PREPARATION AND PROPERTIES OF HIGH DENSITY POLYETHYLENE (HDPE)/SOYA POWDER/KENAF CORE BIOCOMPOSITES

by

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ISO	International Organization for Standardization
MMC	Metal Matrix Composites
CMC	Ceramic Matrix Composites
PMC	Polymer Matrix Composites
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
ULDPE	Ultra Low Density Polyethylene
EVA	Ethylene-Vinyl Acetate
FRIM	Forest Research Institute Malaysia
MAPE	Maleic Anhydride Polyethylene
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
OxPE	Oxidized Polyethylene

PENYEDIAAN DAN SIFAT-SIFAT BIOKOMPOSIT POLIETILENA BERKETUMPATAN TINGGI (HDPE)/SERBUK SOYA/TERAS KENAF

ABSTRAK

Sifat-sifat mekanikal dan morfologi biokomposit HDPE/serbuk soya/teras kenaf terubahsuai dengan maleik anhidrida polietilena (MAPE), γ-aminopropiltrimetoksisilana (γ-APS), asetik anhidrida dan polietilena teroksida (OxPE) telah dikaji. Kesan pembebanan pengisi juga telah dikaji. Biokomposit HDPE/serbuk soya/teras kenaf telah disediakan dengan mencampurkan kenaf teras pada pembebanan yang berlainan (0, 10, 20, 30 dan 40 bsr) ke dalam adunan HDPE/serbuk soya dengan menggunakan pencampur dalaman (Haake PolyLab) untuk 12 min pada suhu 180°C dan kelajuan rotor 50 ppm. Keputusan menunjukkan penggunaan agen pengserasi, agen pengkupel silana, dan pengubahsuaian oleh asetik anhidrida terhadap pengisi kenaf teras telah secara berkesan meningkatkan interaksi antaramuka pengisi-matrik yang lebih baik dan seterusnya meningkatkan sifat-sifat mekanikal biokomposit HDPE/serbuk soya/teras kenaf. Kajian mikroskop penskanan elektron ke atas permukaan patah biokomposit HDPE/serbuk soya/teras kenaf menunjukkan interaksi antaramuka matriks dan pengisi dipertingkatkan dengan penambahan maleik anhidrida polietilena (MAPE), polietilena teroksida (OxPE), γ-aminopropiltrimetoksisilana (γ-APS) dan asetik anhidrida sebagai pengubahsuai kimia. Pengubahsuaian kimia dengan γ-aminopropiltrimetoksisilana (γ-APS) dan asetik anhidrida meningkatkan kestabilan terma biokomposit, manakala penggunaan agen pengserasi maleik anhidrida polietilena (MAPE) dan polietilena teroksida (OxPE) tidak mempamerkan perubahan yang ketara kepada kestabilan terma biokomposit. Pencuacaan buatan terpecut menyebabkan pengurangan yang ketara pada sifat-sifat regangan biokomposit HDPE/serbuk soya/teras kenaf. Walau bagaimanapun, biokomposit HDPE/serbuk soya/teras kenaf terubahsuai dengan maleik anhidrida polietilena (MAPE), γ-aminopropiltrimetoksisilana (γ-APS), asetik anhidrida dan polietilena teroksida (OxPE) masih mengekalkan sifat-sifat regangan yang tinggi berbanding dengan biokomposit HDPE/serbuk soya/teras kenaf tanpa pengubahsuaian. Kajian mikroskop penskanan elektron menunjukkan rekahan bertambah dengan masa pencuacaan. Perubahan warna (ΔE_{ab}) dan pencerahan permukaan (ΔL) yang ketara diperhatikan selepas pencuacaan buatan terpecut. Kehadiran maleik anhidrida polietilena (MAPE), γ-aminopropiltrimetoksisilana (γ-APS), asetik anhidrida dan polietilena teroksida (OxPE) mengurangkan pembentukan rekahan, pengurangan sifat-sifat regangan dan juga pencerahan permukaan biokomposit HDPE/serbuk soya/teras kenaf semasa pencuacaan buatan terpecut.

