

**INVESTIGATION ON THE PROPERTIES OF
RUBBER VULCANIZATES FOR ANTI-
VIBRATION APPLICATIONS: EFFECTS OF
DIFFERENT RUBBER AND PARTICLE SIZE OF
CARBON BLACK**

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UNIVERSITI SAINS MALAYSIA

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CARBON BLACK**

by

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LIST OF SYMBOLS

E'	Storage modulus
E''	Loss modulus
K_d	Dynamic stiffness
K_s	Static stiffness
M_{100}	Stress at modulus 100% strain
M_H	Maximum torque
M_L	Minimum torque
P_o	Wallace plasticity
$\tan \delta$	Tangent delta/ loss tangent
t_{c90}	Time of 90% cure
t_{s2}	Scorch time

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CBS	N-cyclohexyl-2-benzothiozole sulfonamide
CR	Chloroprene Rubber
DCPD	Dicyclopentadiene
DMA	Dynamic mechanical analysis
ENB	Ethylidene norbornene
EPDM	Ethylene Propylene Diene Monomer
JIS	Japanese Industrial Standard
MU	Mooney unit
NBR	Nitrile Butadiene Rubber
NR	Natural Rubber
phr	Part per hundred rubber
PRI	Plasticity retention index
RSS	Ribbed Smoked Sheet
SBR	Styrene Butadiene Rubber
Semi-EV	Semi Efficient Vulcanization
SMR	Standard Malaysian Rubber
TMTD	Tetramethylthiuram disulfide
VNB	Vinyl norbonene

**KAJIAN TERHADAP SIFAT-SIFAT VULKANIZAT GETAH BAGI
APLIKASI ANTI-GEARAN: KESAN PERBEZAAN JENIS-JENIS GETAH
DAN SAIZ ZARAH HITAM KARBON**

ABSTRAK

Kebanyakan industri automotif menghadapi cabaran besar untuk memenuhi permintaan yang berubah-ubah dalam keperluan spesifikasi, prestasi dan ketahanan bahan. Dalam merekabentuk getah bagi aplikasi anti-getaran, sifat mekanikal dan dinamik adalah diperlukan untuk mendapat sifat redaman yang bagus dan menghapuskan taksiran getaran yang terlalu tinggi pada kekerapan frekuensi resonansi sistem. Kajian ini memberi tumpuan kepada kesan jenis-jenis getah (tidak terisi) SMR 60 CV, SMR L, RSS, SBR, NBR, CR dan EPDM dan saiz zarah hitam karbon (terisi) N220, N330, N550, N774 dan N990 dengan getah SMR 60 CV terhadap sifat-sifat mekanikal dan dinamik. Ciri permatangan, sifat mekanikal (ujian tegangan, set mampatan, fatig), dan sifat dinamik (kekakuan statik dan dinamik, delta tangen) telah dianalisis. Keputusan ciri permatangan menunjukkan hubung kait antara sebatian yang tidak terisi dengan tenaga ikatan getah. Masa permatangan yang lebih panjang menunjukkan masa yang lebih lama diambil bagi memutuskan tenaga ikatan yang tinggi dalam rangkaian getah. Sementara itu, untuk sebatian terisi, kadar permatangan meningkat secara berterusan dengan pengurangan permukaan hitam karbon disebabkan oleh had penyebaran dan pergerakan rangkaian yang rendah. Kesan sifat dinamik oleh teori Payne yang dipengaruhi oleh struktur bon getah memberi nilai kekakuan dinamik yang tinggi disebabkan oleh interaksi getah-getah yang baik. Untuk sebatian yang terisi, luas permukaan karbon hitam yang lebih tinggi memberi hasil kekakuan dinamik yang lebih tinggi disebabkan peningkatan dalam interaksi getah-pengisi dan pengisi-pengisi. Oleh itu, kelikatkenyalan getah dan saiz zarah

hitam karbon adalah penting dalam merekabentuk formulasi sebatian untuk aplikasi getah anti-getaran.

INVESTIGATION ON THE PROPERTIES OF RUBBER VULCANIZATES FOR ANTI-VIBRATION APPLICATIONS: EFFECTS OF DIFFERENT RUBBER AND PARTICLE SIZE OF CARBON BLACK

ABSTRACT

Most of the automotive industry facing a major challenge to meet the changing demands in material specifications, performance and durability requirements. In designing rubber for anti-vibration application, the mechanical and dynamic properties are required in order to obtain good damping properties and eliminate the overestimation of the vibration of the resonant frequency of the system. This research work focused on the effect of different rubber types (unfilled) SMR 60 CV, SMR L, RSS, SBR, NBR, CR and EPDM and particle size of carbon black (filled) N220, N330, N550, N774 and N990 with SMR 60 CV rubber on the mechanical and dynamic properties. The curing characteristic, mechanical properties (tensile test, compression set, fatigue), and dynamic properties (static and dynamic stiffness, tan delta) were analyzed. The curing characteristic results show the relationship of unfilled compounds with rubber bond energy. The longer cure time indicates longer times to break the higher bond energy of the rubber chain. Meanwhile, for the filled compound, the cure rates gradually increased with the lower carbon black surface area due to the diffusion limitation and lower chain mobility. The dynamic properties results based on the Payne effect theory influenced by the rubber bond structure that gave higher value of dynamic stiffness due to the better rubber-rubber interaction. For the filled compound, higher surface area of carbon black gave higher dynamic stiffness due to increase in rubber-filler and filler-filler interactions. Thus, the rubber viscoelasticity and carbon black particle size play a big role and a major concern in designing the compound formulation for rubber anti-vibration applications.

CHAPTER 1

INTRODUCTION

1.1 Types of Rubber

Rubber is known as the elastic material that can stretch and shrink. Rubber is classified into two group which are natural rubber (NR) and synthetic rubber. NR commonly known as the rubber that harvested from rubber tree called as *Hevea Brasiliensis* tree. Bristow & Sears (1987) has classified NR based on the levels and ranges of ash, nitrogen, dirt content, volatile matter, plasticity (P_o) and resistance to plasticity index (PRI) properties of rubber bale itself. Meanwhile, the synthetic rubber is an artificial polymer that is made from various petroleum-based. Synthetic rubber can be made to meet the numerous ranges of physical and chemical properties by adjusting its monomer proportion. Brandrup (1999) stated that there are many types of synthetic rubber which depending on the chemical structure of monomer in polymer. These different types of synthetic rubber will gave different properties of the end product.

