SAFE ACCELERATOR INCORPORATED NON-CYTOTOXIC VULCANIZATES BASED ON NATURAL RUBBER

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by

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Safe Accelerator Incorporated Non-Cytotoxic Vulcanizates based on Natural Rubber

Ph.D. Thesis under the Faculty of Technology

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Certificate

This is to certify that the thesis entitled “Safe Accelerator Incorporated Non-cytotoxic Vulcanizates based on Natural Rubber”, which is being submitted by Ms. Abhitha K., in partial fulfillment of the requirements of the degree of Doctor of Philosophy, to Cochin University of Science and Technology (CUSAT), Kochi, Kerala, India, is a record of the bonafide research work carried out by her under my guidance and supervision.

Ms. Abhitha has worked on the research problem for about six years (2011-2017) in the Department of Polymer Science and Rubber Technology of CUSAT. In my opinion, the thesis fulfills all the requirements according to the regulations. The results embodied in this thesis have not been submitted for any other degree or diploma. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral committee have been incorporated in the thesis.

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Declaration

I hereby declare that the thesis entitled "Safe Accelerator Incorporated Non-cytotoxic Vulcanizates based on Natural Rubber" is a record of the original research work carried out by me under the supervision of Dr. Thomas Kurian, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, Kerala, India. No part of this thesis has been presented for any other degree from any other institution.

Kochi **Abhitha K.**
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Preface

Natural rubber is a very versatile material that has been successfully used in engineering applications for over a century. As the rubbers in their virgin forms are too weak for practical applications they are mixed with other materials (compounding ingredients) to improve processability and to develop the properties required for various applications. Vulcanization or curing is an essential step in the manufacture of any rubber product. In the vulcanization reaction of rubbers, accelerators perform the important functions of bringing down the time needed for vulcanization, controlling the scorch safety and managing the type and number of cross links formed.

Of the various chemicals used in the rubber industry, some are known to produce nitrosamines. Some of these nitrosamines (by-products of rubber vulcanization) have been classified as potential human carcinogens by the International Agency for Research on Cancer (IARC). Therefore the rubber industry has to take measures for the control of nitrosamines. One of the options for controlling the nitrosamines is using nitrosamine safe formulations in rubber compounding.

Nitrosamines are of particular relevance to the rubber industry as these materials can be formed in rubber articles through the reactions of many of the accelerators used in formulations. The accelerators and sulphur donors that form hazardous nitrosamines (regulated) are tetramethyl thiurammonosulfide (TMTM), tetramethyl thiuramdisulfide (TMTD), N-oxydiethylenedithiocarbamyl N'-oxydiethylenesulfenamide (OTOS) and N-oxydiethylene 2-benzothiazolesulfenamide (MBS). Certain accelerators, because of their specific structure produce safe or non-regulated nitrosamines. Zincdibenzyl dithiocarbamate (ZBEC), tertiarybutyl benzothiazolesulfenamide

(TBBS), Tetrabenzyl thiuramdisulfide (TBzTD) and Dithio dicaprolactam (DTDC) are some of the non-regulated nitrosamine accelerators.

As per German regulations related to the activities involving hazardous substances including their classification and labelling (Technical Rules for Dangerous Substances (TRGS 522)), TBzTD is a non-regulated accelerator and is safe to replace thiurams such as TMTD. Similarly nitrosamine producing accelerators such as MBS can be replaced by non–regulated nitrosamine producing accelerators such as N-cyclohexyl-2-benzothiazole sulfenamide (CBS), N, N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) and TBBS. In order to study the effect of accelerators on properties of the vulcanizates, it is convenient to select a low sulphur (Efficient Vulcanization (EV)) vulcanization system. For low sulphur vulcanization, thiurams are normally used in combination with sulfenamides as accelerators.

Though the gum natural rubber vulcanizates exhibit good tensile strength, fillers are generally incorporated in commercial rubber compounds for reinforcement, improved processability and cost reduction. The most effective reinforcing filler used in rubber industry is carbon black. One of the non-black reinforcing fillers with reinforcing properties closer to carbon black is precipitated silica. Though the presence of silica in rubber formulations offers high strength, it is accompanied by processing problems such as high viscosity, cure retardation and compound stiffness.

Several modifications of silica filler such as heat treatment, chemical modification of the filler surface groups, grafting of polymers on to the filler surface and use of promoters or coupling agents have been reported to improve the rubber-filler interaction. One of the widely used silane coupling agents is bis(triethoxysilylpropyl) tetrasulfide (TESPT). Epoxidised natural rubber (ENR) shows polarity and bi-functionality. ENR may be considered as an alternative to silanes.

The present work focuses on the preparation of non-cytotoxic vulcanizates based on natural rubber using safe accelerators.

The thesis consists of eight chapters. A concise introduction to the topic is presented in the first chapter. The second chapter describes the details of materials used and experimental procedures used for the study. Chapter 3 has been divided into two parts. This chapter presents the studies on natural rubber gum vulcanizates based on formulations containing regulated binary accelerator (MBS and TMTD) system. Vulcanizate with comparable properties were prepared by replacing MBS with non-regulated (safe) TBBS and TMTD with non-regulated TBzTD. The use of DCBS and N, N-dibenzyl-2-benzothiazolesulfenamide (DBBS) as non-regulated sulfenamide type accelerators is described in Chapter 4. Chapter 5 is divided into two parts. The chapter describes the evaluation of the effect of carbon black and silica on the cure characteristics, mechanical properties, sorption properties, thermal properties and fluid resistance of nitrosamine-safe natural rubber vulcanizates containing TBBS and TBzTD. Chapter 6 is divided into two parts. This chapter discusses the use of epoxidised natural rubber as a modifier in silica filled natural rubber and comparison of the properties of the vulcanizates with that of silane modified silica filled natural rubber vulcanizate. Analysis and comparison of the effect of heat ageing on the properties of natural rubber vulcanizates prepared using antioxidants N-(1, 3-dimethyl butyl)-N’-pheny1-p-phenylenediamine (6PPD), polymerized 1,2-dihydro-2,2,4-trimethyl quinoline (commercial TQ) and dimer-rich high pure grade TQ (HPG) are described in Chapter 7. The evaluation of cytotoxicity of the vulcanizates for detecting the toxicity of the soluble substances present in the rubber vulcanizates has been presented in chapters 3-7. The conclusions of the investigations presented in the thesis are given in chapter 8.

Abstract

Conventional accelerators (N-oxydiethylene 2-benzothiazolesulfenamide (MBS) and tetramethyl thiuramdisulfide (TMTD)) used in rubber vulcanization are listed under the category of cancer producing nitrosamine generating (regulated) chemicals. The vulcanizates prepared using these accelerators are not safe. Safe natural rubber (NR) vulcanizates were prepared using non-regulated (safe) accelerators viz. tertiarybutyl benzothiazolesulfenamide (TBBS) and tetrabenzyl thiuramdisulfide (TBzTD) with properties comparable to that prepared using the conventional accelarators. The results of cytotoxicity testing confirmed the safety of the vulcanizates. Safe natural rubber vulcanizates were also prepared using non-regulated accelerators (either N,N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) or N,N-dibenzyl-2-benzothiazolesulfenamide (DBBS)) as a single accelerator and as binary accelerators (in combination with TBzTD). Mechanical properties of these vulcanizates were compared. Effect of carbon black and precipitated silica on the cure characteristics and mechanical properties of the safe NR vulcanizates prepared using safe accelerators (TBBS and TBzTD) were analysed. Silane coupling agent was incorporated in silica-filled natural rubber compounds to reduce the processing difficulties and to improve the rubber-filler interaction. The role of epoxidised natural rubber (ENR) as an economic substitute for silane coupling agent was also examined. Studies include thermo-oxidative ageing, sorption characteristics, scanning electron microscopy and thermogravimetric analysis. The rubber-filler interaction, fluid resistance and cytotoxicity of the vulcanizates too were evaluated. The efficiency of the antioxidants - commercial polymerized 1,2-dihydro-2,2,4–trimethyl quinoline (TQ), dimer-rich high pure grade TQ (HPG) and N-(1,3-dimethyl butyl)-N’-phenyl-p-phenylenediamine (6PPD) in safe vulcanizates was compared. The cytotoxicity of these vulcanizates was evaluated.

Keywords:

Conventional accelerators, Vulcanization, Nitrosamines, Non-regulated accelerators, Cytotoxicity, Binary accelerators, Carbon black, Precipitated silica, Silane coupling agent, Epoxidised natural rubber, Thermo-oxidative ageing, Sorption characteristics, Scanning electron microscopy, Thermogravimetric analysis, Antioxidants.

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Chapter 1

GENERAL INTRODUCTION

Contents

1.1 Introduction

Elastomers or rubbers constitute an important class of engineering materials, without which modern technology could not have been materialized. The unique and versatile properties of rubber have made it highly indispensable for the modern life. Contribution of rubber in the fields of engineering, space research, medical sciences, etc. is praiseworthy. Among the elastomers, natural rubber (NR) being a renewable agricultural product holds prime position as a raw material for the manufacture of several products.

Part of work presented in this chapter has been communicated to *Progress in Rubber, Plastics and Recycling Technology*.

As the rubbers in their virgin forms are too weak for practical applications they are mixed with many chemicals (compounding ingredients) to improve processability and to acquire specific properties required for various applications. In most of the applications, fillers such as carbon black, silica, etc. are incorporated in rubber formulations to attain the acceptable engineering properties.

Of the various chemicals used for rubber compounding, some are known to produce nitrosamines. Some of these nitrosamines (by-products of rubber vulcanization) have been classified as potential human carcinogens by the International Agency for Research on Cancer (IARC). In this context, the rubber industry has to take measures for the control of nitrosamines. Of different strategies applied, one of the measures adopted for controlling the nitrosamines is the use of nitrosamine safe formulations in rubber compounding.

1.2 Natural rubber – Properties and uses

Natural rubber is an excellent elastomer for many applications that require low heat build-up such as large tyres, carcasses of passenger car tyres, vibration dampers, springs, engine mountings and bearings. It is used for other products such as hoses, conveyer belts, gaskets, seals, rollers, rubberized fabrics, elastic bands, latex foams, adhesives, pharmaceutical products and medical products. Traditionally, NR was considered as a general purpose rubber for the production of virtually all rubber products, because of its well-balanced range of mechanical properties. The natural rubber is cis-1,4 polyisoprene with M_w ranging from 1 to 2.5 x 10^6. Natural rubber has a very high structural regularity, providing it with unique and valuable characteristics. In particular, NR crystallises under strain or at low temperatures and has very low hysteresis and high resilience. Low temperature crystallisation causes stiffening [1], but is easily reversed by warming. The low hysteresis of NR minimises heat build-up and provides good rolling resistance. The phenomenon of strain-induced crystallisation is responsible for the very high tensile strength and tear strength of NR, even in the absence of any filler. Because of the strain–induced crystallisation and high molecular mobility, uncured NR has very high green strength and building tack, which is particularly useful for building tyres [2]. NR is used in the carcass of passenger tyres, for its building tack, ply adhesion and good tear resistance and in belt compounds for steel cord adhesion and crack growth resistance.

Tyre industry consumes about 70 % of the global production of NR [3]. Almost 100 % NR is used for the manufacture of large truck and earthmover tyres, which require maximum cut growth resistance as well as low heat build-up. NR is the ideal elastomer for the manufacture of aircraft tyres. The rubber's polymer network allows elasticity and flexibility to be combined with crystallisation-induced strength and toughness when stretched. The elastic nature of this network also accounts for the exceptional resilience (less kinetic energy lose as heat during repeated stress deformation) of cured rubber products. Products made from natural rubber are less likely to fail from excessive heat build-up or fatigue when exposed to severe dynamic conditions. These properties are exploited in the sidewalls of radial ply tyres [4].

NR is used in blends with halobutyl rubbers in the inner liner of tyres. It is also used in the bead, apex and rim strip compounds. Applications of NR latex in gloves and condoms make use of its high strength in thin-walled unfilled products and its low modulus at low strains.

1.3 Vulcanization

Vulcanization or curing is an essential step in the manufacture of any rubber product [5]. It is the process of insertion of relatively small number of chemical cross links along the polymer chains to fully realize the inherent strength and elastic properties of NR [6]. In short, vulcanization converts a substance that is plastic and moldable into one that is flexible and elastic. Vulcanization increases tensile strength, modulus, hardness, abrasion resistance and rebound resilience and decreases elongation, hysteresis, compression set and solubility. Important characteristics related to the vulcanization process are the time taken before crosslinking starts, the rate of crosslink formation and the extent of crosslinking at the end of the process. There must be sufficient delay or scorch resistance to permit mixing, shaping and flowing in the mould. Then the formation of crosslinks should be rapid and the extent of crosslinking must be controlled. Vulcanization-induced changes are proportional to the number of crosslinks and their length. Excessive crosslinking can convert the elastomer to a hard, brittle solid. Longer crosslinks promote better tensile and tear strength and better fatigue properties. Shorter crosslinks provide better oxidative and thermal stability and lower compression set [4].

A simplified flow diagram, which shows the basic steps in the vulcanization of natural rubber, is shown in Figure 1.1. Starting with the raw rubber, the first step is usually mastication to soften the rubber by mechanical working and heat. Mastication is a combination of extension, disentanglement and oxidative cleavage of polymer chains. In this state it is considerably more receptive to the incorporation of additives so that the rubber’s natural attributes can be modified and optimized as desired. The next step is the mixing or compounding of the softened raw rubber. This is done in an open two roll mill or in an internal mixer for dry rubbers. Rubbers behave as viscoelastic fluids when sheared at elevated temperatures. This enables the incorporation of the various fillers and chemical additives in the process of compounding. Then moulding at suitable temperature and pressure for optimum cure time gives the vulcanized product.

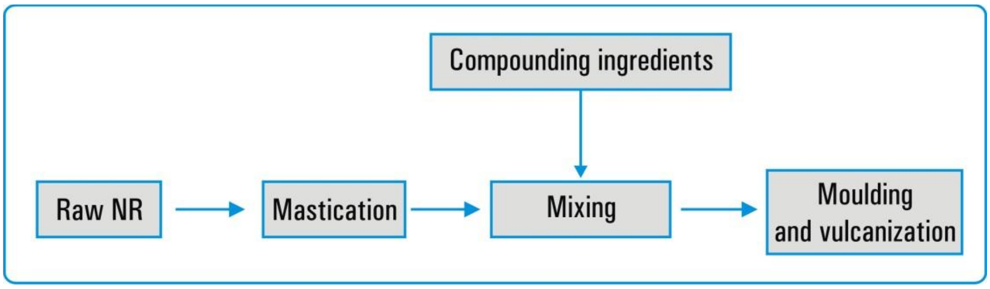


Figure 1.1 Flow diagram for the vulcanization of natural rubber

1.4 Compounding Ingredients

The main objectives of rubber compounding are: to facilitate processing and fabrication, to achieve the required balance in vulcanizate properties and to provide durability, all at lowest possible cost [7]. During this step a wide variety of substances such as vulcanizing agents, accelerators, activators, fillers, processing aids, anti-degradants and a number of special ingredients as per a recipe [8] are mixed with natural rubber to develop a rubber compound. Each component of the recipe apart from the base rubber, have a specific function during processing, vulcanization or service of the product.

1.4.1 Vulcanizing agents

Vulcanizing agents are substances which are added to effect subsequent crosslinking, when the compounded rubber is heated to an appropriate temperature. Sulphur is the most commonly used vulcanizing (curing) agent for elastomers with chemically unsaturated polymer backbones, particularly for the diene rubbers such as NR, styrene butadiene rubber (SBR), polybutadiene rubber (BR), nitrile rubber (NBR), polychloroprene rubber (CR) and polyisoprene rubber (IR) [7]. Sulphur is low priced and less toxic, broadly compatible with other compounding additives and is able to provide the desired vulcanization properties. The oldest method of vulcanization consisted of heating rubber with sulphur for a long duration. Vulcanization of rubber with sulphur alone is a very slow process. Depending on the temperature of vulcanization and the nature of rubber used, it takes several hours or even days to reach optimum cure. The use of sulphur alone is ineffective and requires 45 to 55 sulphur atoms per crosslink and has a strong tendency to produce a large number of intramolecular (cyclic) crosslinks [9]. Sulphur blooming is also a fatal effect accompanying the process of vulcanization with sulphur alone. Vulcanization with sulphur alone is therefore of no technological importance and a major revolution occurred with the discovery of organic nitrogen compounds known as accelerators to achieve rapid sulphur vulcanization. A brief description about different sulphur vulcanization systems are given in the following section.

1.4.1.1 Sulphur vulcanization systems

A typical sulphur vulcanization system is composed of sulphur, a metal oxide (usually zinc oxide), a fatty acid (to solubilize the oxide’s metal) and one or more organic accelerators. Sulphur is available in two forms: amorphous and rhombic. The amorphous form of sulphur (insoluble sulphur) is insoluble in rubber and in most solvents including carbon disulphide. On the other hand, rhombic sulphur (a ring of eight sulphur atoms) is soluble in rubber and it is the form normally used for vulcanization.

Over the year's three special types of sulphur vulcanization systems have been developed based on the relative sulphur and accelerator proportions:

- Efficient vulcanization (EV) systems
- Semi efficient vulcanization (SEV) systems and
- Conventional vulcanization (CV) systems

EV systems are those where a low level of sulphur (0.3 - 0.8 phr) and a correspondingly high level of accelerator (6.0 - 2.0 phr) are used for achieving extremely high heat and reversion resistance in the rubber vulcanizates [6, 10, 11]. In the CV systems, the sulphur dosage is high (2 - 3.5 phr) and the accelerator level is low (1.0 - 0.4 phr). The CV systems provide better flex and dynamic properties but poor thermal and reversion resistance. The bond dissociation energy depending on the number of sulphur atoms within the linkage has been proposed to be the underlying reason for the variation in the properties of the different vulcanizates. The higher the number of sulphur atoms, the lower the bond dissociation energy of the linkages. Thus the vulcanizates containing mainly mono-sulphidic linkages (EV and SEV) have better heat stability and reversion resistance than those containing relatively high poly-sulphidic linkages (CV) [12]. For getting mechanical, dynamic and thermal properties in-between that of CV and EV systems, SEV systems with intermediate level of accelerator (2.5 - 1.0 phr) and sulphur (1.0 - 1.8 phr) are employed [6, 10].

1.4.2 Accelerators and activators

In the vulcanization reaction of elastomers, accelerators perform the important functions of bringing down the time needed for vulcanization, controlling the scorch safety and managing the type and number of cross links formed [9]. The most common vulcanization systems used in industrial applications are based on the accelerated sulphur formulations.

The accelerators require activators like zinc oxide (ZnO) and co-activators like stearic acid in all types of rubbers [13]. These are essential ingredients in rubber compounds to achieve economic rates of vulcanization. The ZnO and stearic acid are used to activate the organic compounds used as vulcanization accelerators.

1.4.3 Fillers

Fillers are classified into two groups: reinforcing and non-reinforcing. Reinforcing fillers are used for enhancement of properties like tear strength, abrasion resistance and tensile strength, thus making it more suitable for a given application [14, 15]. Examples of reinforcing fillers are carbon black, china clay, precipitated silica and silicates. Non-reinforcing fillers are incorporated primarily to cheapen and stiffen the final product. They are unable to provide any increase on these properties and they function merely as diluents [16].

1.4.3.1 Properties of fillers

Fillers with particle size greater than 10,000 nm are generally avoided because they can reduce performance. Fillers with particle sizes between 1000 and 10,000 nm are used primarily as diluents and usually have no significant effect - positive or negative on rubber properties. Semi-reinforcing fillers, which range from 100 to 1000 nm improve strength and modulus. The truly reinforcing fillers, which range from 10 nm to 100 nm significantly, improve rubber properties. The carbon blacks and precipitated silica and silicates are available in various particle sizes that range from semi-reinforcing to highly reinforcing. They generally exist as structural agglomerates or aggregates rather than individual spherical particles.

The level of dispersion of fillers in a rubber matrix is a very important parameter that decides the mechanical and dynamic mechanical properties of rubber products [17, 18]. The mixing of filler and dry rubber includes stages like incorporation, distribution and dispersion. Dispersion involves reduction of the size of agglomerates to their ultimate size: i.e., changing their physical state, while at the same time distributing the primary aggregates formed. This phase is also called dispersive or intensive mixing. Distribution involves the homogenization of the mix by distributing the filler particles within the polymer matrix. This phase is also called simple mixing or extensive mixing. Filler must make intimate contact with the elastomer chains if it is going to contribute to reinforcement. Fillers that have a high surface area have more contact area available and therefore have a higher potential to reinforce the rubber chains. The shape of the particle is also important. Particles with a planar shape have more surfaces available for contacting the rubber than spherical particles with an equivalent average particle diameter. Clays are planar-shaped particles that align with the rubber chains during mixing and processing thus imparting more reinforcement than a spherical-shaped calcium carbonate particle of similar average particle size. In compounds containing fillers with identical surface area and chemical nature but with a substantial difference in shape, modulus increases with increasing anisometry [19]. Particles of carbon black or precipitated silica are generally spherical, but their aggregates are anisometric and are considerably smaller than the particles of clay. Thus they have more surface area per unit weight available to make contact with the polymer. The greatest hardness is also provided by rod-shaped or plate-like particles, which can line up parallel to one another during processing, compared to spherical particles of similar diameter.

The shape of an individual particle of reinforcing filler is of less importance than the filler's effective shape once dispersed in elastomer. The blacks and precipitated inorganics used for reinforcement have generally round primary particles but function as anisometric acicular aggregates. The round particles clump together into chains or bundles that can be very dense or open and lattice-like. These aggregate properties: shape, density and size define their structure (Figure 1.2). The more an aggregate deviates from a solid spherical shape, larger its size and higher its structure. Higher structure indicates greater reinforcing potential.

For reinforcing fillers which exist as aggregates rather than discreet particles (e.g. carbon black and silica), a certain amount of structure that existed at manufacture is lost after compounding. The high shear forces encountered during milling will break down the weaker aggregates and agglomerates. The structure that exists in the rubber compounds affects their processability and properties.

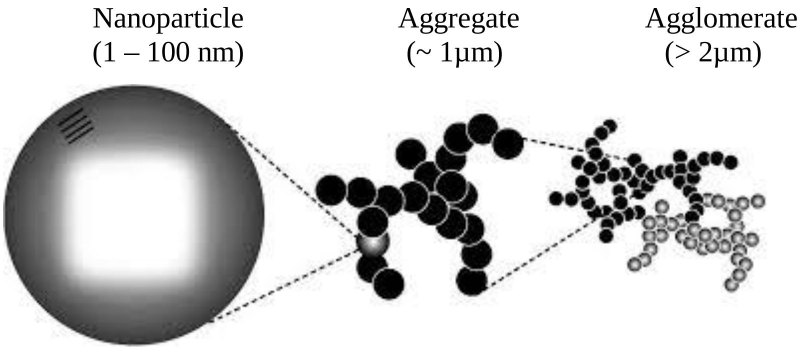


Figure 1.2 Carbon black structural units [20, 21]

A filler can offer high surface area and high structure, but still provide relatively poor reinforcement if it has low specific surface activity [22]. The specific activity of the filler surface is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Non polar fillers are best suited for nonpolar elastomers; polar fillers work best in polar elastomers. Beyond this, chemical compatibility is an essential factor for interaction between the elastomer and active sites on filler surface. Carbon black particles, for example, have carboxyl, lactone, quinone and other organic functional groups as shown in the Figure 1.3, which promote a high affinity of rubber for filler. This together with the high surface area of the carbon black facilitates an intimate elastomer-carbon black contact. The close contact of elastomer and carbon black will allow the active sites of carbon black to chemically react with elastomer chains to form a strong crosslink. The carbon black particle effectively becomes a crosslink. The reinforcing effect of carbon black on rubber is well known [24–33].

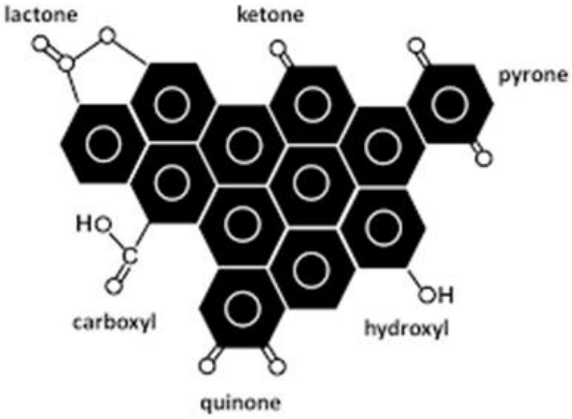


Figure 1.3 Chemical surface of carbon black with various functional groups [23]

1.4.3.2 Carbon black

Carbon black is essentially elemental carbon in the form of fine amorphous particles. Each particle is composed of randomly oriented microcrystalline layered arrays of condensed carbon rings. Because of their random orientation, many arrays expose open layer edges with unsatisfied carbon bonds at the particle surface. This in turn provides the sites for chemical activity. Individual round carbon black particles do not exist as discrete entities but form aggregates. Average particle size and aggregate configuration (structure) are the major determinants of the utility of a given carbon black in a specific rubber compound [4].

Carbon black is classified in several ways. One way to classify carbon black is in accordance with their imparted levels of abrasion resistance to the rubber vulcanizates as super abrasion furnace (SAF), intermediate super abrasion furnace (ISAF) and high abrasion furnace (HAF). Extrusion rate is another way to classify carbon black - fast extrusion furnace (FEF) and general purpose furnace black (GPF) falls in that category. There are other classifications, but basically they all depend on their manufacturing process, structure and surface area. Oil furnace blacks today account for about 95 % of the carbon black used in rubber industry for reinforcement. Thermal blacks are made in large cylindrical furnaces by the thermal decomposition of natural gas in the absence of flame or air. Their relatively large size and low structure enable higher loadings and provide better resilience and lower hysteresis than the more reinforcing blacks. In 1968, the ASTM committee on carbon black established a common nomenclature system consisting of a prefix followed by a three digit number. The prefix is either N, for normal curing or S for slow curing. The first of the three digits indicates the surface area of carbon black as measured by iodine adsorption [8].

1.4.3.3 Non-black fillers

The non-black fillers generally offer less affinity and less surface activity toward the common elastomers. The clays, silicas, and silicates all have surface silica (SiO_2) groups which have hydrolysed to silanols (-SiOH). These silanol groups behave as acids ($-SiO^-H^+$) and are chemically active. The fillers with higher surface area have more silanols available and are thus more active.

Silanols show similarities to carboxylic acid groups in their reactions with amines, alcohols, and metal ions. Most of the accelerators used in sulphur cure systems contain an amine group. Strong adsorption or reaction with filler particles can decrease the amount of accelerator available for vulcanization reactions. This can give slower cure rates and a reduced state of cure. Similar effects can result from the reaction of zinc ions with filler particles. These negative effects on the cure system can be reduced or completely avoided by adding other chemicals that will tie up the silanol groups and reduce their activity. Such additives commonly used in non-black compounds include diethylene glycol (DEG) and polyethylene glycol (PEG), hexamethylene tetramine (Hexa) and triethanolamine (TEA). These are mixed into the compound prior to the addition of the zinc oxide and accelerators. Many of these additives reduce the polarity of the filler surface and thus improve the wetting and dispersion of polar fillers in non-polar polymers.

1.4.3.3.1 Silica

Among various forms of silica that are commercially available, precipitated and fumed silica are commonly used reinforcing fillers in rubber vulcanizates [34]. Fumed silica is manufactured by the flame hydrolysis of silicon tetrachloride [35]. Precipitated silica is an amorphous form of silicon dioxide produced by reacting sodium silicate solution with either sulphuric acid or a mixture of carbon dioxide and hydrochloric acid. The particle size of silica can be divided into agglomerates, aggregates and primary particles as shown in Figure 1.4. The discreet silica particles which initially form the primary particles fuse into aggregates, which in turn form loose agglomerates. The precipitate is filtered, washed of residual sodium sulphate or sodium chloride, dried, and milled. The particle size reported for precipitated silica products is typically that of the primary particles (10 to 30 nm) rather than the aggregates (30 to 150 nm) that are the functional particles. Precipitated silica is silicon dioxide containing about 10-14 % water. They are reinforcing fillers giving composites of high tensile strength, tear resistance, abrasion resistance and hardness.

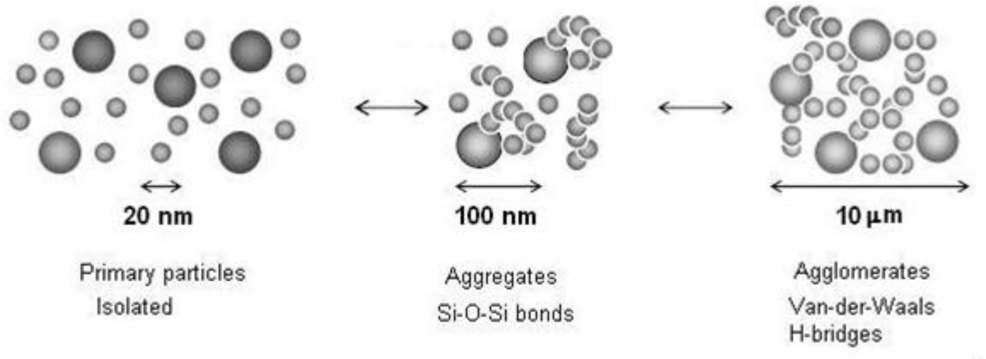


Figure 1.4 Characteristic sizes of silica [36]

Despite similarities in size and structure between precipitated silica and carbon black, fundamental differences exist in their surface activity. The silica surface is highly polar and hydrophilic and contains adsorbed water. The surface hydroxyl groups are acidic and tend to retard cure rate. The silanol groups on the surface of different silica particles interact with each other, resulting in strong agglomerates due to the hydrogen bonds formed between the silanol groups [37, 38].

The moieties on the silica surface also interact with basic accelerators, resulting in reduced curing rates and lower crosslink densities [23, 39]. The tendency of silica surfaces to react with the zinc oxide (activator) is also high. High molecular weight polyethylene glycols are usually used with precipitated silica to reduce its polarity and reactivity towards zinc oxide and organic accelerators. The use of additives to make the surface of precipitated silica less hydrophilic and more “rubberphilic” facilitates incorporation, dispersion, and more intimate filler-elastomer contact during compounding. This provides an improvement in rubber physical properties. However, reinforcement comparable to that obtained with carbon black requires a superior polymer-filler bonding mechanism provided at the carbon black active sites. Addition of a silane can very well create such active sites for strong polymer-filler bonding [4].

1.4.3.4 Effect of fillers on physical properties of rubber

The effect of fillers on the physical properties of rubbers can be related to the number of polymer chains attached to the filler surface and the strength of these polymer-filler bondings. Filler surface area and activity are the main determinants, supplemented by structure. Increasing surface area (decreasing particle size) gives lower resilience and higher Mooney viscosity, tensile strength, abrasion resistance, tear resistance and hysteresis. Increasing surface activity (including surface treatment) gives higher abrasion resistance and hysteresis. Increasing persistent structure gives higher Mooney viscosity and modulus (at 300 % elongation) and lower tear resistance [40]. Modulus is a measure of the force required to stretch a defined specimen of rubber to a given percentage of elongation. Filler with low surface activity will increase resistance to elongation by the viscous drag its surface exerts on the polymer trying to stretch and slide around it. Higher surface area, higher structure and higher loading will increase the modulus [4].

Abrasion resistance is a function of filler structure, particle size and filler–elastomer interaction. At equivalent loadings of filler, large particles will be more easily dislodged from the rubber surface than finer particles. Finer particle sizes provide more uniform distribution and more particles per unit surface area. Loss of a larger particle will expose more of the relatively soft surrounding elastomer matrix to wear. Extent of rubber-filler interaction is determined by the filler surface area, which increases inversely with the particle diameter. Rubber-filler bonds will be better with finely sized fillers which impose much restriction to dislodge them from the matrix [4, 41].

1.4.4 Other chemicals

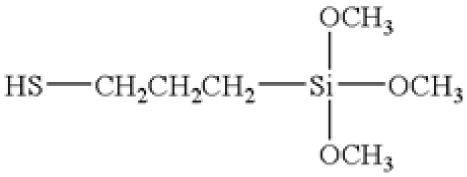
Antioxidants, antiozonants, processing aids, etc. are used in rubber product manufacturing according to the service requirements expected. Antidegradants are added in rubber compounds in order to increase the ability of the vulcanized products to resist the various deteriorative factors like oxygen [42], ozone, sunlight, etc. to which it may be subjected during service. Elastomers with a highly unsaturated backbone like NR and BR are not inherently ozone resistant. Therefore antiozonants and protective waxes are added during compounding to improve the ozone resistance.

The processing aids are generally liquids or resinous materials (e.g. petroleum oils, vegetable oils and synthetics such as esters and high molecular weight sulfonic acids) which mix intimately with rubber and act as softeners to permit incorporation of fillers, improve milling and extrusion, modify the flow behaviour of the rubbers, improve low temperature flexibility and make the vulcanizates softer [4]. The petroleum oils (paraffinic, naphthenic or aromatic) are used primarily with non-polar elastomers based on elastomer compatibility and expected product service conditions. The synthetic ester plasticizers such as dioctyl phthalate and dibutyl phthalate are used with polar elastomers. These additives lower elastic modulus, increase resilience, improve elongation and reduce hysteresis.

1.5 Silane coupling agents

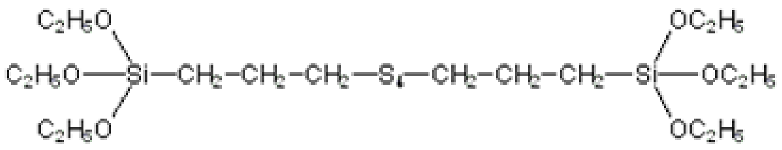
One effective means to modify the surface chemistry of non-black fillers is by the addition of silane coupling agents. Previous researchers have studied the reinforcement of silica filler in natural rubber, in presence of silane coupling agents [43]. Silane coupling agents react with the silanols on the filler surface to give a strong bond, and also contain a functional group that will bond to the rubber during vulcanization. The result is filler-polymer bonding (crosslinking) that increases modulus and tensile strength and improves abrasion resistance. Clays are found to reduce the tensile properties. However silane coupling agent treated clays are found to show improved tensile properties [44, 45].

Any one of the two silane coupling agents is commonly used with non-black fillers in sulphur-cured compounds. These are mercaptosilane and tetrasulfide silane. Chemical structure of mercaptosilane (e.g. mercapto propyl trimethoxy silane) and tetrasulfide silane (e.g. bis (triethoxy silylpropyl) tetrasulfide - TESPT) is shown in Figure 1.5. The methoxy or ethoxy groups of the coupling agent react with the silanol groups on the surface of silica, silicates or clay particles during mixing to give a strong chemical bond. The sulphur containing group of the coupling agent reacts and forms bond with the polymer during vulcanization thus enhancing polymer-filler interaction. The mercaptosilane is more active than tetrasulfide silane.



$HS{-}CH_2CH_2CH_2{-}Si(OCH_3)_3$

Mercapto propyl trimethoxy silane

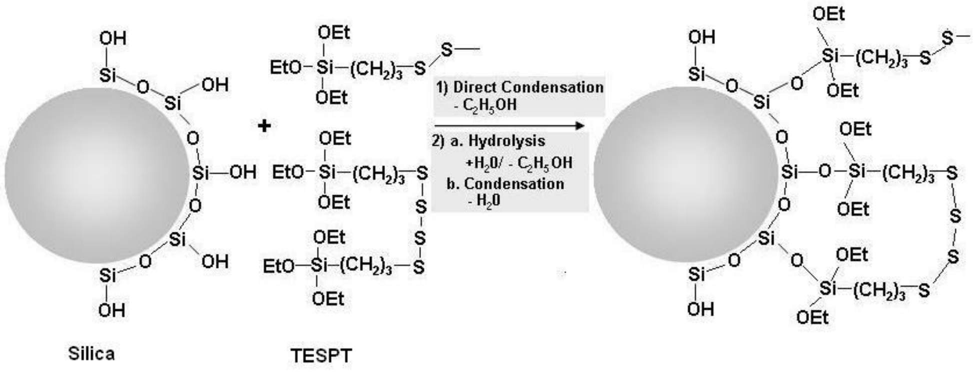


TESPT

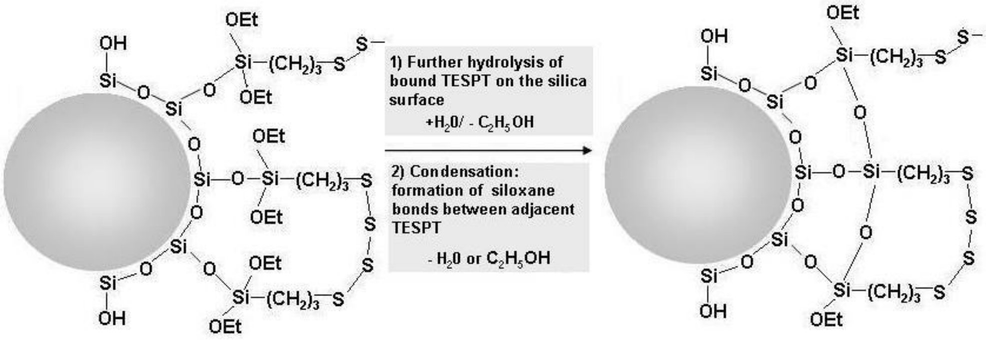
Figure 1.5 Chemical structure of silanes used with non-black fillers

The addition sequence is very important when adding silane coupling agents during mixing of the rubber compound, especially when using the tetrasulfide. To make the most efficient use of these high cost chemicals, it is important to mix the polymer, filler and silane coupling agent for 1 to 2 minutes before adding any other ingredients that will interfere with the reaction between the filler and the silane.

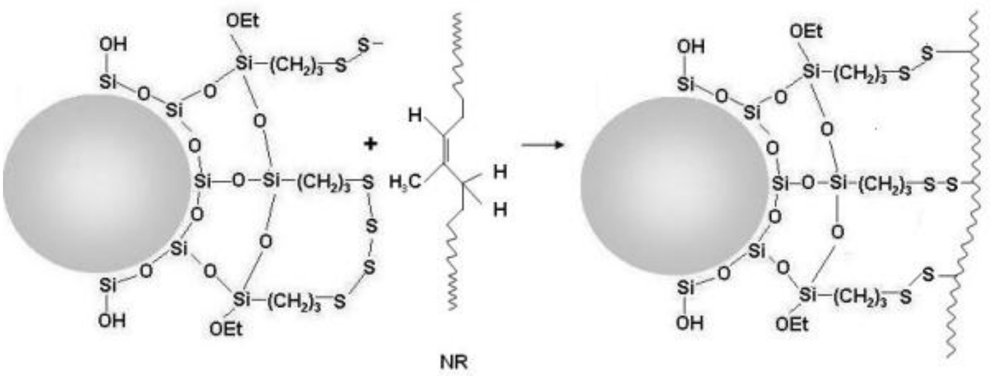
The reaction mechanism between silica, silane coupling agent and rubber has been extensively reviewed [46-51]. The primary and secondary reaction between TESPT and silica, as well as reaction between TESPT and natural rubber are shown in Schemes 1.1, 1.2 and 1.3 [46].



Scheme 1.1 Proposed mechanism for primary reaction between silica and TESPT



Scheme 1.2 Proposed mechanism for secondary reaction between silica and TESPT



Scheme 1.3 Proposed mechanism for reaction between natural rubber and TESPT

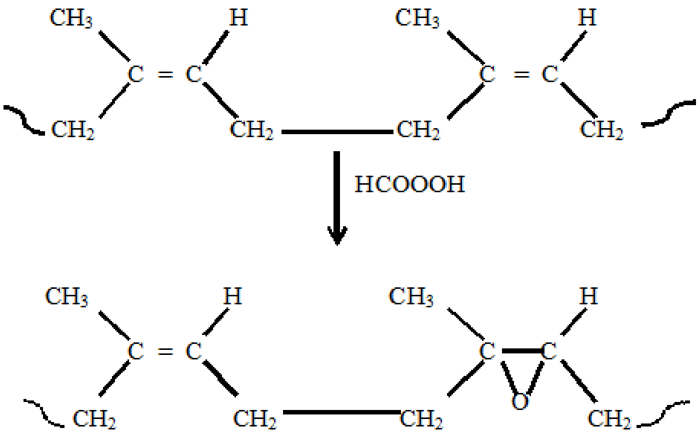
1.6 Epoxidised natural rubber

Various modifications have been done to improve the reinforcing ability of the silica, which include heat treatment, polymer grafting on silica surface and chemical modification. The reports show the feasibility of using epoxidised natural rubber as a reinforcement modifier in silica-filled nitrile rubbers [52]. Epoxidised natural rubber is a modified form of natural rubber with inherent reinforcing ability with silica. Two grades of epoxidised NR: ENR-25 and ENR-50 with 25 and 50 mole percent of epoxidation respectively have attained commercial importance. Unlike NR, epoxidised natural rubber (ENR) can be reinforced with silica without silane coupling agent [53]. Epoxidation of NR latex with hydrogen peroxide and formic acid (Scheme 1.4) is used to produce 25 and 50 mol % epoxidised natural rubber, which are marketed as ENR–25 and ENR–50 respectively [54].

Step 1

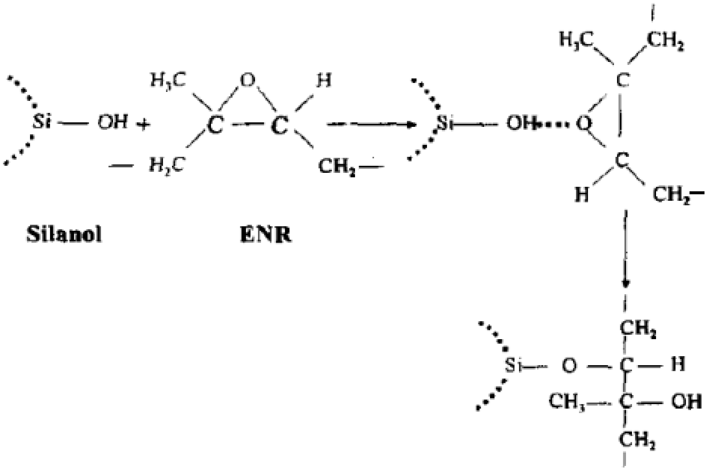
$$HOOH + HCOOH \leftrightarrow HCOOOH + H_2O$$

Step 2



Scheme 1.4 Epoxidation reaction of natural rubber

Silica being strongly polar and hydrophilic reinforcing filler requires a polar rubber matrix to attain better rubber-filler interactions. The polarity and bifunctionality (the oxirane and the unsaturation) of ENR allows establishment of improved rubber-filler interactions. The proposed mechanism of interaction between epoxy and silanol groups is shown in Scheme 1.5 [55].



Scheme 1.5 Proposed mechanism for epoxy-silanol interaction

Epoxidised natural rubber retains the cis-1,4 configuration of natural rubber and hence undergoes strain induced crystallization and high tensile strength. Epoxidation of natural rubber reduces its gas permeability, making it suitable for applications such as tyre inner liners.

1.7 Filler-filler and rubber-filler interaction

1.7.1 Payne effect

Filler-filler interaction is commonly measured by the Payne effect. The introduction of reinforcing fillers into rubbery matrices strongly modifies the viscoelastic behavior of the materials. The dynamic modulus of rubber increases with addition of reinforcing filler. The contribution of the fillers to the modulus of rubber can be divided into two: strain-dependent and strain-independent parts. Filler-filler interaction contributes to the strain-dependence of the modulus. The modulus decreases with increasing strain: the so-called Payne effect, which is due to a partially reversible breakdown of the filler network [56]. The strain-independent part of the modulus is a contribution from the combination of filler-rubber interactions, the crosslinked rubber network and hydrodynamic effect of the filler as illustrated in Figure 1.6 [57-60]. Filler-filler and filler-rubber interactions are two partially competitive processes. A decrease in filler networking would lead to better filler-rubber interaction. Filler-filler interaction is commonly characterized by the Payne effect: the drop in storage modulus and loss modulus in a dynamic mechanical test when the strain (deformation) is increased from low (<1 %) to a high value (100 %) at constant frequency and temperature. This behavior is the result of breakage of physical bonds (i.e. van der Waals forces and hydrogen bonds) among filler particles. The Payne effect is stronger for silica compared with carbon black, as a consequence of the strong interparticle forces between the silica particles [59, 61-64].

Rubber chains can be trapped in the voids of the filler aggregates, and so they are immobilized and shielded from deformation [65, 66]. In addition, the rubber layer attached on the surface of filler particles also exhibits an immobilized and glassy state character [67-69]. The immobilized rubber is due to its physical interactions or chemical interactions with the filler and is called “in-rubber structure” which results in strong rubber-filler interactions.

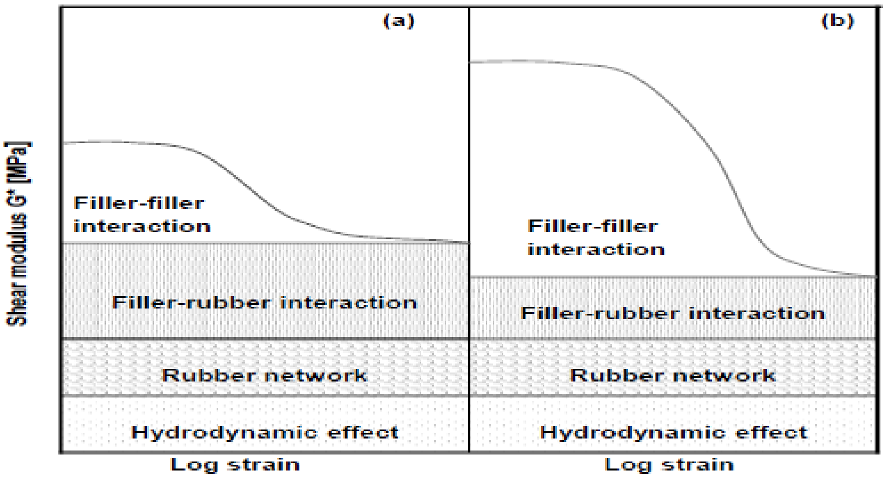


Figure 1.6 Contributions to the shear modulus of filled rubber: (a) carbon black-filled rubber and (b) silica-filled rubber [59]

Hydrodynamic effect is another strain independent contribution to the modulus. It is described as an increment in moduli of rubber compounds caused by the addition of filler particles. The theoretical meaning of hydrodynamic effect is given by the modified form of Guth and Gold equation [70, 71]. The addition of the filler increases the shear modulus (G_0)

of the pure elastomer and results in a higher shear modulus ($G_{f)}$ for the filled compound.

$$G_f = G_0\,(1+ 0.67f_s\varphi + 11.62f_s^2\varphi^2) \text{ ---------------------------------- } (1.1)$$

Where φ is the volume fraction of the particles and the shape factor f_s represents the ratio of the longest dimension to the shortest dimension of the particle. The modulus was calculated by the equation independent of the applied strain [72].

Network of rubber is mainly generated during vulcanization by crosslinking chemicals. This crosslinking is also one of the strain-independent contributions to the modulus. The modulus of the vulcanized rubber is proportional to the crosslink density of the networks, which depends on the vulcanization system.

1.7.2 Bound rubber content

The phenomenon of bound rubber is another evidence for rubber-filler bonds. Polymer-filler bonding, particularly in the case of carbon black, develops through active sites on the filler surface resulting in 'bound rubber' attached to the filler surface. Bound rubber is regarded as the result of rubber to filler interactions which can be considered as a measure of the surface activity and surface area of the black or white fillers [73]. The surface activity of the filler is reflected in the mechanical properties of the rubber such as tensile strength, modulus, abrasion and tear resistance. High structure black generally exhibits larger rubber–filler interaction. In the polymer matrix, above critical concentration (C_{crit}.) filler transforms from dispersed state to a coherent gel. Bound rubber is essentially the gel formed in rubber-filler mix and its estimation is considered to be a practical means of assessing rubber-filler interaction in the uncured state. The gel formed due to polymer-polymer crosslinking is not considered as bound rubber. Bound rubber is generally determined by swelling measurements. Physical as well as chemical interactions are believed to involve in bound rubber formation [23].

The filler-filler aggregates, which get broken down during mixing with the elastomers may get reformed during the post-mixing period. The trapped rubber in such aggregates can also cause bound rubber [74]. Chemical interaction of a filler particle with elastomer can affect the properties of both the uncured mix and the vulcanizate. Covalent bonds between rubber and carbon black contribute to reinforcement, while it is not a necessary condition for bound rubber formation. The bound rubber retained at higher temperature (> 100 °C) is apparently due to rubber-filler covalent bonds [23]. Polarity of the polymer also contributes to enhanced bound rubber formation. Polarization of the unsaturated polymers in the presence of polar fillers also contributes to polymer-filler interactions [75].

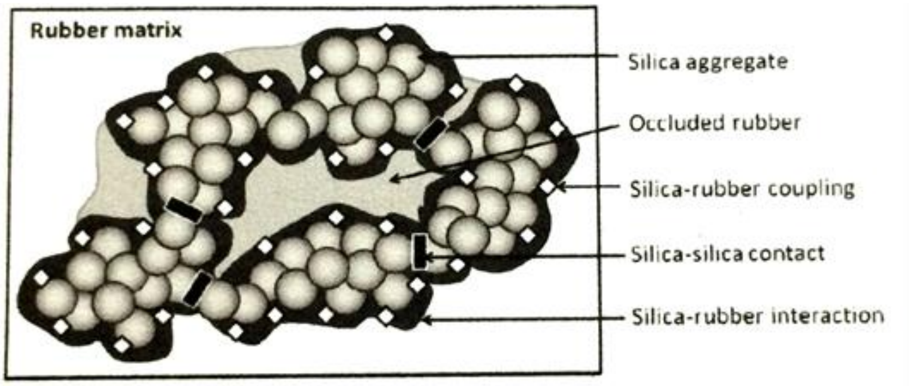


Figure 1.7 Bound rubber model of coupling agent modified silica-filled rubber compound [76]

The model of rubber reinforcement with silica modified by a silane coupling agent is shown in Figure 1.7. The silica aggregates form a network by strong hydrogen bonding. Apart from the occluded rubber, there is a layer of bound rubber chemically bonded to the silica surface by the organo-silane coupling agent. In addition, probably some rubber chains are also loosely adsorbed on the modified surface which also contributes to bound rubber, but rubber-silica interaction is very weak in this case. Under high deformation the filler network partially breaks open leading to the reduction of occluded rubber and hence the deformation of the matrix. However in the presence of coupling agent, the rubber chains are chemically attached to the silica surface and occluded rubber remains totally [76].

1.8 Accelerated Sulphur vulcanization system

A generally accepted scheme for the accelerated sulphur vulcanization reactions [77-79] is shown below:

- Accelerator (Ac] and activator interacts with sulphur to form the active sulphurating agent.

  $Ac + S_8 \rightarrow Ac - S_x - Ac$ (active sulphurating agent) ------- (1.2)

- The rubber chains interact with the sulphurating agent to form polysulphidic pendant groups terminated by accelerator groups.

  $Ac - S_x - Ac + RH \rightarrow AcH + R - S_x - Ac$ (Pendent sulphurating agent)----- (1.3)

  where RH is the rubber chain.

- Polysulphidic crosslinks are formed.

  $R - S_x - Ac + RH \rightarrow AcH + R - S_x - R$ (crosslinks) -------- (1.4)

- Network maturing and competing side reactions and thermal decomposition leads to the following reactions:

  $R - S_x - Ac \rightarrow$ cyclic sulphides + dienes + ZnS (degradation) -- (1.5)

  $R - S_x - Ac \rightarrow S_{x-1} + R - S - Ac$ (desulphuration) ------------ (1.6)

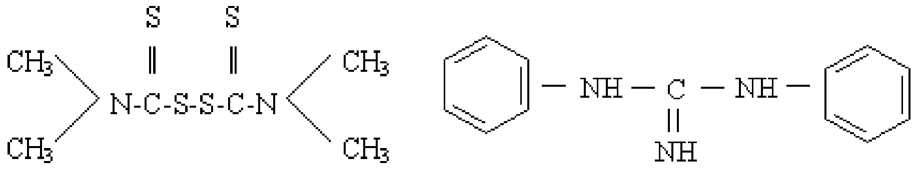
  $R - S_x - R \rightarrow S_{x-1} + R - S - R$ (monosulphidic crosslinks) ----- (1.7)

There are at least three competing reactions (cross linking, desulphuration and degradation) that occur during the cure and network maturing period. The ultimate network structure formed depends on the temperature, accelerator types and concentration. The ratio of types of crosslinks formed (poly, di or mono sulphidic) depends on the ratio of sulphur to accelerator in the formulation.

The accelerators react in the form of their more active zinc salt. The scorch (premature vulcanization) safety, cure rate and the length and number of crosslinks formed in the vulcanizate depend highly on the accelerator used and the speed with which the accelerator is converted to its very active salt form. Different accelerators are compared in Table 1.1 based on its influence on the above mentioned properties. Chemical structures of some of the commonly used vulcanization accelerators are also shown in Figure 1.8.

Table 1.1 Effect of various types of accelerators

Accelerator type	**Scorch safety**	**Cure rate**	**Crosslink length**
None (sulphur alone)	------	very slow	very long
Guanidines	moderate	moderate	medium-long
Mercaptobenzothiazoles	moderate	moderate	medium
Sulfenamides	long	fast	short - medium
Thiurams	short	very fast	short
Dithiocarbamates	least	very fast	short



Tetramethyl thiuramdisulfide Diphenyl Guanidine

2 – Mercaptobenzothiazole (MBT) N-oxydiethylene 2- benzothiazolesulfenamide (MBS)

Figure 1.8 Chemical structure of common vulcanization accelerators

The desired level of scorch safety can be achieved through use of scorch retarders in addition to the chosen accelerators. The traditional retarders are benzoic acid, salicylic acid and phthalic anhydride, which interfere with the activity of the accelerators. These retarders, however slow the cure rate and reduce the ultimate state of cure in addition to reducing the scorch time. The most popular commercial retarder used along with sulfenamide accelerators is N-(cyclohexylthio) phthalimide (CTP). CTP impedes the onset of vulcanization without significantly reducing cure rate or ultimate state of cure.

The length of sulphidic crosslinks formed during vulcanization affect rubber properties. Mono and di sulphidic crosslinks are more stable than poly-sulphidic links and thus promote better thermal and ageing characteristics. Poly-sulphidic links, on the other hand, provide better molecular flexibility which imparts better dynamic fatigue resistance. The more stable crosslinks are often preferred to provide reversion resistance.

Reversion is the cleavage of sulphidic crosslinks during vulcanization due to the extension of cure beyond the optimum cure time.

The choice of accelerator will influence the length of crosslinks, but this can be further controlled by adjusting the accelerator to sulphur ratio. Increasing this ratio progressively favors shorter crosslinks. This can be alternatively accomplished by using sulphur donors instead of the elemental sulphur for vulcanization.

After the mixing and formation of rubber compounds, it is vulcanized. This process involves three stages: induction, curing and reversion (overcure). The induction period is the time during which no measurable crosslinking occurs at the vulcanization temperature. It determines the safety margin of the compound against “scorch” during the processing steps preceding crosslinking. Scorch is premature vulcanization that can occur due to the effects of heat and time. Scorching produces tough and unworkable batch. Cure time is the time required for the compound to reach a state of cure where a desired balance of properties can be attained. When a compound is cured beyond the point where its balance of properties has been optimized it becomes overcured. For most elastomers, overcure means the compound becomes harder, weaker and less elastic. In the case of natural rubber compounds, overcure results in reversion. The compound softens, becoming less elastic and more plastic [4].

1.8.1 Single and Binary accelerator system

The accelerated sulphur systems can further be classified into single accelerator systems and binary accelerator systems. The single accelerator systems are the most widely studied because of the widespread use and simplicity of the mechanism. Binary accelerator formulations involve the use of two different accelerators in the system, often leading to improved properties. One of the advantages of using binary systems is the synergistic behavior of accelerator combinations so that the final properties are better than those produced by either accelerator separately [80-82]. Aprem et al. in his work proved that 1-phenyl 2, 4 dithiobiuret (DTB) along with tertiarybutyl benzothiazolesulfenamide (TBBS) have excellent mechanical properties in both conventional and efficient vulcanization systems [83].

Mutual activity of the binary systems of accelerators during the vulcanization of NR has been explained by Dogadkin and co-workers [84], Skinner and Watson [85], Kempermann [86], and Krymowski and Taylor [87]. Kemperman [88] determined the synergistic effect and the effectiveness of different binary accelerator systems by studying many pairs of vulcanization accelerators in NR compounds. Out of these, majority of the combinations showed strongly positive and few slightly positive synergisms. Debnath et al. [89] and Alam et al. [90] have also done some studies in this area.

1.9 Carcinogenic effects of rubber chemicals

Large numbers of chemicals in huge quantities enter the production processes of rubber industry every day. The toxicological characteristics of these chemicals are largely unknown and their study is complicated due to the use of commercial grade products of low purity or unknown chemical identity or both. Furthermore, during the production of finished rubber goods these chemicals find suitable conditions (high temperatures and large surfaces for reaction with atmospheric oxygen or nitrogen oxide) for cross reactions with the possible generation of new chemical entities with new and unforeseen toxicological characteristics [91].

Recent concern on potential health hazard of different rubber chemicals has thrown the subject quite open to the scientists. Several epidemiological studies, reviewed by the International Agency for Research on Cancer (IARC), indicate that occupation in the rubber industry is significantly related to an increased risk of developing cancer in various organs [92]. Rubber chemicals derived from secondary amines, when exposed in air, form nitrosamines in presence of atmospheric nitrosating agents. These substances are known as genotoxic and carcinogenic [93- 95]

The medical world generally recognizes that the best way to lower human cancer rates is through prevention rather than therapy. Current epidemiology indicates that one way of prevention can be achieved by reducing exposure to nitrosamines [96].

The highest concentrations of nitrosamines in the human environment have been measured in the rubber industry [97-99]. Straif et al. have conducted a study to investigate occupational exposure to nitrosamines and cancer risks among workers in the rubber industry and speculated that nitrosamines may have played a part in the excess risk of cancers in the pharynx, esophagus and urinary bladder [100, 101].

N-nitrosamine release is a major environmental issue in rubber industries due to the feasible reaction of accelerators used in rubber compound formulations with atmospheric nitrogen oxides especially at high temperatures. In the year 1980, more than 90 % of the 300 nitrosamines have been classified as carcinogen or mutagen [102, 103]. The affected or specifically the target organs of nitrosamine attack are the lungs and liver.

Two German researchers - Spiegelhalder and Preussman published results showing the presence of N-nitrosamines in a number of rubber articles [104]. In the year 1982 German Federal Health Office (German BGA) proposed upper limits for N-nitrosamines and N-nitrosatable amines in baby teats and soothers. Regulations of these materials were closely followed by the American FDA and regulatory bodies in several other countries [105].

1.10 Regulated nitrosamine generating accelerators

So far, Germany leads the world in legislation and the elimination of nitrosamines from the work place. Eight suspected carcinogenic nitrosamines that are formed from accelerators commonly used in the rubber vulcanization systems are listed in “Technical Rules for Dangerous Substances” (TRGS 522) of Germany (Table 1.2) [106].

Table 1.2 Carcinogenic nitrosamines and corresponding accelerators (ASTM abbreviations)

Nitrosamine	Accelerators
Nitroso-dibutylamine (NDBA)	ZDBC[a], TBTD[b], DBA[c]
Nitroso-diethylamine (NDEA)	ZDEC[d], TETD[e]
Nitroso-dimethylamine (NDMA)	ZDMC[f], TMTM[g], TMTD, HEXA[h]
Nitroso-diisopropylamine (NDiPA)	DiBS[i]
Nitroso-ethylphenylamine (NEPA)	ZEPC[j]
Nitroso-methylphenylamine (NMPA)	MPTD[k]
Nitroso-morpholine (NMoR)	MBS, DTDM[l], OTOS[m]
Nitroso-piperidine (NPIP)	DPTT[n], Z5MC[o]

([a]ZDBC – Zincdibutyl dithiocarbamate, [b]TBTD – Tetrabutylthiuram disulfide, [c]DBA – Dibutylamine, [d]ZDEC - Zincdiethyl dithiocarbamate, [e]TETD – Tetraethyl thiuram disulfide, [f]ZDMC - Zincdimethyl dithiocarbamate, [g]TMTM - Tetramethyl thiuram monosulfide, [h]HEXA – Hexamethylene tetramine, [i]DiBS – Diisopropyl benzothiazolesulfenamide, [j]ZEPC- Zincethylphenyl dithiocarbamate, [k]MPTD – Dimethyldiphenyl thiuram disulfide, [l]DTDM – 4,4’-Dithiodimorpholine, [m]OTOS – N-Oxydiethylenethiocarbamyl N- oxydiethylenesulfenamide, [n]DPTT – Dipentamethylene thiuramtetrasulfide, [o]Z5MC – Zincpentamethylene dithiocarbamate)

N-nitrosamines are the nitroso derivatives of amines where the nitroso group is bound to the amine nitrogen. N-nitrosamines are compounds with the general structure $R_2N.NO$, where the R is an alkyl or aryl group. N-nitrosamines are formed by the reaction between secondary amines and nitrosating agents (generally an oxide of nitrogen) as given in equation 1.8. Secondary amines are more susceptible to the reaction compared to the primary amines as the derivatives of primary amines are not stable and breakdown to form nitrogen, water and an olefin.

$R_2NH + N_2O_3 \rightarrow R_2N.NO + HNO_2$ ---------------------------- (1.8)

N-nitrosamines are polar and this polarity may also explain their carcinogenic activity, as it may release the ion, R^+. Such ions are thought to be able to alkylate DNA. The carcinogenic activity of this ion decreases as its stability increases. Thus ions with more ∞-hydrogens are less stable. This suggests that among N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA), the former is expected to be carcinogenic, and its toxicity was proved in various animal tests [107]. The chemical structures of NDMA and NDEA are shown in Figure 1.9.

