DEVELOPMENT OF ENR BASED COMPOUNDS FOR GREEN TYRE TREAD APPLICATIONS WITH IMPROVED PERFORMANCE, PROCESSING CHARACTERISTICS AND SUSTAINABILITY.

by

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I am really indebted to my loving wife, Impy Nadia Mohd Ghani and all our sons and daughter for their constant encouragement, support, patience and perseverance throughout the years of completing my PhD study and to our parents for their blessing and patience during the period we were away from them. They are the most important people in my life, and I dedicate this thesis to them.

ABSTRACT

Silica filler is a renewable and environmentally friendly resource. The precipitated silica is the most commonly used as filler in rubber compounds especially in tyre rubbers compounds. Since the introduction of “Green Tyres” in the early 90’s, the use of silica as a reinforcing filler in a polar variant of natural rubber, epoxidized natural rubber (ENR) has grown. The greatest advantage of using silica over carbon black as a reinforcing filler in a tyre tread compound is that a lower rolling resistance is achieved, while maintaining good wet and dry traction. However, a previous study has shown that high silica loading in ENR without any coupling agent results in lack adhesion to the rubber matrix, which in turn affects the processability and physical properties of the rubber compound. In addition, the wear resistance of a silica filled ENR compound also was not as high as those of conventional Oil Extended Styrene Butadiene rubber (OESBR) and NR/BR compounds used in passenger car and truck tyre treads even with the presence of silane.

In this work, with the aim of improving silica filled ENR compound properties, the effect of X50S silane coupling agent concentration, water addition to silica during mixing a silica filled ENR compound and blending butadiene rubber (BR) into a silica filled ENR compound were studied. While, the recovered silica fillers from pyrolysis and geothermal sources, referred to as ‘rSilica’ and ‘geoSilica’ respectively have been used in place of conventional silica in ENR compound in order to determine whether they can be used to improve the sustainability of ‘green’ tyre tread compounds. All silica filled ENR compounds or blends for lab scale mixes were prepared in a Polylab Haake internal mixer and for the extrusion performance evaluation, a medium scale mixer was used to prepare the silica filled ENR compounds. The rheological properties of the compound were measured using a Mooney viscometer and Oscillating Disc Rheometer. The physical properties such as hardness, tensile strength, heat build-up and DIN and Akron abrasion resistance were also measured. The results showed that the ENR/silica compound properties such as tensile strength and hardness were as good as those of the conventional NR/BR compounds used in tyre tread. However, the most important finding was that the heat build–up property and Mooney viscosity decreased significantly with addition of X50S silane coupling agent and water. While the DIN abrasion resistance index increased significantly with BR content, exceeding that of the conventional compound at BR:ENR ratios of greater than 20:80. The rSilica which is recovered silica from pyrolysis of tyres did show reasonably good physical properties such as tensile strength, hardness and abrasion resistance as well as good processing characteristics compared to the commercial grade silica (Zeosil) may have potential to replace Zeosil silica in tyre compounds.

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

T_g - Glass transition temperature

ML - Mooney large rotor

MS - Mooney small rotor

M_L - Minimum torque

M_H - Maximum torque

ts2 - Scorch time

t90 - 90% curing time

t95 - 95% curing time

IRHD - International Rubber Hardness Degree

TESPT - bis(3-(triethoxysilyl)propyl) tetrasulfide

TESPD - bis(3-(triethoxysilyl)propyl) disulphide

6PPD - N-1,3-dimethylbutyl-N’ phenyl-p-henylenediamine

TBBS - N-tert-butylbenzothiozole-2-sulphenamide

TMQ - 1,2-dihydro-2,2,4-trimethylquinoline

TBzTD - Tetrabenzylthiuram disulfide

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CHAPTER 1

INTRODUCTION

1.1 Background

The wheel is considered one of most important product inventions in our history because of the wide range of applications such as, transportation vehicles, construction equipment and internal parts of machinery in engineering works. Wheeled vehicles were recorded in Sumeria in 3500 BC, Assyria in 3000 BC and central Europe towards 1000 BC[1]. Later, the spoked wheel was introduced and then given its first “tyre” consisting of first, a leather and then a copper and iron binding to prevent damage to the wooden wheel frame. Then in 1846, Thompson was granted a patent for an elastomeric air tube, to be fixed onto a wheel to reduce the power to haul a carriage, make motion easier and reduce noise. This achievement in wheel development was much refined in the 1880s when the first pneumatic tyre was developed for use on tricycles. In 1839, the discovery of rubber vulcanization by Charles Goodyear during the industrialization of Europe and North America has enabled the tyre to evolve from a rubberized canvas covering a rubber tube to a complex fabric, steel and elastomer composite[1].

As concern grows regarding climate change and the cost and long-term availability of petroleum oil supplies, there is an increasing desire for materials and products such as tyres to be manufactured in part, or entirely from renewable materials such as natural rubber (NR)[2]. Chemically modified of NR can also be considered a renewable material, including Epoxidized natural rubber (ENR), which is derived from natural rubber through epoxidation. Unlike NR, ENR is a polar rubber which means that ENR has the potential to interact more strongly with silica filler than the conventional non-polar tyre rubbers such as NR, BR and SBR. Silica filler itself can also be considered as a renewable material. This is because silica (silicon dioxide, SiO_2) is very commonly found in nature as quartz in sand. The main industrial use of silica sand is for glassmaking and more silica sand is naturally generated per annum than is used by mankind to produce glass, insulation and other sand-based products. As a result, sand can be considered as rapidly renewable[3]. Sustainability of silica filler can be further improved by using silica recovered from the pyrolysis of tyres and from water used in the renewable geothermal energy industry. ENR reinforced with silica filler, particularly recovered silica, can therefore be considered a highly renewable material to use for tyre treads.

Apart from the use of renewable materials in tyres, there is an additional desire to minimise energy consumption and hence carbon footprint while in use[2]. Lower energy consumption can be achieved by reducing rolling resistance. It is reported that a 3% decrease in rolling resistance is equivalent to a 1% saving in fuel, thus giving green tyres an economic as well as an environmental benefit[4].

In developing green tyre compounds, it was important that low rolling resistance should not be achieved at the cost of wet traction and good wear and tear performance[5]. During the development of silica-filled tyre compounds it was found that silica has a poor interaction with and dispersion in the non-polar tyre rubbers, compared to carbon black[6]. In contrast to carbon black, the surface of precipitated silica is highly polar and hydrophilic due to the presence of numerous silanol groups. The strong intermolecular hydrogen bonds between the hydroxyl groups and the relatively high surface area of the silica, means that agglomeration tends to occur during storage and the vulcanization process[7]. In order to improve the compatibility of silica in non-polar tyre rubbers such as NR and BR and to ensure its good coupling to the polymer matrix, the addition of coupling agents was found to be necessary[8]. Silica with silane coupling agents has enabled tyre manufacturers to satisfy the ‘magic triangle of tyre technology’ where low rolling resistance of a tyre for fuel economy and improved wet grip for easy handling has been achieved, while maintaining the abrasion resistance of the tyre (Figure 1.1). The first durable silica-filled ‘green’ tyre was introduced by Michelin in 1992. However, there are some disadvantages to using coupling agents. Certain silane coupling agents release harmful volatile compounds such as ethanol during the mixing process and coupling agents are also relatively expensive.

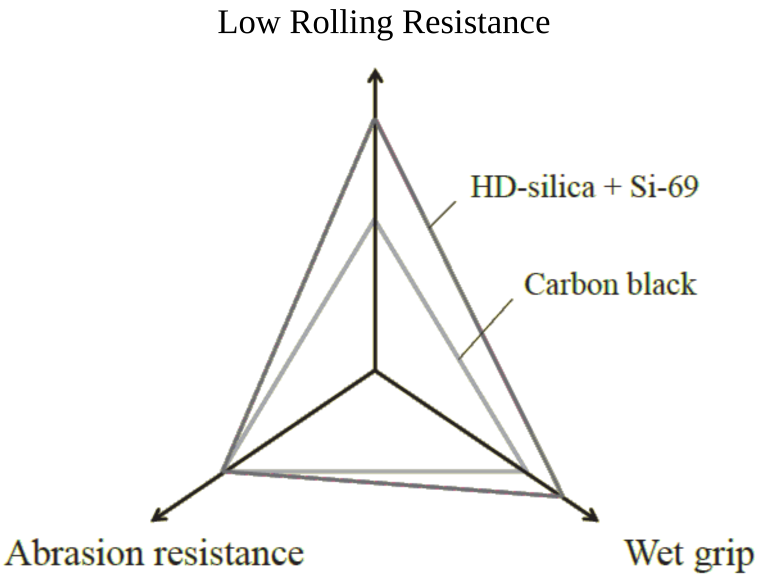

Figure 1.1: Magic Triangle of Tyre properties[9].

As an alternative to using coupling agents it may be possible to use a modified form of natural rubber, Epoxidized natural rubber (ENR) which potentially gives better compatibility to silica, and higher reinforcement for silica compounds compared to natural rubber. The epoxide groups in ENR can interact with the silanol groups on the surface of the silica, so that the use of coupling agents such as silane could be eliminated or greatly reduced[10]. In the 1980s, TARRC developed the first tread using silica-filled epoxidized natural rubber with 25 mol% epoxidation (ENR25). It was shown that ENR25 compounds containing silica or silica/carbon black gave lower rolling resistance than NR and better wet traction than oil extended styrene butadiene rubber (OESBR), providing an ideal combination of these two properties for tyre treads. However, the wear results of ENR25/silica compounds, are still not as good as those of OESBR and NR/BR filled with carbon black and the compounds are relatively difficult to process, having a high viscosity[11]. Today, increased environmental awareness, changes in economic factors and recent technical advances have made the use of silica filled ENR compounds for tyre manufacturing a viable option, especially for marketing as a ‘green’ tyre product. Therefore, the current study focuses mainly on the development of ENR25 based, silica filled compounds with improved performance, processing characteristics and sustainability.

1.2 Research Aims and Objectives

Silica filled ENR compounds are relatively difficult to mix and process, with difficulty in achieving high levels of dispersion and having a high viscosity. It is believed that adding silane coupling agent and water during first stage mixing will help to improve the mixing process by reducing the filler-filler interaction and hence, improve the processability and flow properties of ENR compound. Furthermore, good dispersion of the filler and the introduction of chemical bonds between the filler and silica through the silane may improve properties and hence performance of the vulcanized tyre compound. Blending with BR will be carried out in an attempt to improve the abrasion resistance performance of silica filled ENR25 compound. Last but not least, an investigation will be carried out into the feasibility of improving the sustainability of silica filled ENR25 'green' tyre compounds by using recovered silica fillers in place of the current conventional silica filler.

Specific research objectives and the chapters in which the results are presented and discussed are listed below.

i) To determine whether silane coupling agent and water addition to silica can improve the processing characteristics and physical properties of 'green' tyre compounds produced from Epoxidized natural rubber. (Chapter 4)

ii) To determine whether blending with BR can improve the abrasion resistance and other physical properties of 'green' tyre compounds produced from Epoxidized natural rubber. (Chapter 5)

iii) To determine whether the sustainability of 'green' tyre tread compounds can be improved by using recovered silica fillers from tyre pyrolysis and from geothermal sources. (Chapter 6)

iv) To determine whether results and conclusions about the effect of silane and water on processing obtained in small lab scale mixing are in agreement with a larger mixing scale and in actual rubber processing conditions such as extrusion. (Chapter 7)

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CHAPTER 2

LITERATURE REVIEW

2.1 Rubber Matrices

A rubber or elastomer is a type of polymer which has the ability to undergo large elastic deformations and can return to its original shape in a reversible way after being stretched or deformed. This behaviour is usually known as rubbery elasticity. One essential requirement for a substance to be rubbery and elastic is that it consists of very long flexible chainlike molecules, with very little branching and relatively weak interactions between molecules. The flexibility of the molecules comes from free rotation about the bonds. The 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. Rubber polymers can be divided into two types, natural rubber (NR) and synthetically produced rubber such as silicone rubber (SR), styrene-butadiene rubber (SBR), butyl rubber (IIR) and nitrile rubber (NBR). This project is mainly concerned with Epoxidized natural rubber (ENR), NR and butadiene rubber (BR), which are described in the following sections.

2.1.1 Natural Rubber (NR)

Natural Rubber (NR) is produced from the latex of the *Hevea Basiliensis* rubber tree. Natural rubber is a linear polymer with repeating units of 1,4 isoprene $(C_5H_8)n$, with the structure shown in Figure 2.1. Its glass transition temperature is about -70°C and its specific gravity is 0.93 at 20°C. The NR structure is thought to be completely cis-1,4-polyisoprene except for the chain ends. NR contains small amounts of non-rubber such as fatty acids and protein residues, which act to promote sulphur curing, the main vulcanization system used in the industry[1]. Because NR macromolecules are configured identically (stereoregular), they can spontaneously pack together as crystallites on standing at low temperature, with a maximum crystallisation rate at temperatures around -25°C. NR also crystallizes upon straining and strain-induced crystallization imparts outstanding green strength and tack and also gives NR vulcanizates high resistance to cut growth at severe deformation[2].

NR vulcanizates generally exhibit, low heat build-up, low compression set and stress relaxation, good electrical insulation, good processability, high resilience and excellent dynamic properties and have been used in many applications due to their excellent properties. Like other unsaturated elastomers, NR vulcanizates are susceptible to attack by atmospheric oxygen and ozone. Being non-polar, NR vulcanizates are not resistant to petroleum-based oils and fuels but they can be used with a wide range of organic and inorganic chemicals such as silicon oils, greases, acids, alkalis and salts. NR elastomers remain the best choice for many applications that require low heat build-up such as large tyres of trucks and buses, carcasses of passenger car tyres, anti-vibration mounts and bearings. Other products that may be produced from NR include hoses, conveyor belts, gaskets, seals, rubberized fabrics, elastic bands and pharmaceutical goods[2,3].

There are three basic types of commercially available NR: technically specified rubbers, visually inspected rubbers and specialty rubbers. The specifications of technically specified natural rubbers are defined by the respective producing countries such as Standard Malaysian Rubber (SMR), Standard Indonesian Rubber (SIR) and Thai Technical Rubber (TTS). Examples of visually inspected natural rubber are ribbed smoked sheet (RSS), white and pale crepe and pure smoked blanket crepe. Several examples of specialty rubber or modified natural rubber include liquid natural rubber (LNR), methyl methacrylate grafted rubber (MG rubber), deproteinized natural rubber (DPNR) and Epoxidized natural rubber (ENR)[4]. The last of these, ENR is the main rubber used in the research reported in this Thesis and its structure and properties are described in the next section.

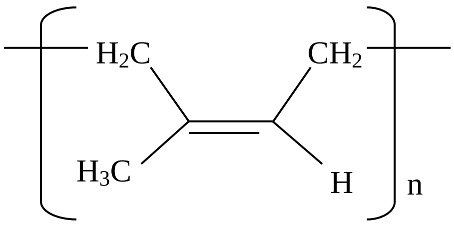


Figure 2.1: Structure of Natural rubber, cis-1, 4 polyisoprene

2.1.2 Epoxidized Natural Rubber (ENR)

In the early to mid-1970s, there was renewed interest in chemical modification of NR to produce other polymeric materials as a result of the crude oil crises. ENR has some properties that are better than NR for many applications such as increased oil resistance, lower gas permeability, enhanced adhesive properties, and for tyres, lower rolling resistance and better wet grip[5].

Epoxidized natural rubber (ENR) is prepared from natural rubber latex through chemical modification of NR. The epoxidation process is defined as the chemical reaction of an olefinically-unsaturated polymer, which involves the addition of an oxygen atom to a proportion of the carbon-carbon double bonds, thereby converting them to an oxirane (epoxide) ring, as shown in Figure 2.2. The epoxidation process is carried out by the chemical reaction between performic acid (hydrogen peroxide + formic acid) and natural rubber latex as schematically shown in Figure 2.3. Epoxidized natural rubber (ENR) is a rubber product which is characterized by its epoxide or oxirane rings randomly distributed along the main chain backbone, among the normal isoprene units[10,11]. The epoxidation of NR causes an increase in the glass transition temperature of the pristine elastomer as shown in Figure 2.4. The T_g of NR will increase by about 0.9˚C per % degree of epoxidation level. The epoxidation process of NR transforms the NR into a new specialty elastomer with extra important rubber vulcanizate properties[5,6].

Epoxidized natural rubber (ENR) is now an established commercial specialty polymer. Two grades are available with different epoxide contents, which are referred to as ENR25 (25 mole % epoxide) and ENR50 (50 mole % epoxide). ENR is still able to undergo strain crystallisation and so offers high strength, while the addition of a polar group results in an increased solubility parameter increased oil resistance, enhanced adhesive properties and reduced gas permeation. The two grades of ENR are significantly different from each other and have properties that are distinct from NR. The combination of good wet grip and low rolling resistance properties of ENR25 has made it attractive for tyre tread applications. ENR50 with good air impermeability is suitable to replace butyl rubbers in tyre inner liners and tubes as well as being used in engineering and mechanical rubber goods due to its high strength and ability to isolate vibration[5,6 ,7].

ENR also has the potential to act as a chemically reactive rubber due to its ability to crosslink with other polymers having functional groups such as chloroprene, chlorosulphonated polyethylene, polyvinyl chloride and carboxylated nitrile rubber without the use of conventional curing agents resulting in self-vulcanising blends[5,8,9].

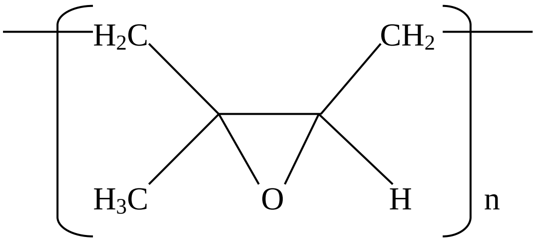


Figure 2.2: Structure of Epoxidized natural rubber (ENR)

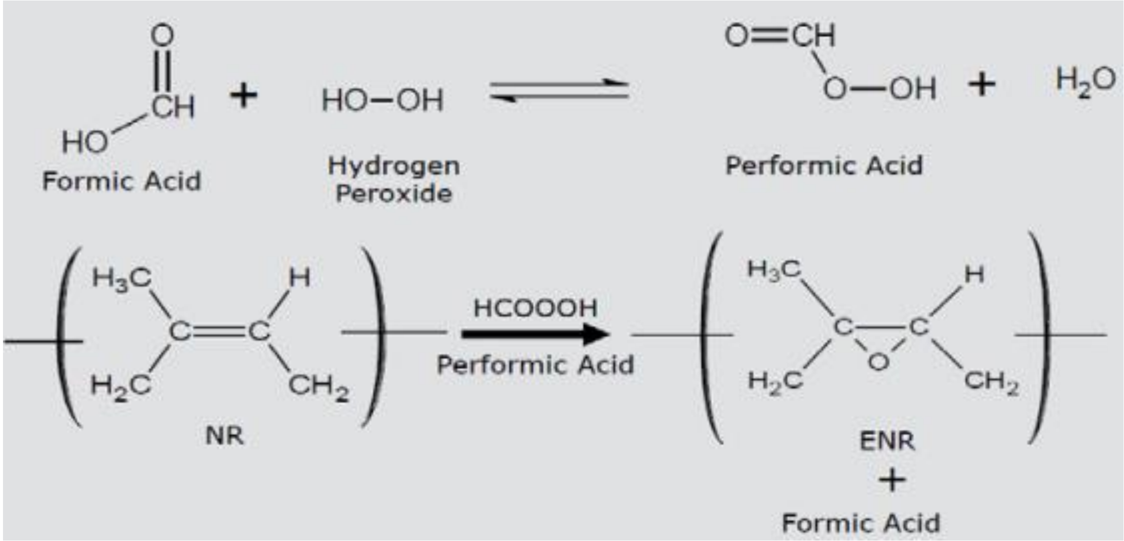


Figure 2.3: Epoxidation of NR through chemical reaction between natural rubber latex and performic acid (hydrogen peroxide + formic acid)[10]

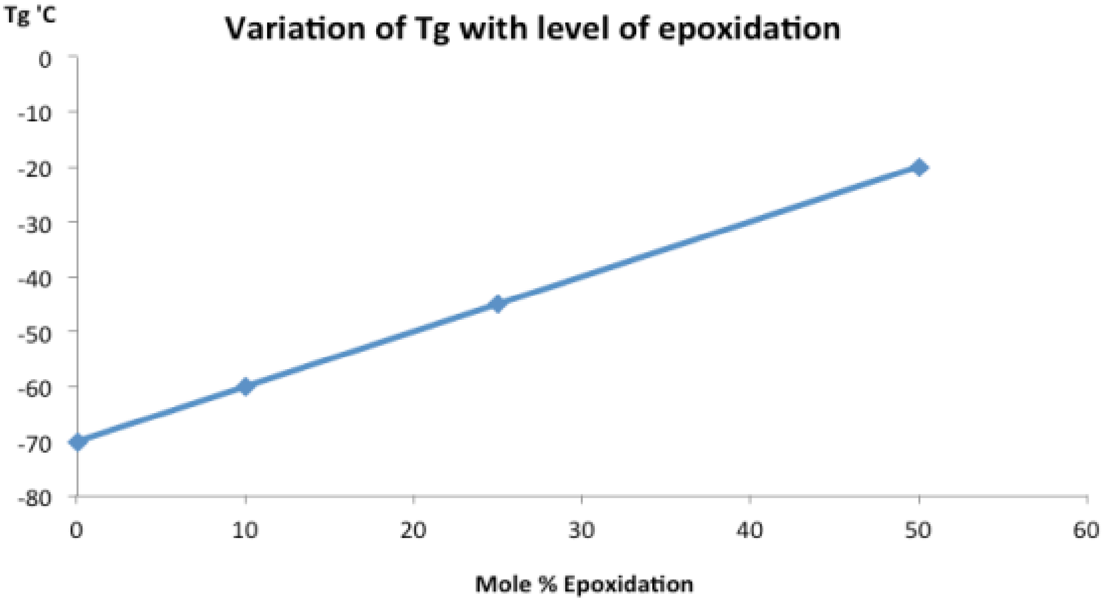


Figure 2.4: The effect of epoxidation level on the glass transition temperature, T_g of ENRs[10]

2.1.3 Butadiene Rubber (BR)

In this research project, butadiene rubber (BR) of grade Buna CB 24 is used in blend compounds with ENR. Buna CB 24 is a solution polymerised high-cis polybutadiene polymer produced with a neodymium catalyst. BR is a homopolymer of butadiene monomer and usually the high cis grades of BR contain approximately 97-98% cis-1,4 butadiene units as shown in Figure 2.5. Butadiene rubber is noted for its high abrasion resistance, low heat build-up, and the highest resilience of all known elastomers as well as a low glass transition temperature (T_g)[2]. Unlike NR, BR is resistant to chain scission during mastication and the mixing process[3]. Butadiene rubber is more difficult to process than NR or SBR, so it is commonly used in blends with other rubbers such as NR, SBR or NBR to improve the abrasion resistance, resilience and low-temperature flexibility. BR is used mainly in the production of tyre tread where it is blended with SBR, for passenger car tyres and with NR for truck tyres. BR is also used in blends with other rubbers such as NBR in manufacturing mechanical and engineering rubber goods[2].

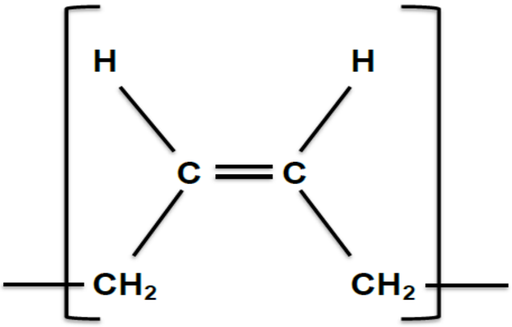


Figure 2.5: Structure of Butadiene rubber, cis 1,4 polybutadiene.

2.2 Tyre Technology Overview

Nowadays, there are tyres for racing vehicles, passenger car vehicles and light trucks. In such tyres, significant quantities of fabric ply are used as reinforcement for the tyre structures. There are also larger tyres such as those used for heavy trucks, farm and agricultural vehicles, earthmoving equipment and large aircraft which tend to comprise both steel wire and fabric reinforcements. Finally, there are a range of specialty tyres which include those used on fork lift trucks, light aircraft, construction equipment and golf cars[11].

A pneumatic tyre is essentially a cord-rubber composite. There are two types of pneumatic tyres that are commonly used, radial ply and cross ply. Tyres have plies of reinforcing cords extending transversely from bead to bead, on top of a belt located below the tread. A range of specialized components are also found in a tyre that serve to ensure the tyre meets its intended design and required performance. High-performance passenger car tyres can have a nylon overlay which is located over the belt package as shown in Figure 2.6. These nylon overlays restrict and control tyre growth resulting from centrifugal forces created at high speeds. The ply turn up is the body ply that wraps around the bead wire and turns up the sidewall, anchors the body plies to the bead bundle and further reinforces the lower sidewall region. A toe guard is a nylon-reinforced rubber component which functions to protect the bead toe from tearing during mounting and dismounting. The chafer is to further protect the bead area from abrading against the rim flange during use[11].

For pneumatic tyres, the rubber part of the composite structure consists of rubber compounds composed of an elastomeric matrix and rigid filler. The exact composition of the compound will depend on the role and application in the tyre architecture. It is common to have more than half dozen different compounds in a tyre, which vary by their polymeric composition and blends as well as the type and amount of filler and other chemicals used[12].

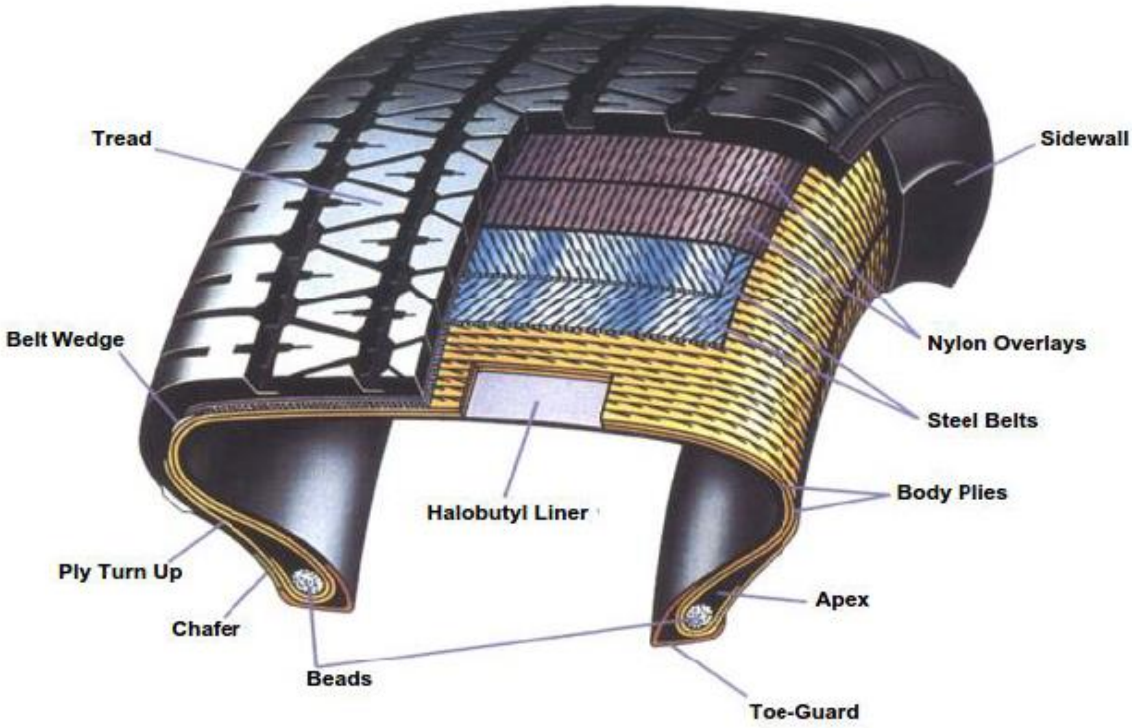


Figure 2.6: Example of a cross-section of a high-performance passenger car tyre[11].

2.2.1 Tyre Performance Criteria

Today the tyre industry is challenged to meet new environmental and safety standards while at the same time maintaining or improving the current vehicle handling, ride and durability that has already been achieved. Three main tyre properties that are very important for the user are treadwear, rolling resistance and wet traction, usually determined by the composition of the tread compound. It has always been difficult to improve all these three properties at the same time merely by compounding[13]. Usually the tyre manufacturer aims to obtain the best possible compromise between the following properties:

i) High abrasion resistance
ii) Low rolling resistance
iii) Good (wet and dry) grip

A low rolling resistance combined with high wet and dry grip properties is very difficult to obtain. Both these properties are determined by internal hysteretic losses within the tyre rubber. The rolling resistance is commonly related to the phase angle δ in dynamic mechanical testing at 60°C, representing an average operation temperature of a tyre at frequencies of the order of 10-30 Hz. In this case a low rolling resistance corresponds to a low value of δ. Good wet grip properties are characterized by much higher frequencies involved in the skidding process. In this case a high value of δ is desired to give good wet grip. The effect of higher frequency can be transformed, by means of the time-temperature superposition principle, to lower frequencies at lower temperature, which are easier to obtain experimentally. Therefore, the tyre manufacturer aims to produce tyre compounds with a high tan δ at 0°C and a low tan δ at 60°C as reported by Noordermeer[14]. An example of tan δ vs temperature obtained from Dynamic Mechanical Thermal Analysis (DMTA) measurement is shown in Figure 2.7.

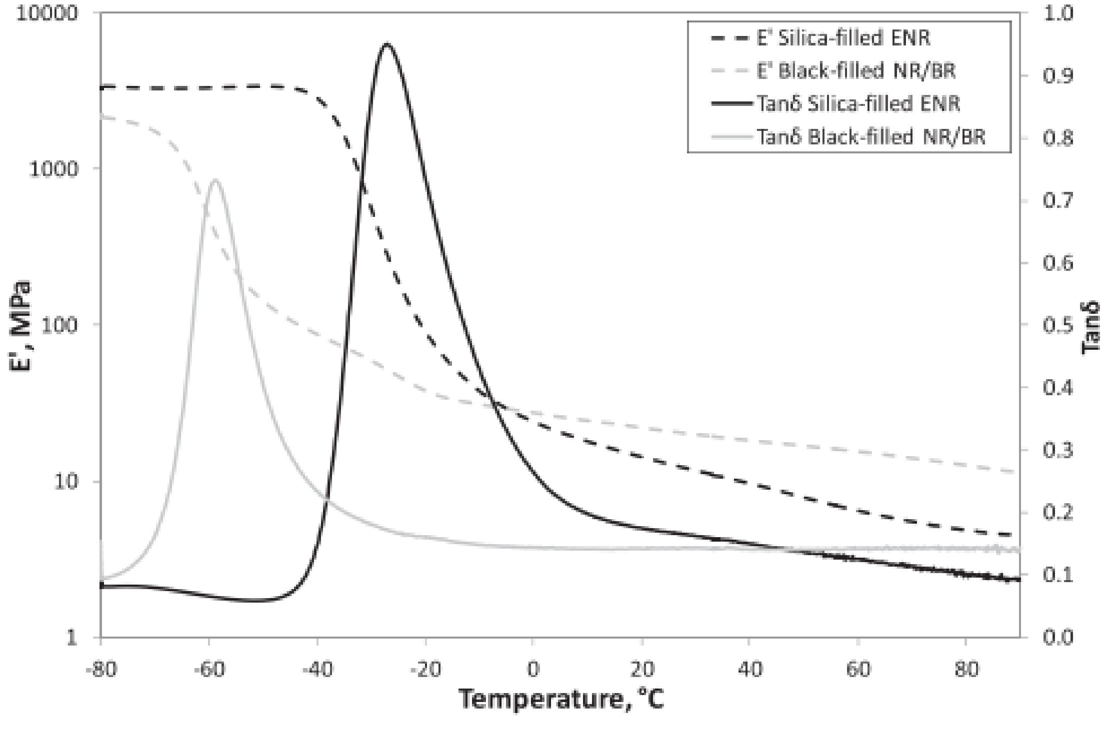


Figure 2.7: Tan δ and E' curve versus temperature of ENR25-silica compound measured by DMTA[15].

Based on the Williams, Landel & Ferry model equation (WLF), the model uses time-temperature superposition to generate master curves that predict the dynamic behaviour of materials at frequencies outside the range of practical measurement. This model relies on the observation that time and temperatures have equivalent effects on the properties of viscoelastic materials. The relationship given by the Williams, Landel & Ferry model equation shows that, for any given rubber, the glass transition temperature increases with the stress frequency, which moves the T_g toward higher temperatures[16].

Sarkawi *et al*[10], reported the temperature dependence of tan δ obtained from DMTA measurement for ENR25-silica and NR/BR carbon black compounds. The paper concluded that, the tan δ at 0˚C of the ENR25-silica compound was higher than that of NR/BR-carbon black compound, indicating a marked improvement of wet grip for the ENR25-silica tread. The range between 30˚C and 70˚C was taken to reflect the running temperatures of a tyre and thus the tan δ in this temperature range correlates with the tyre rolling resistance. A lower tan δ at 60˚C for the ENR25-silica compound as compared to NR/BR-carbon black compound indicated a lower tyre rolling resistance.

The tyre manufacturer has two main variables that they can adjust during design of the compound formulation in order to obtain optimum properties, the rubber polymer and the amount of reinforcing filler[14]. Based on these two main variables, this research project is concerned with the development of a 'green' tyre tread compound using ENR25 as the base polymer and silica as the reinforcing filler. The composition and structure of silica and its function as a reinforcing filler in rubber will be discussed in the following sections.

2.3 Silica

Silica also known as silicon dioxide, SiO_2 is most commonly found in nature as quartz, as well as in various living organisms[17]. Silica is one of the most complex and most abundant families of materials, existing both as several minerals and being produced synthetically.

Synthetic silica is used as a filler for rubber compounds. It is amorphous, consisting of silicon and oxygen atoms arranged in a tetrahedral structure, assembled into a three-dimensional network. Silica fillers are prepared synthetically either by precipitation or by pyrogenic processes. However, the precipitated silica is the most commonly used silica in rubber compounds especially in tyre rubbers compounds. Sand, soda ash, caustic soda and water are the raw materials that are required to produce sodium silicate in a furnace or digester operation. Silica is produced by the controlled neutralization of a dilute sodium silicate solution by using concentrated sulphuric, hydrochloric or carbonic acids to cause the silica to precipitate. During the precipitation, a low solids content slurry of hydrated silica and residual salts such as sodium sulphate, sodium chloride or sodium carbonate are produced. The salts are usually removed by a washing process which reduces the salt content to one or two percent. After filtration, washing and drying, the product is composed of 86-88% of silica with 10-12% of water, about half of which is chemically bound. In most cases the final product (silica) still contains about 6% free water which is roughly the equilibrium free water content at 50% relative humidity[18,19].

After the first invention of synthetic amorphous silica in the late 1940s, silica filler progressed in the next 20 years, from a simple filler used for producing coloured rubber compound and products to an important physical performance additive used for improving rubber compounds properties, especially in tyre applications. In this way, silica manufacturers started to develop and offer various grades of silicas for different rubber product requirements[20].

Recovered silica from the pyrolysis of tyres may also be available as an alternative silica filler. The advent of the European tyre labelling regulation EC/1222/2009 and tightening of the US Corporate Average Fuel Economy (CAFE) regulations have resulted significant improvements in the fuel efficiency offered by tyre manufactures[21]. Therefore, due to these regulations, the utilization of silica filler in place of carbon black in rubber compounds has increased. Based on analysis of a selection of European energy efficient tyres from leading manufacturers highlighted that the tread compounds now contain as little as 2wt% carbon black. This means that pyrolysis of waste tyres, offers an alternative source of silica filler, whilst assisting with the environmental issues associated with end-of-life tyres.

ARTIS[22] produced recovered silica from a pyrolysis process, referred to as ‘rSilica’. The rSilica demonstrated a slight reduction in filler dispersion compared to virgin highly dispersible silica of grade Ultrasil 7000GR. However, the overall compound properties of filled rubber showed an impressive performance compared to the Ultrasil 7000GR control compound, supporting the use of such recovered silica in tyre compounds.

Geothermal energy industries in countries such as New Zealand and Japan can also be one of the potential sources of recovered silica and other minerals and metals, which can be extracted from the geothermal fluids[23,24]. For example, it has been reported that the composition and volume of geothermal fluids in New Zealand offers a considerable potential commercial opportunity for the recovery and sale of a range of materials such as silica, precious metals and various minerals and gases. Although the extracting of products from geothermal fluids is technically feasible, positive economics is the key that driver for commercial success.

In this Thesis, the performance of these recovered silicas from tyre pyrolysis and geothermal sources in an ENR/silica tyre tread compound will be evaluated and will be a novel finding.

2.3.1 Silica as Reinforcing Filler in Rubber

The characteristic structure of silica as a filler can be divided into three levels, primary particles, aggregates and agglomerates. The size of primary particles for silica is between 5 to 40 nm. The silica aggregates are formed by the reaction of primary particles during dehydration and the typical size of silica aggregates is 100 to 500 nm. Within the aggregates the nano-sized primary particles are linked together by siloxane bonds. Agglomerates of silica are formed by the agglomeration of silica aggregates, held together by hydrogen bonding and Van der Waals forces[25].

The reinforcement effect of a reinforcing filler is influenced by its specific surface area, aggregate structure and by the chemical structure of its surface. The specific surface area is the amount of surface area per gram of filler and is the most important factor that determines the reinforcing effect of silica. This is because the specific surface area determines how much contact area is available for physical or chemical interactions between the rubber and filler. The specific surface area is mostly determined by the dimensions of the primary particles of silica, with silica having a smaller primary particle size possessing more specific surface area and hence resulting in a greater reinforcement effect[26]. Surface areas for a range of commercial silica fillers are given in Table 2.1.

Table 2.1: Classification of various commercial silicas based on their surface area and dispersibility (HD = highly dispersible)[20].

CTAB Surface Area (m^2/g)	**100 ± 20**	**160 ± 20**	**200 ± 20**
Conventional	Ultrasil 360 (GR) Ultrasil AS 7, Ultrasil Hubersil 1613, 1633, Hi-Sil 315 Zeosil 125 Gr Zeolex 23, Zeolex 80	Ultrasil VN3 Hubersil 1714, 1715 Hubersil 1743, 1745 Hi-Sil 170, 210, 233 Hi-Sil 255, 243 LD Zeosil 145 GR, 174 G Zeolex 25	Hi-Sil 170 Hi-Sil 185/195 Zeosil 195 GR
Semi- HD	Ultra VN2 (GR) Zeosil 115 Gr Zeosil 1135	Ultrasil 3370 GR Hi-Sil 234 MG Hi-Sil EZ Huberpol 135 Zeosil 145 MP Zeosil 165 Gr	Hi-Sil 190 G Zeosil 195 MP Zeosil 215 GR
HD	Zeosil 1115 MP Zeopol 8715	Ultrasil 7000 GR Zeosil 1165 MP(S) Zeopol 8745 Zeopol 8755	Ultrasil 7005 Zeosil 1205 MP Hi-Sil 2000

The silica surface is composed of siloxane and silanol groups as shown in Figure 2.8, randomly distributed over the whole silica surface. The typical silanol groups present on the silica surface can be divided into three types;[25]:-

i) Isolated or free silanol group (a single hydroxyl group on a silicon atom)

ii) Geminal silanol group (two hydroxyl groups on the same silicon atom)

ii) Vicinal silanol group (two hydroxyl groups on adjacent silicon atoms)

In addition, a siloxane is formed at the silica surface when one oxygen atom is shared by two silicone atoms.

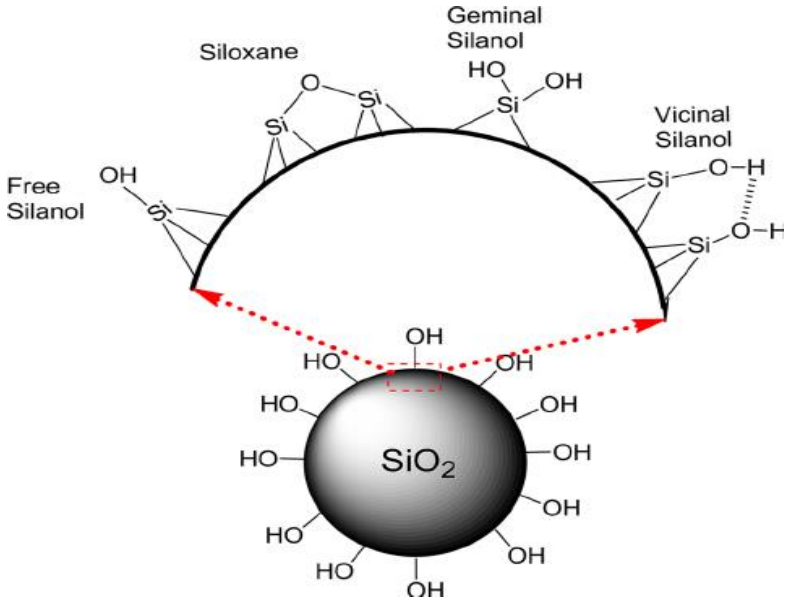


Figure 2.8: The siloxane and silanol groups on a silica surface[27].

The average size of silica aggregates also depends on the concentration of silanol groups on the silica surface. Usually a higher amount of silanol groups per unit surface area will result in an increase of silica aggregate size[26].

