# INVESTIGATION OF PHOSPHATE TYPE ACCELERATOR (ZINC O,O-DIBUTYLPHOSPHORODITHIOATE,ZBPD) AND SILANE (BIS(TRIETHOXYSILYLPROPYL)TETRASULFIDE, TESPT) EFFECT ON THE PHYSICAL AND MECHANICAL PROPERTIES OF CURED RUBBER COMPOUND

Submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons.)

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# APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Hons). The member of the supervisory are as follow.

……

**(Profesor Dr. Qumrul Ahsan)**

# ABSTRAK

Tujuan kajian ini adalah untuk mengkaji kesan jenis fosfat pemecut (ZBPD) dan silana (TESPT) kepada sifat-sifat fizikal dan mekanikal sebatian penawar getah. Pada masa ini dalam pembangunan untuk produk getah kumpulan DECATHLON, pemecut thiazole adalah terhad dalam semua komponen untuk sportwares sentuhan kulit kerana pemecut thiazole datang dengan kesan-kesan risiko bahaya kesihatan manusia yang tinggi. Oleh itu, ZBPD dan TESPT digunakan untuk menggantikan pemecut thiazole kerana fungsi rumusan baru adalah berhampiran dengan fungsi thiazole pemecut iaitu untuk mempercepatkan proses pengawetan getah. Kira-kira tiga Ujian fizikal dan mekanikal (penawar pencirian, tegangan dan kekerasan, sifat bengkak) dan tiga kaedah pencirian (FTIR, SEM, OM) telah digunakan dalam kajian ini. Dalam kajian ini, formulasi getah dengan semasa MBT pemecut rendah dan DPG pemecut menengah sedang berbanding dengan formulasi getah dengan semasa ZBPD, ZDBC dan TESPT silana ejen gandingan. Selepas ujian dan analisis, keputusan menunjukkan bahawa formulasi getah dengan ZBPD menunjukkan sifat-sifat mekanikal yang lebih baik jika dibandingkan dengan formulasi getah konvensional dengan MBT pemecut. Sebaliknya, rumusan getah dengan semasa TESPT tidak meningkatkan sifat-sifat mekanikal perkarangan penawar getah disebabkan oleh suhu pemprosesan yang tidak mencukupi dalam proses pencampuran peringkat pertama menyebabkan sebatian getah untuk menjadi mempunyai luka bakar dan tingkah laku pra-matang. Oleh itu, ZBPD pemecut adalah disyorkan untuk menggantikan MBT pemecut dalam penggubalan getah.

# ABSTRACT

The aim of this research is to investigate the effect of phosphate type accelerator (ZBPD) and silane (TESPT) on the physical and mechanical properties of cure rubber compound. Currently in the development for rubber product of DECATHLON group, thiazole accelerator is restricted in all component for skin contact sportwares due to thiazole accelerator comes with the side-effect of high human health hazard risk. Hence, ZBPD and TESPT is used to replace thiazole accelerator due to the functionality of the new formulation is close to the function of thiazole accelerator which is to accelerate the rubber curing process. About three physical and mechanical testings (cure characterisation, tensile and hardness, swelling properties) and three characterisation methods (FTIR, SEM, OM) have been used in this study. In this research, rubber formulation with the present of MBTS primary accelerator and DPG secondary accelerator is being compared with the rubber formulation with the present of ZBPD, ZDBC and TESPT silane coupling agent. After testing and analysis, result shows that the rubber formulation with ZBPD shows better mechanical properties when compared with the conventional rubber formulation with MBTS accelerator. On the other hand, the rubber formulation with the present of TESPT does not improve the mechanical properties of the cure rubber compound due to insufficient processing temperature in the first stage mixing process causing the rubber compound to be have a scorch and pre-mature behaviour. Hence, ZBPD accelerator is recommended to replace MBTS accelerator in the rubber formulation.

# DEDICATION

I would like to dedicate this work to my.

Beloved parents and family.

Honourable supervisor and lecturers.

Supportive friends.

