

**EFFECTIVENESS OF GLUT PALMITATE SALT  
AS COUPLING AGENT  
COMPARED TO POLYETHYLENE GRAFTED  
MALEIC ANHYDRIDE AND 3-  
AMINOPROPYLTRIMETHOXY SILANE IN  
HIGH DENSITY POLYETHYLENE AND  
NATURAL RUBBER COMPOSITE**

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**UNIVERSITI SAINS MALAYSIA**

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AND NATURAL RUBBER COMPOSITE**

by

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## LIST OF ABBREVIATIONS

<b>Abbreviation</b>	<b>Description</b>
APES	3-Aminopropyl triethoxy silane
APMS	3-Aminopropyl trimethoxy silane
CPMS	3-chloropropyl trimethoxy silane
DSC	Differential Scanning Calorimetry
EDD	Ethylene diamine dilaurate
EVA-g-MAH	Ethylene vinyl acetate grafted maleic anhydride
FTIR	Fourier Transform Infrared Spectroscopy
Gln	Glutamine
GP	Glut palmitate salt
HDPE	High Density Polyethylene
IPPD	N- isopropyl-N'-phenyl-p-phenylenediamine
KB	Kenaf Bast Fibre
LDPE	Low density polyethylene
ISO	International Organization of Standardization
M100	Modulus at 100% elongation
M300	Modulus at 300% elongation
MA	Maleic Anhydride
MBTS	Mercapto Benzothiazolyl disulfide
MDPE	Medium-Density Polyethylene
MDR	Moving Die Rheometer
MFA	Multifunctional additive
MPMS	3-methacryloxypropyl trimethoxy silane
NR	Natural Rubber

PA	Palmitic acid
PBS-g-MAH	Polybutylene succinate grafted maleic anhydride
PDMAEMA	Poly(dimethylamino)ethyl methacrylate
PE	Polyethylene
PEEK	Poly(aryl ether ketone)
PE-g-MAH	Polyethylene grafted maleic anhydride
Phr	Part per hundred rubber / resin
PP-g-MAH	Polypropylene grafted maleic anhydride
S	Silica
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscopy
Semi-EV	Semi-efficient Vulcanizing System
SMR L	L Grade Standard Malaysian Rubber
TGA	Thermogravimetric Analysis
XPS	X-Ray photoelectron spectroscopy
ZnO	Zinc Oxide

## LIST OF SYMBOLS

<b>Symbol</b>	<b>Description</b>
kJ	KiloJoule
g/cm <sup>3</sup>	Gram per cubic centimeter
ts <sub>2</sub>	Scorch time
t <sub>90</sub>	Curing time
°C	Degree celcius
g/mol	Gram per mole
%	Percent
µm	Micrometer
g	Gram
mol	Mole
ml	Mililiter
min	Minute
rpm	Revolutions per minute
cm <sup>-1</sup>	Inverse centimetre
eV	Electron Volt
mA	MiliAmpere
kV	KiloVolt
°	Degree
psi	Pounds per square inch
kN	KiloNewton
mm/min	Milimeter per minute
mm	Milimeter
h	Hour
mg	Miligram

$^{\circ}\text{C} / \text{min}$	Degree celcius per minute
$\text{ml}/\text{min}$	Mililiter per minute
$\text{J}/\text{g}$	Joule per gram
$\text{ml}/\text{mol}$	Mililiter per mole
$\text{cm}$	Centimeter
$M_L$	Minimum torque
$M_H$	Maximum torque
$T_m$	Melting temperature
$\rho$	Density

**PERBANDINGAN KEBERKESANAN GARAM GLUT PALMITAT SEBAGAI  
AGEN PENGGANDING TERHADAP POLIETILENA TERCANGKUK MALEIK  
ANHIDRIDA DAN 3-AMINOPROPIL TRIMETOKSI SILANA DI DALAM  
KOMPOSIT POLIETILENA BERKETUMPATAN TINGGI DAN GETAH ASLI**

**ABSTRAK**

Agen pengganding memainkan peranan yang penting dalam komposit polimer di mana ianya dapat mewujudkan interaksi yang baik antara polimer matrik dan pengisi. Dengan itu, perkembangan dalam penyelidikan agen pengganding adalah selari dengan penghasilan komposit polimer yang baru. Oleh itu dalam penyelidikan ini, satu agen pengkupel yang dipanggil garam Glut Palmitat (GP) yang dapat digunakan untuk meningkatkan antaramuka pengisi dan matrik di dalam sistem komposit polietilena berketumpatan tinggi berpengisi silika (PE/S), komposit polietilena berketumpatan tinggi berpengisi serat kenaf bast (PE/KB), komposit getah asli berpengisi silika (NR/S) dan komposit getah asli berpengisi serat kenaf bast (NR/KB) telah dihasilkan . Agen pengkupel ini dihasilkan daripada asid palmitik dan L-glutamine dengan kaedah titratan asid-alkali. Bagi mengkaji keberkesanan GP ini sebagai agen pengkupel dalam sistem komposit polietilena berketumpatan tinggi (PE) yang berpengisi silika dan serat kenaf bast, GP telah dimasukkan ke dalam komposit dengan kandungan yang berbeza (0.5, 1, 2 dan 3 phr). Kesan kandungan GP dan perbandingan antara agen pengkupel GP dengan polietilena maleik anhidrida (PE-g-MAH) ke atas komposit iaitu pemprosesan tork, sifat mekanikal dan thermal, penyerapan kandungan air, morfologi dan interaksi antara pengisi dan matrik telah dikaji. Kajian mendapati dengan kehadiran GP dan PE-g-MAH di dalam PE/S, menyebabkan kekuatan tensil, modulus, darjah penghabluran dan kestabilan terma meningkat, berbanding komposit tanpa agen pengkupel. Manakala, bagi sistem PE/KB, menunjukkan peningkatan terhadap nilai kekuatan tensil, modulus, darjah penghabluran dan kestabilan terma apabila GP dan PE-g-MAH digunakan. GP pada 1 phr menunjukkan

keberkesannya didalam kekuatan tensil, kekuatan hentakan dan darjah penghabluran berbanding PE-g-MAH pada komposisi yang sama.

