EFFECT OF SKIM LATEX ON MECHANICAL PROPERTIES OF TIRE TREAD COMPOUND

NURUL HUSNA BINTI MOHAMAD JAFRI

UNIVERSITI SAINS MALAYSIA

2022

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

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By

NURUL HUSNA BINTI MOHAMAD JAFRI

Supervisor:

ASSOC. PROF. DR NADRAS BINTI OTHMAN

Dissertation submitted in partial fulfillment of the requirements for the degree of

Bachelor of Engineering with Honours

(Polymer Engineering)

Universiti Sains Malaysia

AUGUST 2022

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled the effect of skim latex on mechanical properties of tire tread compound. 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.

Name of Student: Signature:
Nurul Husna
Date: 19/8/2022

Witness by
Supervisor: Assoc. Prof. Irt. Dr Nadras Othman Signature:
Date: 19/8/2022

ACKNOWLEDGEMENT

First and foremost, I would like to praise and thank the Almighty Allah for the blessing bestowed upon me and granted my wish to complete my final year project within the predetermined time. If it were not for His blessings, I would not possibly be able to complete my final year project.

Apart from the efforts that I have put in, nurtured with patience in completing the assigned project, the success of this thesis substantially depends on the encouragement and guidance of many others. I take this opportunity to express my gratitude and sincere appreciation to my supervisor, Assoc. Prof. Dr. Nadras Othman for her valuable support, guidance and comments withal patience throughout the venture of completing this project. My deepest appreciation to all technician staff of School of Materials and Minerals Resource Engineering especially the polymer engineering technician staff, Mr Mohd Suharudin Sulong and Mr. Shahril Amir Saleh, for the continual help and guidance.

Besides, not to lose sight of the support received from my family, which had me kept going to finish the entire project subsequently at ease. The motivational words given by was inspirational and had pushed me forward until the project comes to the end. Last but not least, I would like to say thank you to my final year course mate who contributed directly and indirectly to my project. I would like to acknowledge their comments, suggestion and motivation, which vitally assist me in completing the project.

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LIST OF SYMBOLS

℃	Degree celcius
%	Percentage
m	Mass in gram of the dried material
m_o	Mass in gram of the test portion
min	Minute
MPa	Mega Pascal
M_H	Maximum torque
M_L	Minimum torque
s	Second(s)
t_{90}	cure time
t_s	Scorch time

LIST OF ABBREVIATION

ARI	Abrasion Resistance Index
SR	Skim Rubber
ASTM	American Society for Testing and Materials
CB	Carbon Black
CRI	Cure Rate Index
CV	Conventional Vulcanization
DRC	Dry Rubber Content
EV	Efficient Vulcanization
FEF	Fast Extrusion Furnace
HA	High Ammonia
HAF	High Abrasion Furnace
HM	High Modulus
HS	High Structure
IPPD	N-Isopropyl-N'-phenyl-1,4-phenylenediamine
ISAF	Intermediate Super Abrasion Furnace
ISO	International Organization for Standardization
MBTS	2-2'-Dithiobis(benzothiazole)
MDR	Monsanto Die Rheometer
MST	Mechanical Stability Time
M_w	Molecular weight
NR	Natural Rubber
NRL	Natural Rubber Latex
pH	potential of Hydrogen
Pphr	Parts per hundred rubber
RT	Room temperature
SA	Stearic acid
SAF	Super Abrasion Furnace

ABSTRAK

KESAN LATEKS SKIM PADA SIFAT MEKANIKAL DAN FIZIKAL SEBATIAN BUNGA TAYAR

Kesan penting penggabungan skim getah dalam sebatian bunga tayar telah disiasat. Kaedah ini telah dikaji dalam beberapa tahun kebelakangan ini bahawa sebatian inklusif yang digabungkan dengan lateks skim sepatutnya mempunyai kesan ke atas menyembuhkan ciri-ciri getah. Terutamanya, pentadbiran kajian ini adalah untuk mengesahkan kebolehterimaan skim lateks untuk diintegrasikan dalam sebatian bunga tayar serta menggantikan getah asli dalam pembangunan sebatian getah. Tujuh variasi nisbah pencampuran SMR 10/skim getah telah disediakan berbeza-beza dari 100:0 hingga 0:100 dan sifat-sifat mekanikal sebatian masing-masing telah diperiksa selepas itu. Secara amnya, beberapa ujian mekanikal telah dilakukan untuk menyiasat sifat-sifat mekanikal campuran lateks SMR 10/skim getah iaitu ujian kehausan, tegangan, ujian kemerosotan indeks, dan sebagainaya. Kaedah eksperimen dan arahan sampel dirujuk kepada ASTM D228, ASTM D412-98, ASTM 624 dan ASTM D3616. Kehadiran protein mendorong pengukuhan pautan silang di dalam rantaian matriks getah yang bersebelahan. Kesimpulannya, getah skim menimbulkan kualiti komposit getah yang lebih rendah kerana prestasi mekanikal merosot dalam surat-menyurat untuk meningkatkan penggabungan getah skim. Prestasi mekanikal yang merangkumi kekuatan tegangan dan lusuh, rintangan lelasan, kekerasan getah dan indeks kemerosotan SMR 10/Skim cenderung menurun dengan ketara apabila bahagian getah skim meningkat dari 20 hingga 100 pphr. Walaupun begitu, ciri penyembuhan dipertingkatkan dengan ketara oleh integrasi getah skim.

ABSTRACT

THE EFFECT OF SKIM LATEX ON MECHANICAL AND PHYSICAL PROPERTIES OF TIRE TREAD COMPOUND

The vital effect of incorporation of skim latex in tire tread compound has been investigated by preparing seven variations of blending ratios of skim rubber/SMR 10 varies form 100:0 to 0:100. The mechanical properties of the rubber vulcanizates have been examined thenceforth. This method has been studied in recent years that the inclusive compound incorporated with skim latex ought to have an effect on curing characteristics of the vulcanizates. Predominantly, the administration of this particular investigation is to validate the admissibility of skim latex to be integrated in tire tread compound as well as substituting natural rubber in the development of rubber compound. A researcher had executed an experimentation correlated to skim latex/NR combination wherein high protein content and fatty acid in skim rubber is distinctly affect the vulcanization conduct of rubber compound. Generally, few testing had been performed to investigate the mechanical properties of skim rubber/SMR 10 blend namely abrasion test, tensile, swelling index test, and tear test. The experimental method and sample instruction were referred to ASTM D228, ASTM D412-98, ASTM 624 and ASTM D3616. The presence of protein is perceived as the strengthening effect, bonding the molecular chain of rubber. However, it was found that the mechanical properties of SMR 10/skim rubber blend prospect to decrement, wherein the abrasion resistance, tear strength and tensile strength has diminished in correspondence to the increasing portion of skim rubber. In spite of that, the cure characteristic of rubber composites significantly increased coherently with the proportional increment of skim rubber from 20 to 100 pphr.