PREPARATION AND PROPERTIES OF HIGH DENSITY POLYETHYLENE (HDPE)/SOYA POWDER/KENAF CORE BIOCOMPOSITES

ABSTRACT

Mechanical, thermal, water absorption properties and morphologies of HDPE/soya powder/kenaf core biocomposites modified with maleic anhydride polyethylene (MAPE), γ-aminopropyltrimethoxysilane (γ-APS), acetic anhydride and oxidized polyethylene (OxPE) were investigated. The effect of filler loading was also studied. HDPE/soya powder/kenaf core biocomposites were prepared by incorporation of kenaf core powder at different filler loading (0, 10, 20, 30 and 40 phr) into HDPE/soya powder biocomposites with an internal mixer (Haake PolyLab) for 12 min at 180ºC and 50 rpm rotor speed. Results showed that the use of compatibilisers, silane coupling agent, and chemical modification by acetic anhydride on kenaf core filler has effectively introduce better matrix-filler interface interaction and consequently improved the mechanical properties of HDPE/soya powder/kenaf core biocomposites. Field Emission Scanning electron microscope (FESEM) studies of tensile fracture surfaces of HDPE/soya powder/kenaf core biocomposites showed that interfacial interaction between kenaf core filler and matrix was improved with the addition of maleic anhydride polyethylene (MAPE), oxidized polyethylene (OxPE), γ-aminopropyltrimethoxysilane (γ-APS) and acetic anhydride as chemical modifiers. Chemical treatment with γ-aminopropyltrimethoxysilane (γ-APS) and acetic anhydride improved the thermal stability of the biocomposites, whereas the use of compatibilisers; maleic anhydride polyethylene (MAPE) and oxidized polyethylene

(OxPE) did not exhibit significant changes on the thermal stability of the biocomposites. The artificial accelerated weathering caused a significant decrease in tensile properties of the HDPE/soya powder/kenaf core biocomposites. However, HDPE/soya powder/kenaf core biocomposites modified with maleic anhydride polyethylene (MAPE), γ-aminopropyltrimethoxysilane (γ-APS), acetic anhydride and oxidized polyethylene (OxPE) still retained higher tensile properties compared to HDPE/soya powder/kenaf core biocomposites without modification. The FESEM results showed that cracks at the surface of the both biocomposites samples increased with the accelerated weathering test time. Significant color changes (ΔE_{ab}) and surface lightening (ΔL) were observed after accelerated weathering test. The presence of maleic anhydride polyethylene (MAPE), γ-aminopropyltrimethoxysilane (γ-APS), acetic anhydride and oxidized polyethylene (OxPE) reduced the cracks formation, deterioration of tensile properties and color changes as well as surface lightening of HDPE/soya powder/kenaf core biocomposites during accelerated weathering test.

CHAPTER I

INTRODUCTION

1.1 Natural fibre reinforced composites

Recently, the use of biodegradable polymers such as soya protein and natural fibre reinforced composites has been widely studied. This increasing interest is due to an increasing awareness of environmental issues worldwide such as air pollution from the incineration of plastics as a means of disposal and marine pollution resulted from discarded plastics into the drainage systems. There are many areas of applications for natural fibre reinforced composites as shown in **Figure 1.1**.

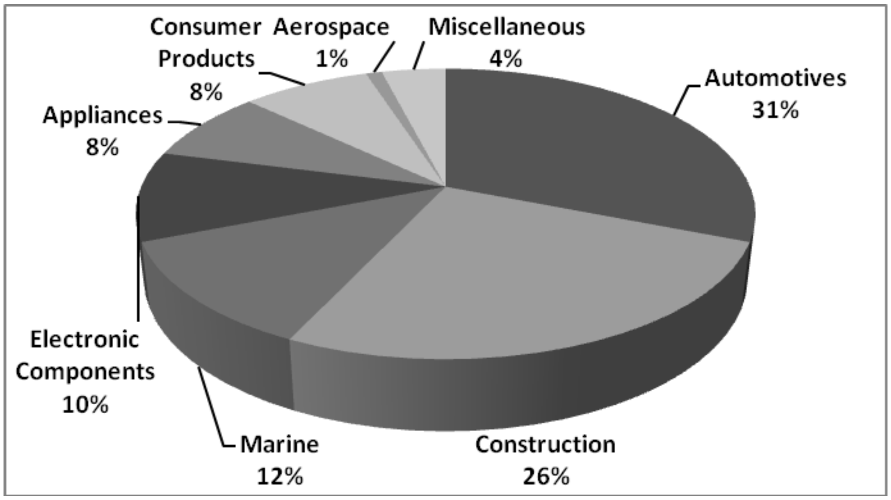


Figure 1.1 : Applications of natural fibre reinforced composites (Ashori, 2008)

