A study of the effects of kaolin, solid filler on the processing, mechanical, and dynamic properties of some industrial rubbers cured with novel sulphur cure system

by

Saad Hasan Sheikh

A doctoral thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

Project Supervisor: Dr Ali Ansarifar

School of Aeronautical, Automotive, Chemical and Materials Engineering

ACKNOWLEDGEMENTS

“Praises be to God, the Lord of the Universe. The Most Gracious, the Most Merciful.”

Source: Sura Al-Fatiha, Al-Quran.

There are so many people I would like to thank for all their support and guidance that I have received during my PhD project. Firstly I would like to show sincere thanks to my supervisor Dr Ali Ansarifar for his support and guidance from the beginning and his motivation to the completion of this project. I would also like to thank my co-supervisors Dr George Weaver and Professor Upul Wijayantha-Kahagala-Gamage from the department of chemistry for their continuous support.

I am very thankful to Mr Ray Owen, Mr Andy Woolley for the training and guidance with all the practical work carried out. I would like to thank everyone in LMCC for their support and assistance throughout this project. I would also like to express my sincere gratitude to all the administrative and secretarial staff at Loughborough University and the department of materials for their friendly attitude and continuous support during my studies.

Last but not the least, I would like to express my deepest gratitude to my parents, my brother, my wife and all family members who have been very supportive and encouraging all my life and I truly appreciate their sacrifices and understanding.

STRUCTURE OF THE THESIS

Chapter 1

This chapter provides background to the present work. Sulphur cure systems and solid fillers are indispensable parts of rubber formulations. The health, safety, cost and environmental issues related to the excessive use of these chemicals in rubber compounds are mentioned. Two novel methods for the sulphur vulcanisation of rubber and mineral kaolin as a potential replacement for the current filler systems in rubber are studied.

Chapter 2

This chapter provides a review of the structure, properties and applications of NR, BR and EPDM rubbers. These rubbers were used in this project. Furthermore, rubber chemical additives were also reviewed with particular emphasis on the chemicals used in the sulphur vulcanisation of rubber and also mineral clays, kaolin, carbon black and silica/silane solid filler systems for rubber reinforcement.

Chapter 3

This chapter reports results on the measurement of the optimum loading of a sulphenamide accelerator for curing some sulphur-filled NR, BR and EPDM rubbers. The optimum loading of zinc oxide activator in the sulphur-filled rubbers with the optimum loading of TBBS was subsequently determined. For each rubber, a new cure system based on the measurement of the optimum loading of TBBS accelerator and ZnO activator at a given loading of sulphur was developed.

Chapter 4

This chapter presents results on combining ZnO with TBBS by functionalising the surface of zinc oxide with TBBS molecules in an organic solvent to produce a convenient single material referred to as powder to cure some sulphur-filled NR. The optimum loading of the powder to fully cure the sulphur-filled rubber was subsequently measured.

Chapter 5

In this chapter, solid kaolin filler pre-treated with a sulphur-bearing mercaptosilane was investigated as a possible replacement for toxic carbon black and expensive silica/silane systems in rubber reinforcement. This method react the sulphur in the silane with the NR chains to produce stable covalent sulphur bonds between the two which is essential for rubber reinforcement. The optimum loading of TBBS required for reacting the sulphur in the silane with the rubber phase was first measured and then an optimum amount of ZnO was also added to improve the efficiency of the TBBS reaction with the sulphur in the silane to achieve full cure of the rubber.

Chapter 6

Using the novel sulphur cure systems developed for NR, BR and EPDM rubbers in Chapter 3, NR, BR and EPDM rubbers were mixed with up to 140 parts per hundred rubber by weight (phr) mineral kaolin solid filler the surface of which was pre-treated with a mercaptosilane. The rubber compounds were subsequently cured and their viscosity, cure and mechanical properties were measured. The mechanical properties measured were, hardness, tensile strength, elongation at break, stored energy density at break, Young’s modulus, tear strength, and compression set. The glass transition temperatures and crosslink density of the rubber vulcanisates were also measured.

Chapter 7

This chapter summarises the conclusions from chapters 3 and 4 on the development of novel sulphur cure systems for NR, BR and EPDM rubbers. Also, conclusions from chapters 5 and 6 on the effect of the silane pre-treated kaolin filler on the mechanical properties of the NR, BR and EPDM rubber vulcanisates were included.

Chapter 8

This chapter provides suggestions for further work. The novel cure systems developed in this study can be used to cure rubbers other than NR, BR and EPDM and produce green rubber compounds for use by the rubber industry. Also, the mineral kaolin filler can be used more extensively in rubber reinforcement as potential replacement for carbon black and silica/silane systems.

ABSTRACT

Two novel methods for the sulphur vulcanisation of NR, BR and EPDM rubbers using N-tert-butyl-2-benzothiazole sulphenamide (TBBS) accelerator and zinc oxide (ZnO) activator have been developed. In one method, the optimum loading of TBBS and ZnO were measured for some sulphur-filled NR, BR and EPDM rubbers. The cure systems for the NR were (S/TBBS/ZnO), (1/1.5/0.2), (2/1.5/0.3), (3/1.5/0.25), and (4/3.5/0.2), for the BR, (0.5/1.75/0.2) and (1/3/0.2), and for the EPDM, (1/1/0.075). The cure was very efficient in spite of reducing the amount of TBBS and ZnO chemicals. In another method which used a single additive component in the form of a powder (TBBS/ZnO: 350mg/1g), the loading of the powder in NR was raised increasingly from 0.63 to 5.63 phr, the scorch time was unchanged and the optimum cure time reduced at 1.25 phr powder. The rate of cure accelerated at 1.25 phr powder. The crosslink density reached its maximum value at 5.63 phr powder. This method reduced the TBBS and ZnO requirement in the cure system by 85wt%.

Solid kaolin filler pre-treated with a sulphur-bearing mercaptosilane was used to reinforce NR, BR and EPDM rubbers. For NR, to react the sulphur in the silane on the kaolin surface with the rubber chains and optimise the reaction between the two, 16 phr TBBS and 0.2 phr ZnO were added to the kaolin-filled rubber. The hardness and Young’s modulus increased and compression set decreased when up to 3 phr elemental sulphur was included in the kaolin-filled rubber with 16 phr TBBS and 0.2 phr ZnO. The tensile strength, elongation at break, stored energy density at break, and tear energy of the rubber vulcanisate reduced when elemental sulphur was added. Notably, the inclusion of elemental sulphur was the key factor in controlling the rubber properties.

In an extended work, 60 phr silane pre-treated kaolin was mixed with NR, BR and EPDM and the rubbers were cured using the novel cure systems developed earlier. The effect of 140 phr kaolin on the properties of NR was also investigated.

For NR, the hardness increased by 64% when 60 phr kaolin was added and the trend continued rising by another 28% when the loading of kaolin reached 140 phr. Similarly, the Young’s modulus rose by 170% with 60 phr kaolin and then by an extra

148% when the full amount of kaolin, i.e. 140 phr, was reached. The tensile strength and tear energy were unchanged and the elongation at break and stored energy density at break deteriorated by a total of 65% and 34%, respectively with 140 phr kaolin. The compression set of the unfilled rubber was 41%, and it then rose to 64% and 71%, when 60 and 140 phr kaolin was added, respectively.

For BR, the hardness increased by 23% and for EPDM, by 34%, respectively when 60 phr kaolin was incorporated in the rubbers. For BR, the tensile strength, elongation at break and Young’s modulus rose by 759%, 256% and 114%, respectively. The compression set of the unfilled BR was 9.4%, and subsequently rose to 26% when 60 phr kaolin was mixed with the rubber.

For EPDM, the tensile strength, elongation at break and Young’s modulus improved by 964%, 332% and 71%, respectively. For BR, the stored energy density at break and tear energy were increased by 2442% and 536%, respectively and for EPDM, by 3133% and 1479%, respectively. The compression set of the unfilled EPDM was 39%, and afterward increased to 48% with 60 phr kaolin.

Kaolin was found to be extending or non-reinforcing filler for the strain-induced crystallising NR and highly reinforcing for the non-crystallising BR and EPDM.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

NR	Natural rubber
BR	Polybutadiene rubber
EPDM	Ethylene-propylene-diene monomer
ZnO	Zinc oxide
Phr	Parts per hundred of rubber
T_g	Glass transition temperature
^oC	Degree Celsius
IIR	Butyl Rubber
SBR	Styrene-Butadiene rubber
CR	Polychloroprene rubber
NBR	Acrylonitrile-Butadiene rubber
DCP	Dicyclopentadiene
ENB	Ethylidene norbornene
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
EV	Efficient vulcanisation
SEV	Semi-efficient vulcanisation
CV	Conventional vulcanisation
IARC	International Agency for Research on Cancer
EPA	Environmental Protection Agency
6PPD	N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine
PAA	Primary Aromatic Amines
RFL	Resorcinol formaldehyde latex
CB	Carbon Black
OECD	Organisation for Economic Co-operation and Development
TESPT	Bis (-triethoxysilylpropyl-) tetrasulphane
TBBS	N-tert-butylbenzothiazole-2-sulphenamide
CBS	N-cyclohexylbenzothiazole-2-sulphenamide
MBT	2-Mercaptobenzothiazoles
MBTS	2,2’-Dithiobenzothiazole
TMTD	Tetramethylthiuram disulphide

TEM	Transmission Electron Microscopy
MPTS	3-mercaptopropyltrimethoxysilane
SRSO	Sodium salt of rubber seed oil
GRAS	Generally Regarded as Safe
CMS	Clay Minerals Society
MMT	montmorillonite Clay
OMMT	Organically modified montmorillonite
XRD	X-ray diffraction
ODR	Oscillating Disc Rheometer
ISO	International Standard Organisation
MU	Mooney Viscosity Units
T_{min}	Minimum torque
T_{max}	Maximum torque
Δtorque	Delta torque (difference between maximum and minimum torque)
T_{s2}	Scorch time
T_{95}	Optimum cure time
min	time in minutes
dNm	deci-Newton meter (unit for Δtorque)
CRI	cure rate index
CLD	cross link density
SMRL	Standard Malaysian Rubber (natural rubber)
SEM	Scanning electron microscopy
MPa	Mega Pascal
mJ/m^3	mili joule per cubic meter
MJ/m^3	Mega joule per cubic meter
KJ/m^2	Kilo joule per square meter
ppm	parts per million
Tanδ	Tangent delta (the ratio between loss modulus and storage modulus)
DMA	Dynamic measurement analyser

Chapter 1 – Introduction

1.1 Background

Natural rubber (NR) and synthetic rubbers such as polybutadiene rubber (BR) and ethylene-propylene-diene rubber (EPDM) are used in many industrial applications. However, for shape retention, rubber must be cured. Rubber formulations have come a long way since Charles Goodyear discovered that heating raw rubber with sulphur modified the rubber to retain its shape. This was subsequently termed vulcanisation. To enhance the efficiency of vulcanisation in rubber, there has been an increasing trend to use more chemical curatives. The availability of new classes of chemicals known as accelerators and activators has speed up this process in recent years. Although it cannot be denied that sulphur vulcanisation is a much more efficient process today than it was at the time of Charles Goodyear, nevertheless serious health and safety issues related to its excessive use in rubber have emerged. Additionally, the chemical curatives are damaging to aquatic life and the environment. Consequently, the use of these chemicals is restricted by the new European chemicals policy, Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) and various legislations for environment, health and safety.

Sulphenamide accelerators and zinc oxide (ZnO) and stearic acid activators are used extensively to cure a wide range of industrial articles. These chemicals are potentially harmful to health, safety and the environment according to the European Directive 2004/73/EC. The exact amount of the chemical curatives in the sulphur vulcanisation of rubber has never been measured accurately and moreover, there is no reason why so many and so much of these chemicals need to be used in rubber compounds today.

This work developed two novel methods for determine the exact amount of some common chemical curatives in the sulphur vulcanisation of NR, BR and EPDM rubbers. Method 1 measured the optimum loading of sulphenamide TBBS accelerator and ZnO activator at a given loading of sulphur. Method 2 combined TBBS and ZnO chemicals into a single additive component referred to as powder and then measured the optimum loading of the powder to fully cure some sulphur-filled rubbers. These two methods helped to reduce the excessive amount of these chemicals in the sulphur vulcanisation of rubber and addressed the health, safety, and environmental issues related to the use of these chemicals in rubber compounds.

Solid fillers such as carbon black and silica/silane systems are used extensively to reinforce the mechanical and dynamic properties of rubbers. Carbon blacks are toxic and silica/silane systems are expensive. This study examined effect of a mineral kaolin solid filler on the viscosity, cure and mechanical properties of NR, BR and EPDM rubbers. The kaolin filler was pre-treated with mercaptosilane to help its dispersion in the rubbers. The NR compounds had 60 and 140 parts per hundred rubber by weight (phr) and the BR and EPDM compounds 60 phr kaolin. The cure systems which were developed in the early part of the study were used to cure the rubbers. As expected, the viscosity of the rubber compounds increased when filler was added, the scorch and optimum cure times as well as the cure rate index benefitted from the addition of the filler. The mechanical properties of the cured BR and EPDM gained significantly from the inclusion of kaolin in the rubbers but surprisingly NR did not benefit from kaolin. It emerged that kaolin was non-reinforcing or extender filler for NR and highly reinforcing for BR and EPDM rubbers.

It was concluded that kaolin in conjunction with the new sulphur cure systems developed in this study is a viable replacement for carbon black and silica/silane systems in rubber reinforcement.

The aim of this study is to develop environmental-friendly green rubber compounds for use in industrial rubber articles. This will be achieved by addressing the aforementioned health, safety, cost and environmental issues related to the excessive use of the chemical curatives in the sulphur vulcanisation of rubber, and finding a safer solid mineral filler to replace petroleum-based carbon black and synthetic silica/silane fillers in rubber reinforcement.

The objectives are as following.

1. To use a novel technique for measuring the optimum loading of accelerators and activators in the cure systems of some industrially important rubbers such as

natural rubber (NR), polybutadiene rubber (BR) and ethylene-propylene-diene rubber (EPDM).

2. For the first time, to combine a sulphenamide accelerator with zinc oxide activator to produce a single additive component to use with sulphur in the cure systems of the rubbers aforementioned.
3. To test a mineral solid kaolin filler the surface of which is pre-treated with a sulphur-bearing mercaptosilane and react the sulphur in the silane with the rubber chains to form stable covalent bonds and study it effects on the viscosity, cure and mechanical properties of natural rubber.
4. To use the mineral solid kaolin filler pre-treated with mercaptosilane in NR, BR and EPDM rubbers in combination with the novel sulphur cure systems measured as described in part 1 above, and determine the viscosity, cure and mechanical properties of the rubbers cured with the new cure systems and reinforced with a high loading of kaolin, i.e. reaching 140 phr.
5. To carry out an evaluation of the potential benefits of this new technology and greener rubber formulations to the rubber industry in terms of costs, health, safety and environmental impacts.

Chapter 2 - Literature review

2.1 Introduction to elastomers and their properties

Elastomers can be defined as of two types;

- ***Very extensible*** (They stretch many times their original length)
- ***Resilient*** (they snap back to their original size and shape after being stretched)

The combination of properties makes them very different from all other materials. The extensibility also makes them very flexible which, in some applications, is more important than great extensibility.

2.1.1 Effect of temperature on elastomers

The flexibility of the molecules inside the elastomer comes from free rotation of the bonds. Rotation generally requires little energy and will occur spontaneously in elastomers at room temperature where they are well above their glass transition temperature, $T_{g.}$ On the other hand, when temperature is decreased the thermal motion of the molecules become slower and the chains are less flexible and so the material becomes stiffer. If temperature gets low enough (approaching T_g) then no rotations in the rubber molecules will take place. The deformation is only by straining of interatomic bonds, requiring very high forces. At this stage, the rubber is glassy and doesn't exhibit rubbery behaviour at all. Elastomers have different T_gs Table 2.1 which indicate major differences in their molecular structure and chemical composition.

Table 2.1 Glass transition temperature of some Industrial rubbers [3]

Elastomers	T_g (°C)
Natural Rubber (NR)	-70
Polybutadiene Rubber (BR)	-108
Butyl Rubber (IIR)	-61
Styrene-Butadiene Rubber (SBR)	-61
Polychloroprene Rubber (CR)	-49
Acrylonitrile-Butadiene Rubber (NBR)	-24

2.2 NR (Natural Rubber)

2.2.1 Origin, molecular structure, chemical composition, properties and applications

Natural rubber is extracted from latex tapped from the Heva Brasiliensis tree (rubber tree). Rubber trees are found in tropical countries such as, Malaysia, India and Brazil. Natural rubber is made of hydrogen and carbon and is known as hydro-carbon polymer. Its chemical composition is $(C_5H_8)_n$ where n is the number of monomers joined together to form a long chain. The monomer of natural rubber is called cis-1-4 polyisoprene Fig. 2.1a. The second naturally occurring polyisoprene polymer is trans-1-4 polyisoprene Fig. 2.1b. Trans 1-4 polyisoprene is rigid at ambient temperature and must be heated to about 60^oC before is soft enough to be processed. So, it is never used. Cis-1-4 polyisoprene is used to manufacture industrial rubber articles such as tyres and hoses. Natural rubber is an unsaturated hydro-carbon, non-polar, with 98% cis 1-4 polyisoprene. The presence of 98% cis makes structure of the rubber very stereo-regular in 3-dimensional space. . Natural rubber has a glass transition temperature of approximately -71^oC. Due to the high cis content, the natural rubber chains can align themselves alongside each other to form internal regular structures called crystallites under the right conditions, for example when tensile strain on the raw rubber exceed 300% or when the rubber is cooled down slowly and progressively towards its Tg or is stored at a constant temperature for up to 320 hours [4].

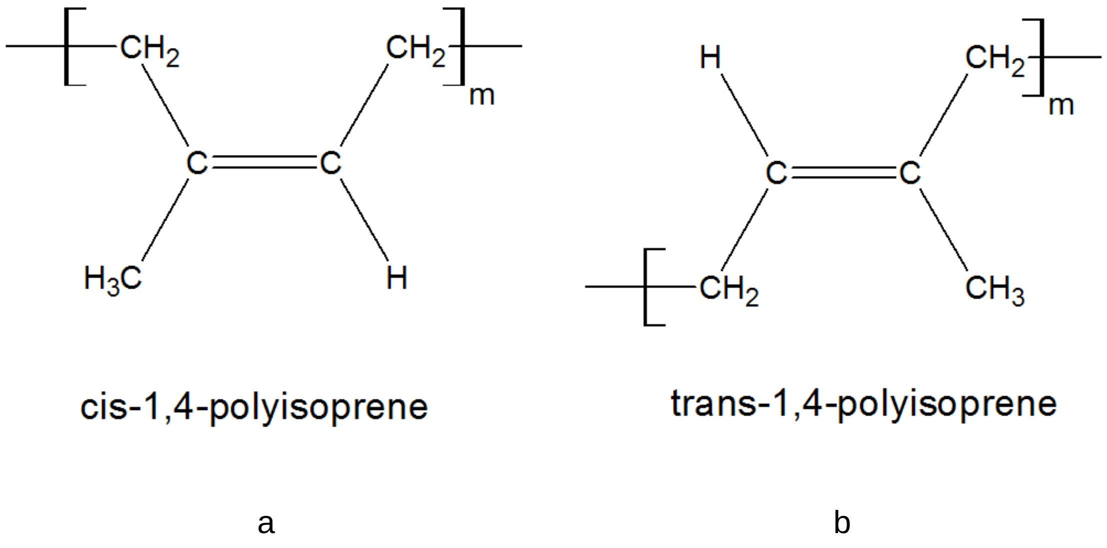


Figure 2.1 a) cis-1,4 polyisoprene, b) trans-1,4 polyisoprene [4]

Natural rubber has high tear strength, long flex and high abrasion resistance. These are due to the ability of the rubber to crystallise when stretched, which reinforces the above properties. The rubber has also high resilience, and low hysteresis, due to its low T_g. It has high compression set resistance because of it low T_g and good low-temperature flexibility as long as it does not crystallise at low temperatures. When natural rubber crystallises at lower temperatures it loses its flexibility and becomes rigid and non-elastic. Natural rubber has moderate to poor resistance to heat because the covalent bonds in the monomer have lower temperature of dissociation and tend to break down as temperature increases too high. The moderate and poor resistance of natural rubber to oxygen and ozone is due to the presence of unsaturation sites or chemically active double- bonds in the monomer. The minimum working temperature of natural rubber is -55^{o}C. This is affected by the T_g of the rubber. The maximum working temperature of natural rubber is 100^{o}C. This is decided by the dissociation temperature of the covalent bonds in the monomer backbone. Natural rubber is used to manufacture tyres, hoses, conveyor belting, anti-vibration mountings, bridge bearings and general purpose goods.

Natural rubber has excellent adhesion to brass-plated steel cord, which is ideal in rubber tyres. It has low hysteresis which leads to low heat generation. It has low rolling resistance with enhanced fuel economy. It has very high resistance to cutting, chipping and tearing [3].

Some important uses of natural rubber are in passenger car cross-ply tyres for its building tack, ply adhesion and good tear resistance. Natural rubber is used in the sidewalls of radial ply tyres for its fatigue resistance and low heat build-up. Large amount of natural rubber is used to make truck and earthmover tyres which require low heat build-up and maximum cut resistance. Natural rubber is widely used in industrial goods such as engineering products, resilient load bearing and shock or vibration absorption components and latex products such as gloves, and adhesives [4].

2.3 BR (Polybutadiene Rubber)

2.3.1 Origin, molecular structure, chemical composition, properties and applications

Polybutadiene (BR) is originally made by emulsion polymerisation. It is available in a wide variety of polymeric materials ranging from general purpose, non-crystallising rubber to highly crystalline plastics. Polybutadiene can be used in a variety of products made from low to high molecular weight and different in microstructure. Comparatively high molecular weight polymers are solids, whereas low molecular weight polymers are liquid. The differences in microstructure determine the properties of both solids and liquids. Commonly used isomers are cis-1-4, trans-1-4 and viny-1-4 polybutadiene Fig. 2.2 [5]. In this work Buna CB 24 high-cis was used which is made with neodymium catalyst and is not oil extended. CB 24 has high- cis content of over 92% [6] and a small portion of vinyl which is less than 4%. It is made using Ziegler-Natta catalysts derived from transition metals [7].

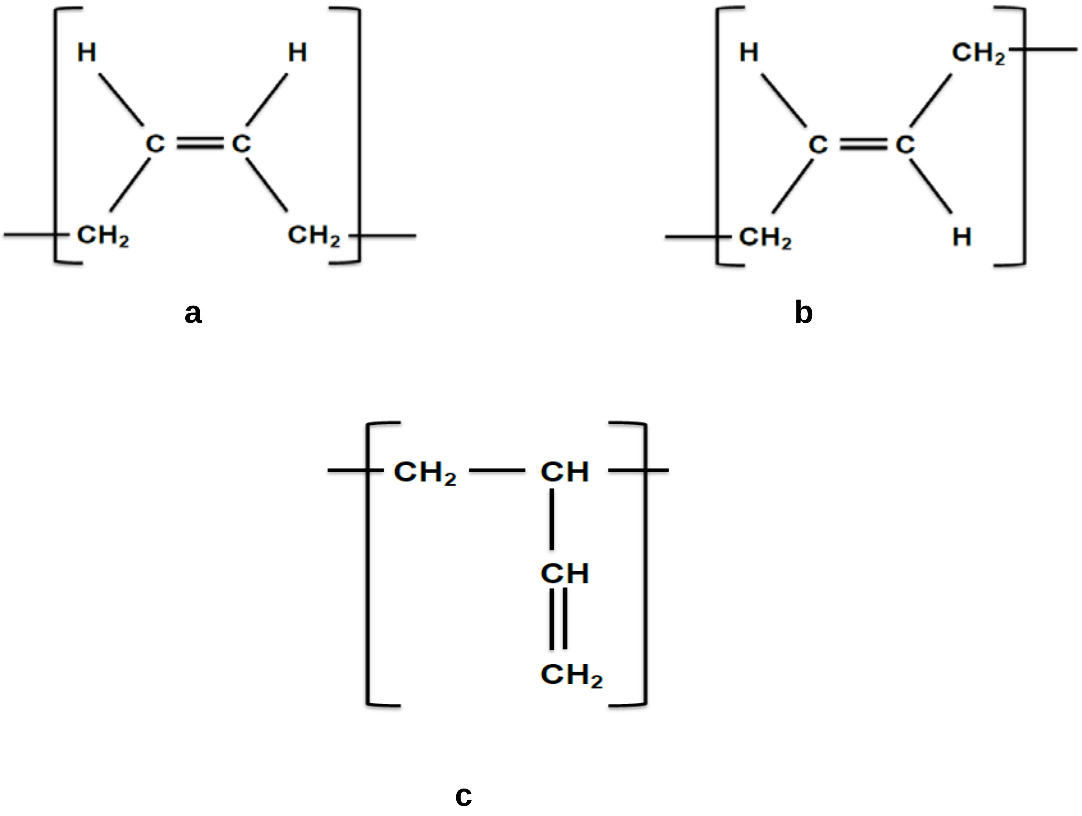


Figure 2.2 a) trans-1-4 Polybutadiene, b) Cis-1-4 Polybutadiene, c) Vinyl-1-4 Polybutadiene [5]

Randomly mixed micro-structured polymers (40-85%) are amorphous, possess intermediate properties and superior low temperature flexibility. Whereas, polymers with uniform (98-100% cis or trans) microstructure are crystalline. High cis polybutadiene possess low hysteresis, excellent dynamic properties and superior abrasion resistance. On the other hand, trans polybutadiene is a tough elastomer with high hardness and thermoplasticity, and poor hysteresis. High vinyl liquid polybutadiene are used to make thermosetting polymers with excellent electrical resistivity, excellent chemical resistance, high thermal distortion temperatures, and low water absorption [5].

Polybutadiene rubbers are commonly used in conjunction with other polymers such as blends which inherently gives good hysteresis properties, abrasion resistance, and good low temperature properties. Typical blends include BR with NR or BR with SBR (styrene butadiene rubber) which give improved resistance to groove cracking, improved reversion resistance on over-cure and enhanced ageing resistance. High BR content in NR or SBR blends helps reduce rolling resistance of tyres and impact favourable ice traction properties. Another application of BR is the solid golf balls made from polybutadiene rubber on its own reinforced with silica pigment and are very tightly cured either by peroxide or sulphur [5].

2.4 EPDM (Ethylene-Propylene Diene Monomer)

2.4.1 Origin, molecular structure, chemical composition, properties and applications

EPDM rubbers are formed by the process of ter-polymerisation. Like other non-crystallising polymers, mechanical properties of the unfilled EPDM are rather poor, therefore reinforcing fillers are added. Generally EPDM is not used to obtain extraordinary mechanical properties for the required application hence easily processable semi-reinforcing fillers are used in EPDM compounds [8]. Due to its low density, high extender oil and high filler loading are used for economy reasons. The EPDM rubber grades containing oil can be used for low hardness compounds. High hardness is usually achieved by using blend of EPDM with NR and blend of EPDM with SBR.

EPDM rubbers do not possess excellent low air permeability like the butyl rubber does, however they are used at fairly low levels in inner tubes to improve low temperature properties, ageing, and processing characteristics. EPDM can be modified to produce different grades of rubber. The commercially available grades can be varying in polymerisation process, Mooney viscosity, relative molecular mass distribution, ethylene/propylene weight ratio, and the third unsaturated monomer (dicyclopentadiene (DCP) or ethylidene norbornene (ENB)) type and amount. Required grades can be chosen according to the application and costs [8].

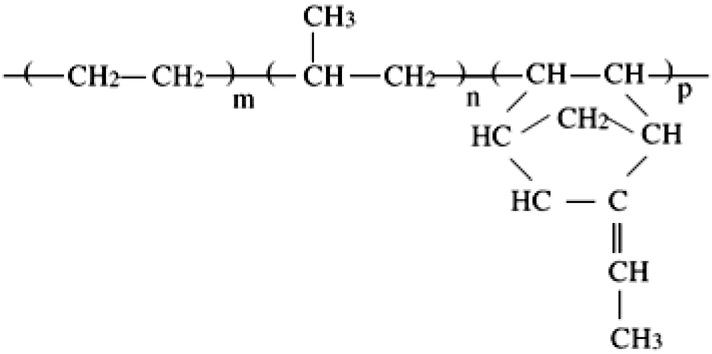


Figure 2.3 Molecular structure of EPDM [8]

The molecular structure of EPDM rubber as shown in Fig. 2.3 contains no double bonds in the chain backbone and thus EPDM does not suffer deterioration due to molecular scission even after extended exposure to ultraviolet (sunlight). These compounds are generally suitable for high ozone environment and outdoor applications with no need for environmental protection in reinforced EPDM. Therefore, NR and SBR which have inferior environmental properties, i.e. poor oxygen ageing, are blended with EPDM for better environmental protection.
EPDM rubbers contain excellent electrical insulation properties, such as high di-electric strength, low power factors and corona discharge resistance, and radiation resistance. Thus, they are used in medium and high voltage cable covers [9]. They also contain good low temperature flexibility and stay flexible at above -50°C [8]. They have very good resistance to water absorption, with combined mechanical properties and relatively low cost, make them good rubbers for use in pond liners.

Finally, EPDM rubbers are one of the most versatile, fast growing and interesting synthetic polymers. Excellent weather ageing, resistance to heat, oxidation, and ozone are expected to fulfil the demand in automotive, construction and mechanical goods applications. The emerging advanced polymerisation technologies provide the ability to design polymers to meet the ever increasing demands for product quality performance and uniformity [10].

2.5 Rubber cure systems

2.5.1 Introduction

Curing is the process of forming stable covalent bonds between the polymer chains. The process is widely used for enhancing the polymer properties. Since Charles Goodyear discovered in 1839 that heating raw rubber with sulphur modified the rubber so that it would retain its shape. In the early stages of his work, sulphur cure took almost 5 h to get a fully cured rubber. Since then the cure system has been improved and a large number of new chemical curatives have been introduced and marketed. In some tyre compounds, e.g. carbon black-filled natural rubber based truck tread compounds, cure system often consists of sulphur, accelerators (primary and secondary) and activators (primary and secondary), adding up to 10.25 parts per hundred (phr) by weight [2]. In addition, some antidegradants and processing aids are also added to tyres for environmental protection and viscosity modification. In some rubber articles, flame retardant (to suppress inflammability) and blowing agents (to produce foam rubber) are also added to achieve certain properties. However, over the years there has been an increasing trend to use more chemical additives to improve processing and mechanical and dynamic properties of raw rubbers [10].

Excessive use of these chemicals is harmful to health, safety and the environment and their use is restricted by the new European REACH chemicals policy and various environment and safety legislation. For example, zinc oxide (ZnO) is used as primary activator in conjunction with stearic acid (secondary activator) in sulphur-cure systems. The presence of ZnO in tyres has come under growing scrutiny because of the environmental concerns [11].

2.5.2 Rubber cure systems

A very wide range of chemicals can be used to produce crosslinks in rubbers. These crosslinks can vary from direct linkage of polymer chains itself, to the use of complex urethanes as bridges. The choice of crosslinks is dependent on the required performance, cost and ease of processing of the rubber. There are a wide range of vulcanising agents which include sulphur, peroxides, metal oxides, phenolic resins, maleimides and urethanes. Most commonly used vulcanising agents are sulphur, peroxides and metal oxides due to their low cost [13].

2.5.3 Sulphur cure systems

2.5.3.1 Elemental sulphur

Vulcanisation using sulphur is the most widely used method for crosslinking unsaturated rubbers such as NR, SBR, synthetic polyisoprene (IR), acrylonitrile-butadiene rubber (NBR) and EPDM, due to its low cost and the flexibility possible in processing conditions, reaction rate and physical properties achievable. Initially, the vulcanisation was accomplished by heating elemental sulphur up to 8 phr at 140^{o}C for about 5 h. The addition of activator such as ZnO significantly reduced the cure time from 5 hours to 3 h. Addition of accelerators in low concentration even helped to reduce the vulcanisation time considerably. The vulcanisation process with sulphur, activators and accelerators were commercialised significantly [12].

Over the years, three different cure systems have been developed. They are named as efficient vulcanisation (EV), semi-efficient vulcanisation (SEV), and conventional vulcanisation (CV) systems. EV system gives relatively high mono-sulphidic and little or no polysulphidic crosslinks as they contain low level of sulphur and correspondingly high level of accelerator. SEV system gives an intermediate (both mono and polysulphidic crosslinks) distribution of sulphur and accelerator. CV system provides relatively high polysulphidic content with little or no monosulphidic crosslinks. The loading of accelerator and sulphur in EV, SEV and CV systems are shown in Table 2.2 below.

Table 2.2 Loading of accelerator and sulphur in EV, SEV and CV systems [12]

Type	Sulphur (phr)	Accelerator (phr)	Accelerator/sulphur ratio
EV	0.4-0.8	2.0-5.0	2.5-12.0
SEV	1.0-1.7	1.2-2.4	0.7-2.5
CV	2.0-3.5	0.4-1.2	0.1-0.6

2.5.3.2 Accelerators

Vulcanisation or crosslinking can take place by heating sulphur in the rubber itself and is a slow process, resulting in poor properties and long curing time. Adding a small amount of organic or inorganic compound can speed up the process quite considerably. These chemicals are called “accelerators” when they are added to rubber containing sulphur, it speeds up the curing reaction and the properties and performance of the rubber will be controlled efficiently [14].

Accelerators plays important role in vulcanising rubber. They control the time to onset of vulcanisation, the rate of vulcanisation and most importantly the type and number of sulphur crosslinks and crosslink density. Accelerators can be divided into two types [15].

- <u>Primary accelerators</u>

  Commonly used primary accelerators are marcapto-based, which impart good processing for rubber compounds and exhibit broad vulcanisation. They also used to delay the scorch time and medium to fast cure rate.
- <u>Secondary accelerators</u>

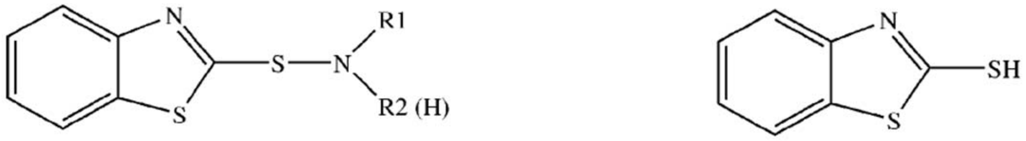
  These accelerators are generally used to give fast cure and contribute positive attributes to general properties of the rubber.

Accelerators are divided into different classes based on chemical structure and the cure rates in sulphur cure systems. Below in Table 2.3, different classes of accelerators are summarised.

Table 2.3 Comparison of accelerators and their classes [16]

Accelerator class	Rate of cure
Sulphenamides	Fast-delayed action
Guanidines	Medium
Thiazoles	Semi-fast
Thiurams	Fast
Dithiocarbamates	Very fast
Aldehyde-amine	Slow
Dithiophosphates	Fast

Habitually, rubber compounds with particularly sulphur cure systems contain a mixture of both primary and secondary accelerators for specific applications. The mixture of these accelerators is determined by applying extensive knowledge of their molecular structure, type and its relevance in each rubber compound. The combination of both accelerators gives good scorch and fast curing of compounds. In addition, rubber vulcanisates exhibit very good tensile and elastic properties which are mainly due to high degree of crosslinking. The chemical structures of some primary and secondary accelerators are given in Fig. 2.4 below [17].



Sulphenamide

Thiazole

Guanidine

Thiuram

Dithiocarbamate

Dithiophosphate

Figure 2.4 Chemical structures of some primary and secondary accelerators [19]

Sulphur cured rubber vulcanisates contain different types of crosslinks which include, mono, di or polysulphidic. The nature of crosslinks in a rubber vulcanisates depends on the type of accelerator used or a combination of primary and secondary accelerators, and sulphur to accelerator ratio. Some of the common accelerators and their chemical structures used in the sulphur vulcanisation are shown in Fig. 2.5 [17].

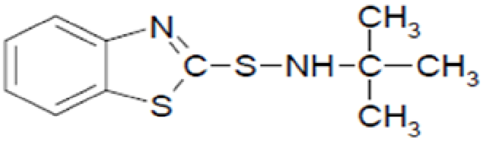
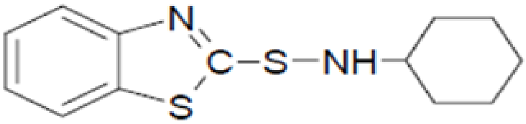
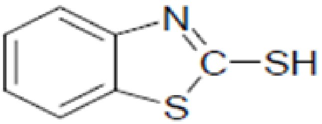
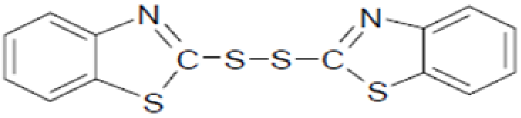
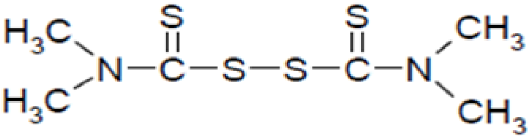
Compound	*Structure*	*Acronyms*
Benzothiazolesulphenamides		
N-tert-butylbenzothiazole-2-sulphenamide		TBBS
N-cyclohexylbenzothiazole-2-sulphenamide		CBS
Benzothiazoles		
2-Mercaptobenzothiazoles		MBT
2,2’-Dithiobenzothiazole		MBTS
Thiurams		
Tetramethylthiuram disulphide		TMTD

Figure 2.5 Important accelerators used in sulphur vulcanisation [19]

TBBS and CBS are primary accelerators which provide considerably scorch delay, medium to fast cure and relatively good modulus development. Whereas, TMTD is a secondary accelerator and is seldom used alone, but commonly used in conjunction with primary accelerators to gain fast cures and shorter scorch time. [18] Sulphenamide accelerators form vulcanisates which have a wide range of crosslink densities and reversion resistant cure. The increased loading of sulphenamide accelerators indicates improvement in state and rate of cure, higher stress-strain properties, and better resilience compared to thiazole accelerators.

2.5.3.3 Activators

Activators are mainly used to enhance the efficiency and effectiveness of accelerators during the curing process. These chemicals increase the rate of vulcanisation by first reacting with accelerators to form rubber-soluble complexes.

These complexes then activate sulphur to form sulphur crosslinks. The most commonly used activators are ZnO and stearic acid for sulphur based vulcanisation [20]. Stearic acid is a fatty acid, which is added to improve the solubility of ZnO in the rubber. ZnO produces zinc ions in the presence of stearic acid, which form chelates with the accelerator and sulphides. This will help to increase the efficiency of vulcanisation process. Other metal oxides have been used for specific purposes such as, lead, cadmium, magnesium etc. ZnO has a melting point of 1975^{o}C and is one of the most commonly used activators for sulphur vulcanisation of unsaturated elastomers such as, NR, BR etc. [21]. The role of ZnO in sulphur vulcanisation has been studied extensively [22-30]. ZnO increased the rate of sulphur vulcanisation and influenced the distribution of different types of crosslinks in the rubber vulcanisates. Stearic acid has a melting point of about 70^{o}C and solubilises zinc in the rubber compound and form zinc stearate which is essential for sulphur cured rubber compound [31-36].

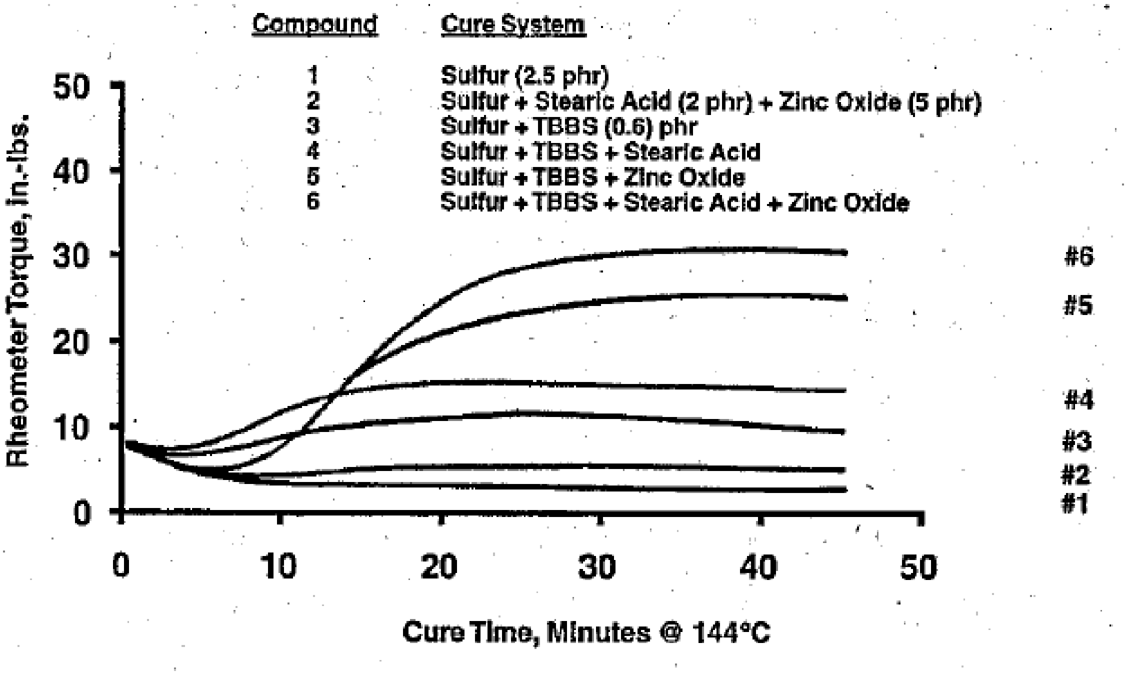


Figure 2.6 Effect of accelerators and activators on the cure rate of NR [20]

Natural rubber normally contains fatty acid to solubilise the zinc salt. However, when the fatty acids are removed from the rubber, it will exhibit a much lower state of cure.

Therefore, fatty acids are added to ensure consistent cure rate. Moreover, sulphenamide accelerators generally require less fatty acid because they release an amine during the vulcanisation process which acts to stabilise the zinc [14].

Zinc oxide and stearic acid are used as primary and secondary activators, respectively, in sulphur cure systems. Some typical examples of rubber articles made by these activators are tyres, conveyor belts and hoses. However, these activators are not effective in the absence of accelerators and cannot increase the cure rate in the rubber compounds. Paris [20] studied the effect of activators in sulphur cure system, as shown in Fig. 2.6 In the absence of accelerator, the activators were ineffective in increasing the number of crosslinks produced (compound 2). However, without activators, sulphenamide accelerators produced significant increase in crosslinks in a reasonable cure time (compound 3). In addition, stearic acid alone produced less crosslinks (compound 4) than adding zinc oxide alone (compound 5).

Sulphur curing with the help of accelerators is the most common technique crosslinking elastomers. The accelerated sulphur crosslinking is applicable for (unsaturated hydrocarbons) containing elastomers including natural rubber, polybutadiene rubber and Styrene butadiene rubber as well as (saturated elastomers) nitrile rubber and EPDM. The typical cur systems for elastomer contain the following chemicals;

Vulcanising agent (sulphur)	0.25-5.0 phr
Activators: stearic acid	0.5-3.0 phr
Zinc oxide	1.0-10.0 phr
One or more accelerators	0.2-5.0 phr
Retarders (as required for adequate scorch safety)	

In sulphur curing, sulphur ring is opened by negative ions to make it active for curing. Negative ion can be from accelerators such as 2-mercaptobenzothiazile or HS^- from hydrogen sulphide. The zinc oxide and stearic acid are involved in forming complexes with the sulphur and accelerator which leads to the attachment of sulphur to the main chains. The reactions normally take place in two stages [122]:

1. Formation of reactive crosslinking species, which defines the processing or scorch time
2. Formation of crosslinks, which defines the cure time

Many studies have been carried out to understand the mechanism of rubber vulcanization with sulphur in the presence of accelerators and activators. Vulcanization is the phenomenon of formation of cross links with rubber macromolecules. These cross links can be made up of sulphur atoms. Transformation of rubber from plastic to elastic state, lack of solubility in organic solvents, limited swelling ability, as well as modification of certain important physico-mechanical properties, like tensile strength, elasticity, elasticity modulus, relative and plastic elongation, plastic compression, heat evolution, swelling stability, permeability to gases, resistance to low temperatures, can be explained by the presence of these cross links.

In the case of natural rubber NR both tensile strength and modulus display a peak followed by a decrease of their values. The latter phenomenon is called Reversion. In the case of styrene-butadiene rubber (SBR) the tensile strength remains approximately constant, while the modulus increases (marching cure) and when the vulcanization time is too long leading to over cure, sudden reduction of elongation at break occurs, which is not observed in the case of natural rubber. The variation of mechanical properties (tensile strength, elasticity modulus) depends on nature of the polymer as shown in Fig 2.7.

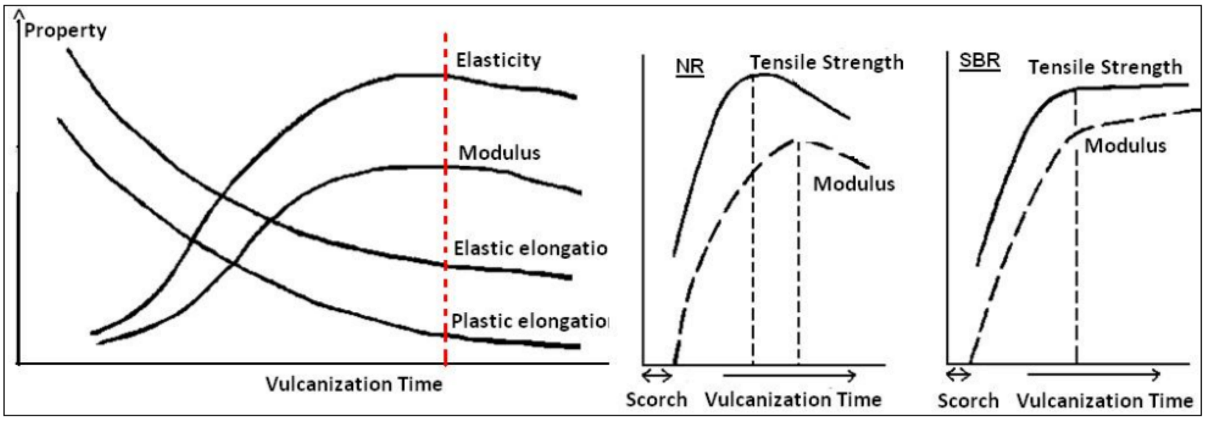


Figure 2.7 Effect of vulcanisation time on the cure and mechanical properties of NR, and SBR [36]

Cross links which form bridges between the chains are stress bearing members contributing to elasticity and strength. Cyclic sulphides, accelerator fragments, vicinal cross links do not contribute to elasticity as shown in Fig. 2.8. ‘Sx’ refers to cross links consisting of more than two sulphur atoms (Polysulphidic cross links). ‘Sx’ gets desulphurated to form di or mono sulphidic cross links with the action of heat (as low as at 90 - 100°C).

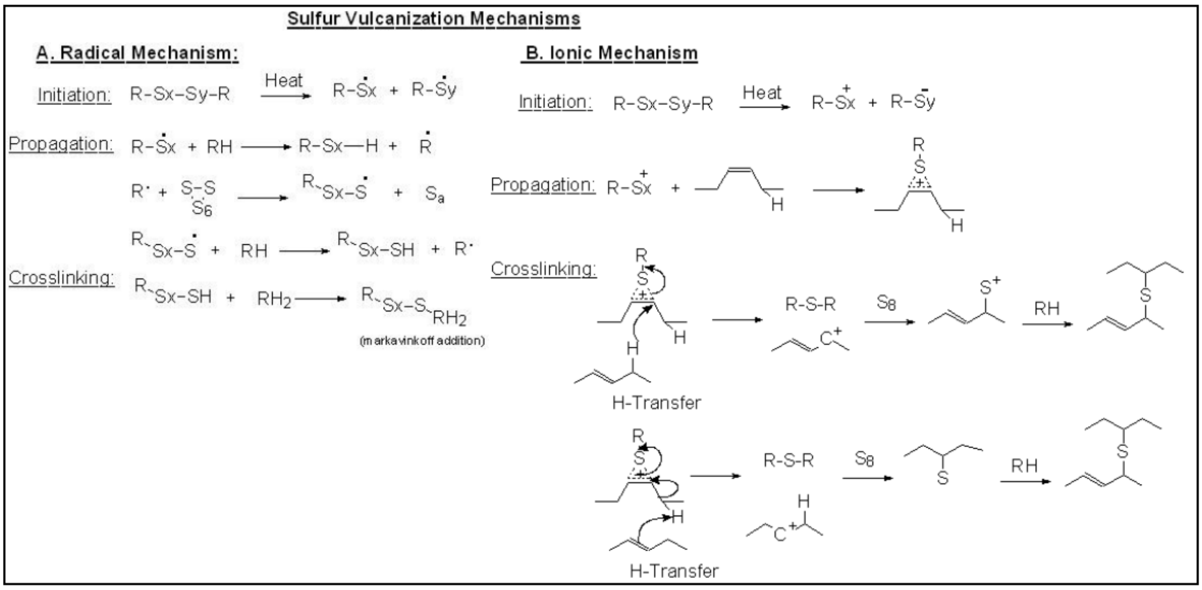


Figure 2.8 Mechanism of sulphur vulcanisation [36]

2.5.3.4 Other ingredients for rubber compounds

Apart from accelerators, activators and sulphur, which form the cure system, rubber compounds also contain a range of other ingredients such as, retarders, antidegradants, processing aids, colour pigments and special purpose additives. Antidegradants play an important role for rubber life. The presence of carbon-carbon double bonds renders rubber susceptible to attack by oxygen, ozone and also thermal degradation. However the oxidation in rubbers is accelerated by various factors such as, heat, heavy metal contamination, light, weather, fatigue, oxygen, ozone and atomic radiation etc. [37]. For instance, the oxidative ageing process causes the physical properties of natural rubber to deteriorate by either chain scission, resulting in reduction of chain length and average molecular weight, or formation of additional crosslinks in the rubber, which results in a three dimensional structure and higher molecular weight. Therefore, natural rubber’s environmental degradation predominantly results in a weak, softened stock, often showing surface tackiness. However, EPDM, BR and nitrile rubbers environmental degradation by oxygen causes more crosslinks to form, which makes the rubber compound brittle with poor flexibility and elongation. To protect these unsaturated rubbers against ageing and to increase the service life of rubber articles, antidegradants, e.g. antioxidants, antiozonants, and waxes, are added to rubber during mixing. Usually waxes protect the rubber by diffusing to the surface and forming a thin solid layer. Whereas, antioxidants diffuse to the rubber surface and react with oxygen and ozone and significantly retard the ageing process [38]. Some commercially available antidegradants are, amine (diphenylamine derivatives), (dihydroquinolines), (ρ-phenylenediamine-di-Alkyl), (ρ-phenylenediamine-Alkylaryl), and mercaptobenzimidazoles). However, phenylenediamines antioxidants provide excellent protection against O_2, O_3 and fatigue. Oxidative is by far the most common ageing process in articles made of unsaturated rubbers.