CHAPTER 1

INTRODUCTION

1.1 Background Study

Wet grip index, rolling resistance and abrasion resistance are three main properties in the development of tire tread compound. The combination of synthetic and natural rubber has become the most in industries of tire tread manufacturing, gives superior performance of the tire. However, the main focus in this study to evaluate the incorporation of skim latex on mechanical properties of tire tread compound by preparing heterogeneous of blending ratios between skim latex and SMR 10. Seven blending variations varies from 100:0 and 0:100 between the ratios of SMR 10 to skim latex.

Fundamentally, gloves, in particular, those have been dipped in NR latex have been regarded preferentially as an efficient barrier against transmitted disease. However, it has been noted that some consumers' suffer severe allergies are triggered by the latex products residual protein (Kalapat, Watthanachote and Nipithakul, 2009). Consequentially, protein ought to be reduced due to the allergenic content commonly by centrifugation process and can be further leached during processing. Correlatively, skim latex is a by-product waste generated upon centrifugation of natural rubber to productize concentrated latex, prompts long-term preserved latex. Thereupon, approximately 5–10% of TSC and a high relative proportion of the natural rubber latex's non–rubber components remain in the serum phase (T. and Rojruthai, 2012).

Skim rubber block principally produced from neutralization of the skim latex with acidic substance develop low dirt rubber bale. Skim rubber block are acquired affixed to consequential process of skim latex destabilization, accumulating coagulant forms hence will be utilized to manufacture lower-grade rubber application. In recent years, it was reported that the curing characteristics of rubber vulcanizates potentially enhanced preceding from inclusive skim rubber incorporation mechanism. High level of non-rubber particles present give rise to rather slow, scorchy cures and high modulus vulcanizates. This latter phenomenon is muchly attributed by the presence of the protein in the skim rubber, which is perceived to enact as reinforcing filler.

It was found that up to 20 phr of skim rubber can be added to natural rubber without the addition of further curatives amidst of retaining a high quality vulcanizate property. Addition of this level of skim rubber has not reported any reversion in curing process. The mechanical properties of skim rubber and smoked sheet rubber blends for a solid tire tread compound has shown up to 25 phr of skim rubber could be blended with natural rubber without affecting the desired properties (BRISTOW, 1990).

1.2 Problem Statement

Prominently, widely used raw rubber materials in tire manufacturing are butadiene rubber (BR) and Styrene Butadiene Rubber (SBR) with the aggregate of NR. The combination of artificial and natural rubber is the most accessible approach in tire industries to accustom the development of particular qualities. As matter of fact, NR imputable for imposing excellent tear and fatigue crack resistant. The exclusion of synthetic rubber in making tire tread is somewhat remain ambiguous, which manufacturer are apparently not attentive to other rubber blend compound in the respective application.

The incorporation of skim latex in composing tire seemingly remains vague and concealed in rubber industries. A study has established that the incorporation of skim rubber might affect curing characteristics of compounded rubber between skim latex with SMR 10 at different proportions due to the presence of excessive protein content and other non-rubber constituents.

Conclusively, up to 20 phr of skim rubber can be introduced to natural rubber to without curatives while keeping high-level vulcanizate properties. Skim rubber incorporated with high degree of metallic components i.e., copper and protein content withal other non-elastomeric components, which considerably federates skim rubber as inferior waste material. The skim NR latex has small rubber particles in the range of 0.05 m with a suggest particle diameter of 0.1 m. In spite of perceivably considered as inferior quality, a prior study has verified that skim rubber has excellent properties at which point that blending SNR with NR concentrate is a deliberate method to offset the inferior effect of skim latex (Rahim *et al.*, 2016)

However, there is antithetical conception on the amalgamation of NR with skim rubber, which susceptible to cause difficulty during processing and the encountered hassle possibly due to high presence of protein and non-rubber constituents. Skim rubber is regarded as low-quality raw natural rubber with industrially undesirable raw rubber properties such as a high Wallace Plasticity Number, a low PRI, and a high nitrogen content. Subsequently, despite its characteristics such as low dirt and light color, skim rubber commands the lowest price of any NR grade. (Senevirathna and Sudusinghe, 2020).

Henceforth, this investigation is emphasized on the interpreting the imperative effect of skim latex on the mechanical properties of Skim latex/SMR 10 blends with dissimilar mixing ratios. In this regard, the characteristics of the respective rubber compound concerning its mechanical and physical properties will be appraised and the acceptability to be used in tire manufacturing can be investigated.

1.3 Research Objective

I. To prepare different variations of Skim latex/NR blend with different composition.
II. To investigate the effect of the presence of skim latex in rubber compounding on the mechanical properties of tire tread compound.

1.4 Thesis Outline

The appended sections of this project are recounted as follows:

Chapter 1

This chapter primarily explains profile of the project, the inclusive description of background of study, problem statement, research target and a brief configuration of the chapters involved.

Chapter 2

Inclusion of the clarification of an intricate ensemble of ingredients utilized in the development of the project included the overview of the general perspective of raw material, carbon black and other ingredients necessary in the compliance of rubber compounding mechanism.

Chapter 3

The project overview specifically on the materials used and research methodological aspect particularly on the inauguration of the compounding process, equipment, and testing detailed-directed procedures in accordance with the ASTM standards complied.

Chapter 4

Congregated results are deliberately discussed in this section preceding from the acquired sequel of the testing and observation within the venture project development.

Chapter 5

A brief consolidation of the entire research outlook along with the justification of the respond to the primary aforementioned objectives upon the pertaining project.