Natural fibres such as kenaf, jute, hemp, sisal, flax, bagasse, and rice husk have been successfully used as reinforcements or fillers in plastic composites (Nishino et al., 2003; Luz et al., 2008; John et al., 2009; Madsen et al., 2007). Natural fibre such as kenaf are attractive because of their low cost, low density, abundance, renewability, biodegradability, environmental friendliness and decreased equipment abrasion (Zampaloni et al., 2007). However, the main disadvantage of using natural fibre in plastic composites is its poor wettability and the incompatibility of hydrophobic matrix with its hydrophilic natural fibres, which is the reason for its low tensile strength (Bledzki and Gassan, 1999; Herrera-Franco and Valadez-González, 2004). However, these problems can be alleviated through the use of suitable compatibilizers and coupling agents (Salmah and Ismail, 2008; Ismail et al., 2002; Vilay et al., 2008). Liu et al. (2009) modified jute fiber with alkali and silane, and found that chemical treatments on the surface of jute fiber have improved the mechanical properties of jute fiber reinforced poly(butylenes succinate) biocomposites.

Another major problem with natural fibre is its high water-absorption properties caused by the hydroxyl groups at the surface of the natural fibre (Bessadok et al., 2008). High water absorption in natural fibres can lead to dimensional changes, cracks and interfacial breakdown (Sgriccia et al., 2008). Resistance to water absorption can be improved by the use of compatibilizers and the treatment of the natural fibres with suitable chemical treatments (Najafi et al., 2006; Arbelaiz et al., 2005; Yang et al., 2006). One method that can be generally used is the acetylation of natural fibres (Alvarez and Vázquez, 2006; Mat Taib et al., 2009; Abdul Khalil et al., 2007). Acetylation replaces hydroxyl groups at the fibre’s surface with acetyl groups making the fibre hydrophobic (Hill et al., 1998). This alteration reduces water absorption (Alvarez and Vázquez , 2006; Mat Taib et al., 2009). The acetylation of natural fibres not only increases the water-resistance properties of natural fibre composite, but it also increases its thermal stability. These increases have been reported by Luz et al. (2008).

In this study, an attempt was made to produce HDPE/soya protein/kenaf core biocomposites. Due to the incompatibility of kenaf core and high-density polyethylene matrix, compatibilizers and coupling agents are used to improve the interactions between the kenaf core and high-density polyethylene.

1.2 Objectives

The main objectives of the study are as follows:

(a) To study the effects of the addition of maleic anhydride polyethylene (MAPE) as a compatibilizer on the properties of HDPE/soya powder/kenaf core biocomposites

(b) To study the effects of silane treatment on the kenaf core on the properties of HDPE/soya powder/kenaf core biocomposites

(c) To study the effects of kenaf core acetylation on the properties of HDPE/soya powder/kenaf core biocomposites

(d) To study the effects of the addition of oxidized polyethylene as a compatibilizer on the properties of HDPE/soya powder/kenaf core biocomposites

(e) To study the effects of filler loading on the properties of HDPE/soya powder/kenaf core biocomposites

1.3 Importance of studies

Recently, more studies are aimed towards achieving the objective of green composites or biodegradable composites. The main reasons for the attention in eco-friendly materials are:

(1) The increases of fuel price

  - The increase of fuel price which is the raw materials for producing plastic cause industries to find new alternative materials to substituting the use of petroleum-based plastics.

(2) Availability of green materials

  - Natural resources such as natural fibres are the most abundant, renewable and inexpensive (Mohanty et al., 2005).

(3) Shortage of landfill availability

  - The need to develop composite materials that is environmental friendly which can degrades if disposed.

(4) Increasing environmental awareness

  - The need to develop composite materials that is environmental friendly, by using renewable raw materials and reducing the amount of petroleum-based plastic in the composition.