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# LIST OF ABBREVIATIONS AND NOMENCLATURES

| | |
|---|---|
| MBTS | Benzothiazole disulphide |
| DPG | Diphenyl Guanidine |
| ZBPD | Zinc-dibutylphosphorodithiate |
| ZDBC | Zinc Dibutyldithiocarbomate |
| TESPT | Bis-(triethoxy-silyl-propyl) tetrasulfide |
| BZT | Benzothiazole |
| MBZT | 2-mercaptobenzothiazole |
| EtOH | Ethanol |
| KBr | Potassium Bromide |
| NaCl | Sodium Chloride |
| FTIR | Fourier Transform Infrared Spectroscopy |
| OM | Optical Microscope |
| SEM | Scanning Electron Microscope |

# LIST OF SYMBOLS

| | | |
|---|---|---|
| % | - | Percentage |
| µm | - | Micrometre |
| A | - | Area |
| cm | - | Centermetre |
| d | - | Density |
| MPa | - | Mega Pascal |
| mm | - | Millimetre |
| N | - | Newton |
| nm | - | Nanometre |
| $^{o}C$ | - | Degree Celcius |
| s | - | Second |

# CHAPTER 1
# INTRODUCTION

## 1.1 Project Background

Curing process is the chemical reaction which involves heating the mixture of natural rubber. Throughout this process, cross-linking of the chains of rubber are chemically bonded to one another to form a network hence turning into an elastic cured rubber compound. Curing process would increase the material properties of rubber by having better crosslinking density, strength and modulus. It involves crosslinking of sulphur atom bonds at both chain where the carbon-to-carbon double bonds existed. (Bauman, 2008).

Accelerator is one of the key factor to ensure fast, greater efficiency and lesser quantity of sulphur required for curing process. Accelerator for curing process are divided into two main groups that are primary accelerator and secondary accelerator. The function of primary accelerator is to provide considerable scorch delay, medium to fast cure and good modulus development. The example of the primary accelerators are sulfenamides and thiazoles. On the other hand, secondary accelerator provides scorch and very fast curing stocks. The example of the secondary accelerator is dithiacarbomate, thiurams and specialty accelerator. In the rubber industry, thiazoles accelerator is commonly use to accelerate the curing process.

Benzothiazole disulphide (MBTS) is one of the thiazoles type accelerator that is widely used in compound for all types of major commercial applications. Activity for MBTS and scorch properties can be controlled over a wide range by using ultra accelerators such as Diphenyl Guanidine, DPG secondary accelerator with MBTS. MBTS acceleration is the ideal starting point in new compound development.

Zinc-dibutylphosphorodithiate (ZBPD) is considered as the phosphate type accelerator. ZBPD is mainly used as for non-blooming, lower cost rubber curing process as it has fast curing ability. Besides, when applying ZBPD in rubber curing process, the cured rubber compounds will have a better reversion resistance property. ZBPD is usually used for translucent food packaging rubber products due to theirs non-blooming and non-discoloring properties.

Bis-(triethoxy-silyl-propyl) tetrasulfide (TESPT) or silane is a silicon based coupling agent that replaces sulphur atoms used for cross-linking in curing process. TESPT could use to replace accelerator by provoking cross-linking reaction between rubber chains. The working mechanism of TESPT could be categorised into two separate reactions which are hydrophobation and silanisation. During the mixing process, TESPT reacts with silica fillers which lead to hydrophobation that reduce the silica network and further lead to polar silica more compatible with the non-polar rubber hence reduce the compound viscosity (Debnath *et al,* 2013). On the other hand, silanisation reaction subsequent coupled reaction between the bound silane splits with the elastomer molecules. (C. Hayichelaeh, 27 May 2018) Combination of the two reaction provide chemical bond between rubber and polar silica filler.

## 1.2 Problem Statement

Accelerators are used in curing process of natural rubber to accelerate and increase the efficiency of the curing process. Nowadays, thaizole accelerator is the most commonly used in natural rubber industry for all type of applications which include footwear products. It is because thaizole accelerator have an ultra-fast scorching speed which results in increase of the cross-linking of sulphur bridge with rubber chains in compound by curing process

Certain accelerators can adversely affect human health risk and cause environmental pollution issue. In the development process of swimming fin product for DECATHLON group in Rubber Leisure Products Sdn. Bhd, thaizole accelerators are restricted in all component or finished goods having skin contact because thaizole accelerator would cause toxicity and lead to human health risk issue.

