APPLICATION OF FELDSPAR FILLER ON CURING CHARACTERISTICS AND PHYSICAL PROPERTIES OF ELASTOMERIC MATERIALS

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2022

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA

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by

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Dissertation submitted in fulfilment of the requirement for the degree of

Bachelor of Engineering with Honours

(Polymer Engineering)

Universiti Sains Malaysia

September 2022

DECLARATION

I hereby declare that I have conducted, and completed the research work and work the dissertation entitled **"Application of Feldspar Filler on Curing Characteristics and Physical Properties of Elastomeric Materials"**. I also declare that it has not been previously submitted for the award of any degree, diploma, or similar titles for any other examining body or university.

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Date: 19 August 2022

Witness by,

Supervisor: Prof. Dr. Azura Binti A. Rashid   Signature:

Date: 19 August 2022

ACKNOWLEDGEMENT

I am indebted to a number of people who made the successful completion of the final year project named “Application of feldspar fillers on curing characteristics and physical properties of styrene butadiene rubber” with their constant guidance and acknowledgement. First of all, I would like to thank Dr. Muhammad Afiq Bin Misman, Technical Manager (Rubber and Latex) of Sibelco and Prof. Dr. Azura A. Rashid,a senior lecturer from Universiti Sains Malaysia for their constant support, advice and guidance throughout the project. I would also like to thank Mr. Shahril Amir and Mr. Suharuddin Sulong, the assistant engineers at the Rubber Lab, School of Material and Mineral Resources Engineering for the technical guidance and arranging all facilities to make the training easier.

Last but not least, I would like to thank this opportunity to thank my family and friends who have been with me and comfort me with their support.

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ABSTRAK

Karbon hitam (CB) dan silika adalah pengisi yang telah digunakan secara meluas di seluruh dunia dalam industri tayar. Penggunaan feldspar dalam pembuatan tayar merupakan salah satu alternatif kepada pengisi konvensional atas sebab kosnya yang efektif dan kelestariannya. Di dalam kajian ini, sebatian getah stirena-butadiena (SBR) yang terisi dengan karbon hitam (CB) dan feldspar telah pun dijalankan untuk menentukan keupayaan feldspar sebagai pengisi penguat dalam aplikasi bunga tayar. Kajian ini juga telah melibatkan kesan penggunaan pelbagai jenis sistem pemvulkanan sulfur seperti sistem pemvulkanan konvensional (CV), pemvulkanan cekap (EV), dan pemvukanan separa cekap (semi-EV) untuk sebatian kawalan dan hibrid. Bagi sebatian kawalan, 40 bahagian per seratus getah (bsg) CB, Silica dan Feldspar telah digunakan dan bagi sebatian hibrid, nisbah antara CB dan pengisi ialah 30:10, 20:20 dan 10:30. Bagi sebatian kawalan, sistem semi-EV telah memendekkan masa skorj dan pematangan bagi sebatian SBR-Feldspar. Bagi sebatian hibrid, SBR-CB-Feldspar dengan pembebanan CB tertinggi, 30 bsg telah pun meningkatkan ciri-ciri pematangan dan sifat-sifat fizikal bahan elastomer seperti kekuatan tensil, kekerasan, daya tahan lantunan, dan rintangan lelasan. Namun, feldspar masih lagi tidak setaraf dengan silica sebagai pengisi penguat. Untuk sistem pengisi hibrid dengan pelbagai jenis bahan elastomer, seperti SMR-L, EPDM, NBR, dan CR, kelakuan getah tersebut berlainan dari segi ciri-ciri pematangan dan sifat-sifat fizikal apabila dibandingkan dengan sebatian SBR kerana sifat asal getah tersebut. Feldspar mungkin boleh dianggap sebagai pengisi separa penguat dan bertindak sebagai *extender* dan pelembut dalam sebatian elastomer.

APPLICATION OF FELDSPAR FILLERS ON CURING CHARACTERISTICS AND PHYSICAL PROPERTIES OF ELASTOMERIC MATERIALS

ABSTRACT

Carbon black (CB) and silica are fillers that have been widely used worldwide in the tire industry. The use of feldspar in tire manufacturing is one alternative to conventional fillers due to its cost effectiveness and sustainability. In this work, a compound of styrene-butadiene rubber (SBR) filled with carbon black (CB) and feldspar has been conducted to determine the ability of feldspar as a reinforcement filler in tire tread applications. This work has also involved investigating the effects of using different types of sulfur vulcanization systems such as conventional vulcanization systems (CV), efficient vulcanization systems (EV), and semi-efficient vulcanization systems (semi-EV) for both control and hybrid compounds. For the control compound, 40 parts per hundred rubber (pphr) of CB, Silica and Feldspar were used and for the hybrid compound, the ratio between CB and filler was 30:10, 20:20 and 10:30. Based on the results, the control compound from semi-EV system has short scorch and cure time for the SBR-Feldspar compound. For the hybrid compound, SBR-CB-Feldspar with the high CB loading, 30 pphr has already improved the curing characteristics and physical properties of the elastomer material such as tensile strength, hardness, rebound resilience, and abrasion resistance. However, feldspar is still not on par with silica as a reinforcement filler. For hybrid filler systems with various types of elastomer materials, such as SMR-L, EPDM, NBR, and CR, the behavior of these rubbers is different in terms of curing characteristics and physical properties when compared to SBR compounds due to the original nature of the rubber involved. Feldspar may be considered as a semi-reinforcing filler and acts as an extender and softener in elastomer compounds.

CHAPTER 1 CHAPTER 1

INTRODUCTION

1.0 Research background

Carbon black (CB) is typically used in the manufacturing of rubber products to enhance the physical properties of the rubber, especially in terms of tear and tensile strength, and also improve the hardness and viscosity of the rubber (Fan et al., 2020).

