SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

CURING CHARACTERISTICS, TENSILE AND MORPHOLOGICAL PROPERTIES OF TEA WASTE FILLED NATURAL RUBBER COMPOSITES

By

NUR ZAFIRAH BINTI HAMDAN

Supervisor: Prof. Dr. Hanafi bin Ismail

Dissertation submitted is partial fulfillment

of the requirements for the degree of Bachelor of Engineering with Honours

(Polymer Engineering)

UNIVERSITI SAINS MALAYSIA

JUNE 2018

DECLARATION

I hereby declared that I have conducted, completed the research work and written the dissertation entitled “Curing Characteristics, Tensile and Morphological Properties of Tea Waste Filled Natural Rubber Composites”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

Name of student : Nur Zafirah binti Hamdan Signature:

Date : 25 June 2018

Witness by

Supervisor : Prof. Dr. Hanafi bin Ismail Signature:

Date : 25 June 2018

ACKNOWLEDGEMENTS

Firstly, I would like to thank God for giving me physical and mental strength in completing this final project and dissertation within a given time frame. While I was completing this thesis, there were many people who helped me directly or indirectly. They were a researchers, academicians, practitioners, friends and family. A very special thanks I wish to Professor Hanafi bin Ismail for being my supervisor during my final year project with all the guidance, cooperation, opinion, suggestion, understanding and constructive of criticism. The cooperation is much indeed appreciated. Besides, I also would like to thank technical staffs in polymer section especially in rubber department, Mr. Shahril Amir bin Saleh and Mr. Mohd Suharudin bin Sulong for their cooperation and willingness in order to help me in my project. Not forgotten, Mr. Faizal, Mr. Shahrizol, Master and PhD students for their valuable helps and guidance.

A huge thanks also to all my lecturers in USM especially lecturer's in Polymer Engineering department for their valuable lessons and guidance since the first day I becoming USM's student. In addition, I also grateful for the opportunities that I had from School of Materials and Mineral Resources to do my degree in Bachelor of Engineering (Polymer Engineering) including my final year project that gives me great experiences and benefits. My thanks also goes to all my friends from classmates, course mates and roommates that help me going through ups and down to completing this final year project.

Last but not least, I would like to gives a big appreciation and thanks to my precious parents, Mr. Hamdan and Mrs. Khadijah. Not forgotten, my siblings for their encouragement, advice, opinions and patience throughout my degree in Universiti Sains Malaysia.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
BKF	2,2 methylene-bis-(4-methyl-6-tert-butylphenol)
CB	Carbon black
CBS	N-cyclohexyl-benzothiazole-2-sulphenamide
EB	Elongation at break
FTIR	Fourier Transform Infrared Spectroscopy
ISO	International Standard for Organization
NR	Natural rubber
SEM	Scanning Electron Microscopy
Si69	Silane coupling agent
SMR 20	Standard Malaysia Rubber grade 20
TW	Tea waste
ZnO	Zinc Oxide

LIST OF SYMBOLS

%	Percentage
a	constant
b	constant
dNm	deci Newton meter
E	Young Modulus
M100	Modulus at 100 % percentage
M300	Modulus at 300 % percentage
M_H	Maximum Torque
M_L	Maximum Torque
MPa	Mega Pascal
Phr	Part per hundred rubber
Q_f/Q_g	Gram of solvent per gram of hydrocarbon
t_{90}	Cure time
t_{s2}	Scorch time
-z	Ratio by weight of filler to rubber hydrocarbon in vulcanizate

CIRI-CIRI KEMATANGAN, TEGANGAN DAN SIFAT MORFOLOGI KOMPOSIT GETAH ASLI TERISI SISA TEH

ABSTRAK

Tujuan eksperimen ini dijalankan adalah untuk mengkaji ciri-ciri kematangan, ciri-ciri tegangan dan morfologi komposit getah asli yang di isi dengan sisa teh. Ciri-ciri serbuk sisa teh dikaji dengan menggunakan ujian Spectroscopy Fourier Transform Infra-Red (FTIR) dan ujian Pengimbasan Mikroskopik (SEM). Ciri-ciri kematangan, sifat tegangan, kajian morfologi permukaan tegangan yang patah dan sejauh mana interaksi pengisi getah komposit getah asli yang di isi oleh sisa buangan teh telah dikaji sebagai fungsi pengisi di dalam Siri 1, kesan ejen gandingan bersama silane dalam Siri 2 dan pengisi hibrid antara sisa teh dan karbon hitam dalam Siri 3. Jumlah sisa teh yang digunakan dalam Siri 1 dan Siri 2 adalah 0, 5, 10, 15, 30 phr dan 0, 5, 10, 15 phr, manakala dalam Siri 3, campuran sisa teh (TW) dengan karbon hitam (CB) (TW + CB) adalah 30 + 0, 30 + 10, 30 + 20 dan 30 + 30 phr. Keputusan menunjukkan bahawa komposit getah asli tanpa kehadiran agen gandingan,Si69 (Siri 1) mempunyai interaksi yang kurang baik antara serbuk sisa buangan dan mengurangkan sifat komposit manakala komposit getah asli dengan kehadiran Si69 (Siri 2) menunjukkan peningkatan sifat-sifat komposit dimana interaksi yang lebih baik berlaku antara getah dan pengisi. Dalam Siri 3, dengan peningkatan jumlah karbon hitam, sifat-sifat komposit getah asli juga meningkat disebabkan penggabungan pengisi penguat dalam penggabungan getah yang meningkatkan sifat getah.