Kajian bagi menguji keberkesanan GP pada matrik yang berbeza iaitu getah asli telah dilakukan, di mana GP dengan kandungan 1, 3, 5, 7, 9, dan 11 phr telah dimasukkan ke dalam komposit getah asli berpengisi silika (NR/S). Kajian mendapati, penggunaan 9 phr GP di dalam komposit getah, masa skorj, tork maksima, ketumpatan sambung silang, kekuatan regangan, modulus, kekerasan dan kestabilan terma menunjukkan nilai yang optima. Manakala, masa pematangan, tork minima dan interaksi pengisi-getah menurun dengan penambahan 9 phr GP. Bagi sistem komposit getah asli berpengisi serat kenaf bast (NR/KB), kandungan GP yang telah diuji adalah 1, 3, 5, dan 7 phr. Nilai optima didapati pada tork maksima, ketumpatan sambung silang, kekuatan tensil, modulus, kekerasan dan kestabilan terma dengan penambahan 3 phr GP di dalam komposit. Penambahan GP didalam NR/S komposit menyebabkan kekuatan tensil, pemanjangan pada takat putus dan kestabilan terma yang tinggi berbanding Aminopropilmetoksi silana (APMS). Keberkesanan agen pengkupel ini dapat dibuktikan dengan ujian imbasan elektron mikroskop (SEM) dimana, mikrograf permukaan kegagalan tensil bagi semua sampel komposit yang ditambahkan agen pengkupel GP, PE-g-MAH dan APMS menunjukkan perlekatan antaramuka antara matrik dan pengisi yang lebih baik berbanding dengan komposit tanpa kehadiran agen pengkupel. Ini disebabkan wujud interaksi di antara matrik, agen pengkupel dan pengisi dan ianya disokong dengan kajian spektroskopi Inframerah Transmisi Fourier (FTIR).

**EFFECTIVENESS OF GLUT PALMITATE SALT AS COUPLING AGENT  
COMPARED TO POLYETHYLENE GRAFTED MALEIC ANHYDRIDE AND 3-  
AMINOPROPYL TRIMETHOXY SILANE IN HIGH DENSITY POLYETHYLENE  
AND NATURAL RUBBER COMPOSITE**

**ABSTRACT**

Coupling agents play an important role in polymers composite where they can enhance the interactions between matrix polymers and fillers. Thus, the growth in the coupling agents' research is in line with the growth of production of new polymers composite. Therefore, in this research, a coupling agent called Glut Palmitate salt (GP), that can be used to enhance matrix and filler interfaces in silica-filled high-density polyethylene composite (PE/S), kenaf bast fibre filled high density polyethylene composites (PE/KB), silica-filled natural rubber composite (NR/S) and kenaf bast fibre filled natural rubber composites (NR/KB) has been produced. GP was synthesized from palmitic acid and L-glutamine by acid-alkali titration method. To investigate the effectiveness of this GP as a coupling agent in a high-density polyethylene composite (PE) system, the GP was incorporated into composites with different contents (0.5, 1, 2 and 3 phr). The effectiveness of GP was compared to polyethylene maleic anhydride (PE-g-MAH) on polyethylene composites by processing torque, mechanical and thermal properties, water absorption, morphology and interaction of matrix-filler interfaces. In the presence of the GP and the PE-g-MAH in PE/S composite, the tensile strength, modulus, degree of crystallinity and thermal stability were increased as compared to control composites. Meanwhile, for the PE/KB composite, it showed an increment in tensile strength, modulus, degree of crystallinity and thermal stability when the GP and the PE-g-MAH are added. In both PE/S and PE/KB composites, the addition of GP at 1 phr resulted in higher tensile strength, impact strength, and degree of crystallinity than the PE-g-MAH at same composition. A study to test the GP efficiency on different matrices that is natural rubber was also



performed, where the GP contents (1, 3, 5, 7, 9, and 11 phr) have been incorporated into silica-filled natural rubber composites (NR/S). The scorch time, maximum torque, crosslink density, tensile strength, modulus, hardness and thermal stability shows the optimum value when 9 phr GP was added. Meanwhile, cure time, minimum torque and rubber-filler interaction decreased with the addition of 9 phr GP. For kenaf bast fibre-filled natural rubber composites (NR/KB) system, the tested GP content is 1, 3, 5, and 7 phr. There was an increment in maximum torque, crosslink density, tensile strength, modulus, hardness and thermal stability with the addition of 3 phr GP in the composite. Addition of GP in NR/S composite resulted in higher tensile strength, elongation at break composites and thermal stability compared with Aminepropyl trimethoxy silane (APMS). Meanwhile in NR/KB, the APMS showed higher tensile strength, and thermal stability with good rubber filler interaction compared with GP as a coupling agent. The effectiveness of coupling agents was proven by Scanning Electron Microscopy (SEM), where the micrograph of tensile failure surface for all composite incorporated with GP, PE-g-MAH and APMS coupling agents showed promote better adhesion between matrix and filler as compared to composites without incorporation of the coupling agent. This is supported by Fourier Transform Infra-Red Spectroscopy (FTIR) study which the absorption peak associate with formation of hydrogen bonding, van der Waals interaction and ester and amide bonds were recorded in the IR spectra when the coupling agents were added in the composites.

## INTRODUCTION

### Research background

A coupling agent is a substance that is placed at a composites material's filler-matrix interface, facilitating interaction between the two components ( i.e the filler and the matrix) (Owen, 2002). Coupling agents help to resolve the issue of different constituent polarities at the interfaces, and are recognised as additives in polymer composites. The development of coupling agents is as important as the development of the polymer composites, since both the present and the future challenges involving every new composites are due to the different constituent polarities at the interfaces (Owen, 2002; Ten Brinke *et al.*, 2003). Composites with superior properties can be synthesized if the constituent interfaces interact well. Thus, it is important to enhance the surface interaction between the polymer composite constituent, by using coupling agents.

Polyethylene grafted maleic anhydride (PE-g-MAH) is a coupling agent, synthesised from a functional maleic anhydride monomer and polyethylene as the base resin. This coupling agent is commonly used in academic research and industry alike, and has distinct advantages in terms of enhanced mechanical and thermal properties as well as good resistance to water absorption in polyethylene based composites (Araujo *et al.*, 2008; Keener *et al.*, 2004; Md Salleh *et al.*, 2014; Mat Taib *et al.*, 2010). This is to be expected as the PE-g-MAH has the same base resin as the composite matrices. The drawback, however is its' limited applicability in other polyolefin composites systems (Li & Matuana, 2003). Aminopropyltrimethoxysilane (APMS) is another type of organosilane that is used extensively in various polymer composite systems (Daud *et al.* 2016; Surya *et al.*, 2014; Mohd Ishak *et al.*, 1998). Although APMS has shown its' efficiency as a coupling agent in a variety

of polymer composites systems, the health considerations while handling the compound will be an issue, as it is labelled as a toxic compound.

This work takes a novel approach, by synthesizing a non toxic coupling agent, based on palmitic acid and glutamine, which can potentially be used in various polymer composites systems. Palmitic acid an amphiphilic chemical compound, with a long hydrocarbon chain (non polar) and a carboxylic acid (polar group), has attracted great interest among researchers for its' suitability in a wide range applications, including biomedical, polymer, chemical, food, coating and printing industries (Alam *et al.*, 2014; Guner *et al.*, 2006; Mutlu & Meire, 2010). It can be obtained from petrochemical feedstock and biomass resources, such as coconut oil, *Jatropha curcas* oil, soybean oil, rapeseed oil, palm oil, linseed, sunflower oil and animal fats (Neyda *et al.*, 2008). Glutamine is an  $\alpha$ -amino acid that occurs naturally in the human body, meat, dairy products, spinach, cabbage and corn. It can also be synthesised by glutamate with ammonia. Glutamine is a dipolar molecule with a unique structure, containing both an amine and a carboxylic group, and may be taken as an oral supplement by individuals whose have undergone abdominal surgery. Palmitic acid and glutamine are non-toxic materials that can be safely used in the production of a coupling agent. This coupling agent could potentially improve the interfacial adhesion between the fillers and the various types of polymer matrices due to palmitic acid's amphiphilic character and glutamine's dipolar character.

