**SCHOOL OF MATERIALS AND MINERAL RESOURCES**
**ENGINEERING UNIVERSITI SAINS MALAYSIA**

# EFFECT OF DIFFERENT RATIO NATURAL RUBBER/ BUTADIENE RUBBER, CARBON BLACK/SILICA AND TYPES OF CARBON BLACK ON PHYSICAL PROPERTIES OF TIRE TREAD FOR OFF ROAD APPLICATION

By

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Dissertation submitted in partial fulfillment

of the requirements for the degree of Bachelor of Engineering with Honours

(Polymer Engineering)

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# DECLARATION

I hereby declare that I have conducted and completed the research work and work the dissertation entitle **“Effect of Different Ratio Natural Rubber/ Butadiene Rubber, Carbon Black/Silica and Types of Carbon Black on Physical Properties of Tire Tread for Off Road Application”.** I also declare that it has not been previously submitted for award of any degree or diploma or other similar title of this for any other examining body or university.

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| Date: | 1 June 2016 | |

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# LIST OF SYMBOLS

| | |
|---|---|
| NR | Natural rubber |
| BR | Polybutadiene rubber |
| CB | Carbon black |
| Si | Silica |
| phr | Parts per hundred rubber |
| SMR | Standard Malaysian Rubber |
| ZnO | Zinc oxide |
| IRHD | International Rubber Hardness Degree |
| ODR | Oscillating Disk Rheometer |

# NOMENCLATURES

| | |
|---|---|
| °C | Degree celcius |
| ° | Degree |
| % | Percentage |
| s | Second |
| $T_s$ | Tear strength in kilonewtons per metre of thickness |
| F | Force |
| d | Thickness |
| mm | Milimeter |
| MPa | Mega pascal |
| dN.m | Deci newton meter |
| $t_{s1}$ | Scorch time |
| $t_{90}$ | Cure time |
| $M_L$ | Minimum torque |
| $M_H$ | Maximum torque |
| Min | Minute |
| lb-in | Pound per inch |

# PENGARUH PERBEZAAN NISBAH GETAH ASLI/ GETAH BUTADIENA, KARBON HITAM/ SILIKA DAN JENIS KARBON HITAM TERHADAP SIFAT-SIFAT FIZIKAL PADA BUNGA TAYAR UNTUK APLIKASI *OFF ROAD*

## ABSTRAK

Kesan nisbah berbeza getah asli / getah butadiena, karbon hitam / silika dan jenis karbon hitam pada sifat fizikal bunga tayar bagi aplikasi *off road* telah dikaji. Pengkompaunan ini telah disediakan dengan menggunakan pengadun dalaman dan *two roll mill*. Ciri pengawetan diukur dengan menggunakan ukuran reologi. ujian tegangan, ujian air mata, indeks rintangan lelasan dan kekerasan untuk menganalisis sifat-sifat fizikal getah. Terdapat tiga nisbah yang berbeza daripada karbon hitam / silika yang S70N228 / 42 (28/42), S70N230 / 44 (30/44) dan S70N232 / 48 (32/48). S70N232 / 48 mempunyai nilai yang optimum dalam rintangan lelasan dan kekuatan koyak kerana polimer-pengisi interaksi yang lebih kukuh dalam kompaun. Nisbah yang berbeza karbon hitam tidak memberi kesan yang besar ke atas kekerasan. Selain itu, dua nisbah getah getah / butadiena semulajadi disiasat dengan nisbah 70/30 dan 80/20. Getah asli / butadiena dengan 80/20 mempunyai sifat-sifat mekanikal yang lebih tinggi berbanding nisbah getah asli / butadiena getah 70/30 kerana interaksi yang baik antara pengisi dan polimer. Tambahan pula, dua jenis karbon hitam juga sedang dikaji yang N220 dan N134. N134 mempunyai yang baik dalam sifat-sifat mekanikal kerana kawasan permukaan yang lebih tinggi berbanding dengan N220.

# EFFECT OF DIFFERENT RATIO NATURAL RUBBER/ BUTADIENE RUBBER, CARBON BLACK/SILICA AND TYPES OF CARBON BLACK ON PHYSICAL PROPERTIES OF TIRE TREAD FOR OFF ROAD APPLICATION

## ABSTRACT

Effect of different ratio natural rubber/butadiene rubber, carbon black/silica and types of carbon black on physical properties of the tire tread for off road application were studied. The compounding was prepared by using internal mixer and two roll mill. The curing characteristic were measured by using Rheometer100 Mosanto. Tensile test, tear test, abrasion resistance index and hardness to analyse the mechanical properties of the rubber. There are three different ratio of the carbon black/silica which are S70N228/42 (28/42), S70N230/44 (30/44) and S70N232/48 (32/48). S70N232/48 has the optimum value in abrasion resistance and tear strength due to the stronger polymer-filler interaction in the compound. The different ratio of carbon black did not give a significant effect on hardness. In addition, two ratio of natural rubber/butadiene rubber are investigated which are 70/30 and 80/20 respectively. Natural rubber/butadiene rubber with 80/20 higher mechanical properties compared to the ratio of natural rubber/butadiene rubber 70/30 due to good interaction between the filler and polymer. Furthermore, two types of carbon black were also being studied which are N220 and N134. N134 had a good in mechanical properties due to the higher surface area compared to the N220.

# CHAPTER 1

# INTRODUCTION

## 1.1. Background of Study

Tire tread was an important part in the tire component and had the greatest effect on the way and the type of use. Tire tread, or the portion of the tire that comes in contact with the road, composed of tread itself, tread shoulder, and tread base. This tread will worn off as the tires being used which it will limiting its effectiveness in traction. The tire tread contains the grooves that call as a tread pattern. The design of the tire tread need to be concerned due to the noise that will be generated once the tire tread being used. There are many factors that effects the tire tread like temperature and type of road (Hogan,1973)

As many years, the tire tread industries had developed the new types of tire tread based on different type of application, for examples like street tires, snow tires \and off road tires. Off-road tire tread features aggressive tread lugs that bite into the loose or muddy surface to give a maximum traction that helps propel the vehicle through muddy ruts and over slippery rocks. The forces can be transmitted once it contact and the contact area plays an important function in describing friction aspects. The performance of the existence of the tire tread also has been improved with higher capabilities and efficacy (Sridharan and Sivaramakrishnan, 2012)

The properties of the rubber products can be enhanced by blending the different types of elastomers. It will be contributed in the physical properties, increase service life, easier processing and reduced product cost. The performance of the elastomer blend can be predicted from the ratios of the respective polymer components. In tire tread production, the blending of the elastomer is needed in order to meet a specific requirement. The blending between natural rubber (NR) and butadiene rubber (BR) enable to improve tread wear and groove cracking resistance without a reduction in resilience (Hess et al.,1985)

Natural rubber contains a long entanglement of hydrocarbon chains which has high molecular weight. Natural rubber is commonly used in rubber industries due to its advantages, such as flexibility. It also has the ability to stick itself and to other material which make it easier to fabricate. Natural rubber also good in tear and tensile strength which this characteristics can be developed due to the capability of this rubber has to crystallize under stress. However, some its properties may fall in certain application like ozone resistance, air permeability, and compression set (Chiu and Tsal, 2006)

Polybutadiene rubber (BR) is essentially a polymerization product of butadiene in solution and formed from the polymerization of the monomer 1,3-butadiene. The type of BR used depends on the properties that required on the compound. Polybutadiene rubber gives a high wear due to the low coefficient of friction which causes a reduction in the resistance to cutting and chipping especially on the rough road or off road application. High-cis BR blended with NR to improve the latter's processing and BR gives many of its desirable properties to the blend (Arayapranee, 2012)

The carbon black and silica is the most preferred in the tire tread industries due to its ability to enhance the strength properties. Silica has a number of hydroxyl groups on the surface that contributes to the strong filler-filler interaction and adsorption of polar materials by hydrogen bonds. Intermolecular hydrogen bonds between hydroxyl groups on the surface of silica is very strong and it can form a tight aggregate. Several approaches to improve the silica dispersion by optimizing the mixing equipment and silica surface treatment ( Kaewsakul et al., 2013)

Carbon black is the most popular filler that is commonly added in rubber compounding. The properties of the carbon blacks are normally controlled by particle size, surface area, surface activity and structure. The degree of reinforcement depends on content and structure of fillers. The choice of carbon black grades is based on the desired physical properties of the end products, processing method and costs. The carbon black that commonly used in rubber industries such as N220, N550 and N234. Different grade of the carbon black will give a different size of the carbon black that influence the surface area, average particle size and the DBP absorption (Bijarimi et al., 2010)

The processing of the rubber compound with filler affect the end properties which can be obtained through a series of experiments that differ the ratios of filler and calculate the effects of hardness. The result of the filler loading is to increase the number of chains. This can be showed in the filled vulcanizates where the efficiency of reinforcement depends on the complex interaction of several filler related to particle size, particle shape, particle dispersion, surface area, structure of filler and bonding quality between filler and rubber matrix (Waqyiuddin, 2010)

The blends of the silica and the carbon black give the benefits from each other. Carbon black has the higher modulus, and it also increase the tensile strength, tear strength and abrasion once it compounded with the rubbers. Silica gives a tear strength, abrasion resistance, aging resistance and adhesion properties in order to give a great combination to carbon black. CB-silica dual phase filler (CSDPF) from Cabot Corporation is a commercial hybrid filler that are produced by pyrolyzing petroleum-and silicon-based feedstock. It has a high surface activity of the carbon domain and high silica surface. CSDPF is described to have an advantages in abrasion resistance and tear strength (Rattanasom et al., 2007)

## 1.2. Problem Statement

The vulcanized blend rubber system of natural rubber and synthetic rubbers used to prepare the tire tread. It also added with the most important materials which is a carbon black and silica as main fillers in the compounding recipe. The common grade for the carbon black to produce the tire tread is N220. These common tire tread was easy to wear off once it used for off road application as shown in Figure 1.1. Therefore, considerable R&D efforts are being carried out of investigation the optimum ratio of NR/BR, N220/ Silica with the different type of the carbon black. The different type of the rubber will give the different effect in properties. Many researchers have studied the effect on the blending of NR/BR and N220/ Silica and type of the carbon black in order to enhance the properties of the product. In this study, the rubber formulation is based on the standard formulation of existing tire tread in the market, but for this work the ratio of the rubber, carbon black, silica are varied. The other type of carbon black, N134 also being used in this experiment.

Figure 1.1: The tire tread wear off

## 1.3. Objectives

i. To identify the optimum of the tensile strength, tear strength, abrasion resistance and hardness properties with different ratio of carbon black/ silica of NR/BR compound.

ii. To investigate effect of different ratio NR/BR on physical and mechanical properties of tire tread for off road application.

iii. To investigate the tensile strength, tear strength of tire tread with different type of carbon black (N134 and N220) of NR/BR compound.

## 1.4. Thesis Outline

This thesis is covered all chapters that consist of

Chapter 1: Consists of introduction of the thesis. It is covers for research background, problem statement, research objectives and also the scope of all the chapter

Chapter 2: Provide literature review of project, extensive review the effect of different ratio carbon black/ silica, SMR/BR, type of carbon black, several material used in compounding and testing that will use in this project

Chapter 3: Consists the detail of the raw materials that used in this research, experimental procedures, machine and the testing that involved in this research

Chapter 4: Encloses results and discussion. It includes the charts, tables which represent the physical properties from the testing and will be described in details

Chapter 5: Summary and conclusion as well as suggestion for future studies

Chapter 6: List of references that used in this research.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1. Blending of Natural Rubber (NR) and Polybutadiene Rubber (BR)

The polymer blends is a virtual method for upgrading of polymer materials and is widely use in engineering plastics, rubber and fiber materials. The combination of two or more rubbers need to be used in the preparation of the compound in order to achieve the special properties. Generally, the blending of elastomeric material to improve the properties, better processing and lower cost. The reported studies on the effect of blending on properties mostly concerned about the general-purpose of elastomers. The influence of blending on processing and cured physical properties is considered, the achievement of best properties depending on successful processing (Castro et al.,2003)

BR used in the rubber industry especially in tire industry. BR provides high abrasion resistance and low hysteresis due to the amount of cis content. Chiu and Tsai (2005), have reported that the deformation of BR is less than of NR under the same load and BR contains a higher compression stiffness than NR. They observed that the aging resistance property of BR is good compare to NR and both tensile and tear strength of NR/BR blends increase with increasing NR content.

The concept of the blending NR/BR received many attentions from many researchers. Amin et al. (2010), investigated the effect of temperature history on the Mullin effect, its recovery behavior and the rate dependence is investigated using NR/BR blend. The investigation revealed that temperature dependence of both the healing and the Mullin effect in rubber with different degrees of crystallinity is determining by considering the melting and recrystallization rates. The rate dependence of the blend is tested under different temperatures via monotonic and cyclic tension under different strains and relaxation test.

## 2.2. Natural Rubber

Natural rubber is extracted in the form of latex from the bark of Harvea tree. The latex needs to undergo several steps involving preservation, concentration, coagulation, dewatering, drying, cleaning and blending. Natural rubber sold in a variety of grades based on purity, viscosity, viscosity stability, oxidation resistance and rate of cure.

Figure 2.2 shows the chemical structure of the naural rubber. Natural rubber is nearly 100% cis-1,4 polyisoprene with molecular weight ranging from 1 to $2.5 \times 10^6$. It tends to crystallize spontaneously at low temperatures due to its high structural regularity. Low temperature crystallization causes stiffening but is easily reverse by warming. Crystallization contributes to the resistance of cutting, tearing, abrasion and high tensile strength (Moldoveanu,1998)

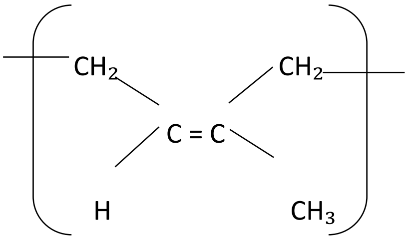


Figure 2.1: Chemical structure of natural rubber (Bartoletti, 2008)

One of the important properties of natural rubber is elasticity. It can be distorted and the rapidity and degree to which it recovers to its original shape and dimensions.

However, it is not perfectly elastic and rapid recovery is not complete. The distortion part is recovered more slowly and part is retained. The polymer network allows elasticity and flexibility to be combined with crystallization-induced strength and toughness when stretched.