NDMA NDEA

Figure 1.9 Chemical structures of N-nitrosodimethylamine and N-nitrosodiethylamine

The secondary amines are formed by the decomposition of many rubber accelerators, and thus can be present in vulcanized rubber articles also. Amines and nitrosating agents may be present in elastomers, fillers and other compounding ingredients. During vulcanization these contribute to the formation of additional nitrosamines, possibly to levels of magnitude above those already existing in the uncured compound. Sometimes, nitrosamines may form during storage, assembling or service [108]. If the vulcanizing or drying ovens on a manufacturing plant are heated by open gas flames, the nitrous oxide, which may be produced during the gas combustion, can provide a route for the formation of N-nitrosamines. Since most nitrosamines are volatile at low temperatures, leaching of nitrosamines into the air of production areas and warehouses poses catastrophic health risks to the employees. Formation of N-nitrosamines is favored by the presence of halides, thiocyanates and thioureas at pH 2.5-3.5 and by the presence of formaldehyde at higher pH values [96].

IARC classifies N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) in Group 2A as probable carcinogens to humans and N-nitrosodipropylamine (NDPA), N-nitrosodibutylamine (NDBA), N-nitrosopiperidine (NPIP), N-nitrosopyrrolidine (NPYR) and N-nitrosomorpholine (NMoR) in Group 2B [109] as possible carcinogens to humans. The chemical structure of NPYR is shown in the Figure 1.10.

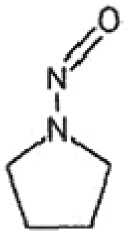


Figure 1.10 Chemical structure of N-nitroso pyrrolidine (NPYR)

Furthermore, N-nitrosodibenzylamine (NDBzA), N-nitroso N-methyl N-phenylamine (NMPhA) and N-nitroso N-ethyl N-phenylamine (NEPhA) have been reported to be mutagenic [110 - 113]. Rubber articles that tend to generate nitrosamines due to the use of nitrosamine generating accelerators (dithiocarbamates, sulfenamides, thiurams, sulphur donors or chemicals containing secondary amines) include athletic shoe soles, baby bottle nipples, condoms, gloves, milking inflations, pacifiers, pharmaceutical items (stoppers, plunger seals, etc.), radiator hoses, sealing systems, tires and windshield washer tubing, to name a few. The secondary amines may be nitrosated by nitrous acid in the atmosphere or if ingested, form the corresponding N-nitrosamine in the stomach. This possible exposure route is alarming, especially for babies and small children. Exposure to skin or mucous membranes through gloves or condoms is thought to cause much less risk. Primary amines also generate nitrosamines, but these are unstable and do not last long enough to do any damage. The N-nitroso primary amines RNH.NO readily get decomposed to the corresponding alcohol (ROH) and nitrogen. Tertiary amines are safe to use as these are not prone to form nitrosamines. Certain secondary amines, because of their specific structure will produce safe or non-regulated nitrosamines.

In addition, diphenylamine type secondary amines are sometimes added as antioxidants. These secondary amines may be nitrosated by nitrous acid in the atmosphere or if ingested form the corresponding N-nitrosamine in the stomach [114,115]. Examination of the relationship between chemical structure and carcinogenic activity suggests that there are receptors in cells, for which N-nitroso compounds are the substitute for the normal substrate. Binding of the N-nitroso compound to the receptor might block normal activity, sending an abnormal signal to the nucleus and initiating cell division at an inappropriate time. This could result in permanent adverse consequences to the host [116].

Nitrosamines have been used as intermediates in a number of industrial processes [117-119] and hence exposure to these compounds may be more widespread than assumed. Animal studies have shown that N-nitrosamines and the related N-nitrosamides are carcinogenic [120, 121] and they may be mutagenic and teratogenic [122] as well. Nitrosamines having a wide variety of molecular structures are carcinogenic; among the approximately 100 compounds tested, 75 produced lesions in test animals [123].

1.10.1 Dithiocarbamates

The dithiocarbamates are secondary accelerators that are used at low phr levels in rubber compounds to boost the cure system to a desired rate of cure. Examples of dithiocarbamates include ZDBC, ZDMC, ZDEC, Telluriumdiethyl dithiocarbamate (TDEC), etc. Almost every dithiocarbamate has the ability to form a regulated nitrosamine in the presence of a nitrosating agent [124].

1.10.2 Sulfenamides

The sulfenamides are primary accelerators that are used at low phr levels in a rubber compound and can influence not only the rate of cure, but also the scorch safety of the compound. Due to this nature, the sulfenamides have been termed as fast-delayed action accelerators [125]. Three of the popular sulfenamides are based on morpholine and can generate the regulated nitroso-morpholine. They are 2-morpholino dithiobenzothiazole (MBSS), N-oxydiethylene-2-benzothiazole sulfenamide (OBTS or MBS) and OTOS [124]

1.10.3 Sulphur donors

Sulphur donors are accelerators that are used in a rubber formulation when improvements in heat ageing and compression set are required. They are unique in that they provide either mono or disulphidic bonds to the rubber compound. Unfortunately, the most common sulphur donor, DTDM, is based on morpholine and just like the three sulfenamides cited above, produces a regulated nitrosamine [124]

1.10.4 Thiurams

The thiurams are secondary accelerators used in a rubber formulation at low phr levels to boost the cure system to a desired rate of cure. Although the thiurams are not as fast as the dithiocarbamates, these act both as accelerator and as sulphur donor. Examples of common thiurams include DPTT, TETD, TMTD and TMTM [125]. Thiuram disulfides, the parent compound of thiuram, either alone or in combination with thiazole group of accelerators [126, 86] have been considered immensely important and popular during last few decades in the rubber industry for their efficient accelerated crosslinking capacity leading to preparation of vulcanized article of desired technological properties. Thiuram compounds, e.g., tetramethyl thiuramdisulfide as derived from secondary amine were reported [127] to have generated carcinogenic nitrosamine. Thiuram disulfides are so important in the rubber industry that they are indispensable. It’s high time to replace the unsafe thiuram disulfides with safe ones as far as human health is considered.

1.10.5 Chemicals containing secondary amines

N-nitrosodiphenylamine (NDPA) has been used as a retarder in the rubber industry. Although it is not known to be carcinogenic it can nitrosate secondary amines by transnitrosation [128].

$Ph_2NNO + R_2NH \rightarrow Ph_2NH + R_2NNO$------------------------ (1.9)

This effect can be quite fatal. It was found that NDMA and NMoR concentration in curing fume could be reduced by two orders of magnitude when NDPA was removed from a rubber compound.

Sodium nitrite which is a nitrosating agent is usually used as a heat transfer agent in salt baths. Any amines present in the cure fumes released from the rubber being vulcanized in such baths are susceptible to nitrosation with the formation of nitrosamines (e.g. 230µg/ m^3 NDMA in direct fumes). So these types of nitrosating agents should be avoided or controlled in the rubber industry.

1.11 Carcinogenecity tests

The safety of the material can be determined by carcinogenicity tests. Thus carcinogenicity tests are used as the method for proving the non-carcinogenicity of a specific material.

Conventional carcinogenicity tests are carried out by administering high doses of the test chemical to a group of animals over a long period. As this can take many years and are expensive, various short term carcinogenicity tests have been developed. Some of the short term *in vitro* carcinogenicity tests are the Ames test and cytotoxicity tests such as extract tests and direct contact tests [99, 129].

1.11.1 The Ames test

This test looks for mutations caused by the test chemical in specially developed mutant strains of *Salmonella typhimurium* bacteria. These strains contain a defect which prevents the bacteria from synthesizing the amino acid histidine, which is required for bacterial growth. The strains will therefore grow only if histidine is supplied to them. The defect in these bacteria can be reversed by chemicals which have mutagenic activity and the bacteria will then grow even in a histidine deficient culture. The test consists of exposing large numbers of these bacteria to a known quantity of the test chemical, incubating at 37 °C for 72 h and counting the number of revertant colonies which have grown. The number of colonies produced is then compared with the number given by controls. Many chemicals become mutagenic (or carcinogenic) only after they have been chemically altered by enzyme systems within the mammalian body. For Ames test, the enzyme activity is induced by adding supplemented liver fraction, S-9, made from livers of rats [99]

1.11.2 Cytotoxicity tests

A carcinogen is any substance that is directly involved in causing cancer. This may be due to the ability of the substance to damage the genome or to disrupt the cellular metabolic processes. The cytotoxicity test is one of the biological evaluation and screening tests that use tissue cells *in vitro* to observe the cell growth, reproduction and morphological effects. With the continuous development of cytotoxicity test, methods, such as detection of cell damage by morphological changes, determination of cell damage, measuring cell growth and metabolic properties, have appeared and have gradually been developed from qualitative evaluation to quantitative

[130-133]. Extract and direct contact tests are cytotoxicity tests stated in the International Organization for Standardization 10993-5 [134].

1.11.2.1 Extract tests

In general, the extract test is suitable for detecting the toxicity of soluble substances (extract) of materials and is usually consistent with the results of animal toxicity tests. Cell viability in the extract can measure by MTT and neutral red uptake assay.

1.11.2.1.1 MTT assay

The mitochondrial dehydrogenase performance measurement, also known as the 3-(4, 5-dimethylthiazol-2-yl)-2,5-diphenyltetrazoliumbromide assay (methylthiazolyl tetrazolium or MTT assay), is a rapid assessment of cell proliferation and cytotoxicity colorimetric assay to measure cell metabolism or function [129, 135]. The assay can be performed entirely in a microtiter plate (MTP). The main principle is as follows: mitochondrial dehydrogenase in the living cells can cleave the tetrazole ring, and the yellow, water-soluble MTT is reduced to produce a purple crystalline formazan. This method involves culturing the cells in a 96-well MTP and incubating the culture with MTT solution for approximately 3 h. During the incubation period, viable cells convert MTT to a water-insoluble formazan dye. This substance is soluble in dimethyl sulfoxide and other organic solvents, but is insoluble in water. The amount of crystals formed has a positive correlation to the number of cells and activity of the viable cells and measuring the absorbance (optical density) value reflects the number of surviving cells and metabolic activity. A microtiter plate after an MTT assay is as shown in Figure 1.11. Increasing amounts of cells resulted in increased purple colouring. The procedure for MTT assay is shown in the Figure 1.12.

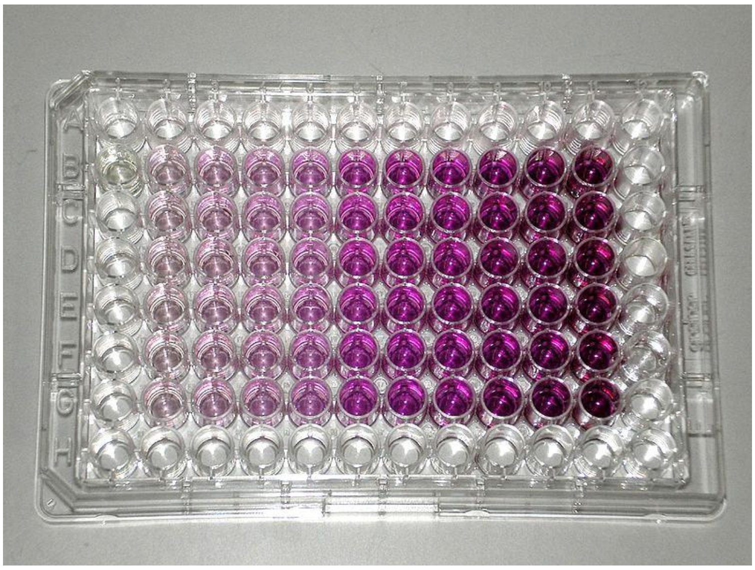


Figure 1.11 A microtiter plate after an MTT assay

Murali et al [129] synthesized N-nitroso-3-(substituted phenylimino) -indolin-2-one and carcinogenic activity was assessed by MTT cell-viability assay. The MTT assay results proved the carcinogenic activities of synthesized compound. This chemical produced nitrosamines and most of the nitrosamine generating chemicals are carcinogenic.

The MTT assay is currently the most commonly used method to test cell growth rate and toxicity of the culture. This method is easy-to-use, safe, has a high reproducibility and is widely used in cytotoxicity tests. Among the enzyme-based assays, the MTT assay is the best known method for determining mitochondrial dehydrogenase activities in the living cells.

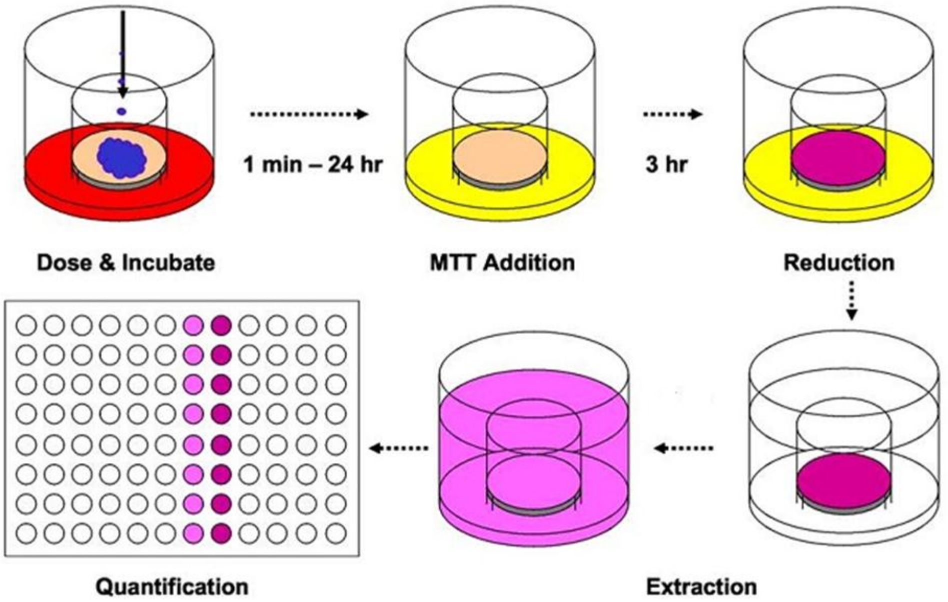


Figure 1.12 Schematic procedure for MTT assay

1.11.2.1.2 Neutral red uptake assay

The neutral red uptake assay provides a quantitative estimation of the number of viable cells in a culture. It is based on the ability of viable cells to incorporate and bind the supravital dye neutral red in the lysosomes. Cells are seeded in 96-well tissue culture plates and the plates are then incubated for 2 h with a medium containing neutral red. The cells are subsequently washed, the dye is extracted in each well and the absorbance is read using a spectrophotometer [136,137]. Oshima et al [138] have done extract test based on neutral red uptake assay [139, 140] for finding out the cytotoxicity in various rubbers. The extracts of ethylene-propylene, butyl and nitrile rubber vulcanizates yielded strong cytotoxicity in extraction method, while chloroprene, fluoro-elastomers, isoprene and silicone rubber vulcanizates showed little cytotoxicity.

1.11.2.2 Direct contact test

The direct contact method yields direct contact of the material to be tested with cultured mammalian cells *in vitro* [99, 129]. The cytotoxic test is done by observing the morphological changes and detecting the changes in the number of cells; it can directly reflect the impact of testing the material on the cells. Eventhough this method is most sensitive for testing the cytotoxicity of the medical devices, suitable medical devices for testing are limited [141]. For example, certain less dense medical devices, such as condoms, float easily in the medium, and as the cells are difficult to access, this law does not apply for testing [142]. Moreover the medical devices even with weak cytotoxicity can be tested [143].

1.12 Alternatives for regulated nitrosamine generating accelerators

There are three basic methods that a rubber compounder can use to reduce or eliminate the production of nitrosamines in a rubber formulation [124]. These are: (i) use of inhibitors, (ii) compounding with accelerators that do not produce nitrosamines and (iii) compounding with accelerators that produce non–regulated nitrosamines. The use of inhibitors has shown promising results in the food industry for reducing the levels of nitrosamine formation. Examples of inhibitors include ascorbic acid, α- tocopherol, etc. Nitrosamine inhibitors disable nitrogen oxides and prevent them from reacting with secondary amines [144, 145]. The amines or amine derivatives which do not give rise to nitrosamines or which give rise to non-carcinogenic nitrosamines are called ‘safe amines’. In this perspective, it is better to replace the unsafe rubber accelerators by the safe rubber accelerators without any appreciable change in their major activity in the rubber vulcanization. Examples of accelerators that do not produce nitrosamines include zinc dialkyl dithio phosphate, diisopropyl xanthogendisulphide and zinc isopropyl xanthate [124].

1.12.1 Compounding with accelerators that produce non–regulated nitrosamines

A non-regulated nitrosamine accelerator is an accelerator that has the potential to generate a nitrosamine that is far non-regulated. Some of the non-regulated nitrosamine accelerators include zincdibenzyl dithiocarbamate (ZBEC), TBBS, TBzTD and dithiodicaprolactam (DTDC) [146].

There are three sulfenamides that do not produce any regulated nitrosamines. These include cyclohexyl benzothiazolesulfenamide (CBS), N,N-dicyclohexyl 2-benzothiazolesulfenamide (DCBS) and TBBS [124].

Safe amines (non-carcinogenic nitrosamines) are produced by replacing chemical groups leading to the formation of carcinogenic nitrosamines like methyl, ethyl, morpholinyl, etc. with either hardly nitrosable alkyl groups like tertiary carbon or phenyl groups [147]. Alam et al. [148] synthesized three safe amine based zinc dithiocarbamates (ZDC), namely zinc (N-benzyl piperazino) dithiocarbamate (ZBPDC), zinc (N-ethyl piperazino) dithiocarbamate (ZEPDC) and zinc (N-phenyl piperazino) dithiocarbamate (ZPPDC). They reported that binary combinations of these accelerators with mercaptobenzothiazole disulfide (MBTS) work as effective accelerator systems for the vulcanization of natural rubber (NR) filled with carbon black grades (N330, N550 and N774). A comparison between the safe amine based zinc dithiocarbamates with the unsafe ZDMC in the light of mechanical and ageing resistance behavior, proved the effectiveness of non-carcinogenic rubber accelerators in the filled vulcanization of rubber. According to their view, ZBPDC-MBTS accelerator system is the suitable substitute for ZDMC-MBTS accelerated system in the filled vulcanization of natural rubber composites as far as their ageing resistance and mechanical properties are concerned [148].

Alam et al. [149,150] synthesized some safe thiuramdisulfides (TD), namely bis(N-ethylpiperazine) thiuramdisulfide (EPTD), bis(N-benzylpiperazine) thiuramdisulfide (BPTD) and bis(N-phenylpiperazine) thiuramdisulfide (PPTD) derived from safe N-substituted piperazine to introduce non-carcinogenic thiuramdisulfide for the vulcanization of natural rubber. These accelerators have achieved strong synergism in combination with mercaptobenzothiazole disulfide (MBTS) in NR gum vulcanization. The effects of the combination of safe accelerators like EPTD, BPTD and PPTD separately with MBTS on the vulcanizate properties were compared with the corresponding unsafe TMTD compounds in the light of mechanical properties in order to replace the unsafe TMTD with the newly synthesized safe thiuram disulfides [149,150].

Virdi discovered three safe accelerators namely N-nitrosodiisononylamine, N-nitrosodibenzylamine and zincdiisononyldithiocarbamate. These accelerators were proved effective and nitrosamine negative in the Ames test for mutagenicity and carcinogenicity. These chemicals are highly soluble in rubbers, thus minimizing the access of nitrosating agents to the amine and the transfer of the amine and/or nitrosamine out of the rubber into the media where human contact is more likely. An associated influence on the low availability of amine and/or nitrosamine is the low volatility of both the compounds [151].

Layer et al. found out that branched and cyclic N,N-dialkyldithiocarbamyl accelerators do not produce any undesirable N-nitrosamines in the sulphur vulcanization of rubber and also showed comparable performance as that of corresponding straight chain N,N-dialkyldithiocarbamyl accelerators. They invented accelerators namely tetraisopropyl thiuramdisulfide, tetraisobutyl thiuramdisulfide, zinchexamethylene dithiocarbamate and N,N'-bis(hexamethylene) thiuramdisulfide. The vulcanizates prepared using these accelerators exhibited good cure characteristics without generating detectable levels of nitrosamine [152].

Residual amines of high molecular weight are less soluble or less extracted in solvents and are believed to be less carcinogenic than their lower molecular weight variants.

1.13 Scope and objectives of the present work

Elastomers have historically been useful in many commercial applications due to their mechanical properties, notably their rubbery behaviour and ability to recover from mechanical deformation. Natural rubber is an important elastomer with the unique attribute of being a renewable agricultural product. In order to obtain better end use properties NR is subjected to vulcanization with varying types and amount of accelerators, sulphur and other compounding ingredients.

Many of the rubber compounding ingredients especially accelerators currently used in rubber industry are reported to be toxic and there should be some restriction to the use of these materials in rubber compounding. Most of the conventional accelerators are regulated nitrosamine generating chemicals and are carcinogenic. There are some accelerators listed under non-regulated group which are safer to use. Recently research works on safe accelerator incorporated vulcanization system has gained considerable scientific interest.

Only a limited number of published works are available on utilization of non-regulated nitrosamine generating accelerators for natural rubber compounding. The objective of the present effort is to replace the unsafe accelerators with safe accelerators without compromising the typical properties of the natural rubber vulcanizates thereby reducing the health hazards associated with rubber processing and rubber products. Since the whole research is based on accelerators, a ratio of moderately high accelerator to sulphur pertaining to the efficient vulcanization system has been chosen.

The specific objectives of the present research are:

- Comparison of the cure characteristics, mechanical properties and ageing properties of the vulcanizates prepared using nitrosamine generating accelerators viz. MBS and TMTD with that of the vulcanizates prepared using non-regulated accelerators namely TBBS and TBzTD.
- Determination of the optimum dosage of TBBS and TBzTD in NR formulations for optimum mechanical properties.
- Comparison of the cure characteristics and mechanical properties of the vulcanizates prepared by incorporating non-regulated accelerators

namely DCBS and N,N-dibenzyl-2-benzothiazolesulfenamide (DBBS) and their binary combination with TBzTD.

- Evaluation of the effect of carbon black and silica on the cure characteristics, mechanical properties, sorption properties, thermal properties and fluid resistance of nitrosamine-safe natural rubber vulcanizates containing TBBS and TBzTD.
- Use of epoxidised natural rubber as a modifier in silica-filled natural rubber and comparison of the properties of the vulcanizates with that of silane modified silica-filled natural rubber vulcanizate.
- Analysis and comparison of the effect of heat ageing on the mechanical properties of natural rubber vulcanizates prepared using antioxidants viz. N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), polymerized 1,2-dihydro-2,2,4-trimethyl quinoline (commercial TQ) and dimer-rich high pure grade TQ (HPG).
- Evaluation of cytotoxicity of the vulcanizates for detecting the toxicity of the soluble substances present in rubber vulcanizates.

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Chapter 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

Contents

This chapter deals with the details of materials used and the experimental techniques adopted. The various tests done on the vulcanizates prepared for the investigations are also described.

2.1 Materials

2.1.1 Natural rubber (NR)

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

Table 2.1 Specifications for ISNR-5 (ISO 2000: 1989 (E))

Characteristics	Limit	Test method
Dirt content, % (m/m) retained on 45 μm sieve, max.	0.05	ISO 249
Ash, % (m/m), max.	0.60	ISO 247
Initial plasticity, min.	30	ISO 2007
Plasticity retention index (PRI), min.	60	ISO 2930
Nitrogen content, % (m/m), max.	0.60	ISO 1656
Volatile matter content, % (m/m), max.	0.80	ISO 248 (Oven method at100 ± 5 °C)

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

2.1.2 Epoxidised natural rubber (ENR 25)

Epoxidised natural rubber (ENR 25) containing 25 mole percent of oxirane rings, obtained from the Rubber Research Institute of India, Kottayam has been used in the study.

2.1.3 Vulcanizing agent - Sulphur

Sulphur with the specifications shown below was supplied by Standard chemicals Co. Pvt. Ltd., Chennai.

Parameter	**Value**
Specific gravity	2.05
Acidity, max (%)	0.01
Solubility in CS_2 (%)	98

2.1.4 Accelerators

2.1.4.1 N-oxydiethylene 2-benzothiazolesulfenamide (MBS)

MBS was obtained from Merchem Ltd., Cochin, India. The specification of MBS is shown below.

Parameter		**Value**
Melting point (°C)	Initial	80
	Final	83
Density (25 °C, kg/m^3)		1400

2.1.4.2 Tertiarybutyl benzothiazolesulfenamide (TBBS)

TBBS was obtained from Merchem Ltd., Cochin, India. The specification of TBBS is as shown below.

Parameter		Value
Melting point (°C)	Initial	105
	Final	107
Density (25 °C, kg/m^3)		1300

2.1.4.3 N, N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS)

DCBS was obtained from Merchem Ltd., Cochin, India. The specification of DCBS is shown below.

Parameter		Value
Melting point (°C)	Initial	99
	Final	101
Density (25 °C, kg/m^3)		1250

2.1.4.4 N, N-dibenzyl-2-benzothiazolesulfenamide (DBBS)

DBBS was obtained from Merchem Ltd., Cochin, India. The specification of DBBS is:

Parameter		Value
Melting point (°C)	Initial	92
	Final	94
Density (25 °C, kg/m^3)		1290

2.1.4.5 Tetramethyl thiuramdisulfide (TMTD)

TMTD was obtained from Merchem Ltd., Cochin, India. The specification of TMTD is as shown below.

Parameter		Value
Melting point (°C)	Initial	144
	Final	148
Density (25 °C, kg/m^3)		1450

2.1.4.6 Tetrabenzyl thiuramdisulfide (TBzTD)

TBzTD was obtained from Merchem Ltd., Cochin, India. The specification of TBzTD is:

Parameter		Value
Melting point (°C)	Initial	126
	Final	130
Density (25 °C, kg/m^3)		1450

2.1.5 Fillers

2.1.5.1 High abrasion furnace black (HAF-black)

High abrasion furnace black (N330) used in the study was supplied by M/s Philips carbon black India Ltd., Cochin, India. The specifications of the black are:

Parameter	Value
Appearance	Black granules
DBP absorption (cc/100g)	102 ± 5
Pour density (kg/m^3)	376
Iodine adsorption number (mg/g)	82

2.1.5.2 Precipitated silica

Precipitated silica of commercial grade supplied by Minar Chemicals, Cochin. The following are the specifications.

Parameter	Value
pH (5 % aqueous solution)	6.3
Density (g/cc)	2.03
SiO_2 content (%)	90

2.1.6 Antioxidants

2.1.6.1 N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)

6PPD was obtained from Merchem Ltd., Cochin, India. The specifications of the 6PPD are:

Parameter		Value
Melting point (°C)	Initial	46
	Final	49
Density (25 °C, kg/m^3)		1090

2.1.6.2 Polymerized 1, 2-dihydro-2,2,4-trimethyl quinoline (TQ)

TQ was obtained from Merchem Ltd., Cochin, India. The specification of TQ is given below.

Parameter	Value
Softening point (°C)	83-97
Dimer content (%)	45
Bis-aniline content (%)	0.2
Density (25 °C, kg/m^3)	1100

2.1.6.3 High pure grade TQ (HPG)

HPG is polymerized 1,2-dihydro-2,2,4-trimethyl quinoline with dimer as the predominant constituent, obtained from Merchem Ltd., Cochin, India. The specification of HPG is shown below.

Parameter	Value
Softening point (°C)	83-100
Dimer + Trimer content (%)	70
Bis-aniline content (%)	0.1
Density (25 °C, kg/m^3)	1100

2.1.7 Other chemicals

2.1.7.1 Zinc oxide (ZnO)

Zinc oxide was supplied by M/s Meta Zinc Ltd., Mumbai. The specifications are:

Parameter	Value
Specific gravity	5.5
ZnO content (%)	98
Acidity (%)	0.4

2.1.7.2 Stearic acid

Stearic acid was supplied by M/s Godrej Soaps Pvt. Ltd., Mumbai. The specifications are as shown below.

Parameter	Value
Specific gravity	0.85
Melting point (°C)	50-69
Acid number	185-210

2.1.7.3 Naphthenic oil

M/s. Hindustan Petroleum Ltd., India, supplied naphthenic oil. The specifications are:

Parameter	Value
Aniline point (°C)	78
Viscosity gravity constant	0.85-0.9
Aromaticity (%)	20

2.1.7.4 Diethylene glycol (DEG)

Diethylene glycol was supplied by M/s Merck Limited, Navi Mumbai, India. The specifications are as shown below.

Parameter	Value
Boiling point (°C)	245
Flash point (°C)	140
Density (at 20 °C)	1.12
Viscosity (at 40 °C, cSt)	43

2.1.7.5 Coupling agent

The coupling agent used was Si69, a product of Degussa AG, Germany. Chemically the product is bis(triethoxysilylpropyl) tetrasulfide. The specifications of the product are shown below [3].

Parameter	Value
Sulphur content (%)	22.7
Volatiles (%)	< 4.0
Average molecular weight (g/mol)	532
Density (g/cc)	2.5
Appearance	Clear yellow liquid

2.1.7.6 Toluene

Toluene (specifications shown below) was supplied by M/s. Fine chemicals Ltd., Mumbai.

Parameter	**Value**
Boiling point (°C)	110
Appearance	Colourless liquid
Odour	Aromatic

2.1.7.7 Diesel oil

Diesel oil (specifications shown below) was of commercial grade purchased from Bharat Petroleum Company Ltd. (BPCL).

Parameter	**Value**
Boiling point (°C)	>110
Flash point (°C)	>35
Density (g/cc)	0.82 - 0.86
Viscosity (kinematic at 40 °C, cSt)	2-5

2.1.7.8 Lube oil

Lube oil (specifications shown below) was of commercial grade supplied by Castrol.

Parameter	**Value**
Boiling point (°C)	>250
Flash point (°C)	>180
Density (g/cc)	<1
Viscosity (kinematic at 40 °C, cSt)	32

2.2 Experimental techniques

2.2.1 Mixing and homogenization of the NR compounds

The natural rubber compounds were prepared on a laboratory size two-roll mixing mill as per ASTM D 3182 [4] at a friction ratio of 1:1.25.

The compounding ingredients were added as per the procedure given in ASTM D 3184 [5].

2.2.2 Cure characteristics

The rheographs of the mixes and their cure characteristics were obtained using RPA 2000 Rubber Processing Analyzer (Alpha Technologies, model - 90AJC2353) as per ASTM D 5289 [6]. The instrument used has two directly heated opposing biconical dies that are designed to achieve a constant shear gradient over the entire sample chamber. The lower die is oscillated at 50 rpm and the torque transducer on the upper die senses the force being transmitted through the rubber. To determine the cure characteristics of the rubber compound, approximately 5 g was placed in the lower die that is oscillated through a small deformation angle ± 0.2° at a frequency of 50 cycles per minute. The torque transducer on the upper die senses the forces being transmitted through the rubber.The torque is plotted as a function of time. A typical cure curve is shown in Figure 2.1.

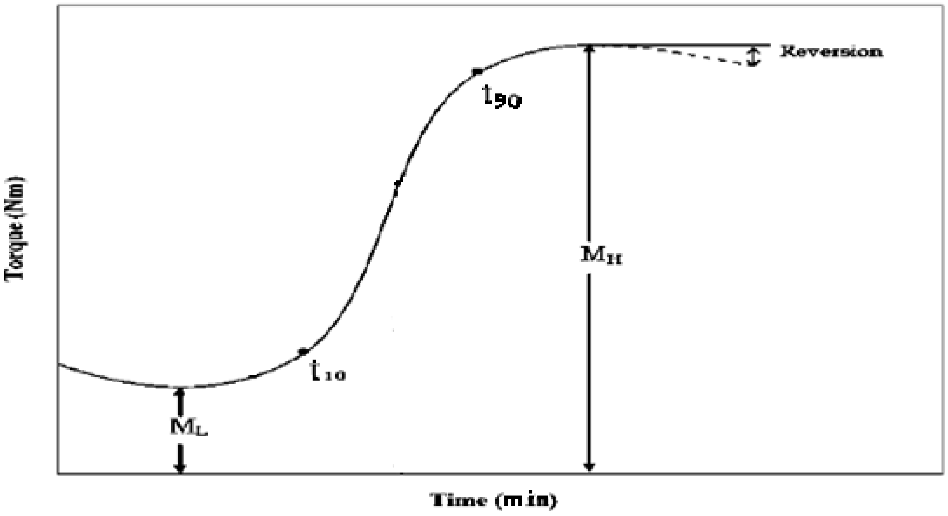


Figure 2.1 Typical cure curve obtained from RPA 2000

The following data can be taken from the cure curve.

a) Minimum torque (M_L): Measure of the stiffness of unvulcanized test specimen. It is the torque shown by the mix at the test temperature before the onset of cure.

b) Maximum torque (M_H): Measure of the stiffness or shear modulus of the fully vulcanized test specimen at the vulcanization temperature. It is the torque recorded after curing of the mix is completed.

c) Scorch time (t_{10}): It is the time taken for attaining 10 % of the maximum torque.

d) Optimum cure time (t_{90}): Time taken for attaining 90 % of the maximum torque. It is the time corresponding to a torque equal to $0.9(M_H – M_L) + M_L$.

e) Cure rate index (CRI): It is a measure of the rate of cure and is calculated using the formula,

$$\mathrm{CRI} = \frac{100}{(t_{90} - t_{10})} \quad \text{---} \quad (2.1)$$

2.2.3 Assessment of rubber-filler interactions

2.2.3.1 Strain-sweep analysis

The strain sweep measurements on the uncured and cured samples were conducted to study the rubber-filler interaction. Rubber Process Analyzer (RPA 2000 - Alpha Technologies) is a purposely modified commercial dynamic rheometer for capturing strain and torque signals, with the assistance of appropriate software [7]. Filled rubber compounds exhibit strong nonlinear viscoelastic behaviour, the well-known Payne effect, i.e., the reduction of elastic modulus with increasing strain amplitude [8]. RPA can do strain-sweep tests in which the variation of storage modulus (G'), loss modulus (G") and complex modulus (G*) with change in strain amplitude are measured. With respect to its measuring principle, the RPA cavity must be loaded with a volume excess of test material. According to ASTM D 5289, the manufacturer recommends to load samples of about 5.0 g for a standard filled rubber compound. Samples for RPA testing were consequently prepared by die cutting 46 mm diameter disks out of around 2 mm 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 0.7 to 70 % keeping the frequency at 0.5 Hz.

For strain sweep studies of the cured samples, uncured samples were taken and immediately after a cure cycle at their optimum cure time within the RPA cavity, strain sweep at 100 °C was carried out.

2.2.3.2 Bound rubber content

The bound rubber that formed in the master batches can be determined by the following procedure [9]. About 0.2 g of uncured master batch (without curatives) was put into a previously weighed metal cage made by stainless steel wire gauze of 280 mesh and immersed in 20 ml of toluene for 72 hours at room temperature. Toluene was renewed every 24 hours.

The sample was removed from toluene after 72 hours, dried at 105 °C for 24 hours and weighed. The bound rubber content was calculated according to the equation:

$$\text{Bound rubber content (\%)} = \left[\frac{(W_{fg} - W_f)}{W_p}\right] \times 100 \quad \text{----------- (2.2)}$$

where W_{fg} is the weight of filler with the bound rubber attached, W_f is the weight of filler in the specimen and W_p is the weight of polymer in the specimen.

2.2.4 Moulding

The test specimens were prepared by moulding in an electrically heated hydraulic press at a pressure of 200 kg/cm^2 and at a temperature of 150 °C for the optimum cure time. The mouldings were cooled quickly in water at the end of the curing cycle and stored for maturation in a cool dark place.

2.3 Tests on vulcanizates

2.3.1 Mechanical properties

2.3.1.1 Stress-strain properties

The tensile strength, elongation at break and modulus at various elongations were determined using dumb-bell shaped specimens punched out from the vulcanized sheet along the mill grain direction using a dumb bell die (C-type). The tensile properties of the specimens were measured according to ASTM D 412 [10] using Shimadzu Universal Testing Machine, model -AG-1 series (10 KN) at a cross head speed of 500 mm/min.

2.3.1.2 Tear strength

The tear strength test was carried out as per ASTM D 624 [11] using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The measurements were carried out on a Shimadzu Universal testing machine (10 KN) with a grip separation of 40 mm, using a crosshead speed of 500 mm/min. The tear strength was reported in N/mm.

2.3.1.3 Thermo-oxidative ageing

The thermo-oxidative ageing of the samples were done in a hot air oven at 70 °C and 100 °C for 24 hours according to ASTM D 573 [12] to determine the effect of elevated temperature and time on stress-strain properties. The aged specimens were kept at room temperature for at least 16 hours before the mechanical properties are tested. These are compared with the properties determined on unaged specimens.

2.3.1.4 Hardness

The hardness (Shore A) of the samples was determined using Mitutoyo hardmatic hardness tester according to ASTM D 2240 [13]. The measurement was done by pressing the indenter against the sample and reading the scale, which is ranging from zero (soft) to 100 (hard). The tests were performed on unstressed samples of 12 mm diameter and 6 mm thickness.

2.3.1.5 Compression set

Compression set at constant strain was measured according to Method B of ASTM D 395 [14]. Samples were compressed to constant strain (25 %) and kept for 22 hours in an air oven at 70 °C. At the end of the test period the test specimens were taken out, kept at room temperature for 30 minutes and the final thickness was measured. The compression set in percentage was calculated as:

$$\text{Compression set (\%)} = \frac{(T_0 - T_1)}{(T_0 - T_S)} \times 100 \text{ ----------------------- (2.3)}$$

where T_0 and T_1 are the initial and the final thickness of the specimen and T_S is the thickness of the spacers used.

2.3.1.6 Rebound resilience

Resilience is the energy returned by a vulcanized elastomer when it is suddenly released from a state of strain or deformation. High resilience causes bounce or snap often associated with products of natural rubber. Resilience is defined as the ratio of energy given up on recovery from deformation to the energy required to produce the deformation. Rebound resilience was determined by vertical rebound method according to ASTM D 2632 [15]. Rebound resilience is defined as the ratio of the energy of the metal plunger after impact to its energy before impact expressed as a percentage and hence, in the case where the plunger falls under gravity, is equal to the ratio of rebound height to the drop height.

$$\text{Rebound resilience}(\%) = \frac{\text{Rebound height}}{\text{Drop height}} \times 100 \text{ ------------ } (2.4)$$

2.3.1.7 Abrasion resistance

The abrasion resistance of the samples was determined using a DIN Abrader (DIN 53, 516). Samples having a diameter of 6 ± 0.2 mm and a thickness of 12 mm were kept on a rotating sample holder and a 10 N load was applied. Abrasion loss was measured as per ASTM D 5963 [16]. Initially a pre run was given for all samples and its weight was taken. The weight after final run was also noted. The difference in weight is the weight loss by its travel through 42 cm on a standard abrasive surface. The abrasion loss in cm^3/ h was calculated using the formula given below:

$$\text{Abrasion loss} = \frac{\text{Loss of weight}\times 60}{\text{Specific gravity}\times 2.2} \text{ -------------------------------- } (2.5)$$

Abrasion resistance is the reciprocal of volume loss on abrasion.

2.3.2 Swelling Studies

Vulcanizate samples weighing about 0.3 g were cut using a sharp edged disc shaped die. The samples were immersed in airtight diffusion bottles containing about 20 ml of toluene maintained at constant temperature (25 °C). Samples were removed from the bottles at periodic intervals, the surfaces were quickly dried using tissue paper, weighed and allowed to swell again until equilibrium swelling [17].

2.3.2.1 Transport properties

The mole percent solvent uptake (Q_t) of the sample was calculated from the diffusion data as [18,19]:

$$Q_t(\%) = \frac{\text{Wt.of the solvent absorbed at a given time/Molecular wt.of the solvent}}{\text{Initial wt.of the rubber specimen}} \times 100 \quad \text{------------ (2.6)}$$

At equilibrium swelling, Q_t becomes Q_α. The mechanism of diffusion was investigated using the equation [20]:

$$\log (Q_t / Q_\alpha) = \log k + n \log t \quad \text{-------------------------------- (2.7)}$$

The value of k depends on the structural features of polymer, whereas the value of n determines diffusion mechanism [21]. In the Fickian mode, case 1, the value of n is 0.5 and it occurs when the rate of diffusion of penetrant molecules is much less than the relaxation rate of the polymer chains. In case 2, i.e. non-Fickian transport, where the n value is 1, the diffusion is rapid when compared with the simultaneous relaxation. However in the case of anomalous transport where the n value is in between 0.5 and 1, both solvent diffusion and polymer relaxation rate are comparable. The effective diffusivity, D of the rubber-solvent system was calculated from the initial portion of the sorption curves using the equation [22, 23]:

$$D = \pi(\frac{h\theta}{4Q_\alpha})^2 \text{ --- } (2.8)$$

Where h is the initial thickness of rubber sample, θ the slope of the linear portion of the sorption curve Q_t versus $t^{½}$. The permeation of a solvent into a polymer membrane will also depend on the sorptivity of the penetrant in the membrane. Hence sorption coefficient (s) has been calculated using the relation [24]

$$s = \frac{W_s}{W} \text{ -- } (2.9)$$

where Ws is the weight of the solvent at equilibrium swelling and W, the initial weight of the polymer sample. Since the permeability depends on both diffusivity and sorptivity, the permeation coefficient has been determined using the relation [25]:

$$P = D \times s \text{ -- } (2.10)$$

The swollen sample was weighed, solvent removed in vacuum, and the sample was weighed again.

2.3.2.2 Crosslink density

As diffusion is influenced by polymer morphology, the molar mass between crosslinks M_c from the sorption data is also determined. The crosslink densities of the vulcanizates ($1/2M_c$) were determined using the equilibrium swelling data [26]. Degree of swelling usually is expressed as V_r. V_r is dependent on the swelling power of the solvent (high swelling power means low V_r) and the cross link density. Higher cross link density results in restraint on the network, which results in lower swelling. The volume fraction (V_r) in the swollen network was calculated by the method reported by Ellis and Welding [27] using the following equation:

$$V_r = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1}+A_0\rho_s^{-1}} \text{---}(2.11)$$

where D is the deswollen weight of the test specimen, T is the weight of the test specimen, F is the weight fraction of insoluble components, A_o is the weight of the solvent absorbed, ρ_r and ρ_s are the densities of the polymer and the solvent respectively. The crosslink density was determined using the Flory-Rehner equation [28]:

$$M_c = \frac{-(\rho_r V_s V_r^{1/3})}{[\ln(1-V_r)+V_r+\chi V_r^2]} \quad \text{---}\ (2.12)$$

where V_s is the molar volume of the solvent and the value of the interaction parameter (χ) for NR-toluene taken was 0.42 [29]. The volume fraction of rubber (V_r) is calculated assuming that the filler does not swell. It is then converted to V_{ro} (the value V_r would have in the absence of filler) according to Cunneen and Russel [30].

$$\frac{V_{r0}}{V_r} = ae^{-z} + b \text{ ---}(2.13)$$

Here a and b are constants characteristic of the system and z is the weight fraction of the filler in the vulcanizate. The values for a and b for HAF black-filled systems are; a = 0.56 and b = 0.44. The corresponding values for silica-filled [31] systems are a = l.4l and b = -0.41.

The values of V_{ro} were then substituted in the Flory-Rehner equation in place of V_r to obtain the crosslink density. Using the value M_c, crosslink density (ν) can be calculated using the equation:

$$\nu = \frac{1}{2M_c} \text{ --- } (2.14)$$

The swelling index was determined by using the equation:

$$\text{Swelling index} = \frac{(W_2 - W_1)}{W_1} \text{--} (2.15)$$

where W_1 and W_2 are the weights of the unswollen and swollen rubber, respectively. The swelling index is a direct measurement of degree of cross linking, the smaller the value, the higher the degree of crosslinking.

2.3.2.3 Gibbs free energy change and entropy change

The expansion of the rubber in the presence of a solvent will significantly modify the conformational entropy (ΔS) and elastic Gibbs free energy (ΔG). The elastic Gibbs free energy can be determined from the Flory-Huggins equation [32].

$$\Delta G = RT\,(\ln(1 - Vr) + Vr + \chi\, Vr^2) \text{ -------------------------- } (2.16)$$

From the statistical theory of rubber elasticity, ΔS can be obtained from the relation [33]:

$$\Delta G = -T\,\Delta S \text{ --} (2.17)$$

which assumes that no change in internal energy of the network occurs upon stretching.

2.3.3 Fluid resistance

The fluid resistance of the vulcanizates was carried out in diesel and lube oil according to the ASTM D 471[34]. Test specimens of circular shape (diameter 20 mm and thickness 2 ± 0.1 mm) were punched out from tensile sheets and initial weight in air was taken to the nearest 1 mg accurately. The test specimens were immersed in oil for 3 days at room temperature. After the immersion time, they were taken out and quickly dipped in acetone, blotted lightly with a filter paper and final weight of the specimens were determined to the nearest 1 mg. The percentage change in mass was calculated as follows:

$$\text{Change in mass}(\%) = \frac{(M_2 - M_1)}{M_1} \times 100 \text{ --------------------(2.18)}$$

M_1 = initial mass of specimen in air

M_2 = mass of specimen in air after immersion

2.3.4 Thermogravimetric analyses

Thermogravimetric analysis (TGA) is a technique by which the mass of the sample is monitored as a function of temperature or time, while the substance is subjected to a controlled temperature program [35]. Thermogravimetric analysis is used to investigate thermal degradation and thus the thermal stability of the samples.

Thermogravimetric analyses of the samples were carried out in a TGA Q-50 thermal analyzer (TA Instruments) under nitrogen atmosphere. The samples were heated from room temperature to 800 °C at a heating rate of 20 °C/min. The chamber (furnace) was continuously swept with nitrogen at a rate of 40-60 cm^3/min. Sample weight varied from 6-10 mg. The weight changes were noted with the help of an ultra sensitive microbalance. The data of weight loss versus temperature and time was recorded online using the TA Instrument’s Q Series Explorer software. The analysis of the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were done using TA Instrument’s Universal Analysis 2000 software version 3.3 B. Thermograms were recorded from room temperature to 800 °C. The onset of degradation temperature (T_i), the temperature at which weight loss is maximum (T_{max}), and weight loss at 500 °C, etc were evaluated.

2.3.5 Scanning electron microscopy (SEM)

SEM was used to investigate the morphology of fractured surfaces [36]. In SEM, the electron beam incident on the specimen surface causes various phenomena of which the emission of secondary electrons is used for the surface analysis. Emitted electron strikes the collector and the resulting current is amplified and used to modulate the brightness of the cathode ray tube. There is one-to-one correspondence between the number of secondary electrons collected from any particular point on the specimen surface and the brightness of the analogous point on the screen and thus an image of the surface is progressively built up on the screen.

In the present study, morphological characterisation of the fractured surfaces of the tensile test specimens was carried out using scanning electron microscope (JEOL Model JSM – 6390 LV) after sputter coating the surface with gold.

2.3.6 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out on a DMA Q 800 dynamic mechanical analyzer (TA instruments) using tension film mode. Samples for DMA measurement were cut from the vulcanized sheets. All samples were tested from 40 to 120 °C at a heating rate of 3 °C/ min at a frequency of 1 Hz. Oscillating strain was set at 0.15 % for all tests.

2.3.7 *In vitro* cytotoxic effect of the NR vulcanizates

Determination of *in vitro* cytotoxic effect of the NR vulcanizates was done in cultured L929 cells as per test procedure based on ISO 10993-5 [37]. L929 (Fibroblast cells) cell lines purchased from NCCS Pune was maintained in Dulbecco's modified eagles media (DMEM - HIMEDIA) which is a medium containing amino acids and nutrients, supplemented with 10 % Fetal Bovine Serum (FBS), which are hormones for cell growth (Invitrogen – brand name). These cells are then grown to confluency at 37 °C in 5 % CO_2 in humidified atmosphere in a CO_2 incubator (NBS, EPPENDORF, GERMANY). The cells were trypsinized (500µl of 0.025 % Trypsin in PBS/ 0.5mM EDTA solution (Himedia)) for 2 minutes and transferred to T flasks (flask for cell culture) in complete aseptic conditions. Trypsinization is the process of cell dissociation using trypsin, a protolytic enzyme which breaks down proteins, to dissociate adherent cells from the vessel in which they are being cultured. PBS is phosphate buffered saline.

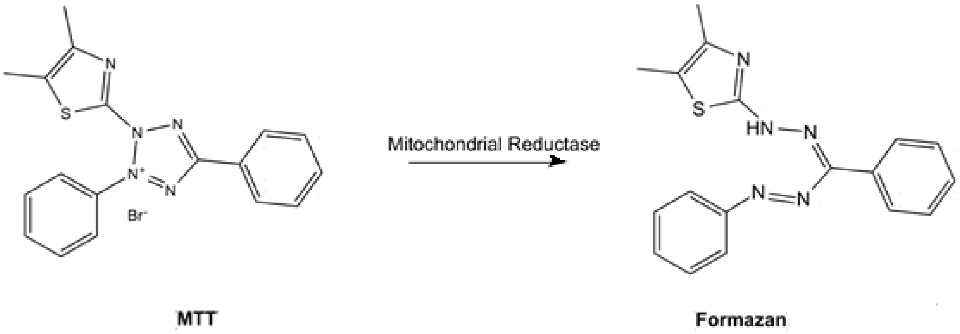
The polymer samples were sterilized in UV chamber for 1 hour. The samples were aseptically transferred to a well plate using sterile forceps. 1 ml of DMEM was added to the plate containing the samples. It was then incubated for 24 hours (one day immersion in medium). The media was removed from the polymer and this medium containing leached polymer was added to 80-90 % confluent cells (kept for 24 hrs). The phase contrast images (under magnification of 20 x) were captured using inverted microscope

(OLYMPUS CKX 41). The cytotoxicity of the polymer samples were determined using MTT assay after 24 hours of incubation.

2.3.7.1 MTT assay

MTT is a colorimetric assay [38] that measures the reduction of yellow 3-(4,5 dimethylthiazol-2-yl)-2,5-diphenyltetrazoliumbromide (MTT) by mitochondrial enzyme succinate dehydrogenase.

The cells were washed with 1x PBS and 30 µl of MTT solution was added to the culture (MTT - 5mg/ml dissolved in PBS). It was then incubated at 37 °C for 3 hours. The MTT enters the cells and passes into the mitochondria where it is reduced to an insoluble, coloured (dark purple) formazan product. MTT reaction in mitochondria of viable cell is as shown in Scheme 2.1 [39].



Scheme 2.1 Formation of formazan from MTT

MTT was removed by washing with 1x PBS and the cells are then solubilised with 200 µl of an organic solvent (dimethyl sulfoxide (DMSO-Himedia)). Incubation was done at room temperature for 30 minutes until the cell got lysed (broken) and coloured solution was obtained. This solution was transferred to centrifuge tubes and centrifuged at top speed (3500-4000 rpm) for 2 minutes to precipitate cell debris. Optical density of the solubilized formazan product was read at 540 nm using DMSO as blank in a microplate reader (ELISASCAN, ERBA).

Since reduction of MTT can only occur in metabolically active cells the level of activity is a measure of the viability of the cells. Control samples used for the MTT assay are the cells (L929 cells) to which polymer solution is not added.

$$\%\ \text{viability} = \frac{\text{Optical density of test specimen}}{\text{Optical density of control}} \times 100 \quad \text{----------}(2.19)$$

The material was graded according to a cytotoxicity scale ranging from 0-3 as per the test procedure based on ISO 10993-5 [37]. The grading was done as follows: If the confluency of healthy cells (% viability) is greater than 80 %, it is graded as '0' (non-cytotoxic); if it is between 60-80 %, the grade given is '1' (mildly cytotoxic); if it is 40-60 %, the material is graded as '2' (moderately cytotoxic) and if it is less than 40 %, a grading of '3' (severely cytotoxic) is given [40, 41].

The MTT assay procedure is as represented by the flow diagram (Figure 2.2) shown below:

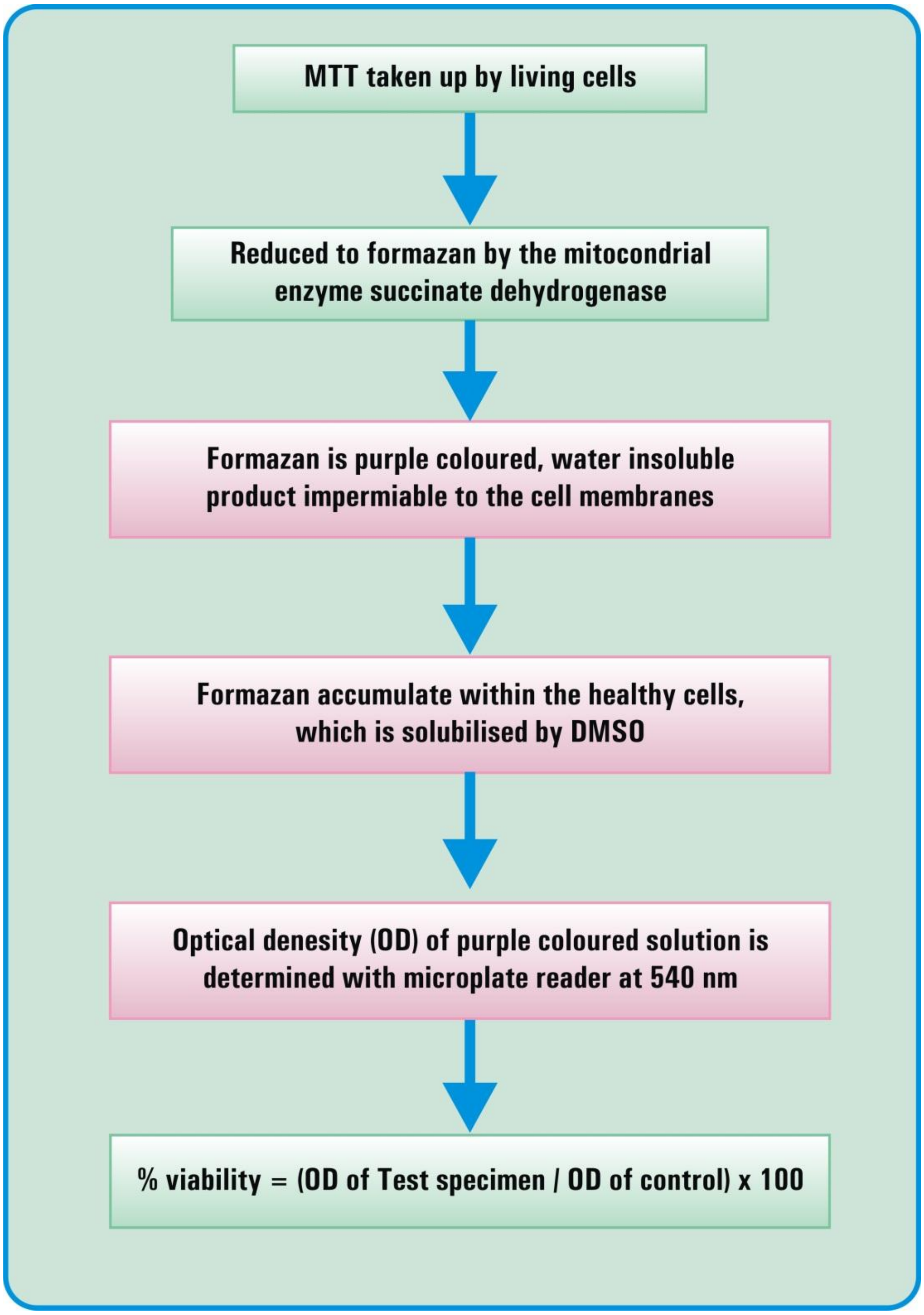


Figure 2.2 Flow diagram for MTT assay procedure

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Chapter 3

NATURAL RUBBER VULCANIZATES PREPARED USING REGULATED (MBS & TMTD)/ NON-REGULATED (TBBS & TBzTD) BINARY ACCELERATORS - A COMPARATIVE STUDY

Contents

Part of work presented in this chapter has been published in:

1) *Progress in Rubber, Plastics and Recycling Technology,* 29(2), (2013), 99-108.
2) *American Journal of Engineering Research (AJER),* 3, (2013), 8-13.
3) *Rubber Science*, 29(2), (2016), 199-206.

In the present work, natural rubber gum vulcanizate based on formulation containing regulated binary accelerator (MBS and TMTD) system was prepared as the control. Comparable NR vulcanizate was prepared by replacing MBS with non-regulated accelerator (TBBS). TMTD too was replaced with TBzTD, the safe accelerator to produce a vulcanizate with properties comparable to the control vulcanizate. Cure characteristics and cure kinetics of the mixes were studied. Studies on the valcunizates include evaluation of mechanical properties, their response to ageing at elevated temperatures, fluid resistance and thermogravimetric analysis. Cytotoxicity testing of the samples was carried out by MTT assay method.

3.1 Introduction

Natural rubber was the only high polymeric material serving humanity until a team headed by Fritz Hofmann working at the Bayer laboratory in Elberfeld, Germany, succeeded in polymerizing methyl isoprene or (2,3-dimethyl-1,3-butadiene), the first synthetic rubber [1, 2]. The vulcanized products made from NR retain high mechanical strength and elasticity. Natural rubber is cis-1,4-polyisoprene and the repeating units are arranged in a highly stereo regular manner. Due to the high structural regularity, NR crystallizes on stretching. This strain induced crystallization gives it the unique high tensile strength in gum and non-reinforcing filler containing vulcanizates [3]. Natural rubber is the preferred polymer in many industrial applications because of its superior building tack, green stock strength, high resilience, excellent dynamic properties, etc.

Sulphur is the most commonly used vulcanizing agent in NR. Vulcanization with sulphur alone is quite inefficient and requires curing time of several hours. In the sulphur vulcanization of rubber, accelerators play an important role in accelerating the chemical process taking place during the vulcanization of rubber.

Vulcanizates of high heat resistance are obtained by using a high ratio of accelerator to sulphur which are usually recommended for products which need improved reversion resistance during vulcanization and for products which are exposed to higher service temperatures. Among thiuram accelerators, tetramethyl thiuramdisulfide (TMTD) is the fastest accelerator. Thiurams act as ultra-accelerators and impart relatively high modulus, good mechanical properties and ageing properties to the vulcanizate [4].

Another class of accelerators most widely used are thiazoles and sulfenamides. The accelerators with the widest application are the thiazoles, a subcategory of which is the delayed-action sulfenamides. Compounds containing sulfenamides as accelerators could be sheared for long times without premature vulcanization. Compared to thiuram accelerators, thiazole and sulfenamide accelerators give compounds with better processing safety. Sulfenamide accelerators act slowly in the beginning of the vulcanization process and subsequently become very active. This is because sulfenamide accelerators are derivatives of mercapto benzothiazole where an amine is oxidatively bound to the mercapto sulphur and these accelerators become active only when the amines are split off during vulcanization. Such vulcanization behaviour is especially desirable in the case of multilayered and complex articles such as automobile tyres. Often a combination of accelerators is used to obtain the desired scorch resistance and cure rate [5].

The use of vulcanization systems composed of two or more accelerators find wide technological applications in recent years. There is no ideal accelerator i.e., one that is absolutely safe at processing temperatures and fast curing at vulcanizing temperatures. Use of suitable binary accelerator system has been found to approach this ideal behaviour to some extent [6-8]. For example, to increase the scorch delay of thiuram systems, usually MBT and sulfenamides are added additionally [9]. Amidino thiourea and its derivatives were found to be effective secondary accelerators to increase the accelerator activity of 2,2'-dithiobis (benzothiazole) (MBTS) and TMTD [10-13].

In order to study the effect of accelerators on properties of the vulcanizates, it is convenient to select a low sulphur (EV) vulcanization system. For low sulphur vulcanization, thiurams are normally used in combination with sulfenamides.

In this chapter, the control formulation consisted of a binary accelerator system with N-oxydiethylene 2-benzothiazolesulfenamide (MBS) and tetramethyl thiuramdisulphide (TMTD) as accelerators. These accelerators are the conventional accelerators used for the production of rubber articles. But these accelerators are listed under the category of cancer producing nitrosamine generating chemicals. The replacement of these chemicals with non-regulated accelerators is necessary for the manufacture of safe rubber products.

Tertiarybutyl benzothiazole sulfenamide (TBBS) is an accelerator grouped under the non-regulated nitrosamine generating chemicals list of Germany [14]. This accelerator can be used as a substitute for the carcinogenic MBS in rubber articles. First session of this chapter presents the effect of using varying dosages of TBBS as replacement for MBS in the control formulation.

TMTD is also listed under carcinogenic chemicals. The second part of this chapter discusses the effect of using various dosages of tetrabenzyl thiuramdisulfide (TBzTD) as a substitute for TMTD.

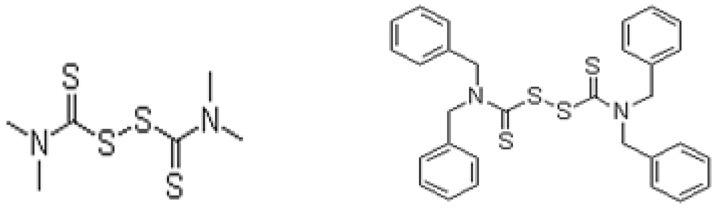

TMTD TBzTD

Figure 3.1 Chemical structures of TMTD and TBzTD

The non-carcinogenicity of TBzTD as compared to TMTD is attributed to the differences in melting point, solubility and the decomposition of the respective thiurams. TMTD and TBzTD releases dimethyl amine and dibenzyl amine as decomposition products, the latter being less volatile is better retained in rubber matrix (respective boiling points are 7 ^{o}C and 300 ^{o}C at 1 atmospheric pressure) [15]. The chemical structures of TMTD and TBzTD are shown in the Figure 3.1.

PART A

REPLACEMENT OF MBS WITH TBBS (SAFE ACCELERATOR)

3.A.1 Preparation of the mixes

Table 3.A.1 shows the composition of various mixes prepared. In all these mixes zinc oxide (5 phr), stearic acid (2 phr) and sulphur (0.3 phr) were incorporated as activator, co-activator and vulcanizing agent respectively. Different dosages of the safe accelerator (TBBS) was used with a constant loading (2 phr) of TMTD so as to find an optimum concentration of TBBS required in binary combinations.

