

**UTILIZATION OF PLASTICIZERS AND
LUBRICANTS DERIVED FROM PALM OIL ON
RHEOLOGICAL AND MECHANICAL
PROPERTIES OF STYRENE BUTADIENE
RUBBER**

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**UTILIZATION OF PLASTICIZERS AND LUBRICANTS DERIVED FROM
PALM OIL ON RHEOLOGICAL AND MECHANICAL PROPERTIES OF
STYRENE BUTADIENE RUBBER**

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled 'Utilization of Plasticizers and Lubricants Derived from Palm Oil on Rheological and Mechanical Properties of Styrene Butadiene Rubber'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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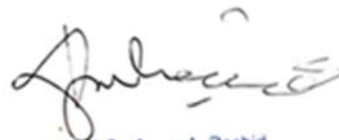
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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CB	Carbon Black
CBS	N-Cyclohexyl-2-Benzothiazole Sulphenamide
CPO	Crude Palm Oil
CNSL	Cashew Nut Shell Liquid
DAE	Distillated Aromatic Extract
DOP	Diethylphthalate
EBS	Ethylene Bis-Steramide
EBO	Ethylene Bis-Oleamide
EESO	Epoxidized Ester Of Soyabean Oil
EG	Expandable Graphite
EPO	Epoxidized Palm Oil
ESBO	Epoxidized Soya Bean Oil
ESFO	Epoxidized Sunflower Oil
GTO	Glycerol Trioleate
FTIR	Fourier Transform Infrared
HNAP	High-Viscosity Naphthenic Oils
IPPD	N-Isopropyl-N'-Phenyl-1,4-Phenylenediamine (IPPD)
LNAP	Mild-Viscosity Naphthenic Oils
M100	Tensile Modulus At 100%
M300	Tensile Modulus At 300%
M500	Tensile Modulus At 500%
MES	Mildly Extracted Solvate
MU	Mooney Unit
NBS	N-Butyl Stearate
NBR	Nitrile Butadiene Rubber
NMO	Standard Mineral Oil
NR	Natural Rubber
OHP	Overhead Protective
PAH	Polycyclic Aromatic Hydrocarbons
PETS	Pentaerythritol Tetrastearate
SBR	Styrene-Butadiene Rubber
TDAE	Treated Distillate Aromatic Extract

TMQ Polymerized 2,2,4-Trimethyl-1,2- Dihydroquinoline
ZnO Zinc Oxide

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
°F	Fahrenheit
cm ⁻¹	Reciprocal Wavelength
g	Gram
hr	Hour
kN	Kilonewton
min	Minutes
ml	Milliter
mm	Milimeter
M _L	Minimum Torques
MPa	Megapascal
M _H	Maximum Torque
N	Newton
ρ	Density
psi	Pounds Per Square Inch
phr	Part Per Hundred Rubber
Rpm	Rotation Per Minute
s	Seconds
T ₉₀	Optimum Cure Time
T _g	Glass Transition Temperature
T _{s2}	Scorch Time
W _u	Weight of the Unswollen Rubber
W _s	Weight of the Unswollen Rubber

**PENGGUNAAN PEMPLASTIK DAN PELINCIR YANG DIPEROLEH
DARIPADA MINYAK KELAPA SAWIT TERHADAP SIFAT-SIFAT REOLOGI
DAN MEKANIKAL GETAH STIRENA BUTADIENA**

ABSTRAK

Penyelidikan semakin tertumpu kepada pelincir dan pemplastik semula jadi kerana kepekatan tinggi hidrokarbon aromatik polisiklik dalam minyak pemprosesan, yang berbahaya kepada kesihatan manusia. Penyelidikan ini memberi tumpuan kepada penggunaan pelincir dan pemplastik yang diperolehi daripada minyak sawit terhadap sifat reologi, mekanikal dan haba penuaan sebatian getah stirena-butadiena (SBR). Pelincir dan pemplastik ini dikenali sebagai *Glycerol Trioleate (GTO)*, *N-Butyl Stearate (NBS)*, *Ethylene Bis-Steramide (EBS)*, *Ethylene Bis-Oleamide (EBO)*, *Pentaerythritol Tetrastearate (PETS)* dan *Stearyl Stearate*. Rintangan lelasan, rupa (visual) dan ciri pematangan untuk sebatian SBR telah diperiksa dan dibandingkan dengan pelincir dan pemplastik mineral. Sebatian SBR (GTO, EBS dan asid stearik) yang mempamerkan ketahanan lelasan dan sifat pematangan yang lebih baik setara dengan pemprosesan sebatian SBR berasaskan minyak telah dipilih untuk kajian lanjut terhadap sifat mekanikal dan sifat penuaan haba. Keputusan sifat tegangan telah menunjukkan sebatian SBR dengan EBS dan EBS dengan GTO mempunyai sifat mekanikal yang serupa daripada SBR yang disebatikan dengan minyak pemprosesan. Ini kerana pelincir dan pemplastik yang berasal daripada minyak sawit mampu menggalakkan penyerakan karbon hitam dalam sebatian SBR. Keputusan penuaan haba menunjukkan bahawa semua sebatian SBR telah terjejas. Walau bagaimanapun, sifat tegangan sebatian SBR dengan pelincir semula jadi dan pemplastik menunjukkan ciri-ciri sampel selepas penuaan yang serupa dengan sebatian SBR dengan minyak pemprosesan. Ini menunjukkan bahawa penggunaan pelincir dan pemplastik yang diperolehi daripada minyak sawit tidak akan menjejaskan sifat tegangan selepas penuaan haba. Berdasarkan kajian, EBS dan EBS dengan GTO sesuai dijadikan pengganti untuk pembantu pemprosesan untuk minyak pemprosesan berasaskan petroleum di dalam sebatian SBR.