Processing aids are added to alter viscosity and mainly consist of oils added during mixing or compounding. Plasticisers such as aromatic oil, paraffinic oil, and naphthenic oil provide flexibility at low temperatures without substantial loss in physical and mechanical properties [39]. Peptisers such as activated dithio-bisbenzanilide reduce the molecular weight of rubber to make mixing easier. Lubricants for example paraffin wax and hydrocarbon based petroleum minimise the friction between rubber and internal wall of processing equipment. Releasing agents are sprayed on the inner surface of a mould to enable it to easily remove compounds after curing. Flame retardants are used to prevent rubbers to burn up to a certain extent and help to suppress the ability of rubbers to burn easily and produce flames. Pigments are added to impart colours to non-black rubber compounds and make them more attractive for users and contain both organic and inorganic pigments which provide good efficiency and brilliancy in colour shades. Blowing agents for instance sodium bicarbonate, ammonium carbonate and bicarbonate are used for producing micro porous and sponge rubber. These blowing agents decompose upon high temperature curing and release neutral gas during vulcanisation which gives rise to pore formation. Reodorants are used to improve the smell of rubber compounds [39].

To conclude, it is abundantly clear that the rubber industry has gained a great deal of benefit from using the above chemicals and additives to process, cure and protect rubber compounds against dynamic, mechanical and environmental ageing. Because of this reason, there are so many rubber articles in service today. However, most of these chemicals are harmful to human health, too costly and are damaging to the environment. The biggest challenge that the rubber formulation scientists and technologists are facing today is to reduce the number and amount of these chemicals, particularly the chemicals in the sulphur cure systems, of rubber articles. There is a fundamental problem with the excessive use of the chemical curatives in rubber compounds. There is no reason why so many and so much of them are in use in industrial rubber articles today.

2.6 Health, safety and environmental issues related to the excessive use of rubber chemicals

Generally, rubber compounds are made from several chemicals as discussed in the above section. These compounds contains up to twelve different chemicals including fillers and curatives. The choice of suitable cure systems in order to ensure good mechanical and dynamic properties for manufactured rubber articles is essential. Following are the few examples of health and safety and environmental concerns and issues related to the excessive use of these harmful chemicals [40].

2.6.1 Fillers

Carbon black used in tyres is mildly toxic by ingestion, inhalation and skin contact. Approximately 65% of carbon black is used in tyre production. The international Agency for Research on Cancer (IARC) conducted a comprehensive study of carbon black and concluded that carbon black could be classified as carcinogenic to humans and definitely carcinogenic to animals [41]. The study also highlighted the respiratory effects on people who worked with carbon black. These tests included cough, sputum production, chest radiographic opacities and lung functions. There is a need to partially or completely replace carbon black with eco-friendly materials or natural minerals. On the other hand, silica is also used as filler for making rubber articles. The fine dust particle of silica can cause fibrosis, i.e. scar tissue formation in lungs. Inhalation of silica dust particles increased the risk of developing pulmonary tuberculosis if exposed to the person with tuberculosis [42].

2.6.2 Activators

Zinc oxide and stearic acid are used as activators in rubber articles. Zinc oxide is added in relatively high concentrations of up to 5 phr. According to the European REACH chemicals policy and various environmental and safety legislation and the US Environmental protection energy (EPA), ZnO is classified as toxic and the earliest symptoms of this metal oxide fume is metallic taste in mouth, accompanied by dryness and irritation of the throat [43-44].

2.6.3 Accelerators

Most commonly used accelerators include, amines and sulphenamides. Thizoles dithiocarbonates etc. contains N-nitrosamines fumes. Many of these N-nitrosamines are carcinogenic [45]. They are formed by the reaction of an amine with a nitrosating agent. Nitrosamines are classified as carcinogenic to humans and animals by international organisations and regulatory authorities (IARC) [45]. It is worth mentioning again that according to European Directive 67/548/EEC, zinc oxide is very toxic to aquatic organisms and stearic acid cause skin and eye irritation and is classified as highly flammable[46].

2.6.4 Antidegradants

These chemicals are generally used to protect the rubber article against environmental degradation such as oxidative ageing. Generally, they are volatile under high temperature conditions, and migrate towards the rubber surface, giving rise to blooming and staining. For instance, antidegradants such as N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (6PPD) partly decomposes and undergoes further reactions, which forms primary aromatic amines (PAA), which is highly critical and has hygiene concern [48].

2.6.5 Curing agents

A large amount of air contaminants are released during the vulcanisation process. Generally, sulphur and peroxide are used to cure most rubber compounds. However, metal oxides, resin curing agents are also used in some applications. Several studies [48-51] have shown that excessive use of curing agents can cause respiratory morbidity. Other symptoms have also been reported such as headache and nausea among the workers who carry out vulcanisation [51-52].

As mentioned above, most chemicals and curatives are harmful to environment, human and animal health alike. Thus, the use of these chemicals in industrial rubber compounds must be restricted or in some cases eliminated altogether.

Recently, Ansarifar and co-workers developed a new technology for the sulphur vulcanisation of rubber compounds, which reduced the excessive use of the chemicals in the cure system significantly [53-55].

In this study, the aim was to measure the optimum amount of the chemical curatives in the sulphur vulcanisation of some commercially important rubbers accurately, and by doing so, reduce the excessive amount of these chemicals and even to eliminate some of the chemicals altogether from the cure system without compromising the dynamic and mechanical properties of the rubber vulcanisates. Previous studies showed that it was possible to remove the secondary accelerator from the cure systems and reduce the amount of ZnO to less than 1 phr. In addition, stearic acid was taken out of the cure system entirely [53-55].

2.7 Fillers

For Industrial rubber applications, vulcanisation is not only determined by the nature and quantity of polymer used, the crosslinking (cure systems), and other ingredients but also by the nature and quantity of solid filler that is used. Vulcanised rubbers without fillers do not possess good mechanical properties such as tensile strength, tear strength, hardness, modulus, and abrasion resistance. Fillers are added to rubber to enhance its properties. There are two types of solid fillers: reinforcing fillers and non-reinforcing or extending fillers. Extending or non-reinforcing fillers are clay, kaolin (China clay) whitening and braites [60], which have little or no effect on the mechanical properties of rubber vulcanisates. On the other hand, reinforcing fillers such as carbon black, silica and fibres improve mechanical and dynamic properties for instance stiffness (hardness) tensile strength, modulus etc. [62]. Extent by which these properties improve rubber properties depends on the quantity and particle size of the filler. The smaller the particle size, the larger is the surface area of the filler. Fillers with large surface area are more reinforcing because rubber chains interact more actively with large surface areas. Other factors such as surface chemical functionality are also important because they determine the strength of the rubber-filler interaction which is essential in rubber reinforcement [65].

2.7.1 Carbon blacks

2.7.1.1 Background

Application of carbon black in rubber compounds is over a hundred years old. During the late 1800 century black colloidal substance consisting wholly amorphous carbon namely lamp black was used as black pigment. In 1872 channel black was discovered and successively replaced the lamp black. Channel black is a type of carbon black which is formed by burning organic raw gas or oil. This process produces a black smoke containing extremely small carbon black particles, which eventually separate from the combustion gases to form intense black powder [2].

2.7.1.2 Manufacturing processes of carbon black

- Furnace black process

This process of producing carbon black was first introduced in 1922 and was continued for 20 years with natural gas as feedstock and with semi-reinforcing furnace black [2]. After that fine furnace black and high modulus furnace black were added to the process. Later in 1940s, aromatic oil feedstock based process outmoded the old natural gas based process. The feedstock is burned in a reactor, producing carbon black and tailgas. After cooling down, the carbon black powder is separated from the tailgas. These gas components include, H_2O, N_2, CO, CO_2, H_2, C_2H_2 etc. and the process of separating is accomplished through the use of various commercially filter bags. After separation, carbon black is processed into varying grades/sizes [56].

- Thermal black process

Thermal process is almost similar to the furnace process. However, in thermal process carbon black is formed in the absence of oxygen. The feedstock in this process can be natural gas. The surface area and structure of carbon black is much lower than carbon black formed in furnace process. Therefore, these blacks are not as reinforcing as furnace carbon blacks. Over 95% of carbon black is produced by furnace process and is used in the rubber industry.

2.7.1.3 Composition, structure and surface activity

During the combustion reaction carbon particles are formed with different dimensions and different grades depending on the specific application [58]. In general, carbon black grades with smaller particle size have better reinforcing qualities than those with larger particle size. Carbon black particles are spherical is shape and are generally termed as nodules as shown in Fig. 2.7

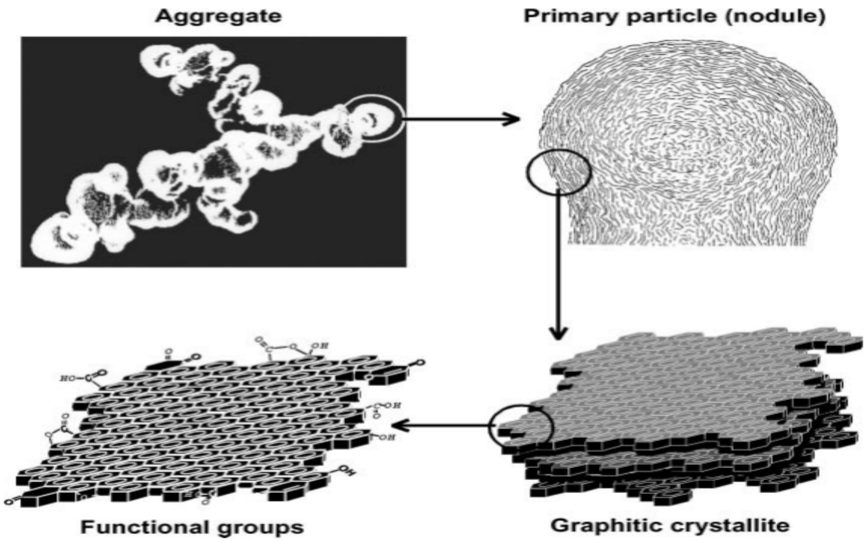


Figure 2.9 Structure of carbon black [57]

In the early days, there was no direct method for measuring carbon black surface activity. The surface of carbon black is influenced by the graphite plane orientation, the type and number of organic side groups. The molecular structure of carbon black is composed of amorphous graphite layer which is created from the microcrystalline arrays of condensed aromatic rings. The orientation of arrays within the amorphous mass appears to be random, consequently a large percentage of arrays have open edges of their layer planes at the surface of the particle. A large number of unsatisfied carbon bonds associated with these open edges provide sites for chemical activity. In addition, other elements such as oxygen, hydrogen and sulphur are also present in a very small quantity [57]. It is not clear that these elements are confined to the surface only or are distributed throughout the carbon black aggregates. Bansal and Donnet [59] proposed several types of functional groups on carbon black surface as shown in Fig. 2.8. Carbon dioxide formed from the functional groups containing lactones and carboxylic acid. However, carbon monoxide is formed upon decomposition of phenols and quinines. In addition, hydrogen gas is likely to be produced from the reduction of -CH or -OH functional groups.

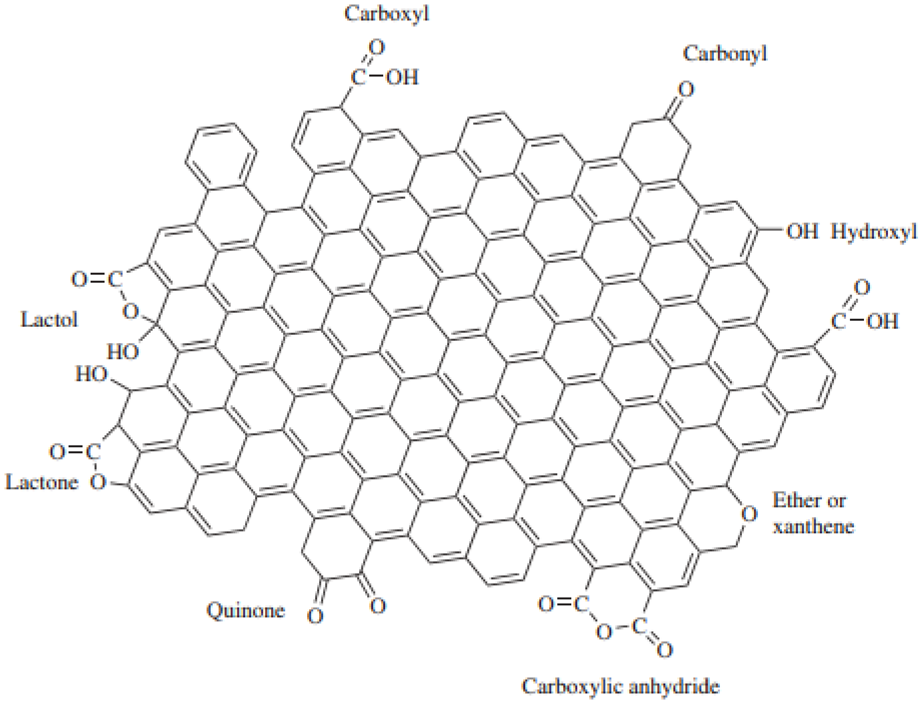


Figure 2.10 Aromatic layer plane with functional groups of carbon black [57]

Wang, Wolff and Donnet [59-50] demonstrated that no direct correlation between the chemical groups on carbon black and rubber properties such as, tensile strength and modulus existed. Filler-rubber interaction was mainly by physical nature i.e. physic-sorption. Wang and Wolff [61] recognised the highest activity on carbon black regions where density of available π electrons from the aromatic system would be greatest.

2.7.1.4 Effect of carbon black on the properties of rubber

Rubber properties can be controlled by three main factors: loading of the filler, the specific surface area and the structure of filler. Typically rubber compounds are made by accelerated sulphur vulcanisation systems (as discussed above in sulphur cure systems) at high temperatures with any grade of carbon black filler and even with small amount of the filler, curing time is reduced significantly. As mentioned above, loading of the filler and specific surface area dominate the reinforcing effect in the rubber. A study was conducted to measure the mechanical properties of raw natural rubber and that of carbon black filled natural rubber composites. Natural rubber was reinforced with carbon black (specific surface area; 36.8 m^2/g and particle size of N550) at a given loading of 24 phr and other compounding ingredients were also added on a two roll mill and the compound was cured at 143°C. Mechanical properties were tested and it was seen that hardens, tensile strength, tear strength of the carbon black filled rubber were significantly higher than those of the raw rubber, indicating the inherent reinforcing potential of carbon black. Whereas, percentage elongation at break of the carbon black filled rubber composites were lower than that of the raw rubber [62]. The effect of particle size and amount of carbon black on the cure characteristics and dynamic mechanical properties of vulcanised natural rubber have been extensively investigated. Results showed that when the particle size of carbon black decreased, the Mooney viscosity was increased effectively and the cure and scorch time were shortened. It was found that the addition of carbon black decreased $\tan\delta_{max}$. The tensile modulus at 100% and 300% elongation were increased when $\tan\delta_{max}$ was decreased [63].
Higher structure of carbon black tends to offer greater reinforcement as observed by higher modulus at high strains in cured rubber. This is due to filled compound is subjected to higher strains, therefore physical properties becomes less influenced by the surface area of the carbon black. Carbon black structure appears to play only a small role in performance at low strains.

An increasing loading of carbon black of any grade, tends to increase strength of the rubber. On the other hand, some properties such as, tensile strength and abrasion resistance, tend to decrease after a certain loading of carbon black. Figure 2.9 shows the relationship between carbon black loading and selected rubber properties [64].

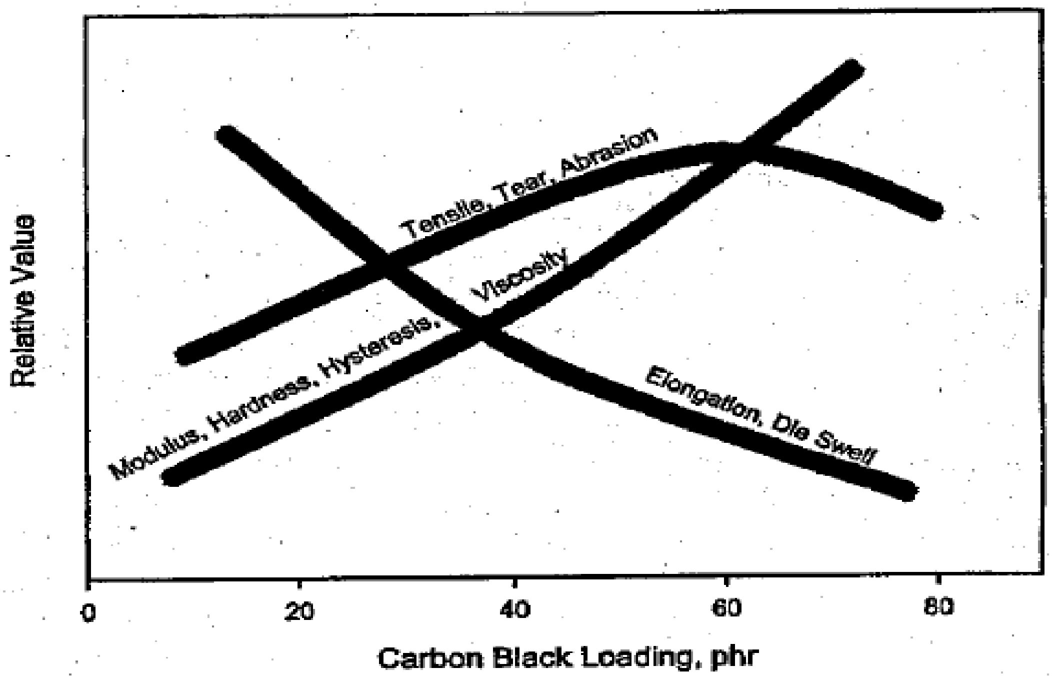


Figure 2.11 Relationship between carbon black loading and some rubber properties [64]

Han *et al.* [65] measured the dynamic mechanical properties over a wide range of temperatures and strains of some vulcanised rubbers filled with carbon black (N330) and a surface modified carbon black, respectively. The surface modified carbon black was prepared by introducing special resorcinol formaldehyde latex (RFL) into N330 carbon black. The main chain of RFL had good compatibility with the rubber matrix, whereas the side chain with pyridine function reacted with the acidic functional groups on the surface of carbon black. The work suggested that surface modified carbon black filled rubber showed better dispersion and the results from the surface modified carbon black in the rubber matrix provided better understanding of the mechanism of reinforcement. Mechanical properties were improved with the surface modified carbon black due to the stronger filler-rubber interaction. The effect of two types of carbon blacks (CBs), N990 and Vulcan XC-72, on the mechanical properties and thermal conductivity of some filled silicone rubbers (SR) were investigated [66]. The result showed that CB particles increased the thermal conductivity, the thermal stability and the tensile strength of the silicon rubber composites. The scanning electron microscope showed that Vulcan XC-72 of higher structure created more conductive networks within the matrix, and the thermal conductivity of the filled composites were superior compared to that of the N990 filled composites at given filler loading. In addition, Vulcan XC-72 enhanced the mechanical properties and electrical conductivity of the composites.

2.7.1.5 Toxicology of reinforcing carbon black

The toxicity of carbon black has been studied by a number of national and international agencies for risk associated with human health. These organisations include Environment and Health Canada, OECD, and the international Agency for Research on Cancer (IARC) [67-69]. The study on animal models shows carbon black was deemed to be a low acute toxicity by oral and inhalation exposure, with mild inflammation in rat lung with an exposure to ultrafine carbon black particles (particle size of 20 nm). However, no inflammation observed in rat lung following exposure to fine carbon black (particle size of 200 nm) [67]. Therefore, particle size of carbon black plays important role in inflammatory effects. OECD has determined that carbon black does not pose a significant health risk and is of low priority for further investigations. IARC has described carbon black as “possibly carcinogenic to humans” but also concluded that there is a limited evidence for carcinogenicity from carbon black based studies on humans. However, these studies are based solely on animals utilising very high exposure concentrations [68].

2.7.2 Silica

2.7.2.1 Background

Silica has been used in rubber formulations since early 20th century [70]. Like carbon black, silica is also reinforcing and has quite comparable reinforcing mechanism to carbon black. Over the years, since 1950s and 1960s, silica became important solid reinforcing filler in almost all kinds of rubber applications. However, silica was not as compatible as carbon black in some certain applications, such as tyre tread in which the dispersion of silica reduced the effectiveness of some of the properties of the rubber vulcanisates. Hydrated precipitated silica is polar and hydrophilic in nature due to having polysiloxane structure and the presence of numerous silanol groups. These groups react with rubber accelerators, causing a detrimental effect on the vulcanisation process. In addition, there is a possibility of having high filler-filler interaction and weak filler-rubber interaction due to silanol groups. As a result poor filler reinforcement and performance was observed when compared with the effect of carbon black.

2.7.2.2 Manufacturing processes of silica

There are two processes of preparing silica fillers;

The precipitation process

The pyrogenic of thermal process (fumed silica)

- The precipitation process

Silica is manufactured from the raw material called alkali-silicate solutions which include, sodium silicate from which the silica is isolated by the addition of sulphuric acid. These precipitates consist of 86-88wt% of SiO_2 and 10-14wt% of water and chemically bonded residues of salts formed at the conversion. The precipitated silica is obtained after filtration, washing and drying. However, properties of the final product can be controlled by the process conditions such as, precipitation time, temperature, electrolyte concentration and pH [2]. Therefore, products can be obtained ranging from silicas to silicates. The surface area of precipitated silica used for rubber applications are ranging from 25-250 m^2/g. Finally, after the precipitation process the separation by filtration is carried out to wash of any salts that were formed during precipitation. Filtered precipitates are then dried in an oven.

- The pyrogenic of thermal process (fumed silica)

This process of fumed silica is produced in a flame consists of microscopic droplets of amorphous silica fused into branched, three dimensional secondary particles which then agglomerate into tertiary particles. A mixture of gas containing $SiCl_4$, hydrogen and oxygen is combusted in a reactor of about 3000^oC.

$H_2 + ½ O_2 \rightarrow H_2O$

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCL$

After the combustion process powder was recovered from the reactor. The resulting powder has extremely low bulk density and non-porous high surface area of about 50-600 m^2/g and the particle size of 5-50 nm.

As mentioned earlier, because of the surface properties of precipitated silica, there is difficulty in using it as reinforcing filler in hydrocarbon rubbers. The hydrophilic groups on the silica surface interact with rubber accelerators, resulting in detrimental effect on the cure time, cure rate and loss in crosslink density in the cured rubber. Although, there is a strong interaction between filler-filler but it has an adverse effect on the rubber reinforcement [71]. Moreover, processing becomes more difficult when a large amount of precipitated silica is added, because the viscosity increases significantly [72-73]. To get the best possible reinforcement and high filler-rubber interaction, surface modification of silicas have been studied over the years.

2.7.2.3 Modification of silica surface with Si69 silane coupling agent

Surface modification of the fillers is by far the most effective way of changing the surface properties to meet the required applications. Bifunctional organosilanes can be used as primers for treating silica surfaces to make the filler more suitable for use in rubber [74]. Bis(-triethoxysilylpropyl-)tetrasulphane (TESPT), also known as Si69 coupling agent, is commonly used to modify surface of silicas. Silica incorporated in hydrocarbon rubber modified with Si69 has shown to improve the filler-rubber interaction. Si69 silane enables silica to be used in many applications and is now a key factor, being a successful replacement for carbon black in for example the tyre tread.

TESPT silane coupling agent possesses tetrasulphane and ethoxy groups. The tetrasulphane groups Fig. 2.10 react with the rubber in the presence of accelerators at elevated temperatures, with or without elemental sulphur being present to form crosslinks in the unsaturated rubbers.

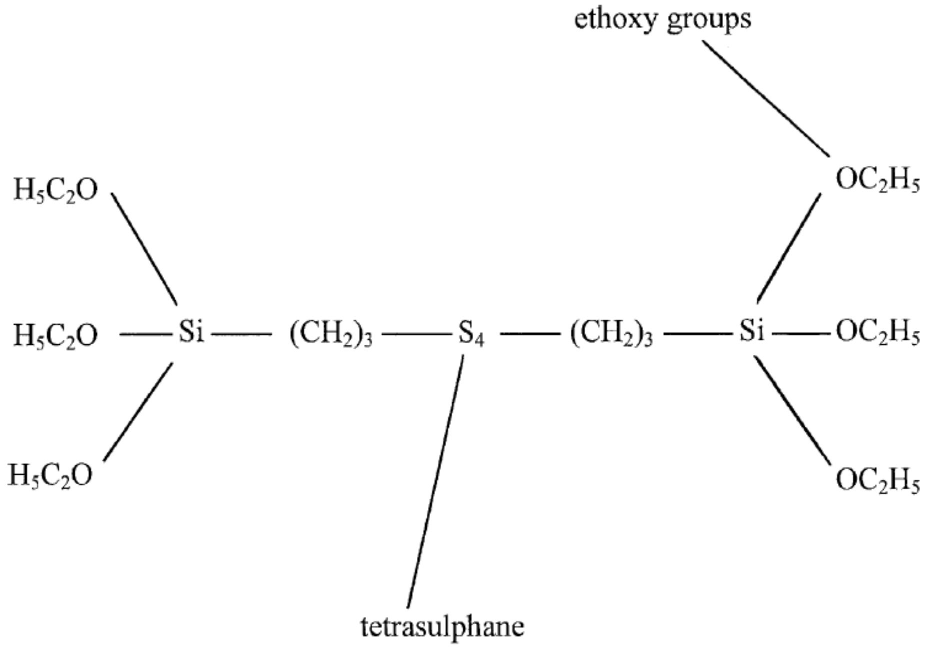


Figure 2.12 Chemical structure of TESPT (Si69 coupling agent) [74]

The ethoxy groups react with silanol groups (present on the surface of silica) during mixing to form stable silane-filler bonds. Additionally, the silane reaction with silanol group Fig. 2.11(a-b) reduces their numbers and the remaining groups become less accessible to the rubber because of steric hindrance [74]. During the compounding and vulcanisation process, tetrasulphane groups (split due to heat treatment and also the influence of the accelerator) react with the rubber chains by forming mono-sulphidic, di-sulphidic and poly-sulphidic covalent bonds.

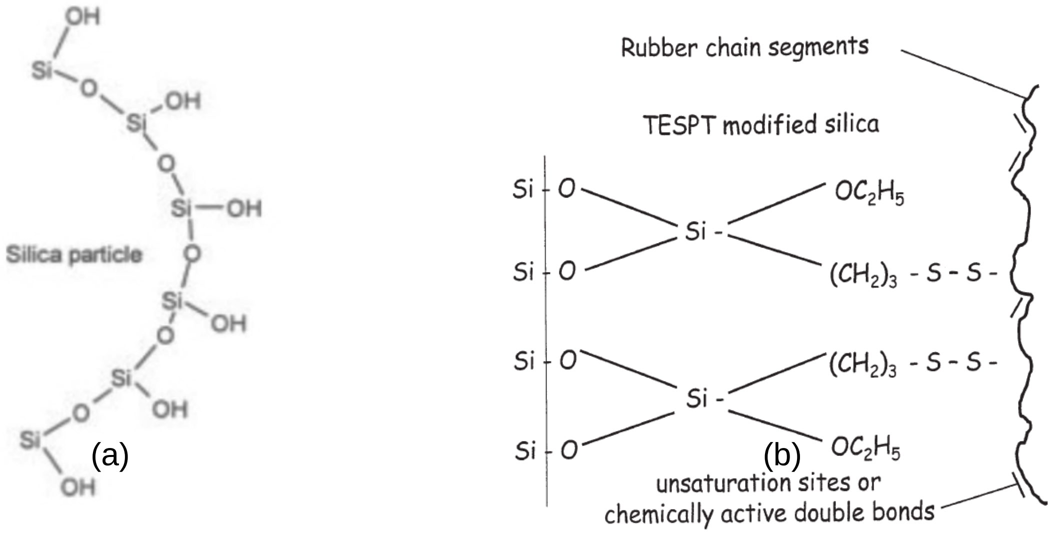


Figure 2.13 a) Silica surface, b) Silanised silica nanofiller pre-treated with TESPT. Tetrasulphane groups react with rubber to form stable covalent sulphur bonds. [74]

2.7.2.4 Effect of silanised silica nanofiller on the properties of rubber

Carbon black and silanised silica reinforcing effects on rubber properties have been extensively studied and generally it has been acknowledged that they can reinforce rubbers to a large degree due to filler-rubber interaction. Voet and co-workers [75] examined the effect of silica–rubber adhesion on the mechanical properties of a sulphur cured styrene–butadiene rubber and showed that hardness and elongation at break were improved when a silane coupling agent was added. This was recognised by the chemical bonding between the filler and rubber, which was facilitated by the coupling agent. Ansarifar and co-workers [76] studied effect of 30 phr precipitated silica on the mechanical properties of a sulphur-cured NR. The filler was introduced with liquid TESPT before it was added to the raw elastomer in the mixer. Results showed that the viscosity of the rubber compound decreased, the cure time shortened and the quality of the filler dispersion enhanced when the TESPT silane was present in the rubber. In addition, the tensile strength, elongation at break, and cohesive tear strength were also improved significantly [76]. The reinforcing effect of a large amount of silanised precipitated amorphous silica nanofiller on the mechanical properties of styrene butadiene rubber was studied. The hardness, tensile strength, elongation at break, stored energy density at break, modulus, crosslink density of the rubber vulcanisate were substantially increased when filler was added. These properties were enhanced because of high filler-rubber interaction which was mainly due to the chemical bonding between rubber and TESPT. Therefore, pre-treated amorphous white silica with TESPT was found to be effective reinforcing filler for SBR. This optimum cure system in the rubber formulation consisted of 3 phr TBBS and 0.5 phr zinc oxide and when up to 0.7 phr elemental sulphur was added, some of the rubber properties improved and others deteriorated. However, it was beneficial to the cure properties t_{S2} and t_{95} were significantly decreased and the rate of cure increased noticeably. [77]. A similar study showed optimisation of the chemical bonding between the rubber and filler required 7.5 phr of TBBS. When zinc oxide was added to the filled rubber with 7.5 phr TBBS the rubber became too brittle. Hence, the addition of zinc oxide and stearic acid offered no benefit to the crosslink density of the rubber. Mechanical properties were improved substantially and bound rubber and crosslink density measurements indicated strong rubber-filler adhesion [78]. Ansarifar *et al* used silanised silica to reduce the excessive amount of rubber curatives in SBR. They studied the reaction between the rubber reactive tetrasulphane groups of TESPT and the rubber chains to optimise cure. Accelerators TMTD and TBBS was used at 5 phr and 3 phr loading, respectively, and also 0.5 phr zinc oxide was added. There was no need to add stearic acid and elemental sulphur to the filled rubber and in fact, stearic acid was detrimental to Δtorque, which indicated the crosslink density changes in the rubber. Cure and some mechanical properties were improved substantially with TMTD. However, tensile strength, elongation at break, and stored energy density at break were inferior. Therefore, chemical bonding or crosslinking between the tetrasulphane groups of TESPT and the rubber chains were optimised with the sulphur bearing TMTD accelerator efficiently. This resulted in the significant reduction in the use of the curing chemicals [79].

2.7.2.5 Toxicology of reinforcing amorphous white silanised silica

The toxicity of commercially available amorphous and synthetic white precipitated silicas has been studied by a number of researchers and organisations including national and international agencies such as, Environmental Protection Agency (EPA) and organisation for Economic Cooperation and Development (OECD). These studies were based on animals with the toxicity related to the use of synthetic amorphous silica and the results were remarkably consistent. The effects of amorphous silicas are transient and include an initial inflammatory response that occurs with exposure to particles [80]. The new European chemicals policy, Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) and various legislations for environment and safety restrict excessive use of chemicals in rubber which are harmful to health, safety and the environment. In order to address the health, safety and environment issues related to rubber compounds, it is essential to use chemical curatives and reinforcing filler more efficiently and effectively. However, there are some deficiencies in using the TESPT and precipitated silica in rubber reinforcement. When silica compounds are modified *in situ* with liquid TESPT, unreacted TESPT could sometimes be identified, indicating and incomplete and uneconomical modification process *in situ*. Also, different mixing equipment results in different mixing conditions gives different properties from those experienced using experimental compounds [81]. When silica reacts with liquid TESPT *in situ*, it generates harmful ethanol during mixing [82-83]. There is also a major concern related to the use of harmful curatives in the cure systems of rubber compounds. For instance, in some EPDM vulcanisates where liquid TESPT and precipitated silica were used [84], the cure system consisted of 5 phr zinc oxide and 1 phr stearic acid (primary and secondary activators), 3.1 phr accelerators (primary and secondary), and 0.8 phr curing agents (sulphur substitute), adding up to 9.9 phr, which as too much. Therefore, using TESPT pre-treated silanised silica filler produced better quality rubber compounds and ethanol free mixing was obtained [85].

2.7.3 Kaolin (China clay)

2.7.3.1 Background

Kaolin belongs to the group of minerals and is derived from the Chinese term “Kauling” which means high ridge. The mineral comprises of hydrated aluminosilicates such as dickite, nacrite, and halloysite [86]. Kaolinite is soft and non-abrasive and has a low conductivity of heat and electricity. The structure of kaolinite consists of alumina octahedral sheet bound on one side to a silica tetrahedral sheet, stacked alternately. The two sheets of kaolinite form a tight fit with the oxygen atoms forming the link between the two layers as shown in Fig. 2.12 [87].

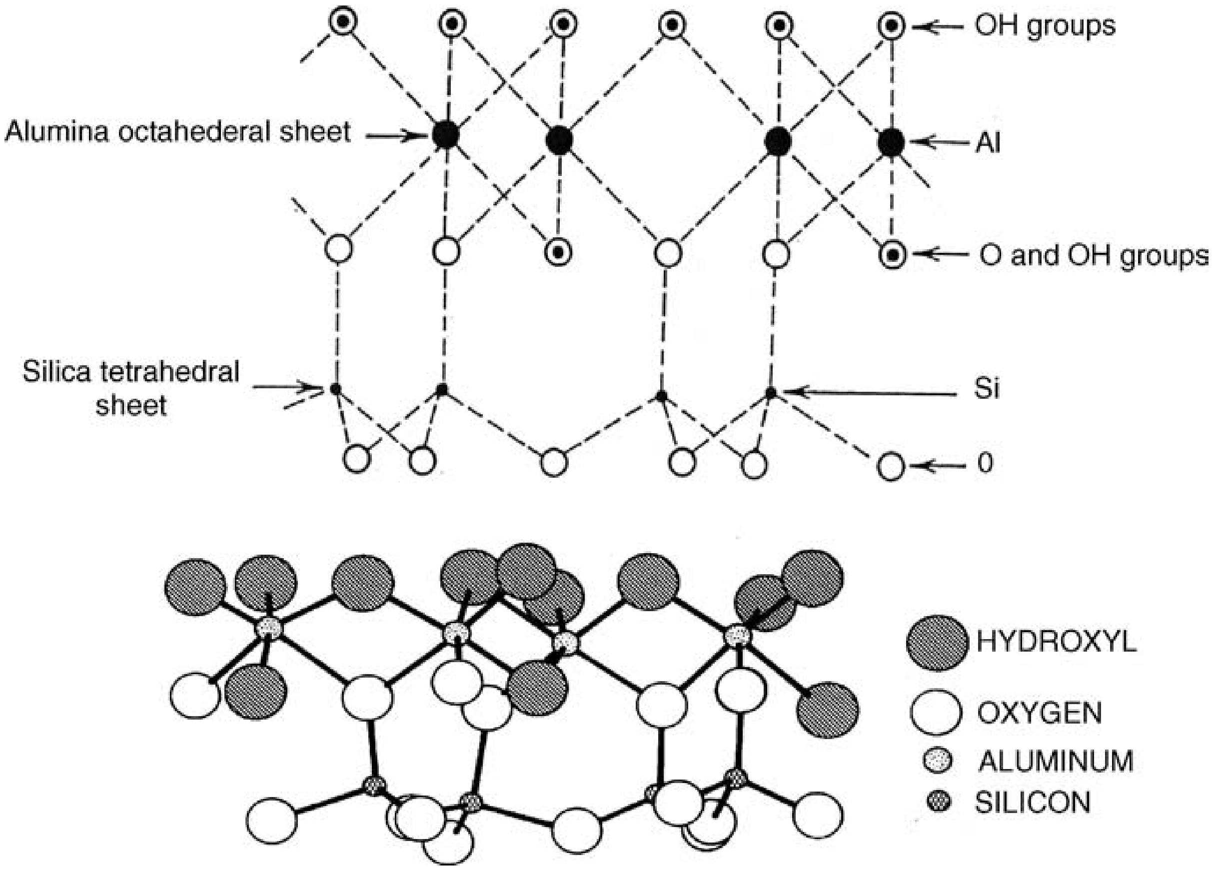


Figure 2.14 Structure of kaolin (China clay) [88]

The composition of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) mineral is 46% SiO_2, 39.8% Al_2O_3 and 13.9% H_2O [89]. Kaolin is considered to be a phyllosilicate mineral. Phyllosilicates are characterised by an indefinitely extended sheet of rings, in which three of the tetrahedral oxygens are shared whereas every fourth oxygen atom is apical and points upward [88]. An individual kaolin particle has a hydroxyl surface on one side and oxygen surface on the other side as shown in Fig. 2.12. Kaolin has a plate like structure as shown in Fig. 2.13 compared to other traditional fillers like carbon black and silica which are spherical in shape. Kaolin is used as filler for many applications such as, paper, coating, paper filling, paints, plastics, and also rubber.

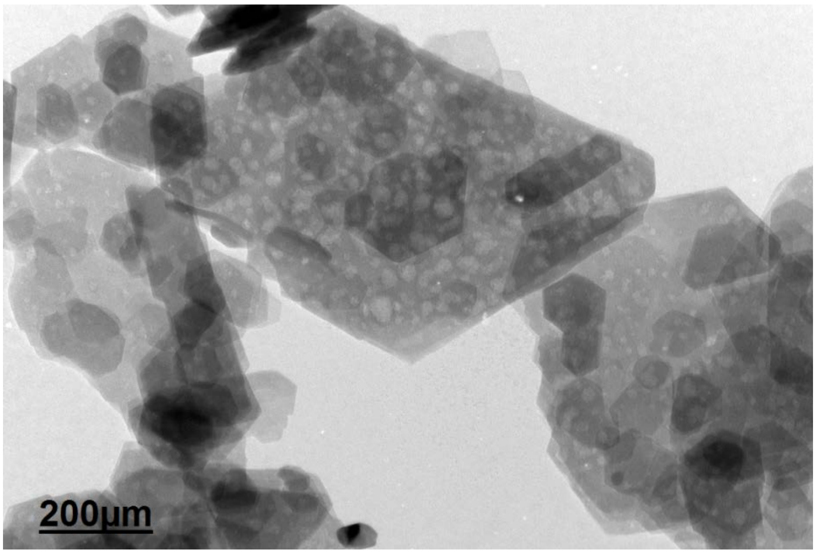


Figure 2.15 TEM image of kaolin particles showing plate like structure [121]

2.7.3.2 Manufacturing processes of kaolin

Kaolins are classified into primary and secondary. Primary kaolins are formed by the alteration of crystalline rocks such as granite where they remain in the place as it forms. Secondary kaolin deposits are sedimentary, formed by erosion of primary deposits. The secondary deposits contain about 85-95wt% more kaolinite than the primary which contains 15-30wt%. The primary deposits consist ore of quartz, muscovite, and fledspar. However, quartz, muscovite, smectite, anatase, pyrite and graphite are present in the secondary deposits. Kaolins deposits occur on every continent but only few of these can be mined and beneficiated to meet the industrial specifications required for use as filler. For instance, deposits are mined in countries like, United States (Georgia, South Carolina, and Texas), Brazil, and East Germany Spain etc.

- Primary processing of kaolin

Different kaolin grades can be produced by two commercialised methods of air floating or wet processing. Kaolin produced by air floating is cheap in which the mineral is crushed, dried and pulverised. It is then floated in an air stream and classified using an air classifier. Finally, finer particles are separated from the coarse particles and nano-kaolin particles. On the other hand, wet process is much more sophisticated and gives high quality consistent particle sizes with maximum purity.

This process starts with the formation of a clay-water suspension in a step referred to as blunging where kaolin slurry is produced that contain 45-50wt% solids. The slurry is then pumped into the processing plant for de-gritting, particle size distribution or morphology, leaching of colour bodies. Finally, apron drying and pulverisation or spray drying into bead form takes place [88].

2.7.3.3 Kaolin surface treatment

Surface modification of kaolin filler is another step that can improve and enhance the performance. Commercially kaolin produced is naturally very hydrophilic in nature due to hydroxyl groups, surface treatment can be applied to make them hydrophobic or organophilic. Surface treated kaolins are very useful in rubber industry. Since kaolin surface contains OH groups which makes it polar and moisture absorbing, surface treatment with silane improves the dispersion of the filler particles in the rubber matrix. One commonly used silane is 3-mercaptopropyltrimethoxysilane (MPTS), which contains less than 2wt% of sulphur. When sulphur reacts with rubber chains in the presence of an accelerator and activator, it produces stable covalent sulphur bonds. This in turn enhances the rubber/filler interaction and is immensely beneficial to the rubber reinforcement [90]. Using kaolin pre-treated with MPTS, a new method has been developed that optimises the reaction between the sulphur in MPTS on the kaolin surface and the rubber chains. This reduces excessive use of the chemical curatives and improves mechanical properties of the rubber vulcanisate. The Mooney viscosity, cure properties, hardness, tensile properties and Young’s modulus, tear strength, and compression set of rubber filled with MPTS pre-treated kaolin were measured [121].

2.7.3.4 Effect of kaolin on the properties of rubber vulcanisates

Numerous studies have looked into potential replacement of tradition fillers with kaolin in rubber compounds. A small amount of kaolin – 10 phr was modified with sodium salt of rubber seed oil (SRSO) and mixed with natural rubber [91]. The SRSO modified kaolin was more strongly bound in a constraint environment within the lamellae of kaolin. The rubber filled with SRSO-modified kaolin cured faster than that of a similar mix containing unmodified kaolin. In addition, the NR vulcanisates containing SRSO-modified kaolin showed considerable increase in tensile modulus, tensile strength, and elongation at break, indicating its potential as an organomodified nano-filler [91]. NR nanocomposites reinforced with 20-50 phr of silane-modified kaolin exhibited outstanding mechanical properties and much higher thermal stability compared with pure NR. The hardness and tensile properties improved with increasing filler loading and an optimum tensile strength was achieved at the highest loading of modified kaolin [92]. The surface of kaolinite clay was modified with different surface modifiers such as methacrylic acid and polymethacrylic acid. Natural rubber and styrene butadiene rubbers were mixed with modified and unmodified kaolins. The rheometric properties and mechanical properties of the rubber vulcanisates were determined. It was noted that there was a significant decrease in both the optimum cure time t_{90} and scorch time ts_2 and an increase in the maximum torque values for both the NR and SBR compounds. Mechanical properties of the rubber vulcanisates were investigated and showed improvement in tensile strength and hardness for both modified and unmodified kaolin [93]. Nano-kaolin powder of different average thickness and specific surface areas were introduced into NR, SBR, BR and EPDM rubbers. The effect of nano-kaolin on the rubbers was evaluated by comparisons with those from precipitated silica. Rheological and mechanical properties were measured. The results showed that nano-kaolin could greatly improve the vulcanisation process by decreasing the optimum cure and scorch times. Mechanical properties, thermal properties and rubber properties were substantially good. Tensile strength was close to that of the rubber filled with precipitated silica, but tear strength and modulus were inferior to those of silica. For natural rubber, tensile strength of nano-kaolin filled rubber was considerably higher than that of the precipitated silica filled one [94]. In a study, importance of the surface organo-modification of kaolin was demonstrated. Metal salt of rubber seed oil (RSO-Na) was used to modify kaolin and then was introduced into NR. Rubber composites mixed with various compositions of pristine and modified kaolin (2–10 phr) were then prepared and tested. The results showed that the modified kaolin improved the cure and mechanical properties of the rubber composite compared to the pristine kaolin-filled rubber. For example, the viscosity and hardness increased with increase in filler concentration. Furthermore, the extent of crosslink density and rubber-filler interaction also improved. It was concluded that the presence of the modified kaolin resulted in the formation of a higher number of crosslinks, which was attributed to the confinement of the rubber chains within the silicate galleries, and consequently to better interaction between the filler and the rubber [95]. Formulation and morphology of novel-kaolin filler rubber composites were investigated [96]. Rubber composites included NR, SBR, BR, NBR, EPDM and CR, with various filler loading displayed superior mechanical and thermal properties such as, tensile strength but weaker elongation at break. It was concluded that kaolin could replace silica in the specific rubber products and was suitable for rubber reinforcement. The cure systems in these compounds consisted of two accelerators, two activators and elemental sulphur. It was clear that after surface treatment kaolin performed a lot better in rubber.

2.7.3.5 Toxicology and environmental effects of kaolin

Kaolin is classified as nontoxic mineral with the exception of possible dust particles. Only an approved dust mask would be highly recommended when using kaolin. The food and drug administration gives kaolin as “Generally Regarded as Safe” status (GRAS) [88]. Kaolin has been used in many consumer products in various industries. It is a very unique mineral that is chemically inert over a relatively high pH range. It has low conductivity of heat and electricity and it is lower in cost and readily available. Kaolin is used by rubber manufacturers due to its reinforcing and stiffening properties. When kaolin was incorporated in rubber it improved mechanical properties such as, tensile strength, tear resistance, abrasion resistance, heat generation, energy rebound, extrusion and plasticity, hardness, ageing characteristics etc. [97].

2.7.4 Other fillers used for rubber reinforcement

2.7.4.1 Fibres

Fibre is a constitute material available to use as a reinforcing agent designed for a particular matrix system to make a composite material [98]. Reinforcement by fibres generally produces good stiffness. There is a variety of fibres used which give several different advantages in particular with their properties. Fibres such as, glass, carbon, talc, silica and high performance fibres, (aramidic) are combined with polymer to make composite materials.

In a study, composites made from SBR and short fibres were prepared. The influence on the vulcanisation process and tensile strength were studied and the results showed that with fibres shorter cure time and a marginal increase in tensile strength was achieved but elongation at break of the compound was decreased [99].

Natural rubber was mixed with short fibres and the reinforcing effect of the fibre on the rubber properties was discussed [100-103]. It was found that the fibre offered a similar level of reinforcement compared to carbon black and silica. In some other studies, tensile strength and elongation at break of natural rubber based composites substantially decreased with the addition of fibres [99]. The effect of aramid, glass and cellulose short fibres on the processing behaviour, crosslink density and mechanical properties of NR, EPDM and SBR was investigated [104]. The result showed aramid fibres were effective reinforcing agents for these rubbers giving rise to a significant increase in mechanical properties, such as tensile modulus and strength, and tear and abrasion resistance. In addition, there was a significant decrease in optimum cure time. The decrease in the cure time indicated that the fibres tended to increase the vulcanisation rate [104]. Another very important parameter of natural fibre was poor compatibility with polymer matrices, i.e. poor adhesion at the interface which ultimately resulted in non-uniform dispersion of fibres within matrix. Natural fibres are very hydrophilic in nature therefore their high moisture content and this led to harsh reduction of mechanical properties or delaminating [105]. In order to obtain optimum properties and to improve the adhesion between the fibre and matrices, adhesion promoters or chemical coupling agents are used. The fibre surface is treated with coupling agents in such a way that bonding between the fibre and matrix will be enhanced.

2.7.4.2 Clays and organo-clays

According to CMS (Clay Minerals Society), clay is a naturally occurring material composed of primarily fine-grained minerals when added as fillers, affects the behaviour of rubbers. The modification of clays with organophilic cations is essentially done to promote compatibility with rubber [106]. Clays are stacked layered inorganic compounds that are joined together by iono-covalent bonds. These layers are bound to each other in a perpendicular direction through weaker forces which can be separated from each other by applying a small amount of energy. However, a remarkable amount of energy is required to break the layers of clay [107].

2.7.4.2.1 Structure of clays

The dispersion of clay in polymer matrix is one of the most important features of polymer nanocomposites. Fig. 2.14 shows the structure of montmorillonite (MMT), the most applied clay for the preparation of polymer nanocomposites.

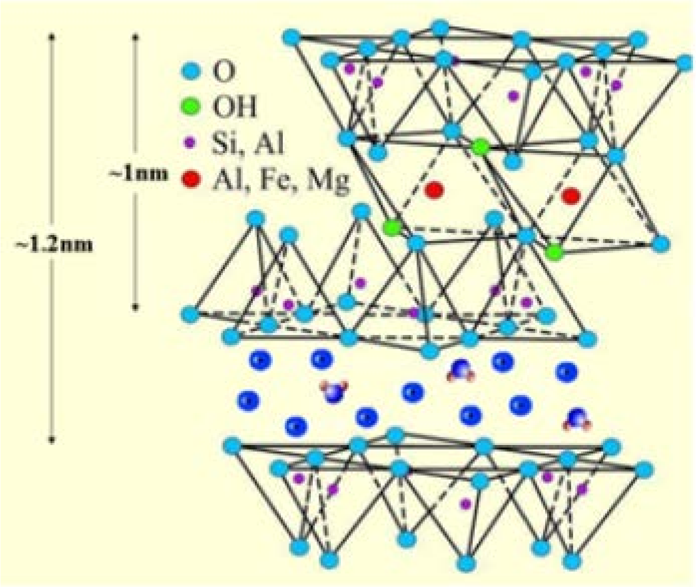


Figure 2.16 Structure of montmorillonite [107]

This montmorillonite clay (MMT) is available in bulk and is very cost effective with high surface area. It contains less than 1wt% of crystalline silica and therefore considered safe and is handled as a standard powder [108].

In a study, natural rubber latex clay nanocomposites reinforced with montmorillonite clay achieved good dispersion and provided better reinforcement. The physio-mechanical properties of composites were measured. The crosslink density of nanocomposites was increased with an increase in clay loading. As a result, low loadings of MMT clay were able to significantly improve the reinforcement, whilst maintaining good elastic properties and barrier properties of the nanocomposites vulcanisates [109]. In another study, nanocomposites were prepared using a non-polar polymer such as, EPDM reinforced with nanoclay at low filler loadings showed improved properties and better dispersion. EPDM and organoclay has been modified to improve the dispersion of clay, provided better thermal stability and decreased swelling [110]. Rubber nanocomposites based on natural rubber and organically modified montmorillonite (OMMT) were prepared by melt intercalation technique, using a laboratory open mill, followed by compression moulding. The dispersion of OMMT in the NR was better for organoclay Cloisite 15A that showed a higher d-spacing. X-ray diffraction (XRD) spectrum showed OMMT was nearly exfoliated in the NR. In addition, the presence of organoclay significantly decreased the cure time and scorch time. Mechanical properties such as, hardness and stresses at low strain of nanocomposites slightly increased with increasing d-spacing of organoclay and swelling behaviour was also increased with increase in d-spacing but elongation at break slightly decreased [111].

2.7.4.3 Calcium carbonate

Calcium carbonate ($CaCO_3$), which is also known as whiting, chalk, limestone and calcite are added to the rubber to make it cost effective and improve hardness of rubber compounds. Calcium carbonate is used in the rubber industry for making electrical wires and cable insulation where low moisture content and natural insulating properties make a perfect choice for rubber compounder to use in rubber compounds. Particle sizes, ranging from 2 to 80 µm, are typically available for use and typical loading of calcium carbonate in rubber compounds ranges from 20 to 300 phr [112].