Table 3.A.1 Formulations of the mixes

Ingredients	**C_c**	**C_{01}**	**C_{02}**	**C_{03}**	**C_{04}**
NR (g)	100	100	100	100	100
ZnO (phr)	5.0	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0	1.0
MBS (phr)	1.0	-	-	-	-
TBBS (phr)	-	1.0	1.25	1.50	1.75
TMTD (phr)	2.0	2.0	2.0	2.0	2.0
Sulphur (phr)	0.3	0.3	0.3	0.3	0.3

3.A.2 Cure characteristics

Table 3.A.2 shows the cure characteristics of the prepared natural rubber compounds and rheographs of the mixes is shown in Figure 3.A.1. The scorch time (t_{10}) is a measure of the premature vulcanization of the material. The mix containing TBBS showed scorch time comparable to the control mix and the scorch time increased with TBBS loading. Highest

scorch safety obtained in the mix containing 1.5 phr TBBS. Optimum cure time (t_{90}) of the compound containing TBBS was shorter compared to the compound containing MBS at equal dosage and then increased as the dosage of TBBS increased. Cure rate index (CRI) is a measure of the speed with which the cure reaction takes place. High CRI is observed in the case of mix containing TBBS compared to the control mix. As the dosage of TBBS increased cure rate decreased. It has been reported that as the dosage of sulfenamide increased the scorch time increased and rate of cure decreased [16, 17]. The CRI value of the mix containing a dosage of 1.5 phr TBBS is higher compared to the other mixes. This shows that the cure reaction in the case of the mix C_{03} is faster along with high scorch safety compared to the other mixes containing TBBS.

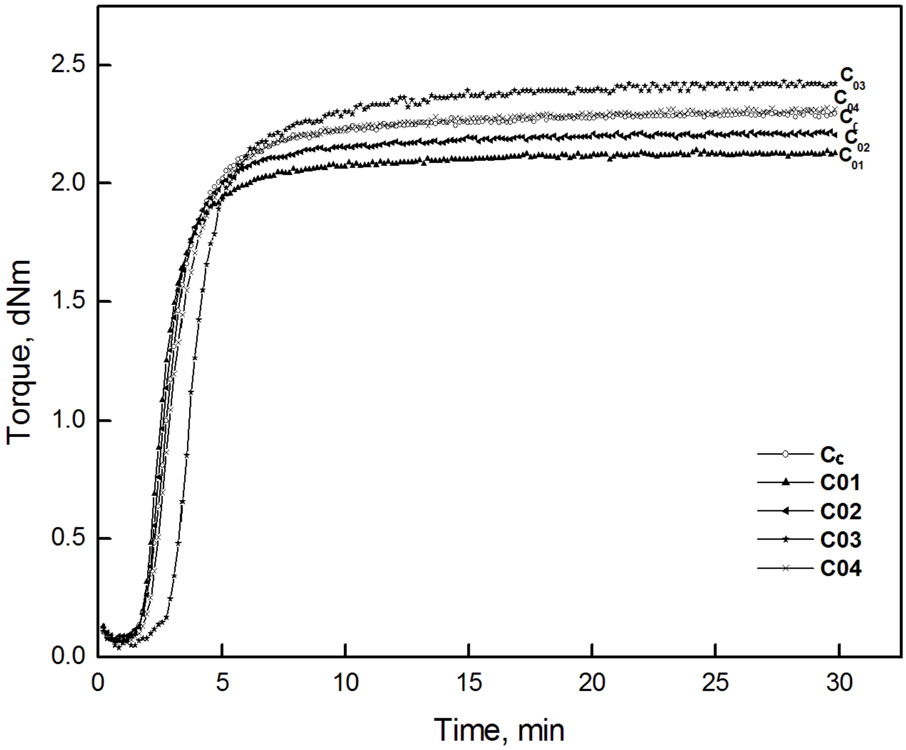


Figure 3.A.1 Rheographs of the mixes

Table 3.A.2 Optimum cure time and scorch time of mixes cured at 150 °C

Properties	**C_c**	**C_{01}**	**C_{02}**	**C_{03}**	**C_{04}**
Scorch time t_{10} (min)	2.01	2.00	2.01	2.96	2.18
Optimum cure time t_{90} (min)	6.52	6.02	6.16	6.82	6.93
Cure Rate Index (CRI, min^{-1})	22.17	24.88	24.09	25.91	21.05
Maximum torque (M_H, dNm)	2.32	2.15	2.23	2.40	2.33

The control sample showed large maximum torque compared to the mix containing TBBS at equal dosage. As the concentration of TBBS increased, the maximum torque value of the compounds also got proportionately increased thus indicating an increase in the stiffness of the vulcanizate. This may be due to an increase in cross link density [18]. However the mix C_{04} showed a slight decrease in the maximum torque value.

3.A.3 Mechanical properties of the vulcanizates

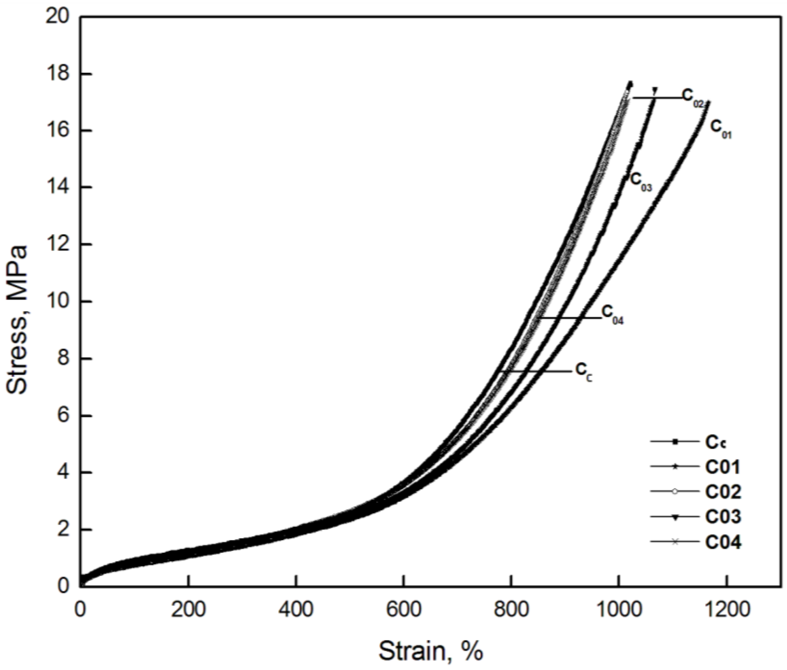


Figure 3.A.2 Stress-strain curves of the vulcanizates

The stress-strain curves of the samples are shown in Figure 3.A.2. All the curves were of typical elastomeric nature. The strain induced crystallisation of NR is apparent in all the mixes irrespective of the accelerator loading. The mechanical properties of the vulcanizates are given in Table 3.A.3. The vulcanizates containing TBBS showed similar tensile strength values as that of control vulcanizate containing MBS (C_c). However among the vulcanizates containing TBBS, C_{03} showed slightly higher tensile strength.

Table 3.A.3 Properties of the natural rubber vulcanizates

Properties	**C_c**	**C_{01}**	**C_{02}**	**C_{03}**	**C_{04}**
Tensile strength (MPa)	17.67	17.04	17.38	17.43	17.01
Modulus at 300 % elongation (MPa)	1.54	1.48	1.52	1.61	1.57
Elongation at break (%)	1021	1126	1026	1051	1026
Tear strength (N/mm)	25.80	25.10	25.15	25.37	25.44
Hardness (Shore A)	30	29	29	29	30
Rebound resilience (%)	66	64	65	65	65
Compression set (%)	15.70	14.80	14.73	14.60	15.26
Crosslink density x10^5 (mol/g rubber hydrocarbon)- from swelling studies	4.19	3.82	3.88	4.34	4.14
Crosslink density x 10^4 (mol/g rubber hydrocarbon)- from stress- strain analysis	3.69	3.19	3.49	3.53	3.51
Swelling index	4.14	4.11	4.04	4.03	4.04

The modulus values of the vulcanizates increased with increase in concentration of TBBS up to a maximum dosage of 1.5 phr (C_{03}). This is in accordance with the cross link density values. Modulus is a measure of the force required to stretch a defined specimen of rubber to a given percent elongation. This can be alternatively viewed as the resistance to a given elongating force [19]. The modulus is related to the crosslinking density of the rubber vulcanizates. These changes are directly associated with changes in the original crosslink structure, such as main chain scission and crosslink modifications [20, 21]. All the vulcanizates containing TBBS showed almost similar hardness, rebound resilience, compressions set and tear strength.

The chemical crosslink densities of the vulcanizates were calculated from swelling measurements while physically effective crosslink density was calculated from stress-strain analyses (Table 3.A.3). The swelling index of the vulcanizates gives a direct measure of the chemical crosslink density. The swelling index of the vulcanizates was found to decrease with increase in the chemical crosslink density. On the other hand, the physically effective crosslink density obtained by stress–strain analyses, could be measured using the Mooney-Rivlin equation [22] as given below:

$$\nu = \frac{F}{2A\rho RT(E - E^{-2})} \text{ --- } (3.1)$$

where ν is the physically effective crosslink density, F is the force at break, A is the area of cross-section, ρ is the density, R is the universal gas constant, T is the absolute temperature and E is the extension ratio of the sample. In this method the crosslink density is related to the extension ratio of the samples, which are subjected to tension.

The trends obtained for the crosslink density of the samples were similar irrespective of the method adopted. However, higher values of crosslink density were obtained from the stress-strain measurements, as expected. This is because the physically effective crosslink density contains contributions from the chemical crosslinks, chain entanglements and loose chain ends acting as crosslinks in rubber while chemical crosslink density obtained from swelling studies takes into account only the pure chemical crosslinks negating the contributions from chain ends and entanglements [23].

Heat resistance of the samples were measured by determining stress-strain properties before and after ageing at 70 °C and 100 °C for 24 hours (Table 3.A.4). The improvement in properties on thermal ageing at 70 °C may be due to the conversion of the small percentage of the polysulphidic crosslinks formed initially in the vulcanizate to monosulphidic and disulphidic linkages [18, 24, 25]. In the case of the vulcanizates prepared using EV system mono and disulphidic linkages are dominant. The mono and disulphidic linkages are relatively stronger and stable at high temperatures [25]. A schematic representation of crosslinks formed by efficient vulcanization system is shown in Figure 3.A.3.

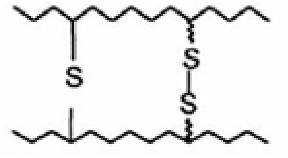


Figure 3.A.3 Efficient vulcanization system

A rubber vulcanizate during the ageing process at high temperature can undergo two different kinds of temporary or reversible changes: expansion and softening. The vulcanizate at high temperature ageing may also undergo irreversible chemical changes such as further crosslinking, cleavage of polymer chains by oxidation and loss of some ingredients by evaporation or migration too. All the compounds are cured for their optimum cure time and thus there is possibility for formation of additional crosslinks during further heating.

The vulcanizates containing MBS/TBBS with TMTD showed an increase in tensile strength with thermal ageing. Vulcanizates prepared using thiurams as accelerators generally show high modulus, good mechanical properties and good resistance to ageing [26]. This may be another reason for good ageing resistance of the vulcanizates.

Table 3.A.4 Stress-strain properties of the natural rubber vulcanizates before and after ageing at 70 °C and 100 °C

Sample	**Tensile strength (MPa)**			**Modulus at 300 % elongation (MPa)**			**Elongation at break (%)**		
	Un aged	**70 °C**	**100 °C**	**Un aged**	**70 °C**	**100 °C**	**Un aged**	**70 °C**	**100 °C**
C_c	17.67	18.96	18.94	1.54	1.79	2.10	1021	944	877
C_{01}	17.04	17.43	17.10	1.48	1.58	1.94	1126	1013	937
C_{02}	17.38	17.51	17.26	1.52	1.60	1.93	1026	1008	860
C_{03}	17.43	17.54	17.75	1.61	1.62	2.12	1051	995	863
C_{04}	17.01	17.50	17.76	1.57	1.63	2.11	1026	959	834

The variation in tensile strength, modulus at 300 % elongation and elongation at break of the control NR vulcanizate and TBBS incorporated vulcanizates after ageing at two different temperatures (70 ^{o}C and 100 ^{o}C) for 24 hours were studied and are shown graphically in Figures 3.A.4, 3.A.5 and 3.A.6.

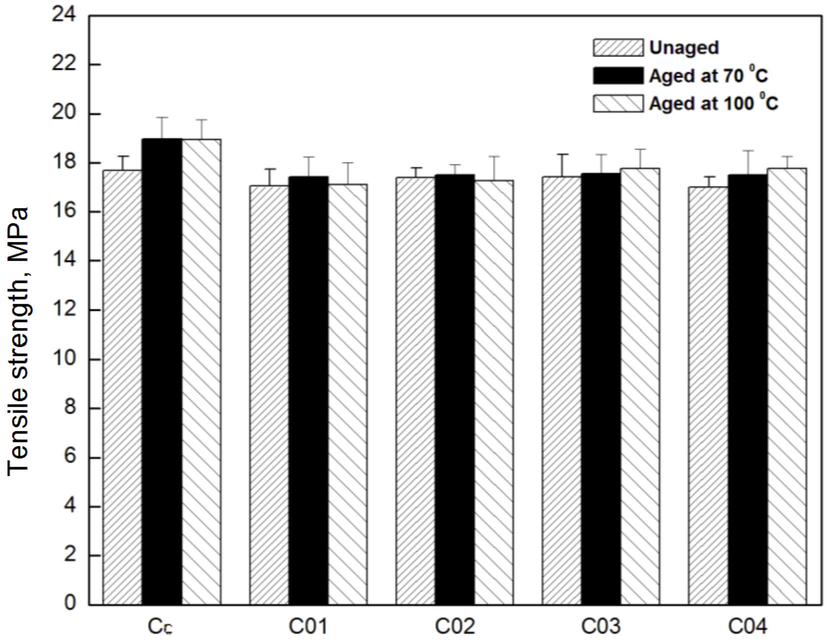


Figure 3.A.4 Variation in tensile strength of the NR vulcanizates before and after ageing

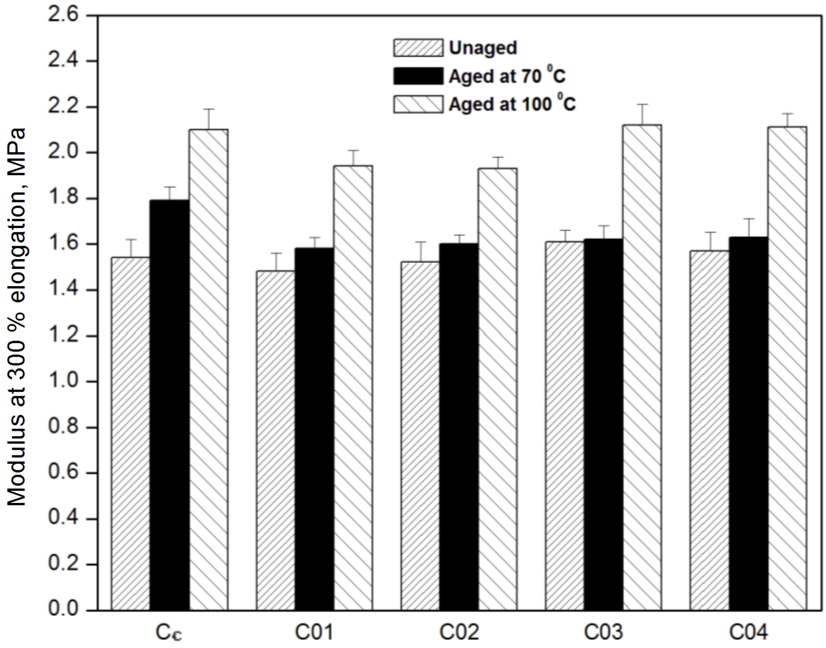


Figure 3.A.5 Variation in modulus at 300 % elongation of the NR vulcanizates before and after ageing

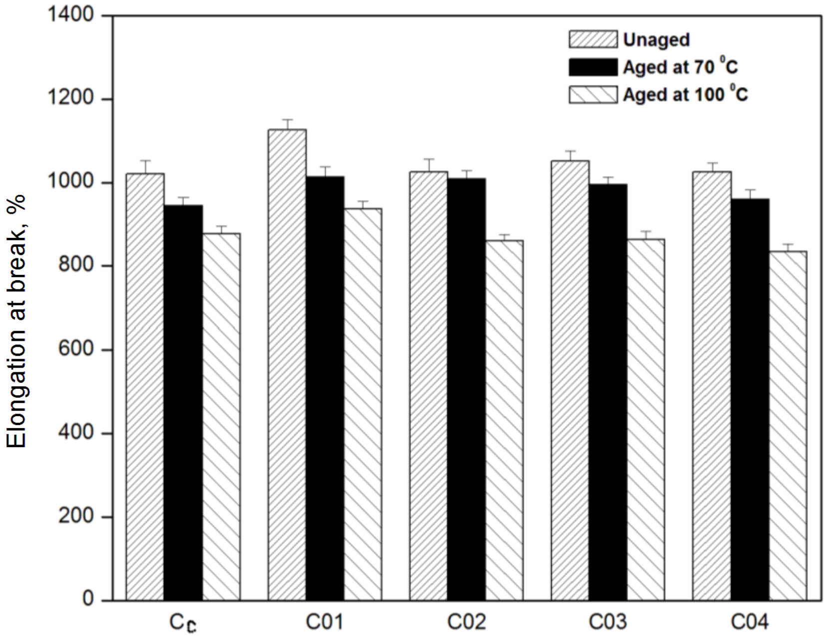


Figure 3.A.6 Variation in elongation at break of the NR vulcanizates before and after ageing

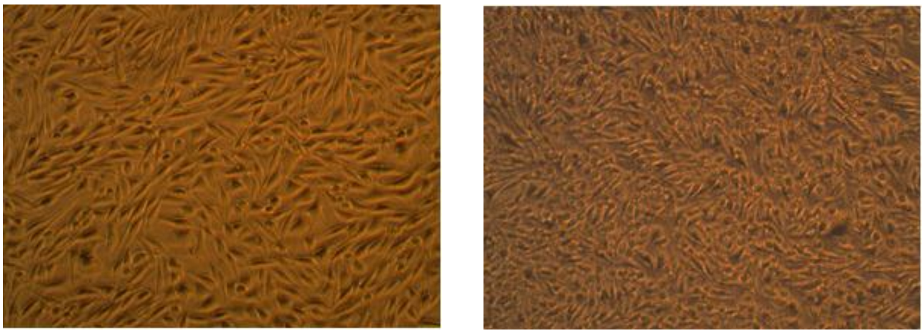
3.A.4 Cytotoxicity (MTT assay) of the vulcanizate containing MBS and TMTD

Phase contrast image for determination of cell morphology of the control of MTT assay and confluent cells containing extract of C_c is shown in Figure 3.A.7. In the control, a large number of elongated cells (fibroblast cells) are observed. In the case of the confluent cells containing the extract of vulcanizate with unsafe accelerators, a major reduction in the number of viable cells can be seen after 24 hours of incubation. The dead cells can be seen as round shape.

Measurement of cell viability forms the basis for *in vitro* MTT assay [27]. Percentage viability is calculated by:

$$\% \text{ viability} = \frac{\text{Optical density of test specimen}}{\text{Optical density of control}} \times 100 \text{ ------------ } (3.2)$$

Absorbance values (i.e. optical density) that are lower than the control cells indicate a reduction in the number of viable cells. The sample containing extract of C_c (containing MBS and TMTD) has 51.53 % of viable cells. It is evident from the MTT assay that the natural rubber vulcanizate containing MBS and TMTD is moderately cytotoxic [28-30] (nearly towards carcinogenic value) and seems to be not safe.



(a) (b)

Figure 3.A.7 Phase contrast image (magnification 20 x) for determination of cell morphology of: (a) control of MTT assay and (b) extract of C_c

PART B

REPLACEMENT OF TMTD WITH TBzTD (SAFE ACCELERATOR)

3.B.1 Preparation of the NR compounds

From the previous session, it was observed that MBS can be replaced by 50 % higher dosage of TBBS in order to get vulcanizates with comparable mechanical properties. This session discusses the efforts to replace the carcinogenic accelerator (TMTD) with the safe accelerator (TBzTD). The vulcanizate containing 1.5 phr TBBS and 2 phr TMTD was taken as the control for the present work (Formulation C). Different loadings of the safe accelerator, TBzTD was tried to find the optimum concentration required in the binary mixture in combination with 1.5 phr TBBS so as to efficiently replace 2 phr carcinogenic TMTD from the NR formulation. The formulations of the mixes are given in Table 3.B.1.

Table 3.B.1 Formulations of the mixes

Ingredients	**C**	**C_1**	**C_2**	**C_3**
NR(g)	100	100	100	100
ZnO (phr)	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0
TBBS (phr)	1.5	1.5	1.5	1.5
TMTD (phr)	2.0	-	-	-
TBzTD (phr)	-	2.0	2.2	2.4
Sulphur (phr)	0.3	0.3	0.3	0.3

3.B.2 Cure characteristics of the mixes

The rheographs of the mixes cured at 150 °C are shown in Figure 3.B.1 and the cure properties are shown in Table 3.B.2. The value of the scorch time of the compound containing 2.2 phr TBzTD (mix C_2) is almost the same as that of compound containing 2.0 phr TMTD (mix C). As the concentration of TBzTD changed from 2.0 (mix C_1) to 2.4 (mix C_3) the optimum cure time reduced. The optimum cure time of the mix C_2 is low; therefore, more crosslinks are formed in shorter time at this concentration [31].

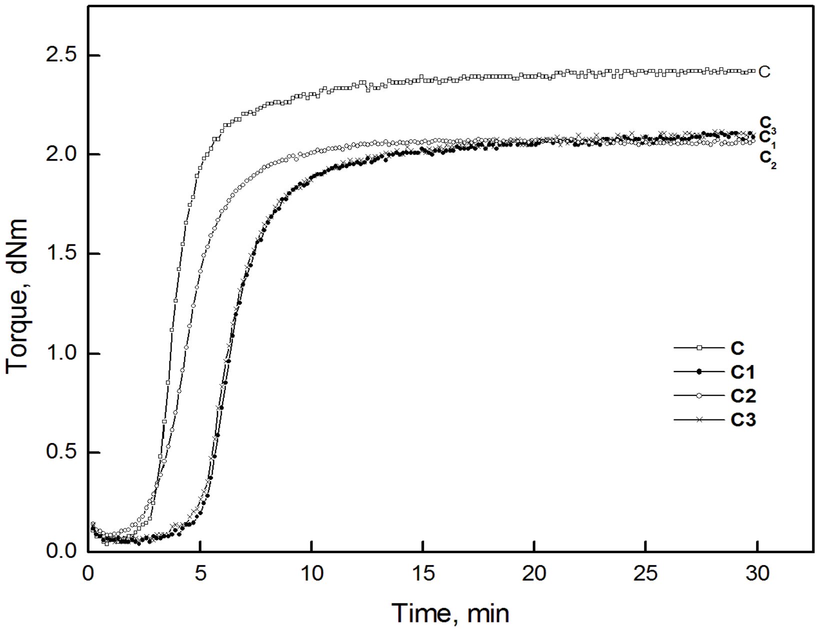


Fig 3.B.1 Rheographs of the mixes cured at 150 °C

Table 3.B.2 Optimum cure time and scorch time of mixes cured at 150 °C

Properties	**C**	**C_1**	**C_2**	**C_3**
Scorch time t_{10} (min)	2.96	5.10	2.89	4.95
Optimum cure time t_{90} (min)	6.82	10.41	7.17	9.83
Cure Rate Index (CRI, min^{-1})	25.91	18.83	23.36	20.49
Minimum torque M_L (dNm)	0.08	0.07	0.08	0.06
Maximum torque M_H (dNm)	2.43	2.09	2.11	2.10

Similarly the CRI values increased with increasing concentration of TBzTD and showed the highest value for the mix C_2. As the concentration of TBzTD increased, the maximum torque value of the compounds also increased. This indicates an increase in the stiffness of the vulcanizates and it may be caused by increase in crosslink density [18]. Marginally high maximum torque value is observed in the case of mix C_2.

3.B.2.1 Kinetics of vulcanization

The kinetics of vulcanization was studied from rheographs by the method given below [32-35]:

The general equation for the kinetics of a first order chemical reaction is:

$$\ln (a - x) = - kt + \ln a \quad \text{---} \quad (3.3)$$

where, a is the initial reactant concentration, x is the reacted quantity of reactant at time t, and k is first order rate constant.

For the vulcanization of rubber, the rate of crosslink formation is monitored by measuring the torque developed during vulcanization. The torque obtained is proportional to the modulus of rubber. Since modulus and torque are analogous, the following substitutions can be made.

$$a - x = M_H - M_t \quad \text{---} \quad (3.4)$$

$$a = M_H - M_L \text{ -- } (3.5)$$

M_H and M_L are the maximum and minimum torques (Table 3.B.2), and M_t, the torque at time t. So the equation becomes:

$$\ln (M_H - M_t) = -kt + \ln (M_H - M_L) \text{ ------------------------- } (3.6)$$

This equation is of the general form of a straight line which means that the cure reaction follows first order kinetics.

The energy of activation E_a of curing was determined using modified Arrhenius equation shown below [36]. Since $1/t_{90}$ is a measure of the cure rate, it is taken as a measure of the rate of cure reaction.

$$(t_{90})^{-1} = Ae^{-Ea/RT} \text{ --- } (3.7)$$

$$-\ln(t_{90}) = \ln A - E_a / RT \text{ -------------------------------------- } (3.8)$$

where, A is the Arrhenius constant, E_a, is the activation energy, R is the universal gas constant and T is the absolute temperature.

For the vulcanization reaction of NR, the rate of crosslink formation is usually monitored by measuring the torque developed during vulcanization. When $\ln (M_H - M_t)$ is plotted against time t, a straight line graph is obtained as shown in the Figure 3.B.2. Even though linearity is claimed for the plots theoretically, deviations from linearity were observed at certain points. The observed linearity in the plots confirm that the cure reaction of the samples follow first order kinetics. The control sample and the samples containing TBzTD, proceed according to first order kinetics.

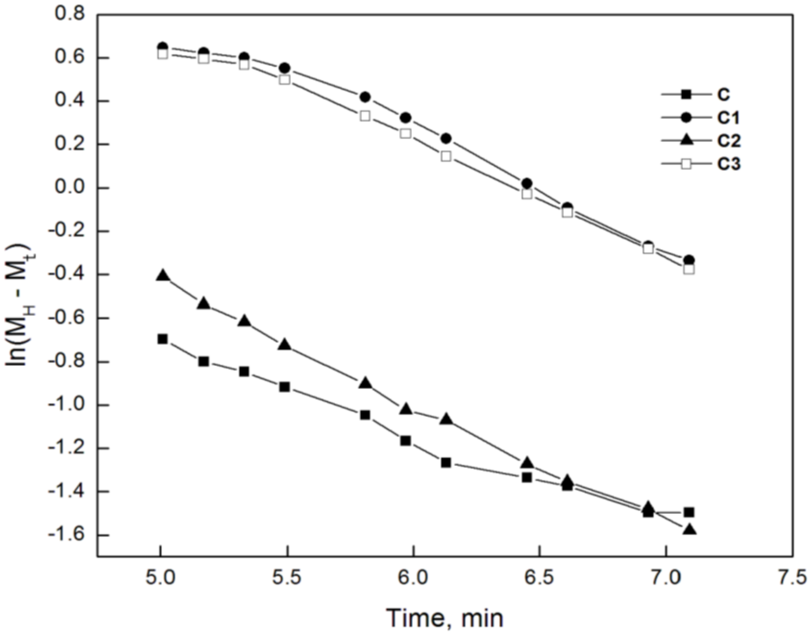


Figure 3.B.2 Plot of ln (M_H – M_t) vs. time of the control and compounds containing TBzTD

Regardless of concentration of TBzTD, the vulcanization reactions proceed according to first order kinetics. The cure reaction rate constant (k) can be obtained from the slope of the respective straight lines.

The Arrhenius equation was used to calculate the activation energy of the cure reaction of the rubber compound containing 2.2 phr of TBzTD. For this composition, optimum cure time of the compound at different temperatures (140 °C, 150 °C and 160 °C) was determined. A plot of -ln t_{90} versus 1/T gives a straight line as shown in the Figure 3.B.3. From the slope of this line, the activation energy (Ea) can be calculated. Thus activation energy obtained for the rubber compound containing 2.2 phr of TBzTD was 83.223 KJ/mol.

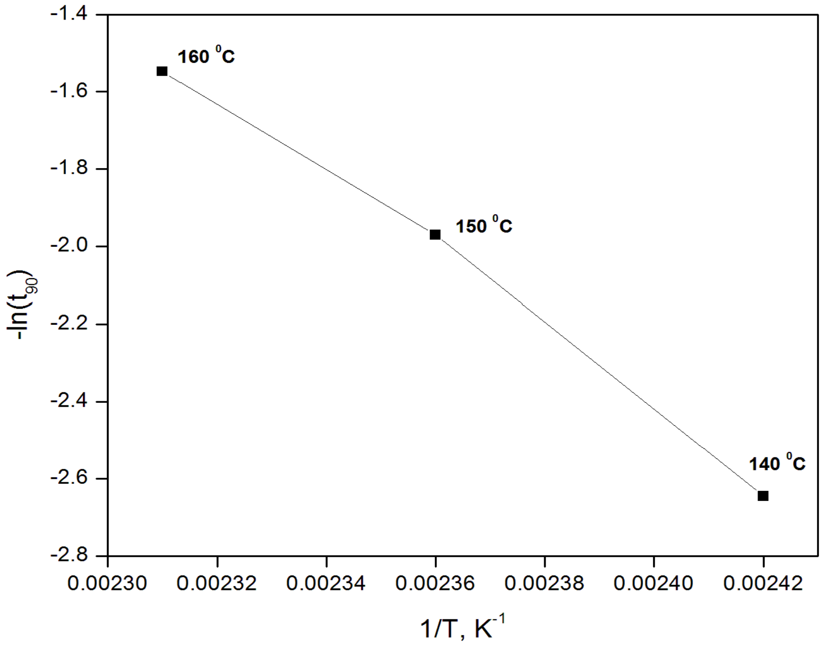


Figure 3.B.3 Arrhenius plot for the mix C_2

3.B.2.2 Reversion resistance

Rheometer torque can be used as an indicator of reversion behaviour. The cure characteristics at different temperatures (140 °C (60 min), 150 °C (45 min) and 160 °C (30 min) of the vulcanizate C_2 for prolonged time is shown in the Figure 3.B.4. From the figure, it is observed that there is no tendency for reversion in the case of the vulcanizate at curing temperatures of 140 °C and 150 °C. But a slight reversion was observed in the case of the vulcanizate at a curing temperature of 160 °C.

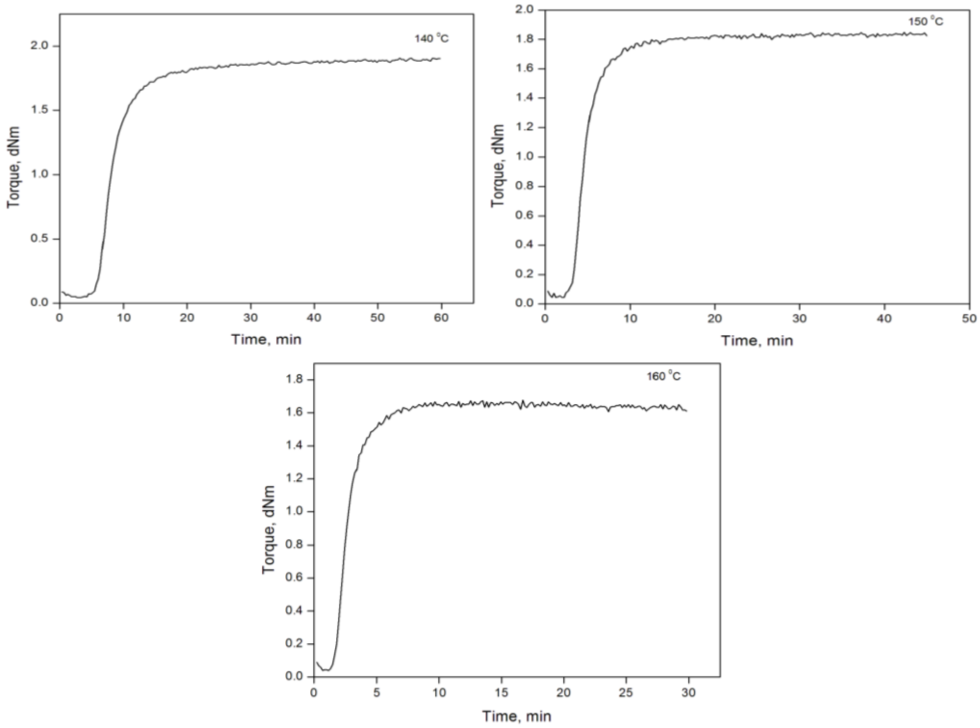


Figure 3.B.4 Cure characteristics of NR vulcanizate (C_2) at different temperatures: (a) 140 °C, (b) 150 °C and (c) 160 °C

3.B.3 Mechanical properties of the vulcanizates

The stress-strain curves of the control and TBzTD incorporated vulcanizates are shown in Figure 3.B.5. Tensile strength of the control C was found to be 17.43 MPa. The tensile strength values are in the order $C_1 < C < C_3 < C_2$ in agreement with the aim of this work, i.e. developing a non-carcinogenic nitrosamine-safe vulcanizate with properties comparable to that of the control vulcanizate. Tensile properties of the samples are tabulated in Table 3.B.3.

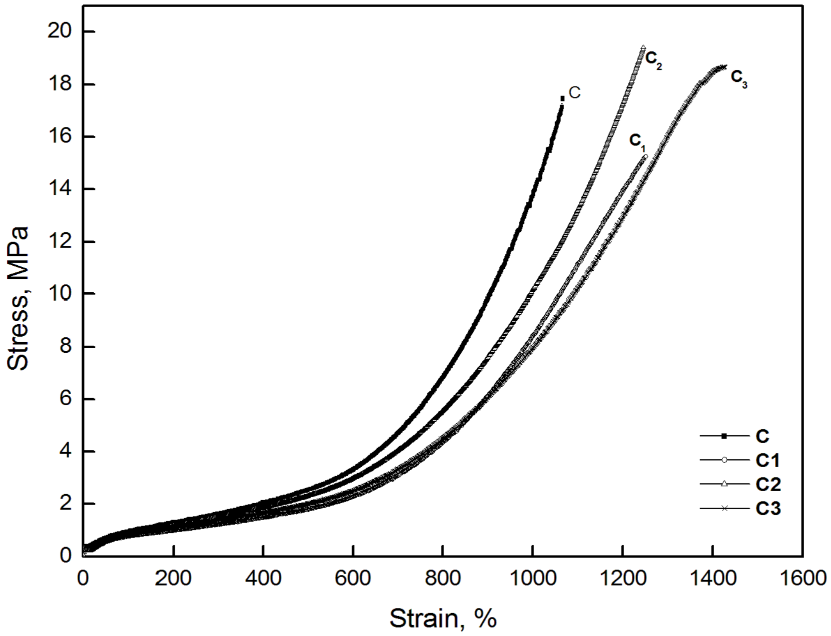


Figure 3.B.5 Stress-strain curves of the vulcanizates containing TMTD (C) and TBzTD (C_1, C_2 and C_3)

The tensile strength values are in exact correlation with the chemical crosslink density values which are explained later in this section (Table 3.B.3). It could be seen that the modulus values increases with increase in concentration of TBzTD and it shows a maximum at a dosage of 2.2 phr. This is in accordance with the crosslink density values.

Table 3.B.3 Properties of the vulcanizates

Properties	**C**	**C_1**	**C_2**	**C_3**
Tensile strength (MPa)	17.43	14.52	19.55	18.97
Modulus at 300 % elongation (MPa)	1.61	1.32	1.46	1.39
Elongation at break (%)	1061	1228	1230	1354
Tear strength (N/mm)	25.37	24.13	26.71	24.96
Hardness (Shore A)	29	28	31	31
Rebound resilience (%)	65	62	65	66
Compression set (%)	14.60	15.97	15.05	17.46
Crosslink density x10^5 (mol/g rubber hydrocarbon)	4.34	4.11	4.38	4.36

The tear strength of the samples C, C_1, C_2 and C_3 are shown in Table 3.B.3. Tear strength indicates the capacity of the vulcanizates to resist cutting, chipping and tearing actions during service. From the result it was observed that the samples C_1 and C_3 have almost the same tear strength and while the tear strength for C_2 was high.

Hardness (Shore A) of the samples C, C_1, C_2 and C_3 are shown in Table 3.B.3. Hardness is a measure of modulus of elasticity at low strain [37]. The hardness value remains practically unchanged. This indicates that the hardness is not adversely affected by the addition of the safe accelerator.

Compression set of rubber vulcanizates results from rearrangement of the network structure, degradation of polymer chains, etc. It is dependent on the type of the polymer and nature of crosslinks [38-40]. Measurement of set under compression provides a practical evaluation of either the creep or the stress relaxation of rubber. A high state of cure is found to reduce set. Compression set values of the vulcanizates is shown in Table 3.B.3. The compression set value of the vulcanizates prepared from the compounds containing TBzTD is slightly higher than that of the control vulcanizate containing TMTD. Compression set is defined as the residual deformation of a material after removal of an applied compressive stress. Low set values mean that the material has recovered nearly to its original height, and there is very little residual deformation. The vulcanizate containing 2.2 phr TBzTD shows lowest value of compression set among the safe vulcanizates studied.

Rebound resilience of the samples C, C_1, C_2 and C_3 are shown in Table 3.B.3. The values are in the order $C_3 > C > C_1$ with marginal difference. The Control sample C and the sample C_2 shows similar rebound resilience values.

The crosslink densities of the vulcanizates calculated from the equilibrium swelling measurements in toluene are shown in Table 3.B.3. The crosslink densities are in the order $C_1 < C < C_3 < C_2$. Crosslink density is an important parameter, which can be related to the physical properties of rubber vulcanizate [41]. The results of the work cited above show that the mechanical properties of the samples such as tensile strength, tear strength, modulus at 300 % elongation and hardness are in accordance with the crosslink density.

The stress-strain properties of the vulcanizates after ageing for 24 hours at 70 °C and 100 °C are shown in Table 3.B.4 and Figures 3.B.6, 3.B.7 and 3.B.8. In all the cases the stress-strain properties improved marginally after ageing at 70 °C. After ageing at 100 °C, the vulcanizates C, C_1 and C_3 show marginal improvement in the properties. The vulcanizates showed comparable properties before and after ageing due to the stability of the mono and di sulphidic linkages. This observation is due to the higher bond energy of mono or di sulphidic linkages [42, 43]. The improvement in properties on thermal ageing at 70 ^{o}C may be due to crosslink maturation reactions, which result in the conversion of small percentage of the polysulphidic crosslinks formed initially in the vulcanizate to monosulphidic and disulphidic linkages [18, 24, 25].

It has been also noticed by earlier workers that thiuram disulfide in presence of zinc oxide forms zinc dithiocarbamates, which act as accelerators as well as antidegradants [44-46]. Good ageing resistance exhibited by all the combinations may be due to the formation of zinc ditiocarbamates. There is increase in modulus of the vulcanizates during ageing, it may assumed that prolonged heating at 70 °C is apt to cause post-vulcanization thereby generating more crosslinks that are also responsible for the increase in tensile strength values during ageing of rubber vulcanizates. With the rise in the number of crosslinks the molecular weight between crosslinks decreases and the network becomes rigid and thus may restrict the elongation at break and actually this was observed for all the vulcanizates subjected to hot air ageing.

Table 3.B.4 Stress-strain properties of the rubber vulcanizates before and after ageing

Sample	Tensile strength (MPa)			Modulus at 300 % elongation (MPa)			Elongation at break (%)		
	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C
C	17.43	17.54	17.75	1.61	1.62	2.12	1061	995	863
C_1	14.52	14.95	14.80	1.32	1.44	1.73	1228	1084	967
C_2	19.55	20.64	19.19	1.46	1.62	2.04	1230	1200	906
C_3	18.97	19.08	19.46	1.39	1.55	1.95	1354	1069	1016

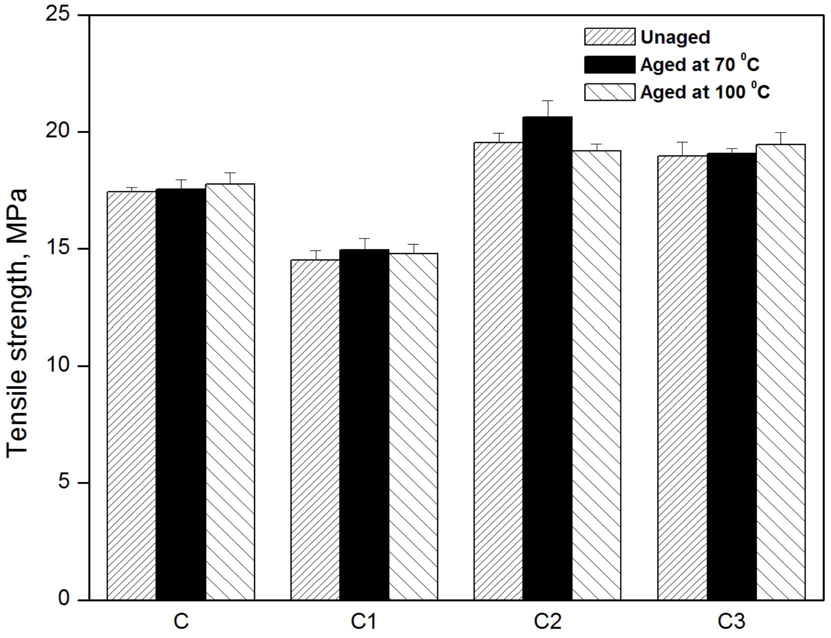


Figure 3.B.6 Variation in tensile strength of the NR vulcanizates before and after ageing

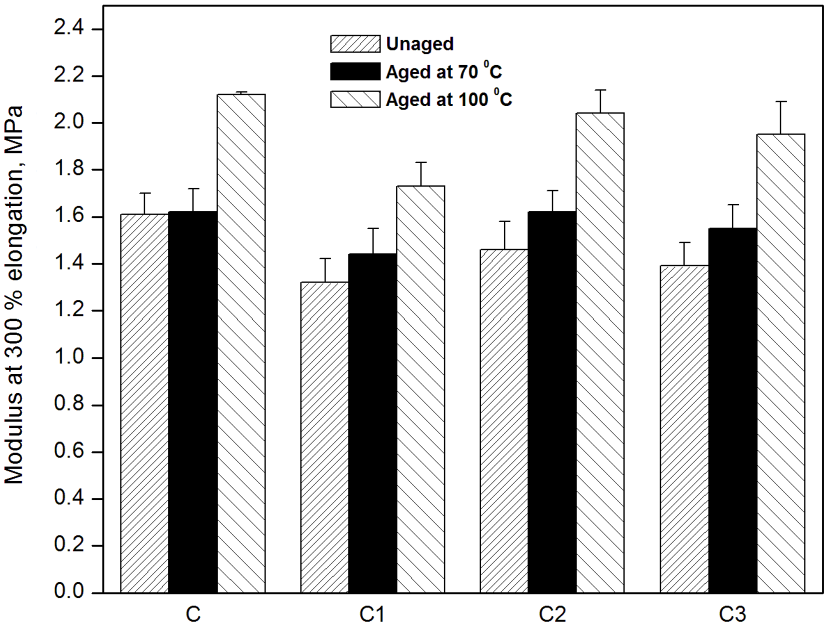


Figure 3.B.7 Variation in modulus at 300 % elongation of the NR vulcanizates before and after ageing

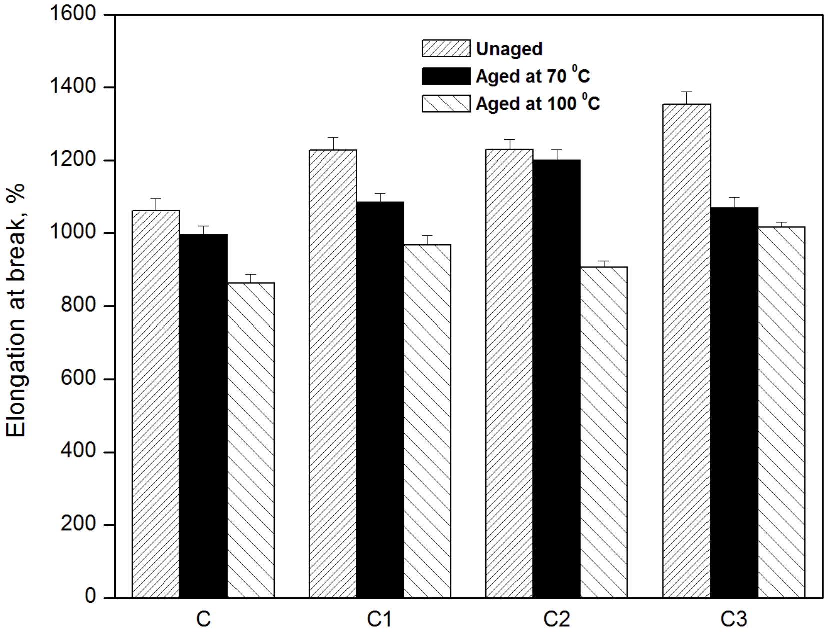


Figure 3.B.8 Variation in elongation at break of the NR vulcanizates before and after ageing

These results prove that TBBS and TBzTD could be used as safe accelerators instead of MBS and TMTD in an efficient vulcanization system for natural rubber without sacrificing the mechanical properties of the vulcanizates. This work establishes that in natural rubber vulcanizates it is possible to develop equivalent and even superior crosslink densities and mechanical properties by replacing MBS and TMTD, which are reported to be carcinogenic, with 50 % higher dosage of TBBS and marginally higher dosage of TBzTD which are non-regulated and safe. Since the molecular weight of TBzTD (544) is high relative to the most common thiuram based accelerator, TMTD (240), higher dosages are needed to achieve the same level of active functional groups to react with the available sulphur for the vulcanization [47].

3.B.4 Fluid resistance

Fluid resistance is a general term describing the extent to which a rubber product retains its original physical characteristics and ability to function when it is exposed to oil, chemicals, water, organic fluids or any liquid which it is likely to encounter in actual service.

The fluid resistance of the vulcanizates containing regulated nitrosamine accelerators (C_c) and non-regulated accelerators (C_2) were determined (Table 3.B.5). Natural rubber does not perform well when exposed to oils and hydrocarbon solvents, as a result of its non-polar character [48]. Nevertheless fluid resistance of the vulcanizate containing the safe accelerators is found to be more than the vulcanizate containing the unsafe accelerators.

Table 3.B.5 Change in mass (%) after soak in diesel and lube oil

Sample	Change in mass (%)	
	Diesel	Lube oil
C_c	233	104
C_2	225	98

It is also observed that the change in mass (%) of the vulcanizates is much lower in lube oil than in the diesel oil. This may be due to the low penetration of the highly viscous lube oil between the rubber chains [49].

3.B.5 Thermogravimetric analysis

The thermal degradation patterns of the NR vulcanizates with safe/unsafe accelerators were determined by the thermogravimetric analyses. The TGA/DTG curves of the natural rubber vulcanizate containing unsafe accelerators (C_c) and that containing safe accelerators (C_2) are shown in Figures 3.B.9 and 3.B.10. The temperature of onset of degradation (T_i), the temperature at which the rate of decomposition is maximum (T_{max}), the decomposition temperature at 50 % weight loss (T_{50}) and weight loss (%) at 500 °C of C_c and C_2 are tabulated in Table 3.B.6.

Table 3.B.6 Thermogram data of control (Cc) and safe natural rubber vulcanizate (C_2)

Sample	T_i (^oC)	T_{50} (^oC)	T_{max} (^oC)	Weight loss (%) at 500 ^oC
C_c	341	392	392	94.5
C_2	341	392	393	94.3

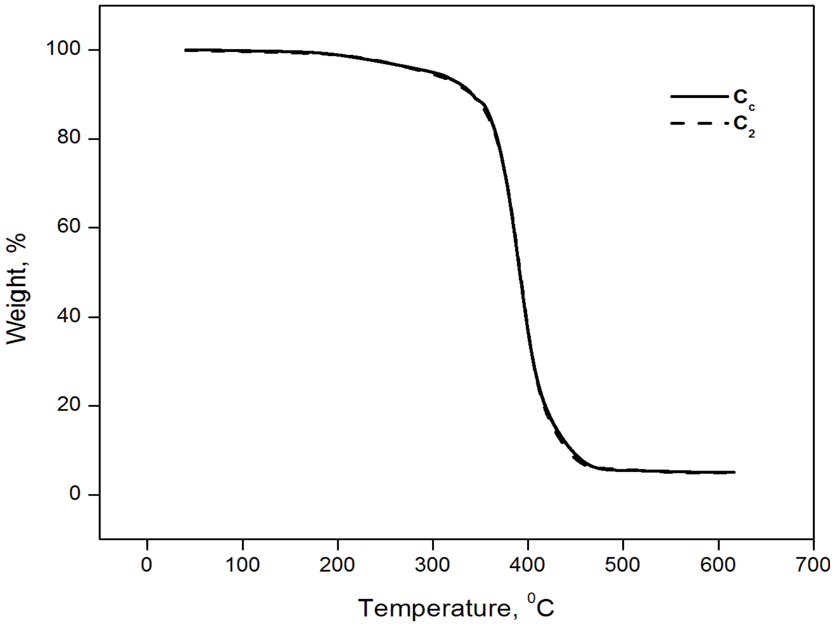


Figure 3.B.9 The thermograms of NR vulcanizates (C_c and C_2)

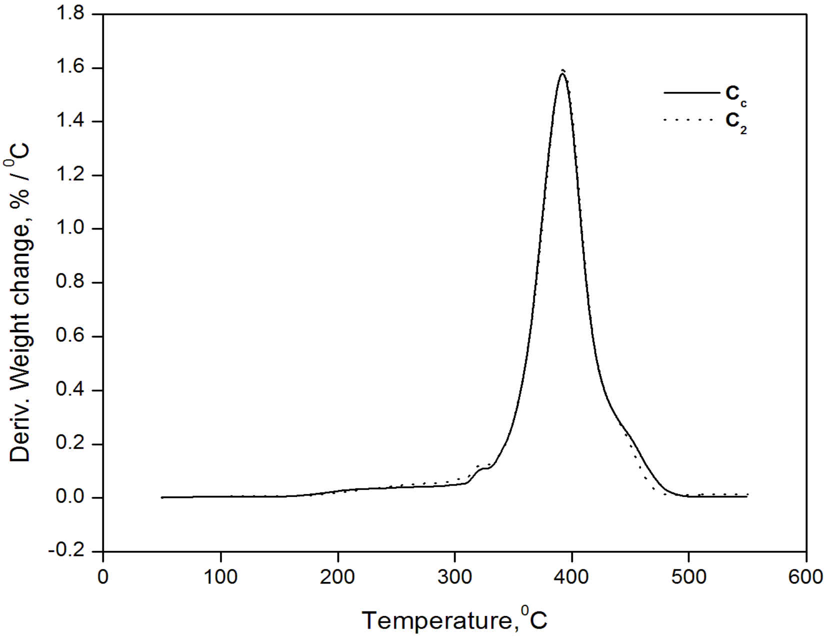


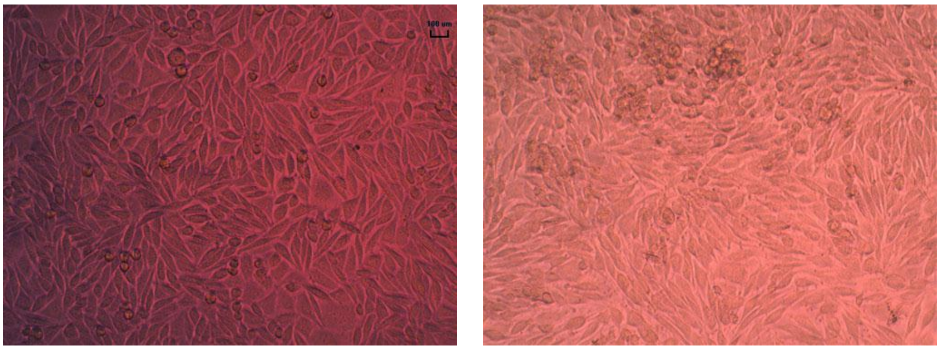
Figure 3.B.10 DTG curves of NR vulcanizates (Cc and C_2)

The thermal stability of the vulcanizate was not adversely affected by replacing MBS and TMTD with safe accelerators TBBS and TBzTD. T_i and T_{max} of both the vulcanizates were almost similar.

3.B.6 Cytotoxicity of the vulcanizate containing non-regulated accelerators

Phase contrast image for determination of cell morphology of control of MTT assay and confluent cells containing extract of C_2 is as shown in Figure 3.B.11. In control, a large number of elongated cells (fibroblast cell) are observed. In the case of the confluent cells with the extract of vulcanizate containing safe accelerators after 24 hours incubation, a small reduction in the number of viable cells can be seen.

Absorbance values (i.e. optical density) that are lower than the control cells indicate a reduction in the number of viable cells. The sample containing extract of C_2 (containing TBBS and TBzTD) has 84.50 % of viable cells. It is evident from the MTT assay that the natural rubber vulcanizate containing TBBS and TBzTD is safe to use and seems to be non-cytotoxic [29, 30].



(a) (b)

Figure 3.B.11 Phase contrast image (magnification 20 x) for determination of cell morphology of: (a) control of MTT assay and (b) extract of C_2

3.2 Summary

The natural rubber compound prepared in an efficient vulcanization system containing TBBS and TMTD showed comparable scorch time and shorter optimum cure time at equal dosages of MBS and TMTD. The optimum cure time increased as the dosage of TBBS increased. The vulcanizate containing TBBS and TMTD showed marginally inferior mechanical properties and crosslink density than the vulcanizate containing equal dosages of MBS and TMTD. However the vulcanizate containing 50 % higher dosage of TBBS provided comparable tensile properties as that of MBS. The use of TBzTD instead of TMTD in natural rubber compound at equal dosage results in better scorch safety. The vulcanization reactions proceeded according to first order kinetics. Vulcanizate with dosage of TBzTD equivalent to TMTD dosage in the control vulcanizate displayed marginally inferior mechanical properties and crosslink density. However the vulcanizate containing 10 % higher dosage of TBzTD showed mechanical properties, ageing resistance and crosslink density comparable to that of the control vulcanizate prepared using TMTD. The vulcanizate containing safe accelerators showed lower percentage increase in mass after soaking in oil compared to the vulcanizate containing unsafe accelerators. Replacement of MBS and TMTD with safe accelerators TBBS and TBzTD has not adversely affected the thermal stability of the vulcanizate. MTT assay and mechanical property results indicate that TBBS and TBzTD are safe (non-carcinogenic) substitutes for MBS and TMTD in natural rubber based formulations.

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Chapter 4

NON-REGULATED ACCELERATOR (DCBS / DBBS) INCORPORATED NATURAL RUBBER VULCANIZATES

Contents

Natural rubber vulcanizates incorporating safe sulfenamide single accelerator (N,N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) or N,N-dibenzyl-2-benzothiazolesulfenamide (DBBS)) and binary accelerators (DCBS or DBBS in combination with tetrabenzyl thiuramdisulfide (TBzTD)) were prepared as per efficient vulcanization recipe. The cure characteristics and cure kinetics of the prepared compounds were studied. Mechanical properties, fluid resistance in oil and cytotoxicity of the vulcanizates were also evaluated.

4.1 Introduction

Generally, sulfenamide type of accelerators exhibit long scorch safety. The superior scorch safety of the sulfenamides is due to the longer time required to thermally decompose to mercaptobenzothiazole (MBT) and amine [1]. N, N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) and N, N-dibenzyl-2-benzothiazole sulfenamide (DBBS) are two accelerators that are coming under this category.

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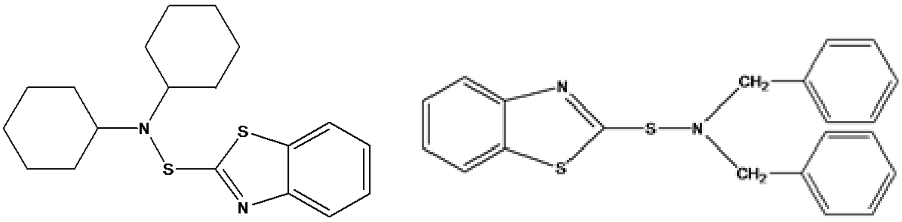
Druckrey and co-workers [2, 3] have showed that DCBS is a safe non-carcinogenic accelerator based on their animal experiments. DBBS is also believed as a safe accelerator since it is an accelerator based on sterically hindered amines [4, 5]. These accelerators are not included in the list of regulated nitrosamine generating accelerators. Chemical structures of DCBS and DBBS are shown in Figure 4.1.



DCBS DBBS

Figure 4.1 Structures of DCBS and DBBS

In compounding of rubbers binary cure systems are generally used for faster cure rate and better reversion resistance [6]. Binary accelerator systems enhance the efficiency of sulphur intake during crosslinking, which in turn improves the mechanical, chemical and service properties of finished rubber goods [7].

The natural rubber formulations based on safe single accelerator (either DCBS or DBBS) and their combination with the non-regulated TBzTD have been used for the work presented in this chapter.

4.2 Preparation of the mixes containing various dosages of DCBS / DBBS

Table 4.1 shows the composition of the various mixes prepared. Minimum dosage of the single accelerator required in the EV system in the case of DCBS and DBBS were used in the formulations D_1 and D_6 and the corresponding maximum dosage of the accelerators were used in the formulations D_2 and D_7. The binary combinations of these accelerators with a fixed dosage of TBzTD (2.2 phr) were used in formulations D_3, D_4, D_5, D_8, D_9 and D_{10}.

Table 4.1 Formulations of the mixes containing various dosages of DCBS / DBBS

Ingredients	**D_1**	**D_2**	**D_3**	**D_4**	**D_5**	**D_6**	**D_7**	**D_8**	**D_9**	**D_{10}**
NR (g)	100	100	100	100	100	100	100	100	100	100
ZnO (phr)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DCBS (phr)	3.0	6.0	1.0	1.5	2.0	-	-	-	-	-
DBBS (phr)	-	-	-	-	-	3.0	6.0	1.0	1.5	2.0
TBzTD (phr)	-	-	2.2	2.2	2.2	-	-	2.2	2.2	2.2
Sulphur (phr)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

4.3 Cure characteristics

The cure characteristics of the mixes containing DCBS or DBBS as single accelerator are shown in the Table 4.2. From the cure characteristics, it is observed that the optimum cure time required for the single accelerator systems are very high and they are not suitable for practical applications.

Table 4.2 Optimum cure time and scorch time of mixes containing single accelerator at 150 °C

Properties	**D_1**	**D_2**	**D_6**	**D_7**
Scorch time t_{10} (min)	9.93	11.57	12.95	21.07
Optimum cure time t_{90} (min)	52.37	85.74	40.82	57.53
Cure Rate Index (CRI, min^{-1})	2.36	1.35	3.59	2.74

When DCBS and DBBS were used in single accelerator system, long scorch time was observed. As the dosage of DCBS or DBBS was increased, the optimum cure time increased with a proportional decrement in the cure rate index. It has been reported that the compounds prepared using DCBS showed high scorch safety and low cure rate index as the dosage increased [8, 9]. DBBS incorporated NR vulcanizates also showed a similar trend.

On the contrary, the binary accelerator systems showed better cure characteristics (Table 4.3). When TBzTD was added as the binary accelerator, scorch time decreased considerably indicating faster cure initiation. The cure rate index (CRI), which is a measure of the rate of the vulcanization process, increased significantly with the addition of TBzTD.

The rheographs of the binary systems containing DCBS or DBBS in combination with TBzTD are shown in Figure 4.2. Addition of the TBzTD reduced the scorch and optimum cure time. However in both the cases, as the dosage of sulfenamide increased the scorch time increased and rate of cure decreased [8, 9]. The vulcanizates containing DBBS showed better scorch safety and cure rate index compared to the vulcanizates containing DCBS.

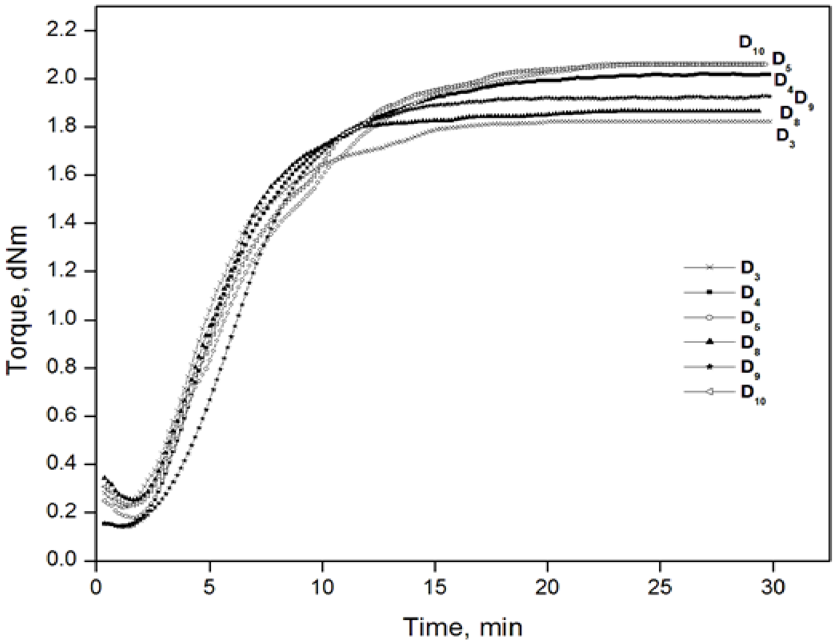


Figure 4.2 Rheographs of the mixes containing binary accelerators (DCBS/DBBS and TBzTD)

Table 4.3 Cure characteristics of the mixes at 150 °C

Properties	**D_3**	**D_4**	**D_5**	**D_8**	**D_9**	**D_{10}**
Scorch time t_{10} (min)	2.77	2.98	3.07	2.90	3.36	3.74
Optimum cure time t_{90} (min)	10.97	12.32	13.47	9.65	10.83	12.99
Cure Rate Index (CRI, min^{-1})	12.19	10.71	9.62	14.80	13.39	10.81
Maximum torque (M_H, dNm)	1.82	2.02	2.06	1.87	1.93	2.06
Minimum torque (M_L, dNm)	0.21	0.14	0.17	0.25	0.15	0.23
$M_H - M_L$ (dNm)	1.61	1.88	1.89	1.62	1.79	1.83

ΔM (i.e. $M_H - M_L$) is considered as the parameter to demonstrate the degree of chemical crosslinking. ΔM is an indication of the chemical interaction between rubber and vulcanizing agent. It shows a marginal increase as the dosage of DCBS and DBBS increases (Table 4.3).

