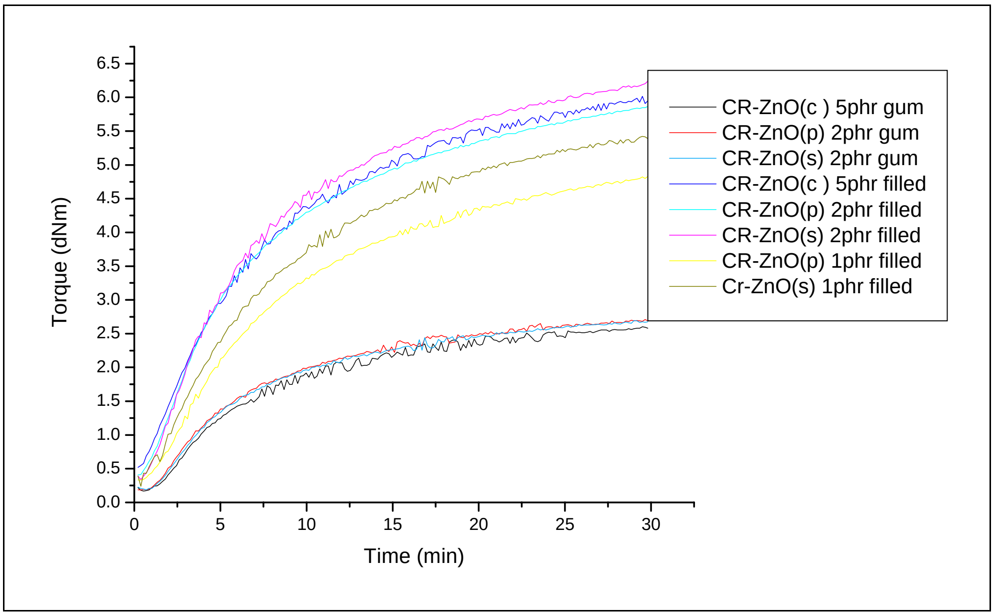


Figure 5.1 Cure graph of neoprene compounds

Cure behaviour of gum and filled compounds are given in the Table 5.3 and in figure 5.1. Compared to the cure values of filled and gum compounds with 2phr and 5phr conventional ZnO, it is found that compounds with 5phr conventional ZnO show better cure values than with 2phr conventional ZnO. Similarly the cure values of filled compounds with 2phr ZnO(p) and ZnO(s) show better cure values than with 1phr ZnO(p) and ZnO(s).

The cure values of gum and filled compounds with 2phr ZnO(p) and 2phr ZnO(s) are equivalent to the compounds with 5phr conventional ZnO(c). This indicates composites with very low dosage of ZnO(p) and ZnO(s) show equivalent cure characteristics as composite with higher dosage of conventional ZnO(c).

5.3.2 Properties of gum composites

Tensile properties

Table 5.4 Tensile properties of CR gum vulcanizates

Composite	Tensile strength MPa	Elongation at break %	Tensile modulus at 300% elongation (Mpa)	Tear strength N/mm
C-1	10.30	1198	1.36	26
C-2	9.58	1192	1.62	28
C-3	10.02	1189	1.66	28
C-4	9.03	1637	1.28	23

Tensile properties of gum vulcanizates with ZnO(c), ZnO(p) and ZnO(s) are shown in Table 5.4. Gum vulcanizate with 2phr conventional ZnO (C-4) has relatively low tensile properties compared to vulcanizate with 5phr conventional ZnO (C-1). Vulcanizates with 2 phr ZnO(p) and ZnO(s) show fairly good modulus and tear strength compared to those containing conventional ZnO vulcanizate. This may be due to increase in crosslink in C-2 and C-3 vulcanizates. Tensile strength and elongation at break of vulcanizates with ZnO(p) and ZnO(s) are comparable to that containing conventional ZnO. These values show that the curative effect of ZnO(p) and ZnO(s) are influenced by the smaller particle size and larger surface area of these prepared ZnO.

Other technological properties

Table: 5.5 Technological properties of gum vulcanizates

Composite	Hardness(shore A)	Compression Set (%)	Abrasion Loss (cc/hr)
C-1	44	23.93	10.71
C-2	44	20.56	7.23
C-3	47	23.02	8.20
C-4	43	25.00	11.27

Other technological properties like hardness, compression set values and abrasion loss for gum vulcanizates are given in Table5.5. Hardness, compression set and abrasion loss for C-1, C-2, and C-3 vulcanizates are superior compared to C-4 vulcanizate. It is clear from the table that the hardness and compression set values of C-2 and C-3 vulcanizates are comparable with C-1 vulcanizate. The abrasion loss values for C-2 and C-3 vulcanizates are reduced compared to C-1 vulcanizate. This indicates that low dosage of ZnO(p) and ZnO(s) are enough to get the same strength as that with higher dosage of conventional ZnO. This may be due to the smaller particle size of ZnO(p) and ZnO(s).[8]

5.3.3 Properties of filled vulcanizates

Tensile properties

Table 5.6 Tensile properties of filled vulcanizates

Composite	Tensile strength MPa	Tensile modulus at300% elongation (MPa)	Elongation at break (%)	Tear strength N/mm
C-5	19.82	8.42	489	53
C-6	18.53	8.46	478	64
C-7	19.48	8.91	468	60
C-8	15.28	7.82	499	50
C-9	14.72	3.68	791	49
C-10	14.91	4.10	712	52

Table 5.6 shows the comparative evaluation of tensile properties of filled vulcanizates.

Filled vulcanizate with 2phr conventional ZnO (C-8) has low tensile properties compared to vulcanizate with 5phr conventional ZnO (C-5). It is seen that tensile properties of C-6 and C-7 vulcanizates are superior to that of C-9 and C-10 vulcanizates. But the values are comparable to that with 5phr conventional ZnO (C-5). This again confirms that the optimum dosage of ZnO(p) and ZnO(s) is 2phr. Tear strength showed more improved values for 2phr ZnO(p) and ZnO(s) vulcanizates. These values are superior to that of conventional ZnO vulcanizate. As the reinforcing capacity increases, generally the elongation at break (%) decreases. Vulcanizates with 2phr ZnO(p) and ZnO(s) show reduced elongation at break values compared to that of vulcanizate with 5phr conventional ZnO. This again shows that 2phr ZnO(p) and ZnO(s) are better curatives than conventional ZnO.

Other technological properties

Table 5.7 Technological properties of filled vulcanizates

Property	C -5	C –6	C-7	C - 8
Hardness (Shore A)	67	69	69	62
Compression set (%)	19.12	16.91	17.36	20.84
Abrasion loss (cc/hr)	2.68	2.40	2.41	2.8
Heat build-up(ΔT)°C	13.2	12.2	13.3	13.9
Flex resistance (k cycles)	35.62	39.44	62.86	30.35

The technological properties like hardness, compression set, abrasion loss, heat build-up and flex resistance were compared for CR vulcanizates with ZnO(p), ZnO(s) and conventional ZnO and is given in the Table 5.7. Hardness, compression set, abrasion loss, heat build-up and flex resistance for C-5, C-6 and C-7 vulcanizates are superior compared to C-8 vulcanizate. Abrasion resistance, compression set and flex resistance are found to be superior for C-6 and C-7 vulcanizates. Hardness and heat build-up values of C-6 and C-7 vulcanizates are comparable with that of C-5 vulcanizate with 5phr conventional ZnO. This indicates low dosage of ZnO(p) and ZnO(s) are better curatives than high dosage of conventional ZnO.

Reinforcing index

Reinforcing index values of composites with respect to tensile strength are given in the Table 5.8.

Table 5.8 Reinforcing index values of composites

Composite	Reinforcing index (%)
C-5	4. 81
C-6	4.83
C-7	4.86
C-8	4.23

Reinforcing index was calculated using the equation, RI = (N/No) (100/m_{filler}) where N and No are the nominal values of the mechanical property (tensile strength) measurements for the sample filled with and without filler respectively.[9] Vulcanizate with 2phr conventional ZnO (C-8) has lesser reinforcing index compared to vulcanizate with 5phr conventional ZnO (C-5). The reinforcing index values of C-6 and C-7 vulcanizates with low dosage of ZnO(p) and ZnO(s) are comparable with C-5 vulcanizate with high dosage of ZnO(c).

5.3.4 Swelling studies

Crosslink density

Crosslink density of filled composites with 2phr of ZnO(p) and ZnO(s) and 5phr of ZnO(c) are shown in Table 5.9.

Table 5.9 Crosslink density of composites

Composite	Crosslink density (mol / g)
C-5	7.38×10^{-05}
C-6	7.55×10^{-05}
C-7	7.94×10^{-05}

Crosslink densities were calculated using Flory–Rehner equation.[10] Swelling studies of composites with 2phr ZnO(p) and ZnO(s) were done to calculate the crosslink density and the values are compared with the crosslink density values of the composite with 5phr conventional ZnO. The crosslink densities of C-6 and C-7 vulcanizates are superior to that of C-5 vulcanizate.

Swelling resistance in solvents and oil

Swelling resistance of gum and filled composites in different solvents and in engine oil are shown in Table 5. 10.

Table 5.10 Swelling index value of composites

Solvent	Swelling index (%)					
	C-1	C-2	C-3	C-5	C-6	C-7
Cyclohexane	86	85	83	43	43	41
Petrol	53	52	52	26	27	25
Diesel	39	39	39	24	25	23
Engine Oil	41	41	38	26	28	24

Several researchers have extensively studied the transport behavior of various organic liquids in polymer composites.[11,12] The phenomenon of transport of liquids through rubbers is controlled by the polymer structure, its crosslink density, presence of fillers, penetrant, size etc. It is clear from the table that the swelling index values of C-2 and C-3 gum vulcanizates are comparable to C-1 gum vulcanizate and the swelling index values of C-6 and C-7 filled vulcanizates are comparable with C-5 filled vulcanizate. This indicates C-2, C-3 and C-6, C-7 vulcanizates with lower dosage of ZnO show equivalent swelling property to that of C-1 and C-5 vulcanizates with higher dosage of ZnO respectively.

5.3.5 Thermal ageing

Ageing resistance of the composites with 2phr ZnO(p), ZnO(s) and 5phr ZnO(c) were measured by measuring the tensile properties after ageing to 72 hrs at 100°C and is given in the Table 5.11.

Table 5.11 Ageing resistance of filled composites

Hours	Tensile strength MPa		
	C-5	C- 6	C-7
24	15.83	16.20	17.41
48	15.91	18.82	18.92
72	16.50	17.29	18.86

During thermal ageing, crosslink formation or crosslink breakage can take place or an existing crosslink may break and a stable linkage can be formed. After ageing tensile strength showed a gradual increase. This indicates better resistance to thermal degradation. The ageing resistances of C-6 and C-7 vulcanizates are superior to C-5 vulcanizate.

5.4 Conclusions

1. Gum and filled composites with 2phr conventional ZnO (C-4 and C-8) showed significant reduction in torque values, tensile properties and other technological properties compared to vulcanizates with 5phr conventional ZnO(C-1 and C-5), 2phr ZnO(p) (C-2 and C-6) and ZnO(s) (C-3 and C-7).
2. Filled vulcanizates with 1phr ZnO(p) and ZnO(s) (C-9 and C-10) showed poor cure characteristics and tensile properties compared to vulcanizates with 2phr ZnO(p) and 2phr ZnO(s) (C-6 and C-7).
3. Vulcanizates with lower dosage (2phr) of ZnO(p) and ZnO(s) were found to have equivalent cure rate and tensile properties compared to vulcanizates with higher dosage (5phr) of conventional ZnO.
4. Tear strength values are superior for vulcanizates with 2phr ZnO(p) and ZnO(s) compared to that of vulcanizates with 5phr conventional ZnO.

5. Hardness, compression set, heat build-up and swelling resistance are found to be comparable for vulcanizates with 2phr ZnO(p), 2phr ZnO(s) and 5phr ZnO(c).
6. Abrasion, flex and thermal ageing resistances are found to be superior for vulcanizates with 2phr ZnO(p) and 2phr ZnO(s) compared to vulcanizate with 5phr ZnO(c).
7. Crosslink density of vulcanizates with 2phr ZnO(p) and 2phr ZnO(s) are slightly higher than vulcanizate with 5phr conventional ZnO.

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Chapter 6

Use of nano zinc oxide in styrene butadiene rubber

Contents

6.1 Introduction

As described in previous chapters, zinc content in rubber products has come under increased scrutiny due to environmental concerns. The trend in rubber industry is therefore to reduce or even completely eliminate the zinc content, although to date no viable alternative for ZnO and zinc containing species for vulcanization purpose has been found.[1] There is general agreement that zinc cations from ZnO and/or zinc compounds react with organic accelerators to give active zinc–accelerator complexes, which is one of the main step in the vulcanization scheme.[2] It has been suggested in many different studies that these active complexes of Zn^{2+} ions with accelerators are more reactive than the free accelerator[3,4] This active sulphurating agent reacts at the allylic sites of the rubber polymer unsaturations to form a rubber bound intermediate, which reacts with another rubber bound intermediate or with another polymer chain to generate a crosslink. The exact activator role of ZnO is highly dependent on the type of accelerator present in the initial vulcanization system.

Fatty acids as co–activators in rubber vulcanization increase the crosslink yield.[5] It is assumed that stearic acid reacts with ZnO to form zinc stearate, which is an essential cure activator. Its function has been the subject of extensive research by Kruger and McGill.[6] Morrison and Porter reported that zinc stearate inhibits zinc promoted decomposition of mono sulphide cross links, though the mechanism is unclear.[7]

It was observed that addition of nano zinc oxide (from precipitation and solid–state pyrolytic method) in polar synthetic rubber has improved the mechanical properties and so the same method was studied in non-polar synthetic rubber, 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 copolymerization of styrene and butadiene under controlled conditions of reaction using different techniques of polymerization and the polymer properties vary with the method of polymerization.

The unsaturation in SBR is less than that in NR and the double bonds are chemically less active 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.[8] All types of SBR require less sulphur than NR for curing. On the other hand SBR requires more accelerators, because of lower unsaturation.

This chapter explains the use of low dosage of ZnO(p) and ZnO(s) as activator in SBR and compares the mechanical properties of the vulcanizates with reference to the vulcanizates prepared from SBR and conventional zinc oxide (ZnO(c)).

6.2 Experimental

Materials:

SBR(1502) with Mooney viscosity (ML 1+4) at 100°C is 52, ZnO(p), ZnO(s), conventional ZnO(c), stearic acid, vulkanox HS, high abrasion furnace black, aromatic oil, CBS, TMTD and sulphur.

Preparation of the composites

The base formulation for the preparation of compounds is given in the Table 6.1.

Table 6.1 Base formulation for SBR compounds

Ingredient (phr)	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10
SBR1502	100	100	100	100	100	100	100	100	100	100
ZnO(c)	4.5	-	-	2	4.5	-	-	2	-	-
ZnO(p)	-	2	-	-	-	2	-	-	1	-
ZnO(s)	-	-	2	-	-	-	2	-	-	1
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HAF	-	-	-	-	40	40	40	40	40	40
Aromatic oil	-	-	-	-	7.0	7.0	7.0	7.0	7.0	7.0
CBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
S	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

Testing

The cure characteristics of the mixes were determined using Rubber Process Analyzer RPA 2000 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 hrs prior to physical testing.

Physical properties such as modulus, tensile strength, elongation at break, tear strength, hardness, heat build-up, compression set, flex resistance, abrasion resistance and ageing resistance were studied as per the relevant ASTM standards. Swelling studies were used to study the crosslink density. The equilibrium swelling studies of the compounds were carried out in toluene and crosslink densities were calculated using Flory-Rehner equation.

6.3 Results and discussion

6.3.1 Cure characteristics

Torque values of gum and filled compounds are shown in Table 6.2.