2.8 Health, safety, environmental and cost issues related to the use of carbon black, silica, mineral fillers and fibres in the rubber

Summary - To enhance the mechanical properties of a rubber such as hardness, tear strength, tensile strength, and elongation at break, fillers with surface areas ranging from 150 to 400 m^2/g are added [113].Among these fillers, short fibres, colloidal carbon blacks, metal oxides, and synthetic silicas are the most widely used materials in rubber reinforcement. Carbon black contains a low level of polycyclic aromatic hydrocarbons (PAHs) within the structure of CB. Many of these PAHs are tightly bound into the structure of the CM aggregate and are not free to migrate, but a small amount are on the surface. PAHs are known to be highly carcinogenic (cause cancer), mutagenic (cause mutation) and teratogenic (cause defects); and therefore there is a considerable health risk associated with their use in the rubber compounds [113].

According to IARC carbon black is classified as 2B rated, possibly carcinogenic to humans and definitely carcinogenic to animals [114-115]. Silica is also used as filler in rubbers. Silica contains silicosis, which has potential health effects such as, respiratory disease of lungs from inhalation of airborne crystalline silica dust. These dust particles cause fibrosis (scar tissue formation) in the lungs. The overall IARC evaluation was that crystalline silica inhaled in the form of quartz or occupational sources is carcinogenic to humans [115]. Traditional fillers such as carbon black and precipitated silica are both classified as harmful and pose serious health concerns. Whereas, natural minerals such as kaolin (China clay) are less harmful solid fillers and pose no considerable health risk associated with their use in rubber. In terms of costs, these natural solid fillers are readily available in the market and compared to carbon black and silica, mineral fillers are very cost effective and much safer to use in rubber composites and provide as good if not better mechanical properties.

2.9 Summary

Excessive use of the curing chemicals is harmful to health, safety, and the environment and their use is restricted by the new European chemicals policy, Regulation, Evaluation, Authorisation, and Restriction of Chemicals (REACH) and various legislation for environment and safety. Reduction in the use of these chemicals in rubber compounds is now a priority. In any rubber formulation, chemical curatives and solid fillers are indispensable. The former provides shape stability, and the latter reinforcement of the dynamic and mechanical properties of the cured rubber, which is essential for the performance, durability, and life of the final product in service [116,117]. According to the European Directive 67/548/EEC, zinc oxide is very toxic to aquatic organisms. Stearic acid causes skin and eye irritation and is classified as highly flammable [118]. Both of these chemicals are used extensively as activator in sulphur vulcanisation [119,120]. Besides, CBs could be highly toxic and pose a considerable health risk associated with their use in rubber compounds [113]. There is a need to replace CB with less harmful solid fillers.

2.10 References

1. L G Hernandez, L M I Rueda, C C Anton, “Magnesium silicate filler in rubber tread compounds”, *Rubber. Chem. Technol*. Vol. 60, No. 4 (1987) pp 606-617

2. W Hofmann, “Rubber Technology Handbook”. *Hanser Publishers*, Munich Germany, (1989)

3. P A Ciullo and N Hewitt, “The Rubber Formulary”. *Noyes Publications*, NY, (1999). pp 110.

4. M L Stuart “Reference book for Composites Technology”. *Technomic Publishing Company* (1989). pp 81-104

5. D Feldman, A Barbalata, “Synthetic Polymers: Technology, Properties, Applications”, 1st *edn. Chapman & Hall*, (1996).

6. J E Logsdon “Kirk-Othmer Encyclopaedia of Chemical Technology”, *John Wiley & Sons, Inc*. (2000)

7. NIIR Board of consultants & Engineers, “Rubber Processing and Compounding Technology”, *Asia Pacific Business Press Inc*. (2008)

8. A Ciesielski, “An Introduction to Rubber Technology”, *Rapra Technology Ltd* (1999).

9. R Karpeles and A V. Grossi, “EPDM Rubber Technology”, Handbook of Elastomers, 2ndEd., A K. Bhowmick and H L Stephens [Editors], pp. 845-876, *Marcel Decker, Inc.,* New York (2001).

10. C Goodyear, Inventor , *US Patent 3633* (1844)

11. R J Miller, H S , Lenihan, E B Muller, N Tseng, S K Hanna, A A Keller, “Impact of metal oxide nanoparticles on marine phytoplankton”. *Environ. Sci. Technol*., Vol.44 No.19 pp 7329-7334 (2010)

12. L Bateman, C G Moore, M Porter, B Saville, “The Chemistry and Physics of Rubber-like Substances” (Ed: L. Bateman), *Maclaren & Sons Ltd., London*, (1963), pp. 449.

13. W. Hofinann, Rubber “Technology Handbook” Vulcanisation and Vulcanising Agents, *Pahnerton Publishing co.Inc*., (1967)

14. J S Dick, “Rubber Technology Compounding and Testing for Performance”, *Hanser Gardner Publication*., (2001)

15. W Hofmann, “Rubber Technology Handbook”, *Hanser Gardner Publications*, (1996), pp 222.

16. B H To, “Rubber Technology”, [Ed: J.S. Dick], *Hanser, Munich* (2001) Ch. 15.

17. P M Visakh, S Thomas, A K Chandra, A P Mathew, “Advances in Elastomers I: Blends and Interpenetrating Networks”, *Springer-Verlag Berlin Heidelberg* (2013)

18. J S Dick, “Rubber Technology Compounding and Testing for Performance”, *Hanser Gardner Publication* (2001)

19. DTechnicalNote- Vulcanisation [online] available at: http://www.nocil.com/Downloadfile/DTechnicalNote-Vulcanisation-Dec10.pdf [Accessed: 1st August 2017]

20. W W Paris, "General catalogue for peroxides and speciality chemicals", Pennwalt Chemicals Co. Buffalo, New York (1977).

21. G Heideman, R N Datta, B van Baarle, J W M Noordermeer, *Rubber Chem. Technol*, Vol.77 pp 512-541 (2004)

22. M H S Gradewell, M J Van Der Merwe, *Rubber Chem. Technol*., Vol.72. No. 1, pp 55-64 (1999)

23. G Heideman, R N Datta, J W M Noordermeer, B Baarle, *Journal of Applied. Polymer Science*, Vol.95, No. 6, pp 1388-1404 (2005)

24. R H Campbell, R W Wise, *Rubber Chem. Technol*., Vol.37, No. 3, pp 635-649, (1964)

25. M H S Gradwell, W J McGill, *Journal of Applied Polymer Science*, Vol.61, No. 9, pp1515-1523 (1996)

26. A Y Coran, “Science and Technology of Rubber”, *Academic Press Inc. San Diego*, *2nd edn.*(1994)

27. P Ghosh, S Katare, P Patkar, J M Caruthers, *Rubber Chem. Technol*. Vol.76, No. 3, pp 592-693 (2003)

28. M H S Gradwell, W J McWill, *Journal of Applied Polymer Science*, Vol.51, No. 4 pp 169-208 (1994)

29. M H S Gradwell, K G Hendrikse, W J McGill, *Journal of Applied Polymer Science*, Vol.72, No. 10, pp 1235-1373 (1999)

30. M H S Gradwell, W J McWill, *Journal of Applied Polymer Science*, Vol.61, No. 9, pp 1515-1523 (1996)

31. W H Kruger, W J McWill, *Journal of Applied Polymer Science*, Vol.45, No. 9, pp 1545-1556 (2003)

32. G Heideman, R N Datta, J W M Noordermeer, B J van Baarle, *Journal of Applied Polymer Science,* Vol.95 pp 1388-1403 (2005)

33. C G Moore, B R Trego, *Journal Applied Polymer Science*, Vol.8,No. 2, pp 581-602 (1964)

34. R W Layer, *Rubber Chemical Technology*, Vol.65 pp 211-222 (1992)

35. R W Layer, *Rubber Chemical Technology*, Vol.65 pp 822-835 (1992)

36. Additives for rubber [online] available at: http://www.nocil.com/downloadfile/DTechnicalNote-vulcanisation-Dec10.pdf [accessed:03/08/2017 September 2015]

37. A Y Coran, *Rubber Chem. Technol.*, Vol.37, No. 3, pp 679-688 (1964)

38. F Ignatz, B H Hoover, “Rubber Compounding: Chemistry and Application, Chapter 11”, *Marcel Decker Inc*. (2004)

39. A Ciesielski, “An Introduction to Rubber Technology”, Chapter 3 *Rapra Technology Ltd.* (1999)

40. S C Jagadale, K Rajkumar, R P Chavan, D N Shinde, C L Patil “Environmental concern of pollution in rubber industry”, *International Journal of Research in Engineering and Technology*, Vol.04, No. 11, pp 187-191 (2015)

41. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Lyon, 7–14 February (2006), (2010) Volume 93 page 189.

42. N Chaiear, *Health and safety in the rubber industry,* Vol. 12, No. 6, pp 21 (2001)

43. R J Lewis Sr., “SaxIs Dangerous Properties of Industrial Materials”, Eighth Edition. Vol.1 (1992)

44. Toxicological review of zinc and compounds, EPA/635/R-05/002, July (2005), pp 60.

45. http://www.hse.gov.uk/research/rrpdf/rr819.pdf , “A small survey of exposure to rubber process dust, rubber fume and N-nitrosamines, Prepared by the Health and Safety Laboratory for the Health and Safety Executive” (2010)

46. http://www.westliberty.edu/health-and-safety/files/2012/08/Stearic-Acid.pdf

47. Hans-Jurgen Kretzschmar, “Hazards in the European Rubber Industry: An Assessment of Exposure Risks”, September (1999), paper 6 page 1.

48. L J Fine, J M Peters, “Respiratory morbidity in rubber workers, I: prevalence of respiratory symptoms and disease in curing workers”. *Arch Environ Health,* Vol. 31, No.1, pp 5-9 (1976)

49. L J Fine, J M Peters, “Respiratory morbidity in rubber workers, I: pulmonary function in curing workers”, *Arch Environ Health,* Vol. 31, No.1, pp 10-14 (1976)

50. J L Weeks, J M Peters, R R Monson, “Screening for occupational health hazards in the rubber industry, part I”. *Am J Ind. Med,* Vol.2, No.2, pp 125-41 (1981)

51. E Zuskin, J Mustajbegovic, E N Schachter, J Doko-Jelinic, A Budak, “Longitudinal study of respiratory findings in rubber workers”. *Am J Ind. Med,* Vol. 30, No. 2, pp 171-179 (1996)

52. J L Weeks, J M Peters, R R Monson, “Screening for occupational health hazards in the rubber industry, part II: health hazards in the curing department”, *Am J Ind. Med,* Vol.2, No. 2, pp 143-151 (1981)

53. S Ostad-Movahed, K A Yasin, A Ansarifar, M Song, S Hameed, *J. Appl. Sci.*, Vol.109, No. 2 pp 869-881 (2008)

54. A Ansarifar, L Wang, R J Ellis, Y Haile-Meskel, *J. Appl. Sci., Vol*. 106, No. 2, pp 1135-1145 (2007)

55. A Ansarifar, L Wang, R J Ellis, S P Kirtley, N Riyazuddin, *J. Appl. Sci.,* Vol.105, No. 2, pp 322-332 (2007)

56. B Rodgers, “Rubber Compounding Chemistry and Applications”, *Marcel Dekker, Inc.,* New York, (2004)

57. W Meng-Jiao, A G Charles, A R Steve, K Mahmud, Y Kutsovsky, Cabot Corporation “Kirk-Othmer Encyclopaedia of Chemical Technology”, *John Wiley & Sons,* Inc. Vol. 4 (2003)

58. J B Donnet, R.C. Bansal, and M.J. Wang, “Carbon Black: Science and Technology”. *CRC Press* (1993)

59. R C Bansal, J B Donnet, “Surface groups on carbon blacks”, In: Donnet J B, Bansal RC, M J Wang, eds. Carbon Black. 2nd Ed. New York: *Marcel Dekker*, (1993)

60. M J Wang, S Wolff, J B Donnet, *Rubber Chem. Technol*., Vol. 64, No. 5, pp 714-736 (1991)

61. M J Wang, S Wolff, “Surface energy of carbon black”, In: Donnet J P, R C Bansal, M J Wang, eds. Carbon Black. 2nd Ed. New York: *Marcel Dekker*, (1993)

62. J J Pandian, T Govindan, "Comparative studies on the mechanical properties of natural rubber and natural rubber carbon black composites", *International Journal of Emerging Technology in Computer Science & Electronics (IJETCSE),* Vol. 13, No. 2 (2015)

63. S Chuyjuljit, A Imvittaya, N NA-RANONG, and P Potiyaraj, "Effects of Particle Size and amount of carbon black and calcium carbonate on curing characteristics and dynamic mechanical properties of natural rubber", *Journal of Metals, Materials and Minerals*. Vol. 12 No. 1 pp. 51-57, (2002)

64. B. Rodgers, “Rubber compounding chemistry and applications”, *Marcel Dekker, Inc.,* New York, (2004)

65. J J Han, X. L He, W H Guo and C F Wu, "Effects of filler–rubber interaction on dynamic mechanical properties and reinforcement of NR vulcanisates", *Plastics, Rubber and Composites Macromolecular Engineering* Vol. 36, No. 4 (2007)

66. J Wang, Li Qiuying, Wu Chifei, and Xu Haiyan, "Thermal Conductivity and Mechanical Properties of Carbon Black Filled Silicone Rubber", *Polymers & Polymer Composites*, Vol. 22, No. 4, pp 393-400 (2014)

67. Organisation for Economic Cooperation and Development (OECD), SIDS Initial Assessment Report for SIAM 21: Carbon Black. (2005).

68. International Agency for Research on Cancer (IARC), Printing Processes and Printing Inks, Carbon Black and Some Nitro Compounds, in IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Vol. 65, (1996)

69. Environment Canada and Health Canada, Carbon Black, in Draft Screening Assessment for the Challenge, (2011)

70. A Voet, J C Morawski, and J B Donnet, *Rubber Chem. Technol.*, Vol. 50, No. 1, pp 242-355 (1977)

71. E M Dannenberg, *Rubber Chem. Technol.*, Vol. 48, No. 3, pp 410-444 (1975)

72. E H Tan, H Wolff, S. Haddeman, S M Gretwatta, H P Wang, *Journal of Rubber Chemical Technology*, Vol. 66, No. 4, pp 594-604 (1993)

73. E M Dannenberg, *Rubber Chem Technol*, Vol. 48, No. 3, pp 410-444 (1975)

74. S Wolff S, U Gorl U, M J Wang, W Wolff. “Silane modified silicas–silica-based tread compounds”, *Rubber Journal* Vol. 16, pp 16-19 (1994)

75. A Voet, J C Morawski, J B Donnet, “Reinforcing of elastomers by silica”, *Rubber Chem Technol.* Vol. 50, No. 2, pp 342-355 (1977)

76. A Ansarifar, A Azhar, M Song, “A new design concept for natural rubber compounds using silanised precipitated silica”, *J Rubber Res* Vol. 6, No. 3 pp 129-152 (2003)

77. A Ansarifar, L Wang, R J Ellis, S P Kirtley, N Riyazuddin, “Enhancing the mechanical properties of styrene-butadiene rubber by optimizing the chemical bonding between silanized silica nanofiller and the rubber”, *Journal of applied polymer science,* Vol. 105, No. 2, pp 322-332 (2007)

78. A Ansarifar, L Wang, R J Ellis, Y Haile-Meskel, “Novel technique for crosslinking and reinforcing high-cis Polybutadiene rubber using a silanized silica nanofiller”, *Journal of applied polymer science*, Vol. 106, No. 2, pp 1135-1145 (2007)

79. A Ansarifar, L Wang, R J Ellis, Y Haile-Meskel, “Using a silanized silica nanofiller to reduce excessive amount of rubber curatives in styrene-

butadiene rubber", *Journal of Applied polymer science*, Vol. 119, pp 922-928 (2011)

80. Organisation for Economic Cooperation and Development (OECD), SIDS Initial Assessment Report for SIAM 19: Synthetic Amorphous Silica and Silicates. (2004)

81. S Wolff, *Rubber Chem. Technol.,* Vol. 55, No. 4, pp 967-989 (1982)

82. E F Cluff, E K Gladding, and R Pariser, *Journal of Polymer Science*, Vol. 45, No. 146, pp 341-345 (1960)

83. S Wolff, M J Wang, E H Tan, *Rubber Chem Technol.,* Vol. 66, No. 2, pp 163-177 (1993)

84. K J Kim, *J. Appl. Polymer. Sci.,* Vol. 116, No. 1, pp 237-246 (2010)

85. A Ansarifar, F Saeed, "Developing ethylene-propylene-diene rubber compounds for industrial applications using a sulphur-bearing silanized silica nanofiller", *Polymer Composites*, Vol. 34, No. 12, pp 2019-2025 (2013)

86. P A Ciullo, "Industrial Minerals and Their Uses – A Handbook and formulary", Noyes Publication, Westwood, NJ. (1996)

87. F Washabaugh, "Kaolins for rubber applications", Engelhard Corp., Iselin, NJ. (1995)

88. M Xanthos, "Functional Fillers for Plastics", Chapter 13 "Kaolin" by J Duca, (2010) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

89. H Murray, *Appl. Clay Sci.,* Vol. 5, No. 3, pp 379–385 (1991)

90. S H Sheikh, A Ansarifar, "Carbon black alternative", *Tire technology international*, pp 96-100 (2015).

91. R Sukumar, A R R Menon, "Organomodified kaolin as a reinforcing filler for natural rubber", *J. Appl. Poly. Sci*. Vol. 107, No. 6, pp 3476-3483 (2008)

92. Q Zhang, Y Zhang, Y Wang, "Mechanical and thermal properties of kaolin/natural rubber nano-composites prepared by the conventional two-roll mill method", *Appl. Mech. & Material.,* Vol.164, pp142-145 (2012)

93. M Sh Zoromba, A A M Belal, A E A Ali, F M Helaly, A A Abd El-Hakim, A S Badran, "Preparation and characterisation of some NR and SBR formulation

containing different modified kaolinite", *Polymer. Plastics. Technology and Engineering,* Vol.46, No. 4-6, pp 529-535 (2007)

94. Q Liu, Y Zhang, H Xu, "Properties of vulcanised rubber nanocomposites filled with nano-kaolin and precipitated silica", *Applied Clay Science*, Vol.42, No. 1-2, pp 232-237 (2008)

95. L E Yahaya, K O Adebowale, and B I Olu-Owolabi, "Cure characteristics and rheological properties of modified kaolin-natural rubber composites". *Am. Chem Sci J* Vol.4, No. 4, pp 472-480 (2014)

96. W. Weili, L Tian, "Formulation and morphology of kaolin-filled rubber composites", *Applied Clay Science*, Vol. 80-81, pp93-97 (2013)

97. Kaolin Clays and Their Industrial Uses, *J. M. Huber Corp*., New York, *2nd edn.* (1955)

98. D Hull, T W Clyne, "Introduction to Composite Materials", *2nd edn*, Cambridge University Press, (1996)

99. N Meissner, W M Rzymski, "Use of short fibres as a filler in rubber compounds", *Autex Research Journal,* Vol. 13, No.2, pp 40-43 (2013)

100. D De, B Adhikari, "The effect of grass fibre filler on curing characteristics and mechanical properties of natural rubber", *Polymer for Advances Technologies*, Vol.15, No. 12, pp 708-715 (2004)

101. V G Geethamma, K T Mathew, R Lakshminaryana, and S Thomas, "Composite of short coir fibres and natural rubber: effect of chemical modification, loading and orientation of fibre" *Polymer*, Vol. 39, No. 6-7, pp 1483-1491 (1998)

102. I Hanafi, H D Rozman, R M Jaffri, Z A Mohd Ishak, "Oil palm wood flour reinforced epoxidised natural rubber composites" The effect of filler content and size, *European Polymer Journal*, Vol. 33, No. 1, pp 1627 1632 (1997)

103. W Zhang, Z Xinxing, L Mei, Lu Canhui," Mechanochemical preparation of surface-acetylated cellulose powder to enhance mechanical properties of cellulose-filler-reinforced NR vulcanisates", *Composites Science and Technology*, Vol. 68, No. 12, pp 2479-2484 (2008)

104. M A Lopez, M Arroyo, "Short fibres as Reinforcement of Rubber Compounds", *Polymer Composites,* Vol. 23, No. 4, pp 479-494 (2004)

105. G Koronis, A Silva, and M Fontul, “Green Composites: A Review of Adequate materials for Automotive and Applications”, *Composites Part B: Engineering*, (2012)

106. F Bergaya, M Jaber, J Lambert, F, “Clays and Clay Minerals”. In: Galimberti M. (Ed.), *Rubber Clay Nanocomposites- Science, Technology and Applications*, Wiley and Sons, New York, Chapter 1344 (2011)

107. A Boczkowska "Advanced Elastomers - Technology, Properties and Applications", book, Chapter 4 Rubber Clay Nanocomposites By Maurizio Galimberti, Published: September 12, (2012)

108. http://www.bsi-global.com/en/Standards-and-Publications/Industry-Sectors/ Nanotechnologies/ PAS-71/Download-PAS-712005Vocabulary-Nanoparticles

109. A Amarasiri, U N Ratnayake, U K De Silva, S Walpalage and S Siriwardene, "Natural rubber latex-clay nanocomposite: use of montmorillonite clay as an alternative for conventional $CaCO_3$", *Journal of the National Science Foundation of Sri Lanka* Vol. 41, No. 4, pp 293-302 (2013)

110. K Donghee, K Dongsik, Y Sung-Hwan, K Dongkyu, B Carol, M Joey, “Properties and dispersion of EPDM/modified-organoclay nanocomposites”, *Macromol. Mater. Eng.* Vol. 292, No. 3, pp 329-338 (2007)

111. M I Fathurrohman, B Soegijono, E Budianto, S Rohman, A Ramadhan, "The effect of organoclay on curing characteristic, mechanical properties, swelling and morphology of natural rubber/organoclay nanocomposites", *Macromol. Symp*, Vol.353, No. 1, pp 62–69, (2015)

112. J S Dick, “Rubber Technology : compounding and testing for performance”, *Hanser Publisher, Munich*, (2014)

113. J Hallet, G Moninot, “Proceedings of 7th international conference on rubber chemicals, compounding and mixing”, Vienna, Austria, *Smithers Rapra Ltd*, paper 1 pp 1-6 (2010)

114. N Chaiear, “Health and Safety in the Rubber Industry”, Rapra Review Reports*, Rapra technology limited* Vol.12, No 6, (2001)

115. IARC, Silica, Some Silicates, Coal Dust and para-Aramid Fibrils, WHO Geneva, *IARC Monographs*, Vol.68 (1997)

116. S Ostad-Movahed, K A Yasin, A Ansarifar, “Comparing effects of silanized silica nanofiller on the crosslinking and mechanical properties of natural

rubber and synthetic polyisoprene". *J Appl. Polym. Sci.* Vol.109. No. 2, pp 869-881 (2008)

117. M J Wang, "Effect of polymer-filler and filler-filler interaction on dynamic properties of filled vulcanisates", *Rubber Chem Technol.* Vol.71, No. 3, pp 520-589 (1998)

118. http://www.westliberty.edu/health-and-safety/files/2012/08/Stearic-Acid.pdf

119. P A Ciullo and N Hewitt, "The Rubber Formulary". New York, NY: Noyes Publications, (1999), pp91.

120. P S Brown, M Porter and A G Thomas, "The dependence of strength properties on cross-linked structure in vulcanized polyisoprenes" *Kautsch Gummi Kunstst* Vol.40 pp 17-19 (1987)

121. S H Sheikh, A Ansarifar, "Carbon black alternative", Tire Technology International, pp 96-100, (2015)

122. M.A. Fath, Rubber World, Vol. 209, No. 1, pp 17-22 (1993)

Chapter 3 - Novel sulphur cure systems for rubber

3.1 Introduction

There are fundamental problems with the sulphur-cure systems in industrial rubber articles such as tyres, conveyor belts and hoses. The chemical curatives have never been measured properly and furthermore, there is no reason why so many and so much of them should be used in tyre compounds. This work was carried out to resolve this important issue and provide a precise method for measuring exact amount of the chemicals in sulphur-cure systems for tyres. Sulphenamide accelerators and zinc oxide (ZnO) and stearic acid activators are used extensively to cure a wide range of industrial articles. For example, in NR-based tyre belt skim compound [1], the cure system consists of sulphur, 5 parts per hundred of rubber by weight (phr); (N,N'-dicyclohexyl-2-benzothiazole sulphenamide) (DCBS) accelerator, 0.7 phr; hexamethoxy methyl melamine (HMMM) accelerator, 2 phr; ZnO, 7 phr; and stearic acid, 1 phr. Zinc oxide and stearic acid can potentially be harmful to health, safety and the environment. According to the European Directive 2004/73/EC, zinc oxide is very toxic to aquatic organisms. Stearic acid causes skin and eye irritation and is classified as highly flammable [2]. DCBS and HMMM accelerators may cause eye, skin and respiratory irritation and are harmful to aquatic life [3,4].

Other formulations such as the one for an IR/EPDM rubber blend used in wiper blades have also many chemical curatives in their cure system [7]. In this blend, the cure system consists of sulphur, 1.5 parts per hundred of rubber by weight (phr); Durax (N-Cyclohexyl-2-benzothiazole sulphenamide) (CBS) accelerator, 1.2 phr; Methyl Tuads (Tetramethylthiuram Disulphide) (TMTD) accelerator, 0.25 phr, ZnO, 7.5 phr; and stearic acid, 2 phr activators. CBS and TMTD accelerators are harmful by inhalation and if swallowed and very toxic to aquatic environment. These chemicals are harmful when contact with skin and eyes. For BR based innerliner compounds [8]. The cure system consists of sulphur, 0.5 phr; magnesium oxide (MgO) accelerator, 0.15 phr; 2-2’-Dithiobis(benzothiazole) (MBTS), 1.5 phr; ZnO, 3 phr; stearic acid, 1 phr activators. MgO and MBTS accelerators can cause irritation to skin and very toxic to aquatic environment. Avoid release to the environment results in irritation to eyes and respiratory system. Previously, Ansarifar and co-workers reported a method for measuring the chemical curatives in sulphur cure systems for rubber, which eliminated stearic acid entirely and reduced the ZnO requirement to less than 1 phr [5,6]. Although it cannot be denied that sulphur vulcanisation is a much more efficient process today than it was at the time of Charles Goodyear, nevertheless serious health and safety issues related to its excessive use in rubber have emerged. Additionally, the chemical curatives are damaging to aquatic life and the environment. Consequently, the use of these chemicals is restricted by the new European chemicals policy, Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) and various legislations for environment, health and safety. It is worth mentioning that the exact amount of the chemical curatives in the sulphur vulcanisation of rubber has never been measured accurately and furthermore, there is no reason why so many and so much of these chemicals need to be used in rubber compounds today.

3.2 Experimental

3.2.1 Materials and mixing

The raw rubbers used were standard Malaysian natural rubber (NR) grade L (98wt%1,4-cis content; SMRL); high cis polybutadiene rubber (96wt% 1,4-cis content; Buna CB24, Bayer, Newbury, UK; not oil extended); ethylene-propylene-diene rubber (EPDM; 48wt% ethylene content, 9wt% ethylidene norbornene content, and 13wt% oil content, Keltan 6251A, Lanxess, The Netherlands). The other ingredients were sulphur (curing agent: Solvay Barium Strontium, Hanover, Germany), N-tert-butyl-2-benzothiazole sulphenamide (a fast-curing delayed action accelerator with a melting point of 105^{o}C) (Santocure TBBS, Sovereign Chemicals, USA), zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK), stearic acid (an activator, Anchor Chemicals Ltd, UK), and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (an antidegradant with a melting point of 45^{o}C, Santoflex 13, Brussels, Belgium). These chemicals are used extensively in tyre compounds.

The raw rubber was mixed with the chemical ingredients in a Haake Rheocord 90 (Berlin, Germany), a small size laboratory mixer with counter-rotating rotors to produce compounds. The Banbury rotors and the mixing chamber were initially set at ambient temperature (23^{o}C) and the rotor speed was set at 45 r.p.m. The volume of the mixing chamber was 78 cm^3, and it was 60% full during mixing. Polylab monitor 4.17 software was used for controlling the mixing condition and storing data. To prepare the compounds, the raw rubber was introduced first in the mixer and then sulphur, TBBS, ZnO and stearic acid were added and mixed for 8 min in total. The temperature of compounds during mixing was 51-56^{o}C.

The viscosity of the compounds was measured at 100^{o}C in a single-speed rotational Mooney viscometer (Wallace Instruments, Surrey, UK) according to British Standard 1673, Part 3, 1969 and the results were expressed as Mooney Units (MU). The cure properties of the compounds were measured at 160 ± 2^{o}C in an oscillating disc rheometer curemeter (ODR, Monsanto, Swindon, UK) at an angular displacement of ± 3^o and a test frequency of 1.7 Hz according to the British Standard ISO 3417.

From the cure traces, scorch time, ts_2, which is the time for the onset of cure, and the optimum cure time, t_{95}, which is the time for the completion of cure were determined. The cure rate index, which is a measure of the rate of cure in the compound, was calculated using the method described in British Standard ISO 3417, 2008. Δtorque was afterwards plotted against the loading of TBBS, ZnO, and stearic acid. ΔTorque is the difference between the maximum and minimum torque values on the cure trace of a compound and is an indication of crosslink density changes in the rubber.

3.3 Methodology

3.3.1 Addition of TBBS and ZnO to the sulphur filled NR, BR and EPDM rubbers

3.3.1.1 Addition of TBBS and ZnO to NR filled with 1, 2, 3 and 4 phr sulphur

For NR with 1 phr sulphur, the loading of TBBS was increased from 0.25 phr to 3.5 phr (Table 3.1).

Table 3.1 Formulation of NR compounds with 1 phr sulphur and an increasing loading of TBBS

Formulation (phr)	**Compound no**							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
SMRL (NR)	100	100	100	100	100	100	100	100
Sulphur	1	1	1	1	1	1	1	1
TBBS	0.25	0.5	1	1.5	2	2.5	3	3.5
	ODR test results at 160°C							
Min torque (dNm)	15	15	15	14	14	14	14	14
Max torque dNm)	20	26	33	37	40	42	44	46
∆Torque (dNm)	5	11	18	23	26	28	30	32
Scorch time t_{s2} (min)	9.5	8.7	9.7	9.7	9.7	11	10.4	10.6
Optimum cure time t_{95} (min)	12.4	12.7	14.8	15.9	16.2	19	18.9	19

The ∆torque values were plotted against the loading of TBBS to determine the optimum amount required to react the sulphur with the rubber (Fig 3.1).

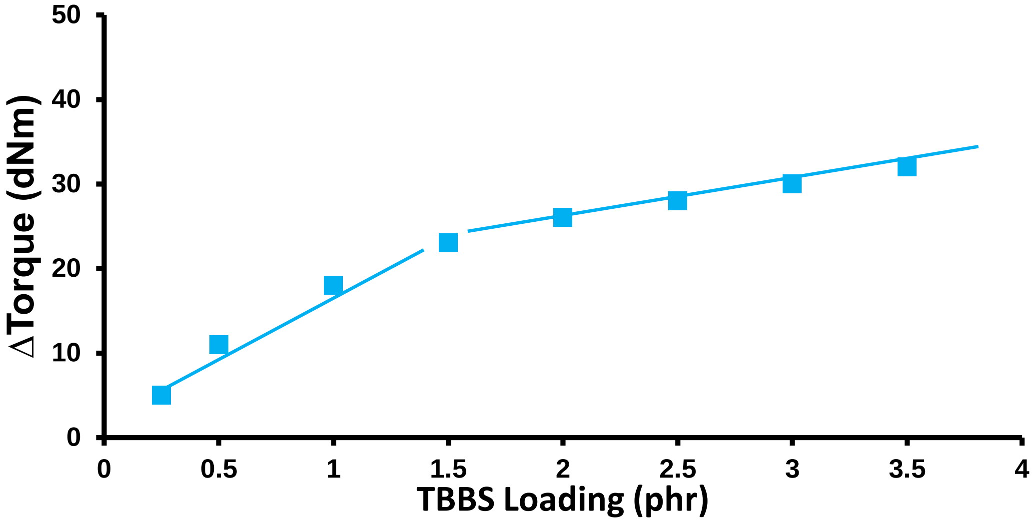


Figure 3.1 ∆Torque versus TBBS loading for the compounds with 1 phr sulphur in NR

Figure 3.1 shows ∆torque as a function of TBBS loading for the rubbers with 1 phr sulphur. ∆torque increased from 5 to 23 dNm as the loading of TBBS was raised to 1.5 phr and it continued rising at a much slower rate to about 32 dNm when the loading of TBBS reached 3.5 phr. The addition of 1.5 phr TBBS was sufficient to react the sulphur with the rubber to from crosslinks. Further increases in the TBBS loading to 3.5 phr had a lesser effect on the ∆torque value, which increased only marginally. Therefore 1.5 phr TBBS was sufficient to fully react the sulphur with the rubber to produce sulphur covalent bonds between the two. There are two types of behaviour in figure 3.1 first ∆torque increases as a function of TBBS loading at a steep rate when up to 1.5 phr of TBBS. Thereafter the increase in ∆torque is less steep. The exact reason for these types of behaviour is not known at this stage. However it may be speculated that above the optimum TBBS loading they may be less TBBS available to react the sulphur with the rubber hence giving lower cross link density as shown by smaller increase in ∆torque.

The cure trace of the rubber with the optimum loading of TBBS (1.5 phr) was examined for proof of full cure (Fig 3.2).

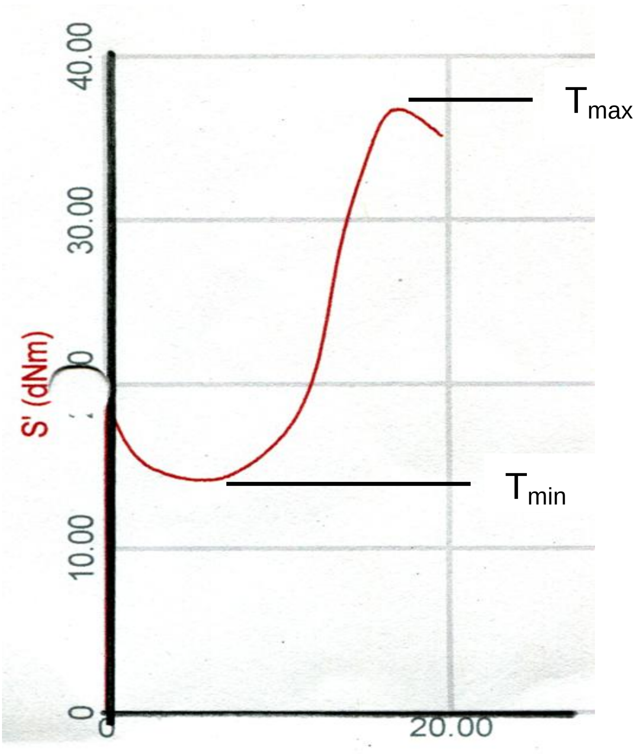


Figure 3.2 cure trace (torque vs time) of the compound with 1 phr sulphur and 1.5 phr TBBS

For NR with 1 phr sulphur, 1.5 phr TBBS, the loading of ZnO was increased from 0.05 phr to 0.5 phr (Table 3.2)

Table 3.2 Formulation of NR compounds with 1 phr sulphur, 1.5 phr TBBS and an increasing loading of ZnO

Formulation (phr)	**Compound no**						
	9	**10**	**11**	**12**	**13**	**14**	**15**
SMRL (NR)	100	100	100	100	100	100	100
Sulphur	1	1	1	1	1	1	1
TBBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	0.05	0.1	0.15	0.2	0.3	0.4	0.5
ODR test results at 160^{o}C							
Min torque (dNm)	15	16	16	16	16	15	15
Max torque dNm)	36	40	41	42	45	46	48
ΔTorque (dNm)	21	24	25	26	29	31	33
Scorch time t_{s2} (min)	9.5	9.4	8.1	8.4	8.1	7.7	7.7
Optimum cure time t_{95} (min)	16.3	15.6	13.4	15.5	14.6	14.3	13.7

Figure 3.3 shows Δtorque as function of ZnO loading for the rubber with 1 .5 phr TBBS and 1 phr sulphur. Δtorque increased from 21 to 26 when the loading of ZnO raised to 0.2 phr and it continued rising at a much slower rate at about 33 dNm when the loading of ZnO reached 0.5 phr. The addition of 0.2 phr ZnO was adequate to improve the efficiency of TBBS as indicated by large increase in Δtorque value.

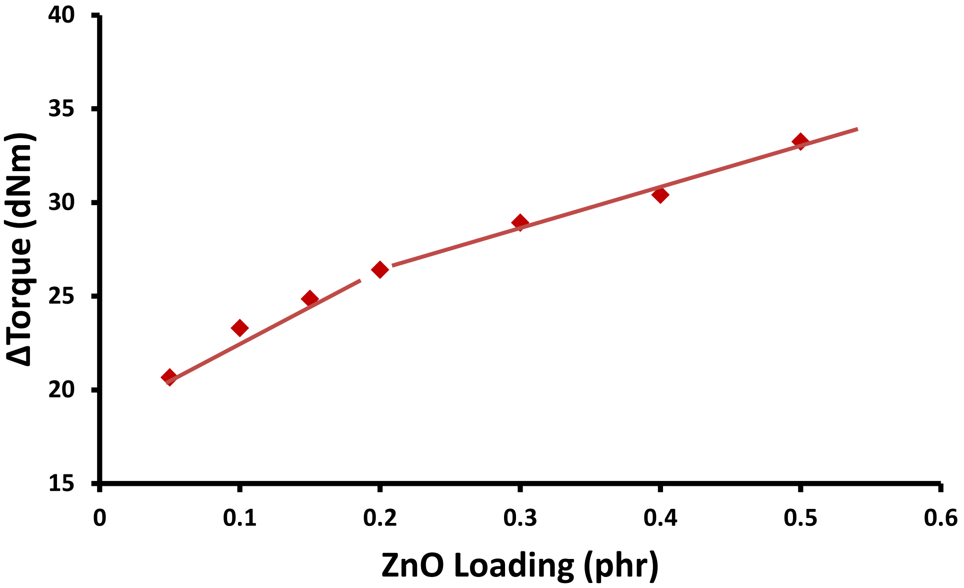


Figure 3.3 ΔTorque versus ZnO loading for the compounds with 1.5 phr TBBS, 1 phr sulphur in NR

The cure trace of the rubber with the optimum loading of TBBS (1.5 phr) and ZnO (0.2 phr) was examined for proof of full cure (Fig 3.4).

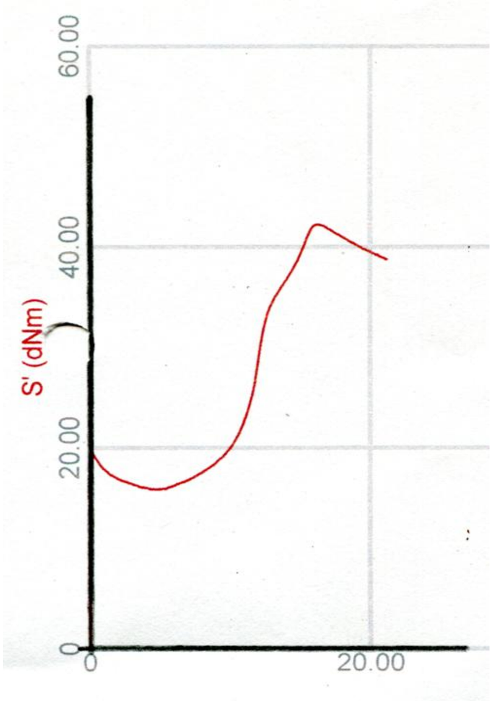


Figure 3.4 cure trace (Torque vs time) of the compound with 1 phr sulphur, 1.5 phr TBBS and 0.2 phr ZnO

For NR with 1 phr sulphur, 1.5 phr TBBS, and 0.2 phr ZnO, the loading of stearic acid was increased progressively from 0 phr to 2.5 phr (Table 3.3)

Table 3.3 Formulation of NR compounds with 1 phr sulphur, 1.5 phr TBBS, 0.2 phr ZnO and an increasing loading of stearic acid

Formulation (phr)	**Compound no**							
	16	**17**	**18**	**19**	**20**	**21**	**22**	**23**
SMRL (NR)	100	100	100	100	100	100	100	100
Sulphur	1	1	1	1	1	1	1	1
TBBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Stearic acid	0	0.5	0.75	1	1.4	1.8	2.1	2.5
	ODR test results at 160°C							
Min torque (dNm)	16	14	14	14	13	13	13	12
Max torque dNm)	42	41	41	41	40	40	40	39
ΔTorque (dNm)	26	27	27	27	27	27	27	27
Scorch time t_{s2} (min)	8.4	8.2	8.6	8.0	7.8	8	8.2	7.5
Optimum cure time t_{95} (min)	15.5	13.7	14	13.9	12.7	12.6	12.7	11.9

Figure 3.5 shows ∆torque versus stearic acid loading. The inclusion of stearic acid in the cure system for NR has no benefit for the ∆torque at all, which stayed constant at about 27 dNm. It is abundantly clear from the results that ZnO is a very effective primary activator in improving the performance of TBBS in the absence of stearic acid (a secondary activator).

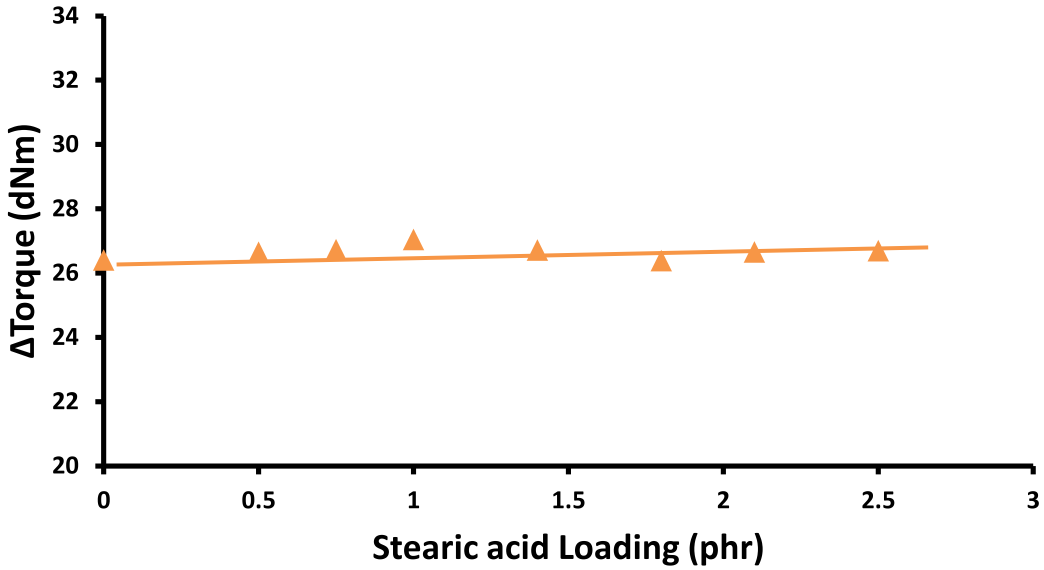


Figure 3.5 ∆Torque versus stearic acid loading for the compounds with 1.5 phr TBBS, 1 phr sulphur, 0.2 phr ZnO in NR

For NR with 2 phr sulphur the loading of TBBS was increased from 0.5 phr to 3.5 phr (Table 3.4).

Table 3.4 Formulation of NR compounds with 2 phr sulphur and an increasing loading of TBBS

Formulation (phr)	**Compound no**						
	24	**25**	**26**	**27**	**28**	**29**	**30**
SMRL (NR)	100	100	100	100	100	100	100
Sulphur	2	2	2	2	2	2	2
TBBS	0.5	1	1.5	2	2.5	3	3.5
	ODR test results at 160^{o}C						
Min torque (dNm)	18	15	15	15	14	14	14
Max torque dNm)	31	36	40	44	46	49	50
∆Torque (dNm)	13	21	25	29	32	35	36
Scorch time t_{s2} (min)	8.3	8.1	8.3	8.5	8.5	8.9	8.9
Optimum cure time t_{95} (min)	23.3	12.6	13.6	14	14.7	15.3	15.7

The ∆torque values were plotted against the loading of TBBS to determine the optimum amount required to react the sulphur with the rubber (Fig 3.6).

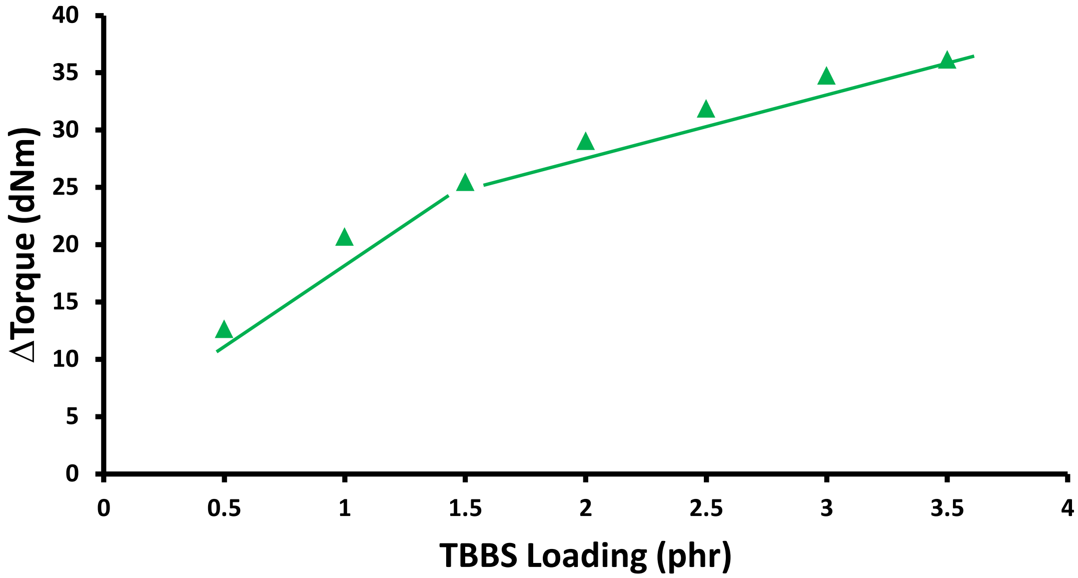


Figure 3.6 ∆Torque versus TBBS loading for the NR compounds with 2 phr sulphur

∆torque increased from 13 to 25 dNm as the loading of TBBS was raised to 1.5 phr and it continued rising at a much slower rate to about 36 dNm when the loading of TBBS reached 3.5 phr. The addition of 1.5 phr TBBS was sufficient to react the sulphur with the rubber to from crosslinks. Further increases in the TBBS loading to 3.5 phr had a lesser effect on the ∆torque value, which increased only marginally. The cure trace of the rubber with the optimum loading of TBBS (1.5 phr) was examined for proof of full cure (Fig 3.7).

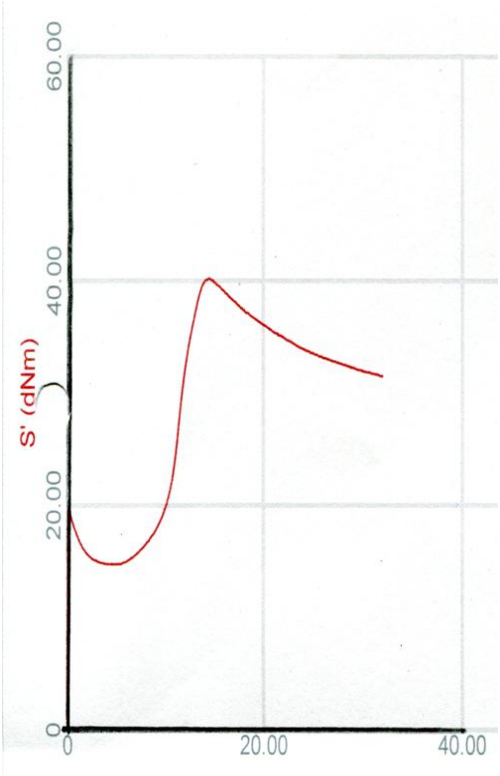


Figure 3.7 cure trace (torque vs time) of the compound with 2 phr sulphur and 1.5 phr TBBS

For NR with 2 phr sulphur and 1.5 phr TBBS, the loading of ZnO was increased progressively from 0.05 phr to 0.5 phr (Table 3.5).

Table 3.5 Formulation of NR compounds with 2 phr sulphur, 1.5 phr TBBS and an increasing loading of ZnO

Formulation (phr)	**Compound no**						
	31	**32**	**33**	**34**	**35**	**36**	**37**
SMRL (NR)	100	100	100	100	100	100	100
Sulphur	2	2	2	2	2	2	2
TBBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	0.05	0.1	0.15	0.2	0.3	0.4	0.5
	ODR test results at 160^{o}C						
Min torque (dNm)	16	17	17	17	17	17	16
Max torque dNm)	41	45	46	48	52	53	55
ΔTorque (dNm)	25	28	29	31	35	36	39
Scorch time t_{s2} (min)	7.7	7.7	7.1	6.9	6.5	6.2	6
Optimum cure time t_{95} (min)	14	13.1	11.9	11.4	10.7	10.3	10

Figure 3.8 shows ∆torque as function of ZnO loading for the rubber with 1.5 phr TBBS and 2 phr sulphur. ∆torque increased from 25 to 31 when the loading of ZnO raised to 0.2 phr and it continued rising at a much slower rate at about 39 dNm when the loading of ZnO reached 0.5 phr. The addition of 0.3 phr ZnO was sufficient to improve the efficiency of TBBS as indicated by large increase in ∆torque value.

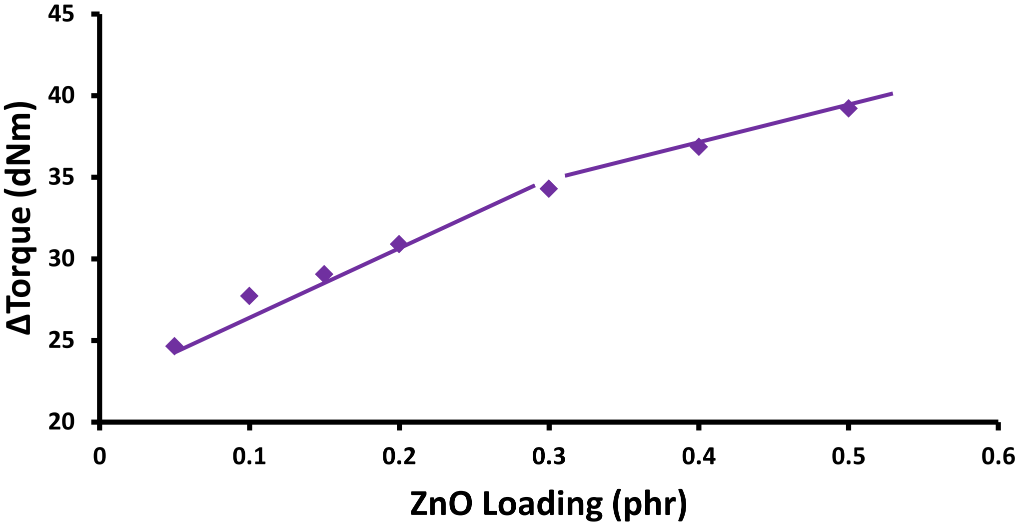


Figure 3.8 ∆Torque versus ZnO loading for the compounds with 1.5 phr TBBS, 2 phr sulphur in NR

The cure trace of the rubber with the optimum loading of TBBS (1.5 phr) and ZnO (0.3 phr) was examined for evidence of full cure (Fig 3.9).

