SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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COMPARISON OF SILANE TREATMENT METHODS ON FILLER REINFORCEMENT IN RUBBER COMPOSTIES

By

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(Polymer Engineering)

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **“Comparison of silane treatment methods on filler reinforcement in rubber composites”**. I also declare that it has not been previously submitted for award of any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

%	Percentage
[X]	Crosslink concentration
^oC	Degree Celcius
dNm	Deci Newton Meter
Eb	Elongation at break
g	Gram
g/mol	Grams per mole
g/cm^3	Grams per centimetre cube
kg	Kilogram
N/mm	Newton per milimetre
mm	Millimetre
Mw	Molecular Weight
MPa	Megapascals
min	Minutes
mdry	Dry natural rubber mass
mwet	Swollen equilibrium mass
pphr	Parts per hundred rubber
rpm	Revolution per minutes
Vo	Molar volume of toluene
Vp	Volume fraction of the particle
Vr	Volume fraction of MREs
wt%	Weight percentage

ρr	Density of natural rubber
ρs	Density of toluene
σ	Stress
χ	Interaction parameter between the rubber and toluene

ABBREVIATIONS

ASTM	American Society for Testing and Materials
CBS	N-Cyelohexy1-2-benzothiazole sulphonamide
NR	Natural rubber
ODR	Oscillating disk rheometer
FTIR	Fourier Transform Infrared Red Spectroscopy
IPPD	N-Isopropyl-N’-Phenyl-P-Phenylenediamine
SEM	Scanning Electron Microscope
SMR	Standard Malaysian Rubber
TESPT	Bis-(3-triethoxysilylpropyl) tetrasulphane
TMTD	Tetramethylthiuram disulphide

PERBANDINGAN KAEDAH RAWATAN SILANA TERHADAP PENGUKUHAN BAHAN PENGISI DALAM KOMPOSIT GETAH

ABSTRAK

Objektif kajian ini adalah untuk membandingkan prestasi kaedah rawatan silana yang berbeza untuk menilai kaedah optimum untuk memperbaiki ikatan antara permukaan pengisi dan matriks. Kaedah yang digunakan adalah kaedah kering, kaedah akues dan kaedah pengadunan leburan. Untuk memeriksa keberkesanan kaedah yang digunakan bagi pengubahsuaian permukaan pengisi, tiga jenis pengisi: silika (saiz nano), ferit (saiz makro), dan kenaf (serat) telah dikaji. Hubungan silana antara pengisi dan matriks getah telah dikenal pasti melalui Spektroskop inframerah jelmaan Fourier (FTIR). Penilaian ketumpatan sambung silang oleh ujian pembengkakkan telah membuktikan bahawa kumpulan tetrasulphane di bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) telah membentuk sambung silang dengan getah rantai molekul. Morfologi permukaan yang patah tidak dirawat dan dirawat telah diperiksa menggunakan pengimbas mikroskop elektron (SEM). Kekuatan tegangan, pemanjangan pada takat putus dan M100 diukur menggunakan ujian tegangan universal. Keputusan mempamerkan kelebihan TESPT sebagai ejen gandingan antara pengisi dan matriks getah dan juga mendedahkan bahawa kaedah kering menghasilkan ikatan antara muka yang optimum berbanding dengan kaedah akues dan kaedah pengadunan leburan.

COMPARISON OF SILANE TREATMENT METHODS ON FILLER REINFORCEMENT IN RUBBER COMPOSITES

ABSTRACT

The objective of this study was to compare the performance of different silane treatment methods to assess the optimum methods for improvement of interfacial bonding between fillers and matrix. The methods used were dry method, aqueous method and melt blending method. In order to check the effectiveness of the applied methods for surface modification of fillers, three different types of fillers: silica (nano size), ferrite (macro size), and kenaf (fibers) were investigated. Evidence that silane linkages between fillers and rubber matrix had occurred was identified by Fourier transform infrared spectroscopy (FTIR). Crosslink density assessment by swelling test provided evidence that the tetrasulphane group of bis-(3-triethoxysilylpropyl) tetrasulphane (TESPT) formed crosslink with the rubber molecular chains. Morphology of the fracture surface of the rubber with untreated and treated filler was examined using scanning electron microscope (SEM). Tensile strength, elongation at break and M100 were measured using the universal tensile tester. The results exhibited the advantages of TESPT as a coupling agent between fillers and rubber matrix and also revealed that the dry method produced the optimum interfacial bonding when compared with aqueous method and melt blending metho

CHAPTER 1

Introduction

1.1 Introduction

Commercial applications of rubber relies thoroughly on the use of fillers to improve the stiffness, strength, and toughness of the final products (Park & Cho, 2003). The most commonly used fillers in rubber include carbon black and minerals such as silica, calcium carbonate (whiting) and clay. Fillers are used as a reinforcement or cost reduction additives for rubber. Fillers can be divided into two categories, reinforcing and non-reinforcing. A reinforcing filler generally increases stiffness and improves tensile strength, tear resistance and abrasion resistances of the final product. The most commonly used reinforcing fillers are carbon black and silica. Non-reinforcing fillers may be used to improve processing and to reduce compound cost (Kamal et al., 2009). Examples of non-reinforcing fillers are clay, mica, talc and calcium carbonate. There are three characteristics, which determine the reinforcing capability of a filler which are particle size, particle shape, and surface activity (Leblanc, 2002). The specific activity of the filler is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Non-polar fillers are best suited to non-polar rubbers and polar fillers work best for polar rubbers. Beyond this, modification of the filler surface is necessary in order to improve ease of adhesion between the rubber matrix and the fillers (Kamal et al., 2009).