Table 6.2 Cure characteristics of SBR compounds

Property	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10
Min torque (dNm)	0.182	0.098	0.124	0.18	0.23	0.33	0.29	0.27	0.34	0.37
Max torque(dNm)	3.239	3.295	3.389	3.03	7.93	8.13	8.06	5.72	5.66	5.70
Δ torque (dNm)	3.057	3.197	3.266	2.85	7.70	7.79	7.76	5.45	5.31	5.32

Compounds with 5phr ZnO(c) showed better torque values compared to compounds with 2phr ZnO(c). The torque values of filled and gum compounds with 2phr ZnO(p) and 2phr ZnO(s) are comparable with that of filled and gum compounds with 5phr of ZnO(c). But the torque values of filled compounds with 2phr of ZnO(p) and ZnO(s) are better than that with 1phr of ZnO(p) and ZnO(s). So compounds with 2phr ZnO(p) and ZnO(s) showed higher cross linking in rubber matrix compared to compounds with 1phr of ZnO(p) and ZnO(s). On evaluating the torque values, 2phr ZnO(p) and ZnO(s) are selected as the optimum dosage of filled compounds that can give better reinforcement.

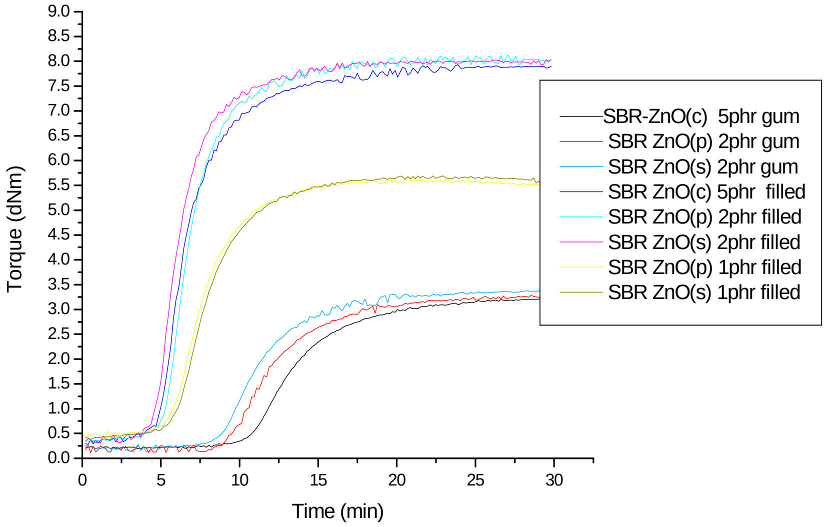


Figure 6.1 Cure graph of styrene butadiene compounds

Figure 6.1 shows the cure graph of styrene butadiene compounds. Cure time of gum and filled SBR compounds with ZnO(p), ZnO(s) and ZnO(c) are given in Table 6.3.

Table 6.3 Cure time values of SBR compounds

Property	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10
Scorch time (t_{s2}), min	11.73	10.08	9.07	14.39	5.64	5.92	5.29	5.10	4.52	4.22
Optimum cure time (t_{90}), min	15.92	14.41	13.13	19.70	11.13	11.27	10.39	12.38	12.12	11.74
Cure rate index ($100/t_{90}$-t_{s2})	23.86	23.09	24.63	18.83	18.21	18.69	19.60	13.73	13.15	13.29

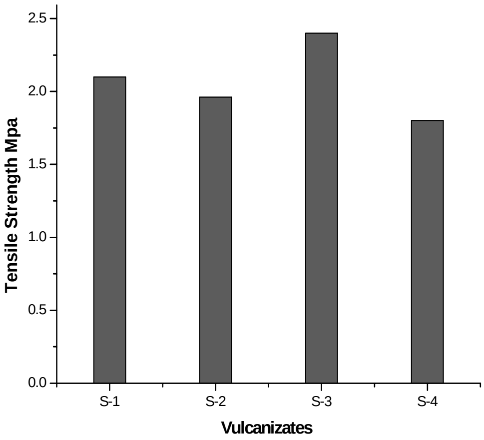
Compared to the cure characteristics of gum and filled compounds of 2phr ZnO(c), the cure properties of compounds with 5phr ZnO(c) are superior. Similarly, compounds with 2phr ZnO(p) and 2phr ZnO(s) are superior compared to compounds with 1phr ZnO(p) and 1phr ZnO(s). The compounds with low dosage (2phr) of ZnO(p) and ZnO(s) showed similar cure characteristics as that with high dosage (5phr) of conventional ZnO(c).

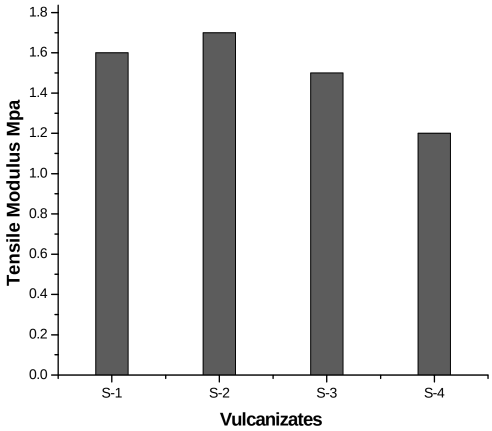
The cure rate index of gum compounds (S-2, S-3) and filled compounds (S-6, S-7) are comparable with that of gum (S-1) and filled (S-5) compounds of 5phr ZnO(c) respectively.

6.3.2 Properties of gum composites

Tensile properties

Tensile properties of gum vulcanizates are shown in Figure 6.2. The tensile properties of vulcanizate with 5phr ZnO(c) is superior compared to the vulcanizate with 2phr ZnO(c). The tensile strength and tensile modulus of gum vulcanizates with 2phr ZnO(p) and 2phr ZnO(s) are comparable to the gum vulcanizate with 5phr of ZnO(c). Tear strength of gum vulcanizates with 2phr of ZnO(p) and 2phr of ZnO(s) are slightly increased compared to gum vulcanizate with 5phr of ZnO(c). Elongation at break of gum vulcanizates with 2phr of ZnO(p) and 2phr of ZnO(s) are reduced compared to gum vulcanizate with 5phr of ZnO(c). This improvement in properties is due to the smaller particle size and larger surface area of ZnO(p) and ZnO(s) compared to ZnO(c).





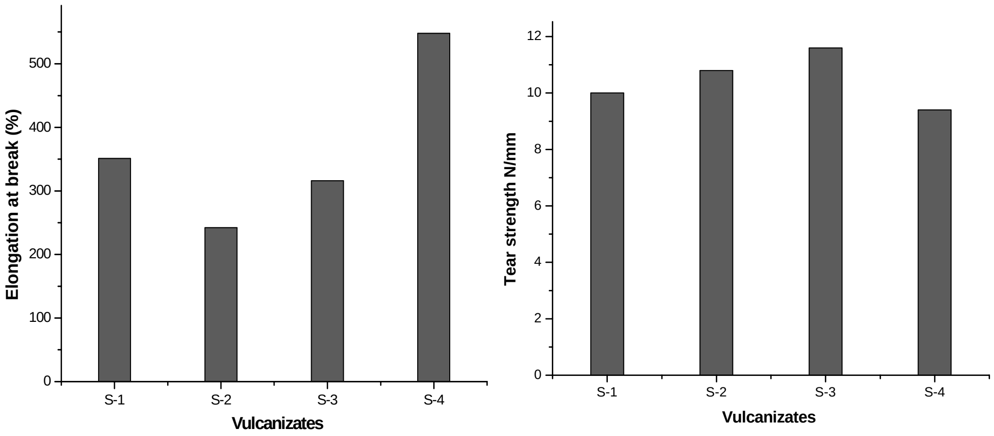


Figure 6.2: Tensile properties of SBR gum vulcanizates

Other mechanical properties

Other mechanical properties like hardness, compression set and abrasion loss of the gum vulcanizates are given in the Table 6.4.

Table 6.4 Other mechanical properties of SBR gum vulcanizates

Composite	Hardness (Shore A)	Compression set (%)	Abrasion loss (cc/hr)
S-1	45	43.02	4.39
S-2	45	39.68	4.07
S-3	45	39.01	3.98
S-3	43	47.12	4.82

The mechanical properties of gum vulcanizate with 5phr ZnO(c) are superior compared to the mechanical properties of vulcanizate with 2phr ZnO(c). Hardness, a measure of the low strain elastic modulus was found to be comparable for vulcanizates with 2phr ZnO(p), ZnO(s) and 5phr ZnO(c). Compression set and abrasion loss of the gum vulcanizates with 2phr ZnO(p), 2phr ZnO(s) are found to be reduced compared to gum vulcanizate with 5phr ZnO(c). This indicates vulcanizates with low dosage of ZnO(p) and ZnO(s) show better mechanical properties compared to vulcanizate with higher dosage (5phr) of ZnO(c).

6.3.3 Properties of filled composites

Tensile properties

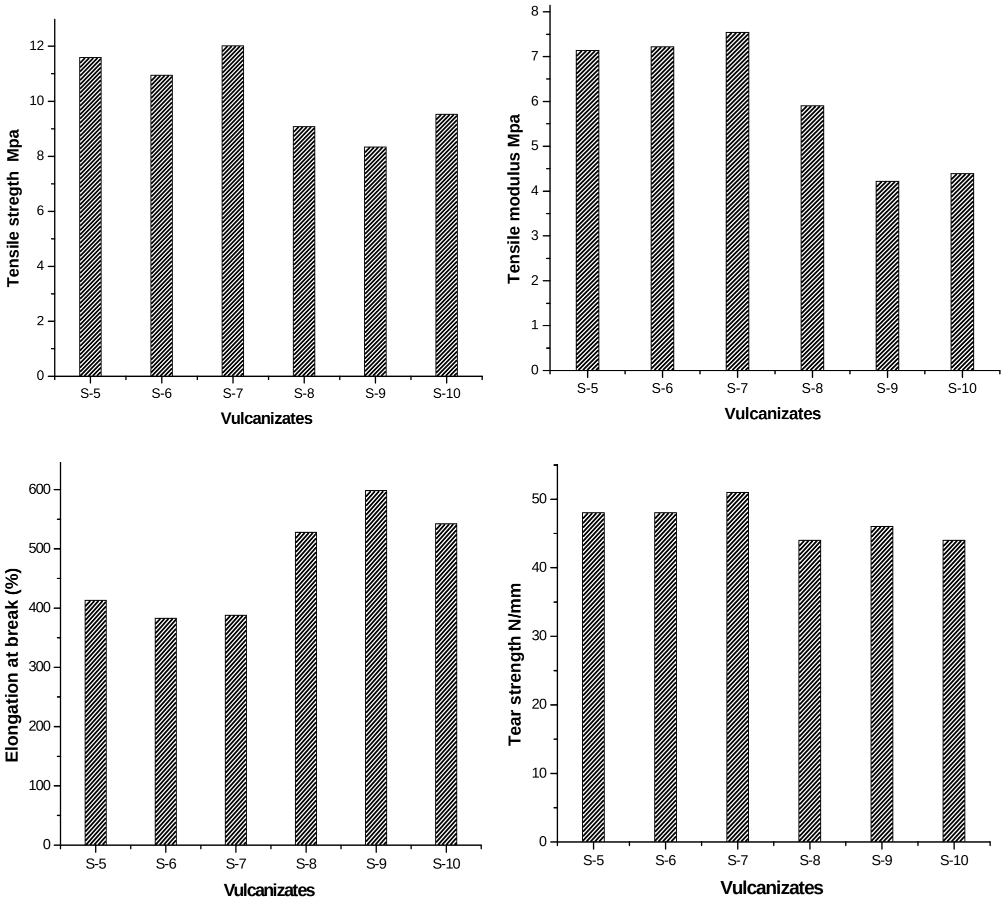


Figure 6.3 Tensile properties of filled vulcanizates of SBR

Tensile properties of SBR filled vulcanizates are shown in Figure 6.3. The tensile properties of vulcanizate with 5phr ZnO(c) is superior compared to the tensile properties of vulcanizate with 2phr ZnO(c). Similarly the tensile properties of vulcanizates with 2phr ZnO(p) and 2phr ZnO(s) are superior compared to the tensile properties of vulcanizates with 1phr ZnO(p) and 1phr ZnO(s). Figure 6.3 shows that the tensile strength, tensile modulus and tear strength values for vulcanizates with 2phr ZnO(p) and 2phr ZnO(s) are comparable to vulcanizate with 5phr ZnO(c). Elongation at break is found to be less for vulcanizates with 2phr ZnO(p) and ZnO(s). This indicates that smaller particle size of ZnO(p) and ZnO(s) leads to an improved distribution in the SBR matrix.

Other mechanical properties

Mechanical properties like hardness, compression set, abrasion loss, heat build-up and flex resistance of filled vulcanizates are given in the Table 6.5.

Table 6.5 Mechanical properties of SBR filled composites

Composite	Hardness (Shore A)	Compression set (%)	Abrasion loss (cc/hr)	Heat build up (Δ T)^{0}C	Flex resistance (k cycle)
S-5	69	22.85	2.64	12.9	28.23
S-6	69	21.73	2.55	11.5	38.39
S-7	69	20.45	2.60	8.8	40.29
S-8	65	24.00	3.08	13.2	26.32

The mechanical properties for filled vulcanizate with 5phr ZnO(c) are superior compared to vulcanizate with 2phr ZnO(c). Vulcanizates with 2phr ZnO(p) and ZnO(s) showed better abrasion resistance, compression set and flex resistance compared to vulcanizate with 5phr ZnO(c). This may be due to smaller particle size of ZnO(p) and ZnO(s). Hardness values are comparable with the conventional ZnO vulcanizates. Heat build-up values are low for vulcanizates with 2phr ZnO(p) and ZnO(s) vulcanizates.

Reinforcing index

Reinforcing index values of SBR vulcanizates with respect to tensile strength are given in the Table 6.6.

Table 6.6 Reinforcing index of SBR vulcanizates

Vulcanizates	Reinforcing index (%)
S-5	13.79
S-6	13.96
S-7	14.04
S-8	12.61

Vulcanizate with 5phr ZnO(c) showed better reinforcing index values compared to vulcanizate with 2phr ZnO(c). Reinforcing index values of vulcanizates with 2phr ZnO(p) and ZnO(s) are slightly increased with that of vulcanizate with 5phr ZnO(c). This shows that low dosage of ZnO(p), ZnO(s) have improved reinforcing capacity compared to that of higher dosage of conventional ZnO(c).

6.3.4 Swelling studies

Crosslink density

Crosslink densities of filled vulcanizates of SBR are given in Table 6.7. Swelling of the vulcanized samples was done in toluene and crosslink densities were calculated using Flory-Rehner equation.[9]

Table 6.7 Crosslink density of filled SBR vulcanizates

Composite	Crosslink density × 10^{-5} moles /g
S-5	7.16
S-6	7.28
S-7	7.36

It can be seen that the vulcanizates with 2phr ZnO(p) and ZnO(s) showed better crosslink density compared to vulcanizate with 5phr conventional ZnO.

Swelling resistance in other solvents

The swelling index of all gum and filled composites in various solvents are given in Table 6.8.

Table 6.8 Swelling index of gum and filled SBR vulcanizates

Solvent	S-1	S-2	S-3	S-5	S-6	S-7
Petrol	1.70	1.73	1.64	0.76	0.74	0.71
Diesel	1.66	1.70	1.65	0.80	0.80	0.80
Cyclohexane	2.37	2.36	2.27	1.05	1.00	1.01

The swelling index of the samples in different solvents was studied by keeping the sample of known weight in solvent for equilibrium swelling. Table 6.8 shows the swelling index of the vulcanizates with 2phr ZnO(p), 2phr ZnO(s) and 5phr ZnO(c). These values are found to be comparable for vulcanizates with 2phr ZnO(p), 2phr ZnO(s) and 5phr ZnO(c).

6.3.5 Thermal ageing

Ageing resistance of the vulcanizates with 2phr ZnO(p), 2phr ZnO(s) and 5phr ZnO(c) are assessed by measuring the tensile properties after ageing to 96 hours and are shown in the Figure 6.4 (a-d).