1.2 Types of Filler

Filler is one of the main ingredients in rubber compound formulation besides raw rubber. It plays an important role in improving the dynamic performance of rubber products. Filler are classified into two general types: reinforcement and non-reinforcement filler. For the reinforcing filler, commonly used is carbon black. As mentioned by Voll & Kleinschmit (2002), commercial carbon black is in the form of solid carbon that classified by its particles size, aggregate size, shape, porosity and surface chemistry. It is usually contains more than 95% pure carbon with minimal quantities of oxygen, hydrogen and nitrogen. Many new ideas, theories, practices,

phenomena, and observations on mechanical properties especially on the filler which improved the dynamic stress-strain response have been presented (Litvinov et al., 2011; Frampton, 2009; Han, 2007). This indicates that the filler influence the dynamic properties of the rubber compound.

1.3 Rubber in Automotive Engineering Application

The automotive or also known as the automobile industry is directly related to the rubber industry. There are various components or parts made of rubber used in automobiles including the high-technology adhesive and sealant products required for the aerospace and other demanding applications in automobiles and automotive industries. Besides that, wheel or tire used in automobiles is also made of rubber. In fact, about 75% of the rubber produced in the world is used in the production of tires (Wang et al. 2018; Chandrasekaran, 2007). In addition, the airbag in vehicles which acts as a cushion during of collision also made from rubber. There are also included the products for dust covers and bumpers which protects the car from external damage. One of most critical rubber product is mainly related to the dynamic application such anti-vibration component used for shock absorption (Kurna et al., 2017; Zhou et al., 2016; Oshima et al., 2007).

An anti-vibration component from rubber based is widely used with the main objectives are to eliminate harmful vibration, reduce noise and absorb shock (Sun et al., 2015; Ishikawa et al., 1980). Rubber is used as anti-vibration based on good absorbing vibration which reduces the effect of the running engine, ensuring smooth humming for automotive anti-vibration components. Previous work by Jung and Kim (2018) and Snowdon (1979) mentioned that the high internal isolating properties of rubber contribute as anti-vibration components. Some examples of anti-

vibration components for automotive application are; rubber bushing, damper, engine mounting, exhaust hanger and others. There are several commonly used rubbers for anti-vibration application including natural rubber (NR), chloroprene rubber (CR), styrene butadiene rubber (SBR), ethylene propylene diene monomer (EPDM) (Phu & Nguyen, 2017 ; Li, 2009; Lewitzke & Lee, 2001).

1.4 Problem Statement

Majority of the rubber industry facing the major challenges and changes to meet the changing demands of the auto industry in order to meet the material specifications, performance and durability requirements. The manufacture of rubber automotive components is a major sector in the rubber industry. Generally, vibrations are normally associated with automotive vehicle applications. It is conceived as unwanted dynamic motions and great effort is made to reduce these motions to improve comfort for passengers and goods together with increased the vehicle component durability (Sjoberg, 2002). The most common way of reducing unwanted vibrations at a receiving structure in between the source and receiver, to either reflect the vibration energy by significantly dissipate or changing the impedance by inducing additional damping.

The dynamic motion in anti-vibration application is correlated to the rubber compound dynamic properties as it responded to the periodic forces applied during application which do not cause failure. The dynamic properties of anti-vibration components refer to the viscoelasticity properties of the rubber compound. Different types of rubbers contribute different viscoelastic properties. By selecting a right type of rubber can produce a good anti-vibration component as it refers to the compound

stiffness and viscoelastic properties (Sjoberg, 2002). The dynamic properties of rubber compounds also contributed from the type of carbon black.

Wang (1998) also stated that the effect of different carbon black fillers on the dynamic properties of a given rubber and cure system, filler networks and strength, are the main parameters to govern the behavior of the filled rubber. The thermodynamic and kinetic of carbon black filler network formation is related to filler-filler, rubber-filler, as well as rubber-rubber interactions that also known as the Payne effect theory. The effect of carbon black grades characteristics is also correlated to dynamic properties with processing conditions and additives. The rubber-filler interaction is not only affected by filler but also the characteristics of rubber such as chemical composition, chain microstructure including molecular weight and molecular weight distribution, configuration, stereo-regularity, monomer unit distribution and sequence, and their functionality also need to be considered (Nicholson et al., 2000). All of these have a substantial influence on the physical and/or chemical interactions of rubbers with other additives and carbon black filler surface area, as well as on the interaction between polymer molecules themselves. These would impact not only the carbon black network formation but also the viscoelastic response of the rubber matrix. In addition, the rubber network structure which was formed during vulcanization and characterized by crosslink density, crosslink structure, and chain modification, is equally important in contributing to the overall dynamic properties of the filled rubber.

In automotive engineering application, rubber is an efficient material to be used as anti-vibration component due to its properties. However, designing a right rubber formulation to meet a critical product specification such as dynamic and

damping properties were difficult. Although there were many previous research studies on the effect of rubber and carbon black types, those studies only limited to the general mechanical properties and less works reported on static and dynamic stiffness for JIS K 6394, N₂ type. Besides that, the influences of the stiffness test of rubber compound towards noise and vibration also become a concern. Due to the limitation of study on dynamic properties in designing rubber anti-vibration, this research work is conducted to study the effect of rubber types and carbon black grades on dynamic properties for rubber anti-vibration application.

1.5 Research Objectives

The objectives of this research work include;

- i. To study the effect of different types of rubber on cure characteristics, mechanical and dynamic properties of rubber compounds.
- ii. To investigate the effect of particle size of carbon black on cure characteristics, mechanical and dynamic properties of filled NR (SMR 60 CV) compounds.

1.6 Thesis Outline

This thesis contains five chapters with each chapter providing essential information regarding the topic of interest.

- **Chapter 1** introduces the research study subject. It includes a brief introduction regarding the research study background, the problem statement, the research objectives and the thesis outline.
- **Chapter 2** comprises the previous published and studied literature review regarding to the research study.