CURING CHARACTERISTICS, TENSILE AND MORPHOLOGICAL PROPERTIES OF TEA WASTE FILLED NATURAL RUBBER COMPOSITES

ABSTRACT

The objective of this research work was to study the curing characteristics, tensile and morphological properties of tea waste filled natural rubber composites. The tea waste powder was characterized by using Fourier Transform Infra-Red (FTIR) Spectroscopy and Scanning Electron Microscopy (SEM) testing. Curing characteristics, tensile properties, morphological studies of tensile fractured surfaces and the extent of rubber-filler interactions of tea waste filled natural rubber (NR) composites were investigated as a function of filler loading in Series 1, the effect of silane coupling agent in Series 2 and the hybrid fillers between tea waste and carbon black in Series 3. The tea waste loading used in Series 1 and Series 2 was 0, 5, 10, 15, 30 phr and 0, 5, 10, 15 phr, respectively while in Series 3, the mixed of tea waste (TW) with carbon black (CB) was in the function of TW + CB which was 30 + 0, 30 + 10, 30 + 20 and 30 + 30 phr. The results indicate that the natural rubber composites without the presence of coupling agent which was Si69 (Series 1) has the poor interaction between tea waste powder hence reduced the properties of the composites while the natural rubber composites with the presence of Si69 (Series 2) showed the improvement in the properties of the composites as the better interaction occurred between rubber and filler. In Series 3, as the amount of carbon black increase, the properties of the natural rubber composites also increased due to the incorporation of reinforcing fillers in the rubber compounding that enhanced the rubber properties.

CHAPTER 1

INTRODUCTION

1.1 Background

Natural rubber (NR) consists of isoprene units $(C_5H_8)_n$ linked together in a 1,4 cis-configuration as shown in Figure 1.1. It has unique properties as a polymer owing to its intrinsic structure, its high molecular weight and there are contributions of minor components, such as proteins, minerals, carbohydrates and lipids, which are all present in the latex (a colloidal suspension of rubber particles) (Jan B. van Beilen and Yves Poirier 2007).

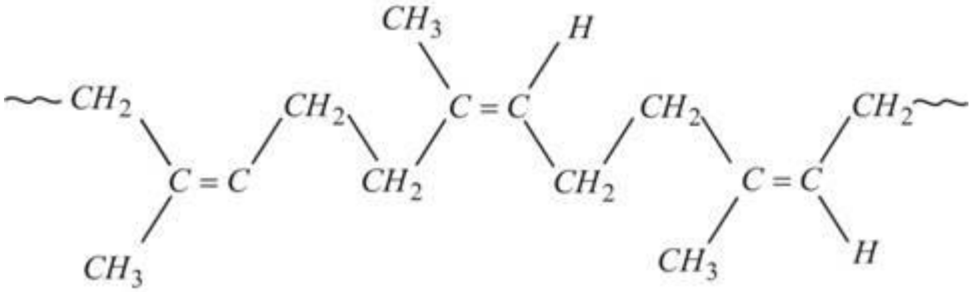

Figure 1.1: Structure of Natural Rubber (NR)

According to Kanokwan Yantaboot and Taweechai Amornsakchai (2017), NR is widely accepted as a material of absolutely necessary. The useful properties of NR are strength, tear resistance and tack which many synthetic rubbers lack. However, the low polarity of NR leads to the poor resistance to non-polar solvents and poor adhesion to polar materials. When it comes to reinforcement of fiber, the low polarity of NR can be significant drawbacks compared with the high polarity rubbers.

Natural rubber (NR) is one of the most important elastomers in the terms of versatility and the application volume owing it to the superior strength, elasticity, resilience, flexibility, and abrasion resistance. Traditionally, it is vulcanized with the reaction of sulphur and sulphur compounds with olefinic substances because it low strength and poor weather resistance in form of original uncured. Further improvement in mechanical properties of NR can be achieved by adding the reinforcing fillers, such as carbon black and silica. There has been a growing interest for the improving the performance of composites by using the reinforcement that derived from the renewable resources (Marcin Maslowski et al., 2017).

As reported by Osabohien and Egboh (2007), to improve strength and reduce the materials cost, fillers that can be incorporated in rubber composites. Fillers become one of the most important components and are added at the second highest portion in the rubber products manufacturing. Fillers can be classified into two type which are reinforcing and non-reinforcing fillers. The reinforcing fillers able to improve the modulus and strength of the rubber products, whereas, non-reinforcing fillers have little or no effect on the rubber properties.

Basically, carbon black (CB) and silica are the main commercially used reinforcing fillers. CB has been the most widely used and studied reinforcing filler for rubber composites since the early 1900s (Fröhlich et al., 2005; Tohsan and Ikeda, 2014). As concerned, commercial fillers used in rubber compounding such as CB and silica has their own drawbacks where they are costly and not renewable.