CHAPTER 2

LITERATURE REVIEW

2.1 Skim Latex

Prominently, Malaysia is well-known for being one of the biggest manufacturers of NR. Field latex is fresh latex tapped from the rubber tree (*Hevea Brisiliensis*), which is a cloudy white and viscous liquid containing rubber proportion and non-rubber elements (Mohamed and Yusof, 2014). As a basic raw material in rubber processing, which necessitates a series of procedures to produce dry rubber or high concentrated latex. Microbial activities inevitably causes colloidal instability, which consequently lead to latex coagulation and evidently unable to be used in latex product manufacturing.

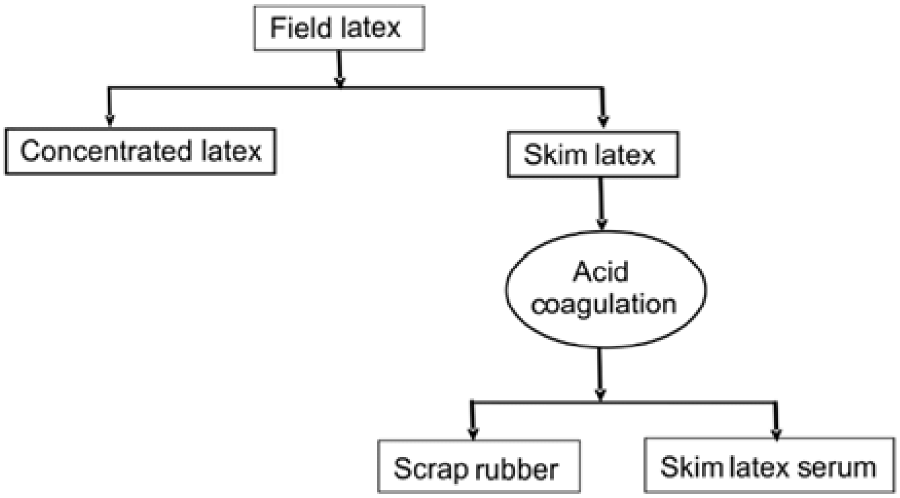


Figure 2.1 Generation of skim latex (Lim, El-Harbawi and Yin, 2017)

The respective figure shows the generation of skim latex primarily from field latex before subjected to centrifugation process. The primary raw material in rubber processing, fresh field latex need to undergo a series of procedures at some point of its conversion to dry rubber, or high concentrated (HA) latex, wherein ammonia is introduced to the field latex to substantially avoid coagulation. The system of centrifugation to attain HA latex, yielded a by-product, recognized as skim latex, considered as low-value by-product and usually discarded as waste effluent. Waste administration and effluent remedy apparently devour variably high value and henceforth another alternative has been delivered to industries by means of reuse the wasteful skim latex (Mardina and Yusof, 2019). Ever since, this approach has elevated the economic savings measures and limit the environmental problems.

Ammonia is the preservative substances used to prepare high concentrated latex as a long-term preservation of field latex to avoid coagulation. The ammoniated latex will be centrifuged afterwards, yielding concentrated latex and a byproduct termed as skim latex. Skim latex is a low-value by-product that is customarily discarded as waste effluent. Rubber manufacturers will eventually have to splurge on waste management and skim latex effluent treatment. As a corollary, employing this wasteful skim latex is one of the capital measures, which might significantly reduce environmental problems (Mardina and Yusof, 2019). Lamentably, skim latex incapable to be recycled into new rubber products and ought to be treated in the effluent treatment reservoir before being released into the stream. Malaysia indisputably still repressed with the striving cost of skim latex waste management and environmental problems despite the higher NR production (Mohamed and Yusof, 2014)

Skim rubber can be recovered from skim latex with the aid of neutralization and coagulation of this latex with the aid of appropriate method then gives skim rubber. Skim block rubber has a low dust content, frequently accompanied by mild color and has exceptionally less odor. The rubber inevitably retains many of elements of the regular materials, in specific the hydrocarbon content material is rather low, generally about 80% in contrast with 93-94% appearing as a reinforcing filler (BRISTOW, 1990). Centrifuged latex comprised of microparticles of a narrow range in which smaller particles yet most of the non-rubber are detached and incorporated into the skim latex fraction during centrifugation, as regards to ultrafiltered latex in which all particles are retained and the film properties have yet to be evaluated (Zairossanif, 2006).

2.1.1 Molecular structure of Skim latex

During the centrifugal process of field latex, approximately 5-8% DRC is left in skim rubber latex, and skim latex has a high non-rubber proportion and ammonia content (Zhang *et al.*, 2015). Skim rubber contains 70-85% rubber component and there are number of proteins contaminate in skim rubber. Customarily, 5-10% acetone-soluble fatty materials and 10-20% proteins, compared with an average of 95% hydrocarbon, 3% fatty materials and 2% protein of skim rubber as contrasted to fresh field latex (T. and Rojruthai, 2012).

It was discovered in the last decade that skim rubber seemingly having no ester content when compared to concentrated rubber, i.e., 0.03 per rubber chain. This implies that the rubber molecules in skim rubber are not terminated by phospholipids, as evidenced by the presence of phospholipids in concentrated rubber molecules. (Kawahara *et al.*, 2000). The illustration of rubber particle in natural rubber is shown in figure 2.2.

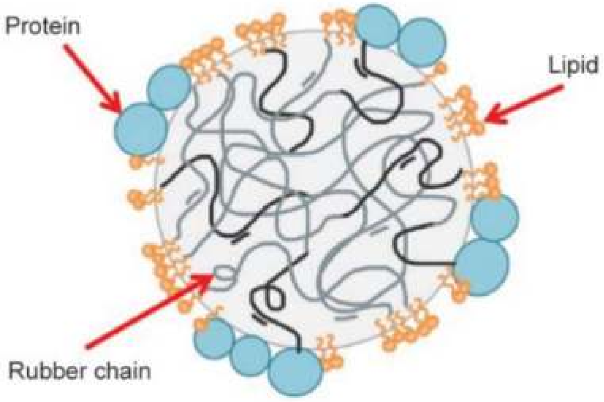


Figure 2.2 Natural rubber particle illustration (Promsung *et al.*, 2021)

The presence of protein and lipid content is indeed particularly notable. The rubber particles are mostly spherical, but also discoverable as pear-shaped, which is found in floating cream and are composed primarily of a hydrophobic core of Polyisoprene surrounded by a monolayer of lipids and proteins, with permeable and fluid membrane (Berthelot *et al.*, 2014). It was found that in afore study that the protein content endeavor the biggest contribution to mechanical properties of rubber compound. Bristow has concluded in his prior research on composition and cure behavior of skim rubber block that the mechanical properties of SMR 10/skim rubber increases with the incremental proportion of skim rubber by 20 pphr. He frequently emphasized on the effect of protein on the enhancement of tensile and tear strength.

