UNIVERSITI TEKNIKAL MALAYSIA MELAKA

CURING CHARACTERISTICS AND MECHANICAL PROPERTIES OF STYRENE BUTADIENE RUBBER (SBR) FILLED WITH INDUSTRIAL WASTE DERNED ASHES

This report is submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering

by

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DECLARATION

I hereby, declare that this thesis entitled "Curing Characteristics and Mechanical Properties of Styrene Butadiene Rubber (SBR) Filled with Industrial Waste Derived Ashes" is the result of my own research except as cited in the references.

Signature : ……………………………….

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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 requirements for the degree of Bachelor of Manufacturing Engineering (Hons.).

The members of the supervisory committee are as follow:

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(Dr. Mohd Edeerozey Bin Abd Manaf)

ABSTRAK

Getah stirena buatdiene (SBR) adalah sejenis getah sintetik yang terdiri daripada monomer stirena dan butadiena. Terutamanya polimer SBR disintesis daripada hasil sampingan petroleum. SBR telah menjadi salah satu daripada getah sintetik yang paling penting di dunia kerana jumlah pengeluarannya yang besar. Kebiasaannya SBR diperkukuh dengan pengisi seperti karbon hitam (CB) untuk meningkatkan sifat-sifat mekanikal sebatian getah untuk tujuan tertentu. Abu terbang (FA) dan abu kelapa sawit (OPA) adalah dua jenis bahan sisa industri yang berpotensi digunakan sebagai pengisi dalam SBR. Kedua-dua abu ini digunakan sebagai pengisi untuk mengurangkan kesan alam sekitar, pencemaran udara dan kawasan lambakan abu sisa industri. Dalam kajian ini, hubungan antara FA, OPA dan CB juga sifat-sifat SBR (sebatian berasaskan) telah dikaji. Sebatian getah dihasilkan menggunakan mesin dua roda pusingan dan proses pengawetan, sebelum dinilai. Kandungan jumlah pengisi telah dipelbagaikan kepada 0, 3, 5 dan 10 phr. Dalam penilaian sebatian getah, fokus utama adalah ciri-ciri pengerasan, sifat-sifat mekanikal dan sifat fizikal sebatian SBR. Ciri-ciri pengerasan bagi sebatian SBR dengan pengisi dari sisa industri diukur dengan menambah jumlah pengisi yang berbeza daripada tiga jenis pengisi kepada sebatian getah. Di samping itu, dua jenis pengisi hybrid iaitu CB-OPA and CB-FA juga dikaji..Dalam keputusan itu, sebatian getah mengandungi CB-OPA dan CB-FA pengisi dipamerkan kekuatan tegangan kedua yang lebih tinggi, pemanjangan pada takat putus, kekuatan lusuh, kelikatan dan kekerasan dan dikaitkan dengan penyebaran pengisi berkesan. Kesimpulan ini disokong oleh mikroskop elektron pengimbas (SEM) dan ujian bengkak.

ABSTRACT

Styrene butadiene rubber (SBR) is a kind of synthetic rubber which is polymerized by using the monomers, styrene and butadiene. SBR are mainly polymers synthesized from petroleum byproducts. SBR has become one of the most important synthetic rubbers in the world because of its huge production. Generally, SBR is reinforced with filler such as carbon black (CB) to increase mechanical properties of rubber compound for specific purpose. Fly ash (FA) and oil palm ash (OPA) are two types of industrial waste that can be potentially used as filler in SBR. Both ashes can be used as filler to reduce environmental effect, air pollution and dumping area of industrial waste ashes. In this study, the relationship between FA, OPA and CB also the properties of SBR (based compounds) was investigated. Rubber compounds were produced by two roll mill and followed with curing process, before evaluated. The total content of fillers was varied at 0, 3, 5 and 10 phr. In the evaluation of the rubber compounds, the main focus was the curing characteristics, mechanical properties and physical properties of the SBR compounds. Curing characteristics of SBR compounds added with waste derived fillers were measured by adding different filler loading of three types of fillers to the rubber compounds. Besides that, two types of hybrid fillers, i.e., CB-OPA and CB-FA were also studied. In the result, the rubber compounds contained CB-OPA and CB-FA filler exhibited second higher tensile strength, elongation at break, tear strength, viscosity and hardness and attributed to effective filler dispersion. These conclusions were supported by the scanning electron microscopy (SEM) and swelling test.

DEDICATION

Only

my beloved father, Allahyarham Mesri Bin Senik
my beloved mother, Zaleha Binti Hamid
my appreciated grandfather, Hamid Bin Bakar
my adored grandmother, Allahyarhamah Tum Binti Lazim

for giving me moral support, money, cooperation, encouragement and also understandings

Thank You So Much & Love You All Forever

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CHAPTER 1

INTRODUCTION

This chapter covers the background, problem statements, objectives to be achieved through the study and scope of the study.