UTILIZATION OF PLASTICIZERS AND LUBRICANTS DERIVED FROM PALM OIL ON RHEOLOGICAL AND MECHANICAL PROPERTIES OF STYRENE BUTADIENE RUBBER

ABSTRACT

Research is increasingly focused on natural lubricants and plasticizers due to the high concentration of polycyclic aromatic hydrocarbon in processing oil, which is harmful to human health. This research focus on utilization of lubricants and plasticizers derived from palm oil on the rheological, mechanical properties and thermal aging of styrene-butadiene rubber (SBR) compounds. These lubricant and plasticizer known as Glycerol Trioleate (GTO), N-Butyl Stearate (NBS), Ethylene Bis-Steramide (EBS) Ethylene Bis-Oleamide (EBO), Pentaerythritol Tetrastearate (PETS) and Stearyl Stearate. The abrasion resistance, appearance (visual), and cure characteristics of these lubricants and plasticizers on SBR were examined and compared with other mineral lubricants and plasticizers. The SBR compounds (GTO, EBS and stearic acid) which exhibited better abrasion resistance and cure properties equivalent to processing oil-based SBR compound were selected for further investigation on the mechanical properties and aging behaviour. Tensile properties results have demonstrated the SBR compounds with EBS and combination of EBS with GTO shows similar mechanical properties than SBR compounded with processing oil. This is because lubricant and plasticizer derived from palm oil able to promote the carbon black dispersion in the SBR compound. The results of thermal ageing demonstrate that all SBR compounds have been adversely affected. However, the tensile properties of SBR compounds with natural lubricants and plasticizers show characteristics of aged samples that are similar to those of SBR compound with processing oils. This indicates that the use of lubricants and plasticizers derived from palm oil would not adversely affect the tensile properties after ageing. Based on the findings, EBS and EBS with GTO are suitable substitutes as processing aids for petroleum-based processing oils in SBR compounds.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE RESEARCH

Rubber is a widely used engineering material with a wide range of applications. Some of them are things we use on a daily basis, especially in the automobile sector. Rubber is used for the production of automotive tires to the extent that it accounts for 70% of all rubber produced (Laroche et al., 2022). The styrene-butadiene rubber (SBR) is a man-made rubber formed by styrene and butadiene monomers that are often used in tire manufacture. (Wang et al., 2021). It is usually used to replace natural rubber (NR) but require a higher amount of reinforcing filler to attain acceptable tensile and tear strengths and durability on par with NR (Şaşmaz et al., 2019). The physical and chemical properties of SBR determine the performance of each component in the tire, as well as the overall performance of the tire, which includes rolling resistance, abrasion, and traction.

SBR has lower resilience as compared to NR which prevents it from being used in lorry tires due to its thicker tire tread which can cause greater build-up of heat during flexing. However, the higher hysteresis loss (energy loss in the form of heat) provides increased wet grip in passenger car tire treads, and this, along with the good abrasion resistance that can be obtained from tire tread compounds (Mao et al., 2019). In tire engineering, a green tire/tread with fuel-saving capabilities such as abrasion resistance is a top priority (Mensah et al., 2018). As the tires tread is the primary component of a vehicle that makes contact with the road, its wear performance is an important factor for tire design. Rubber or tire abrasion processes are exceedingly complex and fundamentally different from those of other materials (Nguyen et al., 2018).

Carbon black is always utilized in tires as a reinforcing filler and pigment. It assists in the removal of heat from the tread and belt areas of the tires which decreases thermal damage and extends the tread life. According to Xu et al. (2018), a pure SBR has a tensile strength of only 2.5 MPa and low abrasion resistance. Its tensile strength is increased to 20 MPa with wear resistance is greatly increased by compounding it with 50% of its weight with carbon black.

However, the viscosity of the rubber compound also increases as the amount of carbon black in the rubber compound increases. There are polar functional groups on the carbon black surface, such as hydroxyl, carboxyl, ketone, and so on, but the amount is extremely minimal (Khodabakhshi et.al., 2020). Due to this carbon black particles regularly interacts with one another and combines to form an agglomeration. Agglomeration can be seen as a challenge in filler dispersion due to its negative effects on the characteristics of rubber compounds (Surya and Hanafi, 2019). Roy et al. (2021) stated that plasticizers and lubricants can increase compatibility between rubber and filler.

A processing additive that acts primarily as an internal lubricant will primarily function as a bulk viscosity modifier and promote filler dispersion is known as a plasticizer and lubricant. In some cases, oils are used in the compounding process and during the rubber production process. Their purpose is to assist in the dispersion of fillers, to reduce uncured compound viscosity, compound cost, vulcanizate stiffness (hardness), and in some cases, to increase the low-temperature flexibility (Intharapat et al., 2020).

1.2 PROBLEM STATEMENT

Rubber compounding is a technique used by rubber manufacturers to improve the rubber's processability, properties, and cost-effectiveness by mixing it with additives.

During rubber compounding, plasticizer and lubricant were usually added to reduce the viscosity of the rubber compound thus improving the processing of the rubber. Plasticizers come from a variety of sources, including wax, petroleum oils or vegetable oils. Petroleum oils are either naphthenic, paraffinic, or aromatic, depending on elastomer compatibility, volatility, and predicted product service conditions (Mannekote et al., 2018).