A non-carbon black filler, such as silica, feldspar, quartz, and kaolin, would be treated with a silane coupling agent, to the polymer-matrix interface (Panaitescu et al., 2018). Other than CB, silica is widely used as a reinforcing filler in rubber industries as it improves the physical properties of the rubber products especially for coloured products.

Hybrid fillers are a combination of two or three fillers in a rubber compound that fulfil the requirements or needed features of rubber vulcanizates. Carbon black and non-carbon black fillers such as silica are the common hybrid fillers that are the common used as the hybrid fillers in rubber manufacturing. In a study by Rattanasom et al., (2007), a natural rubber (NR) vulcanizate shows an improvement on its mechanical properties as the hybrid fillers of CB and Silica, which the rubber compounds contained 20 and 30 phr of Silica as it gives better filler dispersion, also, 20 phr of Silica is good enough for the rubber vulcanizates as the amount of CB (30 phr) were easily incorporated with the NR than the silica.

The vulcanization system also plays a major role in determining the behaviour of the rubber compound. Two types of vulcanization systems typically used in rubber compounding are sulphur and peroxide vulcanization systems. Sulphur vulcanization system focuses on the ratio of sulphur to the accelerator, as for the peroxide vulcanization, only peroxide is used as vulcanizing agent. Sulphur vulcanization which the three types of sulphur vulcanization; efficient, semi-efficient, and conventional vulcanization system.

1.1 Problem statement

In producing tire tread, other than its main ingredient, rubber like styrene-butadiene rubber (SBR), the reinforcing filler such as silica and carbon black were also important to improve the mechanical and physical properties of the tire tread. However, it was found that there is other material that may be able in replacing silica as its economical and abundant of source. The use of feldspar in rubber application is offered as an alternative to conventional filler as its cost-friendly and sustainable as 60% of of the Earth's crust belong to feldspar (Pinton & Pajarito, 2017).

Feldspar, on the other hand, increases Mooney viscosities of rubber (SBR) when incorporated with CB and shows good processability (Kaynak and Şen, 2021). In the study, a hybrid filler system SBR-filled with CB and feldspar was studied. The overall filler used in the rubber is 50 phr, which a filler loading study imposed found that the addition of 10 phr feldspar and 40 phr CB has yielded higher Mooney viscosities than the 50 phr filled CB-SBR. The usage of the hybrid filler system has decreased the minimum torque (ML) rather than the non-hybrid system which stipulated that the rubber vulcanizates with hybrid filler system has good processability. From the study also, the addition of feldspar into the SBR-CB has give good advantage in terms of low-cost material but also, can acts as the fuel saving improvements as it showed great rolling resistance and has a winter traction property. However, the hybrid filler system, does not give any significant different of tensile strength when compared to the 50 phr SBR-CB. Thus, it may be regarded as the semi-reinforcing filler which more suitable used as cheapener, extender, and softener since the incorporation of the feldspar with the SBR increased the Mooney's viscosities of the rubber.

The difference of vulcanization system gives an impact of the curing characteristics and physical properties of the rubber. Three type of vulcanization system have different concentration of polysulfidic, disulfidic, and monosulfidic which affects the behaviour of the rubber. Every vulcanization offers different characteristics based on the sulphur and accelerator dosage which determine the scorch and curing time, tensile properties, crosslink density, rubber aging and fatigue.

In this research project, there were two stages proposed which were Stage 1 and Stage 2. Stage 1 is the compounding of controlled compounds which involved the SBR rubber with three types of sulphur vulcanization system; conventional vulcanization (CV), efficient vulcanization (EV) and semi-efficient vulcanization (semi-EV) system in which for every rubber compounds, 40 phr of fillers; feldspar, silica and carbon black would be tested to determine which system has improved the properties of the rubber. Every result that gained from the systems were compared in order to select which system gave the best-fit result for tire application in terms of curing characteristics and physical properties. The best system would undergo the hybrid filler system which the ratio of the carbon black to feldspar (CB:Feldspar) were 10:30, 20:20 and 30:10. The ratio which meet the expectations would be used in the next stage.

For the Stage 2, SMR-L, EPDM, NBR and CR were compounded using the hybrid filler system to investigate the compatibility of the mixing rubber with the hybrid filler. The recent studies, have shown the feldspar increases the physical properties of the rubber when mixed with feldspar at certain level. In a study by Ismail et al., (2005) stated that the usage of feldspar on SMR-L increased the tensile strength of the rubber vulcanizates up until 10 phr and for ENR 50, its tensile strength increased up until 20 phr. Further loading of the feldspar has caused the rubber vulcanizates to deteriorate gradually. Another literature by (Kaynak & Şen, 2021) in a hybrid filler compound which contains SBR-CB-Feldspar, the minimum torque (ML) was found lower than SBR-CB compound which shows the hybrid compounds shows that the addition of the feldspar offered easy processability.

1.2 Objectives

The aim of this research work is to investigate the application of feldspar on curing characteristics and physical properties of natural and synthetic rubber with the hybrid filler system. The specific objectives of this research are as follows:

a) To determine the effect vulcanization system of the hybrid fillers CB-Feldspar on its curing characteristics and physical properties of SBR vulcanizates.

b) To investigate the effect of the hybrid fillers of CB/Feldspar on curing characteristics and physical properties for different types of rubber which are EPDM, NBR, CR and SMR-L.

1.3 Scope of research

In this research project, the study was divided into two stages which are 'Stage 1' and 'Stage 2'. In Stage 1, the study is to determine which sulphur vulcanization system could give the best-fit impact for the SBR in terms of curing characteristics and physical properties when a hybrid filler system is used. The hybrid filler system is a binary system in which the ratio of CB to the feldspar is imposed. The proposed ratio is 10:30, 20:20, and 30:10. From this research, all the results would be compared to select the best ratio that shall be used in Stage 2. Stage 2 is focused on the compounding of SMR-L, EPDM, NBR and CR with the hybrid filler system. For both stages, the scorch and cure time, tensile properties, hardness, rebound resilience, swelling properties, crosslink density, and abrasion resistance were observed as the expected properties for the rubber application.