1.1. Background of study

World-wide increase in demand for automotive ownership has resulted in an increasing market demand for pneumatic tires. Pneumatic tires are composed of external surface, called tread, under which resides a reinforcement belt, which is consists of a number of steel cords. Tread is the part which directly contacts the road surface, and thus, needs to be strong enough to avoid cracks or tears. In addition, reducing rolling resistance is very important for tread, because rolling resistance is related to fuel consumption with higher rolling resistance resulting in higher energy loss. Tread is made up of a rubber compound.

There are two main types of rubber which are synthetic rubber and natural rubber. Natural rubber is collected from mature rubber trees which have to be planted in damp and hot environments. Therefore, the production of natural rubber is limited and cannot satisfy the overall market need. This is why synthetic rubber was developed during World War II. Styrene Butadiene Rubber (SBR) is a kind of synthetic rubber which is polymerized by using the monomers, styrene and butadiene. SBR are mainly polymers synthesized from petroleum byproducts. SBR has become one of the most important synthetic rubbers in the world because of its huge production. In tire applications, SBR rubber exhibits good abrasion resistance and stability, which is the reason why SBR rubber is usually used in tire tread.

SBR is a mixture of approximately 75 percent butadiene (CH_2=CH-CH=CH_2) and 25 percent styrene (CH_2=CHC_6H_5). In most cases these two compounds are copolymerized in an emulsion process, in which a soap like surface-acting agent disperses, or emulsifies, the materials in a water solution. Copolymerized is single-unit molecules linked to form long, multiple-unit molecules of the two compounds. Other materials in the solution are include free-radical initiators, which begin the polymerization process, and stabilizers, which prevent deterioration of the final product. Upon polymerization, the styrene and butadiene repeating units are arranged in a random manner along the polymer chain. The polymer chains are cross-linked in the vulcanization process.

For many purposes SBR directly replaces natural rubber, the choice depending simply on economics. Its particular advantages include excellent abrasion resistance, crack resistance, and generally better aging characteristics. In SBR, however, the main effect of oxidation is increased interlinking of the polymer chains. So, unlike natural rubber, it tends to harden with age instead to harden with age instead of softening. A large amount of SBR is produced in latex form as a rubbery adhesive for use in applications such as carpet backing. Other applications are in belting, flooring, wire and cable insulation, and footwear.

The concept of reinforcement for rubbers is complex but, generally, reinforcement is added to rubbers to enhance certain properties and at the same time reduces the cost of the rubber compound. Currently, there are more than 100 types of reinforcement that have been reported in the literature, however, only a few have been commercialized and used extensively. The principal advantage of composite materials lies in the possibility of combining physical properties of the constituents to obtain enhanced properties, for example physical, mechanical or optical. The great demand for composite materials in many fields has brought to the forefront the very complex problem of developing new types of composite material in which reinforcement from two or more types of filler/fibres is combined to produce so called hybrid composite materials. The incorporation of hybrid fillers into polymer matrix has been a popular field of research in recent years (Ismail and Shaari 2010).

Filler represent the largest volume category of material added to polymers and may be sub divider into reinforcing or extending type. Reinforcing fillers increase hardness and modulus, improve tensile and tear strength, and provide abrasion resistance. The purpose of extending filler is to lowest cost without sacrificing key performance properties. Many compounds use a mixture of both reinforcing and extending fillers.

Rubber compound fillers typically have multi-purposes. Some filler like carbon black and silica are used to improve the properties of rubber compounds by acting as reinforcement agent. On the other hand, some filler such as calcium carbonates cannot increase the properties of rubber compounds, but are still used to reduce the cost of the tire. Absence of any fillers in the rubber compound, would result in soft and easy to break rubber material. Filler addition typically results in stiffer rubber resistant to abrasion and deformation. Among all kinds of rubber fillers, carbon black is the most traditional and commonly used reinforcing filler. Carbon black is collected from the carbon black oil furnace process. Carbon black has various types with different physical and chemical properties. There are multiples sizes, surface areas, structures and surface activities. Its surface has functional groups like phenolic, ketones, carboxylic, lactones and others. These functional groups will be responsible in interacting with the rubber.

