

**POTENTIAL UTILIZATION OF MODIFIED OIL
PALM ASH AS FILLER IN NATURAL RUBBER
VULCANIZATES**

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**UNIVERSITI SAINS MALAYSIA
2015**

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by

OOI ZHONG XIAN

**Thesis submitted in fulfillment of the requirements for
the degree of Doctor of Philosophy**

January 2015

ACKNOWLEDGEMENT

A special acknowledgement for the Ministry of Science, Technology and Innovation (MOSTI) science fund (Project no. 305/PBAHAN/6013380) for the financial support to proceed this research and also Ministry of Education by offering me the MyPhD scholarship to pursue my PhD degree.

First of all, I would like to express my deepest gratitude to my beloved parents, Ooi Peng Hoi and Chen Yean Phin for their endless love, and tolerance. Not to forget my sister, brothers, and loved one, Yi Peng for their persevering support, encouragement and unconditional support during the period of my studies.

I am greatly indebted to my dedicated supervisor, Prof. Dr. Hanafi Ismail for his support, guidance, encouragement, advice, and also generosity in sharing knowledge during period of my studies. I am grateful and thank Prof. Hanafi very much for driving me towards the correct pathway throughout the course of my PhD research. Also, I am sincere thanks to my co-supervisor, Assoc. Prof. Dr. Azhar Abu Bakar for spending his guidance, effort and valuable time to carry out my PhD research and examine my research paper and thesis to improve the quality prior to submission.

Not forgetting to thank the administrative staff of School of Materials and Mineral Resources Engineering (USM), especially to Prof. Dr. Zainal Arifin Ahmad, Pn. Jamilah, Pn. Asmah, Kak Na, and Kak Shaly. Also, my sincere gratitude to technical staff, Mr. Rashid, Mr. Khairi, Mr. Faizal, Madam Fong, Mr. Sharil, Mr. Joe, Mr.

Norshahrizol, Mr. Che Mat, Mr. Azam. This research would have never been completed in time without their valuable support, help and advice during period of my studies.

Last but not least, I would like to thank my dear friends Dr. Sam, Dr. Ragu, Dr. Razif, Dr. Mathi, Dr. Indrajith, Nabil, Ai Ling, Kak Shida, Kak Rohani, Kak Dalina, Zaid, Boon Peng, Wei Ling, Tao Long, Guat Wei, Ezu, Akmal, Fasahah and Fikri for providing entertainment, support behind me, gave me advices and suggestions to conduct a proper experiment throughout the studies.

To all the people, it is a pleasure to thank those who have helped me throughout my PhD research and completion of thesis, directly or indirectly; your contribution shall not be forgotten. Thank you very much!!!

Ooi Zhong Xian

January 2015

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LIST OF SYMBOLS

Symbol	Description
t_{s2}	-- Scorch time
t_{c90}	-- Cure time
M_H	-- Maximum torque
M_L	-- Minimum torque
M_{100}	-- Tensile modulus at 100 % elongation
M_{300}	-- Tensile modulus at 300 % elongation
W_s	-- Swollen weight of specimen
W_i	-- Initial weight of specimen
W_d	-- Dried weight of specimen
Q	-- Weight of toluene uptake per gram of rubber hydrocarbon
Q_f/Q_g	-- Rubber-filler interaction
M_c	-- Molecular weight between crosslinks
ρ_p	-- density of the natural rubber
V_s	-- Molar volume of the toluene
V_r	-- Volume fraction of the swollen rubber
Q_m	-- Swelling mass of specimen
χ	-- Interaction parameter between the rubber network and the toluene
V_c	-- Degree of crosslink density of specimen
$T_{-x\%}$	-- Temperature at x% weight loss

$T_{\max I}$	--	Temperature at maximum weight loss rate
G'	--	Storage modulus
T_g	--	glass transition temperature
$\tan \delta_{\max}$	--	Maximum value of tan delta

LIST OF ABBREVIATIONS

Abbreviation		Description
ASTM	--	American Society for Testing and Materials
CBS	--	N-Cyclohexyl-2-Benzothiazole Sulfenamide
COAN	--	Oil absorption number compressed
COPA	--	Cetyltrimethylammonium Bromide-modified Oil Palm Ash
CTAB	--	Cetyltrimethylammonium Bromide
DMTA	--	Dynamic Mechanical Thermal Analysis
DTG	--	Derivative Thermogravimetric
EDX	--	Energy Dispersive X-ray
ENR	--	Epoxidized Natural Rubber
FT-IR	--	Fourier Transform Infrared
HCl	--	Hydrochloric Acid
HOPA	--	Hydrochloric Acid-treated Oil Palm Ash
IPPD	--	N-Isopropyl-N'-Phenyl-p-Phenylenediamine
ISO	--	International Organization for Standardization
LENR	--	Liquid Epoxidized Natural Rubber
LOPA	--	Liquid Epoxidized Natural Rubber-coated Oil Palm Ash
MIDA	--	Malaysian Investment Development Authority
MPOB	--	Malaysia Oil Palm Board
NR	--	Natural Rubber
NRL	--	Natural Rubber Latex

NSA	--	Nitrogen Surface Area
OAN	--	Oil Absorption Number
OPA	--	Oil Palm Ash
phr	--	Parts per Hundred Parts of Rubber
SEM	--	Scanning Electron Microscopy
STSA	--	Statistical Thickness Method
TGA	--	Thermogravimetric Analysis
USEPA	--	United States Environmental Protection Agency
XRD	--	X-ray Diffractometer
XRF	--	X-ray Fluorescence