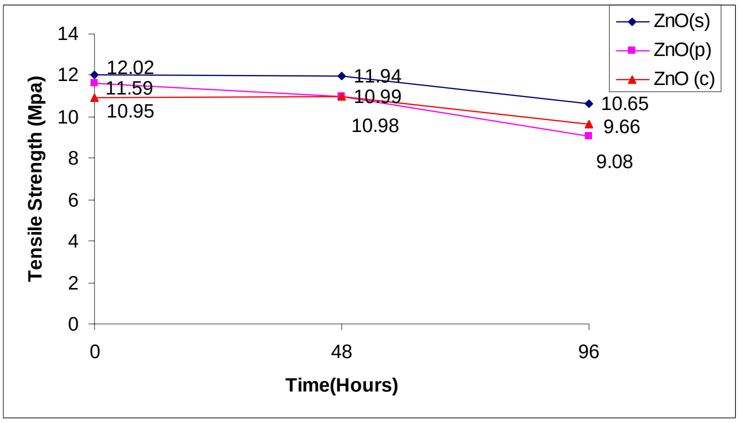


Figure 6.4 (a) Variation in tensile strength of SBR vulcanizates with time of ageing at 100°C

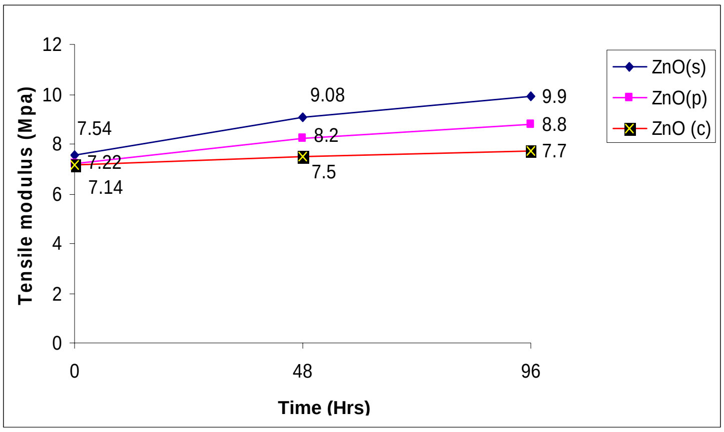


Figure 6.4 (b) Variation in tensile modulus of SBR vulcanizates with time of ageing at 100°C

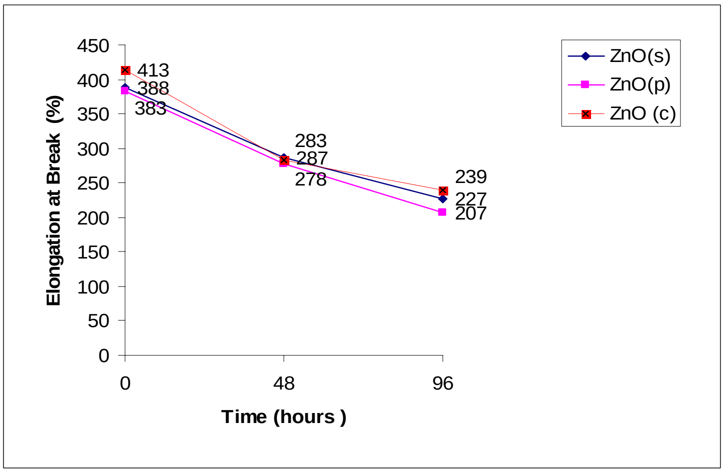


Figure 6.4 (c) Variation in elongation at break of SBR vulcanizates with time of ageing at 100°C

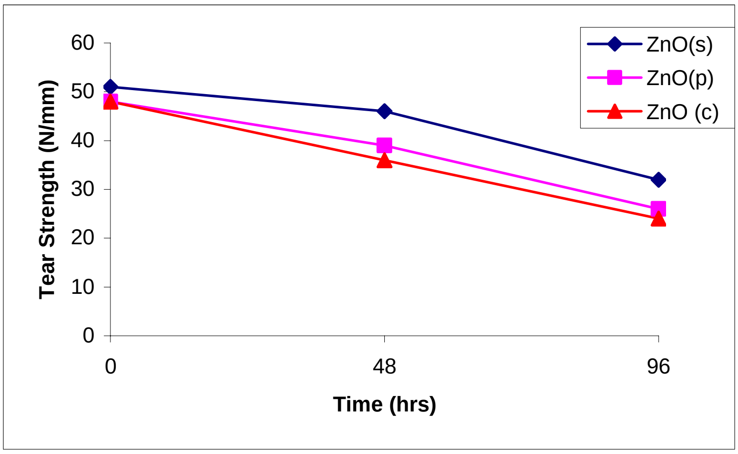


Figure 6.4(d) Variation in tear strength of SBR vulcanizates with time of ageing at 100°C.

Figure 6.4(a) shows the variation in tensile strength of the vulcanizates with time of ageing at 100°C. The vulcanizates with 2phr ZnO(p) and ZnO(s) show fairly good resistance to ageing at 100°C compared to those containing 5phr conventional ZnO.

Figure 6.4(b) shows the modulus of the vulcanizates with time of ageing. The increase in modulus after ageing may be due to increase in crosslink density. 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 changes greatly influence the performance of the vulcanizates. Tensile modulus of vulcanizates with 2phr ZnO(p) and 2phr ZnO(s) are superior compared to vulcanizate with 5phr ZnO(c).

Figure 6.4(c) shows the change in elongation at break of the vulcanizates with time of ageing. Vulcanizates with 2phr ZnO(p) and ZnO(s) showed better retention in elongation at break after ageing. This again shows that vulcanizates with ZnO(p) and ZnO(s) can improve the ageing resistance of SBR vulcanizates.

Figure 6.4(d) shows the tear strength of the vulcanizates with time of ageing at 100°C. Retention in tear strength of the vulcanizates with 2phr ZnO(p) and ZnO(s) after ageing is superior than to vulcanizate with 5phr conventional ZnO.

The above results indicate that low dosage of ZnO(p), ZnO(s) can improve the tensile properties of vulcanizates compared to higher dosage of ZnO(c) vulcanizate.

6.4 Conclusions

1. Gum and filled composites with 5phr conventional ZnO (S-1 and S-5) have better cure characteristics, tensile properties and other technological properties compared to composites with 2phr ZnO(c).
2. Filled composites with 2phr ZnO(p) and ZnO(s) (S-6 and S-7) showed better cure characteristics and tensile properties compared to composites with 1phr ZnO(p) and 1phr ZnO(s) (S-9 and S-10).
3. Compounds with low dosage (2phr) of ZnO(p) and ZnO(s) showed similar cure characteristics as that with high dosage (5phr) of conventional ZnO(c).
4. Tensile properties of composites with optimum dosage of ZnO(p) and ZnO(s) are comparable to vulcanizates with 5phr ZnO(c).
5. Compression set, abrasion loss, heat build-up values are low for vulcanizates with optimum dosage of ZnO(p) and ZnO(s).
6. Retention in tensile properties of the vulcanizates with low dosage of ZnO(p) and ZnO(s) after thermal ageing is superior compared to vulcanizate with 5phr conventional ZnO.
7. Crosslink density of composite with optimum dosage of ZnO(p) and ZnO(s) are slightly higher than vulcanizates with 5phr conventional ZnO.
8. The swelling index values are found to be equivalent for gum and filled vulcanizates with 2phr ZnO(p), 2phr ZnO(s) and 5phr ZnO(c).

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Chapter 7

Use of antioxidant modified precipitated silica in natural rubber, chloroprene rubber and styrene butadiene rubber

Contents

7.1 Introduction

Incorporation of precipitated silica in rubber is quite different from that of carbon black. Carbon black is reinforcing filler for hydrocarbon rubbers.[1] 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 as for as reinforcement is concerned. Precipitated silica is used as reinforcing filler and have particle sizes as small as the carbon black besides an extremely reactive surface.[2] Different 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.[3] Pyrogenic silica is too active and expensive. Precipitated silica is a 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.[4]

However, the silica surface has a tendency to absorb moisture due to its hydrophilic character. This adversely influences the curing reaction and hence the properties of the final product. The hydroxyl groups on the surface of the silica control surface acidity. This intrinsic acidity can influence vulcanization.[5] The higher moisture content increases the dispersion time of silica into the rubber. Absorbed water can decrease cure time, tensile strength, bound rubber content [6] and also abrasion resistance.[7]

Rubber articles under severe service conditions undergo different types of degradations like ozone, oxidation etc. Although ozone is present in the atmosphere at concentration normally in the range 0-7pphm[8], it can severely attack unsaturated rubber products under stress. The general subject of protection of rubber against ozone attack has been reviewed by a number of authors.[9-11] Several theories have appeared in the literature regarding the mechanism of antiozonant protection. The “scavenger” model states that the antiozonant blooms to the surface and preferentially reacts with ozone so that the rubber is not attacked until the antioxidant is exhausted.[11-12]

The protective film theory is similar except that the ozone–antiozonant reaction products form a film on the rubber surface that prevent ozone attack.[13] A third “relinking” theory states that the antiozonant prevents scission of the ozonised rubber recombines several double bonds.[14]

During recent years there has been a gradually increasing demand for antidegradants to give optimum protection of rubber goods. Derivatives of p-phenylenediamine (PPD) offer excellent protection to rubber vulcanizates as antioxidants, antiozonants and antiflex cracking agent. P-phenylenediamine antidegradants function as primary antioxidants and are recognized as the most powerful class of chemical antiozonants, antiflex cracking agents and antioxidants. PPD's are extensively used in tyres belting and molded and extruded rubber products as antiozonants and antiflex cracking agent. PPD's are also used as polymer stabilizer.

Derivatives of p-phenylenediamine fall into three classes:

1) N,N'-dialkyl PPD's 2) N-alkyl-N'-aryl PPD's 3) N,N'-diaryl PPD's Even though N,N'-dialkyl p-phenylenediamines offer excellent static ozone resistance, they are not very effective under dynamic conditions. They are more sensitive to oxygen and hence suffer from lack of persistency and poor shelf life, where as alkyl–aryl PPD's and diaryl PPD's are less volatile than dialkyl PPD's. They are stable and have good shelf life.

To overcome the difficulty in dispersing silica in rubber matrix and also to protect the rubber from deterioration due to heat, light, oxygen and ozone, precipitated silica is modified by antioxidant. This chapter explains the modification of silica with antioxidant and their use as filler in natural rubber and in synthetic rubbers. The mechanical properties and ozone resistance are measured and compared with that containing equivalent amount of antioxidant and silica.

Part - A

USE OF ANTIOXIDANT MODIFIED SILICA IN NATURAL RUBBER

7.2 Experimental

Materials

Natural rubber of grade ISNR-5, conventional zinc oxide, stearic acid, precipitated silica, antioxidants IPPD [N-isopropyl-N′-phenyl-p-phenylenediamine], 6PPD [N-(1,3-dimethylbuty1)–N′-pheny1-p-phenylenediamine], DPPD [N,N′-diphenyl-p-phenylenediamine], naphthenic oil, diethylene glycol (DEG), cyclohexylbenzothiazyl sulfenamide (CBS), tetramethylthiuram disulfide (TMTD), sulphur.

Preparation of antioxidant modified precipitated silica

Antioxidant (1phr) was mixed with precipitated silica (50phr) in torque rheometer (Brabender plasticorder) at 50 rpm for above the melting temperature of antioxidant for 5 minutes. Antioxidants used in this study, to modify silica are IPPD, 6PPD and DPPD.

Preparation of composites

Compounds were prepared as per the formulation given in Table 7.1.

Table 7.1 Formulation of composites

Ingredients (phr)	E-1	E-2	F-1	F-2	G-1	G-2
Natural Rubber	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
stearic acid	2	2	2	2	2	2
Antioxidant modified precipitated silica	51(IPPD)	-	51(6PPD)	-	51 (DPPD)	-
Precipitated silica	-	50	-	50	-	50
IPPD	-	1	-	-	-	-
6PPD	-	-	-	1	-	-
DPPD	-	-	-	-	-	1
Naphthenic oil	8	8	8	8	8	8
DEG	1	1	1	1	1	1
CBS	0.6	0.6	0.6	0.6	0.6	0.6
TMTD	0.1	0.1	0.1	0.1	0.1	0.1
S	2.5	2.5	2.5	2.5	2.5	2.5

Compounds were prepared by mill mixing on a laboratory size (16 x 33 cm) two–roll mill at a friction ratio of 1:1.25 as per ASTM D 3184-89

(2001). After complete mixing of the ingredients the stock was passed out at a fixed nip gap. The samples were kept overnight for maturation.

Testing

The cure characteristics of all mixes were determined using Rubber Process Analyzer as per ASTM standard D 2084-01. Subsequently the rubber compounds were vulcanized upto 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 hrs prior to physical testing.

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

Studies on rubber filler interactions

The strain sweep measurements on unvulcanized samples and vulcanized compounds were conducted to study the rubber-filler interaction. Filled rubber materials need special instruments for rheology. Rubber process analyzer (RPA-2000 Alpha technologies) is a purposely modified commercial dynamic rheometer.[15] The variation of complex modulus with strain was studied for the compounds before and after curing.

Swelling studies

Swelling studies of the composites were conducted in toluene to find their crosslink densities using Flory-Rehner equation.[16]

Ageing studies

Thermal ageing

Thermal ageing was carried out at temperature of 100°C for 48 hrs and 96 hrs as per ASTM D 573-1999.

Ozone resistance

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 12 hrs. The concentration of ozone was maintained at 50 ppm at 20% strain and the inside temperature at 40°C. The ozone cracks developed on the samples were observed by a lens and the photographs were taken.

7.3 Results and discussion

7.3.1 Characterization

Surface area studies

Table 7.2 shows the surface area values of precipitated silica and modified silica. It is found that the surface area is lesser for modified silica compared to the unmodified precipitated silica. This shows that antioxidants are adsorbed on to the surface of silica under physical force of attraction.

Table 7.2 Surface area of silica

Samples	Surface area (m^2/g)
Neat precipitated silica	178
Modified silica	127

7.3.2 Cure characteristics

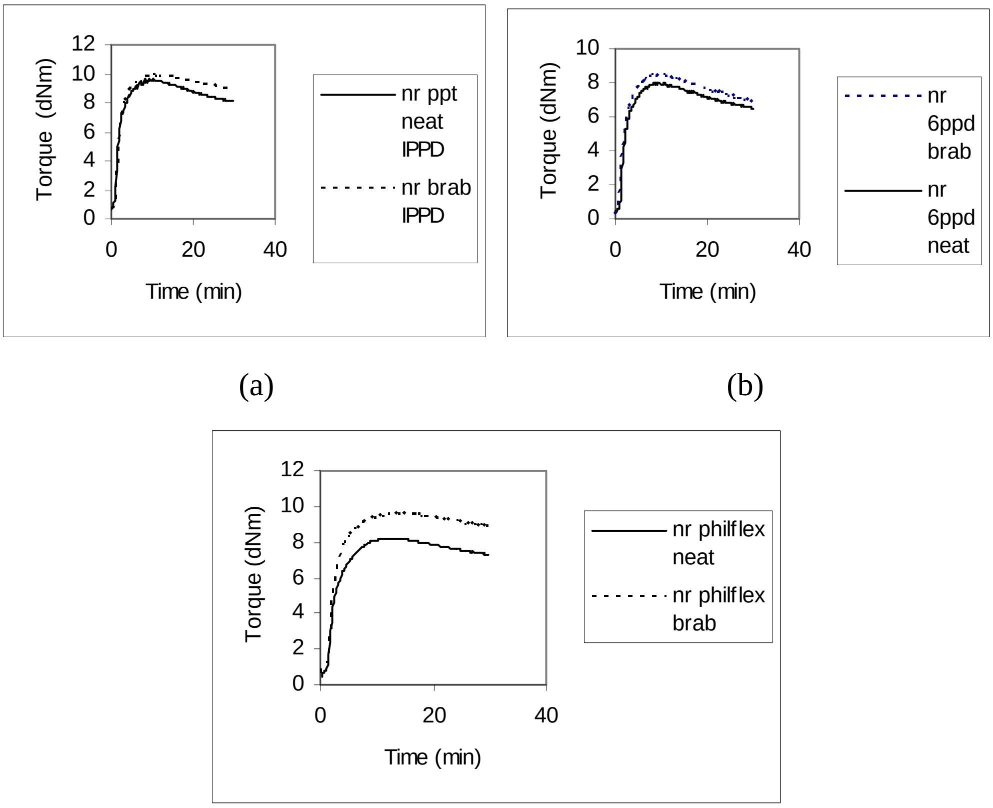
Cure characteristics of the NR compounds with an optimum concentration of 50phr silica and 1phr antioxidant are shown in Table 7.3.