## 2.3. Butadiene rubber

Cis-1,4-polybutadiene rubber which showed in figure 2.2 widely used in tire industry due to its superior dynamic mechanical properties, abrasion resistance, elasticity and flex crack resistance (Gu et al, 2009). The structure of the butadiene rubber hardens at much lower temperature (at Tg of -100℃) compared to the natural rubber and commercial elastomers. This gives better low temperature flexibility and higher resilience at ambient temperatures than most elastomers. Greater resilience will contributes to the less heat buildup during continuous dynamic deformation happen.

$$—\left(CH_2\text{-}CH\text{=}CH\text{-}CH_2\right)—$$

Figure 2.2**:** Chemical structure of butadiene rubber (Sun et.al.,1992)

## 2.4. Black and Non-Black Reinforcing Fillers

In elastomer industries, the importance of filler for the rubber product has been acknowledged. Fillers can be classified into reinforcing and non-reinforcing fillers. Reinforcing fillers commonly have a significant effect on both compound and vulcanizate properties. Fillers can be abled to bond the rubber matrix and consequently improve the processability and final product performance. They are divided into black and non-black types.

The black fillers is including in the formulation to improve the modulus and failure properties (tensile strength, tear resistance, and abrasion resistance) of final vulcanisate, whereas the non-reinforcing fillers are added as extender in the rubber compounds to reduce cost. Figure 2.3 shows the chemical surface of carbon black in the form graphitic basal planes with various functional groups. Non-black fillers also offer to have a rubber finish product with bright colour or white. Non-black fillers can be characterized into four types which are:

1. Calcium carbonate: It can be divided into two group which are ground natural limestone and precipitated calcium carbonate. The ground natural has low aspect ratio and low surface are which contributed to poor abrasion and tear resistance.
2. Kaolin clay: Clay are commonly use in components of tires for fiber adhesive compounds. It also good in reinforcement, moderate cost and good processability.
3. Amorphous silica: Precipitated silica consist of three dimensional network of coagulated primary silica particles. The primary particles can form the aggregation and agglomeration, as consequences can effect on the properties of the rubber itself.

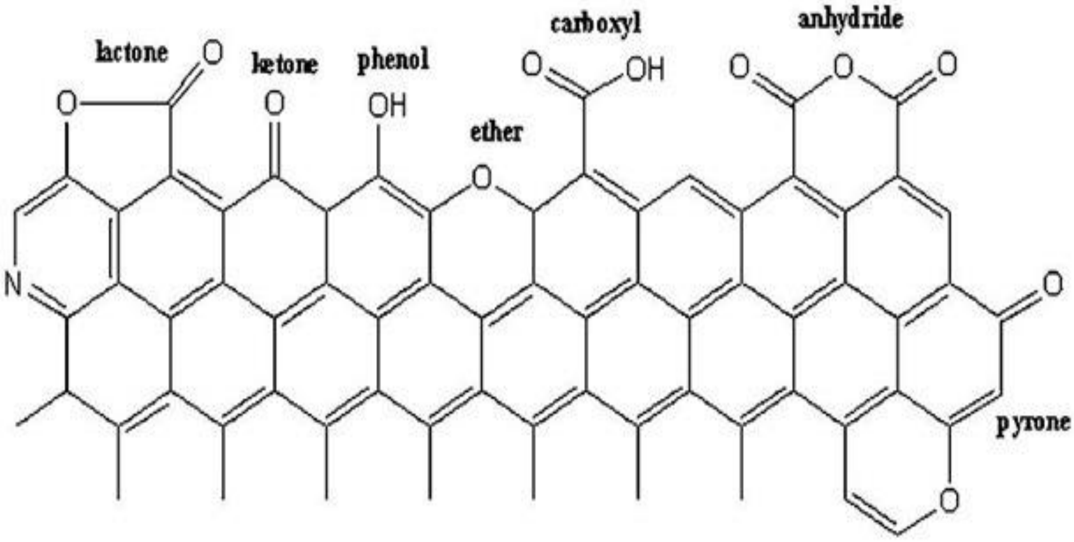


Figure 2.3: Chemical surface of carbon black in the form of graphitic basal planes with various functional groups. (Kaewsakul, 2013)

## 2.5. Filler Effect

The rubber properties can be improved from the particle size, surface area, structure and surface-activity of the filler. The general influence of these three filler characteristics on rubber properties can be categorized into:

1. Increasing surface area by decreasing the particle size gives a lower resilience and higher Mooney Viscosity, tensile strength, abrasion resistance, tear resistance and hysteresis.
2. Increasing surface activity including surface treatment gives a higher abrasion resistance, modulus ( elongation>300%), and hysteresis
3. Increasing persistent structure gives higher Mooney Viscosity, modulus and hysteresis, lower extrusion shrinkage, tear resistance and resilience.

The higher hysteresis of the carbon black at higher temperature is due to the energy dissipation during repeated destruction and reconstruction of filler network. It forms a rapid decrease of tan δ with increasing temperature. The hysteresis of silica-filled rubber increases with increasing temperature, but finally showing a crossover point at 90℃. It may be anticipated from strongly and highly constructed filler cluster. As the temperature increases, the filler-filler interaction become weak and result in an increasing of filler network which can be broken down and reformed during cyclic deformation at low strain amplitudes (Brinke, 2002)

## 2.6. Carbon Black

Carbon black is normally used for reinforcement and normally provides or enhanced the physical and mechanical properties for cured compound. The introduction of carbon black as reinforcing agent lead to strongly increased tread wear resistance. In tire tread industry, since 1912 the zinc oxide replaced by a high loading of carbon black while the small amount of zinc oxide is still needed for the curing purposes (Kaewsakul, 2013)

According Boonsta (1967), the research is based on the mixing of carbon black and polymer on the interaction and reinforcement. A primary agglomerate is formed during the mixing process. The important carbon black properties are surface area, specific activity, structure of the carbon black and porosity of the particles. The carbon black loses its sites of high specific activity when it undergoes heat treatment at 3000℃. The bound rubber is used to measure of specific surface activity. The filler-polymer interaction is evident in reduced swelling solvents. The percentage of swelling is no longer dependent on the amount of filler when it below a critical degree of swelling. The graphitized black vulcanizate happen in all solvents the same degree of swelling as the unfilled vulcanizate and it can be explained by the assumption of mobile adsorption of rubber chains on the carbon black surface. The untreated carbon blacks has a limited mobility on the surface by sites of high energy of adsorption.

Reinforcement is explained by the more homogenous distribution of tension between molecular chains due to slippage on the carbon surface.

## 2.7. Silica

High surface area grades of precipitated gives an alternative to carbon black as a source of reinforcement for natural and synthetic rubber compounds. The use of silica can improve wet skid performance. By incorporating silica in the winter tire, the wet skid performance can be improved by 15% in order to improve the braking distances at the same time. Compounds using silica more elastic and flexible at low temperature. The morphology of silica can be divided into three characteristic structures, primary particles, aggregates and agglomerates. Figure 2.4 shows the characteristic structure of silica. The aggregates are condensed into agglomeration by Van der Waals forces. Silica has a higher structure which give a strong tendency to agglomerate, and is difficult to disperse in rubber and rapidly re-agglomerates after mixing (Brinke, 2002)

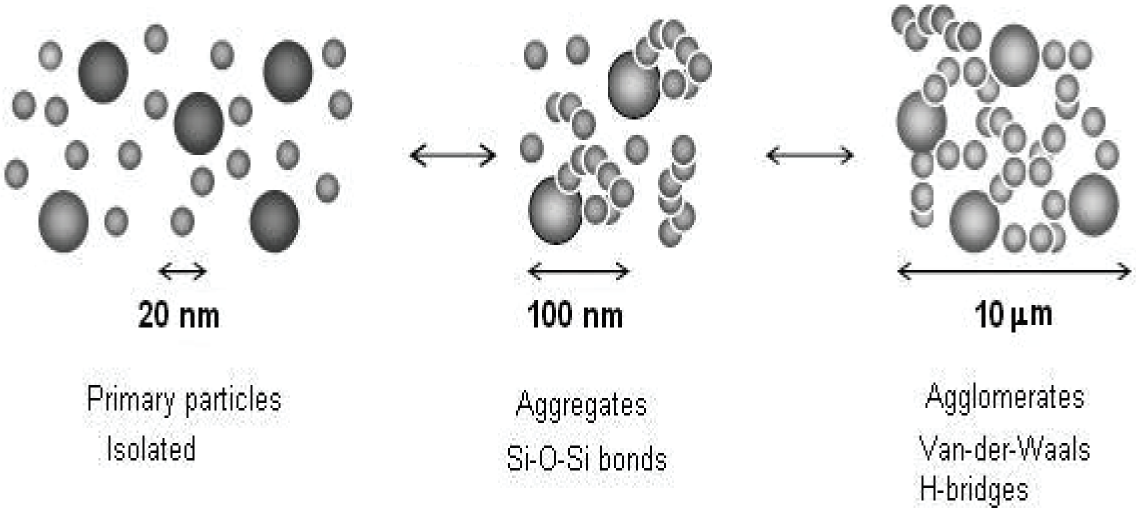


Figure 2.4: The characteristic structure of silica. (Sarkawi et al., 2015)

Hewitt (2007), mentioned that silica still have severe deficiencies in abrasion resistance compare to the carbon black even though the silica provides the highest level of reinforcement among inorganic fillers. The unusual reinforcement behavior led to studies of silica interaction with a normal cure like zinc oxide, stearic acid and glycols. The lack of abrasion resistance was due not to a defect inherent in silica but to silica surface modification by soluble zinc attachment. Although zinc functions as the accelerator activator in the rubber compounding but it also becomes a barrier to effective silica-polymer bonding.

Silica technology used for rubber has long been developed, since silica can reinforce rubber and gives high performance of articles, particularly in tires. The major problem of this combination is that silica has a relatively high polarity by nature and cannot easily be mixed with natural rubber which is a non-polar material. Furthermore, NR is more susceptible to degradation under excessive mixing conditions, compared to its synthetic counterparts. To date, bifunctional organosilane type coupling agents effectively solve the incompatibility with hydrocarbon rubber and to additionally strengthen the interaction between silica and rubber.

## 2.8. Carbon Black/Silica

The different composition of carbon black and silica CB/Si- 0/60, 20/40, 30/30, 40/20 and 60/0 phr in rubber compounding were prepared by Ulfah et al.,(2015). The rheological behavior can be measured by using the Mooney viscosity and cure time. The result revealed that the Mooney viscosity increase as the phr of the carbon black increase. The compound filled with CB/Si of 30/30 and 60/0 showed the cure time decreased suddenly and increase at certain ratio. For mechanical properties, the higher value of carbon black give a low value in hardness which contribute to the higher abrasion resistance. Also, the optimum ratio of filler blended is CB/Si 40/20. The tensile stress at 300% increase as the carbon black filler increase.

Furthermore, Zafarmehrabian et al. (2011), investigated the effect of silica and carbon black ratio on dynamic properties of NR/BR. The value of the phr CB/Si are varied; 60/0, 55/5, 50/10, 40/20. As high amounts of silica will results in reduce of abrasion properties, improve the rolling resistance and decreases the heat buildup. The tensile strength and modulus and wet grip decrease with increasing of silica in rubber compound formulation.

Besides that, Rattanasom et al. (2007), have explored that the use of silica/CB will enhance the mechanical and dynamic properties of NR vulcanizates. In their study, reinforcement of NR with silica/ CB hybrid filler at various ratios was investigated in order to find the optimum silica/CB ratio. The total hybrid filler is 50phr. Based on the result, it shows that the vulcanizates containing 20 and 30 phr of silica in hybrid filler have a better mechanical properties like tensile strength, tear strength, abrasion resistance, crack growth resistance, heat buildup resistance and rolling resistance.

## 2.9. Size of Carbon Black

If the size of filler particles exceeds the polymer inter-chain distance, it introduces an area of localized stress which contribute to elastomer chain rupture on bending or stretching. When filler particles size up to 10,000 nm, the performance of the filler can be less. Fillers with particle size between 1000 and 10,000 nm are used as diluent and have no significant effect on rubber properties. Semi reinforcing filler range from 10 to 100 mm can improves rubber properties.

Figure 2.5 shows the filler classification chart based on the size of the filler. The particles of the carbon black are not discrete but are fused “clusters” of individual particles.The reinforcement of the carbon black is not effect by the size of the clusters but it depends on the size of the particles within it. The particle size of various grades of carbon black is given in the Table 2.1.

Bijarimi et al., 2010, studied the effect of carbon black grades in tire tread compounds. The carbon black grades were N339/N375 and N550/N660. The compounds were classified with the respect to their physical and rheological properties. The carbon black with grade N375 and N339 has a minimal effects to the hardness, rebound resilience, tensile and tear strength. N550 could not directly substituted with N660 in tire tread as it decreases the hardness property. In order to achieve a similar hardness value, the loading of N660 needs to be increased.

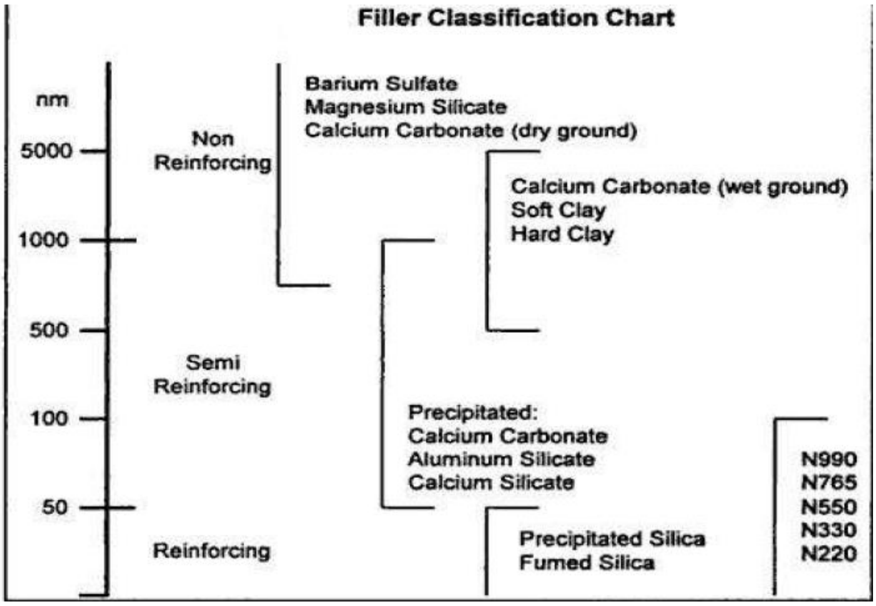


Figure 2.5 :Filler Classification Chart (Kaewsakul et al., 2013)

Table 2.1: Particles size of various type of carbon black fillers. (Niyogi, 2007)

| **Type Name** | **Type Code** | **Average particle diameter (nm)** |
|---|---|---|
| Super abrasion furnace | SAF | 20 (Oil furnace) |
| Intermediate super abrasion furnace | ISAF | 23 (Oil furnace) |
| High abrasion furnace | HAF | 23 (Oil furnace) |
| Fast extrusion furnace | FEF | 40 (Oil furnace) |
| General purpose furnace | GPF | 50 (Oil furnace) |
| Semi-reinforcing furnace | SRF | 60 (Oil furnace ) |
| | | 80 (Gas furnace) |
| High modulus furnace | HMF | 60 (Gas furnace) |
| Fine thermal | FT | 180 |
| Medium thermal | MT | 470 |

## 2.10. Rubber Compounding

In rubber mixing, two major ingredients are important which are rubber itself and filler, combined in such a way to achieve a different objectives. The objectives of the compounding:

1. To enhance some properties in finished products in order to fullfil the service requirement
2. To meet processing characteristics required for efficient utilization of available equipment.
3. To attain the desirable properties and processability at the lowest cost.