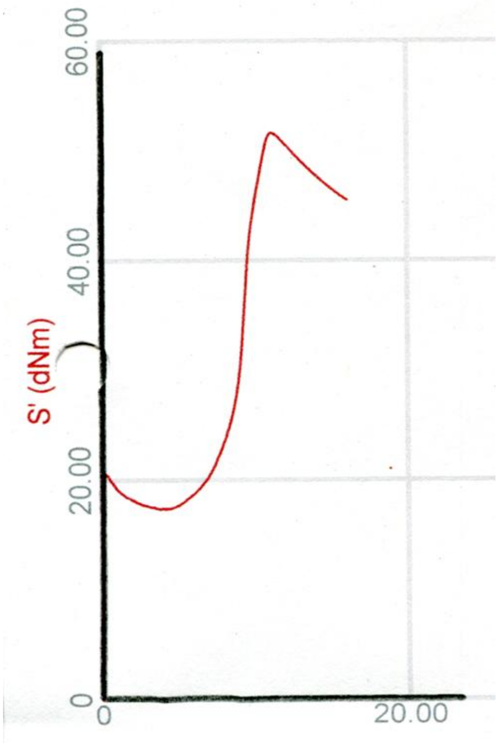


Figure 3.9 cure trace (torque vs time) of the compounds with 2 phr sulphur, 1.5 phr TBBS and 0.3 phr

For NR with 3 phr sulphur the loading of TBBS was increased from 0.5 phr to 3.0 phr (Table 3.6).

Table 3.6 Formulation of NR compounds with 3 phr sulphur and an increasing loading of TBBS

Formulation (phr)	**Compound no**							
	38	**39**	**40**	**41**	**42**	**43**	**44**	**45**
SMRL (NR)	100	100	100	100	100	100	100	100
Sulphur	3	3	3	3	3	3	3	3
TBBS	0.5	0.75	1	1.25	1.5	2	2.5	3
ODR test results at 160^{o}C								
Min torque (dNm)	16	16	15	16	15	15	15	14
Max torque dNm)	34	36	38	40	42	46	48	50
ΔTorque (dNm)	18	20	23	24	27	31	33	36
Scorch time t_{s2} (min)	6.4	6.9	7	7.3	7.2	7.3	7.4	7.8
Optimum cure time t_{95} (min)	25.2	15.6	11.2	12	12.3	13.1	13.4	14.2

Figure 3.10 shows Δtorque as a function of TBBS loading for the rubbers with 3 phr sulphur. Δtorque increased from 18 to 27 dNm as the loading of TBBS was raised to 1.5 phr and it continued rising at a much slower rate to about 36 dNm when the

loading of TBBS reached 3 phr. The addition of 1.5 phr TBBS was sufficient to react the sulphur with the rubber to from crosslinks. Further increases in the TBBS loading to 3 phr had a lesser effect on the ∆torque value, which increased only marginally.

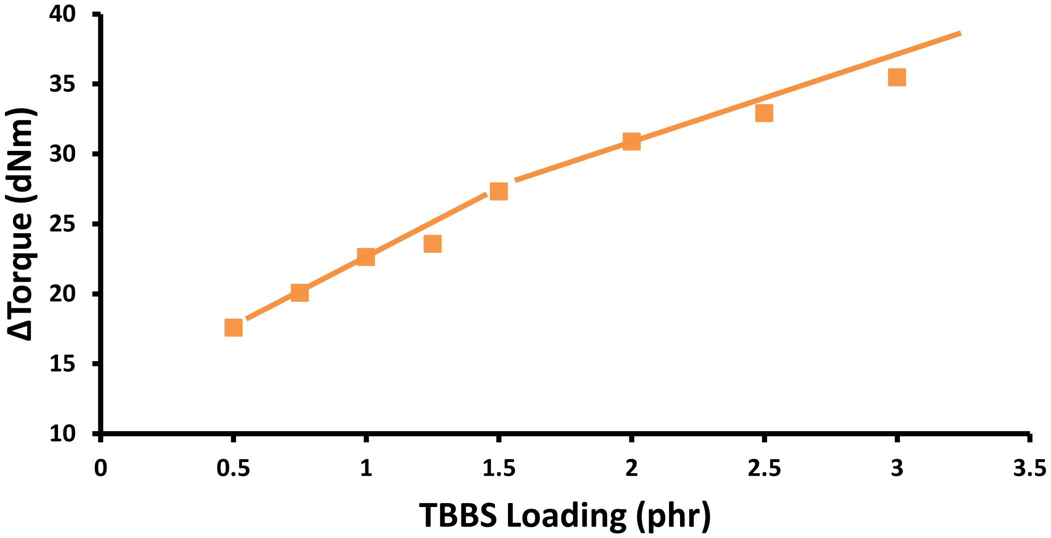


Figure 3.10 ∆Torque versus TBBS loading for the compounds with 3 phr sulphur in NR

The cure trace of the rubber with the optimum loading of TBBS (1.5 phr) was examined for proof of full cure (Fig 3.11).

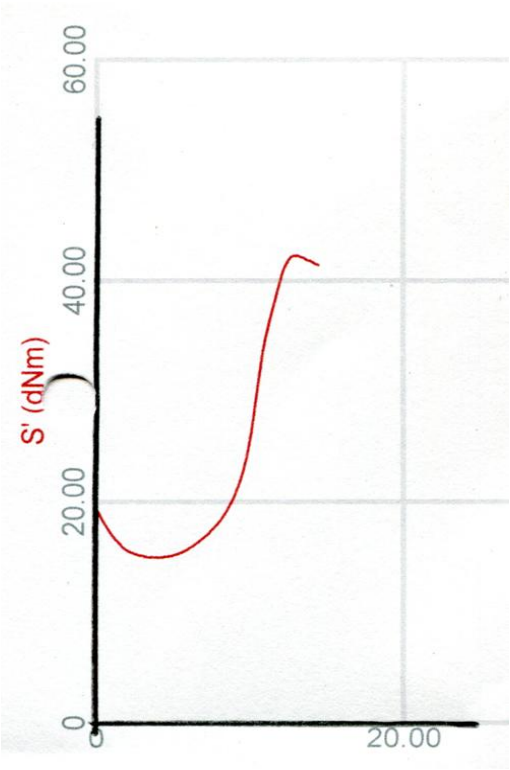


Figure 3.11 Cure trace (torque vs time) of the compounds with 3 phr sulphur and 1.5 phr TBBS

For NR with 3 phr sulphur and 1.5 phr TBBS, the loading of ZnO was increased from 0.05 phr to 0.4 phr (Table 3.7)

Table 3.7 Formulation of NR compounds with 3 phr sulphur, 1.5 phr TBBS and an increasing loading of ZnO

Formulation (phr)	**Compound no**								
	46	**47**	**48**	**49**	**50**	**51**	**52**	**53**	**54**
SMRL (NR)	100	100	100	100	100	100	100	100	100
Sulphur	3	3	3	3	3	3	3	3	3
TBBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	0.05	0.075	0.1	0.125	0.15	0.2	0.25	0.35	0.4
	ODR test results at 160°C								
Min torque (dNm)	16	17	17	16	16	17	16	17	16
Max torque dNm)	43	45	46	47	48	50	54	56	55
∆Torque (dNm)	27	28	29	31	32	33	38	39	39
Scorch time t_{s2} (min)	7.1	6.6	6.4	6.1	6	6	5.5	5.6	5.2
Optimum cure time t_{95} (min)	13.2	11.8	11	10.3	9.6	9.7	9.8	9.7	8.7

Figure 3.12 shows ∆torque as function of ZnO loading for the rubber with 1.5 phr TBBS and 3 phr sulphur. ∆torque increased from 27 to 38 when the loading of ZnO rose to 0.25 phr and it continued rising at a much slower rate at about 39 dNm when the loading of ZnO reached 0.4 phr. The addition of 0.25 phr ZnO was adequate to improve the efficiency of TBBS as indicated by large increase in ∆torque value.

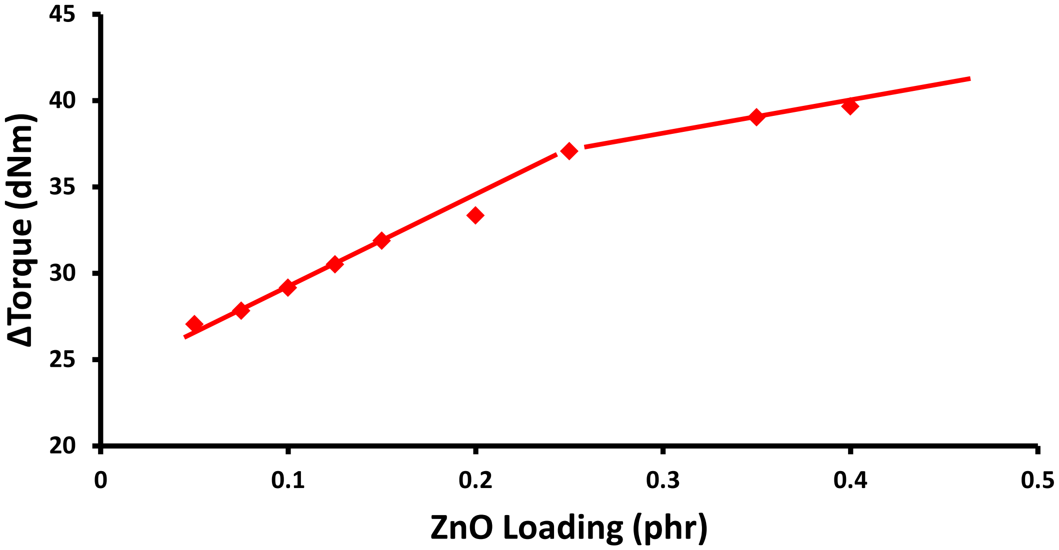


Figure 3.12 ΔTorque versus ZnO loading for the compounds with 1.5 phr TBBS, 3 phr sulphur in NR

The cure trace of the rubber with the optimum loading of TBBS (1.5 phr) and ZnO (0.25 phr) was examined for evidence of full cure (Fig 3.13).

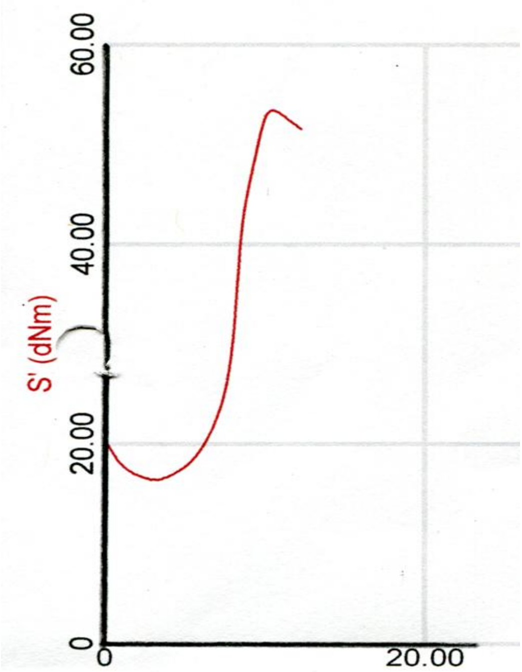


Figure 3.13 cure trace (torque vs time) of the compound with 3 phr sulphur, 1.5 phr TBBS and 0.25 phr ZnO

For NR with 4 phr sulphur the loading of TBBS was increased from 0.5 phr to 3.0 phr (Table 3.8)

Table 3.8 Formulation of NR compounds with 4 phr sulphur and an increasing loading of TBBS

Formulation (phr)	**Compound no**											
	55	**56**	**57**	**58**	**59**	**60**	**61**	**62**	**63**	**64**	**65**	**66**
SMRL (NR)	100	100	100	100	100	100	100	100	100	100	100	100
Sulphur	4	4	4	4	4	4	4	4	4	4	4	4
TBBS	0.5	0.75	1	1.25	1.5	2	2.5	3	3.5	3.8	4.2	4.5
ODR test results at 160°C												
Min torque (dNm)	17	16	16	16	16	15	15	15	14	14	14	13
Max torque dNm)	40	41	41	42	44	48	51	53	55	56	55	57
ΔTorque (dNm)	23	25	25	26	28	33	36	37	41	42	41	44
Scorch time t_{s2} (min)	5.8	6.2	6.4	6.6	6.7	6.7	6.9	7.3	7.2	7.4	7.9	7.7
Optimum cure time t_{95} (min)	28	21	15.5	10.9	11.1	11.6	12.2	13.2	13.3	13.6	15.7	14.8

Figure 3.14 shows Δtorque as a function of TBBS loading for the rubbers with 4 phr sulphur. Δtorque increased from 23 to 41 dNm as the loading of TBBS was raised to 3.5 phr and it continued rising at a much slower rate to about 44 dNm when the loading of TBBS reached 4.5 phr. The addition of 3.5 phr TBBS was sufficient to react the sulphur with the rubber to from crosslinks. Further increases in the TBBS loading to 4.5 phr had a lesser effect on the Δtorque value, which increased only marginally.

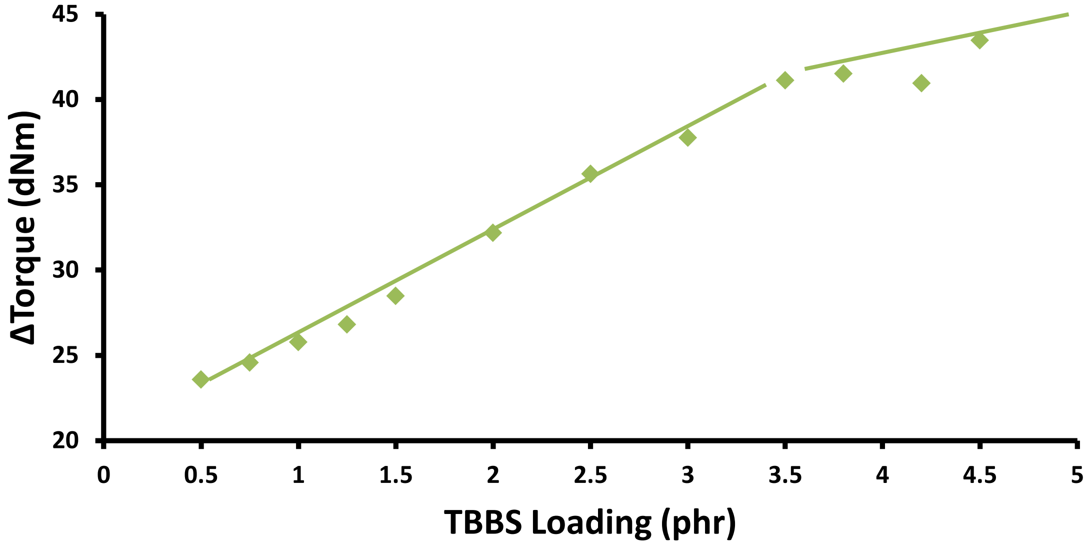


Figure 3.14 ΔTorque versus TBBS loading for the compounds with 4 phr sulphur in NR

The cure trace of the rubber with the optimum loading of TBBS (1.5 phr) and ZnO (0.2 phr) was examined for proof of full cure (Fig 3.15).

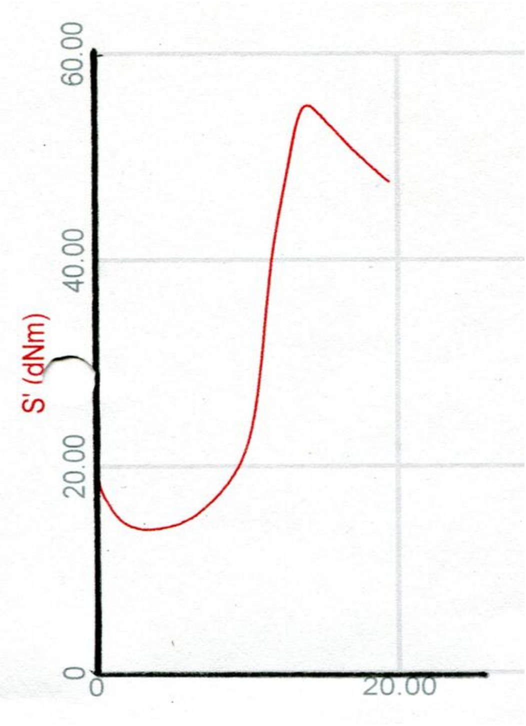


Figure 3.15 cure trace (torque vs time) of the compound with 4 phr sulphur and 3.5 phr TBBS

For NR with 4 phr sulphur and 3.5 phr TBBS, the loading of ZnO was increased from 0.05 phr to 0.4 phr (Table 3.9)

Table 3.9 Formulation of NR compounds with 4 phr sulphur, 3.5 phr TBBS and an increasing loading of ZnO

Formulation (phr)	**Compound no**								
	67	**68**	**69**	**70**	**71**	**72**	**73**	**74**	**75**
SMRL (NR)	100	100	100	100	100	100	100	100	100
Sulphur	4	4	4	4	4	4	4	4	4
TBBS	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
ZnO	0.05	0.075	0.1	0.125	0.15	0.2	0.25	0.3	0.4
ODR test results at 160^{o}C									
Min torque (dNm)	16	16	16	16	16	16	16	16	15
Max torque dNm)	54	57	57	58	61	61	63	63	64
ΔTorque (dNm)	38	41	41	42	45	45	47	47	49
Scorch time t_{s2} (min)	6.4	6.5	6.2	6	6.3	5.2	5.5	5.1	5.1
Optimum cure time t_{95} (min)	14.2	13	12.5	12.3	11.9	10.5	10.4	10.2	10.2

Figure 3.16 shows Δtorque as function of ZnO loading for the rubber with 3.5 phr TBBS and 4 phr sulphur. Δtorque increased from 38 to 45 when the loading of ZnO raised to 0.2 phr and it continued rising at a much slower rate at about 49 dNm when the loading of ZnO reached 0.4 phr. The addition of 0.2 phr ZnO was adequate to improve the efficiency of TBBS as indicated by large increase in Δtorque value.

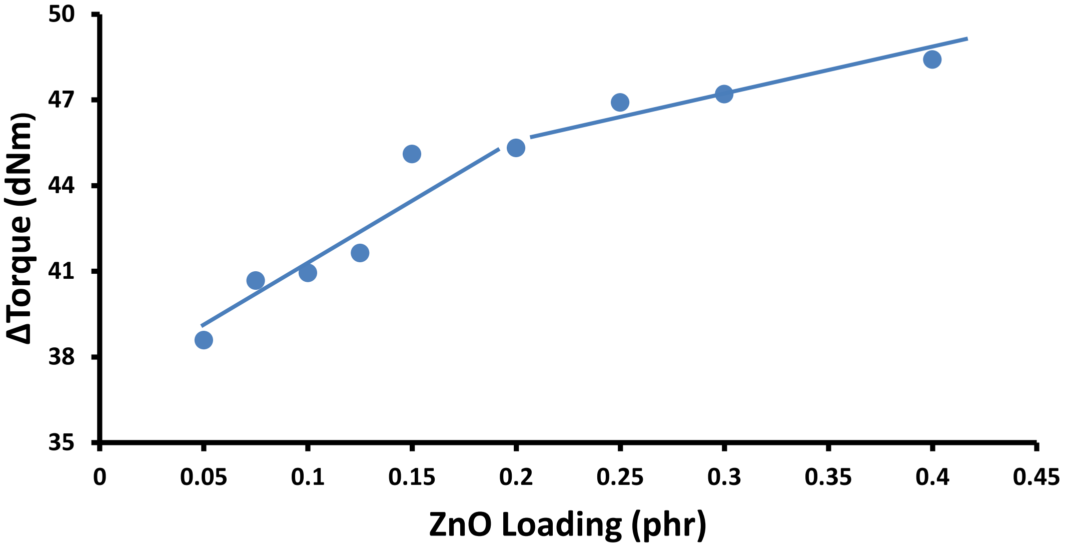


Figure 3.16 ΔTorque versus ZnO loading for the compounds with 3.5 phr TBBS, 4 phr sulphur in NR

The cure trace of the rubber with the optimum loading of TBBS (1.5 phr) and ZnO (0.2 phr) was examined for proof of full cure (Fig 3.17).

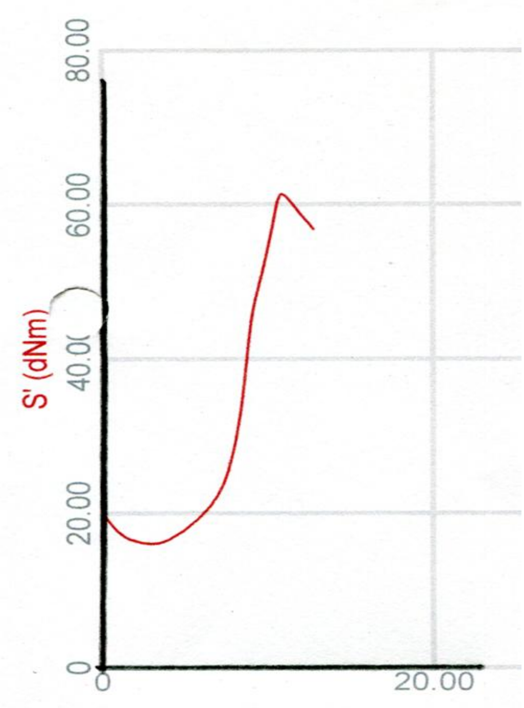


Figure 3.17 cure trace (torque vs time) of the compound with 4 phr sulphur, 3.5 phr TBBS and 0.2 phr ZnO

Figure 3.18 summarises the optimum loading of TBBS for the sulphur-filled NR rubbers. It is interesting that the rubbers with 1, 2, and 3 phr sulphur required 1.5 phr TBBS and the one with 4 phr sulphur, 3.5 phr TBBS for full cure.

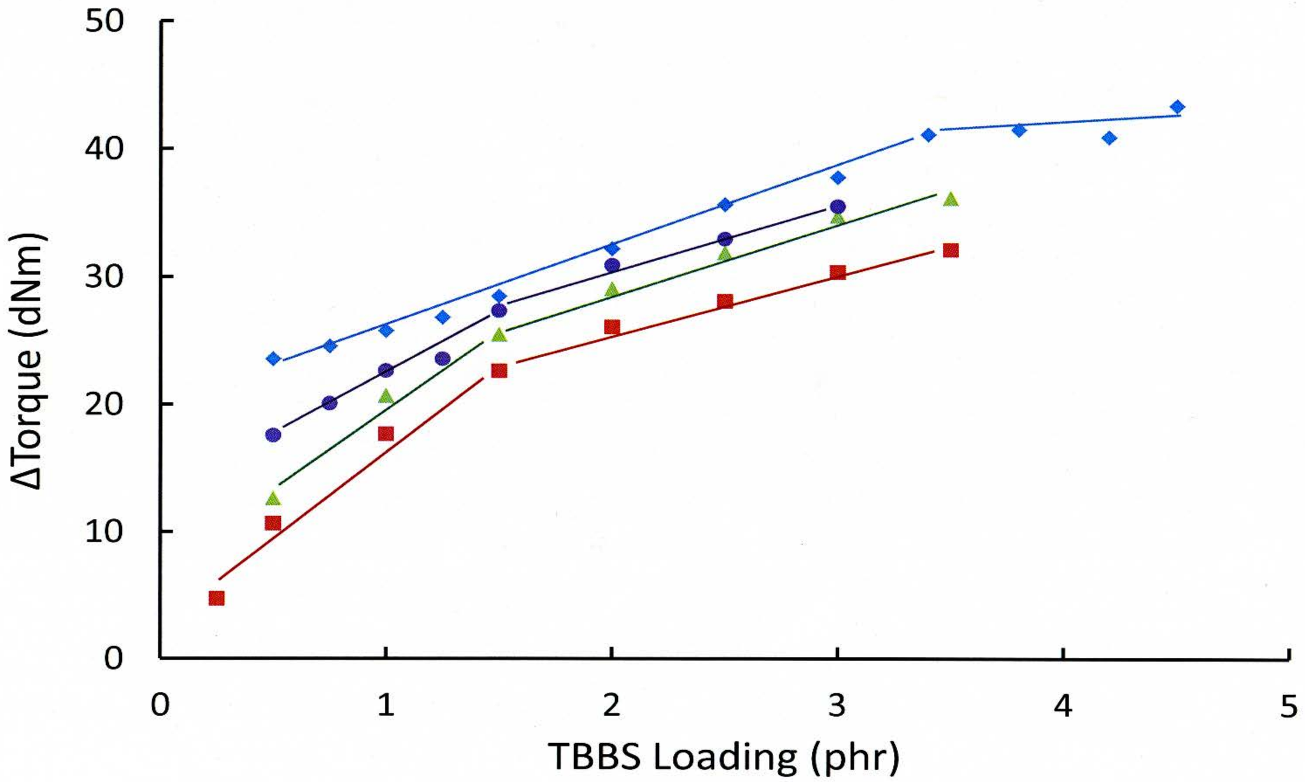


Figure 3.18 ΔTorque versus TBBS loading for the compounds with different amounts of sulphur. (■) compound with 1 phr sulphur, (▲) compound with 2 phr sulphur, (●) compound with 3 phr sulphur, (◆) compound with 4 phr sulphur. Each point on the graph corresponds to one compound

Figure 3.19 summarises the optimum loading of ZnO for the sulphur-filled NR rubbers with the optimum loading of TBBS. It is interesting that the sulphur-filled rubbers with 1.5 phr TBBS needed 0.2-0.3 phr ZnO whereas the sulphur-filled rubber with 3.5 TBBS required a similar amount of ZnO, i.e. 0.2 phr.

There are two types of behaviour in each curve of figure 3.18 first Δtorque increases as a function of TBBS loading at a steep rate when up to optimum loading of TBBS. Thereafter the increase in Δtorque is less steep. The exact reason for these types of behaviour is not known at this stage. However it may be speculated that above the optimum TBBS loading they may be less TBBS available to react the sulphur with the rubber hence giving lower cross link density as shown by smaller increase in Δtorque.

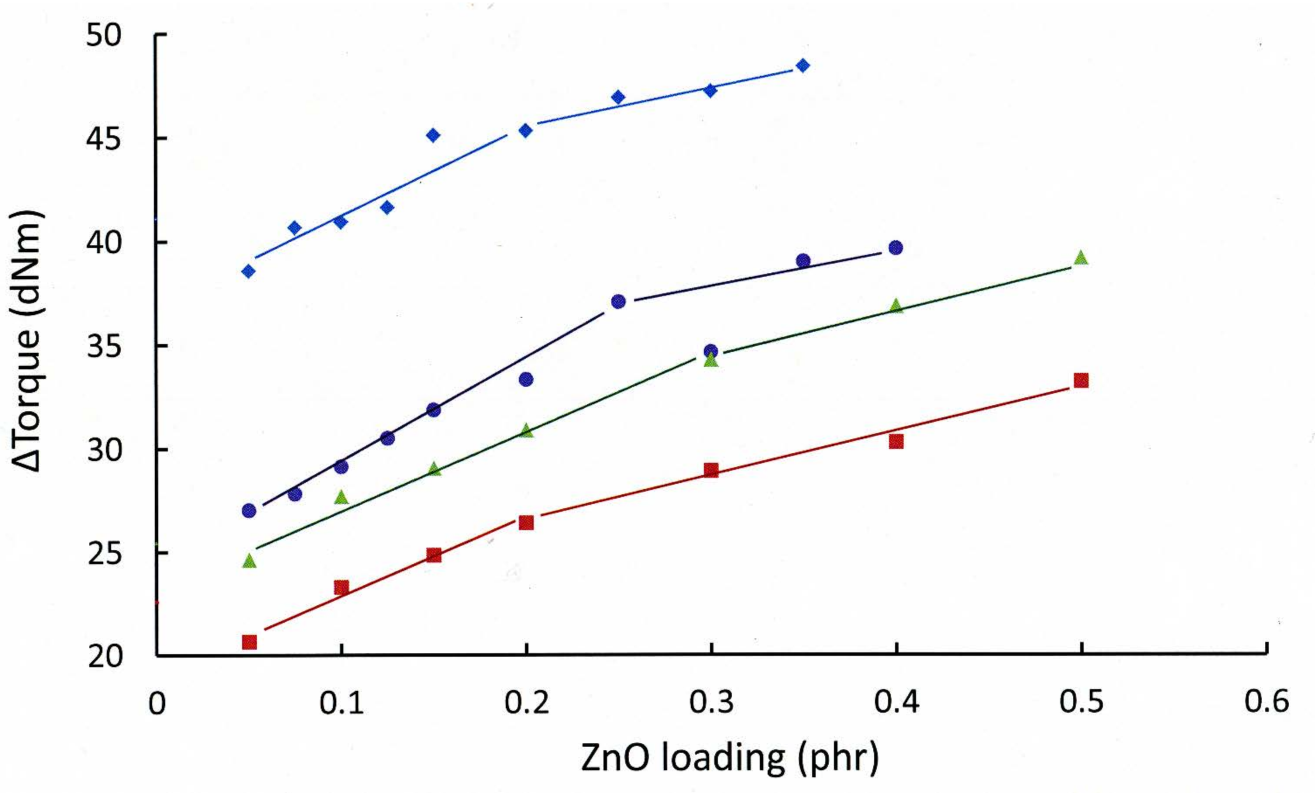


Figure 3.19 ΔTorque versus ZnO loading for the compounds with different amounts of sulphur and TBBS. (■) compound with 1 phr sulphur and 1.5 phr TBBS, (▲) compound with 2 phr sulphur and 1.5 phr TBBS, (●) compound with 3 phr sulphur and 1.5 phr TBBS, (♦) compound with 4 phr sulphur and 3.5 phr TBBS. Each point on the graph corresponds to one compound

3.3.1.2 Measurement of crosslink density of some NR rubber vulcanisates

The crosslink density (CLD) of some NR rubbers containing 1 and 4 phr sulphur and 1.5 phr TBBS and increasing loading of ZnO was determined by swelling technique in an organic solvent. The CLD was then calculated, using the Flory-Rehner equation [11,12]. The aim was to determine correlation between the crosslink density of the rubbers and Δtorque values.

3.3.1.2.1 Method

The solvent used for the crosslink density (CLD) determinations was toluene. For the determination. 1.2 g of rubber was placed in 300 ml of the solvent in labelled bottles and allowed to swell for 50 days at 21^oC. the sample weight was measured every day until it reached equilibrium and the solvent was then removed. The samples were dried in air for 9 h and then in an oven at 80^oC for 24 h, and allowed to stand for an extra 24 h at 23^oC before reweighing. The CLD was calculated using the following equation;

$$-[\ln(1-v_r)+\ v_r+\ x_1 v_r^2]=V_1 n\ \left(v_r^{1/3}-\frac{v_r}{2}\right) \qquad (1)$$

where, v_r is the volume fraction of polymer in the swollen mass, V_1 is the molar volume of the solvent, n is the number of network chain segments bounded on both ends by crosslinks and x_1 is the Flory solvent-polymer interaction term $(x_1 = 0.393)$ [9,10].

The volume fraction of a rubber network in the swollen phase is calculated from equilibrium swelling data as:

$$v_r = \frac{1}{1+Q} \qquad (2)$$

where, Q is equal

$$Q = \frac{(w_1 \times D_p)}{(w_2 \times D_o)} \qquad (3)$$

where, w_1 is the weight of the swelling gel, D_p is the density of the polymer NR was taken as 0.92 g/cm^3, w_2 is the initial weight of polymer, D_o is the density of the solvent 0.867 g/cm^3 for toluene.

3.3.1.2.2 Materials

The rubber formulations selected and the CLD of the rubber vulcanisates are summarised in (Table 3.10). Note that these compounds are the same ones shown in Table 3.1 (compound 8), Table 3.2 (compounds 9, 11, 12, 14), Table 3.8 (compound 66), and Table 3.9 (compounds 69, 70, 72, 73).

Table 3.10 Formulation and crosslink density measurement of selected NR compounds with 1 phr and 4 phr sulphur, TBBS and ZnO loading

Formulation (phr)	**Compound no**									
	8	**9**	**11**	**12**	**14**	**66**	**69**	**70**	**72**	**73**
NR	100	100	100	100	100	100	100	100	100	100
Sulphur	1	1	1	1	1	4	4	4	4	4
TBBS	1.5	1.5	1.5	1.5	1.5	3.5	3.5	3.5	3.5	3.5
ZnO	0.05	0.1	0.2	0.3	0.5	0.05	0.125	0.15	0.2	0.3
ODR test results at 160°C										
Min torque (dNm)	15	16	16	16	15	16	16	16	16	16
Max torque dNm)	36	40	42	45	48	54	58	61	63	63
ΔTorque (dNm)	21	24	26	29	33	38	42	45	47	47
Scorch time t_{s2} (min)	9.5	9.4	8.4	8.1	7.7	6.4	6	6.3	5.5	5.1
Optimum cure time t_{95} (min)	16.3	15.6	15.5	14.6	13.7	14.2	12.3	11.9	10.4	10.2
Crosslink density mol/cm^3	1.94×10^{-5}	1.65×10^{-5}	3.14×10^{-5}	4.28×10^{-5}	6.15×10^{-5}	1.69×10^{-5}	1.62×10^{-5}	1.47×10^{-5}	3.67×10^{-5}	3.28×10^{-5}

3.3.1.2.3 Results and discussion

Figure 3.20 shows crosslink density versus ∆torque for the NR compounds with 1 phr sulphur, 1.5 phr TBBS and increasing loading of ZnO (compounds 8, 9, 11, 12, 14; Table 3.10). As expected, the crosslink density increased when ∆torque increased. Also as shown in Figure 3.21, for the NR with 4 phr sulphur, 3.5 phr TBBS and an increasing loading of ZnO a similar trend emerged (compounds 66, 69, 70, 72 and 73; Table 3.10).

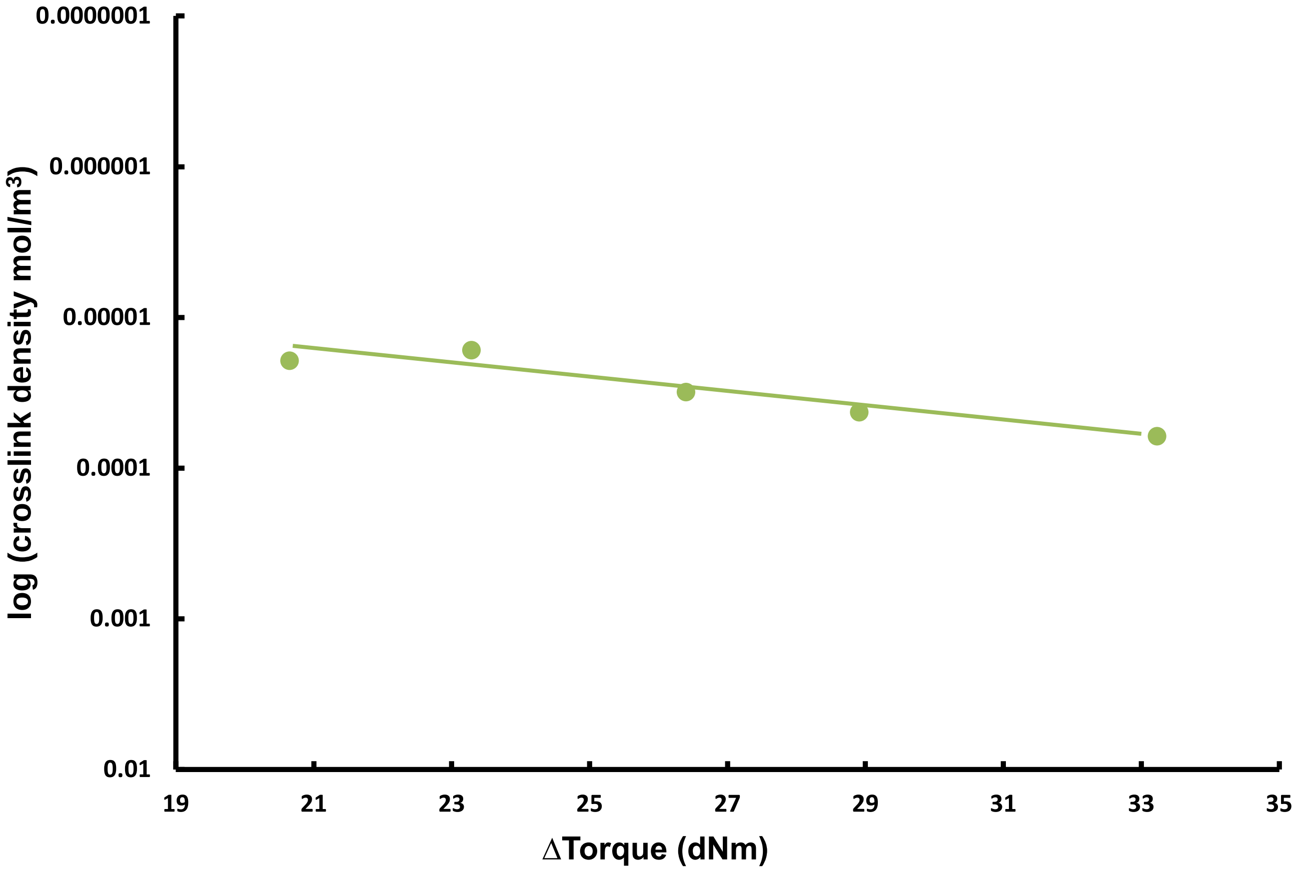


Figure 3.20 Crosslink density vs Torque for compounds 8, 9, 11, 12 and 14 in Table 3.10

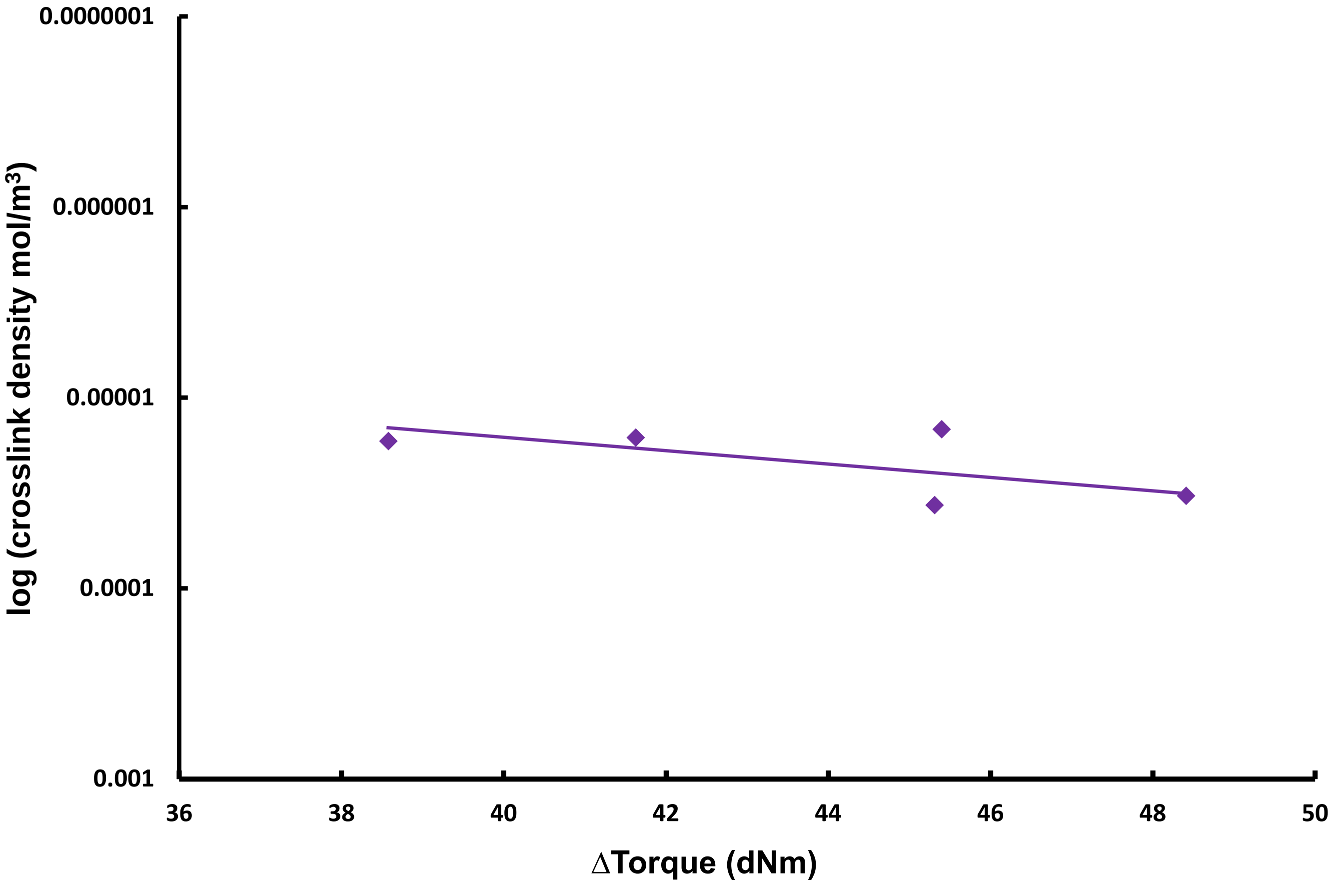


Figure 3.21 Crosslink density measurements for the samples 66, 69, 70, 72 and 73 in Table 3.10

As the figure 3.20 shows, at the lowest crosslink density, i.e. 0.00001939 mol/m^3, the torque is calculated to be 20.65 dNm. Furthermore, at the highest crosslink density, i.e. 0.0000615 mol/m^3, the torque is about 33.23 dNm. This expected since higher crosslink density always correlates with higher torque values. This was expected.

Clearly, there is a direct correlation between crosslink density and Δtorque. This correlation helps to avoid measuring the crosslink density changes by the swelling method, which uses a volatile organic solvent, and resorts to a much safer method on the ODR machine.

3.3.2 Addition of TBBS and ZnO to BR filled with 0.5 and 1 phr sulphur

For BR with 0.5 phr sulphur, the loading of TBBS was increased from 0.5 phr to 3.0 phr to react the sulphur with the rubber chains (Table 3.11)

Table 3.11 Formulation of BR compounds with 0.5 phr sulphur and an increasing loading of TBBS

Formulation (phr)	**Compound no**							
	76	**77**	**78**	**79**	**80**	**81**	**82**	**83**
Buna CB 24 (BR)	100	100	100	100	100	100	100	100
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TBBS	0.5	1	1.25	1.5	1.75	2	2.5	3
	ODR test results at 160°C							
Min torque (dNm)	14	13	14	14	14	13	14	13
Max torque dNm)	39	47	52	56	58	59	58	58
∆Torque (dNm)	25	34	38	42	45	46	44	45
Scorch time t_{s2} (min)	19.2	13.8	13.8	12.8	14.4	11.1	12.7	13
Optimum cure time t_{95} (min)	90.9	78.1	81	76.6	77.7	66.8	73.8	85.4

Figure 3.22 shows ∆torque as a function of TBBS loading for the BR rubbers with 0.5 phr sulphur. ∆torque increased from 25 to 45 dNm as the loading of TBBS was raised to 1.75 phr, and then it stopped rising once the loading of TBBS reached 3 phr. The addition of 1.75 phr TBBS was sufficient to react the sulphur with the rubber to form crosslinks.

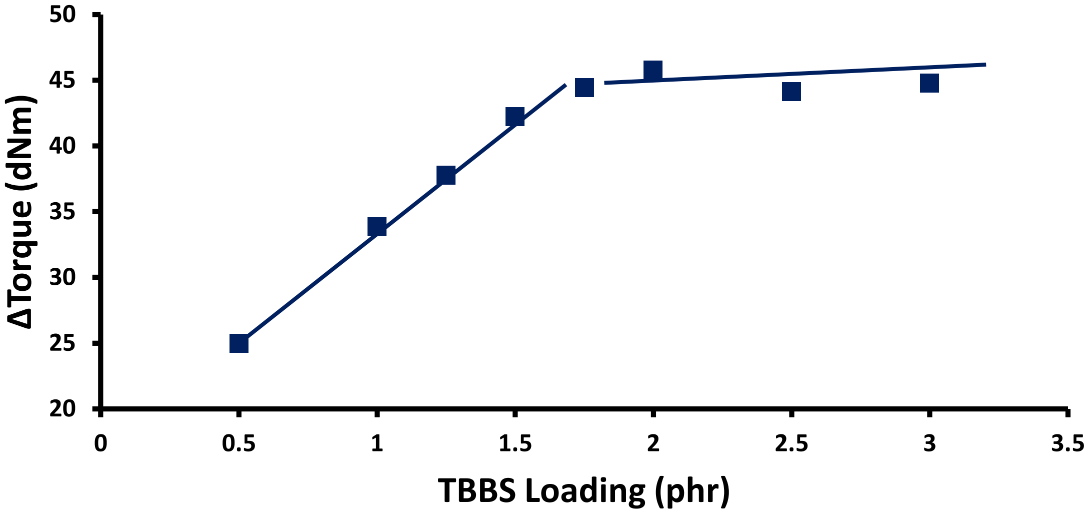


Figure 3.22 ∆Torque versus TBBS loading for the compounds with 0.5 phr sulphur in BR

The cure trace of the rubber with the optimum loading of TBBS (1.75 phr) was examined for proof of full cure (Fig 3.23).

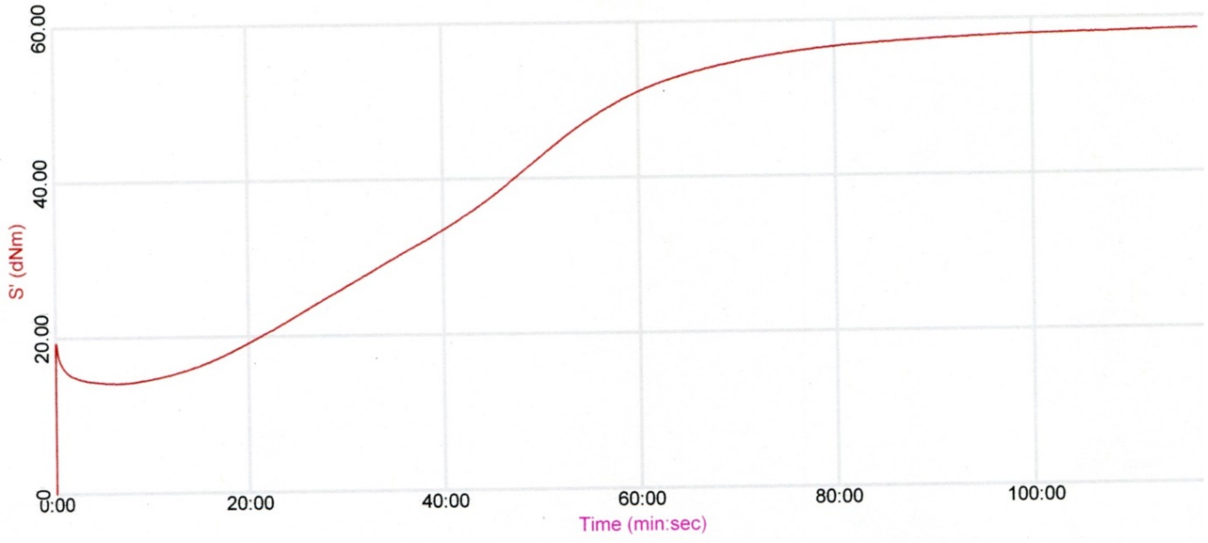


Figure 3.23 cure trace (torque vs time) of the BR compound with 0.5 phr sulphur and 1.75 phr TBBS

For BR with 0.5 phr sulphur and 1.75 phr TBBS, the loading of ZnO was increased from 0.05 phr to 0.35 phr (Table 3.12).

Table 3.12 Formulation of BR compounds with 0.5 phr sulphur, 1.75 phr TBBS and an increasing loading of ZnO

Formulation (phr)	**Compound no**								
	84	**85**	**86**	**87**	**88**	**89**	**90**	**91**	**92**
Buna CB 24 (BR)	100	100	100	100	100	100	100	100	100
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TBBS	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
ZnO	0.05	0.075	0.125	0.15	0.175	0.2	0.25	0.3	0.35
	ODR test results at 160°C								
Min torque (dNm)	14	14	14	14	15	15	15	16	14
Max torque dNm)	76	78	82	83	85	85	83	88	87
ΔTorque (dNm)	62	64	68	69	70	70	68	72	73
Scorch time t_{s2} (min)	15.1	14.4	14.5	14	16.5	13.2	15.2	16.7	13.3
Optimum cure time t_{95} (min)	61.1	60.2	57.9	56.3	62.1	55.7	58.9	65.2	55.5

Figure 3.24 shows ∆torque as function of ZnO loading for the rubber with 0.5 phr TBBS and 1.75 phr sulphur. ∆torque increased from 60 to 70 when the loading of ZnO was raised to 0.2 phr and it continued rising at a much slower rate at about 73 dNm when the loading of ZnO reached 0.35 phr. The addition of 0.2 phr ZnO was adequate to improve the efficiency of TBBS as indicated by large increase in ∆torque value.

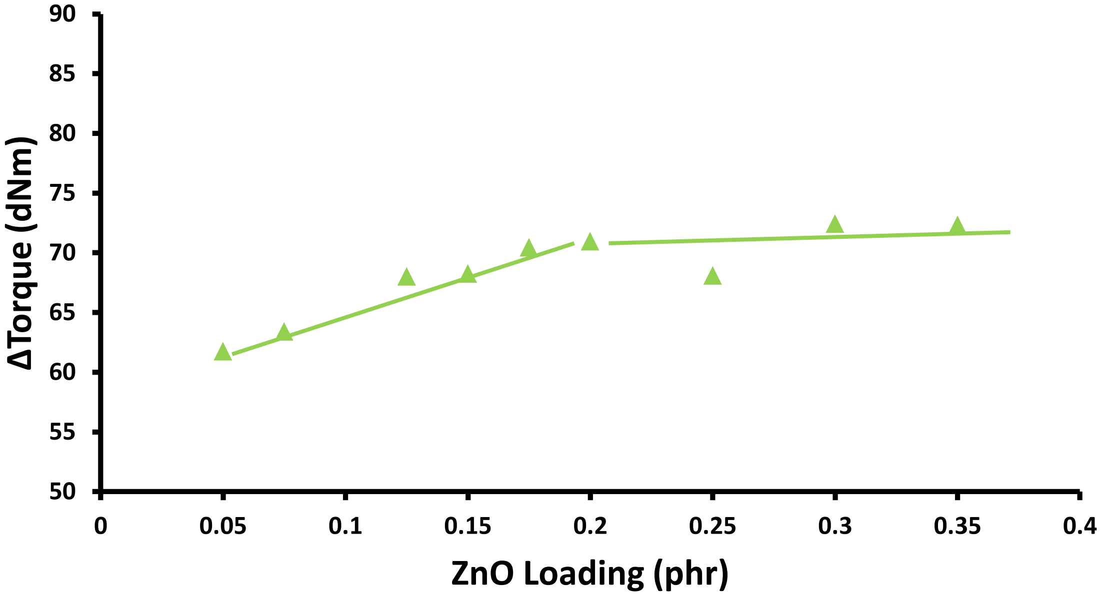


Figure 3.24 ∆Torque versus ZnO loading for the compounds with 0.5 phr sulphur and 1.75 phr TBBS in BR

The cure trace of the rubber with the optimum loading of ZnO (0.2 phr) was examined for evidence of full cure (Fig 3.25).