The silanol groups on the silica surface can interact with each other to form strong agglomerates due to the hydrogen bonds between the silanol groups. Easy incorporation of silica into the rubber mixture and good dispersion of silica particles is important as they can affect the processing and compound performance and properties. Silicas for the rubber industry can be classified according to their dispersion performance into three types, namely conventional, easily dispersible or semi-HD and highly dispersible (HD) silicas, as shown in Table 2.1[20]. The silanol composition on the surface of the three types of silicas remains to be elucidated, but it would be anticipated that HD silicas would have a higher amount of geminal silanols, whereas the conventional silica would have a higher amount of isolated silanols[4]. According to Kaewsakul *et al.* the compounds containing highly dispersible silicas exhibit greater filler–rubber interaction but, the flocculation processes develops faster when compared to the compounds filled with conventional silicas[28].

An important factor that can influence the reinforcement of silica filled compounds is flocculation. This is because the polar silica aggregates tend to flocculate due to their poor compatibility with the mostly non-polar rubbers and their consequent strong tendency for self-association. The flocculation process can occur during compound storage and also at the onset or early stage of vulcanization when no dense rubber network has been formed yet[28,29]. A typical cure curve with a flocculation hump or shoulder that was measured using an RPA 2000 is shown in Figure 2.9. Kaewsakul *et al*[28]. investigated the kinetics of the flocculation process in a silica filled natural rubber (NR) system by determining the change in storage modulus of uncured compound at a low strain amplitude under simulated vulcanization conditions, according to a procedure carried out by *Mihara et al*[30]. The results obtained demonstrated that silica flocculation can be effectively suppressed by increasing compound dump temperature and the amount of silane added, which results in a better degree of dispersion, higher degree of hydrophobation and a higher degree of silica-rubber interaction. It was also stated that epoxidation of NR clearly influences the silica-rubber interaction but there was no clear evidence of a change of flocculation rate[28].

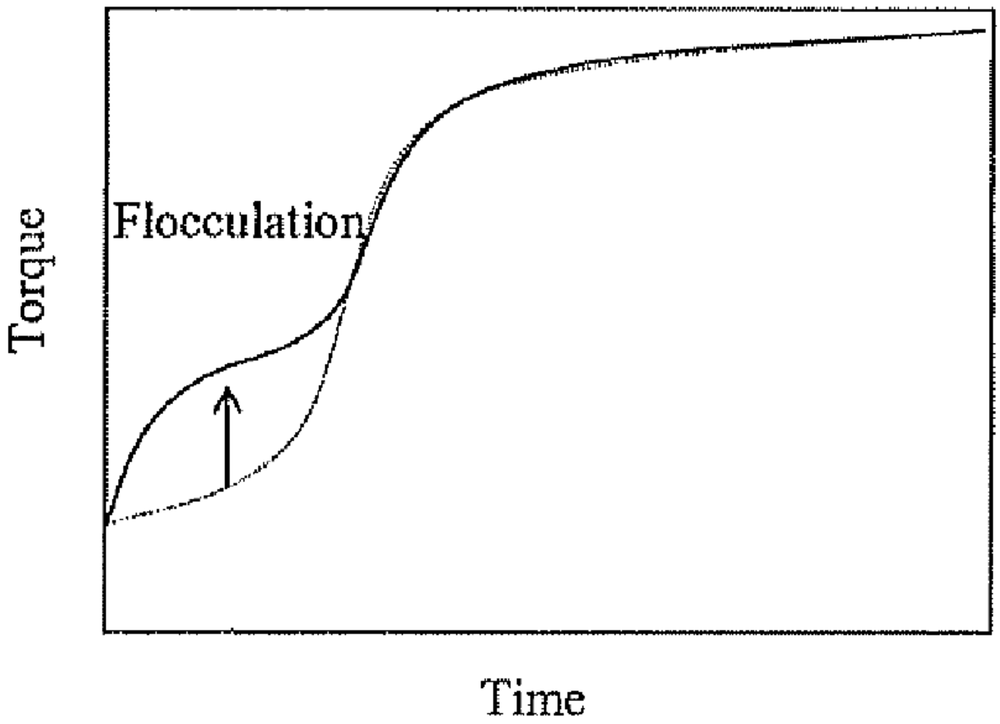
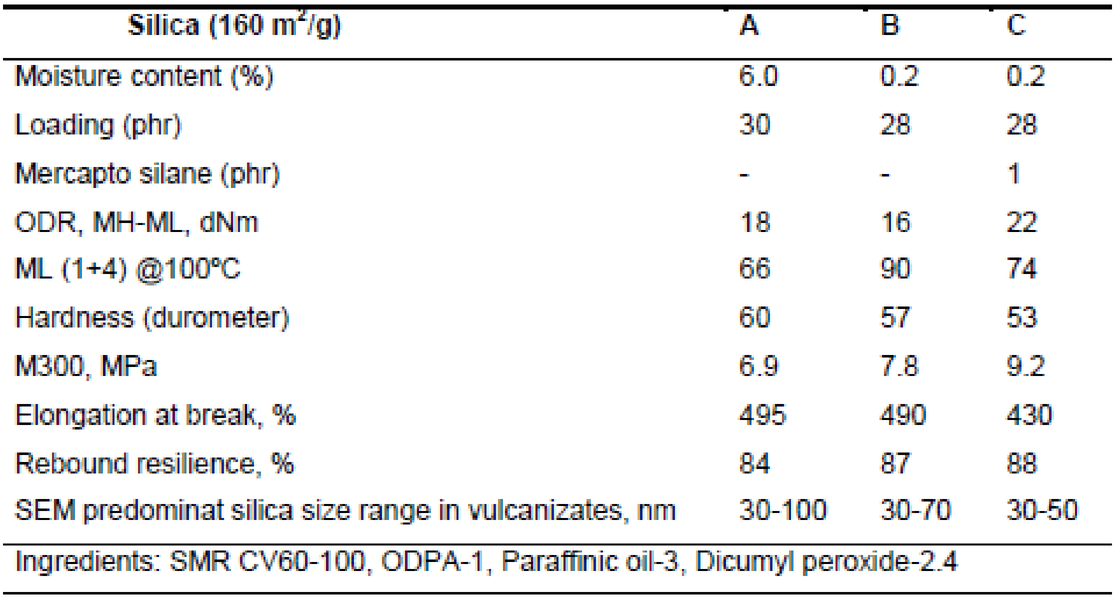


Figure 2.9: Illustration of the cure curves with and without flocculation; dashed line: without flocculation; solid line: with flocculation[30].

The silica surface has a tendency to absorb moisture due to its hydrophilic character and to attain equilibrium with the relative humidity of its environment. Silanol groups on the silica surface are very unstable and the equilibrium is towards forming siloxane groups. Hence, siloxane and silanol groups establish an equilibrium depending upon humidity level. The normal moisture content of silica is in the range of 5 to 7% [18]. Hewitt[18] reported that the larger particle aggregates are reduced in number in dried silica (moisture content less than 1%) and the average diameter of the larger aggregates is reduced from 100 to 70 nm in dried silica. It is also reported that dry silica in the compound increases the Mooney viscosity, slightly reduces the hardness and increases the high-strain modulus of a NR compound as shown in Table 2.2. The author reported that an increase in viscosity with dried silica involves a loss of plasticization due to the removal of the cloud of water which normally surrounds the silica particle. The reduction in viscosity values, shown in Table 2.2, when a silane coupling agent is used to treat the dry silica surfaces indicates that the resulting loss in hydrogen bonded structure between silica particles is the major factor in the viscosity decrease. At water contents above 7% plasticization predominates, with a resulting decrease in Mooney viscosity. The free water also acts as a barrier to reduce the attachment of silica surface silanols (SiOH) to soluble zinc and hydrogen bonded materials[18].

Table 2.2: Effect of moisture/free water content on silica (30phr) filled NR compound with peroxide cure[18].



Silica (160 m^2/g)	A	B	C
Moisture content (%)	6.0	0.2	0.2
Loading (phr)	30	28	28
Mercapto silane (phr)	-	-	1
ODR, MH-ML, dNm	18	16	22
ML (1+4) @100°C	66	90	74
Hardness (durometer)	60	57	53
M300, MPa	6.9	7.8	9.2
Elongation at break, %	495	490	430
Rebound resilience, %	84	87	88
SEM predominat silica size range in vulcanizates, nm	30-100	30-70	30-50
Ingredients: SMR CV60-100, ODPA-1, Paraffinic oil-3, Dicumyl peroxide-2.4			

The acidic surface of silica and the active OH groups tend to bond to and deactivate accelerator molecules, which results in the cure reaction being retarded and lower crosslink densities[19]. In order to maintain a given cure rate, it is necessary to add a higher level of accelerator than in corresponding carbon black formulations. Previously it was common to add a substance which was preferentially absorbed onto the surface of silica filler particle at an early stage of the mixing process and before the addition of accelerator, to shield the accelerator molecules from the silica surface. Diethylene glycol and polyethylene glycol were widely used for this purpose, however these materials have now been largely replaced by silane coupling agents which also have additional functionality[19].

The non-polar elastomers are rubbers without polar groups in their molecules such as NR, BR and SBR, which are widely used in tyre compounds. Silica reinforcement of non-polar rubbers such as SBR and BR without surface modification of filler is not very good. When compared with carbon black filler that have similar specific surface area, silica filled non-polar rubber exhibits a lower degree of reinforcement due to the incompatibility between the polar silanol groups on the silica surface and the non-polar rubber[18]. However, a high level of reinforcement in non-polar rubbers may be achieved with silica, when coupling agents are used (see Section 2.4.1).

Elastomers that have polar groups in their molecules such as NBR and CR are considered more compatible than non-polar elastomers with highly polar fillers such as silica. However, from a previous study of silica filled polar rubbers such as CR and NBR, the results showed that their compound properties are still not as good as those of the corresponding carbon black filled compounds. Therefore, a minimal amount of silane coupling agents is still required for the mixing of silica filled polar rubbers as the compounds with silane coupling agent demonstrated a significant improvement in physical and mechanical properties as well as processing characteristics, compared to silica filled compounds without silane coupling agent[18].

2.3.2 Silica in Epoxidized Natural Rubber

Epoxidized natural rubber is produced by chemical modification of NR, as described in section 2.1.2. The presence of epoxide groups makes epoxidized natural rubber a polar rubber[5] and therefore, it may be expected to have good compatibility with a highly polar filler such as silica. Cook *et al.*[31] from Tun Abdul Razak Research Centre (TARRC) has reported that ENR25, with 25 mol% of epoxidation, develops a strong interaction with silica filler without the use of silane coupling agent, as shown by a high bound rubber content. The silica filled ENR25 based on a tyre tread compound also demonstrated properties associated with low hysteresis, which resulted in a low rolling resistance tread compound being developed. Furthermore, the tread compound based on silica filled ENR25 was also found to provide a very good wet grip property. The excellent rolling resistance and good wet grip properties that were obtained with ENR25 has made silica reinforced ENR25 compound become an important choice in producing ‘green ‘tyre tread compound[29].

Cataldo[32] has carried out research into silica-filled ENR compounds to compare their behaviour with those of silica-filled NR compounds with silane coupling agents. The objective was to study the possibility of preparing a rubber compound filled with silica without the use of a silane coupling agent. In the study, ENR/silica and NR/silica with and without silane compounds were prepared using two grades of ENR with 25 and 50% epoxidation (ENR25 and ENR50) and two grades of silica (VN3 and Ultrasil 7000). Their filler dispersion, mechanical and rheological properties were measured and compared. The results showed poor dispersion for the NR compound in the absence of silane coupling agent and the best results in terms of dispersion were observed with NR/silica with silane coupling agent. However, ENR25/silica and ENR50/silica did show better dispersion than NR/silica without silane coupling agent. This could be an indication of a relatively strong interaction between silica and the epoxy groups of ENR. The DIN abrasion results are in line with the expectation of NR/silica with silane coupling agent performing better than NR/silica without silane and both ENR25 and ENR50 with silica.

However, in all cases, both grades of ENR with silica gave better abrasion resistance than NR/silica without silane, for both grades of silica (VN3 and Ultrasil). ENR50 with silica (Ultrasil) also gave higher abrasion resistance than ENR25 with silica (Utrasil) and it appears quite comparable with NR/silica (Ultrasil) with silane coupling agent. The improvement offered by ENR50 with silica could be due to a stronger interaction between silica and the ENR with a higher epoxidation level. However, the tensile strength follows the trend NR/silica with silane > ENR25/silica > ENR50/silica > NR/silica without silane. This trend may be explained by the fact that epoxidation causes a reduction in molecular weight of the polymer and hence affects the ultimate properties of the rubber compound. According to Cataldo, the compatibility between epoxidized natural rubber and silica involves a hydrogen bonding effect and possibly also some chemical bonding, allowed by the cationic ring opening of the oxirane ring caused by acidity of the silica surface as illustrated in Figure 2.10. Therefore, it is possible to compound ENR with silica without the use of silane coupling agent, although the results may not be as good as a similar compound made with NR-silica and silane[29,32].

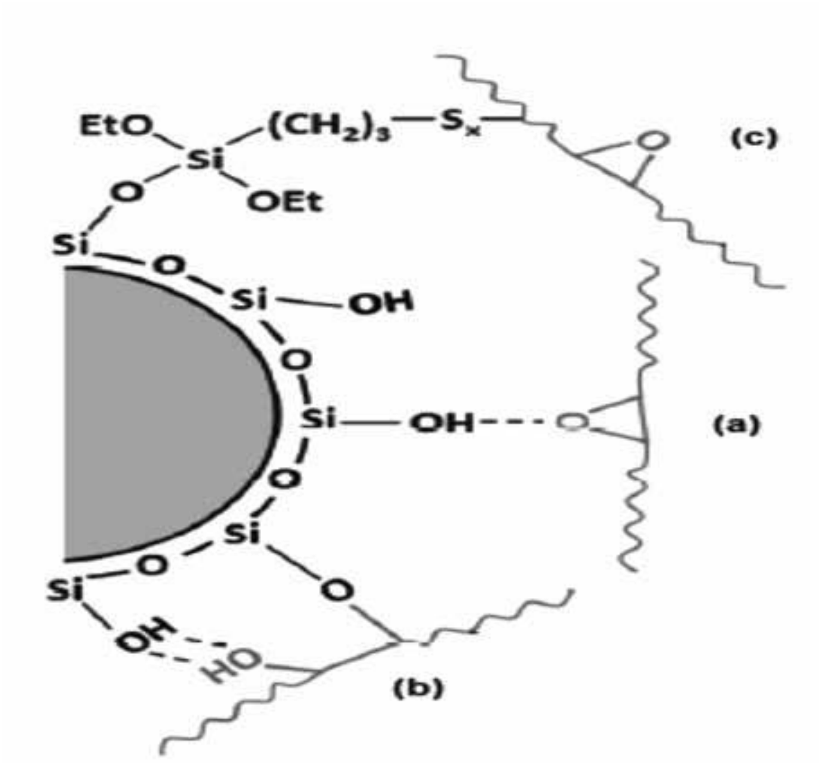


Figure 2.10: Possible interactions and bonding between silanol groups on the silica surface and ENR molecules; a) interaction between silanol groups and epoxide group in ENR, b) coupling of silica with ENR through ring opening of ENR and c) silane coupling bonding (if silane coupling agent present)[33].

Varughese *et al.*[9] carried out a study on the unusual reinforcement mechanism exhibited by silica in epoxidized natural rubber. The higher reinforcement effect could be due to the specific chemical interaction or chemical crosslinking taking place between silica and the epoxy groups while heating the silica filled ENR mix at high temperature. Evidence of higher interaction is established through a rheometric study conducted at 180˚C and a change in the dynamic mechanical characteristic analysis over a wide range temperature using the dynamic viscoelastometer for heated and unheated silica filled ENR mixes. The ENR with 50% mol of epoxidation level was found to have high interaction with silanol groups of silica as evidenced in rheometric and dynamic mechanical analysis. Gelling in one of his papers also reported that the specific interactions through epoxide groups in ENR, results in high degree of reinforcement with silica fillers without the need for coupling agents[5].

There are a number of papers published by researchers from TARRC, about the development of ‘green’ tyre tread compounds from silica reinforced ENR25 compounds. Martin *et al.* reported in their paper that excellent rolling resistance in the tyre tread and hence, reduced fuel consumption, could be obtained with ENR25 reinforced with silica filler[34]. The paper also reported that the micro-dispersion of silica in ENR25 was shown to be exceptional. Micro-dispersion is a measurement of silica particle distribution at very high magnification by using transmission electron microscopy (TEM). Good filler microdispersion in tyre tread compounds is believed to cause improvement in the tread properties, such as reduced wear and rolling resistance[35]. However macro-dispersion of silica in ENR25 is also important. Macro-dispersion is a measurement of silica dispersion in vulcanizates by using reflected light microscopy, namely DisperGrader. The same group of researchers carried out a study into the influence of mixing procedure on the macro dispersion achieved during mixing using an open mill and internal mixer. The objective was to improve the macro-dispersion of silica in ENR and hence, improve properties such as abrasion and wear[34]. Based on the results obtained, the low temperatures and high shear rates achieved when mixing silica filled ENR compounds on an open mill, resulted in exceptionally good macro dispersion as shown in DisperGrader images, which lead to significantly improved abrasion resistance and tensile strength properties. At the same time the Mooney viscosity and bound rubber content were not affected by the high shear rates on the open mill as compared to standard internal mixing, which indicated that there was a minimum effect of mechanical shearing or mastication on the ENR molecular weight and hence viscosity. The bound rubber content results also showed that without the need of silane coupling agent, ENR25 can develop a strong interaction with silica filler.

A comparison study between silica filled ENR25 tyre tread and a silane coupled silica filled SBR/BR blend was also carried out by TARRC[34]. The silica filled ENR25 tread was found to exhibit better rolling resistance and wet traction performance than the silane coupled silica filled SBR/BR. In contrast with standard hydrocarbon rubbers such as SBR and BR, it was thought that the ENR must develop a very high level of interaction with precipitated silica during conventional mixing, without the use of a silane coupling agent. It was supposed that most of the interaction is a result of the hydrogen bonding between the silica and rubber[31]. It was also explained that when curing ENR compounds containing high levels of silica, a shoulder is sometimes observed at the initial part of the cure curve which is similar to that associated with flocculation[5] (Figure 2.7). The result suggests that the silica and ENR25 interaction may not as strong as the silica-silica interaction as demonstrated by the shoulder at initial part of the silica filled ENR25 cure curve. This could be because there is only 25% mol of epoxide group in ENR25.

Baker *et al*. studied and discussed properties of ENR25, and ENR50 containing silica compared with those containing silica and carbon black fillers. Both ENR25 and ENR50 were investigated as tyre tread materials and it was found that ENR25 compound containing silica or silica/carbon black exhibited lower rolling resistance than natural rubber (NR) and better wet traction or grip than OESBR, providing an ideal combination of these two properties for tyre tread application[36]. Although, wear or abrasion resistance data were not included it was anticipated from truck tyre experience, that ENR containing black/silica compounds would have sufficient abrasion resistance. ENR25 and ENR50 with silica and without the use of coupling agent also exhibited equivalent reinforcement to the carbon black filled compound, which means these rubbers have the potential of providing white or coloured vulcanizates[36].

Martin *et al.* in one of her papers also showed that ENR25 with 25% mol epoxidation has a glass transition temperature (T_g) most suitable for tyre tread applications. Silica filled ENR25 tread compounds exhibit lower rolling resistance and enhanced wet and ice traction compared with the benchmark premium passenger or truck treads from carbon black filled compounds[15]. In that paper their main focus was to optimize the wear performance by understanding the correlation between laboratory abrasion testing and on-the-road tyre wear testing. An investigation of silica filled ENR25 tread wear has been carried out at TARRC by using light microscopy and transmission electron microscopy (TEM) to ascertain a mechanistic insight into tread wear for road and laboratory abrasion testing[15]. The results obtained indicate that the mechanism of on-the-road tyre wear is different from that in the laboratory for Akron abrasion tests, where there was a poor correlation between laboratory abrasion and on the road tyre wear. The laboratory and road wear TEM micrographs illustrate that the mechanism of wear is quite dissimilar between Akron abrasion tests and on-the-road tyre wear, where the Akron abrasion test is much more severe than normal tyre wear and the test pieces did not show failure at the rubber-filler interface on the abraded surface. However, the mechanism of on-the-road tyre wear for black filled NR/BR and silica filled ENR demonstrate a similar evidence to each other, of failure at the rubber-filler interface on the tread surface.

The effect of moisture in ENR/silica compounds and in silica filled compounds of NR, BR and sSBR/BR was studied by Martin *et al.*[34]. The cure behaviour of silica-reinforced ENR25, NR, BR and SBR/BR was compared with and without added water and in the presence and absence of a sulphur cure system. It was reported that the cure behaviour of silica filled ENR25 is significantly different when water is present in the compound than when it is absent. The rheometer torque rises earlier, faster and to a greater extent with a significant shoulder before the main cure, which is similar to that associated with flocculation (see Figure 2.7 in section 2.3.1). The steep rise in torque from the start of cure in both compounds with and without curatives, demonstrates that the cure system is not involved in this initial shoulder in the cure curve. The paper suggested that water can change the silica filled compounds rheometer torque by either disrupting rubber-silica hydrogen bond interactions or silica-silica interactions. Dissimilar effects of water on flocculation were observed in the cure behaviour of the others rubber. These differences are thought to reflect the differences in rubber-silica interaction and silica-silica interaction in ENR, NR and BR[34]. The paper reported that the water will disrupt the ENR-silica hydrogen bonding interaction, increasing the scope for silica-silica networking and leading to the largest change in the rheometry results. For NR, a smaller effect on flocculation is observed as there is evidence of few rubber-silica interactions in the NR/silica compound. While in BR, the water may be just disrupting the silica-silica interaction, as a reduction in the flocculation effect is observed.

2.4 Silane Coupling Agents

Inorganic materials based on silicon or metals and organic substances founded on carbon chemistry tend to be incompatible. To increase compatibility between them, chemicals which contain silicon and carbon atoms in a single molecule are generally used. Silanes are an example of this type of chemical, having a unique combination of organic and silicon reactivity. Silanes are a unique class of chemicals that have many applications such as in coatings, adhesives, sealants, elastomers, electronic materials, fiber glass and foundry sand. Plueddemann[37] who had worked for 35 years in the research department of Dow Corning and has published numerous papers about silanes as coupling agents mentions that the most commonly used are bifunctional silanes. After the successful introduction of bifunctional silanes for glass fiber-reinforced composites in the early 1960s, the use of this type of silane in silica-filled rubber compounds started in the late 1960s[20]. A bifunctional organosilane coupling agent is able to chemically bond a polymer matrix to inorganic substrates such as silica through its organo-functional and silicon-functional group. The chemical structure of a bifunctional organosilane coupling agent can be simply described in Figure 2.11 below:

$$X_3 – Si – (CH_2) – Y$$

Figure 2.11: Structure of bifunctional silane coupling agent[20]

Where;
X is the silicon-functional group or hydrolysable group that reacts with inorganic surfaces. The group may be halides, alkoxides or acyloxy, and below are the examples of these groups:

$$\text{-HCl, -OCH}_3\text{, -OC}_2\text{H}_5\text{, -OC}_2\text{H}_4\text{OCH}_{3,}\text{ -OOCR}$$

The silicon-functional group is able to react through hydrolysis and condensation. For example, the chemical reaction of silica with an alkoxysilyl moiety of the coupling agent takes place in a two-step, endothermic reaction. The primary reaction is the reaction of alkoxy groups with silanol groups on the silica surface. Two possible mechanism are reported, one is direct reaction of the silanol groups with the alkoxy groups of the coupling agent, and the other is hydrolysis of the alkoxy groups followed by a condensation reaction with the silanol groups. In the second case, a certain moisture content is required for the reaction of silanization due to the hydrolysis of ethoxy groups of the coupling agent as a precondition for the secondary reaction to take place. The secondary reaction is the condensation reaction between adjacent molecules of the coupling agent on the silica surface or between alkoxy groups of the coupling agent and silanol groups of the silica.[26] (See Figures 2.13 and 2.14 in section 2.4.1)

Y is the organo-functional group that creates bonding with the polymer matrix during the vulcanization. The group can consist of an amino, methacrylate, mercapto, chloro, vinyl or isocyanate group. Below are the examples of these groups:

$-NH_2$, $-C_4H_5O_2$, -SH, -Cl, $-CH=CH_2$, -N=C=O

Organo-functional silane coupling agents can chemically bond to an organic polymer via different reactions or methods as follows:

i) Reaction with terminal or pendant group;

- this reaction can occur for isocyanato, hydroxyl and amine end blocked polymers

ii) Grafting to reactive sites on the backbone;

- this reaction involves the free radical grafting with unsaturated silanes.

iii) Addition or condensation reaction;

- this reaction includes the incorporation within sulphur-crosslinked rubber, free radical-cured acrylates/methacrylates, thermoset epoxy resin and phenolic resin

iv) Formation of interpenetrating polymer networks

2.4.1 Silane Coupling Agents in Silica-Filled Non-Polar Rubber

The reinforcement of rubbers by silane-modified silica fillers is an important application of bifuctional silanes. For the coupling of silica fillers to elastomers, silanes with hydrolysable groups to couple with the filler and organo-functional groups to react or couple with the rubber matrix are needed. This silica-rubber coupling is often achieved by using a trialkoxylsilyl group, preferably a trimethoxy or triethoxylsilyl moiety that will react with silanol groups on the filler surface during the mixing process. For sulphur-cured unsaturated rubber compounds, it is recommended to use sulphur-functional silanes due to their reaction with the rubber in the allyl position to the double bond, during the vulcanization process. For peroxide cured compounds of saturated rubbers, unsaturated silanes such as vinylsilanes bond to the rubber during the vulcanization process. The use of silanes also allows a modification of the polar surface of silica that reduces the silica-silica interaction and hence makes the silica more compatible with rubber matrix. The two functional groups in the silane can be linked by a hydrocarbon spacer, preferably polypropylene groups, which contribute to the hydrophobation of the polar silica surface. The hydrophobation of the silica surface with monofunctional alkylalkoxysilanes, which couple to silica but cannot react with rubber, lead to a strong reduction of the silica network, which results in a reduced Payne effect, lower viscosity and lower hardness[19,20].

For sulphur-cured rubber compounds, there are three types of organo-functional or sulphur-functional silanes that are commonly used as shown below[19]:

i) Di- and polysulfide silanes; $[(RO)_3–Si–CH_2–CH_2–CH_2–S]_2–S_x$
ii) Mercaptosilanes; $(RO)_3–Si–CH_2–CH_2–CH_2–SH$
iii) Blocked mercaptosilanes; $(RO)_3–Si–CH_2–CH_2–CH_2–S–B$

Where; $R = CH_3, C_2H_5$; B = CN; x = 0-8

The main application of di- and polysulfide silanes is in the tyre industry whereas the mercaptosilanes are used widely for industrial rubber goods and also for shoe soles. As shown above, the R group in the coupling agent can be either methyl or ethyl. The trimethoxysilanes show a faster hydrolyzation speed than the ethoxy silanes, but methanol is released during the reaction that can result in serious health and safety problems. Therefore, for most rubber applications the triethoxysilyl group silane is preferred by the rubber industry.

The first successful commercially available silane coupling agent for silica filled rubber was mercaptopropyltri-methoxysilane in the late 1960s. The polysulfidic silane bis(3-(triethoxysilyl)propyl) tetrasulfide (TESPT), tradenamed Si69® from

Degussa was introduced in 1972 and has set the benchmark for significantly improved silica filled rubber compounds. The uses of silica-silane compounds grew slowly until the 1990s. In 1992 the introduction of the “green tyre” by Michelin with a tyre tread based on silica from Rhodia and silane from Degussa was a real breakthrough in tyre innovation and technology[20]. Most published literature concurs that the tensile strength and tear resistance of silica-filled compound with coupling agent is similar to compounds filled with a carbon black such as N339. However, some studies such as Stewart[38] state that the utilizing of silica filler instead of carbon black may adversely affect compound abrasion resistance and lower the 300% modulus. On the other hand, Wagner[39] has stated that these properties are comparable between the two types of filler and the differences are usually due to the choice, level and point of addition of coupling agent in the rubber compound. Wagner also reported that the best results can be obtained if the coupling agent is added to the filler before it is compounded into rubber during the mixing process.

The silane coupling agents may be premixed or pre-reacted with the silica filler or added to the rubber compound during the mixing stage of rubber and silica filler. If the coupling agent and silica are added simultaneously to the rubber compound during the mixing process, the coupling agent will react in-situ with the silica filler. Based on the previous studies, the most commonly and effectively used silane coupling agents in silica filled rubber systems are bis(3-(triethoxysilyl) propyl) tetrasulfide (TESPT) and bis(3-(triethoxysilyl) propyl) disulphide (TESPD)[40]. The chemical structure of TESPT silane coupling agent is shown in Figure 2.12. The use of silanes such as TESPT involves two main chemical reactions that need to take place during rubber processing namely, the silica and silane reaction (silanization) and silane-rubber reaction. The reaction between silane coupling agent and silica results in hydrophobation of the silica surface where this hydrophobation inhibits the formation of a silica-silica network in rubber and makes silica more compatible with non-polar rubbers[40,41].

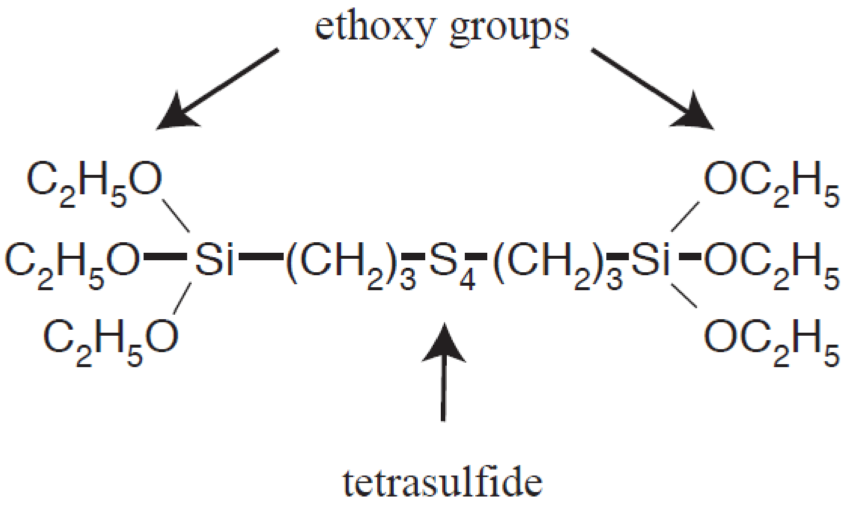


Figure 2.12: Chemical structure of TESPT silane coupling agent[40]

The reaction mechanism between silica, rubber and TESPT silane coupling agent has been extensively reviewed and studied[20,33,40,41,42]. During mixing, the triethoxysilyl groups of TESPT react with the silanol groups on the surface of the silica, with loss of ethanol. The rubber reactive group of TESPT, the tetrasulphane has a strong tendency to form bonds with the rubber during curing of the rubber compounds[40,41,42]. The primary and secondary reaction of TESPT silane coupling agent and silica silanol groups during compounding, as well as the reaction of TESPT and rubber during curing are shown in Figures 2.13 - 2.15 respectively. It is reported also that the reactivity of silane coupling agent is generally influenced by the stability of the hydrolysable group of the silane. For comparison, the methoxy has the highest rate of silanization reaction followed by ethoxy, propoxy and butoxy derivatives. The methoxy groups reacts rapidly but is not used as a silanization agent due to the toxicity of the evolved methanol[40].

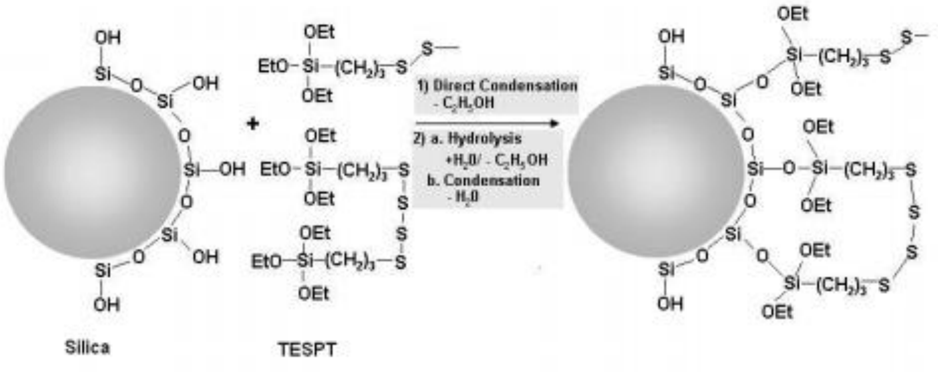


Figure 2.13: Primary reaction between silica and silane coupling agent[40].

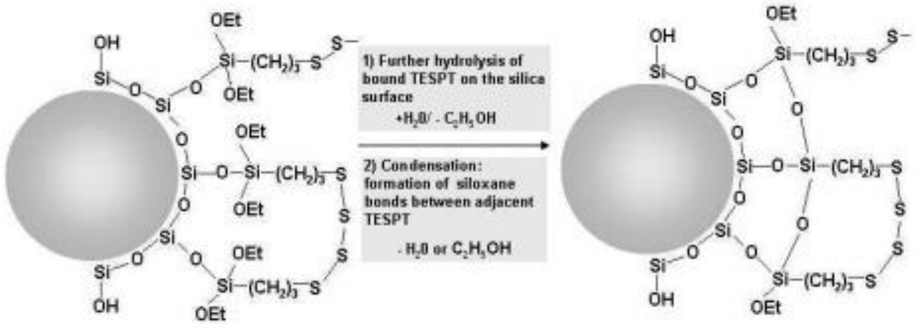


Figure 2.14: Secondary reaction between silica and silane coupling agent[40].

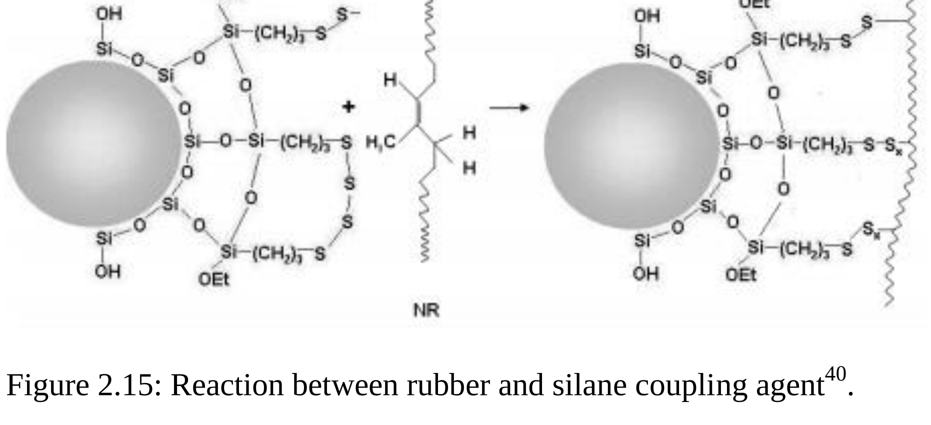


Figure 2.15: Reaction between rubber and silane coupling agent[40].

According to Mihara, silica in rubber compounds tends to flocculate in the early stages of vulcanization even if silane coupling agents are applied. In her study, flocculation was monitored by following the changes of storage modulus at low strain, referred to as the Payne effect (Figure 2.16), using a RPA 2000 dynamic mechanical tester. Then the kinetic parameters, the rate constant and the activation energy of the silica flocculation were determined by using the Arrhenius equation. Based on the value of the activation energy, she concluded that silica flocculation is a purely physical phenomenon[30]. The interfacial interaction layer between silica and rubber with the presence of silane coupling agent, was estimated from bound rubber measurements. It was found that the flocculation rate of silica decreases with increasing interfacial interaction layer on the silica surface. The result indicates that the decrease of the flocculation rate is due to the shielding effect of the silane coupling agent[30].

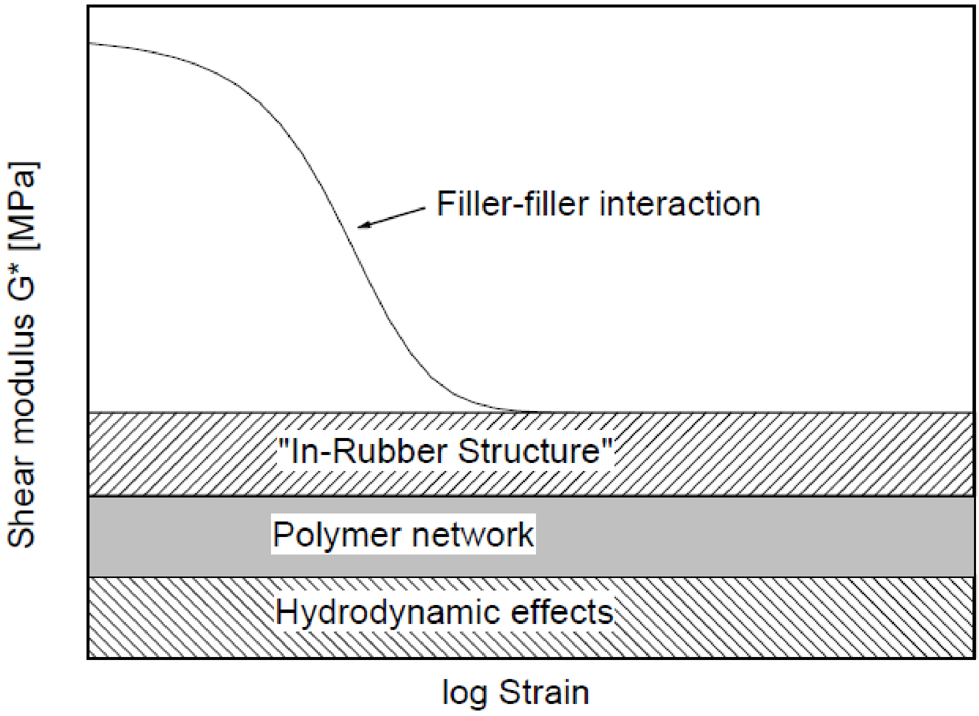


Figure 2.16: An example of Payne-effect obtained from dynamic mechanical tester[26].

A proper silanization of silica during mixing will result in good dispersion of silica. Salina *et al*. had investigated the morphology of silica reinforced natural rubber (NR) in the presence and absence of a silane coupling agent, bis(3-(triethoxysilyl) propyl) tetrasulfide (TESPT). In that study, the micro and nano-dispersion morphologies of silica in NR and deproteinized natural rubber (DPNR) were studied by using transmission electron microscopy (TEM) and atomic force microscopy (AFM). From the TEM images obtained, it was found that vacuoles around the silica particles are formed in the absence of silane coupling agent as a result of weak silica-rubber interaction. While in the presence of silane the strong silica-rubber bonding results in no formation of vacuoles around silica particles[43,44]. In addition, an improvement of the micro-dispersion of silica in the NR and DNPR vulcanizates with the use of silane coupling agent was observed from AFM phase imaging. The results were also supported by the high chemically bound rubber content and low Payne effect of silica in rubber in the presence of TESPT[43].

Salina Sarkawi *et al*. reports that the properties of silica filled compounds with silane coupling agent demonstrate a strong dependence on mixing dump temperature. This is because the silanization reaction and silica dispersion during mixing are the key parameters in this system. It was also reported that the optimal mixing conditions for silica filled NR compounds in the presence of TESPT silane coupling agent are to be dumped at temperature in the range of 135-150˚C. However, if the mixing was performed till dump temperatures above 150˚C were reached, this resulted in a decrease in vulcanizate properties due to NR degradation. Based on the results obtained, it is evident that during mixing of silica filled NR compound in the presence of TESPT silane coupling agent, premature crosslinking reaction also take place beside the silanization reaction. This is due to NR starting to react with sulphur coming from the TESPT molecules at temperatures as low as 120˚C, but this phenomenon did not have an adverse effect on the vulcanizate properties[40].

It has been reported that the addition of organosilane such as bis(3-(triethoxysilyl) propyl) tetrasulfide (TESPT) into silica filled rubber not only improves silica dispersion but also enhances the silica-rubber interaction which results in improvement in rolling resistance and wet grip properties[45]. In order to gain maximum benefit from silane coupling agents, the reaction between silanol groups on silica surfaces and alkoxy groups of silane coupling agents (silanization) must take place sufficiently during the mixing process. Thaptong *et al.* had carried out an investigation on the influence of silanization temperature on the properties of silica filled solution polymerized styrene butadiene rubber with addition of two different types of silica, namely highly dispersible silica (HDSi) and conventional silica (CSi). It was found that increasing the silanization temperature during the mixing process leads to enhanced silica-rubber interaction, filler dispersion and crosslink density. These in turn resulted in an improvement in vulcanizates properties such as modulus, heat build-up (HBU), dynamic set and tyre performance properties such as wet grip, rolling resistance and abrasion resistance[46]. However, it was suggested that great care must be taken during mixing in order to avoid the scorching phenomenon at too high a mixing temperature. The paper also concluded that the best balance of compound properties is found at a silanization temperature of 140˚C. It was found that there were insignificant differences in filler dispersion, wet grip and rolling resistance between the highly dispersible silica (HDSi)and the conventional silica (CSi)[46].

There is much published literature supporting the use of silica fillers in combination with bifunctional organosilane such as bis(3-(triethoxysilyl) propyl) tetrasulfide (TESPT) coupling agent in rubber applications especially in tyre compounds. Wolff reported that the use of silica with TESPT coupling agent gives superior physical vulcanizate properties such as low heat build-up, better performance under continuous deformation and better tear and cutting resistance compared to carbon black filled vulcanizates[47]. Goerls *et al.* also investigated silica in combination with TESPT coupling agent due to their use in tyre treads to improve in rolling resistance and wet grip. In that paper, the reaction of precipitated silica with the silane was investigated in relation to the influence of various parameters such as silane concentration, pH and moisture content. The effect of the variables on the reaction type, degree of reaction and the reaction kinetics were investigated using ^{29}CP/MAS solid state NMR spectroscopy. It was found that increasing the silane concentration exhibited no significant difference in the efficiency of the reaction. However, at low concentrations a greater amount of ethanol was formed per mole silane, indicating a noticeably higher degree of hydrolysis of silane. The use of acidic and alkaline silicas and fillers with higher moisture content favoured the reaction with the silane, with a greater efficiency of reaction observed[45]. Therefore, by use of appropriate organic silanes and controlling mixing conditions, silica has proved workable in tread compound formulation.