Surface modification has been widely applied to lift this limitation of fillers (Tang et al., 2015) and improve the interface between inorganic filler particles and rubber matrix (Thio et al., 2004). Surface modification of inorganic fillers can be achieved using a number of approaches (Wang, 1998); most commonly, the filler surface is chemically modified to become more compatible with the matrix using methods such as polymer coating, surfactant absorption (Jiang et al., 2008) and bifunctional coupling agent treatments (Pickering et al., 2015; Wu et al., 2009). Among various modification approaches, the bifunctional coupling agent treatment using silane based coupling agents is the most successful and cost effective treatment for improving the adhesion between inorganic fillers and rubber matrix.

A silane coupling agent contains functional groups that can react with the rubber and the filler. In this way, the rubber–filler adhesion is increased and consequently the reinforcing effect of the fillers is enhanced. The most commonly used silane coupling agents in rubbers are bis-(3-triethoxysilylpropyl) tetrasulfane (TESPT). TESPT have proven to enhance the filler–rubber interaction reaction. Therefore, inorganic and organic materials can be coupled together with the silane coupling agent acting as a bridge between them.

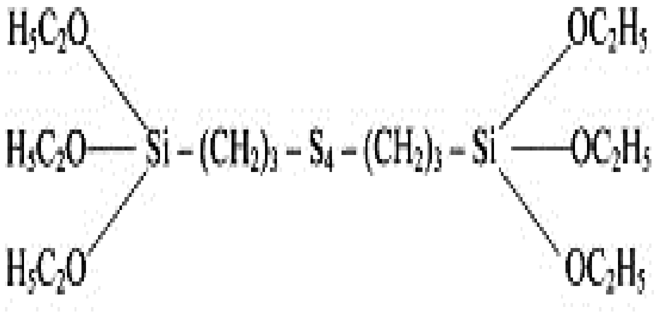


Figure 1.1 Molecular structure of TESPT

In this work, three different methods; dry method, aqueous method and melt blending method were used for silane treatment of the filler. In order to investigate the consistency of the methods for surface modification of fillers, all the method were applied to three different fillers: silica (nano size), ferrite (macro size), and kenaf (fibers). To the author knowledge, limited work is carried out to compare the effectiveness of different silane treatment methods to the performance of interfacial bonding between the rubber and filler.

1.2 Problem statement

The interface between the filler and the rubber matrix plays an important role in determining the properties of rubber composites. Poor interaction between fillers and rubber is expected to influence the final properties of the rubber composites, which mainly through its influence by the dispersion of filler in rubber matrix (Thio et al., 2004). Therefore, the ability to homogeneously disperse the filler in the rubber matrix remains one the most challenging tasks in rubber processing. The increase in modulus and tensile strength is dependent on the filler particle size because smaller the filler particle will affect poor filler dispersion.

The poor interface of filler-rubber interaction is influenced by the surface of fillers which are polar and hydrophilic. This surface has strong tendency to adsorb moisture which adversely influences the curing reaction and hence the properties of vulcanizate rubber. Therefore, surface treatment method could improve the interfacial bonding between the filler and the rubber matrix.

Silane treatment method is the most popular surface treatment for filler which used silane as a coupling agent. Conventionally, there are three different methods used to modify the filler surface which are dry method, aqueous method and melt blending method. In dry method, the fillers and silane coupling agent are placed in a container and rotating rollers are used to disperse the silane coupling agent throughout the inorganic filler surface. A large amount of filler was treated in a short time and generating little waste; however, the dispersion of silane coupling agent might be poor. Aqueous method is the popular method that is widely used in rubber industry. This method has a lot of steps, and it produces a lot of waste of resources especially the solvent because at the end of this method, the mixture need to be filtered and the unreacted coupling agent and the solvent are removed. Melt blending method is an intrinsic treatment of the filler particle which is carried out during compounding process on two roll mill. However, the effectiveness of the silane treatment is limited due to the surface of filler treatment only applied silane coupling agent during compounding and no futher treatment is needed.

1.3 Objectives

The objectives of this research was to compare the performance of different silane treatment methods which are dry method, aqueous method and melt blending method for improvement of interfacial bonding between filler and rubber matrix. The specific objectives are as follows;

1. To investigate the optimum silane treatment methods for filler reinforcement in the rubber composites.
2. To investigate the effect of different silane treatment method for different types of reinforcement; silica (nano size), ferrite (macro size), and kenaf (fibers) in rubber composites.

CHAPTER 2

Literature review

2.1 Rubber

Rubber is an elastomeric material which can be characterized by their ability to have reversible elastic deformation and return rapidly to approximately its initial dimension after substantial elastic deformation on a release of stress (Mark et al., 2013). Rubber is build up from long chains and flexible molecules which chemically crosslinked during the vulcanizing process. The vulcanizing process is a formation of crosslink between rubber molecules that are important to obtain the unique properties and formation of the three-dimensional network. There are many types of rubbers on the market that divided into many groups following different criteria such as saturated and unsaturated, natural and synthetic, polar and non-polar, crystallizing and non-crystallizing (Gent, 2012). Rubber also effective of adhering to fibers and metals; such as rayon, polyamide, polyester, glass or steel cord (Morton, 2013).

2.2 Natural rubber

Natural rubber (NR) is obtained from the latex milk extracted from the tree called Hevea Brasiliensis belonging to Euphorbiaceae family. Their historical origin is from the tree named Hevea Brasiliensis formerly grown in the jungles of Brazil. Natural rubber practically contained of pure cis-1,4-polyisoprene (more than 99.9 %), and the molecular structure is shown in Figure 2.1. Natural rubber also is known as a linear polymer, and it can crystallize when stretched or stored at temperatures below 200^0C due to the regularity of its structure (Baranwal & Stephens, 2001). Fresh latex can be concentrated by centrifuging or creaming. Latex can be coagulated with hydrogen carboxylic acid or acetic acid, to form sheets or granulates and subsequently dried to produce a solid rubber (Rodgers et al., 2000). Natural rubber also contains few percents of non-rubber constituents such as resins, proteins, sugars and fatty acids and weak to oxygen and ozone attack. This weakness is due to ozone and oxygen can react efficiently with natural rubber functional groups (double bonds) and degrade the rubber. However, the ozone and weather resistance can be improved by the addition of antiozonants and protective waxes in the compound (Baranwal & Stephens, 2001).