Mineral plasticizers and lubricants or so-called petroleum-based oils are consistently the most often utilized process oils for tire rubbers due to their good balance properties, better oxidation stability, great compatibility with the majority of available rubbers, and low processing cost. However, it is not a sustainable solution as the petroleum refining process produces petroleum oils that contain polycyclic aromatic hydrocarbons (PAHs) were discovered to be carcinogenic, posing a concern to the environment (Pechurai et. al., 2015). In short, these types of lubricants and plasticizers have poor biodegradability and release toxic materials into the environment.

In addition, after the desired properties of rubber have been achieved through proper rubber compounding, it is important to maintain these properties during service, particularly against oxidation and ozone attack (Agrawal et al., 2005). According to Huntink (2005), there are two types of waxes that are used to preserve rubber from cracking due to exposure to ozone or sunlight which are paraffin and microcrystalline wax. According to Pillion (2016), petroleum wax is defined as paraffin and microcrystalline wax, which are produced during the dewaxing process. Macrocrystalline wax is produced from the distillate lubricating oil fraction, whereas microcrystalline wax is produced from the residual lubricating oil.

Paraffin wax and microcrystalline wax serve as lubricants in rubber compounds, they reduce viscosity and assist in filler dispersion. When a wax-based antioxidant is mixed with rubber, the antioxidant oozes out and forms a thin layer on the surface of the rubber, protecting it from ozone exposure and preventing deterioration (Li and Koeing, 2005). It is important to note that paraffin wax was not just used as an antiozonant, it can be used to minimize friction in rubber because of its lubricating characteristics.

However, petroleum is a limited resource that contributes to a variety of environmental problems, including rising carbon dioxide levels in the atmosphere. In addition, the petroleum-based resources that are non-renewable that used to synthesis paraffin and microcrystalline wax are going depleted. Currently, the need for environmentally acceptable lubricants and plasticizers made from renewable resources such as vegetable or plant oil is growing in response to the problems connected with petroleum-based lubricants and plasticizers (Panchal et al., 2021).

Thus, petroleum must be replaced with alternative green sources. Alternative sources which are vegetable or plant oils can provide a major portion of the feedstock needed to replace petroleum. These types of lubricants and plasticizer is derived from renewable resources which is biodegradable and non-toxic due to the absence of high concentrations of polycyclic aromatic hydrocarbons. Non-toxic lubricants and plasticizers derived from palm oil were expected to replace the aromatic oil and paraffin wax to provide excellent processability and mechanical properties in tire tread application. Not only palm oil, it can be derived from soybean, sunflower, castor oil and etc (Karmakar et al., 2017).

These non-toxic lubricant and plasticizer derived from vegetables oil has a lot of advantages over petroleum-based lubricant and plasticizer such as decreased reliance on

petroleum imports, high flash point, and built-in lubricity in neat form (Demirbas, 2009). However, the higher viscosity of plasticizers and lubricants derived from vegetables is one of their major drawbacks. The usage of non-renewable raw materials has resulted in significant reductions in non-renewable resource availability, continued rises in petroleum costs, environmental repercussions with rising greenhouse gas emissions, and a build-up of non-biodegradable waste worldwide (Abdel-Raouf et.al., 2021).

Moreover, the European Communities Council has proposed a comprehensive ban on the use of PAH-rich petroleum oils in industrial and commercial applications (Roy et al., 2021). The focus of world attention has switched to other sources at the moment. As a result, the use of natural resources that are good for the environment should be used in rubber manufacture as a substitute for petroleum-based products has increased. Hence, this collaboration works with KLK Oleo to utilize the plasticizers and lubricants made from palm oil on the rheological and mechanical characteristics of SBR rubber compounds is carried out.

During storing and operational life, some of the compounded materials bloom and diffuse to the surface of the rubber. In rubber compounds, blooming can be a problem. According to Wręczycki et al. (2018), one of the most common issues tires has been sulphur blooming. As it will result in a lack of tackiness. In addition, SBR are sensitive to the environmental factor as the styrene component inside the SBR may lead to degradation of the rubber. According to Kaneko et al. (2019), the rubber will become stiff and brittle after thermal aging due to the predominant oxidation and cross-links reaction. During the research, it is expected that non-renewable materials would be replaced by sustainable materials with excellent processing and mechanical characteristics.

1.3 OBJECTIVE

The main goal of this research project is to investigate the effect of lubricants and plasticizers derived from palm oil to achieve the desired mechanical properties that can be used for tire tread application. To achieve this goal, there are three main objectives:

1. To compare the effect of lubricants and plasticizers on the abrasion resistance performance, visual inspection, and rheological characteristics of SBR compound.
2. To determine the effect of the selected lubricant and plasticizer on the mechanical properties of the SBR compound.
3. To investigate the effect of selected lubricant and plasticizer on the mechanical properties of SBR compound after subjected to thermal aging at 70°C.

1.4 SCOPE OF RESEARCH

In this research work, three main studies were conducted based on the problem statements mentioned in the previous sub-section. The first was to compare the effect of lubricants on the performance, appearance, and rheological properties of the SBR compound. At this stage, four materials were selected based on their performance, appearance, and rheological properties. Abrasion tests were conducted to test the performance of tire tread application. Besides, the appearance of the rubber compound was also investigated, and it was discovered that blooming occurs when a thin layer of dust or film forms on the surface of rubber compounds. The rheological properties of rubber compounds were also studied as they are sensitive to minor changes in the number of different materials utilized.

The second study was mainly concerned with the effect of the selected lubricant and plasticizer on the mechanical properties of the SBR compound. Swelling index, hardness, compression set, tensile strength, and tear strength were all investigated to develop a greater understanding of the rubber compound's mechanical characteristics. When using different compounding materials, they must meet all of their application requirements such as excellent tensile strength or tear strength. The last research works focus on the effect of thermal aging on the mechanical properties of SBR compounded with selected lubricant and plasticizer and the FTIR was used to study the structural change of the rubber compound after aging.