**POTENSI PENGGUNAAN ABU KELAPA SAWIT TERUBAHSUAI SEBAGAI
PENGISI DI DALAM VULKANIZAT GETAH ASLI**

ABSTRAK

Kajian ini mengkaji kemungkinan untuk menggunakan abu kelapa sawit (OPA) sebagai pengisi untuk memperkuat vulkanizat getah asli. Pembebanan OPA yang digunakan dalam kajian ini adalah antara 0 hingga 9 bsg. Pencirian OPA telah dijalankan sebelum proses pencampuran dengan menggunakan penggiling bergulung dua konvensional. Kajian morfologi menunjukkan bahawa zarah OPA tidak sekata dengan permukaan kasar dan mempunyai struktur berliang. Dua komponen utama mineralogi dalam OPA ialah kuarza dan kalsit yang dibuktikan oleh penyerakan tenaga sinar-X, spektrometri pendafluoran sinar-X, inframerah jelmaan Fourier dan analisis pembelauan sinar-X. Pengisian OPA dalam vulkanizat menunjukkan keputusan bahawa masa skorj dan masa pematangan yang pendek selepas penambahan OPA manakala tork maksimum, modulus tensil dan kekerasan didapati meningkat. Dari sudut perspektif pengukuhan, adalah penting untuk diambil perhatian bahawa kekuatan tensil dipertingkatkan sehingga 16 % apabila 1 bsg OPA telah disebatikan. Bila dibandingkan dengan pengisi-pengisi komersial, vulkanizat terisi OPA ini mempamerkan kekuatan tensil yang setanding dengan pengisian 50 bsg karbon hitam dalam vulkanizat dan lebih tinggi jika dibandingkan dengan vulkanizat terisi silika. Selain itu, penambahan OPA dengan amaun rendah telah meningkatkan pemanjangan pada takat putus manakala pencampuran silika dan karbon hitam telah mengurangkan pemanjangan pada takat putus vulkanizat getah asli. Pengukuran interaksi antara pengisi-getah dan kajian morfologi pada permukaan patah ujian tensil vulkanizat getah asli yang terisi OPA, silika dan karbon hitam telah menyokong keputusan yang diperolehi dari sifat-sifat tensil.

Kestabilan haba dan sifat pengekal selapas penuaan haba telah dipertingkatkan dengan penyebatian OPA dan menjadi lebih tinggi dengan penambahan pembebanan OPA. Analisis Termogravimetri juga menunjukkan kestabilan haba bergantung kepada pembebanan pengisi, maka kestabilan haba didapati lebih tinggi dengan peningkatan pengisi dalam vulkanizat. Akhir sekali, keberkesanan tiga cara pra-rawat yang berbeza telah dijalankan untuk meningkatkan kekuatan tensil vulkanizat terisi OPA. Media pra-rawatan, iaitu bromida cetiltrimetilammonium (CTAB), asid hidroklorik (HCl) dan cecair getah asli terepoksida (LENR) telah meningkatkan kekuatan tensil vulkanizat getah asli. Bagaimanapun, sifat-sifat lain seperti ciri-ciri pematangan, pemanjangan pada takat putus, kekerasan, modulus tensil dan rintangan pembengkakan berubah bergantung kepada media pra-rawatan yang digunakan. Sifat-sifat haba vulkanizat terisi OPA telah terjejas selapas modifikasi CTAB dan LENR, tetapi kaedah pra-rawatan HCl tidak menunjukkan kesan ketara dan berkelakuan hampir sama dengan vulkanizat terisi OPA tanpa rawatan. Kaedah modifikasi CTAB, HCl dan LENR juga menyumbang kesan positif terhadap sifat-sifat pengekal vulkanizat getah asli terisi OPA selapas penuaan haba.

POTENTIAL UTILIZATION OF MODIFIED OIL PALM ASH AS FILLER IN NATURAL RUBBER VULCANIZATES

ABSTRACT

This work studied the possibility of utilizing oil palm ash (OPA) as filler to reinforce the natural rubber vulcanizates. The OPA loading used in this study was ranged from 0 to 9 phr. The characterization of OPA was carried out prior to compounding by using conventional laboratory-sized two roll mills. Morphological study revealed that the OPA particle was irregular with rough surface and porous structure. The two main mineralogical components in OPA were quartz and calcite which elucidated by Energy dispersive X-ray, X-Ray Fluorescence spectrometry, Fourier transform infrared and X-ray diffraction analysis. Results of the OPA-filled vulcanizates showed that the scorch time and cure time decreased with the incorporation of OPA whereas maximum torque, tensile modulus, and hardness increased. From a reinforcement point's perspective, it was worthwhile to note that the tensile strength improved by 16 % when 1 phr OPA was incorporated. When compared to the commercial fillers, this OPA-filled vulcanizate showed comparable strength to the 50 phr carbon black-filled vulcanizate and even higher than silica-filled vulcanizate. Besides, the incorporation of low OPA loading has increased the elongation at break whereas silica and carbon black reduced the elongation at break of the natural rubber vulcanizates. The measurement of rubber-filler interaction and morphological studies of tensile fractured surface of OPA, silica, and carbon black-filled natural rubber vulcanizates supported the result obtained from tensile properties. The thermal stability and retention properties after thermal ageing were notably enhanced with the incorporation of OPA and improved as the OPA loading was increased.

Thermogravimetric analysis also denoted the thermal stability was depending on the filler loading, thus higher thermal stability was found for higher loading of filler-filled vulcanizates. Last but not least, the effectiveness of three different pre-treatment methods was carried out in order to further improve the tensile strength of the OPA-filled vulcanizates. The pre-treatment media, i.e. cetyltrimethylammonium bromide (CTAB), hydrochloric acid (HCl), and liquid epoxidized natural rubber (LENR) improved the tensile strength of natural rubber vulcanizates. However, other properties such as curing characteristics, elongation at break, hardness, tensile modulus, and swelling resistance were varied depend on the pre-treatment media utilized. Thermal properties of OPA-filled vulcanizates have been affected after CTAB and LENR modification, but the HCl pretreatment method showed no significant effect and behaves almost the same manner as raw OPA-filled vulcanizates. The CTAB, HCl, and LENR modification method also contribute the positive effect on retention properties of OPA-filled natural rubber vulcanizates after thermal ageing.

CHAPTER 1

INTRODUCTION

1.1 Overview

In Malaysia, the natural rubber is normally obtained from *Hevea brasiliensis* tree. Up to now, rubber industry is playing a vital role in the Malaysia's economic development and to increase the economic welfare of the population. The reason can be account for the unique physical properties of natural rubber that can't be replaced by other materials in which allows combination of elasticity and crystallization-induced strength when the stretch force is exerted on it. These unique properties was mainly due to the high level of stereoregularity of organic compound which is known as *cis*-1, 4-polyisoprene even though the natural rubber contains small amounts of fatty acids and proteinaceous residues (Hamed, 1992). Besides, the natural rubber is readily molded into complex shapes. Therefore, the vulcanized natural rubber are used to prepare various rubber products such as complex shaped-mechanical goods, hoses, soles, V-belts, seals, gaskets, tyre treads, swimming fin and etc.