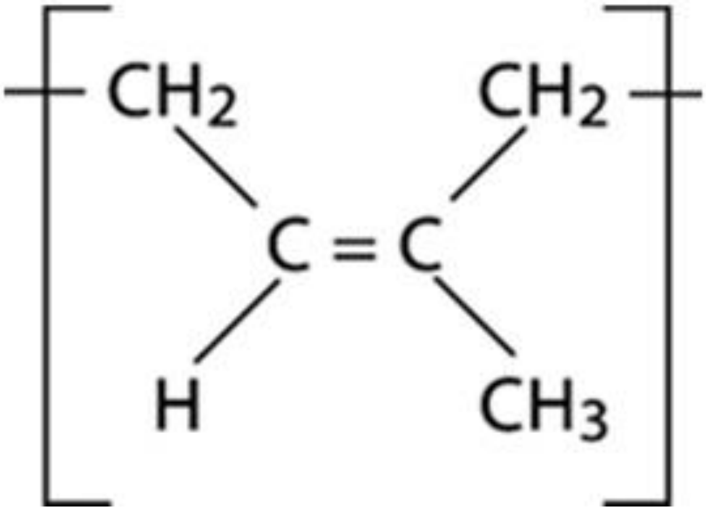


Figure 2.1 Polymer structure of cis-1,4 polyisoprene for natural rubber (Rodgers et al., 2000).

Gum rubber needs to be compounded compounded with other chemical and additives and then is vulcanized to improve the properties of rubber and produce natural rubber products. The most widely used vulcanizing agent for rubber is sulfur. Sulfur usually used together with accelerator and activator at elevated temperatures to form stable covalent bonds between the rubber chains at the carbon–carbon double bonds

(Mark et al., 2013). Vulcanized rubber products have high mechanical properties and also excellent elasticity. Natural rubber also has excellent abrasion resistance with its low cost, and it also has good dynamic mechanical properties which often used in a lot of application such as tires, rubber spring, and vibration mounts. Other products include hoses, conveyor belts, gaskets, seals, rolls, rubberized fabrics, elastic bands and pharmaceutical goods (Nagdi, 1993). Further advantages include low compression set and stress relaxation, good electrical insulation and excellent resistance to abrasion, tear, and fatigue.

Natural rubber available in many grades that related to the dirt content and precise method of production. A National Standard Malaysian Rubber (SMR) scheme was introduced by Malaysia and production and marketing technically specified rubbers based on the ISO 2000 system have been started by all the rubber-producing countries. Moreover, there are a few grades that usually used such as ribbed smoked sheets (RSS) and technically specified rubber such as SIR (Standard Indonesian Rubber), SMR (Standard Malaysian Rubber) and so on. Grades are subgrade by dirt content such RSS1 to RSS5 and SMR5, 10, 20 and 50. The lower the number, the cleaner the rubber grades and also the more expensive (Rodgers et al., 2000).

2.3 Filler

Fillers are defined as materials used in a rubber formulation to reduce the cost of compounding and improve the properties of rubber such as processing and mechanical properties. In fact, fillers can change one or more properties such as improve surface characteristic, optical properties, and color, etc. by far, the most commonly used filler in rubber compounding are carbon black and non-black such as silica, calcium carbonate (whiting) and clay (Kamal et al., 2009). Fillers can be divided into two categories:

1. Reinforcing filler
2. Non-reinforcing filler

2.3.1 Reinforcement concept

The reinforcement mechanism of filled rubber is better understood after the study on the strain dependence of filler-reinforced rubber by Payne (Mark et al., 2013). The studied the relation between the three-dimensional filler aggregates and the dependence of the storage and loss moduli on the strain. The network of aggregates could easily be ruptured even at small strain. Subsequently, the Payne concept has been widely used to characterize the interaction between filler and filler and filler and rubber interaction.

Applying fillers which can interact with the polymer matrix in a physical or chemical leads to improvement of mechanical properties of the material. Interactions between filler and polymer can be mainly physical like in case of carbon black or chemical like in case of silica with a coupling agent. The most important requirement for a strong reinforcing effect is a strong interaction on the interface between filler and polymer.

2.3.2 Filler-filler interactions

When fillers are dispersed in a polymer matrix, they form aggregates which can be connected in a filler-filler network. Between the adherent, not covalently connected filler particles, there is a strong energy dissipation due to friction. Because of physical or weak chemical interactions between the filler particles, the filler-filler network is rather weak, which means that it can be broken under strain. This effect is called Payne effect, and it is an indication of the degree of filler-filler interaction.

The Payne effect is observed in filled rubbers under low shear conditions. The loss and storage modulus of filled rubbers are amplitude-dependent. There is a specific value of shear amplitude at which the loss modulus reaches a maximum and the storage modulus has an inflection point. This effect is independent of the type of polymer but is dependent on the type of filler. Silica filled rubbers, in which the silane coupling agent was not introduced, show a much stronger Payne effect than the rubbers filled with carbon black (Baranwal & Stephens, 2001).

2.3.3 Filler-polymer interactions

When elastomers and reinforcing fillers are mixed, interactions occur and polymer chains are immobilized on the filler surface. This results in a thin layer of polymer (2 – 5 nm), which encapsulates filler particles and aggregates (Andrews, 1963). These interactions can be so strong that even a good solvent for the polymer cannot extract it. The part of rubber that cannot be extracted is called bound rubber.