1.4 Thesis outline

The thesis consists of five chapters;

Chapter 1: Briefly discuss the research overview, problem statement, objectives, and scope of the research work.

Chapter 2: Overview of the previous research findings and literature from journals correlated to the research topic.

Chapter 3: Illustrate the procedure and workflow of the research experiment including materials specification, equipment, working steps, and testing used in the study.

Chapter 4: Study and analyse the results and findings of the research including curing characteristics, mechanical properties, and crosslink density of the rubber when incorporated with the filler and carbon black.

Chapter 5: Summarization of the whole research project findings and recommendations for future works.

CHAPTER 2 CHAPTER 2

LITERATURE REVIEW

2.0 Rubber

2.1.1 Natural rubber (NR)

Natural rubber (NR) or *Hevea brasiliens*is is one of the natural resources that is widely used in producing rubber products. *Hevea brasiliensis*, coming from the para rubber tree typically can be found in South and Southeast Asia countries such as India, Sri Lanka, Malaysia, Indonesia, China, Thailand, Vietnam, and Cambodia.

NR is formed from the polymerization of isoprene (2 methyl-1,3 butadiene) with its major component that consists of C_5H_8 isoprene units in the cis-1,4 configuration. Figure 2.1 illustrated the chemical structure of NR which consist of 93-95% configuration of cis-1,4 polyisoprene (Surya et al., 2018). NR also has been grouped into country's standard and technical specification. For an example, in Malaysia, the SMR is stand for Standard Malaysia Rubber and the rubber will be graded according to its technical specification. The commonly NR used for rubber products are SMR-L, SMR CV 60, STR and SVR. SMR-L (Standard Malaysia Rubber grade L) is one of the NR that is often used in coloured compounds (AkronChem Corporation, n.d) which a very clean and light-coloured rubber that has low content of dirt which improves the quality of the physical properties of the rubber.

NR originally is only capable of holding a low tensile load due to its constituents and yet it has the ability to crystallize. However, with the addition of fillers such as carbon black, mica, and silica improved, the physical properties of the rubber such as hardness, tear resistance, abrasion resistance, and high breaking stress on the product (Farida et al., 2019; Omnès et al., 2008) . Research work by (Farida et al., 2019), has shown that the insertion of the carbon black into the NR has improved its functionality of the NR. Most of the works of the literature suggested that the physical properties of the rubber can be enhanced as the filler loading increases until an optimal value. The usage of 5 and 10 phr of nano-calcium carbonate with organoclay improved the tensile strength of the NR nanocomposites by 350% from 6.83 MPa (unfilled NR nanocomposites) to 30.36 MPa (Sadeghi Ghari & Jalali-Arani, 2016). In a worked by Surya et al., (2015), addition of alkanomide has increased the hardness of the SMR-L from 50 Shore A (0 phr of alkanomide) to 54 Shore A (5 phr of alkanomide), beyond 5 phr, the hardness started to decreased as there was softening effect. SMR-L that is filled with waste tire dust (WTD) and carbon black (CB), shows different effect of mechanical properties with these two fillers (Ismail et al., 2011)The work claimed that CB filled NR improves the rubber vulcanizates mechanical properties compared to the WTD filled NR. The hybrid filler content of 0 phr of WTD and 30 phr of CB has made the tensile strength up until 25 MPa, whilst when the hybrid filler content were 30 phr of WTD and 0 phr of CB, the tensile strength is approximately 15 MPa.

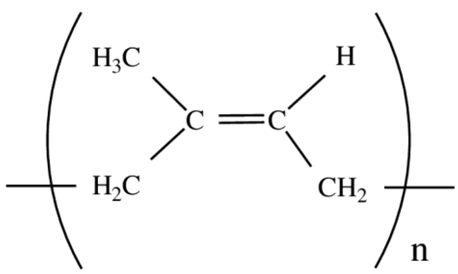

Figure 2.1: Natural rubber chemical structure (Surya et al., 2018)

2.1.2 Synthetic rubber

Synthetic rubbers are generally extracted from crude oil and they also have been used in various rubber applications such as gaskets, seals, tires, hoses, and mats (Morton, 1981). Synthetic rubber which is coming from a synthesis of the polymer under certain conditions has created various kinds of rubber such as styrene-butadiene rubber (SBR), and ethylene-propylene-diene monomer (EPDM), nitrile-butadiene rubber (NBR) and chloroprene rubber (CR). Each rubber has a different monomer before undergoing solution or emulsion polymerization to produce a rubber.

SBR is made up of styrene and butadiene and is well-known in the production of automotive tires and parts. SBR is well known for its comparable to NR properties such as abrasion resistance, good impact strength and resilience, however, it lacks building tack, has poor cohesive and tensile strength, reduced the hot tear strength, reduced the elongation (Martin -Martinez, 2009). The tires are usually reinforced with filler which can maximize the rubber performance. SBR is classed into two categories which are emulsion SBR (ESBR) and solution SBR (SSBR). Unlike the NR which can be crystallized, SBR is a non-crystallized rubber that needs fillers to enhance its mechanical properties (Surya & Edwin, 2020). Carbon black and silica are the common fillers that were used as the reinforcing filler for SBR.

Ethylene-propylene-diene monomer or EPDM is a synthetic rubber that is mostly used in vehicles as the seal for the windows and cars, as cooling system hoses, and as non-slip coatings for decks and playgrounds. Common properties of EPDM are it have fair tensile strength over a wide hardness range, excellent ozone resistance, weathering, chemical attack and have good electrical insulation properties. The blend of EPDM and SBR composites with reinforcing of carbon black and nanosilica improved the mechanical properties of the rubber blends such as tensile properties increased up until 6 phr of the nano-silica before it drops (Vishvanathperumal & Anand, 2022).