The facts that carbon black (CB) are capable to significantly improve the physical properties of rubber that is referred to as reinforcement which provide the largest market today especially in the tire industry. CB are made up from incomplete combustion of organic substances, probably first noted in ancient times by observing the deposits of a black substances on objects close to a burning material. Typically, tire contains 30 %- 35 % of CB, and there are normally several grades of carbon black in the tire. Surely, the uses of CB is not only in the tire industry, it is also used in many non-tire rubber applications owing to its ability to reinforce the rubber and its use as a cost reduction diluent in the compound (Brendan Rodgers, 2015)

Nowadays, it can be seen that many researcher have shown their interest in the study of natural fillers in rubber compounding. The natural fillers reinforcement in polymer was found to be as good as the common fillers for the low load bearing applications (P. Wambua et. al., 2003). The research on developing a new type of filler for rubber composites is by using natural resources, particularly renewable resources like natural fibers. These kind of natural fibers are inexpensive and available in every part of the world that allow countries to use their own natural resources in their processing composites (Ali and Khoo 1995). The advantage of natural fibers are cheap, abundantly available, environmentally friendly, readily, low density than traditional fibers and biodegradable. However, the disadvantage of natural fibers in composites is may results the poor compatibility with hydrophobic matrix (John and Anandjiwala 2008; Li et al. 2007; Saheb and Jog 1999).

Basically, the use of coupling agents can cover up this drawbacks in order to improve the wettability of the natural fiber by polymers and encourage interfacial adhesion (John and Anandjiwala 2008; Xie et al. 2010). Coupling agents contain bi-functional groups that can react with the matrix of natural fiber and polymer by forming a linkage between them. By this, an enhancement in adhesion of natural fiber to polymer will form a uniform structure of composites. An efficient coupling agent for rubber is silane coupling agent (Barry 1977; Xie et al. 2010).

Silane coupling chemicals present three main advantages where firstly, they are commercially available in a large scale. Secondly, at one end, they bear alkoxysilane groups capable to react with OH-rich surface, and lastly at the second end, they have a large number of functional groups which can be tailored as a function of the matrix to be used. Nowadays, the features is to ensure at least a good compatibility between the reinforcing element and the polymer matrix or even covalent bonds between them. Besides, the chemical bonding theory which is the most evident mechanism by which organosilane coupling agents are acting, other theories have been proposed, such as the interpenetrating networks theory which states that the matrix diffuse inside the silane interphase to form an entangled network (M. Abdelmouleh et al. 2006)

Silane coupling agent compatible almost with every kind of organic polymer that range from thermoset resins through elastomers to thermoplastic resins. It may be applied to the substrate which is as a pretreatment or in many systems, the silane may be added to the resin where it migrates to the substrate while normal mixing and application procedures. The silane coupling agents allow the application of promoting the bonding that lead to improve physical and mechanical properties of composites material such as filled and reinforced resins, filled elastomers, and caulks for adhesion of metal and glass, and resin-coated and painted metal (Samuel. Sterman and James G. Marsden, 1966).

Tea dust (TD) powder is a waste material also known as a tea waste (TW) especially in urban areas. It is generally not used for any purpose and is discarded as wet garbage. Used particles of tea waste are advantageous waste materials because they are cheap, light in weight, rich in polyphenols as tannin present in tea leaves, and easily available from natural resources and also exist in large amount of tea industries that can be found in tea stalls or restaurants or residence. Tea waste materials also have the capability of solving environment-related issues and it is described as natural fibers (Pravin Bari et al. 2015).

1.2 Problem Statement

In the modern era of modernization, with the accelerating urban industrial growth, wide quantity of harmful waste products have been released into the atmosphere. Nowadays, pollution is the crucial issues that allowed a lot of problem. One of the most widely consumed beverages in the world is tea that mainly obtained from the leaves of *Camellia sinensis* L. Based on the recent statistics, the production of tea in the world has reached 4.5 million tons annually (Batiancela et al. 2014). Commercially, for example, the preparation of tea drinks, the tea waste will remain after preparation of the tea drink and it is collected as a solid waste product. Tea waste also known as tea fiber. The tons of consumption of tea waste will create a potential pollution problems. The tea waste mostly come from restaurants and stalls as a waste in the large amount, so it is better to make it as a useful wastage such as natural filler at the same time to reduce the environmental pollution. These natural fibers are renewable, biodegradable, abundant and low cost.

The technology of polymer composites nowadays has been one of the major areas of research and development. A polymer composite basically contains a polymer and non-polymer. The use of natural fiber as a filler in polymer composites may cause the reduction of the cost in their production.

In the rubber compounding of tea waste filled natural rubber composites, the interaction between rubber and tea waste powder was poor. In order to give the better interaction between them, the used of silane coupling agent is needed. This is because, silane coupling agents was usually used to enhance the compatibility of rubber and filler.

In particular, the specific case of rubber composites is by using the carbon black (CB) as the most effective reinforcing fillers in the elastomeric compound (Mujkanovic et al., 2009). The CB are essentially an oil by-product used to strength the rubber. It is produced by shooting a hot mist of oil particles into a flame and it is classified as an expensive process that has limited number of competitors in the industry.

As explained by Matthews and Rawlings (1999), there are different approaches that have been applied in order to improve the properties of fiber-reinforced polymer composites. In line with that, the hybrid composites nowadays become common to many researchers as these composites are designed to benefit from the different properties of the fillers employed to give the synergistic enhancements in the composite’s properties.

1.3 Objectives

I. To study the effect of different loading of tea waste on curing characteristics, tensile and morphological properties of natural rubber (NR) composites.