According to (Birkley, 1989), besides a classification in chemically and physically bound rubber, there are two other types. A part of the rubber is trapped in the cavities of the filler structure; this part is called occluded rubber. The other part of the rubber, which is adsorbed onto the external aggregate surface, is called shell rubber. Under increasing deformation, these filler polymer structures can successfully release the rubber which can further transfer the applied load. The filler-polymer interaction depends on the filler particle size: smaller filler particles have a higher contact surface with the polymer, and therefore a higher amount of bound rubber. However, applying very high specific surface area fillers in elastomers leads to difficulties during processing due to an increased blend viscosity.

2.3.4 Reinforcing fillers

The reinforcing fillers are commonly used with rubber matrix during mixing process that can improve the mechanical properties of rubber, such as tensile strength, modulus, elongation at break and so on. The reinforcing fillers also used to achieve the performance requirements depend on the application of rubber product. The higher performance can be achieved by high level of chemical links with the polymer network (Rothon, 2003). Filled rubber polymer has significantly higher stiffness than unfilled rubber polymer at the same degree of deformation. Furthermore, filled rubber polymer has as well as considerably higher strength and deformation to break than unfilled rubber polymer. The examples of reinforcing fillers that widely used such as carbon black, and silica which lead to increases in viscosity of the rubber compound as well as to increase the mechanical properties and the abrasion resistance by increasing the amounts of filler loading (Thomas et al., 2013).

The term of reinforcement refers to an improvement of rubber performance in addition of filler (Kapgate et al., 2015). The influence of reinforcement of filler in the rubber matrix can be summarized as follow:

1. Particle size

   Particle size of a filler is one of the key parameters which strongly affect rubber properties. Silica and carbon black have very small primary particles sizes in the range of 10 – 100 nm which are classified as reinforcing fillers that can improve rubber performance. Fillers with particle size in the range of 100-1000 nm and 1000 – 10000 nm are classified as semi- and non- reinforcing fillers (diluents). When the particle size is greater than 10000 nm, the filler causes an area of localized stress, leading to elastomer chain rupture on flexing or strectching and hence deterioration in rubber properties.

2. Particle surface activity

   Active fillers can give a strong interaction between filler and rubber matrix when compared to inactive fillers, which relates to the affinity for and ability to react with the rubber. Chemical interaction between filler and rubber depends significantly on type or form of the functionality on the surface filler surface. Some fillers need to be modified in order to match the surface chemistry to a rubber matrix. For example, silica, is one of the active fillers which require a surface modification.

3. Concentration of filler where optimum loading effect higher reinforcement.

4. Porosity of filler.

5. Physical and chemical nature of filler.

Furthermore, the stress values and the hardness are increased and other properties also improved such as elongation at break. The reinforcement effect of fillers can change the viscosity of a rubber compound and also the vulcanizate properties with increasing amount of filler loading. The specific activity of the filler is determined by the physical and chemical nature of the filler surface in relation to that of the rubber. Therefore, general chemical compatibility is the potential for specific interaction between the rubber and active sites on the filler surfaces (Rothon, 2003).

2.3.5 Non-reinforcing fillers

Non-reinforcing fillers are known as inert fillers. There most commonly used non-reinforcing fillers in rubber compounding are talcum, calcium carbonate ($CaCO_3$), and clay. Non-reinforcing fillers usually used for reducing the cost of the compound and do not exhibit any reinforcing effect but only increase viscosity of the compound (Grossman, 2012).

2.4 Size and dispersion of the fillers in the matrix

The dispersion of filler in the rubber matrix is one of the most important process that need to be achieve during mixing process. Therefore, the dispersion of filler depend on filler-related parameters including filler size, filler shape and structure of filler. Table 2.1 shows that as the particle size smaller, the surface area increase that which allows and reinforced the rubber more available contact between rubber molecules and the filler particles(Thomas et al., 2013).

Table 2.1 Role of fillers according particle size measurements (Thomas et al., 2013)

Particle size (μm)	Role of filler
1 to 10	Non-reinforcing
0.1 to 1	Semi-reinforcing
0.01 to 0.1	Reinforcing

Fillers are usually made up from primary particles at the smallest size scale which are strongly bonded to other primary particles to form aggregates structures. Aggregates can be defined as assembly of particles which bonded strongly while agglomerates is known as when particles are joined loosely together, they can be simply broken by mechanical forces. The aggregates can interact with other aggregates through weaker secondary bonding to form agglomerates (Boverhof et al., 2015). High structure filler which has a high number of primary particles per aggregates is known as the strong aggregation, while the low structure filler has weak aggregation because of these aggregates may form loose agglomerates that linked by van der Waals interactions(Rothon, 2003). Formation of aggregates and agglomerates reduces the effective reinforcement surface area and reduce the ability of the filler to provide reinforcement to the rubber matrix.