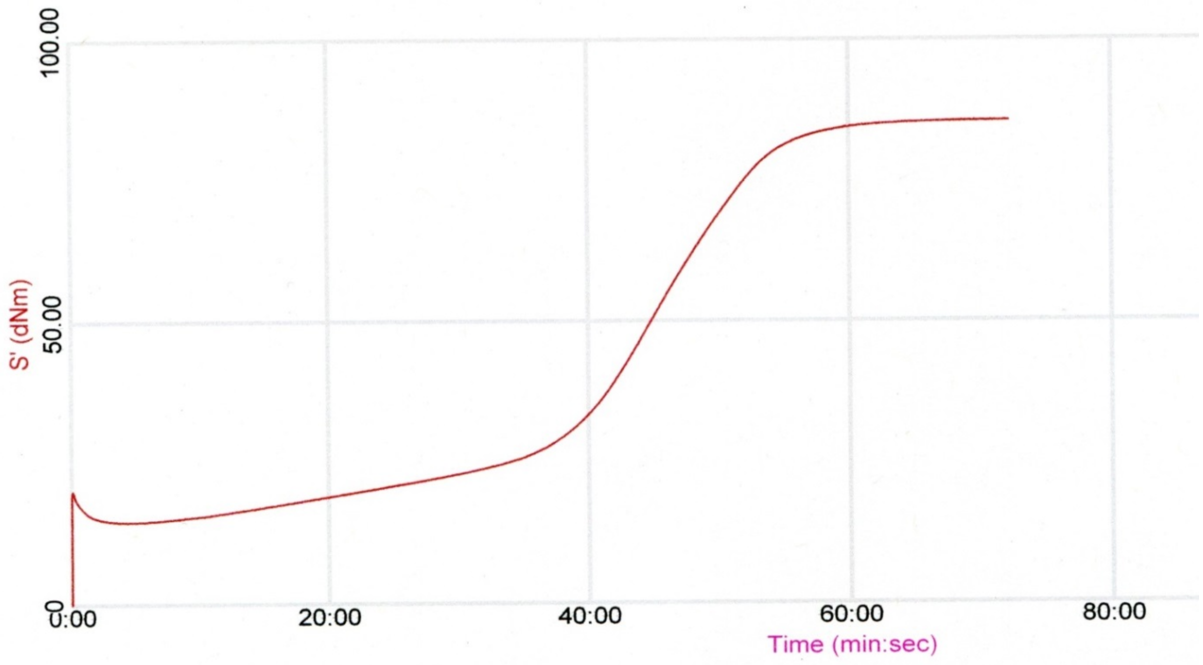


Figure 3.25 cure trace (torque vs time) of the BR compound with 0.5 phr sulphur, 1.75 phr TBBS and 0.2 phr ZnO

For BR with 0.5 phr sulphur, 1.75 phr TBBS and 0.2 phr ZnO, the loading of stearic acid was increased from 0 phr to 3 phr (Table 3.13)

Table 3.13 Formulation of BR compounds with 0.5 phr sulphur, 1.75 phr TBBS, 0.2 phr ZnO and an increasing loading of stearic acid

Formulation (phr)	**Compound no**							
	93	**94**	**95**	**96**	**97**	**98**	**99**	**100**
Buna CB24 (BR)	100	100	100	100	100	100	100	100
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TBBS	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
ZnO	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Stearic acid	0	0.5	0.9	1.3	1.7	2.1	2.5	3
	ODR test results at 160^{o}C							
Min torque (dNm)	15	12	14	12	14	14	14	14
Max torque dNm)	85	62	74	65	71	70	67	64
ΔTorque (dNm)	71	50	60	53	57	56	53	50
Scorch time t_{s2} (min)	13.2	12.1	11.5	10.4	12.6	12	11.8	12.1
Optimum cure time t_{95} (min)	55.7	50.2	52.3	48.3	50.9	44.4	43.5	40.9

Figure 3.26 shows Δtorque versus stearic acid loading. When stearic acid was added to the BR with 0.5 phr sulphur, 1.75 phr TBBS and 0.2 phr ZnO, Δtorque first

decreased sharply from 71 to 50 dNm and then remained almost steady until the loading of stearic acid reached 3 phr. Evidently, small amounts of stearic acid, i.e. up to 0.5 phr, were detrimental to the crosslink density of the rubber as indicated by drop in Δtorque.

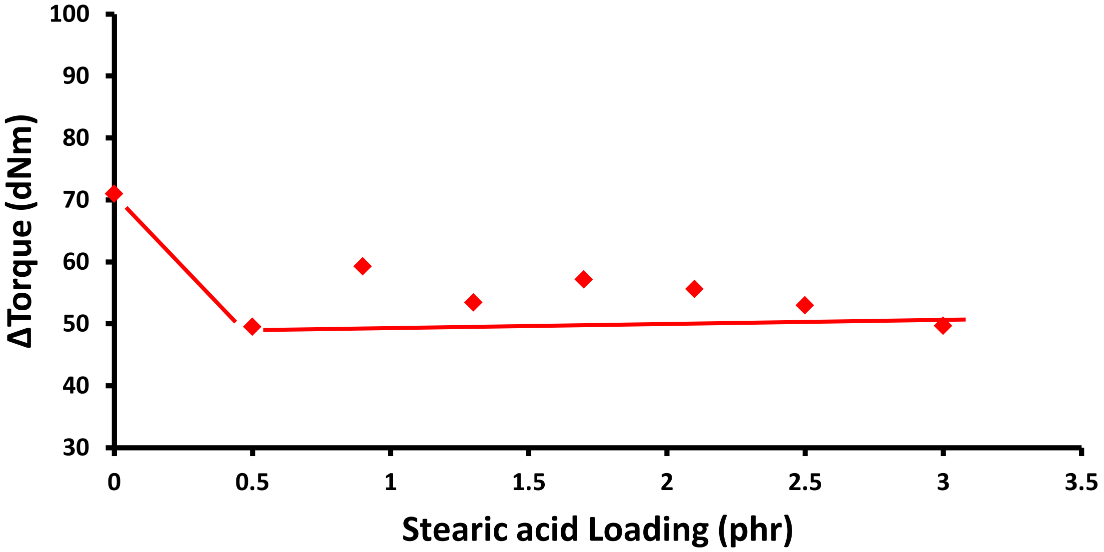


Figure 3.26 ΔTorque versus stearic acid loading for the compounds with 0.5 phr sulphur, 1.75 phr TBBS, 0.2 phr ZnO in BR

For BR with 1 phr sulphur, the loading of TBBS was increased from 0.5 phr to 3.8 phr (Table 3.14).

Table 3.14 Formulation of BR compounds with 1 phr sulphur and an increasing loading of TBBS

Formulation (phr)	**Compound no**									
	101	**102**	**103**	**104**	**105**	**106**	**107**	**108**	**109**	**110**
Buna CB 24 (BR)	100	100	100	100	100	100	100	100	100	100
Sulphur	1	1	1	1	1	1	1	1	1	1
TBBS	0.5	0.75	1	1.25	1.5	2	2.5	3	3.4	3.8
ODR test results at 160°C										
Min torque (dNm)	15	14	14	14	15	13	14	14	14	14
Max torque dNm)	54	57	59	62	63	63	69	74	72	77
∆Torque (dNm)	39	43	45	48	48	50	55	60	58	63
Scorch time t_{s2} (min)	14.3	11.5	11.6	11.6	11.8	10.6	10.3	10.2	10.1	12
Optimum cure time t_{95} (min)	77	45.2	44.6	45.3	48	44.6	50	51.8	55.9	61

Figure 3.27 shows ∆torque as a function of TBBS loading for the BR rubbers with 1 phr sulphur. ∆torque increased from 39 to 60 dNm as the loading of TBBS was raised to 3 phr, and then it stopped rising once the loading of TBBS reached 3.8 phr. The addition of 3 phr TBBS was sufficient to react the sulphur with the rubber to form crosslinks.

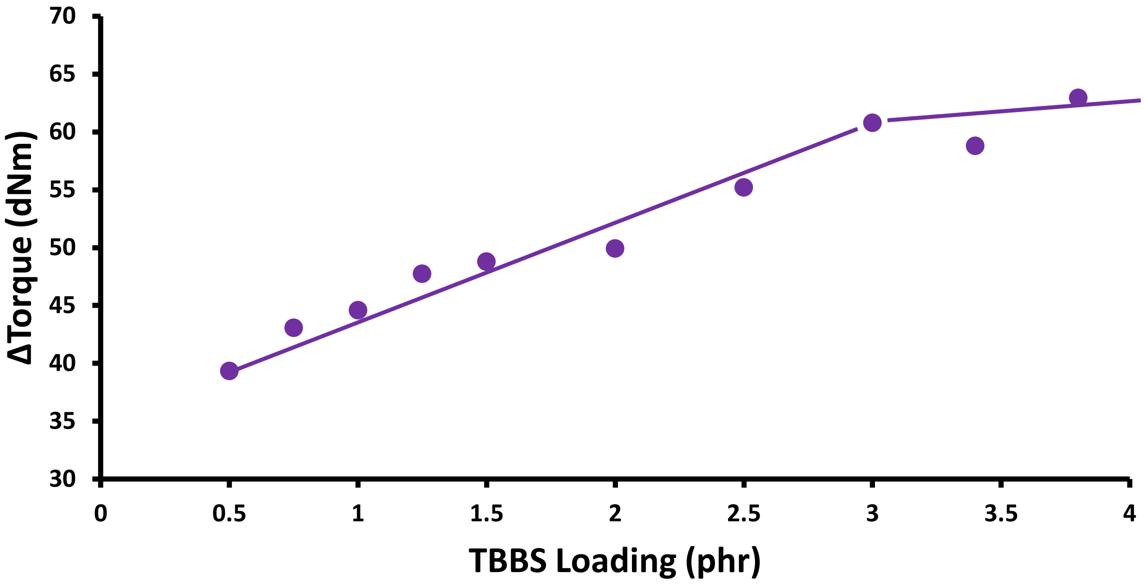


Figure 3.27 ΔTorque versus TBBS loading for the compounds with 1 phr sulphur in BR

Note: The amount of sulphur use in figure 3.22 was 0.5 phr, however in figure 3.27 is 1 phr, there seems to be a correlation between sulphur and TBBS to require optimum ΔTorque.

The cure trace of the rubber with the optimum loading of TBBS (3 phr) was examined for proof of full cure (Fig 3.28).

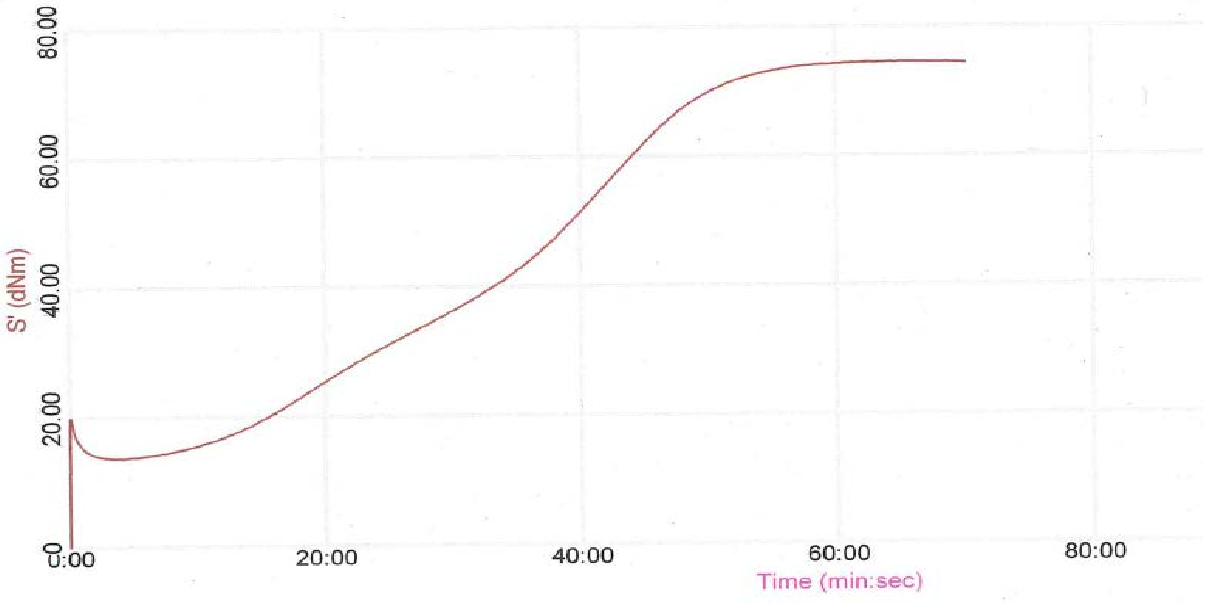


Figure 3.28 cure trace (torque vs time) of the BR compound with 1 phr sulphur and 3 phr TBBS

For BR with 1 phr sulphur and 3 phr TBBS, the loading of ZnO was increased from 0.05 phr to 0.45 phr (Table 3.15).

Table 3.15 Formulation of BR compounds with 0.5 phr sulphur, 1.75 phr TBBS and an increasing loading of ZnO

Formulation (phr)	**Compound no**								
	111	**112**	**113**	**114**	**115**	**116**	**117**	**118**	**119**
Buna CB 24 (BR)	100	100	100	100	100	100	100	100	100
Sulphur	1	1	1	1	1	1	1	1	1
TBBS	3	3	3	3	3	3	3	3	3
ZnO	0.05	0.075	0.1	0.15	0.175	0.2	0.25	0.35	0.45
	ODR test results at 160°C								
Min torque (dNm)	14	14	14	14	14	15	15	14	15
Max torque dNm)	92	94	96	101	103	108	108	109	109
∆Torque (dNm)	78	80	82	87	89	93	93	95	94
Scorch time t_{s2} (min)	10.7	10.3	10.1	9.8	10.3	11.8	10	10	11.8
Optimum cure time t_{95} (min)	48.1	44.7	42.7	39.8	39.2	43.3	40	40.6	46.5

Figure 3.29 shows ∆torque as function of ZnO loading for the rubber with 3 phr TBBS and 1 phr sulphur. ∆torque increased from 78 to 93 dNm when the loading of ZnO raised to 0.2 phr and it continued rising at a much slower rate at about 94 dNm when the loading of ZnO reached 0.45 phr. The addition of 0.2 phr ZnO was adequate to improve the efficiency of TBBS as indicated by large increase in ∆torque value.

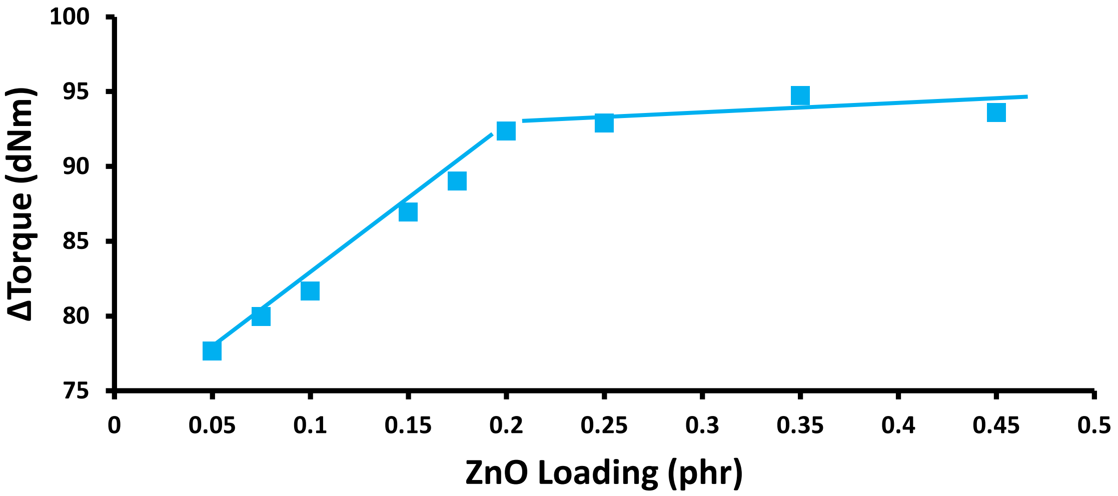


Figure 3.29 ∆Torque versus ZnO loading for the compounds with 1 phr sulphur and 3 phr TBBS in BR

The cure trace of the rubber with the optimum loading of ZnO (0.2 phr) was examined for proof of full cure (Fig 3.30).

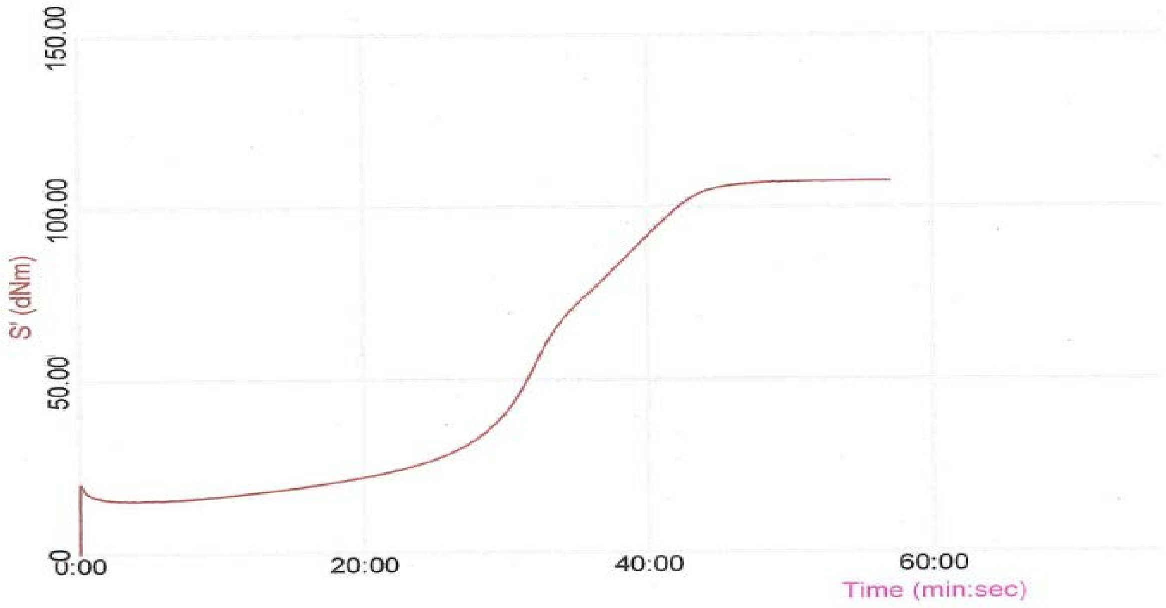


Figure 3.30 cure trace (torque vs time) of the BR compound with 1 phr sulphur, 3 phr TBBS and 0.2 phr ZnO

Figure 3.31 summarises the optimum loading of TBBS for the sulphur-filled BR rubbers. As shown, the rubbers with 0.5 and 1phr sulphur required 1.75 and 3 phr TBBS, respectively for full cure.

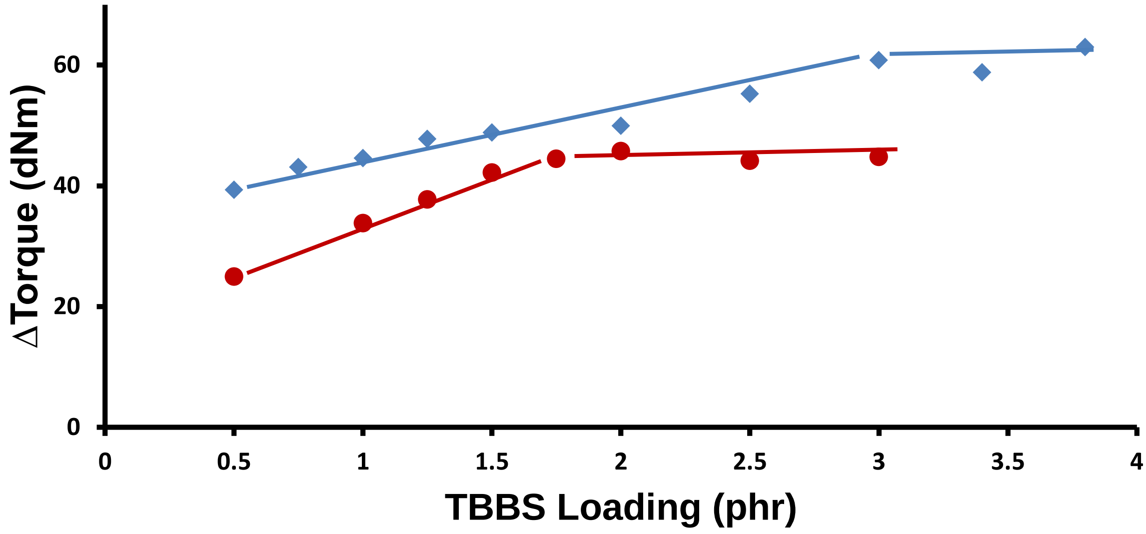


Figure 3.31 ΔTorque versus TBBS loading for the compounds with different amounts of sulphur (●) compound with 0.5 phr sulphur, (◆) compound with 1 phr sulphur. Each point on the graph corresponds to one compound

Figure 3.32 summarises the optimum loading of ZnO for the sulphur-filled BR rubbers with the optimum loading of TBBS. Interestingly, the sulphur-filled rubbers with 1.75 and 3 phr TBBS needed only 0.2 phr ZnO to be fully cured. That suggested that the ZnO requirement was not necessary dependent on the loading of TBBS though the amount of TBBS needed to react the sulphur with the rub was dependent on the sulphur loading.

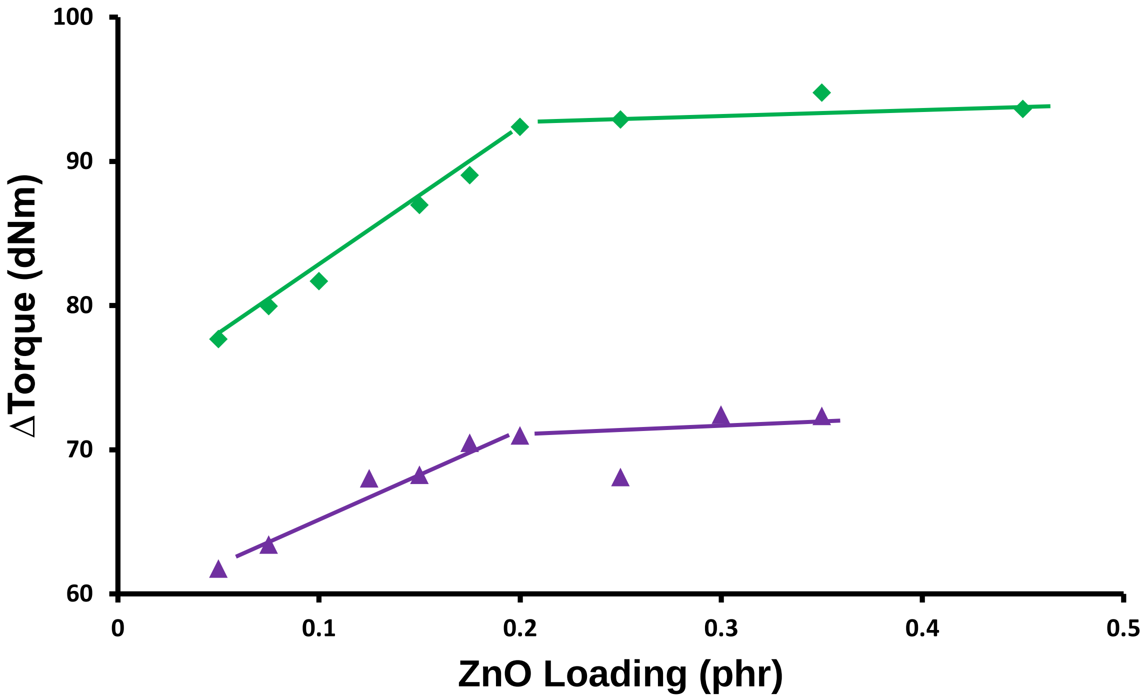


Figure 3.32 ΔTorque versus ZnO loading for the compounds with different amounts of sulphur and TBBS. (▲) compound with 0.5 phr sulphur and 1.75 phr TBBS, (◆) compound with 1 phr sulphur and 3 phr TBBS. Each point on the graph corresponds to one compound

3.3.3 Addition of TBBS and ZnO to EPDM filled with 1 phr sulphur

For EPDM with 1 phr sulphur, the loading of TBBS was increased from 0.25 phr to 3.8 phr (Table 3.16)

Table 3.16 Formulation of EPDM compounds with 1 phr sulphur and an increasing loading of TBBS

Formulation (phr)	**Compound no**								
	120	**121**	**122**	**123**	**124**	**125**	**126**	**127**	**128**
Keltan 3251A (EPDM)	100	100	100	100	100	100	100	100	100
Sulphur	1	1	1	1	1	1	1	1	1
TBBS	0.25	0.5	0.75	1	1.25	1.5	2	2.5	3.8
	ODR test results at 160^{o}C								
Min torque (dNm)	15	16	17	16	16	16	15	15	14
Max torque dNm)	41	49	54	57	59	58	58	56	54
ΔTorque (dNm)	26	33	37	42	43	42	43	41	40
Scorch time t_{s2} (min)	18.7	19.6	24.8	22.1	21.7	20.9	31.4	25	23
Optimum cure time t_{95} (min)	104.8	87.2	59.9	59.5	61.8	64.2	74.1	75.6	751

Figure 3.33 demonstrates Δtorque versus TBBS loading for the EPDM with 1 phr sulphur. ΔTorque increased steeply from 26 to 42 dNm as the loading of TBBS was boosted from 0.25 to 1 phr. Subsequently, there was no improvement in Δtorque once the amount of TBBS reached 3.8 phr. Apparently, 1 phr TBBS was enough to react the sulphur with the rubber.

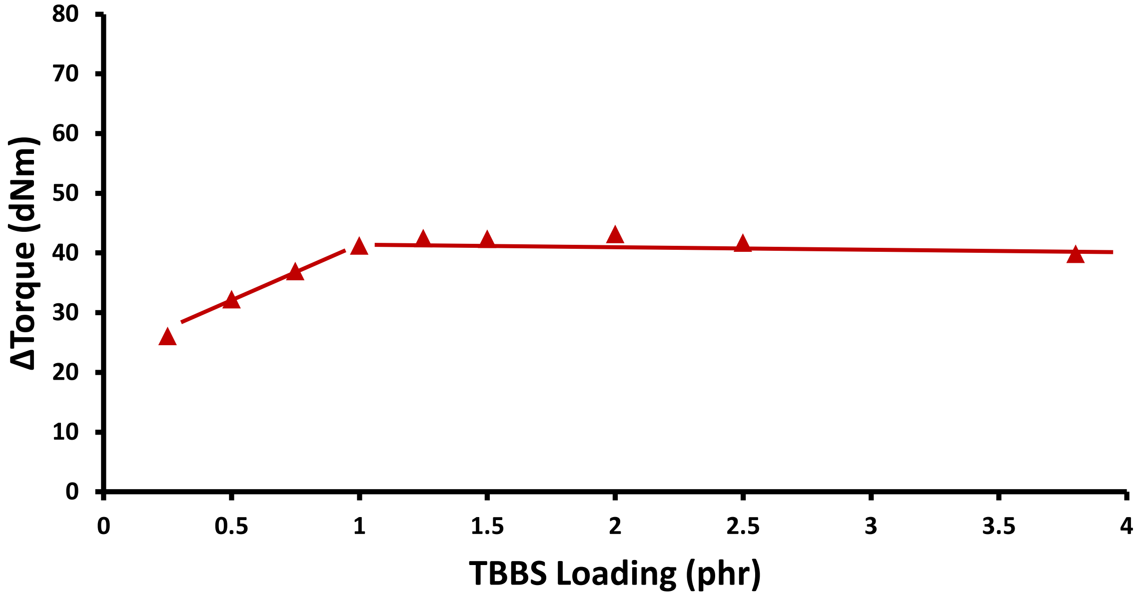


Figure 3.33 ΔTorque versus TBBS loading for the compounds with 1 phr sulphur in EPDM

The cure trace of the rubber with the optimum loading of TBBS (1 phr) was examined for evidence of full cure (Fig 3.34).

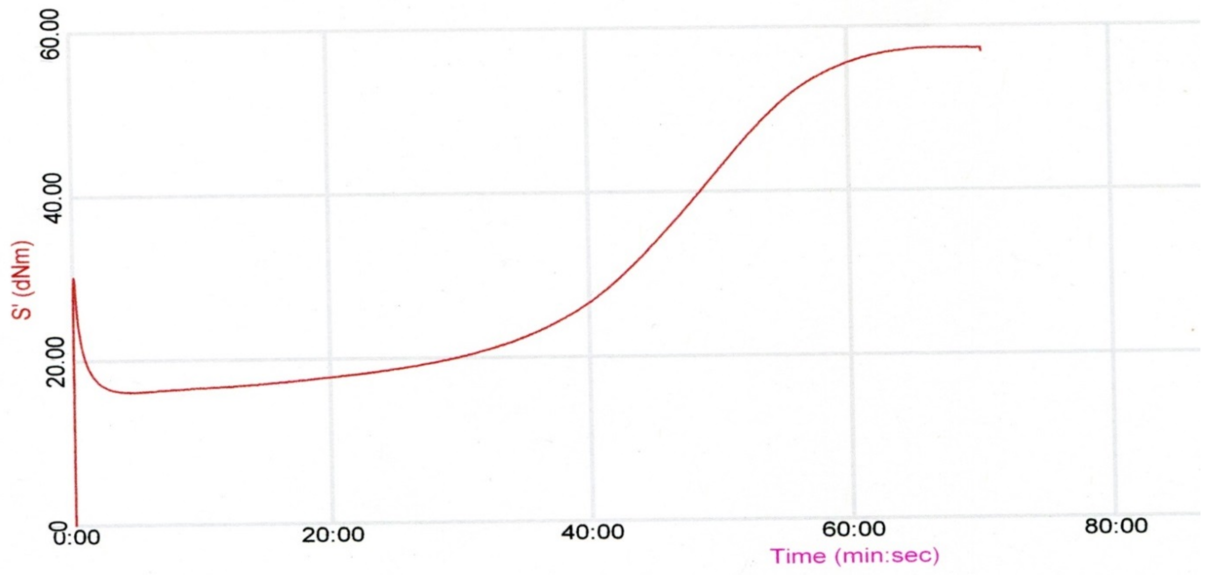


Figure 3.34 cure trace (torque vs time) of the EPDM compound with 1 phr sulphur and 1 phr TBBS

For EPDM with 1 phr sulphur and 1 phr TBBS, the loading of ZnO was increased from 0 phr to 0.4 phr (Table 3.17)

Table 3.17 Formulation of EPDM compounds with 1 phr sulphur, 1 phr TBBS and an increasing loading of ZnO

Formulation (phr)	**Compound no**										
	129	**130**	**131**	**132**	**133**	**134**	**135**	**136**	**137**	**138**	**139**
Keltan 3251A (EPDM)	100	100	100	100	100	100	100	100	100	100	100
Sulphur	1	1	1	1	1	1	1	1	1	1	1
TBBS	1	1	1	1	1	1	1	1	1	1	1
ZnO	0	0.05	0.075	0.1	0.125	0.15	0.2	0.25	0.3	0.35	0.4
	ODR test results at 160^{o}C										
Min torque (dNm)	16	16	16	17	17	16	16	15	15	16	16
Max torque dNm)	57	69	72	70	72	73	71	72	74	81	83
ΔTorque (dNm)	41	53	56	53	55	57	55	57	59	65	67
Scorch time t_{s2} (min)	22.2	18.5	17	17.9	17.3	15	20.6	16.9	16.6	15.1	14.6
Optimum cure time t_{95} (min)	59.5	40.5	37.7	40.2	41.4	37	44.8	41	41	40.1	40.2

Figure 3.35 shows Δtorque vs ZnO loading for rubber with the optimum loading of TBBS. ΔTorque rose noticeably from 41 dNm at 0 phr ZnO to 56 dNm at 0.075 phr ZnO and the rate of increase slowed down significantly thereafter. Δtorque then reached to about 67 dNm when the loading of ZnO was raised by an additional 0.325 phr. It is remarkable that a small amount of ZnO, i.e. as low as 0.075 phr, had such a major influence on the performance of TBBS in the cure system as indicated by a significant rise in Δtorque.

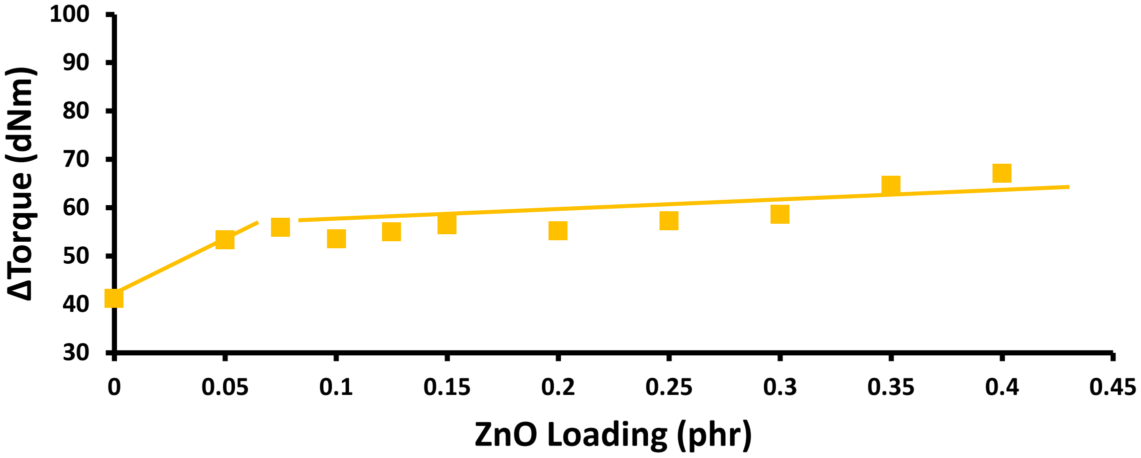


Figure 3.35 ΔTorque versus ZnO loading for the compounds with 1 phr sulphur and 1 phr TBBS in EPDM

The cure trace of the rubber with the optimum loading of ZnO (0.075 phr) was examined for evidence of full cure (Fig 3.36).

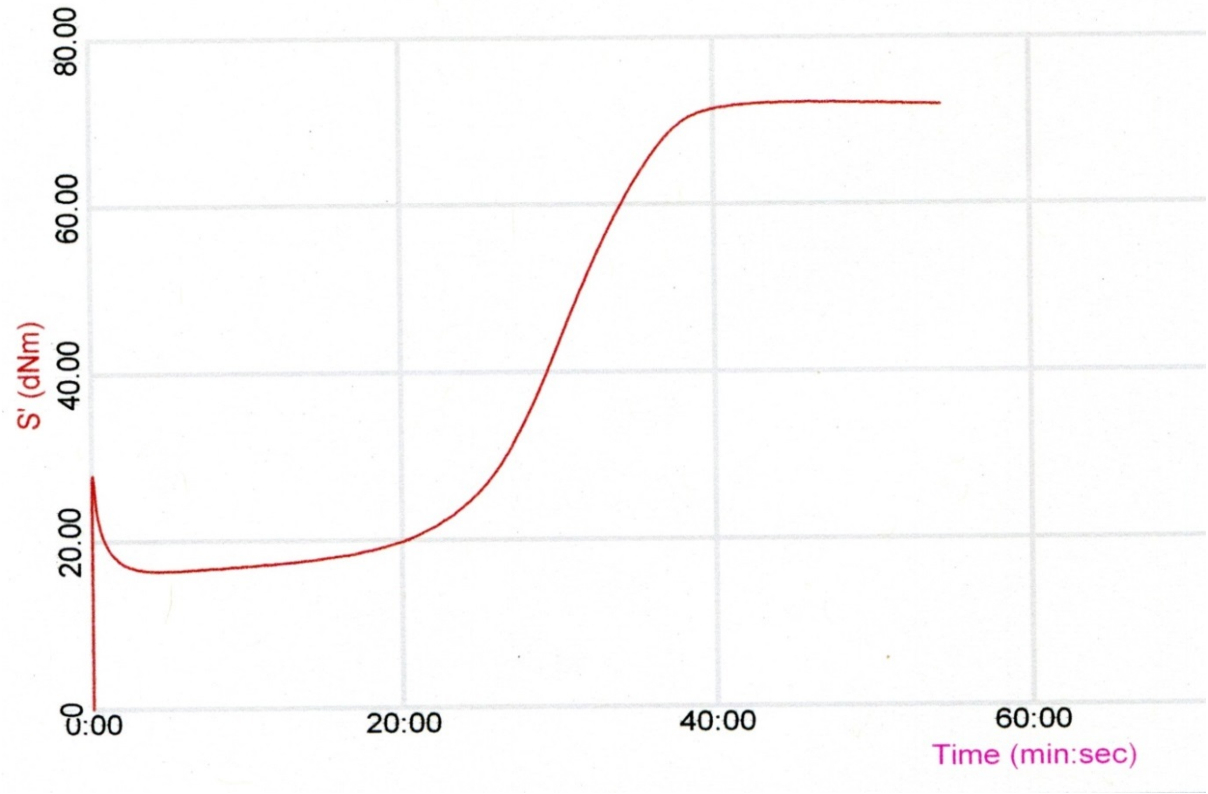


Figure 3.36 Cure trace (torque vs time) of the EPDM compound with 1 phr sulphur, 1 phr TBBS and 0.075 phr ZnO

For EPDM with 1 phr sulphur, 1 phr TBBS, and 0.075 phr ZnO, the loading of stearic acid was increased from 0 phr to 3 phr (Table 3.18)

Table 3.18 Formulation of EPDM compounds with 1 phr sulphur, 1 phr TBBS, 0.2 phr ZnO and an increasing loading of stearic acid

Formulation (phr)	**Compound no**							
	140	**141**	**142**	**143**	**144**	**145**	**146**	**147**
Keltan 3251A (EPDM)	100	100	100	100	100	100	100	100
Sulphur	1	1	1	1	1	1	1	1
TBBS	1	1	1	1	1	1	1	1
ZnO	0.075	0.075	0.075	0.075	0.075	0.075	0.075	0.075
Stearic acid	0	0.5	0.9	1.3	1.7	2.1	2.5	3
	ODR test results at 160°C							
Min torque (dNm)	16	16	15	15	14	14	15	14
Max torque dNm)	72	62	60	59	58	57	57	55
ΔTorque (dNm)	56	47	45	44	44	43	42	41
Scorch time t_{s2} (min)	17	25.6	23	21.9	22.8	19.2	19.1	18.8
Optimum cure time t_{95} (min)	37.7	49.3	45	42.7	46.3	41.8	43.7	40.2

Figure 3.37 when 0.5 phr stearic acid was mixed with the EPDM with 1 phr sulphur, 1 phr TBBS and 0.075 phr ZnO, ∆torque decreased from 56 to 47 dNm and subsequently continued decreasing slowly to about 42 dNm when the amount of stearic acid was raised to 2.5 phr. The crosslink density as shown by Δtorque did not benefit from the addition of stearic acid to the rubber and consequently it can be eliminated from the cure system completely.

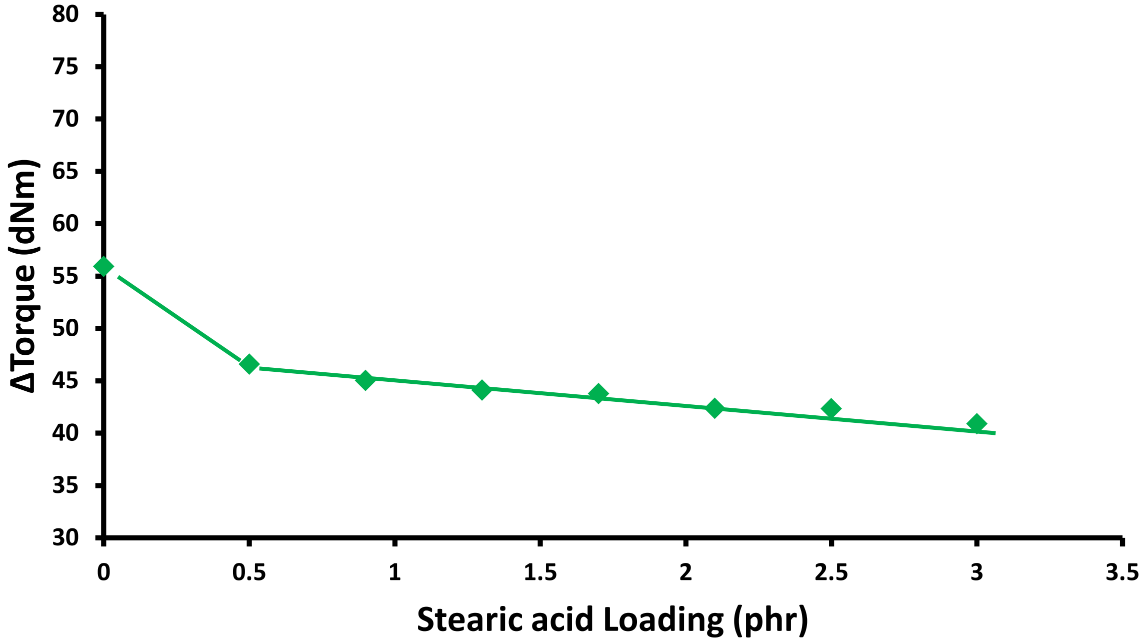


Figure 3.37 ∆Torque versus stearic acid loading for the compounds with 1 phr sulphur, 1 phr TBBS, 0.075 phr ZnO in EPDM

After these measurements were completed, there were seven cure systems depending on the amount of sulphur in the rubber (Table 3.19). The cure systems consisted of sulphur, TBBS and ZnO. For the NR with 1 phr sulphur, the total amount of TBBS and ZnO was 1.7 phr and this increased to 3.7 phr for the NR with 4 phr sulphur (compounds 148-151). For the BR with 0.5 phr sulphur, the total amount of TBBS and ZnO was 1.95 phr and this rose to 3.2 phr for the BR with 1 phr sulphur (compounds 152 &153). For the EPDM with 1 phr sulphur, the total amount of TBBS and ZnO was 1.075 phr (compound 154). Note that there were only three chemicals in the cure systems. This was a significant reduction both in the number and amount of the chemicals in the cure system. Compounds 151, 152 and 154 were then selected for further work. A high loading of mineral kaolin was mixed with these compounds and then they were cured and their mechanical properties measured. The results will appear in Chapter 6.

Table 3.19 Rubber formulations and cure properties of the rubber compounds

Formulation (phr)	**Compound no.**						
	148	**149**	**150**	**151**	**152**	**153**	**154**
SMRL (NR)	100	100	100	100	-	-	-
Buna CB 24 (BR)	-	-	-	-	100	100	-
Keltan 3251A (EPDM)	-	-	-	-	-	-	100
Sulphur	1	2	3	4	0.5	1	1
TBBS	1.5	1.5	1.5	3.5	1.75	3	1
ZnO	0.2	0.3	0.25	0.2	0.2	0.2	0.075
ODR test results at 160^{o}C							
Minimum torque (dNm)	16	17	16	14	15	15	16
Maximum torque (dNm)	42	52	54	58	85	108	72
ΔTorque (dNm)	26	35	38	44	70	93	56
Scorch time, ts_2 (min)	8.4	6.5	5.6	4.9	13.2	11.8	17
Optimum cure time, t_{95} (min)	15.5	10.7	9.8	9.4	55.7	43.3	37.7
Cure rate index (min^{-1})	14.1	23.8	23.8	22.2	2.36	3.18	4.8
Exact Optimum cure system (S/TBBS/ZnO)	(1/1.5/0.2)	(2/1.5/0.3)	(3/1.5/0.25)	(4/3.5/0.2)	(0.5/1.75/0.2)	(1/3/0.2)	(1/1/0.075)

3.4 Conclusions

A new method measured the exact optimum amount of TBBS accelerator and ZnO activator at a given loading of sulphur in the composites of NR, BR and EPDM and eliminated stearic acid from the cure system entirely. The requirement for ZnO was 0.075-0.3 phr. interestingly, in spite of using less chemical curatives in sulphur vulcanisation, the rubber composites were fully cured. The following conclusions were drawn.

1. The optimum loadings of TBBS for the NR with 1, 2, 3 and 4 phr sulphur were 1.5, 1.5, 1.5 and 3.5 phr, respectively.
2. The optimum loading of ZnO for the NR with 1 phr sulphur and 1.5 phr TBBS, the NR with 2 phr sulphur and 1.5 phr TBBS, the NR with 3 phr sulphur and 1.5 phr TBBS, and the NR with 4 phr sulphur and 3.5 phr TBBS were 0.2, 0.3, 0.25, and 0.2 phr, respectively.
3. The optimum loading of TBBS for the BR with 0.5 and 1 phr sulphur were 1.75 and 3 phr, respectively.
4. The optimum loading of ZnO for the BR with 0.5 phr sulphur and 1.75 phr TBBS and the BR with 1 phr sulphur and 3 phr TBBS were 0.2 phr, respectively.
5. The optimum loading of TBBS for the EPDM with 1 phr sulphur was 1 phr.
6. The optimum loading of ZnO for the EPDM with 1 phr sulphur and 1 phr TBBS was 0.075 phr.
7. Relation between Δtorque and mechanical properties will be discussed in chapter 6.

This study measures the optimum loading of TBBS accelerator for curing some sulphur-filled NR, BR and EPDM rubbers. The optimum loading of zinc oxide activator in the sulphur-filled rubbers with the optimum loading of TBBS was subsequently determined. For each rubber, a new cure system based on the measurement of the optimum loading of TBBS accelerator and ZnO activator at a given loading of sulphur was developed.

3.5 References

1. P A Ciullo and N Hewitt, “The rubber formulary”. Noyes publications, NY, 1999. pp79.
2. http://www.westliberty.edu/health-and-safety/files/2012/08/Stearic-Acid.pdf
3. Regulation (EC) No 1272/2008.
4. European Directive 98/24/EC. Risks related to chemical agents at work.
5. A Ansarifar, A Azhar, N Ibrahim, S F Shiah, J M D Lawton, “The use of a silanised silica filler to reinforce and crosslink natural rubber”, *Int J Adhes & Adhes.*, Vol. 25, No. 1, pp 77-86 (2005)
6. S H Sheikh, X Yin, A Ansarifar, K Yendall, “The potential of kaolin as reinforcing filler for rubber composites with new sulphur cure systems”, *J Rein Plast Compos*, Vol. 36, No. 16, pp 1132-1145 (2017)
7. P A Ciullo and N Hewitt, “The rubber formulary”. Noyes publications, NY, 1999. Pp 85.
8. P A Ciullo and N Hewitt, “The rubber formulary”. Noyes publications, NY, 1999. Pp 194.
9. F.P. Baldwin, G.V. Strate, "Polyolefin elastomers based on ethylene and propylene", *Rubb Chem Technol*, Vol. 45, No. 3, pp. 709-881(1972)
10. A. Bani, G. Polacco, G. Gallone, "",Microwave-induced devulcanisation for poly(ethylene–propylene– diene) recycling", *J Appl. Polym Sci*, Vol.120, No. 5, pp. 2904-2911 (2011)
11. P J Flory and R. Rehner, *J. Chem. Phys.* Vol. 11, No. 2, pp 521-526 (1943)
12. L. Mullins (1957) Determination of Degree of Crosslinking in Natural Rubber Vulcanisates. Part I. *Rubber Chemistry and Technology*, Vol. 30, No. 1, pp. 1-10 (1957)

Chapter 4 – Revisiting the sulphur vulcanisation of rubber

4.1 Introduction

As mentioned earlier in Chapter 3, sulphenamide accelerators and zinc oxide (ZnO) activator are used extensively to cure rubber articles [1]. In sulphur cure systems currently in use, these chemicals are used as individual powders and then mixed with the raw rubber to produce rubber compounds [2&3]. However, literature review has indicated that no work has been done to date to study effect of the combined chemicals on the cure properties of rubber. One method of combining these chemicals together to produce a single additive component is by coating the surface of ZnO with the TBBS molecules. This work functionalized ZnO with TBBS accelerator in an organic solvent to produce a single dry powder and then examined its effect on the cure properties of NR. The aim was to minimize use of these two chemicals in the cure system and enhance the efficiency of the sulphur vulcanisation of the rubber.

4.2 Experimental

4.2.1 Materials, mixing and functionalising ZnO with TBBS

The raw rubber and chemicals used were described fully in the Experimental section of Chapter 3. Zinc oxide was coated on TBBS to study the minimum amount of TBBS needed to satisfactorily crosslink the rubber. Adsorbing the TBBS onto the ZnO provided a convenient single material component to use as additive. The quantity of TBBS required to provide monomolecular coverage of the zinc oxide was determined to be 35 mg/g based on the approximate surface areas of the TBBS molecule (6 x 10^{-19} m^2) and the ZnO (50 m^2/g) used. Gradually, the amount of TBBS to coat the zinc oxide was increased from 100 mg/g to 350 mg/g to find a material with optimum properties. The material with 35 mg/g TBBS led to a very slow cure, but material with 350 mg/g gave a good cure comparable to much higher loadings of TBBS as shown in (Table 4.1). A large batch was then prepared with this ratio from 202.0 g of ZnO and 70.7 g of TBBS which was mixed in 100 ml of ethyl acetate solvent (sigma Aldrich, UK) in a 500 ml beaker. The suspension stirred magnetically for 15 min at room temperature (21.5°C). The mixture was filtered under suction using an electric diaphragm vacuum pump (capable of achieving 50 mmHg). The white solid was left to dry overnight and then further dried in a vacuum oven at 50°C. Evaporation of the filtrate on a rotary evaporator indicated the mass lost was 0.110 g, indicating the bulk of the TBBS was absorbed onto the ZnO. The additive will be referred to as the “powder”. In another experiment, the loading of the powder with 350 mg/g of TBBS was increased progressively to determine its effect on the cure properties of the rubber (Table 4.2).

The raw rubber was mixed with the chemical ingredients in a Haake Rheocord 90 intermixer as described in Chapter 3. To prepare the rubber compounds, the raw rubber was introduced first in the mixer and then after 30 seconds, the sulphur and powder were added and mixed for 8 min in total. The temperature of the rubber compounds during mixing was 52-62^{o}C. In total, nineteen rubber compounds were prepared. The cure properties of the rubber compounds were them determined at 160 ± 2^{o}C in an oscillating disc rheometer curemeter according to the British Standard ISO 3417:2008.The tests ran for up to an hour. From the cure traces, the cure properties of the rubber compounds were measured (see also the Experimental section in Chapter 3). Results from these tests are summarised in Tables 4.1 and 4.2. ∆Torque was subsequently plotted against the loading of the powder. Recall that ∆Torque is the difference between the maximum and minimum torque values on the cure trace of a rubber compound and is an indication of crosslink density changes in the rubber.