The new coupling agent can then be incorporated into polymer composites in which comprised of filler and polymer matrices constituent resulting in significant different characteristics from those of the original constituents. Polymer matrices can be classified into three categories namely thermoplastics, thermoset and elastomers and are mostly hydrophobic in nature (Subramaniam, 1987; Xie *et al.*, 2010). Meanwhile, fillers can be classified into mineral and natural fibre fillers which are hydrophilic in nature. In this study, the effects of the synthesised coupling agent on various polymer composite systems were investigated, by evaluating the composites' mechanical and thermal properties, water uptake, coupling agent interaction and morphology. Those tests were performed for a mineral filler and for a natural fibre filler, each filled with thermoplastic composites. Then, the effectiveness of the

synthesised coupling agent was compared to that of the commercial PE-g-MAH. Meanwhile for rubber composites with mineral and fibre fillers, the curing characteristics, the mechanical and the thermal properties, the rubber-filler interaction, the crosslink density, the coupling agent interaction and the rubber composite morphologies were investigated. The synthesised coupling agent's effectiveness was compared to that of the APMS.

### **Problem statement**

Currently, there is significant interest in the development of, and innovations in polymer composites in the industry. The quest for polymer composites with desirable combination properties unavailable in single constituent materials, low costs, as well as eco-friendliness, make the industry a crucial element in the development of new polymer composites. Combining polymer matrices with the low cost mineral or natural fibre fillers may be one of the more promising innovations in the polymer composites (Sarifuddin & Ismail, 2013; Fu *et al.*, 2012; Liu *et al.*, 2002; Ogah & Afiukwa, 2014). Recently, many polymer composites made of mineral and fibre fillers such as silica, calcium carbonate, clay, mica, wollastonite, bamboo, coir, and jute have been patented and are well accepted (Riebel & Tate, 2013; Liu *et al.*, 2005; Dorman & Meyer, 1985). Finding the ideal materials would be the next step in the industrial development of coupling agents to be used with polymer composites.

Coupling agents are used in the polymer composites formulations in order to improve the interface polarity. This problem is due to the hydrophobic nature of polymer matrices and the hydrophilic nature of fillers. These differences could make synthesizing polymer composites with superior composites properties more difficult. This is due to polymer matrices and the fillers being separated by interfaces which plays an important role in transferring stress and energy. Coupling agents acted as bridges between matrices and fillers in the composites, in order to enhance the interfacial interaction between them. The bonding occurring at the

interface may enhance the mechanical properties of the polymer composites (Ramli *et al.*, 2011; Kakou *et al.*, 2014; El-Sabbagh, 2014).

A coupling agent with a functional monomer of maleic anhydride has attracted particular attention as maleic anhydride are monomers which are likely to graft with olefin than homopolymerize with each other (Li & Matuana, 2003). Generally, coupling agents are tailor made for their polymer matrix composites such as PE-g-MAH, polypropylene grafted maleic anhydride (PP-g-MAH), ethylene vinyl acetate grafted maleic anhydride (EVA-g-MAH) and polybutylene succinate grafted maleic anhydride (PBS-g-MAH) were used as coupling agents with high density polyethylene, polypropylene, ethylene vinyl acetate and polybutylene succinate based composites, respectively (Kim *et al.*, 2007; Hoang *et al.*, 2014; Ahmad Thirmizir *et al.*, 2013; Md Salleh *et al.*, 2014). However, these tailor-made coupling agents may not versatile as their usage in polymer composite systems was limited to its based composites. As reported by Li and Matuana (2003), the addition of PE-g-MAH coupling agent in the polyethylene based composite appeared more effective than PP-g-MAH coupling agent in improving the tensile strength. Lai *et al.* (2002) also reported that addition of PP-g-MAH coupling agent in the polyethylene based composite was unsuitable as it resulted in debonding at ductile phase of the PE matrix. Thus, the tailor made PE-g-MAH was fitted to be used with its respective polyethylene based composite but not with other polyolefin based composite.

To date, effective use of organosilane coupling agents has been reported, with various type of polymer composites (Le Moigne *et al.*, 2014; Ansarifar, *et al.*, 2004; Surya, *et al.*, 2014). However, the APMS has been labelled as a toxic material by the Globally Harmonized System of Classification and Labelling of Chemicals as it may cause health hazard. The disadvantages of the PE-g-MAH coupling agent's lack of versatility and the APMS coupling agent's toxicity can be addressed by using a coupling agent synthesised from palmitic acid and glutamine. Palmitic acid compound is amphiphilic, while glutamine is dipolar.

The functionalization of the palmitic acid's carboxylic group with the glutamine's amine group can produce a compound called a glut palmitate salt (GP) salt with properties similar to those of amphiphilic and dipolar molecules. A previous study by Ismail *et al.* (1997)

reported that the addition of fatty diamine resulted in improved tensile strength in rubber composites. According to Suryadiansyah *et al.* (2008), a coupling agent synthesized from lauric acid and ethylene diamine dilaurate was capable of interacting with the polymer matrices and the hydrophilic silica fillers. John *et al.* (2010), in their study zein as an amphiphilic coupling agent, reported that adding zein enhanced the mechanical and the viscoelastic properties in the composites. Chun and Husseinsyah (2014), synthesized a coupling agent from lauric acid (extracted from coconut oil) and ethylene diamine. The study showed that the coupling agent successfully enhanced the filler-matrix interaction and consequently improved the mechanical properties of the composites. Most of the studies on the subject conclude that amphiphilic molecules can act as coupling agents as their chains contain both hydrophobic hydrocarbon groups and hydrophilic. Therefore, the compounds synthesised from palmitic acid and glutamine is a potential coupling agent and can be used in various type of polymer composites such as thermoplastics and rubber, as the long hydrocarbon chain from the palmitic acid can entangle with the hydrophobic polymer matrix and the hydrophilic group from glutamine can interact with the hydrophilic fillers. To date, no studies have been published featuring any coupling agents produces from the amphiphilic molecules palmitic acid and the dipolar glutamine being utilized in silica filled high density polyethylene composites, kenaf filled high density polyethylene composites, silica filled natural rubber composites and in kenaf bast fibre filled natural rubber composites.