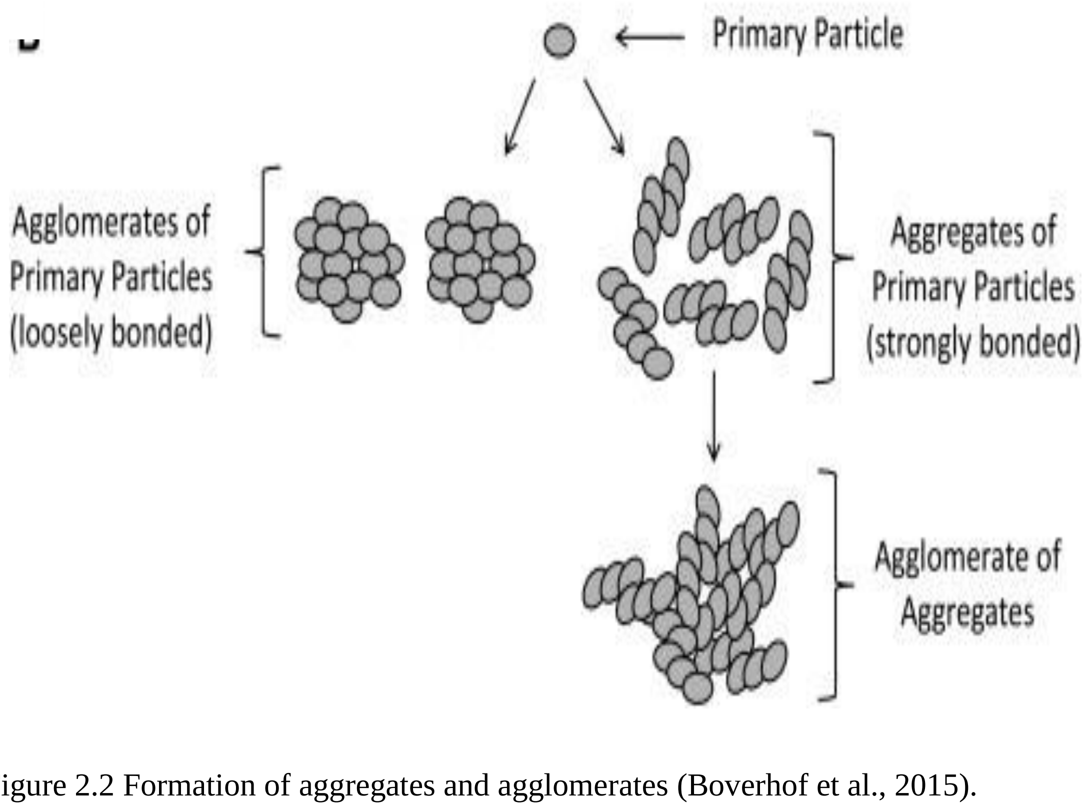


Figure 2.2 Formation of aggregates and agglomerates (Boverhof et al., 2015).

2.5 Interfacial bonding between fillers and matrix

The mechanical properties of rubber composites depends not only on the types of rubber matrix and filler, but also on the level of adhesion between the filler and the rubber matrix. Rubber and filler interaction can be improved by surface modification of filler. This is because surface modification method are the most commonly method used to modify the filler surface and to improve the compatibility between filler and matrix. There are few methods of surface modification that usually used such as polymer coating, surfactant absorption and bifunctional coupling agent treatments. Bifunctional coupling agent treatments are also called as silane treatment. Silane are knowns as efficient coupling agents that has been used widely in composites and adhesive formulation (Xie et al., 2010; Zeng et al., 2009). It also was been proved can be applied in inorganic filler reinforcement of polymer composites such as glass fiber and mineral filled polymer composites. Therefore, silane coupling agents can use as adhesion promoters in many adhesion application that giving stronger adhesion (Mittal, 2007).

2.6 Coupling agents

Coupling is an important chemical modification method, which improves the interfacial adhesion. When two materials are incompatible, it is often possible to bring about compatibility by introducing a third material that has properties intermediate between those of the other two. Strongly polarized cellulose fibre are inherently incompatible with hydrophobic polymers. Therefore, scientists have investigated a variety of coupling agents to improve the compatibility of the fibre and matrix.

2.6.1 Types mechanism of coupling agents

There are several mechanisms of coupling in materials:

- weak boundary layers-coupling agents eliminate weak boundary layers.
- Deformable layers- coupling agents produces a tough, flexible layer
- Restrained layers - coupling agents develop a highly crosslinked interface region, with a modulus intermediate between the substrate and the matrix.
- Wettability - coupling agents which improve the wetting between polymer and substrate
- Chemical bonding - coupling agents form covalent bonds with both materials
- Acid-base effect - coupling agents alter the acidity of the substrate surface.

The development of a definitive theory for the mechanism of bonding by coupling agents in composites is a complex problem. The chemical bonding theory only is not sufficient. The considerations of other concepts which include the morphology of the interface, the acid-base reactions at the surface energy, interface, and the wetting phenomena (Gent, 2012).

2.6.2 Classification of coupling agents

Coupling agents are classified into organic, inorganic and organic-inorganic groups. Organic coupling agents are iso-cynates, anhydrides, amides, imides, acrylates, chlorotriazines, epoxides, organic acids, monomers, polymers, and copolymers. Inorganic coupling agents include silicates while organic-inorganic agents include silanes and titanates.

Organic coupling agents normally have bi- or multifunctional groups in their molecular structure and these functional groups, such as (-N=C=O) of isocynates, [-$(CO)_2O$-] of maleic anhydrides, and (Cl-) of dichloro triazine derivatives, interact with the polar groups [mainly hydroxly groups (-OH)] of fillers to form covalent or hydrogen bonding. Alternatively, organic coupling agents can modify the polymer matrix by graft copolymerization, thus resulting in strong adhesion, even crosslinking at the interface.

Inorganic coupling agents acts as dispersing agents to counteract the surface polarity of filler and improve the compatibility between fillers and rubber. Only a few inorganic coupling agents have been used in wood fibres polymer. Organic-inorganic coupling agents are hybrid compounds in structure. For example, titanates usually contain a titanium centre and an organic part surrounding this inorganic atom. The functionalities of the organic part in these agents determine their coupling effectiveness. Organic-inorganic coupling agents are between organic and inorganic agents in functions.

2.7 Silane coupling agents and mechanism

In rubber compounding technology, silane coupling agent is used to modify the filler surface such as silica and it have ability to form durable bond between rubber and filler. The purpose is to increase the compatibility of the polar filler with the non-polar rubber matrix. Table 2.2 shows others silane coupling agents that can be used in rubber compounding such as TESPT, TESPD, OTES, VTMS and TMSMT. The most commonly used silane coupling agent in rubber is silane was used to act as the bridge of between the filler and rubber (Murakami et al., 2003). A chemical linkages between the filler and the polymer matrix is presence to achieve the desired reinforcement of filler and rubber interaction. Therefore, bis-(3-triethoxysilylpropyl) tetrasulphane (TESPT) (Figure 2.3).