Table 2.2 shows the ingredients and function in rubber compounding. Mixing will incorporate all the ingredients like antioxidant, accelerator, vulcanizing agent and distribute it uniformly with the rubber compounds. The natural rubber usually undergoes the mastication to reduce its viscosity. Different ingredients and mixing sequence of the rubber compound result the different properties and processability. (Schaal et al, 2000)

Table 2.2: Ingredients and function in rubber compounding (Dick and Annicelli,2001)

| Ingredients | Functions |
|---|---|
| Elastomers | Act as a matrix in rubber compounding |
| Vulcanization agent | Ingredients that cause the chemical reaction and results in crosslinking of elastomer molecules |
| Accelerators | To reduce the vulcanization time by increasing the speed of vulcanization |
| Activators | To activate the accelerator in order to improves its effectiveness |
| Anti-degradants | Used to retard the deterioration of rubber compound from oxygen, ozone, light, and heat |
| Filler | To enhance the properties, reduce cost and impart certain processing characteristic |
| Retarders | To reduce the scorchiness of a compound |
| Processing oil | Act as lubricant to reduce the viscosity and ease the processability |

## 2.11. Mixing

Mixing is the first step in manufacturing and type of mixing is depends on the scale of operation. For small scale mixing, the mixing will carried out by two roll mill. A kneader is less expensive compared to internal mixer is sometimes used.

Two roll mill contains the horizontal and parallel of the roll axes and the distance of the rolls can be adjusted by having the bearing blocks of the front roll resting against adjusting screw. The speed of the rolls are different. For natural rubber mixing, a ratio of 1:1. The refining compounds and even-speed rolls on feed mills to calenders use a high friction ratios. For synthetic rubbers, the internal mixer will be used because it is very difficult to mix on two roll mills.

$$\text{Friction Ratio} = \frac{\text{speed of back roll}}{\text{speed of front roll}} \qquad (1)$$

Internal mixers which shown in Figure 2.6 is more efficient mixers than two roll mills. There are two type of internal mixer which known as ‘Banbury mixer’ (tangential) and Francais Shaw ‘Intermix’ (intermeshing). The tangential type has two slightly spiralled rotors revolve side by side towards each other within a chamber shaped like two short cylinders lying together with adjacent sides open. The hopper that function to insert the material can be closed by pneumatic and the bottom gate which can be hydraulic opened to drop out the contents after mixing (Sharma, 2014)

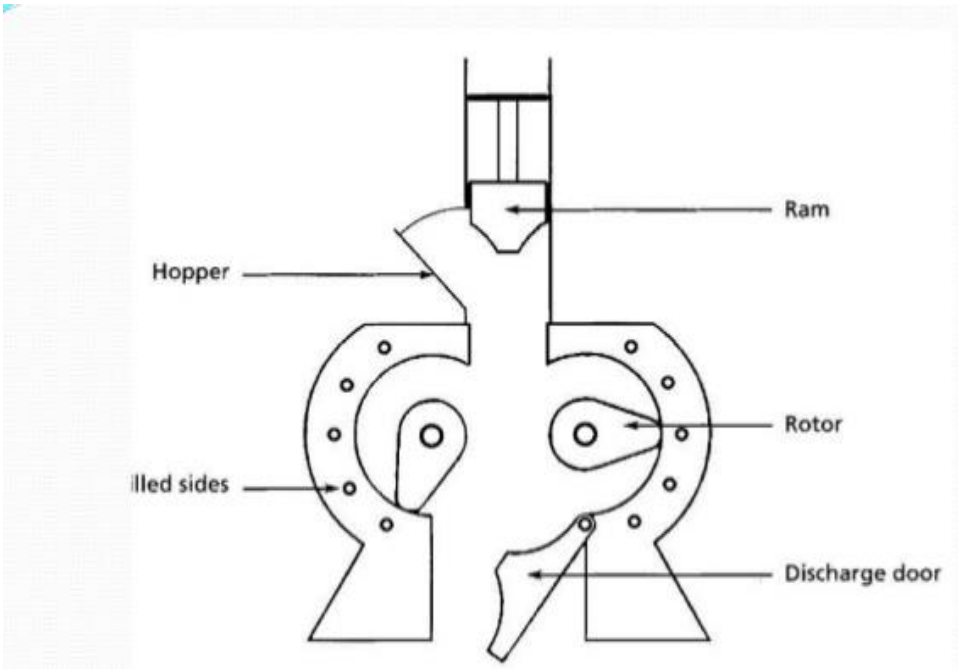


Figure 2.6: Banbury internal mixer (Singh, 2016)

Kneader is a less intensive mixer compared to the internal mixer and intermediate between Banburry mixer and open mill. The kneader is provided with pressurized lid which it functions as a ram. The surface area of lid is wider than the Banbury mixer. The capacity for the soft compound is around 80 to 90% of the mixing volume whereas for harder compound is 75% of the mixing volume.

### 2.12. Additives

Rubber formulations are formed to meet specific requirements. Each parts in the formulation plays an important role to give a good properties at the final products. Castro (2003) discussed about the influence of additives incorporation sequence on NR/BR blends properties. This studied carried out by prepare 50/50 NR/BR by using four different sequence to incorporate the additives and curing under constant conditions. A correlation between the mechanical performance and the blend morphology can be formed by dynamic mechanical thermal analysis and scanning electron microscopy.

## 2.13. Accelerator

Accelerator is a part of additive that had in the rubber compounding. In the absence of the accelerator, 8-10 parts of the sulphur is required and the rate of vulcanization is low. Mostly the sulphur is used in intramolecular rather than crosslinking reactions. The effectiveness of the vulcanization can be happened when 1 phr of the accelerator with 2-3 phr of sulphur being used. It can produced a better in properties.

The selection system normally is based on the properties such as solubility in rubber. The high solubility of rubber can prevent from bloom and improve dispersibility, reversion characteristic and adequate scorch time which required for scorch free processing. The combination these additives create soluble zinc ions which activate intermediate reactions involved in crosslink formation.

The scorch time, cure time and vulcanisation time are the most important characteristics of the accelerator. Scorch time is the time that the crosslinking start to be formed where the accelerator chemistry is involved. Cure time is the time where the stock must be heated at given temperature until it reaches the optimum cure time. Vulcanisation time is the time that required after vulcanization has started until a technical cure is reached. After achieved the maximum torque, it may faces a marching, or reversion or levels off. Stable cures are characterized by flat cure curves which it tends to reach a plateau as vulcanisation progresses.

The changing of the amounts and/ or types of accelerators can reduce the amount of time that required for vulcanization. There are different system of accelerator can used for different applications:

1. Single accelerator system: produce satisfactory cures within specified time.
2. Combinations of two or more accelerators: largest amount of primary accelerator, 10-20% of secondary accelerator in order to activate and improve the properties of the vulcanizate. The combinations of this type produce a synergistic effect as the final properties compared to the accelerator that produced separately.
3. Delayed action: not affected by processing temperatures but produce satisfactory cures at ordinary vulcanization temperatures.

Effects of different accelerators on the cure characteristics and mechanical properties of sulphur-cured natural rubber (NR)-based compounds was performed by Ahsan et al. (2015). Three types of accelerator that being used in this research. Mercaptobenzothiazole disulphide (MBTS) as primary accelerator, diphenylguanidine (DPG) and Zn-2-mercaptobenzothiazoole (ZMBT) as secondary accelerators. The synergistic effect of MBTS/DPG gives the shortest scorch time, highest cure rate and highest crosslink density compared to the MBTS/ZMBT and MBTS/ZMBT/DPG combinations. The tensile strength of MBTS/DPG also increases but not for tear strength. From this researched, it reveals that MBTS/ZMBT/DPG systems is the most effective in enhance the tear strength by 4.5% compared with MBTS/DPG system.

Table 2.3 : Accelerators for sulfur vulcanization (Niyogi, 2007)

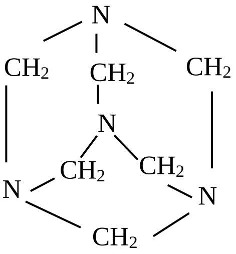
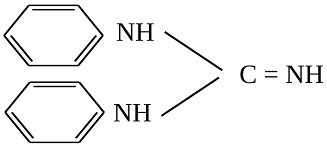
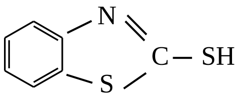
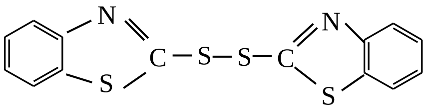
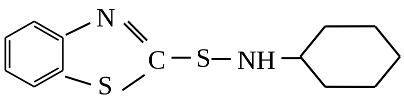
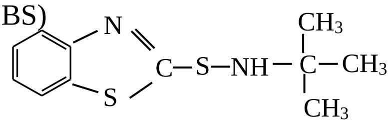
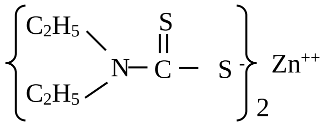
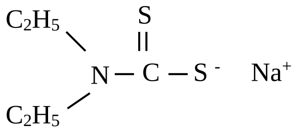
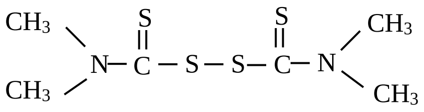
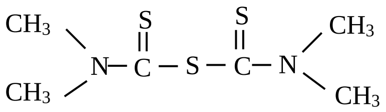
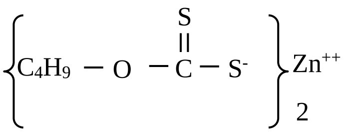
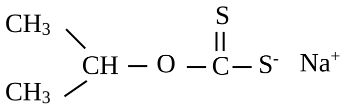
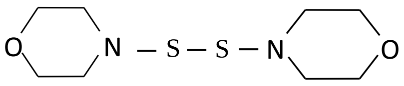
| **Types** | **Examples** | **Remarks** |
|---|---|---|
| Aldehyde – amines | <br>Hexamethylene Tetramine (HMT) | ➢ Moderately test<br>➢ Primary accelerator for NR and synthetic rubbers<br>➢ Occasionally used as secondary plasticizer<br>➢ Used in self curing adhesive |
| Guanidines | <br>1,3 Diphenyl Guanidine (DPG) | ➢ Moderately fast<br>➢ Secondary accelerator for thiazoles, sulfenamides and thiurams |
| Benzothiazoles | <br>Mercaptobenzothiazole (MBT) | ➢ Fast accelerator<br>➢ General purpose<br>➢ Primary accelerators for NR & synthetic rubber |
| | <br>Dibenzothiazyl disulfide (MBTS) | ➢ Delayed action<br>➢ Safe processing<br>➢ Moderate cure rate |
| Sulfenamides | <br>N-cyclohexylbenzothiazyl sulfenamide (CBS) | ➢ Delayed action, semiultra<br>➢ Safe processing<br>➢ Moderate cure |
| | <br>N-t-butyl -2- benzothiazyl sulfenamide(TBBS) | ➢ Delayed action<br>➢ primary accelerator for NR and synthetic rubbers |

Table 2.4 : Accelerators for sulfur vulcanization (Niyogi, 2007) (continue)

| **Types** | **Examples** | **Remarks** |
|---|---|---|
| Dithocarbamates | <br>Zinc diethyldithiocarbamate (ZDC) | ➢ Delayed action<br>➢ Safe processing<br>➢ Ultra accelerator |
|  | <br>Sodium diethyldithiocarbamate (SDC) | ➢ Water soluble ultra accelerator used for latex |
| Thiurams | <br>Tetramethylthiuram disulfide (TMTD) | ➢ Ultra accelerator<br>➢ Excellent for fast press cure |
|  | <br>Tetramethyl thiurum monosulfide (TMTM) | ➢ Ultra accelerator<br>➢ Booster for thiazoles especially for nitrile rubber |
| Xanthates | <br>Zinc butyl xanthate (ZBX) | ➢ Low temperature ultra accelerator |
|  | <br>Sodium isopropyl xanthate (SIX) | ➢ Water soluble ultra accelerator for latex work |
| Morpholines | <br>4,4′ - dithiobismorpholine | ➢ Provides excellent heat ageing properties |

# CHAPTER 3

# METHODOLOGY

This chapter will describe about the material used, the sample preparation and the type of the testing for this project. Three series of investigation were carried out for this project. The first series to compare the properties of the sample by varying the concentration or loading of the carbon black and silica. The second series to investigate the effect of different ratio of NR/BR on the physical and mechanical properties. The third series is to study the physical and mechanical properties of SMR/BR different type of carbon black.

## 3.1. Materials

### 3.1.1. Natural Rubber

Standard Malaysia Rubber with grade 10 (SMR10) was used for this experiment. This natural rubber was purchased from the Lee Rubber Co. which located in Muar Johor. The grade determines 0.054 % of dirt content, 0.25 % of nitrogen and 0.50 % of ash content. SMR10 has the cis-1, 4 configuration which means that carbon atoms 1 and 4 both on the same side of the double bond and glass transition 70℃ with density of 0.91 g/cm$^3$ at room temperature.

### 3.1.2. Butadiene Rubber

Butadiene rubber was selected to be blended with the natural rubber to enhance the performance like abrasion resistance, resilience and low-temperature flexibility. It was produced from Zeon Corporation, Tokyo, Japan. Butadiene rubber is a homopolymer of butadiene and it formed from the polymerization of the monomer 1, 3 - butadiene. It is a high cis grades contain with minimum 97% cis-1,4 butadiene units and volatile matter with maximum 0.5 %.

### 3.1.3. Filler

#### 3.1.3.1. N220

N220 is categorized in intermediate super abrasion furnace (ISAF). It is supplied from Cabot (Malaysia) Sdn. Bhd., Negeri Sembilan. The size of the N220 is between 24 to 33 nm. It used in rubber compounding to improve tensile strength, strip strength and resistance to abrasion. The heat loss of the N220 is maximum 2.5.