Chloroprene or neoprene rubber (CR) is a synthetic rubber that is commonly used in producing domestic goods such as footwear and gloves. CR is consists of homopolymers of chloroprene which its entire polymer chain contains of trans-1,4 configuration which is caused by the high degree of stereoregularity which it would crystallize during stretching. The ability to crystallize during stretching has caused the rubber vulcanizates to have high tensile strength. The existence of chlorine atoms on its structure decreased the reactivity of the double bonds toward many oxidizing agents which is oxygen and ozone. There were few literatures that discover about the chloroprene rubber as the base rubber. CR usually will be blended with other elastomers and polymers. In a study by Azar F. et al., (2017), NR was blends with CR to study the network structure and aging resistance.

Nitrile-butadiene rubber (NBR) or nitrile rubber is yielded from the copolymerization of acrylonitrile and butadiene. NBR is an elastomer that have the oil-resistant properties which is suitable in the production of fuel hose. The general properties of NBR are good resistance towards petroleum-based fluids and hydrocarbon fuels. A recent study by Ateia et al., (2017), claimed that the addition of acrylonitrile butadiene styrene (ABS) into NBR filled with carbon black and silica, has easy processability. The reinforcement of carbon black into NBR has improved the modulus of elasticity (Mostafa et al., 2009).

2.2 Fillers

2.2.1 Feldspar

The fillers in rubber can be categorized as carbon black and non-carbon black. The non-carbon black fillers are usually from minerals such as silica, clay, bentonite, kaolin, quartz, and feldspar. Feldspar is one of the organo-minerals that exist in the earth's crust which is generally related to silicate, titanium and iron minerals which typically possessed high-grade materials in the manufacturing industries, yet, it does not have the similarities in physical-chemical properties with other silicate gauges (Zhang et al., 2018). Figure 2.2 depicted the image of crystalline structure of microline for feldspar which explained the crystal lattice of feldspar that contains corner-sharing AlO_4^{5-} and SiO_4^{4-} tetrahedra linked in an infinite 3D framework to give the representation of feldspar based on its general formula $M^{1+/}M^{2+}$ $(Al,Si)_4O_8$ and the definition of feldspar as tectosilicates or framework silicates.

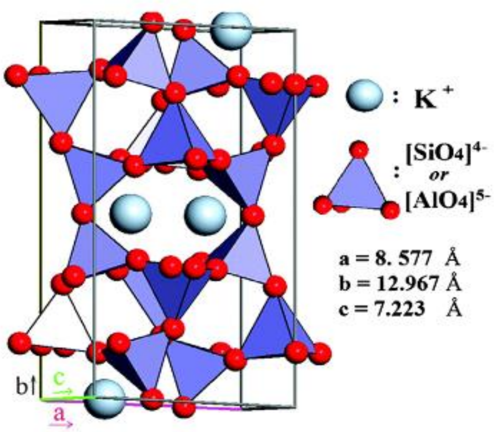

Figure 2.2: Crystalline structure of microline for Feldspar (Skorina & Allanore, 2015)

In addition, feldspar is claimed to have poor adhesion and compatibility between rubber matrix and filler as it has a hydrophilic surface (Pinton & Pajarito,

2017) which resulted in reduction of the mechanical performance of the rubber. Hence, the treatment of the feldspar surface is required and generally, its surface is treated with the silane coupling agent. Surface-treated feldspar gives better tensile strength than untreated feldspar. Treated fillers have influenced the tensile strength by enhancing the interaction of treated fillers and rubber matrix and the adhesion of the rubber matrix and filler increased (Mousa, 2013).

The addition of feldspar as a filler did influence the curing characteristics and physical properties of rubber. The increasing loading of feldspar has increased the scorch, ts2 and optimum curing time, t90, meanwhile for its physical properties, feldspar enhances the tensile strength of natural rubber vulcanizates only at a certain level, 10 phr before the properties of the rubber drops (Ismail et al., 2005). The worked also stated that feldspar functioning well in improving the physical properties at lower loading caused the dispersion of the feldspar and strong interaction of feldspar and rubber in the rubber matrix. In a study by Jaya et al., (2018), in the manufacturing of composite, at different loading, feldspar has shown an improvement in the mechanical performance of composites of potash feldspar and unsaturated polyester when the feldspar loading is up to 5 phr (intermediate level) and decreased as the filler increased. They also claimed that the feldspar improves the adhesion of matrix and filler and could be one of the alternatives for the reinforcement filler as the feldspar is cheaper than another type of filler.

2.2.2 Carbon black (N330)

Carbon black (CB) is a typical reinforcing filler which enhances the performance of elastomers majorly in terms of physical properties. 90% of the carbon black contains carbon elements which are coming from the agglomeration of the tiny and spherical carbon atoms which act as the dispersible unit in the rubber matrix and are often regarded as the reinforcing medium (Fan et al., 2020). Carbon black is also often graded according to its particle size, shape features, and nature of rubber-fillers interaction which strengthens the static and dynamic characteristics of the rubber (Robertson & Hardman, 2021).

In research work by Potiyaraj, (2002), carbon black also improved the curing properties of natural rubber which the high loading of the carbon black increased the Mooney viscosity of the rubber particularly when the particle size of the carbon black is smaller. Also, the study claimed that the scorch time, ts2 and curing time, t90 rise as the filler loading increases. The interaction between rubber and filler also increased when the loading of the carbon black increased up until 60 phr.

The incorporation of natural rubber and carbon black increased when the loading carbon black used is 24 phr the tensile strength of the rubber compounds by 58 times higher than unfilled natural rubber which has lowered the rubber chain elasticity as the carbon black has plunged into the rubber matrix (Pandian, 2015). The study also has alleged that the rubber became stiffer because of the carbon black reinforcement and the hardness also increased as the crosslink density rise. Carbon black which has a small particle size has the ability to raise wear resistance and reduce abrasion loss of the rubber since the interaction of polymer and filler could increase the rubber strength and stiffness (Sivaselvi et al., 2020).