- **Chapter 3** contains important information regarding the material specification, the equipment, the experimental procedures and process flow with include the testing standard use for this research work.
- **Chapter 4** contains the results and discussion for the study of the effects of different rubber and particle size of carbon black on the cure characteristics, mechanical and dynamic properties.
- **Chapter 5** summarizes the conclusion of research based on the research objectives and also mentions some suggestion for further research in this research scope area.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In order to produce a useful rubber end product, rubbers as a base are mixed together with other suitable additives. Usually, the 'phr' unit is used in the formulation as 'parts per hundred rubber' which means the parts by weight of an ingredient per hundred parts by weight of rubber. Rubber is known as the materials that give elastic properties to the end product. These materials essentially have long flexible chain-like molecules knowing as polymers, which the elasticity and polymers have led to the alternative name as elastomers. Gupta et al. (2014) demonstrate that rubbers are characterized by the ability to undergo large reversible deformation under influence of external deformation forces which also known as the hysteresis loops. Researchers have studied the elasticity of rubber that depends on the structure and molecular weight of deformed rubber and also on external conditions of deformation for example rubber can achieve 100 % up to 1000 % at low stress. Generally, there are two major classifications of rubber; natural rubber and synthetic rubber (Sindhu & Anantharaman, 2002; Pokrovky et al., 1998)

2.1.1 Natural Rubber (NR)

Natural rubber is the only non-synthetic elastomer which widely used. It is obtained by coagulation of milk-like liquid knowns as the latex from a *Hevea brasiliensis* tree. Kohjiya & Ikeda (2014) stated that NR is based on the chemical structure of polyisoprene (refer to Figure 2.1). There are two types of structure of polyisoprene based on the position of methylene (-CH₂-) group attached. Generally, NR is available in three basic types: technically specified rubbers, visually inspected

rubbers and specialty rubbers. There are six basic types of coagulated technical specified NR reported by The American Society for Testing and Materials (ASTM), which is processed and compacted into-35 Kg block (bale) (ASTM D2227-96) used tabulated in Table 2.1 (Mark et al. 2013). Basically two constant-viscosity (CV) Standard Malaysian Rubber grades are available, SMR CV50 and SMR CV60. However, only SMR CV60 type being analyzed in this research study.

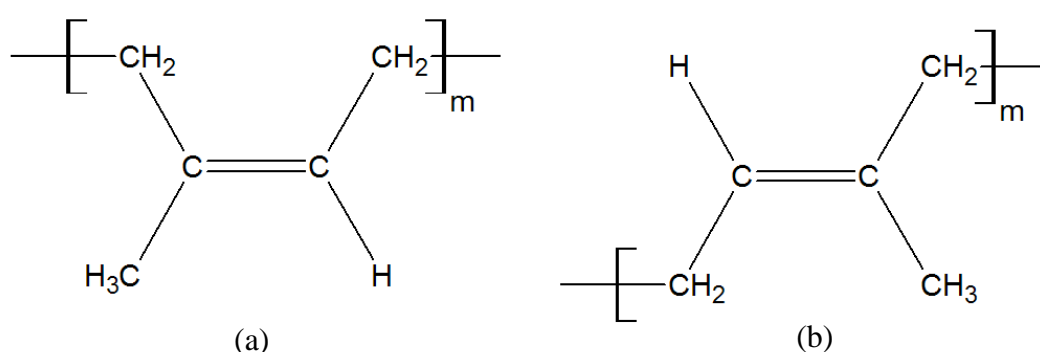


Figure 2.1 Polyisoprene chemical structures (a) cis-1,4-polyisoprene, (b) trans-1,4-polyisoprene (Kohjiya & Ikeda, 2014).

The second category NR which been studied in this research is grading by visual inspection. Rubber Manufacturers Association defines eight types of rubber covered in this category one of it is Ribbed Smoked Sheet (RSS). It is a coagulated sheet of latex that undergoes the process of drying and smoking (Mark et al., 2013). The third category of NR are the specialty materials, which include liquid low molecular weight rubber, methyl methacrylate grafted polymers, oil-extended natural rubber, deproteinized NR (DPNR), epoxidized NR (ENR), and superior processing NR.

Table 2.1 Specification for Technically Graded NR (Mark et al., 2013).

Property	Rubber Grade	
	L	CV
Dirt (% maximum)	0.050	0.050
Ash (% maximum)	0.60	0.60
Volatile matter (%)	0.80	0.80
Nitrogen (%)	0.60	0.60
Plasticity	30	-
Plasticity retention index	60	60
Mooney viscosity (MU)	-	60

More recent studies have confirmed that NR is highly resilient due to the hysteretic properties, little heat buildup during flexing, which suitable for shock and dynamic load requirements. The thermal degradation in vibration absorbing devices is caused by the heat buildup. However, NR also has its shortcomings, such as poor resistance to ozone, high temperatures, weathering, oxidation, oils and concentrated acids and bases (Gupta et al., 2014; Dick, 2001). The higher tensile strength of NR was attributed by the ability to strain-induced crystallization during stretching. As highlighted by Persson et al. (2005) when NR undergoes tension mode, the amorphous chain turns into a semicrystalline material as depicted in Figure 2.2. These crystallites segments are highly oriented along the pulling direction. The increase in tensile strength of NR is due to the crystallites segments acting like filler or crosslinks. There is a consensus among researchers that the crystallization of NR tremendously elevates the tensile strength (Toki et al., 2000; Treloar, 1975; Flory, 1947).