Nevertheless, Sakdapipanich has conducted a study on the molecular structure of skim rubber via H-NMR spectra of fractionated skim rubber and 1-month old seedlings. Skim rubber exhibited three major signals at 1.78, 2.10, and 5.18 ppm, which are assigned to -CH3, -CH2, and =CH of cis-1,4 isoprene units, respectively. Additional signals were detected in the rubber of 1-month-old seedlings at 4.0-4.3 ppm and 1.2 ppm, which have been assigned to terminal -CH2O and long methylene sequence -(CH2)n- of fatty acids (Sakdapipanich, 2007). This study suggests that, unlike concentrated rubber, skim rubber is composed of linear rubber molecules. The absence of both signals in fractionated skim rubber clearly indicates that there is no phospholipid linked to the rubber chain. Phospholipid groups, including long-chain fatty acids, were discovered to be important in the formation of branched structures (Tarachiwin et al., 2005; T. & Rojruthai, 2012).

Evidently, from the foregoing clarification, it is notable that protein alone incapable of imposing induction of high crosslinking network. This latter explains lower mechanical properties of skim rubber than SMR 10.

2.1.2 Non-rubber constituents in Skim Latex

Skim rubber has a nitrogen level indicating a protein content of 10% to 15%, as well as a high level of acetone extractable material, of which a significant amount is made up of a mixture of fatty acids. The carbon number and degree of unsaturation of these acids are identical to those found in normal grades of NR, but the quantities of the various species may differ. The skim samples are significantly cleaner than SMR L in terms of contaminant dirt level, but the ash content, which includes all sorts of mineral debris, is 50 percent more than that observed in latex grades such as SMR L or centrifuged latex concentrate. Despite the high concentration, the copper appears to be oxidation inert (Rahim *et al.*, 2016).

Manganese is metallic element possessing oxidation catalyst potential and is discovered in trace amounts in NR. In spite of its high copper levels found in skim rubber, manganese levels in standard grade SMR L are comparable. The manganese is particularly associated with the rubber phase of the latex, whilst the copper is prevalent in the serum and thus concentrated in the skim latex before being co-precipitated with rubber during coagulation. The presence of high levels of fatty acid and protein distinguishes skim rubber from regular natural rubber. Afore factor has high propensity of affecting rheological behavior of rubber compound. The cure system does not affect the rheometer torque levels observed for skim rubber, and there is no significant correlation between torque and fatty acid content for the various skim samples. Similarly, while the high acid content of skim likely contributes to the low cure rate and addition of stearic acid to the cure system in normal grades of natural rubber does not influence the result observed between MH – ML and t_{90} for skim rubbers (BRISTOW, 1990).

Ultimately, concentrated skim latex is am material which inherits all the smaller rubber particle, non-rubber predominantly proteins with higher molecular weight and minerals. During the ultrafiltration process, SNR loses the aqueous phase along with proteins and lower molecular masses as well as carbohydrate components to the skim serum fraction as permeates.

2.2 Rubber Compounding

Rubber compounding entails the science and engineering of rubbers and rubber additives, such as processing aids, fillers and curing agents, in particular proportions to achieve a uniform combination that will have suitable bodily and chemical properties to meet processing at low value and possible cost. The foremost targets of rubber compounding are prospect to impervious certain properties in finished products, attaining processing characteristics imperative for efficient utilization of available equipment and to subsequently obtain the ideal properties and method capacity at the lower feasible cost.

The quintessential apprehensive step of rubber compounding is commenced with the incipient stage of rubber mastication, which is takes place inside 3-5 minutes observed via incorporation of rubber additives. Homogeneity of filler dispersion necessitates a profound comprehension discerning the admissibility of ultimate favored properties of rubber vulcanizates.

Mixing considerations ought to be taken in account to extensively preclude the recurrence of mixing main difficulty related to the dispersion, scorchiness, contamination and system ability at the two-row mill. Mixing typically requires both dispersive and distributive mixing. Dispersive mixing involves producing high stresses in the melt to decrease extensively the size of any dispersed particles. In the context of distributive, stretching, dividing and reorienting the flow of the polymer melt compound in order to dispose of local variations in material distribution and produce a greater homogeneous mixture.

Raw rubbers are admixed with excellent amount of ensembles of substances in acquiring end product, which is known as compounding. Accelerators, activators, antioxidants, coloring agents, filler and reinforcing agents, retarders, rubber processing oils, softener, and vulcanizing agents are typically used ingredients in rubber compounding process. Other supplementary ingredients specifically dusting and anti-tack dealers such as talc powder and mold lubricants are examples of non-typical rubber compounding complementary element. Rubber compounding is administrated to acquire processing characteristics required for most suitable equipment utilization and permissible to applicable facets at the lowest possible cost. Generally, the most oftentimes used components are illustrated in the table below.

Table 2.1 Rubber Compounding Ingredients (Sapkota, 2011)

MATERIAL	**FORM**	**PURPOSE**
polymer/rubber	bales, chips, pellets or powder	raw rubber material
fillers	powder, pellets	reinforcing, achieve desired properties
plasticizers and lubricants	oil, waxes	processing aids and plasticizer
miscellaneous additives	powder, pellets and fluids	antioxidants, antiozonants, colorants, tacktifiers, releasing agents
vulcanizing agents	powder, pellet	curing agent

2.3 Fillers

The incorporation of fillers in the formulation is an ultimate purpose on undertaking the augmentation of the mechanical properties of the rubber compound especially on the abrasion resistance, strength and tearing resistance. Fillers can be categorized by reinforcing and non-reinforcing filler depends on the predominant purpose of filler integration in rubber compound. Silica and carbon black are unambiguous instance of reinforcing filler, whilst clay, mica and calcium carbonate renowned as non-reinforcing fillers. Non-reinforcing fillers may be used to improve processing and reduce compound cost. There is no resolute definition of reinforcing filler, but it is a filler, which generally increases stiffness and improves failure properties of the acquiring vulcanizate (Ginting *et al.*, 2017).