In addition, carbon black also has benefitted the properties of synthetic rubber. A study of synthetic rubber blends, styrene-butadiene rubber (SBR) and butadiene rubber (BR) that were incorporated with carbon black and silica by Sae-Oui et al., (2017), shows that carbon black is superior in terms of abrasion resistance compared to the silica. In addition, the insertion of another non-carbon black filler also helps to improve the properties of carbon black filled rubber (CB-filled rubber). The insertion of alkanolamide has helped the CB-filled SBR in enhancing the rheometric, the degree of filler dispersion, and the mechanical properties (Surya & Ismail, 2019). The inclusion of carbon black into EPDM decreases the sliding wear and the specific wear rate (Mishra, 2021). Figure 2.3 explains chemical functions on the carbon black surface which contains NaHCO3, Na2CO3, NaOH the carbon black surface function which consist of normality of basis of different strength which were NaHCO3, Na2CO3, NaOH in water, and EtONa in ethanol.

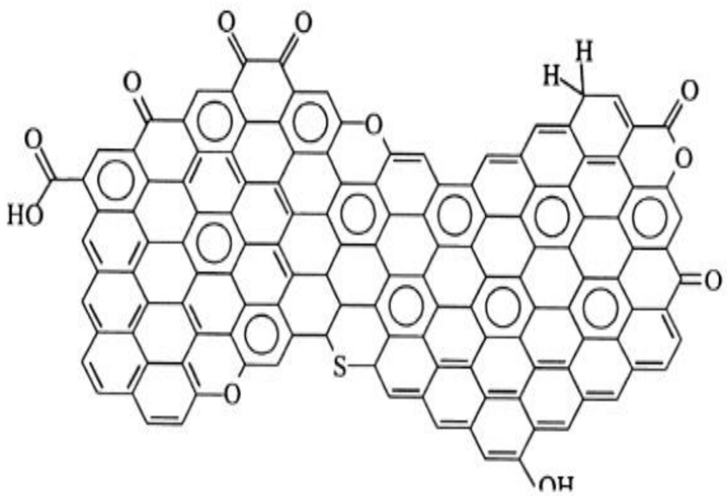

Figure 2.3: Chemical functions on the carbon black surface (F. Bueche, 1960)

2.2.3 Precipitated Silica (Vulkasil S)

Silica and carbon black are the typical reinforcing fillers in the production of rubber products, especially tires. Silica or Si-O2 has been used widely as it has the ability in shaping the performance of the rubber by the dispersion of the silica and interfacial interaction of the silica and rubber (C. Zhang et al., 2018). Silica, as a non-carbon black filler usually treated with a silane coupling agent, such as organo-bifunctional silane (TESPD). Without the interference of silane coupling agent, the interaction of the rubber-filler is unapproachable because of the polarity of the silica and the rubber is non-polar (Dhanorkar et al., 2021). Silica allows the reinforcement of the rubber by its small particle size. The use of the silane coupling agent also gives huge impact on the filler-rubber interaction, filler dispersion in the rubber matrix, and the structure of crosslinking during vulcanization (Park et al., 2018).

Vulkasil S is a silica filler with a reinforcing effect which contains accelerators such as DPG, compounds that consist of hydroxyl groups and all compounds containing basic nitrogen, like triethanolamine and di-cyclohexylamine. Vulkasl S is economical and make the processability of the product easier with silanes treatment and enhances the rolling resistance. Vulkasil S normally blend with carbon black in the rubber manufacturing for tire. It is also suitable in hard, light-colored, colored or transparent articles, such as soles and heels, tubing, profiles, bicycle tires, car and bicycle inner tubes, cable sheathing.

Silica is often pairing with carbon black for a rubber compound to achieve the maximal physical properties in terms of tensile properties, hardness and abrasion resistance. According Sae-Oui et al., (2017), carbon black increased the abrasion resistance while the silica maximized the strength, better wet grip efficiency and reduce rolling resistance. In a study by Khanra et al., (2020), a fluoro-elastomer that filled with silica at 15 phr, its tensile strength obtained is 6 MPa with 7% increment. The utilization of CB and silica as the hybrid filler, also at 15 phr, the tensile strength rise up to 9 MPa. Figure 2.4 shows the chemical structure of silica or silicon dioxide (SiO_2) in tetrahedral form.

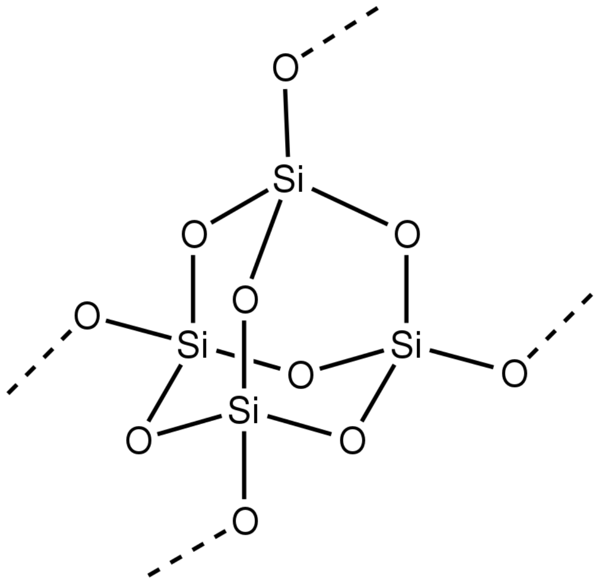

Figure 2.4: Silica chemical structure (Petersen, Reed. 2022).