4.3.1 Kinetics of vulcanization

The kinetics of vulcanization was done by the method reported earlier (section 3.B.2.1). For the vulcanization reaction of NR, the rate of crosslink formation is usually monitored by measuring the torque developed during vulcanization. When ln ($M_H - M_t$) is plotted against time t, a straight line graph is obtained as shown in the Figure 4.3. Even though linearity is claimed for the plots theoretically, minor deviations from linearity are experimentally observed for certain points. The observed linearity in the plots confirm that the cure reaction of the samples follow first order kinetics. Regardless of concentration of DCBS and DBBS, all vulcanization reactions proceeded according to first order kinetics.

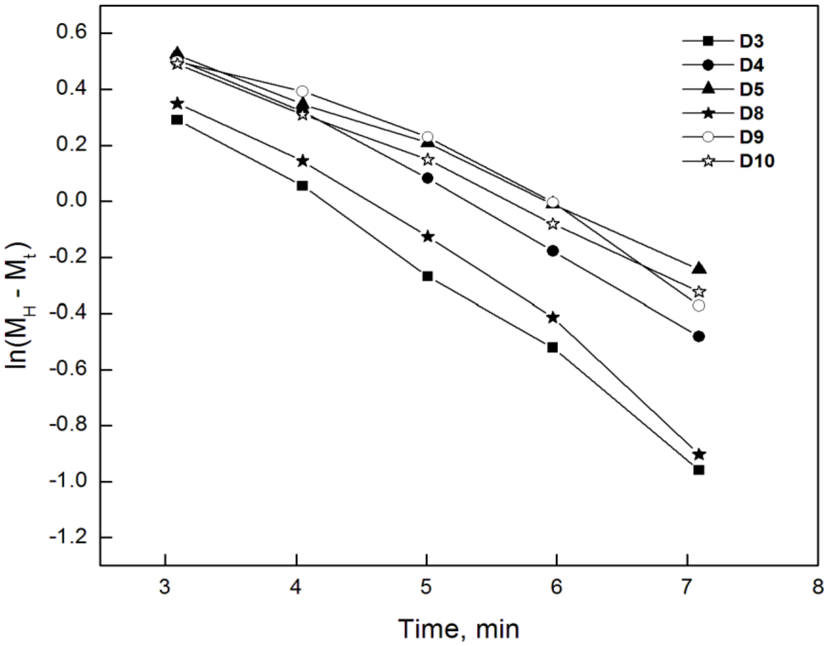


Figure 4.3 Plot of ln(M_H – M_t) vs. time of NR compounds containing binary accelerators (DCBS/DBBS and TBzTD)

4.4 Mechanical properties of the vulcanizates

4.4.1 Mechanical properties of the NR vulcanizates containing DCBS

The mechanical properties of the vulcanizates containing DCBS are given in Table 4.4. The stress-strain curves of the vulcanizates containing DCBS are given in Figure 4.4. The tensile strength values are higher for the binary accelerator based vulcanizates as compared to the single accelerator based vulcanizates. As the concentration of DCBS increased, the modulus values were found to increase for both the single and binary accelerator systems. As compared to the vulcanizates prepared using single accelerator, the vulcanizate prepared by incorporating the binary accelerators showed higher moduli.

Tensile strength and the tear strength of the vulcanizates increased with DCBS loading for both single and binary accelerator systems. Of all the combinations, comparatively high tensile strength was observed for the vulcanizate containing 1.5 phr of DCBS and 2.2 phr of TBzTD. This could be correlated with the observed crosslink density of the vulcanizates.

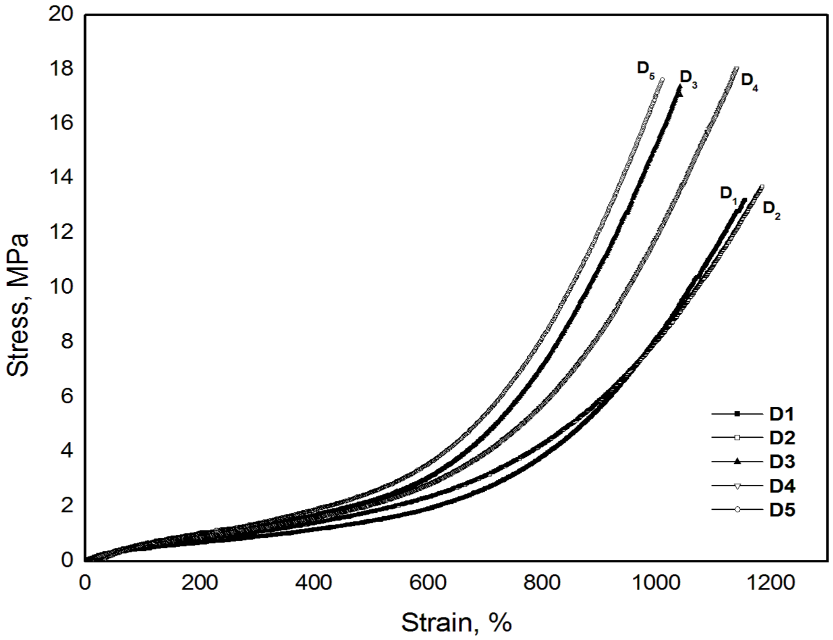


Figure 4.4 Stress-strain curves of NR vulcanizates containing DCBS

The hardness of the single accelerator based vulcanizates increased as the dosage of DCBS increased from 3 phr to 6 phr and the vulcanizates based on the binary accelerators showed more hardness.

Table 4.4 Properties of natural rubber vulcanizates containing DCBS

Properties	**D_1**	**D_2**	**D_3**	**D_4**	**D_5**
Tensile strength (MPa)	13.22	13.40	17.38	18.05	17.63
Modulus at 300 % elongation (MPa)	0.89	1.06	1.12	1.16	1.19
Elongation at break (%)	1156	1186	1043	1140	1012
Tear strength (N/mm)	20.37	22.96	26.34	26.86	26.63
Hardness (Shore A)	25	27	31	31	32
Compression set (%)	17.65	17.52	15.41	15.23	15.74
Rebound resilience (%)	66	65	65	66	66
Crosslink density x10^5 (mol/g rubber hydrocarbon)	2.80	3.20	3.39	3.84	3.67
Swelling index	4.89	4.64	4.35	4.07	4.08

For optimum performance in service, compression set values should be as low as possible [10, 11]. The values of compression set were lower for the vulcanizates containing DCBS and TBzTD compared to the single accelerator based vulcanizates.

Rebound resilience values were comparable for both single and binary accelerator based vulcanizates. Under impulsive loading conditions, the deformation of a viscoelastic matrix is more elastic and hence the systems show better resilience [12].

The swelling ratio of the vulcanizates was evaluated in order to find the extent of crosslinking. The calculated values of the crosslink densities are given in Table 4.4. Crosslink density of the vulcanizate increased when the dosage of DCBS was increased from 3 to 6 phr. The crosslink density was further improved by the addition of TBzTD and highest value was obtained at a dosage of 1.5 phr DCBS in the binary system. The tensile strength and tear strength values were in accordance with the crosslink density values.

Table 4.5 Stress-strain properties of the natural rubber vulcanizates containing DCBS before and after ageing

Sample	Tensile strength (MPa)			Modulus at 300 % elongation (MPa)			Elongation at break (%)		
	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C
D_1	13.22	13.95	13.24	0.89	0.90	0.85	1156	1180	1208
D_2	13.40	13.51	13.33	1.06	1.03	1.19	1186	1182	1100
D_3	17.38	17.45	17.30	1.12	1.10	1.28	1043	1067	990
D_4	18.05	18.10	18.02	1.16	1.23	1.27	1140	1060	1038
D_5	17.63	17.66	17.62	1.19	1.37	1.66	1012	970	917

The thermal ageing of the samples was carried out at 70 ^{o}C and 100 ^{o}C for 24 hours. The stress-strain properties of the vulcanizates are shown in Table 4.5. The tensile strength values registered a slight increase after thermal ageing at 70 ^{o}C for all the samples. The slight increase in tensile strength may be due to the formation of additional crosslinking. This is possible since the samples were cured for optimum cure time, which results in formation of only 90 % of the total crosslinks [13]. Moreover in an efficient vulcanization system, majority of the crosslinks are mono and di sulphidic. These crosslinks are thermally stable [14, 15]. The resistance of the vulcanizates to thermo-oxidative ageing is evident from the Figures 4.5, 4.6 and 4.7.

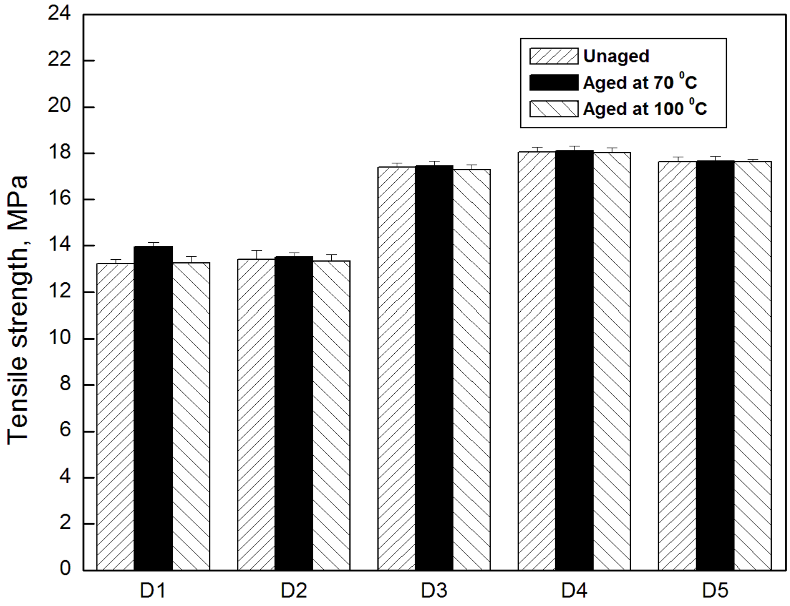


Figure 4.5 Variation in tensile strength of the NR vulcanizates containing DCBS before and after ageing

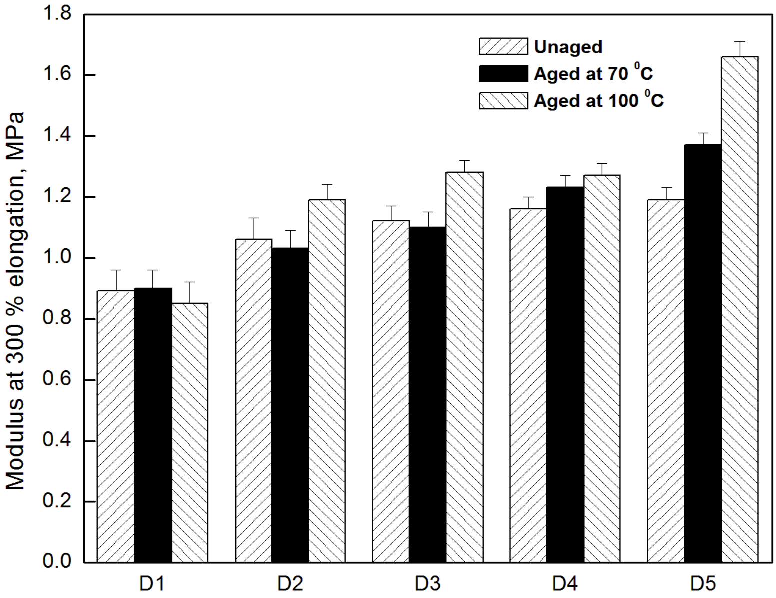


Figure 4.6 Variation in modulus at 300 % elongation of the NR vulcanizates containing DCBS before and after ageing

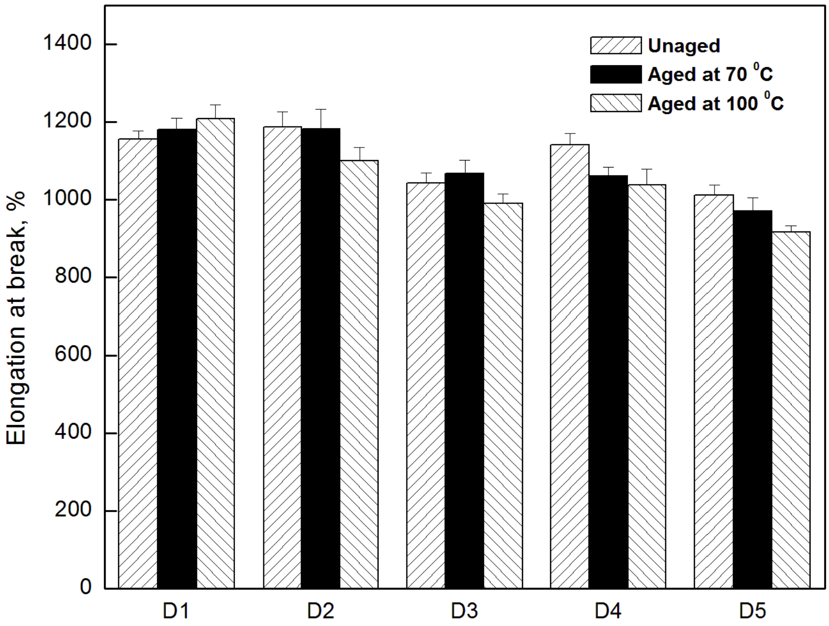


Figure 4.7 Variation in elongation at break of the NR vulcanizates containing DCBS before and after ageing

The vulcanizates aged at 100 °C do not show considerable variation in tensile strength from that of the unaged vulcanizates. Both the single accelerator based vulcanizates and binary accelerator based vulcanizates maintained their mechanical properties even after thermal ageing.

4.4.2 Mechanical properties of the NR vulcanizates containing DBBS

Stress-strain curves of the vulcanizates containing DBBS are shown in Figure 4.8. The binary accelerator based vulcanizates showed better mechanical properties compared to the single accelerator based vulcanizates (Table 4.6). Highest tensile strength was obtained in the case of the vulcanizate containing 1.5 phr of DBBS and 2.2 phr of TBzTD.

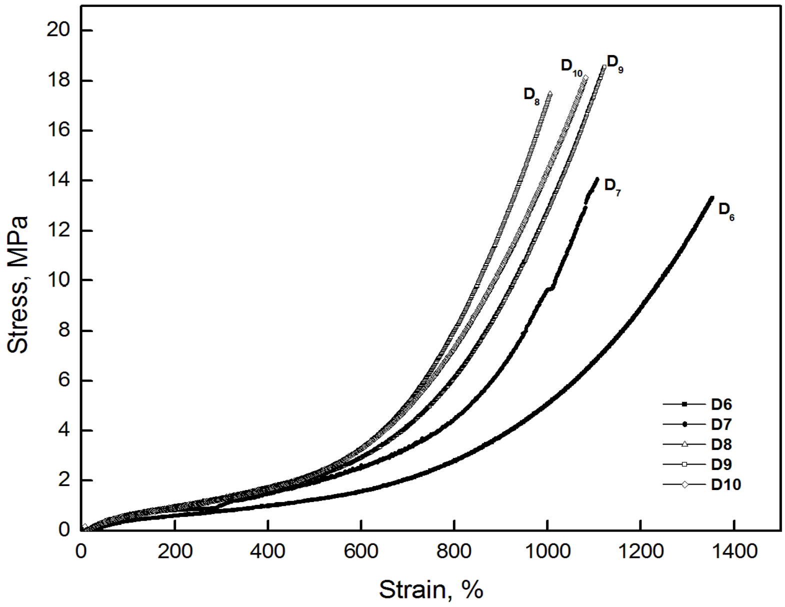


Figure 4.8 Stress-strain curves of NR vulcanizates containing DBBS

Compression set was lowered by the addition of TBzTD and the lowest value was obtained for the vulcanizate containing 1.5 phr of DBBS and 2.2 phr of TBzTD.

Table 4.6 Properties of NR vulcanizates containing DBBS

Properties	**D_6**	**D_7**	**D_8**	**D_9**	**D_{10}**
Tensile strength (MPa)	13.32	14.05	17.48	18.55	18.13
Modulus at 300 % elongation (MPa)	0.78	0.99	1.21	1.24	1.26
Elongation at break (%)	1354	1013	1006	1122	1082
Tear strength (N/mm)	20.05	20.81	28.15	28.22	28.18
Hardness (Shore A)	24	26	32	33	33
Compression set (%)	18.58	17.47	15.68	15.26	15.37
Rebound resilience (%)	65	66	65	66	66
Crosslink density x10^5 (mol/g rubber hydrocarbon)	2.55	2.67	3.63	4.01	3.97
Swelling index	4.98	4.94	4.24	3.92	4.04

The vulcanizates with the single accelerator, DBBS retained the same rebound resilience even after the introduction of TBzTD indicating that this property is not adversely affected by the addition of TBzTD. The crosslink densities of the vulcanizates determined by the equilibrium swelling measurements in toluene are shown in Table 4.6. The reduction in swelling index with the addition of TBzTD indicates an increase in crosslink density of the vulcanizates. This increase in crosslink density has in turn increased the mechanical properties such as tensile strength, modulus at 300 % elongation and tear strength of the binary accelerators (DBBS and TBzTD) incorporated system. The results showed that these properties are in accordance with the crosslink density values.

Table 4.7 Stress-strain properties of NR vulcanizates containing DBBS before and after ageing

Sample	**Tensile strength (MPa)**			**Modulus at 300 % elongation (MPa)**			**Elongation at break (%)**		
	Un aged	**70 °C**	**100 °C**	**Un aged**	**70 °C**	**100 °C**	**Un aged**	**70 °C**	**100 °C**
D_6	13.32	13.82	13.70	0.78	0.91	0.88	1354	1260	1229
D_7	14.05	14.08	14.04	0.99	1.01	1.02	1013	1007	971
D_8	17.48	17.59	17.35	1.21	1.26	1.55	1006	996	919
D_9	18.55	18.53	18.57	1.24	1.31	1.43	1122	1080	987
D_{10}	18.13	18.29	18.30	1.26	1.40	1.73	1082	1000	942

Stress-strain properties of the vulcanizates containing DBBS after ageing at 70 °C and 100 °C for 24 hours are shown in Table 4.7. Variation in tensile strength, modulus at 300 % elongation and elongation at break of the vulcanizates before and after ageing are also shown in Figures 4.9, 4.10 and 4.11. Both the single accelerator based vulcanizates and binary accelerator based vulcanizates maintained their mechanical properties even after thermal ageing.

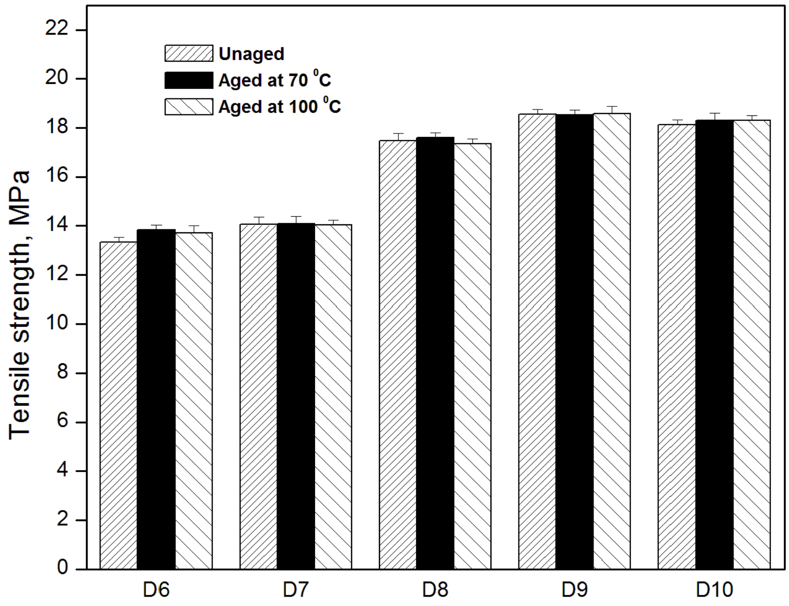


Figure 4.9 Variation in tensile strength of the NR vulcanizates containing DBBS before and after ageing

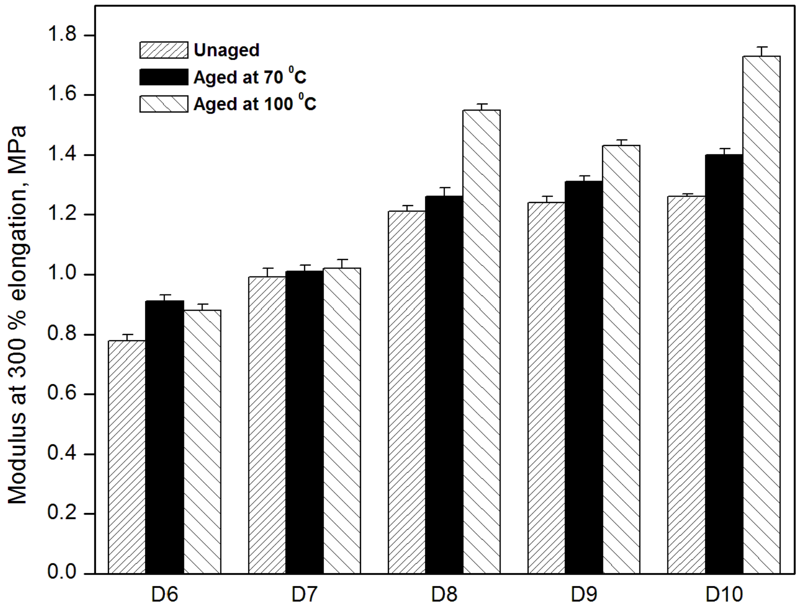


Figure 4.10 Variation in modulus at 300 % elongation of the NR vulcanizates containing DBBS before and after ageing

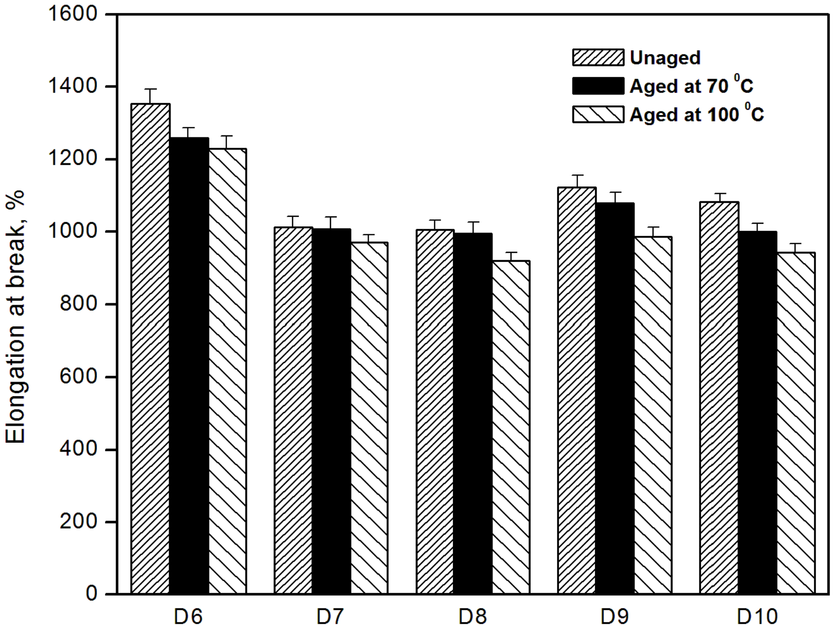


Figure 4.11 Variation in elongation at break of the NR vulcanizates containing DBBS before and after ageing

4.5 Fluid resistance

The fluid resistance of the samples D_4 (1.5 phr DCBS and 2.2 phr of TBzTD) and D_9 (1.5 phr of DBBS and 2.2 phr of TBzTD) were carried out in diesel and lube oil. The percentage change in mass of the gum vulcanizates are shown in the Table 4.8.

Table 4.8 Change in mass (%) of the vulcanizates D_4 and D_9 in diesel and lube oil

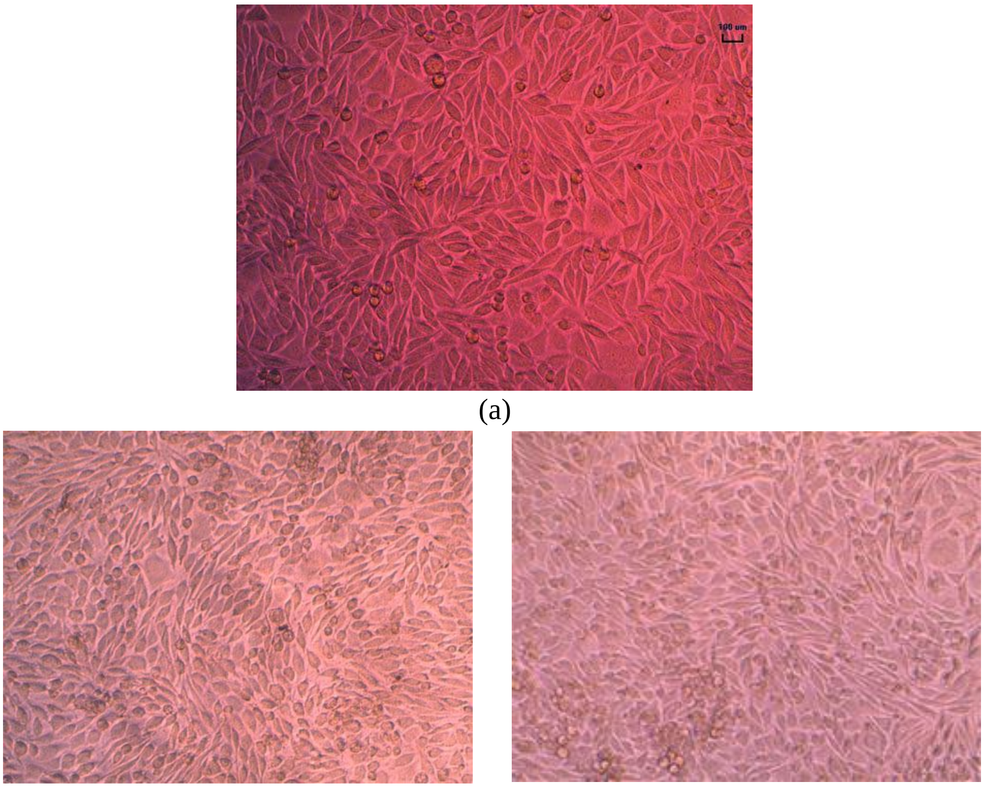
Sample	Change in mass (%)	
	Diesel	Lube oil
D_4	257	114
D_9	254	113

Comparable fluid resistance shown by the vulcanizates after soaking in diesel and lube oil for 72 hours may be attributed to their crosslink densities.

4.6 Cytotoxicity of the vulcanizates containing DCBS / DBBS

Cytotoxicity of the vulcanizates was evaluated by checking the cell viability through MTT assay [16]. Cell morphology of control of MTT assay and confluent cells containing extract of D_4 and D_9 were determined using phase contrast image as shown in Figure 4.12. Control sample of the MTT assay showed large number of fibroblast cells. But in the case of the confluent cells containing the extract of NR vulcanizates containing DCBS or DBBS, a considerable reduction in the number of viable cells was noticed after 24 hours incubation.

A reduction in the number of viable cells in the case of confluent cells containing the extract of vulcanizates was evident from the lower value of optical density as compared to the control cells. The samples containing extract of D_4 (NR vulcanizate conataining DCBS) and D_9 (NR vulcanizate containing DBBS) was found to possess 81.18 % and 81.02 % of viable cells. Thus the results of MTT assay showed that the natural rubber vulcanizates containing DCBS and DBBS were safe (non-cytotoxic) [17, 18].



(a)

(b) (c)

Figure 4.12 Phase contrast image (magnification 20 x) for the determination of cell morphology of: (a) control of MTT assay, (b) extract of NR vulcanizate containing DCBS and (c) extract of NR vulcanizate containing DBBS

4.7 Summary

Natural rubber vulcanizates containing DCBS or DBBS as single accelerator system show very good scorch safety. Addition of TBzTD to the system reduces the scorch time and optimum cure time. As the dosage of DCBS or DBBS increases the optimum cure time increases and cure rate index decreases. Kinetic studies show that the cure reaction follows first order kinetics. Better mechanical properties are obtained for vulcanizates prepared using DCBS or DBBS in binary combination with TBzTD, i.e.

binary accelerator system. Addition of high dosages of DCBS or DBBS improve the mechanical properties of the vulcanizates. The vulcanizates prepared using DCBS or DBBS in binary combination with TBzTD show similar fluid resistance in diesel and lube oil. The MTT assay results verified and confirmed the non-cytotoxic nature of the vulcanizates prepared using DCBS or DBBS.

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Chapter 5

EFFECT OF FILLERS ON PROPERTIES OF SAFE NATURAL RUBBER VULCANIZATES

Contents

PART A

EFFECT OF CARBON BLACK ON PROPERTIES OF SAFE NATURAL RUBBER VULCANIZATES

Contents

Natural rubber masterbatches containing various loadings of carbon black were prepared and their bound rubber content was determined. Cure characteristics, cure kinetics and strain-sweep analysis of the formulations were studied after incorporating safe (non-regulated) curatives. Studies on the vulcanizates include the evaluation of the mechanical properties, ageing resistance, sorption characteristics, fluid resistance and cytotoxicity. Morphological analysis of the tensile fractured surfaces was done by scanning electron microscopy (SEM) and thermal stability of the vulcanizates were studied by thermogravimetric analyses (TGA).

Part of work presented in this chapter has been communicated to *Rubber Chemistry and Technology.*

5.A.1 Introduction

Even though gum natural rubber vulcanizate shows high tensile strength, it is not suitable for many commercial applications. Fillers are generally incorporated for improving processability, reinforcement and cost reduction.

Reinforcement by filler is the enhancement of one or more properties of an elastomer by the incorporation of that filler, thus making it more suitable for applications [1, 2]. Carbon blacks are the most efficient and cost-effective reinforcing fillers used in rubber industry till date. The main reason for the predominant use of carbon black in elastomers is the excellent reinforcement it imparts to the vulcanized rubber [3]. The unique ability of carbon black to enhance the physical properties of elastomers is associated with the size, shape and surface chemistry of its primary aggregates [4]. Reactive groups like acid groups, phenolic groups, quinonic groups and lactone groups capable of persuading adsorption of curatives have been identified on the carbon black surface [5, 6]. During vulcanization, carbon black establishes a chemical link with sulphur, accelerators, etc. participating in the formation of the vulcanized network. Polar rubbers like nitrile rubber exhibits stronger interaction with carbon black as compared to the non-polar olefinic rubbers [7].

The use of tetrabenzyl thiuramdisulfide in conjunction with TBBS as safe and effective accelerators for the gum vulcanization of NR has been reported in the chapter 3. Eventhough the vulcanizates prepared using binary accelerators DCBS/DBBS and TBzTD are safe, the mechanical properties (especially tensile strength) are inferior compared to that prepared using TBBS and TBzTD at the same dosages. So the accelerator combination TBBS (1.5 phr) and TBzTD (2.2 phr) has been chosen for further studies. The objective of the work reported in this chapter is the evaluation of the effect of carbon black on natural rubber vulcanizates prepared using safe binary accelerator (TBBS and TBzTD) combination.

5.A.2 Preparation of carbon black-filled NR compounds

Formulations used in the preparation of the vulcanizates are given in Table 5.A.1. The mix without filler is designated as C_0 and masterbatches with 20, 30, 40 and 50 phr loadings of carbon black were prepared. The mixes prepared after incorporating other ingredients are designated as CB_1, CB_2, CB_3 and CB_4 respectively. Experimental procedures are presented in the section 2.2.1. Mixes with various loadings from 20 to 50 phr of carbon black were prepared on a two-roll mixing mill. Naphthenic oil is used as the process oil for mixes containing carbon black.

Table 5.A.1 Formulations of the mixes containing carbon black

	C_0	**CB_1**	**CB_2**	**CB_3**	**CB_4**
NR (g)	100	100	100	100	100
ZnO (phr)	5.0	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0	1.0
Naphthenic oil (phr)	-	2.0	3.0	4.0	5.0
HAF (phr)	-	20	30	40	50
TBBS (phr)	1.5	1.5	1.5	1.5	1.5
TBzTD (phr)	2.2	2.2	2.2	2.2	2.2
Sulphur (phr)	0.3	0.3	0.3	0.3	0.3

5.A.3 Cure characteristics of the carbon black-filled NR compounds

Figure 5.A.1 shows the rheographs of the natural rubber compounds filled with carbon black and that of the control sample C_0 without any filler. The cure characteristics are given in Table 5.A.2.

Variation of scorch time (t_{10}) and cure time (t_{90}) with the filler loading is shown in Table 5.A.2. In the case of carbon black-filled NR compounds scorch time was found to decrease with filler loading. This may be due to restriction of the chain mobility and deformability of the rubber with the introduction of carbon black.

When compared to gum vulcanizate, the optimum cure time of the carbon black-filled compounds was higher. This may be due to the adsorption of curatives onto the surface of the carbon black [8]. But as the filler loading was increased, the optimum cure time decreased. This was due to the pronounced effect of activating groups like phenolic, quinolic, etc. on the surface of the black which promote a higher affinity of rubber to filler. The subsequent close contact of elastomer and carbon black allowed the active sites on the surface of the black particles to chemically interact with elastomer chains [9, 10].

The maximum torque (M_H) values increased with increase in concentration of the carbon black. The increase in maximum torque with increasing filler content indicated an enhancement in the stiffness of the vulcanizate.

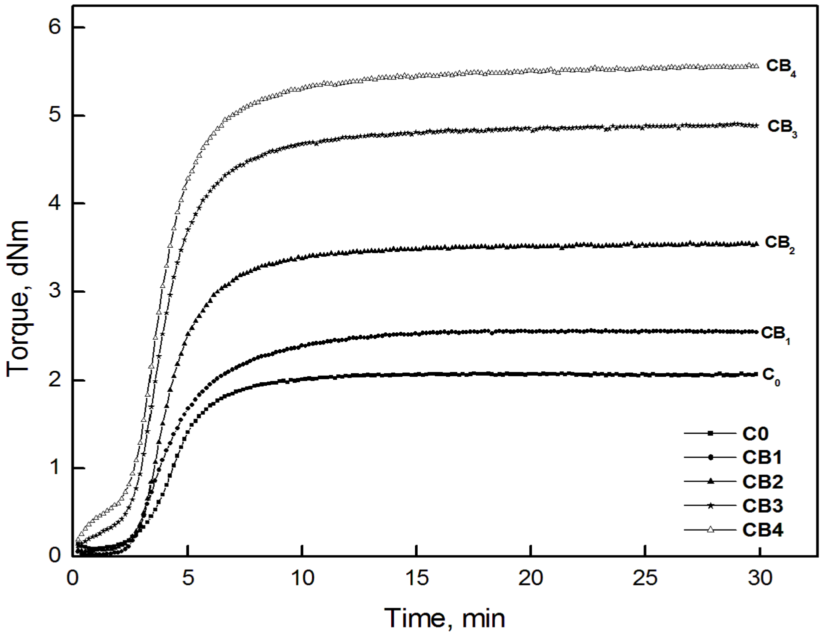


Figure 5.A.1 Effect of carbon black on cure characteristics of NR compounds

The maximum torque is an index of the extent of crosslinking reactions and represents the shear modulus of the fully vulcanized rubber at the vulcanization temperature. It is also a measure of the filler-polymer interaction. Therefore it is anticipated that filler-polymer interactions are improved with increasing dosage of carbon black up to 50 phr.

Table 5.A.2 Cure characteristics of the mixes at 150 °C

Properties	**C_0**	**CB_1**	**CB_2**	**CB_3**	**CB_4**
Scorch time t_{10} (min)	2.89	2.88	2.85	2.56	2.28
Optimum cure time t_{90} (min)	7.17	8.79	7.95	7.19	7.17
Cure rate index (CRI, min^{-1})	23.36	16.92	19.61	21.59	20.45
Minimum torque (M_L, dNm)	0.08	0.09	0.14	0.29	0.37
Maximum torque (M_H, dNm)	2.08	2.68	3.58	5.07	5.54
$M_H - M_L$ (dNm)	2.00	2.65	3.45	4.78	5.17
Relative increase in torque (α_r)	-	0.33	0.73	1.40	1.59

The minimum torque (M_L) (a measure of the viscosity of the compound) was found to increase with filler loading. The increase in viscosity with the addition of filler suggests that incorporation of carbon black considerably reduce the mobility of the rubber chains and processability of the compounds become more and more difficult. M_L is a cure property measured in the uncured state while M_H is the characteristic of the cured rubbers. During the vulcanization process, the chemical crosslinks are formed based on the reaction of rubbers with vulcanizing agent [11]. When we compare the differential torque, ΔM (i.e. $M_H – M_L$) values of gum and the filled vulcanizates (Table 5.A.2) it was found that the values were higher for the filled ones than the gum vulcanizate. ΔM is considered as the parameter to indicate the degree of chemical crosslinking between rubber and the vulcanizing agent. It was found to increase with carbon black loading. It is believed that the accelerator, sulphur and carbon black form an active intermediate complex. The additional amount of crosslinks in the filled vulcanizates as compared to the corresponding gum vulcanizate can be attributed to the formation of this complex [12]. The cure rate index of the vulcanizates too was increased with carbon black filler loadings and showed the highest value for the mix containing 40 phr carbon black.

5.A.3.1 Cure kinetics

A plot of ln ($M_H – M_t$) against time‘t’ gave a straight line for the carbon black-filled NR vulcanizates (Figure 5.A.2). Since the obtained linear plot is the characteristic of a first order reaction, first order cure kinetics was predicted for the filled vulcanizates.

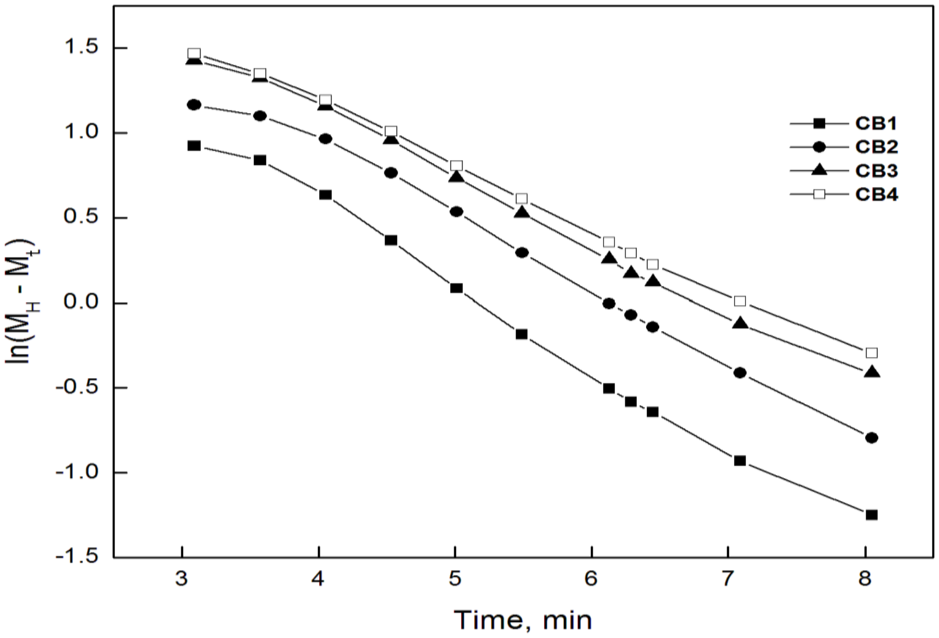


Figure 5.A.2 Plot of $\ln(M_H - M_t)$ versus time of carbon black-filled NR compounds

5.A.3.2 Westlinning-Wolff's equation

A mathematical expression has been proposed by Wolff in terms of rheometric data to characterize the filler structure present in rubber vulcanizates and to evaluate its influence on the crosslinking process [13-15].

When filler is incorporated into a compound, the differential torque, observed during vulcanization increases.

$$\Delta M_f = M_H - M_L \text{ --- } (5.1)$$

The ratio between ΔM_f and ΔM^0 (i.e., the torque variations for the loaded and unloaded compounds respectively) is directly proportional to filler loading. By plotting the relative torque as a function of filler fraction, a straight line is obtained whose slope is defined by Wolf as α_f, according to Westlinning-Wolff's equation given below.

$$\frac{(M_H - M_L)}{(M_H^0 - M_L^0)} - 1 = \alpha_f\left(\frac{m_f}{m_p}\right) \text{--} (5.2)$$

where m_p is the mass of polymer in the compound and m_f is the mass of filler in the compound and α_f is a specific constant for the filler, which is independent of the cure system and closely related to the morphology of the filler [16]. The left hand side of the equation gives the relative increase in torque (α_r) due to the addition of the filler. The parameter α_f represents the final structure of the filler as it exists in the vulcanizates after all possible structure breakdowns that occurred during mixing and vulcanization. The reinforcement of the compounds occurs due to the crosslinking reactions taking place during curing. The application of Westlinning-Wolff's equation allows the correlation of filler specific constant (α_f) to the filler structure, and also predicts whether the crosslink density is affected by the presence of a particular filler or not [17-20].

Wolff equation was applied for the prepared carbon black-filled natural rubber compounds. Figure 5.A.3 represents the relation between differential torque (M_H – M_L) and filler fraction in the natural rubber compounds. The increase in differential torque indicates that the incorporation of carbon black has improved the crosslinking between the polymer chains.

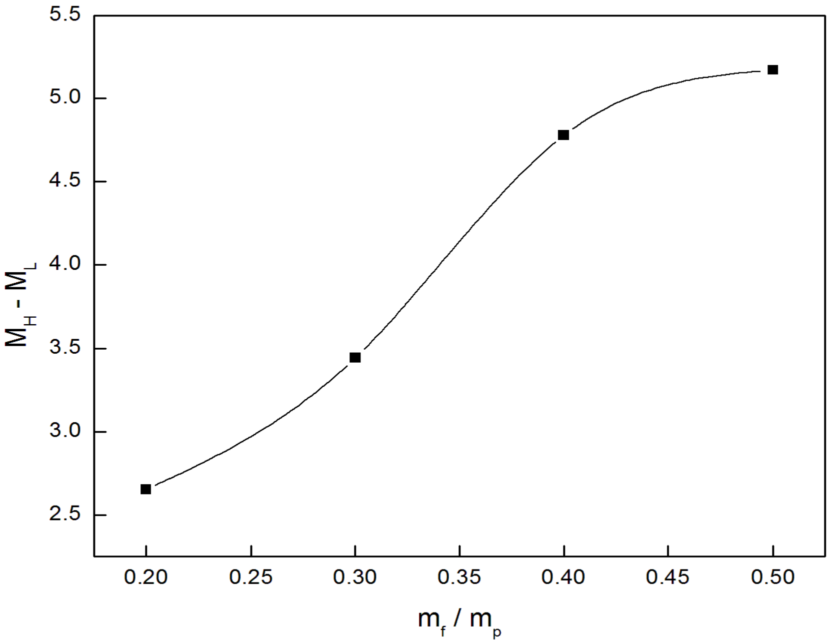


Figure 5.A.3 Plot of differential torque versus carbon black filler fraction

The relative increase in torque (α_r) was also plotted against the filler fraction giving a straight line (Figure 5.A.4). The filler specific constant (α_f) can be obtained from the slope of the line. It is a measure of the structure of the fillers in the matrix. The value of α_f is significant only when comparing different fillers. High structure carbon blacks are easier to disperse than lower structure carbon blacks. So the value of α_f can also be used as an indication of rubber-filler interactions [21]. The relative increase in torque (α_r) of the filled samples increased with increase in carbon black as shown in Table 5.A.2.

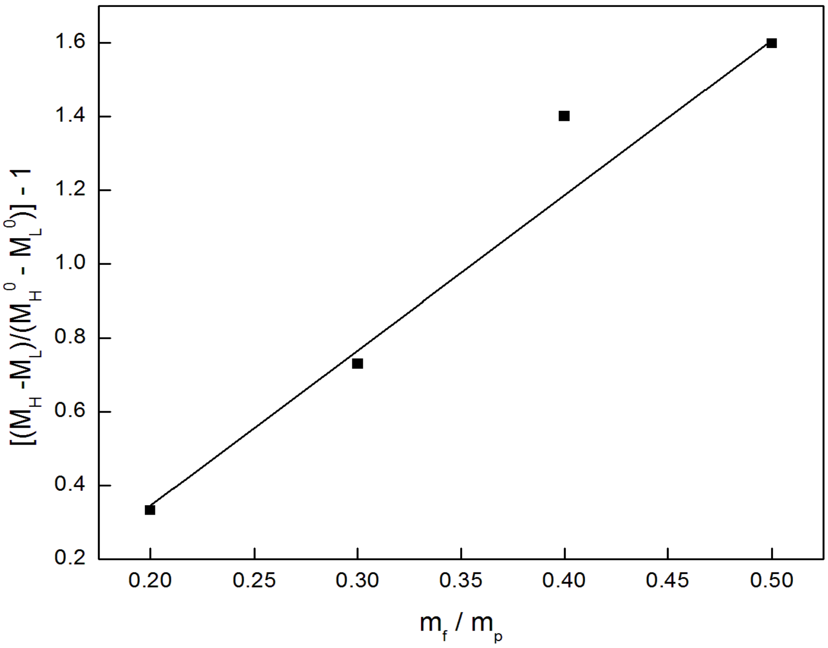


Figure 5.A.4 Plot of relative increase in torque (α_r) as function of carbon black filler fraction

5.A.4 Mechanical properties of the NR vulcanizates containing carbon black

Stress-strain properties of the NR vulcanizates containing carbon black are presented in Figure 5.A.5. The mechanical properties like tensile strength, modulus at 300 % elongation, tear strength and hardness of the vulcanizates improved with carbon black loading (Table 5.A.3). One of the reasons for such improvement is the reduction of the inter-aggregate distance within the fillers, which imposes greater resistance against crack propagation [22]. The natural rubber fills the pores of the porous carbon black filler, adheres to it and gives tremendous reinforcement to the matrix [23].

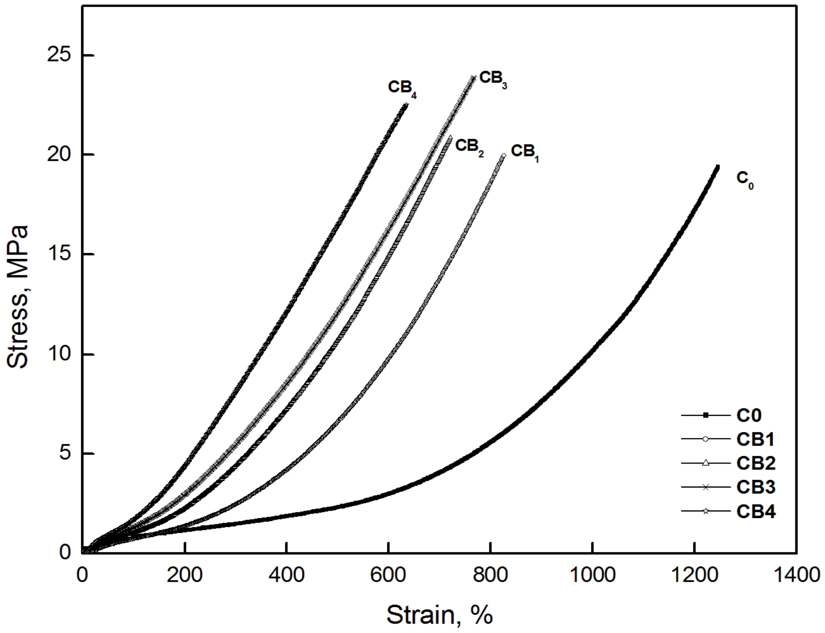


Figure 5.A.5 Stress-strain curves of gum and carbon black-filled NR vulcanizates

The improved tensile strength of the carbon black-filled vulcanizates compared to the gum vulcanizate can be explained in terms of additional resistance offered by carbon black to attain maximum elongation and overcome the applied stress to cleave chain-chain and chain-filler attachments [24]. The improvement in tensile strength indicated a homogeneous dispersion of the fillers with a strong interfacial bonding between them and the polymer matrix. Tensile strength increased with filler content up to the point at which there was sufficient rubber to bind with the filler and thereafter decreased. The initial increase in tensile strength may be due to the successful distribution of load among carbon black adhered natural rubber chains. This increased the resistance of rubber to failure. Optimum tensile strength was obtained for the vulcanizate with 40 phr carbon black loading (19.5 % enhancement as compared to the gum vulcanizate). The enhancement in the tensile strength occurred due to the prevalence of higher polymer-filler interactions than filler-filler interactions. Higher loading than 40 phr carbon black detrimentally affected the stress-strain properties due to the agglomeration of the filler. At 50 phr carbon black loading, 5.4 % depreciation in tensile strength was observed compared to 40 phr loading.

Elongation at break of NR vulcanizates significantly decreased with the addition of carbon black due to the reinforcement effect of the porous filler [25]. Apparently as the filler loading increases, the matrix is filled by filler thereby decreasing the space available for polymer chains to stretch.

Modulus increased with the increment in carbon black loading. Carbon black tends to form agglomerates as its amount in the vulcanizates increase. Hence higher strength will be needed to deform compounds filled with carbon black when compared to that of gum vulcanizate, which results in higher tensile modulus. Therefore higher the amount of carbon black loading, higher will be the tensile modulus [25].

Table 5.A.3 Properties of gum and carbon black-filled NR vulcanizates

Properties	C_0	CB_1	CB_2	CB_3	CB_4
Tensile strength (MPa)	19.55	20.38	21.18	23.36	22.11
Modulus at 300 % elongation (MPa)	1.46	2.40	4.28	5.27	8.22
Elongation at break (%)	1230	838	739	745	620
Tear strength (N/mm)	26.71	43.99	69.89	78.78	85.34
Hardness (Shore A)	31	40	45	50	55
Compression set (%)	15.05	13.57	11.26	9.20	10.30
Rebound resilience (%)	65	49	47	41	37
Crosslink density x10^5 (mol/g rubber hydrocarbon)	4.38	4.94	5.40	6.51	7.59
Molar mass between crosslinks (g/mol)	11416	10121	9259	7680	6588
Swelling index	4.10	3.13	2.75	2.44	2.08
Abrasion loss (cc/h)	-	10.82	7.89	7.69	7.19

Hardness is typically measured as resistance to surface indentation under specific conditions. The hardness of the 20 phr carbon black-filled vulcanizates was considerably higher than the gum vulcanizate. Here the rubber hardness increased with filler loading since the resistance to elastomer chain deformation was increased with filler loading [24].

Tear strength is a measure of resistance to crack. It measures the growth of crack under tension. Tear strength increased by the addition of the filler and the values was increased in proportion with the filler loading. The carbon black particles apparently act as barriers to the propagation of micro cracks thereby providing higher tear strength [24].

From the compression set values, it is clear that residual deformations of the carbon black-filled vulcanizates are low, especially for the vulcanizate containing 40 phr of carbon black. Low compression set of rubber is a requisite criterion for seal applications [24].

Resilience is essentially a measure of rubber elasticity - the characteristic ability to quickly return to original shape following deformation. Unfilled elastomers are at their peak resilience because there is no obstacle to elastomer chain extension and contraction. The introduction of carbon black reduced the resilience of the vulcanizates since the increased polymer-filler interactions pose obstructions to facile polymer chain mobility. Resilience was therefore generally in inverse proportion to filler loading and reinforcement. As more filler was introduced into the rubber, the percentage rubber content in the compound decreased and this further restricted the chain mobility.

If resilience is considered as the ratio of energy released on recovery to the energy impressed on deformation, hysteresis can be viewed as a measure of the amount of impressed energy that is absorbed. An unfilled elastomer will convert most of the energy of deformation into the mechanical energy for returning to the original shape. The degree to which input energy is converted to heat, due to friction from polymer chains sliding past each other, is a function of polymer chain morphology. All fillers increase the hysteresis of rubbers due to the energy consumed at polymer-filler interfaces due to friction and in dislodging polymer segments from active filler surfaces. In short, hysteresis is inversely related to resilience [24]. Lower the resilience of the vulcanizate, lower is the vibration transmitted. Thus carbon black-filled vulcanizates with lower resilience can be applied for damping applications [24].

Abrasion resistance is a function of filler structure, particle size and filler-elastomer adhesion. Greater the rubber-filler interactions, more difficult will be the dislodgement of the vulcanizate under abrasion. As the filler loading increases the rubber-carbon black particle bonds also increase as evident from Table 5.A.3. It has been reported that crosslink density, hardness and modulus of the vulcanizate are important factors controlling the abrasion resistance [26, 27]. The increased crosslink density increases the hardness and modulus of the filled vulcanizates ultimately enhancing their abrasion resistance.

Crosslink density of a rubber vulcanizate determines its physical properties [28]. By increasing the crosslink density, the modulus, hardness, and abrasion resistance of the vulcanizates increase, whereas their elongation at break decreases.

The crosslink density of the carbon black-filled vulcanizates was more compared to that of gum vulcanizate. The reaction of rubbers with vulcanizing agent is merely one specific factor influencing the crosslink density. The other one is the chemical interaction of rubbers with the functional groups on carbon blacks. The chemical interaction of rubbers with carbon black has increased the degree of chemical crosslinking. Apparently this may be the reason for the increase in crosslink density values of the carbon black-filled vulcanizates with the filler loading.

Lorenz and Park equation has been applied to study the rubber-filler interactions in the vulcanizates [29]. According to the equation:

$$Q_f/Q_g = ae^{-z} + b \text{ -- } (5.3)$$

where f and g refer to filled and gum vulcanizates respectively, z is weight fraction of the filler in the vulcanizate and ‘a’ and ‘b’ are constants. In the present work, weight of toluene uptake per gram of rubber hydrocarbon (Q) is:

$$Q = \frac{(W_s - W_d) \times \text{formula weight}}{W_i \times 100} \text{ --}(5.4)$$

where W_s is swollen weight, W_d is dried weight and W_i is the original weight

Q_f/Q_g of carbon black-filled NR vulcanizates with different loadings of the black is given in Table 5.A.4.

Table 5.A.4 Q_f/Q_g of carbon black-filled NR vulcanizates

Sample	Q_f/Q_g
CB_1	0.917
CB_2	0.885
CB_3	0.848
CB_4	0.778

The higher the Q_f/Q_g values, the lower will be the extent of interaction between the filler and the matrix. It is observed that Q_f/Q_g decreased with increment in carbon black loading indicating good interaction between natural rubber and carbon black filler. This good interaction hindered toluene from penetrating through the NR vulcanizate. Therefore the swelling index decreased with the filler loading (Table 5.A.3).

Stress-strain properties of carbon black-filled NR vulcanizates after ageing at 70 °C and 100 °C for 24 hours are shown in Table 5.A.5 and Figures 5.A.6, 5.A.7 and 5.A.8. After ageing at 70 °C and 100 °C for 24 hours, there was a marginal increase in tensile strength and modulus at 300 % elongation. This result confirmed the inherent thermal stability of the efficient vulcanization systems. Modulus enhancement on ageing may be due to additional crosslinking occurred leading to stiffening of the vulcanizates.

Table 5.A.5 Stress-strain properties of gum and carbon black-filled NR vulcanizates after ageing

Sample	Tensile strength (MPa)			Modulus at 300 % elongation (MPa)			Elongation at break (%)		
	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C
C_0	19.55	20.64	19.19	1.46	1.62	2.04	1230	1082	906
C_{B1}	20.38	20.69	20.75	2.40	2.71	3.09	838	867	800
C_{B2}	21.18	23.27	23.72	4.28	4.34	4.77	739	831	742
C_{B3}	23.36	24.25	24.27	5.27	5.62	5.90	745	757	699
C_{B4}	22.11	23.54	23.52	8.22	8.20	9.28	620	649	564

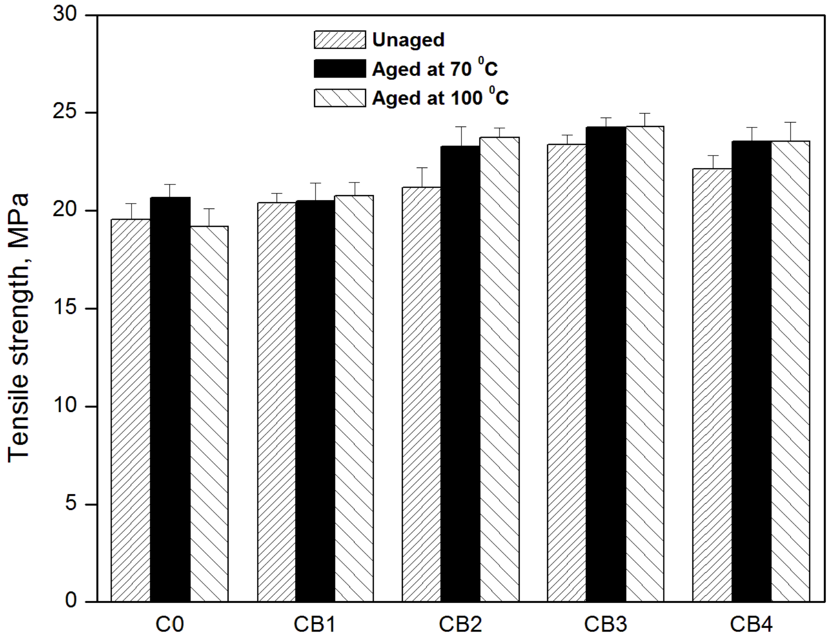


Figure 5.A.6 Variation in tensile strength of gum and carbon black-filled NR vulcanizates before and after ageing

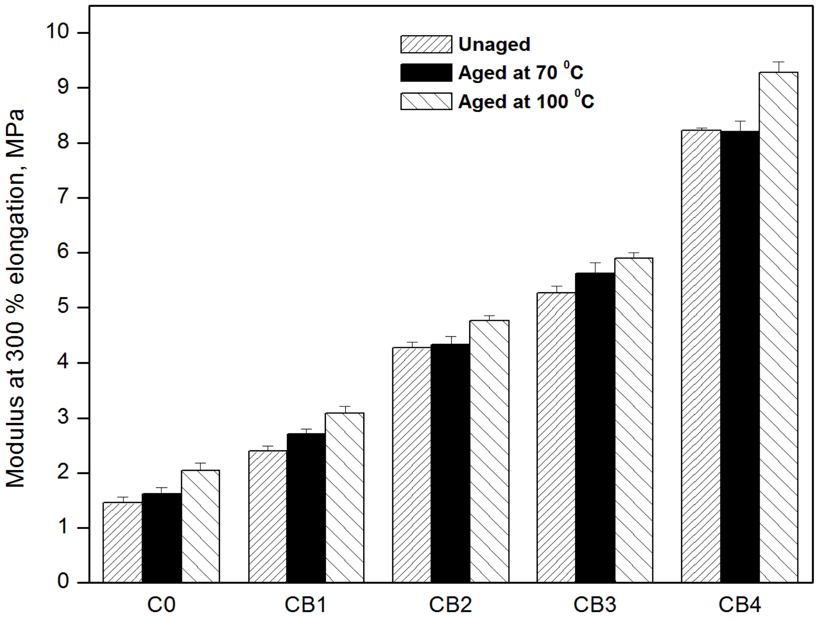


Figure 5.A.7 Variation in modulus at 300 % elongation of gum and carbon black-filled NR vulcanizates before and after ageing

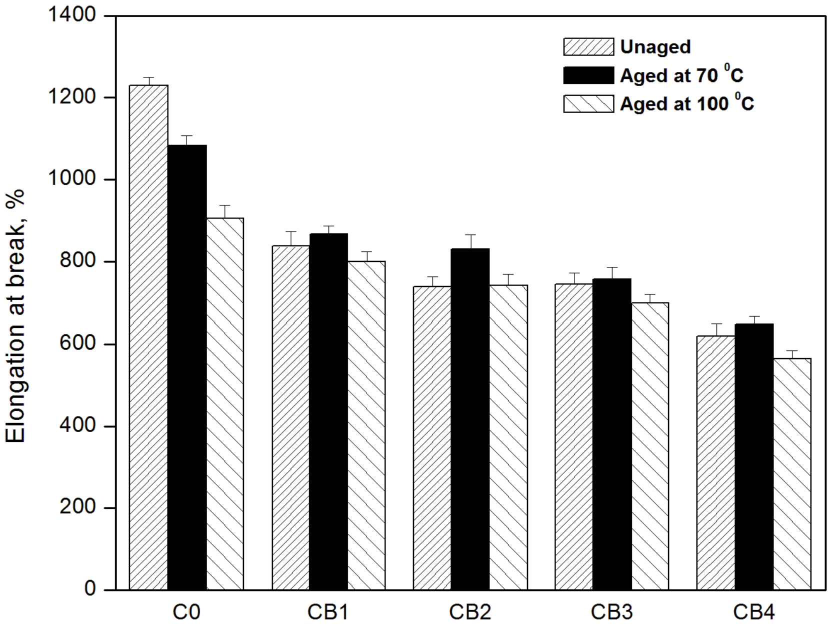


Figure 5.A.8 Variation in elongation at break of gum and carbon black-filled NR vulcanizates before and after ageing

5.A.5 Sorption studies

Swelling studies of the vu1canizates were done in toluene at 25 °C and the diffusion curves (mole percent uptake of penetrant against $t^{1/2}$) for the gum NR vulcanizate and those filled with carbon black at different loadings are given in Figure 5.A.9. Carbon black-filled NR vulcanizates exhibited reduced swelling than the unfilled system. The subsequent addition of carbon black (> 20 phr) further decreased the swelling of the vulcanizates. This may be due to a restriction imparted by the filler-polymer network to the penetration of the solvent molecules into the bulk of the polymer. As filler preferentially reinforces the rubber phase, its introduction reduces the volume swell of the rubber phase and, thus, reduces the overall volume swell of the vulcanizates in solvent [30]. In the case of carbon black -filled vulcanizates, as the filler loading increases Q_t % decreases which may be due to the decrease in volume fraction of rubber with filler loading. The low swelling rate of carbon black-filled vulcanizates was in good agreement with its improved mechanical properties [31].