### **Research objectives**

The aims of this study was to prepare glut palmitate salt (GP) from non-toxic materials which could be used as a coupling agent in thermoplastic composites with mineral or natural fibre fillers, as well as in rubber composites with mineral or natural fibre fillers. The GP's effectiveness was compared to that of commercial coupling agents. Therefore, the research objectives can be outlined as follows:

- i) To synthesise glut palmitate (GP) from palmitic acid and glutamine and characterize the GP by FTIR, XPS DSC, and SEM.
- ii) To compare the effectiveness of GP with the polyethylene grafted anhydride (PE-g-MAH), in terms of the mechanical and thermal properties, the matrix-filler interaction, the water absorption and the morphologies of silica filled high density polyethylene composites as well as in the kenaf bast fibre filled high density polyethylene composites.
- iii) To compare the effectiveness of GP with the 3-Aminopropyltrimethoxysilane (APMS), in terms of the mechanical and thermal properties, the matrix-filler interaction, the cure characteristics, the cross-linked density and the morphologies of silica filled natural rubber composites as well as in the kenaf bast fibre filled natural rubber composites.

### **Thesis outline**

This thesis consists of 9 (nine) chapters and can be summarised as follow;

Chapter 1 provides the research background, the problem statement and the research objectives. The thesis structure also summarized in this chapter.

Chapter 2 provide the literature review on the role of coupling agents in the polymer composites including the introduction of polymer composites and coupling agents, physicochemical characteristics and the measurement of interface properties for matrix-filler interface, and the current scenario of using the coupling agent in the thermoplastic composites as well as in the rubber composites

Chapter 3 describes the materials, the formulation, the equipment, the experimental procedure used in preparing the coupling agent and the testing methods for thermoplastic and rubber composites.

Chapter 4 the preparation and the characterization of the Glut Palmitate (GP).

Chapter 5 compares the effects of the GP and the commercial coupling agent PE-g-MAH on silica filled high density polyethylene composite.

Chapter 6 compares the effects of the GP and the commercial PE-g-MAH coupling agent on the kenaf bast fibre filled high density polyethylene composite.

Chapter 7 compares the effects of the GP and the commercial coupling agent AMPS on the silica filled natural rubber composite.

Chapter 8 compares the effects of the GP and the commercial coupling agent AMPS on the kenaf bast fibre filled natural rubber composite.

Chapter 9 concludes this research works and makes recommendations for the future research.



## LITERATURE REVIEW

### Polymer composites

A polymer composite is a material that consists of two or more distinct components (e.g. matrices and fillers), separated by an interface as shown in Figure 2.1 (Goda *et al.*, 2014). The combinations of the different matrices and fillers create unique properties, unattainable with any of the components alone. Polymer composites have had a great impact on the development of various technologies. The polymer composite industries striving to develop a low-cost, eco-friendly composites with good properties have produced many new composites by mixing polymers with natural fibre and mineral fillers. Examples include calcium carbonate/polyethylene, silica /polypropylene, clay/ natural rubber, kenaf/natural rubber and curau fiber/polyethylene composites (Araújo *et al.*, 2008 ; Rattanasom & Prasertsri, 2009 ; Elleithy *et al.*, 2011; Lee *et al.*, 2013; Ismail *et al.*, 2010 ; Rowell *et al.*, 1999). The factors responsible for significant property enhancement in polymer composites are the properties of the polymer matrices, the fillers and the filler/matrix interfaces (Goda *et al.* 2014). However, the hydrophobic character of the polymer matrices and the hydrophilic nature of mineral and natural fibre filler result in an incompatibility between the polymer matrix and filler interfaces. This, resulted in poor mechanical properties of the composites as the inadequate interfacial strength between the filler and the polymer matrix occurred. Developing and using coupling agents in polymer composites can address these issues. A coupling agent may improve the interaction and the adhesion between the filler and the polymer matrix. Good adhesion may result in superior mechanical properties as stress can be transferred back and forth between the filler and the matrix. For instance, adding maleated anhydride polyolefin and acrylic acid functionalized polyolefin coupling agents in wood flour filled high density polyethylene

composite, enhances their mechanical properties indicating better interaction between the matrices and the filler surfaces (Li & Matuana, 2003).

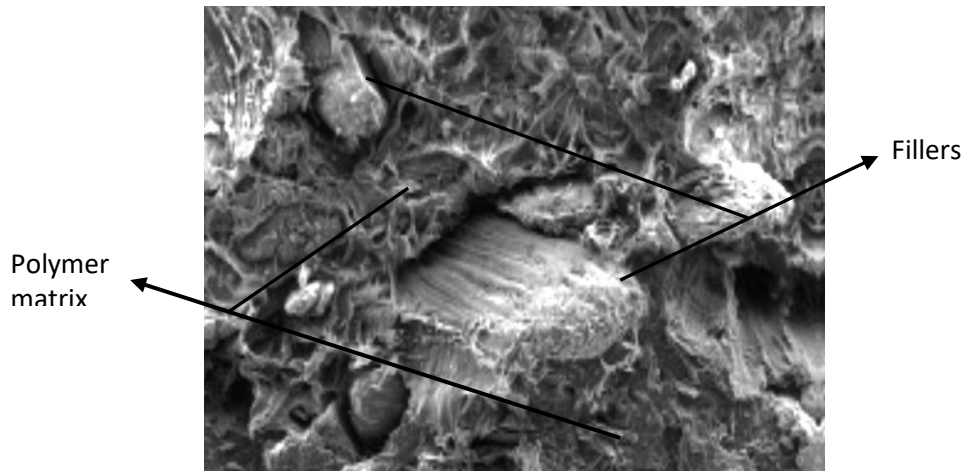


Figure 2.1: Schematic diagram of polymer composites (Adapted: Bettini *et al.*, 2013)

### **Polymer matrix**

A polymer matrix is a continuous phase that binds the filler reinforcement which surround the matrix and supports the filler materials. The matrix can serve to uniformly distribute the applied load and transfer it to the filler, the complete wettability of the filler by the matrix is important in producing polymer composites (Wang *et al.*, 2011). Currently, there are three type of polymer matrices namely thermoplastic, thermosetting plastic and elastomer. Only thermoplastic and elastomer matrices are discussed in detail in this chapter. Due to their fundamentally different properties and processing characteristics, the two types of matrices are suitable in dissimilar applications.

#### **2.1.1(a) Polyethylene**

Polyethylene (PE) is one of the most widely used thermoplastic matrices in the composites due to it's versatility with 37% of the world's polymer products being PE-based (Sagel, 2012). This is due to the low market price compared to other types of plastics and also

the easy processing. The acceptance of PE products among consumer coincided with the PE based composites market development. PE is made from petroleum oil and several different types of PE can be produced by adding different catalysts. Example of different types of PE plastics, include low density polyethylene (LDPE), medium-density polyethylene (MDPE) and high density polyethylene (HDPE). The PE property characteristics such as density, stiffness, tensile strength, flexibility, hardness, brittleness, elongation, creep characteristics and melt viscosity depend on the molecular chain arrangement.

The HDPE manufacturing process was developed in the early 1950s, as the variety of transition metal polymerization catalysts based on molybdenum, chromium and titanium was utilised (Kissin *et al.*, 2015). The HDPE's chemical structure with the density ranging from 0.941 - 0.965 g/cm<sup>3</sup>, is shown in Figure 2.2. HDPE is a non-polar compound. It does not dissolve in polar solvents such as water and is resistant to certain organic acids, inorganic acids, and alkaline solution. The HDPE is not soluble in any solvent at room temperature but at temperature above 80-100 °C, the HDPE can be dissolved in some aromatic, aliphatic, and halogenated hydrocarbons (Kissin *et al.*, 2015). HDPE is characterised as a semi-crystalline polymer as the molecular chain can be densely packed (Gabriel, 1998).