1.4 Organization of the thesis

There are 5 chapters in this thesis and each chapter gives information related to the research interest.

- **Chapter 1** contains introduction of the project. It covers brief introduction about research background, objectives and organization of the thesis.

- **Chapter 2** contains the literature review. It covers brief explanations regarding composites, biocomposites, natural fibres, and degradation.

- **Chapter 3** contains the information about the materials specifications, equipments and experimental procedures used in this study.

- **Chapter 4** contains results and discussion of this study.

- **Chapter 5** concludes the findings in **Chapter 4** with suggestion for future work.

CHAPTER II

LITERATURE REVIEW

2.1 Composites

2.1.1 Definition

Composite material is a combination of two or more constituent materials (reinforcing elements, fillers, and matrix) with dissimilar physical and chemical properties. The constituents maintain their identities, that is, they do not dissolve or merge completely into one another. A lot of composite materials are composed of just two phases; one is termed the matrix, which is continuous and surrounds the other phase, often called the dispersed phase (Callister, 2003). The dispersed material may be either fibres, such as glass fibres, carbon fibres, and natural fibres, or particulate fillers.

2.1.2 Classification of composites

There are various types of composite materials which can be classified based on the type of fibers or matrix used. Based on the type of fibers, composites can be further classified as:

- Continuous fibre reinforced composite,
- Short fibre reinforced composites.

Based on the type of matrix, composites can be broadly classified into three categories:

- Metal matrix composites (MMC),
- Ceramic matrix composites (CMC), and
- Polymer matrix composites (PMC).

Among three types of composites stated above, polymer matrix composites (PMC) are very well known for their widely used and were the focus for discussion in this study. Composite materials also can be divided into several different group based on their reinforcement types as shown in **Figure 2.1**.

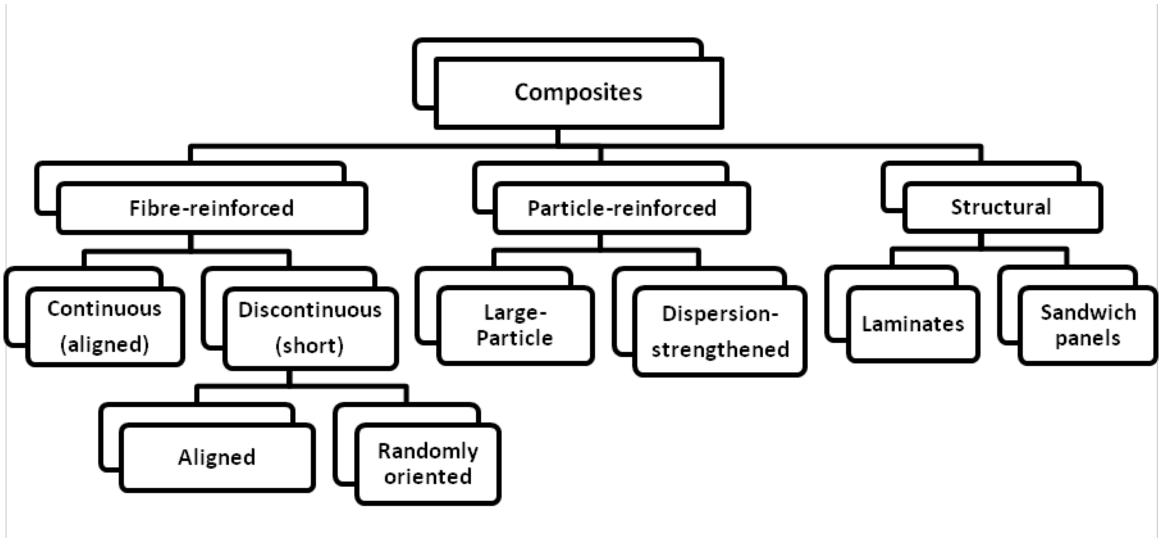


Figure 2.1 : Classification of composite materials (Callister, 2003)

2.1.3 Biocomposites

The use of eco-friendly materials from renewable resources as a reinforcing component in polymer composites has gained further interest in recent years (Ismail et al., 2010; Zampaloni et al., 2007; Nishino et al., 2003). This is due to the advantages of natural fibres in term of biodegradability, renewability, low cost and low density as compared to various conventional reinforcement materials especially fibre glass (La Mantia et al., 2005). Natural fibre reinforced composites or biocomposites have increasing attention in many areas of applications including automotive, housing, and packaging (Ashori, 2008).