The reinforcing capability of a filler determined by their particle size, shape and surface activity. Nonetheless, the magnitude of the effectiveness of the fillers substantially validated from the homogeneity of the filler dispersion within the rubber matrices proceeding from the compounding process. In the context of particle size, the smaller the particle size, the better. This is chiefly because if the filler is larger than the polymer interchain distance, a localized stress area forms, causing the elastomer chain to break when stretched.

The larger the particle surface area, and hence the smaller the particle size, the better. This is because high-surface-area fillers have higher contact area and hence have a greater ability to strengthen rubber links. Furthermore, the greater the particle's width and length, the better. Isometric fillers have round or cubic shape which consider as low aspect ratio whereas fibres that are needle shape and fibrous have high aspect ratio. A filler particle also should have more particle surface activity. A filler may provide poor reinforcement if it has low specific surface activity, that is, affinity for and ability to bond to rubber matrix. Because air gaps indicate the point of permeability and zero strength, adequate matrix-mineral particle interaction is required (Wickham, 1839). The affinity of the filler for the matrix, or the capacity of the rubber matrix to ‘wet' the filler surface, is determined by the surface chemistry of the filler. Increased Mooney viscosity, tensile strength, abrasion and tear resistance, and hysteresis are all benefits of increasing filler surface area while decreasing filler particle size. Moreover, increasing the filler surface activity improves abrasion resistance, chemical adsorption resistance, modulus, and hysteresis. When the filler aspect ratio is increased, the Mooney viscosity, modulus, and hysteresis increase, while the robustness and extrusion shrinkage decrease, and the incorporation time increases.

Apart from the particle size, particle shape and surface activity, surface roughness can also affect rubber reinforcement. The geometric factors of a filler is likelihood of increasing reinforcement effect significantly. Fillers with rough spherical-like shape or polygonal provides smooth surface with lack of porosity, which leads to minimal trapped rubber present to increase the effective filler concentration. The contact angles of the liquids on the material surface depend on the surface energy of the liquid in relation to that of the solid. The greater the contact angle obtained with water indicated greater cohesion between the molecules of the liquid than the molecular adhesion between liquid and solid. The strong hydrogen bonding in water was responsible for its high cohesion and only ionic and high polar surface that offer equivalent or even stronger bonding interactions would be wetted very effectively by water (Wickham, 1839).

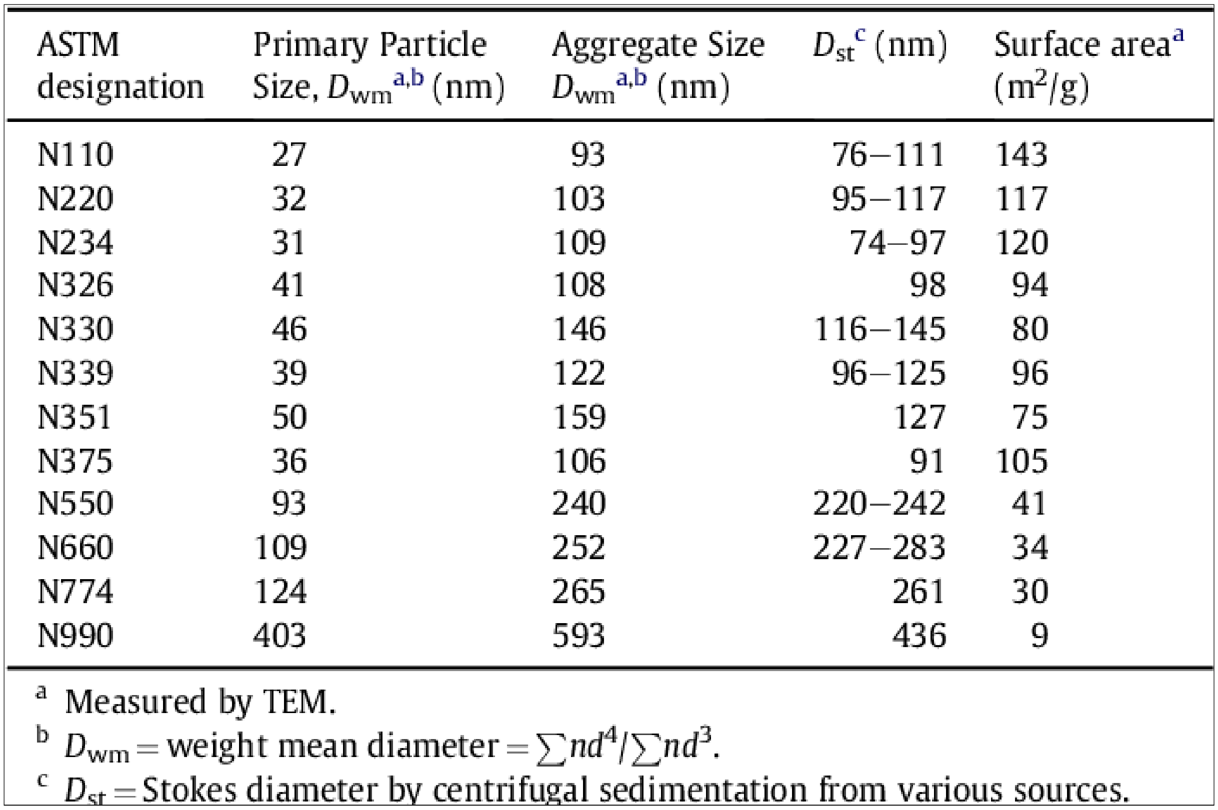
2.3.1 Carbon Black

Natural rubber has limited properties. Modification is required in order to increase the natural rubber properties. Carbon black is one of the types of reinforcing filler utilized in this research study. Carbon black (CB) is a material of major significance in the rubber industry especially for tire manufacture. The CB is essentially elemental carbon in the form of amorphous particles. Carbon black is added in rubber formulation, function to strengthen the tensile strength, tear strength, modulus, abrasion resistant, increase the volume and strengthen vulcanization. These improve properties will only be effective when CB is dispersed well into the matrix of rubber which will give higher bonding of filler with rubber matrix. Carbon black is most frequent type of filler used in rubber compounds. Physical qualities are enhanced with the presence of carbon black fillers especially those with small particle sizes. The addition of carbon black to a compound changes its characteristics, viscosity, and strength. However, using carbon black has the disadvantage of lowering stickiness. Vulcanized rubber's performance can be improved by using carbon black as an active filler (Sapkota, 2011)