1.5 BACKGROUND OF THE RESEARCH

This thesis is consisting of five main chapters:

Chapter 1: This chapter provides a brief overview of the thesis's aims, problem statements, and the historical background.

Chapter 2: This chapter provides a detailed review of the relevant literature as well as earlier study findings.

Chapter 3: The experimental parts of the investigation are covered in this chapter, together with details on the equipment used, the materials utilised, and the general approach of study.

Chapter 4: The entire study results, including the rheological, mechanical, and thermal ageing characteristics of the SBR tire tread, are discussed in this chapter.

Chapter 5: This chapter summarizes the overall research, delivers findings, and makes suggestions for further research.

CHAPTER 2

LITERATURE REVIEW

2.1 SYNTHETIC BUTADIENE RUBBER (SBR)

Nowadays, any material that has properties that are similar to those of natural rubber which independent of its chemical composition is referred to as "rubber". Rubber is divided into two types: natural rubber and synthetic rubber. Natural rubber is produced from latex, a milky sap found in plants such as the *Hevea Brasiliensis* tree and *Castilla Elastica*, whereas synthetic rubber is made from petroleum and natural gas through several processes. According to Qiao et al. (2017), rubber is an important industrial material with numerous applications. It can be found in a variety of consumer items, particularly in the automotive industry such as tire tread.

According to Khan et al. (2022), rubber is the primary component of a tire and that are around 70% of the rubber were produced in Thailand, Indonesia, and Malaysia. In addition, the majority (75%) of the rubber was utilized in the production of passenger car tires. Natural rubber (NR) possesses a variety of desirable characteristics that are comparable to synthetic rubbers, such as good oil resistance, low gas permeability, improved wet grip and rolling resistance, and high strength. Petrochemicals, such as fossil fuels, are the basic building blocks of almost all synthetic rubber. According to Ayar et al. (2021), synthetic rubbers, a new class of polymers generated from fossil sources, experienced a dramatic increase in use since last century.

The synthetic rubber usually used in tire industry is called Styrene Butadiene Rubber (SBR), which is formed by polymerizing a copolymer of styrene and butadiene as shown in Figure 2.1 (Wang et al. 2021). The natural rubber (NR) has known to have an extraordinary ability to crystallized while being stretched, which improves tensile

strength, abrasion resistance, and fatigue resistance. However, when exposed to air, it has adverse effects and has weak chemical stability to oils derived from petroleum. SBR is the first synthetic rubber to be considered as an alternative for NR-based goods due to its low processing cost and superior features (Shesaiah et al., 2022). The various types of SBRs with varying features can be created by modifying the Styrene content and polymerization procedure (Oleiwi et al, 2011). Considering the fact that the majority of factors might affect the performance of the compound, the intrinsic properties of the rubbers serve as the main controlling factors.

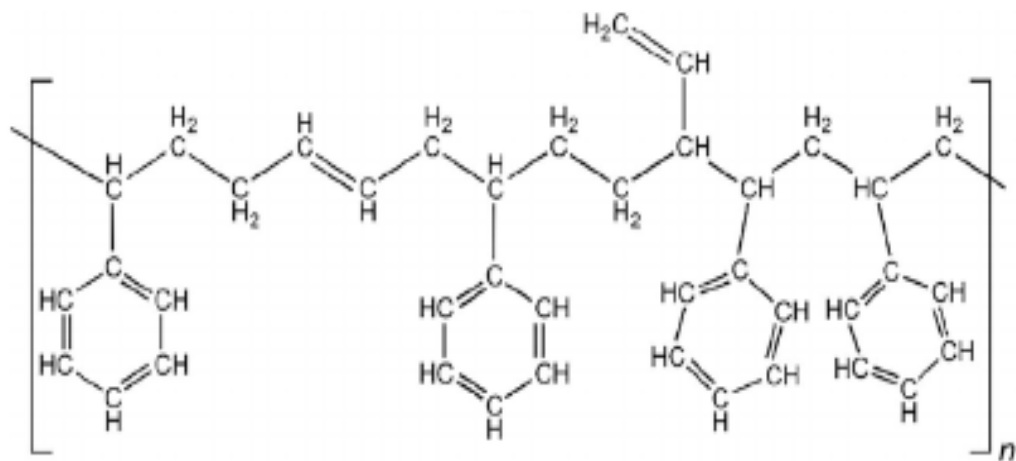


Figure 2.1: Chemical structure of SBR (Wang et. al., 2021)

The wear-resistant portion of a tire that makes contact with the road is known as the tread and is developed or compounded for abrasion resistance, traction, speed, stability, durability and casing protection (Mark, 2013). One of the most crucial features for a tire tread compound among these characteristics is high abrasion resistance. Fillers are a class of compounding materials that are applied to rubber to either strengthen or make the compound appear less expensive. The primary objective of reinforcing is to improve strength and strength-related properties such as abrasion resistance, hardness, and modulus (Vishvanathperumal et al., 2017). Carbon black and silica are the fillers that

are most frequently used to strengthen rubbers during the rubber compounding process because they have a strong interaction with rubber and may transfer stress from rubber to filler (Jong, 2018).

Carbon black (CB) which has a history with tires is typically employed as the primary reinforcing filler for tread compounds due to its enhanced processability and extended tire lifespan (Sae-Oui et al., 2017). The key aspects of carbon blacks are often governed by particle size, surface area, structure, and surface activity, which are typically interrelated. The carbon black has a variety of fine carbon particle types that can provide reinforcement for rubber compounds, with the strength of the reinforcement increasing with decreasing particle size. The tires industry uses a variety of particle fillers for diverse reasons (Pal et al, 2010). One of the most significant fundamental carbon blacks in the rubber industry is N330 which offers strong resilience, simple manufacturing, and ensures good tensile, tear and abrasion resistance properties. Therefore, it is being used in a variety of high severity applications, including tires and mechanical rubber items (Yu et al., 2021).