Biocomposites is composite materials consisting of one or more phase(s) derived from a biological origin (Fowler et al, 2006). At least one of the components has to be bio-based materials in order to classify the final composite as biocomposite. The reinforcement phase may come from natural fibres such as flax, jute, hemp, sisal, cotton and kenaf. The matrix phase may come from the natural resources such as starch and soy protein; or from the biodegradable synthetic plastics (Mohanty et al., 2000) such as polyhydroxyalkanotes, poly(3-hydroxybutyrate), poly(butylenes succinate-co-adipate) and poly(tetramethylene adipate-co-terephthalate). These materials exhibit very good biodegradation properties. However, extensive use could not be implemented because of materials price are too high. At present most matrices used are petroleum based polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC) (Kim et al., 2007; Annie et al., 2008; Habibi et al., 2008).

2.2 Polyethylene as polymer matrix

Polyethylene (PE) was discovered in 1933 by Reginald Gibson and Eric Fawcett at the British industrial giant, Imperial Chemical Industries (ICI). Although it is more than 70 years since it was first produced, it is still a very promising material. This widely used plastic is a polymer of ethylene, $CH_2{=}CH_2$ (Vasile & Pascu, 2005). Chemical structure of polyethylene is shown in **Figure 2.2**.

$$-\!\left[CH_2-CH_2 \right]\!-_n$$

Figure 2.2 : Chemical structure of polyethyelene

There are various types of polyethylene produced by manufacturers all over the world. Polyethylene can be divided into several classes as shown in **Figure 2.3**. Among them, HDPE has the biggest market share based on annual production levels as shown in **Table 2.1**.

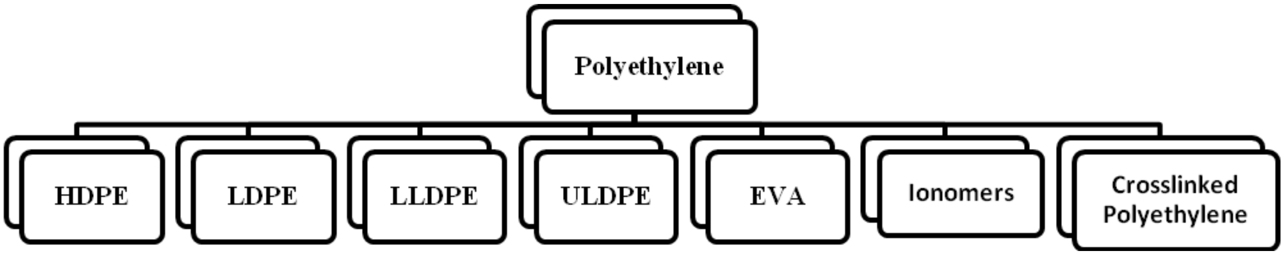


Figure 2.3 : Classes of polyethylene (Peacock, 2000)

Table 2.1 : Annual production levels of polyethylene (White, 2005)

Polyethylene	**Annual Production (million tons)**
HDPE	26
LLDPE	17
LDPE	17

i. High Density Polyethylene (HDPE)

HDPE has the chemical structure closest to pure polyethylene. It has a high degree of linearity because it comprises primarily unbranched chains with very few flaws to mar its linearity. HDPE has a molecular weight below 300,000 g/mol and density around 0.94-0.97 g/cm^3. HDPE resin is a flexible, transparent/waxy material. It is weatherproof, easy to process by most methods, low cost, and has good chemical resistance. Representing the largest portion of PE applications, HDPE offers excellent impact resistance, has low moisture absorption, and has high tensile strength. **Figure 2.4** shows the schematic representations of the HDPE.