#### 3.1.3.2. N134

N134 is very fine particle size, low micro-porosity and high surface activity. The percentage of the ash content in this grade of carbon black is less than 1.5 % and the fines is less than 10 %. It is supplied from Cabot Trading, Shanghai, China.

#### 3.1.3.3. Silica

Silica is known as a silicon dioxide. Silica is classified as a reinforced filler in non-black fillers. Silica has an appearance of white in a powder form. It has a particle hardness 45 maximum and moisture percent maximum to 8.0 %. It also has a high abrasion strength and increased with increasing of surface area.

### 3.1.4. Rubber Processing Oil

Rubber processing oil assist in improving the dispersion of the filler and flow characteristics of the compound. The density of the rubber processing oil is 0.955 g/cm$^3$ with water content 0.04 %. It was supplied by GT Gulf (M) Sdn. Bhd., Petaling Jaya Selangor. The type of the rubber processing oil is confidential.

### 3.1.5. Coupling Agent

Coupling agent was supplied by Behn Meyer Chemical (M) Sdn Bhd. Coupling agent functions as to improve the interaction between the silica fillers and elastomeric material as a matrix. Coupling agent in the form of light yellow transparent to yellow fluid with the specific gravity 1.080. The percentage of Chlorine content is less than 0.6 %. The specific name of coupling agent is not mentioned in this report due to the trade secret of the company.

### 3.1.6. Processing aid

#### 3.1.6.1. Ultra Flow

Ultra flow was traded by Performance Additive Subang Jaya. The percentage of ash content is around 11.5 to 14.0 % and the percentage of zinc content is maximum 10.5 %. It can stabilized free radical formation by improving reversion resistance and tear strength. The density is 1.1 g/cm³. Ultra flow presence in beige pastilles.

#### 3.1.6.2. Ultra Blend

Ultra blend has an appearance of black pastilles. It improved the homogeneity of polymer blends of different viscosities. It contained maximum 2 % of ash content with density 1.06 g/cm³.

### 3.1.7. Activator

Zinc oxide was supplied by Metoxide Malaysia Sdn. Bhd. Butterworth. It had a 99.5% minimum of purity with moisture 0.2 % maximum at 105℃. Zinc oxide form in odorless fine white powder. Stearic acid was supplied by Behn Meyer Chemical (M) Sdn. Bhd. from Subang Jaya. It contained 6.0 maximum of iodine value. Stearic acid also in the form of white to yellow powder.

### 3.1.8. Anti-ozonant

Anti-ozonant was supplied by company Jiang Su Sinorgchem Technology, China. It has a 96.5 % of purity. This chemical had an appearance of grey-brown. The ash content is low than 0.15 %.

### 3.1.9. Anti-Degradant

Anti-degradant was purchased from Luxchem Trading which in the form of grain and amber coloured. The softening point is 94.70℃ and 0.3% maximum of ash content.

### 3.1.10. Accelerator

Two types of accelerator that used in this experiment which are primary accelerator and secondary accelerator. The primary accelerator was supplied from Behn Meyer company. It is in grayish yellow with melting temperature minimum 98℃. The secondary accelerator was purchased from Sin Rubtech Consultancy Sdn. Bhd., Kuala Lumpur. The density of secondary accelerator 1.07 g/cm$^3$- 1.18 g/cm$^3$.

### 3.1.11. Sulphur

Sulphur is in the yellow powder with the 0.05 % maximum of the moisture. It has a density of 2.00 g/cm$^3$ and melting point between 114℃ to 122℃. Sulphur functions as a vulcanization agent in the rubber compounding.

### 3.1.12. Retarders

The retarders supplied from Changdae Ding Yuan Chem. Industrial Limited, China. It is in the form of white orpale yellow crystalline. It contains 0.1% maximum of ash content and 5 maximum of toluene insoluble.

## 3.2. Instruments

The type of instrument that used in this project shown in Table 3.1.

Table 3.1: List of instrument involved.

| Instrument | Model | Test/Process |
|---|---|---|
| Lab mixer | CL-BM16 | Mixing |
| Two roll mill | | Mixing |
| Electronic balance | FX 3000 | Weighing |
| Gotech Rheometer | GT-M2000 | Rheological Measurement |
| Mosanto Rheometer | Rheometer100 Mosanto | Rheological Measurement |
| Hot press | QLB-35X 2 | Vulcanisation |
| Gotech Testing Machine | AI-3000 | Tensile and Tear Test |
| Wallace Tester | L93/HLB 1 | Hardness Test |
| Shore A | L93/HLB2 | Hardness Test |
| U-Can Dynatex | UD-3500 | Carbon Black Dispersion Tester |
| Densimeter | MD-300S | Density |
| Din Abrasion Resistance Tester | GT7012D | Abrasion Tester |

## 3.3. Method

### 3.3.1. Sample Designation

The designation of the formulation in this project shown in Table 3.2.

Table 3.2: Designation of the formulation

| **Code** | **Designation** |
|---|---|
| S70 | NR/BR (70/30) |
| S80 | NR/BR (80/20) |
| N2 | CB N220 |
| N1 | CB N134 |
| 28/42 | phr of CB/Si |
| 30/44 | |
| 32/48 | |

### 3.3.2. Formulation

Table 3.3 representing the formulation by varying the phr NR/ BR, CB/Si and different type of the carbon black (N220 and N134). All the ingredients are weighed as Table 3.3.

Table 3.3: Formulation of different ratio of NR/BR, CB/Si and type of the carbon black (N220 and N134)

| **Ingredients** | **pphr** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | S70N2 28/42 | S70N2 30/44 | S70N2 32/48 | S80N2 28/42 | S80N2 30/44 | S80N2 32/48 | S70N1 28/42 | S70N1 30/44 | S70N1 32/48 | S80N1 28/42 | S80N1 30/44 | S80N1 32/48 |
| NR | 70 | 70 | 70 | 80 | 80 | 80 | 70 | 70 | 70 | 80 | 80 | 80 |
| BR | 30 | 30 | 30 | 20 | 20 | 20 | 30 | 30 | 30 | 20 | 20 | 20 |
| N220 | 28 | 30 | 32 | 28 | 30 | 32 | 28 | 30 | 32 | 28 | 30 | 32 |
| N134 | - | - | - | - | - | - | 42 | 44 | 48 | 42 | 44 | 48 |
| Silica | 42 | 44 | 48 | 42 | 44 | 48 | - | - | - | - | - | - |
| Processing Oil | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Coupling agent | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 |
| Ultra Flow | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Ultra Blend | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Zinc Oxide | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| Stearic Acid | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Anti-ozonant | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Anti-degredant | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Accelerator | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 |
| Accelerator | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| Sulphur | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Retarders | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| **Total** | **199** | **204** | **300** | **199** | **204** | **300** | **199** | **204** | **300** | **199** | **204** | **300** |

### 3.3.3. Mixing

All the experiment required two steps to compound the ingredient which is preparation of the master batch and final mixing in 1.6L lab-use intensive mixer as Figure 3.1 with the temperature at 50℃ and the cooling water at 30℃. After every mixing step, the compound was sheeted out by using two roll mill. The dump temperature was varied due to the mixer's fill factor and rotor speed. Table 3.4 showed the mixing procedures of the master batch and final mixing.

Table 3.4: Mixing Procedures

| Step 1 | |
|---|---|
| Time (sec) | Action |
| 0 | Ram up ; add rubbers ; processing aid ; anti-ozonant ; anti-degradant ; rubber processing oil |
| 60 | Ram down |
| 30 | Ram up ; carbon black ; silica ; coupling agent |
| 40 | Ram down |
| 2 | Ram up |
| 40 | Ram down |
| 10 | Ram up ; drop door open ; dump |
| Step 2 | |
| Time (sec) | Action |
| 0 | Ram up ; add 1/2 compound ; accelerators ; retarders ; sulphur |
| 30 | Ram down |
| 5 | Ram up ; add 1/2 compound |
| 40 | Ram down |
| 2 | Ram up |
| 40 | Ram down |
| 10 | Ram up ; drop door open ; dump |

Based on Table 3.4, the rubber, processing aid, anti-ozonant, anti-degredant and rubber processing oil were mixed for 60 sec and the ram up for 2 sec in between that time to make sure the rubber and other ingredients to mix well. Then, the carbon black and other ingredients was added 80 sec and the ram up for 2 sec in between. The purpose of the ram up for 2 sec is to release the gas that produced from the silica. Finally, the compound was dumped and sheeted out by using two roll mill. The compound was weighed and cooled at room temperature for 24 hours before the final mixing. For final mixing, the compound was added with sulphur, accelerator and retarders.

Figure 3.1: 1.6L lab-use intensive mixer

## 3.4. Cure Characterization

The cure characterization of the rubber compound was tested by using Mosanto Rheometer. The rubber compound was left for one hour in room temperature to stabilize the rubber compound. The Mosanto rheometer was set at 180°C with a torque range 50 (lb-in). The test time for the rubber compound was 5 minutes. The rheograph showed the minimum torque (ML), maximum torque (MH), scorch time ($ts_1$) and cure time ($t_{90}$).

## 3.5. Vulcanization

Vulcanization was carried out by using hot press. 2 sheets of rubber compound were formed and each sheet had 35 g of weight. 3 sample were prepared for the abrasion and each of the sample had 11g in a coin shape.  The mould was heated up to 150℃ and the cure time followed to the $t_{90}$ from the rheograph. The sample is squeezed into a preheat mould follow shape and mould was closed. Bumping is needed before mould is closed in order to remove the trapped air during compression.

## 3.6. Testing

### 3.6.1. Viscosity

This testing described for the Mooney viscosity. Mooney viscosity defined as shearing torque resisting rotation of a cylindrical metal disk embedded in rubber within a cylindrical cavity. The viscosity is depends on the molecular structure, molecular weight, and non-rubber constituents that may be present. This testing was determined by using a Monsanto Mooney Viscometer at 120℃. The preheat time was about 1 minute and 4 minutes for running time with rotation. This testing was based on ASTM D1646-04.

### 3.6.2. Tensile Test

The vulcanized compound was cut into 3 testing specimen in a dumbbell shape. The thickness of the 3 sample was measured by using thickness gauge. Three measurement was made which one at the center and one at each end of the reduced section. The average of the of thickness used in calculating the cross sectional area.

While, the width of the specimen was taken at the distance between the cutting edges of the die in the restricted section. Testing procedure is referred to ASTM D412 and Gotech Instron machine was used. The crossheads speed was 500 mm/min and the distance between the grip separation was 50mm. The tensile test can be determined the tensile strength, elongation at break % and the modulus.

### 3.6.3. Tear test

The vulcanized rubber was cut into three specimens with the angle shape. The thickness of the specimen was measured three places across the width of the specimen. The testing procedure is based on the ASTM D624. The crosshead speed for this test was 50 mm/min with the distance of the grip separation is 40 mm. The tear strength is given by the formula:

$$Ts = \frac{\mathrm{F}}{\mathrm{d}} \tag{2}$$

Ts - Tear strength
F - the maximum force, N
d – thickness of the test piece, mm

### 3.6.4. Hardness

The hardness test measures the penetration of a specified indentor into the material under specified conditions of force and time. The hardness test were tested according to ASTM D2240 by using durometer. The specimen was placed on the hard flat surface. The indentor for the instrument was pressed into the specimen. The hardness is read within one second of firm contact with the specimen. It is usually expressed in Shore A units.

### 3.6.5. Abrasion

The cylindrical test pieces of specifies dimension were prepared for this testing. The test pieces was tested under specified condition of contact pressure, sliding distance and travel speed of the test piece, rotational speed of the drum, and the degree of abrasiveness of abrasion sheet. The abrasion resistance index was evaluated by a cylinder abrader (Gotech Testing Machines, GT-7012-D) according to ASTM D5963-97a. The abrasion resistance index is calculated by using equation:

$$ARI = \frac{\Delta \mathrm{m} \times \mathrm{dt}}{\Delta \mathrm{mt} \times \mathrm{d}} \times 100 \qquad (3)$$

$\Delta \mathrm{m}$ − mass loss of standard rubber

dt − density of test rubber pieces

$\Delta \mathrm{mt}$ − mass of loss of test rubber pieces

d- density of standard rubber

### 3.6.6. Carbon Black Dispersion

Dispersion is calculated by measuring with a light microscope the percentage area covered by black agglomerates in microtomed section of the compound. Some of the physical properties of the compound influenced by the degree of the carbon black dispersion like abrasion and tensile strength. The testing is based on the ASTM D2663-95a. The classification of type of dispersion shown in Table 3.5.

Table 3.5: Classification of type of dispersion,%

| Dispersion, % | Classification |
|---|---|
| Above 99 | Very high |
| 97 to 99 | High |

| | |
|---|---|
| 95 to 97 | Intermediate |
| 92 to 95 | Low |
| Below 92 | Very low |

### 3.6.7. Swelling

The crosslink density of rubber vulcanisate can be determined by using swelling method based on ASTM D471. The specimen with dimension 30mm x 5mm x 2 mm was weighed and immerse in toluene at room temperature for 24 hours. Then, the specimen was removed from the toluene and was weighed. The crosslink density being estimated by using the Flory-Rehner equation.

$$-\{\ln(1 - v_r) + v_r + \chi v_r^2\} = \rho V_o M_c^{-1} v_r^{1/3} \tag{4}$$

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1. The effect of different ratio of CB/Si

### 4.1.1. Curing Characteristics

Table 4.1 summarizes the main curing properties of the studied rubber compounds that were determined from their cure curves. S70N228/42 represented for the ratio CB/Si (28/42), S70N230/44 for the ratio CB/Si (30/44) and S70N232/48 with the ratio CB/Si (32/48). Curing characteristics of the compound were measured at temperature 180℃ by using the Mosanto Rheometer.

Table 4.1: Cure characteristics in the different ratio of Carbon Black/Silica

| Type of the compound | S70N228/42 | S70N230/44 | S70N232/48 |
|---|---|---|---|
| Scorch time, $ts_1$, min:sec | 1:30 | 1:28 | 1:23 |
| Cure time, $tc_{90}$, min:sec | 3.44 | 3.38 | 3.34 |
| Minimum Torque, ML, dN.M | 11.82 | 13.33 | 12.20 |
| Maximum Torque, MH, dN.M | 31.35 | 33.61 | 33.84 |
| Δ(MH-ML), dN.M | 19.53 | 20.28 | 21.64 |

Based on Table 4.1, the scorch time and cure time is slightly decrease as the amount of silica increases. Scorch time, $ts_1$ refers to the premature vulcanization where the compound is partly vulcanized. In the present work, the $ts_1$ is more preferred in the company compared to the $ts_2$ due to the efficiency of the production. If the $ts_2$ are being used as a scorch time, the consumption of time to get the result will affect to the production. Meanwhile, the cure time is the time required during the vulcanization to reach the desired state of the cure.