As was already mentioned, the physical and mechanical properties of the final cured rubber product are significantly influenced not only by the type but also the quantity of carbon black. Carbon blacks with higher specific surface areas will be used by the manufacturer in tyre tread applications as they will lose more heat (hysteresis) and have superior abrasion resistance to rubber than their counterparts with lower specific surface areas. Barlow and Jayasuriya (2014) studied the physical characteristics of the filled rubber compound that are progressively affected by the structure of the carbon black and less by the carbon black's specific surface area as the filled rubber compound is subjected to larger strains (>10%).

Increasing the loading of carbon black also tends to increase the modulus and hardness of the rubber, but some properties, such as tensile strength and abrasion resistance, tend to decrease after a certain loading. Regardless of the grade of carbon black is used, the modulus and hardness of the rubber compound tends to increase as the loading increases, while other properties like tensile strength and abrasion resistance tend to deteriorate once a specific loading was utilized (Franta, 2012). The decrease in the properties was attributed to filler agglomeration and the dilution effect at excessive filler content.

Since the rubber-filler interaction is weak, the filler was unable to transfer stress to the rubber matrix (Srivastava and Mishra, 2018). The correlations between carbon loading and the particular properties that were just addressed are depicted in Figure 2.2. According to Figure 2.2, the modulus, hardness, hysteresis, and viscosity of rubber compounds improve continuously as carbon black loading increases. While tensile, tear, and abrasion values increased with carbon black loading, they decreased after 60 phr loading due to carbon black aggregation. While elongation and die swell decrease as carbon black loading increases due to rubber stiffness improves as carbon black loading increases.

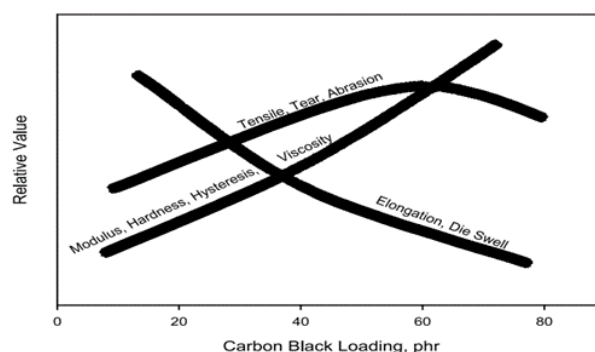


Figure 2.2: The correlation between carbon black loading and properties on rubber compound (Franta, 2012)

2.2 PLASTICIZER AND LUBRICANT

The idea of developing a functional rubber formulation that can be processed and meets or exceeds the specifications of the customer towards the end product is known as rubber compounding. It involves selecting various compounding materials and their amounts. Sisanth (2017) reported that the basic characteristics of the raw rubber inside the compound may be altered by some of the rubber compounding ingredients, such as vulcanizing or cross-linking agents, antidegradants, plasticizers, processing aids, and fillers.

As discussed earlier, carbon black is frequently used as a reinforcing filler in rubber. However, as the loading of carbon black in the rubber system increases, the average distance between carbon black particles decreases, causing agglomeration (Dong et. al, 2017). The buildup of particles might reduce the tensile strength of rubber. The viscosity of the compounded rubber may increase with increasing carbon black loading hence reducing the diffusion rate into the rubber particles.

Jiang and Zukoski (2012) had establish that the plasticizers and lubricants would enhance the processing of the rubber by lowering the viscosity of the rubber compound. Rodgers (2015) claims that plasticizers or lubricants may build up at the rubber-filler interface, improving carbon black dispersion is desired to enhance the mechanical properties of rubber compounds.

Plasticizers or lubricants are usually in the form of liquids, but sometimes solids or semi-solids are known as processing aids that are added to the rubber in order to increase their flexibility and processability. They are functions to reduce intermolecular tensions, which also increases elongation and low-temperature flexibility while decreasing

hardness, glass transition temperature (T_g) of rubber compounds (Dasgupta et al, 2009). According to Ayar et al. (2021), base oils are a key component of lubricants and plasticizers, come in two different forms: mineral (produced from petroleum) and green-based (derived from plants).

2.2.1 Blooming

Blooming occurs when lubricants and plasticizers that are not chemically linked to the rubber chains migrate out of the rubber depend on service conditions with environmental factors such as light, ozone, humidity, or heat (Munasinghe, 2004). Blooming has been attributed to the excess of additives and how differently they solubilized in the rubber matrix. The wax blooming provides an impenetrable physical barrier that shields the vulcanised SBR from ozone attack.

However, the accumulation of oily or powdery particles on the surface of rubber items is detrimental to their visual appeal, interfacial and adhesion properties (Santiago et al., 2016). In fact, Torregrosa-Coque et al (2011) stated that the occurrence of blooming refers to a reduction in the free energy of the vulcanised SBR surface, which might have an adverse effect on both the adhesion of other materials and to itself, especially in the production of multiply products such tire, rubber hose and other products.

According to Yasin et al. (2016), blooming of compounding ingredients was can be related with the solubility and concentration of compounding additives. At the storage or operation temperature of these rubber products, the compounding additives such as curing agents, accelerator, processing aids, and activators must have a concentration larger than this nominal solubility and a limited but considerable solubility in the rubber. The available compounding additives will crystallise when the rubber vulcanizate cools

after the vulcanization process, and as the crystal grows inside the rubber, regions of strain will form around the crystal in bloomed wax concentration.