Table 4.1 Formulations and cure properties of the rubber compounds with an increasing amount of TBBS in the powder

Formulation (phr)	**Compound no**									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
NR	100	100	100	100	100	100	100	100	100	100
Sulphur	4	4	4	4	4	4	4	4	4	4
TBBS Loading in the powder	0.135	0.192	0.247	0.296	0.342	0.351	0.358	0.367	0.376	0.383
ZnO Loading in the powder	1.345	1.288	1.233	1.184	1.138	1.129	1.122	1.113	1.104	1.097
	Curemeter test results at 160^{o}C									
Min torque (dNm)	17	15	15	15	15	16	16	16	15	17
Max torque (dNm)	32	32	31	31	38	46	45	51	50	53
ΔTorque (dNm)	15	17	16	16	23	30	29	35	35	36
t_{s2} (min)	10.7	8.5	10.4	9.1	4.4	3.2	3.2	3.6	3.5	3.6
t_{95} (min)	55.4	54.5	55.5	54.8	41.4	9.9	10.7	8.4	8.1	8.9
CRI (min^{-1})	2.2	2.2	2.2	2.2	2.7	14.9	13.3	20.8	21.7	18.9

phr: parts per hundred rubber by weight

Table 4.2 Formulations and cure properties of the rubber compounds with increasing amounts of the powder

Formulation (phr)	**Compound no**								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
NR	100	100	100	100	100	100	100	100	100
Sulphur	4	4	4	4	4	4	4	4	4
Powder	0.63	1.25	1.88	2.5	3.13	3.75	4.38	5	5.63
	Curemeter test results at 160^{o}C								
Min torque (dNm)	17	16	15	15	15	16	17	16	15
Max torque (dNm)	39	46	56	63	68	75	77	80	80
ΔTorque (dNm)	22	30	41	48	53	59	60	64	65
t_{s2} (min)	4.3	3.4	3.3	3.3	3.4	3.6	3.7	3.8	4.0
t_{95} (min)	30.8	7.7	7.0	6.9	6.8	7.2	7.0	7.1	7.4
CRI (min^{-1})	3.8	23.2	27.0	27.8	29.4	27.8	30.3	30.3	29.4

phr: parts per hundred rubber by weight

4.3 Results and discussion

4.3.1 Effect of an increasing loading of TBBS in the powder on the cure properties of the rubber

As mentioned earlier, in one experiment the loading of TBBS in the powder was raised from 100 mg/g to 350 mg/g (equivalent to an increase of 0.135 phr to 0.383 phr in the formulation, (Table 4.1) to measure the optimum amount required to cure the rubber. When the cure traces of the rubber compounds were examined, the cure was marching until the loading of TBBS in the powder reached 0.351 phr (cf. figures 4.1a and 4.1b). The torque remained at this level until the loading of TBBS in the powder rose to 0.358 phr. Subsequently, the cure experienced reversion when the loading of TBBS in the powder was increased to 0.383 phr (Fig. 4.1c). It is clear that larger amount of TBBS in the powder shortens the cure cycle very substantially. Besides, it was interesting that the cure behaviour was so sensitive to small changes in the amount of TBBS in the powder. As figures 4.1a-4.1c show, the cure was marching first, then reached equilibrium and finally underwent reversion as the loading of TBBS in the powder was increased from 100 mg/g to 350 mg/g.

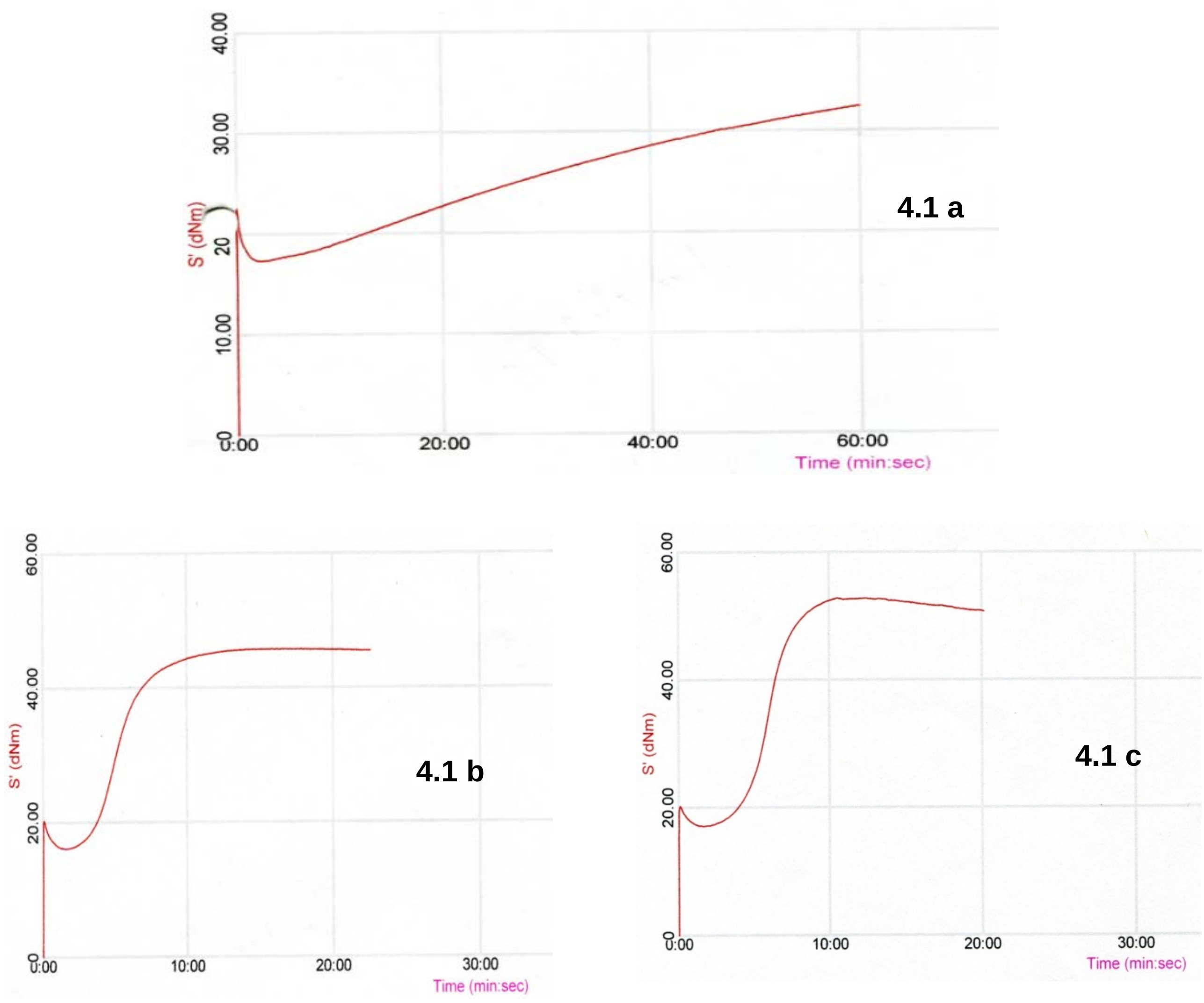


Figure 4.1 Typical cure traces (Torque (dNm) vs Time (min)) of the rubber compounds with an increasing loading of TBBS in the powder. a) compound with 0.135 phr TBBS in the powder; b) compound with 0.351 phr TBBS in the powder; c) compound with 0.383 phr TBBS in the powder

The increase in the loading of TBBS in the powder had a major influence on the crosslink density and cure rate of the rubber as indicated by big rises in the value of ∆torque and CRI, respectively. ∆Torque was almost constant at about 15-17 dNm with up to 0.296 phr TBBS in the powder. It then rose sharply to 36 dNm when the TBBS loading in the powder reached 0.383 phr (Fig 4.2).

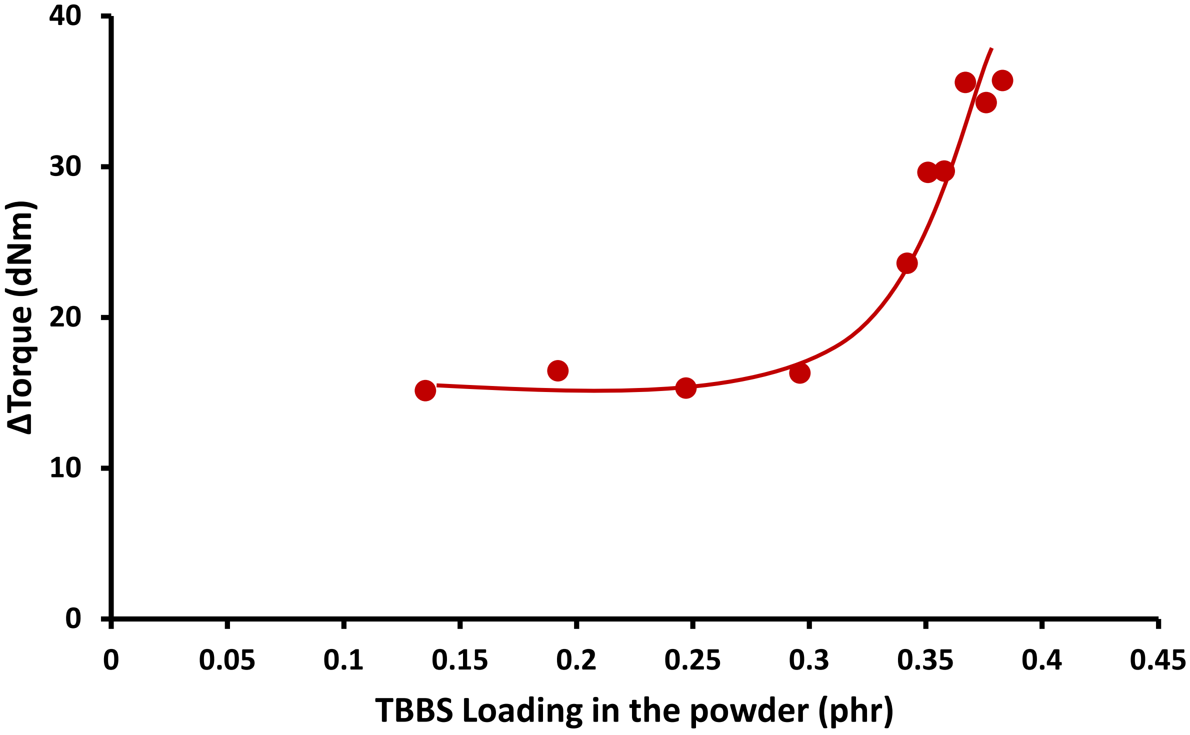


Figure 4.2 ∆Torque vs TBBS loading in the powder for the rubber compounds shown in Table 4.1. Each point on the graph corresponds to one rubber compound

The cure rate index was unaffected by increase in the TBBS loading in the powder up to 0.342 phr but rose sharply to about 21.7 min^{-1} when the TBBS loading in the powder reached 0.376 phr and then decreased to 18.9 min^{-1} at 0.383 phr TBBS loading in the powder (Fig. 4.3).

Although further increase in the loading of TBBS in the powder, could have increased the ∆torque value further in figure 4.2. However, the powder with 350mg of TBBS/1gm of ZnO was efficient in curing the rubber as shown in figure 4.1. Therefore no further increase in the TBBS loading in the powder was considered.

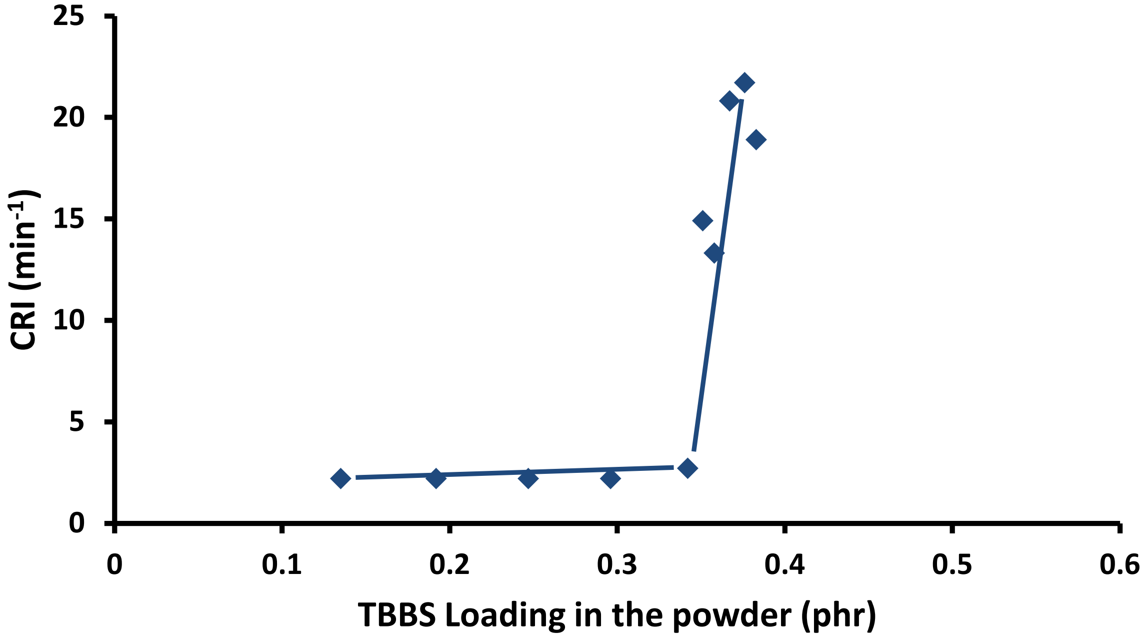


Figure 4.3 Cure rate index vs TBBS loading in the powder for the rubber compounds shown in Table 4.1. Each point on the graph corresponds to one rubber compound

The scorch time was somewhere between 10.7 and 9.1 min with up to 0.296 phr TBBS in the powder and then decreased to 4.4 min at 0.342 phr TBBS in the powder. It subsequently reached a plateau around 3.2-3.6 min when the TBBS loading in the powder was raised to 0.383 phr (Fig 4.4). The increase in the loading of TBBS in the powder for up to 0.296 phr had little or no effect on the optimum cure time which remained essentially unchanged at about 54.5-55.5 min. However, this was followed by a sharp decrease to 41.4 min at 0.342 phr and then to 10.7 min at 0.358 phr TBBS loading in the powder. The optimum cure time attained a constant value at around 8.1-8.9 min when the loading of TBBS in the powder was increased to 0.383 phr.

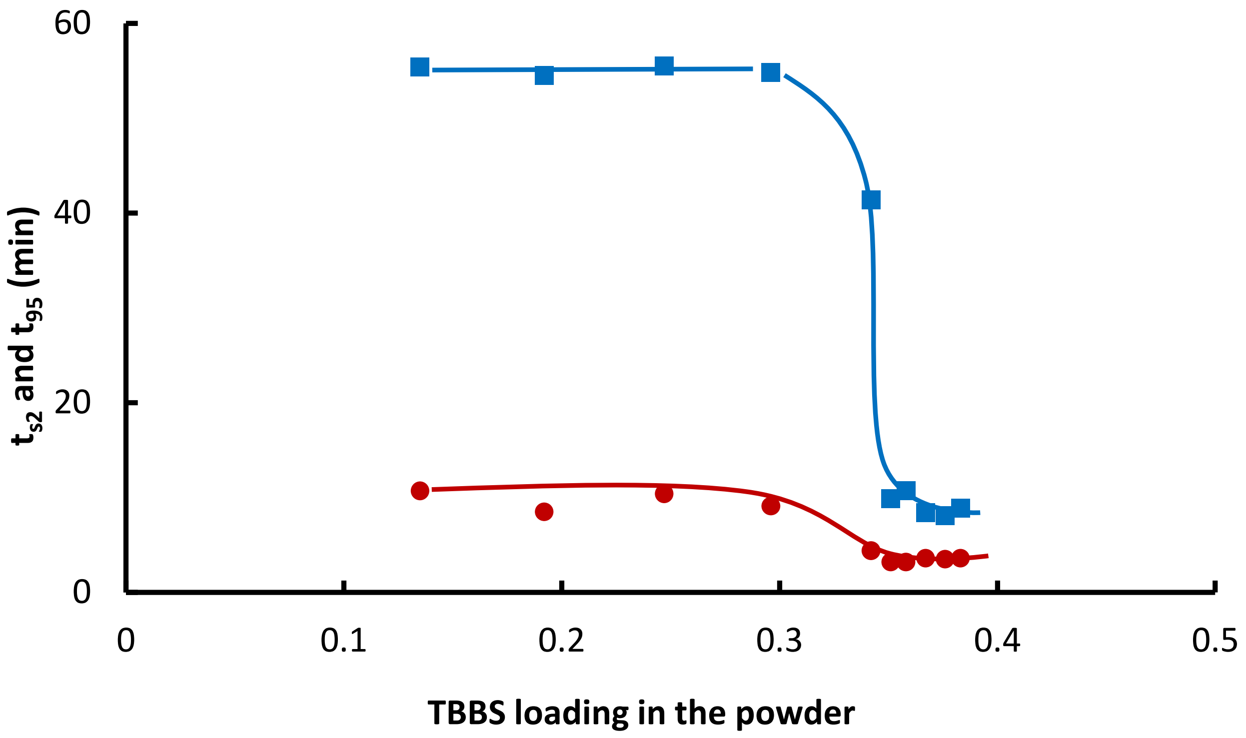


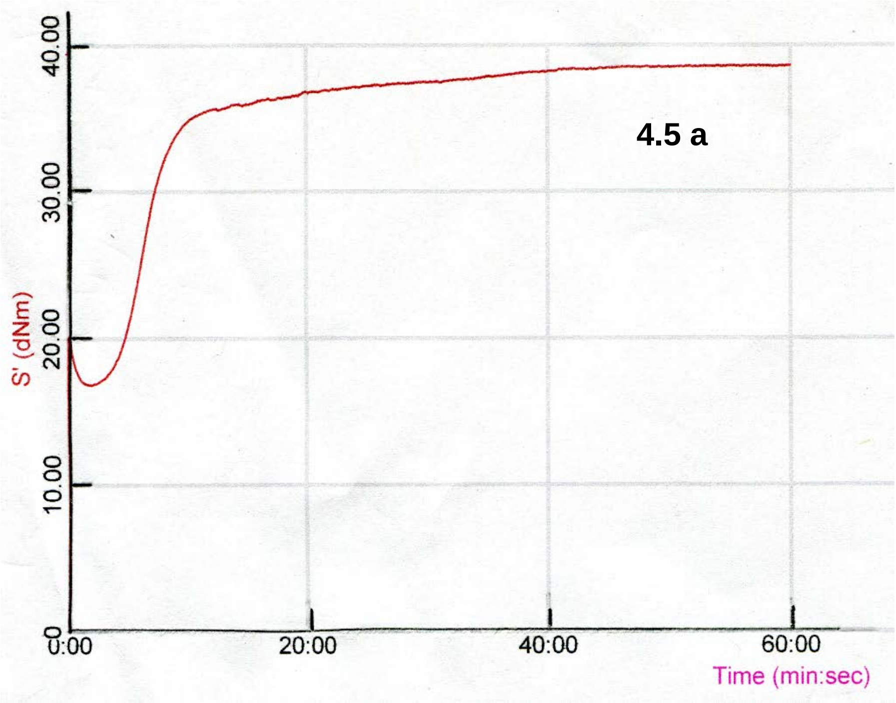
Figure 4.4 Optimum cure time, t_{95}, and scorch time, t_{s2} vs TBBS loading in the powder for the rubber compounds shown in Table 4.1. Each point on the graph corresponds to one rubber compound, optimum cure time (■), scorch time (●)

It was clear that increase in the amount of TBBS in the power to above 0.342 phr was greatly beneficial to the cure cycle of the rubber by significantly reducing the optimum cure time (Fig 4.4). The rate of cure benefitted significantly at above 0.342 phr TBBS in the powder with the highest rate, 21.7 min^{-1}, recorded at 0.376 phr TBBS in the powder. But the cure rate index decreased to 18.9 min^{-1} when the TBBS loading in the powder was raised further to 0.383 phr. The powder with 350 mg/g TBBS (equivalent to 0.383 phr in the formulation) was selected for further work because the rubber compound cured with this powder had the largest Δtorque value, and very short scorch and optimum cure times. For this rubber compound, the cure rate index was 18.9 min^{-1} (Table 4.1)

As figure 4.2-4.4 indicated Δtorque and the cure properties of the rubber, i.e. cure rate index, scorch and optimum cure time are very sensitive to the loading of TBBS in the powder. Therefore, It is clear that the TBBS coverage on the ZnO surface is the determining factor in the cure properties of the rubber. When the TBBS loading in the powder exceeds 0.351 phr (fig 4.3) the cure rate index increased quite substantially. Similarly the scorch and optimum cure time decreased noticeably. It is likely that after full surface coverage is achieved some extra TBBS may be available for reaction with sulphur to produce cross links. However, a full study of the surface coverage of ZnO coated by TBBS will shed light on the results in these figures.

4.3.2 Effect of an increasing loading of the powder on the cure properties of the rubber

In this experiment, the amount of TBBS in the powder was kept constant at 350 mg/g (equivalent to 0.383 phr in the formulation). The loading of the powder in the rubber was subsequently raised from 0.63 phr to 5.63 phr. When the cure traces were examined, for the rubber compound with 0.63 phr powder the cure reached equilibrium after 40 minutes (Fig 4.5a). Though, when the loading of the powder was raised to above 0.63 phr, the cure underwent reversion soon after 8 minutes and the cure cycle was a lot shorter. The cure reversion accelerated when the loading of the powder in the rubber kept rising to its highest level, i.e. 5.63 phr (cf. Figures 4.5b and 4.5c).



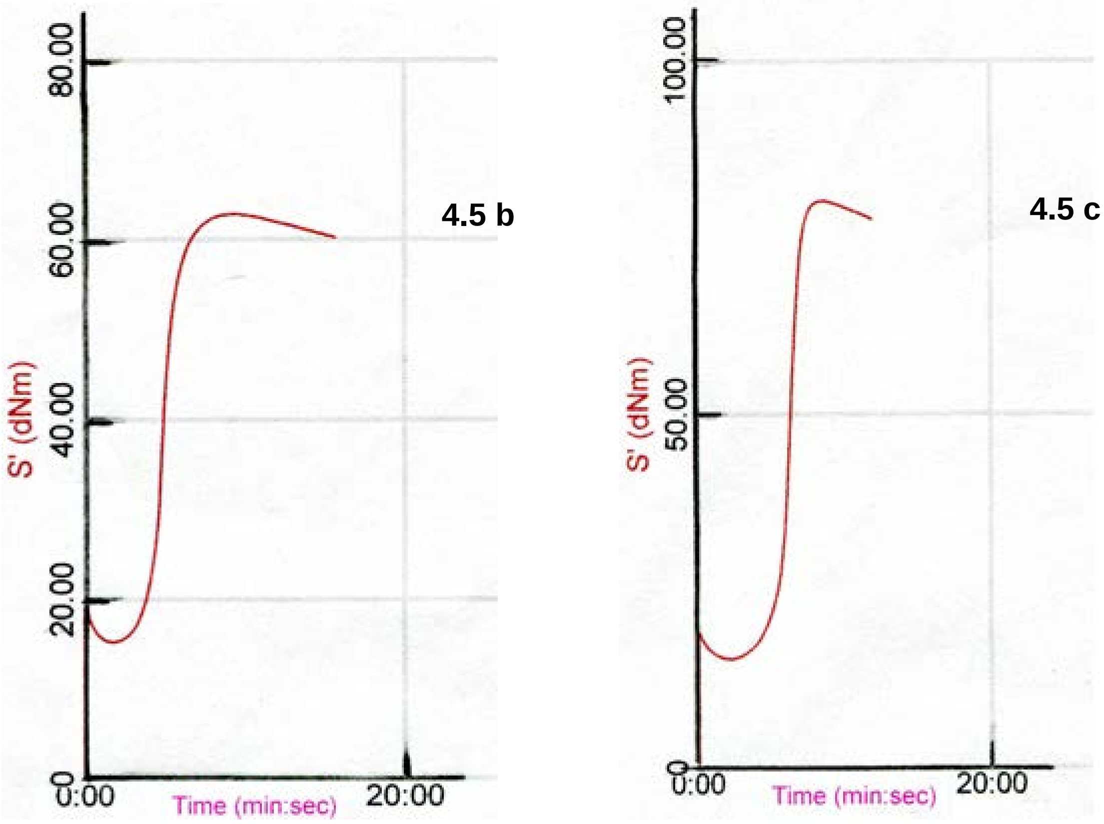


Figure 4.5 Typical cure traces (Torque (dNm) vs Time (min)) of the rubber compounds with an increasing loading of the powder. a) compound with 0.63 phr powder; b) compound with 2.5 phr powder; c) compound with 5.63 phr powder

When solid fillers are added to the rubber they replaced soft rubber and by doing so the viscosity of rubber increased [7]. The increase in viscosity when solid filler is added is due to rubber filler interaction which is due to attractive van der Waals forces. The addition of ZnO is known to increase rubber viscosity [7]. However note that the ZnO used in this work was coated with TBBS and this might have hindered interaction of ZnO with the rubber. However, as fig 4.5 shows the addition of up to 5.63 phr powder has little or no effect on the viscosity of the uncured rubber as indicated by the minimum torque in table 4.2. The minimum torque, T_{min}, was not affected by increase in the loading of the powder in the rubber and remained at around 15-17 dNm. The maximum torque, T_{max}, which shows extend of crosslinks in the rubber, kept rising from 39 to 80 dNm as the loading of the powder was raised from 0.63 to 5.63 phr (Table 4.2). Figure 4.6 shows Δtorque as a function of the powder loading. ∆Torque increased from 22 to 48 dNm when the loading of the powder was raised from 0.63 to 2.5 phr, and it continued rising at a much slower rate to about 65 dNm when the loading of the powder reached 5.63 phr.

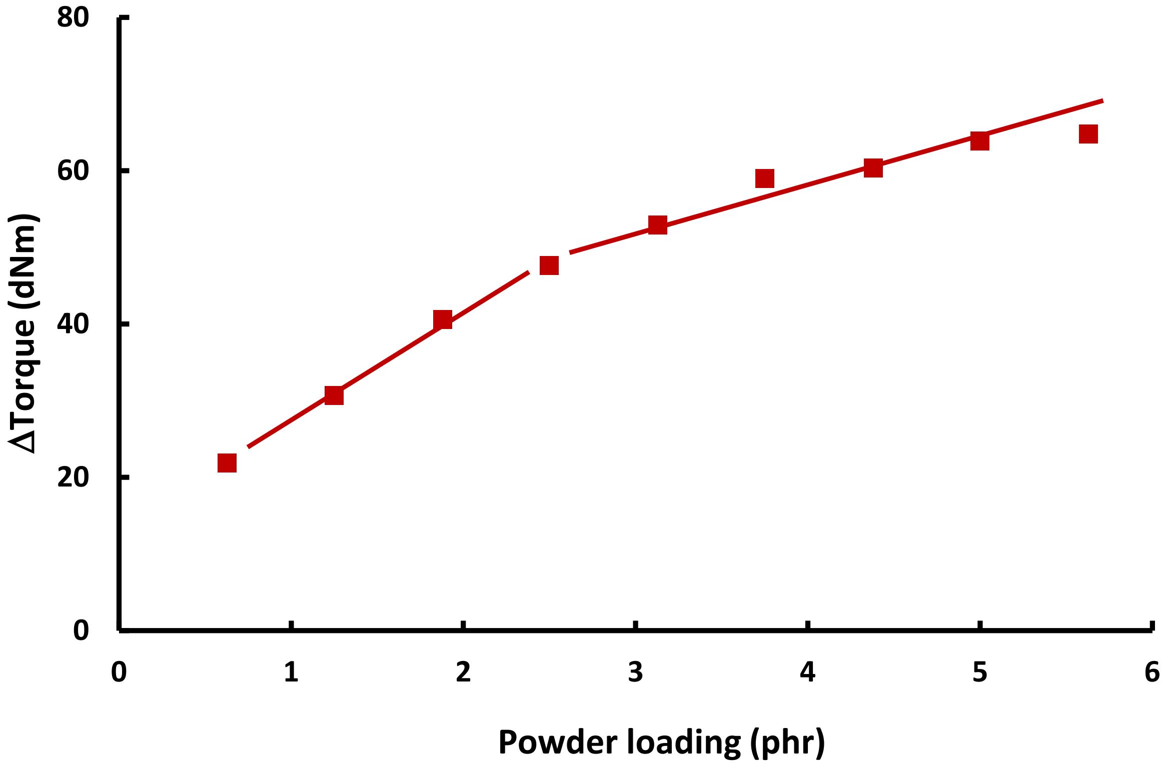


Figure 4.6 ∆Torque vs powder loading for the rubber compounds shown in Table 4.2. Each point on the graph corresponds to one rubber compound

Evidently, the addition of 2.5 phr powder was sufficient to react the sulphur with the rubber to form stable covalent crosslinks or chemical bonds between the rubber chains. As mentioned earlier, the optimum loading of TBBS in the powder was 350 mg/g. Therefore, 26wt% of the powder was TBBS and the remaining 74wt% ZnO. On this basis, the 2.5 phr powder contained 0.65 phr TBBS and 1.85 phr ZnO. In some NR-based industrial articles such as rubber thread and tyre bead filler/apex rubber compound, the loading of accelerators can reach 4.5 phr [5] and that of ZnO to10 phr [6], respectively. Obviously, there is scope to reduce the excessive amount of these chemicals in rubber compounds quite substantially.

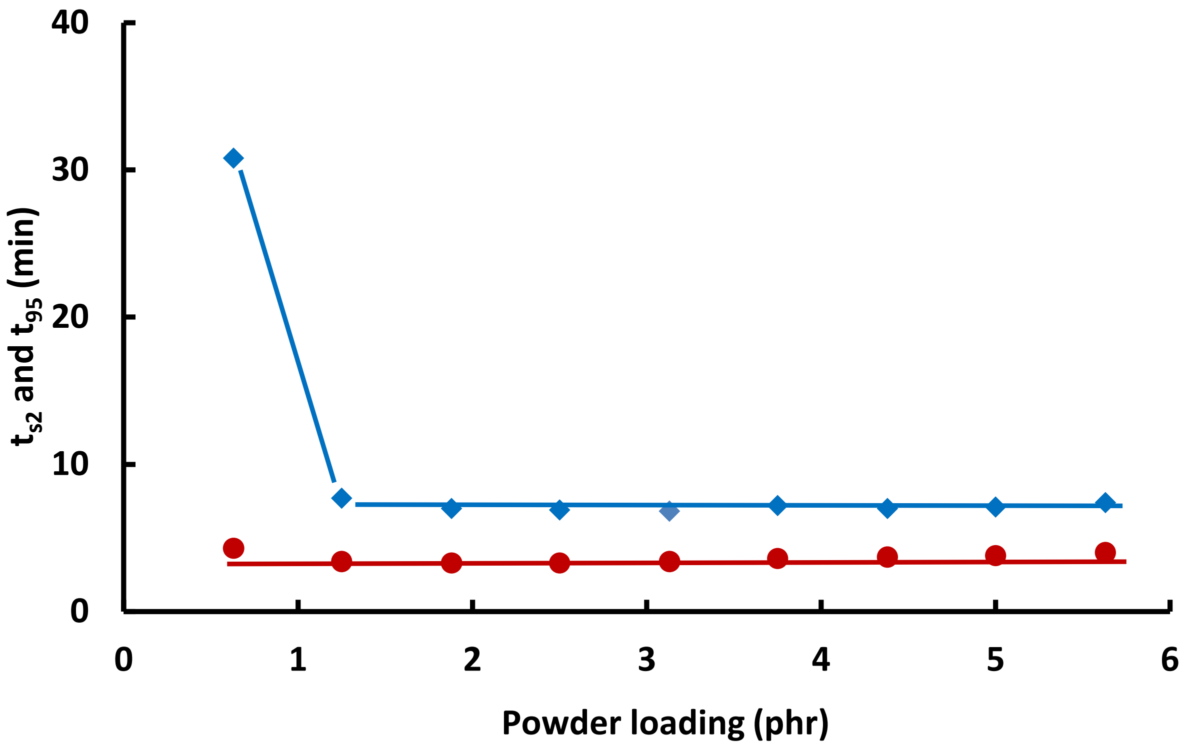


Figure 4.7 optimum cure time, t_{95} and scorch time, t_{s2} vs powder loading for the rubber compounds shown in Table 4.2. Optimum cure time (◆), scorch time (●). Each point on the graph corresponds to one rubber compound

The scorch time was fairly constant about 3.3-4.3 min when the full loading of the powder was added. The optimum cure time decreased sharply from 30.8 to 7.7 min with 1.25 phr powder and afterwards, it showed no obvious trend and remained somewhere between 6.8 and 7.4 min when the loading of the powder was raised to 5.63 phr (Fig 4.7). The rate of cure as indicated by the cure rate index (CRI), benefited significantly from the addition and progressive increase in the amount of the powder. It rose sharply to 23.2 min^{-1} when 1.25 phr powder was added. The increase was about 510%. Afterwards, it continued rising at a much slower rate to 27.8 min^{-1} when the loading of the powder reached 2.5 phr. It subsequently plateaued at about 27.8-30.3 min^{-1} with the full loading of the powder (Fig 4.8). Clearly, above 1.25 phr powder loading, the rate of cure gained not as much, i.e. only 30%.

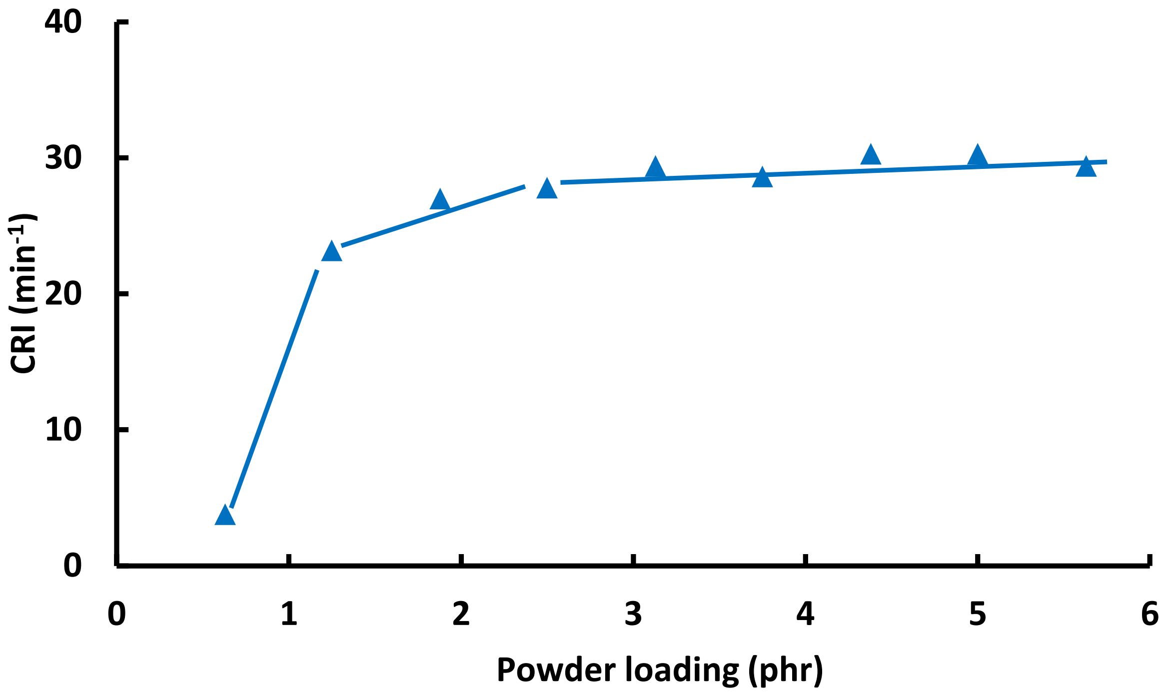


Figure 4.8 cure rate index vs powder loading for the rubber compounds shown in Table 4.2. Each point on the graph corresponds to one rubber compound

4.4 Discussion

For a tyre belt skim compound, which has 5 phr sulphur and 10.7 phr chemical curatives, the scorch time (t_{S2}) and optimum cure time (t_{90}) are 2.6 min and 9.5 min at 160°C, respectively [4]. The cure rate index is 14.5 min^{-1}. It is interesting that with a smaller amount of sulphur, i.e. 4 phr, and only 2.5 phr of the powder (0.65 phr TBBS and 1.85 phr ZnO), shorter scorch and optimum cure times and a much faster rate of cure, i.e. CRI of 27.8 min^{-1}, were recorded for our rubber compound (compound 4, Table 4.2). In fact, 20wt% reduction in sulphur and 77wt% lesser chemical curatives shortened the optimum cure time by 34% (the t_{90} of our rubber compound was 6.3 min) and increased the rate of cure by 130%. But the scorch time (t_{S2}) of our rubber compound was 27% longer than that of the tyre belt skim compound. Note also that no stearic acid was used in the cure system. The trend observed here suggests that a much lesser consumption of the chemical curatives, i.e. TBBS and ZnO, in sulphur vulcanisation, yields significantly shorter cure cycle and hence a more efficient cure. However the increase in ∆torque for tire belt compound was 767% whereas our compound with 2.5 phr increase in ∆torque was 320%, therefore the tire belt skim compound has the high cross link density compound with our compound 4 (2.5 phr) in table 4.2. In addition, for more accurate comparison it is essential that ∆torque should match. Further work is being done to match the ∆torque values by increasing the loading of sulphur in our compounds and measuring the exact amount of the powder loading to the optimum ∆torque values.

Other benefits include improvement in health, safety and the environment as well as major cost reduction. It seems that coating ZnO with TBBS into a single additive is a more efficient method of using these chemicals in rubber vulcanisation than the methods which are currently in use. This has the added advantage of eliminating secondary accelerators and too much ZnO from the cure system. All the signs are that the sulphur cure systems currently in use in industrial rubber compounds such as tyres are basically inefficient, too costly and no longer viable and hence must be improved. Combining the chemical curatives by means of functionalising them undoubtedly is the most effective way in making green compounds for industrial rubber articles.

4.5 Conclusion

Coating ZnO with TBBS to provide a single additive component reduced the excessive use of these chemicals in the sulphur vulcanisations of NR. Some powders were tested and the following conclusions drawn.

1. When the loading of TBBS in the powder was raised progressively to 0.383 phr, the scorch time and optimum cure time of the rubber decreased at 0.351 phr TBBS. The rate of cure as indicated by the cure rate index increased at 0.351 phr TBBS in the powder. The crosslink density as shown by ∆torque rose, reaching its optimum value at 0.383 phr TBBS loading in the powder.
2. When the loading of the powder in the rubber was raised increasingly to 5.63 phr, the scorch time was unchanged and the optimum cure time reduced at 1.25 phr powder. The rate of cure as shown by the cure rate index accelerated at 1.25 phr powder. The crosslink density as indicated by ∆torque rose, reaching its maximum value at 5.63 phr powder.

This study combines ZnO with TBBS by functionalising the surface of zinc oxide with TBBS molecules in an organic solvent to produce a convenient single material referred to as powder to cure some sulphur-filled NR. The optimum loading of the powder to fully cure the sulphur-filled rubber was subsequently measured. Functionalising the surface of ZnO with TBBS reduced the excessive use of these chemicals in the cure system and provided a more efficient way of mixing them with the raw rubber.

4.6 References

1. W Hofmann, “Rubber Technology Handbook”. Hanser Publishers, Munich Germany, 1989. Chapter 2, pp19-20.
2. P A Ciullo and N Hewitt, “The rubber formulary”. Noyes publications, NY, 1999.
3. R N Datta, “Rubber Curing Systems”, Report 144, 12 (12) (2002) pp1-37.
4. R N Datta, “Rubber curing systems”, *Rapra review reports, Report 144* (2002); 12:1-37
5. P A Ciullo and N Hewitt, “The rubber formulary”. Noyes publications, NY, 1999. Pp98.
6. P A Ciullo and N Hewitt, “The rubber formulary”. Noyes publications, NY, 1999. pp78.
7. I M Ulfah, R Fidyaningsih, S Rahayu, D A Fitriani, D A Saputra, D A Winarto, and L A. Wisojodharmo, “Influence of carbon lack and silica filler on the rheological and mechanical properties of natural rubber compound”, Procedia Chemistry 16 (2015) 258-264

Chapter – 5 Kaolin-Filler as a possible reinforcing agent for natural rubber

5.1 Introduction

Carbon black (CB) is one of the most widely used additives in industrial rubber compounds. Some CBs have large surface area, ranging from 30 to140 m^2/g [1], which makes them highly reinforcing and are used extensively in tyres [2]. Mechanical properties such as hardness, tensile strength, tear strength, fatigue life and Young's modulus improved significantly when CB was added to rubber [3]. However, CB is toxic and health risk is associated with its use in rubber compounds [4]. There is a need to replace CB with other less harmful solid fillers. Several studies looked into potential replacement of CB with kaolin (China clay) in rubber compounds. Kaolin has a plate-like structure (Fig 5.1) whereas CB is spherical in shape.

The purpose of this study is to use kaolin pre-treated with MPTS, a new method has been developed that optimises reaction between the sulphur in MPTS on the kaolin surface and natural rubber chains. This reduced excessive use of chemical curatives and improved mechanical properties of the rubber vulcanisate. The Mooney viscosity [7], cure properties [8,9], hardness [10], tensile properties and Young's modulus [11], tear strength [12], and compression set [13] of NR filled with MPTS pre-treated kaolin were measured. The preliminary results indicated that when the reaction between the rubber and kaolin was optimised, the addition of elemental sulphur was the key factor in controlling the rubber properties. This made the MPTS pre-treated kaolin an ideal replacement for CB in tyres.

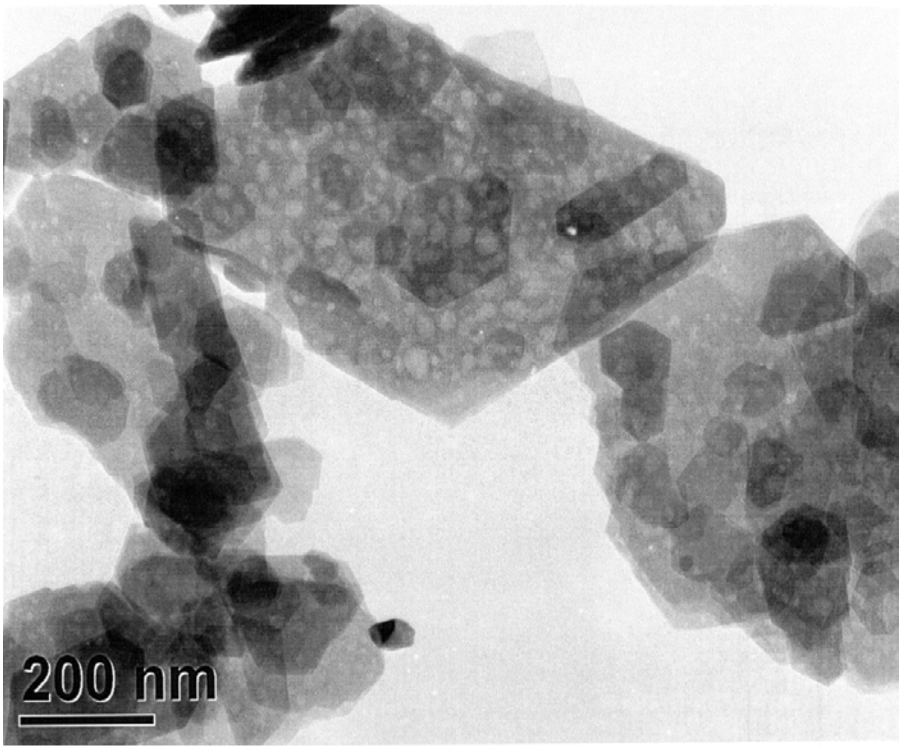


Figure 5.1 TEM micrograph showing kaolin particles [17]

A small amount of kaolin (10 parts per hundred rubber by weight) (phr), was modified with sodium salt of rubber seed oil (SRSO) and mixed with natural rubber (NR). The SRSO-modified kaolin was more strongly bound in a constraint environment within the lamellae of kaolin. The rubber filled with SRSO-modified kaolin cured faster than that of a similar mix containing unmodified kaolin. Besides, the NR vulcanisates containing SRSO-modified kaolin showed considerable increase in tensile modulus, tensile strength, and elongation at break, indicating its potential as organo-modified nanofiller [5]. NR nanocomposites reinforced with 20 to 50 phr of saline-modified kaolin exhibited outstanding mechanical properties and much higher thermal stability compared to the pure NR. The hardness and tensile properties improved with increasing filler loading and an optimum of tensile strength was achieved at the highest loading of the modified kaolin [6]. The cure systems in these compounds consisted of one accelerator, two activators and elemental sulphur [5,6]. Clearly, after surface treatment, kaolin performed better in rubber. Kaolin surface possesses OH groups ($Al_2Si_2O_5(OH)_4$), which make it polar and moisture absorbing. To improve dispersion of the filler particles in rubber, the filler surface is treated with silane. One commonly used silane is 3-mercaptopropyltrimethoxysilane (MPTS) that contains less than 2wt% of sulphur (Fig 5.2). When sulphur reacts with rubber chains in the presence of accelerator and activator, it produces stable covalent sulphur bonds. This in turn enhances the rubber/filler interaction and is immensely beneficial to the rubber reinforcement [6].

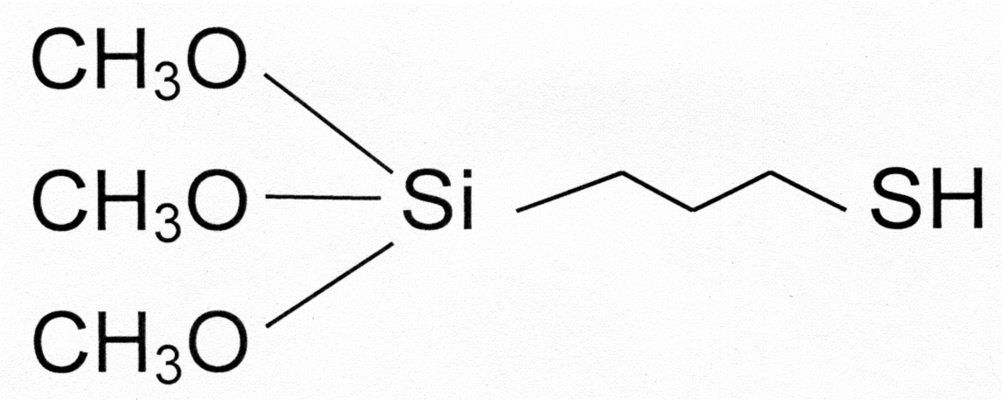


Figure 5.2 Chemical structure of 3-mercaptopropyltrimethoxysilane (MPTS)

Using kaolin pre-treated with MPTS, a new method has been developed that optimises reaction between the sulphur in MPTS on the kaolin surface and natural rubber chains in this work. This reduced excessive use of chemical curatives and improved mechanical properties of the rubber vulcanisate.

5.2 Experimental

5.2.1 Materials and mixing

The raw rubber used was standard Malaysian natural rubber grade L (98 wt. % 1, 4-cis content; SMRL). The reinforcing filler was Mercap 100 (Imerys Ceramics, USA). Mercap 100 is kaolin (China clay) the surface of which had been pre-treated with MPTS and has a 25 m^2/g surface area (measured by N_2 adsorption) (Imerys Ceramics). In addition to the raw rubber and kaolin, the other ingredients were N-tert-butyl-2-benzothiazole sulfenamide (a fast curing delayed action accelerator) (Santocure TBBS, Sovereign Chemical Company, USA), zinc oxide (ZnO; an activator, Sigma-Aldrich Company Ltd, UK), and elemental sulphur (curing agent: Solvay Barium Strontium, Hannover, Germany).

The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small size laboratory mixer with counter rotating rotors. In these experiments, the Banbury rotors and the mixing chamber were initially set at ambient temperature (23^{o}C) and the rotor speed was set at 45 r.p.m. The volume of the mixing chamber was 78 cm^3, and it was 58% full during mixing. Polylab monitor 4.17 software was used for controlling the mixing condition and storing data.

5.2.2 Addition of TBBS to the kaolin-filled rubber

To activate the sulphur in MPTS, TBBS was added. The loading of TBBS in the kaolin-filled rubber was increased from 6 to 30 phr to measure the amount needed to react the sulphur in MPTS with the rubber chains to produce crosslinks and optimise the chemical bonding between the two (Table 5.1). The idea was to add a minimum amount of TBBS to the rubber and produce the largest effect on the ∆torque. ∆Torque (the difference between the maximum and minimum torque values on the cure trace of the rubber) (Fig 5.6a) is an indication of crosslink density changes in the rubber [14,15]. The formation of cross-links may provide good strength between the rubber and filler which is greatly beneficial to the rubber reinforcement [15,16]. In total, 7 rubber compounds were made.

Table 5.1 Formulation of NR compounds filled with 60 phr kaolin and an increasing loading of TBBS

Formulation (phr)	**Compound no**						
	1	**2**	**3**	**4**	**5**	**6**	**7**
SMRL (NR)	100	100	100	100	100	100	100
Kaolin	60	60	60	60	60	60	60
TBBS	6	8	14	16	18	26	30
	ODR test results at 160°C						
Min torque (dNm)	9	7	7	7	7	5	4
Max torque dNm)	16	17	29	33	38	34	32
∆Torque (dNm)	7	10	22	26	31	29	28
Scorch time t_{s2} (min)	39	36.3	34.6	34.9	37.8	37	36.8
Optimum cure time t_{95} (min)	70.7	64.7	61.8	64.5	74.3	76.9	89.9

It has been reported [18] when solid filler is added to raw rubber viscosity will increase. This will depend on strong interaction with the rubber due to attractive van der Waals. However, in the absence of interaction between filler and rubber it is likely that further addition of solid filler may actively reduce the viscosity. The results in Table 5.1 seem to the show this trend. Therefore, the rubber did not adhere to the TBBS solid surface to cause increasing viscosity and had an opposite effect.

5.2.3 Addition of ZnO and elemental sulphur to the kaolin-filled rubber with TBBS

The loading of ZnO was increased progressively from 0 to 2 phr to measure the amount needed to improve the efficiency of TBBS and increase chemical bonds or cross-links between the rubber and MPTS in the kaolin-filled compound (Figure 5.6b). In total, 7 rubber compounds were made Table 5.2. The loading of elemental sulphur was raised gradually from 0 to 4 phr to evaluate its effect on the cure properties of the kaolin-filled rubber compound with TBBS (Figure 5.6c), and the kaolin-filled rubber compound with TBBS and ZnO (Figures 5.7a, 5.7b & 5.7c). In total, 4 rubber compounds were made.