Fly ash is a byproduct of the power generation industries neglected for many years as a potential filler in many different commercial products including the rubber compounds. The fly ash is produced by coal-fired electric and steam generating plants. Typically, coal is pulverized and blown with air into the boiler's combustion chamber where it immediately ignites, generating heat and producing a molten mineral residue. Boiler tubes extract heat from the boiler, cooling the flue gas and causing the molten mineral residue to harden and form ash. Coarse ash particles, referred to as bottom ash or slag, fall to the bottom of the combustion chamber, while the lighter fine ash particles, termed fly ash, remain suspended in the flue gas. The main composition of the fly ash is silica. It can be revealed that silica is also an important reinforcement filler in rubber industry. Therefore, just like the carbon black, fly ash can also be used as a reinforcing filler to improve the mechanical properties of rubber compounds, as investigated over many years.

1.2. Problem statement

The production and use of carbon black may cause environmental problems. Annually, the production of carbon black is about 10 million tons. Carbon dioxide is released into the atmosphere during the production of carbon black. Therefore, carbon black contributes to global warming. In order solve this problem, various methods were invented mainly in two different directions. One direction involves a new process to replace the old method of producing carbon black. For example, S.Rodat et al., reported that carbon black can be produced by solar methane dissociation. The other direction involved replacing the carbon black with other environmental friendly fillers such as in this research, which involved partial replacement of the carbon black with fly ash oil and palm ash.

Annually, a large amount of fly ash is produced from the power stations all over the world. If fly ash is separated by the air and the wind, it will disperse everywhere. In that way, a serious air pollution problem would appear and the risk of getting pulmonary diseases would increase. To solve this problem, solutions have been proposed. Thomas K. Paul, et al. reported that fly ash can increase the mechanical properties of styrene butadiene rubber. It was observed that fly ash has contributed similar reinforcing effect in increasing rubber compound elongation, modulus and hardness when it was compared with carbon black filled styrene butadiene rubber. In this research, fly ash was investigated as a secondary filler along with carbon black and oil palm ash for possible improvements in mechanical properties of rubber compounds.

Malaysian palm oil industry plays an important role as it serves as the largest palm oil producer and exporter in the world (Ismail and Shaari 2010). According to the Malaysian Palm Oil Council (MPOC), Malaysia currently accounts for 51% of world palm oil production and 62% of world exports. The mass production of palm oil generates solid waste, such as palm oil kernels and seeds, which are being used as fuel for a combustion process to generate steam in palm oil mills. The byproduct of the combustion, the ash, is highly abundant in Malaysia and the waste is either transported to an approved dump site or dumped illegally. Dumping requires large areas of land, which is a limited resource, and is an environmentally unfriendly activity. In this research, oil palm ash was investigated as filler along with carbon black and fly ash for possible improvements in mechanical properties of rubber compounds.

Therefore, this research is carried out in order to reduce the cost to handle the industrial waste. The idea is by reinforced SBR filled with available inexpensive waste derived materials such as oil palm ash and fly ash. By utilizing the waste, it will eventually give added value to the waste and reduce cost to handle the industrial waste. Besides that, it also increased the properties to SBR.

1.3. Objectives

- To study curing characteristics of styrene butadiene rubber (SBR) filled with different type of filler, i.e, fly ash, oil palm ash, carbon black.
- To compare mechanical and physical properties of styrene butadiene rubber (SBR) filled with different type of filler, i.e, fly ash, oil palm ash, carbon black.
- To correlate the morphological characteristics of the fracture surfaces of the rubber blends by using scanning electron microscopy (SEM) with their properties.

1.4. Scope

The key focus of this research is to investigate curing characteristics and mechanical properties of SBR filled with industrial waste derived fillers. The waste fillers used are oil palm ash, fly ash and carbon black.

Firstly, the various SBR reinforced with industrial waste derived filler are prepared by compounding them together using two roll mill. The formulation of the SBR and filler used is very important because the different amount of filler, SBR will give different effect to the sample produced.

Then, the SBR rubbers blended with different type and amount of filler undergo curing process by using hydraulic press at high temperature. Next, the samples are shaped by using dumb bell shape puncher to proceed for testing.

The third stage is cure characterization followed with mechanical and physical testing. For mechanical properties, the rubber blend samples are tested with tensile test, tear strength, hardness and Mooney Viscosity test. Meanwhile for physical testing the rubber blend samples undergo swelling test. Lastly, the tested samples undergo microstructure observation by scanning electron microscopy (SEM).

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

The section revises the scope of earlier research works related on styrene butadiene rubber (SBR) filled with different types of fillers from a few years back. In recent years, there are also some research works reported on mechanical properties of SBR filled with the ashes. However, until today there are limited source of information especially on the SBR reinforce OPA or FA

2.2. Rubber

Generally rubbers are divided into two types. First type is thermosets and second type is thermoplastics. Three dimensional molecular networks, with the long molecules control along by chemical bonds known as thermosets. The three dimensional molecular networks absorb swell and solvent. However, the three dimensional molecular networks do not dissolve. Moreover, heating cannot reprocessed the three dimensional molecular networks. The molecules of thermoplastic rubbers, are not connected by primary chemical bonds. Instead, they are joined by the physical aggregation of components of the molecules into arduous domains. Hence, thermoplastic rubbers dissolve unsuitable solvents and soften on heating, in order that they can be processed repeatedly.