2.2.2 Mineral Lubricant and Plasticizer

Mineral lubricants or plasticizers are currently the most frequently used commercial lubricants and plasticizers globally. It is made up of a complex blend of paraffinic (linear/branch), olefinic, naphthenic, and aromatic hydrocarbons with 20 to 50 carbon atoms (Karmakar et al, 2017). In comparison to other lubricants and plasticizers, it is less costly and relatively stable as it has greater oxidation stability.

High aromatic oils have historically been the most popular process oils for tires manufacturing, according to research work by Ezzoddin et al. (2013). Their popularity can be attributed to the fact that they have a great combination of qualities and are less expensive than other kinds of process oils. Polycyclic aromatic compounds are not permitted to be used as rubber additive material in the European Union due to potential health hazards (Schneider, et al., 2020).

Kuta et al (2010) claim that due to the high concentrations of polycyclic aromatic compounds (PAHs) found in these oils, some of them have been identified as probable carcinogens. Since 2010, only lubricants or primers with low levels of polycyclic aromatic hydrocarbons (PAHs) will qualify as non-carcinogenic in new tyres produced or imported into the European Union Ezzoddin et al. (2013).

However, the direct substitution of aromatic oils is not a workable option since the new compounds do not completely satisfy the criteria of original compound. Research work by Myhre et al. (2012) on the replacement of 10 phr of free aromatic process oil in

an SBR tread compound with 10 phr of three different hydrocarbon resins shows the addition of resins has slightly increased the cure time from 12.3 minutes to 13 minutes.

Based on their finding, although crosslink densities of the new compounds were equivalent to those of the control no changes were made to the physical characteristics of rubber compound including rebound, Shore A hardness, compression set, abrasion wear, or tensile strength. The findings are shown in Table 2.1 which outlines the basic formulations and the physical characteristics of SBR tire tread compound with processing oil and 3 different hydrocarbon resins.

Table 2.1: The formulations and the physical characteristics of SBR tire tread compound with processing oil and 3 different hydrocarbon resins (Myhre et al., 2012).

Component	Control	A	B	C
SBR	100	100	100	100
Stearic acid	1	1	1	1
Zinc oxide	3	3	3	3
N-234 carbon black	52	52	52	52
Sundex 790 process oil	10	10	10	10
C5 resin	-	7	-	-
DCPD resin	-	-	7	-
C9 resin	-	-	-	7
TMQ	1	1	1	1
TMTD	0.18	0.18	0.18	0.18
TBBS	0.75	0.75	0.75	0.75
Sulphur	1.8	1.8	1.8	1.8
Processability				
Physical, cured T90 at 320 ° F				
M300 (psi)	1863	1460	1178	1360
Tensile strength (psi)	3368	3546	3286	3499
Elongation (%)	469	573	610	594
Hardness, Shore A	70	69	69	69

The plasticization and reliability properties of two different low and high oil-extended tyre formulations were examined by Ezzoddin et al. (2013) using four types of low aromatic petroleum-based process oils, including mild and high-viscosity naphthenic oils (LNAP and HNAP), treated-distillate aromatic extract (TDAE), and mildly extracted solvate (MES). In contrast, high aromatic oil was prepared from distillate aromatic extracts (DAEs). The results showed that the use of non-carcinogenic lubricants enhanced a variety of qualities, including abrasion resistance as shown in Figure 2.3.

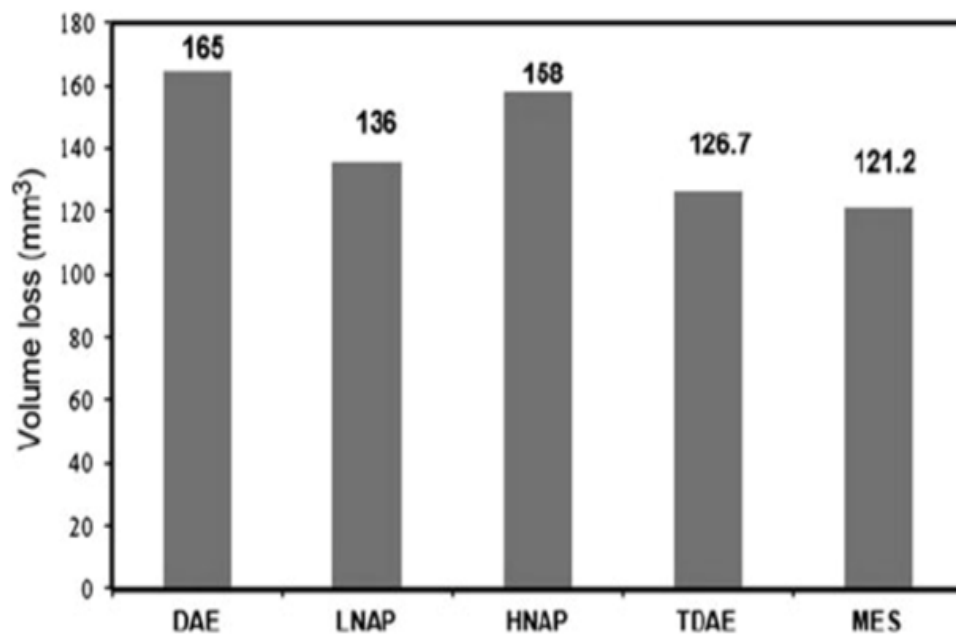


Figure 2.3: Volume loss of tire tread compound with high and low aromatic oils (Ezzoddin et al., 2013)

Another study was conducted by Petchkaew (2015), who found that when low PAH process oil such as treated distilled aromatic extract (TDAE), mild extracted solvate (MES), and naphthenic (NAP oils) were used to replace high PAH distilled aromatic extract (DAE) process oil in carbon black and silica filled tire tread compounds, the results shown that the tread compounds has comparable tensile strength, modulus,

and hardness, reduced rolling resistance, but less effective wet traction when compared to the DAE compound.