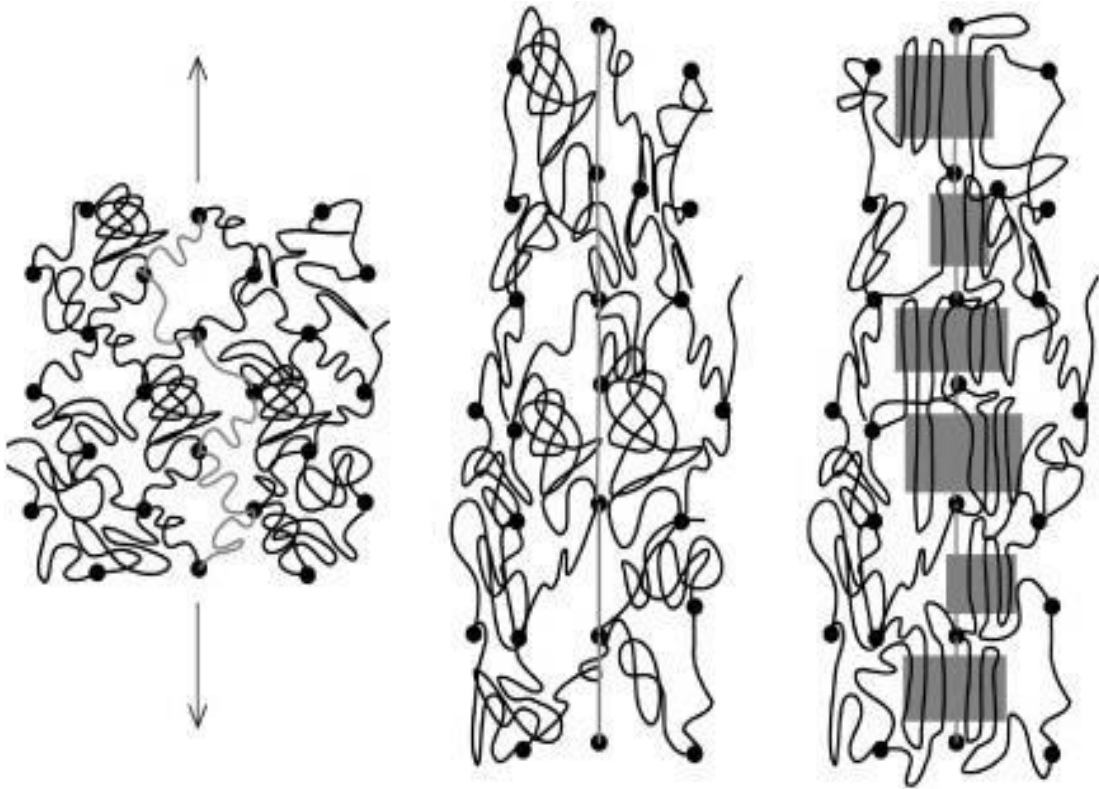


Figure 2.2 The strain-induced crystallization process of NR when undergo tensile test (Persson et al., 2005).

2.1.2 Synthetic Rubber

Unlike NR, the synthetic rubbers are artificial elastomers. These are mainly polymers synthesized from petroleum by-products. Generally, the synthetic rubbers are often produced by means of the reaction of the polymer chain. The great part of them is achieved by the chain polyreaction, namely; radical, or ionic, or by polymerization and copolymerization; emulsion, solution or suspension (Matador, 2007). Various proportions can be used to polymerize or copolymerize the synthetic rubber to produce a high range of mechanical and chemical properties products. The past decade has seen the increasingly rapid development of synthetic rubber in the automotive industry, for example, anti-vibration part, tires, sealant, hoses and many more (Threadingham et al., 2000).

2.1.2 (a) Styrene Butadiene Rubber (SBR)

Styrene butadiene rubbers (SBR) is the most commonly used synthetic rubber. It is the copolymer of styrene and butadiene (refer to Figure 2.3). Generally, its properties are mainly influenced by micro and macrostructure of the polymer chain and also by styrene/butadiene ratio content. The arrangement of styrene and butadiene units can be a random, partially-block or block character. Increasing the styrene content lead to an increase in glass transition temperature (T_g) as the hardness of SBR increases. As highlighted by Gupta et al. (2014) the dynamic properties decrease when styrene monomers increase while increased in hardness is observed.

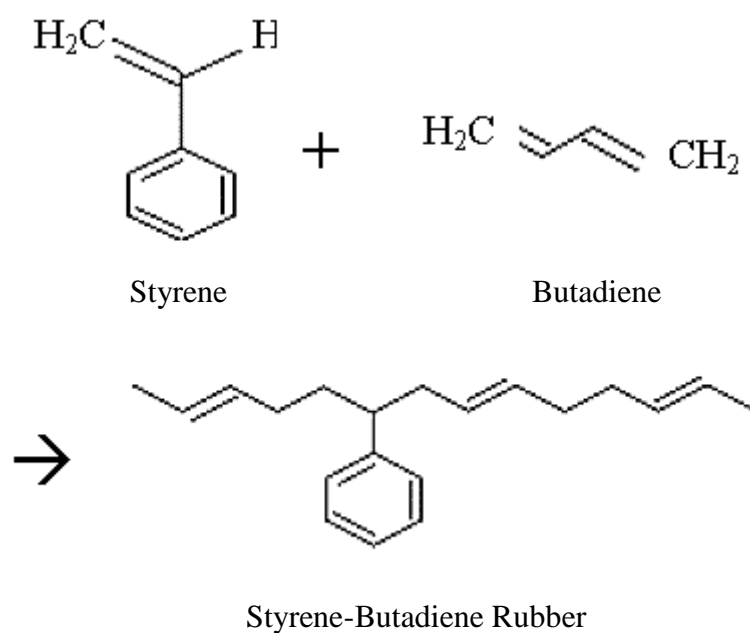


Figure 2.3 Polymerization of styrene butadiene rubber (Gardner & Hongladaromp, 1994).

The commonly available SBR grades contain 23.5 % by weight of styrene and 76.5 % by weight of butadiene. Considering the appropriate combination of elastic and plastic properties, the most used SBR with styrene content in the range of

23 to 25 %. SBR has good abrasion resistance and good ageing stability compared to NR when protected by additives (antioxidant and antiozonant). This is due to the lower unsaturation level compared to NR. However, in order to improve original low strength, SBR must be reinforced usually by fillers to provide acceptable tensile strength and tear resistance. SBR is used for the production of car tires and products for the automotive industries (Sommer, 2013; Gardener & Hongladaromp, 1994).

Today the most commonly used SBR is produced through free radical copolymerization in an emulsion. Emulsion polymerized styrene butadiene rubber (E-SBR) is widely used in mechanical goods application. E-SBR is available in a wide range of viscosity grades where lower viscosity grades SBR are easy to process. They allow the forming of a band on the mill and incorporate fillers and oil more readily, showing less heat generation during mixing. Low viscosity SBR also give higher extrusion rates and better extrudate appearance than the higher viscosity grades (Sommer, 2013).

2.1.2 (b) Nitrile Butadiene Rubber (NBR)

Nitrile butadiene rubber is a synthetic rubber usually known as nitrile rubber. It is also known as Buna-N, Perbunan and acrylonitrile butadiene rubber. As illustrated in Figure 2.4, NBR is a copolymer of butadiene with 15 to 45 % acrylonitrile (ACN) monomers manufactured by advanced free-radical emulsion polymerization technology either hot (hot rubber) or cold (cold rubber). NBR is an unsaturated polymer due to the presence of the butadiene unit. The unsaturated backbones of NBR give the disadvantages as it subjected to attack by oxygen and ozone (Sommer, 2013).