Benzothiazole (BZT) and 2-mercaptobenzothiazole (2-MBZT) are the restricted thaizole accelerator that would lead to high human health hazard risk. BZT exerts acute toxicity and is a respiratory irritant and dermal sensitizer. In a genetic toxicity assay BZT was positive in Salmonella in the presence of metabolic activation. On the other hand, MBZT may relate to the occurrence of human bladder cancer. (Brian, Gary, & Tara, 2011).

Therefore, the swimming fin products for DECATHLON group should be accelerator free to avoid the product produced by Rubber Leisure Products Sdn. Bhd is rejected from the DECATHLON group. Hence, phosphate type accelerator, ZBPD and TESPT/ Silane are taken into consideration in the production of pocket part of swimming fin. TESPT is considered as a silane based coupling agent which could provoke the cross-linking reaction between rubber chain that formed by ZBPD, a fast curing accelerator.

Hence, ZBPD and TESPT is expected to replace the role of thaizole accelerator in accelerating the curing process and improve the mechanical properties of cured rubber compound. ZBPD and TEST are free from toxicological and ecotoxicological classification from DECATHLON group.

## 1.3 Objectives

The objectives of this research project are as below:

1. To evaluate the effect of ZBPD accelerator and TESPT silane coupling agent on the cure characteristics of rubber compounds.

2. To analyze the mechanical properties of the cured rubber compounds.

## 1.4 Scope

The scope of this research is the comparison study between the MBTS type accelerator with ZBPD accelerator and TESPT silanizated in vulcanization. Therefore, the cure characteristic during vulcanization is determined by rheometer. Besides that, the experimental studies of the mechanical properties and the hardness of the vulcanizate are being tested under the hardness machine and tensile testing machine. On the other hands, the qualitative information on the molecular components and structure of the vulcanizate are being obtained by using the Fourier Transform Infrared Spectroscopy (FTIR). The swelling properties for each vulcanized are being determine using the swelling test and lastly the tear path and fracture surface morphology are being determined with optical and scanning electron microscopy respectively.

# CHAPTER 2
# LITERATURE REVIEW

This chapter emphasized on the theory of current curing process in rubber industries. The main purpose of this chapter is to provide a detailed explanation in a chronological order from material and the process involved for the testing and characterization. In addition, the role of silane is also being discussed figure.2.1.

## 2.1 Natural Rubber Curing Process

Natural rubber curing process also known as the vulcanisation of natural rubber is being defined as the chemical process that produce network junctures by the insertion of crosslinking between polymer chains (Eirich, 2014). This process is usually carried out by heating the rubber under a mold under pressure. The atom used for the crosslinking process is depend on the atoms used for the curing. For example, group of sulphur atoms in a short chain, carbon-to-carbon bonding, silicon bonding and others type of bonding.

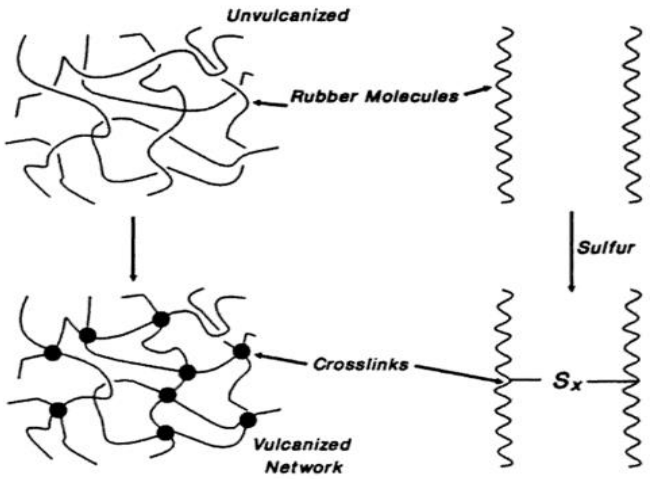


Figure 2.1: Network formation in curing process (Eirich, 2014)

Through the curing process, the long rubber molecules chain is linked together with junctures spaced along the polymeric chains. Curing process is the major factor that effect the mechanical and physical properties of rubber. The use-related properties could be illustrated by the correlation between the vulcanizate property and the crosslink density.