Although DAE oil may be replaced th petroleum-based process oils also known as low aromatic oil like TDAE and NAP without sacrificing any essential properties, the cost of these mineral oils is higher than the original DAE which determined by fuel prices. According to Niemczyk (2012), even some relatively harmless petroleum-based oils might contain carcinogens. Hayichelaeh (2020), Kukreja et al. (2003) and Fernandez et al. (2015) attempts to minimize fuel use have sparked a search for more environmentally friendly oils, such as plant, vegetable oils and their derivatives.

2.2.3 Natural Lubricant and Plasticizer

The tire and rubber industries have invested a great deal of effort over the past 20 to 30 years to develop new applications for recycled or out-of-date materials. Natural lubricants and plasticizers are preferable to mineral lubricants and plasticizers as processing aids because they are portable, conveniently available, renewable, improve combustion efficiency, have a lower aromatic content, and are more biodegradable. The main benefits of biodiesel are its domestic production, decreased reliance on petroleum imports, high flash point, and built-in lubricity in neat form (Demirbas, 2009). According to Hayichelaeh et al (2020), palm, soybean, and rapeseed oils are some of the most important natural oils on the earth due to their large global output and affordability for extensive industrial application. Natural lubricants and plasticizers have recently attracted significant interest in a variety of small- and large-scale industries, including paints, lubricants, biofuels, soaps, etc.

There are several studies that compared various natural oils to mineral oil. According to research by Abbas and Ong (2019), they used crude palm oil (CPO) with various loadings to examine how it affected the mechanical properties of natural rubber (NR) in comparison to paraffin oil. Due to the world's largest oil palm industry in Malaysia and the growing acceptance of CPO on the global markets. As a result, CPO, one of the top four vegetable oils commercialized, has a good prospect as a substitute for processing oils derived from petroleum in rubber compounds. Kukreja et al. (2003) used castor oils in a variety of dosages along with other oils such as paraffin and cashew nut shell liquid (CNSL) at a constant dose (1 phr) to improve the interaction of rubber with carbon black. They investigate on how it affected the physical, mechanical, and adhesion characteristics of carbon black/rubber compounds.

In the study published by Fernandez et al. (2015), they employed linseed oil as a plasticizer for nitrile rubber/expandable graphite (NBR/EG) and naphthenic oil as a reference. The effect of linseed oil on the rubber's cure and mechanical characteristics was carried out. It can be used as a replacement for mineral oil due to the rise in oil costs and the harm that mineral oil does to the environment.

The influence of natural and mineral oils on the rheometric, swelling, and mechanical properties of rubber composite before and after thermo-oxidative aging was investigated by Kalaf et al (2015). The goal of their work is to investigate how natural oils from orange and olive, as well as petroleum derived Dioctylphthalate (DOP), which is used to enhance rubber's processing properties of acrylonitrile-butadiene rubber (NBR). Physical and mechanical studies revealed that olive and orange oils offer stronger mechanical properties, hardness, and ageing resistance than DOP for NBR vulcanizates. Chandrasekara et al. (2011) also examined at the use of epoxidized palm, soybean, and

sunflower oils as processing aids in natural rubber for truck tires. They conducted an experiment to determine the curing characteristics, processability, and physical features of standard rubber compound, which is composed of minerals oil and has been banned due to its exceedingly hazardous consequences.

2.3 CHARACTERIZATIONS OF RUBBER COMPOUNDED WITH NATURAL LUBRICANT AND PLASTICIZER

2.3.1 Cure Characteristics

The cure characteristics of rubber vulcanizates, such as the scorch time (T_{s2}), optimum cure time (T_{90}), maximum and minimum torques (MH and ML), is important in the rubber and tire industries. According to Moresco et al. (2016), ML are important since they are used to evaluate the viscosity of the compound before rubber is vulcanized. This value reveals how easily rubber flows during production. While the cross-link density of rubber vulcanizate is determined by MH. For the T_{s2} , this is the period of time during which the torque increased per 2 units and the determination of the starting point of vulcanization. T_{90} was the point at which the rubber has vulcanized to a 90% degree. It is also the time that provides vulcanizates with the highest possible tensile strength.

Table 2.2 shown the cure characteristics of paraffin oil (PO) and crude palm oil (CPO) at different loading in NR compounds. According to Abbas and Ong's (2019), the ML of CPO is greater than the PO at 1 phr loading. However, the ML value drops while CPO loading is increased, and the contrary has occurred for PO. This is because PO lacks polarity to interact with NR, which results in a weak plasticizing effect when PO loading is increased (Khalaf et al., 2015). Since CPO contains a lot of unsaturated fatty acids, it has a stronger plasticizing effect with NR.

Table 2.2: The cure characteristics of paraffin oil (PO) and crude palm oil (CPO) in SMR with 1, 3 and 5 phr loading (Abbas and Ong, 2019).