II. To study the effect of silane coupling agent of different loading of tea waste on curing characteristics, tensile and morphological properties of natural rubber (NR) composites.

III. To study the effect of hybrid fillers of carbon black (CB) loading with tea waste on curing characteristics, tensile and morphological properties of natural rubber (NR) composites.

1.4 Thesis Outline

The experiment consists of three series namely Series 1, Series 2 and Series 3. 12 compound were prepared for these three series. For Series 1, five compound were prepared with different tea waste loading which consist of 0 phr, 5 phr, 10 phr, 15 phr and 30 phr. While four compound were prepared for Series 2 with different tea waste loading of 5 phr, 10 phr, 15 phr and 30 phr with the addition of 1.0 phr of silane coupling agent. Series 3 were the hybrid of tea waste (TW) and carbon black (CB) with different loading. The filler loading of TW + CB were 30 + 0, 30 + 10, 30 + 20 and 30 + 30. Each series has a different scope of study.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Rubber (NR)

According to C. H. Chan et al. (2013), Natural Rubber (NR) also known as *cis*-1,4-poly(isoprene) where the chemical structure of isoprene is 2-methyl-1,3-butadiene. Originally, NR is an elastomer derived from a milky colloidal suspension from the sap of some plants that called NR latex. The sap cultivated from the *Hevea brasiliensis* tree is only commercially importance. *Hevea* is originated from Brazil and it produces high molecular weight of 97 % *cis*- 1,4-poly(isoprene) which roughly about 20 000 units of isoprene. This signifies that NR polymer chain continues on the same side of double bond. The double bonds along the backbone of NR allow attachment of pendant groups and/or provide chemically reactive sites for crosslinking. NR is naturally soft and sticky solid with low tensile strength and low elasticity due to weak van der Waals forces of its attraction of intermolecular and occasional crosslinking. It is soften during room temperature in tropical countries but harden during cold weather and it is highly crystallizable upon stretching. In some organic solvents such as toluene, tetrahydrofuran, chloroform, methyl ethyl ketone, acetone, benzene and many more, NR is soluble. NR properties is deteriorate drastically by sunlight, ozone, and oxygen according to its high level of unsaturation, and such a material is of minimal interest in the industry. The addition of carbon black (CB), antiozonants and waxes towards NR enhances its resistance to UV and ozone, respectively.

In 1496, Christopher Columbus has returned from his second voyage and brought back the first balls of NR from the West Indies to the Iberian Peninsula. In 1736, Charles Marie de La Condamine introduced the samples of NR and he reported the properties of NR to the Academic Royale des Science of France. Charles proposed that the NR can be used as a flexible tubes. Afterwards, in 1770, an English Chemist, Joseph Priestley suggested the possibility of using NR as an eraser because of the capability to rub pencil mark off the paper and this become the first recorded use of NR. In 1791, Samuel patented a method of waterproofing cloth by coating the cloth in turpentine with a solution of NR. A British industrialist, Nadier, produced NR threads for clothing accessories in 1820. Thomas Hancock invented a mastication machine to mix and soften the NR to enable it to be shaped in London. In 1823, in a plant of Glasgow, Charles Macintosh produced waterproof garments by coating cloth with a solution of NR in benzene. However, NR did not achieved any commercial value until nearly a century later. In 1839, the first important chemical modification of NR was vulcanization. It is generally credited independently to Charles Goodyear (USA) and Thomas Hancock (England). The introduction of crosslinks into NR chains in the vulcanization process by heating up the NR with addition of sulfur, accelerator, fillers and antioxidants as shown in Figure 2.1. The vulcanization turns NR into non-sticky and hard material of polymeric with increased tensile strength and higher resistance to organic solvents. This is the landmark in the NR history that led to multibillion global NR industries (C. H. Chan et al., 2013).

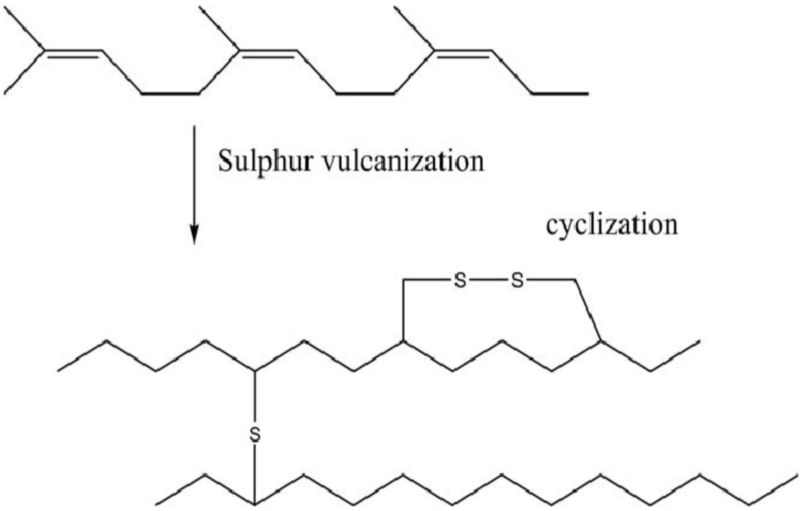

Figure 2.1: The schematic of sulfur vulcanization of NR. Adapted from (P. Saendee and P. Tangboriboonrat, 2006)