TESPT produces a covalent bonding between filler and rubber matrix which increase the compatability and influence the mechanical of the materials. (Rodgers et al., 2000).

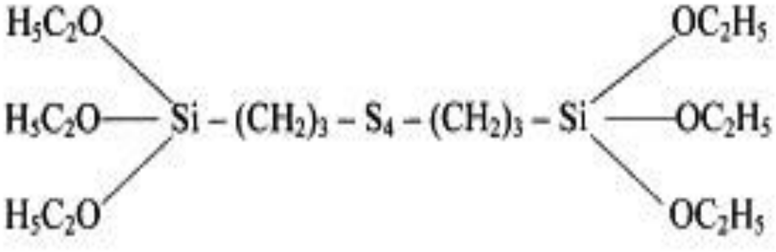
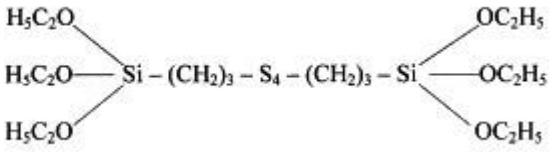
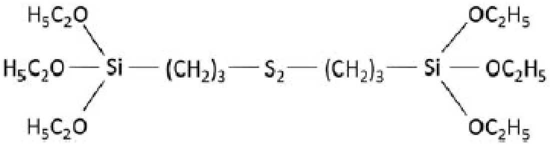
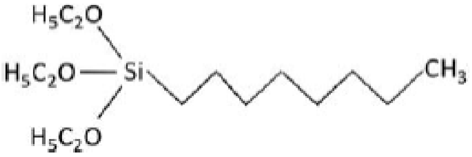
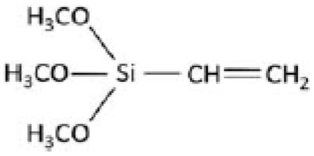
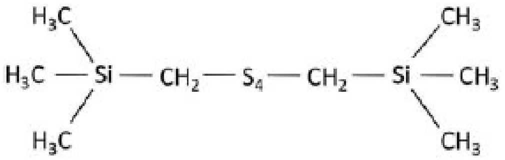


Figure 2.3 Bis(triethoxylsiylpropyl)-tetrasulfide (TESPT) (Pickering et al., 2015).

Table 2.2 Silane coupling agent that can used in rubber compounding (Mittal, 2007).

Silane coupling agent	**Abbreviation**	**Structure**
Bis-triethoxysilylpropyl tetrasulfide	TESPT	
Bis-triethoxysilylpropyl disulfide	TESPD	
Octyltriethoxysilane	OTES	

Vinyltrimethoxysilane	VTMS	
Bis-trimethylsilylmethyl tetrasulfide	TMSMT	

The most effective method of silane treatment involves treating the inorganic fillers, prior to mixing it with rubber matrix. The effectiveness of silane coupling agents for various inorganic fillers can be seen in Table 2.3.

Table 2.3 Degree of effectiveness for various inorganic fillers

Degree of effectiveness	Inorganic fillers
Highly effective	Glass, silica, aluminium oxide
Effective	Talc, clay, aluminium, mica
Slightly effective	Zinc oxide, iron oxide, asbestos
Almost no effect	Carbon black, calcium carbide, graphite

2.7.1 General mechanism of silane treatment

Organofunctional silanes are widely used as silane coupling agent due to its ability to form interfacial bond between the rubber and the filler. Basic formula of silane coupling agents that commonly used is $X(CH_2)_nSi(OR)_3$ (Figure 2.4) where the R group reacts with hydroxyl groups such as methoxy or ethoxy and X represents the organofunctional group such as amine. In majority of application, the alkoxy group of the trialkoxysilanes are hydrolysed to form a reactive silanol group (Mittal, 2007). Moreover, this reaction involves four steps;

1. Hydrolysis of the three alkoxy groups.
2. Condensation to oligomer occurred.
3. The oligomer then react hydrogen bond with hydroxyl group of filler.
4. A covalent linkages is formed with filler which related to loss of water. (This reaction happen simultaneously after initial hydrolysis step)