Although natural rubber is known to shows outstanding properties due to its ability to crystallize under strain, the addition of many ingredients are generally required during rubber compounding as well as fillers in order to modify the cure rate, enhance the physical properties (i.e. strength, modulus and etc.) and prominently reduce the cost of rubber vulcanizates (Ismail et al., 2005). A wide variety of particulate fillers are studied and explored in the rubber compounding recipes, there are more than 100 types of filler, either organic or inorganic fillers, have been studied and reported in the

previous literature (Nugay and Erman, 2001). Fillers such as carbon black, silica, calcium carbonate, talc and clay are used in large quantities in rubber compounding in order to reduce the compounding cost as well as modify the physical properties of vulcanized rubber. It is known that the reinforcement efficiency of filler used in rubber compounding depends on the rubber-filler interaction in terms of particle size, particle dispersion and structure of filler itself (Ismail et al., 2005). However, among the several types of fillers, only the carbon black and silica was claimed as the most promising reinforcing filler (Iqbal et al., 2008).

From the previous to present, the consideration research interest is focused on the utilization of filler derived from the agricultural waste such as acai fiber (Martins et al., 2008), baggase (Osarenmwinda and Abode, 2010), rice husk (Attharangsarn et al., 2012), and bamboo cellulose pulp (Visakh et al., 2012) as an alternative way to replace the carbon black and silica with the target to reduce the cost of rubber products while maintaining their desired properties. The advantage of utilizing agricultural waste such as low cost, highly abundantly, availability have encouraged the researchers to utilize the waste from agricultural industries and incorporated in rubber matrix. Otherwise, the agricultural waste can only be sent to landfill. Therefore, the best option is to utilize agricultural waste for rubber applications.

Other than hevea tree, oil palm is another tropical tree in Malaysia that is commonly used in commercial agriculture to produce palm oil. Million hectares of land in Malaysia planted with oil palm tree in order to produce the palm oil for exporting to oversea. The growth of the palm oil industry has been phenomenal, and the global

production of palm oil has increased more than 9 times since 1980 (Teoh, 2010). Malaysia emerged as one of the world's biggest palm oil producer and exporter with about 352,385 hectares of plantation (Abdul Khalil et al., 2008). The current production of crude palm oil is 19 million metric tonnes and this amount adding 8 % to the gross national income of Malaysia as reported by Malaysian Palm Oil Board (2012) and Zwart (2013).

In spite of the obvious benefits, the harvesting and extracting the oil from fresh oil palm fruits will result in millions tonnes of oil palm biomass in the form of empty fruit bunches, oil palm fronds, and oil palm shells. Due to its highly abundant, the utilization of oil palm biomass as a source of filler deserved the unending attention by most of the rubber technologist in their utilization to solve the environmental issues and reduce the rubber compounding cost. In addition, the utilization of oil palm biomass at no or very low cost led to reduction in the product cost. The investigation of oil palm biomass filled in natural rubber vulcanizates was carried out by previous researchers (Jacob et al., 2004; Joseph et al., 2010; Egwaikhide et al., 2013). However, the usage of oil palm biomasses as an alternative fuel to produce steam for electricity generation (Borhan et al., 2010) is most desirable for oil palm mill industries and this process will generate another by-product known as oil palm ash (OPA).

OPA is the by-product from the combustion of oil palm biomasses and normally considered as waste. The large quantity of OPA produced, has contributed to the rapid increase in the cost of ash disposal services (either in landfill or transportation). Thus, transforming the ash into valuable product has been advocated as a solution to

admonishing environmental issues. There are a number of possibilities to convert the OPA into more valuable end products. As reported by Yin et al. (2008), the OPA can be used as a material to replace cement, concrete additive as well as an absorbent for removing aqueous or gaseous pollutants, but there is no evidence of any commercial return yet. Also, the OPA can be utilized as fertilizer since it contains high percentage of potassium to supply minerals that required for plant growth and high pH to neutralize the acidity of soils (Harun et al., 2008). Additional research studies are still be required to expand the potential utilization of OPA in numerous fields. Foo and Hameed (2009) reviewed that morphology of OPA is presented with spongy and porous structure in nature. This indicated that OPA favorable to be filler to reinforce the polymeric matrix.

Thus, the usage of OPA as filler in the natural rubber compounding recipe is encouraged and seeks for the potential ability to reinforce the natural rubber vulcanizates. The OPA-filled natural rubber vulcanizates were investigated in terms of curing characteristics, tensile properties, swelling measurement, rubber-filler interaction, morphological of tensile fractured surface, thermal stability and the attention was also given on thermal ageing resistance.

1.2 Problem Statement

The generated OPA after combustion of oil palm biomasses can only be sent to landfill due to limited utilization of OPA in industrial application. In Malaysia, it was reported that about 4 million tonnes of OPA was produced annually and dumped into open fields or disposed in landfills (Foo and Hameed, 2009) and this number is expected

to increase with the increasing of global demand for palm oil commodity. The disposal of OPA causing a serious environmental problem; therefore converting them into value-added products or incorporating them onto original products is one of the solution methods.

Many efforts have been made to find profitable and potential used for OPA in polymer application. However, an early investigation reported that the incorporation of high loading OPA ranged from 10 phr to 40 phr had significantly reduced the properties (such as tensile strength and elongation at break) of the natural rubber vulcanizates (Ismail et al., 2008) and also ethylene vinyl acetate/natural rubber blends (Najib et al., 2009) due to agglomeration effect becomes dominant. The yielding of poor properties to the natural rubber vulcanizates or thermoplastic elastomer blends are restricting the efforts of rubber technologist to further utilize the OPA in rubber industry. However, according to Bhat and Khalil (2011) who explored the utilization of OPA in polypropylene composites and the result indicated that low OPA loading (ranged from 1 – 7 %) favorable to the interfacial properties leading to the high values of tensile strength. The good wetting of OPA in polypropylene matrix resulted better adhesion of the OPA when the stress was applied on it which is supported by the SEM results.

Therefore, the solution by combining of economical, ecological and performance demands has led to the idea to utilize the low OPA loading in the natural rubber vulcanizates. It is believed that the low OPA loading is prone to filler-polymer interaction than filler-filler interaction in which the agglomeration effect is reduced and

thereby leading to better interfacial properties. Also, this is an alternative way to minimize the OPA disposal problems.