Early studies by Gupta et al. (2014) shows that the physical and chemical properties of nitrile rubber depend on the total ACN content in the rubber. Higher content of ACN contribute to high plastic nature which resulted in better oil and fuel resistance but poorer low temperature properties. Better oil resistance properties of NBR resulted from increased in polarity. Due to highly resistant to oil, it is capable to be used for fuel hose, shoe soles and also for automotive parts. Usually, rubber grades NBR (medium acrylonitrile polymer) is used in the automotive industry to make fuel and oil handling hoses, seals and grommets. Depending on the ACN content, the temperature range of applications of NBR is between -40 °C to +100 °C. This property gives an advantage for NBR to be an ideal material for automotive application. However, the NBR is more resistant to oils and acids resistant compared to NR with lower in elastic properties (Ciesielski, 1999).

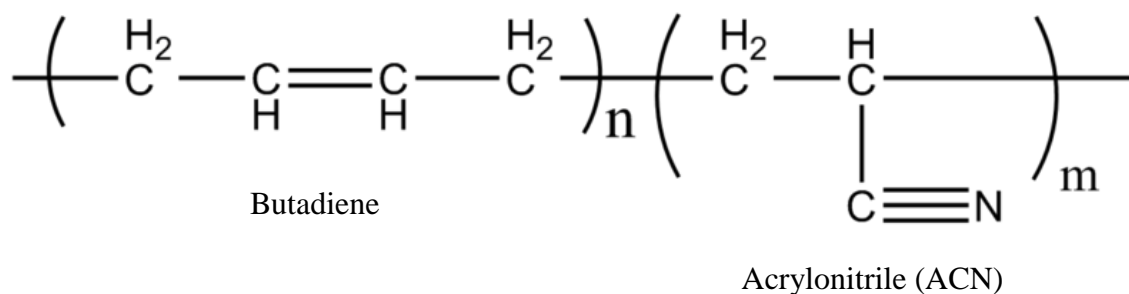


Figure 2.4 Nitrile Butadiene Rubber (NBR) with butadiene and acrylonitrile monomer (Ciesielski, 1999).

2.1.2 (c) Chloroprene Rubber (CR)

Chloroprene rubber is commonly known under the trade name DuPont Neoprene. It is also the synthetic rubber with the chemical structure of poly(2-chloro-1,3-butadiene). The presence of the allylic chlorine (refer Figure 2.5) atom in CR almost deactivates the unsaturation of CR. Due to this; it contributes to very high weather resistance properties. The presence of chlorine (Cl) improves the adhesion

properties of CR rubber. CR rubber also shows the ability to strain-induced crystallization like NR, thus resulting in very high green strength, which leads to the wide application as adhesive. CR rubber vulcanizate shows good elasticity, although it does not reach the level of NR (Klingender, 2008). The Cl atoms in the backbone also contribute to the very low flammability of CR rubber. During decomposition at high temperature, CR liberates HCl gas which reduces the oxygen at the burning area. This helps to improve resistance to flammability properties of CR (Bhowmick & Stephens, 2000).

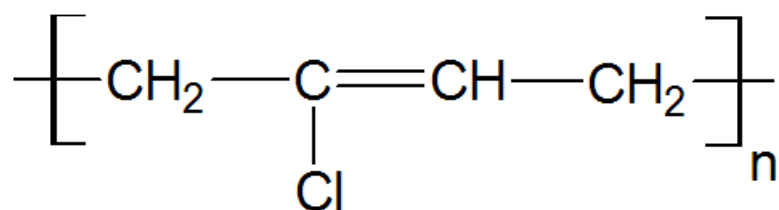


Figure 2.5 Polymer structure of Chloroprene rubber (CR) (Bhowmick & Stephens, 2000).

Typical working temperature range for CR is between -35 °C to + 100 °C. Thus, CR vulcanizates possess a good in mechanical strength, better ozone, sunlight and weather resistance, high dynamic load-bearing capacity, improved ageing resistance, favorable flame resistance, low gas permeability, good resistance toward chemicals, moderate oil and fuel resistance, and good adhesion to rigid substrates, such as metals and textiles (Gupta et al., 2014).

2.1.2 (d) Ethylene Propylene Diene Monomer (EPDM)

EPDM is a type synthetic rubber with a terpolymer of ethylene, propylene and diene monomers. Generally, it has been characterized by a wide range of

application. Commonly, the ethylene content is around 45 to 85 %. Higher ethylene content contributes to high loading possibilities of the rubber, thus give better mixing and extrusion (Avalos et al., 2017; Gupta et al., 2014). Processability of EPDM rubber is very much influenced by its molecular structure. There are three types of diene used to manufactured EPDM; dicyclopentadiene (DCPD), ethylidene norbornene (ENB) and vinyl norbornene (VNB). One of the most popular grades of EPDM is that with ENB as a diene (refer to Figure 2.6).

EPDM is well known for its better performance in heat, ozone, and weather resistance properties which are due to a saturated polymer backbone. The steam ageing and electrical insulator properties are also commendable for EPDM. In addition, EPDM rubber is also compatible with polar substances such as hydraulic fluids, ketones, hot and cold water and also alkalis. It is incompatible with hydrocarbon substances like oils, kerosene, aromatic, gasoline, as well as halogenated solvents (Mitra et al., 2006).

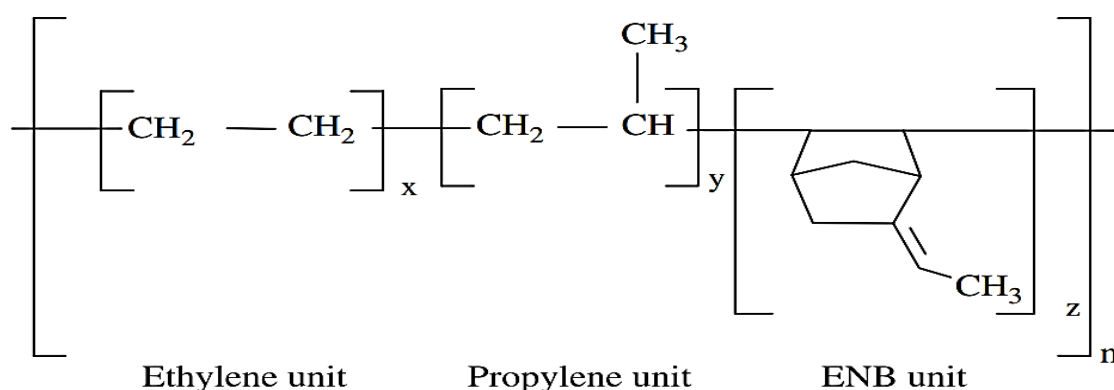


Figure 2.6 Terpolymer monomers of ethylene propylene diene monomer rubber (EPDM) containing ENB as a diene (Mitra et al., 2006).