Table 5.2 Formulation of NR compounds filled with 60 phr kaolin, 16 phr TBBS and an increasing loading of ZnO

Formulation (phr)	Compound no.						
	8	**9**	**10**	**11**	**12**	**13**	**14**
SMRL (NR)	100	100	100	100	100	100	100
Kaolin	60	60	60	60	60	60	60
TBBS	16	16	16	16	16	16	16
ZnO	0	0.05	0.1	0.35	1.0	1.5	2.0
	ODR test results at 160°C						
Min torque (dNm)	7	6	7	7	7	7	7
Max torque dNm)	33	22	40	43	44	45	47
∆Torque (dNm)	26	16	33	36	37	38	40
Scorch time t_{s2} (min)	34.9	46	35.4	33.1	34.6	32.7	30.2
Optimum cure time t_{95} (min)	64.5	68.8	68.6	56.3	58.7	58.1	71.2

After these measurements were completed, 5 rubber compounds were prepared for further tests (compounds 1-5; Table 5.3). The raw rubber was placed in the mixing chamber and mixed for 2 min, and then kaolin was put in and mixed for another 8 min. Finally, after 10 min mixing, TBBS, ZnO and elemental sulphur were added and mixed for another 5 min. The total mixing time was 15 min because this time was long enough to fully disperse the kaolin particles in the rubber matrix (Figure 5.3). When mixing ended, the compound was removed from the mixer and allowed to cool down to ambient temperature (21°C). Temperature of the compounds during mixing was 48-58°C. The compounds were kept at ambient temperature (21±2°C) for at least 24 h before their viscosity and cure properties were determined. They were later cured at 160^{o}C for 64 min to produce sheets of rubber approximately 2.4 mm thick and cylindrical samples 5.9 mm thick and 15.3 mm in diameter for measuring mechanical properties and hardness, respectively.

The Mooney viscosity [7], cure properties [8,9], hardness [10], tensile properties and Young's modulus [11], tear strength [12], and compression set [13] of NR filled with MPTS pre-treated kaolin were measured.

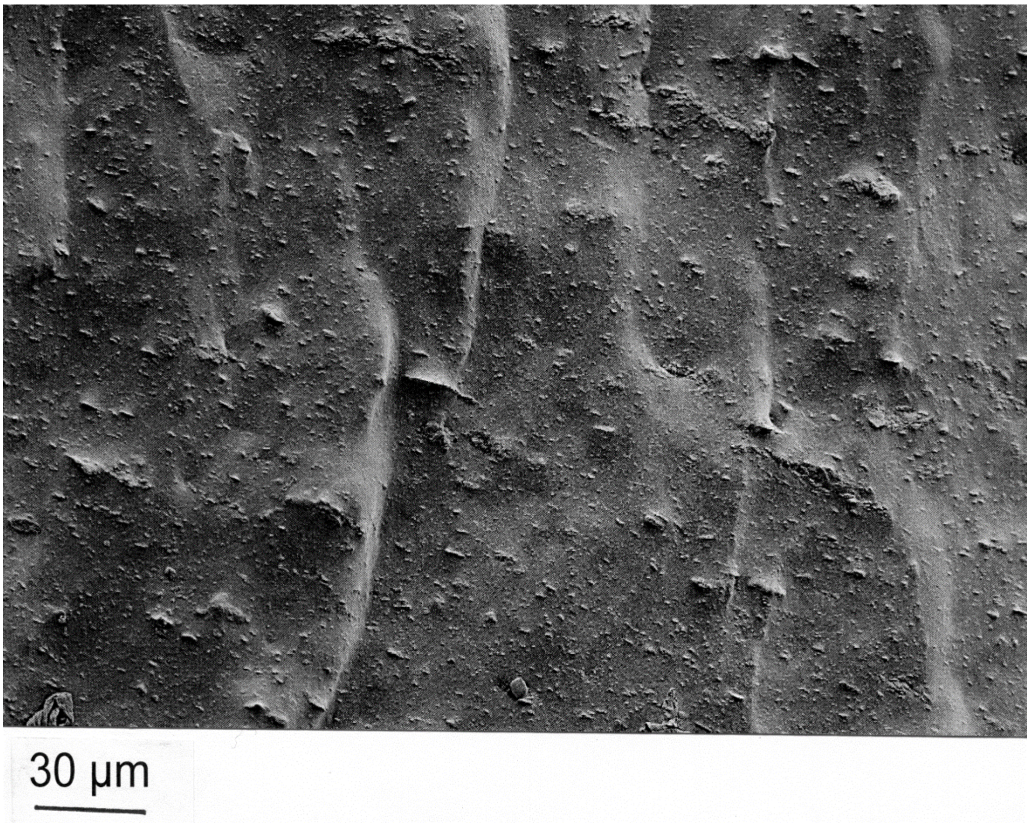


Figure 5.3 SEM micrograph showing dispersion of the kaolin in the rubber after 15 min mixing time [17]

5.3 Results and Discussion

Figure 5.4 shows ∆torque as a function of TBBS loading for the kaolin-filled rubber. ∆Torque increased from 6.5 to 26 dN m as the loading of TBBS was raised from 6 to 16 phr, and it continued rising at a much slower rate to about 27 dN m when the loading of TBBS reached 30 phr. Evidently, the addition of 16 phr TBBS to the kaolin-filled rubber was sufficient to react the sulphur in MPTS with the rubber chains to form cross-links or chemical bonds between the two.

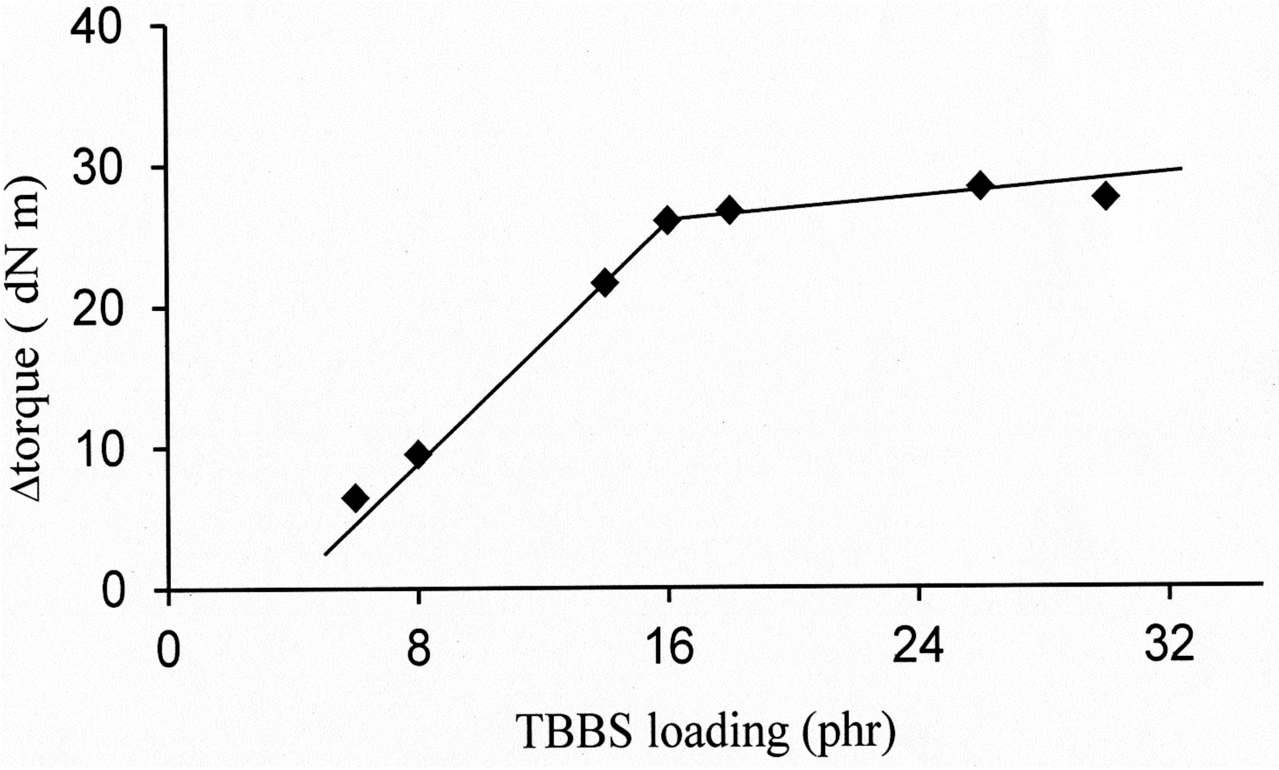


Figure 5.4 ΔTorque versus TBBS loading for the kaolin-filled rubber. Each point on the graph corresponds to one compound

To enhance the efficiency of TBBS in the kaolin-filled rubber, ZnO was added. ΔTorque increased from 26 to 35 dNm when 0.2 phr ZnO was included, and it continued rising at a much slower rate to 40 dNm when the loading of ZnO reached 2 phr (Fig 5.5). The inclusion of 0.2 phr ZnO was sufficient to optimise the efficiency of TBBS and increase chemical bonding between MPTS and the rubber.

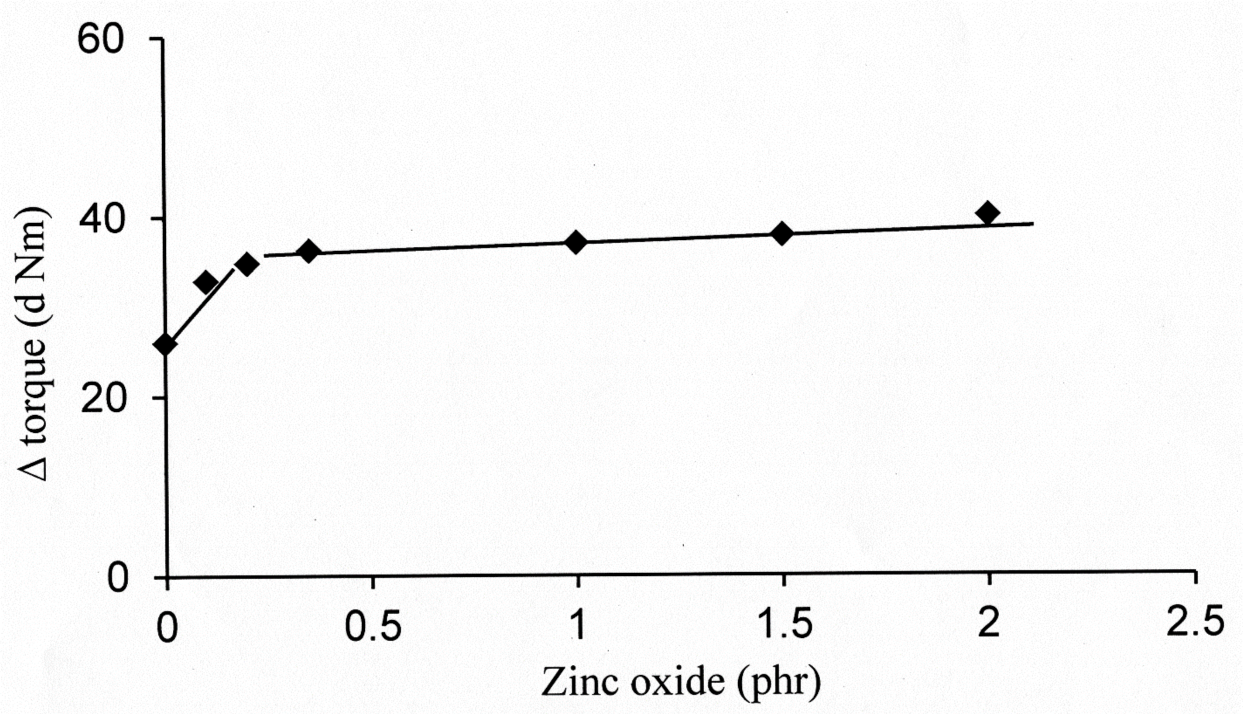


Figure 5.5 ΔTorque versus ZnO loading for the kaolin-filled rubber with 16 phr TBBS. Each point on the graph corresponds to one compound

ΔTorque increased from 26 to 72 dNm when 4 phr of elemental sulphur was added to the kaolin-filled rubber with 16 phr TBBS. The cure characteristics were also affected (Table 5.3). The scorch time, ts2, and optimum cure time, t_{95}, decreased from 35 to 5 min and from 64 to 12 min, respectively. The rate of cure increased sharply, with the cure rate index rising from 3.5 to14.3 min^{-1} (cf. Fig 5.6a and Fig 5.6c).

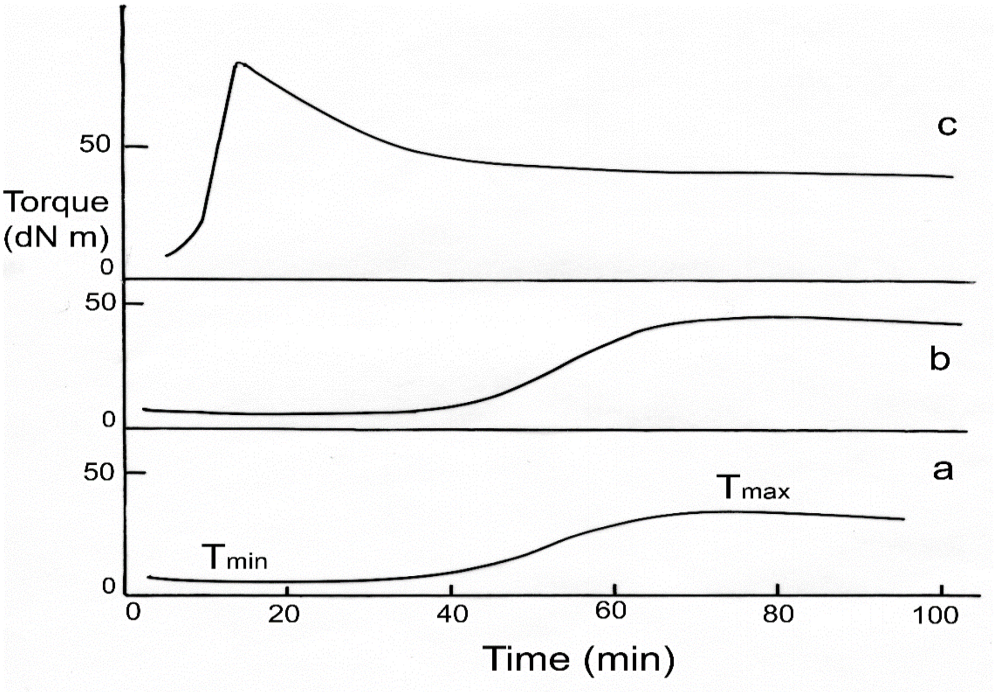


Figure 5.6 Typical cure traces of the kaolin-filled compounds with a) 16 phr TBBS, b) 16 phr TBBS and 0.2 phr ZnO, c) 16 phr TBBS and 4 phr elemental sulphur

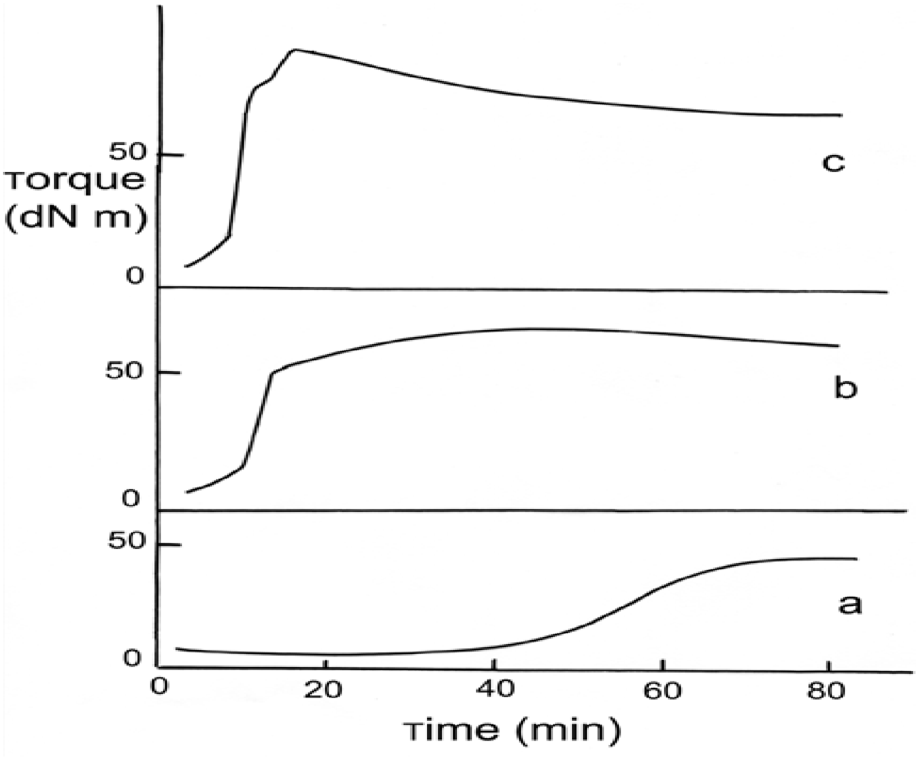


Figure 5.7 Typical cure traces of the kaolin-filled compounds with a) 16 phr TBBS. 0.2 phr ZnO and 0 phr elemental sulphur, b) 16 phr TBBS, 0.2 phr ZnO and 1.5 phr elemental sulphur, c) 16 phr TBBS, 0.2 phr ZnO, and 3 phr elemental sulphur

Probably, the most interesting feature in Figures 5.6a and 5.6c was the fact that the sulphur in MPTS had a much longer reaction cycle, i.e. longer optimum cure time, than elemental sulphur at the same temperature (cf. compound 1 and compound 2; Table 5.3). This highlighted a fundamental problem with the use of sulphur-bearing silane in rubber compounding. In tyre making often silica, liquid silane, e.g. 3-(triethoxysilylpropyl)-tetrasulphane (TESPT), and elemental sulphur are used to reinforce and cure rubber compounds, respectively [3]. Previous studies [15] showed that silica-filled rubber compounds containing liquid TESPT had short optimum cure times when elemental sulphur was present and this did not allow sufficient time for sulphur in TESPT to react fully with the rubber chains to produce strong stable sulphur covalent bonds, which were essential for rubber reinforcement. In this study a similar problem albeit more acutely, was also encountered in the use of MPTS-pre-treated kaolin in NR.

In addition to compounds 1& 2, three more kaolin-filled compounds containing 16 phr TBBS and 0.2 phr ZnO with 0 phr, 1.5 phr and 3.0 phr elemental sulphur were also prepared (compound 3-5; Table 5.3) and cured for 64 min. This allowed sufficient time for the sulphur in MPTS to fully react with the rubber chains and at the same time, the compounds also benefitted from cross-links formed between the rubber chains when elemental sulphur was added. The mechanical properties of compounds 3-5 were later measured (Table 5.3). Compounds 1 and 2 were excluded from further work. Note that only one accelerator, one activator and elemental sulphur were used to cure the rubber compounds. Traditionally, two accelerators and two activators have been used with elemental sulphur to cure rubber compounds for tyres [3].

Table 5.3 Rubber formulations and Mooney viscosity, ODR test results at 160^{o}C hardness, tensile properties, Young's modulus, tear strength, and compression set carried out on the 3 rubber compounds

Formulation (phr)	**Compound no.**				
	1	**2**	**3**	**4**	**5**
SMRL (NR)	100	100	100	100	100
Kaolin	60	60	60	60	60
TBBS	16	16	16	16	16
ZnO	0	0	0.2	0.2	0.2
Elemental Sulphur	0	4	0	1.5	3.0
ODR test results at 160^{o}C					
Minimum torque T_{min} (dNm)	7	8	6	7	7
Maximum torque T_{max} (dNm)	33	80	41	67	88
ΔTorque (dNm)	26	72	35	60	81
Scorch time, ts_2 (min)	35	5	34	6	6
Optimum cure time, t_{95} (min)	64	12	65	35	15
Cure rate index (min^{-1})	3.5	14.3	3.2	3.5	11.1
Mooney viscosity, hardness, tensile properties, Young's modulus, tear strength, and compression set carried out on the 3 rubber compounds					
Mooney viscosity ML (1+4) at 100^{o}C	-	-	26	27	28
Hardness (Shore A)	-	-	36	53	58
Tensile strength (MPa)	-	-	11.7	12.7	8.6
Elongation at break (%)	-	-	1025	721	608
Stored energy density at break (MJ/m^{3})	-	-	50.4	45.0	29.4
Youngs modulus (MPa)	-	-	2.3	3.5	3.9
Tear energy (kJ/m^{2})	-	-	9.8	7.5	7.0
Range of values (kJ/m^{2})	-	-	9.2-10.1	6.6-7.8	6.4-9.6
Compression set (%)	-	-	76	47	42

Compounds 3, 4 and 5 were cured for 64 min.

The properties that gained the largest benefit from the addition of elemental sulphur to the kaolin-filled rubber with 16 phr TBBS and 0.2 phr ZnO were hardness, Young's modulus and compression set. The hardness increased by 61%, the Young's modulus by 70% and the compression set decreased by 42% when the full amount of elemental sulphur was added. The tensile strength showed a marginal improvement, i.e. 9%, when 1.5 phr of elemental sulphur was included and then deteriorated by 32% after the amount of elemental sulphur reached its full amount. The elongation at break, stored energy density at break, and tear energy reduced by almost 41%, 42%, and 29%, respectively when up to 3 phr elemental sulphur was incorporated into the rubber (cf. compound 3 with compound 4 and compound 5; Table 5.3).

In a study, silica, nanoclay and carbon black filled (EPDM) mixtures were prepared and subsequently vulcanised. Rheological property measurements indicated the storage modulus, loss modulus, and complex dynamic viscosity of silica-filled EPDM mixtures were much higher than those of CB-filled EPDM mixtures. The optimum cure time of silica- and nanoclay-filled EPDM mixtures increased with filler loading, whereas the values for CB-filled mixtures slightly decreased with loading. The hardness, modulus, elongation at break, and tensile strength of all the vulcanisates increased with increasing filler loading. The elongation at break of CB-filled EPDM vulcanisates increased insignificantly with CB loading. Among the three fillers, the increase of the tensile strength and elongation at break was most significant for silica-filled EPDM vulcanisates. Remarkably, for 30 phr silica-filled EPDM vulcanisates, a tensile strength and elongation at break of 23.5 MPa and 1045% was achieved, respectively [19]. Therefore to conclude, MPTS pre-treated kaolin could be a viable replacement for CB in tyre applications and besides, adding elemental sulphur is the key factor in controlling the mechanical properties of the rubber.

5.4 Conclusions

1. To react the sulphur in MPTS on the kaolin surface with the NR chains and optimise the reaction between the two, 16 phr TBBS and 0.2 phr ZnO were added to the kaolin-filled rubber.

2. The hardness and Young's modulus increased and compression set decreased when up to 3 phr elemental sulphur was included in the kaolin-filled rubber with 16 phr TBBS and 0.2 phr ZnO. The tensile strength, elongation at break, stored energy density at break, and tear energy of the rubber vulcanisate reduced when elemental sulphur was added. Notably, the inclusion of elemental sulphur was the key factor in controlling the rubber properties.

3. The preliminary results indicated that when the reaction between the rubber and kaolin was optimised, the addition of elemental sulphur was the key factor in controlling the rubber properties. This made the MPTS pre-treated kaolin an ideal replacement for CB in tyres.

From the current study, sulphur-bearing silanised mineral kaolin solid filler as a possible replacement for toxic carbon black in rubber reinforcement was investigated. This method reacts the sulphur in the silane with the NR chains to produce stable covalent sulphur bonds between the two which is essential for rubber reinforcement. The optimum loading of TBBS required for reacting the sulphur in the silane with the rubber phase was first measured and then an optimum amount of ZnO was also added to improve the efficiency of the TBBS reaction with the sulphur in the silane to achieve full cure of the rubber.

5.5 References

1. L H Cohan, “The mechanism of reinforcement of elastomers by pigments”, Rubb. Chem. Technol., 21, pp667-681, (1948)
2. J B Donnet, “Black and white fillers and tyre compound”, Rubb. Chem. Technol., 71, pp323-341, (1998)
3. J T Byres, “Fillers for balancing passenger tyre tread properties”, Rubb. Chem. Technol., 75, pp527-547, (2002)
4. J Hallet, G Moninot, “Proceedings of the 7th International Conference on Rubber Chemicals, Compounding and Mixing”, Vienna, Austria, Smithers Rapra Ltd, paper 1, pp1-6, (2010)
5. R Sukumar, & A R R Menon, “Organomodified kaolin as a reinforcing filler for natural rubber”, J. Appl. Polym. Sci., 107, pp3476-3483, (2008)
6. Q Zhang, Y Zhang, & Y Wang, “Mechanical and thermal properties of kaolin/Natural rubber nanocomposites prepared by the conventional two-roll mill method”, Appl. Mech. & Mater., 164, pp142-145, (2012)
7. British standard 1673: Part 3, (1969)
8. British standard 1673: Part 10, (1977)
9. British standard 903: Part A60: Section 60.1, (1996)
10. British standard 903: Part A26, (1995)
11. British standard 903: Part A2, (1995)
12. British standard 903: Part A3, (1995)
13. British standard 903: Part A51, (1986)
14. S Wolff, U Görl, M J Wang, W Wolff, “Silica-based tread compounds”, Eur. Rubb. J. 16, pp16-19, (1994)
15. S Wolff, “Chemical aspects of rubber reinforcement by filler”, Rubb. Chem. Techno., 69, pp325-346, (1996)
16. S Ostad-Movahed, K Ansar Yasin, A Ansarifar, M Song, S Hameed, “Comparing effects of silanized silica nanofiller on the crosslinking and mechanical properties of natural rubber and synthetic polyisoprene”, J. Appl. Polym. Sci., 109, pp869-881, (2008)
17. S H Sheikh, A Ansarifar, “Carbon black alternative”, Tire Technology International, pp 96-100, (2015)
18. I M Ulfah, R Fidyaningsih, S Rahayu, D A Fitriani, D A Saputra, D A Winarto, and L A. Wisojodharmo, “Influence of carbon lack and silica filler on the rheological

and mechanical properties of natural rubber compound", Procedia Chemistry Vol.16, pp258-264, (2015)

19. H Tan, A I Isayev, "Comparative study of silica, nanoclay and carbon black filled EPDM rubbers", *Journal of Applied Polymer Science*, Vol. 109, pp 767–774 (2008)

Chapter – 6 The potential of kaolin as reinforcing filler for rubber composites with new sulphur cure systems

6.1 Introduction

Solid fillers and curing chemicals perform two distinct functions in rubber compounds. Fillers increase the dynamic and mechanical properties [1-2] and curing chemicals produce crosslinks between the rubber chains at elevated temperatures, i.e., 140-220^{o}C [3-4]. Since the discovery of their reinforcing qualities almost 100 years ago, petroleum-based colloidal carbon blacks (CB) have been used extensively in rubber reinforcement [5-6]. The term reinforcement is defined as the increases in properties such as tensile strength, tear strength, hardness, abrasion resistance and modulus [7]. Synthetic silicas have been replacing CBs in some applications for example tyre tread compound [8] and proved to be as effective as CBs. However, the surfaces of silicas possess siloxane and silanol groups, which make the filler acidic [9] and moisture adsorbing [10]. Acidity and moisture are both detrimental to the cure of rubber compounds [11] and can also cause loss of crosslink density in sulphur-cured rubbers [12]. Bifunctional organosilanes, known also as coupling agent, remedy the problems aforementioned and are used to enhance the reinforcing capability of silicas in rubber [12]. Other fillers such as layer silicates [13-18], carbon nanotubes [19-21], and exfoliated graphene [22-23] have been intensively researched as a potential reinforcing agent in rubber. Several examples of reviews [24-27] suggest that the nanofillers mentioned above are a promising reinforcing agent to improve mechanical and dynamic properties of rubber particularly at low filler loading. Among the fillers, hydrous aluminium phyllosilicates or clay minerals such as montmorillonite (MMT) and kaolin have received much attention in recent years because they are relatively inexpensive and also non-carcinogenic. Since MMT consists of a triple-layer sandwich structure, hence its dispersion mechanism in rubber is different from carbon black and silica which have a spherical shape [28]. As reported in literature [28-32] intercalation and exfoliation morphologies are used to characterise the clay layer dispersion in clay/polymer nanocomposites. The latter morphology is more desirable due to its high surface area, which is important in rubber reinforcement. Nevertheless, producing a high level of clay dispersion in rubber is still a challenge.

Several studies have looked into potential replacement of CB and silica with kaolin. Similar to silica, the kaolin surface possesses OH groups, which makes it polar and moisture adsorbing. To improve dispersion of the kaolin particles in rubber, the filler surface is often treated with silane [33].

In a study, importance of the surface organo-modification of kaolin was demonstrated [34]. Metal salt of rubber seed oil (RSO-Na) was used to modify kaolin and then was introduced into NR. Rubber composites mixed with various compositions of pristine and modified kaolin (2-10 phr) were then prepared and tested. The results showed that the modified kaolin improved the cure and mechanical properties of the rubber composite compared to the pristine kaolin-filled rubber. For example, the viscosity and hardness increased with increase in filler concentration. Furthermore, the extent of crosslink density and rubber-filler interaction also improved. It was concluded that the presence of the modified kaolin resulted in the formation of a higher number of crosslinks, which was attributed to the confinement of the rubber chains within the silicate galleries and consequently, to better interaction between the filler and the rubber.

Typical rubber formulation for commercial products such as NR-based conveyor belt cover consists of up to eleven different chemical additives including cure system and reinforcing filler. The cure system is made of sulphur, three accelerators (primary and secondary), and primary and secondary activators (zinc oxide and stearic acid), respectively), adding up to 9.7 parts per hundred rubber (phr) by weight [35]. The reinforcing filler is carbon black (CB) [35]. In any rubber formulation, chemical curatives and solid fillers are indispensable. The former provides shape stability and the latter, reinforcement of the dynamic and mechanical properties of the cured rubber, which is essential for the performance, durability and life of the final product in service [36-37].

The aim of this study was to investigate effect of up to 140 phr of kaolin modified with a mercaptosilane on the viscosity, cure and mechanical properties of some commercially important rubber composites. The study used a new method described in chapter 3 for measuring the exact amount of the chemical curatives required in the sulphur vulcanisation of the rubbers. The idea was to substantially reduce the usage of these harmful chemicals and replace toxic carbon black and silica/silane filler systems with the much safer mineral kaolin.

6.2 Experimental

6.2.1 Materials and mixing

The raw rubbers used were NR, BR and EPDM. Full details were provided in the Experimental section of Chapter 3. The reinforcing filler was Mercap 100 the surface of which had been pre-treated with 3-mercaptopropyl-trimethoxysilane (MPTS) to reduce its polarity and prevent it from adsorbing moisture. As mentioned earlier, surface polarity and moisture are detrimental to the dispersion of filler particles in rubber and sulphur vulcanisation of rubber compounds [9-12]. MPTS contains less than 2wt% of sulphur. Mercap 100 has a very fine particle size of about 0.3 micron and 25 m^2/g surface area measured by nitrogen adsorption (Imerys Ceramics, USA). It contains approximately 90 parts per million (ppm) of sulphur, which primarily comes from trace secondary minerals, mainly pyrite (FeS_2) with a melting point of 1,100^{o}C. The kaolin was supplied in a plastic bag. The powder was placed in an oven at 80^{o}C for at least 48 h to remove moisture if any before mixing it with the rubbers.

In addition to the raw rubbers and kaolin, the other ingredients were elemental sulphur (curing agent, Solvay Barium Strontium, Hannover, Germany), TBBS accelerator, ZnO activator, and N-(1,3-dimethylbutyl)-N′-phenyl-*p*-phenylene-diamine (6PPD) (an antidegradant with a melting point of 45-51^{o}C, Santoflex 13, Brussels, Belgium).

The raw rubbers were mixed with the chemical ingredients in a Haake Rheocord 90. To prepare the unfilled NR, BR and EPDM compounds, the raw rubber was introduced first into the mixer and mixed for 1 min and then sulphur, TBBS, ZnO, stearic acid and antidegradant were added and mixed for another 12 min. A similar procedure was used for making the kaolin-filled compounds where kaolin was added 3 min after mixing started. The temperature of the compounds during mixing was 58-62°C. Table 6.1 shows the rubber formulations, their viscosity and cure properties.

Table 6.1 Formulations, Mooney viscosity and cure properties of the rubber compounds

Formulation (phr)	Compound no						
	1	2	3	4	5	6	7
NR*	100	100	100	-	-	-	-
BR*	-	-	-	100	100	-	-
EPDM*	-	-	-	-	-	100	100
Sulphur	4	4	4	0.5	0.5	1	1
TBBS	3.5	3.5	3.5	1.75	1.75	1	1
ZnO	0.2	0.2	0.2	0.2	0.2	0.075	0.075
Santoflex 13	1	1	1	1	1	1	1
Kaolin	0	60	140	0	60	0	60
Mooney viscosity	**ML(1+4, 100^{o}C)**						
	44	52	85	42	66	70	89
	Curemeter data at 160^{o}C						
T_{min} (dNm)	12	15	20	15	19	16	19.5
T_{max} (dNm)	55	79	89	87	75	71	64
ΔTorque (dNm)	43	64	69	72	56	55	44.5
t_{s2} (min)	4.7	3.2	2.1	11.3	3.5	6.2	2.6
t_{95} (min)	8.3	4.8	3.1	47.5	12.5	21.5	40
CRI (min^{-1})	27.8	62.5	100	2.8	11.1	6.5	2.7

*The viscosity of the raw NR, BR and EPDM rubbers were 89, 46, and 88 MU, respectively.

In chapter 5 the reaction between the sulphur in the silane present on the surface of kaolin was reacted with the rubber chain by first adding on increasing loading of TBBS and then ZnO. In the first instant the optimum loading of TBBS was reacting the sulphur in the silane with the rubber was determined by plotting Δtorque against the TBBS loading to optimise the efficiency of TBBS reaction with the sulphur. To produce chemical sulphur cross links with the rubber ZnO was added. The loading of ZnO was increased to determine the optimum loading. However, In Chapter 6 the cure system was determined in the absence of kaolin and elemental sulphur was used as curing agent. In each case Δtorque was plotted against the TBBS loading. To determine optimum loading of TBBS and then ZnO was added to optimise the efficiency of TBBS and the correct amount of TBBS and ZnO for optimum cure kaolin was then added to reinforce the rubber.

6.2.2 Viscosity, cure properties, hardness, tensile properties, tear energy and compression set of the rubber vulcanisates

The viscosity, cure properties, hardness, tensile properties and tear energy of the rubbers were measured according to the procedures described in the British Standards.

- Viscosity: British Standard 1673, Part 3 (1969), using a Mooney viscometer (Wallace Instruments, Surrey, UK) and the results were expressed as Mooney Units (MU).
- Cure properties: British Standard 1673: Part 10 (1977), using oscillating disc rheometer curemeter (ODR, Monsanto, Swindon, UK) at 160 ± 2^{o}C. From the cure traces (e.g. Fig 6.1), scorch time, ts_2, which is the time for the onset of cure, and the optimum cure time, t_{95}, which is the time for the completion of cure were determined. ΔTorque which is the difference between the maximum and minimum torque values on the cure trace of a compound and is an indication of crosslink density changes in the rubber [38] was also measured. Δtorque was afterwards plotted against the loading of TBBS, ZnO, and stearic acid.
- Cure rate index (CRI): British Standard 903: Part A60: Section 60.1. (1996). CRI is an indication of the rate of cure in the rubber.
- Hardness*:* British Standard 903: Part A26 (1995), using cylindrical samples 6 mm thick and 15 mm in diameter, in a Shore A Durometer hardness tester (The Shore Instrument & MFG, Co., New York). The test temperature was 23.5^{o}C.
- Tensile stress-strain properties (tensile strength, elongation at break, stored energy at break and Young’s modulus: British Standard 903: Part A2 (1995), in a LR50K plus materials testing machine (Lloyd Instrument, UK), using standard dumbbell test pieces. Lloyd Nexygen 4.5.1 was used to process and store the data. The test temperature was 22^{o}C and the crosshead speed was set at 100 mm/min.
- Tear energy: British Standard 903: Part A3 (1995), in a LR50K plus materials testing machine (Lloyd Instruments, UK), using trouser test pieces. The test temperature was at ambient (23^{o}C), tear angle 180^o, and crosshead speed was set at 50 mm/min.
- Compression set: British Standard 903: Part A6 (1992), in circular steel compression set jig, 210 mm in diameter, at 25% compression for 24 h at 70^{o}C,

using cylindrical samples 6 mm thick and 15 mm in diameter. At the end of each test, the sample was removed and allowed to cool down at room temperature (20^{o}C) for 30 min before the set was measured.

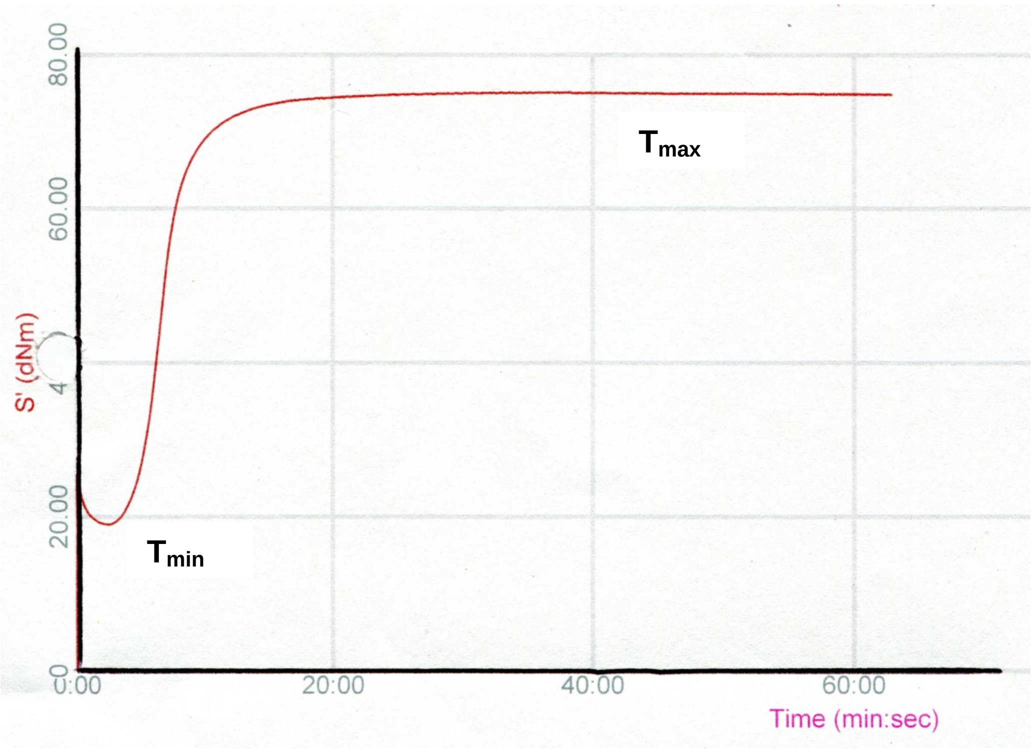


Figure 6.1 typical torque vs time cure trace produced by ODR at 160^{o}C. Data for compound 5 in Table 6.1 ΔTorque = $T_{max} – T_{min}$

6.2.3 Glass transition temperature of the rubber composites

When solid filler is added to rubber for e.g. kaolin, it interacts with rubber chains. This interaction could be either chemical for e.g. formation of sulphur bonds between the rubber and filler as described in chapter 5 or it could be physical interaction due to van der Waal forces. To assist the effect of the filler on the rubber T_g is essential to determine how solid filler affect glass transition temperature. Tan δ is the ratio between loss modulus and elastic modulus. The loss modulus represents the viscous component of modulus and includes all the energy dissipation processes during dynamic strain. The loss modulus, storage modulus and tan δ were measured in DMAQ800 model CFL-50 (TA Instruments, USA), using Universal Analysis 2000 Software Version 4.3A. Test pieces 35 mm long, 10 mm wide and approximately 2.8 mm thick were used. The tests were performed at 1Hz frequency. The samples were deflected 256 µm (nominal peak to peak displacement) during the test, and the sample temperature was raised from -130°C to 30°C at 3°C/min steps. The measurements were repeated to ensure reproducibility of the results. The glass transition temperature of the rubber composites was subsequently determined from the peak values on the tanδ vs temperature traces (Fig 6.10).

6.2.4 Swelling tests in solvent

The organic solvent used for the swelling tests was a laboratory reagent grade Toluene (Fisher Scientific, UK). In these tests, approximately 1.5 g of rubber was placed in 60 ml of the solvent in labelled bottles and allowed to swell for 50 days at 20°C. The weight of the sample was measured every day until it reached equilibrium. The mass of the rubber in the kaolin-filled sample was calculated before it was placed in the solvent. Increase in the weight of the sample in the solvent was attributed to the swelling of the rubber phase. This excluded the dilution effect of the unswellable rigid kaolin from the measurements. The degree of swelling or solvent intake of the rubber in percentage was calculated, using the following expression:

$$\text{Degree of swelling} = \frac{Wsr - Wdr}{Wdr} \times 100 \qquad (1)$$

where W_{sr} is the weight of the swollen rubber and W_{dr} the weight of the dry rubber in the sample.

6.2.5 X-ray diffraction analysis of the kaolin powder and internal structure of the NR composites

The X-ray diffraction (XRD) patterns of the layered kaolin and NR composites (compounds 1-3; Table 6.1) were produced on a Bruker D2 diffractometer (Bruker, Germany). The diffractometer was equipped with Cu Kα radiation (λ= 0.15418 nm), 10 mA of current and 30 kV of voltage. A minimum of 3 g of dried kaolin powder was used to carry out the X-ray analysis of the mineral clay. Square flat sheets, 20 mm by 20 mm and 2.8 mm thick, of the cured rubbers were used for the X-ray analysis of the NR composites. The experiment was performed at low angle in the range 2θ = 1-10°C with the scan rate of 0.02°/s. In addition, the spacing between the structural layers of the kaolin was measured according to the Bragg's law (eq. (2)),

$$n \lambda = 2 d \sin \theta \qquad (2)$$

where n is an integer, λ is the X-ray wavelength, d is the interlayer spacing, and θ is the angle of diffraction. Some XRD diffraction patterns of the solid kaolin particles and NR composites were subsequently produced (Fig 6.8 and Fig 6.9).

6.2.6 Assessment of the kaolin filler and dispersion of the kaolin particles in the rubbers by electron microscopy

The kaolin was investigated by a transmission electron microscope (TEM) model 2000FX (JEOL, Japan). A small amount of the dry kaolin powder, approximately 0.1 g in weight, was placed in a glass tube and mixed with 3 ml of a HPLC grade methanol solvent (Fisher Scientific, UK). The glass tube was then placed in an ultrasonic machine for 15 minutes in order to disperse the kaolin particles in the solvent. After this time elapsed, an electron transparent standard holey carbon film 10-20 nm thick was placed on a copper mesh grid 25 microns thick for TEM samples and inserted in the tube to collect the kaolin nanoparticles. The grid was recovered and placed on a clean tissue paper to remove excess solvent and left in a clean cabinet at room temperature (~20^{o}C) for 24 hours to allow the solvent to fully evaporate before placing it in the TEM. Some micrographs were then prepared for final analysis (Fig 6.6).

To select a suitable mixing time for incorporating the kaolin in the rubbers, the mixing time was increased to 24 min to disperse the kaolin particles fully in the rubber. Twenty-four hours after the mixing ended, the rubbers were examined in a scanning electron microscope (SEM) to assess the filler dispersion. Dispersion of the kaolin particles in the rubber was assessed by a Cambridge Instruments Stereo scan 360 Tungsten filament scanning electron microscope. Small pieces of the uncured rubber were placed in liquid nitrogen for 3 min and then fractured to create two fresh surfaces. The samples, 9 mm^2 in area and 7 mm thick, were coated with gold and then examined and photographed in the SEM. The degree of dispersion of the kaolin particles in the rubber was then studied from SEM micrographs. After the micrographs were examined, a total mixing time of 13 min was found to be sufficient to fully disperse the kaolin particles in the rubbers (Fig 6.7). This mixing time was then used to make rubber compounds for this study.

6.3 Results and discussion

Three cure systems were selected for further work. For NR, the cure system consisted of 4 phr sulphur, 3.5 phr TBBS, and 0.2 phr ZnO; for BR, 0.5 phr sulphur, 1.75 phr TBBS and 0.2 phr ZnO; for EPDM, 1 phr sulphur, 1 phr TBBS and 0.075 phr ZnO. The procedure for measuring the optimum loading of TBBS and ZnO in the sulphur filled NR, BR and EPDM rubber were described fully in chapter 3. To protect the rubbers against environmental ageing, 1 phr antidegradant (6PPD) was also added. Note that there were only three chemicals in the cure systems, i.e. sulphur, TBBS and ZnO, which added up to 7.7 phr in the NR compounds, 2.45 phr in the BR compounds and 2.075 phr in the EPDM compound. This is a significant reduction both in the number and amount of the chemicals in the cure system. In addition to the chemical curatives, the NR compounds had 60 and 140 phr kaolin and the BR and EPDM compounds 60 phr kaolin (compounds 1-7, Table 6.1). These compounds were mixed as described already and their viscosity and cure properties measured. They were then cured at 160^{o}C and their hardness, tensile properties and tear energy determined.

6.3.1 Effect of kaolin on the viscosity and cure properties of the rubber compounds

The inclusion of kaolin affected the viscosity and cure properties of the rubbers not in the same way. The viscosity of NR increased from 44 to 85 MU when 140 phr kaolin was added (Fig 6.2). A similar trend was also observed for BR and EPDM where the viscosity rose from 42 to 66 MU and from 70 to 89 MU, respectively after 60 phr kaolin was mixed (Table 6.1). This was expected, since the inclusion of solid particles in raw rubber raises the rubber viscosity [39].

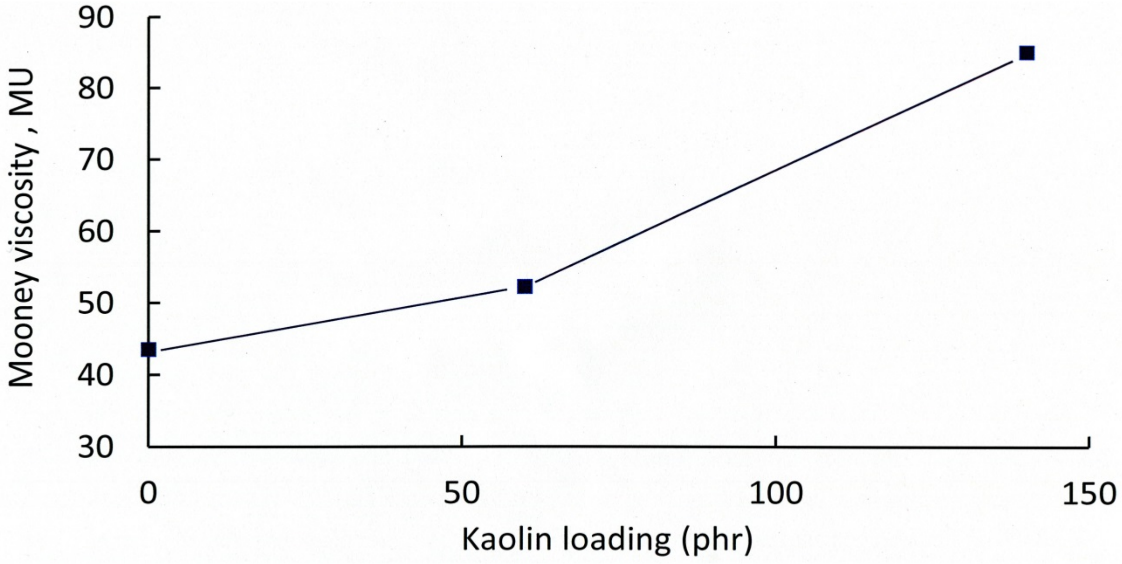


Figure 6.2 Mooney viscosities versus kaolin loading for composites 1-3 in Table 6.1

The t_{S2} and t_{95} of NR shortened from 4.7 to 2.1 min and 8.3 to 3.1 min, respectively with 140 phr kaolin (Fig 6.3).

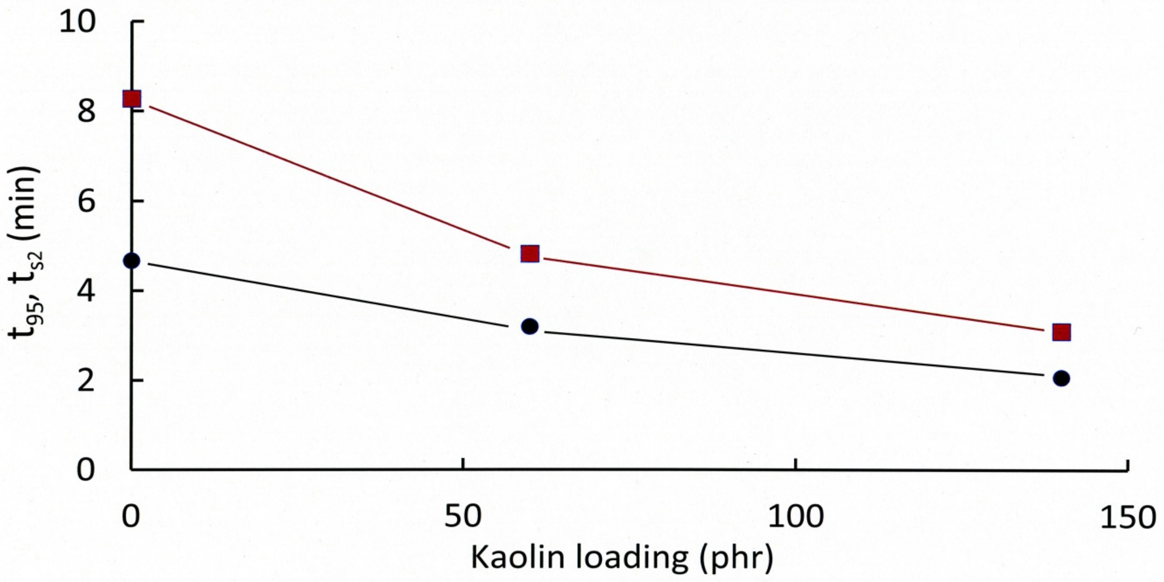


Figure 6.3 Optimum cure time, t_{95} and scorch time, t_{S2} versus kaolin loading for composites 1-3 in Table 6.1. Optimum cure time (🟥), scorch time (●)

The rate of cure as indicated by CRI benefitted greatly from kaolin and increased from 27.8 at 0 phr kaolin to 100 min^{-1} at 140 phr kaolin loading (Fig 6.4). Probably, this was the highest cure rate ever reported for a sulphur-cured NR-based compound.