1.3 Research Objectives

The aim of this research is concerned with utilization of OPA and ability of OPA to improve the properties of natural rubber vulcanizates. The objectives for this research work are:

- i. To determine the physical properties and characteristics of OPA and study the effect of OPA loading on the properties of natural rubber vulcanizates.
- ii. To compare the effectiveness of OPA as filler against optimum loading of two commercial reinforcing fillers (that is silica and carbon black)
- iii. To evaluate the modification effect of cetyltrimethylammonium bromide (CTAB) onto OPA particles and investigate its efficiency to the properties in filled natural rubber vulcanizates.
- iv. To determine the chemical composition changes of OPA after pre-treated by hydrochloric acid (HCl) solution and evaluate its feasibility on the properties in filled natural rubber vulcanizates.
- v. To investigate the effect of a liquid epoxidized natural rubber (LENR) coating method on the properties of OPA-filled natural rubber vulcanizates.

1.4 Scope of Research

The preface of this research study was to assess the potential ability of oil palm ash (OPA) as filler with and without modification to be filled in natural rubber vulcanizates. The curing characteristics, tensile properties, swelling measurement, rubber-filler interaction, morphological of tensile fractured surface, as well as the attention was also given to the thermal properties of OPA-filled natural rubber vulcanizates.

Firstly, characterization of OPA was carried out using X-Ray Fluorescence (XRF) and X-ray diffraction (XRD) in order to determine the presence of major and minor constituents that contained in OPA used in this research work. At the same time, the pH and surface morphological of OPA particles were also investigated. Then, the effect of low OPA loading on properties (i.e. curing characteristics, tensile properties, swelling measurement, rubber-filler interaction) of natural rubber vulcanizates was examined in order to understand the properties affected with the incorporation of OPA.

When the optimum loading for OPA was discovered — which improved the strength of natural rubber vulcanizates, the tensile properties were compared against reinforcement effect as implicated by two other types of commercial fillers (that is, silica and carbon black which are well known as reinforcing fillers) to show the capability of OPA as reinforcing filler in natural rubber vulcanizates.

The surface modification on OPA particles was also applied in this research work in order to enhance the interfacial properties between OPA particles and natural rubber

matrix as well as the strength improvement. The common method used for filler treatment is applied on filler surface by adding the silane (Si-69) coupling agents and this technique had proved to enhance the filler-rubber interaction. However to date, this method had been reported in several previous works (Ismail et al., 1999a; Alkadasi et al., 2004; Thongsang and Sombatsompop, 2006; Idrus et al., 2011b). An alternative pre-treatment method was then encouraged to be applied to alter the surface characteristics of the OPA.

Therefore, in the present research work, there were three different pre-treatment method was utilized separately and their effect to the changing of OPA particles either physical or chemical changes was described. The effect of different pre-treated OPA on the properties of natural rubber vulcanizates was then investigated in order to study effectiveness of pre-treatment method to the properties of OPA-filled natural rubber vulcanizates.

The first pre-treatment media prepared in this research was cetyltrimethylammonium bromide (CTAB) solution in which alkylammonium ion (cationic surfactant) of CTAB (Turro, 2002) suggested to induce the electrostatic interaction with hydrophilic OPA and thereby adsorb onto the OPA surface as well as modify the surface characteristic of OPA filler. This would minimize the polarity gap and facilitate the dispersion of OPA in natural rubber matrix. At the same time, the micro voids within natural rubber and CTAB-modified OPA would be reduced. Besides, Melsom (2003) also reported that the CTAB can be absorbed and attached onto silica whereas the CTAB absorbed are available to react with the rubber.

Generally, OPA contained various mineralogical compositions which can affect the curing characteristic, thermal properties as well as hindered higher tensile properties of rubber vulcanizates. For instance, the incorporation of various metal oxides in EPDM compounds was carried out by Heideman et al. (2005) and reported that the existence of calcium oxide and magnesium oxide will slightly lowering the tensile strength but increase the elongation at break of EPDM vulcanizates. Hence, a new approaches using the HCl solution to treat the surface characteristic as well as mineralogical composition of OPA. The preliminary aim for this pre-treatment media is to seek for the changes in mineralogical compositions of OPA since the varying of mineralogical composition that contained in the OPA. The impurities (owing to the different types of metal oxides) contained in the OPA could affect the strength as well as crosslink density of natural rubber vulcanizates. Thus, it is believed that the impurities in the OPA could be reduced after pre-treated by the hydrochloric acid solution and consequently increased the abilities to further reinforce the rubber vulcanizates.

Furthermore, natural rubber latex (NRL) modification on filler is one of method to improve the interface adhesion within filler and polymer matrices and reported by the previous researchers (Sreekala et al., 2000; Kalia et al., 2009; Nabil and Ismail, 2014). The NRL could forms mechanical locking and improves the elasticity by penetrating into surface pores of filler and thereby withstanding the specimen failure even after major internal failure as reported by Sreekala et al. (2000). Also, Teh et al. (2006) studied the presence of Epoxidized Natural Rubber with 50 mol % epoxidation (ENR-50) as compatibilizer in natural rubber/organoclay composites and found that ENR-50

resulted faster curing and significant improvement in tensile properties. So, both concept was combined and applied in the present study but the media modification used was Liquid epoxidized natural rubber (LENR).

LENR was deemed preferable instead of natural rubber, due to its chemical structure of isoprene units with regular oxirane groups which can improve the compatibility with hydrophilic OPA, whilst the liquid phase of Epoxidized Natural Rubber could penetrate more easily into the porous-surfaced OPA and wet the outer-layer of the OPA more effectively. Therefore, ENR was selected in this work by dissolving it in toluene and converting it into liquid phase (so-called LENR) for facilitating the penetration of ENR since OPA exhibit micro-pores on its surface.

1.5 Organization of the Thesis

There are five chapters in this thesis and each chapter gives information related to the research interest as following:

- **Chapter 1** describes the introduction of the project. It covers brief introduction about research background, problem statement, and research objectives.
- **Chapter 2** shows introduction and development of respective natural rubber and oil palm plantation, the highly abundant of OPA in Malaysia, and factors affecting the rubber vulcanizate properties. It also covers the previous research

findings that have been done regarding to the OPA utilization and filler modification.