Silica filled rubber compounds present considerable difficulties in processing and processability as reported by Lin *et al.* These difficulties include higher compound Mooney viscosity (ML 1+4), short scorch time and environmental problems related to alcohol evolution[48]. The high viscosity and poor processability of silica filled compounds are believed to be associated with silica reaggregation or self-aggregation after the rubber compounding process[49]. Therefore, Lin *et al.* carried out studies on the change in Mooney viscosity with aging time for silica filled compounds containing various silanes and polar additives. Several mechanisms for aging stability are postulated and evaluated in the experiments. It was found that the type of silane or polar additive used can cause the Mooney viscosity to increase or decrease during aging. The rate of increase in Mooney viscosity is strongly dependent on the ambient moisture, mixing and processing temperatures, the extent of connection between silica and polymer, and the strength of the association of silica-dispersing agent to filler and to polymer. It was also reported that when bis(triethoxy silanes) were used in silica filled rubber compounds, the Mooney viscosity increased during aging. Silica-silica bridging (silica-TESPT-silica) was found to be responsible for the Mooney viscosity growth during aging in rubber compounds containing TESPT silane coupling agent. When TESPT was used, a fraction of TESPT was attached to the unsaturated rubber to give rubber-silica attachments which further increased the Mooney viscosity during aging. The secondary reaction of the silane occurring during storage can lead to the formation of a three-dimensional linkage between the silica aggregates themselves or between the polymer and silica (polymer-silica coupling). This sequence increases the silica aggregate-aggregate interactions and leads to a more developed silica network which results in an increase in Mooney viscosity. These processes are greatly accelerated by the presence of high water content in the rubber as demonstrated by faster growth of Mooney viscosity during the humidity aging condition[48].

However, it was found that chemically coating the silica with mono functional silane such as N, N-dimethyl-1-octadecanamine or physical coating with a trialkyl amine compound could effectively stop the viscosity increase upon aging. It was also reported that a reduction in the Mooney viscosity could be realized by absorption of ambient moisture as the viscosity of silica filled compounds decreased upon humidity aging. The decrease in viscosity of silica filled compounds was attributed to the absorbed water in the aged compound stocks helping to weaken silica-silica interactions. This is because of the water having a strong affinity to silica and acting as an additional silica-shielding agent. The paper also concluded that processing difficulties (higher Mooney viscosity) encountered in the silica filled rubbers containing TESPT are primarily due to the higher degree of functionalization of the polymer (TESPT-polymer) by the reaction of the polysulfane and not because of polymer crosslinking. The authors suggest that this degree of functionalization can be reduced by lowering the mixing temperature and by the proper choice of silanes such as TESPD (more thermally stable polysulfane) or by the use of dispersing agents[48].

It has also been pointed out that TESPT silane coupling agent used in a silica filled compound has two functions, as a coupling agent to improve filler reinforcement and as a crosslinking agent. This is because the silica filled rubber can be cured by using the sulphur in the TESPT with the cure being optimised by the addition of sulphonamide accelerator and zinc oxide[50]. In addition, Zhang *et al.* reported that the sulphur released by the TESPT coupling agent also participated in the vulcanisation reaction which resulted in a higher crosslink density and higher concentration of polysulfidic bonds compared with other type silane coupling agents evaluated[51].

2.4.2 Silane Coupling Agents in Silica-Filled Epoxidized Natural Rubber (ENR)

A lot of studies have been dedicated to ENR filled with silica due to the polarity of ENR, its compatibility with silica and the unique properties of silica filled ENR compound that make it suitable for green tyre tread applications[29,33,34,36,52,53,54]. As discussed in section 2.3.2, there is a potentially strong interaction between the epoxide groups in ENR and silica filler and even the possibility of a reaction between them which should enhance mechanical properties. Unfortunately their mechanical properties such as tensile strength, elongation and abrasion resistance, although better than silica filled NR compound without silane, are still generally lower than silica filled NR compounds with silane coupling agent[5]. Therefore, a silane coupling agent may improve mechanical properties of silica filled compounds, even when a polar natural rubber such as ENR is adopted.

Salina *et al.*[33] carried out a study on silica filled ENR with TESPT silane coupling agent. The silica filled ENR compounds were prepared based on truck tyre tread formulations and their results were compared with carbon black filled NR/BR compound, as it is the common tread compound used by the industry. The amount of TESPT silane used in the truck tyre tread formulation was 5wt.% relative to silica content (phr). The results showed that ENR/silica compounds in the presence of TESPT silane coupling agent gave a faster cure. This is due to the silane coupling agent reacting with silanol groups on the silica surface which decreases the number of silanol groups available to interact and interfere with the accelerators. The bound rubber content results showed that the ENR/silica-silane compound had a higher bound rubber content than the NR/BR /carbon black compound, indicating a strong rubber to filler interaction between ENR and silica in the presence of silane. In terms of physical properties, ENR/silica-silane compounds had inferior tensile strength, lower elongation at break and higher modulus than the NR/BR-carbon black compound. However, the dynamic test showed the ENR/silica-silane vulcanizate exhibited a higher tan delta at 0ºC and lower tan delta at 60ºC as compared to the NR/BR-carbon black vulcanizate, giving an indication of good wet grip and lower rolling resistance for the ENR/silica vulcanizate. Varughese *et al.* also reported that the interaction between ENR and silica is increased with the addition of TESPT silane coupling agent as evidenced in rheometric results[9]. The paper reported that the rheometer curves of ENR50 with 50 phr silica without silane and curing agents showed a rise in rheometer torque values at a temperature of 150˚C, which indicates there is a chemical reaction between silica and ENR50 and that there is a slight crosslinking. However for the ENR50 with 50 phr silica in the presence of 2 phr TESPT silane coupling agent, a further increase in rheometer torque is observed which indicates that the crosslinking reaction is further accelerated by the presence of silane[9].

Manna *et al.* carried out studies on the role of N-3(N-vinyl benzyl amino) ethyl-γ-amino propyl trimethoxy silane monohydrogen chloride in the bonding between precipitated silica and epoxidized natural rubber (ENR). Based on the results obtained from Monsanto rheometic studies and physical property measurements, it was concluded that precipitated silica interacts chemically with epoxidized natural rubber (ENR) during high temperature molding at 180˚C and the extent of chemical interaction increases in the presence of the silane coupling agent[55]. Fourier transform infrared spectroscopic results were presented to demonstrate that the silica was bonded to ENR through formation of Si— O—C bonds, whereas in the presence of silane coupling agent, silica is bonded to the coupling agent through Si—O—Si bonds and ENR is bonded to the coupling agent through C—N—C bond formation. The paper concludes that the silanol groups on the silica surface interact strongly with ENR and the extent of the chemical interaction is dependent on the molding time. Addition of the silane coupling agent N-3(N-vynyl benzyl amino) ethyl-γ-amino propyl trimethoxy silane monohydrogen chloride also enhances the chemical interaction through the formation of coupling bonds. It is believed that HCl is liberated from the coupling agent during molding and opens up the epoxy groups of ENR, hence facilitating the reaction between the amino groups of the coupling agent and the epoxy groups of ENR. The authors showed that the formation of these coupling bonds resulted in improved mechanical properties of the silica filled vulcanizates even in the absence of a curing agent such as sulphur[55].

Manna *et al.* also reported in another paper, that ENR reacted chemically with precipitated silica when a mix of silica with ENR was extruded at high temperature (150-170˚C) using a Monsanto Processability Tester (MPT). They concluded that extent of the interaction increases with increase in the volume fraction of filler, shear rates and addition of the silane coupling agent, N-3(N-vinyl benzyl amino) ethyl-γ-amino propyl trimethoxy silane monohydrochloride[56].

Studies involving various levels of epoxidation on natural rubber (ENR) both without coupling agent and with different concentrations of TESPT coupling agent, have provided a better understanding of the various factors that can affect the properties of silica filled ENR compounds. Kaewsakul *et al.* carried out studies on the influence of epoxide content in ENRs in the absence and presence of silane coupling agent (TESPT) at different concentration (loading) on the overall properties of silica filled ENR compounds such as filler-filler interaction, network contributions, Mooney viscosity, cure characteristics and dynamic and mechanical properties of the compound and vulcanizates[57]. From the overall results obtained, it was found that silica filled ENR without coupling agent cannot provide properties to match those of silica filled unmodified NR with TESPT coupling agent. However, with the right combination of epoxide group level and TESPT silane coupling agent, properties similar to those of a silica/TESPT filled unmodified NR system can be obtained, with the advantage of reducing the required silane coupling agent concentration to half or even lower. Kaewsakul *et al.* also concluded that the best possible combination to optimize processability, to reduce filler-filler interaction and improve vulcanization rate and vulcanizates properties, is to use ENR with an epoxide content between 20 and 30 mol% of epoxidation level, together with a small amount of TESPT silane coupling agent at about 2-4 wt.% of the silica content. This lead a reduction of 60-80% of TESPT silane coupling agent used as compared to the TESPT used in silica filled unmodified NR compound, where the optimal loading of TESPT used was 9 wt.% of the silica content[57].

In other studies, Kaewsakul *et al.* carried out experiments to confirm the type of linkage responsible for the filler to rubber interaction in silica filled NR and ENR compounds with and without the presence of TESPT silane coupling agent. The experiment was carried out by using unmodified squalene (Sq) and epoxidized squalene (ESq) as a model for natural rubber (NR) and epoxidized natural rubber (ENR) respectively. They were mixed with silica filler in a reactor at 140-145˚C, which corresponds to the optimal mixing dump temperature of silica filled NR or ENR compounds[58]. The mixtures were prepared with and without TESPT silane coupling agent. Based on the Fourier-transform infrared spectroscopy (FTIR) results of the bound silica extracted from the mixtures, Sq and ESq can chemically link to the silica surface with the help of TESPT silane coupling agent, because the FTIR spectra of purified bound silica showed absorption of peaks of hydrocarbon structures. However, for the mixtures without TESPT silane coupling agent, the epoxidized squalene could still produce a chemical interaction with silica, but to a lesser extent than the one with TESPT, as indicated by the absorption intensity. There was no noticeable chemical interaction observed for the silica in squalene mixture without TESPT silane coupling agent. Therefore, the results conclude that the ability of ENR to create chemical silica-rubber interactions in ENR/silica compounds under high thermal condition during mixing and vulcanization than in compounds based on unmodified NR in either with presence or absence of TESPT silane coupling agent[58].

A similar study was also carried out by Wang *et al.* on the properties and interfacial interaction of Epoxidized natural rubber with precipitated silica composites[59]. In that study, the ENR 40, with 40 mol% epoxidation, was mixed with precipitated silica on an open two-roll laboratory mixing mill at 50 – 60˚C. The ENR40/silica compounds were extracted in toluene to obtain the bound rubber content and then the interaction was investigated by using Fourier-transform infrared spectroscopy (FTIR). The results indicated that during the mixing process, hydrogen bonding and chemical interaction occurred between the ENR40 and silica, as bound rubber increased with the increase in silica loading. The FTIR results also showed that there was epoxy ring opening during mixing, and there were hydrogen bonds and Si-O-C bonds between the ENR40 and silica[59].

Based on the literature reviewed above, it can be concluded that ENR may undergo ring opening during mixing and that there is potentially some chemical reaction or linking with the silica. However, differences in temperature required for the reaction are reported by different authors and the extent of reaction is relatively small compared to that obtained when silane coupling agents are used. Overall the conclusion is that the optimum tyre tread properties would be expected with silica filled ENR25 including some silane coupling agent such as TESPT silane.

2.5 Rubber Blends

The use of blends of two or more elastomers generally stems from an understandable interest to combine the best features or properties, either technical or economic, of the two elastomers which can result in improvement on a variety of physical and chemical properties of the constituent elastomers[60,61]. The technological blending of elastomers allows access to properties of the final blended and vulcanized elastomer which are not possible from a single, commercially available elastomer alone. Elastomer blending technology is largely focused on the selecting of individual elastomers and the creation of blends to achieve a set of final required properties. Theoretically, the combinations of elastomers can result in changes in compound properties due to either intrinsic differences in the constituents or differences in the reinforcement and vulcanization of the constituents. Blends also are often used to improve the processability of rubbers by either lowering the viscosity or producing a material less prone to melt fracture during flow. Secondary elastic effects such as die swell can also be affected by blending. In general, elastomer blends can be divided into two types as shown below[62]:

i) Miscible Elastomer Blends;
  - blends that consist of a single elastomeric phase
  - microscopically uniform crosslinking
  - uniform distribution of reinforcing agents
  - a common example of miscible blends is those of ethylene-propylene diene monomers (EPDM)

ii) Immiscible Elastomer Blends;
  - shows more than one elastomeric phase due to microscopically inhomogeneous phase structure of the two elastomers
  - two separate phases typically have differences in the retention of fillers, plasticizers and vulcanization in the presence of curative

The use of elastomers blends has been very beneficial to the rubber industry, especially the blends of general-purpose rubbers such as NR / BR and SBR / NR used in tyre treads. In other instances more guile has been required for a successful outcome and there are a good number of desirable combinations which have not yet proved successful, such as blending of general purpose rubber with speciality of rubbers[62].

There have been extensive investigations by various researchers with the aim of establishing optimum compositions for green tyre tread compounds[63,64 ,65 ,66]. In these studies, blends of NR with at least one or more synthetic rubbers selected from the category of cis 1,4-polybutadiene (BR), NR/cis 1,4 polyisoprene rubber (IR), styrene-butadiene rubber (SBR) and their derivatives have been reinforced with fillers such as carbon black and silanized silica or hybrid fillers[33,63]. In the current research, blends with ENR are of particular interest and are covered in the following section.

2.5.1 ENR-Silica Blending with other Rubbers

Ahmadi Sholi *et al.*[67] carried out studies on a nanocomposite based on an ENR50/SBR rubber blend with rubber ratio of 50:50 and containing nanoclay filler with and without carbon black. The microstructure of the nanocomposite samples were investigated using X-ray diffraction (XRD), melt rheo-mechanical spectroscopy (RMS) and scanning electron microscopy (SEM). The dynamic mechanical behaviour and mechanical properties of the nanocomposites were also evaluated. Based on the overall results obtained, the paper concluded that, the ENR50/SBR-nanoclay/carbon black blend compound containing 10 phr nanoclay and 20 phr carbon black demonstrated the best dynamic mechanical properties, hardness, abrasion and rolling resistance, making it suitable for a tyre tread compound application[67]. Ismail *et al.*[68] in his paper had reported that the incorporation of ENR50 in the blends had improved processability, stiffness, resilience and reduced the damping property of ENR50/SBR blends. In term of curing characteristics, the rheometer results showed that scorch time and curing time decrease with increasing ENR content in ENR50/SBR blends, which is attributed to the induction effect of ENR50 in blend compounds that produces more activated precursors to crosslinks, thus improving the interphase crosslinking[68]. Blending of ENR50 with NR also has been evaluated with emphasis on the safety aspect of motorcycle tyres as well as a replacement for butyl rubbers in tyre inner liners and tubes application[5].

It has been reported by Gelling[5] that an improvement in abrasion resistance or wear can be obtained by blending silica filled ENR25 with butadiene rubber (BR). Although there is a slight reduction in wet traction, the tyre tread based on ENR25 blended with 30 phr BR showed rolling resistance similar to that of NR and wet grip and wear properties that are comparable to that of an OESBR compound. In this Thesis blending of BR with ENR at different loadings has been carried out to determine the optimum level of BR to add to increase abrasion resistance while maintaining other tyre properties at the required level as well as the processing characteristics. One of the main objectives of this Thesis is to address the remaining issues of relatively poor wear properties and processability of silica filled ENR compounds identified in the literature review. A combined approach of blending with BR, addition of silane coupling agent and water was used to improve the abrasion resistance and processing properties of these ‘green’ tyre compounds. An additional and particularly novel aspect of the study was to determine whether the sustainability of the ‘green’ tyre tread compounds could be improved by using recovered silica fillers from tyre pyrolysis and from geothermal sources.

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CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The following polymers were used for this study: 25% Epoxidized natural rubber (EKOPRENA-25) and standard Malaysian rubber (SMR 10) supplied by the Malaysian Rubber Board. The fillers used for this study include: precipitated silica filler (Zeosil 1165MP) supplied by Solvay and Carbon Black N330 supplied by Orion. The X50S silane coupling agent was supplied by Evonik Industries. The X50S is a blend of the bifunctional sulfur-containing organosilane (Si69) and N330 type carbon black in the ratio 1:1 by weight. The other chemicals such as zinc oxide, stearic acid, antioxidant and rubber accelerators were commercial grade rubber chemicals. A recovered silicas from tyre pyrolysis and geothermal industries sources namely rSilica and geoSilica respectively were also used for this study. rSilica filler was supplied by ARTIS and geoSilica filler supplier is not to disclose here due to confidentiality agreement.

3.2 Compound Formulation

3.2.1 Effect of Silane Coupling Agent Concentration on the Properties of the Silica Filled ENR Compound

The compound formulations below were used to assess the effect of X50S silane coupling agent concentration on the properties of silica filled ENR compounds. The compound formulation is based on a typical truck tyre tread formulation, with ENR as the base elastomer and silica as the filler. The X50S silane concentration used in this study was varied from 2phr to 8phr loading. In addition to the X50S silane, 1 phr Si69 was added in the final stage compound as this had been previously shown to reduce cure reversion. Water addition was fixed at 4 wt.%, as a percentage of silica weight. A conventional carbon black filled NR/BR truck tyre tread compound was also prepared for comparison purposes (benchmark), as shown in Table 3.1. The reason why truck tyres was used as a benchmark and not passenger car tyres is because this thesis is targeting the potential of EKOPRENA-25 rubber in retread tyre industries, an area dominated by truck tyres.

Table 3.1: Formulations of silica filled ENR compounds with varying X50S silane concentration and carbon black filled NR/BR compound

Ingredients	0phr X50S	2phr X50S	4phr X50S	6phr X50S	8phr X50S	NR70:BR30
ENR-25	100	100	100	100	100	
SMR 10						70
BR 40						30
Silica Zeosil 1165MP	55	55	55	55	55	
N330 Black	3	3	3	3	3	
N234 Black						53
Zinc oxide	3	3	3	3	3	3.5
Stearic acid	3	3	3	3	3	2.5
Calcium stearate	2	2	2	2	2	
Santoflex 13, 6PPD	1	1	1	1	1	2.5
Antioxidant, TMQ	1	1	1	1	1	1
Antilux 654 (Wax)	1	1	1	1	1	1
X50S (50% Si69 on CB)	**-**	**2**	**4**	**6**	**8**	
Water (% on Silica)	2.2(4%)	2.2(4%)	2.2(4%)	2.2(4%)	2.2(4%)	
Sulphur	0.7	0.7	0.7	0.7	0.7	1.2
TBBS	1.5	1.5	1.5	1.5	1.5	1
TBzTD	0.25	0.25	0.25	0.25	0.25	
Silane Si69	1	1	1	1	1	

6PPD: N-1,3-dimethylbutyl-N’ phenyl-p-henylenediamine
TBBS: N-tert-butylbenzothiozole-2-sulphenamide
TMQ: 1,2-dihydro-2,2,4-trimethylquinoline
TBzTD: Tetrabenzylthiuram disulfide

3.2.2 Effect of Water Addition to Silica on the Properties of the Silica Filled ENR Compound

The compound formulations below were used to assess the effect of water addition to silica on the processing and other properties of a silica filled ENR compounds. The addition of water was varied from 0 to 20 wt.%, as a percentage of silica weight. The X50S silane content was fixed at 4.4 phr. The formulations and materials used in this study are given in Table 3.2.

Table 3.2: Formulations of silica filled ENR compounds with varying amounts of water % added to the silica

Ingredients	0% water	4% water	6% water	10% water	15% water	20% water
ENR-25	100	100	100	100	100	100
Silica Zeosil 1165MP	55	55	55	55	55	55
N330 Black	3	3	3	3	3	3
N234 Black						
Zinc oxide	3	3	3	3	3	3
Stearic acid	3	3	3	3	3	3
Calcium stearate	2	2	2	2	2	2
Santoflex 13, 6PPD	1	1	1	1	1	1
Antioxidant, TMQ	1	1	1	1	1	1
Antilux 654 (Wax)	1	1	1	1	1	1
X50S (50% Si69 on CB)	4.4	4.4	4.4	4.4	4.4	4.4
Water (% on Silica)	**0(0%)**	**2.2(4%)**	**3.3(6%)**	**5.5(10%)**	**8.3(15%)**	**11(20%)**
Sulphur	0.7	0.7	0.7	0.7	0.7	0.7
TBBS	1.5	1.5	1.5	1.5	1.5	1.5
TBzTD	0.25	0.25	0.25	0.25	0.25	0.25
Silane Si69	1	1	1	1	1	1

6PPD: N-1,3-dimethylbutyl-N’ phenyl-p-henylenediamine
TBBS: N-tert-butylbenzothiozole-2-sulphenamide
TMQ: 1,2-dihydro-2,2,4-trimethylquinoline
TBzTD: Tetrabenzylthiuram disulfide

3.2.3 Effect of Butadiene Rubber Loading on the Properties of Silica Filled ENR/BR Blends.

The compound formulations below were used to assess the effect of butadiene rubber loading on the properties of silica filled ENR/BR blends. The butadiene rubber loading used in this study was varied from 0phr to 30phr. A conventional truck tyre tread compound containing NR, BR and filled with carbon black was also prepared for comparison purposes. The formulations and materials used in this study are given in Table 3.3.

Table 3.3: Formulations of silica filled ENR blends with varying BR loading and carbon black filled NR/BR compound

Ingredients	ENR100:BR0	ENR90:BR10	ENR80:BR20	ENR70:BR30	NR70:BR30
ENR-25	100	90	80	70	
SMR 10					70
BR 40	**0**	**10**	**20**	**30**	30
Silica Zeosil 1165MP	55	55	55	55	
N330 Black	3	3	3	3	
N234 Black					53
Zinc oxide	3	3	3	3	3.5
Stearic acid	3	3	3	3	2.5
Calcium stearate	2	2	2	2	
Santoflex 13, 6PPD	1	1	1	1	2.5
Antioxidant, TMQ	1	1	1	1	1
Antilux 654 (Wax)	1	1	1	1	1
X50S (50% Si69 on CB)	4.4	4.4	4.4	4.4	
Water (% on Silica)	2.2(4%)	2.2(4%)	2.2(4%)	2.2(4%)	
Sulphur	0.7	0.7	0.7	0.7	1.2
TBBS	1.5	1.5	1.5	1.5	1
TBzTD	0.25	0.25	0.25	0.25	
Silane Si69	1	1	1	1	

6PPD: N-1,3-dimethylbutyl-N’ phenyl-p-henylenediamine
TBBS: N-tert-butylbenzothiozole-2-sulphenamide
TMQ: 1,2-dihydro-2,2,4-trimethylquinoline
TBzTD: Tetrabenzylthiuram disulfide

3.2.4 Comparison of Silica Fillers Recovered from Geothermal and Pyrolysis Sources with Commercial Grade Silica.

The effect of using silica recovered by a geothermal and pyrolysis process as the filler in an ENR compound with and without X50S silane was investigated using the formulation shown in Table 3.4. The silica recovered by geothermal and pyrolysis processes are referred to as geoSilica and rSilica respectively. As a comparison, Zeosil silica filled ENR compounds were also prepared using the same formulation.

Table 3.4: Formulations of silica filled ENR compounds for comparing silica recovered by pyrolysis (rSilica) and geothermal processes (geoSilica) with conventional commercial silica (Zeosil)

Ingredients	rSilica	geoSilica	Zeosil	rSilica + X50S	geoSilica + X50S	Zeosil + X50S
ENR-25	100	100	100	100	100	100
rSilica (Pyrolysis)	55			55		
geoSilica (Geothermal)		55			55	
Silica Zeosil 1165MP			55			55
N330 Black	3	3	3	3	3	3
N234 Black						
Zinc oxide	3	3	3	3	3	3
Stearic acid	3	3	3	3	3	3
Calcium stearate	2	2	2	2	2	2
Santoflex 13, 6PPD	1	1	1	1	1	1
Antioxidant, TMQ	1	1	1	1	1	1
Antilux 654 (Wax)	1	1	1	1	1	1
X50S (50% Si69 on CB)	-	-	-	4.4	4.4	4.4
Sulphur	0.7	0.7	0.7	0.7	0.7	0.7
TBBS	1.5	1.5	1.5	1.5	1.5	1.5
TBzTD	0.25	0.25	0.25	0.25	0.25	0.25
Silane Si69	1	1	1	1	1	1

6PPD: N-1,3-dimethylbutyl-N’ phenyl-p-henylenediamine
TBBS: N-tert-butylbenzothiozole-2-sulphenamide
TMQ: 1,2-dihydro-2,2,4-trimethylquinoline
TBzTD: Tetrabenzylthiuram disulfide

3.2.5 Evaluation of Extrusion Performance and Shear Viscosity Properties of Medium Scale Mixes of Silica Filled ENR Masterbatches.

The evaluation of extrusion performance and shear viscosity of silica filled ENR masterbatches was investigated using the formulation as shown in Table 3.5. For the extrusion studies it was necessary to prepare larger batches than in the other studies, so compounds were prepared by using a medium scale Banbury internal mixer (4300 cm^3 volume capacity) at Tun Abdul Razak Research Centre, London. The X50S silane concentration used in this study was varied from 0phr to 8phr loading and water added to the silica was varied from 0 to 10 wt.% of silica.

Table 3.5: Formulations of silica filled ENR compounds with varying X50S silane and water concentration.

Ingredients	0phr X50S			4phr X50S			8phr X50S		
	0% water	6%water	10%water	0% water	6%water	10%water	0% water	6%water	10%water
ENR-25	100	100	100	100	100	100	100	100	100
Silica Zeosil 1165MP	55	55	55	55	55	55	55	55	55
N330 Black	3	3	3	3	3	3	3	3	3
N234 Black									
Zinc oxide	3	3	3	3	3	3	3	3	3
Stearic acid	3	3	3	3	3	3	3	3	3
Calcium stearate	2	2	2	2	2	2	2	2	2
Santoflex 13, 6PPD	1	1	1	1	1	1	1	1	1
Antioxidant, TMQ	1	1	1	1	1	1	1	1	1
Antilux 654 (Wax)	1	1	1	1	1	1	1	1	1
X50S (50%Si69 on CB)	**-**	**-**	**-**	**4**	**4**	**4**	**8**	**8**	**8**

Water (% on Silica)	-	3.3(6%)	5.5(10%)	-	3.3(6%)	5.5(10%)	-	3.3(6%)	5.5(10%)
Sulphur	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
TBBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TBzTD	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Silane Si69	1	1	1	1	1	1	1	1	1

6PPD: N-1,3-dimethylbutyl-N’ phenyl-p-henylenediamine
TBBS: N-tert-butylbenzothiozole-2-sulphenamide
TMQ: 1,2-dihydro-2,2,4-trimethylquinoline
TBzTD: Tetrabenzylthiuram disulfide

3.3 Mixing

3.3.1 Mixing Process for Silica Filled ENR Compounds with Varying Amounts of X50S Silane and Water Added to Silica.

All the mixing of the compounds was carried out in three stages in a Polylab OS Haake Rheomix 3000 fitted with Banbury rotors and with a 379 cm^3 chamber volume. For the X50S silane study, the amount of X50S silane was varied from 0phr to 8phr. For the water % added to silica, the amount of water % was varied from 0 to 20wt.% (on silica). The sequence of mixing stages and mixing conditions are summarised in Table 3.6. Each mixing stage was carried out on a different mixing day. Silica and carbon black were added in 2 portions to improve incorporation. The silica was divided into 2/3 and 1/3 portions. The X50S and water also were divided into 2/3 and 1/3 portions and were pre-blended with 2/3 silica and 1/3 silica filler, respectively prior to mixing. In the first stage of mixing, a 0.6 fill factor, 70 rpm rotor speed and starting temperature of 80°C was employed. The dumping time was set for 3 minutes after the indicated temperature reached 140°C or a maximum of 7 minutes mixing time. Later, the masterbatches were sheeted out on a warm two-roll mill with minimal passes.

In the second stage, the masterbatches were remilled in the same mixer for 3 minutes with a rotor speed of 80 rpm and starting temperature of 80°C. Then the masterbatches were sheeted out on a warm two-roll mill with minimal passes. Finally, the mixing was completed in 2 minutes of mixing when the curatives agents were added, with a mixer temperature and rotor speed of 40°C and 50 rpm respectively. Then the compounds were sheeted out on a warm two-roll mill with minimal passes.

Table 3.6: Summary of mixing stages for silica filled ENR compounds

Mixing steps	Mixer rotor speed, rpm	Temperature, °C
First stage mixing	70	80
2nd stage mixing	80	80
Final stage mixing (finalizing)	50	40

The mixing cycle used for the study of effect of X50S silane concentration and water percentage added on silica in silica filled ENR compounds are shown in Table 3.7.

Table 3.7: Mixing cycle for silica filled ENR compounds with varying X50S silane and water concentration and carbon black filled NR/BR compound

Mixing cycle 1st stage	ENR/silica	NR70:BR30
0	Rubber + powders + c. black	Rubber
¾ mins		$^1/_2$ c.black
1 mins	$^2/_3$ Silica	
$1^{1/}{}_2$ mins		$^1/_2$ c.black
$2^{1/}{}_4$ mins	$^1/_3$ Silica	Powders
3 mins		Sweep
$3^{1/}{}_2$ mins	Sweep	
(Dump*) mins	Dump at $6^{1/}{}_2$ mins	Dump at 4 mins
Mixing cycle 2nd stage		
0	Master-batch	Master-batch
3 mins	Dump	Dump
Mixing cycle Final stage		
0	Remill + powders + Si69	Remill + powders
1 mins	Sweep	Sweep
2 mins	Dump	Dump

* Dump after 3 minutes above 140°C for silica filled ENR mixes

3.3.2 Mixing Process for Silica Filled ENR Blends with Varying Butadiene Rubber Loading.

The butadiene rubber loading was varied from 0 to 30phr. The mixing conditions are the same as described in section 3.3.1 and the sequence of mixing stages and mixing cycle are summarised in Table 3.8.

Table 3.8: Mixing cycle for silica filled ENR blends with varying BR loading and carbon black filled NR/BR compound

Mixing cycle 1st stage	ENR/BR Blend	NR70:BR30
0	Rubber + powders + c. black	Rubber
¾ mins		$^{1}/_{2}$ c.black
1 mins	$^{2}/_{3}$ Silica	
$1^{1}/_{2}$ mins		$^{1}/_{2}$ c.black
$^{1}/_{4}$ mins	$^{1}/_{3}$ Silica+	Powders
3 mins		Sweep
$3^{1}/_{2}$ mins	Sweep	
(Dump*) mins	Dump at $6^{1}/_{2}$ mins	Dump at 4 mins
Mixing cycle 2nd stage		
0	Master-batch	Master-batch
3 mins	Dump	Dump
Mixing cycle Final stage		
0	Remill + powders + Si69	Remill + powders
1 mins	Sweep	Sweep
2 mins	Dump	Dump

* Dump after 3 minutes above 140°C for silica filled ENR mixes

3.3.3 Mixing Process for Silica Filled ENR Compounds for Comparing Silica Recovered by Pyrolysis (rSilica) and Geothermal (geoSilica) with Commercial Silica (Zeosil).

The silica filled ENR compounds were prepared with addition of X50S silane and without silane for each type of silica. The mixing conditions are the same as described in section 3.3.1 and the sequence of mixing stages and mixing cycle are summarised in Table 3.9.

Table 3.9: Mixing cycle for rSilica (pyrolysis), geoSilica (geothermal) and Zeosil silica filled ENR compounds

Mixing cycle 1st stage	Silica filled ENR compounds
0	Rubber + powders + c. black
1 mins	$^{2}/_{3}$ Silica
$2^{1/}{}_{4}$ mins	$^{1}/_{3}$ Silica
$3^{1/}{}_{2}$ mins	Sweep
(Dump*) mins	Dump at $6^{1/}{}_{2}$ mins
Mixing cycle 2nd stage	
0	Master-batch
3 mins	Dump
Mixing cycle Final stage	
0	Remill + powders + Si69
1 mins	Sweep
2 mins	Dump

* Dump after 3 minutes above 140°C for silica filled ENR mixes

3.3.4 Mixing Process for Medium Scale Mixes of Silica Filled ENR Masterbatches with Varying Amounts of X50S Silane and Water % Added to Silica.

For the study of extrusion performance and shear viscosity properties of silica filled ENR masterbatches, the mixing was carried out in two stages in a 00C Banbury internal mixer with a 4300 cm^3 chamber volume. The amount of X50S silane was varied from 0phr to 8phr and the amount of water % was varied from 0 to 10wt.% (on silica). The sequence of mixing stages and mixing conditions are summarised in Table 3.10. Each mixing stage was carried out on a different mixing day. Silica and carbon black were added in 2 portions to improve incorporation. The silica was divided into 2/3 and 1/3 portions. The X50S and water also were divided into 2/3 and 1/3 portions and were pre-blended with 2/3 silica and 1/3 silica filler, respectively prior to mixing. In the first stage of mixing, a 0.72 fill factor, 70 rpm of rotor speed and starting temperature of 40°C were employed. The dumping time was set for 3 minutes after the indicated temperature reached 140°C or after a maximum 7 minutes mixing time. Later, the masterbatches were sheeted out on a warm two-roll mill with minimal passes.

In the second stage, the masterbatches were remilled in the same mixer for 3 minutes with a rotor speed of 50 rpm and starting temperature of 40°C. Then the masterbatches were sheeted out on warm two-roll mill with minimal passes. Then the masterbacthes were cut into a long strip form.

Table 3.10: Summary of mixing stages for silica filled ENR masterbatches

Mixing steps	Mixer rotor speed, rpm	Temperature, °C
First stage mixing	70	40
2nd stage mixing	50	40

The summary of mixing cycles used for the study of medium scale mixes of Silica filled ENR masterbatches with varying amounts of X50S silane concentration and water % added to silica is shown in Table 3.11.

Table 3.11: Mixing cycle for medium scale mixes of silica filled ENR masterbatches with varying X50S silane concentration and water % added to silica.

Mixing cycle 1st stage	Silica filled ENR masterbatches
0	Rubber + powders + c. black
1 mins	$^{2}/_{3}$ Silica
$2^{1/}{}_{4}$ mins	$^{1}/_{3}$ Silica
$3^{1/}{}_{2}$ mins	Sweep
(Dump*) mins	Dump after 3 minutes temp reached 140˚C or maximum 7 minutes mixing time
Mixing cycle 2nd stage	
0	Master-batch
3 mins	Dump

3.4 Mixing Performance (Using Polylab OS Haake Rheomix 3000 mixer).

During mixing, torque, temperature and energy were logged so that mixing performance could be assessed.

3.5 Mooney Viscosity, ML or MS (1 + 4) at 100ºC

Mooney viscosity measurements were carried out using a Wallace MKIII viscometer at 100°C. The sample weights were in the range of 25-30g. The Mooney viscosity was recorded for compounds at the masterbatch, remill and finalised stage. Due to high Mooney viscosity of ENR/silica samples, the small rotor was used and the results MS (1+4) were converted using the equation ML = 2.1031MS – 14.911[1] to give equivalent large rotor values. The testing was conducted based on the ISO 289-1:2005 standard.

3.6 Cure Characteristics

The cure properties of the samples were assessed at 150°C for 30 minutes, using a Monsanto MDR 2000 rheometer with 3° arc and at at a frequency of 1.667 Hertz based on the ISO 6502 standard.

3.7 Filler Dispersion (Macrodispersion Analysis)

Macrodispersion analysis was carried out on vulcanized compounds using a DisperGrader^{TM} 1000NT based on the standard ISO 11345:2006. Sample preparation involved cutting of a hardness test piece sample to generate a 'fresh face' for analysis. For this analysis, three measurements were performed for each vulcanized compound. The magnification of the instrument was set at 100 times magnification and the images of the compounds were compared to reference images from the instrument.

3.8 BET Surface Area.

The specific surface areas (BET) of each type of silica used in this study were measured using Micromeritics Tristar 3000 equipment. BET analysis provides a precise specific surface area by nitrogen gas adsorption measured as a function of relative pressure. The volume of nitrogen gas absorbed to the surface of the silica particles is measured at the boiling point of nitrogen (-196°C). The surface area is determined by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface of the silica. The technique encompasses external area and pore area evaluations to determine the total specific surface area. Before the analysis, a small amount of silica (about 0.5 g) was weigh in sample tube and was degassed first at 90˚C and 150˚C for 1 hour and 3 hours respectively. A degassing unit is used to remove any contaminants which may have adsorbed to the surface or pores of silica samples. After sample has been degassed, it was transferred to an analysis port of Micromeritics Tristar 3000 for begin the analysis and measurement.

3.9 Transmission Electron Microscopy (TEM).

A Tecnai F20 FEG(S) transmission electron microscope was used to evaluate all particle sizes of silicas in this study. For the sample preparation, the silicas were suspended in the distilled water first, followed by treatment in an ultrasonic bath for few minutes. Then a few drops of the distilled water containing silica was dropped onto the TEM copper grid before was dried and loaded into the microscope. Bright field images were recorded for all samples with particle sizes up to nano scale.

3.10 Thermogravimetric Analysis (TGA).

The thermogravimetric analysis in this study was carry out using TGA Q5000IR equipment. During the analysis, the silica samples weighing approximately 10-30g were heated under nitrogen gas from room temperature to 800˚C. The heating rate was set at 10˚C/minute.

3.11 Physical & Mechanical Properties

The physical and mechanical properties tested as listed below were conducted according to Standard Methods as tabulated in Table 3.12. All the samples were cured at a temperature of 150°C and according to t_{90} curing time. All the physical and mechanical testing below were carried out by using facilities at Tun Abdul Razak Research Centre (TARRC).

i) Tensile Strength

- Is the ability of a material to withstand a pulling (tensile) force. Tensile strength is measured in units of force per unit area. The ultimate tensile strength of a material is the force per unit area at which it breaks in two.

ii) Hardness (IRHD)

- A measure of the indentation resistance of elastomeric or rubber materials based on the depth of penetration of a ball indentor. An initial contact force is applied to an indentor and the penetration is set to zero.

iii) DIN Abrasion Resistance

- ISO 4649 refers to the DIN Abrader, based on the German Standard. The rubber test piece with a holder is traversed over the surface of a rotating cylinder covered with a sheet of the abradant paper. By allowing the sample holder to move the test piece across the drum as it rotates, there is less chance of rubber buildup on the abradant paper. This method, used extensively in Europe, is very convenient and rapid and well suited to quality control the uniformity of a specific material. The achieved test results provide important parameters in respect to the wear of rubbers in practical use.

iv) AKRON Abrasion Resistance

- British Standard BS903: Part A9 still describes as the Akron Abrader. The rubber test piece is a moulded wheel which is positioned against an abrasive cylinder under constant speeds and held against the abrasive wheel by a constant force. The Akron Abrader has the advantage of allowing variation in the degree of slip in the test by varying the angle of the test piece. Usually Akron abrasion resistance will give higher abrasion resistance index value than DIN abrasion resistance of the same material or vulcanizate.

v) Heat Build Up

The Metrovib DMA+2000 series instrument is dynamic testing machine dedicated to the fatigue and the viscoelastic properties analysis of advanced materials. The testing was carried out at temperature 23°C and and frequency 30Hz with constant-strain amplitude for the determination of the temperature rise and resistance to fatigue of vulcanized rubber.

Table 3.12: Standard methods used for physical and mechanical property tests

Physical & Mechanical Properties Test	**Standard Method**
Tensile Strength	BS ISO 37:2011
Hardness (IRHD)	ISO 48-2:2010
DIN Abrasion Resistance Index	ISO 4649:2010
AKRON Abrasion Resistance Index	BS 903:A9:1988
Heat Build Up	ISO 4666-3:2010

3.12 Rheological & Flow Properties.

For rheological and flow behaviour analysis, the shear viscosity test was carried out using a Rosand RH7 Flowmaster capillary rheometer. In this study, the test temperature was set at 100°C. The shear rate was set between 10 to 10000 sec^{-1}. A die measuring 1mm diameter and 10mm length was used to conduct this test. The sample was inserted into the barrel, compressed and packed before the testing was started.

The actual viscosity of rubber (η), is given by below equation:

$$\text{Viscosity, } \eta = \frac{\tau}{\dot{\gamma}}$$

Where; τ is the true shear stress (in unit Pascal) and $\dot{\gamma}$ is the corrected shear rate (in units of 1/second). As rubber is a non-Newtonian material, the true shear stress was obtained by using the Bagley equation correction and the shear rate was corrected using the Rabinowitch equation[2].

3.13 Extrudability Performance.

The evaluation of extrudability performance and characteristics of silica filled ENR masterbatches was carried out using a Francis Shaw 30mm single screw-type extruder equipped with an ASTM Extrusion Garvey type Die, based on ASTM D2230-96: 2002. The extrusion was carried out at two different screw speeds (20 rpm and 30 rpm) with the set temperatures at barrel zone and die head zone of 75˚C and 95˚C respectively. This test method is designed to allow the observation of the extrusion process. During the extrusion process, the reading of power (W) and die head melt pressure (MPa) were recorded.