2.2.4 Hybrid filler system

A hybrid filler system is a system where the use of more than one filler in the rubber compound. The number of fillers that are combined is called the binary system (two types of fillers) and tertiary system (three types of fillers). The constituents of the fillers can be varied into several type of fillers. The most common hybrid filler system is carbon black and non-carbon black fillers such as kaolin, silica and calcium carbonate. The use of a binary system is able to make an extraordinary effect on the mechanical properties of the rubber (Abdul Salim et al., 2018). The most common binary system used for rubber compounding is carbon black and silica. According to Choi et al., (2004), the filled rubber compounds with reinforcing fillers enhanced the properties of the rubber. This is because carbon black and silica have different surface chemistries which help to improve the filler-filler interaction.

In a study by Khanra et al., (2020), the hybrid filler of CB/Silica with the ratio of CB and silica is 1:1, and the cure time, t90, of the rubber compounds was shortened when the filler content is 10 phr. But, as the filler content is increased to 15 phr, the t90 gradually increased as the silica dominated the filler-rubber network and caused the viscosity of the rubber to increase. The hybrid filler system also shows outstanding performance in terms of mechanical properties such as tensile strength, elongation at break, tear strength, and hardness. The tensile and tear strength, except for hybrid system and carbon black (at 15 phr), silica-filled rubber gained relatively poor results for all filler loading. For the hybrid filler, the tensile and tear strength has surged up from 5 phr until 15 phr. The surge of the tensile and tear strength has stipulated the increases in filler agglomeration when the filler content increased. Also, the hardness of the rubber compound steadily increased as the filler content increased.

Figure 2.5 illustrated the cure curves for, A, silica filled, B, carbon black filled and, C, silica/carbon black hybrid filler filled composites. The cure time of the carbon black composite has low value as it exhibits physical crosslinking which fasten the curing process. For the hybrid filler compound, the cure time reduced when the filler is up to 10 phr. Beyond 10 phr, the effect of silica content dominating the compound which increased the cure time. Furthermore, silica exhibits more filler-filler interaction rather than rubber-filler interaction. The interaction leads to filler agglomeration which increases the viscosity.

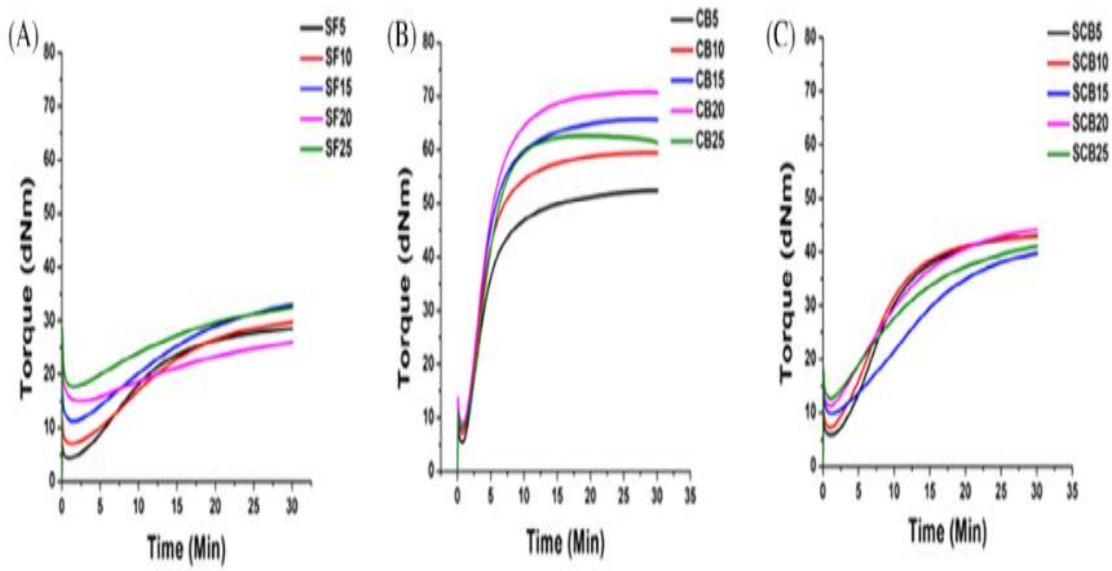

Figure 2.5: Cure curves for, A, silica filled, B, carbon black filled and, C, silica/carbon black hybrid filler filled composites (Khanra et al., 2020)

The hybrid of CB and organo-clay fillers that were compounded in NR has improved the strength, modulus, tear and hardness of the rubber vulcanizates (Liu et al., 2010). Based on their finding, the tensile strength, modulus, tear and hardness show impressive results when using the hybrid filler system. The hybrid filler system approached it maximum strength at 25.7 MPa when the CB content is 21 phr and the organo-clay is 4 phr.

In a worked by Mamauod et al., (2017), the hybrid filler system consisted of 50 phr for every rubber and the nano-calcium carbonate content was 0, 2, 4, 6, 8, and 10 phr. The curing characteristics of NR and SBR blends compound were discussed and found that at 4 phr of nano-calcium carbonate, the rubber vulcanizate achieved its highest value of MH, ML, and MH-ML. In addition, the swelling properties of the rubber blends show the increase of the nano-calcium carbonate in the rubber vulcanizates reduced the swelling capability. Figure 2.6 explains the tensile strength of the nano-calcium carbonate (NCC) with carbon black reinforced NR/SBR blends which shows that at 4 phr of the NCC, its achieved the highest tensile strength, 24.7 MPa. This denoted the optimal value for the filler loading is at 4 phr as beyond the value, the tensile strength started to decreased.