Swelling measurements are useful in characterizing the network degradation. In the case of unfilled rubbers, the swelling restriction is due to the crosslinks connecting the polymer chains, but in filled systems filler-polymer interaction also may interfere. The variation of crosslink density with filler loading for the vulcanizates is shown in Table 5.A.3. The crosslink density was found to increase with filler loading.

The transport properties of organic solvents and gases through polymers are of great technological importance. The diffusion and transport properties of polymers are found to be strongly dependent on the additives and the type of crosslinking [32]. The diffusion process depends on the free volume within the material, segmental mobility of polymer chains and the size of the penetrant molecule [33].

In order to determine how the carbon black content affected the permeability, the transport properties like diffusion coefficient, permeation coefficient and sorption coefficient of the samples were calculated using the equations given in section 2.3.2.1. Table 5.A.6 gives the variation in diffusion coefficient (D), sorption coefficient (s) and permeation coefficient (P) as a function of filler loading. The variation of D depends on the solvent uptake, which shows a maximum for the gum vulcanizate. Addition of carbon black in the natural rubber resulted in a progressive decrease of D value. The value of D decreased further with increase in carbon black content. This proved the strong interaction between the filler and the matrix, which limited the toluene diffusivity. The permeation of a solvent into a polymer membrane will also depend on the sorptivity of the penetrant in the membrane. The sorption coefficient values were slightly higher for the gum vulcanizate than the carbon black-filled vulcanizates.

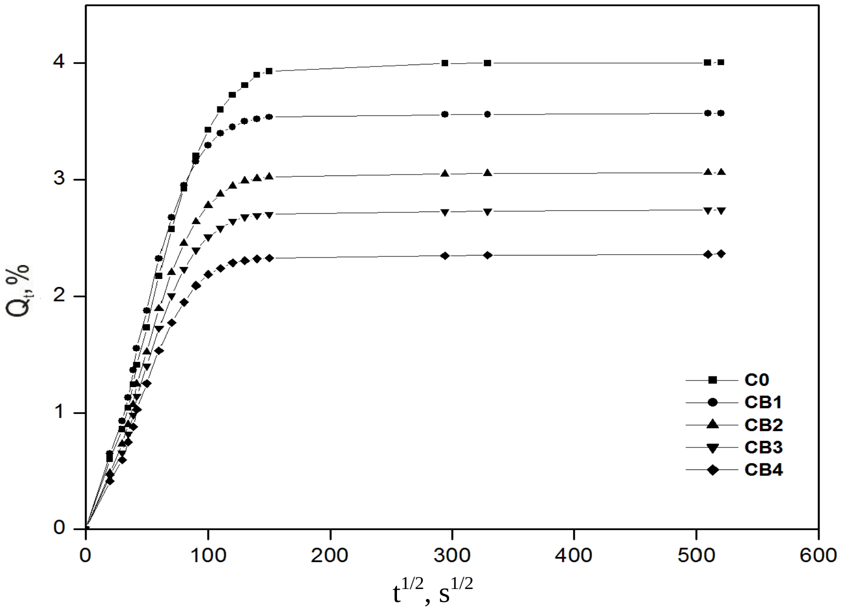


Figure 5.A.9 Q_t vs. $t^{1/2}$ of carbon black-filled NR vulcanizates

The permeation coefficient is the net effect of sorption and diffusion process [30]. The values obtained for P are given in the Table 5.A.6. The formation of the filler network may have contributed to the decrease in permeability. With the build-up of the filler network, the rubber becomes trapped within the filler agglomerates leading to an increase in the effective filler volume fraction. The sorption coefficient, as shown in the Table 5.A.6, decreased with carbon black loading which was the reflection of concomitant decrease in volume fraction of absorbing phase with increased loading. Evidently permeation of the solvent was decreased with carbon black loading since it is a collective phenomenon consisting of both diffusion and sorption.

Thermodynamic effects occurring during swelling of the elastomer chains were also analysed. The thermodynamic approach is of great importance for understanding the rubber-filler interaction in the vulcanizates. Swelling of a vulcanized rubber depends on the crosslink density and the solvent used. The expansion of the rubber in the presence of a solvent will significantly modify the conformational entropy (ΔS) and the elastic Gibbs free energy (ΔG).

The swelling of rubber by a liquid is a mixing process. Two substances mix when the free energy of mixing (ΔG) is negative. The equation for ΔG is given below.

$$\Delta G = \Delta H - T\,\Delta S \quad \text{--} \quad (5.5)$$

where ΔH is the change in enthalpy and T is the absolute temperature.

In simple terms, mixing is favoured by minimum or negative enthalpy change and maximum entropy change [34, 35]. As the network is swollen by the absorption of solvent, the chains between network junctions are stretched and a force analogous to the elastic retractive force in rubber consequently develops in opposition to the swelling process. As swelling proceeds this opposing force also increases. Ultimately a state of equilibrium swelling is reached where these two opposing forces are balanced. The deformation of rubber during swelling is expected to occur without an appreciable change in internal energy of the network structure. Thus the elastic Gibbs free energy can be equated to –TΔS omitting the enthalpy part, where ΔS represents entropy change associated with the change in configuration of the network [36].

The thermodynamical parameter ΔG and ΔS of the studied material is reported in Table 5.A.6. It should be noted that -ΔG increased in the presence of carbon black. It is assumed that ΔG is closely related to the elastic behaviour of the material i.e., the filled vulcanizate shows a better elasticity than the gum compound and it increases with increase in carbon black content. These results can be attributed to better compatibility between the carbon black and rubber. There was noticeable increase in entropy for the filled vulcanizates as compared to the gum vulcanizate [37].

Table 5.A.6 Sorption data of NR vulcanizates filled with carbon black

Sample	**D X 10^7 (cm^2/s)**	**s**	**P X 10^6 (cm^2/s)**	**n**	**k**	**ΔG (J/ mol)**	**ΔS X 10^2 (J/mol K)**
C_0	8.57	4.03	3.46	0.59	0.05	-11.70	3.93
CB_1	7.81	3.30	2.58	0.57	0.07	-14.37	4.82
CB_2	7.72	2.83	2.18	0.61	0.06	-17.83	5.98
CB_3	7.64	2.53	1.93	0.60	0.06	-22.26	7.47
CB_4	7.43	2.18	1.62	0.59	0.07	-27.68	9.29

5.A.5.1 Transport mechanism

The transport properties of polymeric membranes can be checked by using the empirical equation [38, 39]:

$$\text{Log}\,(Q_t/Q_\infty) = \log k + n \log t \quad \text{---------------------------------} \quad (5.6)$$

The slope of the plot log (Q_t/Q_∞) vs. log t gives the value of n, which determines the diffusion mechanism, and its y-intercept is the value of k, which depends upon the structure of the polymer as well as its interaction with the solvent. According to the n values obtained from the above equation, three basic modes of transport are distinguished (section 2.3.2.1). Table 5.A.6 presents the ‘n’ and ‘k’ values of the carbon black-filled NR vulcanizates, in toluene. From the ‘n’ and ‘k’ values of the vulcanizates, it is inferred that the gum vulcanizate and carbon black-filled NR vulcanizates exhibit anomalous behaviour. The longer time taken by the rubber segments to accommodate the solvent molecules may be the reason for the deviations of the NR vulcanizates from the Fickian sorption behaviour. Moreover, the reinforcement with the filler particle imparts a high degree of restriction to the rearrangement of rubber chains and to the diffusion of solvent molecules. These may be the reasons for the vulcanizates showing anomalous behaviour [40]. The low ‘k’ values of the vulcanizates indicate poor polymer-solvent interaction.

5.A.6 Fluid resistance

The fluid resistance of the samples were carried out in diesel and lube oil according to the ASTM D 471. The percentage change in mass for the gum vulcanizate and the vulcanizates containing carbon black is as shown in Table 5.A.7.

Table 5.A.7 Change in mass (%) of the vulcanizates in diesel and lube oil

Sample	Change in mass (%)	
	Diesel	Lube oil
C_0	225	98
CB_1	197	76
CB_2	177	73
CB_3	155	72
CB_4	150	71

Addition of carbon black filler has decreased the percentage swelling of the vulcanizates in diesel and lube oil as a result of improved rubber-filler interactions. This can be explained in terms of the fact that improved rubber-filler interactions make the fluid transport path more tortuous thereby reducing the net available transport area. It was also observed that the change in mass (%) of the vulcanizates is much lower in lube oil than in the diesel oil. It may be due to the high viscosity of lube oil.

5.A.7 Assessment of rubber-filler interactions

5.A.7.1 Strain-sweep studies

The complex modulus (G*) values obtained for the uncured and cured compounds are shown in Figures 5.A.10 and 5.A.11. The elastic modulus of a filled rubber is strongly dependent on the deformation and decreases substantially at higher strains. This phenomenon is known as the Payne effect and is attributed to the breakdown of the filler network present in the compound during deformation. But investigations performed with both experimental and theoretical approaches has proved that the decrease in G* with amplitude of deformation (strain) is attributed to the destruction and reformation of the percolating network of the filler that can also involve polymer-filler bond formation [41].

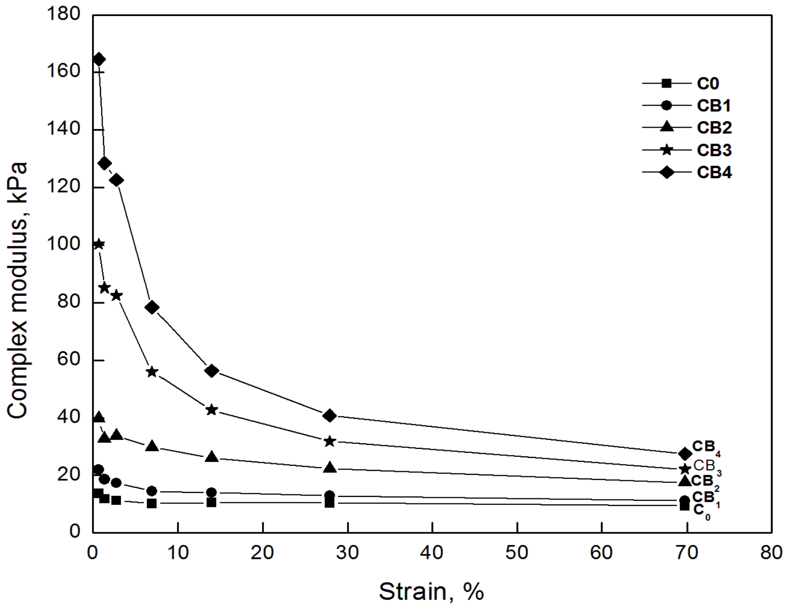


Figure 5.A.10 Dependence of complex modulus (G*) on strain amplitude of uncured carbon black-filled natural rubber compounds at different loadings

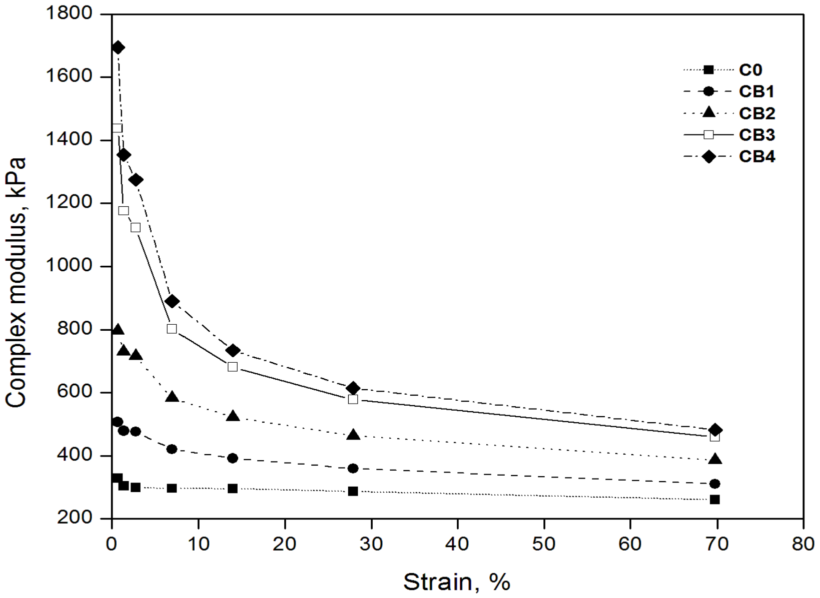


Figure 5.A.11 Dependence of complex modulus (G*) on strain amplitude of cured carbon black-filled natural rubber compounds at different loadings

The complex modulus values at low strains (15 %) are a measure of the filler-polymer interactions [42]. The limiting values at high strains are due to polymer network formation and hydrodynamic effect. Polymer networks are the same for a fixed mass of rubber. But the hydrodynamic effect varies with nature and amount of the filler. The theoretical meaning of hydrodynamic effect is given by the modified form of Guth and Gold equation [43, 44]. The addition of filler increases the shear modulus of the pure elastomer, G_0 and results in a shear modulus, G_f for the filled compound.

$$G_f = G_0\,(1+ 0.67f_s\varphi + 11.62f_s^2\varphi^2) \quad \text{-------------------------} \quad (5.7)$$

where φ is the volume fraction of the particles and the shape factor f_s represents the ratio of the longest dimension to the shortest dimension of the particle. The modulus was calculated by the equation independent of the applied strain [45].

5.A.7.2 Bound rubber content

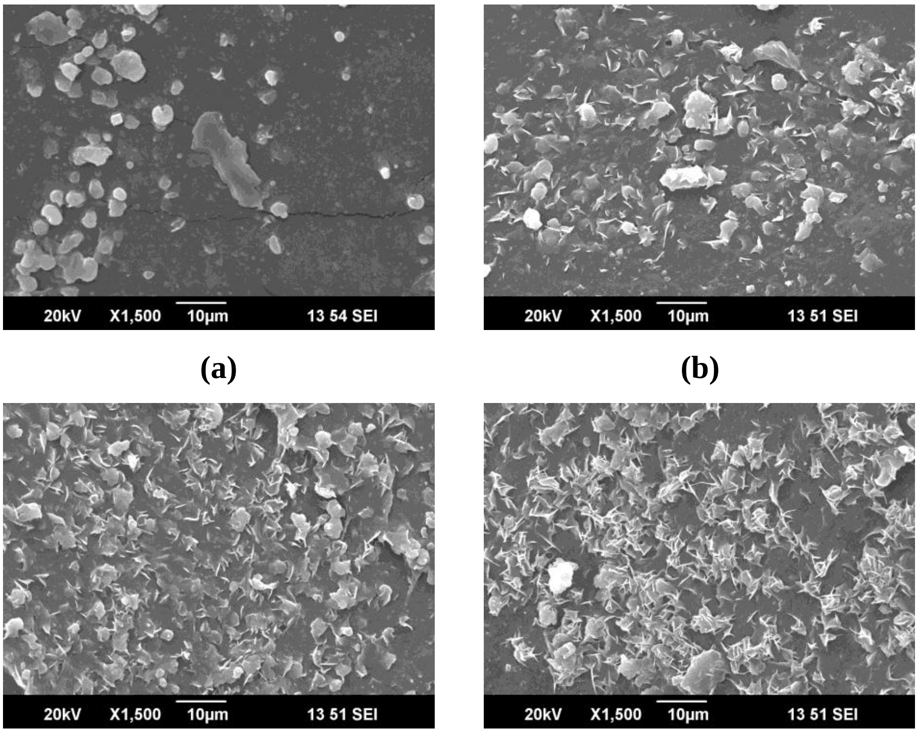
Assessment of the bound rubber content is an indirect method to study the elastomer-filler interactions since bound rubber is essentially the gel formed in the filled rubber compounds due to rubber-filler interactions [46, 47]. The gel formed due to polymer-polymer crosslinking is not considered as bound rubber. Bound rubber of the uncured masterbatches determined by swelling measurements is shown in the Table 5.A.8.

The mechanism of formation of bound rubber is not very clear [48, 49]. The bound rubber content depends on characteristics of filler such as its surface area, structure and surface activity. When the rubber-filler interactions are increased, the bound rubber content also proportionately increases. In our case also, the bound rubber content showed considerable increment with carbon black loading indicating an improved rubber-filler interaction.

Table 5.A.8 Bound rubber contents of uncured masterbatches

Sample	**Bound rubber content, %**
CB_1	38.81
CB_2	40.72
CB_3	43.82
CB_4	49.72

5.A.8 Scanning electron microscopy



(a) **(b)**

(c) **(d)**

Figure 5.A.12 SEM images of fractured surface of tensile samples of CB_1, CB_2, CB_3 and CB_4

SEM micrographs of fractured surfaces of tensile samples of the carbon black-filled vulcanizates are shown in Figure 5.A.12. As it can be seen, CB_1 and CB_2 samples do not show good dispersion and distribution of carbon black particles within the matrix. In the case of vulcanizates containing 40 phr carbon black (CB_3), the particles were dispersed more uniformly than that of CB_4 vulcanizates with 50 phr loading of carbon black. This may be due to the greater rubber-filler interactions present in the vulcanizate CB_3.

5.A.9 Thermogravimetric analysis (TGA)

The TGA and DTG mass loss curves of the samples of natural rubber vulcanizates is as shown in the Figure 5.A.13 and Figure 5.A.14 respectively. The temperature onset of degradation (T_i), the temperature at which the rate of decomposition is maximum (T_{max}), the decomposition temperature at 50 % weight loss T_{50} and weight loss (%) at 500 °C are given in Table 5.A.9. The initial decomposition temperature is used to predict the thermal stability of the rubber vulcanizates.

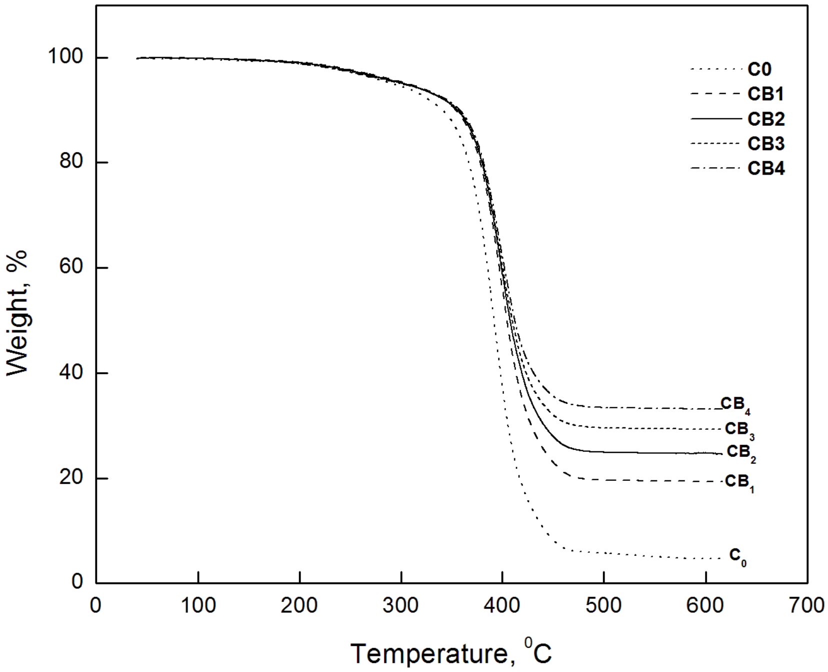


Figure 5.A.13 The thermograms of gum and carbon black-filled natural rubber vulcanizates

As it can be seen in Figure 5.A.13, the degradation of gum vulcanizate started at 341 °C. Hence the sample can be considered as stable up to 341 °C in nitrogen atmosphere. In the case of 20 phr carbon black-filled vulcanizates the degradation started at around 354 °C and gets completed almost at 475 °C.

The onset of degradation showed a slight shift to higher temperatures on further increasing the filler content. The maximum decomposition temperatures of all the compounds were similar as they contain the same type of elastomer.

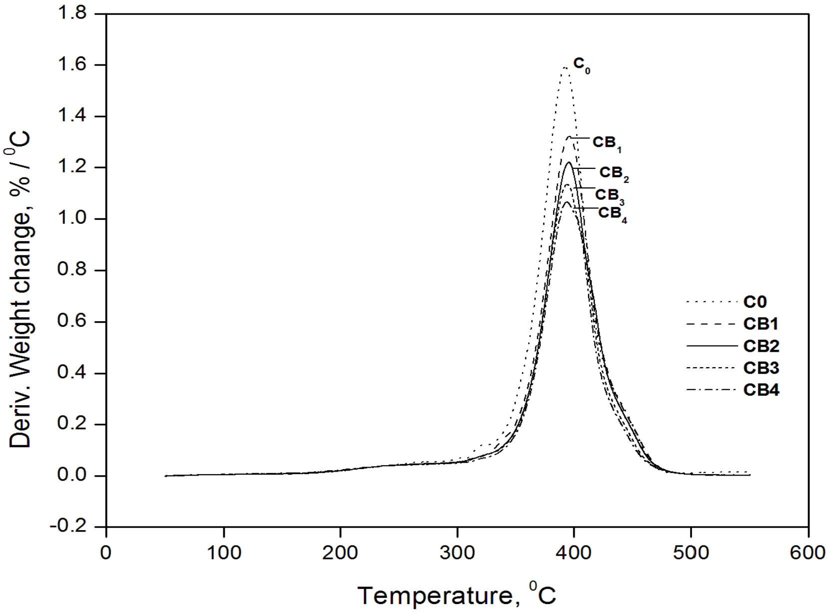


Figure 5.A.14 The derivative thermograms of gum and carbon black-filled natural rubber vulcanizates

The peak of the DTG curve gives the temperature of maximum degradation (T_{max}). T_{max} of the gum vulcanizate was obtained at 393 °C. The thermal degradation of the rubber results in the scission of crosslinking network and the chain cleavage, which in turn decreases the crosslink density and molecular weight of the vulcanizate. This reduces the mechanical strength and application value of the rubbers.

It can be seen from Table 5.A.9 that degradation temperature corresponding to 50 % weight loss increases gradually with the addition of carbon black in the vulcanizate. At 500 °C, the percentage of weight retained is higher for the carbon black-filled vulcanizates. As the percentage of the carbon black in the vulcanizate increased, a gradual decrease of weight loss at 500 °C was noticed. This confirmed the improved thermal stability of the vulcanizates upon incorporation of carbon black which resulted from the strong interactions between the dispersed carbon black particles and rubber molecules.

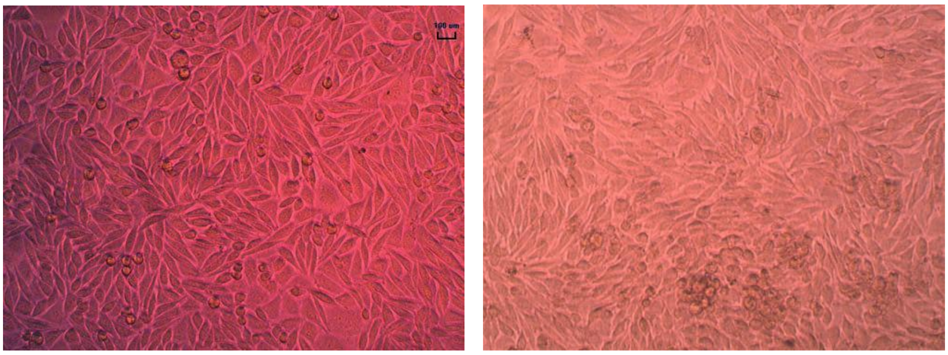
Table 5.A.9 Thermogram data of gum and carbon black-filled NR vulcanizates

Sample	T_i (°C)	T_{50} (°C)	T_{max} (°C)	Weight loss at 500 °C (%)
C_0	341	392	393	94.3
CB_1	354	401	395	80.4
CB_2	355	404	395	75.1
CB_3	356	406	394	70.4
CB_4	358	408	393	66.5

5.A.10 Cytotoxicity of the carbon black-filled NR vulcanizate

Phase contrast images were taken for determination of cell morphology of control of MTT assay and confluent cells containing extract of carbon black-filled NR vulcanizate (CB_3) as shown in Figure 5.A.15. Control of the assay displayed large number of elongated viable cells (fibroblast cells) after 24 hours incubation. But in the case of the confluent cells containing the extract of carbon black-filled vulcanizate, a small reduction in the number of viable cells was observed.

The optical density of the carbon black-filled vulcanizate was lower than the control cells indicating a reduction in the number of sustainable cells. The sample containing extract of CB_3 (NR vulcanizate containing carbon black) possessed 83.15 % of viable cells. It was evident from the MTT assay that the natural rubber vulcanizates filled with carbon black are safe to use and non-cytotoxic [50, 51].



(a) (b)

Figure 5.A.15 Phase contrast image (magnification 20 x) for determination of cell morphology of: (a) control of the MTT assay (b) extract of carbon black-filled NR vulcanizate (CB_3)

5.A.11 Summary

Safe accelerators incorporated natural rubber compounds prepared with various dosages of carbon black shows lower scorch time and longer optimum cure time as compared to the corresponding gum compound. The optimum cure time decreased with filler loading. An increase in maximum torque with increase in carbon black content was also observed in the case of the black filled vulcanizates. The cure reaction for the carbon black-filled natural rubber compounds followed first order kinetics. In the presence of carbon black-filled compounds, cure rate index increased up to 40 phr loading, beyond which, the value decreased. Natural rubber vulcanizates with desired mechanical properties can be obtained with the incorporation of carbon black. The tear and abrasion resistance of the vulcanizates were enhanced with carbon black loading. Among the filled vulcanizates, better tensile strength was observed for CB_3 vulcanizate indicating increased interaction between the filler and rubber at 40 phr of carbon black loading. The percentage of compression set value was also lower at this loading. Permeation, diffusion and sorption coefficients of NR vulcanizates decreased as the filler loading increased. SEM images confirmed the proper dispersion of the filler in the CB_3 vulcanizates. TGA results proved the better thermal stability of carbon black-filled vulcanizates. Thermal stability of the vulcanizates increased as the carbon black dosage increased. Non-cytotoxic nature of the carbon black-filled vulcanizate was proved by the MTT assay. In short, safe carbon black-filled NR vulcanizate at 40 phr loading showed optimum mechanical properties.

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PART B

EFFECT OF PRECIPITATED SILICA ON PROPERTIES OF SAFE NATURAL RUBBER VULCANIZATES

Contents

Natural rubber vulcanizates containing various loadings of precipitated silica were prepared and their bound rubber content was determined from the corresponding masterbatches. Cure characteristics, cure kinetics and strain-sweep analysis of the mixes were studied after incorporating safe (non-regulated) curatives. Mechanical properties, effect of thermal ageing, sorption characteristics, fluid resistance, scanning electron microscopy (SEM), thermogravimetric analyses (TGA) and cytotoxicity test of the vulcanizates were evaluated.

5.B.1 Introduction

In hydrocarbon rubbers carbon black provides high strength, wear resistance and durability. Among non-black reinforcing fillers, precipitated silica holds a supreme position with reinforcing properties closer to carbon black. Silica has extremely reactive surface and fine particle size as that of carbon black. One distinct advantage imparted by silica to many rubbers is the increased resistance to air ageing at elevated temperatures [1]. Precipitated silica is one of the most promising alternatives to carbon black, as silica reduces the rolling resistance in automobile tyres and hence helps to reduce fuel consumption [2]. So silica has evolved as a material of greater importance in tyre industry. Though silica in rubber offers high strength, it is accompanied by processing problems such as high viscosity, cure retardation and compound stiffness. Addition of glycols, amines or guanidines to silica compounds can overcome its cure retarding effect [3]. For a filler to be effective in rubber as a reinforcing agent, it has to be well dispersed. It should also create large rubber-filler interface with good interfacial adhesion. Filler dispersion depends on the balance between two opposing interactions viz., (i) filler-filler interactions that keep filler particles in agglomerate or aggregate form and (ii) filler-matrix interactions, which in turn, depend on the surface energies of the rubber and filler [4]. The latter mentioned chemical compatibility between rubber and filler has been identified as an important factor in achieving a fine dispersion of filler in rubber [5].

Chemical nature of the rubber can also determine the level of filler reinforcement. Reinforcement by filler is achieved generally by the immobilization of polymer segments bonded on the filler surface [6]. Silica produces greater reinforcement in polar elastomers such as NBR, CR, etc. [3]. In acrylonitrile butadiene rubber, strong specific interaction of the acrylonitrile group (ACN) with the silica surface groups result in increased polymer-filler interaction and less filler networking [7].

The influence of silica in safe TBzTD-TBBS based NR vulcanizates is discussed in this chapter. Since the dispersion of silica is difficult in NR, its higher loadings were not used in the present work.

5.B.2 Preparation of silica-filled NR compounds

Formulations used for the preparation of the compounds are given in the Table 5.B.1. Experimental procedures are presented in section 2.2.1. Compounds with various loadings of precipitated silica from 10 to 25 phr were prepared on a two-roll mixing mill. When silica is used as filler in rubber compounds, the polar silanol groups on the surface of the filler can form hydrogen bond with the basic accelerators and can reduce the amount of accelerator added initially. This usually results in undesirable long cure times and slow cure rates. So in order to normalise the cure rate, diethylene glycol (DEG) (5 % of total weight of silica taken) was also added in the compound preparation.

Table 5.B.1 Formulations of the mixes containing precipitated silica

Ingredients	**C_0**	**S_1**	**S_2**	**S_3**	**S_4**
NR (g)	100	100	100	100	100
ZnO (phr)	5.0	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0	1.0
Precipitataed silica (phr)	-	10	15	20	25
DEG (phr)	-	0.5	0.75	1.0	1.25
TBBS (phr)	1.5	1.5	1.5	1.5	1.5
TBzTD (phr)	2.2	2.2	2.2	2.2	2.2
Sulphur (phr)	0.3	0.3	0.3	0.3	0.3

Compared to carbon black, silica creates many mixing problems. Silica has a stronger tendency to agglomerate, difficult to disperse in non-polar rubber and rapidly reagglomerates after mixing [8, 9]. To obtain a fine dispersion of silica in the rubber, higher shear stress is required. But high shear stress can result in excessive energy dissipation in the compound, causing substantial rise in the compound temperature. According to Boonstra and Medalia [10] the total filled volume should include not only the filler but also the rubber that is occluded within the agglomerates. During the dispersive mixing stage, these agglomerates are broken down, the amount of occluded rubber decreases, and thus the filled volume decreases, leading to lower viscosity [11-14].

5.B.3 Cure characteristics

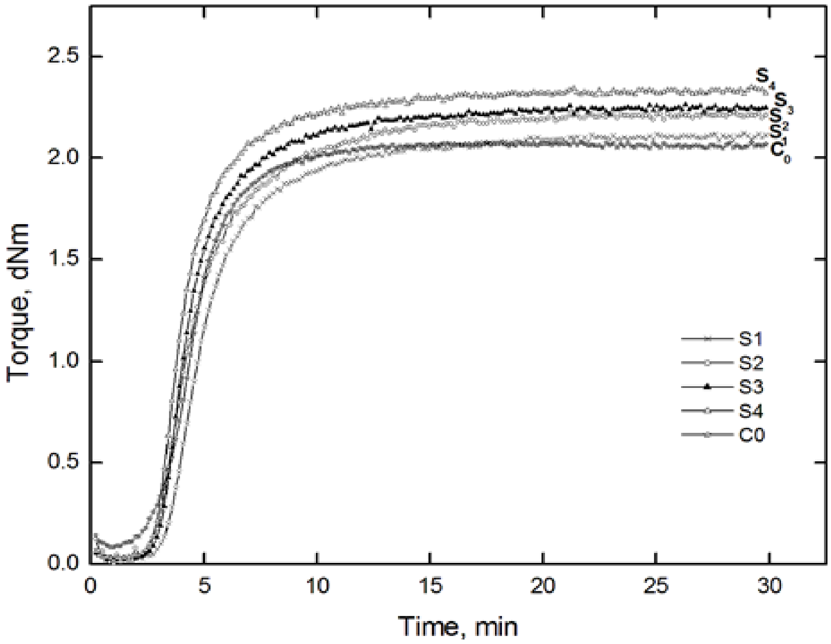


Figure 5.B.1 Rheographs of the gum and silica-filled NR compounds

Silica-filled rubber compounds showed more scorch safety than gum compound as shown in the Table 5.B.2. But t_{10} slightly decreased as the dosage of silica was increased. This may be due to the restriction of the chain mobility and deformability of the rubber on further addition of silica.

Table 5.B.2 Cure characteristics of gum and silica-filled NR compounds at 150 °C

Properties	**C_0**	**S_1**	**S_2**	**S_3**	**S_4**
Scorch time t_{10} (min)	2.89	3.51	3.24	3.19	2.98
Optimum cure time t_{90} (min)	7.17	9.46	9.12	8.14	7.70
Cure Rate Index (CRI, min^{-1})	23.36	16.81	17.01	20.20	21.19
Minimum torque (M_L, dNm)	0.08	0.01	0.04	0.02	0.02
Maximum torque (M_H, dNm)	2.08	2.12	2.22	2.27	2.35
$M_H - M_L$ (dNm)	2.00	2.11	2.18	2.25	2.33
Relative increase in torque (α_r)	-	0.06	0.09	0.13	0.17

Cure characteristics of the gum and silica-filled NR compounds are given in Table 5.B.2. Optimum cure times of silica-filled compounds are higher compared to the gum compound. The incorporation of silica to the NR has also decreased the vulcanization rate due to the adsorption of curatives onto the surface of silica. Moreover silica being highly polar is incompatible with the non-polar natural rubber. Studies on silica-filled sulphur cured NR compounds have shown that the presence of moisture on the filler surface detrimentally affects the scorch and cure times of these compounds. Even a lower level of moisture can prolong the cure times significantly [3].

It can be observed from Table 5.B.2 that optimum cure time exhibits a decreasing trend as the amount of silica increases from 10 to 25 phr. However, the cure rate index was lower than the gum compound and increased gradually as the dosage of silica increased.

The maximum torque developed was less in silica-filled natural rubber compounds compared to carbon black-filled natural rubber compounds (See Table 5.B.2 and Table 5.A.2). As the silica loading increased, the maximum torque value was also increased. The increase in maximum torque can occur for either of the following two reasons: (1) increase in some physical crosslinks or reinforcement with increase in silica loading or (2) the fillers may form agglomerates which ultimately increase the stiffness of the compound.

5.B.3.1 Cure kinetics

The plot of ln (M_H – M_t) against time ‘t’ of silica-filled NR compounds at 150 °C is as shown in Figure 5.B.2. The plots were found to be linear which proved the first-order kinetics of the cure reactions. The cure reaction rate constant can be obtained from the slope of the corresponding straight lines.

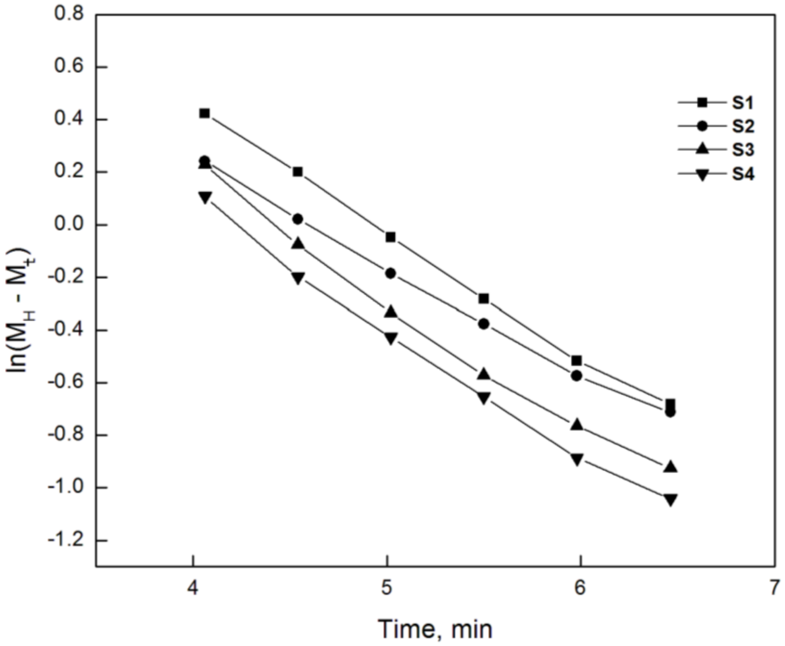


Figure 5.B.2 Plot of ln(M_H – M_t) versus time of silica-filled NR compounds

5.B.3.2 Westlinning-Wolff’s equation

Maximum torque during vulcanization increased as the filler dosage increased in the case of silica-filled compounds. Figure 5.B.3 represents the relation between $M_H - M_L$ against filler loading of the safe natural rubber compounds. The increase in differential torque indicates that the incorporation of silica has affected the crosslinking between the polymer chains.

The plot (Figure 5.B.4) of the relative increase in torque versus silica loading can be defined by Westlinning-Wolff's equation. The slope (α_f) of this linear plot gives an indication about the filler structure and the network formed due to the silica-rubber interaction. The parameter α_f represents the final structure of the filler as it exists in the vulcanizates after all possible structure breakdowns that occurred during mixing and vulcanization. High α_f indicates good rubber-filler interaction. The relative increase in torque (α_r) has increased with silica loading (Table 5.B.2).

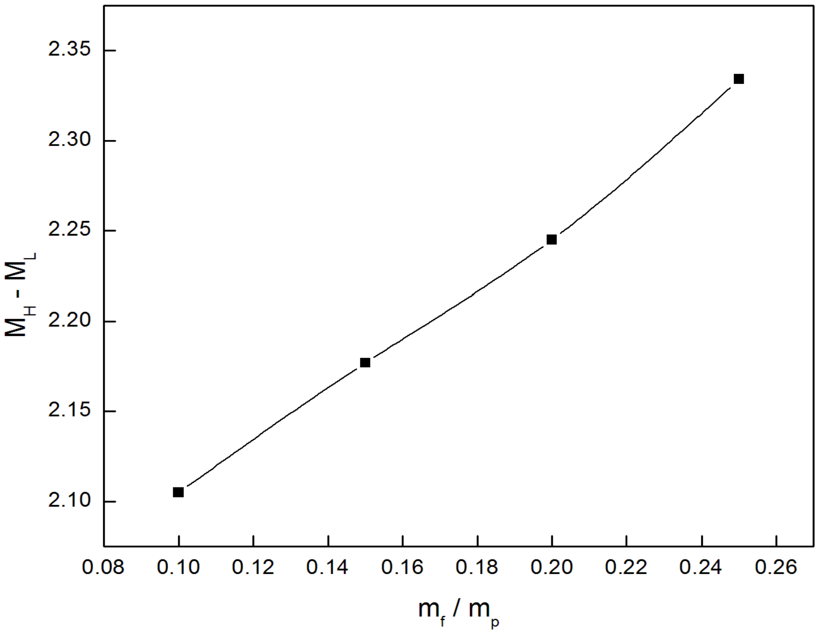


Figure 5.B.3 Plot of differential torque versus silica filler fraction

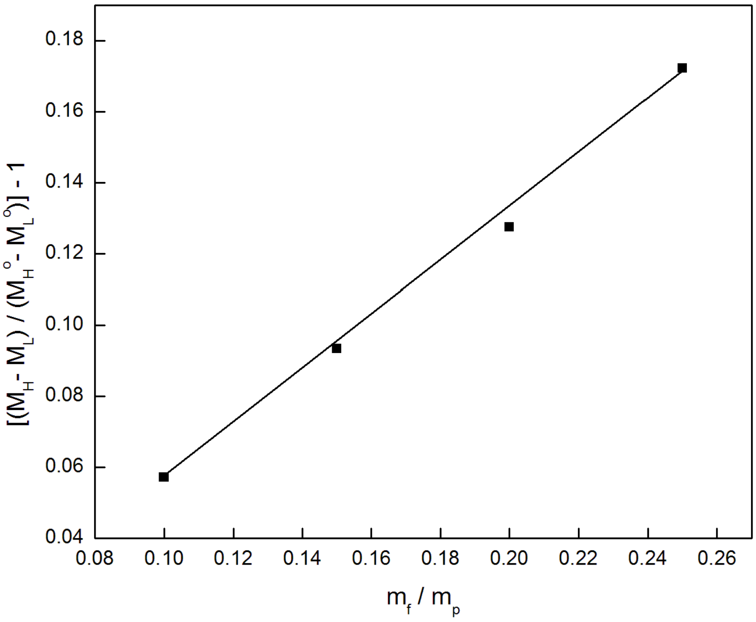


Figure 5.B.4 Plot of relative increase in torque as a function of silica filler fraction

5.B.4 Mechanical properties of the silica-filled NR vulcanizates

Stress-strain curves of the gum and silica-filled NR vulcanizates are shown in Figure 5.B.5. The mechanical properties of the silica-filled vulcanizates are given in Table 5.B.3. High tensile strength was obtained for the vulcanizate with 15 phr of silica loading. But further loadings of silica have resulted in a marginal decrease in the tensile strength due to the agglomeration of the filler particles. Development of high strength was due to the increased ability of NR to dissipate strain energy near the tip of the growing crack by viscoelastic processes in the presence of silica [15]. The dispersed filler particles deflect or arrest growing cracks in addition to providing energy dissipation, thereby delaying the onset of catastrophic failure.

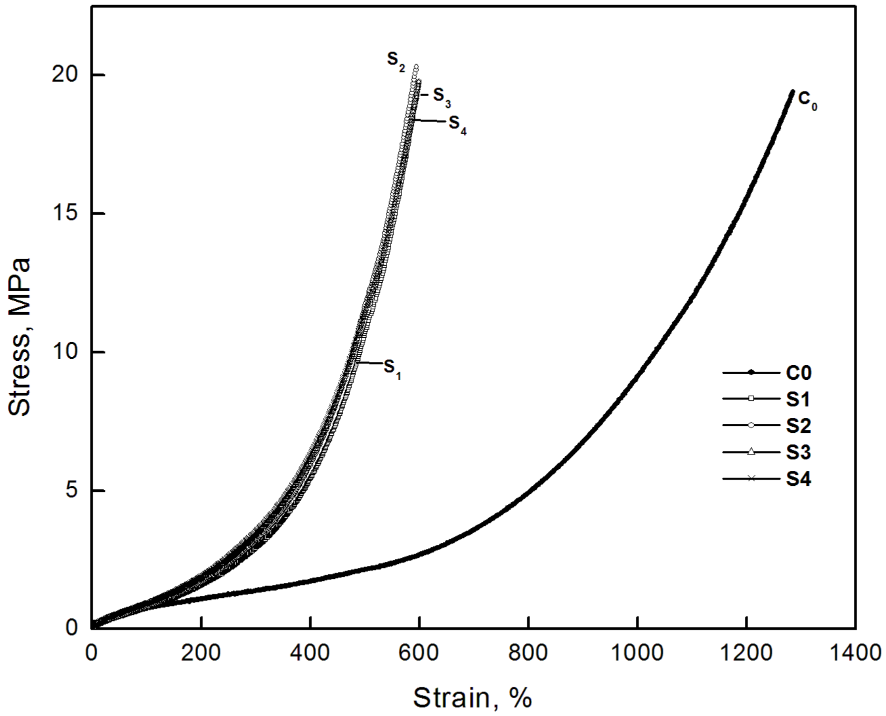


Figure 5.B.5 Stress-strain curves of the gum and silica-filled NR vulcanizates

Generally silica-filled NR vulcanizates show better tear properties [16]. Likewise, the tear strength of the silica-filled safe vulcanizates was higher than the gum vulcanizates and the strength was found to increase proportionally with silica loading. A similar trend was observed in the case of hardness too [15, 16]. This was due to the better interaction of silica particles with NR matrix. It can be seen from the table that the tensile strength and elongation at break changed only marginally with increased loading of silica. The modulus at 300 % elongation increased significantly as the filler was added. The modulus improved further as the loading of the filler increased.

Table 5.B.3 Properties of the gum and silica-filled natural rubber vulcanizates

Properties	**C_0**	**S_1**	**S_2**	**S_3**	**S_4**
Tensile strength (MPa)	19.55	19.74	20.30	19.77	19.68
Modulus at 300 % elongation (MPa)	1.46	2.95	3.19	3.48	3.56
Elongation at break (%)	1230	599	595	598	598
Tear strength (N/mm)	26.71	30.08	31.90	32.08	33.28
Hardness (Shore A)	31	33	35	37	39
Compression set (%)	15.05	20.45	23.90	27.80	31.3
Rebound resilience (%)	65	60	60	59	59
Crosslink density x10^5 (mol/g rubber hydrocarbon)	4.38	4.39	4.91	4.89	4.83
Molar mass between crosslinks (g/mol)	11416	11390	10183	10225	10352
Swelling index	4.10	4.07	3.71	3.76	4.00
Abrasion loss (cc/h)	-	11.01	10.96	10.94	10.93

Modulus is the resistance of the elastomer to a given elongating force. Compared to unfilled NR vulcanizate, 10 phr silica-filled vulcanizate showed 100 % higher tensile modulus. This can be attributed to the establishment of additional crosslinks between NR and silica which in turn imposed greater resistance to elongation [17]. As the filler content increases the stiffness of the rubber increases due to greater interaction between free polymer chain ends and filler. This interaction between polymer and silica has also increased the hardness of the rubber. On the contrary, the rebound resilience of silica-filled vulcanizates decreased marginally as the dosage of the filler was increased since the increased polymer-filler interactions cause hindrances to polymer chain mobility.

Compression set values was higher for the silica-filled NR vulcanizates as compared to the gum vulcanizate. Compression set increased as the filler loading increased. It was concluded that the crosslinks which might have formed between the rubber and silica had little or no effect on the chains movement within the bulk of the rubber. This may adversely affect the elastic properties especially at elevated temperatures and the compression set was affected mainly by the formation of crosslinks between the rubber chains [18]. The compression set of the silica-filled vulcanizates kept on increasing with the filler loading since their elastic recovery was decreased continuously with increase in silica loading.

There was notable reduction in the abrasion loss of the silica-filled compounds with increase in silica loading. Reinforcing fillers like silica interact preferentially with the natural rubber phase and probably the reduced abrasion loss was due to the better silica-rubber interfacial interactions [19, 20].

Reinforcing fillers like carbon black are known to have significant effect on the network structure of filled vulcanizates while semi-reinforcing fillers such as silica do not have similar effect on rubber-network [21, 22]. Moreover, reports show that silica causes a reduction in crosslinking efficiency in accelerated sulphur systems, which may be due to the adsorption of accelerator by the filler itself [23]. Crosslink density values are as shown in the Table 5.B.3. As expected the crosslink density values was in accordance with the tensile strength values. Crosslink density values showed an infinitesimal increase up to 15 phr filler loading and above it no further increment was noticed apparently due to the poor dispersion of silica. The swelling of rubber in a solvent is affected by the incorporation of filler. The swelling indices of the silica-filled vulcanizates in toluene was reduced marginally upto 15 phr silica loading in proportion with the increment in crosslink density.

The results presented above indicated 15 phr as the optimum concentration of precipitated silica for the preparation of silica-filled safe accelerator incorporated NR vulcanizates.

Thermo-oxidative ageing of the unfilled and silica-filled NR vulcanizates was carried out at temperatures of 70 °C and 100 °C for 24 hours as per ASTM D 573 and the results are shown in Table 5.B.4.

Table 5.B.4 Stress-strain properties of the unfilled and silica-filled NR vulcanizates after ageing at 70 °C and 100 °C for 24 hours

Sample	Tensile strength (MPa)			Modulus at 300 % elongation (MPa)			Elongation at break (%)		
	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C
C_0	19.55	20.64	19.19	1.46	1.62	2.04	1230	1082	906
S_1	19.74	20.25	19.96	2.95	3.02	3.11	599	636	648
S_2	20.30	20.48	20.36	3.19	3.28	3.43	595	606	716
S_3	19.77	20.47	20.01	3.48	3.56	3.69	598	607	726
S_4	19.68	19.74	19.71	3.56	3.73	3.75	598	756	690

The graphical representations of the variation in stress-strain properties after ageing are given in the Figures 5.B.6, 5.B.7 and 5.B.8. During thermal ageing, crosslink formation or crosslink breakage can take place or an existing crosslink may break and get transformed to more stable linkage. The incorporation of silica has not affected the ageing resistance of the vulcanizates but has improved it to a certain extent. Tensile strength and modulus showed increase after 24 hours of ageing at 70 °C and 100 °C may be due to the inherent thermal stability of the efficient vulcanization systems. The increase in modulus may be due to the increased crosslink formation on ageing. Elongation at break of the silica-filled vulcanizates showed increase even after 24 hours of heating at both the temperatures while the gum vulcanizate showed considerable reduction in the elongation at break values after ageing. This may be due to the establishment of more rubber-silica interactions than crosslink scission in the vulcanizates during ageing.

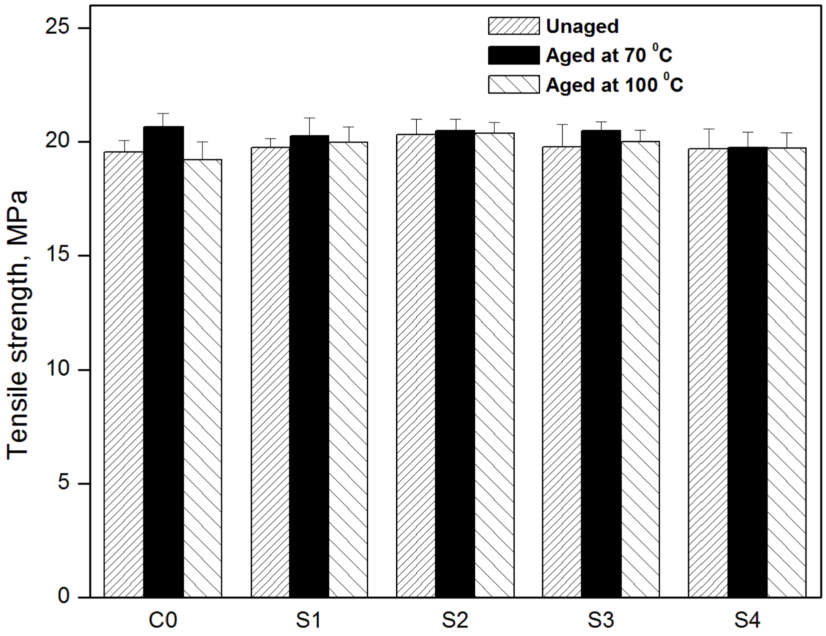


Figure 5.B.6 Variation in tensile strength of the unfilled and silica-filled NR vulcanizates before and after ageing

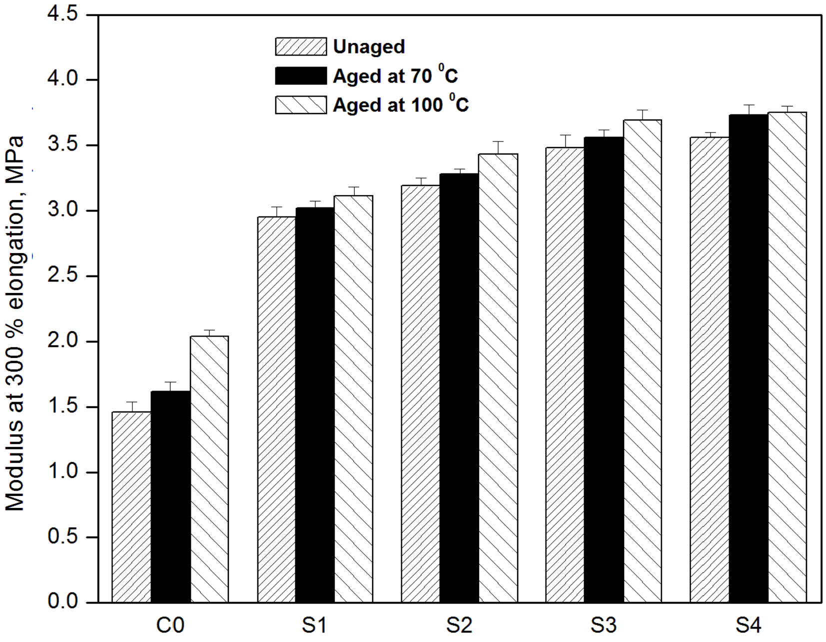


Figure 5.B.7 Variation in modulus at 300 % elongation of the unfilled and silica-filled NR vulcanizates before and after ageing

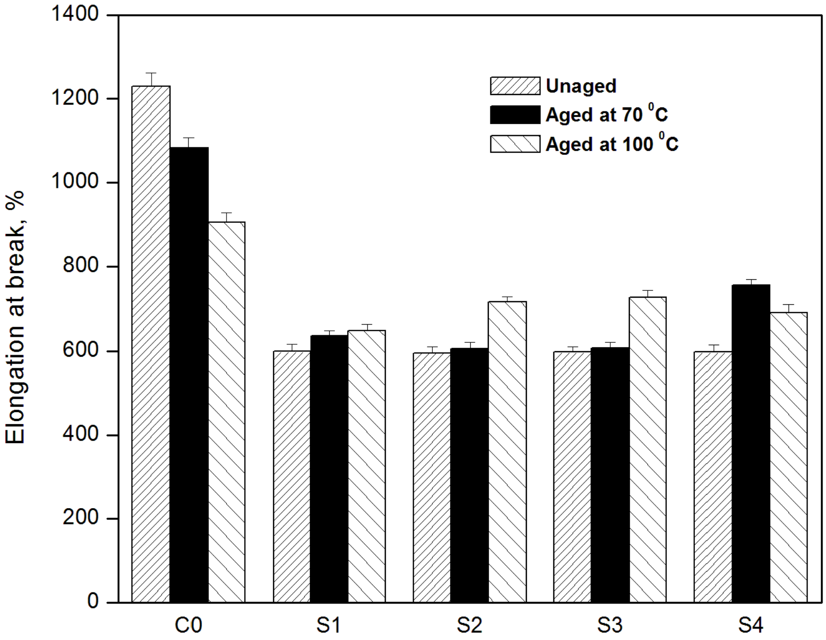


Figure 5.B.8 Variation in elongation at break of the unfilled and silica-filled NR vulcanizates before and after ageing

5.B.5 Sorption studies

Molecular interaction between rubber and filler has a pronounce effect in the polymer reinforcement. This interaction can increase the effective degree of crosslinking which can be measured by equilibrium swelling analyses. Equilibrium swelling analysis of rubber vulcanizate is known to indicate the number of effective network chains per unit volume of rubber.

The swelling percentage is a measurement of the degree of crosslinking. A reduction in the swelling (reduction in solvent uptake) indicates an increase in crosslink density. The diffusion curves for silica-filled and unfilled NR vulcanizates are given in Figure 5.B.9. The curves are plotted as the mole percentage uptake of the penetrant against $t^{1/2}$. Silica-filled NR vulcanizates exhibited reduced swelling than the unfilled vulcanizate. Initial swelling was very high for all the systems. After this the sorption rate decreased leading to a plateau, corresponding to equilibrium swelling.

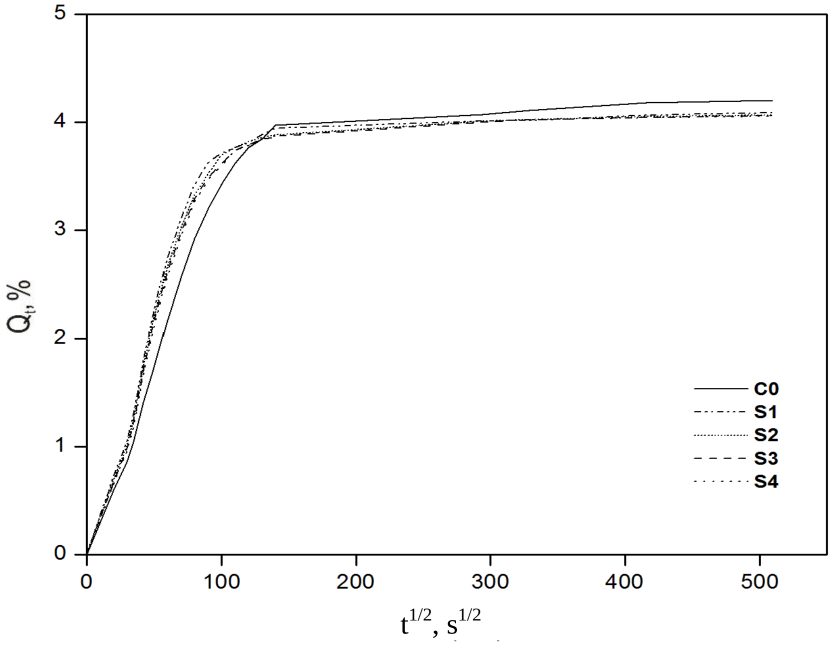


Figure 5.B.9 Q_t vs. $t^{1/2}$ of unfilled and silica-filled NR vulcanizates

Addition of silica particles decreased the swelling rate of NR vulcanizates in toluene. This can be attributed to the restriction of toluene uptake by the introduction of silica. The low swelling rate of silica-filled NR vulcanizates was in good agreement with its improved mechanical properties [24].

Swelling measurements are very useful in measuring the crosslink density of the vulcanizates. In the case of unfilled rubbers, the swelling restriction is due to the crosslinks connecting the polymer chains, but in filled systems filler-polymer interaction also may interfere. The variation of crosslink density with filler loading for the vulcanizates is shown in Table

5.B.3. The crosslink density was found to increase slightly with filler loading and showed high value for 15 phr silica loading.

The process of diffusion is a kinetic parameter related to the penetrant size and to the polymer segment mobility. Table 5.B.5 gives the variation in the diffusion coefficient (D), sorption coefficient (s) and permeation coefficient (P) as a function of filler loading. The unfilled matrix presented the maximum diffusion coefficient of around 8.57 x 10^{-7} cm^2/s. Addition of silica to the natural rubber matrix resulted in a progressive decrease of D value (31 % reduction for 10 phr silica) and decreases with increase in silica content. Thus the silica-filled vulcanizates exhibited lower diffusivity of solvent due to the strong interaction between silica and NR matrix.

It was observed that the permeation coefficient and sorption coefficient also decreased with increase in silica loading. The permeation of a solvent into a polymer membrane depends on the sorptivity and diffusivity of the penetrant in the membrane [25]. The sorption coefficient value was slightly higher for the gum than the filled vulcanizates which reflected a decrease in the volume fraction of absorbing phase (due to introduction of polar silica particles) with increased loading of silica.

Table 5.B.5 Sorption data of the gum and silica-filled NR vulcanizates

Sample	D X 10^7 (cm^2/s)	s	P X 10^6 (cm^2/s)	n	k	ΔG (J/mol)	ΔS X 10^2 (J/mol K)
C_0	8.57	4.03	3.46	0.59	0.05	-11.70	3.93
S_1	5.89	3.77	2.22	0.59	0.07	-13.42	4.50
S_2	5.73	3.76	2.15	0.60	0.06	-14.78	4.96
S_3	5.70	3.75	2.14	0.61	0.06	-15.21	5.10
S_4	5.67	3.74	2.12	0.61	0.06	-15.27	5.12

From the ‘n’ and ‘k’ values it was inferred that gum vulcanizate and silica-filled NR vulcanizates exhibited anomalous behaviour. Thus the observed anomalous diffusion involved the counteraction between the ability of the rubber segments to rearrange in the presence of solvents and the restriction imparted to this by the reinforcing silica particles [26].

Thermodynamic effects occurring during swelling of the elastomer chains were also analysed. Table 5.B.5 demonstrates the influence of the silica loading on the Gibbs free energy (ΔG) and entropy of mixing (ΔS) of the NR vulcanizates swollen in toluene. As ΔG represents the elastic behaviour, the increase in -ΔG for the silica-filled vulcanizates suggested an increased number of possible rearrangements in the NR vulcanizates at high degree of crosslinking. This implies that a typical network structure with good compatibility between silica and rubber was formed in the silica-filled NR vulcanizates. An increase in entropy was obtained for the filled vulcanizates as compared to the gum vulcanizate [27].

5.B.6 Fluid resistance

The percentage change in mass for the gum vulcanizate and the vulcanizates containing silica after swelling in diesel and lube oil for 72 hours is shown in Table 5.B.6.

Table 5.B.6 Change in mass (%) of the vulcanizates after swelling in diesel and lube oil

Sample	Change in mass (%)	
	Diesel	Lube oil
C_0	225	98
S_1	222	92
S_2	220	88
S_3	218	84
S_4	214	81

Enhanced silica-NR interactions have reduced the fluid transport area and apparently the transportation path has become more tortuous. As a result, the percentage swelling after soaking in diesel and lube oil was lower for silica-filled vulcanizates as compared to the unfilled ones.