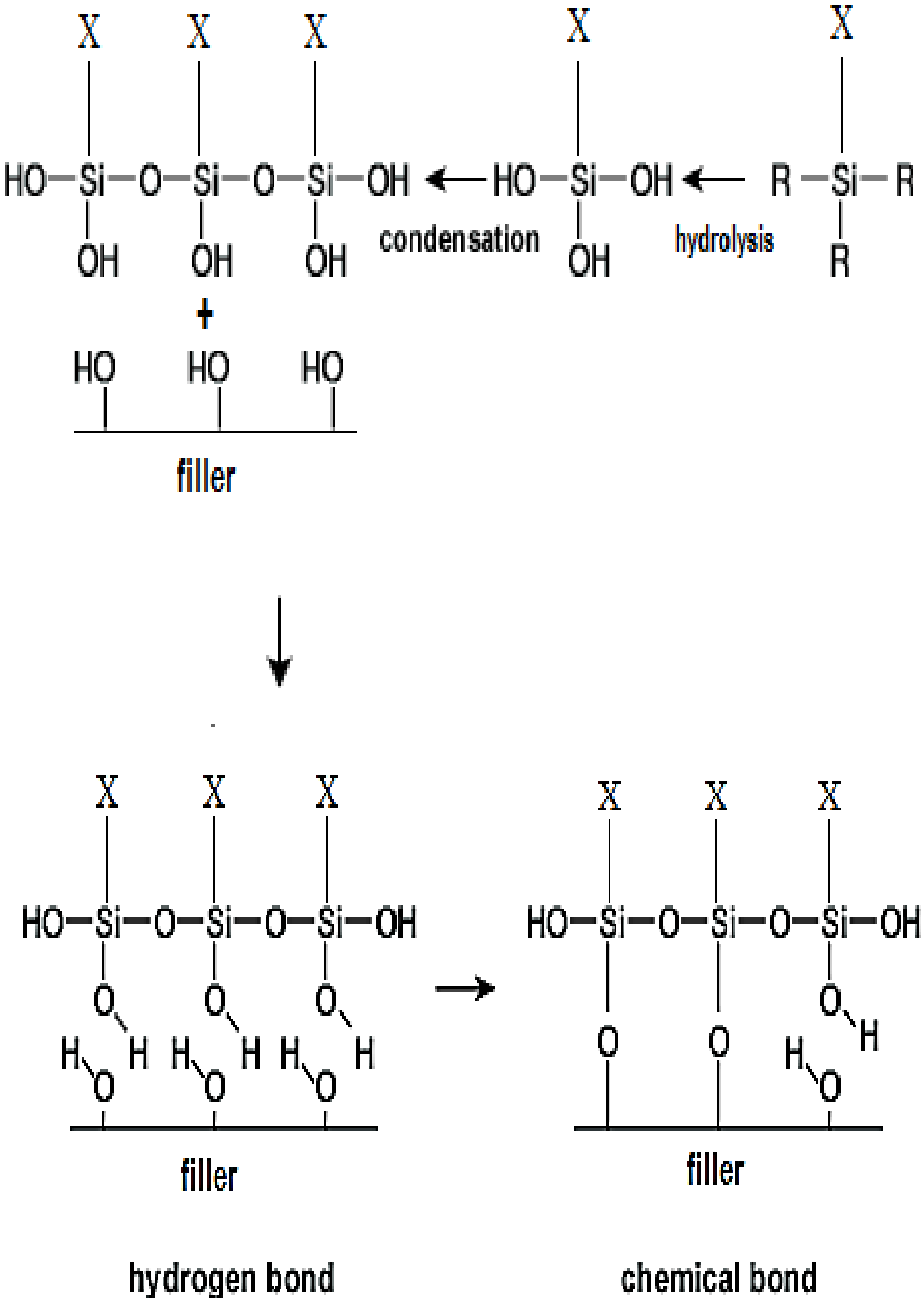
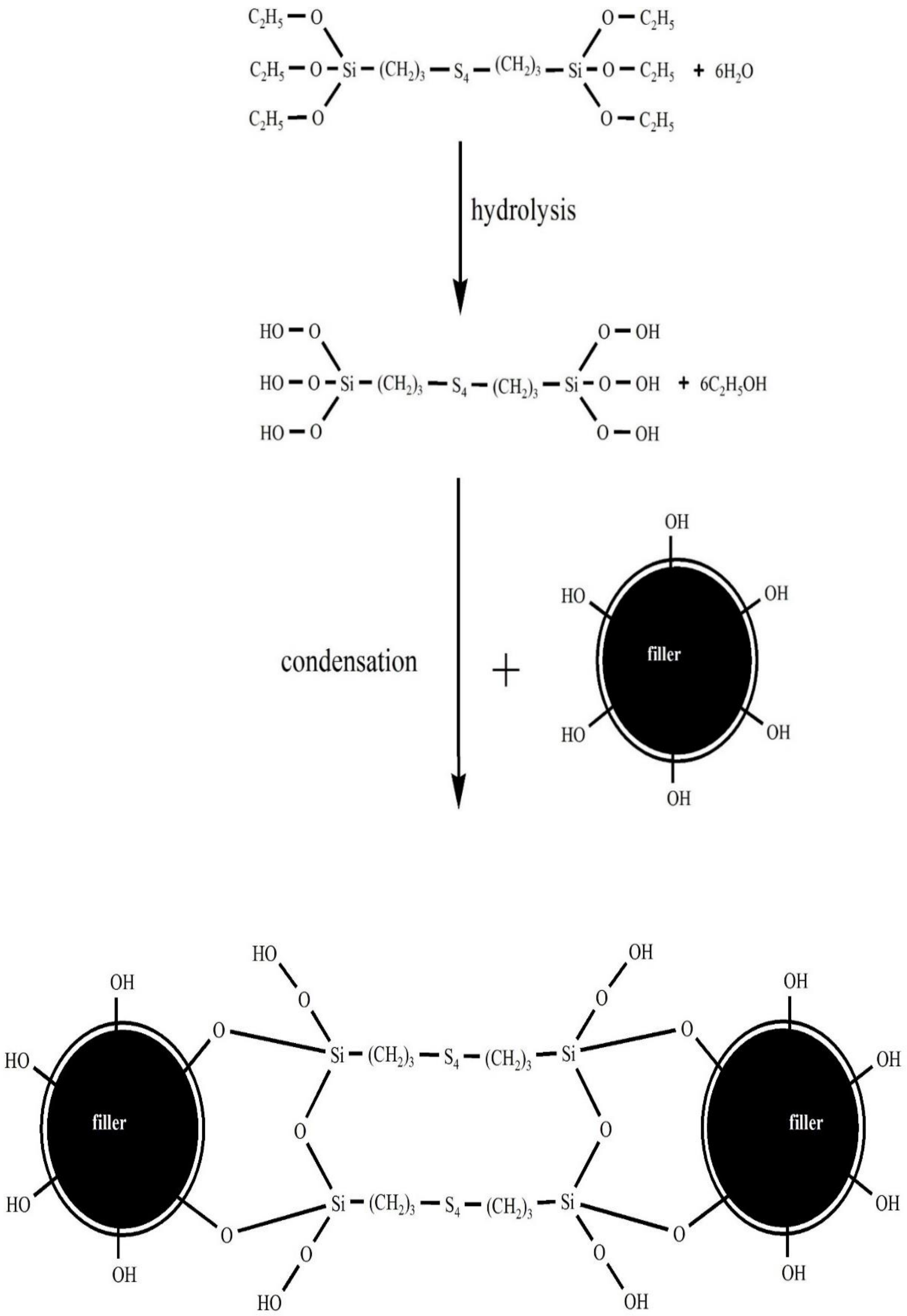