Materials	1phr PO	3 phr PO	5 phr PO	1phr CPO	3 CPO	phr 5phr CPO
ML (dNm)	3.70	4.00	4.20	4.90	3.60	2.00
MH (dNm)	31.22	35.70	36.5	32.3	38.7	34.5
ML-MH (dNm)	27.52	31.7	32.3	27.4	34.1	32.5
Ts2 (min)	4.00	3.21	3.38	4.13	3.52	4.03
T90 (min)	11.23	10.91	11.39	12.47	12.56	12.15
CRI (min- 1)	13.82	12.98	12.48	11.99	11.06	12.32

When the loading of PO increased, it was observed that the MH value increased. As a result, it was found that the loading of PO and the crosslink density in the NR are related. However, when the CPO loading is 3 phr, the MH value for CPO is at its maximum. This showed that 3 phr is the ideal loading time for the CPO. However, since the Ts2 is not significantly different, it can be said that both CPO and PO will not have an impact on the Ts2 value. While the T90 data demonstrate that PO cures more quickly than CPO for both different loadings. Akolisaibemesi (2007) suggests that it may contribute from the unsaturated fatty acids in CPO reduce the impact of carbon black's interaction with rubber, while the sulphur is more likely to react with the double bond in CPO. As a result, it is shown that the cure rate for CPO is lower and the cure duration is longer.

Similar findings were observed by Fernandez et al. (2015), The curing characteristics of linseed oil (LO) and naphthenic oil (NO) with different loading was shown in Table 2.3. The cure time of LO increases with an increase in the loading of LO in NR/EG vulcanizates. They suggested that the Increase in the LO loading was due to

the non-compatibility of the oil, which outweighs the effect of favorable unsaturated fatty acids. It also can be observed that with 2 phr of LO, the rubber vulcanizate exhibited a maximum torque which decreased with an increase in the loading of LO. This may be due to the fact that the double bond present in the LO can participate in the crosslink interaction between the EG and rubber.

Table 2.3: Cure characteristics of LO and NO in NR/EG (Fernandez et al., 2015)

Sample	T90/min	Ts2/min	ML (dNm)	MH (dNm)
NR/EG	5.51	2.11	0.35	7.92
L2	5.43	2.11	0.31	8.12
L4	5.42	2.21	0.25	8.04
L6	5.44	2.20	0.24	7.45
L8	5.40	2.28	0.23	6.71
L10	6.04	2.35	0.21	6.57
N2	6.22	2.33	0.04	6.82
N4	6.35	2.58	0.08	6.66
N6	6.38	2.37	0.13	6.70
N8	6.17	2.49	0.16	6.75
N10	6.14	2.55	0.16	6.79

The results of Chandrasekara et al. (2011)'s study demonstrate that the scorch time values of rubber vulcanizate compounded with epoxidized vegetable oils are lower than those of aromatic oils as shown in Table 2.4. The amount of time that passes before the beginning of the cure is what determines processing safety. To enable shaping, forming, and flowing in the mould, which improves the tire's grip, there must be enough delay or scorch resistance when preparing the tread. For standard mineral oil (NMO) and

Epoxidized soya bean oil (ESBO), the scorch time is longer, correspondingly. As a result, they demonstrate greater processing safety than Epoxidized palm oil (EPO) and Epoxidized sunflower oil (ESFO). For EPO, the shortest scorch time is attained. This indicates that the production of crosslinks begins quickly in the compound containing EPO and that EPO, followed by ESFO, contributes the most to the activation of the vulcanization rate.

The compound containing EPO cures in a comparable amount of time to the compound containing NMO. The former has the maximum cross-link density at T90, demonstrating the ability to process rubber with equal energy efficiency to the NMO. Crosslink density rises along with delta cure. In comparison to other natural oils examined, compounds containing EPO had the highest cross-link density.

Table 2.4: Cure characteristics of Epoxidized vegetables oils (Chandrasekara et al., 2011)

Processing Aids	Scorch Time/ min	Cure Time/Min	Cure Rate Index/min-1	Maximum Torque/ Nm	Delta Cure/Nm
NMO	2.60	6.09	28.65	9.48	8.09
EPO	2.12	6.09	25.19	9.20	8.27
ESBO	2.38	6.41	24.81	8.78	7.71
ESFO	1.93	6.39	22.42	7.88	6.42

Table 2.5 shows the cure characteristics between mineral oil and biodiesel done by Cataldo et al, (2013). Based on Table 2.5 it is shown that the maximum torque (MH) is reduced by biodiesel and therefore the crosslinking density of the compound is also decreased. This can be supported by the lower value of the MH-ML when compared to Mineral Oil.

The outcome of the result indicates that biodiesel, which is made up of unsaturated methyl esters of fatty acids as reactive plasticizers susceptible to sulphur-based vulcanization. The methyl esters of fatty acids are highly reactive with the sulphur used in the curing process and take away some of the sulphur that would otherwise be added to the crosslinking of the rubber chains, causing a decrease in modulus and tensile strength with an increase in elongation.

Table 2.5: Cure characteristic of biodiesel and mineral oil loaded rubber vulcanizate (Cataldo et al, 2013)

Rheometer Test at 160°C	Aromatic Oil	Biodiesel
ML (dNm)	3.07	3.13
MH (dNm)	15.04	13.24
ML-MH (dNm)	12.0	10.1
Ts2 (min)	3.34	3.25
T90 (min)	8.19	7.34

2.3.2 Swelling Index

The swelling index is an indication of crosslink density, which in turn correlates with the physical properties of the various vulcanizates. The swelling index of rubber compound containing various epoxidized vegetable oils are shown in Table 2.6. According to findings from Chandrasekara et al. (2011), rubber compounds using vegetable oil show greater swelling resistance and crosslink density. Vegetable oils commonly include unsaturated long-chain fatty esters that interact well with the surface-active polar groups of carbon black while doing the same for rubber molecules at their non-polar hydrocarbon chain ends. High unsaturation enhances the crosslink density, which also facilitates the degradation of the double bonds in the oil.