References for Chapter 3

1. P.J. Martin, A. V. Chapman, S. Cook, R. T. Davies and A. Kępas-Suwara, Grenn Tire Tread Compounds with Improved Dispersion Based on Silica-Reinforced Epoxidized Natural Rubber, *Fall 180th Technical Meeting of the Rubber Division of the American Chemical Society Inc,* Cleveland, OH October 11-13, 2011.

2. T.A. Osswald and N. Rudolph, Polymer Rheology: Fundamentals and Applications, Hanser Publishers, Munich, Hanser Publication, Cincinnati, 2015.

3. ISO 370:2011 Rubber, vulcanized or thermoplastic – Determination of Tensile Stress-Strain Properties.

4. ISO 48-2:2010 Rubber, vulcanized or thermoplastic – Determination of Hardness (Hardness between 10 IRHD and 100 IRHD).

5. ISO 4649:2010 Rubber, vulcanized or thermoplastic – Determination of Abrasion Resistance Using a Rotating Cylindrical Drum Device.

6. BS 903:A9:1988 Physical testing of rubber. Determination of Abrasion Resistance.

7. ISO 4666-3:2010 Rubber, vulcanized – Determination of Temperature Rise and Resistance to Fatigue in Flexometer Testing – Part 3: Compression Flexometer (Costant Strain Type).

8. ISO 289-1:2014 Rubber, unvulcanized – Determinations Using a Shearing Disc Viscometer – Part 1: Determination of Mooney Viscosity.

9. ISO 6502:1999 Rubber – Guide to The Use of Curemeters.

10. ISO 11345:2006 Rubber – Assessment of Carbon Black and Carbon Black/Silica Dispersion – Rapid Comparative Method.

11. ASTM D2230-96:2002 Standard Test Method for Rubber Property – Extrudability of Unvulcanized Compounds.

CHAPTER 4

EFFECT OF SILANE COUPLING AGENT AND WATER ADDITION ON A SILICA FILLED ENR COMPOUND.

4.1 Effect of Silane Coupling Agent Concentration on the Properties of a Silica Filled ENR Compound.

In this study, silica filled ENR compounds with different X50S silane concentrations (0 to 8 phr), were prepared and the effect of silane concentration on their properties determined. The reason why this study was carried out is because of the processing difficulty of silica filled ENR compound due to its high viscosity and also its poor abrasion resistance. It was considered possible that the use of a silane coupling agent could reduce viscosity and improve properties such as abrasion resistance and heat build -up. The main role of silane coupling agents in silica here is to modified silica surfaces and hence enhance the compatibility between silica and rubber through a chemical bond between TESPT and rubber. Improvement in silica compatibility in the rubber compound will result in a better rolling resistance property. The physical and mechanical properties of the silica filled ENR compounds have been compared with a conventional carbon black filled NR/BR truck tyre tread compound, used as a benchmark for its more favourable processing and abrasion resistance properties.

4.1.1 Mixing Performance

Mixing performance evaluation was carried out based on the mixing data recorded by the Polylab OS Haake Rheomix 3000 mixer. The values such as torque, mixing energy, temperature and time were used to analyse the mixing performance of the masterbach, remilling and final compound.

The final mixing energy and dump temperature at the end of the first, second and final stages of mixing of ENR/silica compounds with different X50S silane concentration are shown in Table 4.1. While the torque curves and mixing time obtained from the first, second and final stages of the mixing process are presented in Figures 4.1 to 4.3.

The benchmark carbon black filled NR/BR masterbatch is also shown in Figures 4.1 to 4.3 as comparison. It can be observed that the ENR/silica masterbatches in the first stage of mixing gave higher torque curves after incorporation of silica filler than the NR/BR masterbatch, but all the torque values gradually reduced to similar levels at the end of mixing. The lower final mixing energy and dump temperature of NR/BR masterbatch compared to the ENR/silica masterbatches is probably because the carbon black filler has less strong inter-particle interactions and so is relatively easily dispersed and has less tendency to agglomerate[1]. In terms of practical and industrial significance, the low mixing energy and dump temperature mean that the mixing process uses less energy (energy saving) and the compound is less likely to overheat.

It is observed that there is no significant difference or clear trend in mixer torque with increase in X50S silane coupling agent from 0 to 8 phr for all ENR/silica masterbatches, remilling and final stage compounds. However, there is a general trend of decreasing mixing energy with increasing silane content, although it is not very great. There is no significant difference in dump temperatures for compounds with different silane content for all mixing stages.

Table 4.1: Mixing properties of ENR/silica masterbatch with X50S silane at different concentration

Mixing properties	Stages	0phr X50S	2phr X50S	4phr X50S	6phr X50S	8phr X50S	NR70:BR30
Final Mixing Energy, KJ	1st	486	426	435	456	445	288
	2nd	257	220	219	182	235	181
	3rd	154	166	160	161	155	163
Dump Temperature, °C	1st	148	152	146	144	146	139
	2nd	131	132	132	126	131	128
	3rd	86	87	86	84	83	80

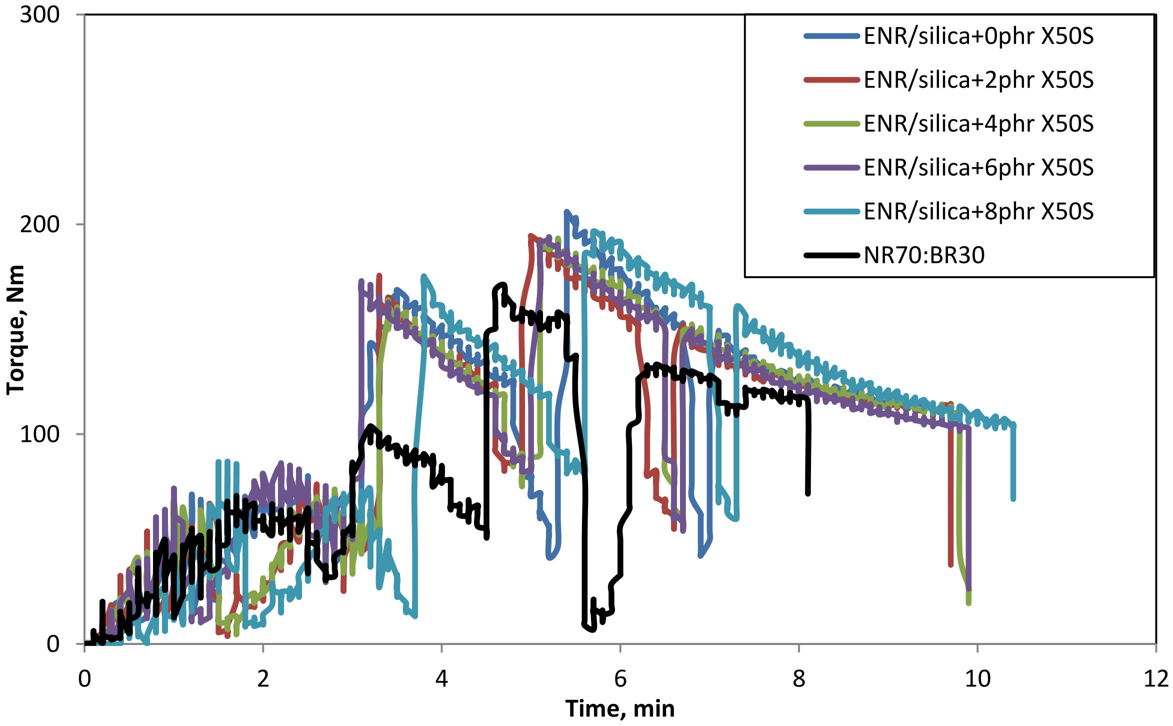

Figure 4.1: Torques curves of ENR/silica mixes with different X50S silane concentration in the first stage mixing.

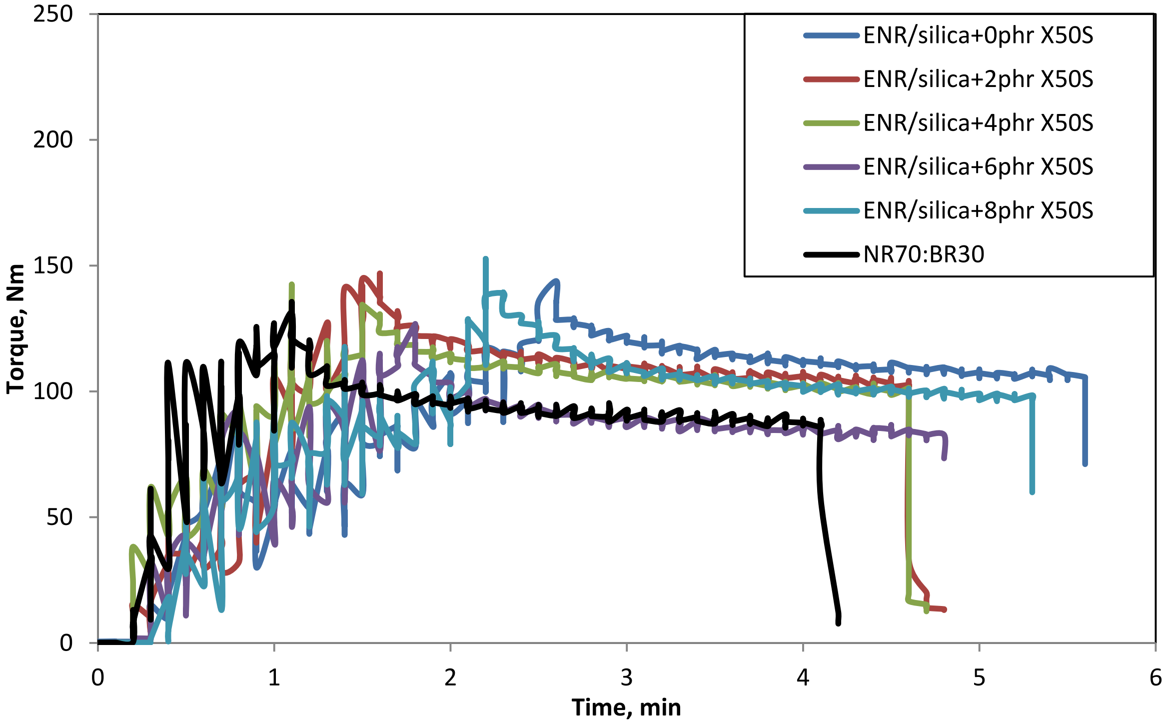

Figure 4.2: Torques curves of ENR/silica mixes with different X50S silane concentration in the second stage mixing.

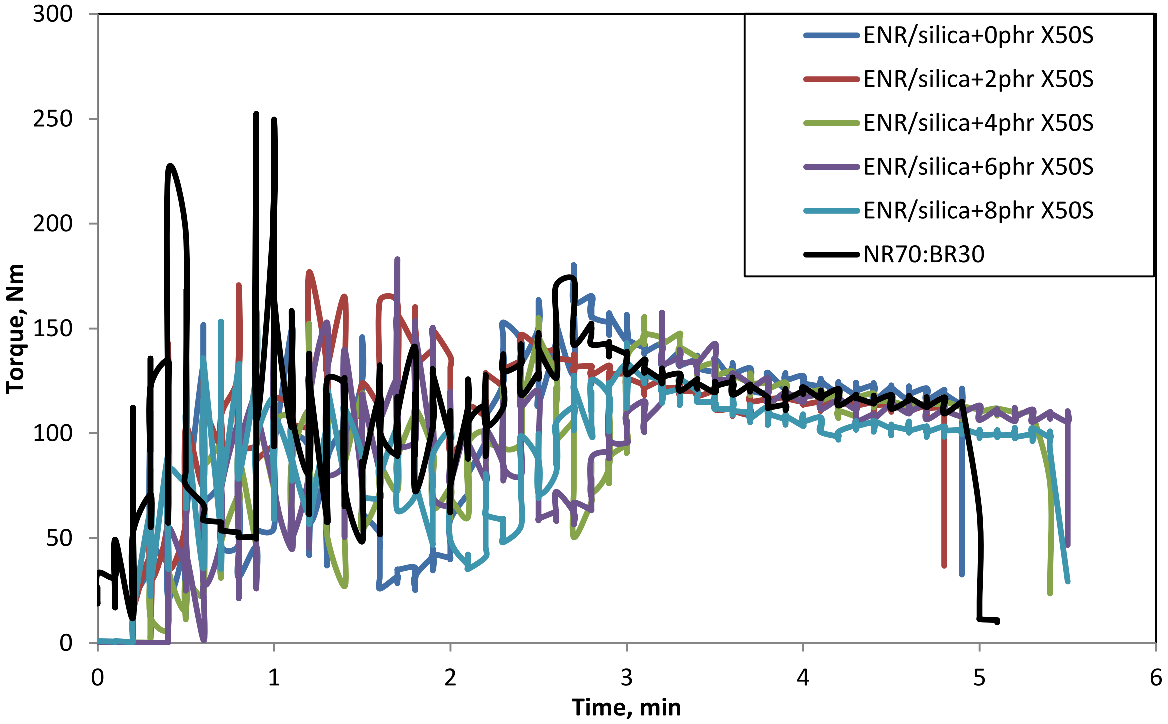

Figure 4.3: Torques curves of ENR/silica mixes with different X50S silane concentration in the final stage mixing.

4.1.2 Mooney viscosity

The Mooney viscosity of the masterbatches and compounds with different concentrations of silane coupling agent are shown in Table 4.2 and Figure 4.4. As expected, the carbon black filled NR/BR compound gave the lowest Mooney viscosities for all masterbacth, remilling and final compounds. For the masterbatch, addition of 2 phr silane resulted in a significant reduction in viscosity, but further increases in silane appeared to have little significant effect. However, increasing the X50S silane concentration resulted in a slight decrease in the Mooney viscosities of remilling and final stage mixes. The reduction in viscosity caused by the addition of silane may be due to either an improvement in filler dispersion or a reduced filler-filler interaction. Usually lower Mooney viscosity is an indirect indication of good processability and flow properties of the rubber mix. Therefore, the results suggest that the addition of silane may improve the processability and flow properties of the ENR/silica compounds by reducing their viscosity. However, the reduction in viscosity is relatively small and so the effect on processing may also be quite small. This is supported by the mixing data in the previous section, which shows only relatively small differences in mixing energy with different silane contents.

Table 4.2: Mooney viscosity of ENR/silica compounds with different X50S silane phr

Mooney Viscosity	0phr X50S	2phr X50S	4phr X50S	6phr X50S	8phr X50S	NR70:BR30
Masterbatch viscosity	159	133	125	130	133	99
Remilling viscosity	124	113	106	103	102	74
Final Compound viscosity	93	91	85	80	78	68

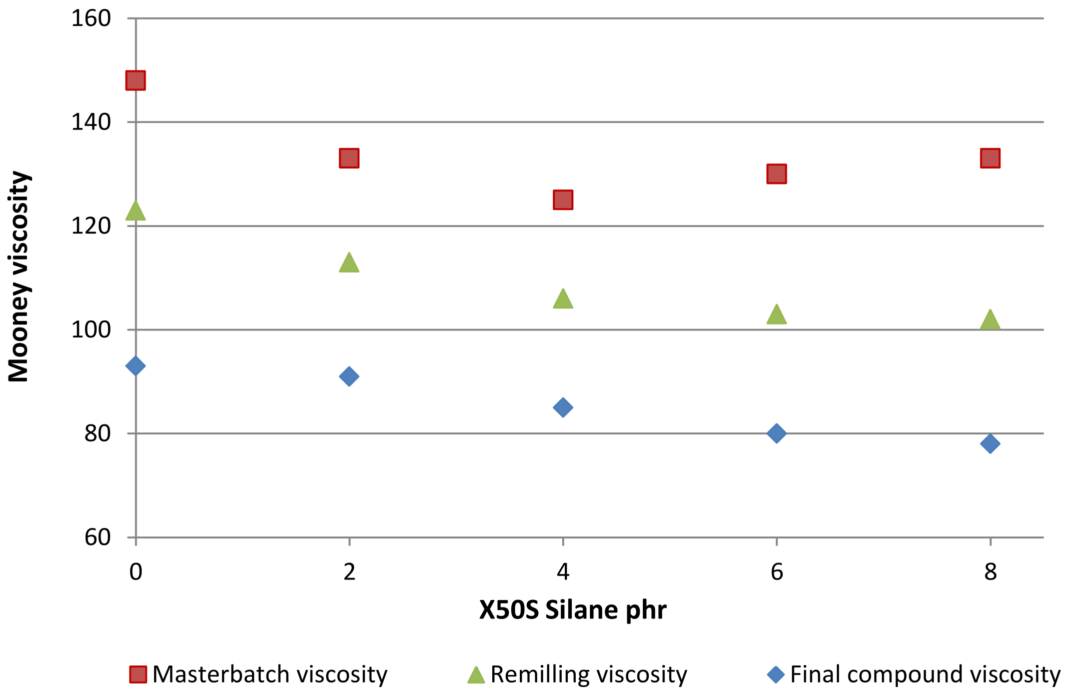

Figure 4.4: Mooney viscosity of ENR/silica mixes with different X50S silane contents

4.1.3 Cure Characteristics

The rheometer curves and cure characteristics of ENR/silica compounds with different concentrations of silane coupling agent are presented in Table 4.3 and Figure 4.5 respectively. The minimum torque decreases with increase in silane content, which is consistent with the trend for Mooney viscosity. The maximum torque shows only a slight indication of an increase trend with increase in silane. The Δ torque values (M_H - M_L) increase significantly with increasing silane addition, showing that the crosslink density of ENR/silica compounds were increased by addition of the silane coupling agent. The combination of reduction in minimum torque and increase in maximum torque indicates that the coupling agent is effectively reacting with both the silica surface and the rubber to increase crosslink density in the cured compound. ENR/silica with 8phr X50S silane gave the highest values of torque as compared to all ENR/silica and NR/BR compounds which indicate this compound have higher stiffness and crosslink density. It is also observed that silica filled ENR compounds with silane do not show any reversion on the torque cure curves. Therefore, the result suggests that the sulphur in the silane coupling agent may have improved the heat resistance of silica filled ENR compounds by compensating the degradation or oxidation of newly formed sulphur bridges of rubber network[2]. The carbon black filled NR/BR compound still gave the highest values of Δ torque as compared to ENR/silica compounds as well as the lowest M_L value among all ENR/silica compounds. This could be due to good carbon black filler dispersion in the NR/BR compound and hence improved rubber-filler interaction and compound crosslink network[1].

Table 4.3: Curing characteristics of ENR/silica compounds with different amounts of X50S silane.

Mix	**M_L** (dNm)	**M_H** (dNm)	**ts2** (min)	**t90** (min)	**t95** (min)	**M_H-M_L** (dNm)	**Torque at 30 min** (dNm)
0phr X50S	29.96	76.04	14.16	19:01	19:24	46.08	73.29
2phr X50S	28.67	76.20	12.39	18:11	18:39	47.53	75.98
4phr X50S	26.97	79.37	10:43	16:38	18:55	52.40	79.37
6phr X50S	21.26	78.16	9:50	17:50	21:45	56.90	78.16
8phr X50S	20.70	83.86	9:07	19:13	23:13	63.16	83.84
NR70:BR30	17.60	81.79	6:14	15:15	17:23	64.19	81.71

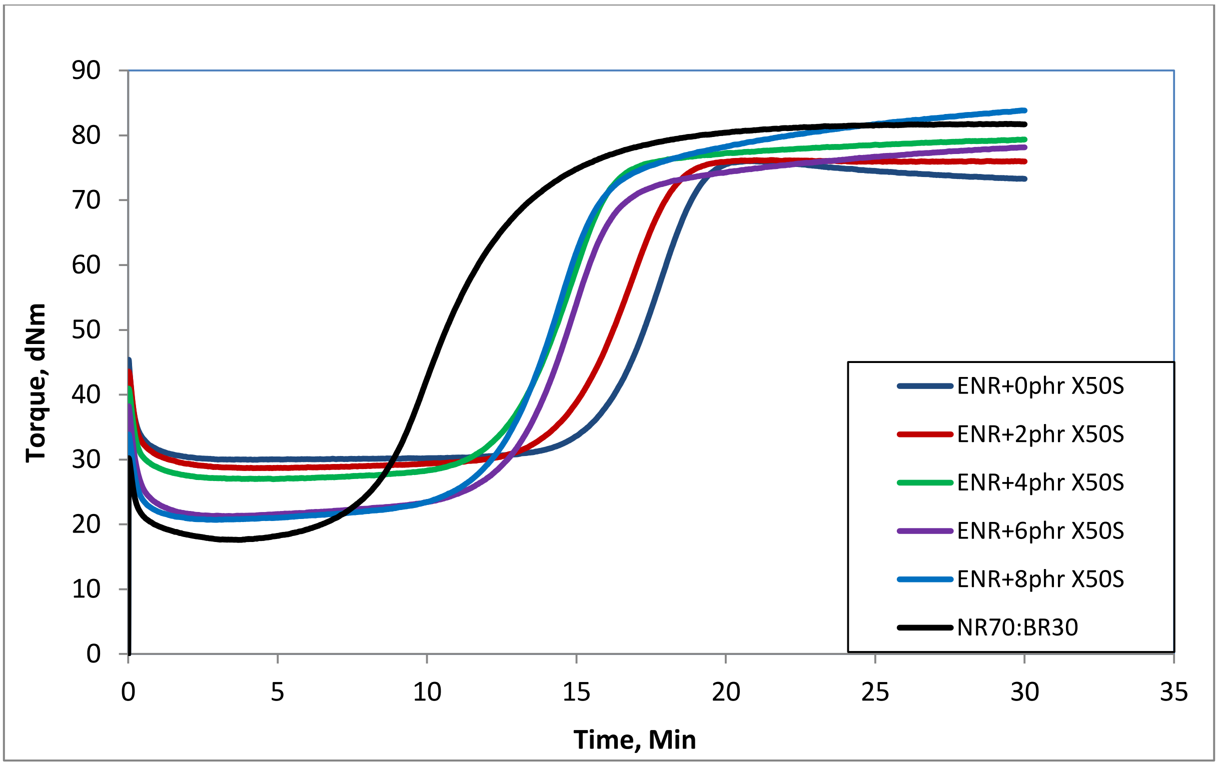

Figure 4.5: Rheometer curves of ENR/silica compounds with different X50S silane phr

4.1.4 Filler Dispersion (Macrodispersion Analysis)

The results of a filler macrodispersion study of ENR/silica vulcanizates both without and with different concentrations of X50S silane coupling agent are shown in Table 4.4. The carbon black filled NR/BR vulcanizate gave the highest percentage of filler dispersion as well as the lowest average aggregate size. This is expected as it is known that carbon black filler is relatively easily dispersed in rubber during mixing. The results show that silica dispersion in ENR is reasonably good, over 92%, but slightly lower than carbon black dispersion in NR.

However, the surprising result is that silane concentration does not have any significant effect on silica dispersion in ENR compounds. It could be that even with silane present the silica surface is still polar and silica-silica interactions may result in flocculation while the compound is at rest during storage[3]. Furthermore, when the surface of the silica reacts initially with the silane, one or two of the ethoxysilyl units per triethoxysilyl group remain unreacted. The unreacted ethoxysilyl groups also can react with moisture or water during storage which results in the silane forming a bridge between silica aggregates[4] to develop silica network that stabilising the silica flocculent. The dispersion results indicate that differences in viscosity and stiffness of compounds with and without silane are not due to different levels of filler dispersion, but most likely due to differences in silica-silica interaction.

Table 4.4: Filler dispersion of ENR/silica compounds with different X50S silane phr

Parameter	0phr X50S	2phr X50S	4phr X50S	6phr X50S	8phr X50S	NR70:BR30
Avg. Ag. Size, micron	12.4	12.3	12.9	12.3	12.9	9.1
Dispersion, %	93	95	94	95	94	99

4.1.5 Physical & Mechanical Properties

The physical and mechanical properties of ENR/silica compounds with different concentration of silane coupling agent are shown in Figures 4.6 to 4.11. From these results, it is observed that there is no significant change in hardness with increase of silane with all the hardness properties are still within the specification for the truck tyre compound (60-72 IRHD), as well as no consistent trend in modulus M100 with increase of silane as shown in Figure 4.6 and Figures 4.7 respectively. This is in agreement with the rheometer results discussed earlier where it can be observed that maximum torque (MH) values do not change very much with increase of silane. It seems that with an increase in silane concentration the silica-silica interaction decreases but the crosslinking between silica and rubber increases, resulting in overall little change in stiffness.

For the heat build-up temperature result, it is interesting to note that the heat build-up temperatures of ENR/silica vulcanizates are much lower than carbon black filled NR/BR vulcanizate. The good heat build-up property is one of the advantages of using silica filler over carbon black filler. It can be observed also that the ENR/silica vulcanizates heat build-up is decreased with increased silane concentration as shown in Figure 4.8. This could be due to less silica-silica interaction and more sulphur crosslinking between silica and rubber with a higher silane concentration[2].

It is observed that the ENR/silica vulcanizates exhibit a slight indication of an increase in tensile strength with increase of silane concentration as shown in Figure 4.9, but all values are below the strength of the NR/BR compound. However, all the vulcanizates still showed tensile strength well within specification for the truck tyre compound which is not below than 14 MPa.

It is also observed that the ENR/silica vulcanizates exhibit a slight indication of an increase in abrasion resistance with silane coupling agent (Figures 4.10 and 4.11) but it is not very convincing and is still very much below the level of the NR/BR vulcanizate. However, the ENR/silica vulcanizate containing 8phr silane exhibits the highest properties of abrasion resistance index compared to all the ENR/silica compounds. This could be due to both the reduced heat build-up and to the better crosslinking between the rubber and silica following the increased chemical reaction between silica and silane as the X50S silane coupling agent concentration increases[5]. This result is in agreement with the tensile strength and heat build-up results above

Based on all these results, it can be said that silane coupling agent reduces silica-silica interactions and improves the crosslink network of the silica filled ENR vulcanizates, by chemically bonding between the silica and the rubber. The reduced filler-filler interaction and improved crosslink network results in reduced heat build-up and a slight increase in tensile strength and abrasion resistance, however hardness and modulus values are not significantly affected. Slight improvements in compound processability can be gained by decreasing its Mooney viscosity with increase of silane concentration. However, it is suggested that 4 to 6 phr of X50S silane coupling could be the best practical amount to add into an ENR/silica compound to enhance physical properties and processability while not increasing compound cost too much.

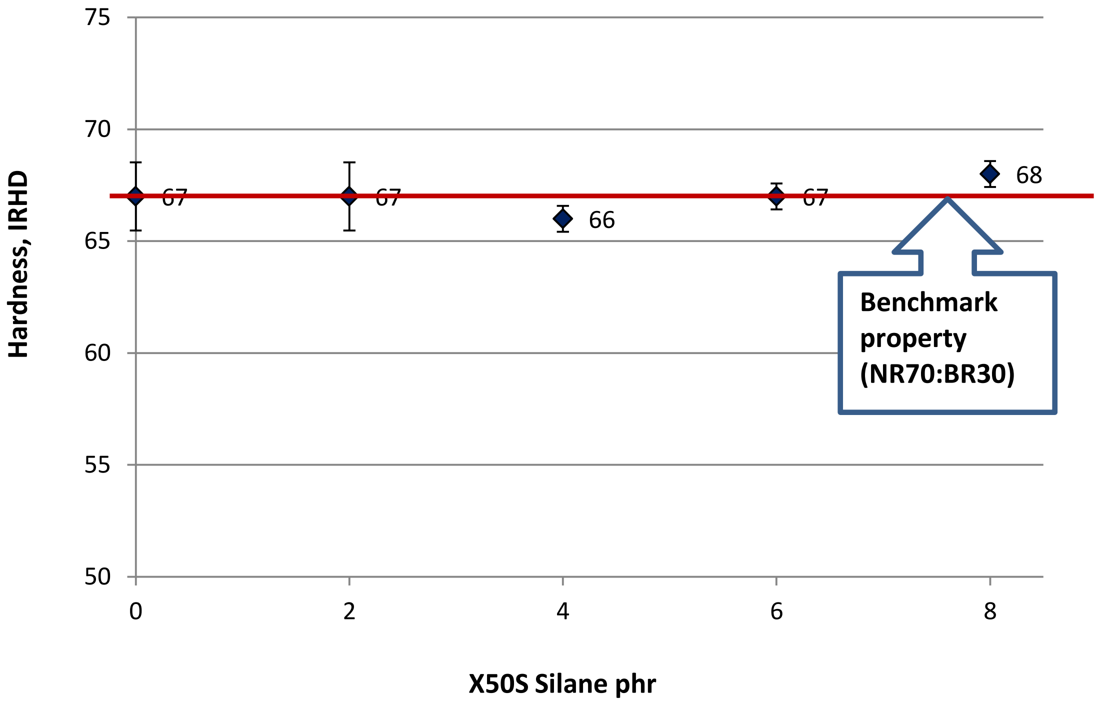

Figure 4.6: Hardness of ENR/silica compounds with different silane phr

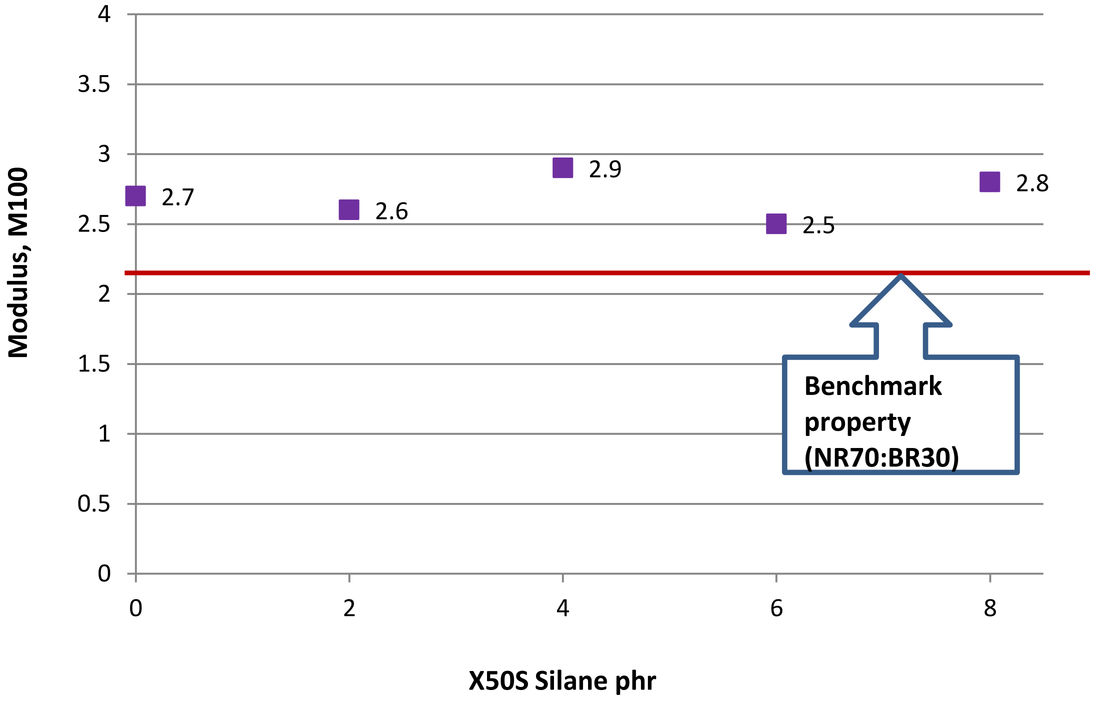

Figure 4.7: Modulus M100 of ENR/silica compounds with different silane phr

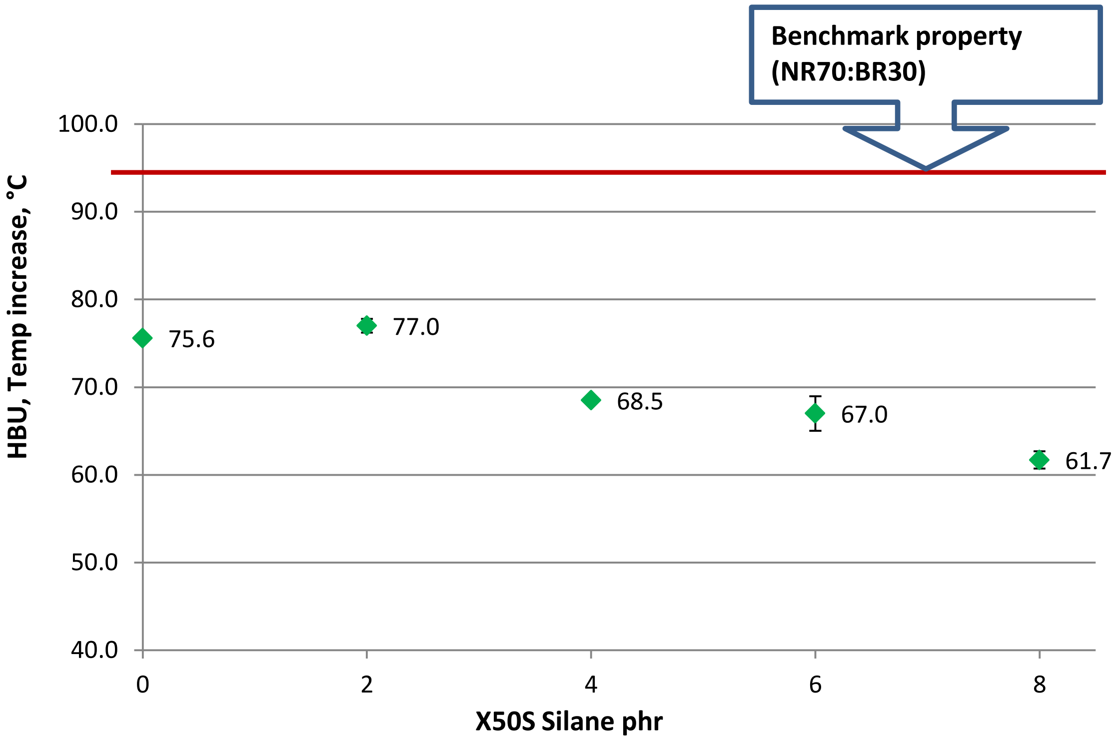

Figure 4.8: HBU (temperature increase) of ENR/silica compounds with different silane phr

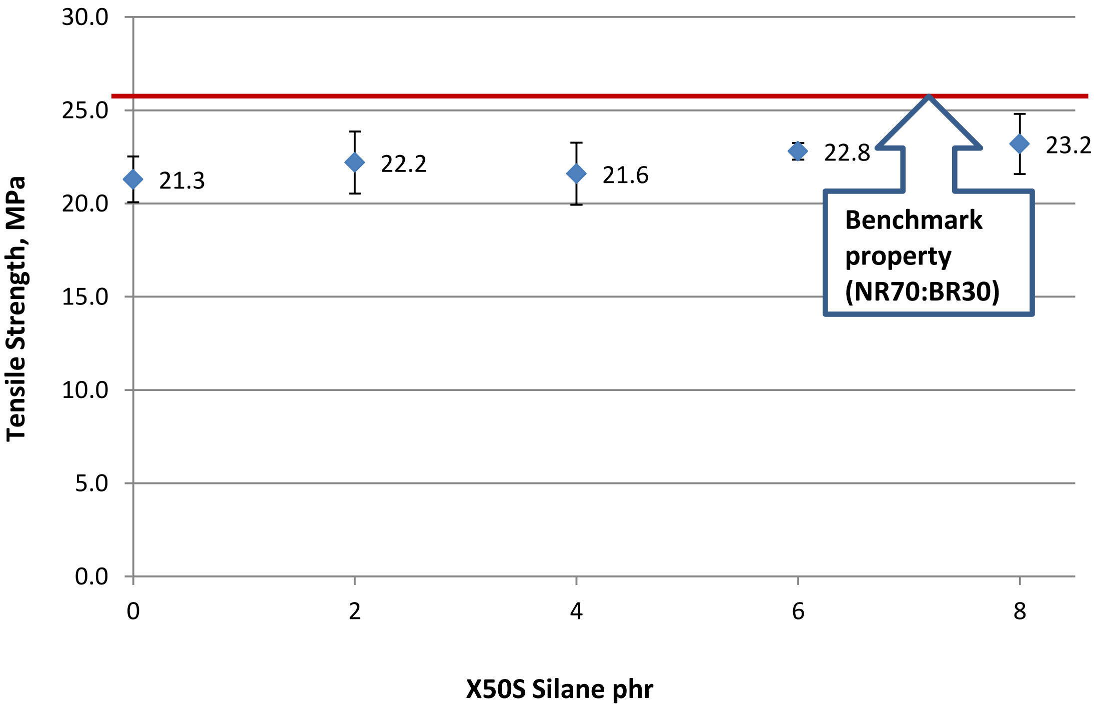

Figure 4.9: Tensile strength of ENR/silica compounds with different silane phr

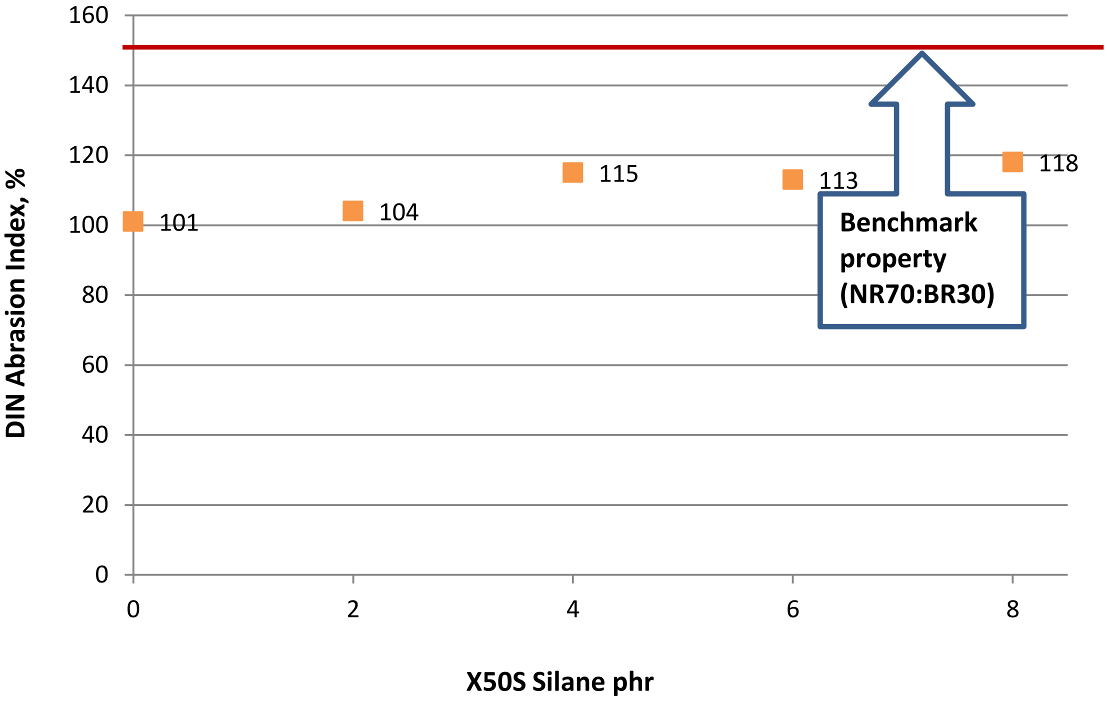

Figure 4.10: DIN abrasion resistance index of ENR/silica compounds with different silane phr

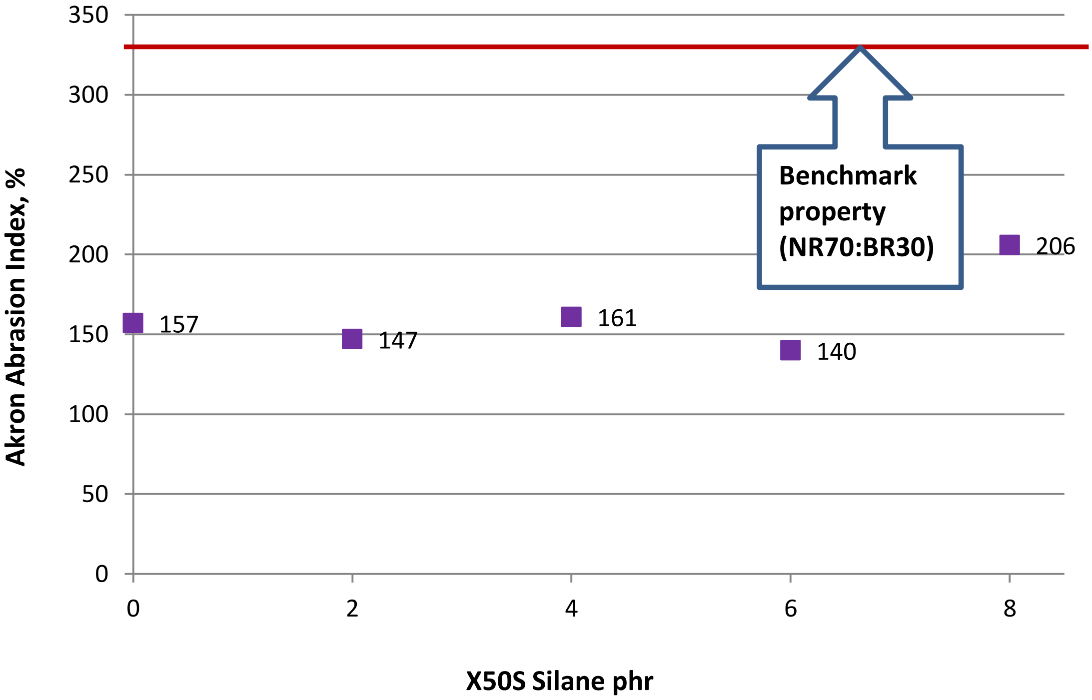

Figure 4.11: Akron abrasion resistance index of ENR/silica compounds with different silane phr

4.2 Effect of Water Addition to Silica on the Properties of Silica Filled ENR Compounds

The reason why this study was carried out is because it had been shown in previous studies^6 and preliminary studies that water added to silica could influence the silica filled ENR compound properties. To quantify the effect of water in this study, silica filled ENR compounds with different amounts of water added to the silica (0-20 wt.% of silica) were prepared and the effect of water addition on the properties determined. As in the previous section, results have been compared with the conventional truck tyre tread, carbon black filled NR/BR compound (benchmark compound).