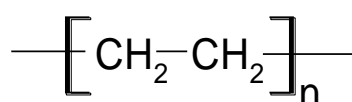


Figure 2.2: Chemical structure of High Density Polyethylene (HDPE)

Given its' safe plastic materials, ease of processability and good chemical stability, HDPE is been widely used in various applications such as bottles, film, toys, prosthetic devices, automobile parts, construction household, wire and cable coating, pipes and foams.

### 2.1.1(b) Natural rubber

Natural rubber (NR) is an example of a polymer matrix that has been used in the production of rubber composites. The NR, poly (cis-1,4-isoprene) as shown in Figure 2.3 consists of isoprene units in cis configuration. The NR is a non-polar polymer and therefore tends to dissolve in a non-polar solvents such as aromatic and aliphatic solvents. NR contains small amounts of fatty acids and proteinaceous residue which promote sulphur vulcanization (Kawahara *et al.*, 2000).

NR when chemically modified by vulcanization has high mechanical strength and excellent elasticity which enables to substantially return to its' original shape after being stretched (Subramaniam, 1987). The NR vulcanization was discovered by Charles Goodyear and Thomas Hancock in 1839. The vulcanization of rubber involves adding sulphur occurs mainly at the C=C bond and the process takes around 6 hours at 140 °C to complete. Using accelerators in the rubber compounding formulations can overcome slow vulcanization speed

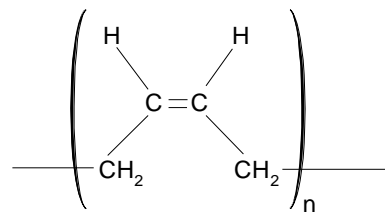


Figure 2.3: Chemical structure of natural rubber

NR has good abrasion resistance, dynamical mechanical properties, low-temperature resistance, and electrical insulation but poor weather resistance (UV light and ozone). With all the inherent properties of the tree gum, the NR is a suitable choice in the applications, such as slurry pump liners, impellers, tank linings, tires, inner tubes, rubber springs and vibration mounts, conveyor, and toys (Ciesielski, 1999).

## Fillers

Fillers are added to polymers in the polymer composites formulations to either reduce the cost or to modify the final properties of the end product. Generally, fillers can be classified into mineral fillers and natural fibre fillers. Silica, alumina, talc, and sepiolite are examples of mineral fillers. Meanwhile, wood flour, kenaf fibre, jute fibre, bamboo fibre, and feather are example of natural fibre fillers. The properties of the composites are influenced by the fillers' characteristics namely particle size and distribution, specific surface area and surface energy, particle shape and chemical composition (Moczo & Pukanszky, 2008). According to Moczo and Pukanszky (2008), large particle fillers easily debond from the matrices but smaller particle fillers have a tendency to aggregate. The aggregation may be responsible for crack initiation due to the inhomogeneous dispersion of fillers in composites. Meanwhile, the surface energy of the fillers significantly influences the matrix/ filler interaction and the particle/particle interaction. There are three main particle shapes namely spherical, rods and plate-like. These shape have pronounced reinforcing effects onto the composites (Idrus *et. al.*, 2011).

### 2.1.2(a) Silica

Silica also known as silicon dioxide ( $\text{SiO}_2$ ) is rapidly gaining acceptance as a filler in the thermoplastic and rubber composites industries. The commercial silica is available in ground, precipitated, fumed and gels forms. Silica may be crystalline or amorphous (Jesionowski *et. al.*, 2002). The silica surface consists of silanol (Si-OH) and siloxane (Si-O-Si) groups as shown in Figure 2.5. There are approximately 3-4.5 hydrophilic silanol groups per square nanometer of the silica's surface, therefore, it exhibits hydrophilic character. When the silica surface consisted primarily of hydrophobic siloxane groups, on the other hands, the silica would have exhibit hydrophobic character. Heating the silica to 105 °C can remove water

molecules at its outer part and if the sample is heated further until the temperature exceed 175 °C, the silanol group can be condensed to form siloxane bond and water is evolved (Iler, 1979). According to Jesionowski *et al.* (2002), hydrogen bonding between active silanol groups enables the silica molecules to aggregate and agglomerate. Also, the silanol group allows chemical modifications on the silica surfaces by the means of electrophilic and nucleophilic substitutions. Weak networks that are linked together in coherent aggregates of silica particles can be easily broken by mechanically. The hydrogen bonds between the OH groups of silanol molecules are formed as the OH groups get closer together and produce broad infrared absorption peaks at 3540-3550  $\text{cm}^{-1}$  (Iler,1979).

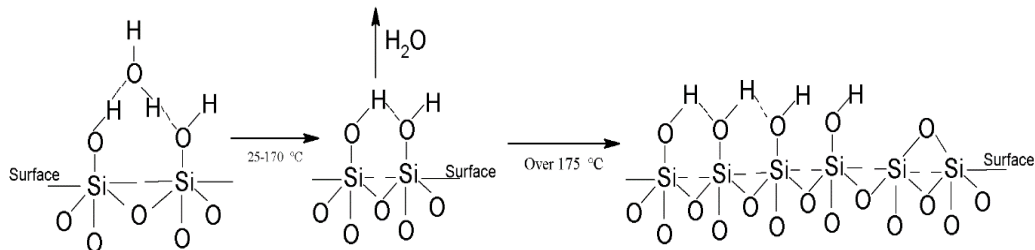


Figure 2.4: Silica surface consist silanol and siloxane (adapted from Iler, Ralph.K, 1979)

The use of silica as a reinforcing filler or an extended filler in the composites mostly depends on the specific industry (Rodgers & Waddell, 2013). Silica's high stiffness is responsible for the high moduli of compounded polymers which can be employed in a wide range of applications from a components in the food and the cosmetics industries, to microelectronics, structural and packaging materials, and the automotive industry.

### 2.1.2(b) Kenaf fibre

The acceptance of natural fibres in the polymer industry has grown as more research has been published over the years. Given their low cost, renewability, non-toxicity, reduce abrasion to processing equipment, biodegradability, and minimum waste disposal problems,

natural fibres have been used to replace synthetic fibres as fillers in composites. Natural fibres can be categorised into plant-based fibres, animal based fibres and fibres from mineral. Many studies have been done on composites with plant based fibres in the last two decades. As plant based fibre are abundantly available and low cost compared to other fibres, they are the most commonly used fillers in composites (Ahmad *et al.*, 2015). In their review of fibres as reinforcement materials in composites, Summerscales *et al.* (2010), claimed that for practical purposes, the limiting fibre volume fraction incorporated into the composites were approximately 75% for unidirectional, 65% for the woven and 30% for those with random orientation.