S70N232/48 shows the shortest scorch and cure time while the S70N228/42 shows the longest scorch and cure time in Table 4.1. S70N232/48 has the shortest scorch and cure time due to the ratio of the silica amount is higher compared to the S70N230/44 and S70N228/42.

According to Ulfah et al. (2015), silica has a high density of the silanol groups on the surface. The ethoxy group from the coupling agent will react with the silanol group to form siloxane bond and reduce the chemical reactivity on the silica surface. The crosslink between the rubber and filler are formed when the sulfide group of the coupling agent bonded to the filler is dissociated and react to the rubber. The amount of zinc complex and the both combination of the accelerators trapped by silica surface contributes to the faster curing rates. Hence, the increase amount of silica gives the scorch time and cure time shorter.

There is some contradiction in article published by Choi et al. (2003). The authors stated that the cure time increase with increasing the silica content in the compound. This is due to the adsorption of curatives on the silica surface. Silica has a high density of the silanol groups on the silica surface where the cure accelerator is adsorbed by hydrogen bond. This leads to slow cure characteristics.

It is known that the minimum torque (ML) can be determined on the Moving Die Rheometer which gives the reading of the viscosity of the rubber compound. The value of the minimum torque at the S70N228/42 and S70N232/48 is lower compared to the S70N230/44. This showed that S70N228/42 and S70N232/48 has lower viscosity due to the intermingling of the carbon black and the silica particles which prevent the formation of the hydrogen bonds between the silanol groups of the rubber compound. The silica aggregate less and the filler disperse well in the rubber matrix and it causes low in viscosity. Thus, the decrease of the ML is due to the good filler dispersion.

S70N232/48 which has a higher carbon black and silica loading show the highest maximum torque which indicates the highest stiffness Silica has a number of hydroxyl groups on the surface which result in strong filler-filler interaction, it can aggregate tightly. Meanwhile, carbon black surface has some polar functional groups such as hydroxyl and carboxyl, but the quantity is very small. The filler-filler interaction of silica is much stronger than the carbon black. When filler networks in the stator meet the counterparts in the rotor, more shearing force are required to break the strong filler-filler interaction. These statement can be supported by Al-Hartomy et al. (2016), where the mixture with silica in the presence of the silane coupling agent has the higher viscosity. These silica will faced the agglomeration due to the Van der Waals forces. The formation of hydrogen bonds between the particles of the filler leads the stronger filler-filler interaction. Thus, the MH increase as the number of silica loading increase.

In addition, when the scorch time and cure time are decreases, the compound have experienced greater thermal history during mixing and result in the higher compound viscosities. The shear heating is increases once the silica loading is increased due to increase of compound viscosity (Rattanasom, 2007).

### 4.1.2. Viscosity Characteristics

Table 4.2 represents the effect of different ratio of CB/Si on the Mooney Viscosity. The result shows S70N230/44 has the higher value of Mooney viscosity once the CB/Si (30/44) is added. The viscosity noticeably influences the Mooney viscosity. The Mooney viscosity is depends on the number of crosslinking that form in the compound and also interaction between matrix and filler. S70N230/44 contains higher in formation of rubber bond in the compound. Difficulties in flow results in higher Mooney viscosity.

Based on Table 4.2, S70N230/44 has the highest value compared to the S70N228/42 and S70N232/48. This can be explained by the effect on carbon black. Carbon black surface has some polar functional groups such as hydroxyl, carboxyl and ketone. Carbon black has weak filler-filler interaction compared to the silica which it can easier to fill rubber bonds. Thus, S70N230/44 has higher value of Mooney viscosity due to the filler-rubber interaction is strong.

Table 4.2: Mooney Viscosity at different ratio of CB/Si

| Type of the compound | Mooney Viscosity, MU |
|---|---|
| S70N228/42 | 57.6 |
| S70N230/44 | 61.6 |
| S70N232/48 | 56.9 |

### 4.1.3. Swelling Characteristics

The crosslink density of the elastomers can be determined by swelling test. Crosslink density is the number of crosslink per unit volume. Percentage of Swelling, equilibrium volume fraction of rubber and crosslink density of different ratio CB/Si shows in Table 4.3, Table 4.4 and

Table 4.5.

Table 4.3 shows as the number of CB/Si increases, the percentage of swelling is decreases. Table 4.4 and 4.5 show as the higher CB/Si the equilibrium volume fraction and crosslink density are increase. The decrease in filler-rubber interaction cause the reduction in swelling as silica loading increases. Silica has strong filler-filler interaction and hence decrease in filler-rubber interaction.

Table 4.3: Percentage of swelling of the compound in the different ratio of CB/Si

| Type of the compound | Percentage of Swelling (%) |
|---|---|
| S70N228/42 | 50.89 |
| S70N230/44 | 49.58 |
| S70N232/48 | 48.77 |

Table 4.4: Equilibrium volume fraction of rubber in the different ratio of CB/Si

| Type of the compound | Equilibrium volume fraction of rubber, Vr |
|---|---|
| S70N228/42 | 0.1853 |
| S70N230/44 | 0.1933 |
| S70N232/48 | 0.1982 |

Table 4.5: Crosslink density of the compound in the different ratio of CB/Si

| Type of the compound | Crosslink density ($x10^{-5}$) g/mol |
|---|---|
| S70N228/42 | 3.7146 |
| S70N230/44 | 4.0120 |
| S70N232/48 | 4.215 |

S70N228/42 has low crosslink density where it absorb more solvent between the rubber chains. The high mobility of rubber chains realigns to maximize the free volume in molecular network. The compound with low crosslink density will be more flexible due to the formation of free volume. Meanwhile, S70N232/48 has the higher crosslink density where the degree of swelling is low. The small amount of solvent diffuse in the rubber due to the less volume is available for solvent diffusion activity.

The crosslinking has a big influence in the mechanical properties of the compounds. The crosslinking will creating a branched molecule and broader the molecular distribution where it will influence the molecular weight. The input energy is stored elastically in the chains when elastomer is deformed by external force. At high crosslink levels, chains become restricted and tight network is incapable of dissipating much energy. Crosslink must be high enough to prevent failure by viscous flow but low enough to avoid brittle fracture.

### 4.1.4. Tensile Properties

#### 4.1.4.1. Tensile Strength

The tensile strength of different ratio carbon black and silica are showed in the Figure 4.1. The tensile strength is related to the resistance of the material to overcome from break. The tensile strength decreases as the ratio of the carbon black increases. S70N228/42 with the ratio of carbon black 28 phr is slightly higher compared to the S70N230/44 and S70N232/48.

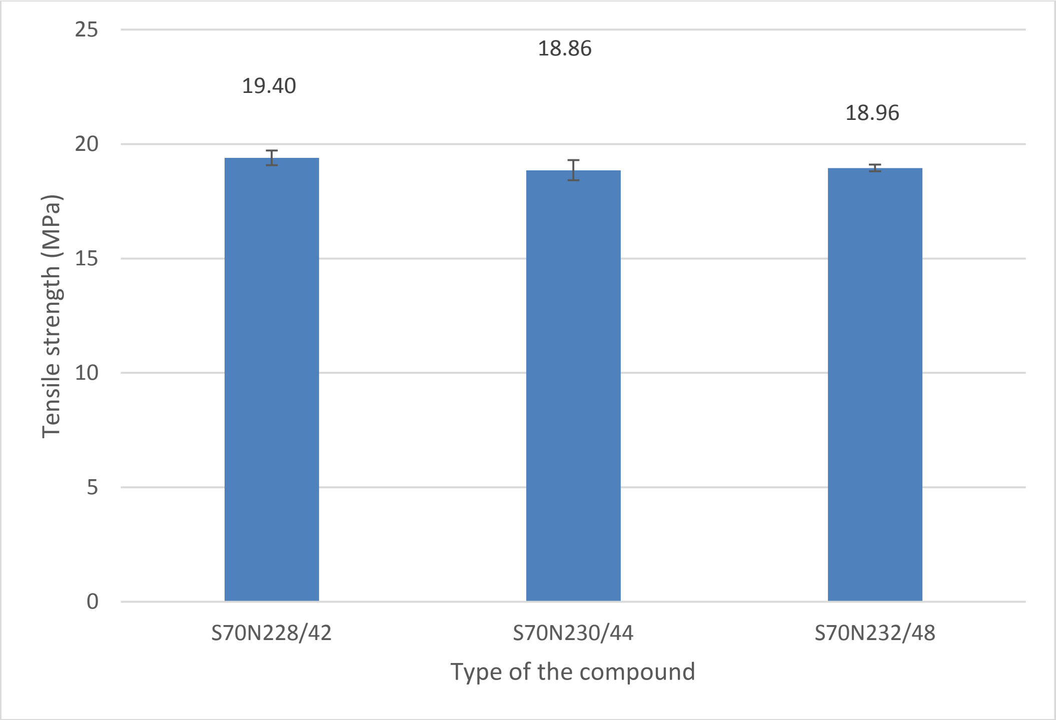


Figure 4.1: Tensile strength in a different ratio of CB/Si

The quality of the carbon black is depends on the degree of dispersion achieve inside the rubber matrix. As the value of the carbon black increases, the tendency of the agglomeration to be happen also increases. The carbon black aggregates and re-agglomerate during vulcanization and cause the ability to wet of the carbon black with the polymer is reduced. In general, the increasing of the carbon black will initiate the onset of the tensile failure. (Dai et. al, 2007)

In addition, as the value of silica loading increases, the tendency of silica to agglomerate also increase and resulted in low filler dispersion. The coupling agent that being used in this project are remained constant which is 4.2 phr and 10 phr even as the number of silica loading is increased. The intermolecular hydrogen bond between hydroxyl groups on the silica surface are very strong and the silica will aggregate tightly. The value of coupling agent is not enough to make the surface treatment of the silica.

Theoretically, the compound with the higher crosslink has higher value in tensile strength. The compound is stiff and increase in hardness. It can overcome the stress that applied on the surface.

#### 4.1.4.2. Elongation at break

Figure 4.2 shows the percentage of elongation at break different ratio of carbon black and silica. S70N228/42 has the highest value of the percentage of elongation at break which is 598.33% followed by S70N230/44 which elongate to 652.36% and S70N232/48 elongate to 598.33%. The percentage of the elongation at break slightly decrease as the number of CB/Si loading increase.

S70N228/42 consist of low crosslink density which contributes to the higher of free volume where the molecule has more spaces to move. The rubber chain becomes more flexible and can realign to the direction of tension applied. S70N232/48 has a low percentage elongation at break due to the formation of the physical bond between the filler particles which contribute to the high crosslink density. The polymer matrix are stiffening by the filler. The mobility of the molecule is restricted and unable to dissipate much energy. It will exhibit the fracture at low elongation. The compound become stiff and easy to break which contributes to the low percentage of elongation at break. Thus, as the number of silica increases, the percentage of elongation at break is decreases.

These statement can be supported by Evans (2001) which stated that the high crosslink density will restrict the movement of the rubber chains. The fillers were restricted the rotation of the chain segment and alignment of the rubber chains. Hence, the mobility and flexibility of the rubber chain is decrease.

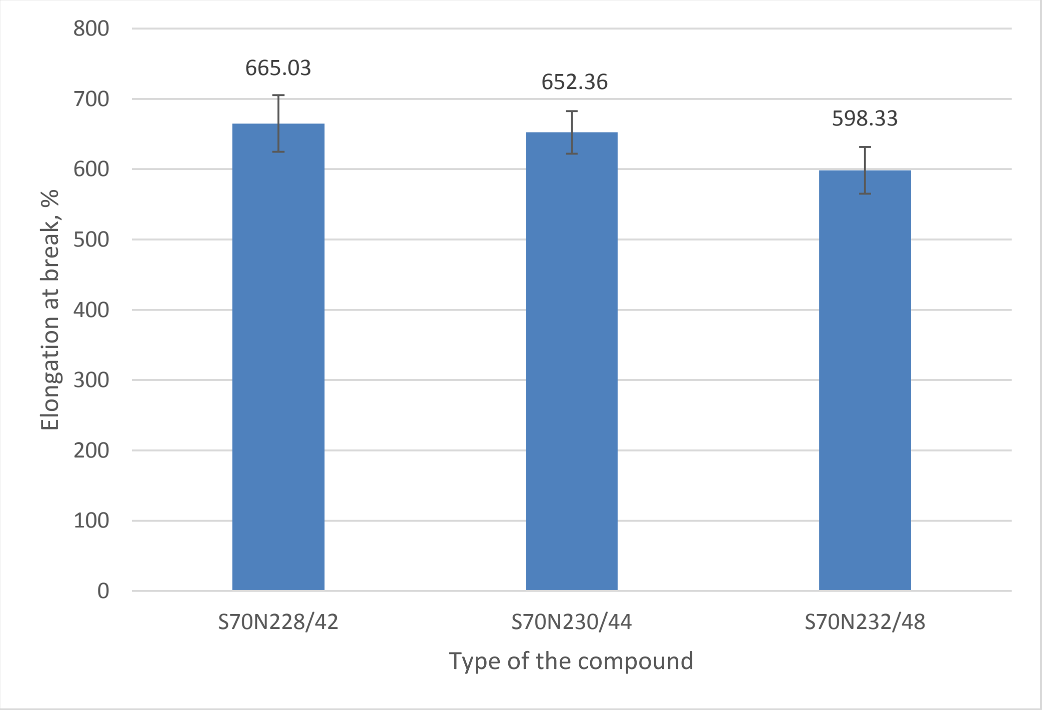


Figure 4.2: Percentage of elongation at break at different ratio of NR/BR

#### 4.1.4.3. Modulus

Figure 4.3 and Figure 4.4 show the modulus $M_{100}$ and $M_{300}$. As the value of carbon black and silica increases, the $M_{100}$ and $M_{300}$ also increases. S70N232/48 has the highest value of M100 and M300 followed by S70N230/44 and S70N228/42.

S70N228/42 has low in modulus due to poor interaction between rubber and filler. As ratio of filler increases, the formation of the occluded rubber may be happened. The formation of the occluded rubber where the aggregates or agglomerates of active fillers can form filler-filler network by self -association in the rubber matrix and trap some part of rubber in the void of structure. The filler aggregates with occluded rubber act as large filler particles. The trapped rubber does not contribute to the elastic behaviour of the matrix at lower strain. Thus, the $M_{100}$ and $M_{300}$ decrease as the number of CB/Si loading decreases.