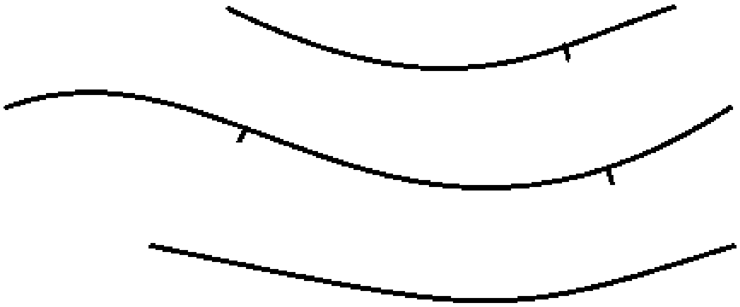


Figure 2.4 : Schematic representations of the HDPE

ii. Low Density Polyethylene (LDPE)

LDPE contains substantial concentrations of branches that hinder the crystallization process, resulting low density comparative to other types of polyethylene. Low density polyethylene resins typically have densities around 0-90-0.94 g/cm^3. **Figure 2.5** shows the schematic representations of the LDPE.

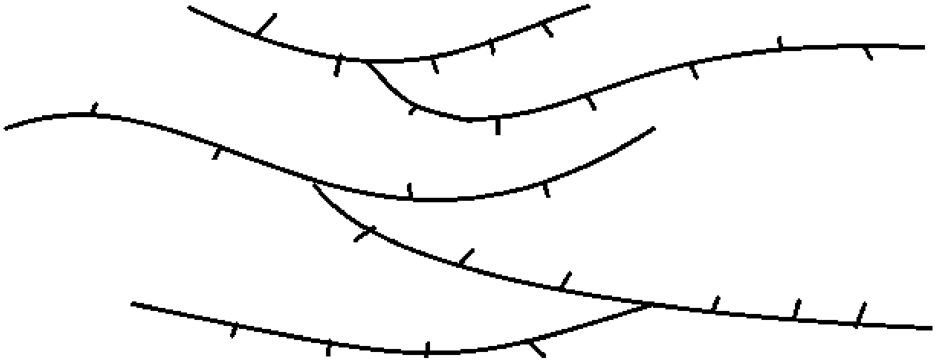


Figure 2.5 : Schematic representations of the LDPE

iii. Linear Low Density Polyethylene (LLDPE)

LLDPE consist of chains with linear polyethylene backbones to which are attached short alkyl groups at random intervals. The density of LLDPE is around 0-90-0.94 g/cm^3. **Figure 2.6** shows the schematic representations of the LLDPE.

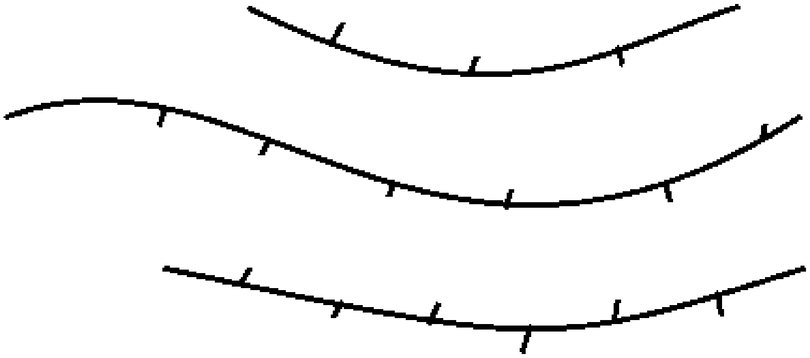


Figure 2.6 : Schematic representations of the LLDPE

iv. Ultra Low Density Polyethylene (ULDPE)

ULDPE consist of high concentration of short-chain branches and have densities approximately 0.86-0.90 g/cm^3. **Figure 2.7** shows the schematic representations of the ULDPE.

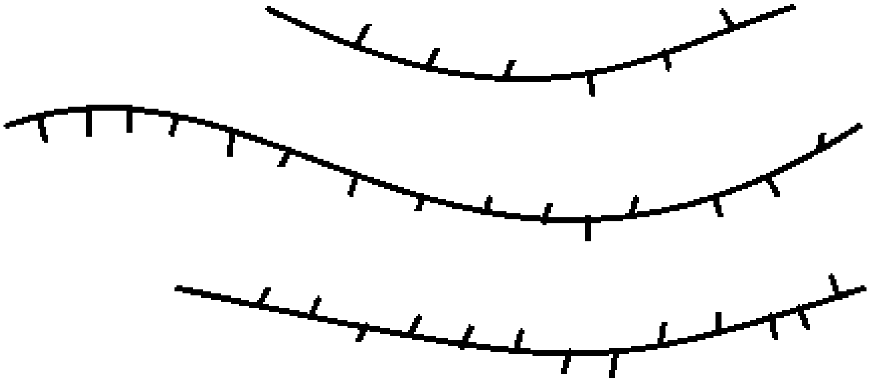


Figure 2.7 : Schematic representations of the ULDPE

v. Ethylene-Vinyl Acetate (EVA)