- **Chapter 3** contains the information about the materials and equipments specification used in this research. The experimental procedure and the different pre-treatment method were described. This chapter also contains the properties evaluation and characterization methods of samples.
- **Chapter 4** determines the physicochemical of OPA in terms of pH, particle size, morphological, elemental as well as mineralogical compositions that exist in OPA particles. This chapter also examines the FT-IR transmission spectra of OPA.
- **Chapter 5** discusses the effect of various OPA loading filled in natural rubber vulcanizates on curing characteristics, tensile properties, hardness, morphological studies, swelling, thermal stability and retention properties after thermal ageing.
- **Chapter 6** compares the reinforcement effect of optimum loading of OPA in natural rubber vulcanizates against optimum loading of silica and carbon black on curing characteristics, tensile properties, hardness, morphological studies, swelling, thermal stability and retention properties after thermal ageing. This chapter also discusses the thermal stability and retention properties of OPA,

silica and carbon black at similar loading in order to prove the thermal properties of natural rubber vulcanizates was much affected by the filler loading amount and not to the filler types.

- **Chapter 7** characterizes the changes of OPA particles after modified by CTAB, followed by investigating the properties of CTAB-modified OPA-filled natural rubber vulcanizates in term of its tensile properties, hardness, morphological studies, swelling, thermal stability, and retention properties under severe ageing condition.
- **Chapter 8** reviews the pre-treatment effect of HCl solution to the chemical composition changes of OPA and the properties of HCl-treated OPA-filled natural rubber vulcanizates.
- **Chapter 9** investigates the effect of LENR coating to the properties of OPA-filled natural rubber vulcanizates.
- **Chapter 10** concludes the findings of the research based on results and discussion in **Chapter 4–9** with suggestions for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Development of Natural Rubber in Malaysia

Among the natural rubber producer in this world, Malaysia is the fourth largest producer after Thailand, Indonesia, and Vietnam and the exportation of rubber products recording positive growth annually owing to its high quality, competitively priced to the international market (Federation of Malaysia Manufacturers, 2014).

2.1.1 Brief history of natural rubber

Natural rubber is an elastomeric material which playing a significant role either individually or combination with other materials for the products nowadays. Rubber is known by the indigenous peoples in America long before the arrival of European explorers, on that time the rubber was used to make elastic ball to be played by ancient tribes' people in an important ritual game called Tlachtlic (Vijayaram, 2009). According to Ciesielsky (1999) and Myers-EI (2008) recorded that Christopher Columbus and Spaniards are the first European to discover natural rubber during his fourth voyage to the Americas. They found the indigenous in Haiti playing ball and bewitch to the bouncing effect. Furthermore, Myers-EI (2008) did mentioned that Padre d Anghiera had seen Mexican tribes people playing with elastic ball in year 1525. However, the first scientific study of rubber was undertaken in 1735 by Charles de la Condamine (French scientist) who extracts the milky liquid (known as latex) and sent the samples to Europe. This milky liquid was used as an eraser which is believed suggested by Jean de Magellan in 1752. Later on, this finding was popularized in England by Joseph Priestley

suggested that milky liquid to be named as “rubber” since its ability to rub away the pencil marks (Vijayaram, 2009; Chennakrishnan, 2012). This means that the rubber has been made long before the discovery of Charles Goodyear’s vulcanized rubber in year 1839.

2.1.2 Rubber cultivation in Malaysia

Thousands of plant species contain natural cis-1,4-polyisoprene, the most well known species is from *Hevea Brasiliensis* which have been commercially cultivated in modern time to produce natural rubber for processing and implied that this species provide major primary source of natural rubber worldwide. The *Hevea Brasiliensis* rubber tree is believed indigenous to the Amazon forests of South America (De Vis et al., 2006). Date back to the latter half of 19th century, the rubber price is relatively high and British search for a cash crop for its Eastern colonies at that time (Hong, 1999). Rubber trees are only thrives in the country near equator as it requires hot and humid climate and also heavy rainfall for optimum growth, thus the rubber tree is identified as one of the potential crops to be cultivated in Singapore and Malaysia. In year 1876, Henry Wickham (British planter) smuggled and shipped 70,000 rubber seeds to London’s Kew Gardens from which 2,700 of them successful germinated and almost 2,000 seedlings from Kew were then shipped to Sri Lanka (Headrick, 1990).

In 1877, another 22 seedlings were sent from Sri Lanka to Singapore Botanical Gardens and nine of these rubber plants were transported to Kuala Kangsar in Perak and planted behind the house of Sir Hugh Low, British resident (Headrick, 1990; Hong, 1999; Kiam 2002). From that time, rubber cultivation started in Malaysia. The rubber

tree took about 6 years to start producing rubber had evaded away most of the planters in Malaysia who interested in quick return. Regardless of considerable opposition among planters, Henry Nicholas Ridley (Director of Singapore Botanic Garden), who began experimenting with new method of tapping and he proved that careful nurtured and proper tapping method can be more productive (Headrick, 1990). Until today, this method of tapping work has not been basically changed.

Under encouragement of Henry Nicholas Ridley, Kinderley brothers started to cultivate 2 hectares of rubber in their coffee estate in 1895 whereas Mr. Tan Chay Yan cultivated rubber plant in his tapioca estate in 1896 and gained the initial success. This was motivated him to cultivate rubber plant in a large scale (3,000 acre) and subsequently formed Malacca Rubber Plantations Ltd under the agency of Guthrie & Co. Thereafter, rubber gradually takes the place of coffee and tapioca as become the dominant crop in Malaysia up to 1989 before oil palm exceeded rubber (Siew, 2010). From the statistic of rubber cultivated in Malaysia shown in Table 2.1, the rubber tree cultivation was decreased and this may due to the some planter converting to more profitable crops such as oil palm. However, according to Malaysian Rubber Board (2013), the natural rubber consumption are steadily increased from 2000 (7,340,000 tonnes) to 2012 (11,042,000 tonnes).