The listed performance properties allow EPDM to be used in many industrial applications including the automotive and electrical insulator industries as the

polymer for window seals, gaskets, cable insulation, and exhaust hanger. As EPDM contains ethylene and propylene, it also shows good dimensional stability (Mitra et al., 2006).

2.1.3 Bond Energy and Glass Transition Temperature (T_g) of Rubber

The bond energy of rubber compound generally based on polymer-analogical. It also measures the bond strength of the chemical bond in the polymer chain. When a rubber undergoes mechanical test, the inter-chemical chain reaction occurs; polymer molecular bonds are shifted and broken and form another different molecule. This phenomenon can be related to the self-induced crystallization reaction that occurred for NR and CR rubber (Zumdaahl & DeCoste, 2018). The chemical bond energies are listed in Table 2.2.

Table 2.2 Average bond energy for chemical bonding (Zumdaahl & DeCoste, 2018).

Chemical bond	Average bond energies (kJ/mol)
C – H	413
C – C	347
C – Cl	339
C = C	614
C ≡ N	891
Covalent	60 – 700
Ionic	600 – 1000
Van der Waals	0.1 – 40
Polar	4 – 20
Hydrogen	Up to 40

In order to break the bond, the energy is always required. This energy is known as bond energy. The bond energy related to the polymer chemical structure

and characteristic of the molecule in the rubber compound. The stronger the bond energy, the higher the energy needed to break the bond where the triple bond takes a lot of energy to break. Generally, the bond energy is correlated to the bond order and bond length. When the bond order is lower, bond length is longer. The bond energy is also associated with the average of bond dissociation energies in a molecule. As mentioned by Luo (2007), energy is absorbed and released when subjected to a mechanical test. These absorption and energy loss are definite as an exothermic and endothermic reaction. Generally, the testing that involves both exothermic and endothermic reaction is dynamic mode testing such as fatigue test and dynamic stiffness test.

Glass transition temperature, T_g is the transition temperature of rubber from the glassy state to the rubbery state as depicted in Figure 2.7. The T_g of rubber describes the range of temperatures at which glass transition occurs. It also defines as the flexibility of the rubber chain. In glassy state, the rubber becomes hard and brittle which is consisting of short-range vibrational and limited movement of polymer chain similar to plastomers. When heated, rubber chains from highly elastic state change to viscoelastic and above the softening temperature where rubber can flow (Harper, 2006).

At low temperature, a rubber with low T_g will freely rotate around the simple chemical bonds. The higher flexibility of the rubber backbone chain will tend to reduce the rubber T_g . The Increasing of a free volume in rubber polymer chain contribute to increase the flexibility of rubber chain at low temperature. Commonly, the presence of bulky substitutes like styrene in SBR and irregular structure, polar group or side group, double bonds or aromatic chain groups in polymer chains tends

to increase the T_g value. These bulky group substitutes of pendant group to have higher impact on the chain mobility and known as a fish hook or boat anchor. These substitutes usually act as a hook that catches the nearby molecule when the rubber chains slide past each other and reduce the mobility of rubber chain. Furthermore, the bulky groups sometimes act as the load to rubber chain and slow down the rubber chain movement. However, the big pendant group can also lower the T_g . These big pendant groups introduce free volume area known as ‘elbow room’ (Arrighi et al., 2003). It limits the rubber chain to pack closely together and increase the free volume area which can work similar as plasticizer where the more free volume with the lower T_g is observed (Geethamma et al., 2014). Due to these factors, the different rubber will have different T_g values as listed in Table 2.3.

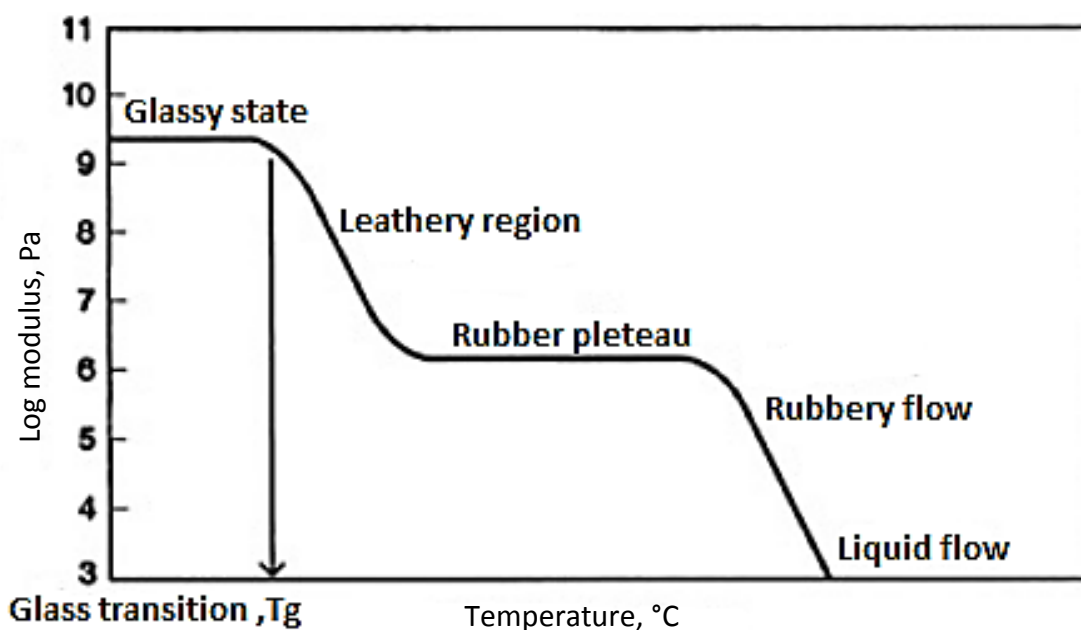


Figure 2.7 The transition state of rubber at various temperatures (Harper, 2006).