Kenaf, also known as *Hibiscus cannabinus* (shown in Figure 2.5), is a plant based natural fibre, well-known among researchers and in industry. Originally planted in Asia and Africa it has a growing cycle of 150-180 days (4-5 months). The main chemical constituents in kenaf fibres are cellulose (58–63 %), hemicelluloses (21–24 %), and lignin (12–14 %). The minor constituents are fats and waxes (0.4–0.8 %), inorganic matter (0.6–1.2 %) , and nitrogenous matter (0.8–1.5 %) (Monti & Alexopoulou, 2013). Each kenaf fibre's chemical composition depends on the plant's maturity and climatic conditions (Ramesh, 2016). There are two distinct types of kenaf fibres, bast and core comprising 35% and 65% of the total, respectively. Raju *et al.* (2008), comparing bast and core fibres, found that bast fibre were stronger than core fibres, as the bast fibre filled natural rubber in their study had higher tensile strength. In another study, Ishak *et al.* (2010), found that the bast fibres with higher content of cellulose gives higher tensile strength than core fibres.

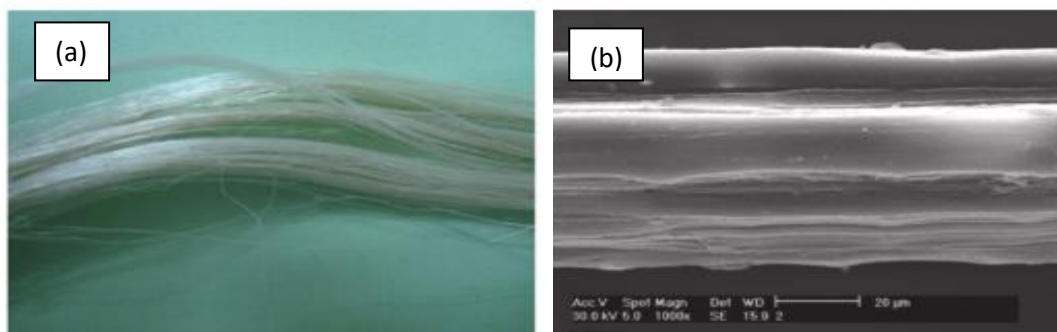


Figure 2.5: (a) Kenaf fibre (b) SEM micrograph of kenaf fibre at magnification of 1000× (adapted from Mahjoub *et al.* 2014)

Cellulose, as shown in Figure 2.6, consist of long polymer anhydrofructose unit which contain alcoholic hydroxyl groups. Hemicellulose with multiple branches, easily degradable and volatile. Meanwhile, lignin consists of multiple aromatic rings with various branches resulting a wide degradation temperature range (100-900 °C)(Yang *et al.*, 2007). The hydroxyl groups on the cellulose chain make it hydrophilic and provide active site for kenaf's chemical reactivity (Cannche-Escamilla *et al.*, 2002; Mahjoub *et al.*, 2014). Several attempts have been made to exploit these active sites, by modifying them with silane, maleated coupling agents and other chemical treatments (Noranizan *et al.*, 2012; Mohanty *et al.*, 2002; Sgriccia *et al.*, 2008; Islam *et al.*, 2015).

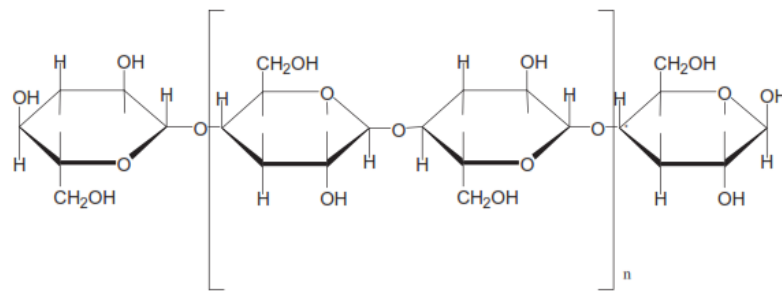


Figure 2.6: Chemical structure of cellulose (adapted from Akil *et al.*, 2011)

Kenaf fibres, as a fillers in the polymer composites technology can be applied in many industrial sectors, such as textile industries, pulp and paper industries, packaging industries, automotive industries, light weight construction industries and others (Ahmad *et al.*, 2015; Monti & Alexopoulou, 2013; Keshk *et al.*, 2006; Mohammed *et al.*, 2015).

### Matrix-filler interface

In polymer composites, the hydrophobicity of the polymer matrix and the filler are very important as differences in the matrix and the fillers hydrophobicity values produce flaws and gaps at the matrix-filler interfaces. This significantly affects the mechanical and the thermal properties and also the water uptake of the composites (Panthapulakkal *et al.*, 2006;



Colom *et al.*, 2003; Md Salleh *et al.*, 2014; Fu *et al.*, 2008; Dányádi *et al.*, 2007; Mojtaba *et al.*, 2014).

Numerous studies have established direct relationship between the mechanical properties of composites and the matrix filler interface properties. The relationship between the filler-matrix properties and the strength of the composites has been widely investigated (Fu *et al.*, 2008; Moczo & Pukanszky, 2008 ; Sobczak *et al.*, 2013; Park & Cho, 2003). Fu *et al.* (2008), present an in-depth review of the effects of particle-matrix interaction on the mechanical properties of a particulate polymer composite and conclude that the adhesion due to the particle-matrix interaction in the composites determines the effectiveness of the stress transfer between the components. The stress from the load is transferred from the matrix to the filler. If the filler and matrix interaction is strong, the filler may carry a part of the stress and consequently the polymer composites' strength increases. Thus, the particle-matrix interfacial adhesion significantly affects the strength and the toughness of the composites. On the other hand, the modulus is independent of the interfacial adhesion as Young's modulus is measured at relatively low deformation.

The tensile strength is one of the parameters that have always been studied as part of the research on the interfacial interaction between matrices and fillers. Bula and Jesionowski (2010), reported an increase in this property in PE-SiO<sub>2</sub> composites when PE-g-MAH was used as a coupling agent. Ahmed *et al.* (2013), in their study of the mechanical properties of a polypropylene/ marble sludge, reported the same results. Research by Kakou *et al.* (2014), involved introducing maleated polypropylene coupling agent into natural fibre filled thermoplastic composites, and an increase in the tensile strength was also reported. In a study of rubber composites reinforced with silica fillers, Pattanawanidchai *et al.* (2014) also reported enhanced tensile strength due to improved interaction between the filler and the rubber matrix when the coupling agent, zinc salt of dixanthated silica (ZMS) was added. The ZMS successfully reduce the hydrophilicity of the silica surface thus enhancing the dispersion in the rubber matrix and exhibiting the C=S bonding in the broad range from 1250 to 1190 cm<sup>-1</sup>.

Park and Cho (2003), studying the influence of silane coupling agents on silica/rubber composites report that when the coupling agents are incorporated into the rubber composites, two interfaces exist between the silica and the rubber in each composite; one between the silane and the silica, and another between the silane and the rubber. The presence of the silane increases the crosslinked density since when the silica surface reacts with the silane, the accelerator can directly interact with the rubber.