Table 7.3 Cure characteristics of the mixes

Mix	Min torque dNm	Max torque dNm	Scorch time (min)	Optimum cure time (min)	Cure rate index (%)
E-1	0.481	9.88	1.39	4.77	29.58
E-2	0.559	9.69	1.06	5.07	24.93
F-1	0.251	8.52	1.15	5.11	25.20
F-2	0.392	8.01	1.10	5.18	24.50
G-1	0.643	9.64	1.55	6.37	20.72
G-2	0.457	8.23	1.39	6.49	19.60

From the Table, it is seen that the cure values of compounds filled with antioxidants modified silica exhibit higher cure rate and extent of cure over that of compounds with neat precipitated silica. Chemical surface groups on fillers play an important role in their effect on rate of cure, with many vulcanized 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 or silica- zinc ion interaction leads to slowing down of the curing reaction.[17] But in the case of antioxidant modified silica, the -OH groups on the surface are already hydrogen bonded with the NH group of the substituted phenylenediamine antioxidant.

Cure graphs of the three types of antioxidants filled compounds are shown in the Figure 7.1(a-c). The maximum torque is a measure of crosslink density and stiffness in the rubber.[18] In general, for all the mixes, the torque initially decreases and then increases. The increase in torque is due to the cross linking of rubber. It is found that the antioxidant modified silica increases the torque compared to the neat precipitated silica. This increase is due to the presence of silica- rubber crosslink that imparts more restriction to deformation.



(a) (b)

(c)

Figure 7.1 Cure graphs of compounds filled with antioxidant modified silica (nr IPPD, 6PPD,DPPD(philflex) brabender mixed) and with neat silica (nr IPPD,6PPD,DPPD(philflex) neat)

7.3.3 Tensile properties

Tensile properties of NR vulcanizates with antioxidant modified silica and with neat silica are shown in Table 7.4.

Table 7.4 Tensile properties of NR vulcanizates

Vulcanizate	Tensile strength, Mpa	Tensile modulus at 300% elongation, Mpa	Elongation at break %	Tear strength (N/mm)
E-1	23.28	3.50	966	59
E-2	22.60	3.27	1027	54
F-1	21.05	2.93	1017	60
F-2	20.58	2.76	1066	56
G-1	16.27	2.60	995	56
G-2	16.19	2.52	1036	54

The tensile strength behavior of vulcanizates filled with antioxidant modified silica and with neat silica are similar. But there is considerable improvement in other properties for antioxidant modified silica vulcanizates. The antioxidant modified silica vulcanizates showed considerable improvement in tear strength. This can be attributed to the better dispersion and improved filler rubber interaction. The tensile modulus values also show the similar behavior indicating better reinforcement. Elongation at break of different vulcanizates showed that the elongation at break is less for antioxidant modified silica vulcanizates compared to neat silica vulcanizates. Improved tensile strength and reduced elongation at break are considered as criteria for higher filler reinforcement.[19] The improvement in tensile properties for antioxidant modified silica vulcanizates proves the better dispersion of filler in the rubber matrix.

7.3.4 Other technological properties

Other properties like hardness, compression set, abrasion loss and flex resistance were compared for the vulcanizates with antioxidant modified silica and with neat silica and is given in the Table 7.5.

Antioxidant modified silica vulcanizates showed better abrasion resistance. This is due to the strong adhesion of silica particles on rubber chains. Hardness also showed the same improvement. Compression set are found to be comparatively low for antioxidant modified silica composites. This indicates lower elasticity of antioxidant modified silica vulcanizates.

Table 7.5 Technological properties of vulcanizates

Property	E-1	E-2	F-1	F-2	G-1	G-2
Hardness (shore A)	60	54	65	65	62	60
Compression set (%)	54.40	61.78	56.90	64.28	55.63	56.58
Abrasion loss (cc/hr)	5.42	5.94	6.26	6.35	5.66	5.97
Flex resistance (k cycles)	35.7	28.6	24.3	24.1	26.6	25

The number of flex cycles required for crack initiation was noted and it is comparatively high for antioxidant modified silica vulcanizates, indicating that antioxidant modification improves the distribution of antioxidant and silica in rubber.

Reinforcing index

Reinforcing index (RI) values of NR vulcanizates are given in the figure 7.2. Reinforcing index is calculated using the equation RI = $(N/No) \times (100/m_{\text{filler content}})$ where N and No are the nominal values of the mechanical property (tensile strength) measurement for the sample filled with and without silica respectively.[20]

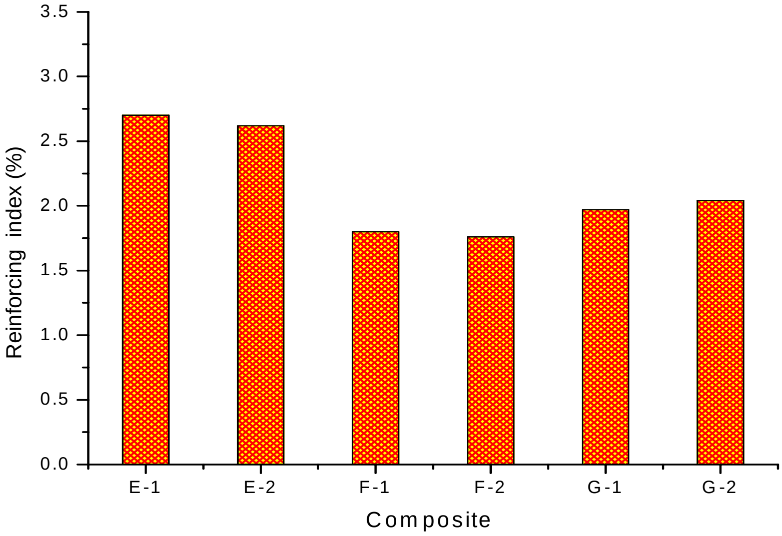


Figure.7.2 Reinforcing index of NR vulcanizates

The values of antioxidant modified silica vulcanizates are comparable with that of neat silica vulcanizates. This shows that antioxidant modified silica filled vulcanizates have reinforcing capacity equivalent to that of neat silica filled vulcanizates.

Crosslink density

The crosslink density of vulcanizates with antioxidant modified silica and with neat silica is shown in figure 7.3. It is seen that the antioxidant (IPPD) modified silica has better value. The increased crosslink density of antioxidant modified silica filled vulcanizates indicates a better adhesion between the rubber and silica particles.

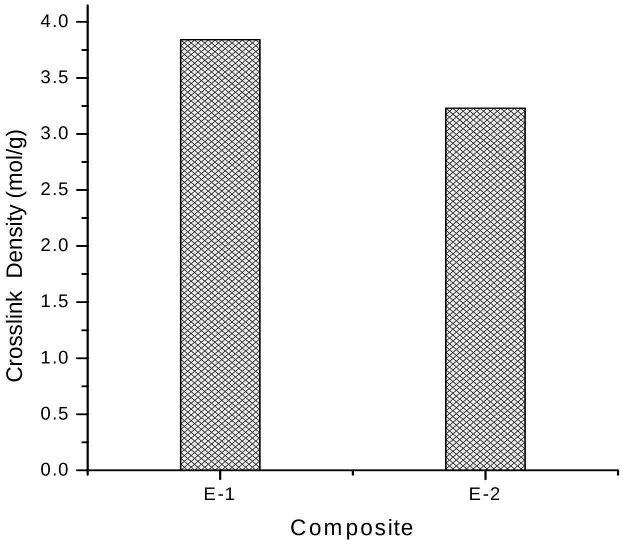


Figure.7.3 Crosslink density of vulcanizates

Heat build-up

Heat build-up values of vulcanizates with antioxidant modified silica and with neat silica are shown in Table 7.6.

Table 7.6 Heat build-up values of vulcanizates

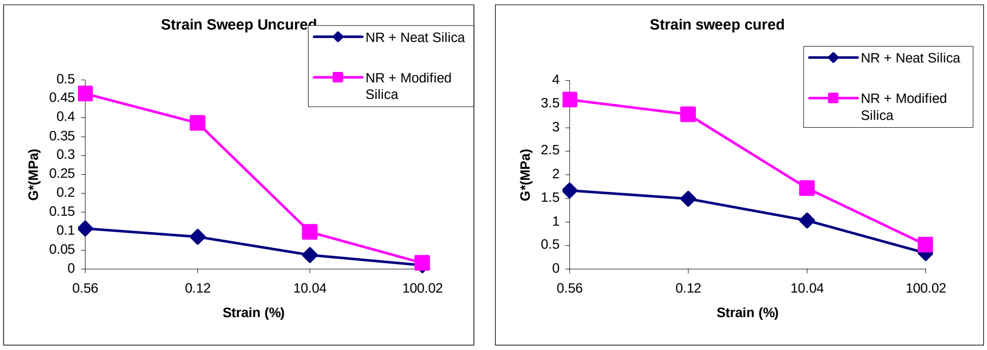
Vulcanizates	Heat build-up (ΔT)°C
E-1	19.7
E-2	26.8

Heat build-up value for vulcanizate filled with antioxidant modified silica is lesser than vulcanizate filled with neat silica. Friction between the silica particles are reduced by the antioxidant which acts as lubricants. So it reduces the heat developed by the frictional strain.

7.3.5 Rubber-filler interaction studies

With antioxidant IPPD

The complex modulus G* of composites containing antioxidant modified silica and neat silica were measured before and after curing. The variation of G* with strain for uncured and cured samples are shown in figure 7.4(a,b) respectively. The complex modulus at low strains is a measure of the filler-polymer interaction.[21-23] At low strains the complex modulus of antioxidant modified silica filled composite are remarkably high compared to higher strain. This may be due to the hydrogen bonding between silanol groups and –NH groups in the antioxidant at lower strain.



(a) **(b)**

Figure 7.4 (a) Variation of complex modulus with strain for uncured compounds **(b)** Variation of complex modulus with strain for cured compounds

7.3.6 Ageing studies

a) Thermal ageing studies

Figure 7.5(a) shows variation in the tensile strength of the filled vulcanizates of NR with time of ageing. The vulcanizate containing IPPD modified silica shows good resistance when the ageing time is increased to 96 hrs. This shows that antioxidant is getting coated over the silica surface and gets uniformly distributed in the rubber matrix.

Figure 7.5(b) shows the change in modulus of the vulcanizates with ageing time. The increase in modulus after 96 hrs may be due to the increase in total crosslink density.

Figure 7.5(c) shows the change in elongation at break of the vulcanizates with ageing time. The vulcanizate filled with antioxidant modified silica shows better retention in elongation at break after ageing. This again shows that antioxidant modified silica can improve the ageing resistance of the NR vulcanizate.

Figure 7.5(d) shows the tear strength of the vulcanizates with time of ageing. The vulcanizates containing antioxidant modified silica shows good resistance when the ageing time is increased to 96 hrs. This may be due to the increased rubber filler interactions in antioxidant modified silica vulcanizates.

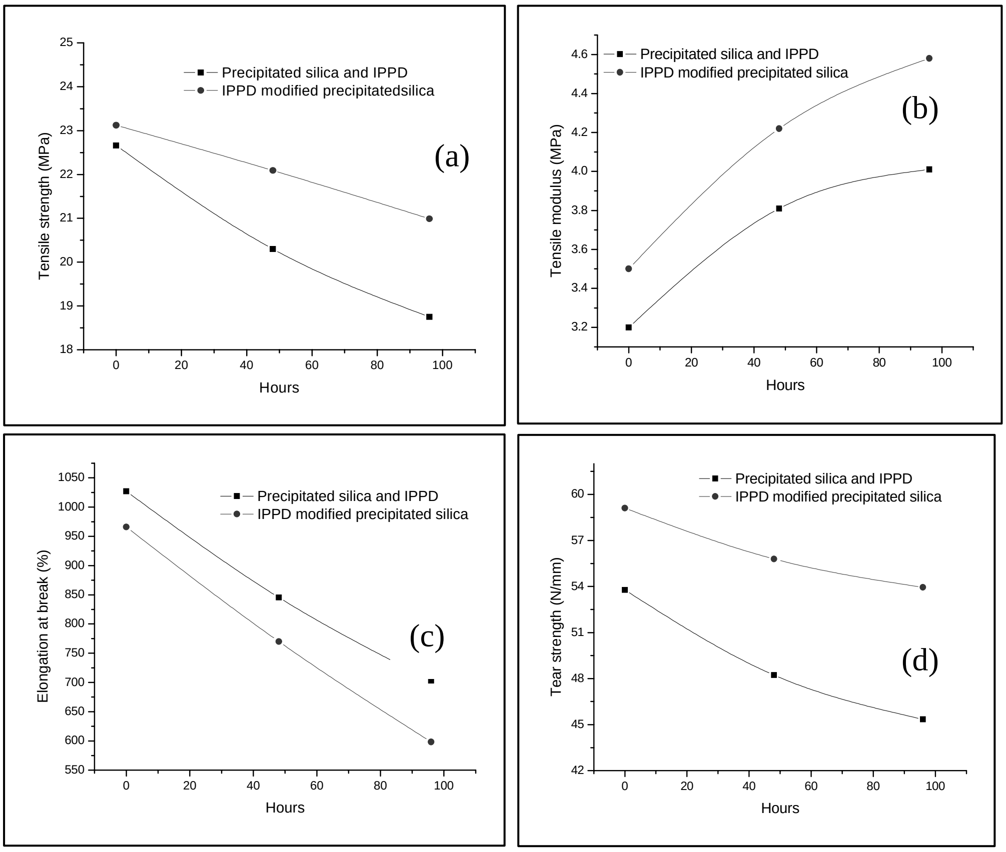


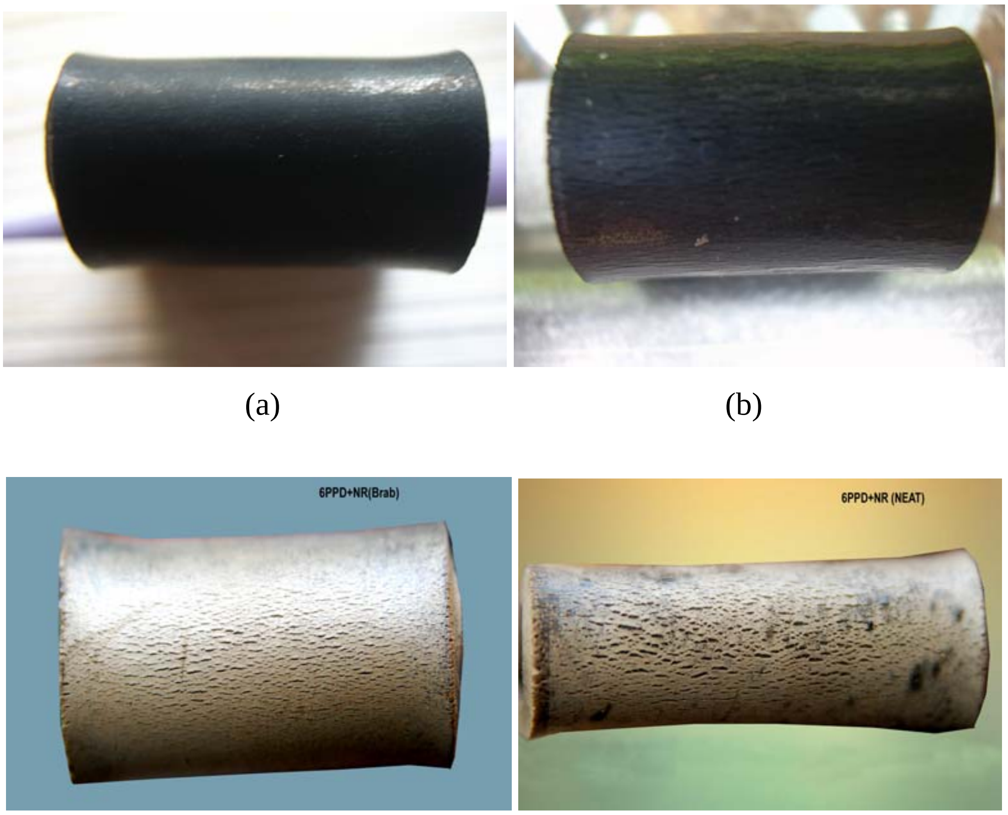
Figure 7.5 Variation in tensile properties of NR vulcanizates with time of ageing at 100°C

b) Ozone ageing

Figure 7.6 (a-f) shows the photographs of ozone cracked surface of NR vulcanizates after 7 hours in an ozone chamber. Photographs clearly show that vulcanizates filled with antioxidants modified silica develop lesser cracks compared to vulcanizates with neat silica and antioxidant. Table 7.7 shows that all vulcanizates except vulcanizate filled with IPPD modified silica cracked in 6 hours. This shows better resistance to ozone attack for the composites filled with antioxidants modified silica.