Table 2.1: Rubber tree (hectare) cultivated in Malaysia (Malaysian Rubber Board, 2013)

Year	Rubber tree ('000 hectare)		
	Estates	Small Holdings	Malaysia Total
2000	123.78	1306.90	1430.68
2001	95.52	1293.80	1389.32
2002	84.81	1264.00	1348.81
2003	78.46	1247.41	1325.60
2004	64.42	1214.41	1278.83
2005	57.37	1213.93	1271.30
2006	54.15	1209.44	1263.59
2007	53.35	1194.69	1248.04
2008	61.10	1185.93	1247.03
2009	61.10	967.14	1028.24
2010	64.20	956.18	1020.38
2011	64.20	962.84	1027.04
2012	64.20	977.34	1041.54
2013*	64.20	983.96	1048.16

*forecast

2.2 Natural Rubber and Its Molecular Structure

Normally, naturally occurring rubber (cis-1,4-polyisoprene) is collected mainly in the form of milky liquid (latex) from a tapped rubber tree. It consists of rubber hydrocarbon, lipids, proteins, carbohydrates, ash, and dirt as listed in Table 2.2. In 20th century, the chemists had discovered the use of Ziegler-Natta catalyst for producing synthetic cis-polyisoprene; however, the discovery of the Ziegler-Natta catalyst and even much other efforts have been made to replace the natural rubber by producing synthetic cis-polyisoprene, but has never been achieved; and today natural rubber accounts for about 40% of the total rubber consumed worldwide (Eng and Ong, 2001). With the synthetic rubber industries will generate and consume the huge quantities of toxic waste and energy respectively, therefore natural rubber is considered as more environmental friendly and sustainable raw material (Jones, 1994; Eng and Ong, 2001).

Table 2.2: Typical components contained in natural rubber (Eng and Ong, 2001)

Components	Weight percentage (wt %)
Rubber hydrocarbon	93.7
Lipids	3.4
Proteins	2.2
Carbohydrates	0.4
Ash	0.2
Others	0.1

Natural rubber is normally processed into either latex or dry rubber, but the raw material input may affect the quality of natural rubber and thus classification of natural rubber according to different types and grades are required and they are summarized in Figure 2.1. The premium product from a rubber tree is latex whereas the cuplump is the by-product of tapping process in which the latex drip collected at alternate days after collection of latex and hence the cupclump will be mixed with small amounts of tree lace. The important of technical classification was introduced to classify the grades of rubber based on parameters such as dirt retained, ash content, and other related specification in the development of natural rubber processing industry to meet the processability and technological properties of natural rubber. In Malaysia, the natural rubber produced is graded by Standard Malaysia Rubber (SMR). One of the grades of natural rubber produced from high quality of latex is light-colored Malaysian rubber (SMR L). Table 2.3 shows the specification scheme and typical rubber values of SMR L.

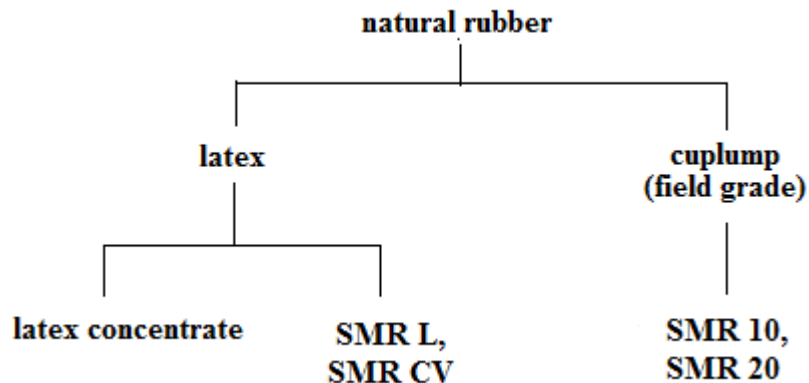


Figure 2.1: General types and grades of commercial natural rubber (Eng and Ong, 2001).

Table 2.3: SMR L specification scheme mandatory from October 1991 and typical rubber values (Eng and Ong, 2001).

Parameter	SMR L	
	Specification Scheme	Typical Values in Range
Dirt retained (% wt)	<0.02	0.004-0.005
Ash content (% wt)	<0.50	0.14-0.28
Nitrogen (% wt)	<0.60	0.33-0.50
Volatile matter (% wt)	<0.50	0.14-0.32
Wallace rapid plasticity (Po)	>35.0	37.0-51.0
Plasticity retention index (%)	>60.0	82-96
Color (Lavibond scale)	<6.0	3.0-5.0

The basic for chemical structure of natural rubber was discovered in 1942 and found that it exists with CH_2 groups on the same side of double bond known as cis-1,4-polyisoprene (Goodman et al., 1974) as shown in Figure 2.2. It is inspected that the chain forming is tangled which complicates to align and here gives natural rubber its elastomeric character because this kind of chain forming allows for mobility of one chain respect to another.

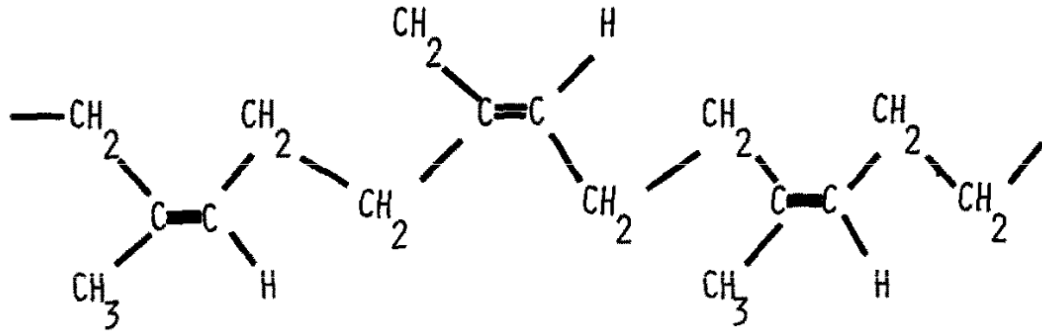


Figure 2.2: Chemical structure of natural rubber (cis-1,4-polyisoprene) (Goodman et al., 1974).