In addition to the tensile strength, the effects of the matrix-filler interface properties on the thermal properties of polymer composites has also been studied extensively (Dorigato *et al.*, 2012; Motaung & Luyt, 2010; Abdul Wahab *et al.*, 2012). Shen *et al.* (2007), in their investigation on the thermal properties of polymer composites, with the addition of different types of maleated anhydride coupling agent, point out that the strong interaction between polypropylene matrix and  $Mg(OH)_2$  fillers may activate the nucleation points on the filler surfaces and result in synergisms effect of heterogeneous nucleation in the matrix.

Espert *et al.* (2004) discuss the importance of matrix-filler interfaces in the water uptake of composites. They point out that the gaps and the flaws at the filler-matrix interfaces, micro cracks formed in composites during processing, as well as environmental or service effects could result in the exposure to and the penetration of moisture into composites. Good interfacial interaction (i.e. no gaps or flaws at the interfaces ), on the other hand, prevents the direct diffusion of the moisture into hydrophilic fillers, consequently decreasing the water absorption rate in the interphase regions of the composites (Colom *et al.*, 2003). When the coupling agent is incorporated into the composite system, the interaction between the filler and matrix improves. The matrix may prevent the filler's hydroxyl group from interacting with the water molecules, thus reducing the water absorption of the polymer composites. The existence of chemical bonds from the reaction between the fillers and the coupling agents also helps to reduce the moisture thus minimizing fibre debonding (Mohanty *et al.*, 2002). Ahmad Thirmizi *et al.* (2013), in their study of the effects of adding Polybutylene succinate grafted maleic anhydride (PBS-g-MA) on the water absorption properties of poly(butylene

succinate)/kenaf bast fibre composites report that the improvement in the fibre matrix interfacial interaction reduces the composites' water absorption.

In rubber composites, the extent of the interaction between the fibre and the rubber matrix can be evaluated by using the Lorez and Park equation whereby the value of filler-rubber interaction index ratio ( $Q_f/Q_g$ ) indicates the interaction between the fibre and the matrix. The low  $Q_f/Q_g$  value indicates the good interaction between the filler and the rubber. Meanwhile, the high  $Q_f/Q_g$  value, indicates the poor interaction between the filler and the rubber. Many researchers have used this equation to investigate the restrictions on the swelling exerted by reinforced composites (Ismail *et al.*, 2010; Haseena *et al.*, 2004). Ismail *et al.* (2010) in their study of treated and untreated kenaf fibres in natural rubber compounds reported that the  $Q_f/Q_g$  values for the untreated kenaf rubber composites were higher than those for the treated kenaf rubber composites. The treated kenaf fibres showed better interaction with the rubber matrix than the untreated kenaf fibres did, as supported by the tensile strength results and the SEM morphologies of the rubber composites. Haseena *et al.* (2004), in their study of interfacial adhesion of fibres on the natural rubber composites, examined the degree of interfacial adhesion by using the restricted equilibrium swelling technique. A mixture of hexamethylene tetramine and resorcinol was used as a coupling agent for the natural composites. Due to the good interfacial adhesion between the fibre and the rubber, bound by the coupling agent, the free volume and the number of micro voids was restricted to penetrate the moisture. Thus the rubber composites with the coupling agent absorbed less toluene at equilibrium than those without the coupling agent. The low  $Q_f/Q_g$  ratio, calculated using the Lorenz and Parks equation also supported the hypothesis that adding a coupling agent would enhance the interaction between the constituents.

## **Coupling agents**

### **Introduction**

A coupling agent is a chemical compound, capable of reacting with both the polymer matrix and the filler (Li *et al.*, 2007). Coupling agents have been used as additives in the polymer composites to improve the interfacial activity consequently, strengthening interfacial adhesion and enhancing composites' properties. (Pattanawanidchai, *et al.*, 2014; Chen *et al.*, 2013; Ahmed *et al.*, 2009; Zabihzadeh, 2010). A coupling agent can link a hydrophobic polymer matrix with a hydrophilic filler surface by the one or more of the following mechanisms; covalent bonding, secondary bonding (hydrogen bonding and Van der Waals forces) and physical chain entanglement (Lu *et al.*, 2005; Le Moigne *et al.*, 2014).

With the development of polymer composites, a number of new coupling agents for improving composites properties have been introduced. For example, Mohanty *et al.* (2002), successfully developed a novel hybrid coupling agent for natural fibre reinforced polypropylene composites. This coupling agent made from mixture of amino-silane and PP-g-MAH successfully strengthened the resulting composite. Currently, maleated anhydride grafted polymers and silane are two well-known types of coupling agents that have been used in polymer composites.

### **Copolymer maleic anhydrides (MA)**

In 1972, maleic anhydride (MA) copolymers and their preparation method were patented by Gaylord (Gaylord, 1970). MA is an unsaturated carbonyl compound that can be conjugated with an unsaturated polymer matrix using a radical catalyst. It has been developed to be grafted onto various polymer substrates (Gaylord, 1975) such as polyethylene grafted maleic anhydride (PE-g-MAH) as shown in Figure 2.7.

Many studies published on the topic feature the MA grafted onto polyolefin such as PE-g-MAH and propylene grafted maleic anhydride (PP-g-MAH) (Fu *et al.*, 2008; El-Sabbagh, 2014; Keener *et al.*, 2004). The maleic anhydride was purposely grafted onto the same type of polymer and to the respective composite polymer matrix to improve the adhesion between the polymer matrix and the fillers (Lee *et al.*, 2013; Nachtigall *et al.*, 2007; Bula & Jesionowski, 2010; Grigoryeva & Karger-Kocsis, 2000). However, it was affected by the graft yield of the MA on the polyolefin (Chen *et al.*, 2008). The challenge in manufacturing maleic anhydride copolymer lies in the proper balance of molecular weight and number of grafted. A maleic anhydride copolymer may not interact sufficiently with a given polyolefin if the molecular weight is too low. Meanwhile, if the molecular weight is too high, it cannot reside at the interface (Keener *et al.*, 2004).

These coupling agents have demonstrated their effectiveness in both mineral filler filled and natural fibre filled thermoplastic composites.

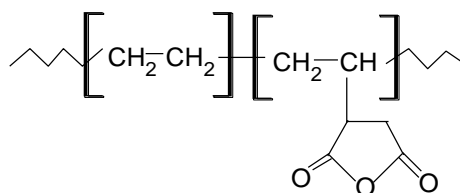


Figure 2.7: Chemical structure of polyethylene grafted maleic anhydride (PE-g-MAH)

As a coupling agent, the MA was used to modify the polymer matrices. The MA chemical structure consisting of a short chain, however, reduce ability to improve interfacial adhesion. Modifications can be made to an MA copolymer, grafted onto a polymer matrix by using in-situ polymerization in which a radical catalyst and maleic anhydride are mixed with polyolefin and clay in a Brabender plasticorder. Hydrogen bonding and/ or esterification take place between the maleic anhydride and the clay (Gaylord, 1975). The previous study by Lu *et al.* (2005), also reports that ester linkages and hydrogen bonds form when the functionalized acid in the MA reacts with the hydrophilic filler surface, as shown in Figure 2.8. However, the

acid number, the molecular weight and the concentration are three important properties influencing the effectiveness of MA as coupling agent. An MA copolymer coupling agent needs enough acid functionality to attract the filler and enough molecular weight to entangle to the polymer matrix (Keener *et al.*, 2004). Couplers interact with hydrophilic filler surface and entangled with the polymer matrix to achieve better interfacial and mechanical properties in composites (Lu, *et al.*, 2005; Li, *et al.*, 2007; El-Sabbagh, 2014).