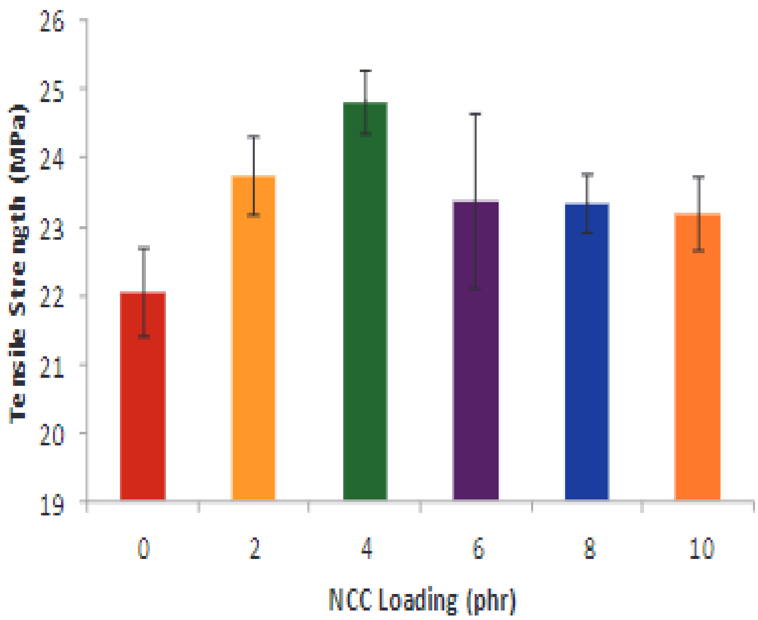

Figure 2.6: Tensile strength of NCC/CB reinforced NR/SBR blends (Mamauod et al.,2017)

An SBR filled with CB and feldspar is investigates by Kaynak & Şen, (2021), which the worked claimed the hybrid filler system has increased the Mooney viscosity of the rubber. Figure 2.7 depicted the Mooney viscosities of the carbon black and feldspar loaded SBR/CB compounds. The overall filler content used in the rubber compound is 50 phr. By replacing 10 phr of the CB with the feldspar, the rubber vulcanizates gained higher Mooney viscosity than the 50 phr of CB. Another finding revealed that the hybrid filler compound obtained lower minimum torque (ML) than the non-hybrid filler system which specifies the rubber has good processability. Figure 2.8 illustrated the stress strain curve of the SBR filled CB using the hybrid filler system. The hybrid filler reinforced composites showed the tensile strength decreased when compared to 50 CB composite.

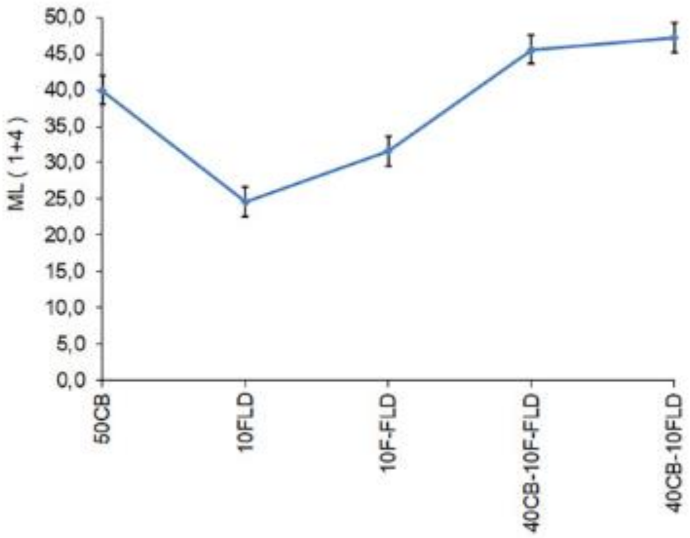

Figure 2.7: Mooney viscosity hybrid filler system of SBR filled CB (Kaynak and Sen, 2021)

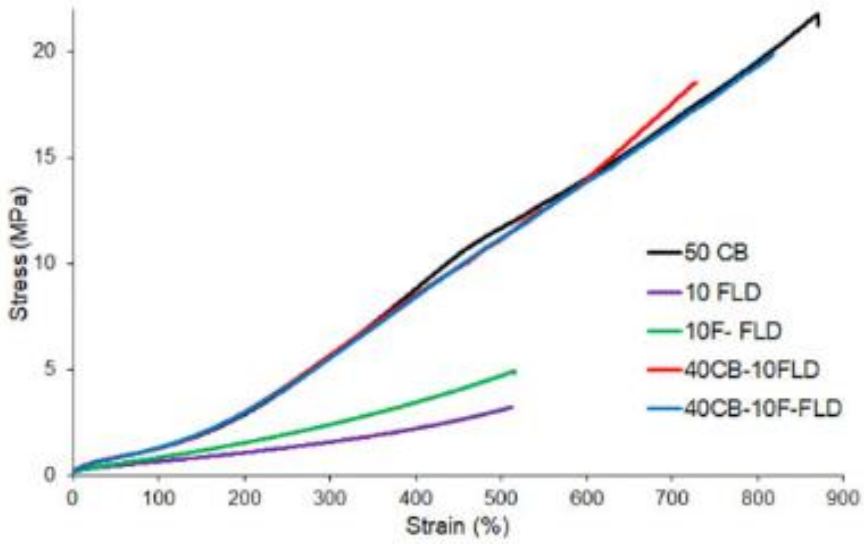

Figure 2.8: Stress strain curve of the SBR filled CB using the hybrid filler system (Kaynak and Sen, 2021)

However, there is also a study that claimed the incorporation of carbon black and bentonite has reduced the tensile properties of the rubber compound. In a study by Ginting et al., (2017), the tensile strength values of the CB-bentonite (20 phr of CB and 10 phr of CB) compound have been reduced due to the constituents of carbon in Na-bentonite siliceous which has caused the crosslinks density to be reduced.