Natural rubber is long linear polymer chains that composed of molecules of different sizes. Thus, the average molecular weight of natural rubber obtained from rubber trees is typically in the ranges from 30,000 to about 10,000,000 (Mathew, 1992) with a broad molecular weight distribution. As reported by Sen (2001), natural rubber possesses excellent processing behavior due to its broad molecular weight distribution. Subramaniam (1972) had revealed that the molecular weight distribution of natural rubber from fresh latex is obviously bimodal distribution using gel permeation chromatography. Although the actual molecular weight is expected to be much higher than result obtained from gel permeation chromatography analysis since the fresh latex contains high molecular weight insoluble microgel that normally filtered and discarded during sample preparation (Eng and Ong, 2001). In addition, the high molecular weight can be broken down during mastication process in order to facilitate the processability of natural rubber.

2.3 Rubber Compounding

Elastomer is the most important group for rubber compounding. The typical formulation for rubber compound consist of 5 or more ingredient to alter the physical or mechanical properties, curing time, deterioration period and etc. to meet the customer's requirements. Table 2.4 show the basic function of ingredients in rubber compounds. Normally, the amounts for the respective ingredients of rubber formulation are given based on a total of 100 parts of rubber. Currently, the use of common ingredients such as vulcanizing activator, co-activators, and organic vulcanizing accelerators are found in any rubber compound formulation to reduce the curing rate and improve the properties of final products.

The flow of rubber compounding process and the problems might occurred during corresponding process is shown in Figure 2.3. During mastication process, the rubber will be softened prior the incorporation of curing ingredients and the widely used equipment in rubber industry is two roll mills. The mastication process will induce high shear force to break down the polymeric chain and consequently the molecular weight and viscosity of raw rubber would be reduced. The low viscosity assist wetting of ingredient/additives, which is essential to achieve uniform and high level of additive dispersion in the mixed rubber compound. After the mastication process, the weight of the compounds needs to be checked and found that the weight of the batch is 0.5 % less than initial weighing ingredients, then the batch has to be rejected (Morton, 1987). The details of the vulcanization process will be discussed in next section.

Table 2.4: The ingredients and its function in rubber compounds (Allen, 1972; Metherell, 1992; India Rubber Directory, 2014).

Groups	Chemicals	Function
Elastomer	-Natural rubber -Synthetic rubber	Provide main characteristic of rubber compound
Vulcanizing agent	-Sulphur -Peroxide	To interconnected between adjacent long polymeric chains through chemical crosslinking process
Activators	-Inorganic compound such as zinc oxide -High molecular weight monobasic acid such as stearic acid -Amines	To trigger and improve the efficiency of accelerators
Accelerators	-guanidines, amines, thioureas, thiozoles, thiurams, sulfenamide, dithiocarbamates and xanthates	To reduce the time for rubber vulcanization
Additives	-Filler -Colorants	To reduce the cost and/or alter the appearances and properties of rubber product
Antidegradants	-P-phenyldiamines	To prolong the service life of rubber product.

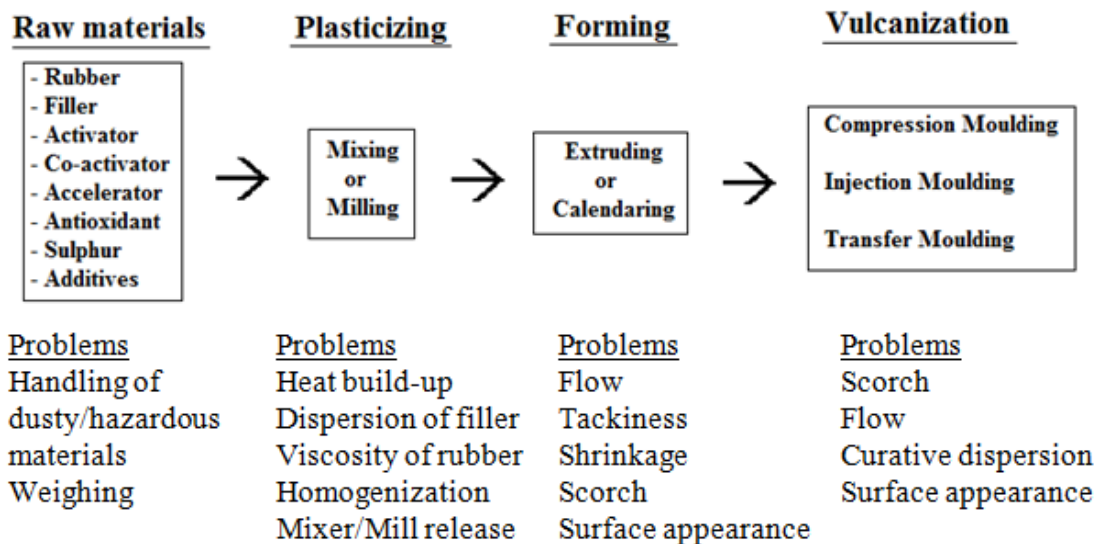


Figure 2.3: Stages involved in rubber processing and the corresponding problems (Hepburn, 1997).

2.4 Vulcanization Process of Natural Rubber

An un-vulcanized rubber is tacky substances which lacks of structural integrity and there is no improvement in the physical properties of rubber compound can be occurred; low tensile strength and elasticity are obtained. However, after vulcanization the chemical bonds formed between adjacent polymeric chains and subsequently induce dimensional stability and strength to the rubber vulcanizate (Schaefer, 2002).

Vulcanization is a chemical cross-linking process in which long linear polymer chains are interconnected between adjacent polymeric chains through vulcanizing agent (sulphur) and heat applied as shown in Figure 2.4. By cross-linking, it will tie together the rubber molecules and allow them to be stretchable and return to its original shape after stretching. The process of cross-linking with sulphur was discovered independently by Charles Goodyear in 1839 and he found that the formation of cross-linked bridge composed of variety sulphur atoms. The reason may account to the fact that sulphur occurs naturally as an eight-membered ring and this ring can be cleaved in smaller parts with varying numbers of sulphur atoms to form radicals (hemolytic cleavage) or ions (heterolytic cleavage) leads to sulphur cross-linked (Krejsa and Koenig, 1993).

However, the actual mechanism of the sulphur cross-link reaction is still not fully understood and it is envisaged via an ionic route (Cowie, 1991; Chanda and Roy 2012). The use of sulphur alone would slow down the vulcanization process, and thus vulcanization rate with elemental sulphur normally increased by incorporation of accelerators and activators which known as accelerated sulphur vulcanization.