Table 2.3 Glass transition temperature (T_g) for rubbers (Geethamma et al., 2014).

Rubber	T _g (°C)
NR	-73
EPDM	-55
SBR	-50
CR	-50
NBR	-40

2.2 Fillers

Generally, there are two classifications of filler; reinforcing and inert fillers. They can be either black or non-black fillers. The reinforcing fillers have an impact on the physical properties of rubber, such as tensile properties, stiffness, abrasion resistance and fatigue resistance. The examples of reinforcing fillers are carbon black, zinc oxide, magnesium carbonate and china clay. The inert fillers for example; ebonite dust and graphite powder do not have an effect on these properties. However, Chandrasekaran (2007) explained that the inert fillers perform a number of useful function such as increasing chemical resistance, heat resistance, and ease of processing, providing rigidity or hardness products and most important reduced the cost of the compound. Usually, in designing an anti-vibration component, carbon black filler is used in order to enhance the end properties of the rubber product (Ouyang, 2006).

2.2.1 Carbon Black

In most rubber products, carbon black is often added not only as filler for cost reduction but also as an important ingredient for reinforcement (Smith & March, 2007). Figure 2.8 shows the chemical structure of carbon black filler. Ouyang (2006)

presented a comprehensive review of tire applications where this reinforcement filler is critical importance in improving performances, such as traction and handling, as well as durability, for example, treadwear mileage and cut resistance. In another study, Yasir et al. (2015) highlighted that the use of carbon black reinforced filler in rubber is very common in automotive applications for example cab mounts, suspension bushes, engine mount, exhaust hanger and many more.

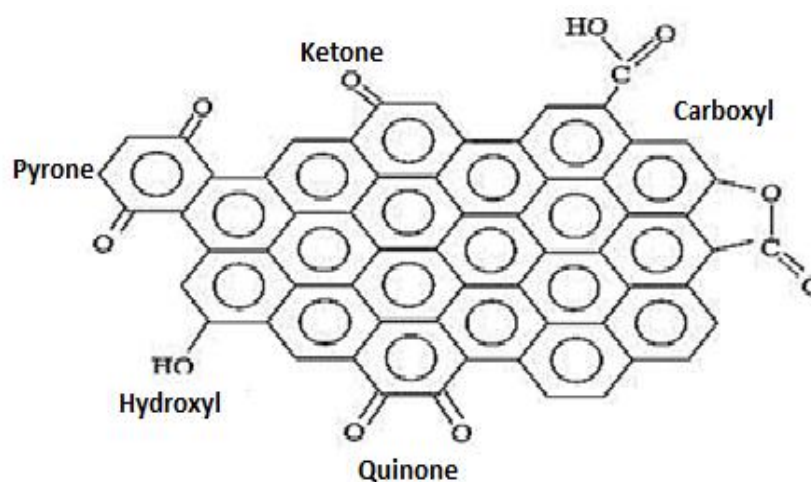


Figure 2.8 Chemical structure of carbon black filler (Smith & March, 2007).

2.2.1(a) The Particle, Aggregate and Agglomerate

Carbon black is in the form of colloidal made of elemental carbon that owes its reinforcing character. Lopez-de-Uralde et al. (2010) mentioned that the particles of carbon black filler can occur in three different forms; primary particles, aggregate and agglomerate. Figure 2.9 depicted that a simple analogy of carbon black filler formation of aggregate and agglomerate. According to Dick (2014), the primary particle is usually a single piece of carbon black that known as an individual particle. In this analogy, the individual primary particles of carbon black are ‘cemented’ together to build the carbon black aggregate in the crystalline area. A group of aggregates together is called agglomerate. In another study by Chandrasekaran

(2007), mentioned that agglomerates are included loose bound primary particles and aggregates that joined together at crystal corners and edges. The individual particles of carbon black can fused together which the aggregate is the smallest dispersible unit of carbon black.

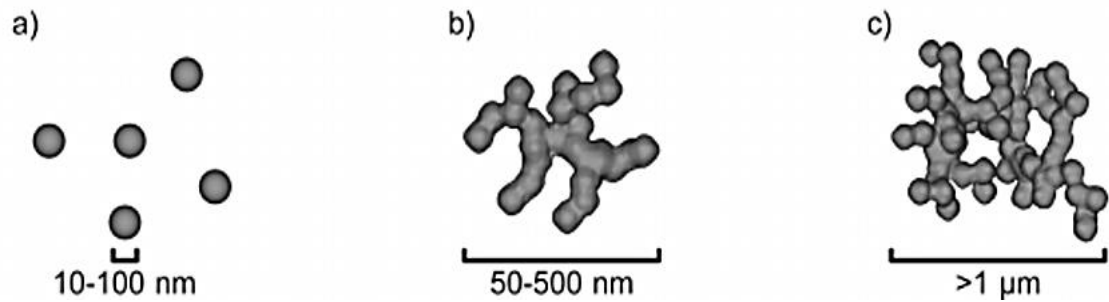


Figure 2.9 Carbon black filler (a) primary particles, (b) aggregate, and (c) agglomerate (Lopez-de-Uralde et al., 2010).

The electron microscopic image is usually used to observe carbon black particles. Figure 2.10, shows a study by Karl (2015) using different types of carbon black tested under the electron microscope shows that the carbon black particles have a complicated structure with the primary particle that is combined together. The size of the spherical or round particle is known as particle size and size of particle chain known as the structure.

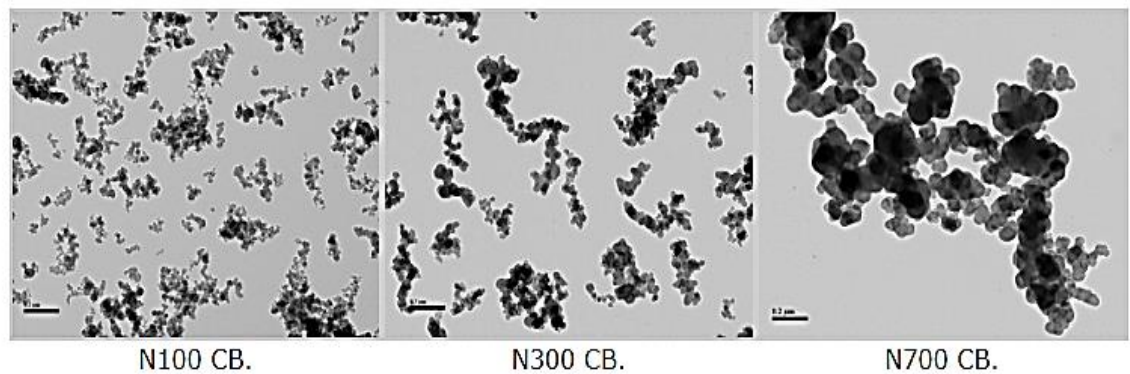


Figure 2.10 Resemblance of carbon black filler aggregate using electron photomicrographs (Karl, 2015).