2.1.1 Standard Malaysian Rubber

Natural Rubber (NR) has many grades from ribbed smoked sheets (RSS) that are made up from coagulated field latex, to pale crepe which is made up from a latex that has been preserved to prevent enzyme darkening, to technically specified (TSR) grades. The Malaysian rubber industry introduced these grades and also known as Standard Malaysian Rubbers (SMR) grades where there are standard rubber grades from Indonesia (SIR), Thailand (STR) and Sri Lanka (SLR) as well. These are the grades of NR that are cleaned and turned to a crumb, rather than a sheet rubber. To achieve such properties as a constant viscosity (SMR-CV), light color (SMR-L) or specified grades of dirt and ash content (SMR 5, 10, 20 and 50), the processed are further for them. The grades of TSR have more consistent properties compared to conventional rubbers made from coagulated field latex. The properties of SMR grades are tabulated in Table 2.1 (Sadhan K. De and Jim R. White, 2001).

Table 2.1: Grades of Standard Malaysian rubber

	SMR-L	SMR-5	SMR-10	SMR-20	SMR-50
Dirt retained, %	0.03	0.05	0.10	0.20	0.50
Ash content, %	0.50	0.60	0.75	1.00	1.50
Plasticity Retention Index (PRI)	60	60	50	40	30

Standard Malaysian Rubber grade 20 (SMR 20) contain the percentage of dirt retained and ash content of 0.20 and 1.00, respectively. An assurance that the rubber is adequately dry and should be reduce by limiting the volatile matter to maximum 0.8 %. The Plasticity Retention Index (PRI) are usually expressed as a percentage and it is measure of, for example, the resistance of raw natural rubber to oxidation (The PRI for SMR 20 is 40 % (A. Whelan and Tony Whelan, 1994)

2.2 Fillers

2.2.1 Fibers

2.2.1.1 Natural Fibers

Layth Mohammed et al. (2015) reported that one of the materials that is considered as an environmentally friendly is natural fiber that having a good properties compared to synthetic fiber. In 2010, a late current industry research identified that the worldwide natural fiber reinforced polymer composites industry sector reached U$2.1 billion. The simple definition of natural fibers are fibers that are not man-made or synthetic. Plants or animals can be their sourced. Natural fiber uses from both resources, renewable and non-renewable for example, oil palm, jute, sisal and flax to produce composite materials. In the last decades, they gained considerable attention, so far. The plants that producing the cellulose fibers are classified in bast fibers (jute, flax, hemp, kenaf and ramie), seed fibers (kapok, cotton and coir), leaf fibers (pineapple, sisal and abaca), grass and reed fibers (corn, rice and wheat), and core fibers (kenaf, jute and hemp) as well as all other kinds (roots and wood).

In numerous applications, fiber reinforced polymer matrix got considerably attention due to good properties and superior advantages of natural fiber over synthetic fibers in the terms of relatively low cost, low weight, less damage to processing equipment, good mechanical properties such as tensile modulus and flexural modulus, improved surface finish of composite molded parts, renewable resources, abundant, flexibility during processing, biodegradability and minimal hazards of health. However, natural fibers also has the drawbacks and they have notable deficits in properties. It is consists of structure of (cellulose, hemicellulose, lignin, pectin, and waxy substances) and also allowed moisture absorption from the surroundings that causes the weak bindings between the fiber and the polymer. Besides, the couplings between natural fiber and polymer are considered a challenge because the structure of the chemical for both fibers and matrix are various. Hence, specific treatments are certainly necessary for the modifications of natural fibers. Generally, these modifications centered on utilization of functional groups reagent which it have the ability for responding of the fiber structures and changing their composition. Fiber modifications will cause the reduction of moisture absorption of the natural fibers as the results, which lead to an excellent enhancement incompatibility between the fiber and polymer matrix. In a review of natural fibers chemical treatments, Kabir agree that treatment is an important factor that need to be considered in the natural rubber processing. They observed that fiber loose hydroxyl groups based on the different chemical treatments, then decreasing the hydrophilic behavior of the fibers and causing the enhancement in mechanical strength as well as dimensional stability of natural fiber reinforced polymer composites (Layth Mohammed et al., 2015).

Based on Wirasak Smitthipong et al. (2014), natural rubber normally, has poor thermal resistance. The incorporation of fibers in the matrix of rubber prevent the initiation of crack and hinders the propagation of crack. The direction of the fibers should be oriented perpendicular of the propagation of crack and the good bonding will exist between the fiber and the rubber.

2.2.1.2 Tea waste fiber

Tea has become one of the most consumed non-alcoholic beverages worldwide by Lin et al., (2015) and also well-known as for its extraordinary health promoting effects such as anti-cancer, anti-virus, anti-obesity, anti-inflammatory, neuro-protective activities, anti-hypertensive effect and so on according to Cabrera (2006) and Stagg (2010). The amount of production of tea in the world was 5,305,000 tons include 2,270,000 tons from China in 2015 due to Li et al., (2017). Zheng et al., (2017) stated that a large amount of tea waste would be generated during tea deep-processing. Ahmad et al. (2015) reported that currently, most of tea waste has been disposed by composting, incineration or in landfills. However, tea waste was hard to degrade and it has posed pressure on the environment and cause huge loss of beneficial components as observed by Ahmad et al., (2015) and Duan et al., (2016).