2.3 Vulcanization system of rubber

The vulcanization system of the rubber is divided into two categories which are sulphur and peroxide vulcanization systems. Figure 2.9 depicted the formation of a crosslinked molecular network. There are three types of sulphur vulcanization systems; a) conventional vulcanization (CV), b) efficient vulcanization (EV), and c) semi-efficient vulcanization (semi-EV) systems. The type of vulcanization system can be differentiated by determining the ratio of sulphur (S) to the accelerator (A) in the elastomer formulation. On the other hand, in the peroxide vulcanization system, the addition of organic peroxide as the curing agent such as dicumyl peroxide (DCP), without the involvement of accelerator or sulphur.

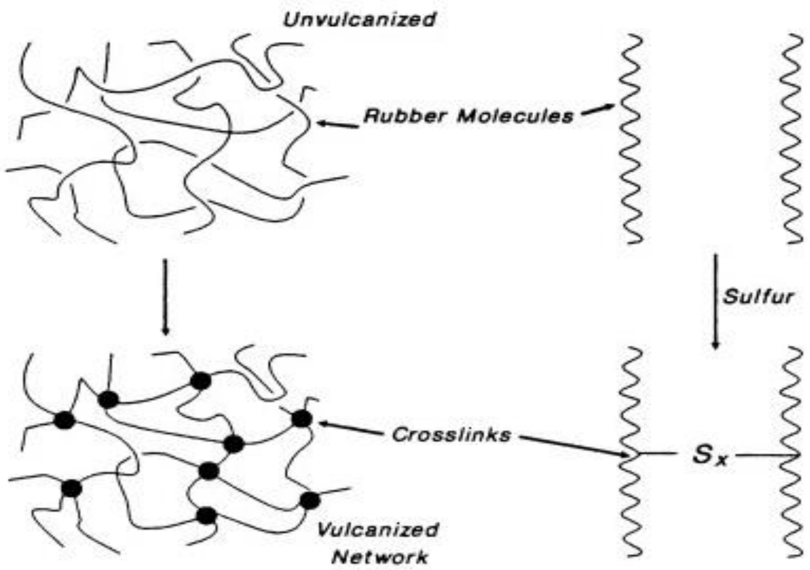

Figure 2.9: The formation of a crosslinked molecular network (Coran, 2013).

2.3.1 Conventional vulcanization (CV) system

CV system is applied as the content of sulphur is higher than the accelerator, in which, the sulphur is in the range of 2.0-2.5 phr and the accelerator is 0.4-1.2 phr. In the CV system, the accelerator affects the crosslink density and crosslink structure which will give changes to the mechanical properties and gives rise to vulcanization time as the accelerator increases (Pietrzak et al., 2020). Moreover, the high content of sulphur in the CV system allows more formation of polysulfide which weakened the crosslink network structure.

2.3.2 Efficient vulcanization (EV) system

EV system offers good mechanical properties and thermal resistance, as the sulphur linkages in the rubber have shortened which enhances the thermal resistance, and yet, since there was reducing of the crosslink density, there is a reduction in the mechanical properties (Naebpetch et al., 2017). To increase the mechanical properties of the rubber vulcanizates, the reinforcing filler is added to the rubber compound. In the same literature, the SBR filled with CB, the torque difference is higher with the increasing of CB loading, which created strong rubber-filler interaction. Using non-carbon black filler, such as silica, the results are similar with the carbon black with different reinforcing activity as the silane coupling agent helps the reinforcement of silica to the rubber. In natural rubber, the EV system offered low tensile strength as the ratio of sulphur and accelerator is lower, hence, the crosslinking of the rubber is weak as the system predominantly by monosulfidic linkages which did not provide stress relieving mechanism (Abdul Wahab et al., 2022).

The usage of the EV system in nitrile rubber has given an impact on the compression set of the rubber vulcanizates (Ostad Movahed et al., 2015). In the study, the nitrile rubber was compounded with carbon black and silica/silane fillers. The study used various amounts of the thiuram and sulfenamide accelerator and sulphur. The finding in the study found that the high loading of the accelerator, CBS and TMTD in the CB-filled nitrile rubber has resulted in the rubber vulcanizates having low compression set. The weight ratio of the CBS and TMTD used varies from 0.33 to 3 whilst the sulphur content is 0.335 phr. The compression set dropped as the accelerator increased.

2.3.3 Semi-Efficient Vulcanization (semi-EV) system

Semi-EV system, which its ratio of Sulphur to the accelerator (S/A) is in between 1.0 and 1.7 phr for the sulphur content and 1.2 to 2.4 phr for the accelerator content, has the highest mechanical properties among the other Sulphur vulcanization system in a study of the devulcanized green NR compound (Ghorai et al., 2018). They also found that the semi-EV system has a lower scorch time and optimum curing time and the highest CRI compared to others. This can be related to the presence of a high amount of mono-sulfidic crosslinks. In the form of mechanical properties, the semi-EV system offered the best modulus, tensile strength, elongation at break, and hardness of the rubber rather than the CV and EV system. Semi-EV system has the highest crosslink density in which resulting from the high content of monosulfidic and disulfidic crosslinks in the rubber matrix which decreased the chain mobility and stiffen the rubber.

Every vulcanization system has its own benefit according to the rubber application. In a work by Mayasari et al., (2016), in EPDM-filled carbon black, the EV system offered a shorter vulcanization time than the CV and Semi-EV system, the semi-EV system hardened the EPDM blends better while the CV system have the lowest swelling index. The cure time, t90 can be shortened due to the high content of the accelerator which the crosslinking can be formed faster. The hardness of the rubber increased in a semi-EV system is resulting from the formation of crosslinking where the sulphur content is slightly higher than the accelerator. On the other hand, CV, which contains a high amount of sulphur dosage required more time for the formation of crosslink.

Semi-EV systems, are generally provided optimum mechanical properties and thermal aging characteristics due to the interchangeable amount of the sulphur and accelerators in the rubber compounds (Rabiei & Shojaei, 2016). In the incorporation of the nanodiamond with rubber blends of NR and SBR, the semi-EV system shows a compromised result on the crosslink density. The finding stated that the interaction of