EVA contains both short-chain and long-chain branches in addition to acetate groups. Density for EVA is around 0.92-0.94 g/cm^3. **Figure 2.8** shows the schematic representations of the EVA.

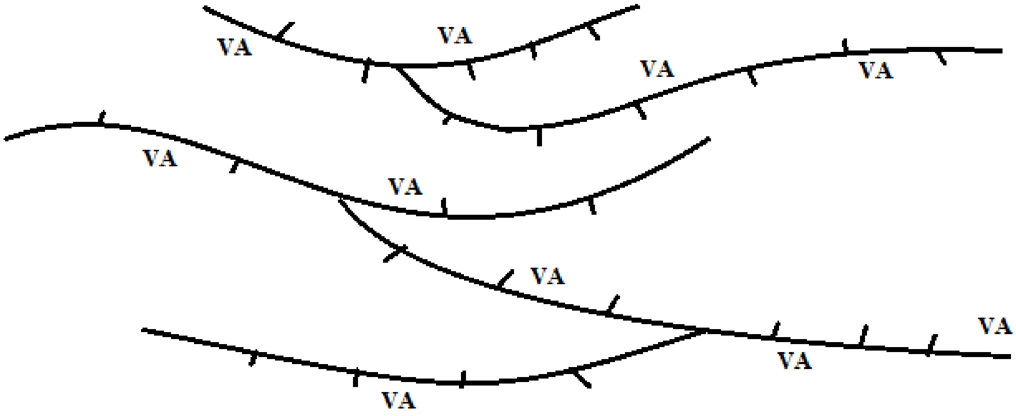


Figure 2.8 : Schematic representations of the EVA

vi. Ionomers

Ionomers are copolymers of ethylene and acrylic acids that have been neutralized to form metal salts. Ionomers contain all the branches normally associated with LDPE.

vii. Cross-Linked Polyethylene (XLPE)

XLPE consists of polyethylene that has been chemically modified to covalently link adjacent chains. Cross-links greatly hinder crystallization, limiting free movement of chains required to organize into crystallites resulted in cross-linked polyethylene with lower density that its original polyethylene resins. **Figure 2.9** shows the schematic representations of the XLPE.

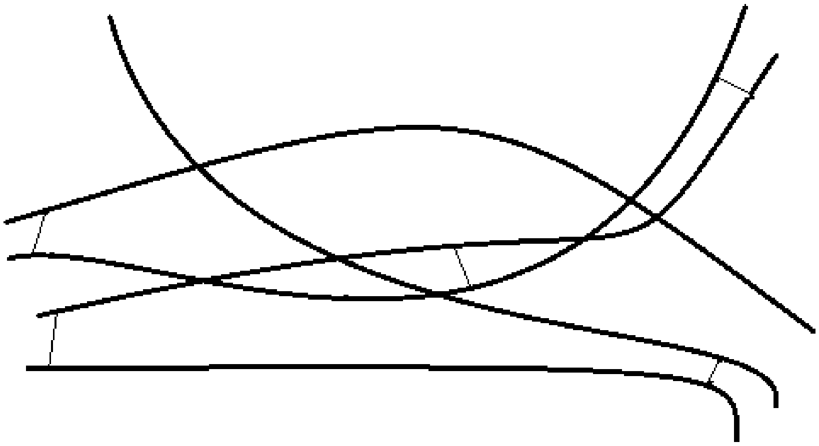


Figure 2.9 : Schematic representations of the XLPE

Different types of polyethylene exhibit a wide range of properties as shown in **Table 2.2**. There is overlapping between the ranges of properties for the different polyethylene types.