Nowadays, the utilization of tea waste has received considerable attention. It was reported that the tea waste sand adsorbents prepared by using tea waste like magnetic porous carbonaceous material and activated carbon were effective in removing the heavy metals for example, Ni (II), Cu (II), Pb (II), As (V), Cr (VI), etc. as studied by Malkoc et al. (2005) and organic pollutants such as methylene blue, acid blue and azo dyes from waste due to Auta et al., (2011). Furthermore, tea waste could be serve as an effective functional food or additive of animal diets to enhance the efficiency of digestion, fat metabolism and immune cell proliferation as reported by Ahmad et al., (2015). Liu and Huang (2016) stated that when preparing tea waste into biological composite hydrogel with soluble starch, it also has good performance on loading and releasing of sodium salicylate.

2.3 Natural Fibers (Fillers) Filled Natural Rubber (NR) Composites

Previously, the research about the effect of tea waste on the physical properties of NR was carried out by Wattana Sukhlaaeid and Sa-Ad Riyajan (2010). By using NR grade STR 5L, they found that the tensile strength and elongation at break of the NR compound decreased while the modulus, increased with the increasing of tea waste in the compounding. Hence, the addition of tea waste and carbon black on the NR compound exhibits excellent thermal properties. From Scanning Electron Microscopy (SEM), they observed that the particle size of tea waste was about 20-30 micron after the milling by using a laboratory blender. They found out that the shape of the tea waste was not spherical. In addition, they investigated that the tensile strength of the NR compound in the presence of tea waste was about 3.5 MPa and then increased to 8 MPa after the addition of Carbon Black with tea waste in the NR compounding.

The past decade, there are rapid development of the use of natural fillers in the research of rubber compound. Ismail et al., (2001) investigated the effects of the various bonding agents on the properties of oil palm wood flour filled natural rubber composites. Jacob et al., (2004) has discussed that the process ability characteristics and mechanical properties of sisa/oil palm hybrid filler reinforced natural rubber composites. Jamil et al., (2006) studied the effect of rice husk filler on the mechanical and thermal properties of the liquid natural rubber compatibilized High Density Polyethylene (HDPE)/natural rubber blends. The modified starch paste showed an obvious reinforcement on both natural rubber/starch composites and the matrix of natural rubber with the improving of mechanical properties in optimum starch content that pointed out by Liu et al., (2008).

Besides, Ismail and Haw (2000) found out that the tensile properties and fatigue life of NR composites reduced with the palm ash incorporation. However, the properties of the palm ash NR composite were increased with the presence of the maleate NR. The possibilities by the using of bagasse fiber ash as alternative secondary filler in NR compounds that contains precipitated silica and CB as primary filler was studied by Kanking et al., (2012) and Sereena et al. (2012) found out that the peanut shell powder could be used as semi reinforcing filler the industry of rubber. The guinea corn husks could serve replacement for N 330 CB in the production of product with low strength, for example, soles and foot mats that has been concluded by Tenebe et al., (2013). In addition from another study, the ground pistachio shell was found to be an environmental friendly and low cost alternative filler for the compounding of rubber, especially for some specific applications such as abrasion resistance.

Ali and Khoo (1995) stated that in Malaysia, rattan has been in large quantities and it is considered as the most important product of non-wood forest where it has been extensively used in the industry of furniture. The large amount of the rattan canes waste that gained from the furniture industry has spurred interest in its possible use as a filler in NR composites. Previously, Ismail et al., (2012) reported that the curing characteristics, tensile properties, rubber filler interaction, and morphological study of the rattan powder filled NR composites. As the results, John and Anandjiwala (2008) concluded that the rattan powder incorporation in NR tended to decrease the tensile properties due to the weaker rubber-filler interaction. Usually, the problem faced by NR is in adhesion and compatibility with the matrix of polymer because of an inherent polar and characteristics of hydrophilic of natural fibers that make them incompatible with non-polar polymer matrix materials. The results from this consequences is poor dispersion of fibers within the matrix and poor interfacial adhesion between fibers and matrix that can create the poorer properties of composites.

According to Kanking et al., (2012), the reinforcement effect of hybrid composites has been extensively study conducted by many researchers. His investigated that the use of bagasse fiber ash as a secondary filler in carbon black or silica filled NR composites.

Based on Cespedes et al., 2010, generally, plants are recognized as a major sources of natural antioxidants based on their phytochemical substances that include the flavonoids and other polyphenols. Nowadays, there are many researchers done the study of the enhancement of the properties offered by natural antioxidants as compared to the commercial antioxidants in several industries, for example, cashew nut shell liquid, pomegranates and grapes. There are widely studied about the effect of natural antioxidants on the properties of polymer by using the different types of plants.

Shuhaimi et al., (2013) studied that the properties offered by the extraction of oil palm leaves as an antioxidant for the NR vulcanizates compared with the commercial antioxidants. In the study by Komethi et al., (2012) and and Shuhaimi et al., (2013) they found out that the oil palm leave's extract has the tendency to substitute the commercial antioxidants (2,2,4-trimethyl-1,2-dihydroquinoline in the rubber compounds. There are variety of fruits that have been proved to have high antioxidant activity, some fruits show the better antioxidant activity on the peel rather than the pulp and seeds. Zadernowski et al., (2009) had confirmed that the mangosteen peel has higher phenolic content than its pulp. The mangosteen peel contains various bioactive substances such as phenolic acids and flavonoids, which possess medicinal and biological properties especially the properties of antioxidants, hence it is considered to be one of the potential anti-oxidative agents.