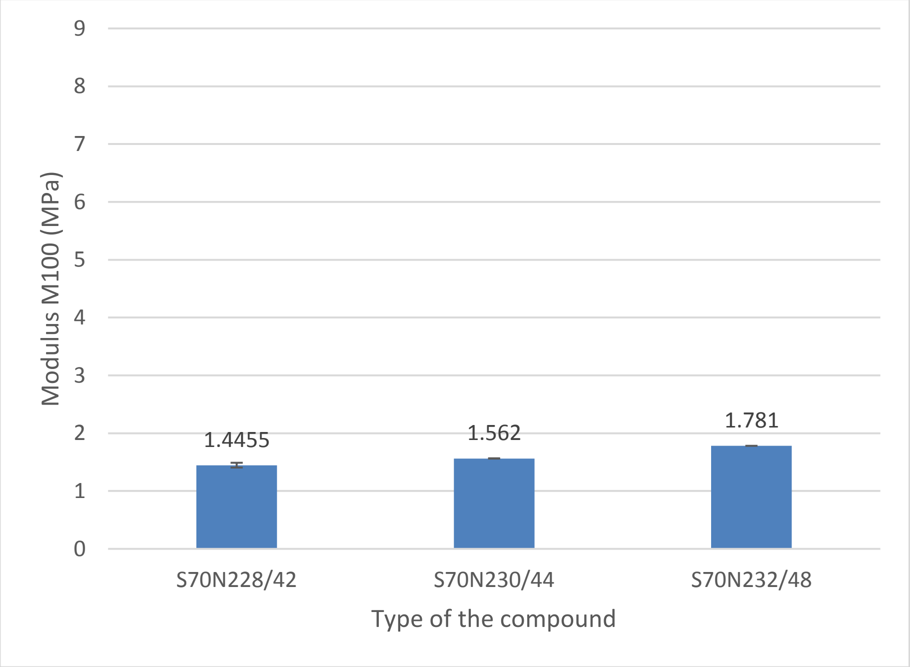


Figure 4.3: Modulus M100 with different ratio of CB/Si

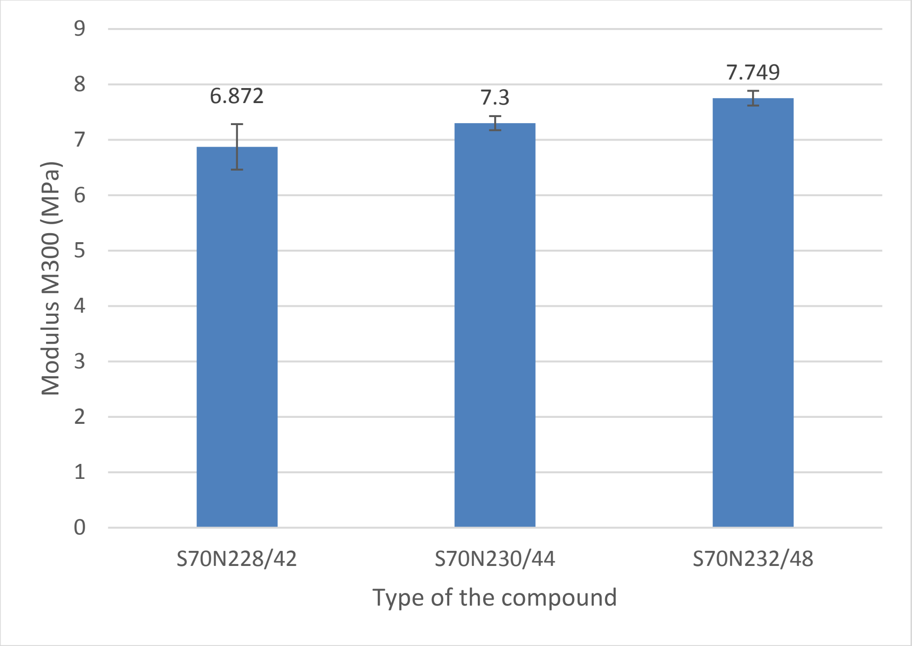


Figure 4.4: Modulus $M_{300}$ with different ratio of CB/Si

### 4.1.5. Tear Resistance

The trends for influence of different ratio of carbon black and silica loading on tear strength are shown in Figure 4.5. The highest value of tear strength are observed at S70N232/48. The tear strength increases by 4% with increase in carbon black to 32phr and silica to 48phr.

The increase in tear strength might be due to the good dispersion between the filler and rubber. The filler and rubber will form a crosslink in the compound. The good interaction between the rubber and filler contribute to the sample difficult to tear off. The matrix transfer the stress to the filler. The crosslink needs more forces to break the interaction between the bonds.

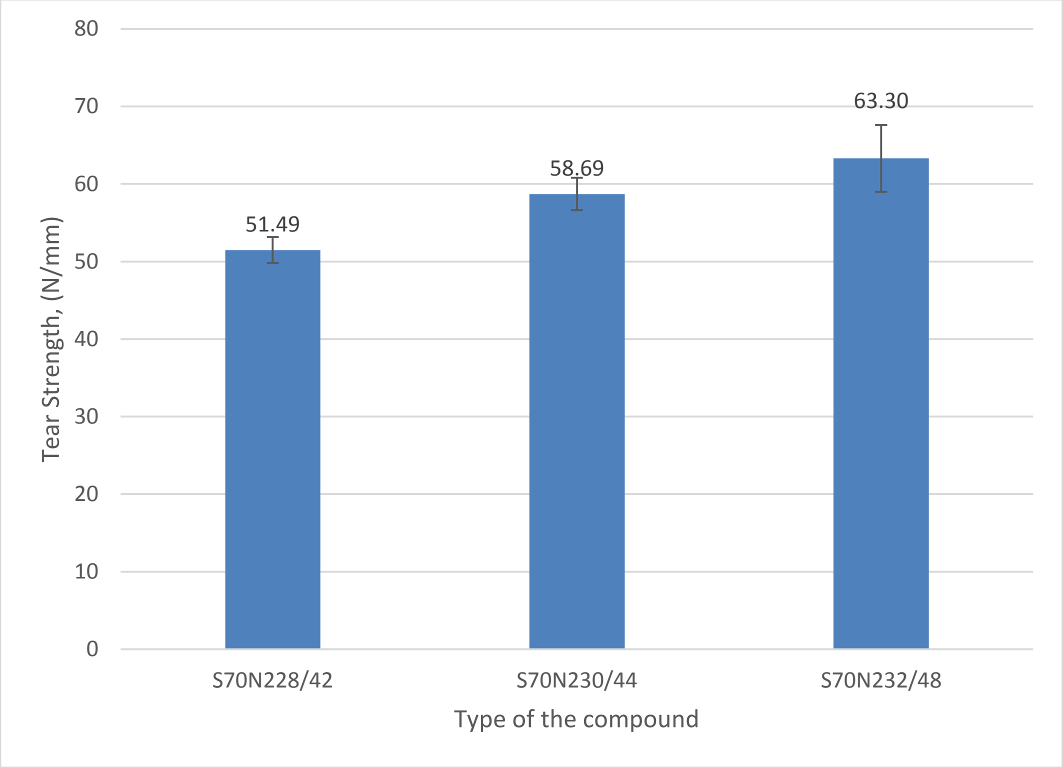


Figure 4.5: Tear strength with different ratio of CB/Si

### 4.1.6. Hardness

Table 4.6 shows the variation of the hardness with different carbon black and silica content which measured by using Shore A. It can be seen that the value of hardness do not change substantially with varying the ratio of the two fillers.

Table 4.6: Hardness with different ratio of CB/Si

| Type of the compound | Hardness (Shore A) |
|---|---|
| S70N228/42 | 62 |
| S70N230/44 | 65 |
| S70N232/48 | 64 |

S70N230/44 shows slightly higher value of hardness which is 65 Shore A due to the distance of the silica aggregates becomes close enough to induce the strong interaction between aggregate giving rise to an additional network which called as filler-filler network. This filler-filler network result in a sharp increase in hardness. This also can be explained due to the crosslink density which is increase. According to Costa et al. (2001), once the filler particles are introduced to the rubber, the elasticity of the rubber chains is reduced which resulting in more rigid vulcanisates. This also can be observed by the decrease in elongation at break.

The result that was obtained are also supported by Ulfah et al., 2012 which studied about influence of carbon black and silica filler on the rheological and mechanical properties of Natural Rubber Compound. The researcher mentioned that as a number of silica loading in the rubber are sufficiently high loading, the hardness of the rubber compound is increased. The silica filler contributes ½ hardness of the rubber compound while the medium carbon black contribute 1/3 hardness of the compound. When both of the filler are being used, it will contribute in hardness value. The higher ratio CB/Si decrease contribution of silica, results in smaller of hardness value.

### 4.1.7. Abrasion

Another important parameter obtained in abrasion resistance index test where it measured by using different ratio of carbon black and silica as shown in Figure 4.6. As can be seen S70N232/48 has the higher abrasion resistance index compared to S70N228/42 and S70230/44. S70N232/48 increased 1.17% of abrasion resistance index compared to the S70N230/44.

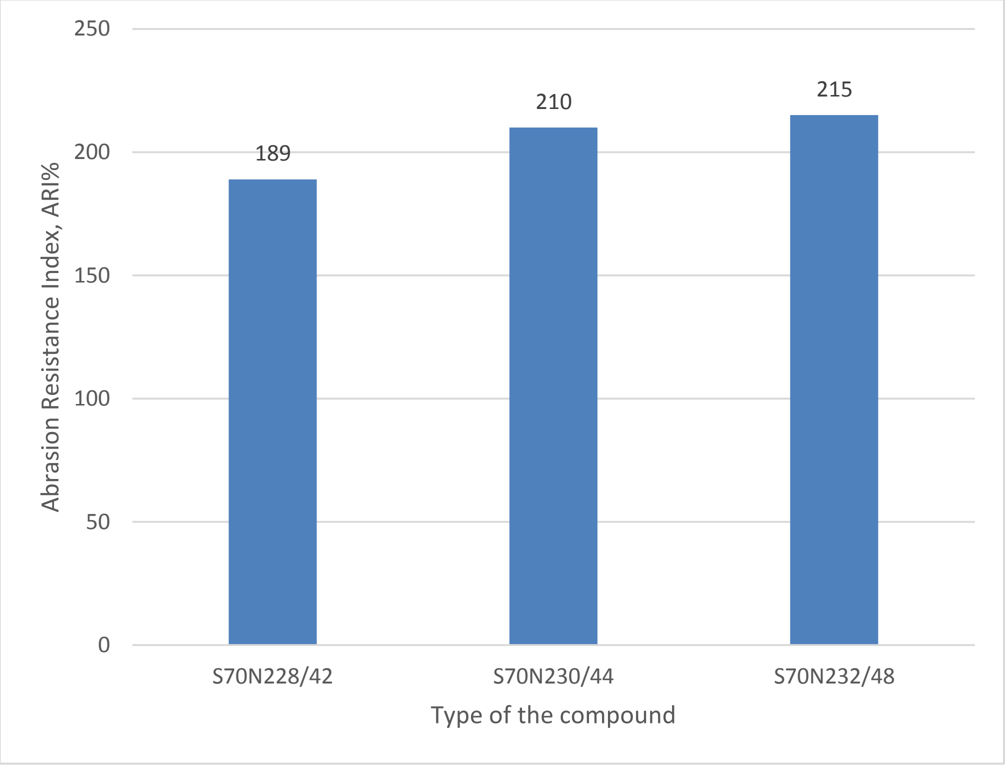


Figure 4.6: Abrasion Resistance Index with different ratio of CB/Si

Based on the result, the higher the value of the carbon black and silica content give the higher abrasion resistance. The carbon black and silica particles mixed together and cause the formation of hydrogen bonds between the silanol groups of silica particles. Thus, the aggregation of silica particles is less and the filler disperses better in the rubber matrix. This contributes to a stronger polymer-filler interaction determined by the presence of the coupling agent.

S70N228/42 has the lowest abrasion resistance index due to the crosslink that form between rubber chain and filler is decrease. The hardness of the compound also decreases which tends to wear easily. Oleiwi et al.,(2013) stated that the key parameter in determining the amount of material removal is depends on the hardness of the composites by sliding the abrasives on a solid surface result in volume removal and wear mechanism.

According to the Rattanasom et al.(2007) obtained that as the abrasion resistance tends to decrease when silica content is more than 10phr. Higher modulus and lower friction coefficient give the vulcanizates with better abrasion resistance. A vulcanizate with good filler dispersion need to have a better property than that with poor dispersion. Thus, poor silica dispersion or strong silica-silica interaction is be another reason for dramatic reduction in abrasion resistance at high silica content.

## 4.2. Effect different ratio NR/BR on physical mechanical properties of tire tread for off road application

### 4.2.1. Mooney Viscosity

Figure 4.7 shows the Mooney viscosity at different ratio of NR/BR. S70N232/48 represents for the NR/BR (70/30) whereas S80N232/48 represents for NR/BR (80/20). S80N232/48 has the highest value of viscosity compared to the S70N232/48.

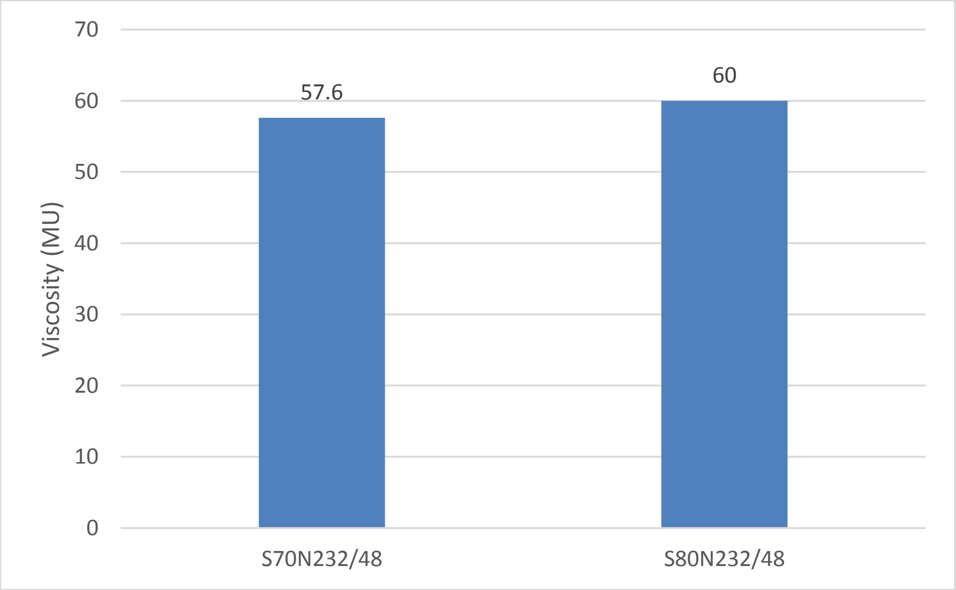


Figure 4.7: Mooney Viscosity at different ratio of NR/BR

Mooney viscosity operate by rubber compounds get heated and slowly the viscosity decrease due to the temperature and torque starts rising due to the formation crosslink bonds between the rubber molecules. Based on Figure 4.7, Mooney viscosity of S80N232/48 is higher compared to the S70N232/48 may due to the structure of the compound. S80N232/48 might be formed a long chain and has more formation of crosslinking. Thus, S80N232/48 indicates that it difficult to process compared to the S70N232/48.