4.2.1 Mixing Performance

The mixing data such as torque, mixing energy, temperature and time were used to analyse the mixing performance of the masterbach and compounds.

The final mixing energy and dump temperature of ENR/silica masterbatches during first stage, second stage and final stage mixing are shown in Table 4.5. The torque curves obtained from all mixing stages are presented in Figures 4.12 to 4.14. Overall, the mixing torque curves, the final mixing energy and dump temperatures for the first stage mixing do not vary significantly with increasing water percentage. However, for the second and final stages of mixing, the mixing torque curves, final mixing energy and to a lesser extent, dump temperatures, did show a significant decreasing trend with increasing water percentage up to 15%. This could be due to the water reducing filler-filler interaction possibly increasing filler dispersion and, hence reducing viscosity.

It also can be observed that at 15% water the silica filled ENR compound gave the lowest final mixing energy and dump temperature of second and final stages compound. However, during mixing it was observed that there was water running out of the mixer during mixing of 15% and 20% water compounds. Therefore, it is important to not add water more than necessary into the silica when trying to improve the processing of the compound and minimise energy used. In particular, it is recognised that the normal moisture/water content of silica is already in the range of 5 to 7% (chapter 2 page 22).

Table 4.5: Mixing energy and dump temperatures of ENR/silica masterbatches with different water wt.% (on silica)

Mixing properties	Stages	0% water	4% water	6% water	10% water	15% water	20% water
Final Mixing Energy, KJ	1st	468	456	456	468	488	486
	2nd	268	238	200	182	172	174
	3rd	162	153	113	102	97	103
Dump Temperature, °C	1st	145	144	145	145	145	145
	2nd	129	133	125	122	120	121
	3rd	81	85	82	79	77	78

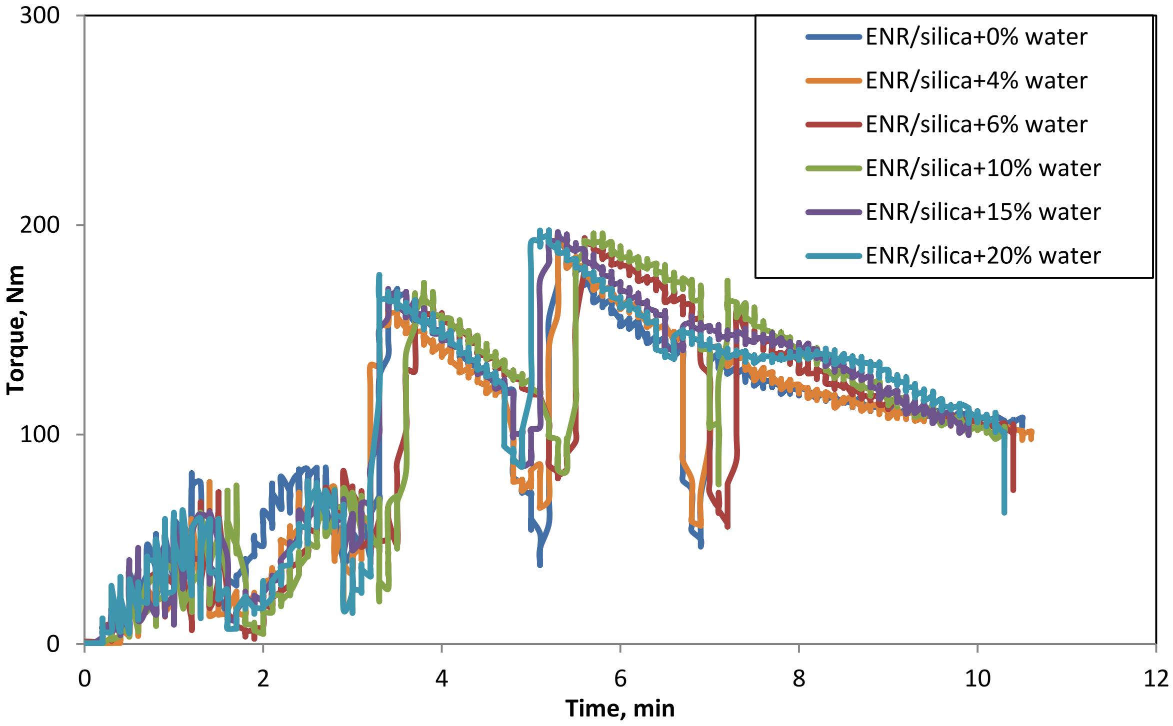

Figure 4.12: Torques curves of ENR/silica mixes with different water wt.% (on silica) in the first stage mixing.

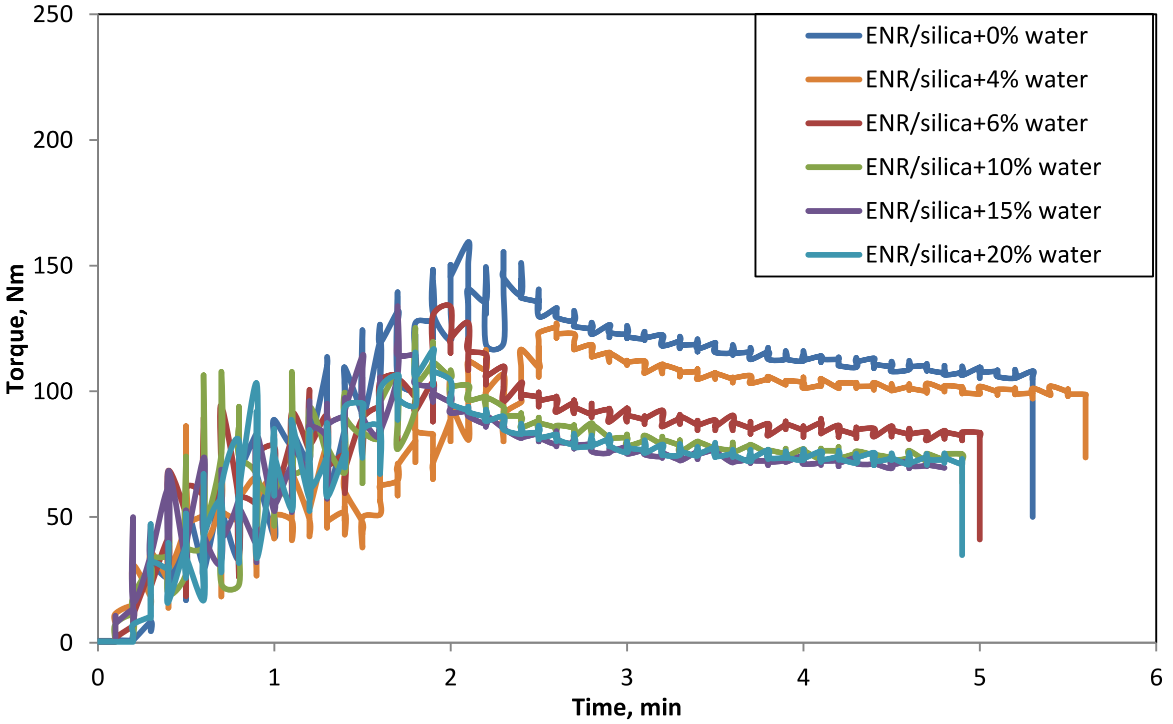

Figure 4.13: Torques curves of ENR/silica mixes with different water wt.% (on silica) in the second stage mixing.

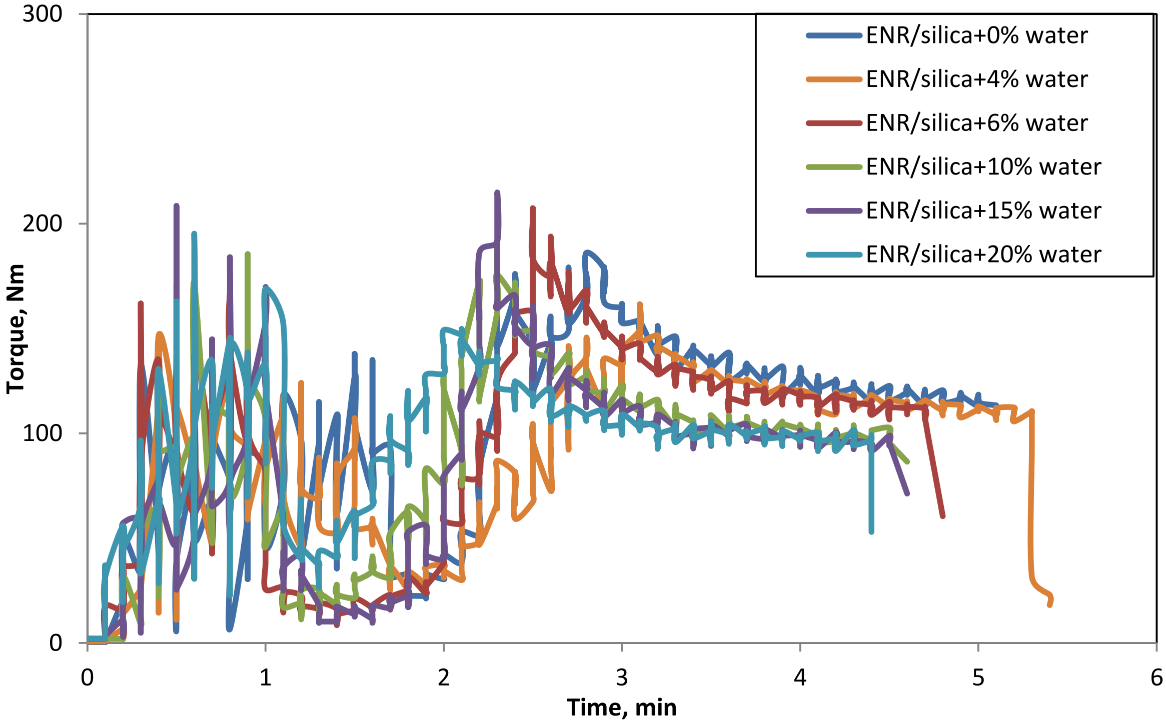

Figure 4.14: Torques curves of ENR/silica mixes with different water wt.% (on silica) in the final stage mixing.

4.2.2 Mooney viscosity

The Mooney viscosity of masterbatches and compounds of ENR/silica mixes with addition of water are shown in Table 4.6 and Figure 4.15. It was found that the Mooney viscosity of the masterbatch reduced significantly with increasing water percentage up to 15% during 1st stage mixing. The water is expected to interact strongly with the silica surface through hydrogen bonding and would therefore reduce the silica-silica interaction, reducing viscosity[7]. It is also possible that the presence of water during first stage mixing may help to reduce filler-filler interaction in the ENR/silica compound by accelerating the reaction of silane with the silica surface through hydrolysing the alkoxysilane and hence reduce viscosity[4,8]. The final compound Mooney viscosity does not show a decrease in viscosity with increase in water content up to 6%. This may be because the relatively small amount of added water has evaporated from these compounds during mixing. There is a slight indication of a decreasing trend with increase in water percentage from 6 to 15% as shown in Figure 4.15, suggesting that some water may remain in these compounds.

These results indicate that the addition of water during mixing of silica filled ENR compounds may improve the mixing processability and to a lesser extent, the flow properties of the compounds after mixing, by reducing their viscosity. Improving in mixing processability and molding or extrusion processability will result in energy saving.

Table 4.6: Mooney viscosity of ENR/silica compounds with different water wt.% (on silica)

Mooney Viscosity	0% water	4% water	6% water	10% water	15% water	20% water
Masterbatch viscosity	150	134	126	109	94	97
Remilling viscosity	119	116	105	106	76	78
Final Compound viscosity	81	85	86	71	63	65

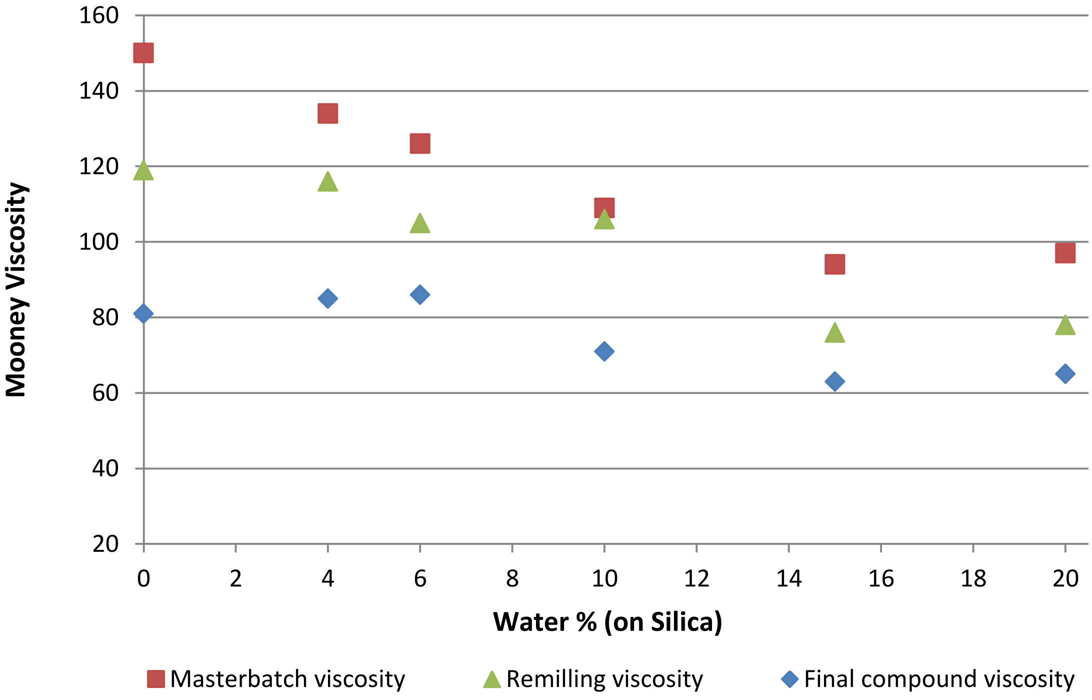

Figure 4.15: Mooney viscosity of ENR/silica mixes with different water wt.% (on silica)

4.2.3 Cure Characteristics

The rheometer curves and cure characteristics of ENR/silica compounds with different amounts of added water are presented in Table 4.7 and Figure 4.16 respectively. There is no significant difference in M_L and M_H values when adding water at up to 6%. However, above 6% water, the minimum torque (M_L) and maximum torque (M_H) reduced significantly with increasing water percentage. The trends in M_L values with increased water percentage are in agreement with the Mooney viscosity results discussed earlier. The low M_H values of the compounds indicates that the low stiffness carries through to the cured compound. The lower stiffness could be because water addition has resulted in an improvement of filler dispersion by reducing silica-silica interaction. Alternatively, it could be that some water still remains in the cured compound, reducing its stiffness by plasticisation[6]. It can be observed in the rheometer curves in Figure 4.16 that the addition of water also increased significantly the scorch time (ts2) and cure time (t95), the whole curve being shifted to longer times. All the compounds with different water contents showed a similar crosslink density (M_H-M_L). The crosslink density is due to the crosslinking reaction of sulfur and silane coupling agent with silica filler and rubber matrix and this result indicates that the extent of these reactions is not significantly affected by the addition of water to the silica in the mixing stage. From all these results it can be concluded that the addition of water delays the start of the crosslinking reaction but does not significantly affect the rate or extent of crosslinking. The longer ts_2 time may be better for rubber processing as there is extra time available for extrusion or molding before it starts to crosslink.

Table 4.7: Rheometer and curing characteristics of ENR/silica compounds with different water wt.% (on silica)

Mix	**M_L** (dNm)	**M_H** (dNm)	**ts2** (min:sec)	**t90** (min:sec)	**t95** (min:sec)	**M_H-M_L** (dNm)	**Torque at 30 min** (dNm)
0% water	23.08	75.35	7:55	14:40	15:23	52.27	75.28
4% water	23.81	73.62	10:13	16:41	18:31	49.81	73.62
6% water	24.44	75.98	9:21	16:27	17:46	51.54	75.82

10% water	18.81	69.86	10:23	17:47	20:46	51.05	69.86
15% water	16.87	67.82	10:33	18:20	21:35	50.98	67.80
20% water	16.71	67.86	10:17	17:57	21:34	51.15	67.86

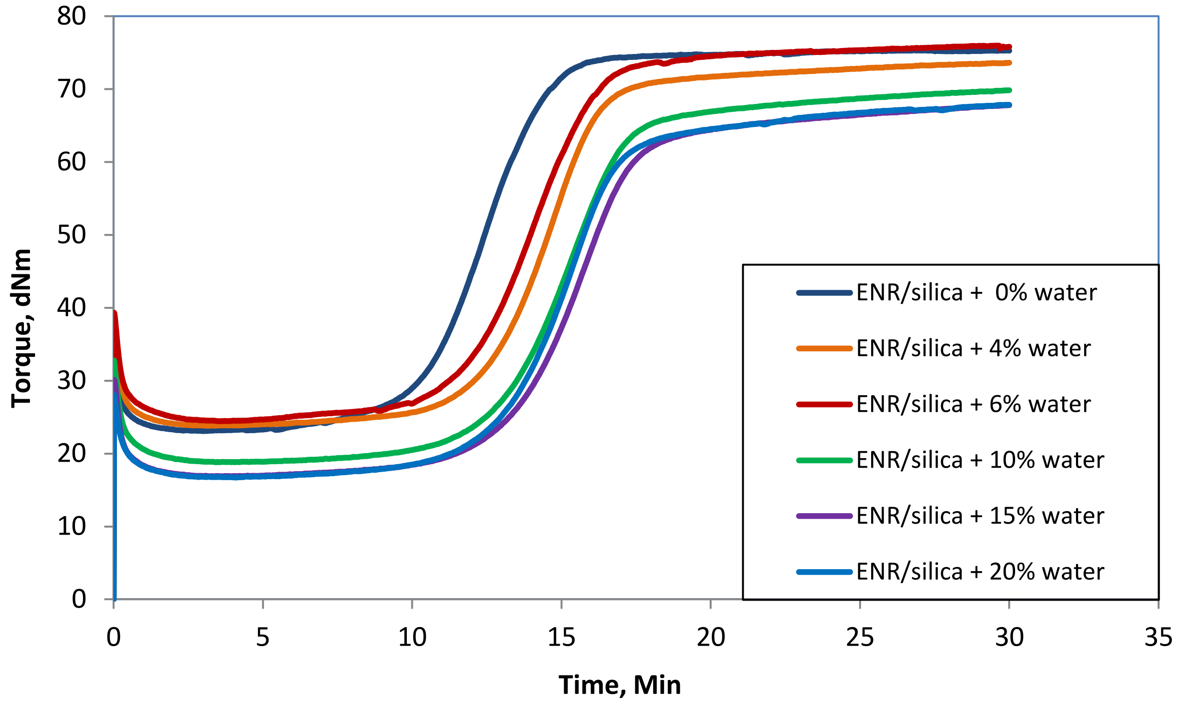

Figure 4.16: Rheometer curves of ENR/silica compounds with different water wt.% (on silica)

4.2.4 Filler Dispersion (Macrodispersion Analysis)

The results of a filler macrodispersion study of ENR/silica vulcanizates using a DisperGrader^{TM} 1000NT, are shown in Table 4.8. It was found that the presence of water during 1st stage mixing of ENR/silica mixes showed no significant effect on the percentage of filler dispersion as all the silica filled ENR vulcanizates show high percentage filler dispersion, all above 95%. The average aggregate size of all the compounds was below 11 μm size and was also unaffected by the water content of the silica. The similar levels of filler dispersion suggest that any differences in properties between the compounds are not due to dispersion, but may be due to differences in filler-filler or polymer-filler interaction. It was noted that the filler dispersion measured in this experiment (95 to 98%) was significantly greater than that observed in the silane experiment discussed in the previous section (93 to 95%). This could not be due to water addition, since the compound without water addition also showed a good dispersion. It is thought that the reason for the difference is that there was a longer time between mixing and curing in the silane experiment and that this allowed more flocculation of the silica to occur, reducing the filler dispersion for all the samples. In the future it will be useful to investigate the effect of time between mixing and curing on filler dispersion.

Table 4.8: Filler dispersion of ENR/silica compounds with different water wt.% (on silica)

Parameter	0% water	4% water	6% water	10% water	15% water	20% water
Avg. Ag. Size, µm	10.2	10.8	11.1	10.2	10.4	10.8
Dispersion, %	98	96	95	95	98	96

4.2.5 Physical & Mechanical Properties

The physical and mechanical properties of ENR/silica compounds are shown Figures 4.17 to 4.21. From these results, it is observed that modulus (M100) of ENR/silica vulcanizates exhibit no consistent trend with increased of water percentage but there is a slight indication of a decrease in hardness with increased water percentage (Figure 4.17) with all the hardness properties are still within the specification for the truck tyre compound which is 60-72 IRHD. The decrease in hardness is in agreement with cure curves which showed a decreasing trend in minimum and maximum torques as well as a decrease in Mooney viscosity with increased of water addition. As the previous section indicates that there is no difference in filler dispersion, the reduced stiffness is probably due to small amounts of water remaining in the compound, adsorbed to the silica surface and reducing the filler-filler or polymer-filler interactions, plasticising the compound.

There is significant decrease in heat build-up temperature with increased water percentage up to 6% in silica as shown and observed in Figure 4.19. This could also be due to the water reducing the silica-silica interactions in the compound.

The tensile strength of ENR/silica vulcanizate exhibit no consistent trend with increased water percentage, but all the compounds still showed tensile strength properties well within specification for the truck tyre compound which is not below than 14 MPa, as shown in Figure 4.20.

The DIN abrasion resistance index (Figure 4.21), shows no consistent trend with increased water percentage. The Akron abrasion resistance index is significantly higher for water percentages above 6% (Figure 4.22). However, both abrasion resistance results do not show very convincing trends and they are very much below the level of the NR/BR vulcanizate.

The most important findings from the water addition experiment are the significant decrease in heat build-up temperature and Mooney viscosity with increased water percentage. This will be very valuable in the development of a new tyre tread compound due to the possibility of having a lower hysteresis compound with improved processability properties. The compound with low heat build-up may also result in an improvement in tyre durability[9].

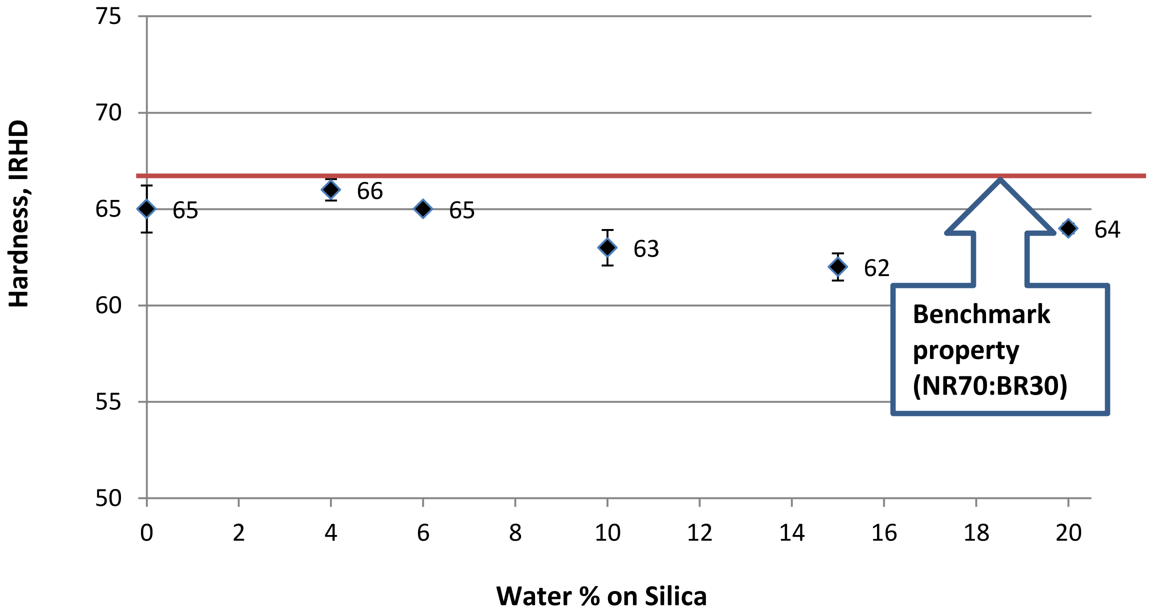

Figure 4.17: Hardness of ENR/silica compounds with different water wt.% (on silica).

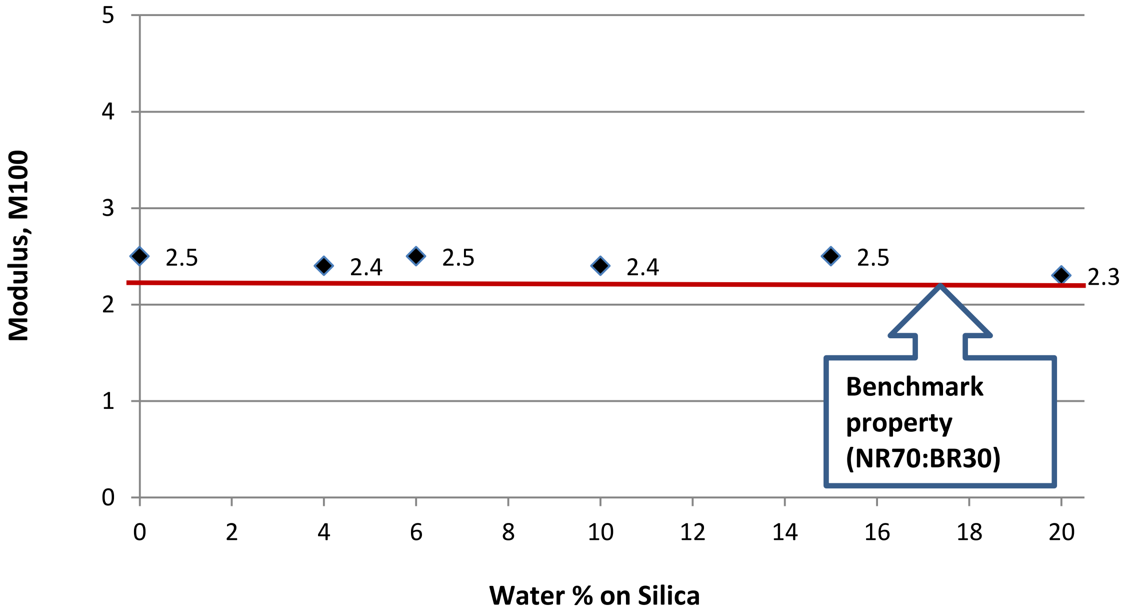

Figure 4.18: Modulus M100 of ENR/silica compounds with different water wt.% (on silica).

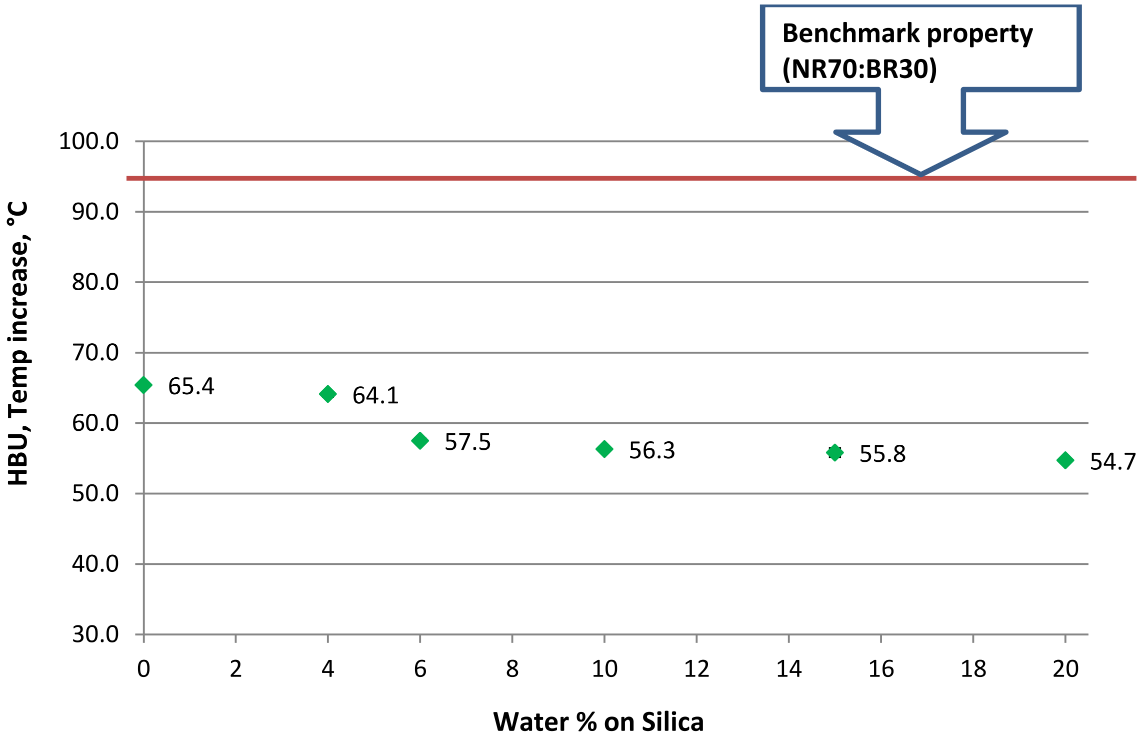

Figure 4.19: HBU (temperature increase) of ENR/silica compounds with different water wt.% (on silica).

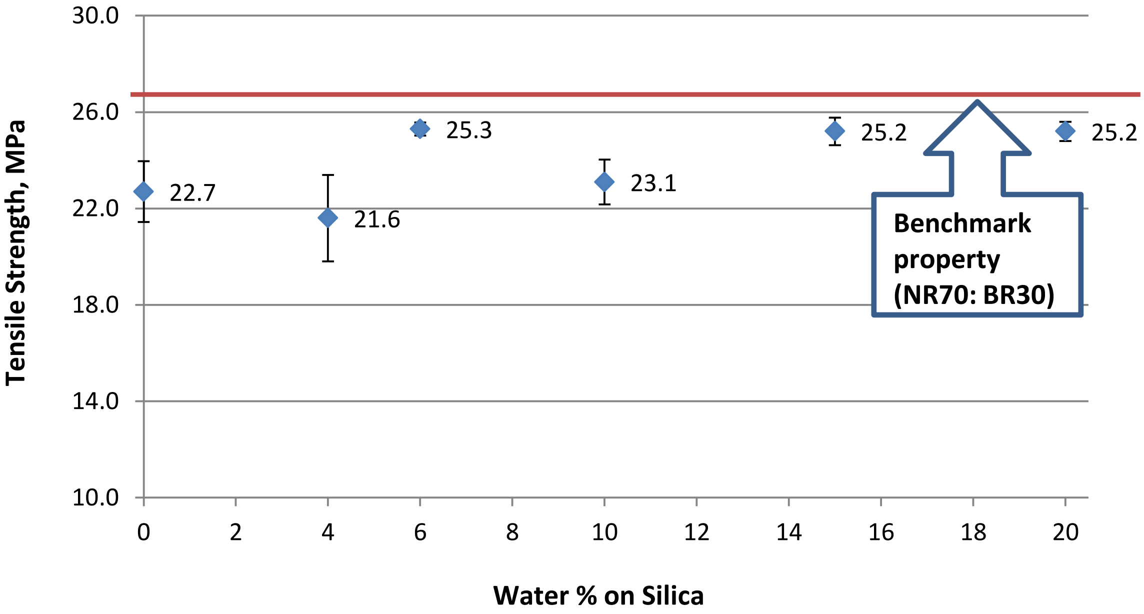

Figure 4.20: Tensile strength of ENR/silica compounds with different water % (on silica).

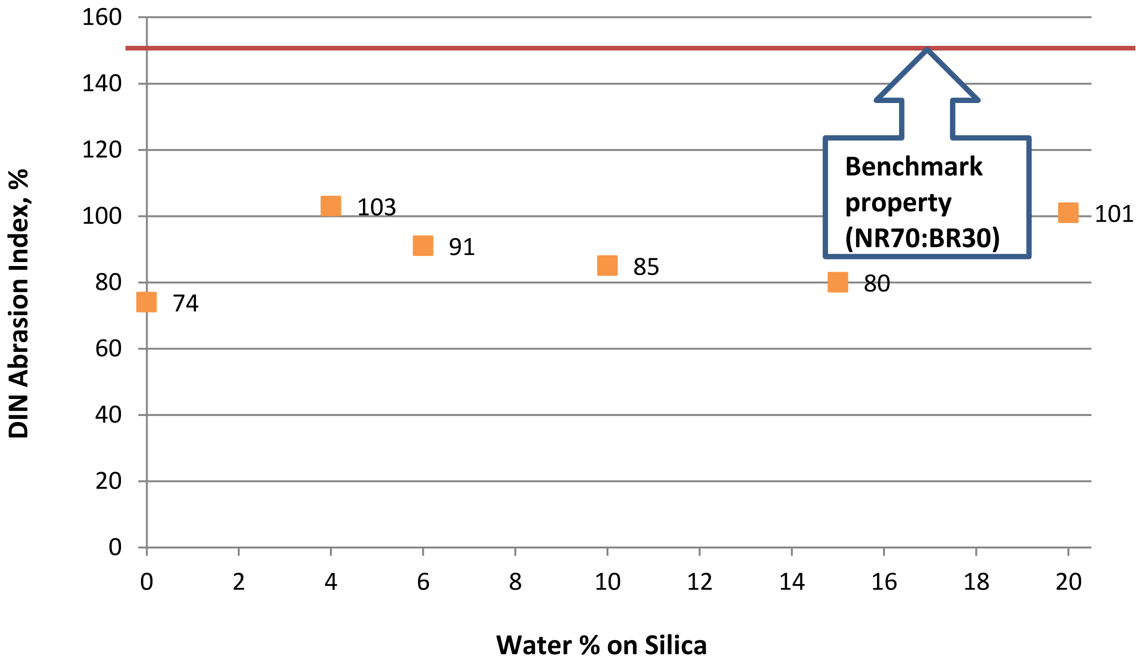

Figure 4.21: DIN abrasion resistance index of ENR/silica compounds with different water % (on silica).

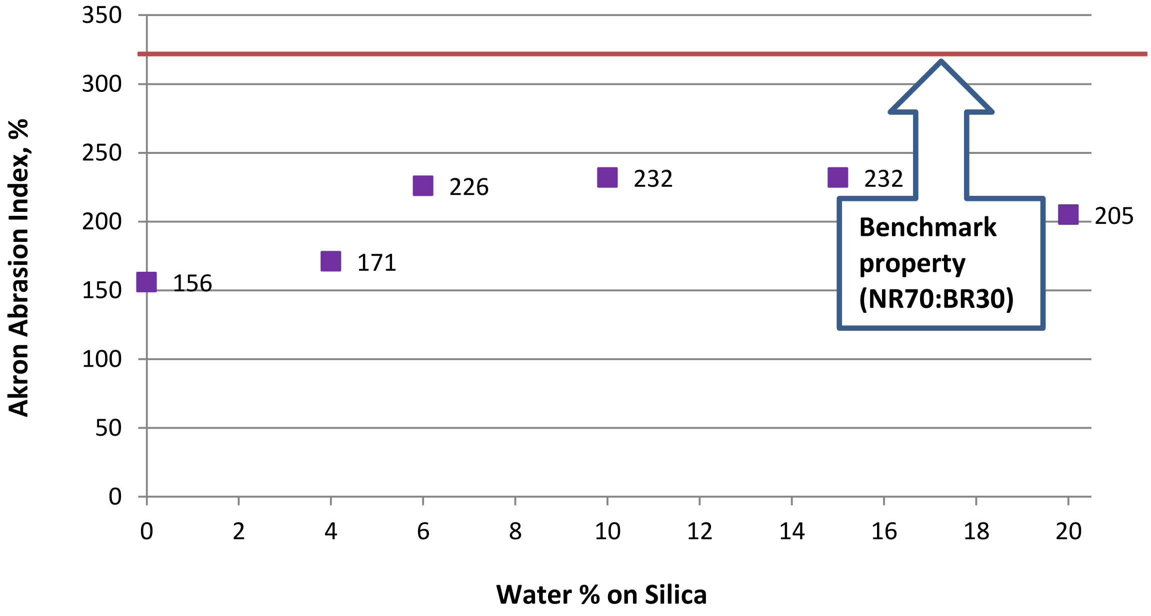

Figure 4.22: Akron abrasion resistance index of ENR/silica compounds with different water % (on silica).

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CHAPTER 5

BLENDING WITH BUTADIENE RUBBER TO IMPROVE ABRASION RESISTANCE

5.1 Effect on Properties of Blending Butadiene Rubber into a Silica Filled ENR Compound

In this chapter, silica filled ENR/BR blend compounds with different BR content from 0 to 30 phr have been prepared in order to determine whether blending with BR can improve the abrasion resistance of ‘green’ tyre compounds produced from Epoxidized natural rubber. Improvement is necessary because the established ‘green’ tyre tread formulation produced from silica filled ENR compound still has an issue with abrasion resistance. All the silica filled ENR/BR blend compounds in this study are prepared with the addition of silane coupling agent (phr) and water (% on silica) during the first stage mixing. The physical and mechanical properties of the silica filled ENR/BR blend compounds have been measured and all the results obtained have been compared with the carbon black filled NR/BR compound which is the conventional truck tyre tread compound (benchmark compound).

5.1.1 Mixing Performance

Mixing performance evaluation was carried out based on the mixing data and results recorded by the Polylab OS Haake Rheomix 3000 mixer. Four mixes of silica filled ENR/BR blends and one NR/BR carbon black mix were prepared in this study. The final mixing energy and dump temperature of the compounds during first stage mixing are shown in Table 5.1. The torque curves obtained from the first stage mixing process are presented in two figures for easier comparison (Figures 5.1-5.2).

For silica filled ENR/BR blends with different ENR:BR ratios, a comparison of torque curves is presented in Figure 5.1. The final torque values of the ENR/BR blends do not vary significantly with BR content. The final mixing energy and dump temperature also do not show a consistent trend with increase of BR loading as shown in Table 5.1.

The comparison of mixing torque curves between the benchmark mix NR70:BR30, and silica filled ENR70:BR30 mix are shown in Figure 5.2. It can be observed that the ENR/BR blend gave a significantly higher torque than the NR/BR compound. The reduced mixing torque results in a much lower mixing energy and dump temperature for the carbon black filled compound compared to the silica filled ENR blends as shown in Table 5.1. The lower mixing torque of carbon black filled NR/BR compound is because carbon black filler is non-polar, unlike silica and has relatively low filler-filler interactions and so is easy to disperse during mixing[1].

Table 5.1: Mixing energy and dump temperatures of silica filled ENR/BR compounds and carbon black filled NR/BR compound

Mixing properties	ENR100:BR0	ENR90:BR10	ENR80:BR20	ENR70:BR30	NR70:BR30
Final Mixing Energy, KJ	451	475	449	398	280
Dump Temperature, °C	148	151	151	147	138

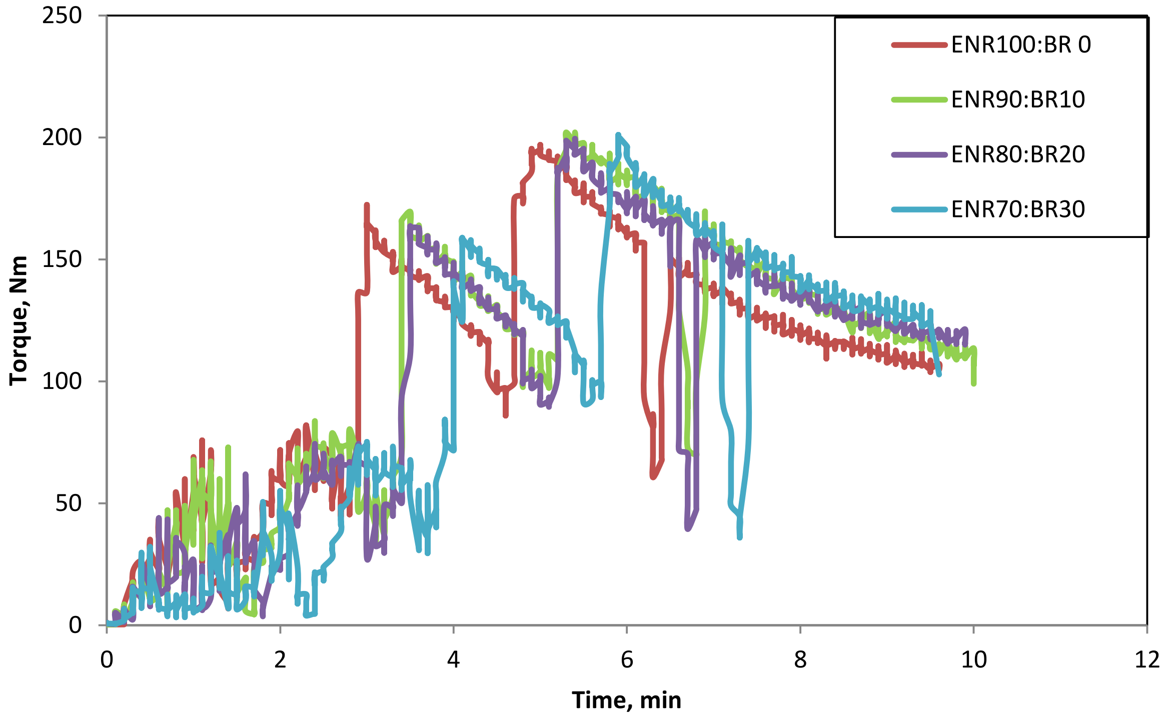

Figure 5.1: Torques curves of silica filled ENR/BR blends with different ratios.