2.2.1(b) Surface Area, Structure and Surface Chemistry

The reinforcing character and properties of carbon black filler are influenced by the size, shape and surface chemistry of the primary particles and aggregates as shown in Figure 2.11. Usually, the particle size of carbon black filler is in the nanoscale range. The classifications of a grade number of carbon blacks are based on surface area and structure measurement. The surface area of carbon black is correlated to the particle size. As mentioned by Chandrasekaran (2007) the surface area measurement gives indirect carbon black classification.

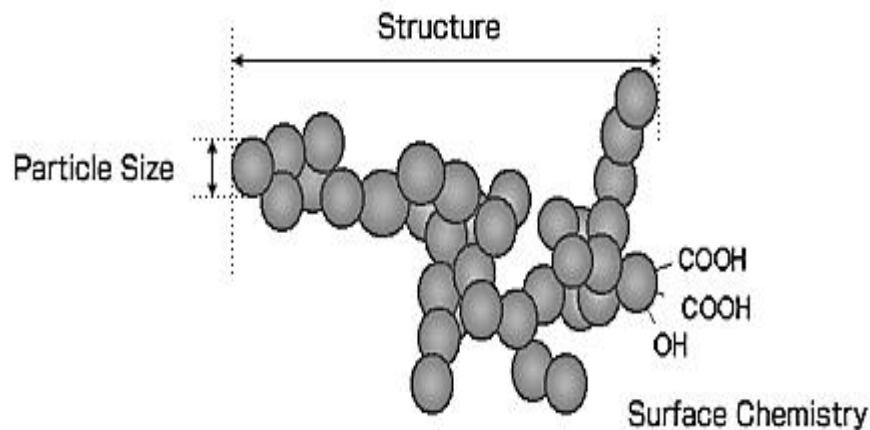


Figure 2.11 Particle size and shape of carbon black filler (Spahr & Rothon, 2017).

The surface area affected the blackness and dispersibility of carbon black filler. The structure of carbon black filler generally refers to the formation aggregation and agglomeration of particles. The structure of the carbon black filler also affected the blackness and dispersibility (Spahr & Rothon, 2017). The higher the structure size tends to improve dispersibility and reduces the blackness. Various functional groups exist on carbon black's surface such as hydroxyl or carboxyl group as depicted in Figure 2.8. These functional groups will affect the reinforcing properties of the carbon black filler.

2.2.1(c) Characterization of Carbon Black

The characterization of carbon black filler is based on various parameters such as particle size, surface area and activity, structure and porosity. These parameters have a large effect on the properties of the rubber compound. They also defined the classification of thermal black and furnace black type of carbon black filler. Table 2.4 provides the characterization and classification of carbon black filler. The (N) symbol in ASTM classification refers to a normal curing material (Gordana & Visakh, 2016).

Table 2.4 The characterization of carbon black filler (Gordana & Visakh, 2016).

Name	Abbreviation	ASTM	Particle size (nm)	Surface area (m ² g ⁻¹)
Intermediate Super Abrasion Furnace	ISAF	N220	24 - 33	117
High Abrasion Furnace	HAF	N330	28 - 36	80
Fast Extruding Furnace	FEF	N550	39 – 55	41
Semi-Reinforcing Furnace	SRF	N774	70 – 96	21
Medium Thermal	MT	N990	250 - 350	9

Based on the particle size and surface area of the carbon black filler, the N990 is classified as a thermal black while, the N220 - N774 are denoted as furnace black. The higher particles size of thermal black contributes to the lowest surface area. In contrast, the furnace black has a lower particle size but higher surface area. The comparison of particle size of carbon black filler is depicted in Figure 2.12.

The finer particles size of carbon black filler which is N220 type lead to increase the reinforcement of filler properties. The smaller particles size of carbon black diameter rise to the higher surface area and lead to improvements in rubber compound strength (Gordana & Visakh 2016; Donet, 1993). Furthermore, Dick (2014) showed that increased in carbon black surface area will contribute to improving abrasion resistance and tensile strength.

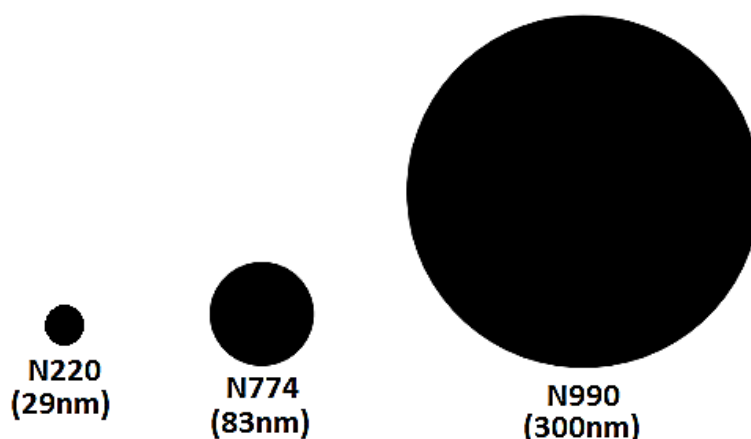


Figure 2.12 The comparison of mean diameter of carbon black particle size (Donnet, 1993).

Figure 2.13 illustrates the comparison of carbon black structure of N990, N774 and N220. The N990 which is the thermal black carbon black type shows a larger primary particles. The aggregation of particles is very limited and consists of very few fused particles. Meanwhile, the furnace black with fall within N220 – N774 do not consist the individual particle of carbon but exhibit the aggregation of carbon black. These aggregations are fused together in a form of a grape-like cluster. Kraus (1984) raised several concerns about the carbon black structure. He mentioned that the increase in carbon black structure will tend to increase the modulus, hardness, however, the viscosity of rubber compound also increased.