CB helps to improve qualities that are vital in tire manufacture and tire performance. It is crucial to choose the right CB for each tire component in order to achieve the best balance of attributes. Addition of CB to tire compounding improve the UV resistance. Furthermore, the addition of CB as an ozone scavenger stabilizes the tire rubber's resistance to UV light and oxidation, preventing fissuring and cracking. Addition of CB prevents electrostatic charge and helps to transmit heat away from hot patches on the tire, which can become quite hot while driving (Long, Nascarella and Valberg, 2013). As a result, the tire’s lifespan is extended by reducing thermal damage. Carbon black is available at various physical and chemical properties, which can be produce at different particle size, surface area and surface activity as well as structures. There are many classifications of carbon black in accordance to ASTM standards.

Table 2.2 shows a few classifications of CB in accordance to ASTM standards. Figure 2.2 shows the illustrations of general trends for tire tread grade carbon black loading and the effect on compound physical properties. Increases in compound heat build-up and hardness, as well as rolling resistance and wet skid characteristic admissible when CB levels rise. Tensile strength, compound process ability, and abrasion resistance, on the other hand, reach a peak after which they decline (Kim *et al.*, 2020). Swor and co-workers (1985) have developed a new-technology N220 series CB that they claim will give better balance 29 of tire performance properties and the general principles will be applicable to a range of tire designs, centralizing on the results of work such as that of Hess and Klamp (1983) in improving tire rolling resistance. (Hess & Kemp, 1983; Al-Hartomy *et al.*, 2016). In this case, carbon black grade N220 (ISAF) will be used in this research project due to it can provide desired properties suitable for tire tread application.

Table 2.2 Carbon black with different grade (Long et al., 2013; Wang et al., 2003)



ASTM designation	Primary Particle Size, D_{wm}[a,b] (nm)	Aggregate Size D_{wm}[a,b] (nm)	D_{st}[c] (nm)	Surface area[a] (m^2/g)
N110	27	93	76−111	143
N220	32	103	95−117	117
N234	31	109	74−97	120
N326	41	108	98	94
N330	46	146	116−145	80
N339	39	122	96−125	96
N351	50	159	127	75
N375	36	106	91	105
N550	93	240	220−242	41
N660	109	252	227−283	34
N774	124	265	261	30
N990	403	593	436	9

[a] Measured by TEM.

[b] D_{wm} = weight mean diameter = $\sum nd^4/\sum nd^3$.

[c] D_{st} = Stokes diameter by centrifugal sedimentation from various sources.

2.3.2 Accelerators

Accelerators are ingredients that are used to shorten the vulcanization or cure time by increasing the rate of vulcanization. The majority of accelerator elements used are derived primarily from organic substances containing both nitrogen and sulphur. Although it is usually a very small part of the compound, an accelerator has a significant impact on the nature of crosslinking formation. As a result, it will determine physical properties such as tensile strength, modulus, resilience, and so on (Kim *et al.*, 2020). The type of accelerators used in rubber compounding has a significant impact on processing characteristics such as scorchiness and cure rate.

Table 2.3 Classification of accelerators commonly found in rubber industries (Whitby and Simmons, 1925).

Accelerators	Chemical Group	Vulcanization Speed
BA, HMT	Aldehyde Amine	Slow
DPG, DOTG	Guanidine	Slow
MBT, MBTS, ZMBT	Thiazole	Semi Ultra-Fast
ZBDP	Thiophosphate	Ultra-fast
CBS, TBBS, MBS, DCBS	Sulfenamides	Fast-Delayed action
ETU, DPTU, DBTU	Thiourea	Ultra-fast
TMTM, TMTD, DPTT	Thiuram	Ultra-fast
ZMDC, ZDEC, ZDBC	Dithiocarbamate	Ultra-fast

Prominently, Accelerators are ingredients that are used to shorten the vulcanization or cure time by increasing the rate of vulcanization. The majority of accelerator elements used are derived primarily from organic substances containing both nitrogen and Sulphur. Although it is usually a very small part of the compound, an accelerator has a significant impact on the nature of crosslinking formation (Whitby and Simmons, 1925). As a result, this latter will determine the physical properties of rubber vulcanizate i.e., as tensile strength, modulus, resilience so on and so forth. The type of accelerators used in rubber compounding has a significant impact on processing characteristics such as scorchiness and cure rate.

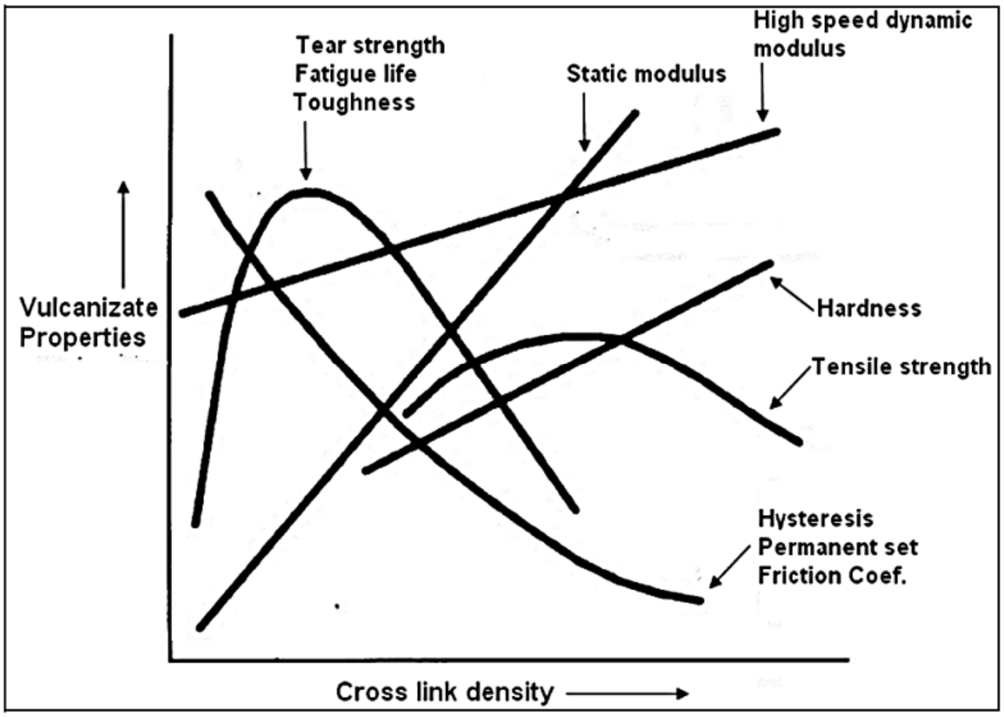


Figure 2.3 Relationship between crosslink density and vulcanizate properties attributed by accelerator (Whitby and Simmons, 1925).