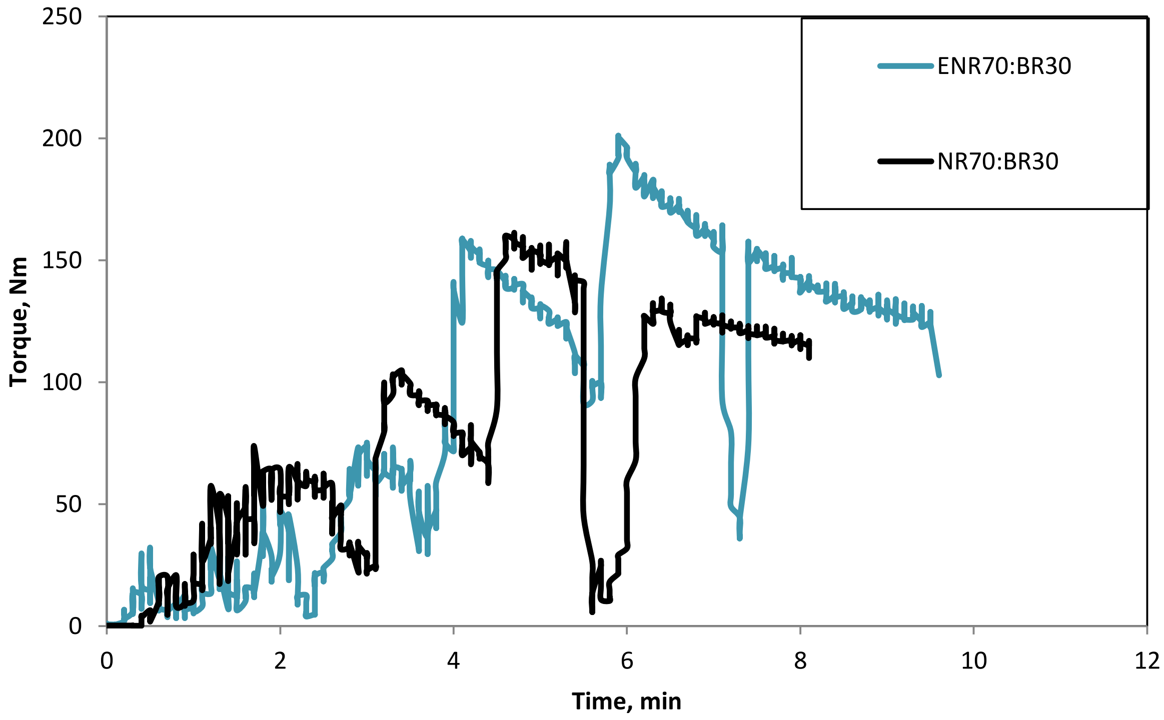

Figure 5.2: Torques curves of ENR/BR-silica and NR/BR-carbon black compounds.

5.1.2 Mooney viscosity

The Mooney viscosity of the masterbatches and compounds are shown in Table 5.2 and Figure 5.3. The NR/BR compound which is a conventional truck tyre tread formulation still gave the lowest Mooney viscosities for both masterbatch and final compound, agreeing with the lowest torque and energy values for mixing. Usually lower Mooney viscosity is an indirect indication of good processability and flow properties of rubber mix. So, in terms of processability, carbon black filled NR/BR compound still exhibited better properties than silica filled ENR/BR blends.

It can be observed that the Mooney viscosity of ENR/BR blends increases as the BR percentage in ENR increased. The increase of Mooney viscosity with BR content is not due to the high Mooney viscosity of butadiene rubber (37-43 Mooney Units)[2] but is more likely due to the resistance to heat degradation and mechanical shearing force (mastication) during mixing of butadiene rubber.

Table 5.2: Mooney viscosity of ENR/BR-silica blends

Mooney Viscosity	ENR100:BR0	ENR90:BR10	ENR80:BR20	ENR70:BR30	NR70:BR30
Masterbatch viscosity	111	116	138	157	90
Final Compound viscosity	70	76	90	97	63

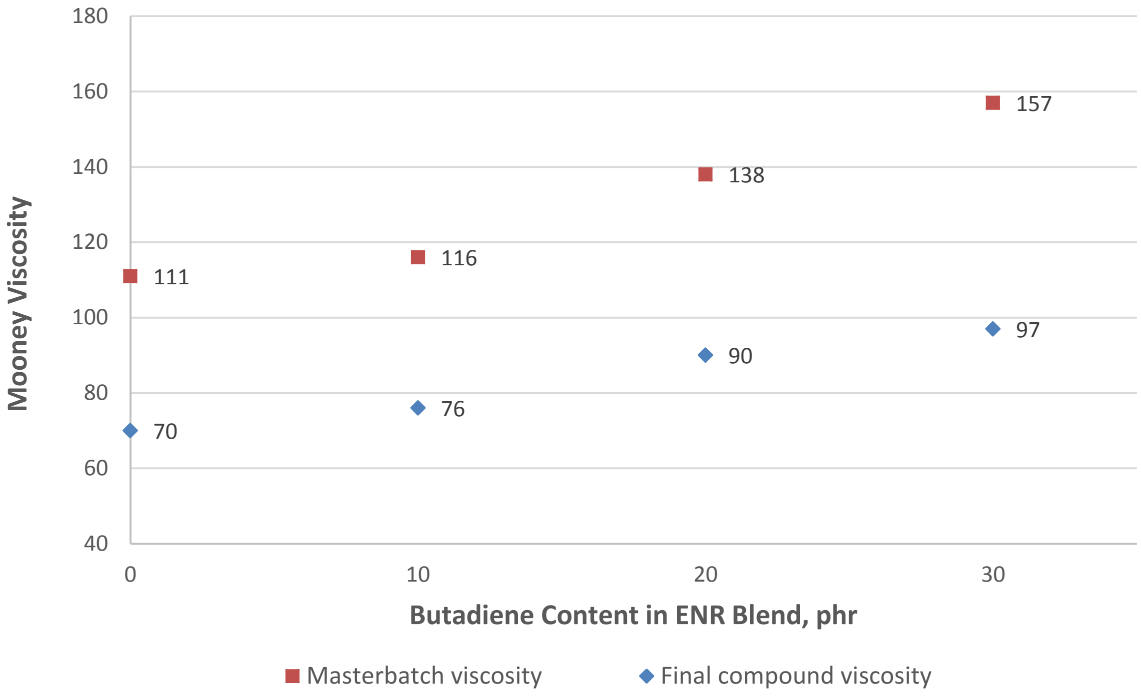

Figure 5.3: Mooney viscosity of ENR/BR-silica blends.

5.1.3 Cure Characteristics

The rheometer curves and cure characteristics of ENR/silica and ENR/BR blend compounds are presented in Table 5.3 and Figure 5.4 respectively. It can be observed that the silica filled ENR/BR compounds exhibit significant higher torque values (M_H and M_L) with increased of butadiene content. This may be expected since the addition of BR in ENR blends increases the Mooney viscosity and hence is also likely to increase the stiffness. However, there is only a slight increase in Δ torque value (M_H - M_L) with increasing BR content, showing that the BR does not significantly influence the crosslink density.

NR/BR carbon black compound still gave the highest values of Δ torque as compared to all compounds as well as the lowest M_L value among all compounds. This indicates that carbon black filled NR/BR compound still gave the highest compound crosslink density, probably because of the interference of silica with the sulphur cure system[3].

Table 5.3: Rheometer and curing characteristics of ENR/BR-silica blend compounds

Mix	**M_L** (dNm)	**M_H** (dNm)	**ts2** (min)	**t90** (min)	**t95** (min)	**M_H-M_L** (dNm)	**Torque at 30 min** (dNm)
ENR100:BR0	19.97	67.92	11.07	22:25	23:48	47.95	67.92
ENR90:BR10	22.58	71.90	10:24	23:07	24:48	49.32	71.90
ENR80:BR20	27.60	77.62	10:40	23:14	25:03	50.02	77.61
ENR70:BR30	30.51	80.34	9:48	24:26	26:01	49.84	80.34
NR70:BR30	16.60	83.32	8:04	17:37	19:41	66.72	83.27

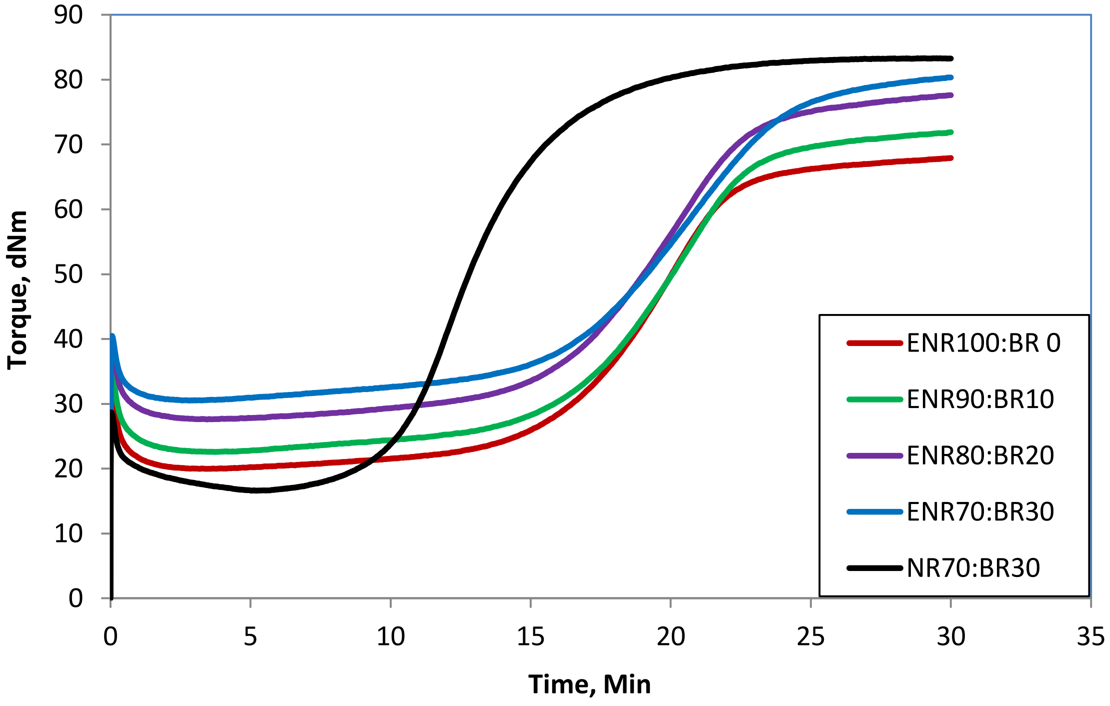

Figure 5.4: Rheometer curves of ENR/BR-silica blend compounds.

5.1.4 Filler Dispersion (Macrodispersion Analysis)

The results of a filler macrodispersion study of ENR/silica and ENR/BR blend vulcanizates using a DisperGrader^{TM} 1000NT, are shown in Table 5.4. The filler dispersion results show that there is a slight decrease in percentage filler dispersion with increase of BR content in ENR/BR blend vulcanizates. This could be because the non-polar butadiene rubber affected the compatibility of silica in ENR/BR blend vulcanizates due to different polarity. However, all silica filled ENR/BR blend vulcanizates still showed above 91% filler dispersion, which still can be considered as an acceptable level of dispersion.

Table 5.4: Filler dispersion of ENR/BR-silica blend compounds

Parameter	ENR100:BR0	ENR90/BR10	ENR80/BR20	ENR70/BR30	NR70/BR30
Avg. Ag. Size, micron	12.0	12.4	12.4	12.4	9.4
Dispersion, %	96.5	93.2	92.2	91.9	99.3

5.1.5 Physical & Mechanical Properties

The physical and mechanical properties of ENR/BR blend compounds are shown in Figures 5.5 - 5.10. From these results, it is observed that silica filled ENR vulcanizates containing BR exhibit no consistent trend in hardness and modulus M100 properties with increase of BR content (Figures 5.5 and 5.6). However, the slightly higher hardness of the compounds with the highest amount of BR (ENR80:BR20 and ENR70:BR30) is in agreement with rheometer curves which showed an increase in maximum torque with increase in BR content.

It can be observed that silica filled ENR/BR vulcanizate heat build-up values are not significantly affected by the BR content in the ENR/BR blends. All the ENR/BR vulcanizates show a significantly lower heat build-up temperature than the

NR/BR benchmark compound, as shown in Figure 5.7. It is very important to maintain the current excellent heat build-up property of the silica filled ENR compound as its related with the tyre rolling resistance.

For the tensile strength of the ENR/BR vulcanizate, the results exhibit no consistent trend with increase of BR content (Figure 5.8) and all tensile strength values are below the strength of the NR/BR compound. However, all the vulcanizates still showed tensile strength well within specification for the truck tyre compound.

There is a significant increase in DIN and Akron abrasion resistance indexes with increase of BR content as shown in Figures 5.9 and 5.10 respectively. It is interesting to note that the DIN abrasion resistance index of ENR80:BR20 and ENR70:BR30 blend vulcanizates are higher than that of the NR/BR benchmark compound. The Akron abrasion resistance index of the ENR70:BR30 blend vulcanizate shows a similar abrasion resistance index to the NR/BR vulcanizate. The positive effect of BR on abrasion resistance is a very valuable finding in the development of a new tyre tread compound. The results indicate that relatively small amounts of BR can be blended into the silica filled ENR compound to dramatically increase abrasion resistance while not significantly affecting other vulcanizate properties. The abrasion resistance of rubber has been related to segment flexibility which increases with an increase in the difference between the T_g and the test temperature. Therefore, due to butadiene rubber having a very low glass transition temperature, it has good vulcanizates abrasion resistance[4,5]. In addition, butadiene rubber also good in resistance to heat and thermal degradation. The only disadvantages of blending with BR are a potential slight decrease in processability due to increased the viscosity and the fact that the BR itself is not a renewable material.

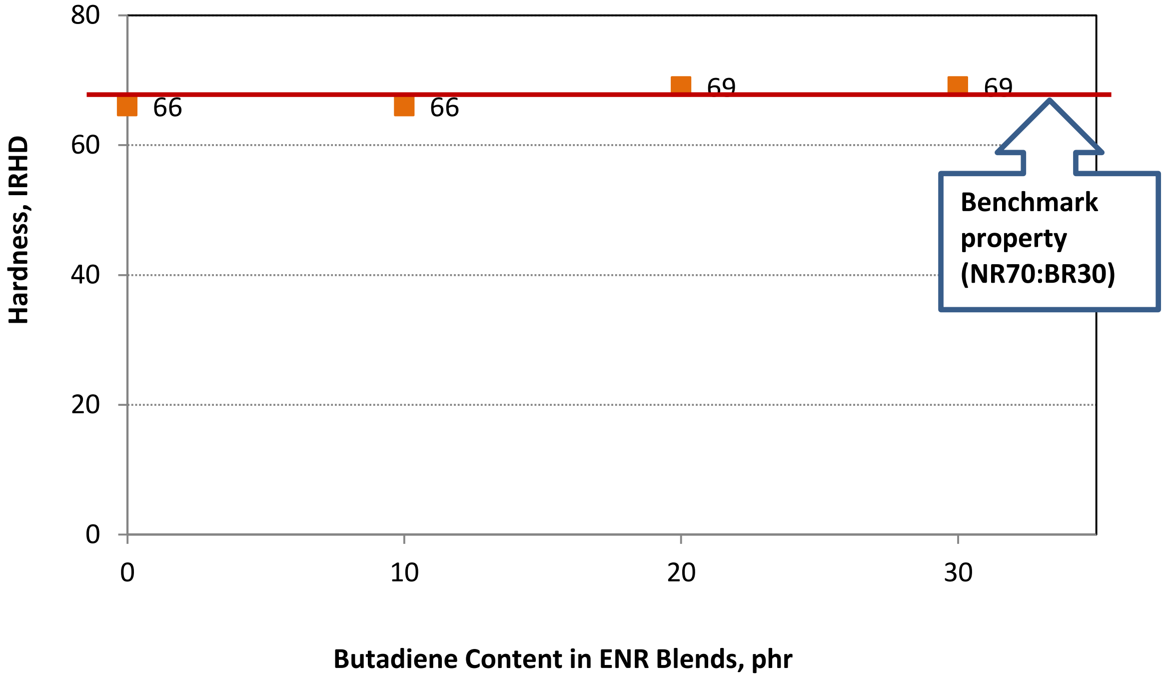

Figure 5.5: Effect of BR content on hardness of ENR/silica blends.

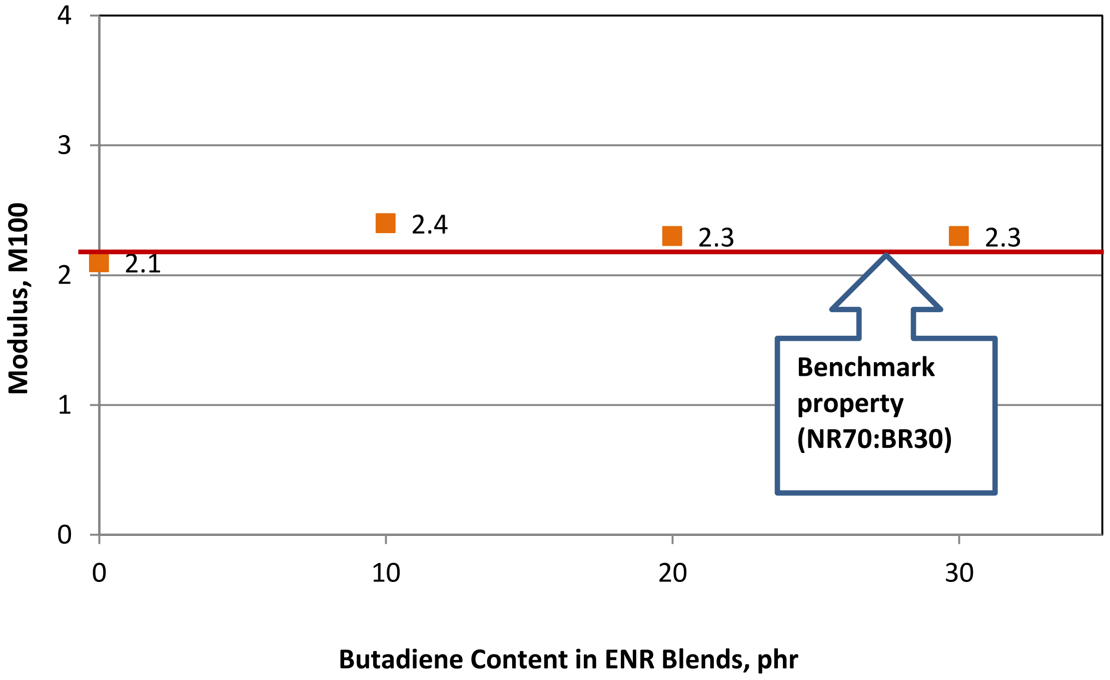

Figure 5.6: Effect of BR content on Modulus M100 of ENR/silica blends.

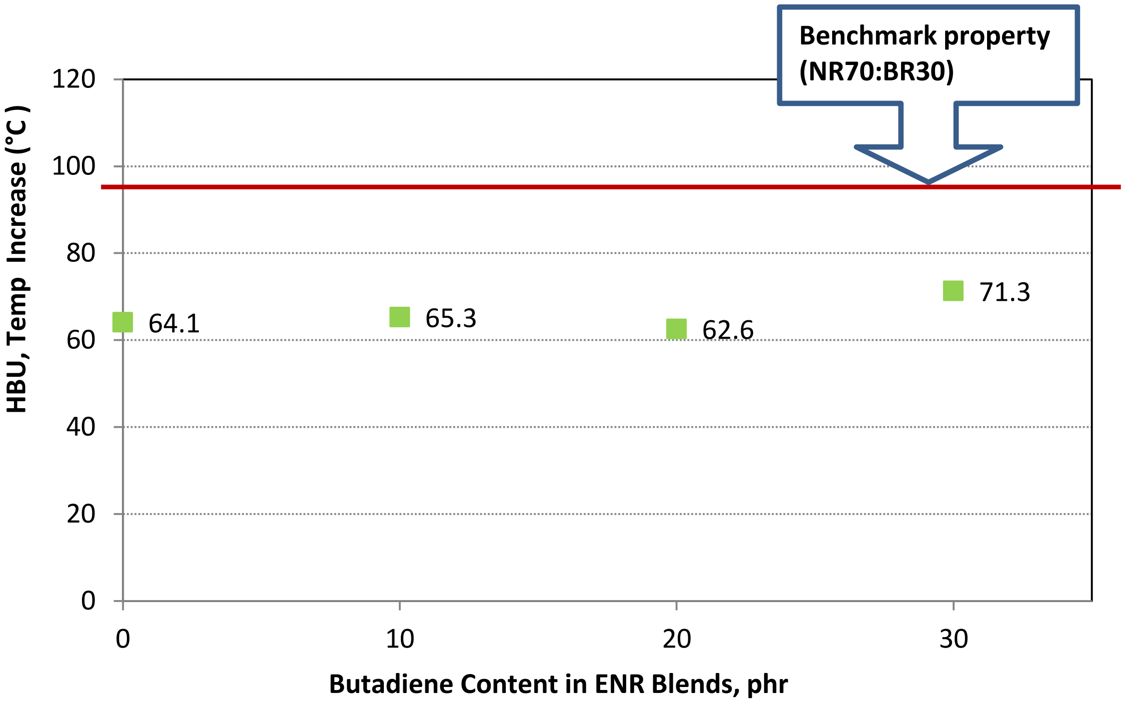

Figure 5.7: Effect of BR content on heat build-up of ENR/silica blends.

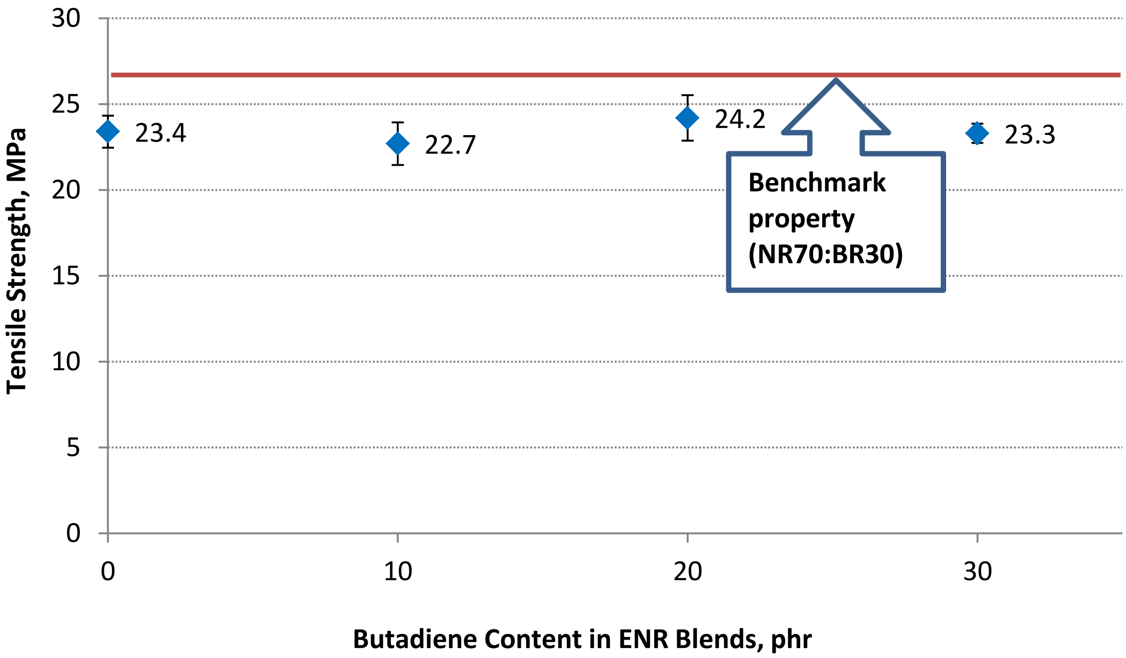

Figure 5.8: Effect of BR content on tensile strength of ENR/silica blends.

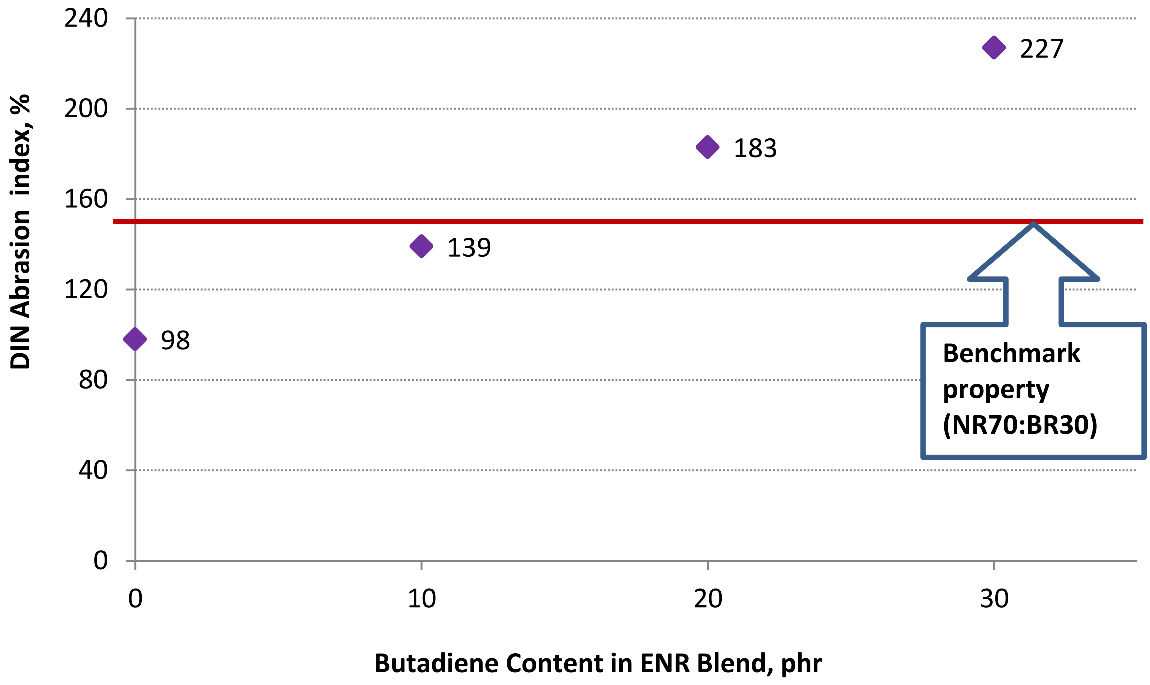

Figure 5.9: Effect of BR content on DIN abrasion resistance index of ENR/silica blends.

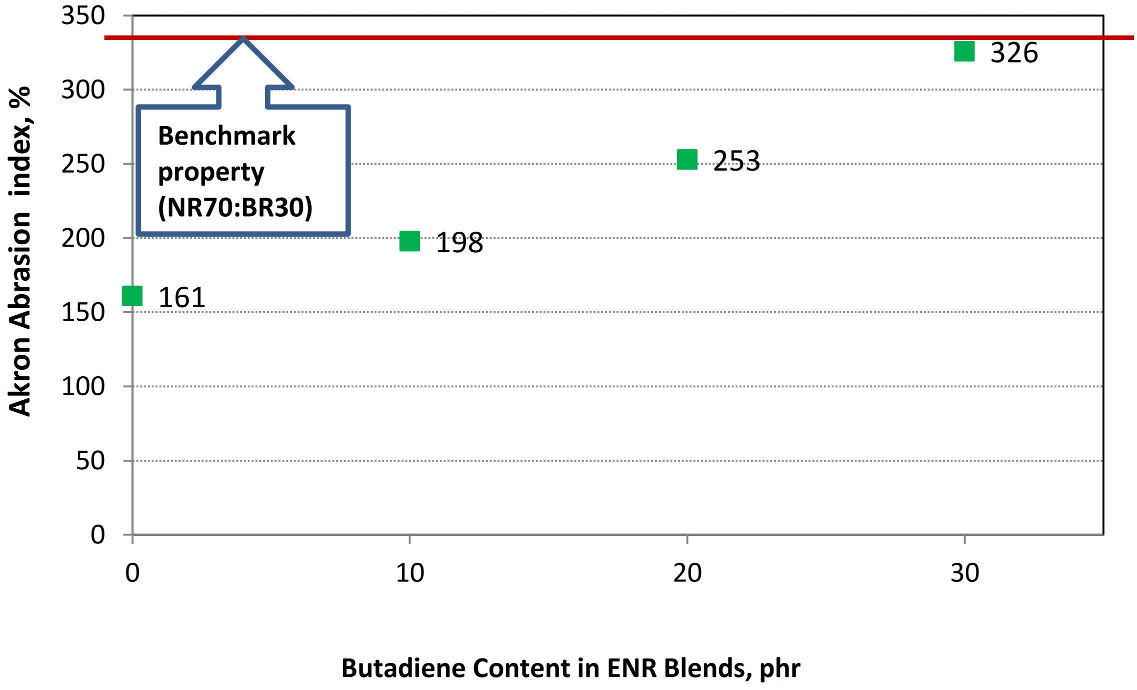

Figure 5.10: Effect of BR content on Akron abrasion resistance index of ENR/silica blends.

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CHAPTER 6

IMPROVING SUSTAINABILITY BY USING RECOVERED SILICA

6.1 Comparison of silica recovered from geothermal and pyrolysis sources with commercial grade silica

In this chapter, recovered silica fillers from pyrolysis and geothermal sources, referred to as ‘rSilica’ and ‘geoSilica’ respectively, have been mixed with epoxidized natural rubber (ENR) in order to determine whether they can be used to improve the sustainability of ‘green’ tyre tread compounds. Both recovered silicas have been characterised and the physical and mechanical properties of the filled ENR compounds measured. All the results obtained have been compared with the industrial silica grade of Zeosil 1165.

6.1.1 Particle size and surface area of the silicas

The silica recovered from both tyre pyrolysis and geothermal water sources were analysed by BET surface area measurement and transmission electron microscopy (TEM). All the results obtained are shown in Table 6.1 and Figure 6.1.

Specific surface area is one of the parameters that can influence the reinforcing effect of a filler because it determines how much contact area is available for interaction between the silica and rubber. The specific surface area is mainly determined by the dimensions of the ultimate silica particles (the smallest particles in the aggregates). A silica filler with small ultimate particles possesses a higher specific surface area than a silica filler with bigger primary particles[1]. The TEM images in Figure 6.1 show that Zeosil and rSilica have an ultimate particle diameter of about 20 nm. From the TEM images, it can be assumed that the pyrolysis process does not significantly affect the rSilica ultimate particle size. For geoSilica there are no small spherical particles, but the silica is in a thin film form. It is likely that this thin film form of geoSilica will have an effect on the mixing process and the compound reinforcement, mostly depending on how easily it can be dispersed in the ENR compound.

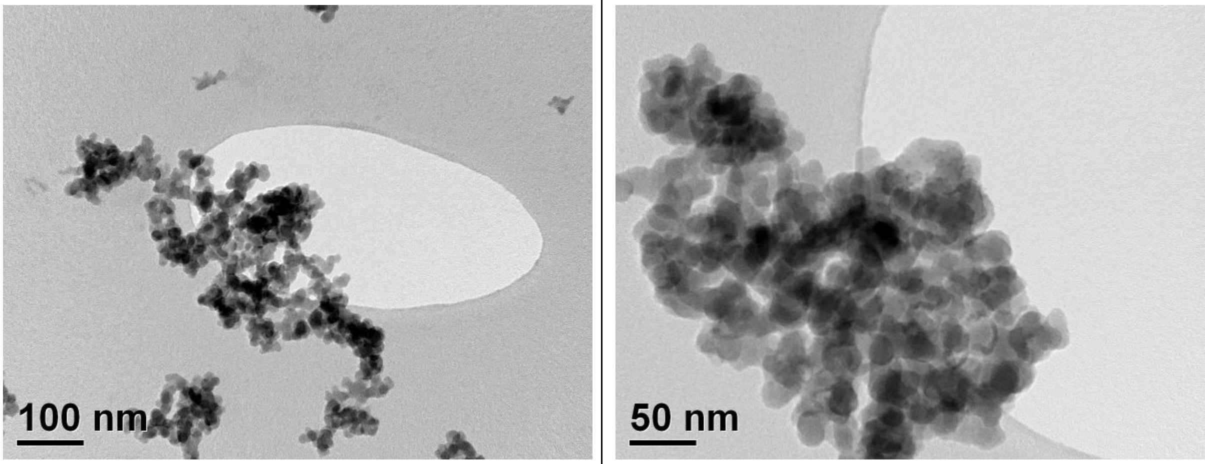
The surface area of fillers available for interaction with the rubber can also be determined by nitrogen gas adsorption using the BET method. However, this may not be accurate if the silica is microporous, because micropores are not available for interaction with the rubber. From these results, it is observed that geoSilica exhibits the highest BET specific surface area. This could be because it is in the form of a very thin film (Figure 6.1) but could also be due to its higher micropore volume as shown in the Table 6.1.

The high specific surface area with low micropore volume of Zeosil indicates a large available surface for interaction with the rubber, which explains its good reinforcing effect on rubber. The two batches of rSilica exhibit slightly lower specific surface area and micropore volume than Zeosil silica. This could be due to the variation of silica grades in the rSilica sources or could be because of the pyrolysis process. Since the rSilica specific surface area is only about 18% lower than Zeosil and has a similar morphology to Zeosil, it still has good potential for compound reinforcement.

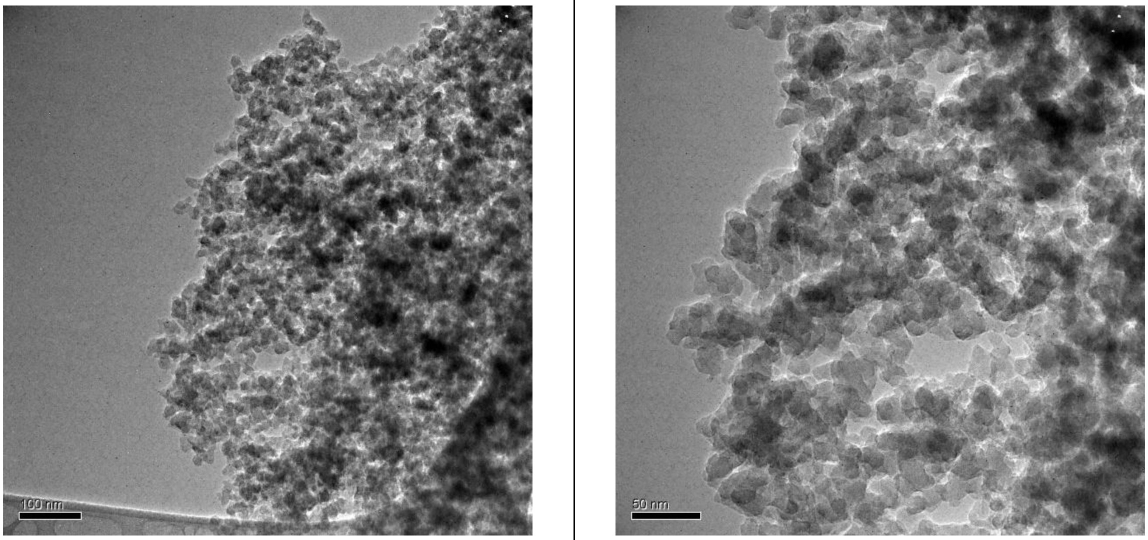
Table 6.1: Surface area and micropore volume of recovered silica fillers (geothermal and pyrolysis) and Zeosil silica.

Parameter	**geoSilica** (Geothermal)	**rSilica 1** (Pyrolysis)	**rSilica 2** (Pyrolysis)	**Zeosil 1165** (Industrial)
BET Surface Area, m^2/g	177	116	113	138
Micropore Volume, cm^3/g	0.0175	0.0042	0.0042	0.0068

rSilica | rSilica



Zeosil silica (scale bar = 100 nm) | Zeosil silica (scale bar = 50 nm)



geoSilica (scale bar = 100 nm) | geoSilica (scale bar = 50 nm)

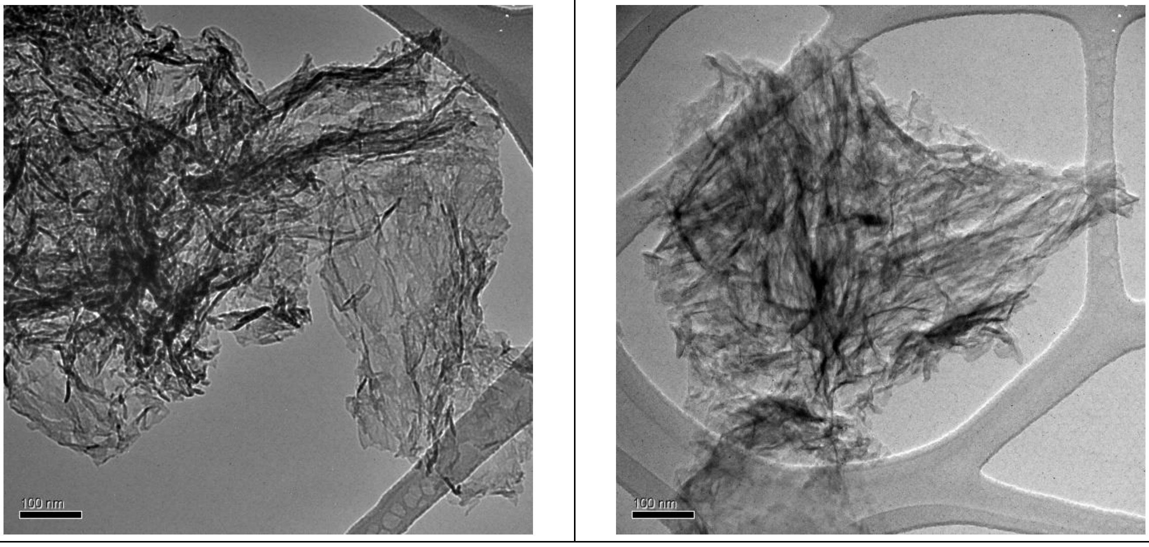


Figure 6.1: TEM images of recovered silica fillers (geothermal and pyrolysis) and Zeosil silica.

6.1.2 Surface chemistry of the silicas investigated by thermogravimetric analysis (TGA)

The thermogravimetry (TGA) results, are shown in Figure 6.2. TGA was used to measure the amount and rate of change in the mass of silica samples as a function of temperature. All the silica samples were heated from room temperature to 800˚C. It is assumed that the weight loss is due to water, because there should be nothing else volatile or chemically unstable in the samples. From the TGA curves shown in Figure 6.2, the first steep decrease in all curves is attributed to the loss of physically absorbed water from all the silicas at temperatures of 100 - 120˚C as reported by Zhuralvlev[2]. This is followed by a broad region of weight loss (shallow decrease) which may be due to a dehydroxylation process (loss of silanol groups from the silica surface as water). Two adjacent silanol groups can react with each other to form siloxane and water during heating at a high temperature as shown in Figure 6.3[2]. For geoSilica the TGA curve showed a steep decrease again at temperatures of 550 - 700˚C which could be due to further dehydroxylation of more stable silanol groups present in geoSilica, but not the other silicas. The more stable silanol groups in the geoSilica surface that react at this very high temperature range could be free isolated silanol group and germinal silanol group types[2].

The lowest weight loss was for rSilica, which could be due to the silica already having undergone a pyrolysis process during recovery, which may have resulted in dihydroxylation and so less silanol groups being left on the silica surface than in the original silica. Under normal temperature and humidity conditions, water can absorb through hydrogen bonding to silanol groups at the silica surface (see Figure 6.4). So, with less silanol groups on the silica surface, less water will be absorbed. From the TGA curves, it can be observed that the rSilica and Zeosil lose all the physically absorbed water at temperatures around 100-120˚C while the geoSilica continues to lose water to a higher temperature. According to Okkerse[3] all physically absorbed water is possible to be removed at 120˚C only if the silica sample is free of micropores. When silica contains micropores, the absorbed water can be retained in the micropores at temperature up to 180˚C. Therefore, the TGA curve of geoSilica obtained here suggests that this silica contains a high micropore volume, as indicated also by the surface area results (Table 6.1).

Based on the silica structure and surface chemistry results above, it can be concluded that the reinforcing capability of all these silicas is likely to be influenced by the differences in ultimate primary particle size, BET surface area, micropore volume and amount of silanol groups on the silica surface. The rSilica showed lower BET surface area than Zeosil, but it may have a potential of similar reinforcement with Zeosil as rSilica has similar ultimate particle size and lower micropore volume than Zeosil. However, in term of surface chemistry, rSilica has less silanol groups than Zeosil as shown in TGA curves which also can influence the reinforcing effect of silica in rubber, especially in the presence of silane coupling agent. This is because the silanol groups on silica surface will react with silane coupling agent during mixing and hence improve the rubber-filler interaction[4]. While geoSilica did show a higher BET surface area than rSilica and Zeosil, this could be due to geoSilica being in the form of a very thin film and also its higher micropore volume. If the higher BET surface area of geoSilica is due to the micropore volume, it is expected that geoSilica may have a less reinforcing effect in rubber than rSilica and Zeosil.