5.B.7 Scanning electron microscopy

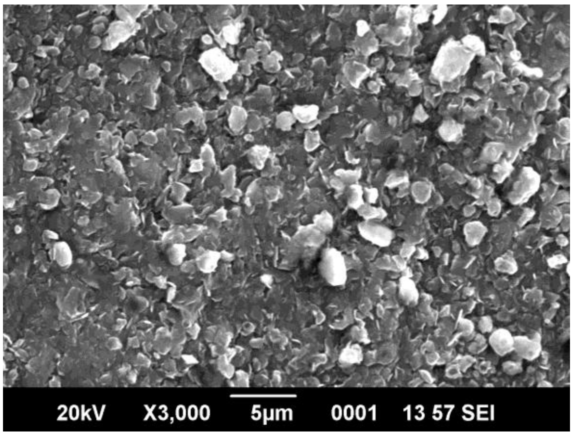


Figure 5.B.10 SEM images of fractured surface of tensile sample containing 15 phr silica

Scanning electron microscopy can be used as a tool to characterise the filler distribution in the rubber matrix. The scanning electron photomicrographs of the fractured surface of tensile sample with 15 phr silica filler is shown in Figure 5.B.10. The SEM photographs show an even distribution of silica in the natural rubber matrix.

5.B.8 Thermogravimetric analysis

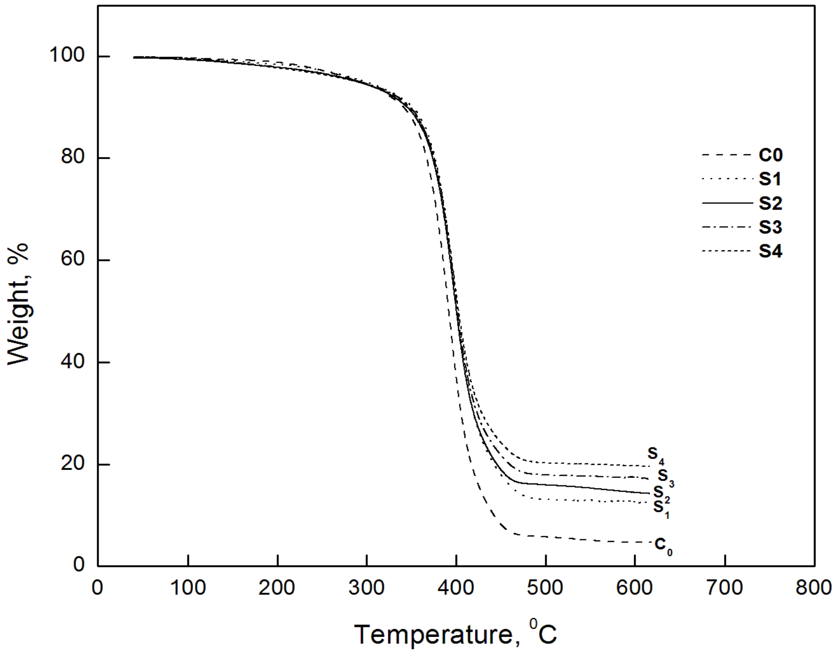


Figure 5.B.11 The thermograms of gum and silica-filled natural rubber vulcanizates

The thermogram and derivative thermogram of silica-filled NR vulcanizates are given in Figure 5.B.11 and 5.B.12 respectively. Analysed thermal data is given in Table 5.B.7. The addition of silica caused a marginal increase in the thermal stability of the elastomer, as evident from TGA thermograms.

Gum natural rubber vulcanizate exhibited maximum degradation (T_{max}) at 393 °C. T_{max} of the silica-filled vulcanizates were almost similar to that of gum vulcanizate. Weight loss at 500 °C was decreased by the addition of silica filler and the loss decreased further on increasing the filler content. The residue percentage (Figure 5.B.11) showed a proportional increment with silica loading.

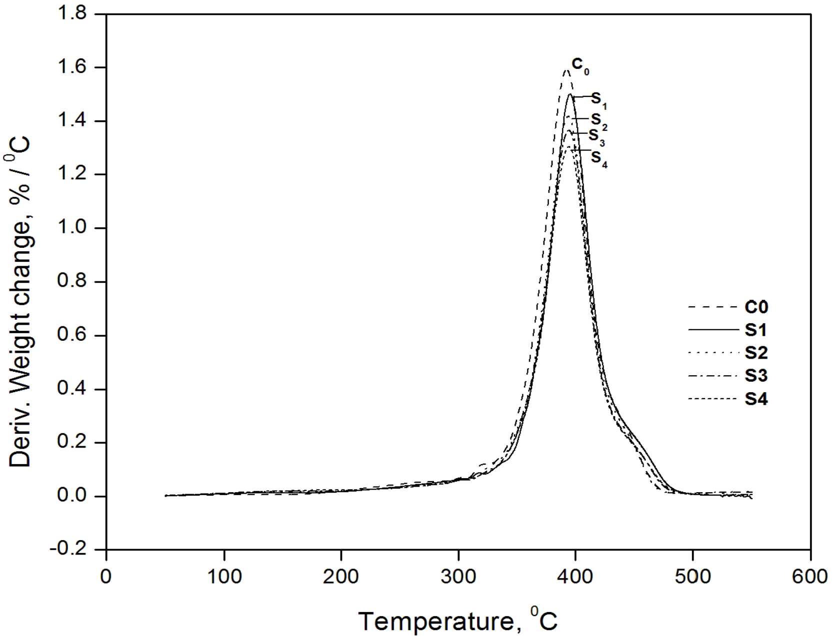


Figure 5.B.12 The derivative thermograms of gum and silica-filled natural rubber vulcanizates

Table 5.B.7 Thermogram data of gum and silica-filled NR vulcanizates

Sample	Ti (°C)	T_{50} (°C)	T_{max} (°C)	Weight loss (%) at 500 °C
C_0	341	392	393	94.3
S_1	351	402	394	86.9
S_2	353	402	394	84.0
S_3	354	402	394	82.1
S_4	358	403	394	79.7

5.B.9 Assessment of rubber-filler interactions

5.B.9.1 Bound rubber content

Bound rubber is the polymer portion that remains bound to the filler when the masterbatches are extracted with a good solvent such as toluene. When immersed in sufficient quantity of toluene, silica-filled NR masterbatches formed a gel in spite of dissolving completely in the solvent. This indicated that the filler-polymer interaction was present to a great extent in the sample containing precipitated silica. The bound rubber content values of the silica-filled NR masterbatches are given in the Table 5.B.8. It is clear from the table that considerable increment in bound rubber was obtained with increased dosage of silica.

Table 5.B.8 Bound rubber content of uncured silica-filled NR masterbatches

Sample	Bound rubber content (%)
S_1	29.15
S_2	30.32
S_3	31.69
S_4	32.30

5.B.9.2 Strain-sweep analysis

Variation of complex modulus (G*) with strain for the uncured and cured compounds with different filler loadings are plotted in Figures 5.B.13 and 5.B.14. From the figures, it is found that the complex modulus (G*) values of silica-filled compounds were higher than the unfilled compounds. The increase in modulus can be credited to the variation in hydrodynamic effect after the inclusion of rigid filler particles in the soft rubber matrix. The elastic modulus of a filled rubber is strongly dependent on its deformation, and it decreases substantially with strain. This phenomenon is known as the Payne effect [28] and is attributed to the breakdown of the formed filler network during deformation. The high values of G* can be due to higher filler-filler or filler-polymer interactions.

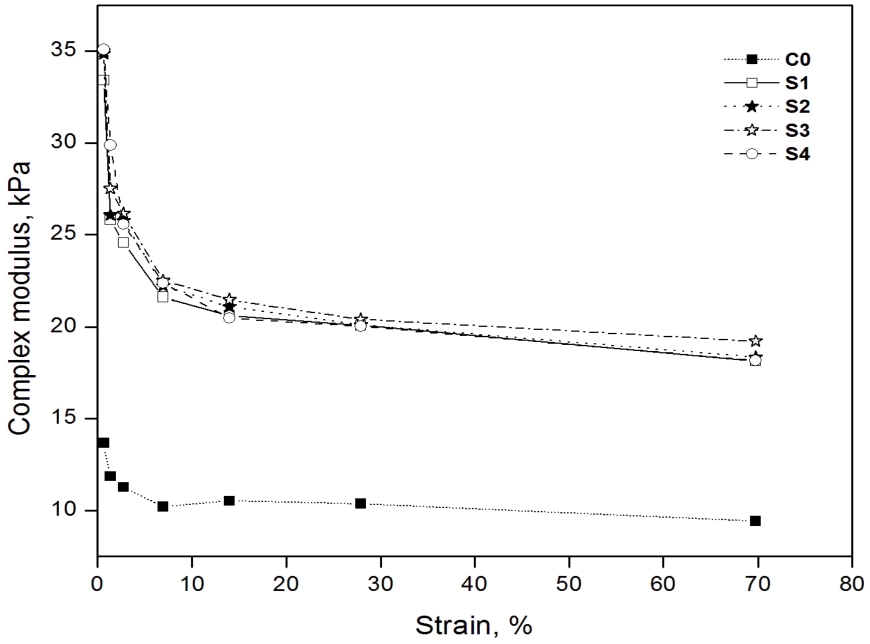


Figure 5.B.13 Dependence of complex modulus (G*) on strain amplitude of uncured silica-filled natural rubber compounds at different loadings

A factor which contributes to the reinforcement of rubber is the formation of filler network. Filler aggregates in the polymer matrix have a tendency to associate and form agglomerates, especially at high loading, leading to chain-like filler structures or clusters which are termed filler networks [29]. This networking is formed by filler-filler interactions in the case of highly polar fillers such as silica, or via strong interactions between filler and rubber in the case of non-polar fillers such as carbon black. Destruction of this networking occurs by the application of strain producing a reduction in complex modulus.

The complex modulus value of the silica-filled compound at low strain ($S_{3,}$ i.e. 35 kPa) was higher when compared with the same quantity of carbon black-filled compound ($CB_{1,}$ i.e. 22 kPa). The reason for this may be that Van der Waals forces are responsible for filler-filler interactions in the case of carbon black but in the case of silica the filler-filler interactions were due to the much stronger hydrogen bonds.

The complex modulus at low strains is high while at high strains (>15 %) it decreases. This can be explained with the help of Payne effect. The Payne effect in filled rubber is a phenomenon of strain dependent dynamic modulus. At low strains the decrease in modulus may be due to the destruction-reformation of the filler network. As the strain increased, the modulus decreased continuously and finally was maintained more or less a constant. This was due to the adsorption-desorption of polymeric chains at the filler interface and subsequent disentanglement of bulk polymer from the rubber bounded to the surface. However a slight reduction in modulus at high strains is accounted to the strain-softening of the polymer in the compounds and it will be present in both the unfilled and filled compounds.

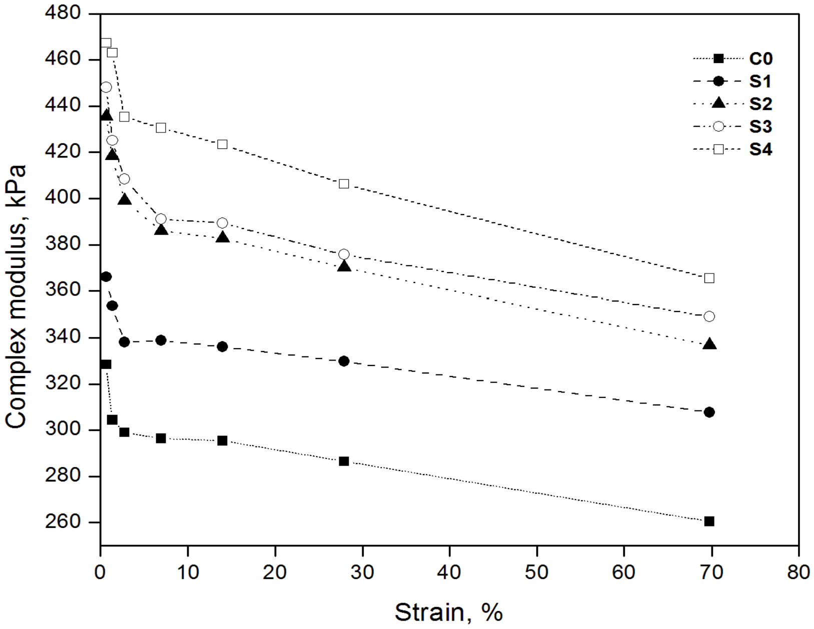


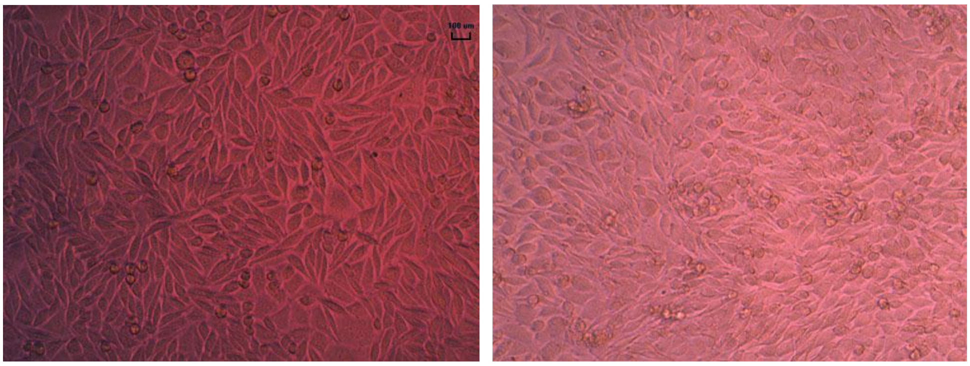
Figure 5.B.14 Dependence of complex modulus (G*) on strain amplitude of cured silica-filled natural rubber compounds at different loadings

The strain sweep studies after curing showed similar trend as that of the uncured compounds. Since the compounds are cured the modulus values were high but the behaviour was the same as that of the uncured compounds. It is seen that the complex modulus at low strains for the silica-filled samples were higher than the unfilled sample and this values increased with increase in the dosage of silica. The higher values of modulus of the cured samples at low strains indicated the improved rubber-filler interactions present in the vulcanizate than in an uncured compound. The complex modulus values at high strains were due to polymer networks formed and its hydrodynamic effect (which is dependent on the particle size and shape of the filler incorporated) [30].

5.B.10 Cytotoxicity of the silica-filled NR vulcanizate

Phase contrast images were taken for determination of cell morphology of control of MTT assay [31] and confluent cells containing extract of S_2 as shown in Figure 5.B.15. In the control, a large number of elongated cells (fibroblast cells) were observed. In the case of the confluent cells containing the extract of silica-filled vulcanizate after 24 hours incubation, a small reduction in the number of viable cells was observed.

The sample containing extract of S_2 (silica-filled NR vulcanizate) contained 81.75 % of viable cells. It was evident from the MTT assay that the natural rubber vulcanizates containing silica were safe to use and are non-cytotoxic [32, 33].



(a) (b)

Figure 5.B.15 Phase contrast image (magnification 20 x) for determination of cell morphology of: (a) control of MTT assay (b) extract of silica-filled NR vulcanizate (S_2)

5.B.11 Summary

Different loadings of precipitated silica were incorporated into the NR formulation containing the safe accelerators. The natural rubber compounds containing silica filler showed more scorch safety than gum compound, but required longer cure times. The cure reactions proceed according to first-order kinetics. Better tensile strength, modulus at 300 % elongation, tear strength and hardness were obtained by the incorporation of silica in the natural rubber compounds. Abrasion loss was reduced with increase in the dosage of silica. From the mechanical property results, optimum mechanical properties were obtained for the 15 phr precipitated silica-filled vulcanizate. Improvement in tensile strength was observed for the silica-filled NR vulcanizates after thermo-oxidative ageing at 70 °C and 100 °C for 24 hours. A reduction in diffusion coefficient, sorption coefficient and permeation coefficient was observed with increase in silica content. Both the gum vulcanizate and silica-filled NR vulcanizates exhibited anomalous transport behaviour. The silica-filled NR vulcanizates showed better fluid resistance in diesel and lube oil compared to the gum vulcanizate. The SEM photographs showed an even distribution of filler in the rubber matrix. The addition of silica caused a marginal increase in the thermal stability of the elastomer. Bound rubber content results indicated predominant polymer-filler interactions in the silica-filled natural rubber masterbatches. Payne effect was explained from the strain-sweep analysis. The MTT assay results confirmed the non-cytotoxicity of the silica-filled natural rubber vulcanizates.

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Chapter 6

EPOXIDISED NATURAL RUBBER - A SUBSTITUTE FOR SILANE COUPLING AGENT IN SAFE SILICA-FILLED NATURAL RUBBER FORMULATIONS

Contents

Part of work presented in this chapter has been communicated to *Polymers for Advanced Technologies.*

Silica-filled natural rubber masterbatches were prepared by incorporating different loadings of silane coupling agent. Bound rubber content of the masterbatches was determined. Cure characteristics and cure kinetics of the compounds prepared from the masterbatches using safe accelerators (TBBS and TBzTD) were studied. The studies on the vulcanizates include measurement of mechanical properties, thermo-oxidative ageing, sorption characteristics, fluid resistance, scanning electron microscopy, thermogravimetric analysis, strain-sweep, dynamic mechanical analysis and cytotoxicity. The role of epoxidised natural rubber (ENR) as a substitute for silane coupling agent too was explored.

6.1 Introduction

Carbon black and silica are the two important reinforcing fillers used in the rubber industry. Unlike carbon black, silica reinforcement of rubbers especially hydrocarbon rubbers suffer from technical difficulties such as poor processability, due to the differences in the surface energies of silica and rubber. Carbon black, which is non-polar, exhibits good rubber-filler interaction whereas silica which is polar, exhibits higher filler-filler interaction rather than good rubber-filler interaction.

Silica has high surface area and high percentage of void volume within the filler particle. As a direct interaction between the filler and the polymer is difficult to achieve, polymer chains can be connected to the filler by physical process only. In polymer-filler mixes polymer is generally trapped in the voids of the filler structure resulting in occluded rubber [1]. During mixing the structure of the filler has to be broken in order to increase the interaction between filler and polymer, thus releasing a part of the occluded rubber. At the same time, the filler should not be broken to the level of primary particles also [2].

Several modifications of silica filler such as heat treatment, chemical modification of the filler surface groups, grafting of polymers on to the filler surface and use of promoters or coupling agents have been reported to improve the rubber-filler interaction [3, 4]. Esterification or alkylation of silica improves its compatibility, wetting and dispersion in hydrocarbon rubbers [3, 5]. Silane modification is the most widely practised technique for improving silica-rubber bonding [6, 7]. The modification of silica with a bifunctional silane during the mixing operation is known as *in situ* modification [8]. *In situ* modification with silane-coupling agent is an effective method to improve silica dispersion and reduce agglomeration of silica particles by chemical interfacial interactions. Natural rubber modified with N-(3-triethoxy silylpropyl)carbamyl azoformate, exhibited improved silica reinforcement [9, 10]. The application of coupling agents is believed to result in the formation of interpenetrating filler-polymer and polymer-polymer networks [11]. However, the high cost of silane is a limitation to its widespread acceptance. One of the widely used silane-coupling agent is bis-(triethoxysilylpropyl)tetrasulfide (TESPT) [4, 12]. Ansarifar and co-workers [13] have examined the effect of treating the silica with TESPT in sulphur-cured NR.

Hydroxy functionalised SBR and epoxy functionalised NBR exhibited improved reinforcement with silica as compared to the unmodified rubber [9, 14]. Silica exhibits good reinforcement in carboxylated nitrile rubber through the carboxyl and silanol entities [15]. Silica exhibits better reinforcement in polydimethyl siloxane due to the interaction between silanol and siloxane groups [16].

Epoxidised natural rubber (ENR) shows polarity and bifunctionality. ENR may be considered as an alternative to silanes. ENR in small proportions has been used as a reinforcing modifier for silica-filled nitrile rubber (NBR) [17].

Part A of this chapter discusses the effect of silane coupling agent (TESPT or Si69) on the properties of silica-filled natural rubber vulcanizates. Part B discusses the effect of epoxidised natural rubber on the properties of silica-filled natural rubber vulcanizates and the feasibility of using ENR as a coupling agent in place of silane in silica-filled NR formulations.

PART A

EFFECT OF SILANE COUPLING AGENT ON PROPERTIES OF SILICA-FILLED NR COMPOUNDS

6.A.1 Preparation of silane modified silica-filled natural rubber compounds

It was concluded from chapter 5 part B that the concentration of silica required to impart optimum mechanical properties to the safe NR vulcanizates is 15 phr. Therefore 15 phr has been selected as the optimum concentration of silica for preparing modified vulcanizates using silane coupling agent.

Silica was incorporated into the masticated natural rubber along with diethylene glycol and silane coupling agent on a two-roll open mill. The mixes were prepared by adding the silane coupling agent at dosages of 8 %, 10 % and 12 % of the weight of silica. Other ingredients were added as per the formulation shown in the Table 6.A.1.

Table 6.A.1 Formulations of the mixes

Ingredients	**S**	**Si_1**	**Si_2**	**Si_3**
NR (g)	100	100	100	100
ZnO (phr)	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0
Precipitated silica (phr)	15	15	15	15
DEG (phr)	0.75	0.75	0.75	0.75
Si69 (phr)	-	1.2	1.5	1.8
TBBS (phr)	1.5	1.5	1.5	1.5
TBzTD (phr)	2.2	2.2	2.2	2.2
Sulphur (phr)	0.3	0.3	0.3	0.3

6.A.2 Cure characteristics

Cure curves of silica-filled NR with and without silane coupling agent are shown in Figure 6.A.1. Silane-treated silica-filled NR compounds show shorter scorch time and cure time (Table 6.A.2). In the case of unmodified silica-filled compounds, silanol groups on silica surface can interact with polar materials such as accelerators resulting in long scorch and cure times.

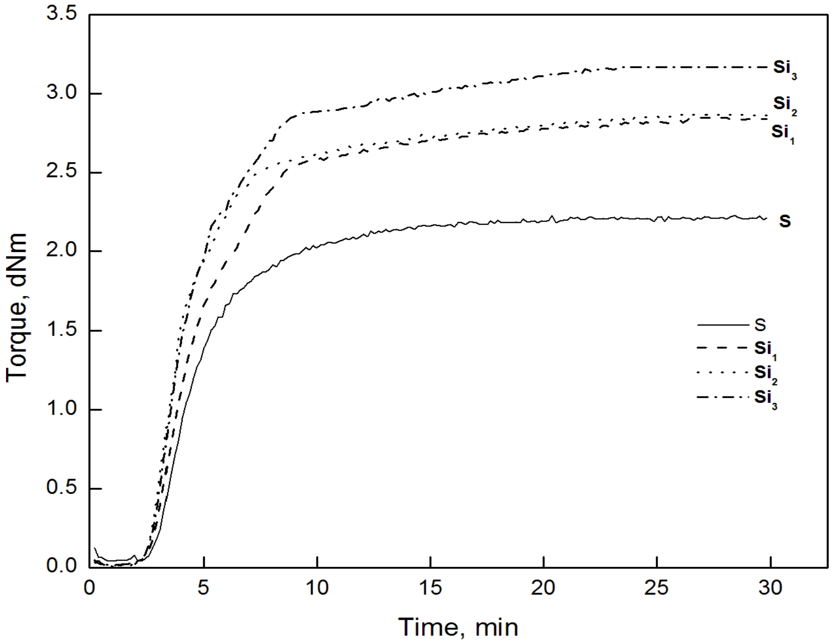


Figure 6.A.1 Rheographs of unmodified and silane modified silica-filled NR compounds

In silane-treated compounds, the ethoxy groups of silane undergoes condensation reaction with silanol groups on silica surface resulting in less adsorption of accelerator [18-21]. Therefore, shorter scorch and cure times are observed in the case of silane modified silica-filled vulcanizates.

Table 6.A.2 Cure characteristics of unmodified and silane modified silica-filled NR compounds at 150 °C

Properties	**S**	**Si_1**	**Si_2**	**Si_3**
Scorch time t_{10} (min)	3.24	2.96	2.79	2.73
Optimum cure time t_{90} (min)	9.12	9.10	9.01	8.94
Maximum torque (M_H, dNm)	2.22	2.83	2.87	3.16
Minimum torque (M_L, dNm)	0.04	0.01	0.009	0.005
$M_H - M_L$ (dNm)	2.18	2.82	2.86	3.16

Addition of silane lowered the minimum torque. The minimum torque is a measure of the stock viscosity. This indicates that the processability of the silane modified compound is better as compared to the unmodified silica-filled compound. As the coupling agent covers the surfaces of the silica particles, it reduces the filler-filler interactions and thus leads to low viscosity [22]. During mixing of a silica-filled rubber compound, the silane coupling agent reacts with the silica resulting in hydrophobation of the silica surface. This hydrophobation reduces the silica-silica network and makes the polar silica more dispersed and compatible with the non-polar rubber.

An increase in maximum torque value is observed when the silica is modified with silane coupling agent. This increase in maximum torque value is a direct measure of the increase in modulus of the vulcanizates. The ΔM value (i.e. $M_H - M_L$) is higher for the compounds with silane treated silica. This is because of the formation of a higher number of crosslinks and better interactions between the filler and the elastomers compared to silica-filled vulcanizate without silane coupling agent.

6.A.2.1 Cure kinetics

The plot of ln (M_H – M_t) versus time of silica-filled natural rubber compounds with and without silane modification is shown in Figure 6.A.2. Straight line plots are obtained for all the compounds confirming that the cure reaction of the samples follow first order kinetics [23, 24].

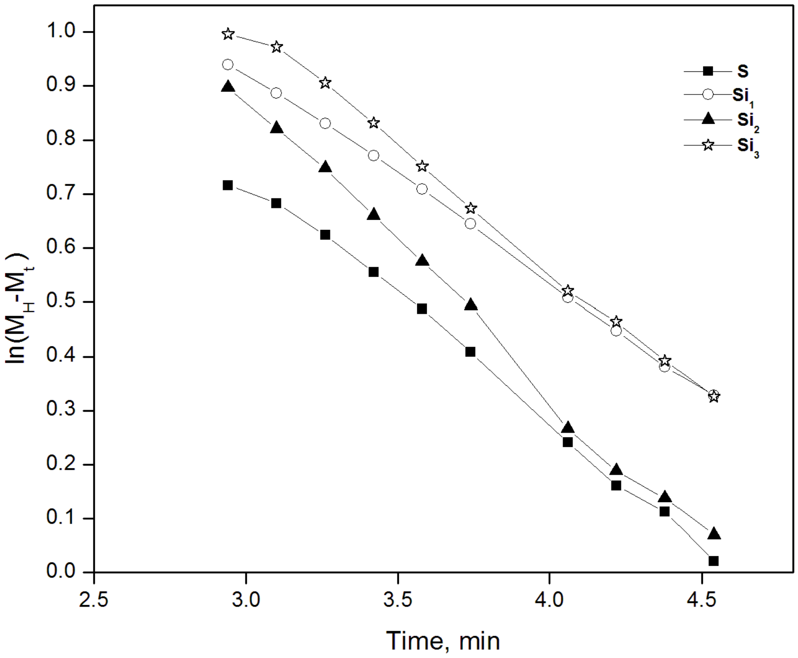


Figure 6.A.2 Plot of ln (M_H – M_t) vs. time for silica-filled NR compounds with and without silane modification

6.A.3 Mechanical properties of silane modified silica-filled NR vulcanizates

The effect of silane coupling agent on the stress-strain properties of the silica-filled NR vulcanizates was studied and is depicted in Figure 6.A.3. Silane modification improved the tensile strength, as can be seen from the

Table 6.A.3. Coupling agent, being a crosslinking agent as well [25], might have contributed to higher crosslink density and improved tensile strength.

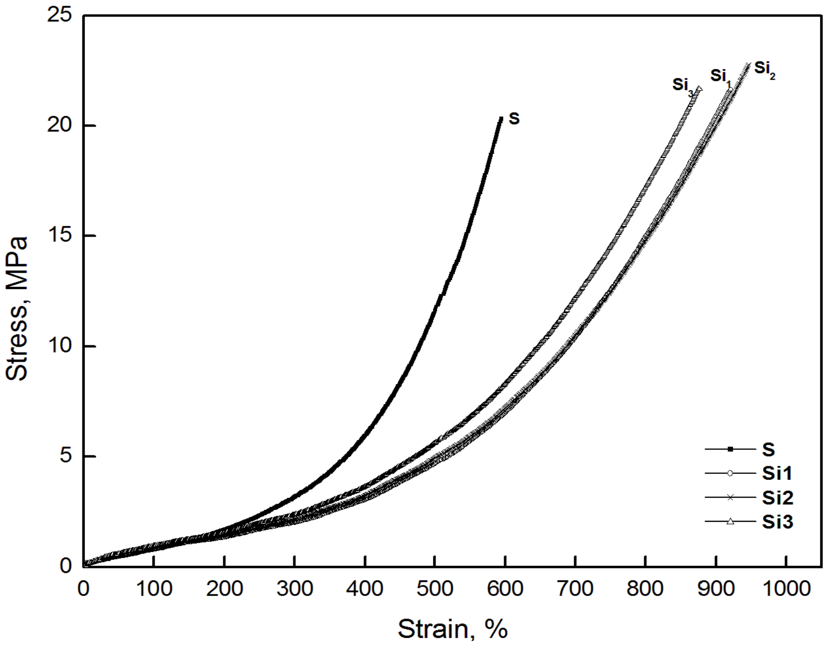


Figure 6.A.3 Stress-strain curves of the unmodified and silane modified silica-filled NR vulcanizates

The tensile strength increases when silane concentration increases from 1.2 phr to 1.5 phr due to the establishment of better rubber-silica interaction and crosslinking, but the strength declines as the concentration increases to 1.8 phr. An increment of 16.5 % in tensile strength is observed in the case of the 15 phr silica-filled vulcanizate containing 1.5 phr silane coupling agent as compared to the pure NR gum vulcanizate. The corresponding increment in tensile strength in the case of the 15 phr silica-filled vulcanizate without coupling agent was only 3.8 %. The higher tensile strength shown by silane modified silica-filled NR vulcanizates may be attributed to the higher strain-induced crystallisation achieved by the incorporation of silane coupling agent [26].

Table 6.A.3 Properties of the unmodified and silane modified silica-filled NR vulcanizates

Properties	**S**	**Si_1**	**Si_2**	**Si_3**
Tensile strength (MPa)	20.30	21.66	22.77	21.68
Modulus at 300% elongation (MPa)	3.19	2.01	2.14	2.40
Elongation at break (%)	595	921	945	877
Tear strength (N/mm)	31.90	34.04	35.59	39.86
Hardness (Shore A)	35	36	37	36
Compression set (%)	23.90	17.69	16.28	15.63
Rebound resilience (%)	60	64	65	68
Crosslink density x10^5 (mol/g rubber hydrocarbon)	4.91	7.05	7.79	7.58
Swelling index	3.71	3.22	3.16	3.17
Abrasion loss (cc/h)	10.96	8.29	7.94	8.17

On incorporation of the coupling agent the modulus at 300 % elongation showed lower values compared to the vulcanizate containing unmodified silica. This may be due to the mild plasticizing effect imparted by the liquid coupling agent. Vulcanizates prepared with the coupling agent shows higher elongation at break as compared to the silica-filled vulcanizate without the coupling agent apparently due to the reason cited above.

An improvement in tear strength and hardness too (Table 6.A.3) was observed for the vulcanizates prepared with silane-treated silica. Abrasion loss decreased with silane modification and minimum abrasion loss was observed in the case of the vulcanizate containing 1.5 phr of coupling agent. Thus silane incorporation has improved the abrasion resistance of silica-filled natural rubber as can be seen from the Table 6.A.3. Improved tear strength and abrasion resistance are considered as a measure of enhanced filler reinforcement [27].

When silica is modified by silane coupling agent, more uniform distribution of silica particles in the NR matrix is obtained [7, 28]. This results in stronger interfacial interaction between rubber and fillers, which would lead to an improvement in mechanical properties of the vulcanizates. The tensile strength and abrasion resistance values are in accordance with the crosslink density values (Table 6.A.3). The interfacial adhesion between the modified silica and the rubber chains is enhanced due to the release of sulphur atoms by Si69 which also take part in the vulcanization reaction of NR [25, 29- 34].

Compression set depends strongly on the elastic recovery of the sample. Silane modified vulcanizates exhibited lower compression set due to their higher network density. A 32 % decrease in compression set value was observed for the silica-filled NR vulcanizates containing 1.5 phr Si69 as compared to silica-filled NR vulcanizate without Si69. The high value of compression set in the case of the vulcanizate containing unmodified silica is due to the friction between filler and matrix and between filler particles that restricts the movement of the rubber chains after the release of the compressive load [35]. The agglomeration tendency between silica particles decreases with the silane modification of silica, and the filler distribution become more uniform. The better rubber-filler interactions reduce the breakdown and reformation of the network under prolonged thermal compression giving a lower compression set. As the dosage of silane coupling agent was increased the compression set values also decreased.

Low rebound resilience of a vulcanizate gives rise to permanent deformation of rubber products under service conditions. The rebound resilience value increased with the addition of silane coupling agent thereby reducing the permanent deformation.

Addition of silane coupling agent has increased the crosslink density (Table 6.A.3) of the silica-filled NR vulcanizate apparently due to an increase in the interaction between silica and rubber. The other reason for the increase in crosslink density may be the reduction in the adsorption of accelerator and sulphur by modified silica. Thus the coupling agent strengthens the rubber-filler interaction, increases the crosslink density and improves the mechanical properties. The increased crosslink density results in the enhancement of abrasion resistance as shown in the Table 6.A.3. Swelling ratio (swelling index) is an indirect measure of the crosslink density.

Stress-strain properties of the silica-filled NR vulcanizates with and without silane modification before and after ageing are shown in the Table 6.A.4 and in Figures 6.A.4, 6.A.5 and 6.A.6. In the case of silane modified silica-filled natural rubber vulcanizates, ageing at 70 °C and 100 °C for 24 hours, did not deteriorate the mechanical properties. This may be due to the thermal stability imparted by the efficient vulcanization system. The increase in modulus on ageing in the case of the vulcanizates prepared using the silane coupling agents may be attributed to the stronger interaction between NR and silica.

Table 6.A.4 Stress-strain properties of the unmodified and silane modified silica-filled NR vulcanizates before and after ageing at 70 °C and 100 °C for 24 hours

Sample	**Tensile strength (MPa)**			**Modulus at 300 % elongation (MPa)**			**Elongation at break (%)**		
	Un aged	**70 °C**	**100 °C**	**Un aged**	**70 °C**	**100 °C**	**Un aged**	**70 °C**	**100 °C**
S	20.30	20.48	20.36	3.19	3.28	3.43	595	606	716
Si_1	21.66	21.75	21.62	2.01	2.09	3.70	921	847	704
Si_2	22.77	22.86	22.71	2.14	2.76	3.93	945	816	708
Si_3	21.68	21.76	21.19	2.40	2.85	4.02	877	814	718

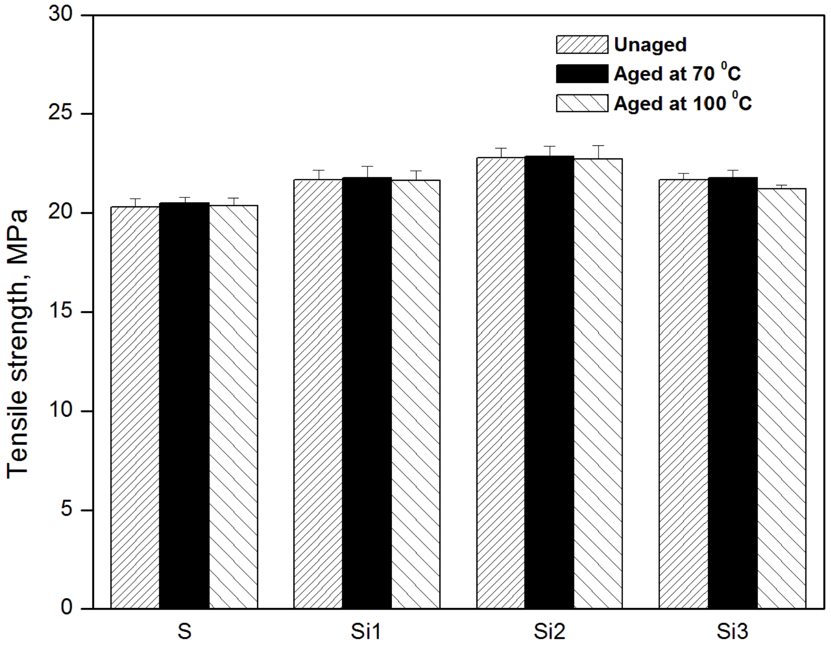


Figure 6.A.4 Variation in tensile strength of the unmodified and silane modified silica-filled NR vulcanizates before and after ageing

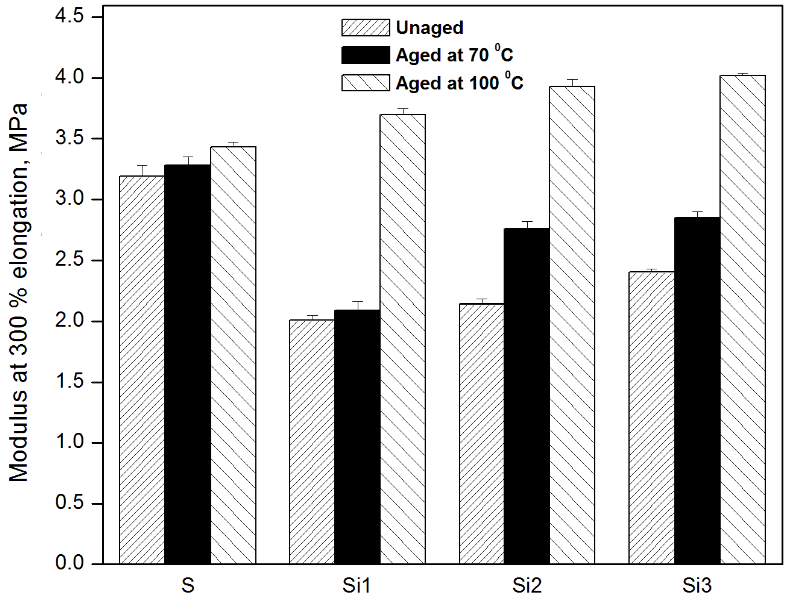


Figure 6.A.5 Variation in modulus at 300 % elongation of the unmodified and silane modified silica-filled NR vulcanizates before and after ageing

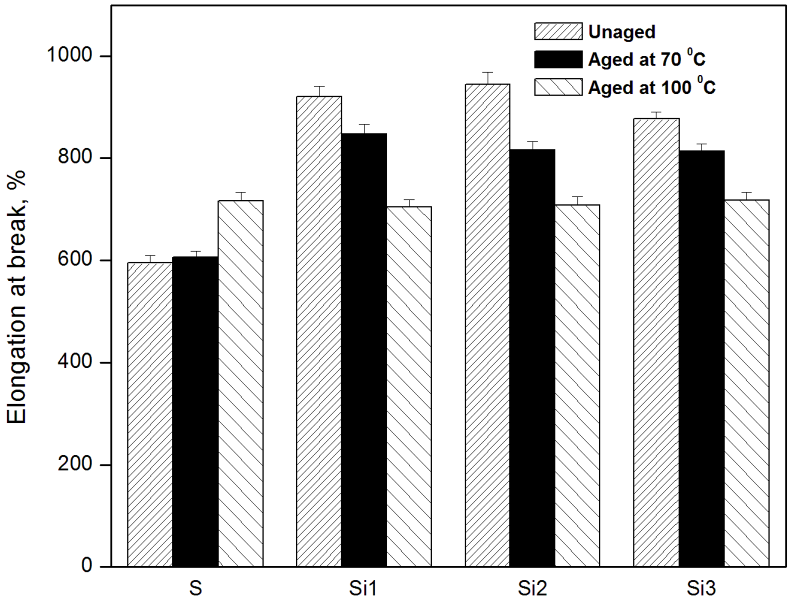


Figure 6.A.6 Variation in elongation at break of the unmodified and silane modified silica-filled NR vulcanizates before and after ageing

6.A.4 Sorption studies

Swelling studies of the vulcanizates prepared by incorporating silica with and without silane modification were done in toluene. Detailed procedure used for the measurement is given in section 2.3.2. Sorption curves of the vulcanizates that are obtained by plotting Q_t against $t^{½}$ are shown in Figure 6.A.7. For all compositions, the uptake is rapid in the initial zone. After this, the sorption rate decreases leading to a plateau corresponding to equilibrium swelling.

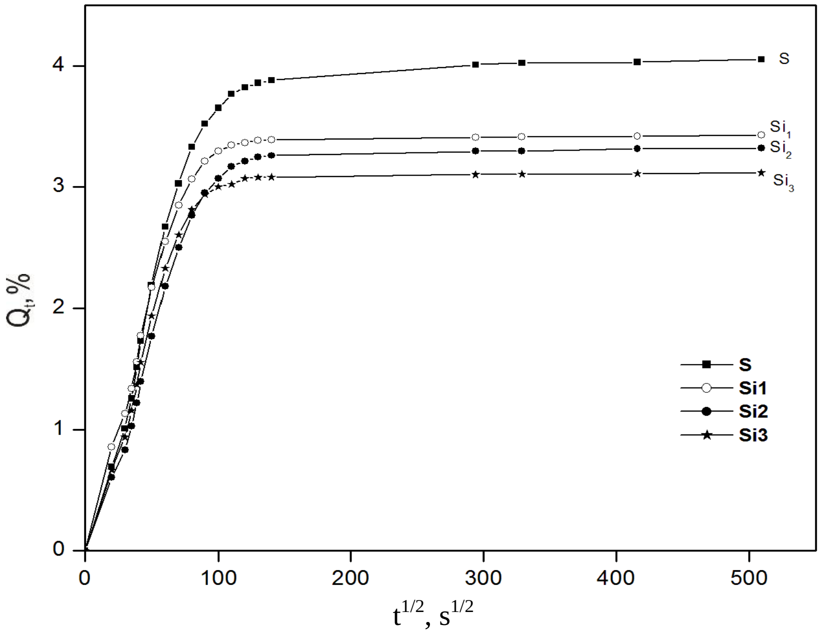


Figure 6.A.7 Q_t vs. $t^{1/2}$ of unmodified and silane modified silica-filled NR vulcanizates

It may be clearly seen from the figure that solvent uptake depends on the extent of crosslinking. Silane modified silica-filled NR vulcanizates show lower uptake of solvent as compared to the unmodified silica-filled vulcanizate. This may be attributed to the fewer crosslinks in the unmodified silica-filled vulcanizate.

In order to determine how the silane modified silica affects the permeability, the transport properties (diffusion coefficient, permeation coefficient and sorption coefficient) of the samples were calculated using the relations given in section 2.3.2.1. Transport of penetrant molecules through polymer proceeds via two stages: sorption and diffusion process. At first, the penetrant molecules are sorbed by the polymer followed by diffusion. Diffusivity is a kinetic parameter which depends on the polymer segmental mobility. The diffusion coefficient decreased marginally with increase in dosage of silane coupling agent. The good interaction between filler and matrix by the addition of coupling agent limits the toluene diffusivity. As the dosage of the coupling agent is increased interaction between filler and rubber increases. This results in gradual reduction in the penetration of solvent through the vulcanizate. This explains the reduction in permeability and diffusivity of the silane modified silica-filled NR vulcanizates with the increase in the dosage of the silane coupling agent (Table 6.A.5).

Table 6.A.5 Sorption data of the unmodified and silane modified silica-filled NR vulcanizates

Sample	**D X 10^7 (cm^2/s)**	**s**	**P X 10^6 (cm^2/s)**	**n**	**k**	**ΔG (J/mol)**	**ΔS X 10^2 (J/mol K)**
S	5.73	3.76	2.15	0.60	0.06	-14.78	4.96
Si_1	5.72	3.17	1.81	0.50	0.11	-21.65	7.27
Si_2	5.71	3.07	1.75	0.55	0.09	-23.68	7.95
Si_3	5.70	2.88	1.64	0.58	0.07	-24.11	8.09

The sorption and permeation of toluene through the silane modified silica-filled vulcanizates decreased with an increased dosage of silane, which is clearly a reflection of decrease in volume fraction of absorbing phase with increased silane loading. Permeation decreased since it is a collective phenomenon consisting of both diffusion and sorption.

The value of k depends on the structural features of polymer, whereas the value of n determines diffusion mechanism (Section 2.3.2.1). The n values for silica-filled NR vulcanizate with and without silane modification are shown in Table 6.A.5. Fickian transport was exhibited by 1.2 phr silane coupling agent incorporated vulcanizate while the others showed anomalous transport.

Thermodynamic effects occurring during swelling of the elastomer chains were also analysed. The thermodynamic approach is of great importance for understanding the rubber-filler interaction in the vulcanizates. Equilibrium swelling of a vulcanized rubber depends on the crosslink density and the solvent used [36]. The expansion of the rubber in the presence of a solvent will significantly modify the conformational entropy (ΔS) and the elastic Gibbs free energy (ΔG). Both the thermodynamic parameters, ΔS and ΔG of the silica-filled vulcanizates with and without silane modification are reported in Table 6.A.5. It should be noted that $-\Delta G$ increases in the presence of silane coupling agent. It is assumed that ΔG is closely related to the elasticity of the material. i.e., the silane modified silica-filled vulcanizate showed a better elastic behaviour than the unmodified silica-filled vulcanizate and it increased with increase in silane coupling agent content. Increase in entropy change was also observed. These results give credence to the better compatibility between silica and rubber.

6.A.5 Fluid resistance

The fluid resistance of the samples were carried out in diesel and lube oil according to ASTM D 471. The percentage change in mass for the silica-filled vulcanizate without coupling agent and with silane coupling agent is shown in the Table 6.A.6.

Table 6.A.6 Change in mass (%) of the unmodified and silane modified silica-filled NR vulcanizates

Sample	Change in mass (%)	
	Diesel	Lube oil
S	220	88
Si_1	192	77
Si_2	185	65
Si_3	176	61

The incorporation of silane coupling agent to the silica-filled natural rubber compound enhanced the fluid resistance of the vulcanizates in diesel and lube oil. Addition of the silane coupling agent further improves the fluid resistance property of the vulcanizates.

6.A.6 Scanning electron microscopy

When the silane coupling agent was incorporated into the silica-filled NR compound, relatively good distribution of silica filler in NR was observed in the SEM photomicrograph as compared to the vulcanizate containing unmodified silica (Figure 6.A.8). Stronger interfacial interaction between rubber and filler is evident in the micrograph of the silane modified vulcanizate. The silane modification provides comparatively better filler distribution with less number of agglomerates.

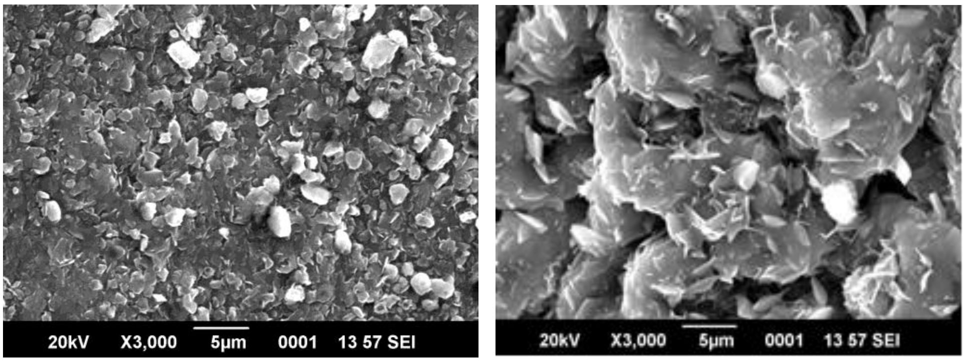


Figure 6.A.8 SEM images of fractured surface of tensile samples of unmodified and silane modified (Si_2) silica-filled NR vulcanizates

6.A.7 Thermogravimetric analysis

The Figure 6.A.9 shows the degradation behaviour of the NR vulcanizates containing silica filler and silane modified silica filler. The results of TGA are summarised in Table 6.A.7. The degradation behaviour of the materials could be clearly read from the differential thermogravimetry (DTG) curves shown in Figure 6.A.10. The temperature onset of degradation (T_i), the temperature at which the rate of decomposition is maximum (T_{max}), the decomposition temperature at 50 % weight loss T_{50} (°C) and weight loss (%) at 500 °C are given in Table 6.A.7.

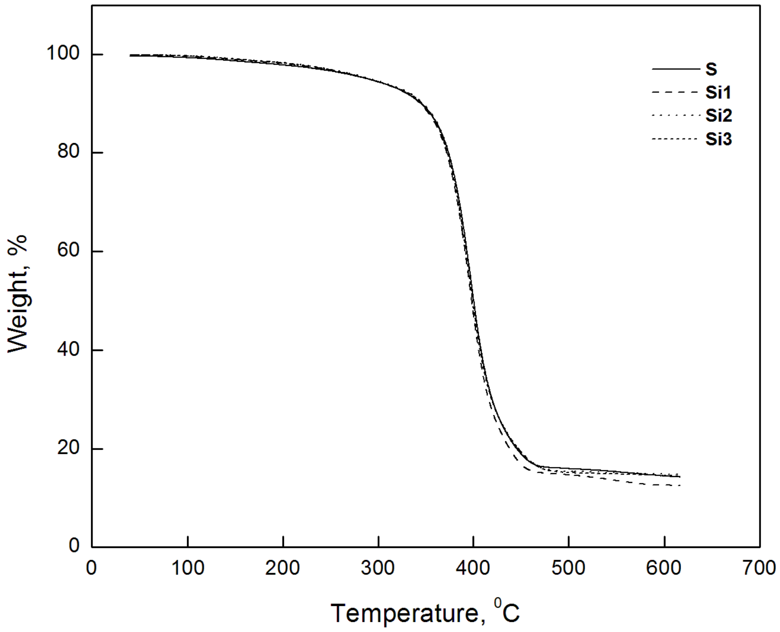


Figure 6.A.9 The thermograms of unmodified and silane modified silica-filled natural rubber vulcanizates

The onset of degradation temperature of the unmodified and silane modified silica-filled NR vulcanizates was almost similar. Similarly, the silica-filled vulcanizates with and without silane modification showed the same maximum degradation temperature. The results showed that the addition of silane coupling agent does not contribute any change in the thermal stability of the vulcanizates.

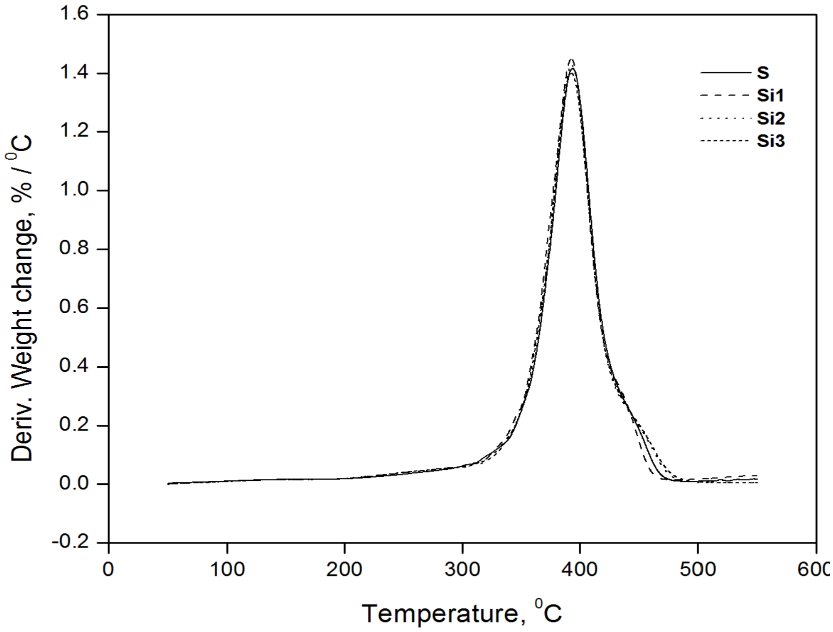


Figure 6.A.10 The derivative thermograms of unmodified and silane modified silica-filled natural rubber vulcanizates

Table 6.A.7 Thermal degradation data of unmodified and silane modified silica-filled NR vulcanizates

Sample	T_i (°C)	T_{50} (°C)	T_{max} (°C)	Weight loss (%) at 500 °C
S	353	402	394	84.0
Si_1	354	398	393	84.9
Si_2	354	400	393	84.6
Si_3	354	399	393	84.8

6.A.8 Assessment of rubber-filler interactions

6.A.8.1 Bound rubber content

The bound rubber content in the unmodified and silane modified silica-filled NR masterbatches was measured and are shown in Table 6.A.8. The silane modification of silica enhanced the bound rubber content of the compounds, indicating that the modification has greatly improved the dispersion of silica and the interaction between silica and natural rubber.

Table 6.A.8 Bound rubber contents of unmodified and silane modified silica-filled NR masterbatches

Sample	Bound rubber content (%)
S	30.32
Si_1	32.77
Si_2	33.78
Si_3	35.89

The better interaction of silica with rubber in the silane modified mix is due to the silanol-ethoxy interaction. The bound rubber formed in NR-TESPT-silica compound was chemically bound to the silica due to the hydrophobation of the silica surface as a result of silanization with TESPT. The increase in silica-TESPT coupling consequently resulted in more filler-rubber interactions. Thus increase in dosage of TESPT resulted in high bound rubber content contributed by the high filler-rubber interactions [4, 25].

6.A.8.2 Strain-sweep analysis

Variation of complex modulus (G*) with strain for the uncured silane modified and unmodified silica-filled NR compounds are plotted in Figures 6.A.11 and 6.A.12.

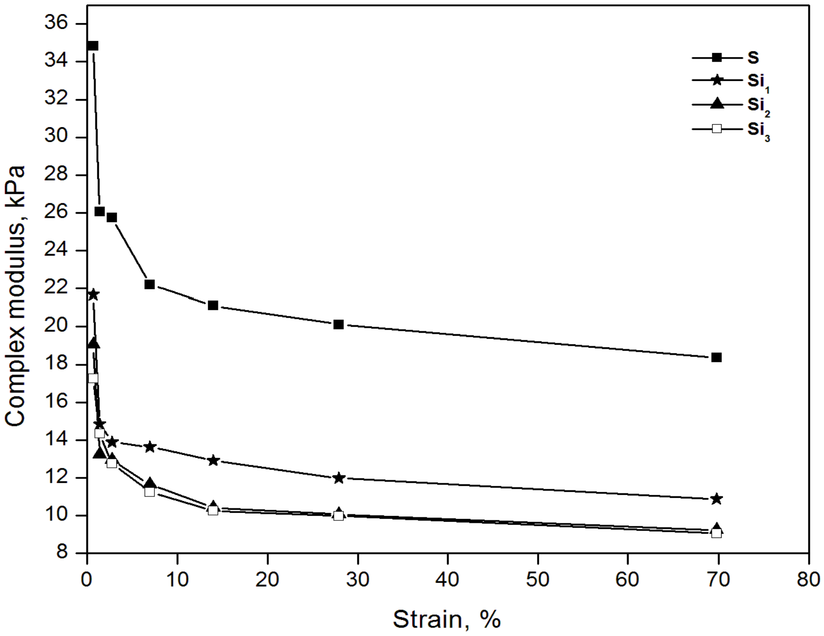


Figure 6.A.11 Dependence of complex modulus (G*) on strain amplitude of uncured silane modified and unmodified silica-filled natural rubber compounds at different loadings

At low strains, filler-filler contacts contribute much more to G* than filler-rubber contacts. The complex modulus of filled rubber drastically decreases as strain increases as the result of breakage of physical bonds between filler particles, for example van der Waals interactions, hydrogen bonds and London forces. This widely accepted phenomenon is called ‘Payne effect’ which is mainly related to the filler network formed in the rubber matrix. The rubber trapped or caged in the filler network would at least be partially ‘dead,’ behaving like filler. Therefore effective volume of the silica would increase substantially upon filler networking. At very low strains, the complex modulus of the uncured compound without silane coupling agent is much higher than that of the compounds with silane, which is attributed to poor dispersion and strong filler–filler interaction of the silica in the NR matrix.

However, with TESPT modification, the Payne effect of the silica-filled compounds has greatly reduced as more silica surface is hydrophobized by TESPT resulting in the disruption of the silica-silica network [37].

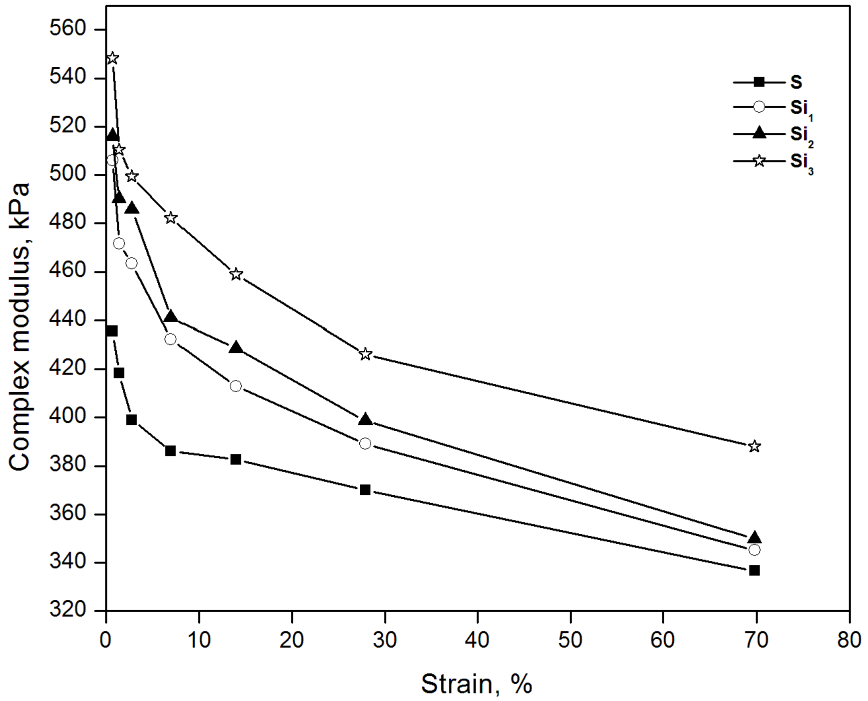


Figure 6.A.12 Dependence of complex modulus (G*) on strain amplitude of cured silane modified and unmodified silica-filled natural rubber compounds at different loadings

The difference between G* at very low and high strains is always used as an indication of the Payne effect. A larger Payne effect (a larger difference in complex modulus at 0.7 and 70 % strain) suggests larger degrees of filler-filler interactions [21]. When the TESPT concentration was increased, modulus difference at very low and high strains was considerably reduced due to increased silica-TESPT coupling resulting in better dispersion of silica in the NR matrix and greater filler-rubber interactions

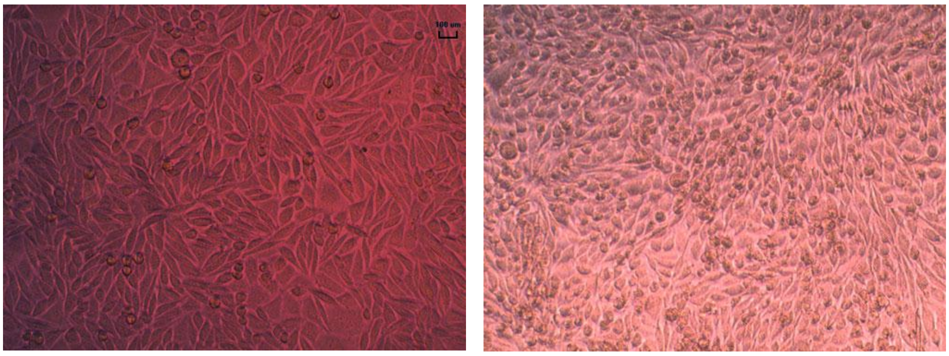
[4]. Accordingly, a lower Payne effect was obtained for the TESPT modified silica compounds.

Owing to the increased rubber-filler interaction in silane modified silica-filled NR compounds, the cured compounds exhibited higher modulus than that without silane modification.

6.A.9 Cytotoxicity (MTT assay) of silane modified silica-filled NR vulcanizate

Cytotoxicity of the vulcanizate was determined by MTT assay [38, 39]. Phase contrast image for determination of cell morphology of control of MTT assay and confluent cells containing extract of silane modified silica-filled natural rubber vulcanizate is shown in Figure 6.A.13. Large number of fibroblast cells were visible in the control of the MTT assay while the number of viable cells got reduced in the case of the confluent cells containing the extract of silane modified silica-filled natural rubber vulcanizate after 24 hours incubation.

If the percentage viability of cells is between 60-80 % then the samples may be considered as mildly cytotoxic [39, 40]. The sample containing extract of Si_2 (NR vulcanizate containing silane modified silica) was found to contain 76.51 % of viable cells. Therefore the MTT assay has proved the mild cytotoxicity of the natural rubber vulcanizate filled with silane modified silica.



(a) (b)

Figure 6.A.13 Phase contrast image (magnification 20 x) for the determination of cell morphology of: (a) control of the MTT assay and (b) extract of silane modified silica-filled NR vulcanizate

PART B

EFFECT OF EPOXIDISED NATURAL RUBBER (ENR) ON PROPERTIES OF SILICA-FILLED NR COMPOUNDS

6.B.1 Preparation of ENR modified silica-filled NR compounds

Epoxidised natural rubber (ENR 25) was incorporated into the NR on a two-roll mill prior to the addition of other ingredients. The dosage of ENR (1.5 g) in the compound E_0 (Table 6.B.1) is equivalent to that of silane coupling agent (1.5phr) in compound $Si_{2.}$ Higher dosages of ENR were incorporated in compounds E_1, E_2, E_3, E_4 and E_5. The mixes were prepared by adding the ingredients as per the formulations in accordance with the ASTM D 3184.

Table 6.B.1 Formulations of the mixes

Ingredients	**Si_2**	**E_0**	**E_1**	**E_2**	**E_3**	**E_4**	**E_5**
NR (g)	100	98.5	98	97	96	95	94
ENR (g)	-	1.5	2.0	3.0	4.0	5.0	6.0
ZnO (phr)	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Precipitated silica (phr)	15	15	15	15	15	15	15
DEG (phr)	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Si69 (phr)	1.5	-	-	-	-	-	-
TBBS (phr)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TBzTD (phr)	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Sulphur (phr)	0.3	0.3	0.3	0.3	0.3	0.3	0.3

6.B.2 Cure characteristics

Rheographs of the silica-filled NR compounds modified with silane coupling agent and epoxidised natural rubber are shown in the Figure 6.B.1. The cure characteristics of the mixes are shown in the Table 6.B.2.