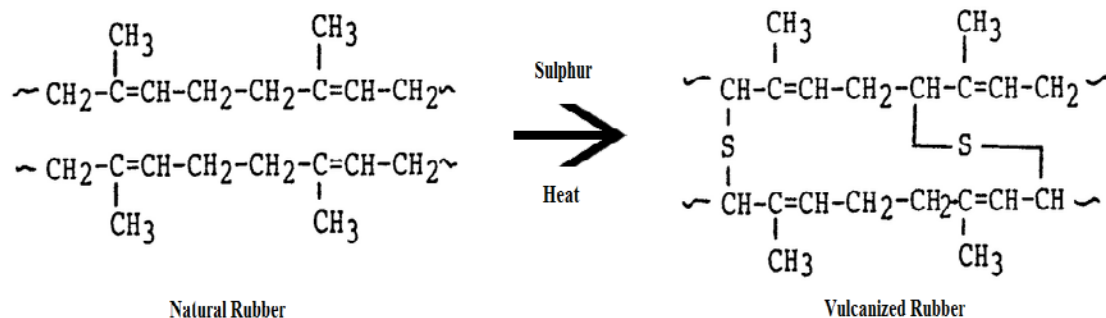


Figure 2.4: Typical cross-linking reaction of natural rubber through sulphur (Winter and Tomic, 1983).

The accelerators are also classified based on the functional group that they belong to and the aspect considerations for the activity speed of accelerator in sulphur vulcanization are summarized in Figure 2.5. Figure 2.6 shows an example of mechanism for N-cyclohexyl-2-benzothiazole sulphenamide (CBS) accelerated sulphur vulcanization. The CBS will decompose into mercaptobenzothiazole (MBT) in the presence of heat and sulphur and then MBT will catalytically react with other CBS molecules to form dibenzothiazole disulphide (MBTS). These reactions consequently offer the delayed to the scorch.

Three classifications for sulphur vulcanization system are used in rubber technology, i.e. conventional vulcanization (CV), semi-efficient vulcanization (semi-EV), and efficient vulcanization (EV). These three categories are classified based on the ratio of accelerator to sulphur as listed in Table 2.5. The different of sulphur vulcanization system will influences the vulcanizate properties especially cross-link types. The combined sulphur with rubber molecules in CV system exists predominantly in the form of polysulphidic cross-links whereas EV system produces a thermally stable

monosulphidic and disulphidic cross-links. Semi-EV system compromises between CV system and EV system.

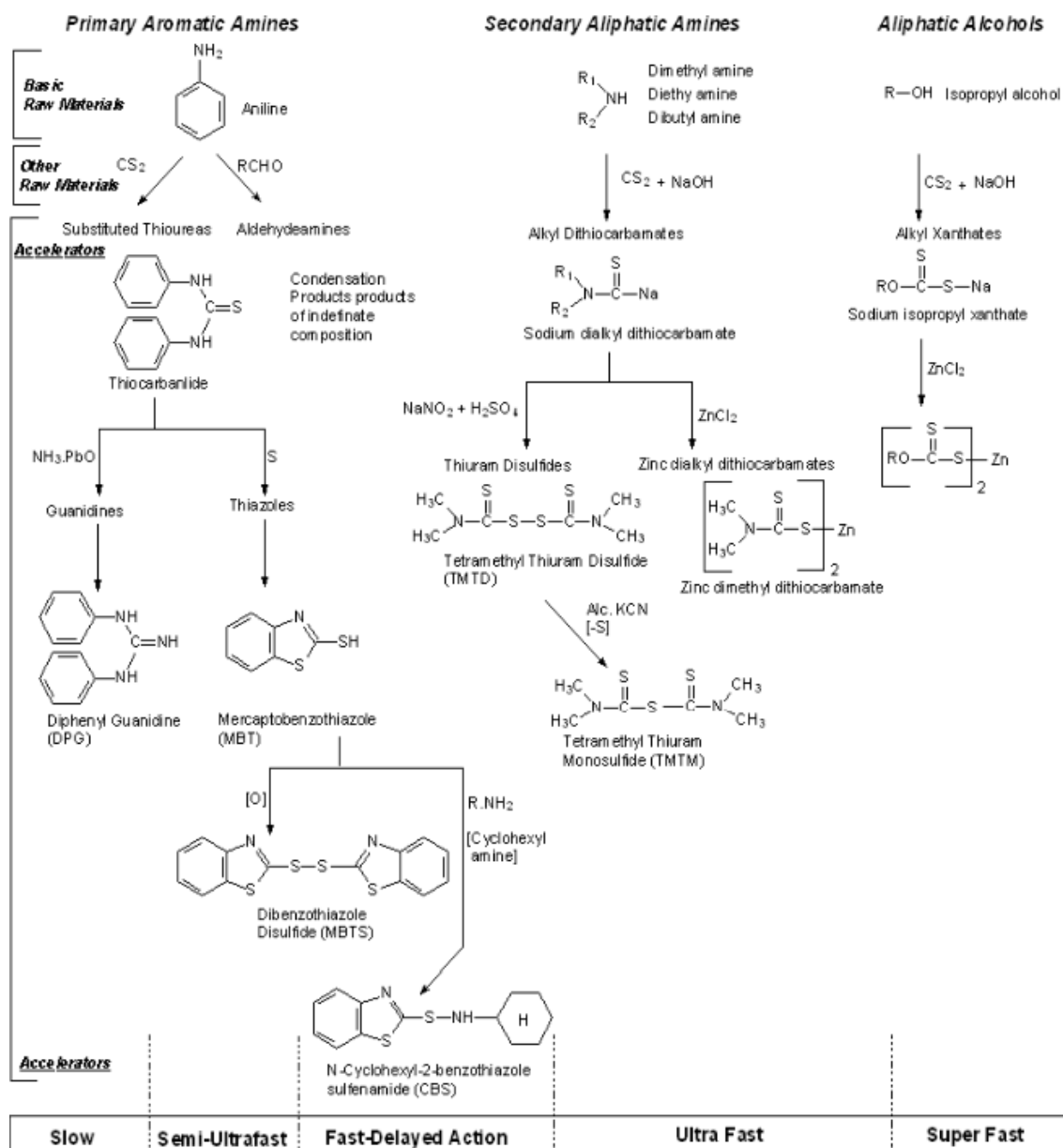


Figure 2.5: Classification of accelerators based on functional group and its activity speed (Arvind Mafatlal Group, 2010).