Vitally, Thiazoles and sulfonamide accelerators, in general, play a role as Primary Accelerators due to their characteristics such as good processing safety, a broad vulcanization plateau, optimal crosslink density, and desired reversion delay. In most rubber compounds, the primary Accelerators are used at 0.5 to 1.5 phr dosages. Secondary accelerators such as Guanidines, Thiurams, and Dithiocarbamites are used to activate the primary accelerators. Secondary accelerators significantly increase vulcanization speed at the expense of scorch safety. Secondary accelerator dosages are typically 10-40% of the primary accelerator dosage.

MBTS particles promptly respond with Sulphur in the presence of heat to generate monomeric polysulfides, which are sulfurating agents. Polysulfide Sulfurating Agent molecules react with rubber molecules to generate sulfurated polymeric polysulfides and release MBT molecules. Two MBT molecules recombine to produce MBTS. The sulfurated rubber decomposes into rubber-Sx* type radicals, which are the forerunners of fibrils and are in the process of releasing MBT molecules. Two MBT molecules recombine to produce MBTS. Rubber-Sx-Rubber Crosslink is formed when a crosslink precursor connects with another rubber molecule.

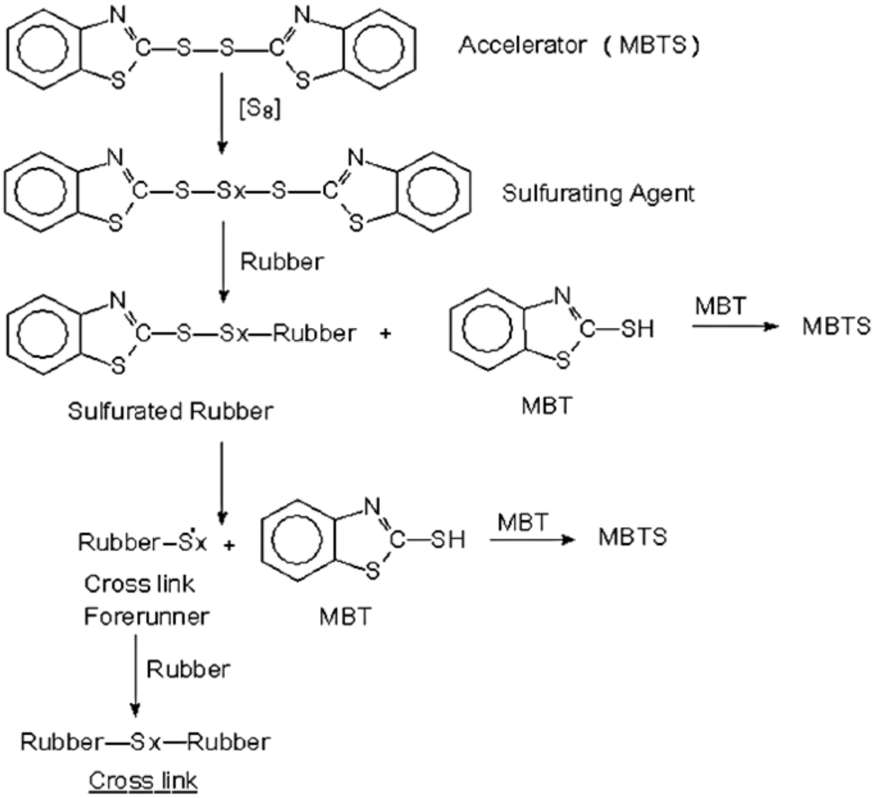


Figure 2.4 Thiazole accelerated sulfur vulcanization (Whitsby & Simmons, 1925).

2.3.3 Antioxidant and Anti-degradant

Rubber items deteriorate when subjected to degradative environments such as storage ageing, oxidizer, Ultraviolet radiation, and weathering. These factors degrade rubbers, causing substantial changes in their technical qualities that eventually lead to service failure or, in the absence of antioxidants, shorten the expected service life (Whitby and Simmons, 1925). The most prevalent cause of rubber breakdown is oxidation. To counteract this, antioxidants are used as inhibitors throughout the rubber compounding process. Commercially available antioxidants are classified into two types, i.e., amines and phenolics. Those formed from amines, often aniline or diphenylamine, are referred to as staining antioxidants because they tend to discolor nonblack vulcanizates when exposed to light, whereas products derived from phenol are referred to as antioxidants.

Antioxidants are extremely potent compounds that, despite their modest concentrations, have a considerable influence on the service life of rubber products. The usual antioxidant dose in a typical rubber product is between 0.5 and 3.5 pphr. IPPD will be used as an antioxidant in this study since it has desirable features such as good resistance to ozone, flex fatigue, heat, and oxidation. IPPD is a stable and long-lasting material that is commonly used in the manufacture of tires or as components of pneumatic tires, solid tires, belts, hoses, cables, and general mechanical products that require ozone protection and it has a strong antioxidant property with high temperature resistance (Budiarto, 2017). The color of IPPD will vary in the sun, but it will retain its properties.

TMQs are antidegradants that are composed by polymerized Aniline-Acetone condensation products. The degree of polymerization and Dimer + Trimer + Tetramer Contents vary amongst products. TMQs are primary antioxidants that are a well-known and potent class of chemical antioxidants that are used to preserve rubber items against atmospheric oxygen breakdown at higher temperatures. The typical dosage of adding TMQ in typical rubber tire ranges between 0.5 – 2.5 pphr (Whitby & Simmons, 1925; Budiarto, 2017)

2.3.4 Curative Agent

Vulcanization, often known as curing, is the process of converting a thermoplastic rubber combination into a highly elastic product called vulcanizate. Almost every rubber product must be cured before it can be utilised in a practical application. The creation of chemical cross-links between rubber chain segments results in the production of a three-dimensional network inside the rubber matrix via interactions between the functional groups of elastomer chains and appropriate curing chemicals. This network can maintain the chains in place after they have been subjected to lengthy deformation stresses, hence providing the essential stability. Furthermore, this network increases elasticity, strength, and modulus while decreasing hysteresis and plasticity (Kvasničáková *et al.*, 2020).