In addition, the factors affecting the rubber materials' initial fluidity are the type of the rubber, its composition, processing procedures. In industry, the fluidity of green rubber is evaluated by using Mooney viscosity. There is some contradiction in article published by Chiu et. al (2007). The authors reported that the NR has a lower Mooney viscosity, and its initial fluidity is superior to BR. NR/BR blends have less Mooney viscosity as NR content is increased which results in the lower viscosity of NR/BR blends.

### 4.2.2. Curing Characteristics

In Table 4.7, it can be seen that the value for the curing characteristics do not change significantly with changing the quantitative ratio between two tested rubber.

As seen in Table 4.7, the value of scorch time and cure time of S80N228/42 is almost same with S70N228/42. This may due to the quantity of the natural rubber. As a number of natural rubber content increase, it needs longer time to make a crosslinking between rubber and other ingredients.

The ratio of the NR will influence the cure time. As a ratio of NR increase, the cure time should be shorter. The result obtained agreed with previous work carried out by Bebb (1976). This is due to the activating effect of the methyl group of the natural rubber. Natural rubber contains the allylic or hydrogen atom are the most reactive which contribute to the faster in curing time. The higher ratio of NR will give a higher number of hydrogen bond. Thus, higher number of hydrogen bond gives a shorter curing time.

Table 4.7: Curing Characteristics in different ratio of NR/BR

| Type of the compound | S70N232/48 | S80N232/48 |
|---|---|---|
| Scorch time, ts1, min:sec | 1.23 | 1:30 |
| Cure time, tc90, min:sec | 3.34 | 3.38 |
| Minimum Torque, ML, dN.M | 12.20 | 9.05 |
| Maximum Torque, MH, dN.M | 33.84 | 27.59 |
| Δ(MH-ML), dN.M | 21.64 | 18.54 |

This also in agreement with similar research by Chough and Chang (1995) which stated that the reactivity of the hydrogen in a carbon chains become higher in order of primary< secondary<tertiary carbon due to the difference stabilization of the corresponding radicals via hy-perconjugation. Hydrogens of allyl are much reactive that of tertiary carbon due to the resonance stabilization. Natural rubber have many allylic hydrogens which shown in Figure 4.8, sulfur radicals can react with the allylic hydrogen much easier than any hydrogens in rubber molecules. Therefore, the vulcanization rate depends upon the number of allylic hydrogens.

The delta torque is the difference of the maximum torque and the minimum torque. The delta torque is directly proportional to the state of cure or total crosslink density. S70N232/48 has the higher value of delta torque due to the higher formation of crosslink in the compound. The increase of crosslink resulting in higher torque to make mobilize the chain segments between crosslink. This statement can be supported by the evidence in the Table 4.9.

### 4.2.3. Swelling Characteristics

Table 4.8,Table 4.9 and Table 4.10 show the swelling characteristics at different ratio of NR and BR. Based on the tables, the value for the percentage of swelling, equilibrium volume fraction and crosslink density is not significantly effect by different ratio of NR/BR. S80N232/48 is slightly higher for percentage of swelling and lower at the equilibrium volume of fraction and crosslink density.

Table 4.8: Percentage of swelling at different ratio of NR/BR

| Type of the compound | Percentage of Swelling (%) |
|---|---|
| S70N232/48 | 48.77 |
| S80N232/48 | 48.87 |

Table 4.9: Equilibrium volume fraction at different ratio of NR/BR

| Type of the compound | Equilibrium volume fraction of rubber, Vr |
|---|---|
| S70N232/48 | 0.1982 |
| S80N232/48 | 0.1977 |

Table 4.10: Crosslink density of the compound in the different ratio of NR/BR

| Type of the compound | Crosslink density ($x10^{-5}$) g/mol |
|---|---|
| S70N232/48 | 4.215 |
| S80N232/48 | 4.166 |

Normally, the percentage of swelling is inversely proportional to the volume fraction of rubber and crosslink density. The compound that has a good interaction between natural rubber matrix and silica particles because of the differences in polarity. The rubber with strong polarity showed a good interaction with silica can improved the restriction extensibility of the rubber chains and made the diffusion of oil into the voids become difficult. In addition, the degree of crosslink density of rubber vuulcanizated indicates in physical and mechanical properties. Hence, the compound that has low percentage of swelling due to the crosslinking that form between filler and rubber in the compound.

### 4.2.4. Tensile Properties

#### 4.2.4.1. Tensile Strength

The tensile properties as mentioned in Figure 4.8 were measured using Gotech Testing Machine. It can be seen contribution of the higher natural rubber content has an influence on tensile properties.

The higher tensile strength was shown by S80N232/48 which due to strain induced crystallization. Different chemical structures of NR and BR contributes to the properties of the compounds. During vulcanization, NR had more reactive site to form crosslinks which were more reactive to improve tensile strength. The polymer network of NR allows the elasticity and flexibility to be combined with crystallization-induced strength and toughness when stretched. The increasing of the NR and decreasing of the BR content will contributes to the higher tensile strength due to the properties of the NR. When the molecular chains are stretched under stress, the non-oriented molecular chains arranged straight which results in strain crystallization. Thus, increasing of NR gives a higher tensile strength.

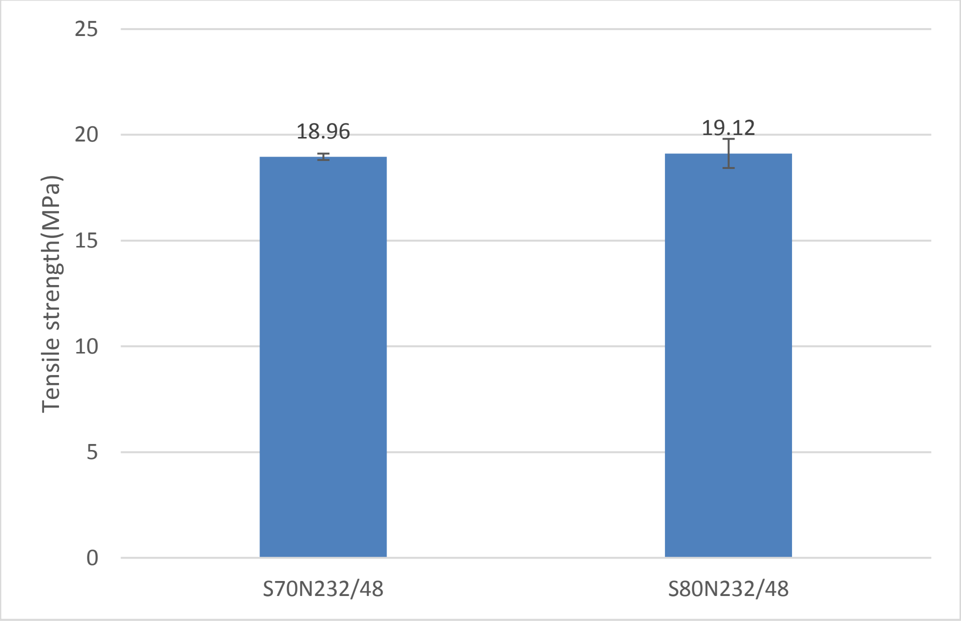


Figure 4.8: Tensile strength at different ratio of NR/BR

#### 4.2.4.2. Elongation at break

Figure 4.9 shows the percentage of elongation at break of S80N228/42 is higher compared to the S70N228/42. It was increase by 5% at the ratio NR/BR 80/20 (S80N232/42).

S70N232/48 has low percentage of the elongation at break due to formation of the crosslink in the compound. The higher formation of the crosslink make the chain motion become restricted where the tight network is unable to dissipate much energy. Hence, S70N232/48 faced a brittle fracture at low elongation. However, S80N232/48 are more flexible and can realign parallel to the direction of tension applied. The crosslink density in S80N232/48 is low and it may have more free volume. The tendency of the rubber chain to realign is increase and resulted to the higher elongation at break.

The mechanical properties of the NR including tensile strength and elongation at break are clearly superior to those of BR. This statement also supported by Chiu and Tsai (2005). While NR being stretched by applying stress across the arranged direction of its molecular chains, the molecular chains would develop an oriented arrangement under stress. This will contributes in improving the tensile strength.

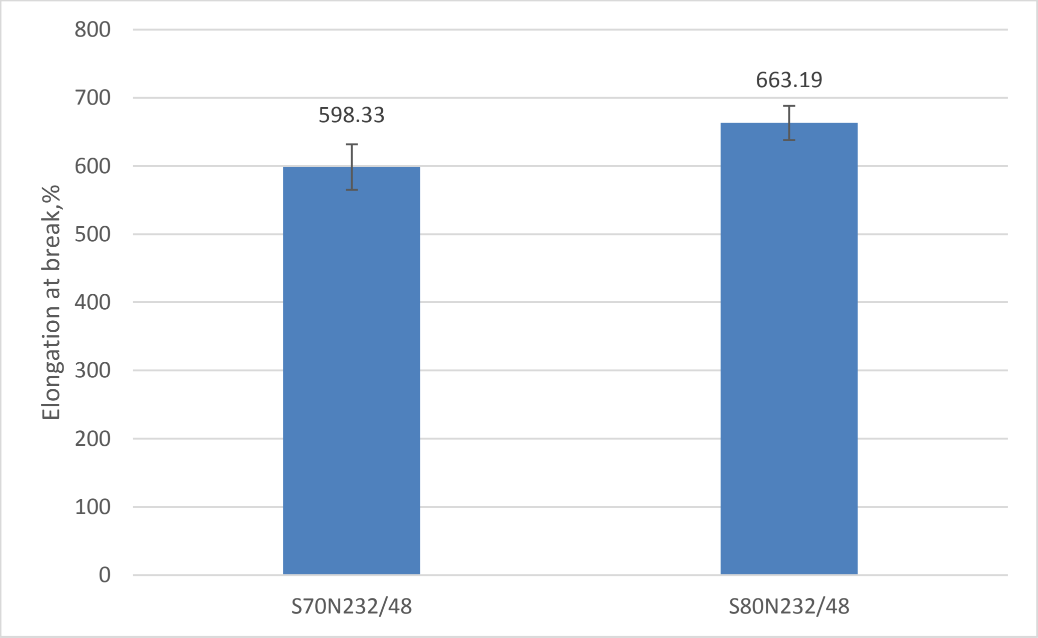


Figure 4.9: Elongation at break at different ratio of NR/BR

#### 4.2.4.3. Modulus

Figure 4.10 and Figure 4.11 represent M100 and M300 for different ratio of NR/BR. S70N232/48 has a higher M100 and M300 compared to the S80232/48. The NR/BR is more compatible in S70N232/48 compared to the S80N232/48. In NR/BR blends, with an NR content that is higher that of BR, the domain of BR is distributed into NR. NR has the properties of strain crystallization, when its molecular chains are stretched under stress, the non-oriented molecular chains will arranged straight. Thus, the blending of NR/BR improve the tensile modulus.

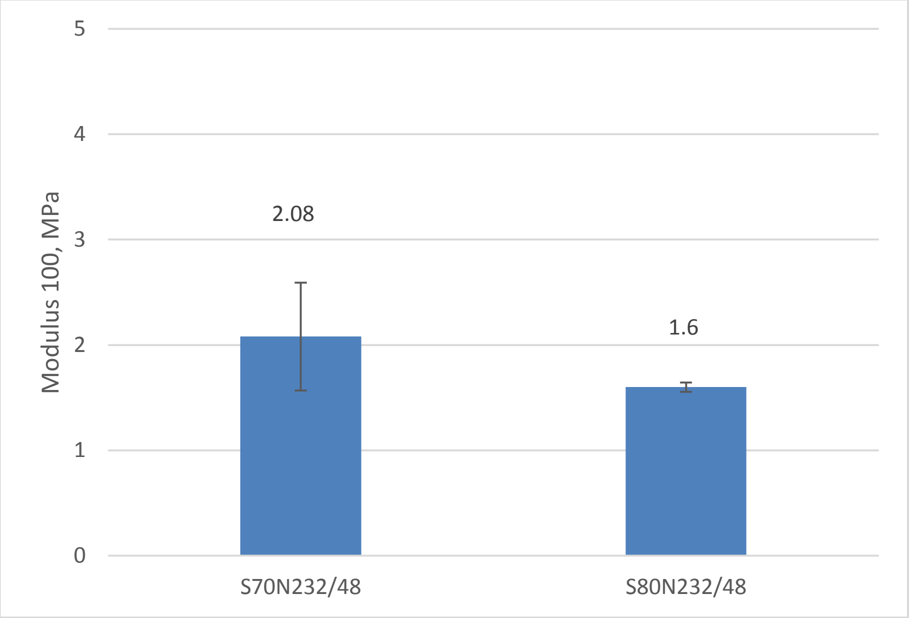


Figure 4.10: M100 at different ratio of NR/BR

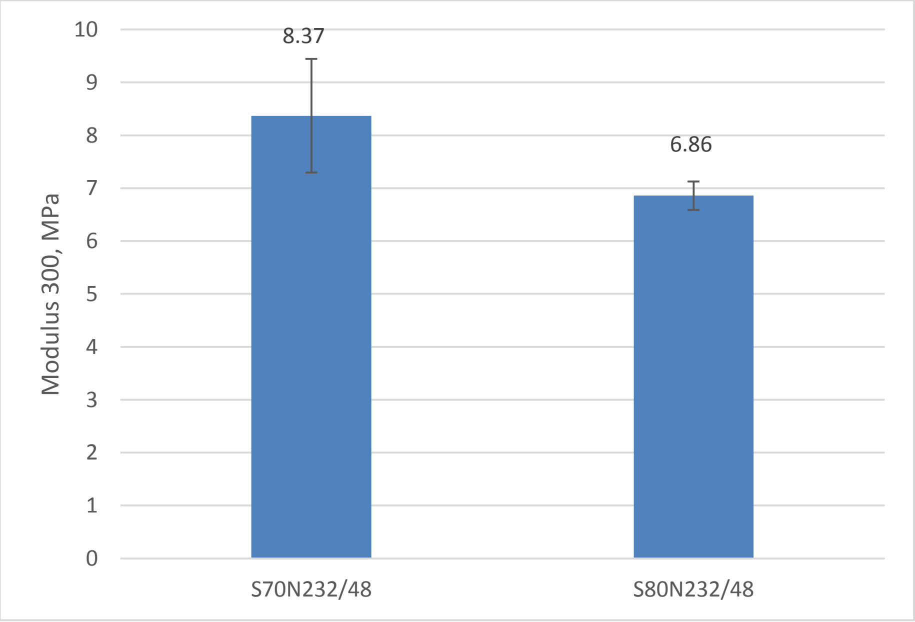


Figure 4.11: M300 at different ratio of NR/BR

### 4.2.5. Tear Strength

Figure 4.12 presents the result of tear strength of different ratio of NR/BR. It can be seen that the tear strength increased with higher natural rubber loading.