Table 7.7 Time for the crack initiation of various samples on ozone ageing

Sample	E-1	E-2	F-1	F-2	G-1	G-2
Time (hrs)	>7	6	6	6	6	6



(a) (b)

(c) (d)

(e) (f)

Figure 7.6 (a-f): The photographs of ozone cracked surface of NR vulcanizates after 7 hours

7.3.7 Incorporation of silica

Mixing sequence of IPPD modified silica and with neat silica and IPPD in natural rubber is shown in figure 7.7. During mixing it is observed that the IPPD modified silica gets easily incorporated into the rubber matrix in lesser time compared to neat silica. This may be due to the lower hydrophilic nature of modified silica.

(a) Neat silica **IPPD modified silica**

After 1 second

(b) Neat silica **IPPD modified silica**

After 5 seconds

(c) Neat silica **IPPD modified silica**

After 15 seconds

(d) Neat silica **IPPD modified silica**

After 25 seconds

(e) Neat silica **IPPD modified silica**

After 30 seconds

(f) Neat silica **IPPD modified silica**

After 40 seconds

(g) Neat silica **IPPD modified silica**

After 45 seconds

(h) Neat silica **(i) Neat silica**

After 50 seconds **After 60 seconds**

Figure 7.7 Mixing sequence of IPPD modified silica and with neat silica + IPPD in natural rubber

7.3.8 Nature of ash of NR compounds

(a) With modified silica **(b) With neat silica**

FIGURE 7.8 Nature of ash of compounds containing antioxidant modified silica and with neat silica

Figure 7.8 show the nature of ash of compounds containing antioxidant modified silica and with neat silica. Nature of ash indicates the uniform distribution of IPPD modified silica in rubber matrix compared to neat silica and antioxidant.

Part - B

USE OF ANTIOXIDANT MODIFIED SILICA IN CHLOROPRENE RUBBER

7.4 Experimental

Materials:

Neoprene W, light magnesium oxide, stearic acid, precipitated silica, antioxidant IPPD, dioctyl phthalate (DOP), conventional zinc oxide, Na22.

Preparation of compounds

Antioxidant modified silica and neat precipitated silica were mixed with neoprene W as per the formulation given in the Table 7.8.

Table 7.8 Formulation of the mixes

Ingredients (phr)	H-1	H-2
Neoprene W	100	100
Light MgO	4.0	4.0
Stearic acid	1.0	1.0
Antioxidant modified silica	51	-
Precipitated silica	-	50
Antioxidant IPPD	-	1.0
Dioctyl phthalate	8.0	8.0
Zinc oxide	5.0	5.0
Na22	0.5	0.5

Compounds were prepared by mill mixing on a laboratory size (16 x 33 cm) two roll mill at a friction ratio of 1:1.25 as per ASTM D 3184-89 (2001). After complete mixing of the ingredients the stock was passed out at a fixed nip gap. The samples were kept overnight for maturation.

Testing

The cure characteristics of all mixes were determined using Rubber Process Analyzer RPA 2000, as per ASTM standard D 2084-01. Subsequently the rubber compounds were vulcanized upto 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 hrs prior to physical testing.

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

Thermal ageing studies

Thermal ageing was carried out at temperature of 100°C for 48 hrs, 72 hrs and 96 hrs as per the ASTM D 573-1999.

7.5 Results and discussion

7.5.1 Cure characteristics

Table 7.9 Cure characteristics of CR compounds

Mix	Min torque (dNm)	Max torque (dNm)	Scorch time (min)	Optimum cure time (min)	Cure rate index (%)
H-1	2.97	45.18	1.71	30	3.53
H-2	3.56	36.90	1.98	30	3.56

Table 7.9 gives the cure characteristics of the neoprene compounds with an optimum concentration of 50phr silica and 1phr antioxidant (IPPD). H-1 mix is with 51phr of prepared antioxidant modified silica and H-2 mix is with 50phr of neat precipitated silica and 1phr of antioxidant (IPPD). Compounds containing antioxidant modified silica and with neat precipitated silica shows comparable cure rate. It is found that antioxidant modified silica

mix increases the torque values. The maximum torque is the measure of crosslink density and stiffness in the rubber. This increase in torque value for antioxidant modified silica mix may be due to the surface modification of silica with antioxidant.

7.5.2 Tensile properties

Tensile properties of CR vulcanizates with antioxidant (IPPD) modified silica and with neat precipitated silica are shown in Table 7.10.

Table 7.10: Tensile properties of CR vulcanizates

Mix	Tensile strength Mpa	300% Tensile modulus, Mpa	Elongation at break (%)	Tear strength N/mm
H-1	16.05	2.70	1237	42
H-2	15.01	2.56	1275	40

The tensile properties of CR vulcanizates with antioxidant modified silica and with neat silica are comparable.

7.5.3 Other technological properties

Other technological properties like hardness, abrasion loss, heat build-up and flex resistance of the CR vulcanizates are given in the Table 7.11.

Table 7.11: Other Technological properties

Mix	Hardness (shore A)	Compression set (%)	Abrasion loss (cc/hr)	Heat build-up $(\Delta T)^0C$	Flex resistance (cycles)
H-1	65	48	1.39	20.1	92539
H-2	65	50	1.40	22.3	72284

Hardness was found to be comparable for vulcanizates with antioxidant modified silica and with neat silica. Compression set, abrasion loss and heat build-up are found to be comparatively low for vulcanizate with antioxidant modified silica. Changes in compression set, abrasion loss and heat build-up are attributed to the lower elasticity of vulcanizate with antioxidant modified silica. Flex resistance for vulcanizate with antioxidant modified silica are higher compared to vulcanizate filled with neat silica. This is due to the improved distribution of antioxidant modified silica in rubber matrix compared to neat silica in rubber matrix.

7.5.4 Thermal ageing studies

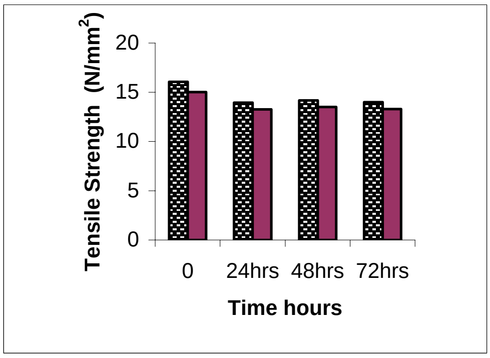


Figure.7.8 (a) Variation of tensile strength of CR vulcanizates (H-1 and H-2) with time of ageing at 100°C

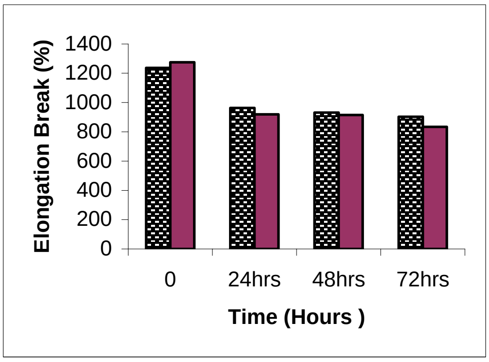


Figure 7.8(b) Variation of Elongation at break of CR vulcanizates (H-1and H-2) with time of ageing at 100°C.

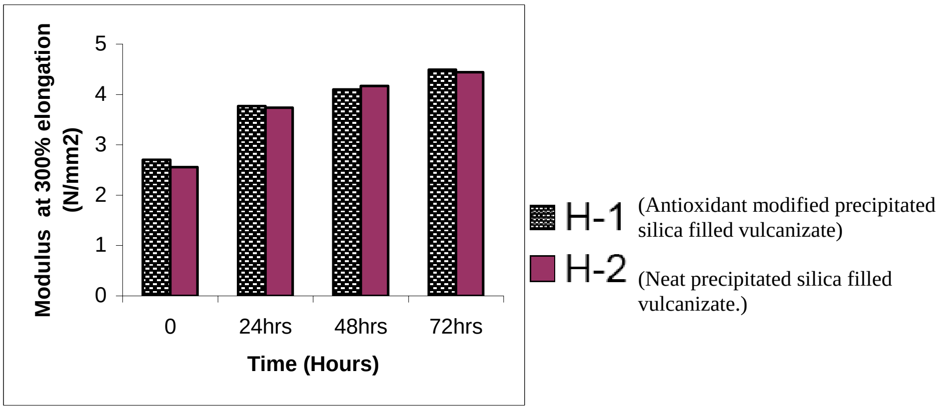


Figure 7.8(c) Variation of modulus at 300% elongation of the CR vulcanizate (H-1 and H-2) with time of ageing at 100°C

Figure 7.8(a,b,c) shows the variation of tensile strength, elongation at break and modulus at 300% elongation of vulcanizates with antioxidant modified silica (H-1) and with neat silica (H-2). Tensile strength showed a decrease while modulus showed gradual increase. Modulus enhancement on ageing may be due to additional cross linking during ageing. It can be seen from the figures that the thermal ageing resistance are found to be comparable for both vulcanizates filled with antioxidant modified silica and with neat silica.

Part - C

USE OF ANTIOXIDANT MODIFIED SILICA IN STYRENE BUTADIENE RUBBER

7.6 Experimental

Materials:

Styrene butadiene rubber (SBR 1502), conventional zinc oxide, stearic acid, precipitated silica, antioxidant IPPD, naphthenic oil, diethylene glycol, cyclohexylbenzothiazyl sulfenamide (CBS), tetramethylthiuram disulfide (TMTD) and sulphur.

Preparation of SBR compounds

Antioxidant modified silica and neat precipitated silica were mixed with styrene butadiene rubber as per the formulation given in Table 7.12.

Table 7.12: Formulation of the mixes

Ingredients (phr)	I-1	I-2
SBR 1502	100	100
Zinc oxide	5.0	5.0
Stearic acid	2.0	2.0
Antioxidant modified silica	51	-
Precipitated silica	-	50
Antioxidant IPPD	-	1.0
Naphthenic oil	8.0	8.0
Diethylene glycol	1.0	1.0
CBS	0.8	0.8
TMTD	0.25	0.25
Sulphur	2.0	2.0

Compounds were prepared on a laboratory size (16 x 33 cm) two roll mill at a friction ratio of 1:1.25 as per ASTM 3184-89 (2001). After complete mixing of the ingredients, the stock was passed out at fixed nip gap. The samples were kept over night for maturation.

The cure characteristics of all mixes were determined using Rubber Process Analyser RPA 2000, as per ASTM standard D 2084-01. Subsequently the rubber compounds were vulcanized upto 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 hrs prior to physical testing.

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

Thermal ageing studies

Thermal ageing was carried out at temperature of 100°C for 48, 72 and 96 hrs as per ASTM D 573-1999.

7.7 Results and discussion

7.7.1: Cure characteristics

Cure characteristics of the SBR compounds with an optimum concentration of 50phr precipitated silica and 1phr antioxidant IPPD are shown in the Table 7.13.

Table 7.13 Cure characteristics of SBR compounds

Mix	Min torque (dNm)	Max torque (dNm)	Scorch time (min)	Optimum cure time (min)	Cure rate index (%)
I-1	2.28	18.98	3.73	8.53	20.83
I-2	2.08	17.73	5.52	14.17	11.56

Antioxidant modified silica filled compounds showed higher cure rate and extent of cure over that of neat silica filled compounds. The optimum cure time was found to be lower for antioxidant modified silica compounds. This is due to the improved rubber-filler interaction. Silica surface has a tendency to absorb moisture and curatives which influences the curing reaction and the properties of the final product. This problem can be overcome by modifying silica with antioxidant. The antioxidant coating prevents silica from further absorption of moisture and curatives. The antioxidant coating improves the dispersion of silica in rubber matrix further.

7.7.2 Tensile properties

Tensile properties of SBR vulcanizates with antioxidant (IPPD) modified silica and with neat silica are shown in Table 7.14.

Table 7.14: Tensile properties of styrene butadiene vulcanizates

Mix	Tensile strength Mpa	300% Tensile modulus, Mpa	Elongation at break (%)	Tear strength N/mm
I-1	12.20	2.63	956	33
I-2	8.28	2.18	945	29

Tensile properties of vulcanizates with antioxidant modified silica are better than that of vulcanizates with neat silica. This indicates that antioxidant modified silica has better polymer-filler interaction resulting in better reinforcement than neat silica. This improvement is due to the fine distribution of modified silica particles in the rubber matrix and reduction in the size of the filler particles during antioxidant modified silica preparation, which has resulted in improved rubber-filler interaction.

7.7.3 Other technological properties

The technological properties like hardness, compression test, abrasion loss, heat build-up and flex-crack resistance were compared for the vulcanizates with antioxidant modified silica and neat silica and are given in the Table 7.15.

Table 7.15 Other technological properties

Mix	Hardness (shore A)	Compression set (%)	Abrasion loss (cc/hr)	Heat build-up(ΔT) ^0C	Flex crack resistance (cycles)
I-1	67	51	5.63	11.1	34477
I-2	62	55	6.79	14.8	20929

Hardness, a measure of the low strain elastic modulus, was found to be higher for the vulcanizates with antioxidant modified silica. Compression set, abrasion loss and heat build-up are found to be comparatively low for the vulcanizates with antioxidant modified precipitated silica. The lower compression set may be due to the better rubber-filler interaction and the better abrasion resistance also points towards better bonding with the silica filler. The lower heat build-up may be due to the smooth surface of silica filler due to the antioxidant coating which acts as lubricant. The number of flex cycles required for crack initiation was noted and it is comparatively high for vulcanizates filled with antioxidant modified silica. The flex resistance is dependent on the network of the vulcanizates and it is found to be superior for the vulcanizate with antioxidant modified silica.

7.7.4 Thermal ageing studies

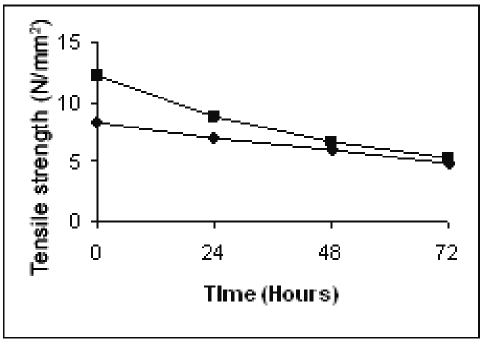


Figure 7.9 (a) Variation of tensile strength of SBR vulcanizates (I-1 and I-2) with time of ageing at 100°C

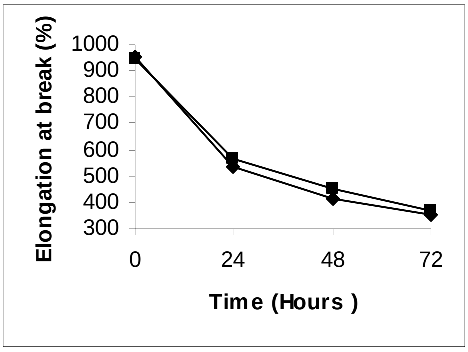


Figure 7.9(b) Variation of elongation at break of SBR vulcanizates (I-1 and I-2) with time of ageing at 100°C.