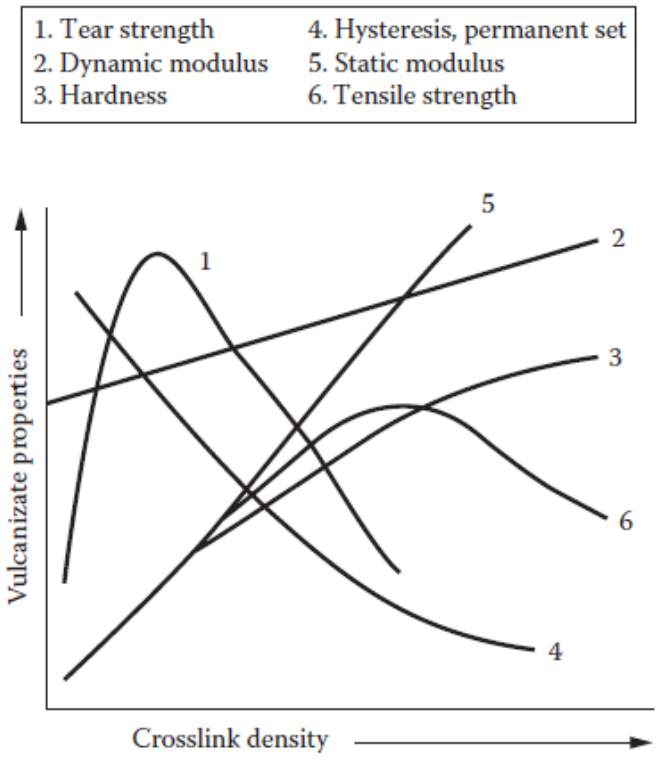


Figure 2.2: : Vulcanizate properties as a function of the extent of curing process. (rodgers, 2016)

From the Figure 1.2 as the cross-linkage density of the vulcanizate increases the elastic properties such as dynamic modulus, tear and tensile strength, resilience and hardness while the hysteresis decrease. (rodgers, 2016). Hysteresis is referred to stress softening which cause energy dissipation of vulcanized rubber. The hysteresis of rubber through curing process is reduced with the incensement of crosslink formation (Eirich, 2014). Further increase in crosslink density will produce vulcanizates that tend toward brittle behaviour. Thus, at higher crosslink densities elastic properties of natural rubber begin to decrease. (rodgers, 2016)

The changes of physical properties of natural rubber is due to the covalent interlinking of the long flexible rubber chain. These chains have a number-average molecular weight of a few hundred thousand and form of randomly coiled molecular structure. Hence, deformation of these coiled molecular structure which results in a fair degree of plastic flow with limited elastic recovery when the deforming force is removed. During curing, the individual molecules become cross-linked to form three-dimensional network in which some molecular alignment on deformation is still possible and resistant to lateral movement. (S.Oae, 2012) .

The chemistry of un-accelerated curing process is not commercial significance due to it requires long period of vulcanization. For example, un-accelerated curing process could be accomplished by using elemental sulphur required 5 hours at 140$^{o}$C of vulcanisation period. (Eirich, 2014) Hence to increase the speed of vulcanisation, accelerator is one of the essential factor for a commercial significance curing process in the industries.

## 2.2 Thiazoles-based Accelerator.

An accelerator is a chemical used in small amount with curing agent to reduce the time of the vulcanisation process. The most comment used accelerator system in the industries is the sulphur accelerator system are used to control the onset, speed and extent of reaction between sulphur and elastomer. Accelerator is divided into two group of accelerators that are primary and secondary accelerator. Compounds that used to increase the rate at which rubber vulcanize with sulphur are referred as primary accelerator.

On the other hand, secondary accelerator also called as booster is used to further increase the rate of sulphur vulcanisation. Although the chemical structure of various accelerator are different, the basic features of the accelerator are similar with composition of one or two sulphur atoms between a pair of organic end group, N = C – S (Heideman, N. Datta, & W. M. Noordermeer,, 2004) .

Accelerator system are chosen based on their ability to control the performance properties of rubber compound. For example, the time delay before vulcanisation begins