Vulcanizing agents are components that must be present in order to create a chemical reaction that causes elastomer molecules to crosslink. The elastomeric compound is transformed from a soft, sticky thermoplastic to a robust temperature-stable thermoset in the presence of crosslinking. The most common vulcanizing agent is sulfur. To improve heat resistance of a product, sulfur donor materials such as thiuram disulfides (TMTD) and *dithiodimorpholine* (DTDM) are utilized as entire or partial replacements for elemental sulfur in a low sulfur or less-sulfur cure method. The second most critical aspect of compounding is choosing the cure system, vulcanizing agents, and accelerators. A compound will not develop its optimum characteristics and process capabilities unless a suitable vulcanizing agent is employed in the right concentration.

In other point of view, vulcanization is the chemical process through which natural rubber and other Polydiene elastomers are converted into cross-linked polymers. Sulfur is the most often used vulcanization agent. When heated with rubber, it generates bridges between individual polymer molecules. To speed up the vulcanization process, a catalyst and initiator are frequently used. Cross-linked elastomers offer significantly increased mechanical characteristics. Non-vulcanized rubber, in essence, has weak mechanical qualities and is not particularly durable. Cross-linking is an intricate method that demands a series of reactions. Ultimately, a free-radical mechanism was postulated, which has been well characterized by Paul J. Flory (1953).

2.3.4.1 Sulfur Vulcanizing Agent

The polysulfide crosslinks formed by these reactions may consist of four to six sulphur atoms at low temperatures, but at higher reaction temperatures, shorter sulphur bridges are constituted. Rubber vulcanization by sulphur alone is extremely slow, taking a few hours at high temperatures (140°C or higher). This is problematic because prolonged heat and oxygen exposure causes oxidative deterioration, resulting in poor mechanical properties. It is also not very cost effective. Accelerators are commonly used to slow down the vulcanization process and reduce rubber deterioration. An accelerator is a chemical that speeds up vulcanization and allows it to occur at lower temperatures and with greater efficiency. The amount of sulphur required for cross-linking also reduced by the accelerator. (Kim *et al.*, 2020)

Vulcanization system forsooth considered as the biggest contribution to the development of crosslinking, which essentially influence the mechanical properties of the rubber vulcanizate. This consideration should be contemplated based on the desired properties dependable on the application specified. The mechanism of the formation of sulfidic crosslink can be comprehended from figure 2.4, which indicates the formation of polysulfidic crosslink.

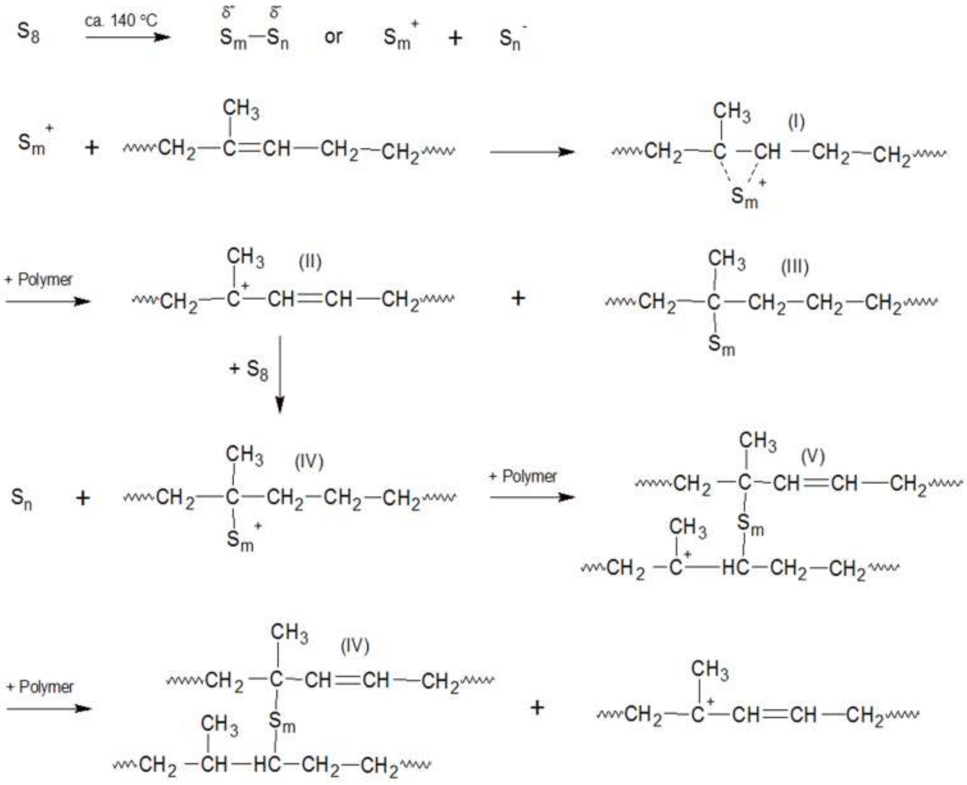


Figure 2.5 Polysulfidic crosslink formed by the reaction (Joseph *et al.*, 2015)

Sulphur as a crosslinking agent necessitates the presence of carbon-carbon double bonds, and the covalent crosslinks formed can be poly-sulfidic chains or mono- and di-sulfidic chains. Sulfidic crosslink types are ascertained by Sulphur level, accelerator type, accelerator and Sulphur ratio, and cure time. It is remarkable that longer cure times and a higher accelerator to Sulphur ratio will give rise to increase of the concentration of mono-sulfidic and di-sulfidic linkages. Predominantly, mono-sulfidic and di-sulfidic crosslinks have higher solvent and heat resistance, set resistance, and reversion resistance, but are stiffer in general, resulting in lower tensile strength and crack resistance. Polysulphidic crosslinks have higher tensile strength, are