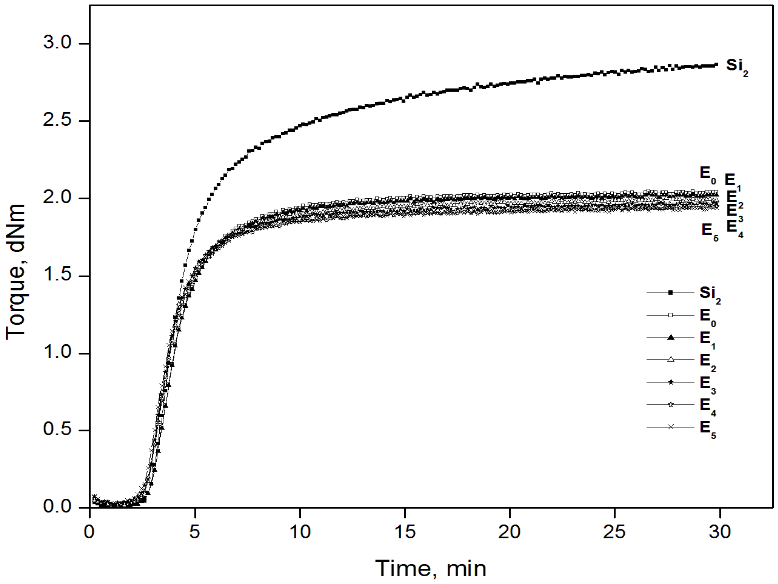


Figure 6.B.1 Rheographs of the silica-filled NR compounds modified with silane coupling agent and ENR

Table 6.B.2 Cure characteristics of the silica-filled NR compounds modified with silane coupling agent and ENR at 150 ºC

Properties	Si_2	E_0	E_1	E_2	E_3	E_4	E_5
Scorch time t_{10} (min)	2.79	2.96	2.93	2.85	2.83	2.78	2.71
Optimum cure time t_{90} (min)	9.01	7.58	7.51	7.27	7.11	6.79	6.72
Cure Rate Index (CRI, min^{-1})	16.08	21.65	21.83	22.62	23.36	24.93	24.94
Minimum torque (M_L, dNm)	0.009	0.013	0.013	0.016	0.016	0.025	0.025
Maximum torque (M_H, dNm)	2.87	2.04	2.03	2.00	1.97	1.95	1.94
$M_H - M_L$ (dNm)	2.86	2.031	2.013	1.984	1.954	1.925	1.913

ENR modified vulcanizates showed lower optimum cure time and higher cure rate index as compared to the silane modified NR vulcanizate. Optimum cure time decreased as the dosage of ENR was increased: thus forming more crosslinks in shorter time [41]. Improvements noted in the cure behaviour of the ENR modified natural rubber compounds might have resulted from the preferential interaction of the epoxy group with the silanol groups [42]. This may reduce the chances of interaction of the silanol group with the accelerator and other compounding ingredients. Thus the added accelerators and compounding ingredients are completely available for curing in the ENR modified compounds.

Minimum torque (M_L) observed in the case of ENR modified compounds were lower than the unmodified compound (Table 6.A.2) but higher than the silane modified compound. This shows that the processability is in the order silane modified compound > ENR modified compounds > unmodified silica-filled NR compound. The minimum torque of the compounds increased while the maximum torque was found to decrease with increase in the dosage of ENR. The ENR modified NR compounds show lower maximum torque values than silane modified NR compound. Decrease in maximum torque value with increase in the dosage of ENR showed the plasticizing effect of ENR which contributes to the improved processing performance of the compounds.

In short, the addition of ENR can promote rubber vulcanization and accelerate the vulcanization rate.

6.B.2.1 Cure kinetics

Plot of $\ln(M_H - M_t)$ versus time is shown in Figure 6.B.2. All the mixes gave straight lines; therefore the cure reaction was found to follow first-order kinetics.

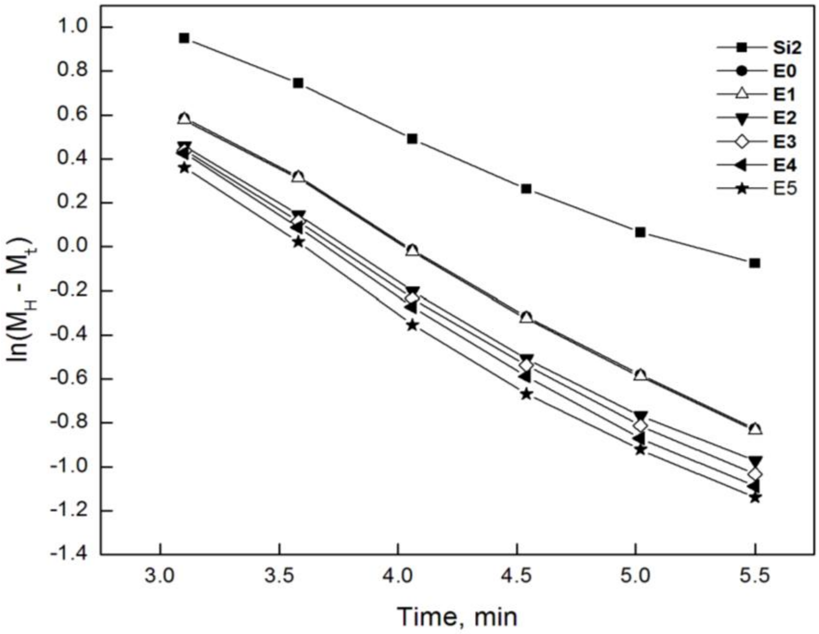


Figure 6.B.2 Plot of ln(M_H – M_t) vs. time of silane modified and ENR modified silica-filled NR compounds

6.B.3 Mechanical properties of ENR modified silica-filled NR vulcanizates

The stress-strain curves of the silane modified and ENR modified silica-filled NR vulcanizates are shown in Figure 6.B.3. Mechanical properties of the vulcanizates are shown in the Table 6.B.3. It is observed that the ENR modified silica-filled NR vulcanizates possess inferior mechanical properties in comparison to the vulcanizate containing corresponding dosage of silane coupling agent. However, as the dosage of ENR increased the vulcanizates showed improvement in mechanical properties. The vulcanizate containing 4 g ENR showed highest tensile strength and tear strength (similar to the vulcanizate containing 1.5 phr silane coupling agent). However, higher dosage of ENR resulted in marginal decline in mechanical properties.

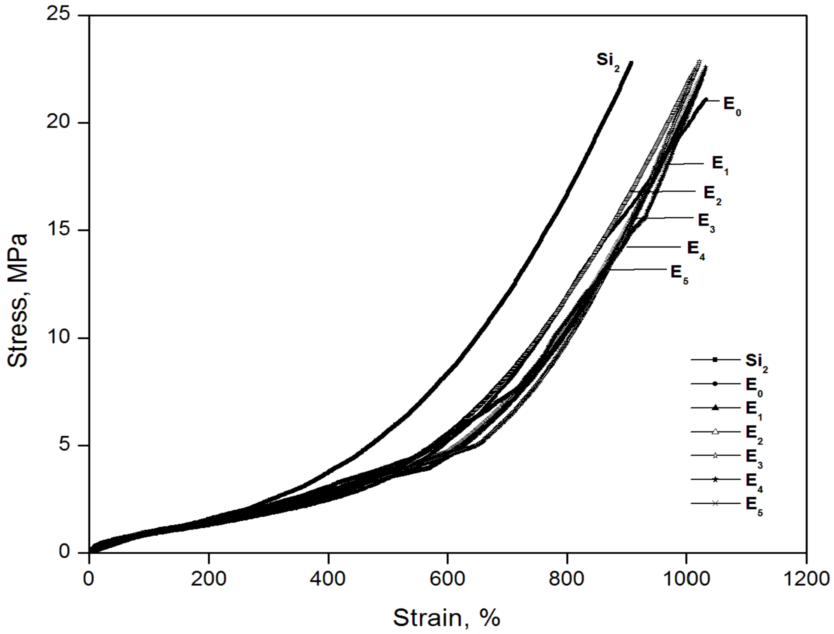


Figure 6.B.3 Stress-strain curves of the silane modified and ENR modified silica-filled NR vulcanizates

Table 6.B.3 Properties of the silane modified and ENR modified silica-filled natural rubber vulcanizates

Properties	**Si_2**	**E_0**	**E_1**	**E_2**	**E_3**	**E_4**	**E_5**
Tensile strength (MPa)	22.77	21.08	22.04	22.46	22.84	22.58	22.36
Modulus at 300 % elongation (MPa)	2.14	1.83	1.87	2.08	2.20	2.20	2.06
Elongation at break (%)	945	1033	1025	1012	1021	1031	1029
Tear strength (N/mm)	35.59	32.35	33.18	33.76	34.85	34.26	34.03
Hardness (Shore A)	36	32	32	33	33	34	34
Compression set (%)	16.28	23.01	22.40	21.65	21.64	22.02	22.55
Rebound resilience (%)	65	59	59	60	60	61	62
Crosslink density x10^5 (mol/g rubber hydrocarbon)	7.79	4.92	4.93	5.06	5.12	5.09	5.01
Swelling index	3.16	3.83	3.78	3.77	3.75	3.76	3.80
Abrasion loss (cc/h)	7.94	12.06	11.91	11.75	11.29	11.91	12.09

Silica-filled NR vulcanizate modified with ENR showed higher tensile strength as compared to the silica-filled natural rubber vulcanizate without any modification (Table 6.A.3). Incorporation of higher dosage of ENR (4 g) resulted in tensile strength comparable to that of silane modified (1.5 phr) silica-filled NR vulcanizate. Thus slightly higher dosage of epoxidised natural rubber could be a better substitute for the expensive silane coupling agent in silica-filled natural rubber formulations. The polarity and bifunctionality (the oxirane and the unsaturation) of ENR facilitates greater interaction of ENR with silica leading to improved rubber-filler interaction [43]. Xue et al. have reported that the silanol groups can open the epoxy rings [42]. Chemical interaction or chemical crosslinks between the epoxy group and silanol groups has been proposed to be the reason for this unusual reinforcement [44]. The hydrocarbon part of ENR makes contact with the NR matrix, thus acting as a coupling agent. The enhanced tensile strength with ENR incorporation might be a result of the better rubber-silica interaction.

The elongation at break was higher in the case of ENR modified vulcanizates as compared to the silane modified vulcanizate. This may be due to the plasticization effect of epoxidised natural rubber. Modulus at 300 % elongation of the ENR modified vulcanizates showed a marginal increase with the increase in concentration of ENR. This may be due to the increased rubber-filler bonding between the epoxy groups of ENR and silanol groups of silica. Although considerable stiffening of the vulcanizates resulting in an improvement in modulus was observed with the addition of ENR up to 4 g, the trend showed marginal reversion on further addition of higher dosages.

The ENR modified samples showed improvement in tear strength as compared to the unmodified silica-filled NR vulcanizate (Table 6.A.3). This further confirms the coupling effect of ENR. However the tear strength values of the silane modified vulcanizates were higher than ENR modified vulcanizates, which may be due to the rubber-filler covalent bonding achieved through sulphur bridges in the former. The improved tear strength shown by the ENR and silane modified vulcanizates may be attributed to the improved wetting and interaction of the filler with the rubber [42].

Though the tensile strength and the modulus of ENR (4 g and 5 g) modified silica-filled vulcanizates were comparable to that of the silane modified NR vulcanizate, their abrasion resistance was inferior, which may be credited to the higher glass transition temperature of ENR [45-48]. Among all the ENR incorporated vulcanizates, the vulcanizate with 4 g ENR showed comparatively higher abrasion resistance.

When compared to silane modified silica-filled NR vulcanizate a reduction in resilience was observed in the case of ENR modified silica-filled vulcanizates due to the higher glass transition temperature of ENR [45, 46, 49]. The lower resilience shown by the ENR modified NR vulcanizates may also be due to the inherent damping character imparted by ENR and restrictions imposed on the polymer segmental mobility by increased rubber-filler bonds. The resilience of the vulcanizates depends on the concentration of ENR and was found to increase marginally with increased ENR dosage [50].

The hardness of the ENR modified vulcanizates was lower compared to that of the silane modified silica-filled vulcanizate (Table 6.B.3). This may be due to the rubber-filler covalent bonding through sulphur bridges in silane modified silica-filled NR vulcanizates.

Crosslink densities of the ENR modified silica-filled NR vulcanizates were higher compared to that of the unmodified silica-filled NR vulcanizate (Table 6.A.3). This may be attributed to the fact that ENR can chemically react with both silica and rubber, improving the filler-rubber interactions. This in turn increases the crosslink density of the vulcanizates [42]. The obtained stress-strain properties of the ENR modified NR vulcanizates were in accordance with the crosslink densities. Silane modified vulcanizate exhibited lower compression set than ENR modified vulcanizates, which can be attributed to the higher network density. A marginal reduction in compression set was noted for the ENR modified vulcanizates upto 4 g dosage and thereafter increased with still higher dosage. A similar trend was observed in the case of swelling index also.

Variation of the stress-strain properties of the vulcanizates after ageing for 24 hours at 70 °C and 100 °C is depicted in Table 6.B.4 and in Figures 6.B.4, 6.B.5 and 6.B.6. Tensile strength and modulus show increment after ageing for 24 hours at 70 °C and 100 °C. The elongation at break decreased on ageing. This may be due to the larger chemical interactions between the natural rubber and silica in the presence of ENR at these temperatures. This causes hindrance to the stretching of the rubber molecules.

Table 6.B.4 Stress-strain properties of the silane modified and ENR modified silica-filled NR vulcanizates before and after ageing

Sample	**Tensile strength (MPa)**			**Modulus at 300 % elongation (MPa)**			**Elongation at break (%)**		
	Un aged	**70 °C**	**100 °C**	**Un aged**	**70 °C**	**100 °C**	**Un aged**	**70 °C**	**100 °C**
Si$_2$	22.77	22.86	22.71	2.14	2.76	3.93	945	816	708
E$_0$	21.08	21.38	22.08	1.83	1.98	2.52	1033	932	850
E$_1$	22.04	22.28	22.58	1.87	2.01	2.54	1025	968	808
E$_2$	22.46	22.63	22.76	2.08	2.22	2.56	1012	970	848
E$_3$	22.84	22.94	22.97	2.20	2.34	2.56	1021	994	843
E$_4$	22.58	22.68	22.98	2.20	2.40	2.62	1031	996	858
E$_5$	22.36	22.64	22.59	2.06	2.19	2.50	1029	1009	836

The addition of ENR did not produce any adverse effect on thermo-oxidative ageing resistance of the vulcanizates. Thus the addition of ENR may be considered as a good choice for the compounders instead of the expensive silane coupling agent.

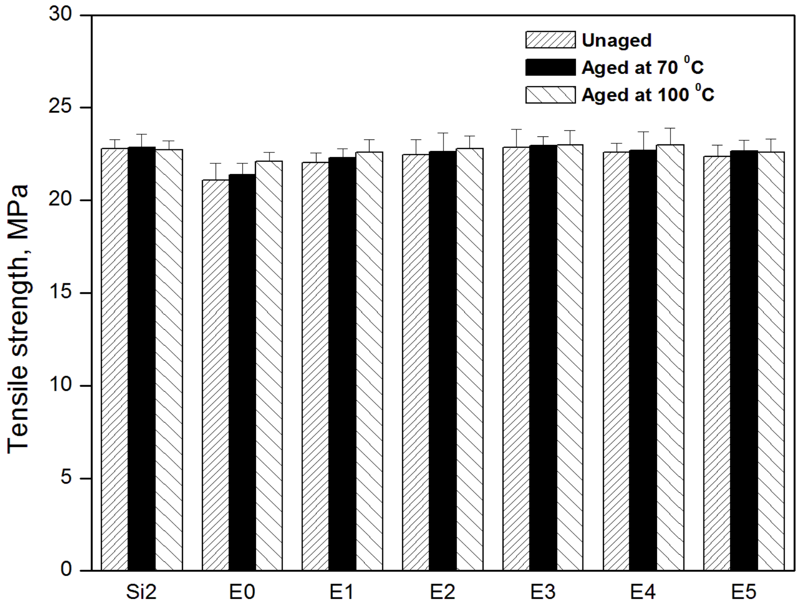


Figure 6.B.4 Variation in tensile strength of the silane modified and ENR modified silica-filled NR vulcanizates before and after ageing

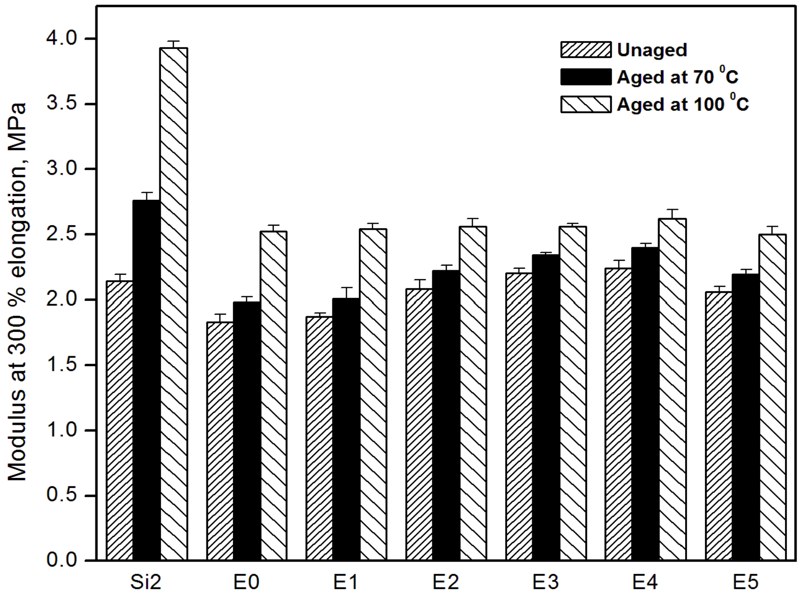


Figure 6.B.5 Variation in modulus at 300 % elongation of the silane modified and ENR modified silica-filled NR vulcanizates before and after ageing

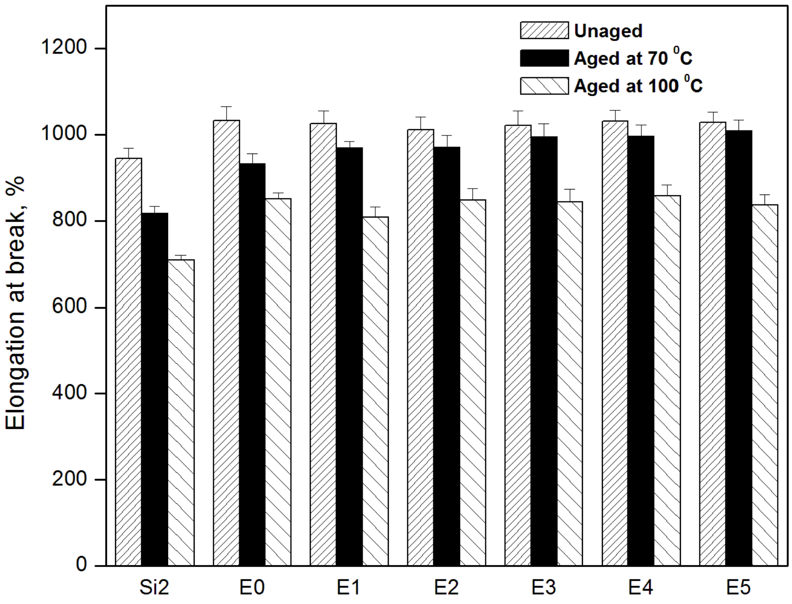


Figure 6.B.6 Variation in elongation at break of the silane modified and ENR modified silica-flled NR vulcanizates before and after ageing

6.B.4 Sorption studies

Swelling studies of the vu1canizates were done in toluene at 25 °C. The diffusion curves of the silica-filled NR vulcanizates modified with silane coupling agent and epoxidised natural rubber are shown in Figure 6.B.7. Silane modified silica-filled NR vulcanizate exhibited reduced swelling as compared to the ENR modified silica-filled NR vulcanizates. There is increase in solvent uptake (%) at equilibrium swelling of ENR modified silica-filled vulcanizates compared to the corresponding silane modified silica-filled NR vulcanizate. This may be attributed to the large number of crosslinks in the silane modified silica-filled NR vulcanizate. The diffusion of penetrant depends greatly upon the concentration of available space that is large enough to accommodate the penetrant molecule. A penetrant molecule may exist in a hole of sufficient size and can jump into a neighbouring hole once it acquires sufficient energy. When there is gap between the polymers it will increase the availability of spaces and enhance the mobility of chain segments.

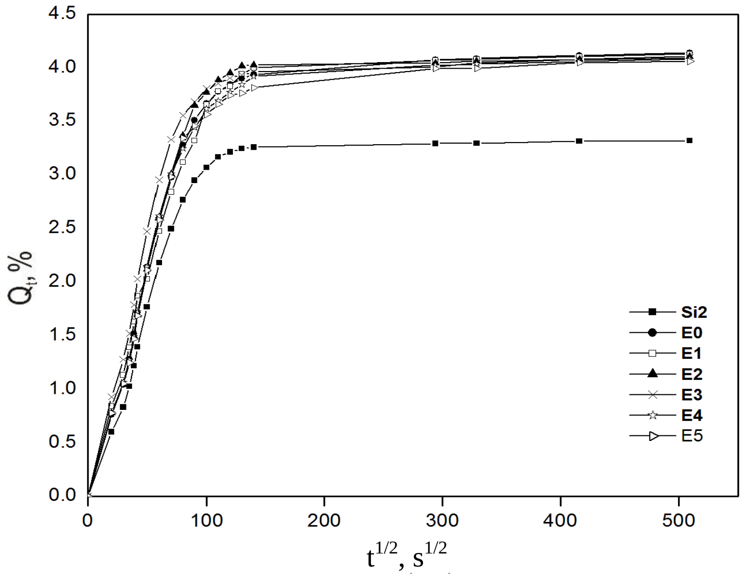


Figure 6.B.7 Q_t vs. $t^{1/2}$ of silane modified and ENR modified silica-filled NR vulcanizates

Table 6.B.5 gives the variation in diffusion coefficient, sorption coefficient and permeation coefficient of unmodified silica-filled vulcanizate, silane modified and ENR modified silica-filled NR vulcanizates. The diffusion coefficient decreased with increase in dosage of ENR. The strong interaction between filler and matrix achieved by the addition of ENR limit the toluene diffusivity. The diffusion coefficient, sorption coefficient and permeation coefficient of the ENR modified silica-filled NR vulcanizates did not show large variation from the coefficients of the unmodified silica-filled NR vulcanizate. However the coefficients of silane modified vulcanizate was smaller than the unmodified and ENR modified silica-filled vulcanizates. The sorption coefficient of ENR modified vulcanizates decreased marginally with increased ENR dosage which reflects a decrease in the volume fraction of absorbing phase with increased loading. Permeation coefficient was decreased with ENR loading which was quite obvious since it is a collective phenomenon consisting of both diffusion and sorption.

Table 6.B.5 Sorption data of the unmodified, silane modified and ENR modified silica-filled NR vulcanizates

Sample	D X 10^7 (cm^2/s)	s	P X 10^6 (cm^2/s)	n	k	ΔG (J/mol)	ΔS X 10^2 (J/mol K)
S	5.73	3.76	2.15	0.60	0.06	-14.78	4.96
Si_2	5.71	3.07	1.75	0.55	0.09	-23.68	7.95
E_0	5.73	3.83	2.19	0.56	0.07	-15.06	5.05
E_1	5.69	3.82	2.17	0.50	0.09	-15.10	5.06
E_2	5.68	3.80	2.16	0.56	0.07	-15.12	5.07
E_3	5.66	3.78	2.14	0.51	0.10	-15.15	5.08
E_4	5.66	3.77	2.14	0.55	0.07	-15.17	5.09
E_5	5.65	3.75	2.12	0.56	0.07	-15.19	5.10

The thermodynamical parameters ΔS and ΔG of the material are reported in Table 6.B.5. ΔS and -ΔG values of the ENR modified and unmodified silica-filled NR vulcanizates were almost the same, but was lower in comparison to the silane modified silica-filled vulcanizate. It is noted that -ΔG increased with increase in the dosage of ENR. It is assumed that ΔG is closely related to the elastic behaviour of the material [51] i.e., the vulcanizates containing ENR show lower elasticity than the silane modified silica-filled NR vulcanizate and it increases with increase in ENR content.

6.B.5 Fluid resistance

The vulcanizates containing silane coupling agent and ENR were soaked in diesel and lube oil for 72 hours to determine the fluid resistance as per ASTM D 471. The percentage changes in mass of the unmodified silica-filled NR vulcanizate, optimum dosage of silane coupling agent modified silica-filled NR vulcanizate and ENR modified silica-filled NR vulcanizates with various ENR dosages are shown in the Table 6.B.6.

Table 6.B.6 Change in mass (%) of the unmodified, silane modified and ENR modified silica-filled NR vulcanizates

Sample	Change in mass (%)	
	Diesel	Lube oil
S	220	88
Si_2	185	65
E_0	208	85
E_1	206	83
E_2	204	80
E_3	203	74
E_4	202	73
E_5	199	72

The change in mass (%) of the ENR modified vulcanizates were greater compared to the silane modified vulcanizates. Apparently the volume fraction of absorbing phase is more exposed to oil in the case of ENR modified vulcanizates as evident from the higher value of change in mass as compared to silane modified vulcanizate. But increase in mass of the ENR modified vulcanizates was lower in comparison to the unmodified silica-filled NR vulcanizate. Change in mass of the ENR modified vulcanizates after equilibrium swelling decreased with increase in the dosage of ENR apparently due to the increase in the interaction between silica and rubber. This reduces the fluid transport area and the transportation path become more tortuous. Therefore percentage swelling after soaking in diesel and lube oil was decreased.

6.B.6 Filler-rubber interaction

6.B.6.1 Bound rubber content

Bound rubber content in the silane modified and ENR modified silica-filled NR masterbatches are shown in the Table 6.B.7. A measurement of bound rubber indicates how much rubber is associated with the filler [47]. Measurements of bound rubber content of ENR modified silica-filled NR masterbatches by swelling in toluene showed that a high level of ENR-25 and NR are bound to silica. A probable explanation is that the hydrophilic proteins on the NR are hydrogen bonded to the silica. A strong association between ENR-25 and silica also cannot be ruled out considering the relatively polar nature of ENR-25. ENR contains 25 mol % epoxy groups and a small proportion of ring opened species containing hydroxyl and furan functionality [52]. It is proposed that these polar groups associate through hydrogen bonding to the silanol group on the surface of the silica to effectively couple the ENR-25 to the silica [48]. Closer values of bound rubber for the ENR modified silica-filled systems and silane modified silica-filled system indicate similar rubber-filler networking status for both. Thus ENR acts as an interface between silica and rubber enhancing the rubber-filler interaction. During mixing, a preferential adsorption of ENR over the silica surface might have taken place through the epoxy-silanol interaction or hydrogen bonding. This facilitates a good dispersion of silica in the ENR modified NR matrix establishing a better rubber-silica binding.

Table 6.B.7 Bound rubber content of silane modified and ENR modified silica-filled NR masterbatches

Property	**Si_2**	**E_0**	**E_1**	**E_2**	**E_3**	**E_4**	**E_5**
Bound rubber content, %	33.78	31.01	31.98	32.08	32.43	33.21	33.32

It is clear from the table that for the same concentration of silica, the bound rubber content tends to increase with increase in the dosage of ENR. This may be due to a preferential adsorption of more ENR over the silica surface resulting in an increased rubber-filler interaction. This gives supplementary evidence for the coupling effect of ENR between silica and rubber.

6.B.6.2 Strain-sweep analysis

The variation of complex modulus (G*) with strain for all the compounds before curing are shown in the Figure 6.B.8. The complex modulus values at low strains (≤ 15%) are a measure of the filler-filler and filler-polymer interactions [53, 54]. In comparison with the silane coupled silica-filled compounds, ENR modified silica-filled NR compounds showed higher modulus at low strains. This may be due to the reduction of the interaction of filler aggregates by the addition of silane coupling agent. In this perspective, silane enhances the interaction between NR and filler and improves the processing performance of the silica-filled NR compounds. ENR also has the capacity to enhance the interactions between NR and filler, but it was not up to the level imparted by the silane coupling agent.

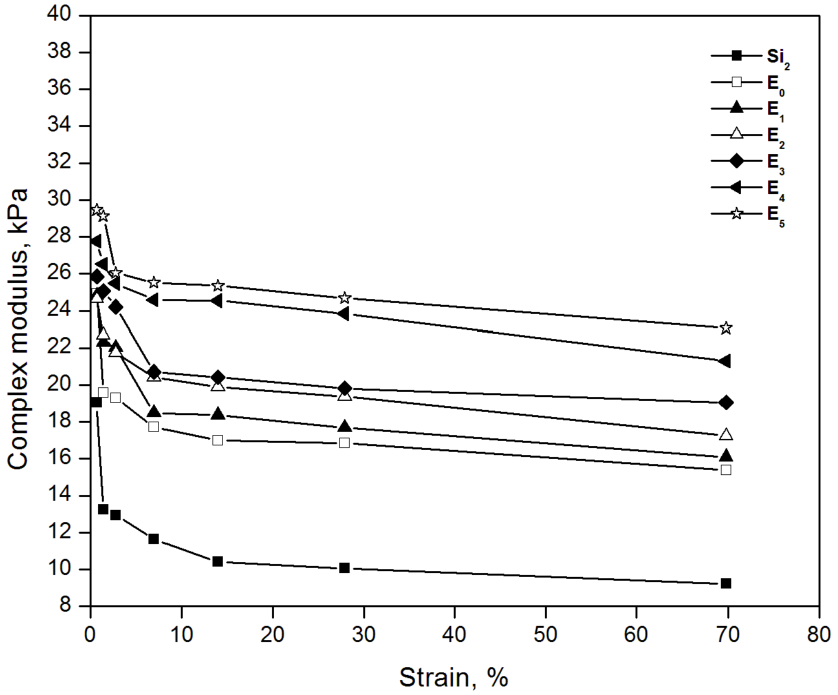


Figure 6.B.8 Dependence of complex modulus (G*) on strain amplitude of uncured silane modified and ENR modified silica-filled natural rubber compounds at different loadings

But in comparison with the unmodified silica-filled compounds, the ENR modified silica-filled compounds displayed lower modulus at low strains (see Figure 6.A.11). The reduction of filler-filler interaction in ENR modified silica-filled NR compounds can again be attributed to the interactions between the silanol groups of silica and epoxide groups of ENR through hydrogen bonding [55].

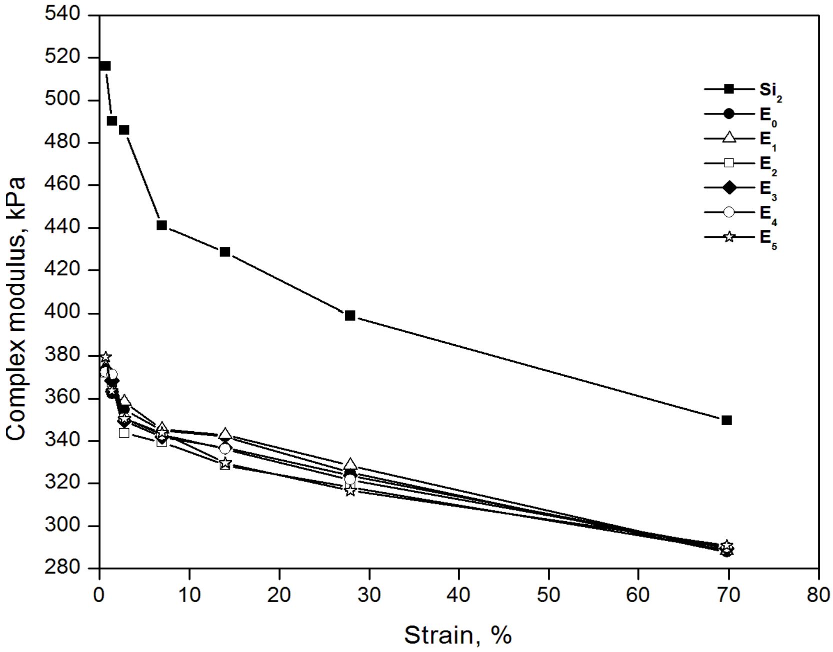


Figure 6.B.9 Dependence of complex modulus (G*) on strain amplitude of cured silane modified and ENR modified silica-filled natural rubber compounds at different loadings

The Figure 6.B.9 shows the variation of complex modulus (G*) with strain for cured compounds. In strain-sweep analysis of the cured samples, silane modified silica-filled NR compounds showed higher modulus compared to that of ENR modified compounds. This may be due to the high crosslinking in the silane modified vulcanizate.

6.B.7 Scanning electron microscopy

Figure 6.B.10 shows the SEM images of the tensile fractured surfaces of the unmodified and ENR modified silica-filled NR vulcanizates. From the SEM micrographs of samples, it could be inferred that ENR modification provides good filler distribution with less number of agglomerates. The morphological evidence gives firm support to the

coupling effect of ENR and further substantiates the better tensile strength obtained for the ENR modified silica-filled NR compounds.

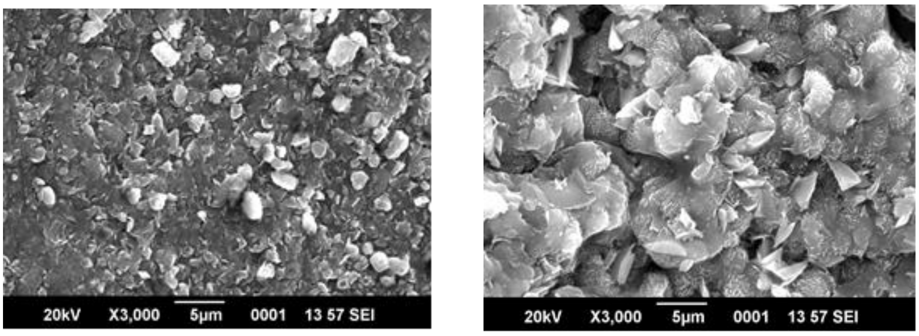


Figure 6.B.10 SEM images of fractured surface of tensile samples of unmodified and ENR modified (E_3) silica-filled NR vulcanizates

6.B.8 Thermogravimetric analysis

TGA thermogram and derivative thermogram of silane modified and ENR modified silica-filled NR vuIcanizates are shown in Figure 6.B.11 and 6.B.12. Table 6.B.8 shows the thermogravimetric data. From the table it is observed that the onset of degradation temperature, temperature of maximum degradation and temperature of 50 % degradation are almost similar for silane modified silica-filled NR vulcanizate and the corresponding dosage of ENR modified silica-filled NR vulcanizate. The results in the Table 6.B.8 and 6.A.7 show that epoxidised natural rubber and silane coupling agent did not contribute much to the thermal stability of silica-filled NR vulcanizates.

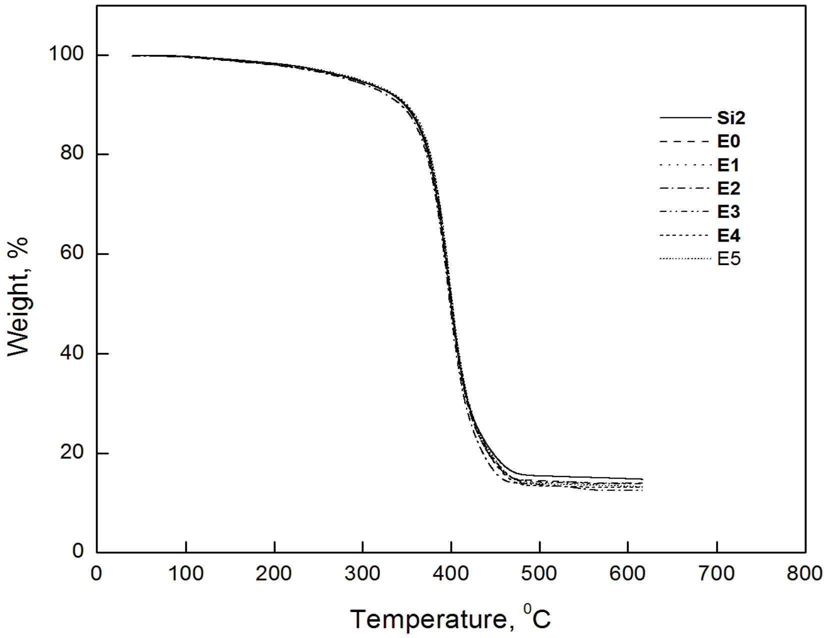


Figure 6.B.11 The Thermograms of silane modified and ENR modified silica-filled natural rubber vulcanizates

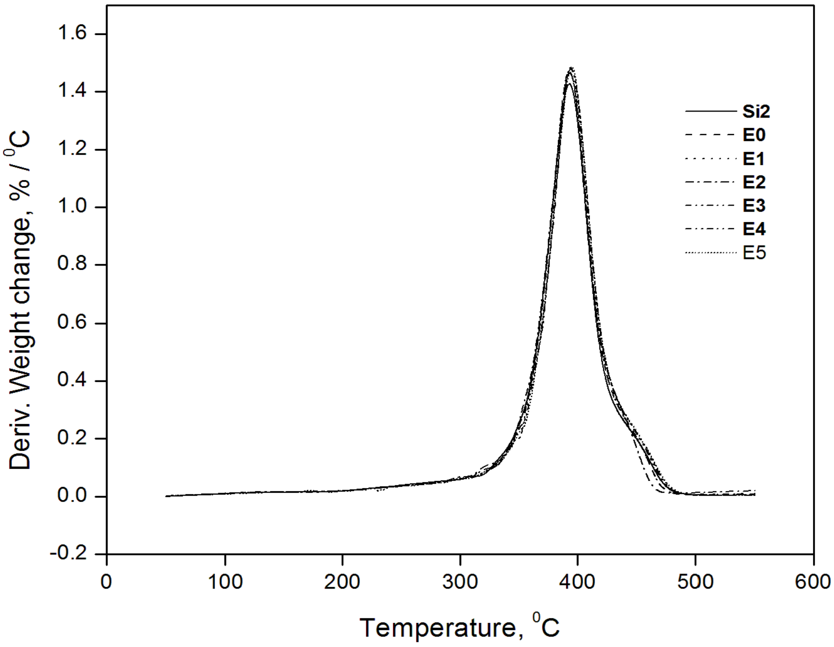


Figure 6.B.12 The derivative thermograms of silane modified and ENR modified silica-filled natural rubber vulcanizates

Further addition of ENR (4 g, 5 g and 6 g) increases marginally the onset of degradation and maximum degradation temperatures of the vulcanizates. The ENR modification of NR contributes to the effective interaction between the filler and the matrix and hence improves the interfacial adhesion. This makes the matrix thermally more stable in the presence of ENR at higher dosages.

Table 6.B.8 Thermal degradation data of silane modified and ENR modified silica-filled NR vulcanizates

Sample	T_i (°C)	T_{50} (°C)	T_{max} (°C)	Weight loss (%) at 500 °C
Si_2	354	400	393	84.6
E_0	353	400	392	85.6
E_1	353	400	393	85.6
E_2	353	401	393	85.6
E_3	355	401	393	85.9
E_4	358	401	394	86.6
E_5	358	401	395	86.2

6.B.9 Dynamic mechanical analysis

Dynamic mechanical properties of the vulcanizates: silica-filled NR, silane modified silica-filled NR and ENR modified silica-filled NR was determined at a temperature range of 40-120 ºC. Loss tangent (tan δ), the ratio of viscous (or loss) modulus to elastic (or storage) modulus of a compound, is a significant property obtained by dynamic mechanical analysis. It reveals the heat generation behaviour of a rubber compound. Value of tan δ at 60 °C gives information on rolling resistance. High performance rolling materials generally exhibit low tan δ at 60 °C and hence low rolling resistance.

Table 6.B.9 tan δ values of unmodified, silane modified and ENR modified silica-filled NR vulcanizates at 60 °C

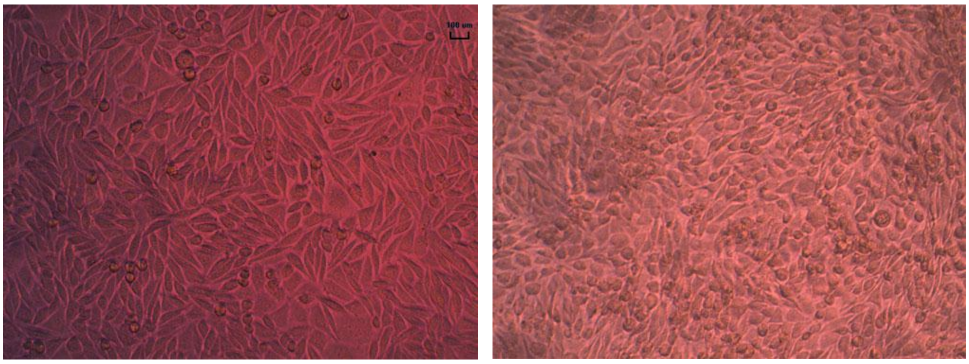
Sample	tan δ at 60 °C
S	0.07
Si_2	0.05
E_3	0.06

Lower the tan δ value at 60 °C, lower the rolling resistance expected in real performance of a material [56]. It is observed from the Table 6.B.9 that silane and ENR modified silica-filled NR vulcanizates show lower rolling resistance compared to the unmodified silica-filled NR vulcanizate.

6.B.10 Cytotoxicity of ENR modified silica-filled NR vulcanizate

Cytotoxicity of the NR vulcanizates was determined by MTT assay [39]. From the phase contrast images of the control of MTT assay and confluent cells containing extract of ENR modified silica-filled NR vulcanizate, taken after 24 hours of incubation (Figure 6.B.13), showed that the control of MTT assay contains large number of elongated viable cells than the latter. The round shape observed in the cell morphology images symbolise the dead cells.

The sample containing extract of E_3 (ENR modified silica-filled NR vulcanizate) have 70.17 % of viable cells. Therefore it was evident from the MTT assay that the ENR modified silica-filled natural rubber vulcanizate is mildly cytotoxic. These vulcanizates have the potential to cause long-term effects, eventhough they may not cause any immediate injury. But repeated exposures through careless handling or misuse can greatly increase the risk of chronic adverse effects [57].



(a) (b)

Figure 6.B.13 Phase contrast image (magnification 20 x) for the determination of cell morphology of: (a) control of the MTT assay and (b) extract of ENR modified silica-filled NR vulcanizate

6.2 Summary

Effect of silane coupling agent on the cure characteristics and mechanical properties of the silica-filled natural rubber compounds were analysed. Use of epoxidised natural rubber as a replacement for silane coupling agent was also studied. Silane treated silica-filled NR compounds show shorter scorch time and cure time compared to the unmodified silica-filled compound. ENR modified compounds show lower optimum cure time as compared to silane modified NR compounds. The cure kinetics study of both the silane modified and ENR modified silica-filled NR compounds revealed that the cure reaction was of first order. The silane modification increases the crosslink density of the silica-filled NR vulcanizate. This in turn improves the tensile strength and reduces the penetration of solvent through the vulcanizate. Silica-filled NR vulcanizates modified with ENR show higher tensile strength in comparison to the unmodified silica-filled natural rubber vulcanizate and comparable tensile strength to that of silane modified silica-filled vulcanizate at a slightly higher dosage. Addition of the silane coupling agent and ENR enhances the bound rubber content of the compounds and improves the fluid resistance of the vulcanizates. A uniform distribution of silica filler without the formation of any aggregates was observed in SEM photomicrographs of silane modified and ENR modified silica-filled vulcanizates. With TESPT modification, the Payne effect of the silica-filled compounds is greatly reduced. Strain-sweep analyses of uncured silane modified and ENR modified silica-filled NR compounds revealed good polymer-filler interaction. The thermal stability of the silica-filled vulcanizate shows marginal improvement with the incorporation of higher dosages of ENR. Addition of silane coupling agent and ENR results in low rolling resistance in the safe silica-filled NR vulcanizates. From the MTT assay it is observed that the silica-filled natural rubber vulcanizates modified with silane or ENR are found to be mildly cytotoxic.

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Chapter 7

EFFECT OF ANTIOXIDANTS ON THERMO-OXIDATIVE AGEING PROPERTIES OF SAFE ACCELERATOR INCORPORATED NATURAL RUBBER VULCANIZATES

Contents

Safe accelerator incorporated natural rubber vulcanizates were prepared using different dosages of commercial TQ (polymerized 1,2-dihydro-2,2,4-trimethyl quinoline) and high pure grade TQ, i.e. HPG (polymerized 1,2-dihydro-2,2,4-trimethyl quinoline with dimer as the predominant constituent) as antioxidant. The mechanical properties of the vulcanizates were compared with the properties of the vulcanizate prepared using N-(1,3-dimethylbuty1)-N$^{'}$-pheny1-p-phenylenediamine (6PPD) as control antioxidant. Stress-strain properties of the vulcanizates after ageing at 70 °C and 100 °C were compared. The studies on the vulcanizates include the evaluation of the cure characteristics, fluid resistance, thermogravimetric analyses and cytotoxicity tests.

7.1 Introduction

Elastomers are susceptible to oxidation. Nevertheless unsaturated elastomers oxidise more readily than saturated elastomers. Oxidation is a cyclic free radical chain process that proceeds through two mechanisms: chain scission and radical-induced crosslinking [1]. Chain scission of the polymer backbone causes softening and weakening while radical- induced crosslinking causes hardening and embrittlement of the polymer. Chain scission is the primary oxidation mechanism in natural rubber while radical-induced crosslinking is predominant in styrene butadiene rubber. Degradation of natural rubber can be caused by a variety of environmental factors such as elevated temperature, humidity, impurities, mechanical load, irradiation and chemicals. The useful lifetime of many polymer products is limited due to the prevalence of oxidative reactions in the presence of atmospheric oxygen [2].

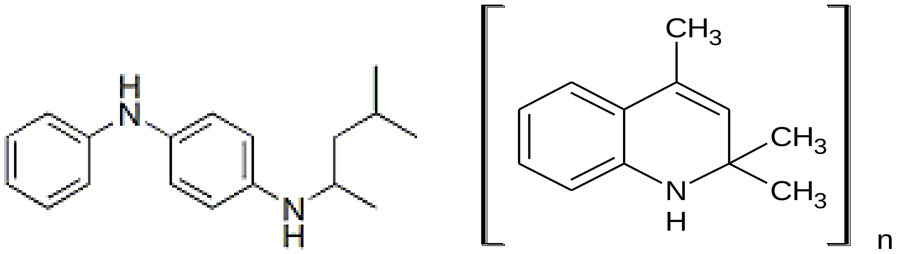
Free radical attack on the polymer chain causes chain scission, crosslink formation and crosslink breakage. Changes in the properties of polymers with ageing depend on the extent of such reactions [3]. The external manifestations of these reactions are changes in physico-chemical properties that include decrease in strength, elongation at break, change in resistivity and colour. Thus the degradative processes impair the useful properties of polymers. The resistance of natural rubber to heat, oxygen and ozone is poor due to the presence of double bonds in every repeating unit of the chemical structure [4, 5].

Oxidative degradation of polymers can be retarded by the addition of suitable antioxidants. NR products are usually protected by suitable antioxidants/antiozonants, such as p-phenylenediamines, dihydroquinolines, phenolic derivatives and waxes [6].

This chapter presents the effect of commercial TQ and high pure grade TQ, i.e HPG (polymerized 1,2-dihydro-2,2,4-trimethyl quinoline with dimer as the predominant constituent) on the mechanical properties and thermal ageing resistance of safe accelerator incorporated natural rubber vulcanizates. The properties of these vulcanizates are compared with that of the natural rubber vulcanizates prepared using N-(1, 3-dimethylbuty1)-N$^{'}$-pheny1-p-phenylenediamine (6PPD). Higher content of dimer in the HPG is believed to contribute better antioxidant property.

7.2 Formulations of the mixes containing 6PPD, commercial TQ and HPG

Table 7.1 shows the formulations of the various mixes prepared using 6PPD, commercial TQ and HPG as antioxidant. The control sample C_0 contains 6PPD as antioxidant. Various dosages of TQ were used in the mixes A_1, A_2 and A_3. The mixes A_4, A_5 and A_6 contain corresponding dosages of HPG. The structure of 6PPD and polymerized 1,2-dihydro-2,2,4-trimethyl quinoline is shown in the Figure 7.1.



(a) (b)

Figure 7.1 Structures of 6PPD and polymerized 1,2-dihydro-2,2,4-trimethyl quinoline

Table 7.1 Formulations of the mixes

Ingredients	**C_0**	**A_1**	**A_2**	**A_3**	**A_4**	**A_5**	**A_6**
NR (g)	100	100	100	100	100	100	100
ZnO (phr)	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	-	-	-	-	-	-
TQ (phr)	-	1.0	1.5	2.0	-	-	-
HPG (phr)	-	-	-	-	1.0	1.5	2.0
TBBS (phr)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TBzTD (phr)	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Sulphur (phr)	0.3	0.3	0.3	0.3	0.3	0.3	0.3

7.3 Cure characteristics

The rheographs of the mixes cured at 150 °C are shown in Figure 7.2. Table 7.2 lists the cure characteristics of natural rubber compounds prepared by incorporating the antioxidants 6PPD, TQ and its pure grade HPG at different dosages. 6PPD is slightly basic in nature and hence influence scorch and cure characteristics [7]. This may be the reason for the low scorch and cure time of the vulcanizate containing 6PPD compared to the vulcanizates containing TQ and HPG.

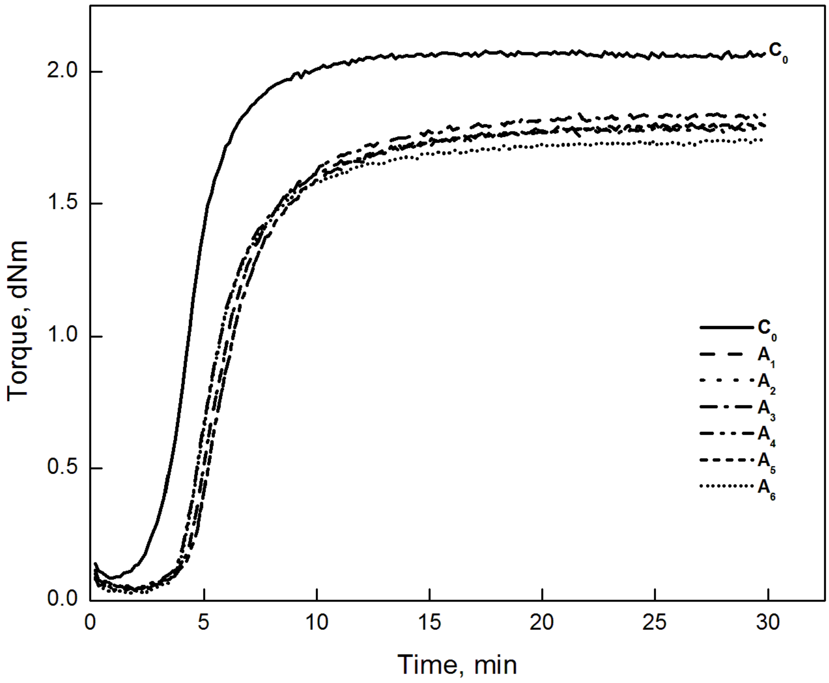


Figure 7.2 Rheographs of the mixes containing antioxidants 6PPD, TQ and HPG

The content of undesirable components like bisaniline (Section 2.1.6.2 and 2.1.6.3) and other primary amine-terminated oligomers and aromatics are very low in HPG compared to commercial TQ. These amine impurities are believed to be responsible for fast scorching, sulphur blooming and increase of stock viscosity at the processing temperature. Scorch time and optimum cure time of the mixes containing HPG are marginally higher compared to that containing TQ. This may be due to the lower amine type impurities present in the HPG.

Table 7.2 Cure characteristics of the mixes at 150 °C

Properties	**C_0**	**A_1**	**A_2**	**A_3**	**A_4**	**A_5**	**A_6**
Scorch time t_{10} (min)	2.89	4.26	4.26	4.25	4.35	4.37	4.34
Optimum cure time t_{90} (min)	7.17	10.70	10.72	10.72	10.86	10.81	10.85

7.4 Mechanical properties of the vulcanizates containing 6PPD, commercial TQ and HPG

The stress-strain properties of the vulcanizates containing 6PPD, TQ and HPG are shown in Figure 7.3. The properties of the vulcanizates with 6PPD, TQ and HPG as antioxidant are tabulated in Table 7.3. The vulcanizate containing 6PPD showed better mechanical properties compared to the vulcanizates containing TQ and HPG. Since bisaniline and other primary amine-terminated oligomers and aromatics are present in slightly higher amount in TQ as compared to HPG, chances of sulphur blooming cannot be ruled out. Sulphur blooming may cause reduction in mechanical properties and crosslink density since only less sulphur is available for crosslinking. The vulcanizates containing HPG showed marginally high tensile strength and tear strength values compared to the vulcanizate containing commercial TQ. The optimum tensile strength and tear strength were obtained for the vulcanizates A_2 (containing 1.5 phr TQ) and A_5 (containing 1.5 phr HPG).

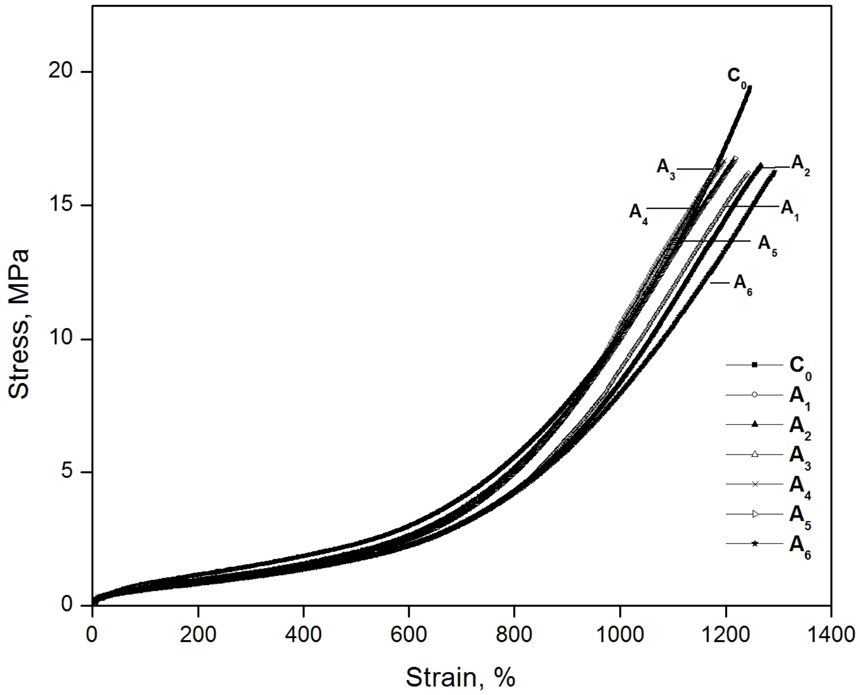


Figure 7.3 Stress-strain curves of the vulcanizates with 6PPD, TQ and HPG as antioxidant

As the dosage of the antioxidants (TQ and HPG) was increased, a marginal decrement in the compression set was observed (Table 7.3). As compression set results from the degradation of polymer chains at elevated temperature under compression [8, 9], the decrease in compression set may be due to the thermo-oxidative stability of the vulcanizates with the increase in the dosage of antioxidant.

As the dosage of TQ and HPG increased the values of rebound resilience and hardness showed no appreciable changes. The chemical crosslink densities of the vulcanizates and swelling index values calculated from swelling measurements are shown in the Table 7.3. Swelling index gave an indirect measure of crosslink density. The materials with high crosslink density showed low swelling index. Tensile strength and tear strength values of the vulcanizates containing TQ and HPG are in correlation with the crosslink density values.

Table 7.3 Properties of the rubber vulcanizates with 6PPD, TQ and HPG as antioxidant

Properties	**C_0**	**A_1**	**A_2**	**A_3**	**A_4**	**A_5**	**A_6**
Tensile strength(MPa)	19.55	16.22	16.51	16.36	16.67	16.76	16.26
Modulus at 300 % elongation (MPa)	1.46	1.07	1.12	1.19	1.18	1.20	1.09
Elongation at break (%)	1230	1229	1244	1178	1197	1218	1292
Tear strength (N/mm)	26.71	23.68	25.97	24.42	24.93	26.56	26.20
Hardness (Shore A)	31	28	28	29	27	28	28
Compression set (%)	15.05	15.60	15.38	15.27	15.55	15.26	15.17
Rebound resilience (%)	65	64	63	63	64	63	63
Crosslink density x10^5 (mol/g rubber hydrocarbon)	4.38	3.14	3.23	3.13	3.15	3.23	3.02
Swelling index	4.10	4.31	4.30	4.37	4.40	4.39	4.51

The stress-strain properties of the samples before and after ageing are shown in Figures 7.4, 7.5 and 7.6. The results are tabulated in Table 7.4. The vulcanizates showed comparable tensile strength before and after ageing at 70 °C and 100 °C for 24 hours due to the stability of the predominant mono and di sulphidic linkages present in the efficient vulcanizates. The elongation at break of the vulcanizates decreased on thermal ageing at both the temperatures.

Table 7.4 Effect of 6PPD, TQ and HPG on stress-strain properties of the NR vulcanizates after ageing at 70 °C and 100 °C (24 hours)

Sample	Tensile strength (MPa)			Modulus at 300 % elongation (MPa)			Elongation at break (%)		
	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C
C_0	19.55	20.64	19.19	1.46	1.62	2.04	1230	1200	906
A_1	16.22	16.33	16.26	1.07	1.20	1.24	1229	957	968
A_2	16.51	16.86	17.14	1.12	1.28	1.53	1244	1150	1007
A_3	16.36	16.52	16.91	1.19	1.40	1.67	1178	1046	902
A_4	16.67	16.65	16.67	1.18	1.21	1.24	1197	902	890
A_5	16.76	16.88	17.21	1.20	1.24	1.47	1218	1158	1034
A_6	16.26	16.35	16.61	1.09	1.28	1.5	1292	1108	1053

The modulus at 300 % elongation increased after ageing at 70 °C and 100 °C. This may be due to the formation of additional crosslinks. The modulus at 300 % elongation was found to increase as the duration of accelerated ageing was increased up to 96 hours at 70 °C (Table 7.5). The modulus is related to the crosslink density of the rubber vulcanizates. These changes are directly associated with the marginal increase in the crosslink density on ageing as shown later in this chapter (Table 7.6) [2, 4, 10].

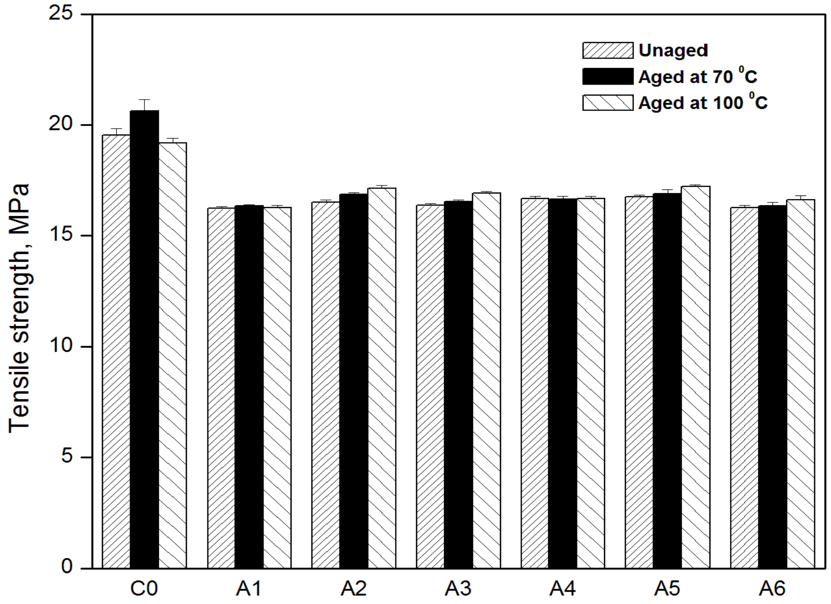


Figure 7.4 Variation in tensile strength before and after ageing of the NR vulcanizates containing 6PPD, TQ and HPG as antioxidant

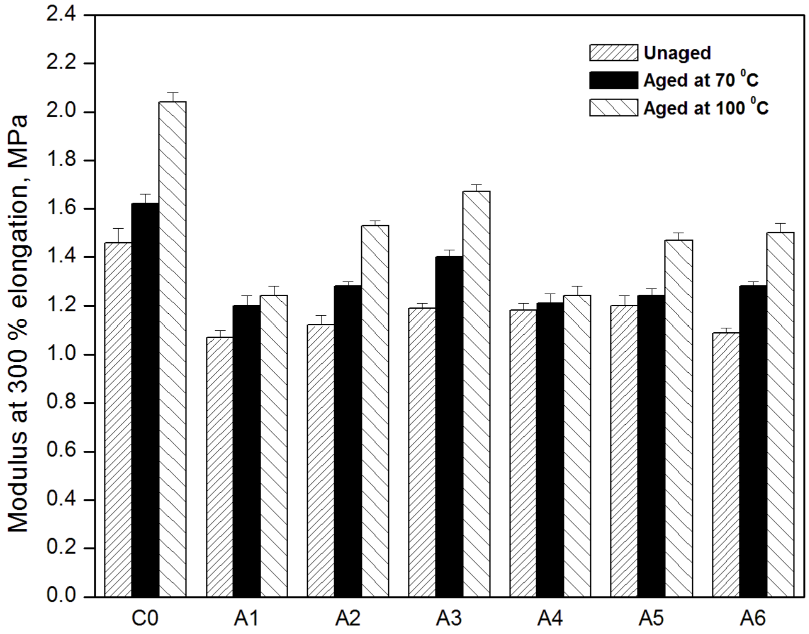


Figure 7.5 Variation in modulus at 300 % elongation before and after ageing of the NR vulcanizates containing 6PPD, TQ and HPG as antioxidant

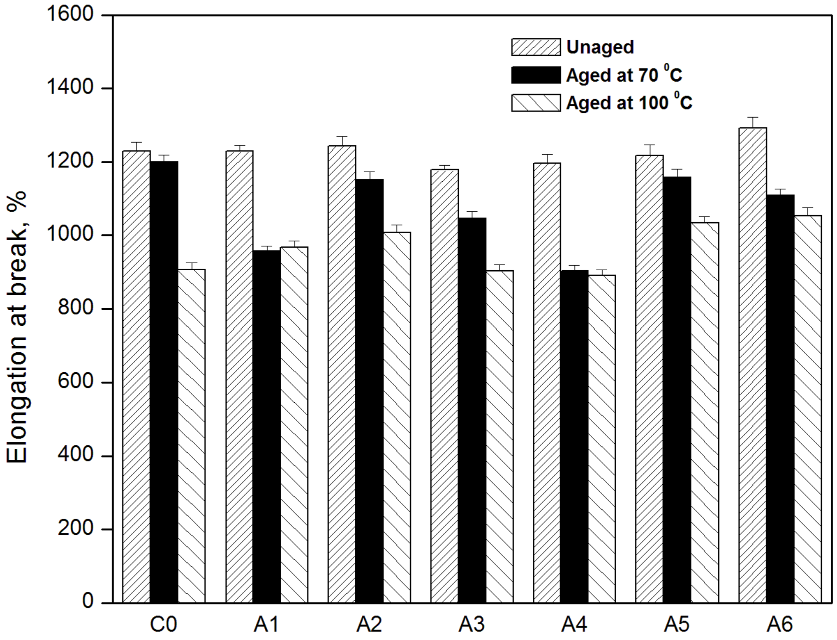


Figure 7.6 Variation in elongation at break before and after ageing of the NR vulcanizates containing 6PPD, TQ and HPG as antioxidant

Thermo-oxidative ageing of the vulcanizates was carried out for extended durations of 24, 48, 72 and 96 hours at a temperature of 70 °C. The stress-strain properties of the NR vulcanizates containing 6PPD, TQ and HPG after ageing at 70 °C are shown in Table 7.5. The variation in tensile strength, modulus at 300 % elongation and elongation at break after ageing at 70 °C for 24 h, 48 h, 72 h and 96 h are shown in Figures 7.7, 7.8 and 7.9. The tensile strength of the vulcanizates did not decrease even after 96 hours of thermo-oxidative ageing at 70 °C. This establishes the effectiveness of the antioxidants, TQ and HPG. Elongation at break decreased after ageing for all the vulcanizates. When the number of crosslinks increases, the networks become rigid and restrict the facile elongation of all the vulcanizates subjected to hot air ageing.