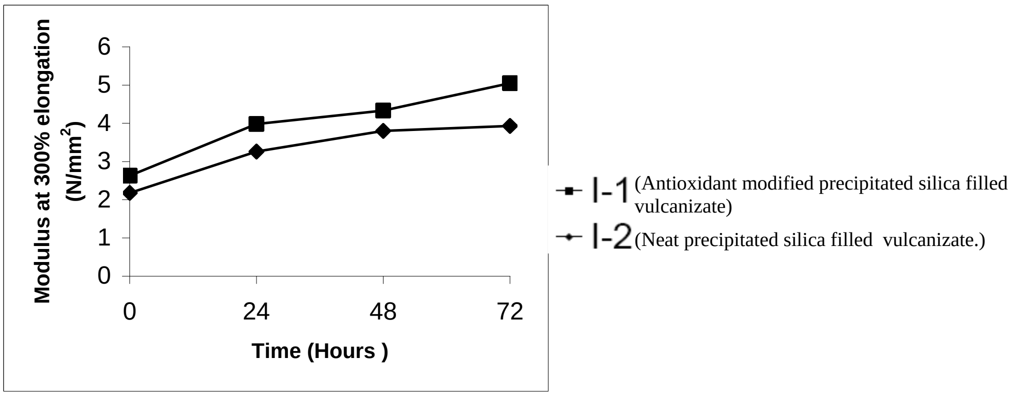


Figure 7.9(c) Variation of modulus of the SBR vulcanizates (I -1 and I-2) with time of ageing at 100°C

Figure 7.9(a,b,c) shows the variation of tensile strength, elongation at break and modulus at 300% elongation of vulcanizates filled with antioxidant modified silica (I-1) and with neat silica (I-2). Tensile strength showed a decrease while modulus showed a gradual increase. Modulus enhancement on ageing may be due to the additional cross linking during ageing. It can be seen from the figures that the vulcanizates with antioxidant modified silica showed a better resistance to thermal degradation compared to vulcanizates with neat silica. This may be due to the increased rubber-filler interactions and improved distribution of antioxidant in the polymer matrix.

7.8 Conclusions

1. Modification of silica with antioxidants gives improved mechanical properties like tensile strength, tear strength, modulus etc.
2. Flex crack resistance, ozone resistance, abrasion resistance and hardness are also found to be increased.
3. Lower heat build-up, lower compression set is also observed for vulcanizates with modified silica compared to neat silica.
4. Modified silica gets easily incorporated and the filler distribution is found to be more uniform compared to neat silica.

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Chapter 8

Products from rice husk as filler in natural rubber

Contents

8.1 Introduction

Rice husk is a widely available agricultural waste. India produces around 25 million tons of rice husks. It is largely used as a fuel in small scale, and in large scale for electrical power generation and thermal needs. Rice husk contains 20% ash and leaves large amount of residue (about 25%). This husk can be used as a fertilizer in agriculture [1] or as an additive for cement and concrete fabrication.[2,3] Due to its high silicon content, rice husk has become a source for preparation of elementary silicon[4-5] and a number of silicon compounds[6] especially silica,[7,8] silicon carbide[9,10] and silicon nitride. Therefore, the rice husks are one of the excellent sources of high grade amorphous silica.

There are several methods to prepare amorphous silica such as chemical pre-treatment with acid or base and combined with pyrolysis, thermal treatment and biological treatment with enzyme. However the chemical pre–treatment with acid before combustion was most frequently implemented method for preparing high pure amorphous silica with low energy process.

Silica has been used as an important reinforcing agent in rubber compounds together with carbon black.[11-15] Mixing of silica into rubber compound offers a number of advantages in tear strength, abrasion, heat resistance, hardness, high modulus, high resilience, improved rolling resistance, reduction in heat build–up and increase in the compound adhesion of multi component products. Reinforcement is usually defined as improvement in abrasion, tear, cutting and rupture resistance, in stiffness and hardness of vulcanized compounds through the incorporation of finely divided mineral particles. The most important factor in the capability of certain minerals to impart reinforcement to elastomers is the average particle size. Reinforcement is readily obtained with particle sizes smaller than 100nm and semi reinforcement with particle sizes smaller than 1000 nm. Particles larger than 10^3 nm do not have reinforcing capabilities or have detrimental action.[16] But the particles chemical structure is also a decisive factor. Silica has a number of hydroxyl groups on its surface, which results in strong filler-filler interactions and adsorption of polar materials by hydrogen bonds. Since intermolecular hydrogen bonds between hydroxyl groups on the surface of silica are very strong, silica can aggregate tightly exhibiting a complex geometry, from elementary particles to aggregates, agglomerates and clusters with dimensions from 0.05 to 40 μm. This property can cause a poor dispersion of silica in a rubber compound.[17]

Nowadays many attempts have been made to prepare mesoporous silica from the natural resources because of cost saving and environmental issue. From rice husk, soluble sodium silicate is extracted using caustic soda. The development of new mesoporous silica with properties different than the precipitated silica, especially their high BET surface areas and their organized pore structures with pore sizes between 1.5-10 nm, make them potential materials in rubber reinforcing.

Supra molecular surfactant aggregates are used as surface directing agent for in-organics during condensation leading to mesoscopically ordered surfactant–inorganic composite. Porosity can be induced in the inorganic part by removal of the surfactant portion through thermal or chemical means.

In this study, we describe the preparation of mesoporous silica and rice husk silica from rice husk and their use as filler in natural rubber compounds in the modified form. Mesoporous silica is prepared from sodium silicate which in turn was prepared from fully burnt rice hull ash and rice husk silica (RHsilica) is prepared directly from rice husk.

This mesoporous silica and rice husk silica (RHsilica) are modified with antioxidant IPPD (N-Phenyl–N'-isopropyl)–p-phenylenediamine. The natural rubber vulcanizates with antioxidant modified mesoporous silica and precipitated silica are compared for bound rubber content and mechanical properties. Also the natural rubber vulcanizate with antioxidant modified RHsilica are compared with vulcanizate filled with neat RHsilica for mechanical properties.

Part - D

USE OF ANTIOXIDANT MODIFIED MESOPOROUS SILICA IN NATURAL RUBBER

8.2 Experimental

Materials

Sodium silicate solution (commercial grade 27% SiO_2, 11.9% Na_2O), pluronic acid P_{123}, nitric acid, natural rubber, conventional zinc oxide, antioxidant

IPPD, stearic acid, precipitated silica, CBS (N-Cyclohexylbenzothiazyl sulphenamide) and sulphur.

Preparation of mesoporous silica

For the preparation of silica sphere, 2gm of triblock co-polymer P_{123} (poly–ethylene oxide bis poly-propylene oxide bis poly–ethylene oxide) was dissolved in 30-80 gm of aqueous nitric acid at 30°C. This solution was then quickly added to a mixture of 5.2 gm of sodium silicate solution and 15 gm of deionized water at 30°C with stirring at 600 rpm for 2 hrs. The solid product was filtered and washed repeatedly with warm deionized water, dried and then calcined at 600°C for one hour in air.

Preparation of antioxidant (IPPD) modified mesoporous silica

IPPD (antioxidant) was mixed with mesoporous silica in torque rheometer (brabender plasticorder) at 50 rpm, 80°C for 5 minutes.

Characterization of mesoporous silica

Small angle XRD is generally used to probe the mesopore structural ordering of the material and to determine the phase structure of the developed material. Powder XRD of mesoporous silica was taken on a Rigaku D/max–c system with Ni–filtered Cu K α radiation (λ - 1.5406 A°, within the 2θ range 0-6 at speed of 1°/minute). The Brunauer, Emmet and Teller method has been adopted as a standard procedure for surface area determination of powdered samples. Surface area analysis was done using micromeritics BJH surface analyzer tristar 3000. Measurements were carried out under nitrogen adsorption at liquid nitrogen temperature. Infrared absorption spectrum was collected using ThermoAvtar 370 spectrometer. The morphology of mesoporous silica was observed using transmission electron microscope (TEM). The transmission electron microscope (TEM) images were taken on a JEOL GEM 3010 transmission electron microscope operating at 300 KV.

Rubber compounding

The natural rubber was compounded on a laboratory two roll mixing mill (16 x 33 cm) as per the formulation given in Table 8.1.

Table 8.1 Base formulation for NR compounds

Ingredients phr	Mix A	Mix B
Natural rubber	100	100
ZnO	5	5
Stearic acid	2	2
IPPD	-	1
Precipitated silica	-	1.6
Mesoporous silica with IPPD	2.6	-
CBS	0.6	0.6
S	2.5	2.5

After complete mixing of the ingredients, the stock was passed six times through tight nip gap 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 process analyzer RPA 2000, 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 hrs prior to physical testing.

Thermal ageing

Thermal ageing was carried out at a temperature of 100°C for 24 hrs, 48 hrs and 96 hrs as per ASTM D 573-1999. Tensile testing before and after thermal ageing were carried out according to ASTM D 628- 54 standard.

Bound rubber content

Mesoporous silica is incorporated into natural rubber by mixing 20 parts of mesoporous silica into 100 parts of natural rubber on a laboratory two roll mixing mill (16 x 33 cm) at room temperature (Sample I). Sample II of natural rubber and precipitated silica, commonly used as reinforcement load for rubber, was prepared in the same way and used as reference for comparison with the result obtained with the mesoporous silica. The compounded samples were cut in small pieces and put over a stainless steel sieve (40 µm meshes), then extracted with the toluene. The toluene is changed with fresh toluene three times during 4 days and finally dried for one day at 80°C. Bound rubber content is determined by using the following equation 8.1.

$$\text{BRC}\ \% = [(b-a)/\ (m-a)] \times 100 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \ (8.1)$$

The BRC is calculated from the weight of the residue after extraction (b), the weight of the initial mixture (m) and the amount of silica present in the initial mixture (a), determined by calcination at 600°C.

Thermogravimetric analysis

The thermograms of natural rubber and silica composites are recorded with a thermogravimetric 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 a temperatures in the range of 30°C to 800°C with a heating rate of 10°C/minute and the corresponding weight changes were noted with the help of an ultra sensitive microbalance Air and nitrogen were used as purge gases.

Soxhlet extraction

Weighed (W_1) small pieces of vulcanized samples from mix A and mix B and placed inside thick filter paper. This is then loaded into the main chamber of soxhlet extractor. Soxhlet extractor is placed onto a flask containing the extraction solvent acetone. The solvent is heated to reflux for 16 hrs. The nonsoluble portion of the sample in filter paper is weighed (W_2).

$$\text{Acetone extractable (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \qquad \text{......................} \ (8.2)$$

Using equation (8.2) acetone extractable in percentage is calculated

8.3. Results and discussion

8.3.1 Characterization of mesoporous silica

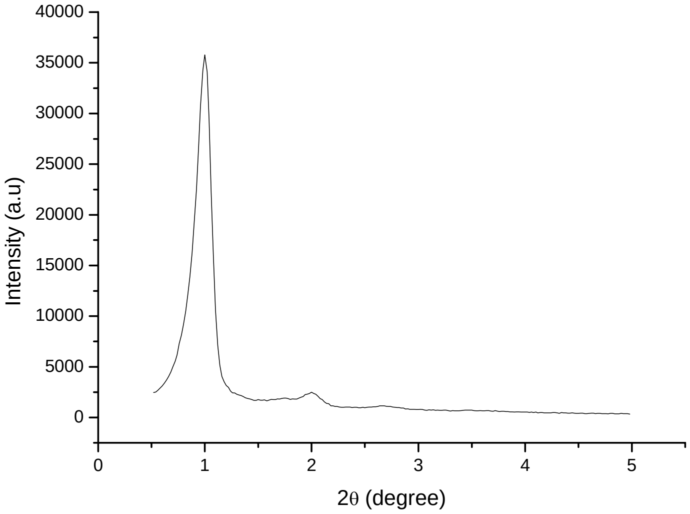

Figure 8.1 Low angle XRD pattern of mesoporous silica

Figure 8.1 shows low angle XRD pattern of mesoporous silica. Well resolved peak at 100 plane and two weak peaks at 110 and 200 planes indicates well ordered mesoporous silica with 2D hexagonal structure.[18-21.]

Mesoporous silica has BET surface area of about 507 m²/g and pore size distribution around 5.5 nm. But precipitated silica has BET surface area of about 67 m²/g.

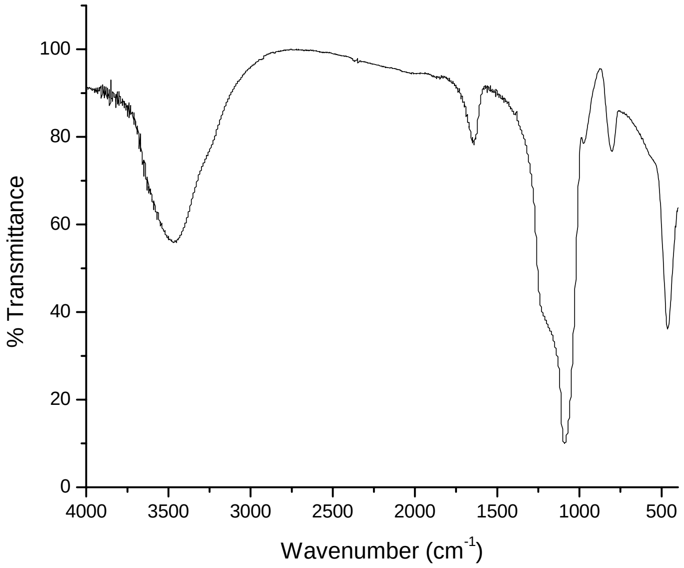

Figure 8.2 FTIR spectrum of mesoporous silica

Figure 8.2 shows FTIR spectrum of mesoporous silica. Spectrum shows a wide O-H stretching band around 3400 cm^{-1}, due to freely vibrating OH groups and a band at 1637 cm^{-1} due to O-H bending vibration. The peak at 1090 cm^{-1} is due to Si–O-Si asymmetric stretching vibration. The peak at 967 cm^{-1} is due to Si–OH stretching vibration. The peaks at 800 cm^{-1} and 463 cm^{-1} are due to Si–O–Si symmetric stretching and bending vibrations respectively.

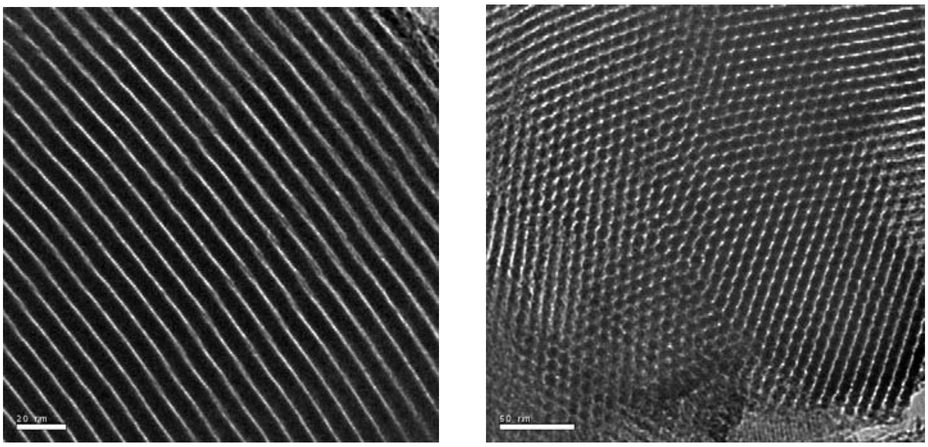

Figure 8.3 Transmission electron microscopic (TEM) images of mesoporous silica

Figure 8.3 shows transmission electron microscopic (TEM) image for mesoporous silica. The TEM image also indicates that the material has a highly ordered 2-D hexagonal structure similar to that of SBA15 obtained from tetraethylorthosilicate (TEOS) .[20, 21]

8.3.2 Cure characteristics

Cure characteristics of the mixes A and B are given in the Table 8.2.

Table 8.2 Cure characteristics of mixes

Property	Mix A	Mix B
Scorch time ,min	4.82	4.10
Optimum cure time, (t_{90}) min	9.15	9.28
Cure rate index (%)	23.09	19.30
Min torque, dNm	0.101	0.078
Max torque, dNm	5.18	4.90
Δ torque, dNm	5.08	4.83

Antioxidant modified mesoporous silica filled composites exhibited higher rate and extent of cure over that of conventional silica. Generally the polar nature of silica surface adsorbs a part of the curative and or silica- zinc ion interaction leads to slowing down of the curing reaction.[22] This will result in an increased cure time and a reduced cure rate index. But the cure characteristics of antioxidant modified mesoporous silica composite indicate improvement in these values.