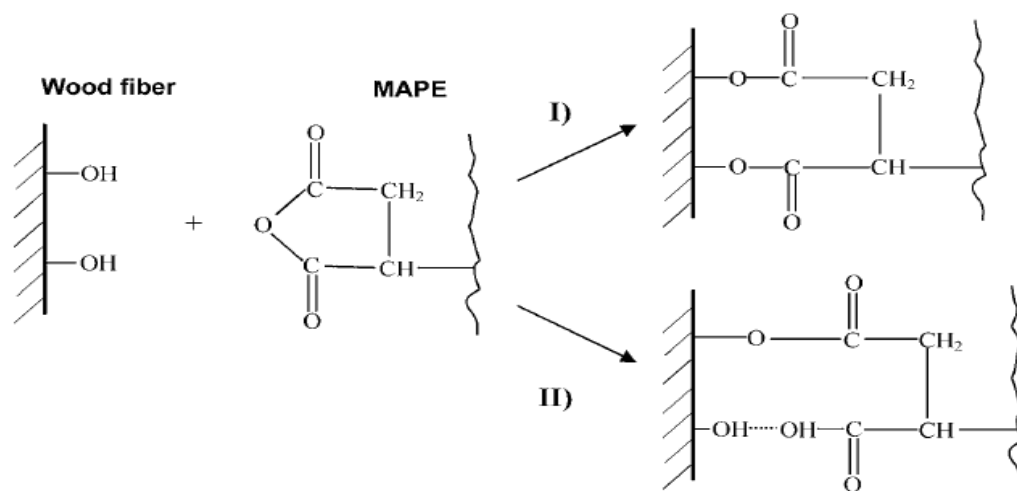


Figure 2.8: Interaction between the PE-g-MAH and the hydrophilic filler surfaces. (I) Succinic bridge structure and (II) half succinic bridge structure. (Adapted from Lu *et al.* 2005)

Almost every paper published on the interaction of copolymer MA coupling agents with filler surface reported that the presence of ester linkages from esterification reaction could be identified between 1800 and 1650  $\text{cm}^{-1}$  on Fourier Transform Infra-Red (FTIR) spectra. (Lu *et al.*, 2005; Kakou *et al.*, 2014; De la Orden *et al.*, 2010). The formation of chemical bonds between filler surfaces and polymer matrix was found to corroborate with the enhancement of composites' mechanical properties (Li & Matuana, 2003; Kakou *et al.*, 2014; Noranizan, 2012).

### 2.3.3 Silanes

Silane coupling agent has the general formula X-R -Si - (OR')<sub>3</sub> where R' is alkoxy group, X represents an organofunctional group and R is an alkyl. The organofunctional groups are typically amino, mercapto, glycidoxy, vinyl, or methacryloxy groups. The most common alkoxy groups are usually ethoxy or methoxy groups (Xie *et al.*, 2010; Shokoohi *et al.*, 2008). The methoxy group is hydrolyzed more rapidly than the ethoxy group (Kang *et al.*, 1990). The R' group is usually hydrolyzed during the filler pretreatment further interacting with the filler forming ether bonds or hydrogen bonds. (Sobczak *et al.*, 2013). Meanwhile, the organofunctional group has the capability to react with the polymer matrix.

Various types of silane have been tested as a coupling agents and it effectively to be used in thermoplastic, thermoset and in rubber composites (Deepthi *et al.*, 2010; Surya *et al.*, 2014; Ismail *et al.*, 2011). Table 2.1 lists the silanes types with their corresponding types of polymer matrix and fillers.

Table 2.1: Types of silane use for polymer composites.

Silanes	Abbrev	Matrix	Filler	Reference
3-aminopropyl triethoxysilane	APES	SBR	Silica	Park & Cho, 2003
3-chloropropyl trimethoxysilane	CPMS	SBR	Silica	Park & Cho, 2003
3-methacryloxypropyl trimethoxysilane	MPMS	SBR	Silica	Park & Cho, 2003
3-aminopropyl triethoxysilane	APES	NR	Silica	Surya, <i>et al.</i> , 2014
3-aminopropyl trimethoxysilane	APMS	NR	Palm kernel shell powder	Daud <i>et al.</i> , 2016

The silane is can be added to the system in a solvent or in-situ in the polymer composite compounding. (Daud *et al.*, 2016; Surya *et al.*, 2014; Park & Cho, 2003). Yang *et al.* (2003), demonstrate that alkoxy silanes are been able to directly react with inorganic filler namely, Mg(OH)<sub>2</sub> and CaCO<sub>3</sub> to form Si-O-Mg and Si-O-C bonds, respectively. Manna *et al.*

(1999), in their study of silica, claims that the Si-O-Si bond is formed when the alkoxy silanes functionality react with the silica. Meanwhile, in the case of a natural fibre as a filler, the silane attaches to the hydroxyl group of cellulose by hydrogen bonding or ether linkage (Li *et al.*, 2007).

The amino bearing silane coupling agent can self-hydrolysed silanol group upon hydrolysis of silane coupling agent (Brochier *et al.*, 2011). The hydrolysis of silane to form silanol is crucial as the actual coupling process is the condensation of silanol with the filler surface groups (Shokoohi *et al.*, 2008). As for this advantage, the 3-aminopropyltrimethoxysilane (APMS) shown in Figure 2.9 has been chosen to be the coupling agent in this work. Reactive alkoxide group bonding with the surface group and the cross-linking between the silanes may occur.

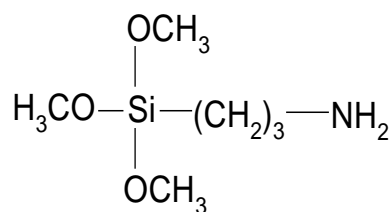


Figure 2.9: Chemical structure of aminopropyltrimethoxysilane (APMS)

A scheme of the AMPS hydroxylation and the possible chemical bonding of the AMPS with the OH groups on the filler surface is shown in Figure 2.10. The hydrolysis of the alkoxy group in the APMS releases methanol which is toxic and harmful to the environment. In order to achieve complete hydrolysis and form silanol groups, additional water is required. Thus, the silanol groups may react with the hydroxyl groups on the fillers' surfaces and eventually form Si-O-C bonds (Xie *et al.*, 2010).