Figure 2.4 General mechanism of silane with filler (Thomas et al., 2013)

2.7.2 TESPT reaction mechanism

Figure 4.1 shows a schematic of the potential reaction mechanisms of TESPT with filler and rubber matrix. In the present of water, the ethoxy reactive groups on the TESPT are hydrolysed forming silanol group (Si-O-OH) which are a reactive intermediate that can potentially bonds with the filler. When the fillers was added, the reactive silanol groups react with the hydroxyl groups on the filler surface forming stable siloxane bonds (Si-O-filler) which are expected to be covalent bonds (Pickering et al., 2015). The tetrasulphane groups of TESPT could have been dissociated during the compounding process on two roll mill to produce sulfidic radicals which subsequently react with the rubber molecular chains either directly or through sulphur crosslinking agent of the rubber in the presence of accelerators to form crosslink with the rubber molecules (Pickering et al., 2015). The formation of siloxane bonds between TESPT with the fillers at one end and the formation of the sulphur crosslinks between tetrasulphane group of TESPT with rubber molecules at the other hands coupled the filler and the matrix together with TESPT acting as a bridge between them (Pickering et al., 2015).



C_2H_5-O
$C_2H_5-O-Si-(CH_2)_3-S_4-(CH_2)_3-Si-O-C_2H_5$ + $6H_2O$
hydrolysis
$HO-O-Si-(CH_2)_3-S_4-(CH_2)_3-Si-O-OH$ + $6C_2H_5OH$
condensation
+
filler
OH
HO
O
Si
$(CH_2)_3$
S_4

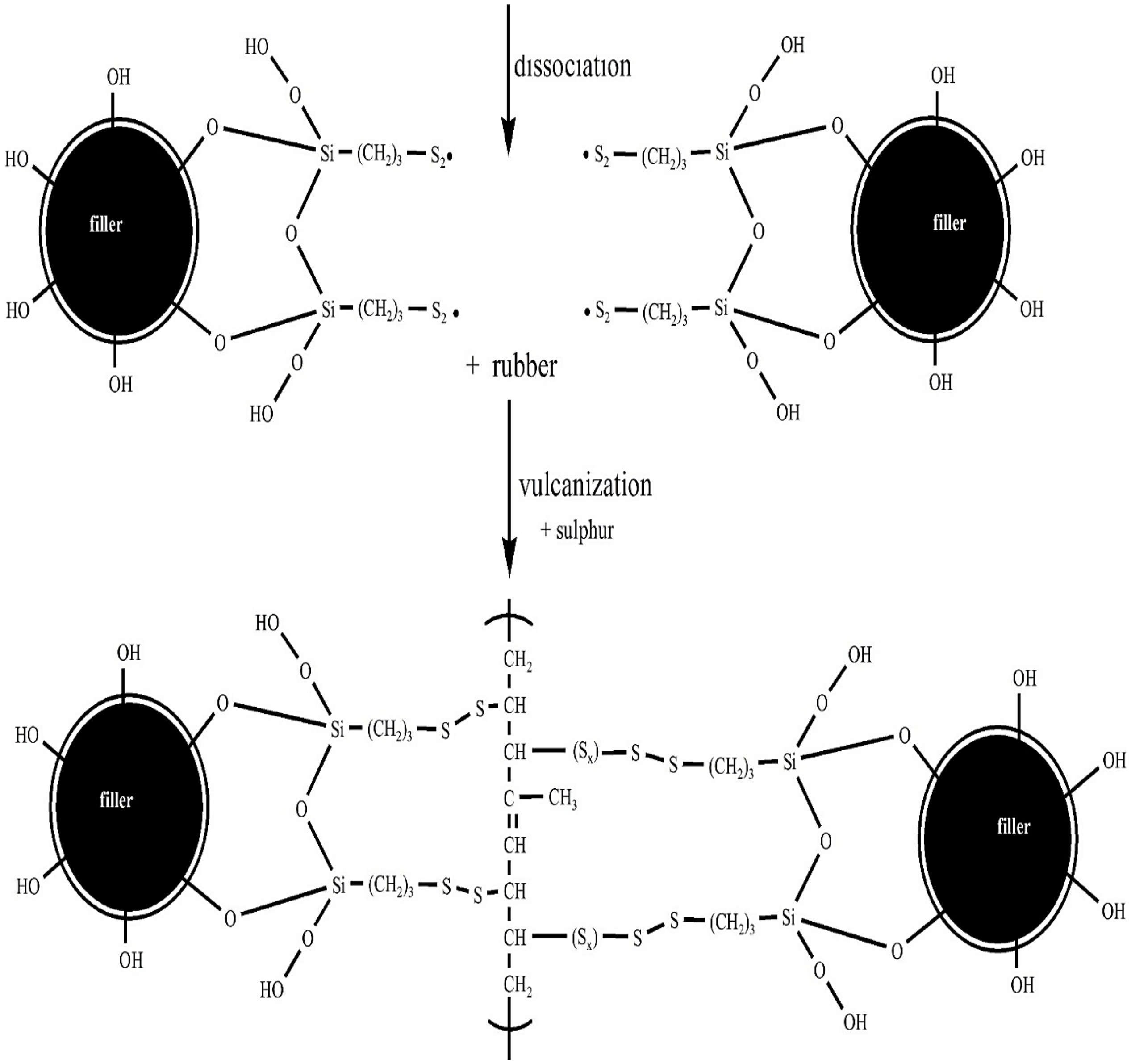


Figure 2.5 Mechanism of TESPT with natural rubber (Pickering et al., 2015).