Scorch safety has increased and cure time was found to be lower for antioxidant modified mesoporous silica compound. This might have resulted from the improved rubber–filler interaction.

8.3.3 Thermal ageing studies

Variation of tensile strength of vulcanizates of mix A and mix B before and after ageing at 100 °C for 96 hours are shown in Figure 8.4.

Retention in property is slightly improved for IPPD bound mesoporous silica. Higher concentration of antioxidants may be incorporated in the pores of mesoporous silica which indicates slow leaching of antioxidant IPPD from the pores of mesoporous silica.

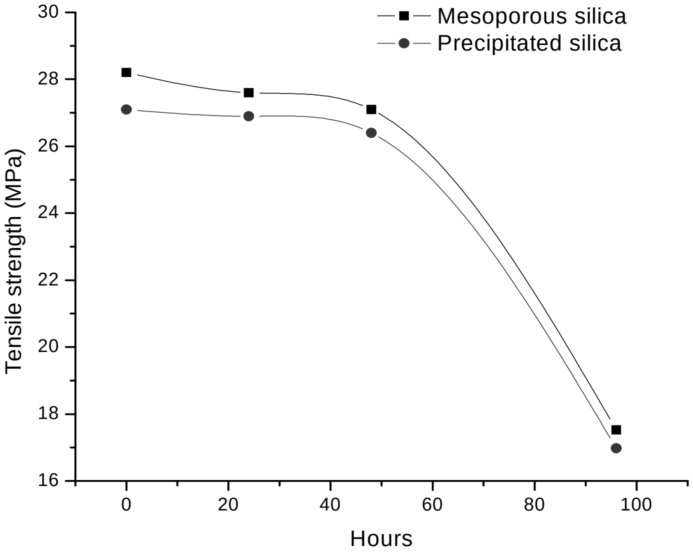

Figure 8.4 Variation of tensile strength of vulcanizates of mix A and mix B before and after ageing at 100°C for 96 hours

8.3.4 Bound rubber content

Bound rubber content of samples I and II are shown in Table 8.3. This determination is based on the assumption that the fraction of polymer, which does not interact or is not bonded to the silica, is soluble in toluene. Bound rubber is the rubber that is trapped by the filler aggregates after mixing. The rubber chains are attracted either physically or chemically to form a rubber shell on the surface of the silica particles. The bound rubber fraction of an uncured compound is the amount of rubber that is not extracted when it is exposed to a good solvent. It is observed that BRC increases with increasing the BET surface area of the silica.[23.]

Table 8.3 Bound rubber content

Mix	Bound rubber content (%)
Mesoporous silica + NR	21.05
Precipitated silica + NR	6.65

It can be concluded that sample I with mesoporous silica gives a higher percentage of bound rubber content compared to that containing precipitated silica (sample II). The high bound rubber content values show that there will be a higher rubber-filler interaction with the mesoporous silica compared to conventional precipitated silica.

8.3.5 Thermogravimetric analysis

The thermograms of natural rubber with precipitated silica and mesoporous silica are recorded. Figure 8.5 shows the thermograms of NR with precipitated silica and mesoporous silica. It can be seen that initiation of degradation is found delayed for mesoporous silica composite. This indicates that NR is more stabilized by mesoporous silica. It is clear from the Table 8.4 that the temperature of complete degradation has improved with mesoporous silica. There is slight increase in maximum degradation temperature for mesoporous silica composite. The rate of degradation showed no considerable change.

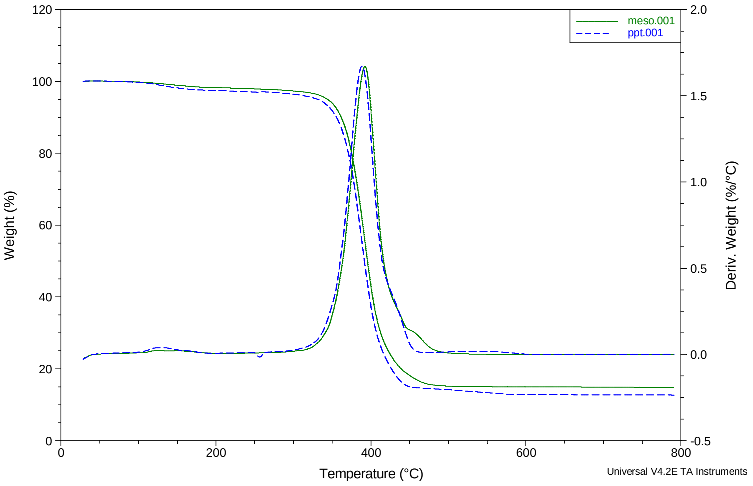

Figure 8.5 Thermograms of the composites

Table 8.4 Thermogravimetric values of composites

Sample	Initiation temp.^{0}C	Max.deg temp. ^{0}C	Rate at max deg. %/ ^{0}C	Completion temp. ^{0}C	25% degg Temp ^{0}C	Residue %
Sample I (meso)	321.7	391.97	1.670	495.36	321.79	14.81
Sample II (ppt)	316.2	388.17	1.672	461.05	316.26	12.69

8.3.6 Soxhlet extraction studies

Acetone extractable of NR vulcanizates is shown in Table 8.5.

Table 8.5 Acetone extractable of NR vulcanizates

Vulcanizates	Acetone extractable (%)
A	5.93
B	6.47

Soxhlet extraction studies also shows that percentage of acetone extractable in vulcanizate A is lesser than vulcanizate B which indicates that mesoporous silica interact with polymer strongly compared to precipitated silica.

8.4 Conclusions

1. Mesoporous silica prepared from commercially available sodium silicate (which in turn was prepared from fully burnt rice hull ash) exhibits specific properties, such as very fine size and good dispersion of the particles besides of its high surface area and porosity can give rise to strong interactions with natural rubber.
2. Retention in tensile strength on thermal ageing is improved for IPPD bound mesoporous silica composite.
3. Bound rubber content is increased for mix with mesoporous silica compared to mix with precipitated silica.
4. Percentage of acetone extractable is found to be lesser for vulcanizate with mesoporous silica compared to vulcanizate with conventional precipitated silica.

Part - E

USE OF ANTIOXIDANT MODIFIED RICE HUSK SILICA IN NATURAL RUBBER

8.5 Experimental

RHsilica Preparation[24]

Rice husk was thoroughly cleaned with tap water. The cleaned husk was mixed with 0.4 M hydrochloric acid in the ratio of 100 g husk per 1 litre acid and heated until boiled for 30 minutes. Then the mixture was maintained at 105°C for 3 hours. During this step, the color of the husk gradually changed from yellow to dark brown. After the reaction, the acid was completely removed from the husk by washing with tap water. It was then dried overnight in an oven at 110°C. The treated husk was burnt in an electric furnace by controlling the temperature so that it reached 600°C in one hour. After burning at 600°C for 6 hours, silica was obtained in the form of white ash. The shape of the silica is similar to the shape of the husk, but smaller in size. It was then grind to fine powder to get silica in smaller particle size.

(a) **(b)** **(c)**

Figure 8.6 (a) rice husk (b) rice husk after treatment with acid (c) RHsilica

Preparation of antioxidant modified RHsilica

1phr of antioxidant (IPPD) was mixed with 50phr of RHsilica in torque rheometer (brabender plasticorder) at 50 rpm, 80°C for 5 minutes.

Rubber compounding

The natural rubber was compounded with antioxidant modified RHsilica and neat RHsilica on a laboratory two roll mixing mill (16 x 33 cm) as per the formulation given in Table 8.6.

Table 8.6 Compounding formulation of mixes

Ingredients (phr)	Mix C	Mix D
Natural Rubber	100	100
ZnO	5.0	5.0
Stearic acid	2.0	2.0
RHsilica	-	50
Modified RHsilica	51	-
IPPD	-	1.0
Naphthenic oil	8.0	8.0
DEG	1.0	1.0
CBS	0.6	0.6
TMTD	0.1	0.1
Sulphur	2.5	2.5

After complete mixing of the ingredients, the stock was passed six times through tight nip gap 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 process analyzer as per ASTM standard, D 2084-01, subsequently, the rubber compound were vulcanized up to the optimum cure time at 150°C in an electrically heated hydraulic press. The moldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 hrs prior to physical testing.

8.6. Results and Discussion

8.6.1 Characterization of RHsilica

Bulk density

Bulk density is defined as the weight per unit volume of a material. It is primarily used for powders or pellets. The test can provide a gross measure of particle size and dispersion, which can affect material flow consistency and reflect packaging quantity. Bulk densities of silica samples are given in Table 8.7. The bulk density of RHsilica is found to be higher due to the smaller particle size of RHsilica compared to precipitated silica.

Table 8.7 Bulk density of silica samples

Samples	Bulk Density m^2/g
Commercial silica	0.96
RHsilica	1.34

BET surface area measurements

The Brunauer-Emmett-Teller method was used for the analysis of surface area of RHsilica and commercial silica at liquid nitrogen temperature. Rice husk silica exhibits surface area of 224 m^2/g whereas the surface area of commercial silica is found to be 178 m^2/g.

Powder X-ray diffraction

The X-ray diffraction pattern of rice husk silica is presented in figure 8.7.

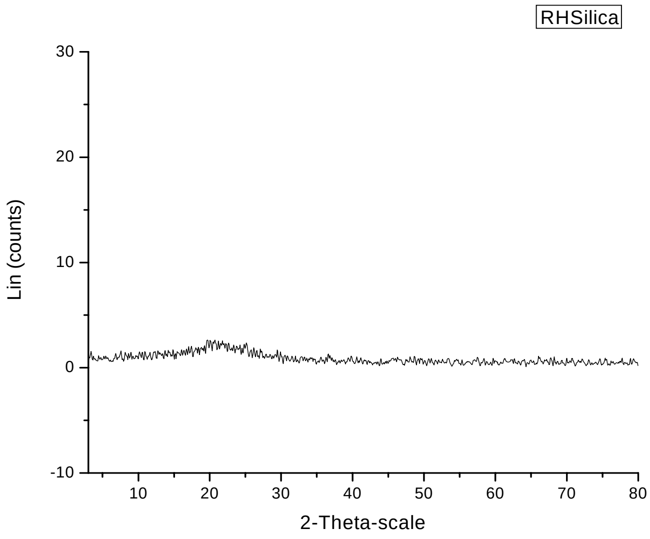

Figure 8.7 X-ray diffraction pattern of rice husk silica

Silica obtained from rice husk is found to be completely amorphous with a broad diffraction peak centered on 2θ/degrees ≈ 22. From XRD analysis the crystallite size of rice husk silica is found to be around 20 nm.

Fourier Transform Infra-red Spectroscopy

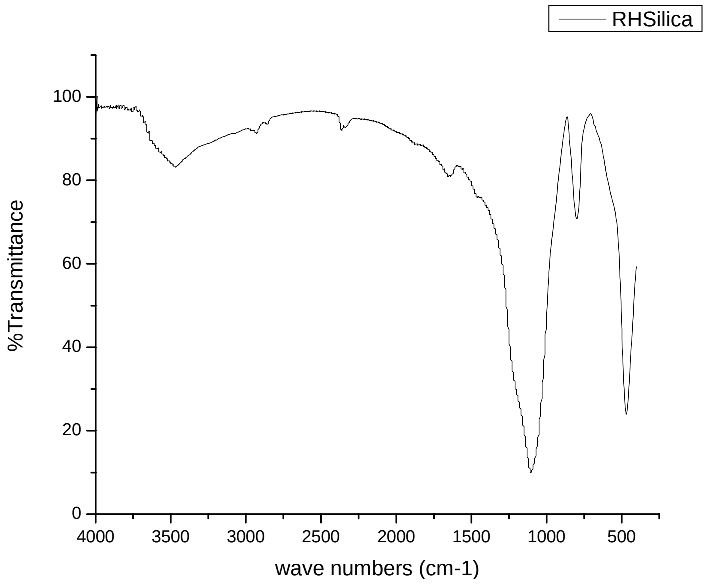

Figure 8.8 – FTIR spectrum of RHsilica

According to Wagner's report,[22] the strong band at approximately 1100 cm^{-1} is assigned to Si-O vibration. The bands at 798 cm^{-1} and 470 cm^{-1} are the characteristic bands of amorphous silica.[25] However the broad absorption band at 3200-3750 cm^{-1} is found only on silica. This band is attributed mainly to the vibration of silanol groups and the hydrogen bonding interaction between water and adjacent silanol groups. Unlike silica, the results reveal the lower number of hydroxyl or silanol groups on the surface of RHsilica and hence reduced silica-silica agglomeration.

8.6.2 Cure characteristics

Cure characteristics of the mixes C and D are given in the Table 8.8.

Table 8.8 Cure characteristics of mixes C and D

Property	Mix C	Mix D
Scorch time, min	0.438	0.51
Optimum cure time(t_{90}) min	4.45	4.98
Cure rate index (%)	24.92	22.37
Min torque, dNm	0.042	0.052
Max Torque, dNm	6.279	4.723
∆ torque, dNm	6.237	4.671

Compound with antioxidant modified RHsilica exhibited higher rate and extent of cure over that of compound with neat RHsilica. The cure graph of the compound with antioxidant modified RHsilica (nr rhs brab) and with neat RHsilica (nr rhs neat) is shown in figure 8.9.

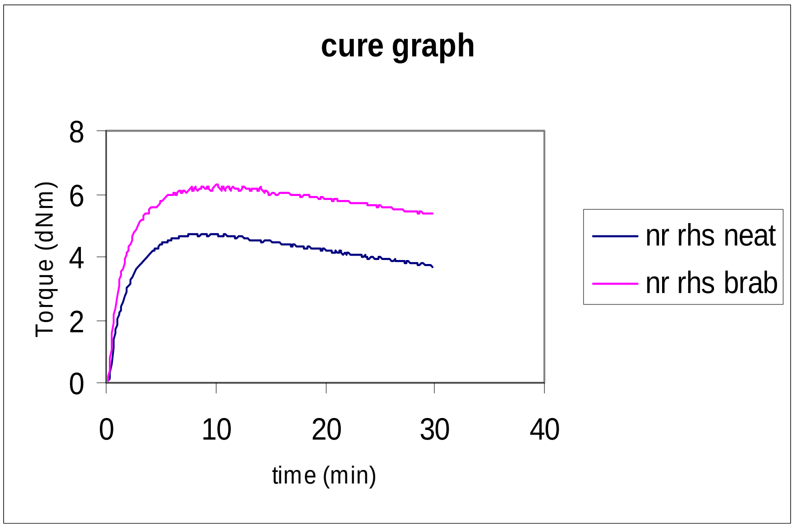

Figure 8.9 Cure graph of the compounds with modified RHsilica (nr rhs brab) and neat RHsilica (nr rhs neat)

The maximum torque is a measure of crosslink density and stiffness in the rubber.[26] It is found that compound with modified RHsilica increases the torque values compared to neat RHsilica compound. This increase is due to the presence of silica rubber crosslink that imparts more restriction to deformation. Antioxidant modified RHsilica compound shows higher cure rate due to the adsorption of antioxidant on to the surface of RHsilica. From the industrial view point, this is an advantage, since time and energy consumption during production could be reduced

8.6.3 Mechanical properties

Vulcanizate reinforced with modified RHsilica had a higher tensile modulus than the vulcanizate reinforced with neat RHsilica. The results are shown in Figure. 8.10.