The mechanical properties of pineapple leaf fiber are prominent compared to other natural fibers and it is closed to aramid and glass fiber, hence it become very attractive as a reinforcement of rubbers. The mechanical properties of a composite usually due to the matrix and the fiber properties, for example, dispersion, strength, content, orientation and aspect ratio. And it is also depending on the mechanism of the stress transfer from the matrix to the fiber. In this journal, they are published the use of short pineapple leaf fiber for the nitrile rubber (NBR) and natural rubber (NR) reinforcement. They found that the improvement level in mechanical properties obtained in NBR is more than that obtained from NR composites. This is because of the greater difference in polarity among the rubber matrix and the fiber reinforcing. By decreasing the molecular weight of NR, there are significant improvement of the mechanical properties in the regions of low strain that can be obtained. But, by using the low molecular weight of NR as the matrix would become the disadvantageous as the mechanical properties of the final composites remain poor at very high strains. However, this latter point can be overcome by using the hybrid particulate filler (Kanokwan Yantaboot and Taweechai Amornsakchai, 2017).

2.4 Compounding Ingredients

Based on Maziar Ramezani and Zaidi M. Ripin (2012), in order to obtain the desired properties, the addition of certain chemicals to the raw rubber are called as a rubber compounding or formulation. Crosslinking agents, reinforcements, colorants and degradants are the well-known chemicals in rubber compounding. K.S. Sisanth et al., 2017 stated that the special class of polymeric materials is elastomers which have unique properties such as toughness, flexibility and elasticity. Natural rubber (NR), synthetic rubber (SR), and other polymeric materials like thermoplastic elastomers are included as an elastomeric materials. The rubber compounding involves science and engineering of rubbers and the additives of rubber, for example, curing agents, fillers and processing aids, in definite proportions in order to obtain a uniform mixture that will have desirable physical and chemical properties to meet processing at low cost and end use performance. The nature of elastomer and the characteristics of these ingredients can affect the final properties of rubber products.

2.4.1 Activator

Barlow, 1993 stated that activators is the substances that can improved the effects of the accelerator. To prevent the premature vulcanization under the processing conditions to the stock, the addition of retarders are allowed. Zinc oxide and stearic acid are the most common and popular activator system. It seem that the reaction of zinc oxide with the stearic acid is to form zinc stearate which is soluble in the rubber where the latter can be considered to be an organic solvent and in this form the process of crosslinking become more easy. It is vital to have zinc ions in the soluble form.

Zinc oxide can reduce the sulfidic crosslink while encouraging the C-C bonds formation and it becoming such an efficient and popular kind of activator. These bond formation in turn increases thermal stability of the vulcanizates (Kogel et al., 2006). Historically, it was the general practice that the addition of 5 parts of zinc oxide when it was used as an activator. Recently, the tendency to use the zinc oxide has been 2-4 parts. The studies have indicated that there is little if any gain in activation function beyond 4 parts, and 3 parts is adequate for most purposes. This decreasing is due to the cost of zinc oxide is relatively expensive pigment and has a high density. Meanwhile, there is more reason for reducing the usage of zinc oxide dosage. The U.S. Environmental Protection Agency (EPA) has determined that the zinc oxide is a toxic chemical where the less used, the less difficulty in disposing of waste rubber compounds (Barlow, 1993).

Stearic acid is naturally occurring that derives from residues of animal product processing. It is in a range of materials that is available from cheap products. Normally, it is added at a 2 phr level to a rubber compound. By reducing the stearic acid level, the problems comes from naturally occurring constituents of natural rubber that include the fatty acids as these can fluctuate depending on the source supply. If the total of fatty acid level is too low, it can affect the cure system that can become too sensitive to other inherent materials (R. B. Simpson, 2002).

2.4.2 Accelerator

Accelerator is a chemical that used only in the small amounts with a vulcanizing agent for reducing time in the process of vulcanization. Nowadays, in the vulcanization of sulfur, the uses of accelerator are to control the speed, onset, and extent the reaction between elastomer and sulfur (Brendan Rodgers, 2015).

In the crosslinking of rubber compounds, the accelerators are used. They can be classified as slow, medium-fast, fast, semi-ultrafast and ultrafast where very rapid accelerators are called ultra-accelerators. They also can be divided into direct or delayed action types. The behavior of end-use or physical property can be obtained by combining the different accelerators. The accelerators can improve the efficiency of vulcanization because they are promoting the formation of mono- and di-sulphide crosslinks rather than intra-molecular reactions. By using them at 1 phr, the required sulphur content is considerably reduced. By the uses of delayed action accelerator, the rapid and efficient vulcanization can be obtained at high moulding temperatures without scorching, at the lower, mixing or shaping temperatures that more than one accelerator may be used to obtain the desired characteristics. In the conjunction with the rubber accelerators, activator are usually use with it. This is because, the function of the accelerator may be efficient in the presence of activator. Natural rubber vulcanizes more quickly compared to synthetic rubber hence the need of the more expensive accelerator system become less (A. Whelan, 2012).