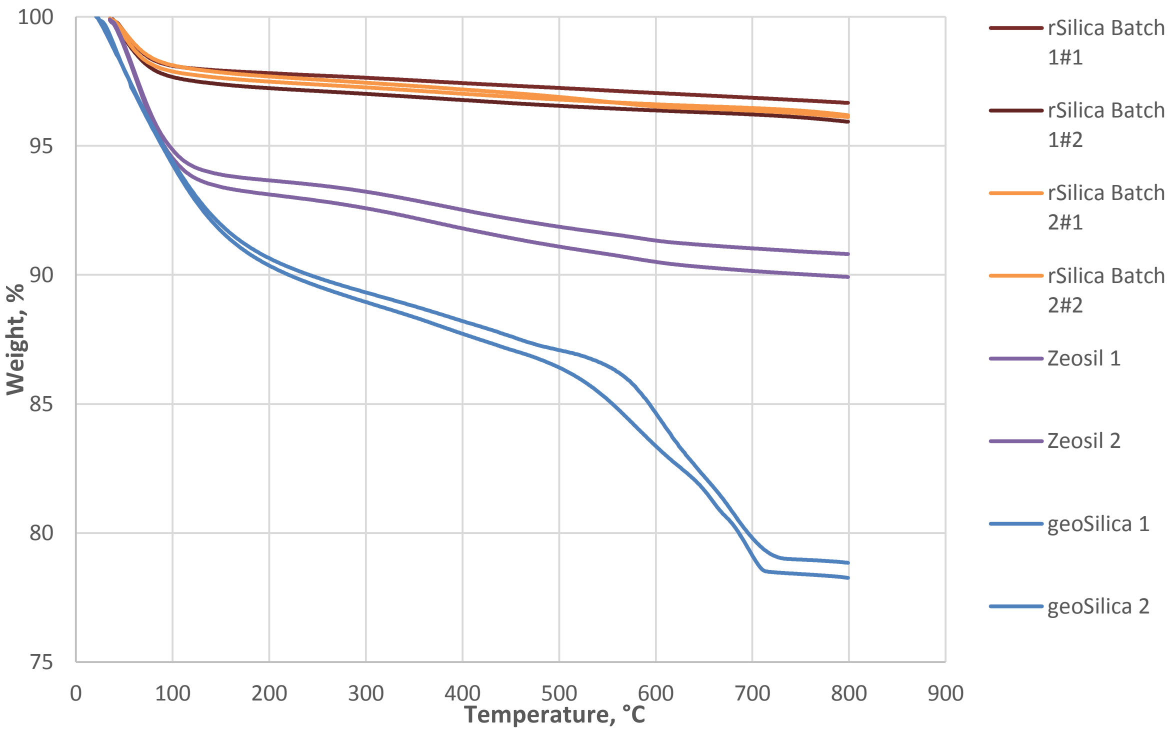


Figure 6.2: Thermogravimetry analysis (TGA) of recovered silica fillers (geothermal and pyrolysis) and Zeosil silica.

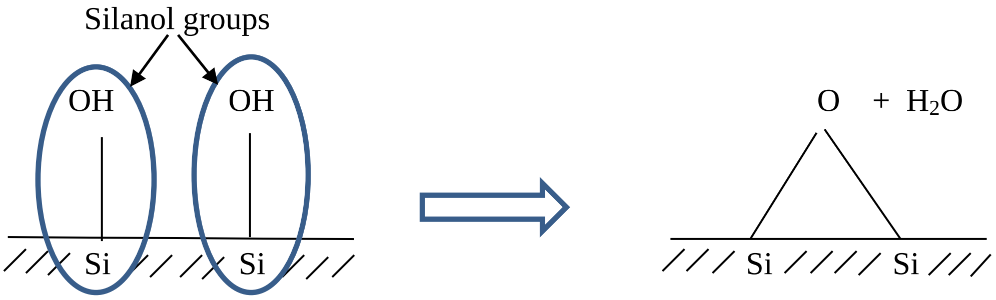


Figure 6.3: Two adjacent silanol group react with each other to form siloxane and water (dehydroxylation of OH).

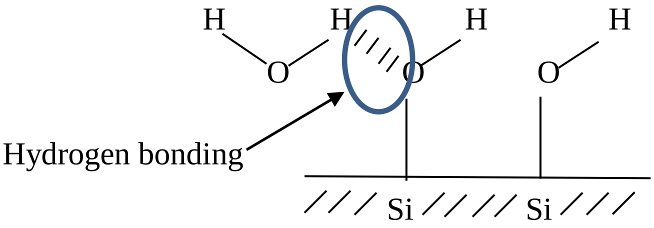


Figure 6.4: Water absorbed through hydrogen bonding to silanol groups at the silica surface.

6.1.3 Mixing Performance

Mixing performance evaluation was carried out based on the mixing data recorded by the Polylab OS Haake Rheomix 3000 mixer. The values of torque, mixing energy and temperature as they changed with time were used to analyse the mixing performance of the masterbach and compound. The final mixing energy and dump temperature of rSilica, geoSilica and Zeosil silica filled ENR masterbatch during the first stage of mixing are shown in Table 6.2. The variation of torque with mixing time obtained from the first stage mixing process are presented in Figures 6.5 to 6.6 and are divided into compounds mixed without silane and with silane.

It is interesting to note that the rSilica filled ENR compounds exhibit a slightly lower final mixing energy compared to geoSilica and Zeosil silica filled ENR compounds either without or with silane. The torque curves show that rSilica exhibits the lowest torque curve, which is consistent with the lower final energy of mixing. This could be due to the smaller number of silanol groups on the rSilica surface, which results in less silica-silica interaction during mixing and therefore better dispersion or less agglomeration of the silica particles. The results suggest that the rSilica filler slightly improves the processability of the ENR compound compared to geoSilica and Zeosil silica. The higher mixing energy for the geoSilica is most likely due to the longer time required to incorporate the filler as it had a very "fluffy" form.

It is also observed that the ENR compounds filled with recovered silica and with silane coupling agent present have lower final mixing energy compared to compounds without silane as shown in Table 6.2. The lower final mixing energy is likely to be due to the silane coupling agent helping to reduce silica-silica interaction through the reaction of silane with silanol groups on silica surface during mixing[5]. The fact that the silane is more effective in the rSilica than the Zeosil compound may be because there are fewer silanol groups on the rSilica surface and so after reacting with silane the surface is a lot less polar.

Table 6.2: Mixing energy and dump temperatures of rSilica, geoSilica and Zeosil silica filled ENR masterbatch compounds

Mixing properties	rSilica	geoSilica	Zeosil	rSilica+X50S	geoSilica+X50S	Zeosil+X50S
Final Mixing Energy, KJ	442.9	513.8	473.1	396.3	442	468
Dump Temperature, ˚C	140	157	148	142.5	157.8	144.7

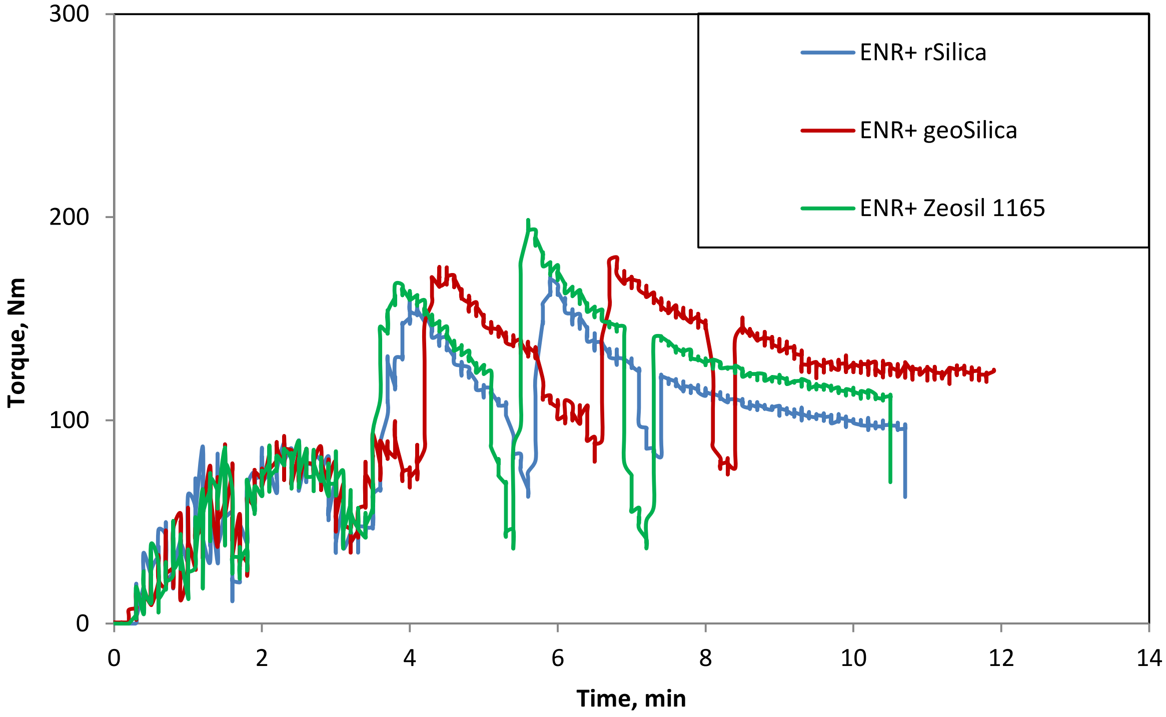


Figure 6.5: Torques curves of rSilica, geoSilica and Zeosil silica filled ENR masterbatch compounds without silane coupling agent.

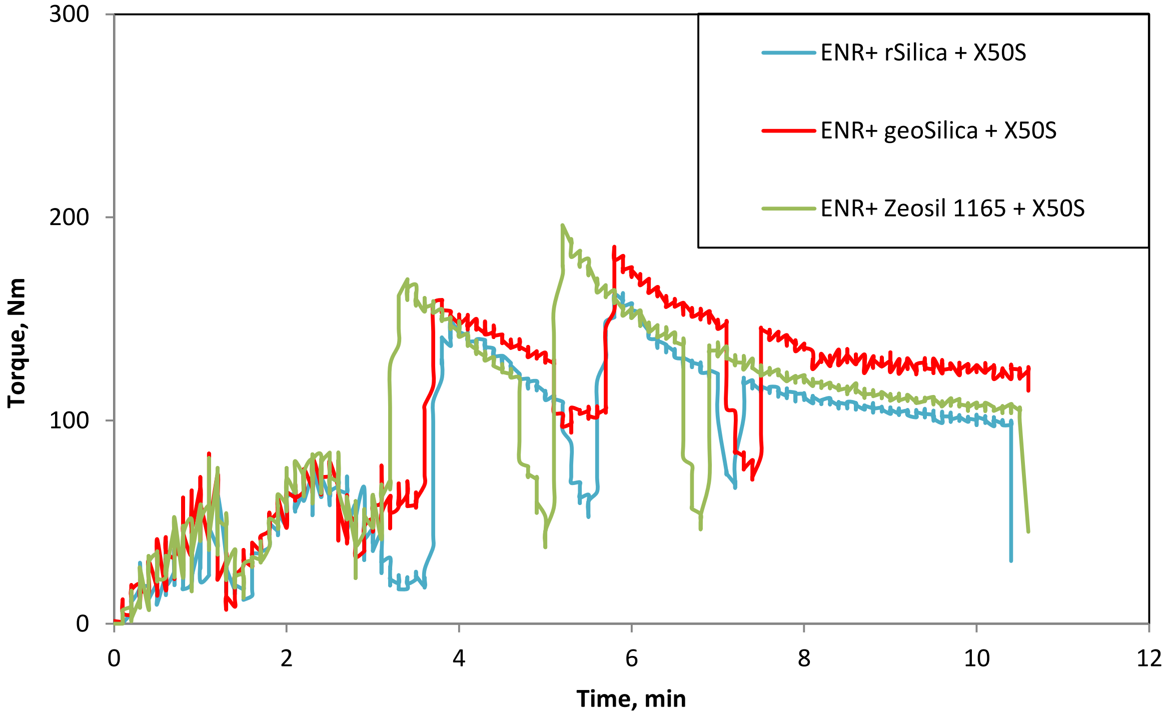


Figure 6.6: Torques curves of rSilica, geoSilica and Zeosil silica filled ENR masterbatch compounds with silane coupling agent.

6.1.4 Mooney viscosity

The Mooney viscosity of masterbatches and compounds of rSilica, geoSilica and Zeosil silica filled ENR compounds with and without silane coupling agent are shown in Table 6.3. For the masterbatch, remilling and final compound, the rSilica filled ENR compounds exhibit significantly lower Mooney viscosities than the Zeosil silica filled ENR compounds for both compounds without and with silane coupling agent. The viscosity result is consistent with the mixing energy and torque values as discussed above, supporting the idea that the lower silanol content of the rSilica results in less silica-silica interaction. GeoSilica filled ENR compounds exhibit significantly higher Mooney viscosities than the Zeosil silica filled ENR compounds for both compounds without and with silane coupling agent, which is also in agreement with the mixing torque value results above. This could be due to poor dispersion of geoSilica filler caused by higher silica-silica interaction in this compound, due to their higher surface silanol content. It was also observed that the geoSilica was very fluffy and took a longer time to incorporate during mixing, which could also lead to a lower dispersion.

It was found that addition of silane coupling agent in Zeosil silica filled ENR compound resulted in a slight decrease in the Mooney viscosities of masterbatch, remilling and final stage mixes as discussed earlier in Chapter 4. It was concluded that reaction of the silane with the silica reduced viscosity by reducing the silica-silica interaction. However, the opposite trend was observed for rSilica filled ENR compounds as the addition of silane increased the Mooney viscosities of masterbatch, remilling and final stage mixes. It is possible that, with the lower silanol concentrations on the silica surface, the silane coupling agent not greatly reduced the silica-silica interaction, but has increased the silica-elastomer interaction, resulting in an increase in viscosity. For the geoSilica filled ENR compound, the addition of silane results in no significant change in Mooney viscosity especially on the final compound viscosity. It is possible that there are so many silanol groups present on the silica surface that reaction with silane does not significantly reduce the number, so that the silica-silica interaction in not significantly reduced. Aternatively, the supplier of the geoSilica suggested that this could be due to the presence of calcium ions in geoSilica which may be expected to interfere with the silane coupling reaction. It is also possible that the silanol groups are not accessible to the silane, perhaps being in the microporosity. The morphology and surface chemistry of the geoSilica should to studied further if it is to be used as a replacement filler for commercial silica.

Table 6.3: Mooney viscosity of rSilica, geoSilica and Zeosil silica filled ENR compounds.

Mooney Viscosity	rSilica	geoSilica	Zeosil	rSilica+X50S	geoSilica+X50S	Zeosil+X50S
Masterbatch viscosity	113	178	159	124	181	150
Remilling viscosity	94	141	124	111	148	119
Final Compound viscosity	65	100	93	69	100	81

6.1.5 Cure Characteristics

The cure curves and cure characteristics of rSilica, geoSilica and Zeosil silica filled ENR compounds with and without silane coupling agent are presented in Table 6.4 and Figure 6.7. However, the presence of silane results in a significant reduction in minimum torque for the Zeosil silica filled ENR compound. These results are consistent with the trend for Mooney viscosity and indicate that the silane has resulted in reduced filler-filler interactions[5], as discussed in Chapter 4. It is observed that the presence of silane does not significantly change the minimum torque of rSilica and geoSilica filled ENR compounds, which is in agreement with the Mooney viscosity results.

The rSilica and Zeosil fillers showed higher Δ torque values (M_H - M_L) in the presence of silane, showing the the silane coupling agent is effectively reacting with rSilica and Zeosil silicas surface and the rubber to increase crosslink density in both cured compounds. The Δ torque value (M_H - M_L) for geoSilica filled ENR compounds is almost identical between the compound with and without silane, which indicates that the silane is not effectively reacting with this geoSilica and this also explains the reversion curve is observed in both compounds. This could be due to the presence of calcium ions in geoSilica that are expected to interfere with the silane coupling reaction as discussed in the section above.

Table 6.4: Rheometer and curing characteristics of rSilica, geoSilica and Zeosil silica filled ENR compounds.

Mix	**M_L** (dNm)	**M_H** (dNm)	**ts2** (min:sec)	**t90** (min:sec)	**t95** (min:sec)	**M_H-M_L** (dNm)	**Torque at 30 min** (dNm)
rSilica	16.74	61.17	14:39	20:03	20:27	44.44	56.39
geoSilica	21.66	69.54	6:38	10:41	11:04	47.88	56.93
Zeosil	28.8	77.65	6:53	16:07	16:29	48.84	74.84
rSilica+X50S	18.20	70.89	11:07	17:40	20:43	52.69	70.89
geoSilica+X50S	22.29	69.38	6:29	10:42	11:04	47.09	57.14
Zeosil+X50S	23.08	75.35	7:55	14:40	15:23	52.27	75.28

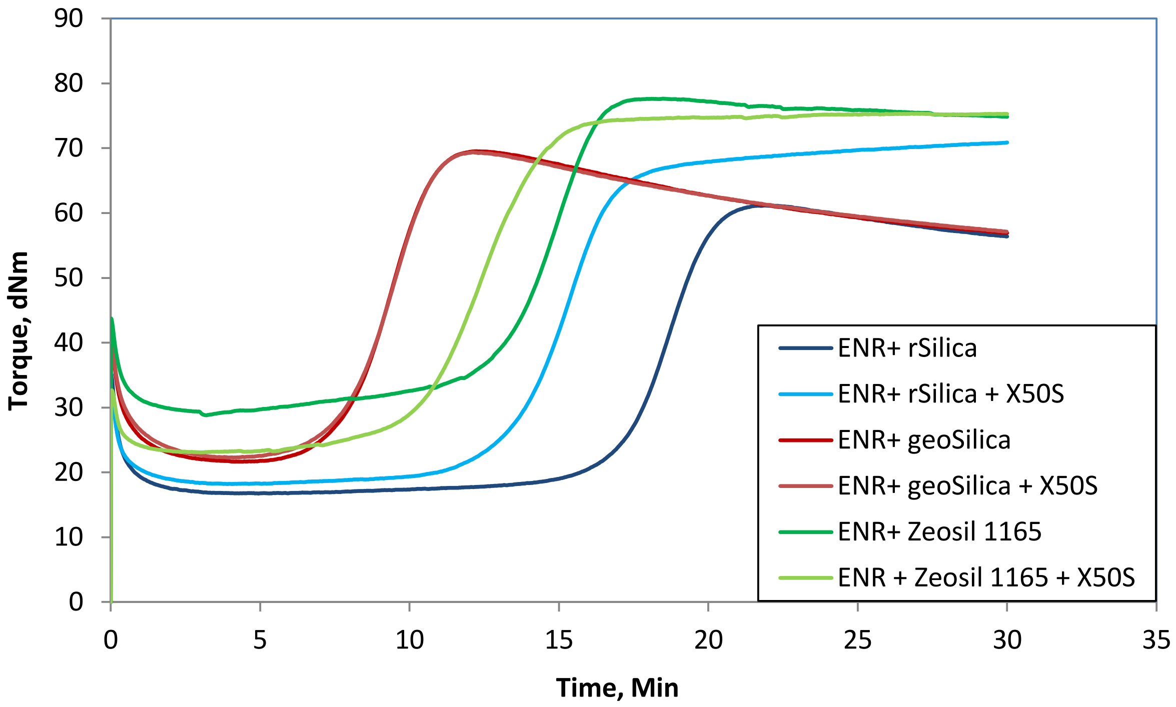


Figure 6.7: Rheometer curves of rSilica, geoSilica and Zeosil silica filled ENR compounds.

6.1.6 Filler Dispersion (Macrodispersion Analysis)

The results of a filler macrodispersion study of rSilica, geoSilica and Zeosil silica filled ENR vulcanizates with and without silane coupling agent are shown in Table 6.5. Overall, Zeosil silica has showed better filler dispersion than rSilica and geoSilica in ENR vulcanizates for compound without and with silane. It was found that the dispersion of rSilica, and Zeosil silica with the presence of silane do show a slight indication of an increase silica dispersion in ENR vulcanizates. Both rSilica and Zeosil silica vulcanizates with silane did show good filler dispersion, above 92%. This dispersion results, as in the previous chapters, indicate that differences in viscosity and stiffness of compounds with and without silane are not due to levels of filler dispersion but are due to differences in interaction between silica particles and/or between the silica and the rubber.

Table 6.5: Filler dispersion of rSilica, geoSilica and Zeosil silica filled ENR compounds (DisperGrader^{TM} 1000NT)

Parameter	rSilica	geoSilica	Zeosil	rSilica+X50S	geoSilica+X50S	Zeosil+X50S
Avg. Ag. Size, Micron	14.0	11.8	12.1	12.4	12.7	10.2
Dispersion, %	85±2.6	89±1.7	95±2.2	92±1.6	85±1.1	98±2.8

6.1.7 Physical & Mechanical Properties

The hardness and M100 modulus of rSilica, geoSilica and Zeosil silica filled ENR compounds with and without silane coupling agent are shown in Figure 6.8 and Figure 6.9 respectively. There is little difference in hardness and M100 between the different silicas and between the compounds with and without silane coupling agent.

Heat build-up property is the determination of the temperature rise and resistance to fatigue of vulcanized rubber. The heat build-up properties of rSilica, geoSilica and Zeosil silica filled ENR compounds with and without silane coupling agent are shown in Figure 6.10. The rSilica filled ENR vulcanizates with addition of silane exhibited good properties of heat build-up, similar to Zeosil with silane. The heat build-up of the rSilica vulcanizate without silane and geoSilica filled ENR vulcanizates with and without silane, could not be measured due to the test pieces breaking. The break or blown out of the test pieces could be due to very high internal heat generation when a constant strain amplitude was applied to the samples or could be due to weakness of the sample under these conditions. The geoSilica filled ENR vulcanizate in the presence of silane may be weak because there is no effective silane coupling reaction between reaction which results higher internal friction between silica and silica or silica and rubber together with a low crosslink density[6].

The tensile strength of rSilica, geoSilica and Zeosil silica filled ENR compounds with and without silane coupling agent are shown in Figure 6.11. For the non-silane vulcanizates, the geoSilica filler exhibited the lowest tensile strength, While, rSilica filler showed a similar tensile strength to Zeosil silica. It is observed also, there is a slight indication of an increase in tensile strength when silane coupling agent is added for rSilica and Zeosil silica filled ENR vulcanizates. The increase in tensile strength could be due to the increase in crosslink density resulting from the reaction of the silane coupling agent, as indicated by the Δ torque in the curemeter results[7].

Abrasion resistance properties of rSilica, geoSilica and Zeosil silica filled ENR compounds with and without silane coupling agent are shown in Figure 6.12 and Figure 6.13. For both abrasion resistance index results, it can be observed that geoSilica filler exhibited the lowest abrasion index result followed by rSilica and Zeosil without silane. There is a slight improvement in abrasion resistance index when silane coupling agent is added for rSilica and Zeosil silica filled ENR vulcanizates. However the opposite trend was observed for geoSilica when the silane compound exhibited slightly lower abrasion resistance index than non-silane compound. Improvement in the abrasion properties especially for Zeosil silica could be due to the better rubber-filler interaction and crosslink network in ENR/silica compounds with silane as discussed above.

Overall, from the results obtained above, it can be concluded that rSilica, which is silica recovered from pyrolysis of tyres, did show reasonably good physical properties such as tensile strength, hardness and abrasion resistance as well as good processing characteristics compared to the commercial grade silica (Zeosil). It can be said that rSilica filler may have potential to replace Zeosil silica in the ENR compound. rSilica filled ENR compounds with silane also showed better physical properties than the non-silane compound, which indicates that rSilica still can react with the silane, despite the fact that the amount of silanol groups on the rSilica surface were reduced by the pyrolysis process. However, for the geoSilica filler there is little reinforcement of the ENR compounds for both with and without silane. Further analysis and treatment on this geoSilica probably is needed in order to improve its reinforcing capability in rubber.

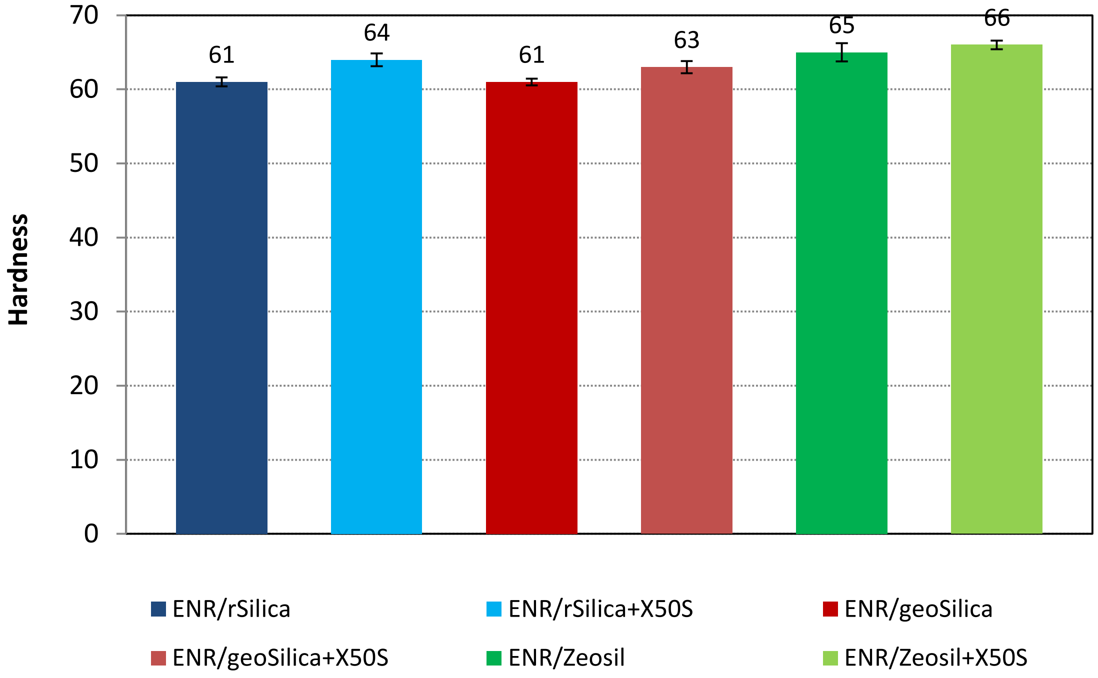


Figure 6.8: Hardness of rSilica, geoSilica and Zeosil silica filled ENR compounds.

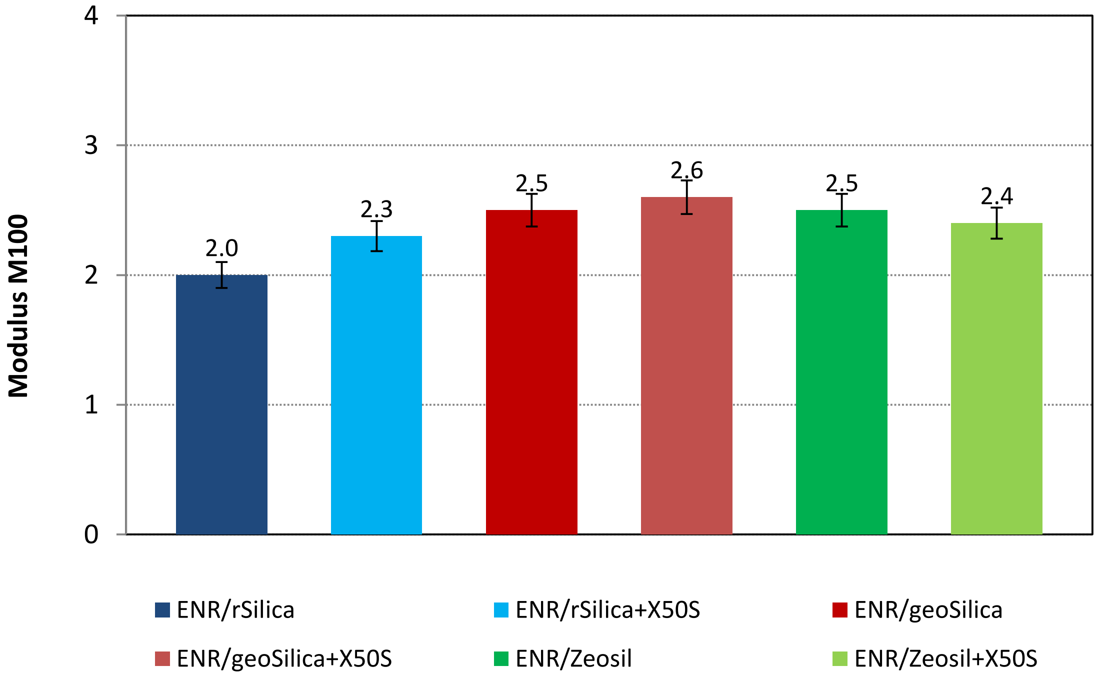


Figure 6.9: Modulus M100 of rSilica, geoSilica and Zeosil silica filled ENR compounds.

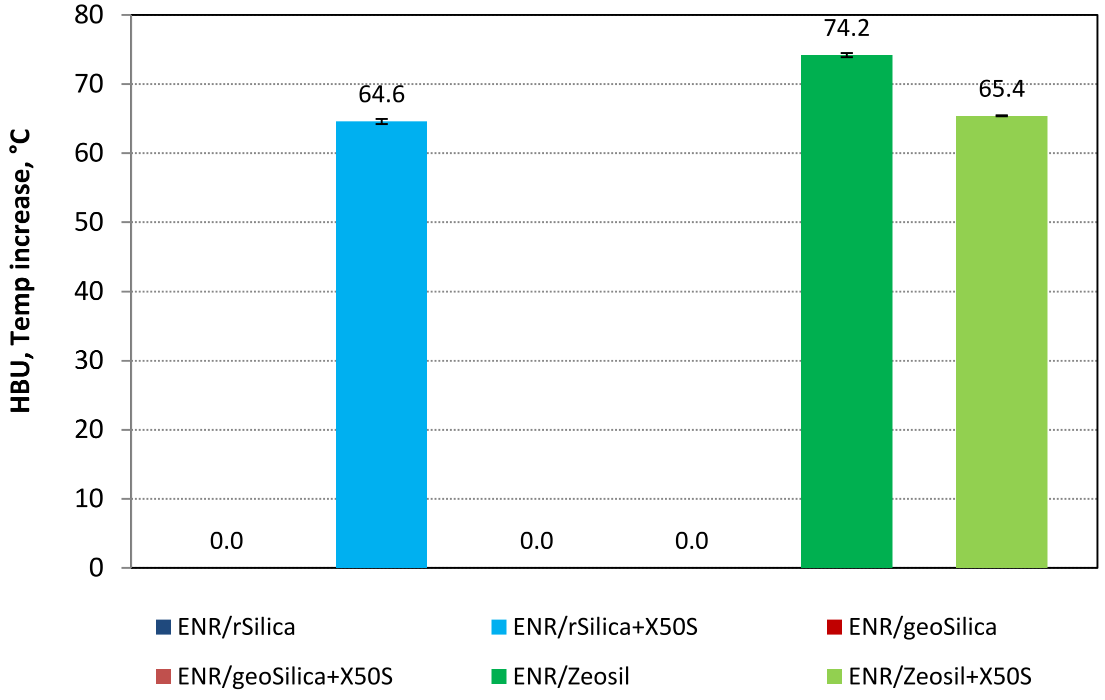


Figure 6.10: HBU (temperature increase) of rSilica, geoSilica and Zeosil silica filled ENR compounds.

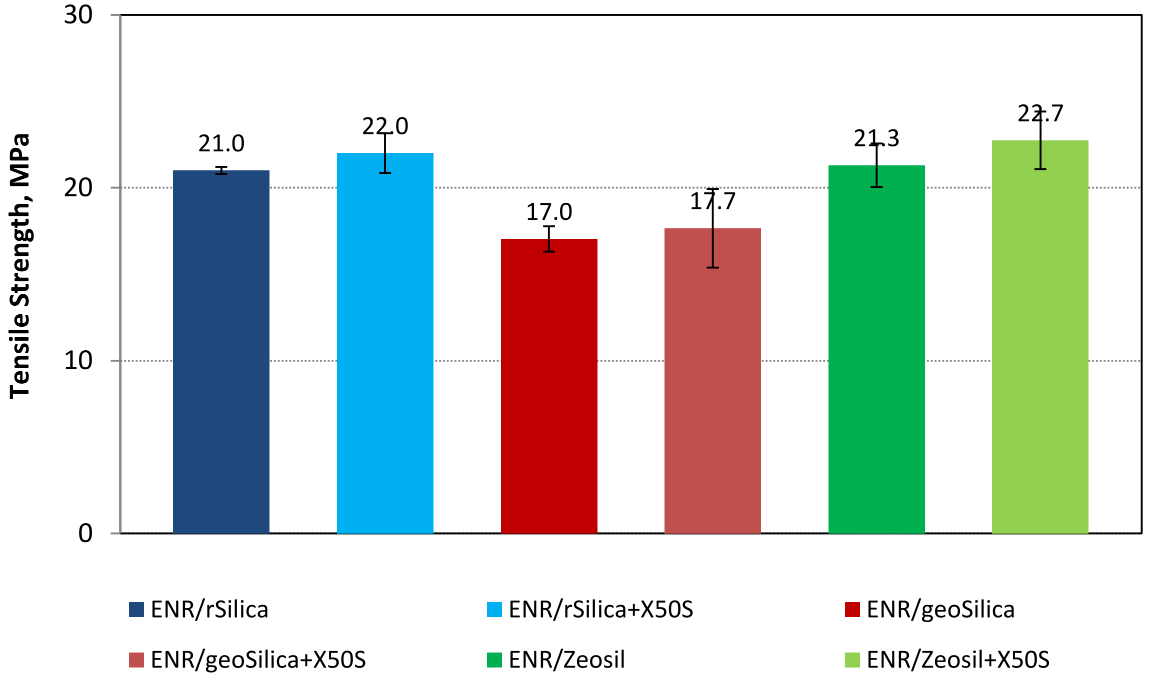


Figure 6.11: Tensile strength of rSilica, geoSilica and Zeosil silica filled ENR compounds.

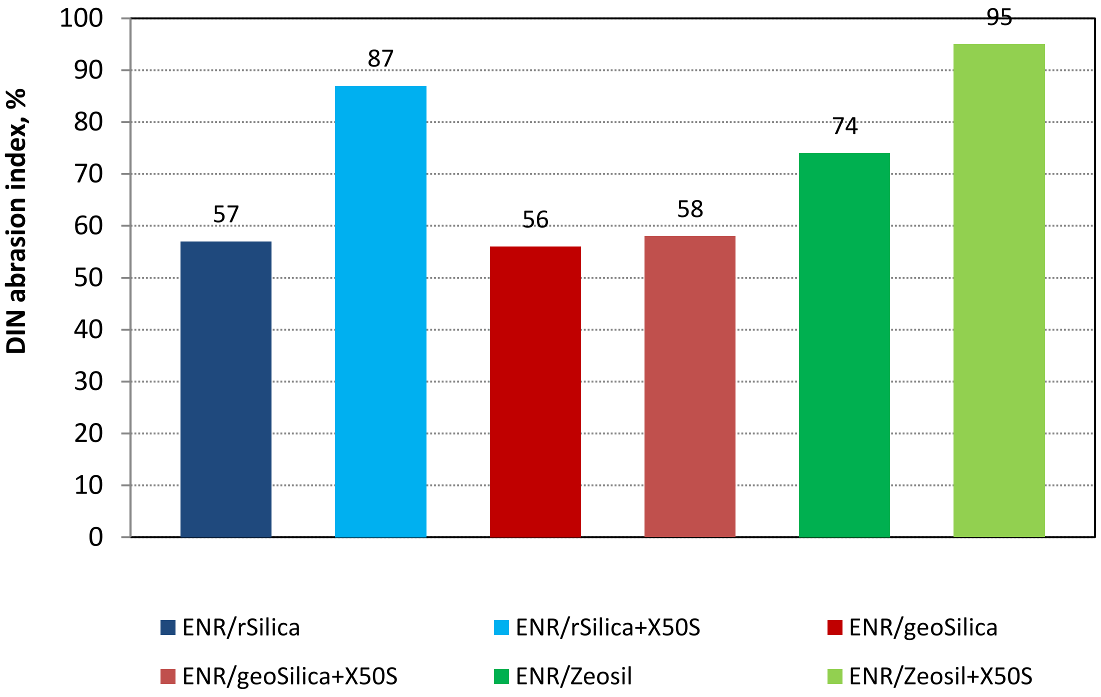


Figure 6.12: DIN abrasion resistance index of rSilica, geoSilica and Zeosil silica filled ENR compounds.

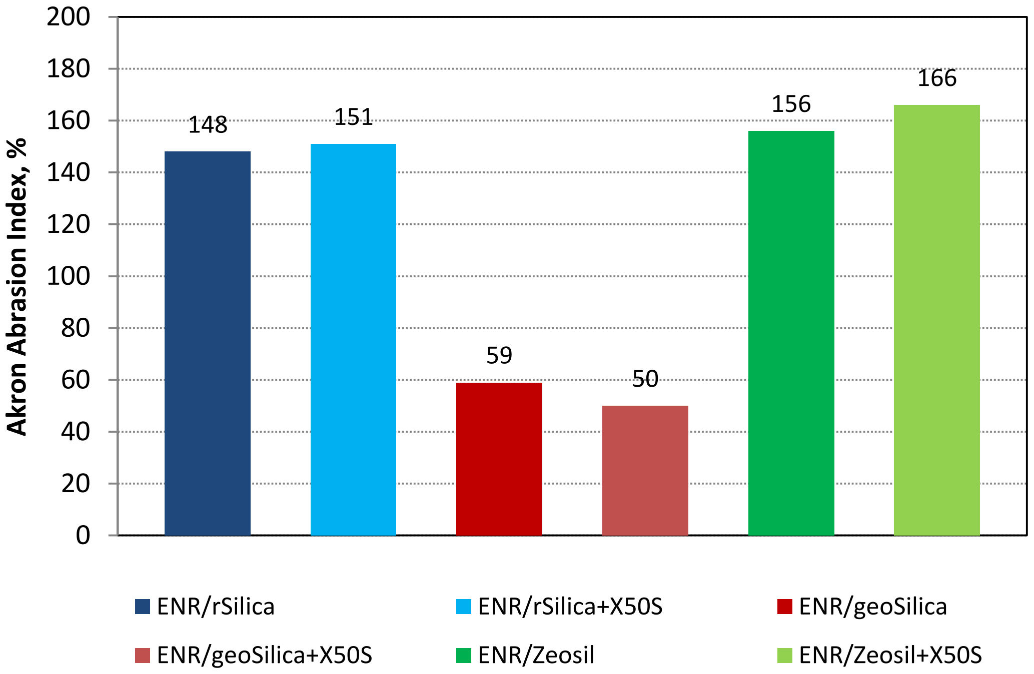


Figure 6.13: Akron abrasion resistance index of rSilica, geoSilica and Zeosil silica filled ENR compounds.

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CHAPTER 7

SCALE-UP OF EFFECT OF SILANE AND WATER ON PROCESSING

7.1 Effect of Water and Silane on Extrusion Performance and Shear Viscosity of Silica Filled ENR Masterbatches.

In this chapter, the effect of water and silane on the extrudability performance and rheological properties of silica filled ENR masterbatches at a range of strain rates is investigated. The reason why this study was carried out is to determine whether results and conclusions from the laboratory scale studies are in agreement with a larger mixing scale and also in actual rubber processing conditions, such as extrusion. The extrudability property is a very relevant property in tyre manufacturing because many of the tyre components pass through an extrusion stage for example tread liners, sidewall and inner liners. The evaluation of extrudability flow characteristics was carried out using a single screw extruder equipped with ASTM Extrusion Garvey die. A Rosand RH7 Flowmaster capillary rheometer was used to characterise the rheological properties.

7.1.1 Extrudability performance of ENR/silica

Rubber extrusion is a process used to create product of a fixed cross-sectional profile by passing it through a die of the desired cross-section. A tyre tread compound is extruded before being added to the tyre in the building process. The extrudability performance, in terms of power and die head pressure for silica filled ENR masterbatches with differing amounts of water and silane at two different screw speeds (20 rpm and 30 rpm) are shown in Tables 7.1-7.2 and Figures 7.1-7.2.

At 20 rpm screw speed, it can be observed that the power and die head melt pressure decrease with increasing water addition, as shown in Figure 7.1 and 7.2. This result clearly confirms that the addition of water to silica during the mixing process helps the processability and flow properties of the ENR/silica masterbatches, as suggested by the Mooney viscosity results in the chapter 4. The results also indicate that the addition of water may reduce the energy used during the extrusion process.

The power and die head pressure values either showed little effect or a slight increase with increase in X50S silane content, as shown in Figures 7.1 and 7.2. This result is surprising, since the addition of silane was shown to slightly reduce Mooney viscosity of a masterbatch compound (Chapter 4).