Table 7.5 Stress-strain properties of the rubber vulcanizates containing 6PPD, TQ and HPG as antioxidant after ageing at 70 °C

Sample	Tensile strength (MPa)			Modulus at 300 % elongation (MPa)			Elongation at break (%)		
	48 h	72 h	96 h	48 h	72 h	96 h	48 h	72 h	96 h
C_0	20.95	21.04	21.16	1.86	1.92	1.98	1120	1040	1020
A_1	16.62	16.94	17.09	1.28	1.42	1.45	948	940	922
A_2	17.44	17.27	17.24	1.36	1.43	1.49	1073	933	920
A_3	17.26	18.78	18.83	1.46	1.74	1.62	1068	984	983
A_4	16.74	16.99	17.12	1.23	1.38	1.44	896	884	880
A_5	17.03	17.13	17.19	1.29	1.49	1.52	1118	973	945
A_6	16.67	18.31	18.71	1.34	1.60	1.66	1179	1019	983

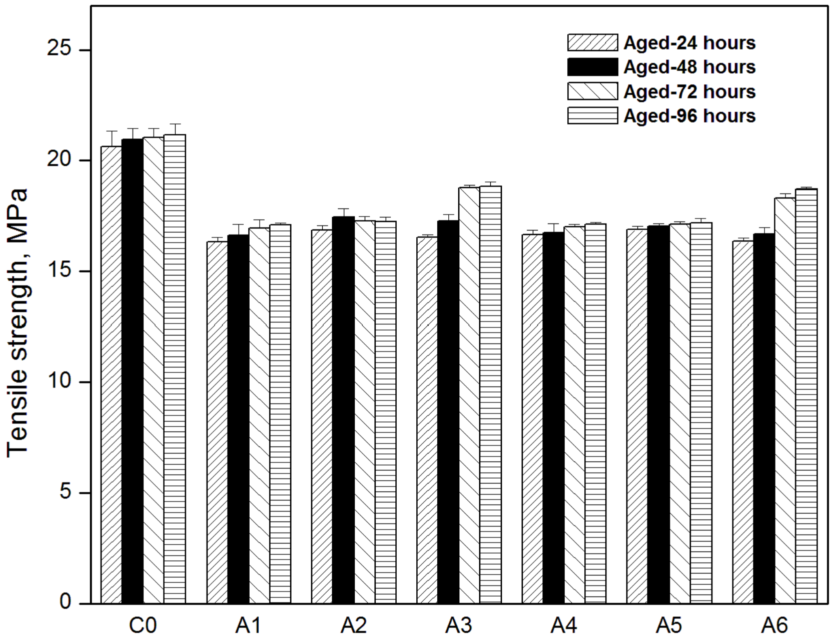


Figure 7.7 Variation in tensile strength of the NR vulcanizates after ageing at 70 °C for 24h, 48h, 72h and 96h

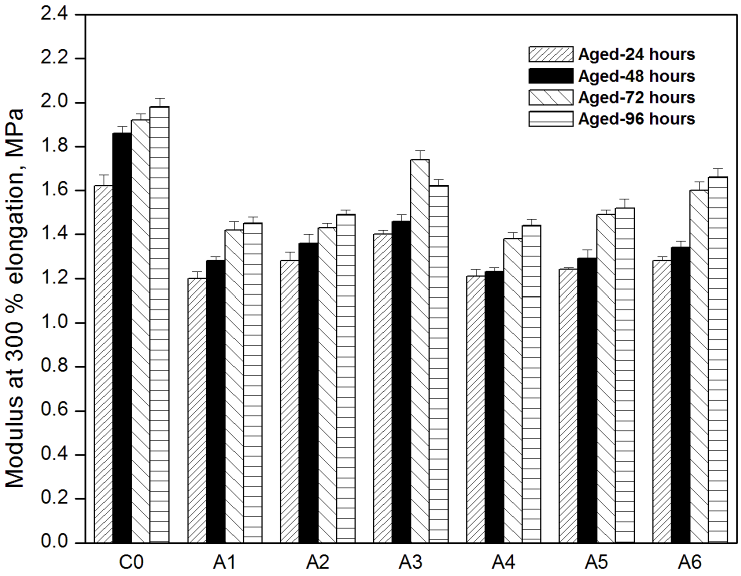


Figure 7.8 Variation in modulus at 300 % elongation of the NR vulcanizates after ageing at 70 °C for 24h, 48h, 72h and 96h

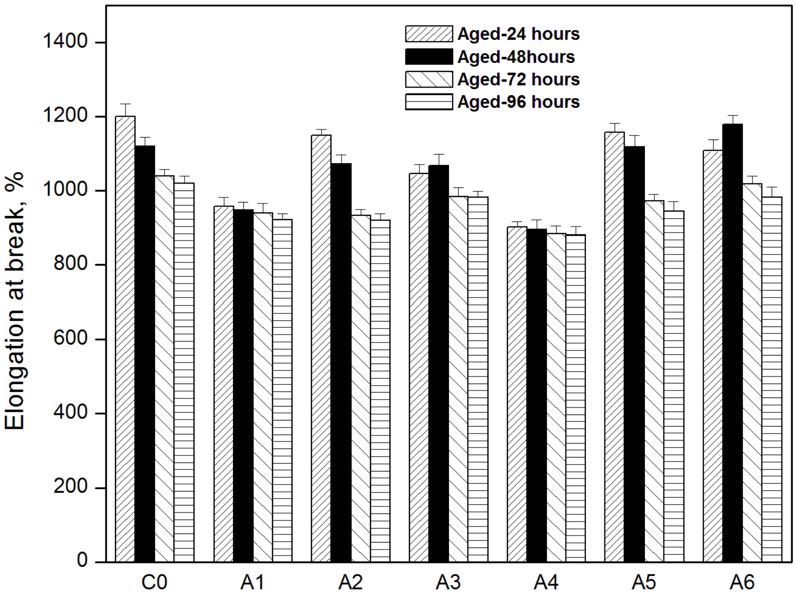


Figure 7.9 Variation in elongation at break of the NR vulcanizates after ageing at 70 °C for 24h, 48h, 72h and 96h

7.4.1 Ageing mechanism

Ahagon et al. [11] proposed three types of ageing mechanisms in the case of natural rubber vulcnizates: Type I – aerobic or anaerobic at lower temperatures, Type II – anaerobic at higher temperatures, and Type III – aerobic at higher temperatures. They have shown in their work that it is possible to distinguish the three ageing mechanisms by analysing the relation between elongation at break ratio (E) and 100 % modulus (M_{100}) in a log E vs. log M_{100} plot known as Ahagon plot [11]. Raising the ageing temperature results in deviations from linearity and ultimately in a completely different behaviour. Instead of the modulus increasing and the elongation at break decreasing with increasing oxidation, for anaerobic degradation both the modulus and elongation at break decrease with increasing degradation. These observations are completely consistent with the basics of aerobic and anaerobic degradation process. Oxidation causes an overall increase in crosslink density and a decrease in elasticity. In contrast, anaerobic degradation typically results in crosslink scission. This leads to a decrease in modulus and elasticity. Figure 7.10 shows a schematic Ahagon plot and the three ageing mechanisms.

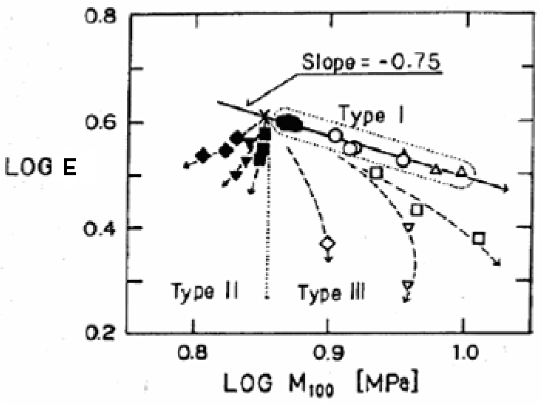


Figure 7.10 Schematic Ahagon Plot [11]

It was also shown by Ahagon that in Type I ageing the M_{100} increased and E decreased following the equation given below:

$E = A \times (M_{100})^{-0.75}$ -- (7.1)

In this type of ageing the process is like the one observed during vulcanization, which is simply an increase in the crosslink density.

In type II ageing, a decrease or marginal increase in M_{100} is observed with a higher reduction in E. This trend makes the curve deviate from the Equation. In type III, the behaviour deviates from the curve given by the equation, because the M_{100} increases/slightly decreases while E value has a severe reduction.

Figures 7.11, 7.12 and 7.13 display the plot of log E vs. log M_{100} of the vulcanizates prepared using 6PPD, TQ and HPG. The slope of log E vs. log M_{100} plot for the C_0, A_2 and A_5 vulcanizates showed the values -0.557, -0.656 and -0.587 respectively. Thus the results establish the preponderance of Type I ageing in these vulcanizates.

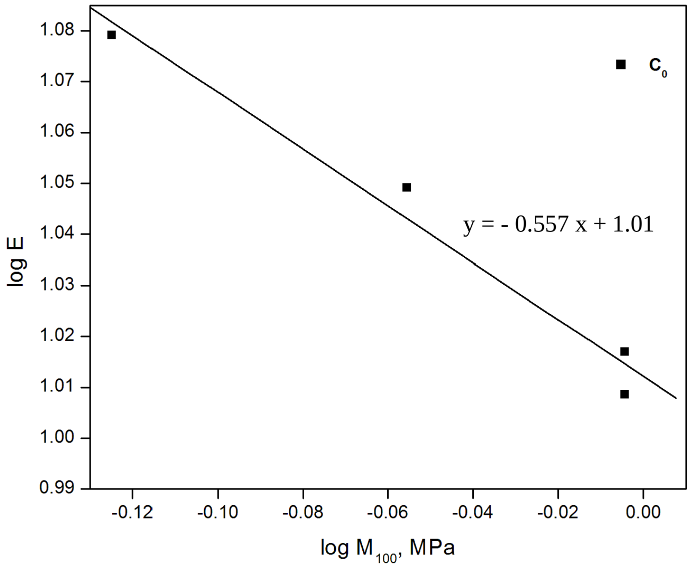


Figure 7.11 Ahagon plot of the NR vulcanizate containing 6PPD (C_0)

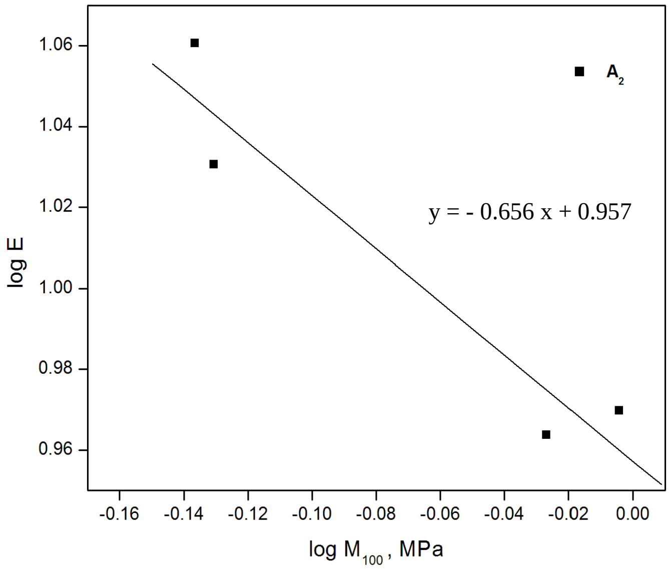


Figure 7.12 Ahagon plot of the NR vulcanizate containing TQ (A_2)

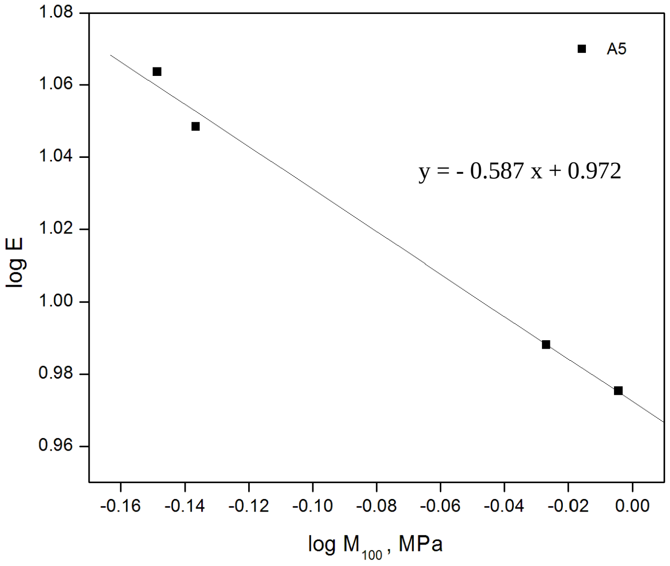


Figure 7.13 Ahagon plot of the NR vulcanizate containing HPG (A_5)

Since the thermo-oxidative ageing is a diffusion-controlled process, the plot of M_{100} versus square root of ageing time ($t^{1/2}$) is expected to be a straight line where the slope represents the rate of change in crosslink density [12].

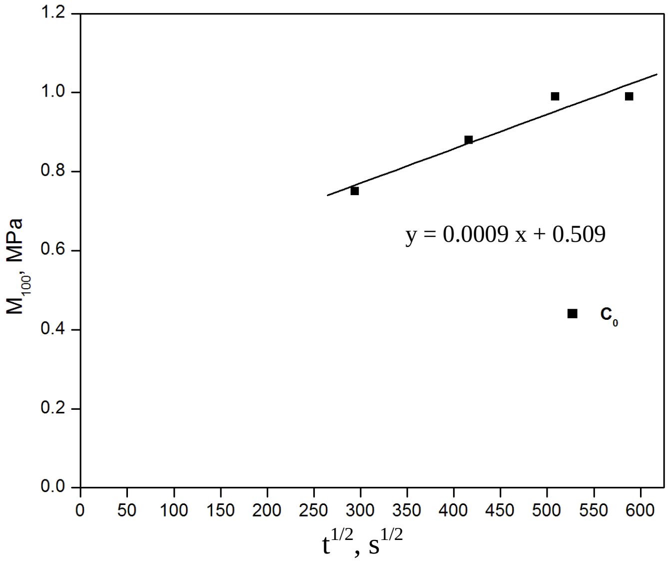


Figure 7.14 Plot of M_{100} vs. $t^{1/2}$ of the NR vulcanizate C_0

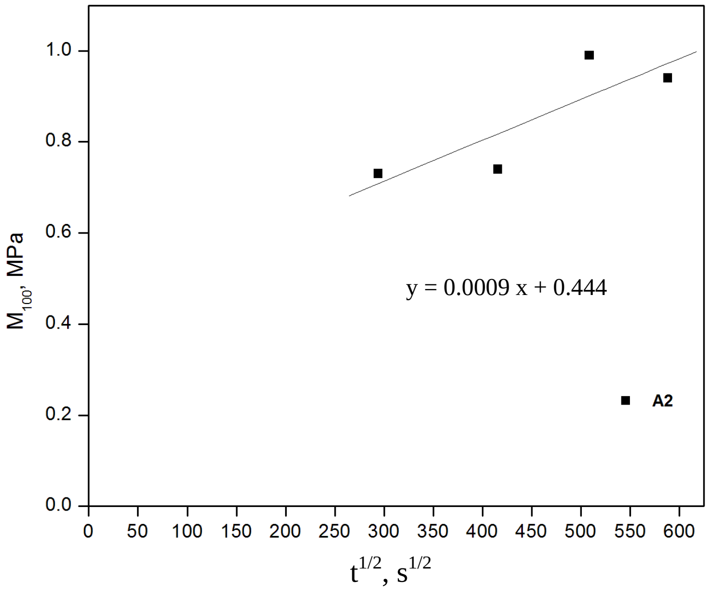


Figure 7.15 Plot of M_{100} vs. $t^{1/2}$ of the NR vulcanizate A_2

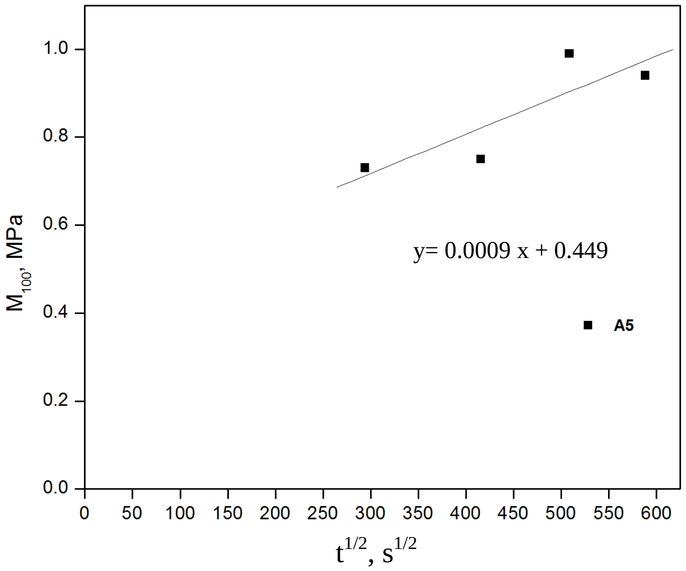


Figure 7.16 Plot of M_{100} vs. $t^{1/2}$ of the NR vulcanizate A_5

The plot of M_{100} vs. $t^{1/2}$ of the aged samples C_0, A_2 and A_5 is shown in Figures 7.14, 7.15 and 7.16. The slope of the plot (rate of change in crosslink density) was obtained from the appropriate equation of the line shown in the above mentioned figures. In an aerobic low temperature condition, M_{100} increases with time, indicating an increasing trend in crosslink density. The rate of change in crosslink density of C_0, A_2 and A_5 is almost the same (0. 9 kPa $s^{-1/2}$) predicting similar ageing resistance for these vulcanizates.

7.4.2 Crosslink density of the aged vulcanizates

Crosslink density of the aged samples (at 70 °C for 24 hours, 48 hours, 72 hours and 96 hours) were calculated from equilibrium swelling data and is shown in the Table 7.6. There was increment in the crosslink densities of the vulcanizates even after thermal ageing at 70 °C for 96 h.

Table 7.6 Crosslink density of the NR vulcanizates C_0, A_2 and A_5 after ageing at 70 °C for 24 h, 48 h, 72 h and 96 h

Sample	**Crosslink density x 10^5 (mol / g rubber hydrocarbon)**			
	24 h	**48 h**	**72 h**	**96 h**
C_0	5.14	5.16	5.21	5.37
A_2	3.75	3.78	3.82	3.90
A_5	3.78	3.80	3.83	3.92

It can be observed from Figure 7.17 that the change in crosslink density of the vulcanizate C_0 is considerably higher than that of A_5 while it was slightly higher than that of the vulcanizate A_2, thus indicating a greater ageing resistance for the vulcanizate C_0. The crosslink density change (ΔX_c) was calculated by dividing the difference in the crosslink densities of the vulcanizates after and before the thermal ageing, by the initial crosslink density.

$$\Delta X_c = \frac{(X_c^{aged} - X_c^{initial}) \times 100}{X_c^{initial}} \text{ ---(7.2)}$$

where the X_c^{aged} and $X_c^{initial}$ indicate the crosslink densities of the vulcanizates after and before the thermal ageing, respectively.

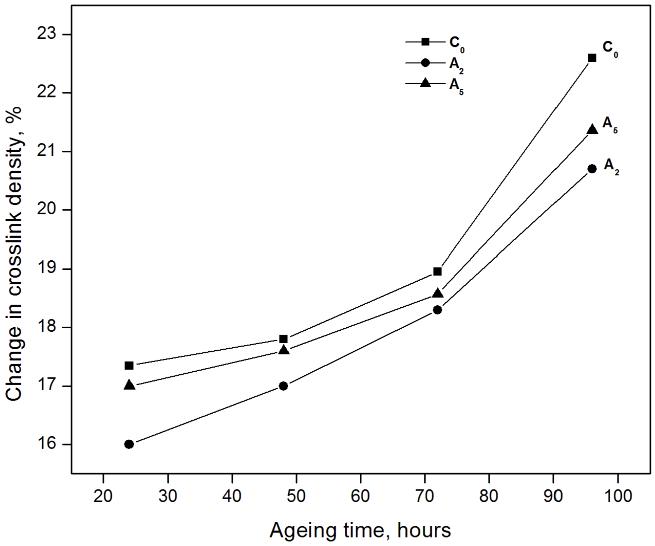


Figure 7.17 Change in crosslink density of the vulcanizates C_0, A_2 and A_5 after thermal ageing at 70 °C

The increased crosslink density after the thermal ageing can be explained with the formations of new crosslinks by free curative residues such as elemental sulphur, cure accelerator residues and zinc complexes remaining unutilized in the vulcanizate [13-15,4]. From the Figure 7.17 and the Table 7.6 it is observed that the vulcanizate containing HPG has more ageing resistance than the vulcanizate containing TQ. This may be due to the low monomer content in HPG. HPG has high dimer and high molecular oligomeric components. It also has minimum contents of undesirable components like bisaniline, primary amine-terminated components and monomer. These factors also contribute to the improved ageing properties of the vulcanizate containing HPG.

7.5 Fluid resistance

The fluid resistance of the vulcanizates were performed in diesel and lube oil according to the ASTM D 471. The percentage change in mass of the vulcanizates containing 6PPD (C_0), TQ (A_2) and HPG (A_5) is shown in the Table 7.7.

Table 7.7 Change in mass (%) of C_0, A_2 and A_5 in diesel and lube oil

Sample	Change in mass (%)	
	Diesel	Lube oil
C_0	225	98
A_2	265	100
A_5	266	103

The fluid resistance of the vulcanizate containing 6PPD was high compared to the vulcanizates containing TQ and HPG. This may be due to the high crosslink density of the vulcanizate C_0 (Table 7.3). The percentage increase in mass of the vulcanizates A_2 and A_5 was almost the same after immersing in diesel and lube oil. The increase in mass of both the vulcanizates in lube oil was lower than obtained in diesel. This may be due to the low penetration of the highly viscous lube oil between the rubber chains [16].

7.6 Thermogravimetric analysis

Figures 7.18 and 7.19 show the thermograms and derivative thermograms of the natural rubber vulcanizates containing the antioxidants 6PPD (C_0), TQ (A_2) and HPG (A_5). The T_i of C_0 and A_5 was 341 °C and 321 °C respectively while that of A_2 was considerably lower (297 °C) (Table 7.8). Improvement in thermal stability of C_0 and A_5 vulcanizates were also evident from their higher values of peak degradation temperature. On comparing the decomposition patterns, thermal stability of the NR vulcanizates were in the order $C_0 > A_5 > A_2$.

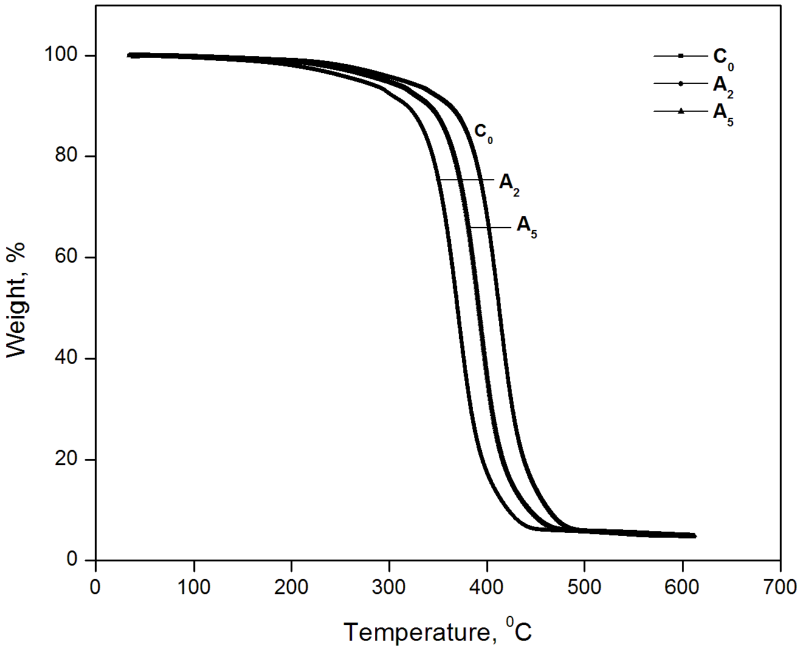


Figure 7.18 The thermograms of natural rubber vulcanizates ontaining 6PPD (C_0), TQ (A_2) and HPG (A_5) antioxidants

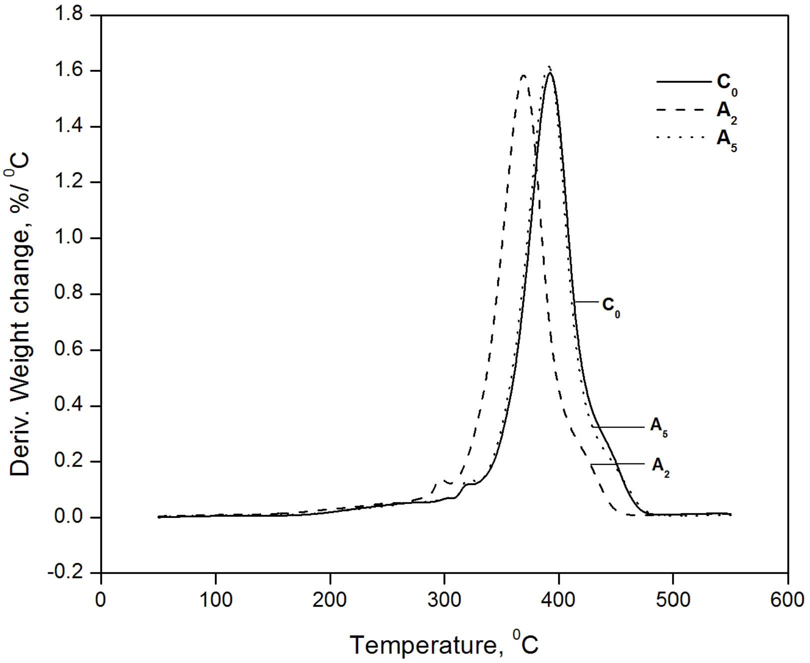


Figure 7.19 The derivative thermograms of natural rubber vulcanizates containing 6PPD (C_0), TQ (A_2) and HPG (A_5)

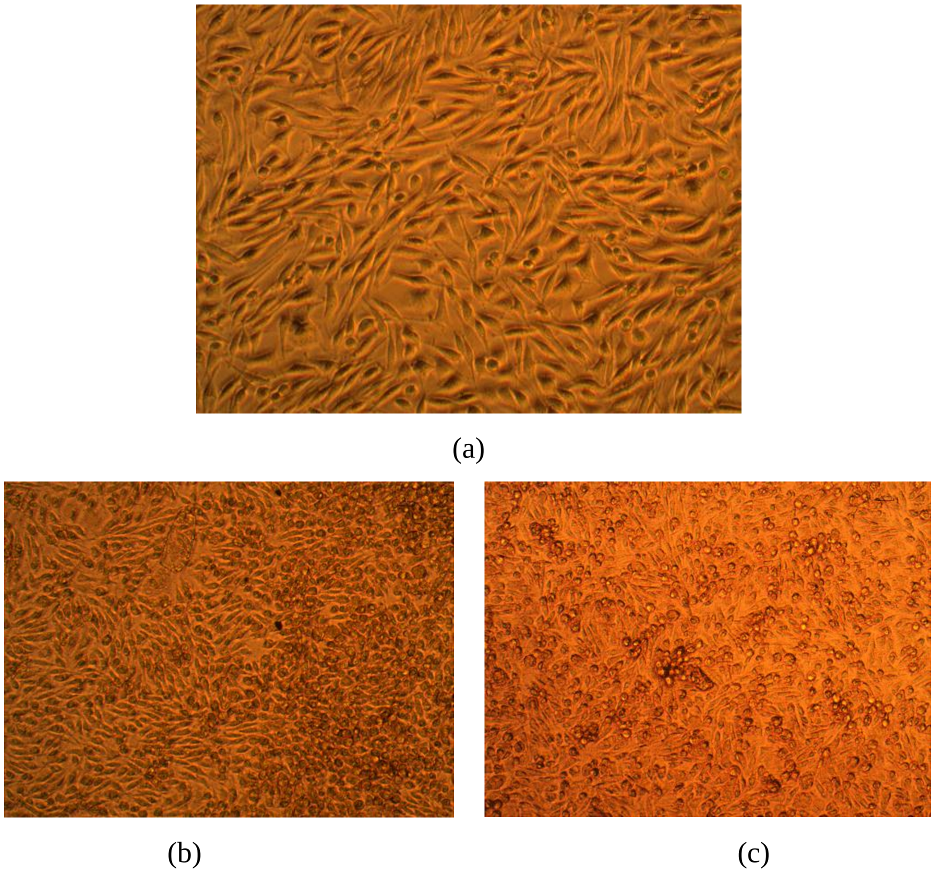
Table 7.8 Thermogram data of the vulcanizates containing 6PPD, TQ and HPG

Sample	T_i (°C)	T_{50} (°C)	T_{max} (°C)	Weight loss (%) at 500 °C
C_0	341	392	393	94.3
A_2	297	349	376	94.5
A_5	321	371	389	94.3

7.7 Cytotoxicity of the vulcanizates containing commercial TQ and HPG

Phase contrast images for determining the cell morphology of control of MTT assay [17] and confluent cells containing extract of A_2 and A_5 after 24 hours incubation, are shown in Figure 7.20. In the control of MTT assay, a large number of fibroblast cells were observed and the corresponding absorbance values were also higher. However in the case of the confluent cells containing the extract of vulcanizates with TQ and HPG as antioxidant, a small reduction in the number of viable cells and absorbance values were observed.

Since the absorbance values reflect the number of surviving cells and its metabolic activity, lower absorbance values in the case of cells containing extracts of A_2 and A_5 than the control cells indicate a reduction in the number of viable cells. Measurement of cell viability forms the basis for *in vitro* MTT assay. Carcinogenic materials reduce the number of viable cells and thereby lower the percentage viability of cells. The cell viability of the samples containing extract of A_2 (containing TQ) and A_5 (containing HPG) are found to be 70.31 % and 76.40 % respectively. It is evident from the MTT assay that the natural rubber vulcanizates containing TQ and HPG was mild cytotoxic while that containing 6PPD was non-cytotoxic in nature (Section 3.B.6) [18, 19]. Incorporation of TQ and HPG to the safe (non-regulated) accelerator incorporated formulation induced mild cytotoxicity in the NR vulcanizates. Nevertheless the incorporation of TQ and HPG has not induced moderate/severe toxicity (< 60 % viable cells) in the cells. Thus the vulcanizates can be believed as safe. These vulcanizates may not be immediately carcinogenic, but repeated exposures through careless handling or misuse can seriously increase the risk of chronic diseases [20].



(a)

(b) (c)

Figure 7.20 Phase contrast image (magnification 20 x) for the determination of cell morphology of: (a) control of the MTT assay (b) extract of NR vulcanizate containing TQ and (c) extract of NR vulcanizate containing HPG

7.8 Summary

Narural rubber based safe vulcanizates incorporating different dosages of TQ and HPG were prepared. Safe NR vulcanizate with 1 phr 6PPD was set as the control vulcanizate. The natural rubber compounds containing TQ and HPG shows higher scorch time and optimum cure time as compared to the control vulcanizate. However the scorch safety of the compounds containing HPG was slightly better compared to the compounds containing TQ. The vulcanizates containing 6PPD show better mechanical properties compared to those containing TQ and HPG. Yet the vulcanizates prepared using high pure grade TQ showed slightly high tensile strength and tear strength compared to that prepared using commercial TQ. The tensile strength and modulus at 300 % elongation of all the vulcanizates were further increased upon thermal ageing at 70 °C and 100 °C for 24 hours. The vulcanizates retained their tensile strength and crosslink density even after ageing at 70 °C for 96 hours. Ahagon plot of the vulcanizates indicated the occurrence of Type I ageing (i.e. increased M_{100} and decreased elongation at break after ageing). The vulcanizates containing commercial TQ and HPG showed similar percentage increase in mass after immersing in diesel and lube oil. Thermogravimetric analysis of the vulcanizates containing 6PPD and HPG established better efficiency of these materials compared to the commercial TQ. The natural rubber vulcanizates containing TQ and HPG were mild cytotoxic while the vulcanizate containing 6PPD was non-cytotoxic.

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Chapter 8

CONCLUSIONS

This chapter provides a glimpse of the conclusions drawn from the research work carried out on natural rubber vulcanizates prepared using safe accelerators and the scope for the future work on non-regulated accelerators incorporated synthetic rubber vulcanizates. The primary objective of the study was to develop safe binary accelerators incorporated natural rubber vulcanizates with mechanical properties comparable to that of the NR vulcanizates prepared using conventional regulated nitrosamine generating accelerators. The results of MTT assay show that tertiarybutyl benzothiazolesulfenamide (TBBS) and tetrabenzyl thiuramdisulfide (TBzTD) are safe (non-carcinogenic) substitutes for N-oxydiethylene 2-benzothiazolesulfenamide (MBS) and tetramethyl thiuramdisulfide (TMTD) in natural rubber based formulations.

Safe natural rubber vulcanizates can be prepared using N, N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) or N, N-dibenzyl-2-benzothiazolesulfenamide (DBBS) too. Though the vulcanizates prepared using DCBS or DBBS in binary combination with TBzTD are non-cytotoxic, the mechanical properties are inferior compared to the vulcanizates prepared using TBBS and TBzTD. So for the further studies TBBS and TBzTD were chosen as the safe accelerators.

Commercial applications of rubbers require the use of particulate fillers such as carbon black, silica, etc. Natural rubber vulcanizates with desired mechanical properties could be obtained by mixing carbon black.

The addition of carbon black improved the tensile strength, tear strength and abrasion resistance. Swelling studies in toluene show that the addition of carbon black decreases the diffusion, permeation and sorption coefficients in NR vulcanizates. Rubber-filler interactions of the carbon black-filled NR compounds were confirmed through bound rubber content and strain-sweep analysis. SEM images confirmed the proper dispersion of the filler in the vulcanizates. Thermogravimetric analysis results show better thermal stability of the carbon black-filled NR vulcanizates compared to the gum vulcanizate. Non-cytotoxic nature of the carbon black-filled NR vulcanizate was proved by the MTT assay. The safe black-filled vulcanizate containing 40 phr filler shows optimum mechanical properties.

One of the non-black reinforcing fillers with reinforcing properties closer to carbon black is precipitated silica. The natural rubber compounds containing silica filler show more scorch safety compared to the gum compound, but require longer cure times. Incorporation of silica to the natural rubber compound improved the tensile strength, modulus at 300 % elongation, tear strength and hardness. Abrasion resistance increased as the dosage of silica increased. Optimum properties were obtained with 15 phr of precipitated silica. Swelling studies in toluene show reduction in diffusion coefficient, sorption coefficient and permeation coefficient with increase in silica content. Incorporation of silica in NR compounds improved the fluid resistance of the vulcanizates in diesel and lube oil. The MTT assay results confirmed the non-cytotoxicity of the silica-filled natural rubber vulcanizates.

For a filler to be effective in rubber as a reinforcing agent it has to be well dispersed. Several modifications of silica filler such as heat treatment, chemical modification of the filler surface groups, grafting of polymers on to the filler surface and use of promoters or coupling agents have been reported to improve the rubber-filler interaction. Conventionally silica-reinforced rubber vulcanizates are prepared by mechanical mixing of rubber and silica with silane coupling agent (Si69), which provides a chemical link between silica and rubber. A promising alternative method for proper dispersion of silica in the natural rubber matrix is the incorporation of small dosages of epoxidised natural rubber (ENR). Evaluation of epoxidised natural rubber as a reinforcement modifier in precipitated silica-filled NR was made and compared with silane modified silica-filled NR. Presence of ENR in the rubber matrix during mixing of silica has improved the distribution of silica in the rubber matrix. The mechanical properties of the ENR modified silica-filled vulcanizates were compared with that of the Si69 modified silica-filled vulcanizates. The results of mechanical properties indicate that ENR has a coupling effect in silica-filled rubber vulcanizates.

Relatively good distribution of silica-filler with less number of agglomerates in the NR was observed in the SEM photomicrograph of the vulcanizates prepared using silane coupling agent and ENR. Addition of the silane coupling agent and ENR enhanced the bound rubber content of the compounds and improved the fluid resistance of the vulcanizates. Addition of silane coupling agent and ENR results in low rolling resistance in the safe silica-filled NR vulcanizates. It is observed that the ENR modified silica-filled NR vulcanizates give reinforcement equivalent to that of silane modified silica-filled NR vulcanizate at dosages of ENR more than double that of Si69. ENR can be considered as an alternative to the expensive silane coupling agent. From the MTT assay it is observed that the silica-filled natural rubber vulcanizates modified with silane and ENR are found to be mildly cytotoxic, but safe to use. The repeated exposures through careless handling or misuse of the vulcanizates may increase the risk of adverse effects.

The mechanical properties of the vulcanizates prepared using commercial TQ (polymerized 1,2-dihydro-2,2,4-trimethyl quinoline) or high pure grade TQ, i.e. HPG (polymerized 1,2-dihydro-2,2,4-trimethyl quinoline with dimer as the predominant constituent) as antioxidant were compared with that of the vulcanizate prepared using N-(1,3-dimethyl buty1)-N’-pheny1-p-phenylenediamine (6PPD) as control antioxidant. The vulcanizates containing 6PPD show better mechanical properties compared to that containing TQ and HPG. The vulcanizate prepared using HPG show slightly high tensile strength and tear strength compared to that prepared using commercial TQ. All the vulcanizates show improved tensile strength after ageing at 70 °C and 100 °C for 24 hours and retained the tensile strength even after ageing at 70 °C for 96 hours. Thermogravimetric analysis of the vulcanizates containing 6PPD and HPG establishes better efficiency of these materials as antioxidants compared to the commercial TQ. The MTT assay results show that the natural rubber vulcanizates containing TQ and HPG produce mild cytotoxicity and the vulcanizate containing 6PPD is non-cytotoxic.

Suggestions for future work

Future prospects of these studies include:

- Preparation of safe vulcanizates by incorporating nitrosamine-safe accelerators (TBBS and TBzTD) into synthetic rubbers such as styrene butadiene rubber (SBR), nitrile rubber (NBR) and ethylene-propylene-diene monomer rubbers (EPDM).

- Use of zincdibenzyl dithiocarbamate (ZBEC) - a nitrosamine safe accelerator - for the preparation of vulcanizates based on synthetic rubbers (SBR, Butyl rubber (IIR), EPDM) and also on NR and SBR lattices.
- Evaluation of the mechanical properties and cytotoxicity of the proposed safe accelerator incorporated vulcanizates.

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List of Symbols and Abbreviations

ASTM - American Society for Testing and Materials
BR - Polybutadiene rubber
CBS - N-cyclohexyl-2-benzothiazolesulfenamide
CRI - Cure rate index
CR - Polychloroprene rubber
CV - Conventional vulcanization
D - Diffusivity
DBBS - N, N-dibenzyl-2-benzothiazolesulfenamide
DCBS - N, N-dicyclohexyl-2-benzothiazolesulfenamide
DEG - Diethylene glycol
DMA - Dynamic mechanical analysis
DTDC - Dithiodicaprolactam
DTG - Derivative thermogravimetry
E - Extension ratio
E_a - Activation energy
ENR - Epoxidised natural rubber
EV - Efficient vulcanization
FDA - Food and drug administration
FEF - Fast extrusion furnace
GPF - General purpose furnace black
HAF or N330 - High abrasion furnace
Hexa - Hexamethylene tetramine
HPG - High Pure Grade TQ
IARC - International Agency for Research on Cancer
IR - Polyisoprene rubber

ISAF	-	Intermediate super abrasion furnace
ISO	-	International organization for standardization
k	-	Cure reaction rate constant
M_{100}	-	Modulus at 100 % elongation
MBS	-	N-oxydiethylene 2-benzothiazolesulfenamide
MPa	-	Mega pascal
MTP	-	Microtiter plate
MTT	-	Methylthiazolyl tetrazolium
M_w	-	Weight average molecular weight
NBR	-	Nitrile rubber
NR	-	Natural rubber
P	-	Permeation coefficient
PEG	-	Polyethylene glycol
6PPD	-	N-(1, 3-dimethyl buty1)-N'-pheny1-p-phenylenediamine
Q_t	-	Mole percent solvent uptake
R	-	Universal gas constant
RPA	-	Rubber process analyzer
s	-	Sorption coefficient
SAF	-	Super abrasion furnace
SBR	-	Styrene butadiene rubber
SEM	-	Scanning electron microscope
SEV	-	Semi efficient vulcanization
T	-	Absolute temperature
tan δ	-	Loss tangent
TBBS	-	Tertiarybutyl benzothiazolesulfenamide
TBzTD	-	Tetrabenzyl thiuramdisulfide
TEA	-	Triethanolamine

TESPT or Si69	-	Bis (triethoxysilylpropyl)tetrasulfide
TGA	-	Thermogravimetric analysis
T_i	-	Onset of degradation temperature
TMTD	-	Tetramethyl thiuramdisulfide
TQ	-	Polymerized 1,2-dihydro-2,2,4–trimethyl quinoline
ZBEC	-	Zincdibenzyl dithiocarbamate
ZnO	-	Zinc oxide
cc/hr	-	Cubic centimeter per hour
cSt	-	Centistokes
°C	-	Degree celsius
°C/min	-	Degree Celsius per minute
dNm	-	Deci newton meter
f_s	-	Shape factor of filler
g/cc	-	Gram per cubic centimeter
G'	-	Storage modulus
G"	-	Loss modulus
G*	-	Complex modulus
G_0	-	Shear modulus of pure elastomer
G_f	-	Shear modulus of filled compound
ΔG	-	Elastic Gibbs free energy change
Hz	-	Hertz
ΔH	-	Change in enthalpy
J/mol K	-	Joule per mole Kelvin
kg/m^3	-	Kilogram per cubic meter
KJ/mol	-	Kilo joule per mole
KN	-	Kilo newton
M_H	-	Maximum torque

M_L - Minimum torque
ml - Milli litre
nm - Nanometer
phr - Parts per hundred rubber
ΔS - Entropy change
t_{10} - Scorch time
t_{90} - Optimum cure time
V_r - Volume fraction of rubber
V_s - Molar volume of the solvent
Xc^{aged} - Crosslink density after ageing
Xc^{ini} - Crosslink density before ageing
ΔXc - Crosslink density change
α_f - Filler specific constant
µm - Micrometer
φ - Volume fraction of filler
χ - Interaction parameter

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Publications

List of Publications in International Journals

[1] Studies on non-regulated safe binary accelerator system for efficient vulcanisation of natural rubber, **Abhitha K.**, Philip Kurian, Thomas Kurian and L. Jayabalan, ***Progress in Rubber, Plastics and Recycling Technology***, **29**(2), (2013), 99-108.

[2] Safe vulcanisation system for heat resistant natural rubber products for engineering applications, **Abhitha K.** and Thomas Kurian, ***American Journal of Engineering Research (AJER),*** **3,**(2013), 8-13.

[3] Evaluation of TBBS and TBzTD based binary accelerator systems in natural rubber compounds, **Abhitha K.**, Thomas Kurian and Jayabalan L., ***Rubber Science***, **29**(2), (2016), 199-206.

[4] Non-regulated Accelerator (DCBS/DBBS) Incorporated Natural Rubber Formulations - Cure Characteristics and Mechanical Properties, **Abhitha K.** and Thomas Kurian, ***International Journal of Research and Scientific Innovation (IJRSI)***. **(In Press)**

[5] Non-carcinogenic Accelerators for Natural Rubber Vulcanization, **Abhitha K.** and Thomas Kurian, ***Progress in Rubber, Plastics and Recycling Technology***. **(Communicated)**

[6] Effect of carbon black on safe binary accelerator incorporated natural rubber vulcanizates, **Abhitha K.** and Thomas Kurian, ***Rubber Chemistry and Technology***. **(Communicated)**

[7] Epoxidised natural rubber - a substitute for silane coupling agent in safe silica-filled natural rubber formulations, **Abhitha K.** and Thomas Kurian, ***Polymers for Advanced Technologies.*** **(Communicated)**

List of Papers Presented at Conferences

[1] Non – carcinogenic cure system for natural rubber, **Abhitha K.**, Philip Kurian, Thomas Kurian and L. Jayabalan, ***National conference on 'Recent Trends in Material Science and Technology (NCMST 2013)*** organized by Department of Chemistry, Indian Institute of Space Science and Technology, Thiruvananthapuram, Kerala, India, July 10 – 12, 2013.

[2] Efficient vulcanisation of natural rubber using safe (non - carcinogenic) accelerator system, **Abhitha K.**, Philip Kurian, Thomas Kurian and L. Jayabalan, ***Third International Conference on 'Materials for the Future' Innovative Materials, Processes, Products & Applications (ICMF 2013)*** organized by GEC, Thrissur, Kerala, India, Nov 6-8, 2013.

[3] Non - carcinogenic binary accelerator based vulcanization system for natural rubber, **Abhitha K.**, Philip Kurian, Thomas Kurian and L. Jayabalan, ***12th Prof. K.V.Thomas Endowment National Seminar Novel Concepts in Computational and Supramolecular Chemistry*** organized by Department of Chemistry, Sacred Heart College, Kochi, Kerala, India, Dec 11-12, 2013.

[4] Safe vulcanisation system for heat resistant natural rubber products for engineering applications, **Abhitha K.**, Philip Kurian, Thomas Kurian and L. Jayabalan, ***CUSAT National Conference on Recent Advances in Structural Engineering RASE 2013***, Kochi, Kerala, India, Dec 13-15, 2013.

[5] Effect of safe non – regulated accelerators in gum and carbon black filled NR vulcanisates, **Abhitha K.**, Philip Kurian, Thomas Kurian and L. Jayabalan, ***National Seminar on Recent Advances in Polymer Technology (RAPT – 2K15)*** organized by Department of Polymer Engineering, School of Technology and Applied Sciences, Mahatma Gandhi University, Kottayam, Kerala, India, March 12-13, 2015.

[6] Influence of non-carcinogenic thiuram and sulphenamide accelerators on the properties of NR vulcanisates, **Abhitha K.**, Thomas Kurian and L. Jayabalan, ***National Seminar Chemistry in Cancer Research (CCR 2015)***, organized by St. Alberts College, Ernakulam, Kerala, India, Oct 8-9, 2015.

[7] Benzoylpyrrolidinylthiourea:A new binary accelerator for the vulcanisation of natural rubber, Molice Thomas, K.Kurien Thomas, Thomas Kurian and **Abhitha K., *52nd Annual convention of Chemists and International conference on Recent Advances in Chemical Sciences, JECRC University, Jaipur, Rajasthan,*** Dec 28-30, 2015.

[8] Rheological and mechanical properties of nitrosamine safe carbon black filled natural rubber vulcanisates, **Abhitha K.**, Thomas Kurian and L. Jayabalan, ***International conference on Advances in applied Mathematics,Materials science and Nano technology for Engineering and Industrial Applications (IC-AMMN-2K16)*** organized by Federal Institute of Science and Technology, Angamaly, Kerala, India, Jan 7-9, 2016.

[9] Effect of carbon black and silica on the cure characteristics and mechanical properties of nitrosamine - safe natural rubber vulcanisates, **Abhitha K.** and Thomas Kurian, ***International conference on Science and Technology: Future Challenges and Solutions (STFCS- 2016)***, organized by University of Mysore, Karnataka, India, August 8-9, 2016.

[10] Effect of Terephthalic Acid Hydrazone synthesized from PET Bottle Wastes on the Thermo-oxidative Aging of Natural Rubber, Neena George, **Abhitha K.** and Thomas Kurian, ***International conference on Science and Technology: Future Challenges and Solutions (STFCS- 2016)***, organized by University of Mysore, Karnataka, India, August 8-9, 2016.

[11] Influence of Silane Coupling agent on Cure characteristics and Mechanical properties of Silica-filled Nitrosamine-safe Natural Rubber Vulcanizates, **Abhitha K.** and Thomas Kurian, ***Prof. K.V. Thomas Endowment International Symposium- New Trends in Applied Chemistry (NTAC-2017)***, organized by Sacred Heart College, Kochi, Kerala, India, February 9-11, 2017.

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Curriculum Vitae

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ACADEMIC PROFILE

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ANNEXURE BASED ON THE SUGGESTIONS OF THE EXAMINERS

1) **For all the MTT assay, presentation of the results in bar chart form would give better correlation between the type of modification and the resulting cytotoxicity.**

MTT assay results in bar chart form is shown in Figure 1

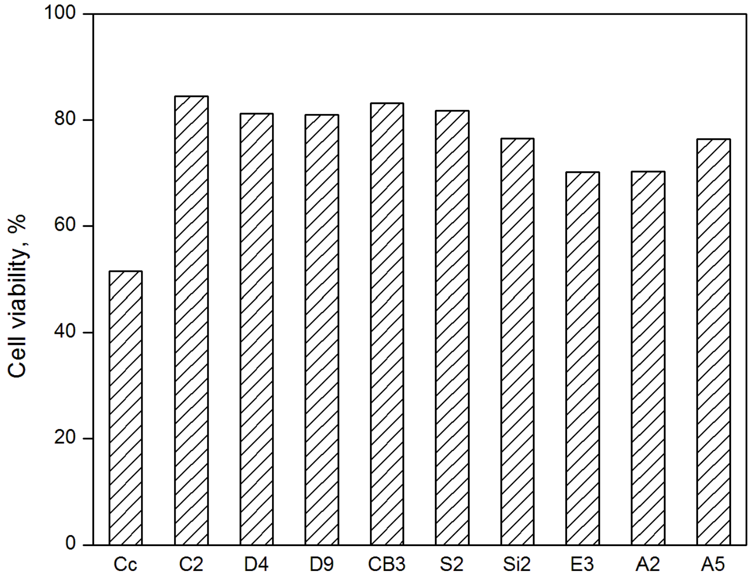

Figure 1 Cell viability (%) of the samples containing extracts of unsafe (C_c) and safe (C_2, D_4, D_9, CB_3, S_2, Si_2, E_3, A_2 & A_5) vulcanizates

2) **What are the molecular weights of NR and ENR used?**

Weight average molecular weight of NR = 8×10^5- 8.5×10^5 g/mol

Weight average molecular weight of ENR= 8×10^5 – 8.2×10^5 g/mol

3) **Precautionary statement codes/hazard statement codes required under the work health and safety (WHS) laws could have been added for the ingredients, as the focus of the thesis is on safe chemicals.**

Table 1 Hazard statement codes and precautionary statement codes of chemicals

Chemical Name	Hazard statement codes		Precautionary statement codes	
Sulphur	H228	Flammable	P210	Keep away from heat/sparks/open flames/hot surfaces.
	H315	Causes skin irritation		
			P264	Wash thoroughly after handling
			P370 +P378	In case of fire: Use dry chemical, CO_2, water spray or foam.
N-oxydiethylene 2-benzothiazolesulfenamide (MBS)	H315	Causes skin irritation.	P264	Wash hands thoroughly after handling.
	H411	Toxic to aquatic life with long lasting effects	P302 + P352	If on skin: wash with plenty of soap and water.
Tertiarybutylbenzothiazolesulfenamide (TBBS)	H317	May cause an allergic skin reaction	P273	Avoid release to the environment.
	H410	Very toxic to aquatic life with long lasting effects.	P302 +P352	If on skin: Wash with plenty of soap and water.
N, N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS)	H317	May cause an allergic skin reaction	P262	Avoid contact with the skin, eyes and clothing.
	H410	Very toxic to aquatic life with long lasting effects	P273	Avoid release to the environment.
N, N-dibenzyl-2-benzothiazolesulfenamide (DBBS)	Not marketed yet. May cause an allergic skin reaction.		Avoid contact with the skin, eyes and clothing.	
Tetramethylthiuramdisulfide (TMTD)	H302	Harmful if swallowed.	P264	Wash hands thoroughly after handling.
	H317	May cause an allergic skin reaction.	P273	Avoid release to the environment
	H319	Causes serious eye irritation.		.
	H341	May cause mutagenic effects		
	H410	Very toxic to aquatic life with long lasting effects.		
Tetrabenzylthiuramdisulfide (TBzTD)	H413	May cause long lasting harmful effects to aquatic life.	P273	Avoid release to the environment.
High abrasion furnace black (HAF-black)	Moderate toxicity. Moderate body contact irritation. Low reactivity.		Wash skin with mild soap and water. Rinse eyes thoroughly with large volumes of water keeping eyelids open	
Precipitated silica	Causes irritation to eyes. May cause irritation and discomfort to skin.		Rinse thoroughly with plenty of water. Wash skin with soap and water.	
N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)	H317	May cause an allergic skin reaction.	P273	Avoid release to the environment.
	H410	Very toxic to aquatic life with long lasting effects.	P302 +P352	If on skin: Wash with plenty of soap and water.
Polymerized 1, 2-dihydro-2,2,4-trimethyl quinoline (TQ)	H412	Harmful to aquatic life with long lasting effects.	P273	Avoid release to the environment.

High pure grade TQ (HPG)	H412	Harmful to aquatic life with long lasting effects.	P273	Avoid release to the environment.
Zinc oxide (ZnO)	May cause eye and skin irritation.		Flush eyes and skin with plenty of water.	
Stearic acid	H315	Causes skin irritation.	P264	Wash hands thoroughly after handling.
Naphthenic oil	May cause eye irritation. Prolonged contact may produce mild irritation to skin.		Flush thoroughly with water. Wash with soap and water.	
Diethylene glycol (DEG)	Skin irritant. Slightly hazardous in case of eye contact.		Immediately flush eyes with running water. Wash immediately with plenty of water.	
Bis(triethoxysilylpropyl) tetrasulfide	May cause eye irritation. Prolonged contact may produce mild irritation to skin.		Flush thoroughly with water. Wash with soap and water.	
Toluene	Hazardous in case of: skin contact, eye contact (irritant), ingestion and inhalation. Flammable.		Immediately flush skin and eyes with plenty of water. If inhaled, move the victim to fresh air. Keep away from heat.	
Diesel oil	Excessive inhalation of vapours causes rapid breathing, headache, nausea and vomiting. Skin-dryness and cracking. Eye irritation. Flammable.		In case of excessive inhalation move the victim to fresh air. If problem in breathing persists, give artificial respiration. In case of eye or skin contact, flush with plenty of water. Keep away from heat	
Lube oil	May cause eye irritation. Prolonged contact may produce mild irritation to skin.		Flush thoroughly with water. Wash with soap and water.	

4) What is the mechanism proposed for the variation in cure time between C_c and C_{01}?

Cure time of C_c (containing MBS) is greater than C_{01} (containing TBBS)[1]. The compounds containing TBBS is more basic than that containing MBS. Thus the compound C_{01} shows faster cure rate as compared to the compound C_c. The sterically hindered amine in MBS may be the reason for slow cure rate.

5) **The incorporation of a discussion on the distinction between physical crosslinks and those introduced via vulcanization (chemical crosslinks), based on the difference in the crosslink density values, could have been more impressive.**

Comparison of physical and chemical crosslink density of carbon black-filled NR Vulcanizates is shown in Table 2

Table 2 Comparison of physical and chemical crosslink density of carbon black-filled NR Vulcanizates

Properties	**C_0**	**CB_1**	**CB_2**	**CB_3**	**CB_4**
Crosslink density x10^5 (mol/g rubber hydrocarbon) – from equilibrium swelling	4.38	4.94	5.40	6.51	7.59
Crosslink density x 10^4 (mol/g rubber hydrocarbon)- from stress- strain analysis	3.34	4.70	5.52	6.00	6.59

6) **What is the particle size of precipitated silica used?**

Average particle size of precipitated silica: 8-10 µm

7) **Why is the crosslink density of Si_3 less than that of Si_2? Fig 6.A.7 shows a reduced solvent uptake for the former**

Inorder to activate short chain polysulfide in the Si69 for the coupling reaction, the addition of sulphur and accelerators is needed. The presence of sulphur and accelerator favours both the matrix (rubber) crosslinking and silane coupling. Once the free sulphur is consumed for both crosslinking reactions, no further bonds are built up (after 1.5phr Si69). So crosslink density decreases thereafter (Si_3).

Increase in amount of silane coupling agent leads to an increase in amount of silica-to-rubber bonds resulting in a lower matrix crosslink density. These silica-rubber bonds make the solvent path tortuous and decrease the solvent uptake [2].

8) Candidate could have added FTIR evidences for comparing silanecoupling agent and ENR modifications.

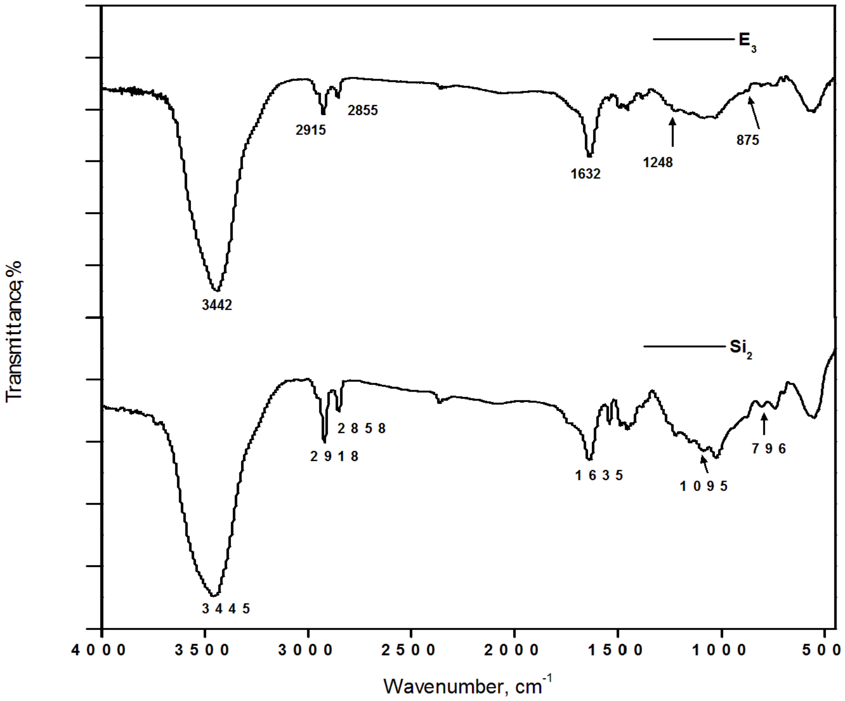

Figure 2 FTIR spectra of silane modified (Si$_2$) and ENR modified (E$_3$) silica-filled NR vulcanizates

Table 3 Important FTIR peaks and assignments for silane modified and ENR modified silica-Filled NR vulcanizates

Wavenumber (cm^{-1})	Functional groups
875	Asymmetric C–O–C stretching vibrations of epoxy groups[3,4]
1248	Deformation vibration of epoxy[5]
2930-2830	C-H stretching[6]
1632,1635	C=C stretching
1095	Si-O-C stretching[7,8]
1300-900	Si-O-Si asymmetrical stretching vibration[9,10]
796	Si-O symmetric stretching vibration [11]
3500-3000	-0H stretching

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