Table 2.2: Classification of accelerators

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, TBzTD	Thiuram	Ultra-fast
ZDMC, ZDEC, ZDBC, ZBEC	Dithiocarbamate	Ultra-fast
ZIX	Xanthates	Ultra-fast

Accelerators are also classified as Primary and / or Secondary accelerators based on the role they play in a given compound. Generally, Thiazoles and Sulfenamide accelerators play a role of being Primary Accelerators due to their characteristics such as good processing safety, a broad vulcanization plateau and optimum cross link density as well as desired reversion delay that they offer. The Primary Accelerators are used at 0.5 to 1.5 phr dosages in most rubber compounds. The basic accelerators such as Guanidines, Thiurams, and Dithiocarbamates are used as Secondary accelerators to activate the primary accelerators. The use of secondary accelerators increases the speed of vulcanization substantially but at the expense of scorch safety. The dosages of the secondary accelerators are generally between 10-40% of the primary accelerator.

2.4.3 Antioxidant

According to Rees and William (1935), antioxidant has few effect on the rubber under some circumstances while under the other conditions, it can increase the tensile strength and longer the lifespan of rubber to a marked extent. It is not impossible to compare between the functions of antioxidant because it is depending on the specific conditions and no single material appears the best under all the circumstances. In the sense of practical, the word of antioxidant is understood to mean as a substances that is added into rubber to increase its useful lifespan. As their summary, the useful life of rubber compounds increased with the addition of all antioxidants under practically all of the conditions of test. Besides, the effectiveness of the antioxidants varied between wide range of limits that depend upon the conditions of exposure, the type of compound and the used of particular antioxidant.

Based on NPCS Board of Consultant & Engineers (2009), a substances that is capable to slower down the oxidation rate in autoxidizable materials is defined by the terms of antioxidant. Usually, an antioxidants are referred to the general term which is anti-degradants. The addition of antioxidant in the rubber compounding is to prolong the useful life cured rubber or plastics by decreasing the oxidative changes that happen over a long period of service.

Sung (2004) stated that nowadays, many antioxidants available like others ingredients in the market. 2,2 methylene-bis-(4-methyl-6-tert-butylphenol) also known as BKF is a non-staining antioxidant from the type of phenolic. Antioxidant can be grouped into a number of chemical classes which the group are amine and phenolic. These phenolic type from BKF is more effective compared to monophenols and it is suitable for the stabilization of elastomers, polymers, lattice and paints. To protect the polymers and rubber compound from oxidation, there are specific way for each antioxidants to perform. Their performance related to their chemical reactivity, their rate of staining or migration to the vulcanized rubber or polymer surface and their volatility.

2.4.4 Vulcanizing Agent

In 1839, Charles Goodyear (1800-1860) an American inventor accidentally discovered the vulcanization process when he dropped some rubber that contain sulfur onto hot stove. To converting rubber or related polymers into durable materials by adding the sulfur or other curative, this chemical process is called vulcanization or curing. This process can help to decrease the effect of heat, cold or solvents on the rubber compound properties and for creating the good and useful mechanical properties (Dick, 2001).

Process of an irreversible during which a rubber compound through a change in its chemical structure such as crosslinking becomes less plastic and more resistant to swelling by organic liquids while the elastic properties are conferred, improved or extended, over a greater range of the temperature is the ASTM definition for vulcanization. Including the irradiation, there are variety of agents that can brought the change. Commonly, there are four curing agents or systems used and they are sulfur systems, peroxides, urethane cross-linkers and metallic oxides (used only in vulcanizing of neoprene). However, sulfur is the most common vulcanizing methods (Barlow, 1993).

Based on Gent (2000), in the conjunction of the accelerators and activators, sulfur is widely used as the vulcanizing agent. Sulfur that used in the vulcanization formed into two type which is soluble (rhombic crystals) and insoluble (amorphous and polymeric sulfur). R.

B. Simpson (2002) reported that rhombic is the most stable form, at least up to 96°C that the other type of revert to this form of stable are at a dependent rate upon temperature. In the different type of rubber, the degree of solubility also different for a normal rhombic sulfur. The required proportion for crosslinking dissolves relatively rapidly at room temperature for the NR and SBR. As one would expect, as the temperature increase, the sulfur solubility within the rubber also increase. The problems that may occur if the sulfur level in a compound is higher than the necessary for the required crosslinking degree is bloom. As the increasing temperature during the compound mixing, the sulfur amount become soluble within the rubber greatly exceeds the sulfur solubility level within the rubber at room temperature. However, either the un-vulcanized or vulcanized surfaces, sulfur not dissolving into the rubber will maintain within the matrix of rubber and will not bloom. Sulfur dissolved into the rubber in the excess of its level of solubility for example, a super saturated solution at elevated temperature will form unwanted bloom on the surface of rubber compound at ambient temperatures. The crystallization rate of the excess sulfur from the super saturated solution depending on the type of rubber, ambient temperature and other factors as the fingerprints on the surface of rubber.

According to Dick (2001), the system for accelerated sulfur vulcanizing can be classified into three systems that depending on the uses of relative amounts of sulfur and the accelerator. The systems are:

1. Conventional Vulcanization (CV)
2. Semi-efficient Vulcanization (Semi EV)
3. Efficient Vulcanization (EV)