In several cases thermoplastic and thermoset rubbers may be used interchangeably. However, in exacting uses like as in tires, engine mounts, and springs, thermoset elastomers are used completely due to their better elasticity, resistance to set, and durability. The addition of assorted the chemicals to raw rubber to impart fascinating properties is termed rubber combination or formulation.

Rubber and elastomers are a number of the foremost common materials considerably acknowledged for its flexibility and their ability to soak up particle like carbon black, silica and clay in enhancing and getting the required properties for specific applications wherever resistance to impact or toughness are desired (Mohamed, Mohd Nurazzi, and Huzaifah 2017).

2.2.1 Natural Rubber

Natural rubber is an elastic substance contained in the milky juice (latex) of any various plants of the genus Hevea, especially the rubber tree (H. brasiliensis) (Harald 2004). Latex consists of an aqueous dispersion of cis-1, 4-polyisoprene, $(C_5H_8)_n$, an unsaturated, high molecular weight hydrocarbon for commercial purposes. This latex is coagulated by adding acetic or formic acid or sodium hexaflurosilicate and subsequently concentrated by evaporation or centrifugation. The processed latex is usually dried and converted into sheets of crude rubber. Besides, ulvulcanized natural rubber has poor mechanical properties and chemical and environmental resistance but these are significantly improved by crosslinking (or vulcanizing). Usually the improvement through treatment with sulphur or special chemicals.

Natural rubber (NR) is the second largest type of rubber utilized in the world (Jayaraj et al. n.d.). NR based product have a high demand due to remarkable properties of NR that not exist in other materials. Excellent mechanical properties are maintained by NR with the addition of fillers, vulcanizing system and other specialty chemicals. NR was a well-known polymer that has been widely used in a spread of commercial and engineering applications (George et al. 2000). The strain-induced crystallization behavior makes NR distinctive among elastomers as so much as strength properties are concerned. NR has better strength and lower heat buildup than SBR and shows better performance at low temperature (Aprem et al. 2003).

Natural rubber is well-known for its strain- induced crystallization behavior (Ismail et al, 2010). Therefore, it exhibits excellent properties such as green strength. In addition, NR also demonstrates abrasion resistance and good hysteric properties. However, it is essential for NR to be reinforced with fillers to achieve specific properties.

2.2.2 Synthetic rubber

Synthetic rubber refers to any of a group of elastomers that resemble natural rubber in physical and chemical properties (Harald 2004). It is trusted that it also have its unique properties of deformation such as high elasticity yield strain.

Besides that, the unique properties are elastic recovery after vulcanization with sulphur or other crosslinking agents. Synthetic rubber can be produced from various starting materials in particular by polymerization of unsaturated compounds but also by addition and condensation polymerization of suitable starting products. It is often distinguished from natural rubber by its improved properties such as higher resistance to abrasion, gasoline oil, oxygen and heat and lower gas permeability. Examples of include butadiene and styrene butadiene rubber, nitrile rubber, isoprene rubber, chloroprene rubber and silicon rubber.

2.2.2.1 Styrene Butadiene Rubber

(Guo, Zhou, and Lv 2013) stated that one of the most widely used synthetic rubbers is the copolymer styrene butadiene rubber (SBR). This polymer is mainly used as a cured material in industrial applications as compounds in tires, membranes, wires, and cables. In the majority of these applications, SBR compounds are vulcanized using sulphur and accelerator as cure system. Although vulcanization takes place by heat and pressure in presence of sulphur, the process is relatively slow. The inclusion of small amounts of chemicals known as accelerators in the compound formulation makes the vulcanization process faster.

Styrene butadiene rubber (SBR) is a random copolymer of styrene and butadiene made either by polymerization in emulsion in the presence of peroxide-type catalyst at elevated temperatures, by polymerization in the presence of metal peroxides at relatively low temperature (cold rubber) or by polymerization in solution with stereospecific organolithium compounds (Harald 2004).

It has good physical properties when reinforced with carbon black and other fillers, excellent abrasion and impact resistance, tensile strength, good electrical and thermal properties, moderate fatigue resistance, poor oil, ozone and weather resistance and poor general chemical resistance. SBR is often sold under trade names and trademarks such as Buna CB and Buna S, Budene, Dyradene, Intene and lastly Krylene or Polysar. Application of SBR are used for