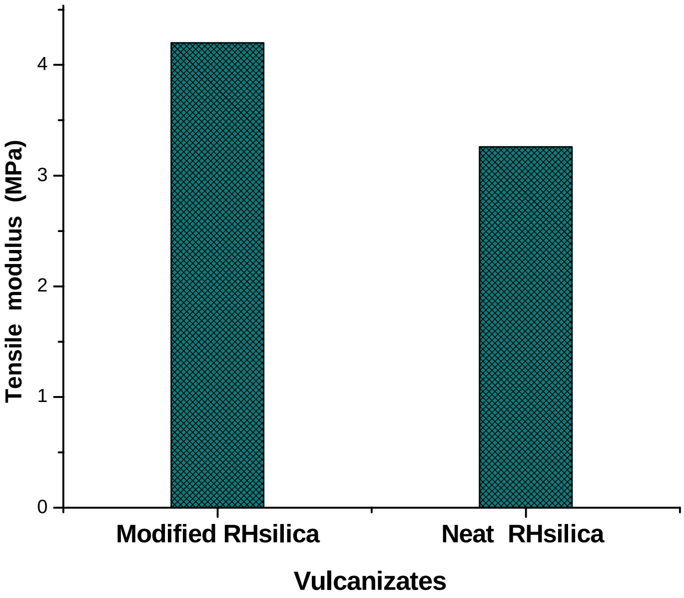

Figure: 8.10; Tensile modulus of the NR vulcanizates with RHsilica

Vulcanizate reinforced with modified RHsilica also showed improved tear strength as presented in Figure 8.11.

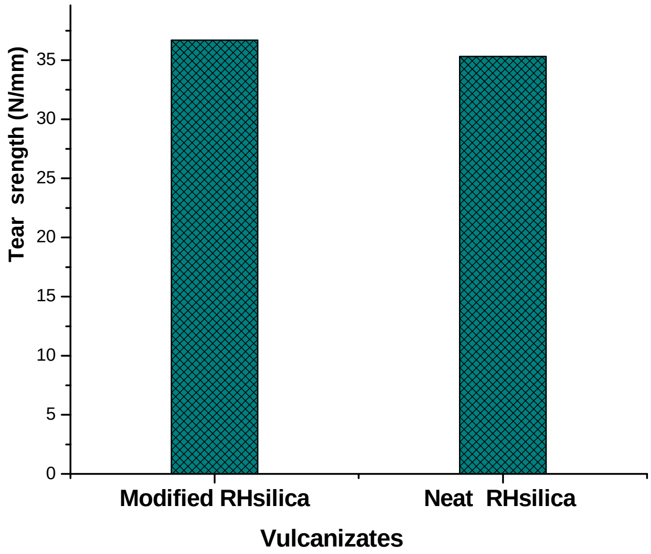

Figure 8.11 Tear strength of the NR vulcanizates with RHsilica

The abrasion resistance is higher for vulcanizate filled with modified RHsilica compared to vulcanizate with unmodified silica. This is shown in figure 8.12.

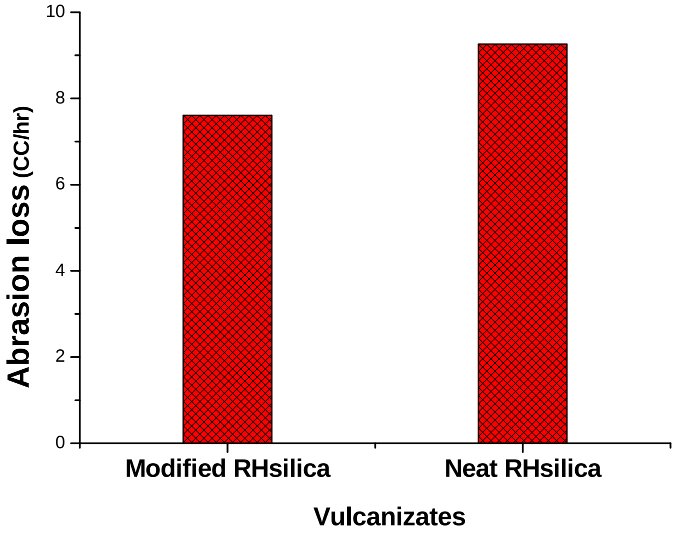

Figure 8.12 Abrasion resistance of NR vulcanizates with RHsilica

Hardness of the composites filled with modified RHsilica and with neat RHsilica is shown in Figure 8.13.

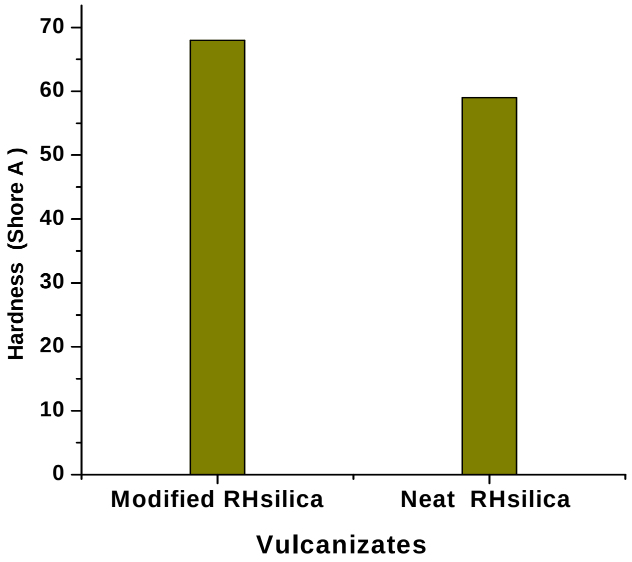

Figure 8.13 Hardness of NR vulcanizates with RHsilica

Figure 8.14 shows the results of the compression set test. It is found that vulcanizate reinforced with modified RHsilica demonstrated better compression set compared to vulcanizate filled with neat RHsilica.

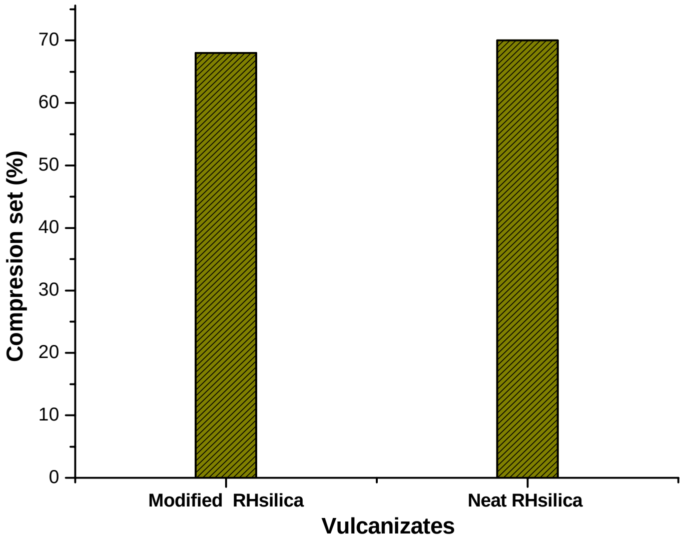

Figure 8.14 Compression set test of the NR vulcanizates with RHsilica

8.7 Conclusions

1. The compounds with IPPD modified RHsilica exhibited higher cure rate than compounds with neat RHsilica. From the industrial view point, this is an advantage since time and energy consumption during production could be reduced.

2. The overall mechanical properties of vulcanizates with IPPD modified RHsilica were found to be better than vulcanizates with neat RHsilica. These properties are tensile modulus, tear strength, abrasion resistance, compression set and hardness. Thus IPPD modified RHsilica has great potential for use as reinforcing filler in natural rubber products.

8.8 References

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Chapter 9

Summary and Conclusions

Polymers are the most versatile of engineering materials because of their ability to be tailor-made to suit specific requirements. Fillers play a dominant role in modifying the properties of the base polymer and nano fillers are the last name in fillers because of their ability to modify properties at very low levels. The primary objective of this study has been to upgrade the performance of rubbers like natural rubber, polychloroprene rubber, and styrene butadiene rubber by modifying with nano zinc oxide and nano silica. This study may be divided into two parts. The first part of the work is the preparation and use of nano zinc oxide in natural rubber, polychloroprene rubber and styrene butadiene rubber. The second part of the work is the use of surface modified silica particles in natural rubber, polychloroprene rubber, and styrene butadiene rubber.

An introduction about various rubbers, their compounding with emphasis on fillers and nano fillers is presented in chapter 1. The use of zinc oxide, antioxidants and various types of silica particles in rubber compounding is presented in detail. The scope and objective of the study are also included in this chapter.

The specifications of all the materials used in the study and the details of the different experimental techniques employed in this study are given in chapter 2. The rubber compounds were prepared on a two roll mixing mill as per the ASTM D 3182-89. The cure characteristics of the compounds were studied using a rubber process analyzer. These compounds were compression moulded in an electrically heated hydraulic press. The tensile properties of the vulcanizates were studied using a universal testing machine. The ageing resistance was studied as per ASTM 573-88. The abrasion resistance of the vulcanizates was studied using a DIN abrader as per DIN standard. The compression set of the samples were determined as per ASTM D 395. The chemical crosslink density was determined by equilibrium swelling method. The heat build-up of the vulcanizates was determined using Goodrich flexometer. The flex resistance was determined using Wallace De Mattia flexing machine.

In the present study nano zinc oxides were prepared by two methods, namely, precipitation method and by solid-state pyrolytic method. Nano zinc oxides from precipitation method (ZnO(p)) and solid-state pyrolytic method (ZnO(s)) were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM), BET adsorption and infrared spectroscopy. Nano zinc oxides prepared by these methods had particle size lower than that of the conventional zinc oxide (ZnO(c)). Bulk density values are found to be higher for zinc oxides prepared in the laboratory compared to the conventional ZnO.

Natural rubber composites were prepared using ZnO(p) and ZnO(s) as activator. The cure characteristics of the natural rubber compounds containing a low dosage of ZnO(p) and ZnO(s) were compared with those of natural rubber compound containing conventional zinc oxide. The cure characteristics were found to be comparable. The mechanical properties of vulcanizates with ZnO(p) and ZnO(s) were compared with those of vulcanizates with conventional ZnO. Abrasion resistance, heat build-up and flex resistance were found to be superior for vulcanizates with ZnO(p) and ZnO(s). It has been observed that use of a low dosage of ZnO(p) and ZnO(s) as activator in natural rubber composites improved the cure properties and mechanical properties of NR composites. So low dosages of ZnO(p) and ZnO(s) were used as curative in a selected synthetic polar rubber (chloroprene rubber) compounds and in a selected synthetic non-polar rubber (styrene butadiene) compounds. The cure characteristics of polychloroprene compounds and styrene butadiene compounds containing low dosages of ZnO(p) and ZnO(s) were compared with those of polychloroprene and styrene butadiene compounds containing conventional zinc oxide. The cure characteristics of both compounds (CR and SBR) were found to be comparable. The tensile properties of the vulcanizates with ZnO(p) and ZnO(s) were comparable with those of the vulcanizates containing conventional zinc oxide. Compression set, heat build-up and flex resistance were found to be superior for SBR vulcanizates with ZnO(p) and ZnO(s) and they were found to be comparable for CR vulcanizates.

Since silica is hydrophilic and rubber is hydrophobic, uniformly dispersing silica in rubber is difficult and gives rise to problems like high initial viscosity. Silica has a number of hydroxyl groups, which results in filler-filler particle agglomeration and reagglomeration. Incorporation of silica in rubber is quite difficult compared to incorporation of carbon black. Since carbon black is hydrophobic in nature similar to hydrocarbon rubbers, incorporation of carbon black is easy. To make the incorporation of silica easy, silica surface was modified with antioxidants. Modification was done by mixing precipitated silica with antioxidants (derivatives of paraphenylene diamine) in a torque rheometer at 50rpm and above the melting temperature of antioxidant for 5 minutes. Compounds were then prepared with this modified silica as filler in natural rubber, polychloroprene rubber and styrene butadiene rubber. The cure and mechanical properties were compared with conventional compounds containing unmodified silica and antioxidant at the same dosage in natural rubber, polychloroprene rubber and styrene butadiene rubber. The cure and mechanical properties of the compounds containing modified silica were found to be superior to the conventional compounds. Incorporation of modified silica was also found to be easier compared to that of unmodified silica and the filler distribution was found to be more uniform compared to unmodified silica.

Mesoporous silica and rice husk silica were prepared from a low cost silica source i.e., rice husk. Mesoporous silica and rice husk silica were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM), BET adsorption and infrared spectroscopy. Mesoporous silica and rice husk silica were found to have larger surface area compared to precipitated silica. Natural rubber compounds were prepared using antioxidant modified mesoporous silica and rice husk silica as filler. The cure and mechanical properties were compared with unmodified precipitated and rice husk silica. Bound rubber content values were found to be greater for mesoporous silica compound compared to precipitated silica compound. The higher bound rubber content values indicate higher rubber-filler interaction with mesoporous silica compared to conventional precipitated silica. The cure and mechanical properties were found to be superior for modified mesoporous and rice husk silica composites compared to unmodified silica composites.

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List of Abbreviations and Symbols

ASTM	American Society for Testing and Materials
BET	Brunauer, Emmett and Teller
BIS	Bureau of Indian Standards
CBS	N-cyclohexyl-2-benzothiazyl sulphenamide
CR	Chloroprene rubber
CRI	Cure rate index
cc	Cubic centimeter
dNm	Deci Newton meter
DEG	Diethylene Glycol
DPPD	N,N′-diphenyl-p-phenylenediamine
DSC	Differential scanning calorimetry
DOP	Dioctyl Phthalate
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
IPPD	N-isopropyl-N′-phenyl-p-phenylenediamine
ISNR	Indian Standard Natural Rubber
min	minutes
M_H	Maximum torque
M_L	Minimum torque

MPa : Mega Pascal
NR : Natural Rubber
N/mm : Newton/Millimeter
nm : Nano meter
P123 : Poly–ethylene oxide bis poly-propylene oxide bis poly–ethylene oxide
phr : Parts per hundred rubber
pphm : Parts per hundred million
6PPD : N-(1,3-dimethyl buty1)–N′-pheny1-p-phenylenediamine
Pa : Pascal
RHsilica : Silica from rice husk
SBR : Styrene butadiene rubber
SEM : Scanning Electron Microscope
SiO_2 : Silica
TEM : Transmission Electron Microscope
Tg : Glass transition temperature
TMTD : Tetramethylthiuram disulphide
TGA : Thermogravimetric analysis
UTM : Universal testing machine
V_f : Volume fraction of rubber in swollen sample
Vi : Volume fraction of rubber in unswollen sample
Vτ : Change in volume fraction of rubber due to swelling
ZnO(c) : Commercial zinc oxide
ZnO(p) : Zinc oxide from precipitation method
ZnO(s) : Zinc oxide from solid-state pyrolytic method
% : Percentage
°C : Degree Celsius
µm : Micro meter
A : Angstron

List of publications

A. International/National journals

1. Preparation of nano zinc oxide, its characterization and use in Natural Rubber, **Progress in Rubber, Plastics and Recycling Technology, Vol:24, No:2, 2008**.
2. Controlled release of antioxidant for improved long term aging resistance, **Fall 172nd Technical Meeting of the Rubber Division of the American Chemical Society, Inc, Cleveland, 17-10-2007** (communicated)
3. Preparation and use of Nano Zinc oxide in Neoprene Rubber, **International Journal of Polymeric Materials, Vol: 57, 12, 1083-1094, 2008.**
4. Mesoporous Silica from rice husk as filler in Natural Rubber: **Progress in Rubber Plastics and Recycling Technology** (in Press)
5. Use of antioxidant modification of rice husk silica in natural rubber. **Journal of Applied Polymer Science** (in Press)

B.International/National conference papers

1. Preparation of nano zinc oxide, its characterization and use in Natural Rubber, **Asia Rub Tech Expo 2006, Kochi 23-25** Nov, Organized by Indian Rubber Institute, Kerala- Mumbai branches.

2. Thermal diffusion in natural rubber dispersed with zinc oxide nano particles, **International conference on Materials for the millennium**, organized by Cochin University of Science and Technology, March 1-3, 2007.

3. Preparation and use of nano Zno in Styrene-Butadiene Rubber, **National Conference on Eco-friendly Plastic and Rubber Systems**

(NCEPRS) Macro-08, organized by Sri Jeyachamarajendra college of Engineering, Mysore,19-20th May 2008.

4. Preparation and use of nano zinc oxide in natural rubber and neoprene rubber, **International conference on Rubber and Rubber like materials,** organized by Indian Institute of Technology, Kharagpur, Jan 8-10, 2008.
5. Antioxidant modification of Silica: A novel method for incorporation and improvement of mechanical properties of NR, CR, SBR, **National Conference on Novel polymeric Materials,** organized by Stella Maris College Chennai, Jan 20-21, 2009.

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Conferences attended	5 presentations in various conferences

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