Factors affecting tear strength include the content of the carbon black, chemical structure of the rubber itself and fillers. The tearing behaviour is influenced by the viscoelastic properties of the polymer. There is close relationship between increase of tear energy and strain crystallization. This indicates that the natural rubber tends to crystallize due to its high structural regularity. The crystallization gives natural rubber resistance to cutting, tearing and abrasion.

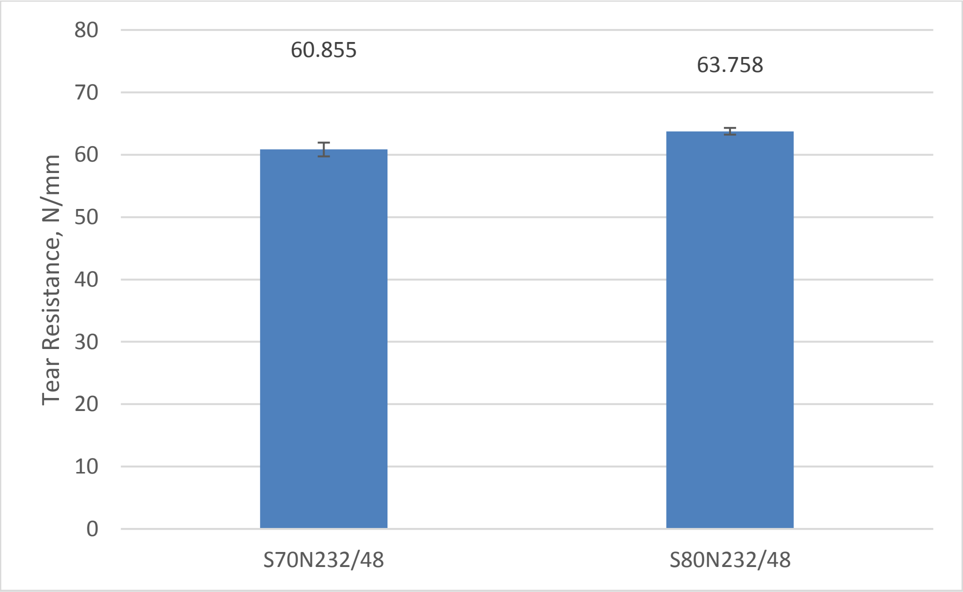


Figure 4.12: Tear Resistance with different ratio of NR/BR

### 4.2.6. Abrasion

Abrasion is refer to a process of wear which there is displacement of material from a surface during relative motion against sharp projections. Table 4.11 shows the different ratio of NR/BR results for the abrasion resistance index. It can be seen in the

Table 4.11 that the addition of the natural rubber to the compound results in decrease of abrasion resistance index value.

Table 4.11: Abrasion Resistance Index with different ratio of NR/BR

| **Type of the compound** | **S70N228/42** | **S80N228/42** |
|---|---|---|
| Abrasion Resistance Index | 189 | 144 |

Based on Table 4.11, increment in abrasion resistance index could be attributed to coefficient friction. Mathew and De (1983) reported that the coefficient friction of the BR is lower than that of NR. The coefficient friction of the blend NR/BR blends may be assumed to decrease with increase in the proportion of BR. As the coefficient friction decrease, the abrasion resistance increase with increase in BR loading. Therefore, S70N228/42 with higher BR loading has higher abrasion resistance compared to the S80N228/42.

Similar findings have been observed in other studies. According to Kim et al. (1999) in Abrasion of Selected Rubber Compounds with a Din Abrader, the wear rates of the BR is lower compared to the NR for carbon black-filled. A linear relation between wear rate and the frictional force are obtained.

## 4.3. Effect different type of carbon black (N220 and N134) on properties of tire tread for off road application

### 4.3.1. Curing Characteristics

The effect of carbon black –rubber interactions on cure rate was determined in this testing. In this Table 4.12 shows the cure characteristics result for the different type of carbon black N220 and N134 in NR/BR (80/20) and NR/BR(70/30) by using rheometer. N228 refers to the type of carbon black (CB) N220. N128 refers to the type of carbon black (CB) 134.

Table 4.12: Cure characteristics for different type of carbon black (N220 and N134) in ratio of NR/BR (80/20) and NR/BR(70/30)

| Type of the compound | S70N228/42 | S70N128/42 | S80N228/42 | S80N128/42 |
|---|---|---|---|---|
| Scorch time, ts1, min:sec | 1:30 | 1:28 | 1:30 | 1:16 |
| Cure time, tc90, min:sec | 3.44 | 3.45 | 3.48 | 3.16 |
| Minimum Torque, ML, dN.M | 11.82 | 8.95 | 7.94 | 11.07 |
| Maximum Torque, MH, dN.M | 31.35 | 31.06 | 26.57 | 32.68 |
| ∆(MH-ML), dN.M | 19.55 | 22.11 | 18.63 | 21.61 |

Based on Table 4.12 for ratio NR/BR (80/20) shows the minimum torque (ML) and maximum torque (MH) of N134 is higher compared to the N220. This is due to the particle size of N134 is lower compared to the N228 and gives a surface area of the N134 is higher. The cure time for both type of carbon black is similar. According to Li et al., (2008), ML increases with the increasing surface area of carbon black as a number of rubber chains immobilized on the carbon black surfaces increases. N134 has the surface area 131m²/g, meanwhile N220 has a surface area 120m²/g. The higher size of the filler, the surface area will be decrease which contribute to ineffective reinforcement. The surface area of the carbon black gives an important role for influencing the ML of NR/BR and type of the carbon black.

ΔM is the curing characteristic of the cured rubbers. The chemical crosslinking forms between rubber and the vulcanizing agent. The crosslinking process can be form from the chemical bonding of rubbers with functional groups on the carbon black. The crosslinking can be formed with appropriate temperature, zinc oxide and sulphur donor. N134 has the large surface area gives the content of the sulphur on the N134 is higher compared to the N220 which allow the increase in crosslinking.

For NR/BR (70/30), the minimum torque (ML) of N220 is higher compared to the N134 where it does not gives a same result in Table 4.12. This may be due to the ratio of the rubber as previously discussed in 4.2.2.

### 4.3.2. Carbon Black Dispersion

Table 4.13 shows the percentage of the carbon black in different type of the carbon black. The percentage of the carbon black dispersion of N134 is lower about 2-4%. Theoretically, the total surface area of the N134 is higher compared to the N220. As the higher surface area, the carbon black disperse well in the rubber matrix. The properties of the compound increased as function of the carbon black act as a reinforcing agent. Thus, the higher total surface area, the carbon black dispersion also increases.

Table 4.13: Percentage of the carbon black dispersion in different type of the CB.

| NR/BR loading | Type of the compound | CB dispersion, % |
|---|---|---|
| 80/20 | S80N228/42 | 96.13 |
| | S80N128/42 | 92.15 |
| 70/30 | S70N228/42 | 87.41 |
| | S70N128/42 | 81.82 |

### 4.3.3. Hardness

Evidence for hardness was provided by hardness test by using a Shore A as shown in Table 4.14. It shows the different type of CB in NR/BR 80/20 and ratio NR/BR 70/30. N134 higher in hardness compared to the N220 for both figures.

Table 4.14: Percentage of the carbon black dispersion in different type of the CB.

| NR/BR loading | Type of the compound | Hardness, Shore A |
|---|---|---|
| 80/20 | S80N228/42 | 57 |
| | S80N128/42 | 68 |
| 70/30 | S70N228/42 | 58 |
| | S70N128/42 | 65 |

Based on the table, N134 has the higher hardness compared to the N220 due to the structure of the filler. Filler structure describes the number of particles that fuse to form aggregate where it measured by dibutyl phthalate (DBP) absorption value. If many prime particles considerable branching and chaining are aggregates, the shape will be more complex and more voids volume are formed. The polymer can be filled to these void. Thus, N134 which has higher structure and the increase in hardness was expected. The higher surface area of the CB forms a rigid shell between the rubber chains and carbon black. The rubber chains will entangle with the CB and aggregates to form a rigid shell. The rigid shell causes the enhancement of the hardness. (Li et al., 2008).

### 4.3.4. Tensile Properties

#### 4.3.4.1. Elongation at break

Table 4.15 shows the value of the elongation at break at different type of carbon black. N228 represents for CB N220 and N128 represents the CB N134. N134 has lower elongation at break compared to the N220.

The larger surface of N134 contributes to the higher irregularity and more bound rubber. The possibility of immobilization of rubber molecules on the surface is increase dramatically. The compound change from soft to stiff and the mobility of polymer chains decrease. The flexibility of the rubber matrix also decreased. Thus, N134 tends to shorten the elongation at break compared to the N220.

Table 4.15: Elongation at break of different type of carbon black in NR/BR 70/30 and NR/BR 80/20

| NR/BR loading | Type of the compound | Elongation at break, % |
|---|---|---|
| 80/20 | S80N228/42 | 634.95 |
| | S80N128/42 | 620.65 |
| 70/30 | S70N228/42 | 686.64 |
| | S70N128/42 | 611.60 |

### 4.3.5. Tensile Strength and modulus

The effect of different type of carbon black on tensile strength, modulus 100% and 300% show in the Table 4.16. The tensile strength, modulus 100% and modulus 300% in NR/BR 80/20 does not show the obvious effect on the different type of carbon black. Meanwhile, the N134 shows the higher value of tensile strength, modulus 100% and modulus 300% compared to N220.

Table 4.16: Tensile strength, M100, M300 of different type of carbon black in NR/BR 70/30 and NR/BR 80/200

| NR/BR loading | Type of the compound | Tensile Strength, MPa | Modulus100,MPa | Modulus300,MPa |
|---|---|---|---|---|
| 80/20 | S80N228/42 | 21.73 | 2.03 | 8.28 |
| | S80N128/42 | 21.21 | 1.97 | 8.22 |
| 70/30 | S70N228/42 | 19.22 | 1.45 | 6.25 |
| | S70N128/42 | 21.41 | 1.81 | 8.41 |

When a distance between aggregates is taken into account, filler networking affected by the surface area of the carbon black. The inter-aggregate distance at constant filler loading inversely proportional to the surface area. The higher surface area of the carbon black, the inter-aggregate distance is shorter. It has a strong attraction between fillers which it contributes to the higher tensile strength and modulus. The compound need higher energy to break the formation of the bond. In addition, the rubber which fills the void space within each aggregate is occluded and shielded from deformation and acts as part of filler rather than as part of the deformable matrix. The effective volume of filler is increased and enhance the strength. S70N128/42 has higher surface area contributes to the higher tensile strength and modulus.

### 4.3.6. Abrasion Resistance

The abrasion resistance of different type of carbon black in NR/BR is shown in Table 4.17. The abrasion resistance N134 is higher compared to the N220. The surface area of N134 is higher allows more crosslink between filler and rubber where increase the hardness. The stiffness of the rubber gives the rubber to loss in abrasion is decrease. In contrast N220 has lower abrasion resistance index compare to N134 due to the less formation of crosslink.

Table 4.17: Percentage of the abrasion resistance index in different type of the CB.

| NR/BR loading | Type of the compound | Abrasion Resistance Index |
|---|---|---|
| 80/20 | S80N228/42 | 144 |
| | S80N128/42 | 201 |
| 70/30 | S70N228/42 | 189 |
| | S70N128/42 | 221 |

# CHAPTER 5

# CONCLUSIONS AND FUTURE STUDIES

## 5.1. Conclusion

In summary, this project has presented studies on the effect of different ratio NR/BR, CB/Si and types of carbon black on physical properties of tire tread for off road application. It believed that that combination of the fillers and rubbers gives a good impact to the process of the compound. Furthermore, the optimum ratio on different ratio of carbon black/silica was studied to attain optimum properties. Two types of ratio been formed which are ratio of carbon black (CB)/silica (Si) and ratio of natural rubber (NR)/butadiene rubber (BR). Another type of investigation was carried out by different type of carbon black which are N134 and N220.

Curing characteristics was carried out to study the cure characteristic on different ratio of fillers, rubber and different types of carbon black. Swelling test, hardness, tear test and abrasion resistance was carried out to study the physical properties. The swelling test was carried out to proven the trend of tensile strength and modulus. Besides that, carbon black dispersion tester to check the efficiency of the carbon black to distribute evenly. The aggregates that have a high structure have a higher degree of branching and chain. The degree of agglomeration of carbon black affects the final properties of filled elastomers.

Mooney viscosity was conducted to study the effect on ratio of CB/Si and NR/BR S70N230 showed the highest viscosity on different ratio CB/Si while for different ratio of NR/BR, S80N232/48 showed the highest value of Mooney viscosity. The higher viscosity indicates good interaction between filler and matrix.

In general, S70N232/48 indicates as optimum ratio of physical properties with different ratio of CB/Si because it has higher value on tear strength and abrasion resistance index. Meanwhile, S70N228/42 be an optimum ratio for the tensile strength. The different ratio of CB/Si has a little significant effect on hardness.

In addition, the cure characteristics does not give so much different in different ratio of NR/BR. it also found that S70N232/42 exhibits the higher crosslink density which contributes to the higher in abrasion resistance index only. S80N232/42 has higher in tensile strength and tear strength due to the higher ratio of natural rubber compared to the butadiene rubber.

The size of the carbon black has significant effect on the properties. N134 indicates the shorter curing time, higher in hardness, abrasion resistance and tensile properties. The filler with higher total surface area indicates an excellent in physical and mechanical properties.

S70N130/44 has good in properties like tensile strength, tear strength, abrasion resistance and hardness.

## 5.2. Future Studies

After conducting this research, some improvements are required to improve the properties of the compound:

1. Varying the type of the rubber and more ratio of the rubber are introduced. Less ratio of NR/BR not strongly enough to prove the mechanical properties
2. Trying another type of rubber and processing oil in order to make the filler to incorporate with rubber efficiently.

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