Table 7.1: Extrudability performance ENR/silica masterbatches at 20 rpm screw speed

ENR/Silica Mix	**Power** (W)	**Die Head Melt Pressure** (MPa)
0%water + 0phr X50S	1280	6.2
6%water + 0phr X50S	1120	4.8
10%water + 0phr X50S	937.5	4.5
0%water + 4phr X50S	1280	6.2
6%water + 4phr X50S	1120	6.2
10%water + 4phr X50S	1014	5.5
0%water + 8phr X50S	1240	6.9
6%water + 8phr X50S	1200	6.9
10%water + 8phr X50S	1027	5.5

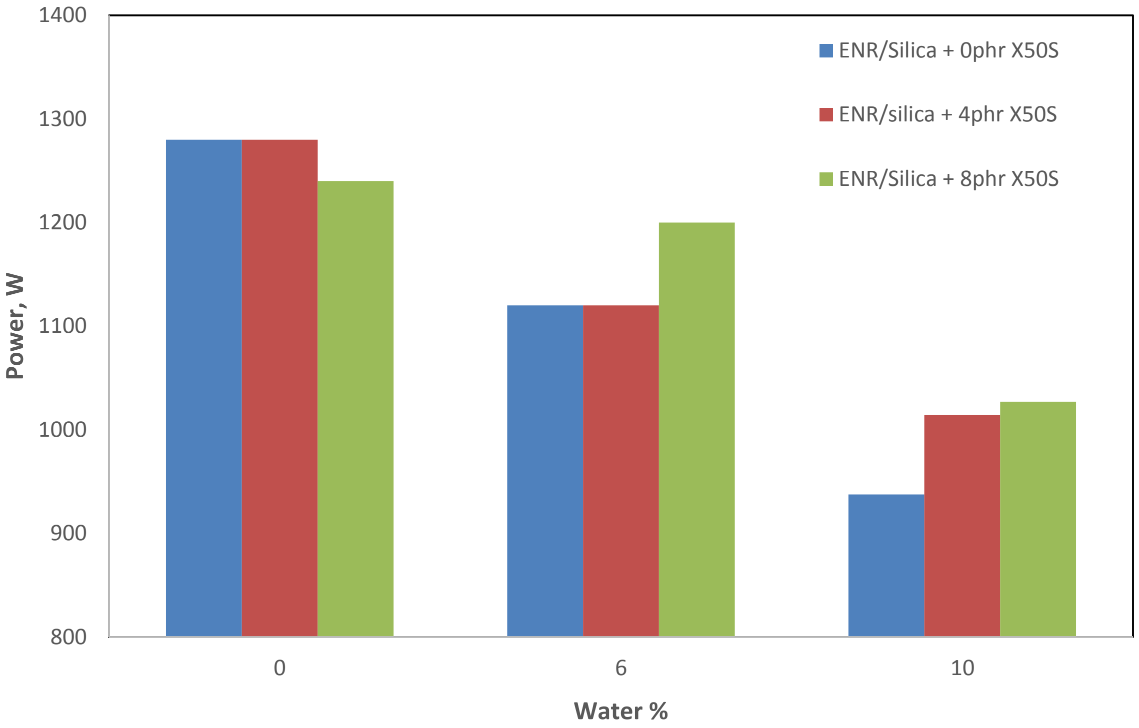

Figure 7.1: Power of ENR/silica masterbatches during extrusion at 20 rpm screw speed.

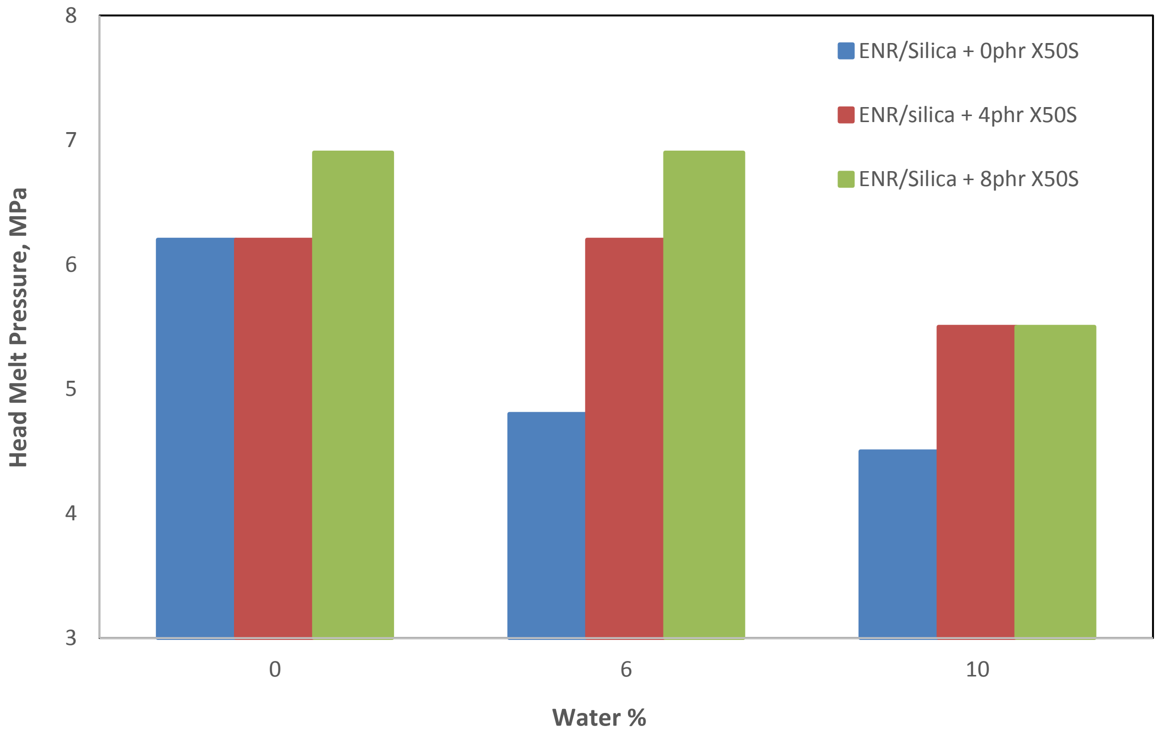

Figure 7.2: Die Head Melt Pressure of ENR/silica masterbatches during extrusion at 20 rpm screw speed.

At a 30 rpm screw speed (Figures 7.3 and 7.4), similar trends to those with a 20 rpm screw speed were observed, as power and die head melt pressure decreased with increase in added water. Again, increases of silane content, generally resulted in little change or in an increase in power and die head pressure.

Overall, ENR/silica masterbatches showed slightly better extrusion processability and flow properties for both screw speeds with addition of 6% and 10% water. The addition of X50S silane did not show an improvement in processability and flow properties of the masterbatches and may even have a negative effect on processability.

Table 7.2: Extrudability performance ENR/silica masterbatches at 30 rpm screw speed

Mix	**Power** (W)	**Head Melt Pressure** (MPa)
0%water + 0phr X50S	1870	6.2
6%water + 0phr X50S	1540	5.2
10%water + 0phr X50S	1458	5.2
0%water + 4phr X50S	1870	7.6
6%water + 4phr X50S	1760	5.5
10%water + 4phr X50S	1512	5.5
0%water + 8phr X50S	1760	7.6
6%water + 8phr X50S	1760	7.6
10%water + 8phr X50S	1512	6.2

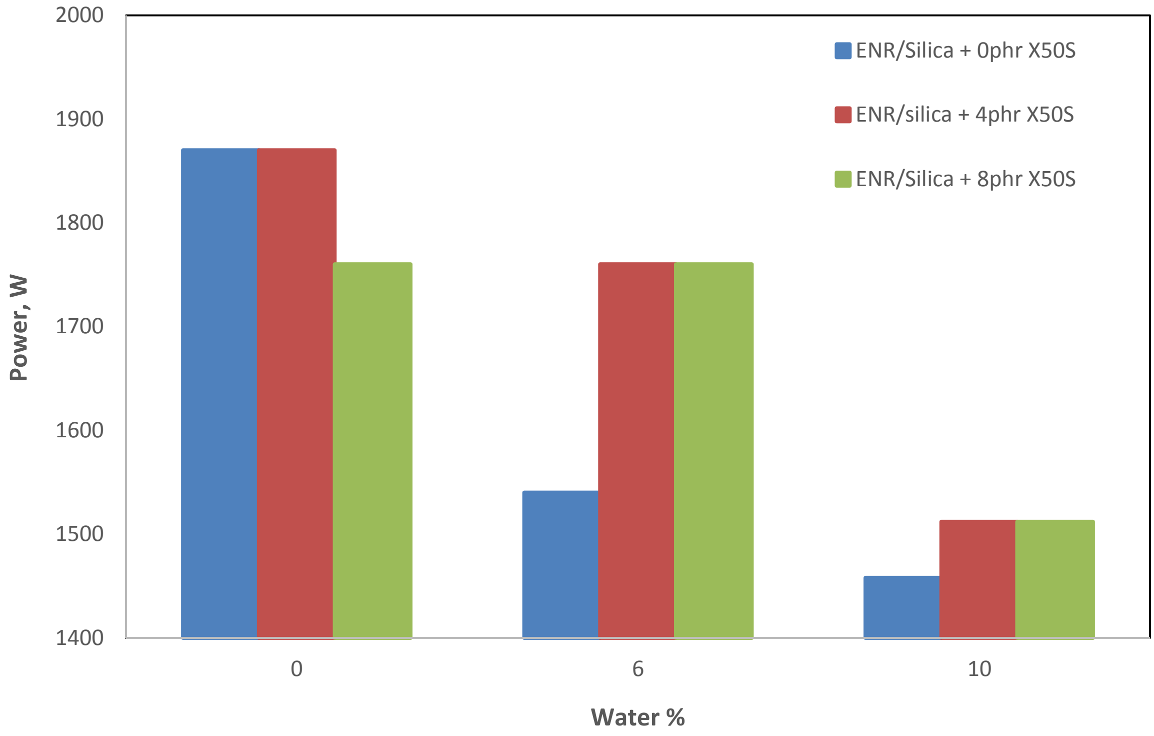

Figure 7.3: Power of ENR/silica masterbatches during extrusion at 30 rpm screw speed.

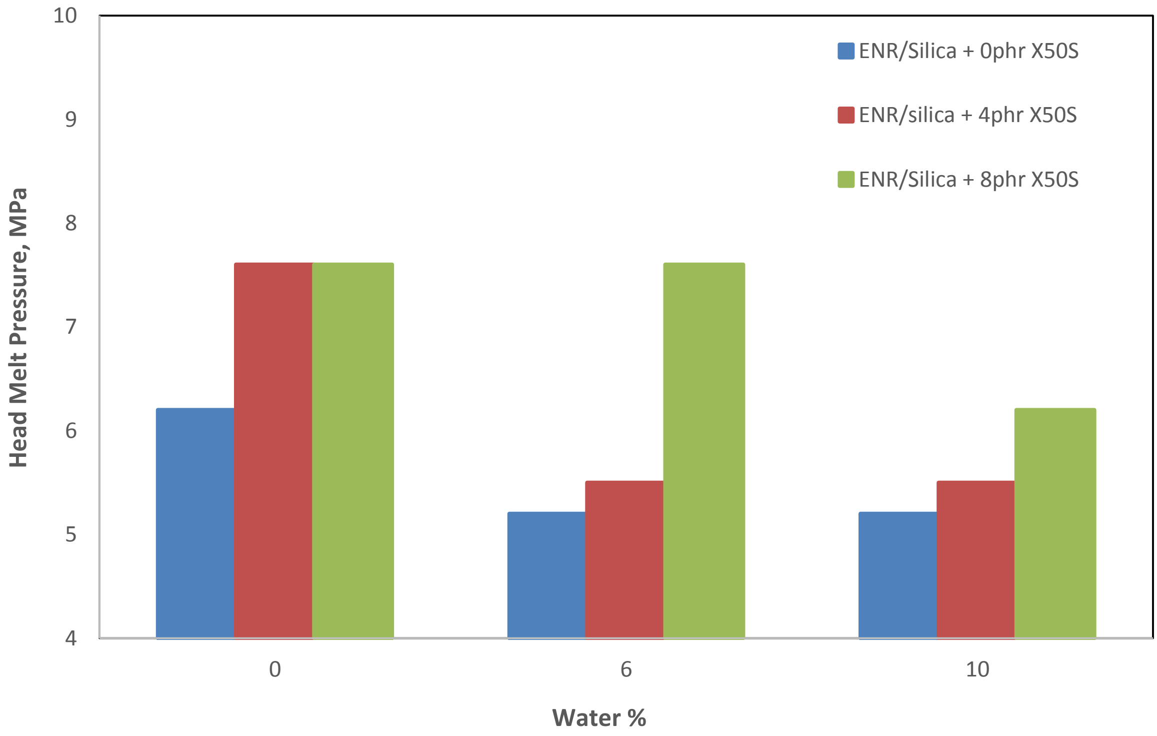

Figure 7.4: Die Head Melt Pressure of ENR/silica masterbatches during extrusion at 30 rpm screw speed.

7.1.2 Rheological properties of ENR/silica masterbatches over a range of shear rates.

Shear viscosity was measured using a Rosand RH7 Flowmaster capillary rheometer. The testing was conducted at different shear rates ranging from 10 to 10000s^{-1} shear rates to study the flow behaviour of rubbers when high shear rates and shear stress are applied such as in injection molding and extrusion processes. The shear viscosity curves of the nine ENR/silica masterbatches are presented in six figures for easier comparison (Figures 7.5-7.10). For better understanding, Figures 7.5-7.7 are showing the effect of X50S silane with specific water contents. Figures 7.8-7.10 are showing the effect of water addition with a specific amount of X50S silane. All the results show shear thinning or pseudoplastic behaviour, with viscosity decreasing as shear rate increases[1].

With no water added, as shown in Figure 7.5, it can be observed that the addition of 4 phr X50S silane does not significantly affect shear viscosity at low shear rates but reduces shear viscosity at high shear rates. This indicates that at very high shear rates, addition of X50S silane will improve processability and flow behaviour of the ENR/silica masterbatch. At 6% water, there is no clear trend or significant change of shear viscosity with increase of silane at low shear rates. However, at high shear rates, it can be observed that there is a slight indication of an increase of shear viscosity with increase of silane (Figure 7.6) which agrees with the power and die head pressure results as discussed earlier. The result suggests that the addition of silane interferes with the viscosity reducing effect of water. At 10% water addition there is no significant change of shear viscosity with silane content at any shear rate (Figure 7.7).

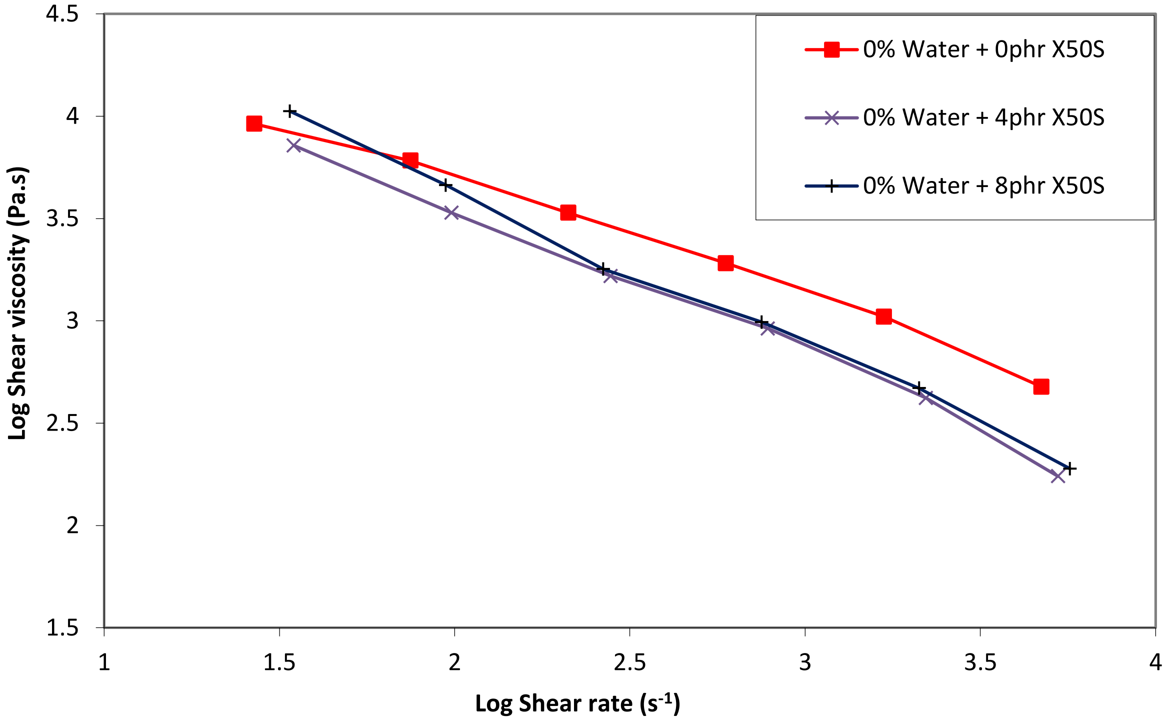

Figure 7.5: Shear viscosity curves of ENR 25/silica masterbatches: Effect of X50S silane with 0% water (on silica).

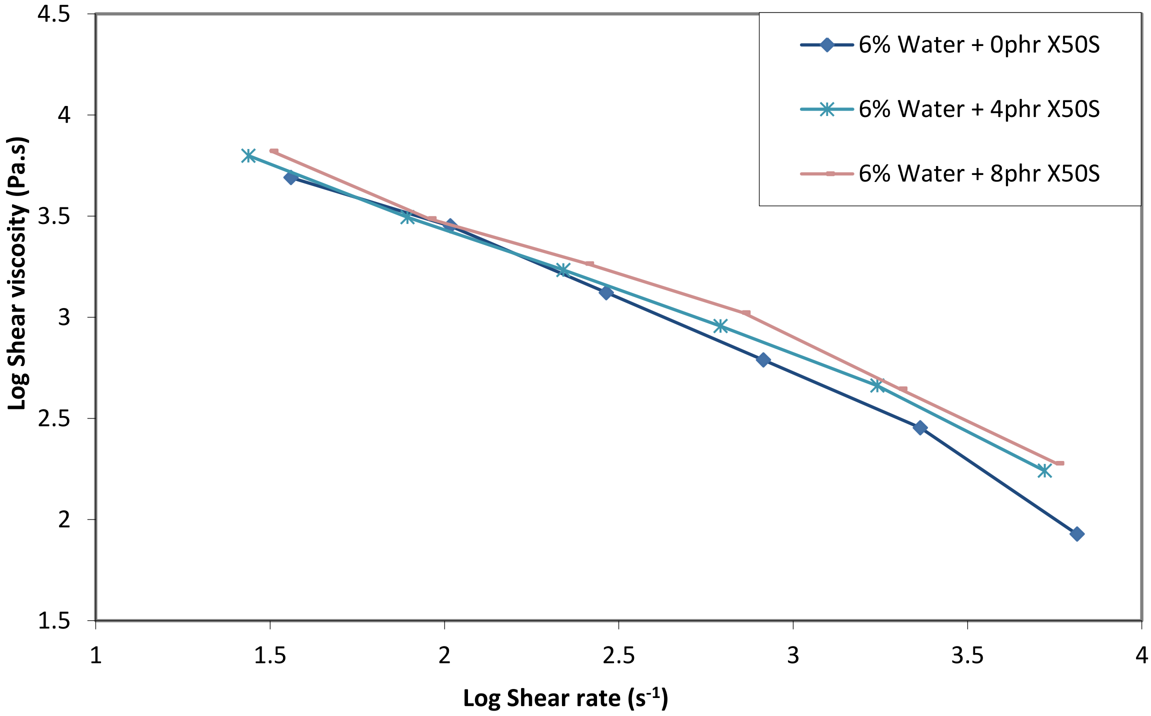

Figure 7.6: Shear viscosity curves of ENR 25/silica masterbatches: Effect of X50S silane with 6% water (on silica).

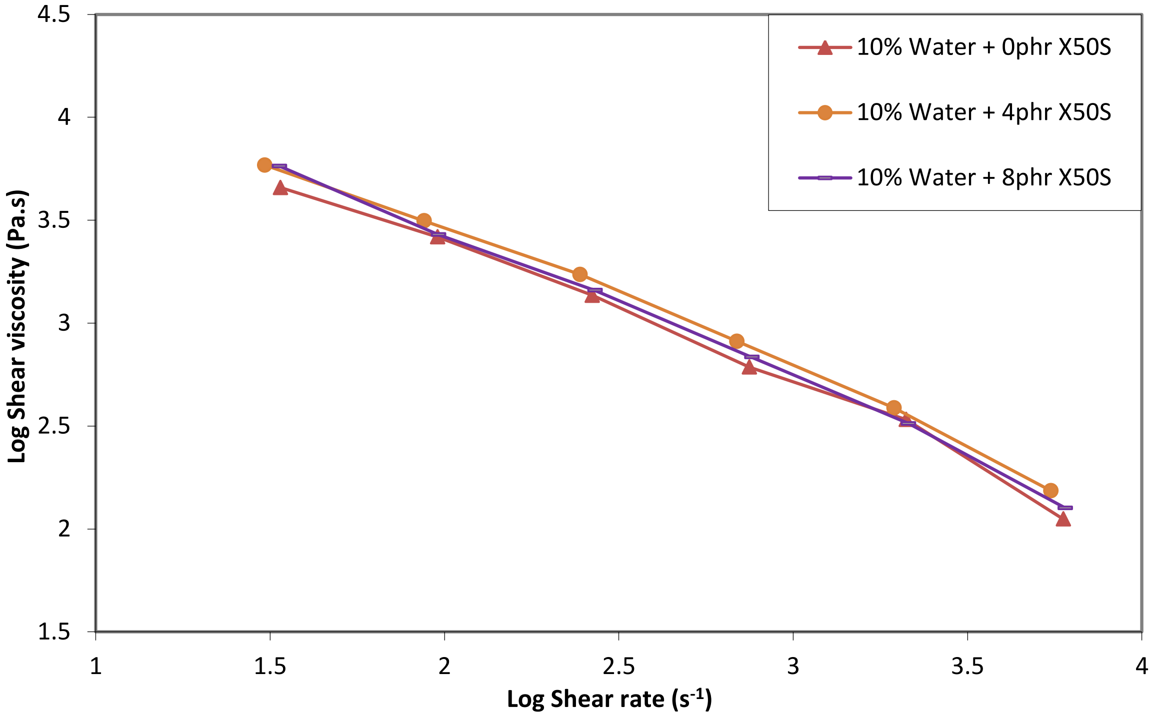

Figure 7.7: Shear viscosity curves of ENR 25/silica masterbatches: Effect of X50S silane with 10% water (on silica).

At 0phr X50S silane as shown in Figure 7.8, it can be observed that there is a significant decrease in shear viscosity with addition of 6% water across the whole shear rate range. Figure 7.8 also shows that both 6% and 10% water addition exhibit similar shear viscosity curves across the shear rate range. This indicates that addition of 6% water in the silica filler can improve the processability and flow behaviour of an ENR/silica masterbatch which also in general agrees with power and die head pressure results as discussed earlier. This result also suggests that at 6% water could be the optimum amount of water to be added as there is no further decrease of shear viscosity when more water is added. At 4phr X50S silane, there is only a slight indication of a decrease in shear viscosity with increase of water addition (Figure 7.9). This could be due to the effect of X50S silane which has already reduced the viscosity of the masterbatches and so water addition has less effect on viscosity. At 8phr X50S silane the addition of 6% water shows a decrease of shear viscosity only at low shear rates, while for 10% water addition, there is a significant decrease of shear viscosity across the whole shear rate range (Figure 7.10).

Overall, it can be deduced that both water and X50S silane addition can improve the processability and flow properties of ENR/silica masterbatches by reducing its shear viscosity and at the same time can give lower energy consumption, which in general agrees with the Mooney viscosity results in Chapter 4. This is because the lower the viscosity, the lower the flow resistance of the melt materials and consequently the lower the elastic strain related to flow within the die[2]. However, the results also suggest that there is an antagonistic effect of silane and water when both are added together in silica filled ENR masterbatches. It is also useful to know the different rheological behaviour in particular shear rate regimes (from low to high shear rates), as this will reflect behaviour in actual rubber processing (e.g. in an extruder or injection moulding machine) more accurately[3].

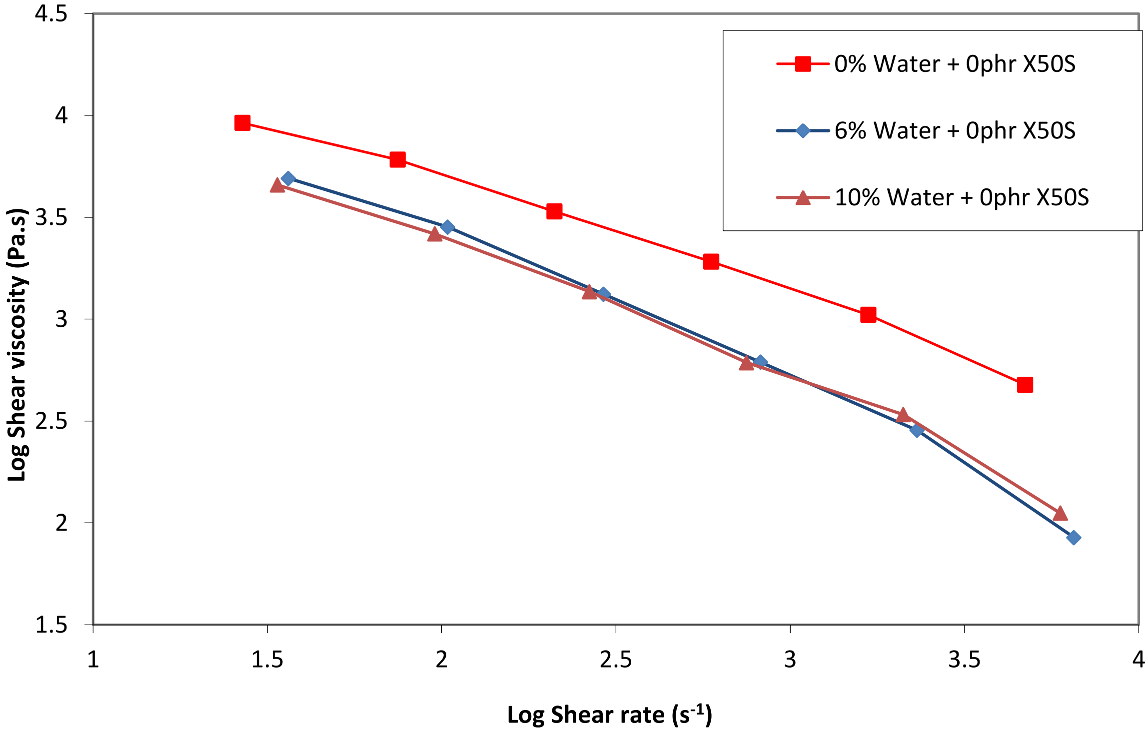

Figure 7.8: Shear viscosity curves of ENR 25/silica masterbatches: Effect of Water % (on silica) with 0phr X50S silane.

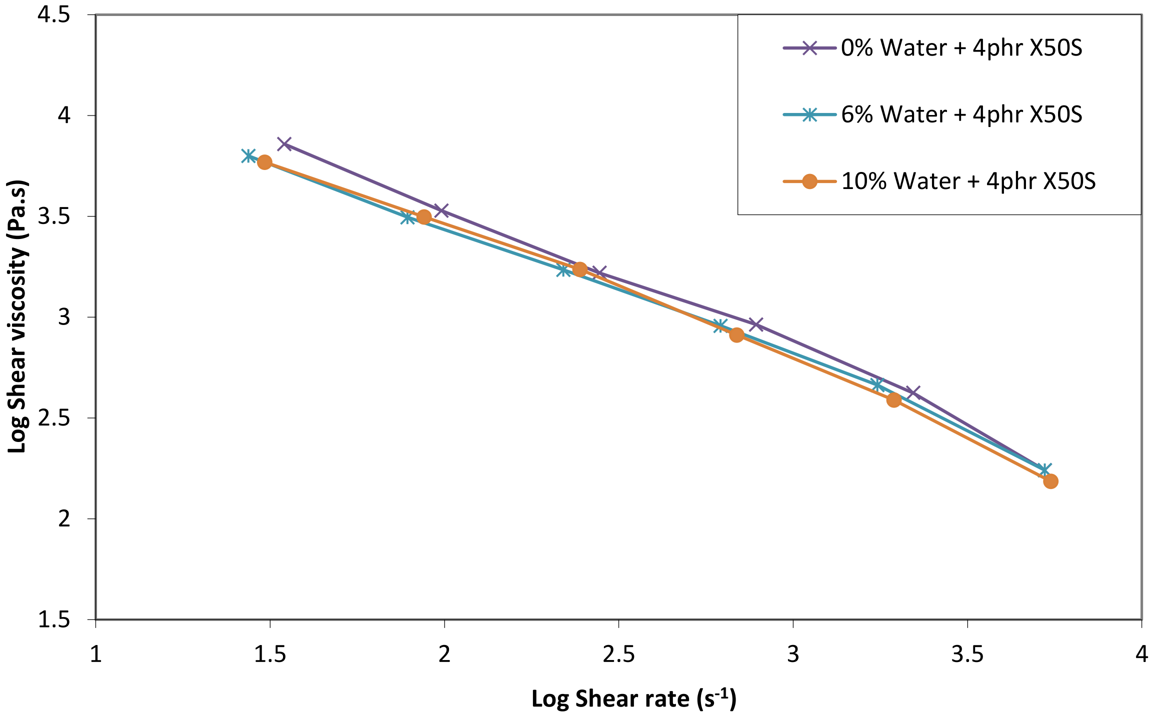

Figure 7.9: Shear viscosity curves of ENR 25/silica masterbatches: Effect of Water % (on silica) with 4phr X50S silane.

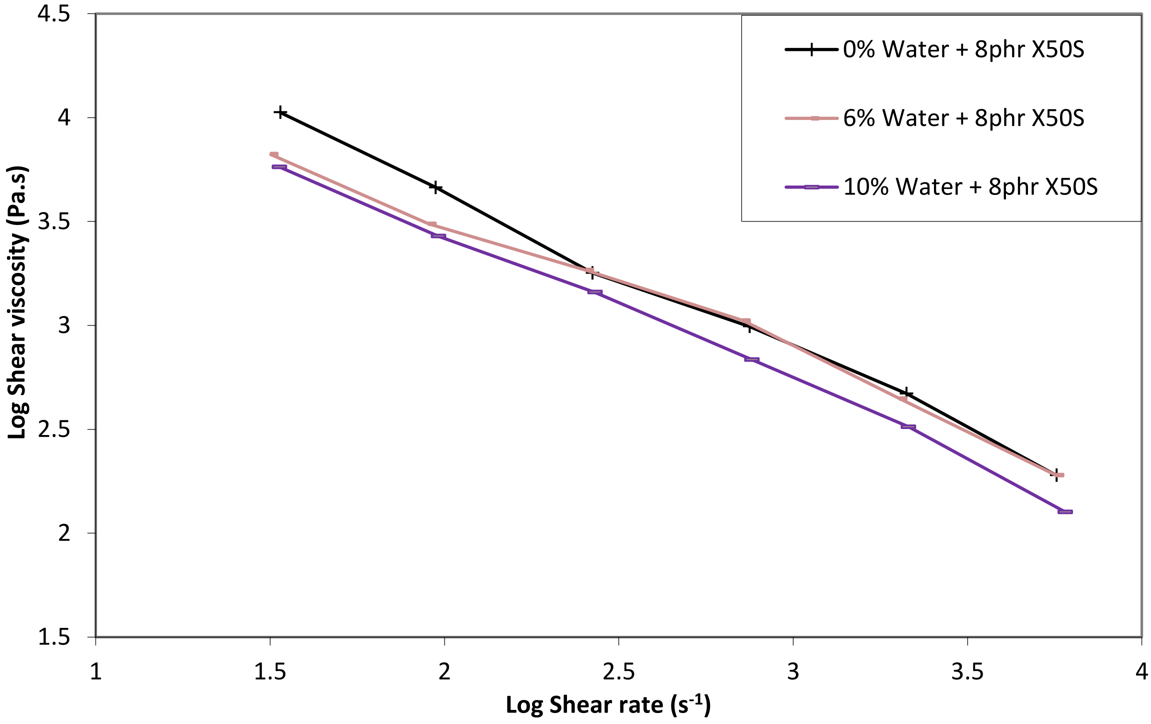

Figure 7.10: Shear viscosity curves of ENR 25/silica masterbatches: Effect of Water % (on silica) with 8phr X50S silane.

References for Chapter 7

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2. J.L. Leblanc, Factors Affecting the Extrudate Swell and melt fracture Phenomena of Rubber Compounds, *Rubber Chemistry and Technology,* Vol. 54, No. 5, 905-929, 1981.

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CHAPTER 8

CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

Results from the experiments showed that processing characteristics such as Mooney viscosity and shear viscosity and mechanical properties such as heat build-up can be improved by the addition of silane coupling agents or water to silica filled ENR25 compounds used in “green” tyre tread applications. It was also shown that an improvement in abrasion resistance can be obtained by blending ENR25 with butadiene rubber. Furthermore, the sustainability of the compound can be increased by using rSilica, recovered from tyre pyrolysis, in place of conventional silica. Specific conclusions are given below.

1. The Mooney viscosity results showed that the addition of silane may improve the processability and flow properties of the ENR/silica compound by reducing its viscosity, through the reduction of silica-silica interactions, when silane reacts with silanol groups on the silica surface. However, the reduction in viscosity is relatively small and so the effect on processing may also be quite small, as supported by the mixing data, which shows only small decreases in mixing energy with addition of silane.
2. The addition of water during mixing of silica filled ENR mixes may also improve the processability and flow properties of the compounds by reducing its viscosity. The presence of water during first stage mixing may help to reduce silica-silica interactions in the ENR/silica compound by weakening the hydrogen bonding within the silica agglomerates.

Improving processability in mixing, moulding or extrusion by reducing viscosity will result in energy saving.

3. For the curing characteristics, the combination of reduction in minimum torque and increase in maximum torque in the presence of silane indicates that the coupling agent is effectively reacting with both the silica surface and the rubber to increase crosslink density in the cured compound.

4. The addition of water during mixing delays the start of the crosslinking reaction but does not significantly affect the rate or extent of crosslinking. The longer t_{S2} time may be better for rubber processing as there is extra time available for extrusion or moulding before the compound starts to crosslink.

5. A filler macrodispersion study of ENR/silica vulcanizates both without and with X50S silane coupling agent does show a reasonably good dispersion, over 92%, for all ENR/silica compounds. However, this is significantly lower than the level of dispersion typically achieved with carbon black filled compounds. The silane concentration does not show any significant effect on silica dispersion in the compounds. This is thought to be because although silane can reduce silica-silica interaction during mixing, it is does not prevent the flocculation of the silica aggregates during storage and/or curing.

6. Addition of water during 1st stage mixing of ENR/silica mixes showed no significant effect on the level of filler dispersion. This is likely to be for the same reason as with silane, due to flocculation of the silica aggregates during storage and/or curing.

7. For physical and mechanical properties, silane coupling agent improves the crosslink network of the silica filled ENR vulcanizates, by chemically bonding between the silica and the rubber. The improved crosslink network results in reduced heat build-up and a slight increase in tensile strength and abrasion resistance, however hardness and modulus values are not significantly affected.

8. The significant decrease in heat build-up temperature with increased water percentage in the ENR/silica compound will be a very valuable finding in the development of a new tyre tread compound as the low hysteresis can result in lower tyre rolling resistance. The Akron abrasion resistance index did show a significantly higher abrasion index for water percentages above 6%, while the DIN abrasion resistance index showed no consistent trend with increased water percentage. However, all the abrasion results were still worse than of the NR/BR vulcanizate, indicating that water addition is not a good way of improving abrasion resistance.

9. The Mooney viscosity of ENR/BR blends increased as the BR percentage increased. The increase of viscosity with BR content is not due to the high Mooney viscosity of Butadiene rubber (43 Mooney Unit) but is more likely due to the resistance to heat degradation and mechanical shearing force (mastication) during mixing of butadiene rubber.

10. For the curing characteristics, the silica filled ENR/BR compounds exhibit significantly higher torque values (M_H and $M_{L)}$ with increase of butadiene content, which is expected since the addition of BR in ENR blends increases the Mooney viscosity. However, there no significant increase in Δ torque value (M_H - M_L) with increasing BR content, showing that the BR does not significantly influence the crosslink density.

11. There is a slight decrease in percentage filler dispersion with increase of BR content in ENR/BR blend vulcanizates, which could be due to the non-polar butadiene rubber affecting the compatibility of silica in the blend vulcanizates. However, all silica filled ENR/BR blend vulcanizates still showed above 91% filler dispersion, which still can be considered as a reasonable level of dispersion.

12. Abrasion resistance results showed a significant increase in DIN and Akron abrasion resistance indexes with increase of BR content. The DIN abrasion resistance index of ENR80:BR20 and ENR70:BR30 blend vulcanizates are higher than that of the NR/BR benchmark compound. The Akron abrasion resistance index of the ENR70:BR30 blend vulcanizate

showed a similar abrasion resistance index to the NR/BR vulcanizate. This positive effect of BR on abrasion resistance of ENR blend vulcanizates is a very valuable finding for the development of a new tyre tread compound.

13. The silica structure and surface chemistry results showed that, the reinforcing capability of rSilica (recovered by pyrolysis), geoSilica (recovered from geothermal water) and Zeosil is likely to be influenced by the differences in ultimate primary particle size, BET surface area, micropore volume and amount of silanol and siloxane bonds on the silica surface.

14. The rSilica showed a lower BET surface area than Zeosil, but it may have a potential of similar reinforcement as Zeosil, as rSilica has a similar ultimate particle size and lower micropore volume than Zeosil. In terms of surface chemistry, rSilica has less silanol groups than Zeosil as shown in TGA curves, which suggests that there may be less reinforcement when silane is present.

15. The geoSilica did show a higher BET surface area than rSilica and Zeosil but this could be due to geoSilica being in the form of a very thin film and also its higher micropore volume. If the higher BET surface area of geoSilica is due to the micropore volume, it is expected that geoSilica may have less reinforcing effect in rubber than rSilica and Zeosil.

16. The lower Mooney viscosity of the compound containing rSilica is consistent with the mixing energy and torque values, supporting the idea that the lower silanol content of the rSilica results in less silica-silica interaction. GeoSilica filled ENR compounds exhibit significantly higher Mooney viscosities than the Zeosil silica filled ENR compounds for both compounds without and with silane coupling agent, which is also in agreement with the mixing torque results. This could be due to poor filler dispersion caused by higher silica-silica interaction, due to its higher

surface silanol content and possibly also its thin film rather than particulate morphology.

17. The rSilica and Zeosil fillers showed higher Δ torque values (M_H - M_L) in the presence of silane. This shows the silane coupling agent is effectively reacting with rSilica and Zeosil silicas and the rubber to increase crosslink density in both cured compounds.

18. The Δ torque value (M_H - M_L) for geoSilica filled ENR compounds is almost identical between the compound with and without silane and a reversion curve is observed in both compounds, which indicates that the silane is not effectively reacting with this geoSilica.

19. The rSilica filled compounds did show reasonably good physical properties such as tensile strength, hardness and abrasion resistance compared to the commercial grade silica (Zeosil). rSilica filler may thus have the potential to replace Zeosil silica in ENR compounds. rSilica filled ENR compound with silane also showed better physical properties than the non-silane compound, which indicated that rSilica still can react with the silane, despite the fact that the amount of silanol groups on the rSilica surface was reduced by the pyrolysis process.

20. For the geoSilica filler, both without and with silane, the reinforcement of ENR compounds was much less than for the Zeosil filled compounds. It is most likely that an improvement of the geoSilica morphology is needed in order to improve its reinforcing capability in rubber.

21. For a larger mixing scale, ENR/silica masterbatches showed slightly better extrusion processability and flow properties for both screw speeds (20 and 30rpm) with increased water percentage (on silica) for 0phr, 4phr and 8phr silane masterbatches. However, the addition of X50S silane did show a little improvement in processability and flow properties of the masterbatches only at 0% water and may even have a negative effect on processability at additions of 6% to 10% water.

22. For capillary rheometer, the addition of 4 phr X50S silane at 0% water does not significantly affect shear viscosity at low shear rates but reduces shear viscosity towards the high shear rates range. This indicates that at very high shear rates, addition of X50S silane will improve processability and flow behaviour of the ENR/silica masterbatch. For 0 phr X50S silane, there is a significant decrease in shear viscosity with addition of 6% water across the whole shear rate range, indicating that addition of 6% water can improve the processability and flow behaviour of an ENR/silica masterbatch.

23. Overall, it can be concluded that silane reduces shear viscosity in the absence of water and water reduces shear viscosity in the absence of silane. However, the results suggest that there is an antagonistic effect of silane and water when both are added together in silica filled ENR masterbatches and the advantages on reducing viscosity are decreased.

8.2 Recommendations for Future Work

The following recommendations for future work in this area are based on the outcomes of the investigations reported in this thesis.

1. A surprising conclusion of the Thesis was that the addition of silane or water during mixing did not improve dispersion of the silica, even though the viscosity of the compounds was reduced, suggesting a decrease in silica:silica interaction. The relatively lower level of dispersion of silica, compared to carbon black, may be due to flocculation of the silica in the period between mixing and curing. In future studies the compound could be cured after different time periods following mixing to determine whether dispersion improved with decrease in time between mixing and curing. If higher levels of dispersion can be achieved in this way, the effect on properties could also be determined, as better filler dispersion is expected to result in improved properties.

2. The rSilica which is from a pyrolysis source did show promising results however, further analysis of the surface chemistry of recovered silicas could be done to further understand how it can affect the mixing process and compound reinforcement.

3. Since the lab scale mixing of silica ENR25/BR demonstrates good abrasion resistance, even better than the NR/BR benchmark compound, it is useful to confirm the result by carrying out large scale mixing with the same blend compound formulations.

4. Further investigation on the antagonistic effect of silane and water in silica filled ENR masterbatches could be carried out using a multifactorial experiment design to determine the interaction effects and so determine optimum combinations.

5. Last but not least is to carry out an investigation of tyre performance on silica filled ENR/BR compound used in the tyre tread, to confirm the results obtained in the lab scale experiment.