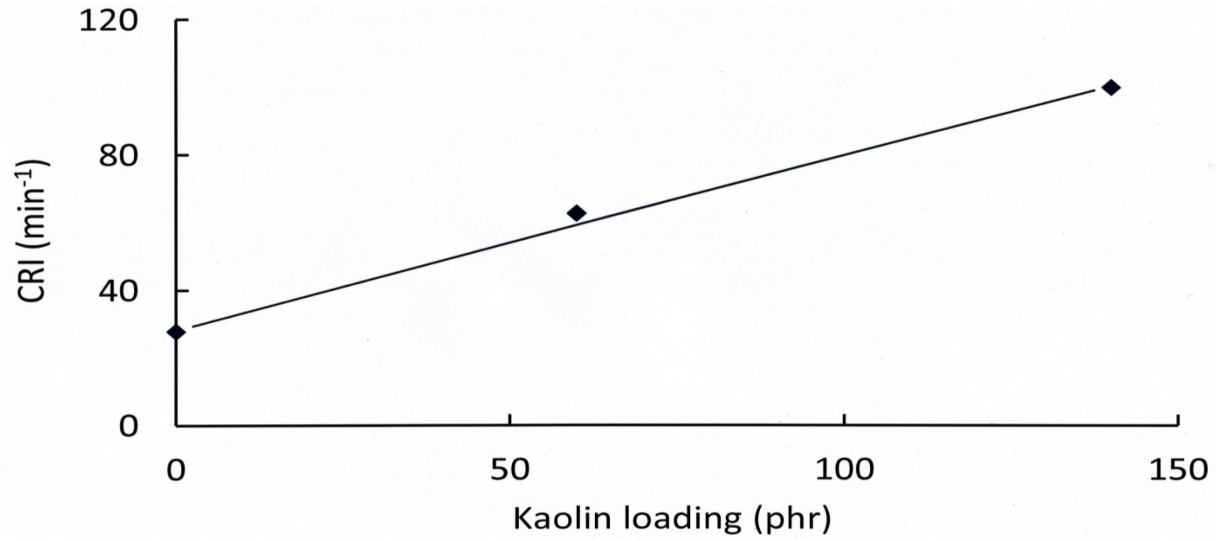


Figure 6.4 Cure rate index versus kaolin loading for composites 1-3 in Table 6.1

As mentioned earlier, Δtorque is an indication of crosslink density changes in the rubber. Δtorque for NR increased from 43 to 69 dNm as the loading of kaolin was raised from 0 phr to 140 phr , which indicated a large rise in the crosslink density of the rubber (Fig 6.5).

Cure characteristics of rubber vulcanisates are show in Table 6.1. Minimum torque increases steadily with increase in filler concentration for vulcanisates. Since minimum torque can be regarded as a measure of stock viscosity, the addition of kaolin of a smaller size tend to impose extra resistance to flow due to a higher restriction of molecular motion of the nanocomposites [53]. The implication of this is that incorporation of modified kaolin increases the viscosity of the vulcanisate. Whereas, the maximum torque which is correlated with hardness also increases with increasing kaolin loading. Since the modulus of kaolin is higher than the rubber matrix, the incorporation of kaolin will increase the stiffness of the nanocomposites. Similar trend was observed for the difference in torque i.e. Δtorque and this indicates the extent of cross linking and rubber-filler interaction of the nanocomposites.

Torque difference is a measure of the shear dynamic modulus, which indirectly relates to the crosslink density of the nanocomposites [54,55]. The presence of the kaolin has therefore resulted in increase in the torque value caused by the formation of a higher number of crosslinks, which could be attributed to the confinement of the elastomer chains within the silicate galleries and consequently, to better interaction between the filler and the natural rubber. Maximum torque can be regarded as a measure of composite modulus. The significantly increased values in maximum torque with filler are indirect evidence.

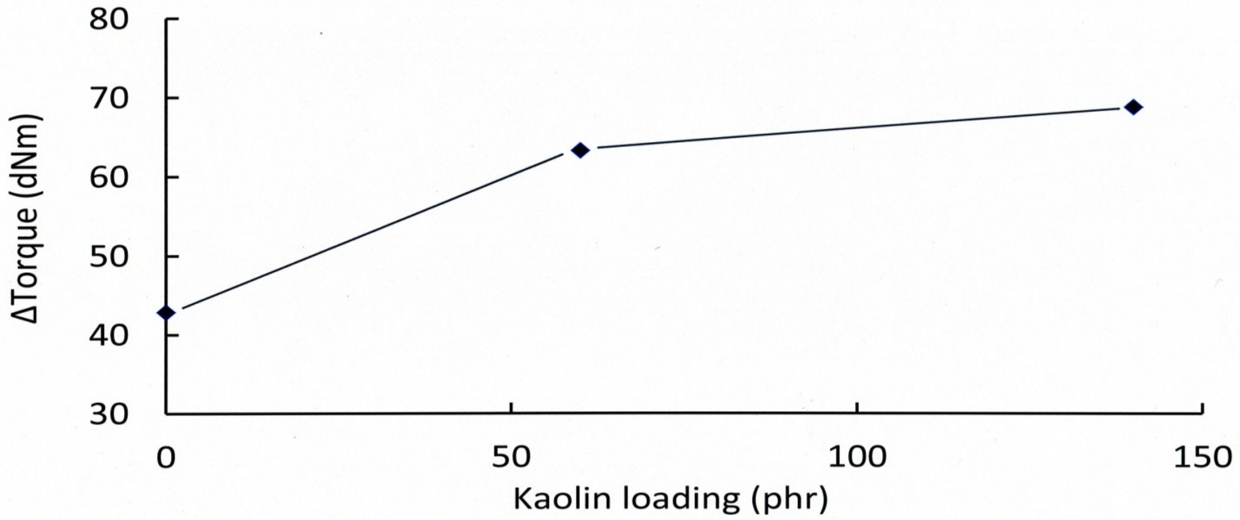


Figure 6.5 ΔTorque versus kaolin loading for composites 1-3 in Table 6.1

For BR, the addition of kaolin shortened the t_{s2} and t_{95} from 11.3 to 3.5 min and 47.5 to 12.5 min, respectively. The rate of cure also improved from 2.8 to 11.1 min^{-1}. Though, kaolin had a detrimental effect on the crosslink density of the rubber because Δtorque decreased from 72 to 56 dNm (Table 6.1).

For EPDM, the t_{s2} decreased from 6.2 to 2.6 min but surprisingly, the t_{95} increased from 21.5 to 40 min when 60 phr kaolin was added. Compound 7 had a marching cure and the torque kept increasing as a function of time. To calculate an optimum cure time for this compound, an arbitrary maximum torque value was considered. Hence, there was some uncertainty regarding the exact optimum cure time of this compound. But, it was evident that kaolin retarded the cure, causing it to march indefinitely. It is worth mentioning that the remaining compounds in Table 6.1 had equilibrium cure (Fig 6.1). The rate of cure declined as shown by a large fall in CRI from 6.5 to 2.7 min^{-1}. The rubber lost some crosslinks as demonstrated by reduction in Δtorque from 55 to 44.5 dNm Table 6.1. This revealed the damaging effect of kaolin on the crosslink density of both BR and EPDM.

6.3.2 Effect of kaolin on the hardness and mechanical properties of the rubber composites

Table 6.2 summarises the hardness and mechanical properties of the rubber composites.

Table 6.2 Hardness and mechanical properties of the rubber vulcanisates

Properties	**Compound no**						
	1	**2**	**3**	**4**	**5**	**6**	**7**
NR	100	100	100	-	-	-	-
BR	-	-	-	100	100	-	-
EPDM	-	-	-	-	-	100	100
Kaolin	0	60	140	0	60	0	60
∆Torque	43	64	69	72	56	55	44.5
Hardness (Shore A)	33	54	69	44	54	41	55
Range of values (Shore A)	32-35	51-55	68-70	43-44	54-56	41-42	55-56
Tensile strength (MPa)	22	22	20	1.7	14.6	1.4	14.9
Range of values (MPa)	21-22	21-22	18-21	1.5-1.8	14.5-15.5	1.3-1.7	14.7-17.5
Elongation at break (%)	1667	997	587	250	889	350	1512
Range of values (%)	1645-1669	994-999	577-628	239-283	878-950	333-370	1492-1651
Young’s modulus (MPa)	1.0	2.7	6.7	1.4	3.0	1.4	2.4
Range of values (MPa)	1.0-1.1	2.3-3.2	5.8-11.6	1.4-1.7	2.8-3.0	1.3-1.4	1.8-2.7
Compression set (%)	41	64	71	9.4	26	39	48
Range of values (%)	39-42	61-65	71-71	9.4-9.4	26-28	37.5-39	46-50
Stored energy density at break (MJ/m^3)	90	90	59	2.4	61	3.0	97
Range of values (MJ/m^3)	90-91	86-91	54-65	2.4-3.0	60-70	2.9-3.7	96-121
Tear energy (KJ/m^2)	13	13	14	1.1	7	1.9	30
Range of values (KJ/m^2)	11-15	11-20	11-20	0.76-1.7	4.6-11.5	1.3-2.0	26-32
Glass transition temperature, Tg (^{o}C)	-41	-43	-42	-100	-97	-42	-40
Degree of swelling (%)	489	347	335	360	428	263	323

The properties benefitted to a great extent from the addition and progressive increases in the loading of kaolin. For e.g. NR, the hardness increased by 64% when 60 phr kaolin was added and the trend continued rising by another 28% when the loading of kaolin reached 140 phr. Similarly, the Young's modulus rose by 170% with 60 phr kaolin and then by an extra 148% when the full amount of kaolin, i.e. 140 phr, was reached. This was expected, since when soft rubber is replaced with solid filler, the rubber becomes harder, causing the Young's modulus to increase. The tensile strength and tear energy were unchanged and the elongation at break and stored energy density at break deteriorated by a total of 65% and 34%, respectively when 140 phr kaolin was mixed with the rubber. Notably, the compression set of the rubber was adversely affected by the addition of kaolin. For the unfilled rubber, the set was 41%, and it then rose to 64% and 71%, when 60 and 140 phr kaolin was added, respectively.

Kaolin was very beneficial to the properties of BR and EPDM. For BR, the hardness increased by 23% and for EPDM, by 34%, respectively when 60 phr kaolin was incorporated in the rubbers. For BR, the tensile strength, elongation at break and Young's modulus rose by 759%, 256% and 114%, respectively. The compression set of the unfilled rubber was 9.4%, and subsequently rose to 26% when 60 phr kaolin was mixed with the rubber.

The effect of kaolin on the properties of EPDM was even more impressive. For this rubber, the tensile strength, elongation at break and Young's modulus improved by 964%, 332% and 71%, respectively. The properties related to fracture were also enhanced very substantially. For BR, the stored energy density at break and tear energy were increased by 2442% and 536%, respectively and for EPDM, by 3133% and 1479%, respectively. The compression set of the unfilled rubber was 39%, and afterward increased to 48% with 60 phr kaolin. Hence kaolin was detrimental to the compression set resistance of these rubbers.

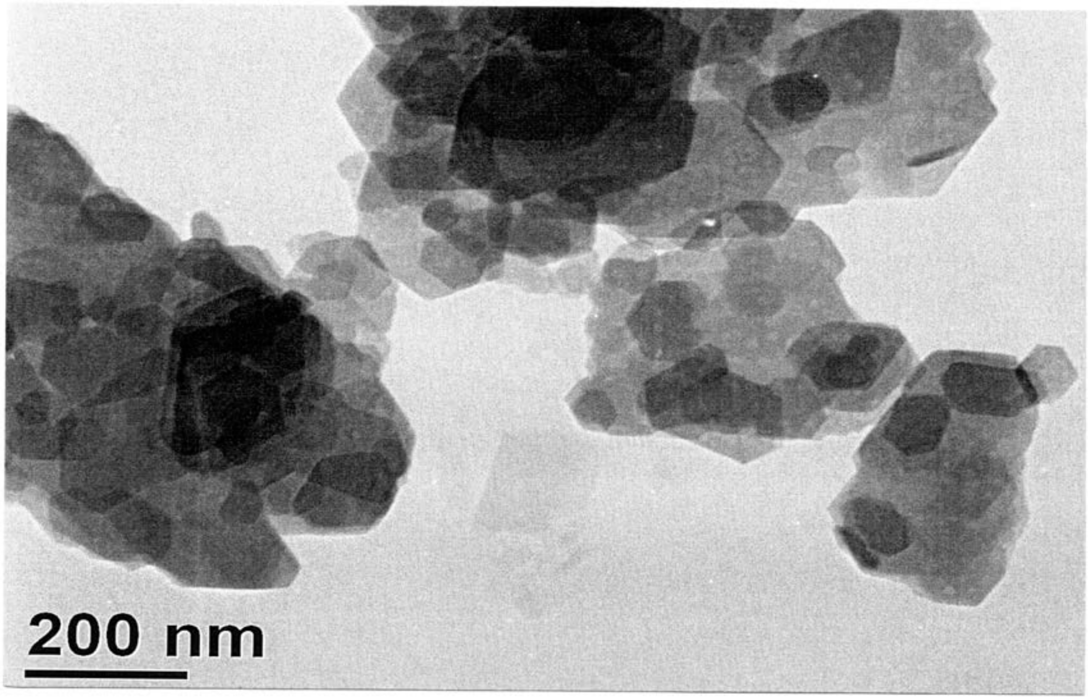


Figure 6.6 Transmission electron micrograph showing kaolin particles

Evidently, kaolin is extending or non-reinforcing filler for the strain-induced crystallizing NR, and highly reinforcing for the non-crystallizing BR and EPDM. Since kaolin has a platelet structure (Fig 6.6), it may be assumed that the mechanism by which rubber is reinforced may be different to that by spherical particles such as CB and silica. The results suggest that strain-induced crystallizing NR benefits less from kaolin than the non-crystallizing BR and EPDM do. In a study [40], some rubber composites were obtained by mixing NR, BR, and EPDM with up to 60 phr kaolin. The cure system consisted of 3 phr primary and secondary accelerators and 4 phr primary and secondary activators, adding up to 7 phr, as well as 2.5 phr sulphur. The kaolin-filled rubber composites had outstanding mechanical and thermal properties. For the NR composite, the highest hardness (38 Shore A), tensile strength (10.10 MPa) and elongation at break (296%) were recorded at 40 phr loading of kaolin. For the BR composite, the highest hardness (58 Shore A), tensile strength (7.75 MPa) and elongation at break (53%) were measured at 50 phr loading of kaolin. Finally, for the EPDM composite, the highest hardness (58 Shore A), tensile strength (9.26 MPa) and elongation at break (208%) were determined at 50 phr kaolin, respectively. Our results compared well with the reported ones above. For instance, the filled EPDM composite had a hardness of 55 Shore A, tensile strength of 14.9 MPa and an elongation at break of 1512%, significantly better than those reported for the EPDM above, in spite of the cure system having one accelerator and one activator, adding up to 2.075 phr (Table 6.1). All the indications are that kaolin reinforces rubber effectively, and reduction in the use of the chemical curatives in the vulcanisation process does not affect the mechanical properties of the rubbers adversely.

There are various factors which affect reinforcement of rubbers by solid fillers. They are filler-rubber interaction [41-42], filler-filler interaction [43], and formation of crosslinks in rubber [4]. Increasing mixing time is an effective way to disperse solid fillers in rubber compounds [44].

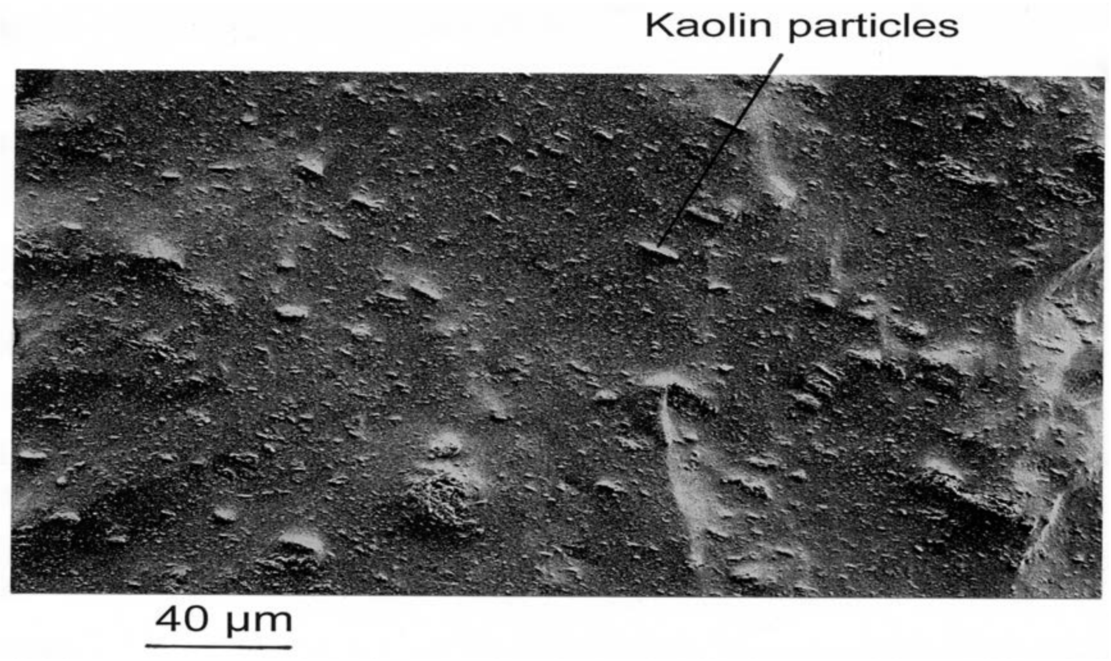


Figure 6.7 scanning electron micrograph showing good dispersion of the kaolin particles in rubber matrix, Data for the NR composite with 60 phr kaolin after 13 min mixing time

As Figure 6.7 shows, the kaolin particles dispersed well in the rubber matrix. The reinforcing effect of kaolin on the mechanical properties was optimized through good dispersion [45] and consequently the filler-filler interaction was minimal. The rubber breaks down during mixing, which causes reduction in molecular weight and viscosity. This is often compensated by the reinforcing effect of the filler. The reduction in molecular weight is attributed to the mechanical rupture of the primary carbon-carbon bonds that are present along the backbone of the rubber chains [46]. For example, for unfilled NR, a mixing time of 11 min reduced the molecular weight by roughly 25% [47] and its viscosity by 13% [48]. As the results in Table 6.2 show, in spite of a long mixing, i.e. 13 min, the mechanical properties of the BR and EPDM composites improved significantly when kaolin was added. This showed the reinforcing capabilities of kaolin.

Although, mixing of the rubber-nanocomposites compound for more than 10 min results in the degradation of macromolecules in all structures of rubber.

The influence of filler on this process is evident. The effect of molecular weight vs mixing time probably is a result of two processes; the first was related to scission mechanism of macromolecules, making possible the mechano-chemical transformations during mastication of rubber. It reduces molecular weight, especially the longest chains, and generates macro radicals. Second, this process consists of both branching of macromolecules because of macroradical recombination and networking because of interferences of macroradicals with the surface of filler. It gives a growth of the molecular weight of rubber. Competition of these processes in the change of the molecular weight gives a maximum in the resulting function [56].

Solid fillers reinforce rubber properties because of their large surface area. There were at least two contributions made to the rubber-kaolin interaction. Kaolin had a surface area of 25 m^2/g and this provided area for bound rubber to form. The formation of bound rubber increases with factors such as temperature, time, surface activity and surface area of the filler [5]. A mixing temperature of 58-62^{o}C and a mixing time of 13 min provided a favourable condition for bound rubber to form in the composites. In addition, the silanisation of the kaolin surface with MPTS, helped to improve the filler dispersion and increased the available surface area for rubber to interact with the filler to form bound rubber. Viscosity increases as a function of bound rubber, and bound rubber improves as a function of filler surface area and filler loading [49]. The results in Table 6.1show large increases in the viscosity for the kaolin-filled rubbers, signifying bound rubber formation in the composites. Effect of bound rubber on the filler-rubber interaction has been studied extensively and all the results suggest major enhancement of this property when bound rubber forms [5].

In a study, modified kaolin was introduced into NR and cured at 140^{o}C for 10 min to produce some composites [34]. The interspacing between the kaolin layers measured by XRD was from 7 to 14 A^o. The result showed as layered structure for kaolin with the interspacing up to 14 A^o this is similar to the interspacing of our kaolin. The presence of the modified kaolin resulted in increase in the torque value caused by the formation of a higher number of crosslinks, which was attributed to the confinement of the rubber chains within the silicate galleries and hence to better interaction between the filler and the rubber. The XRD indicated a gallery spacing of about 7 A^o for the kaolin used in this study. Since the size of a carbon atom along the backbone of hydrocarbon rubber is about 3 A^o [50], it is likely that some segments of the rubber chains entered into the kaolin galleries during mixing, causing strong interaction between the two. This in turn, could have enhanced the kaolin-rubber interaction and improved the properties of the BR and EPDM composites Table 6.2. It seems that confinement of the rubber chains within a layered structure is a major factor in the ability of mineral fillers such as kaolin to reinforce the rubber properties. Apparently, this was not so for the NR composite.

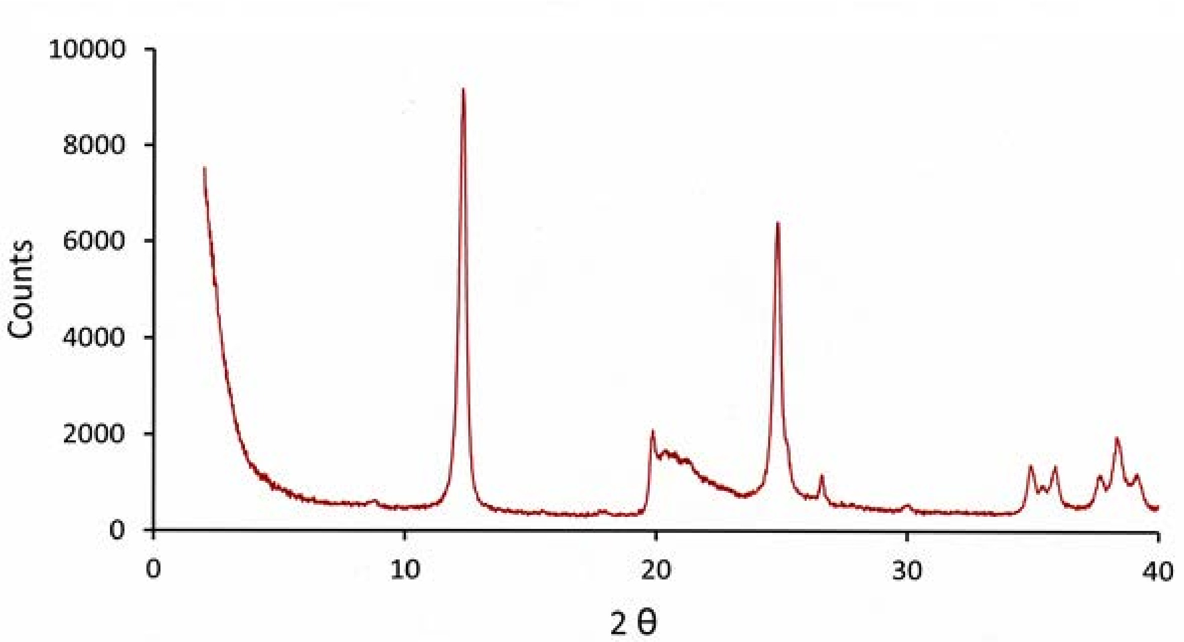


Figure 6.8 XRD diffraction pattern for the solid kaolin particles

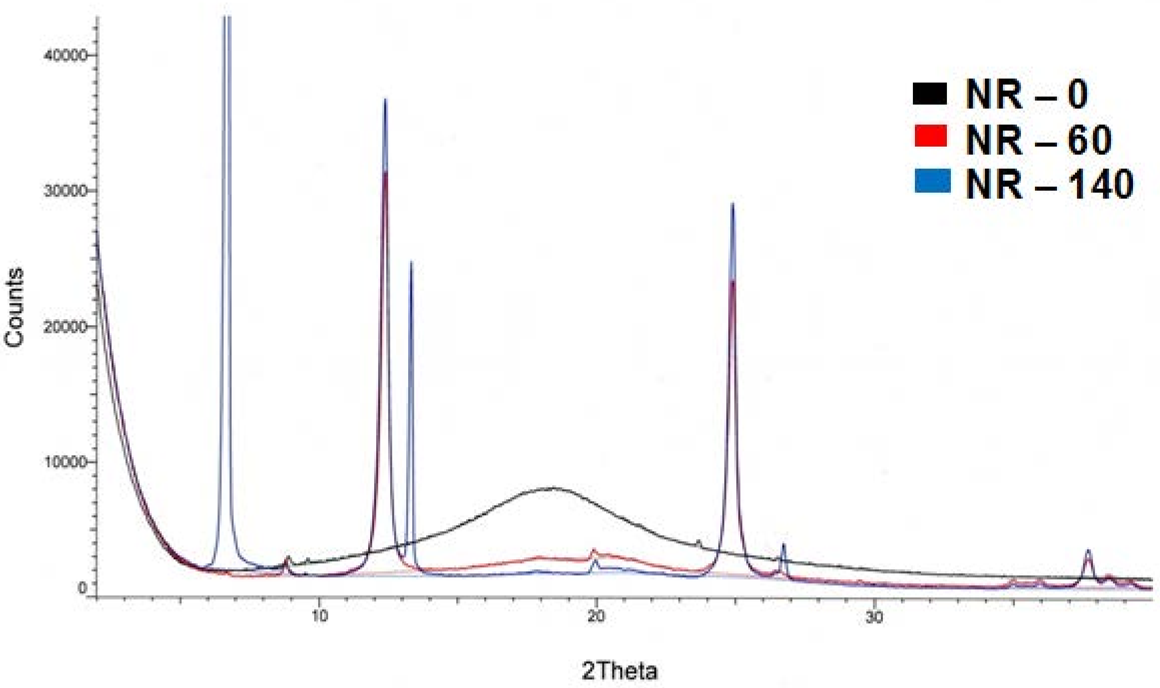


Figure 6.9 XRD diffraction patterns for the NR composites (kaolin in phr) (compounds 1-3 Table 6.1)

The NR viscosity increased by approximately 64% when the loading of kaolin was raised from 60 to 140 phr (Table 6.1). When the viscosity rose, higher shear forces were produced in the rubber, resulting in a more efficient break down of the filler aggregates, better dispersion of the filler particles and more surface area for the rubber chains to interact with (Fig 6.7). Consequently, more bound rubber was formed in the kaolin-filled composites. Furthermore for NR, the peaks on the XRD patterns of the kaolin-filled composites were the same as the ones appearing on the XRD pattern of the kaolin particles but getting larger as more kaolin was added (cf. Fig 6.8 with Fig 6.9). It was concluded that there was no evidence of crystallisation in the rubber. Small amounts of suitable impurities accelerate the crystallisation process markedly in NR in the absence of strain, presumably by promoting crystal nucleation [51]. Clearly, this was not the case with kaolin.

As mentioned earlier, Δtorque is an indication of crosslink density changes in rubber. The Δtorque of the NR composites increased from 43 to 69 dNm when the loading of kaolin was raised from 0 to 140 phr, respectively (Table 6.1). This indicated a significant rise in the crosslink density of the composite. For the BR and EPDM composites, ∆torque decreased by approximately 22% and 19%, respectively when 60 phr kaolin was added (Table 6.1).

The compression set of the composites increased when kaolin was incorporated in the rubber (Table 6.2). In the swelling tests, the unfilled NR composite solvent intake was 489%, and decreased to 347% and 335% for the composites with 60 and 140 phr kaolin, respectively. The decrease in solvent intake correlated well with the increase in ∆torque (Table 6.1), since higher crosslink density inhibits chain mobility and reduces swelling [39]. But the compression set increased by 73% when the kaolin loading was raised to 140 phr. However, higher loading of filler is known to increased compression set [52]. This trend did not match that of the ∆torque (Table 6.2) because higher crosslink density should have reduced the set. The reason for this discrepancy is not immediately clear but it is likely that the NR composites had more physical links and less chemical crosslinks, which affected both the extent of swelling and Δtorque.

For the unfilled and filled BR and unfilled and filled EPDM composites, the solvent intake was 360% and 428%, and 263% and 323%, respectively. The higher solvent intake indicated lesser crosslink density or lower ∆torque than the unfilled counterparts. This meant higher compression set for the filled composites. As shown in Table 6.2, the filled BR and EPDM composites did have lower ∆torques, which implied lesser crosslink density and higher compression set. It appeared that kaolin was detrimental to the crosslink density of these composites. It is expected that swelling of the BR and EPDM composites was affected mostly by the chemical crosslinks and less by the physical ones. Therefore, chemical and physical crosslinks influenced the ∆torque and solvent intake in these composites though the exact contribution to the crosslink density remains to be determined.

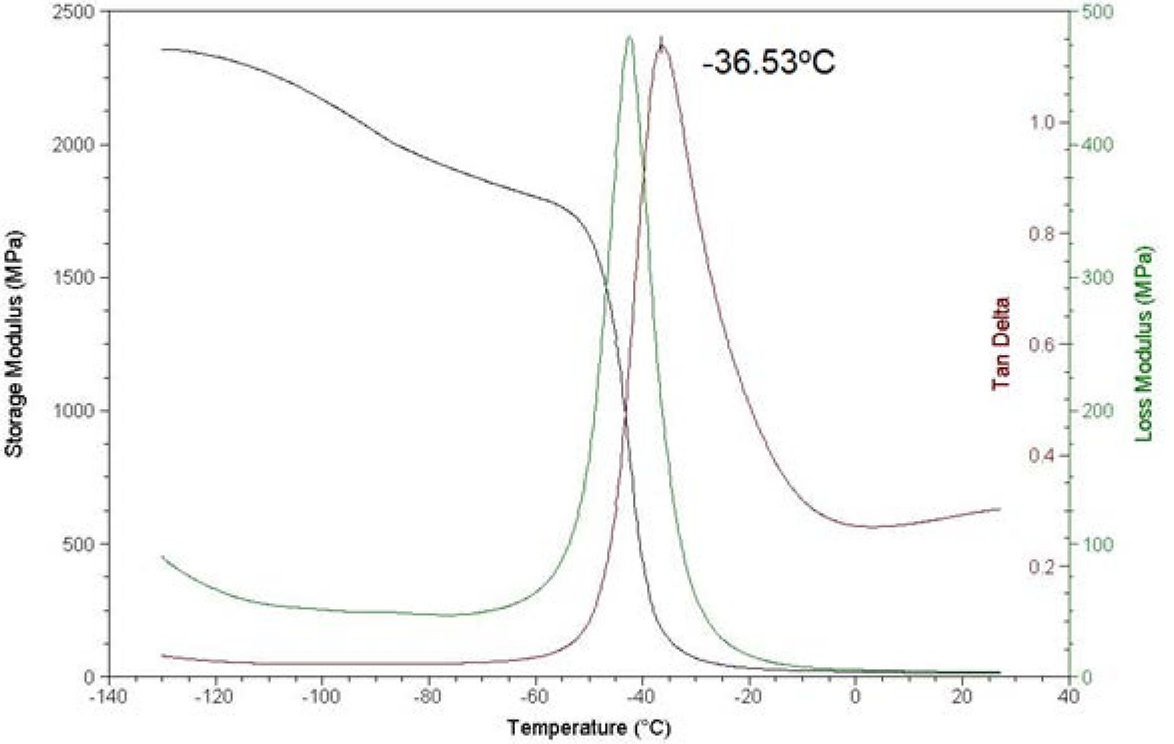


Figure 6.10 Typical DMA traces for the NR composite with140 phr kaolin

Glass transition temperature is governed by the extent of chain mobility within the rubber network. When chain mobility is inhibited, e.g. by the presence of chemical and/or physical crosslinks between the rubber chains and strong rubber-filler interaction, T_g rises [51]. The T_g of the unfilled NR composite was -41^{o}C and rose to about -42 and -43^{o}C when the filler loading was 60 phr and 140 phr, respectively (Table 6.2). The T_g for the unfilled and filled BR composites and unfilled and filled EPDM composites were -100^{o}C and -97^{o}C, and -42^{o}C and -40^{o}C, respectively. The kaolin filler raised the T_g of the composites by up to three degrees centigrade (Figure 6.10).

6.4 Conclusions

From this study, the following main conclusions can be drawn.

1. A new method measured the exact optimum amount of TBBS accelerator and ZnO activator at a given loading of sulphur in the composites of NR, BR and EPDM and eliminated stearic acid from the cure system entirely. The requirement for ZnO was 0.075-0.2 phr. interestingly, in spite of using less chemical curatives in sulphur vulcanisation, the rubber composites were fully cured with outstanding properties.
2. Kaolin was extending or non-reinforcing filler for the strain-induced crystallizing NR and highly reinforcing for the non-crystallizing BR and EPDM.

It is predictable that reduction in the use of ZnO and stearic acid will improve health and safety at work-place, reduce cost, and minimise damage to the environment. The use of MPTS pre-tread kaolin in conjunction with the new method for measuring the exact amount of the curatives in sulphur vulcanisation provides an effective means for designing green composites for industrial applications. The indications are that MPTS pre-treated kaolin is an ideal replacement for carbon black and silica/silane systems in rubber reinforcement, at least for non-crystallising BR and EPDM rubbers.

In the current study, The novel sulphur cure systems developed for NR, BR and EPDM rubbers in Chapter 3, NR, BR and EPDM rubbers were mixed with a high loading of mineral kaolin solid filler which was pre-treated with a mercaptosilane. The rubber compounds were subsequently cured and their mechanical properties measured. The results suggested that kaolin was non-reinforcing or extending filler for NR and highly reinforcing filler for BR and EPDM. Significant benefit to the mechanical properties of the rubbers from kaolin in combination with the efficient sulphur cure systems developed here are the right steps towards developing green compounds for the rubber industry.

6.5 References

1. D D Dunnom, "Use of reinforcing silicas". *Rubber Age* (1968); 100: 49-57.
2. E M Dannenberg, "Carbon black dispersion and reinforcement". *Rubber ChemTechnol* (1982); 25: 843-857.
3. G M Bristow, & R F Tiller, "Correlation of structure and properties of natural rubber vulcanisates". *Kautsch Gummi Kunstst* (1970); 23: 55-9.
4. M Nasir, & G K The, "The effects of various types of crosslinks on the physical properties of natural rubber", *Eur Polym J (*1988); 24: 733-736.
5. S Wolff, M J Wang, & E H Tan, "Filler-elastomer interactions. Part VII. Study on bound rubber", *Rubber Chem Technol* (1993); 66: 163-177.
6. E M Dannenberg, "The effects of surface chemical interactions on the properties of filler-reinforced rubbers", *Rubber Chem Technol* (1975); 48: 410-443.
7. E H Andrews, "Reinforcing of rubber by fillers". *Rubber Chem Technol* (1963); 36: 325-336.
8. F Saeed, A Ansarifar, & R J Ellis, et al. "Two advanced styrene-butadiene/ polybutadiene rubber blends filled with a silanized silica nanofiller for potential use in passenger car tyre tread compound", *J Apply Polym Sci* (2012); 123: 1518-1529.
9. M L Hair, W Hertl, "Acidity of surface hydroxyl groups", *J Phys Chem* (1970); 74: 91-94.
10. J A Hockey, & B A Pethica, "Surface hydration of silicas", *Trans Faraday Soc* (1961); 57: 2247-2262.
11. S Wolff, U GÖrl, M J Wang, W Wolff, "Silane modified silicas-silica-based tread compounds", *Eur. Rubber J* (1994); 16: 16-19.
12. S Wolff, "Chemical aspects of rubber reinforcement by fillers", *Rubber Chem Technol* (1996); 69: 325-346.
13. P Li, L Wang, G Song, et al. "Characterisation of high-performance exfoliated natural rubber/organoclay nanocomposites", *J Appl Poly Sci* (2008); 109: 3831-3838.
14. P L Teh, Z A Mohd Ishak, A S Hashim, et al. "Physical properties of natural rubber/organoclay nanocomposites compatibilised with epoxidised natural rubber", *J Apply Polym Sci* (2006); 100: 1083-1092.

15. E T Thostenson, C Li, & TW Chou, “Nanocomposites in context”. *Comp Sci Technol (*2005); 65: 491-516.
16. S Varghese, J Karger-Kocsis, & K G Gatos, “Melt compounded epoxidised natural rubber/layered silicate nanocomposites: structure-properties relationships”, *Polymer* (2003); 44: 3977-3983.
17. N Rattanasom, S Prasertsri, & T Ruangritnumchai, “Comparison of the mechanical properties at similar hardness level of natural rubber filled with various reinforcing-fillers”, *Polymer Test* (2009); 28: 8-12.
18. D Jia, L Liu, X Wang, et al. “Advances in natural rubber/montmorillonite nanocomposites, in Biodegradable polymer blends and composites from renewable resources”, NJ: John Wiley & Son, Inc., Hoboken, (2008).
19. T P Chua, M Mariatti, A Azizan, et al. “Effects of surface-functionalized multi-walled carbon nanotubes on the properties of poly(dimethyl siloxane) nanocomposites”, *Comp Sci Technol* (2010); 70: 671-677.
20. R Verdejo, C Saiz-Arroyo, J Carretero-Gonzalez, et al. “Physical properties of silicone foams filled with carbon nanotubes and functionalized graphene sheets”. *Eur Polym J* (2008); 44: 2790-2797.
21. L Bokobza, “Multiwall carbon nanotube elastomeric composites”. A review *Polymer* (2007); 48:4907-4920.
22. Y Zhan, J K Wu, H S Xia, et al. “Dispersion and Exfoliation of Graphene in Rubber by an Ultrasonically-Assisted Latex Mixing and In situ Reduction Process” *Macromol Mater Eng.* (2011); 296: 590-602.
23. J P Lewicki, J J Liggat, & M Patel, “The thermal degradation behaviour of polydimethylsiloxane/montmorillonite nanocomposites”, *Polym Degrade Stab* (2009); 94: 1548-1557.
24. R Sengupta, S Chakraborty, S Bandyopadhyay, et al. “A short review on rubber/clay nanocomposites with emphasis on mechanical properties”, *Polym Eng. Sci* (2007); 47: 1956-1974.
25. J K Kim, K Pal & V Sridhar, “Recent advances in elastomeric nanocomposites: Advanced structured materials”, Verlag, Berlin, Heidelberg, (2011), 5.
26. L Bokobza, “The Reinforcement of Elastomeric Networks by Fillers”, *Macromol Mater Eng.* (2004); 289: 607-621.
27. A Das, K W Stockelhuber, R Jurk, et al. “Routes to Rubber Nanocomposites”. *Macromol Symp* (2010); 291-292: 95-105.

28. R Stephen, & S Thomas, “Rubber nanocomposites: Preparation, properties and applications”, Wiley, New Jersey (2010) Chapter 1.
29. D R Paul, & L M Robeson, “Polymer nanotechnology: Nanocomposites”, *Polymer* (2008); 49: 3187-3204.
30. S J Ahmadi, Y Huang, & W Li, “Fabrication and physical properties of EPDM-organoclay nanocomposites”, *Comp Sci Technol* (2005); 65: 1069-1076.
31. C Labruyère, G Gorrasi, F Monteverde, et al. “Transport properties of organic vapours in silicone/clay nanocomposites”, *Polymer (*2009); 50: 3626-3637.
32. S Horsch, G Serhatkulu, E Gulari, et al. “Supercritical CO_2 dispersion of nano-clays and clay/polymer nanocomposites”, *Polymer* (2006); 47: 7485-7496.
33. Sh M Zoromba, A A M Belal, A E M Ali, et al. “Preparation and characterisation of some NR and SBR formulations containing different modified kaolinite”, *Polym-Plast Technol Eng.* (2007); 46:529-535.
34. L E Yahaya, K O Adebowale & B I Olu-Owolabi, “Cure characteristics and rheological properties of modified kaolin-natural rubber composites”, *Am Chem Sci J* (2014); 4: 472-480.
35. P A Ciullo, & N Hewitt, “The Rubber Formulary”, Noyes Publications, New York, (1999), 91.
36. S Ostad-Movahed, K Ansar Yasin, A Ansarifar, et al. “Comparing effects of silanized silica nanofiller on the crosslinking and mechanical properties of natural rubber and synthetic polyisoprene”. *J Appl. Poly. Sci* (2008); 109:869-881.
37. M J Wang, “Effect of polymer-filler and filler-filler interaction on dynamic properties of filled vulcanisates”, *Rubber Chem. Technol* (1998); 71: 520-589.
38. S O Movahed, A Ansarifar & F Mirzaie, “Effect of various efficient vulcanisation cure systems on the compression set of a nitrile rubber filled with different fillers”. *J. Appl. Poly. Sci.(*2015); 132:1-10.
39. A Ansarifar & F Saeed, “Developing ethylene-propylene-diene rubber compounds for industrial applications using a sulphur-bearing silanized silica nanofiller”, *Polym Compos* (2013); 34: 2019-2025.
40. W Wu & L Tian, “Formulation and morphology of kaolin-filled rubber composites”. *Appl Clay Sci* (2013); 80-81: 93-97.
41. J L Leblanc, “Elastomer–filler interactions and the rheology of filled rubber compounds”, *J Appl Polym Sci* (2000); 78: 1541-1550.

42. M J Wang, S Wolff, & J B Donnet, “Filler-elastomer interactions. Part I: Silica surface energies and interactions with model compounds”, *Rubber Chem Technol* (1991); 64:559-576.
43. J FrÖhlich, W Niedermeier & H D Luginsland, “The effect of filler–filler and filler-elastomer interaction on rubber reinforcement”, *Composites Parts A* (2005); 36: 449-460.
44. S Wolff, “Optimisation of silane-silica OTR compounds. Pat I: variation of mixing temperature and time during the modification of silica with bis-(3-triethyoxysilyl-propyl)-tetrasulphide”, *Rubber Chem Technol* (1982); 55: 967-989.
45. P Cochet, P Barruel, I Barriquand, et al. “Dispersibility measurements of pre. silicas. Influence of dispersion on mechanical properties”, *Rubber World* (1994); 219: 20-24.
46. A Ahagon, “Evaluation of Chain Scission during Mixing of Filled Compounds”, *Rubber Chem Technol* (1996); 69: 742-751.
47. D J Harmon, & H L Jacobs, “Degradation of natural rubber during mill mastication”, *J Appl Polym* Sci (1966); 10: 253-257.
48. H Fries, & R R Pandit, “Mastication of rubber”, *Rubber Chem Technol* (1982); 55: 309-327.
49. I Pliskin, & N Tokita, “Bound rubber in elastomers: Analysis of elastomer filler interaction and its effect on viscosity and modulus of composite systems” *J. Appl. Poly. Sci* (1972); 16: 473-492.
50. http://hyperphysics.phy-astr.gsu.edu/hbase/Particles/atomsiz.html.

51. A N Gent, “Crystallisation in natural rubber. II: The influence of impurities”, *Transactions* (1954); 30: 139-143.

52. S. Vishvanathperumal and S. Gopalakannan, "Swelling Properties, Compression Set Behavior and Abrasion Resistance of Ethylene-propylene-diene Rubber/Styrene Butadiene Rubber Blend Nanocomposites" Polymer(Korea), Vol. 41, No.3, pp 433-442 (2017)

53. Ishak ZAM, Bakar AA. "An investigation on the potentials of rice husk ash as filler for epoxidized natural rubber", European Polymer Journal, VOl.31, No. 3, pp 259-269 (1995).

54. Ismail H, Freakley PK. "Determination of the Modes of Action of A Cationic for Property Development in Silica Filled Natural Rubber Compounds", European Polymer Journal, Vol. , pp 321-411, (1996)

55. Ismail H, Chia HH. "The effect of multi- functional and vulcanization systems on silica filled epoxidized natural compounds", European Polymer Journal, Vol. 34, No. 12, pp 1857-1863 (1998)

56. B. JURKOWSKA, Y. A. OLKHOV, B. JURKOWSKI, O. M. OLKHOVA, "Study of Butadiene Rubber Mastication and Mixing with Carbon Black", Journal of Applied Polymer Science, Vol. 71, pp 729 –737 (1999)

Chapter 7 – Conclusions

From this study, the following conclusions were drawn.

7.1. Novel sulphur cure systems for NR, BR and EPDM rubbers.

1. The optimum loadings of TBBS for the NR with 1, 2, 3 and 4 phr sulphur were 1.5, 1.5, 1.5 and 3.5 phr, respectively.
2. The optimum loading of ZnO for the NR with 1 phr sulphur and 1.5 phr TBBS, the NR with 2 phr sulphur and 1.5 phr TBBS, the NR with 3 phr sulphur and 1.5 phr TBBS, and the NR with 4 phr sulphur and 3.5 phr TBBS were 0.2, 0.3, 0.25, and 0.2 phr, respectively.
3. The optimum loading of TBBS for the BR with 0.5 and 1 phr sulphur were 1.75 and 3 phr, respectively.
4. The optimum loading of ZnO for the BR with 0.5 phr sulphur and 1.75 phr TBBS and the BR with 1 phr sulphur and 3 phr TBBS were 0.2 phr, respectively.
5. The optimum loading of TBBS for the EPDM with 1 phr sulphur was 1 phr.
6. The optimum loading of ZnO for the EPDM with 1 phr sulphur and 1 phr TBBS was 0.075 phr.
7. When the loading of TBBS in the powder was raised progressively from 0.135 to 0.383 phr, the scorch time and optimum cure time of the rubber decreased at 0.351 phr TBBS. The rate of cure as indicated by the cure rate index increased at 0.351 phr TBBS in the powder. The crosslink density as shown by ∆torque rose, reaching its optimum value at 0.383 phr TBBS loading in the powder.
8. When the loading of the powder (TBBS/ZnO:350mg/1g) in the rubber was raised increasingly to 5.63 phr, the scorch time was unchanged and the optimum cure time reduced at 1.25 phr powder. The rate of cure as shown by the cure rate index accelerated at 1.25 phr powder. The crosslink density as indicated by ∆torque rose, reaching its maximum value at 5.63 phr powder.

- All the indications are that methods 1 and 2 offer a significantly more efficient use of TBBS and ZnO chemicals in the sulphur vulcanisation of NR, BR and

EPDM rubbers. This helps to reduce excessive use of these chemicals and offers a more efficient cure cycle for these rubbers.

7.2 Reinforcing capabilities of mineral kaolin for NR, BR and EPDM rubbers

9. To react the sulphur in MPTS on the kaolin surface with the NR chains and optimise the reaction between the two, 16 phr TBBS and 0.2 phr ZnO were added to the kaolin-filled rubber.
10. The hardness and Young's modulus increased and compression set decreased when up to 3 phr elemental sulphur was included in the kaolin-filled rubber with 16 phr TBBS and 0.2 phr ZnO. The tensile strength, elongation at break, stored energy density at break, and tear energy of the rubber vulcanisate reduced when elemental sulphur was added. Notably, the inclusion of elemental sulphur was the key factor in controlling the rubber properties.

11. Kaolin was extending or non-reinforcing filler for the strain-induced crystallizing NR and highly reinforcing for the non-crystallizing BR and EPDM.
    Although both methods showed that kaolin was a reinforcing filler, but method 1 used significantly more TBBS, i.e., 16 phr for curing NR. Therefore, method 2 may be the preferred one, since it uses a great deal less TBBS for NR, i.e. up to 3.5 phr.
    - It is predictable that reduction in the use of TBBS and ZnO and elimination of stearic acid from the cure system will improve health and safety at work-place, reduce cost, and minimise damage to the environment. The use of MPTS pre-tread kaolin in conjunction with the use of the novel cure systems developed in Chapters 3 and 4 provide an effective means for designing green rubber composites for industrial applications. The indications are that MPTS pre-treated kaolin is an ideal replacement for toxic carbon black and expensive silica/silane systems in rubber reinforcement, at least for non-crystallising BR and EPDM rubbers.

Chapter 8 – Suggestions for further work

8.1 – Use of novel sulphur cure systems in NR, BR and EPDM

In Chapter 3, the optimum loading of TBBS and ZnO were measured for NR at 1, 2, 3 and 4 phr loading of sulphur. However, for BR the optimum loading of TBBS and ZnO were determined at 0.5 and 1 phr loading of sulphur. For EPDM, the optimum loading of TBBS and ZnO were measured at 1 phr sulphur loading. Therefore, a future work should aim to measure the optimum loading of TBBS and ZnO at 2, 3, and 4 phr sulphur loading for this rubber.

In Chapter 4, the optimum loading of the powder (TBBS/ZnO: 350mg/1g) was measured for the NR with 4 phr sulphur. The cure efficiency was excellent. Hence a future work should repeat a similar study for the NR, BR and EPDM rubbers at different loading of sulphur, e.g. 1, 2, 3, and 4.

8.2 – Exploring the reinforcing properties of mineral kaolin

In Chapter 6, the reinforcing capabilities of mineral kaolin on NR, BR and EPDM properties were studied. As the results showed, kaolin was highly reinforcing filler for non-crystallising BR and EPDM but non-reinforcing filler for NR. The results for crystallising NR were puzzling. So a future study should examine why kaolin did not reinforce the mechanical properties of the NR vulcanisate. Also, in BR and EPDM rubbers, the loading of kaolin was limited to 60 phr in this study. A future work should increase the amount of kaolin in BR and EPDM and also styrene-butadiene rubber (SBR), which is used extensively in passenger car tyres to above 100 phr to investigate its effects on the rubber properties.

APPENDIX

Presentation and attendance at international conferences

1. Saad H. Sheikh, Ali Ansarifar, “Reinforcement of natural rubber with kaolin for tyres”, Invited paper presented at the Tire Technology Expo, Cologne, Germany February (2015).
2. Saad H. Sheikh, Ali Ansarifar, “A novel method for reinforcing rubber with a sulphur-bearing silane pre-treated kaolin”, Invited paper presented at the 11th conference on Intelligent Tire Technol., Dresden, Germany November (2015).
3. Saad H. Sheikh, Ali Ansarifar, “Poster Presentation at Innovations in Rubber Design conference”, London, Dec (2016).
4. Saad H Sheikh, Ali Ansarifar, Jonathan Dushyanthan, George W Waver and Kahagala Gamage Upul Wijayantha, “Revisiting the sulphur vulcanisation of rubber”, Tire Technology Expo February 2018, Hannover, Germany.

Publications

1. Saad H. Sheikh, Ali Ansarifar, “Carbon black alternative”, Tire Technol. Inter. magazine, The annual review of tire materials and tire manufacturing technology, pp. 96-100 (2015).
2. Saad H. Sheikh, Ali Ansarifar, “Novel sulphur cure systems”, Tire Technol. Inter. The annual review of tire materials and tire manufacturing technology, pp. 84-87 (2016)
3. Saad H. Sheikh, Ali Ansarifar, “Kaolin reinforcement of some rubbers and optimisation of the sulphur cure system”, Gummi Fasern Kunststoffe, pp. 323-330 (2017).
4. Saad H. Sheikh, Ali Ansarifar, “Kaolin reinforcement of some rubbers and optimisation of the sulphur cure system”, Rubber Fibres Plastics International magazine for the Polymer Industry of Germany, (2018) In press
5. Saad H. Sheikh, Ali Ansarifar, “The potential of kaolin as reinforcing filler for rubbers with new sulphur cure systems”, Journal of Reinforced Plastics and Composites, 36(16), pp.1132-1145, (2017). This was an invited paper and

was published in special issue: Reinforced Polymers and Advanced Composites.

6. Saad H Sheikh, Ali Ansarifar, Jonathan Dushyanthan, George W Weaver and Kahagala Gamage Upul Wijayantha, “Revisiting the sulphur vulcanisation of rubber”, Gummi Fasern Kunststoffe magazine of Germany, 01/2018 (February) In press
7. Saad H Sheikh, Ali Ansarifar, Jonathan Dushyanthan, George W Weaver and Kahagala Gamage Upul Wijayantha, “Revisiting the sulphur vulcanisation of rubber”, Rubber fibres and plastics International magazine of Germany, 02/2018 (April) In press