Table 2.2 : Properties of different types of polyethylene (Peacock, 2000)

Property	**HDPE**	**LDPE**	**LLDPE**	**ULDPE**	**EVA**	**Ionomer**
Density (g/cm^3)	0.94-0.97	0.91-0.94	0.90-0.94	0.86-0.90	0.92-0.94	0.93-0.96
Degree of Crystallinity (%)	62-82	42-62	34-62	4-34	-	-
Melting Temperature (°C)	125-132	98-115	100-125	60-100	103-110	81-96

2.3 Reinforcement/Filler

Polymeric materials can be filled or reinforced by the addition of organic or inorganic materials named fillers/fibres. Reinforcement occurs when the values for the mechanical strength and tensile modulus of the composite are higher than the corresponding values for the unreinforced matrix (Erhard, 2006). If the additive does not reinforce the composite, the additive is typically described as fillers. However, it is not easy to make a clear distinction between fillers and reinforcing materials, because fillers may also have a reinforcing effect on certain properties. There are various types of reinforcing materials/fillers as shown in **Figure 2.10**. For this study, natural fibre was used as filler in the polymer composites.

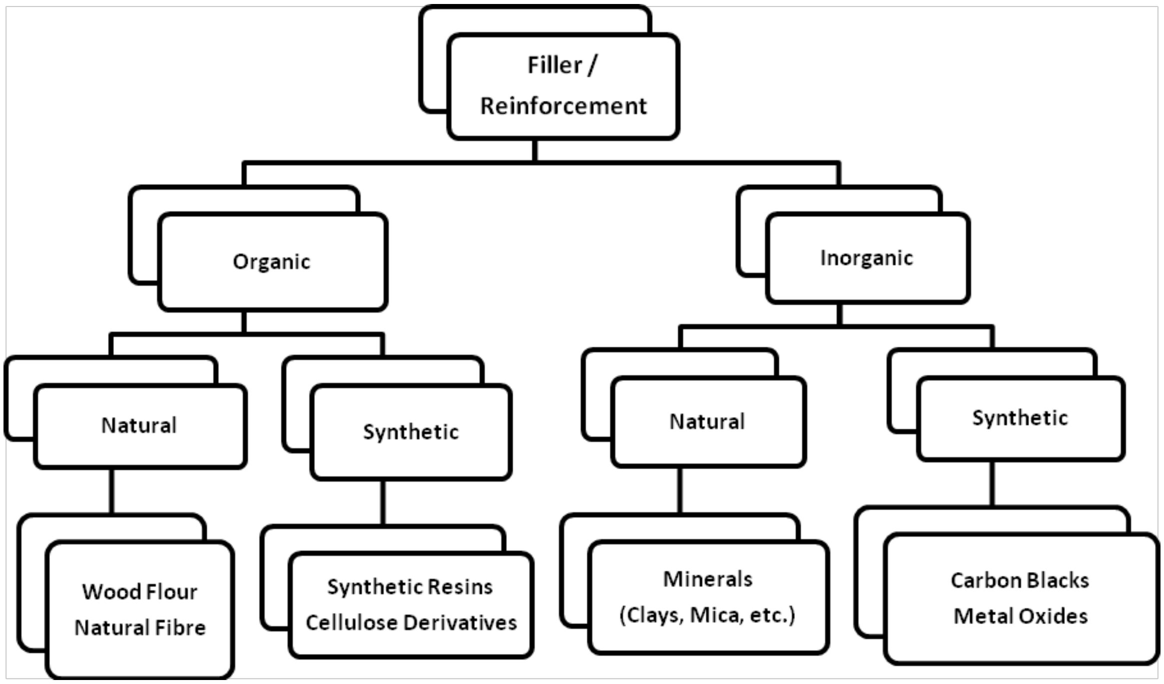


Figure 2.10 : Classifications of fillers/reinforcements

2.4 Natural Fibres

2.4.1 Classification of Natural Fibres

Figure 2.11 shows the general classification of natural fibres and they are divided into three groups according to its origin; animal, vegetable, and mineral fibres (John & Thomas, 2008). Animal fibres consist largely of particular proteins. Instances are silk, hair and feathers. Vegetable fibres are generally comprised mainly of cellulose: often with lignin examples include cotton, linen, jute, flax, ramie, sisal, and hemp. Mineral fibres include asbestos, wollastonite and halloysite.

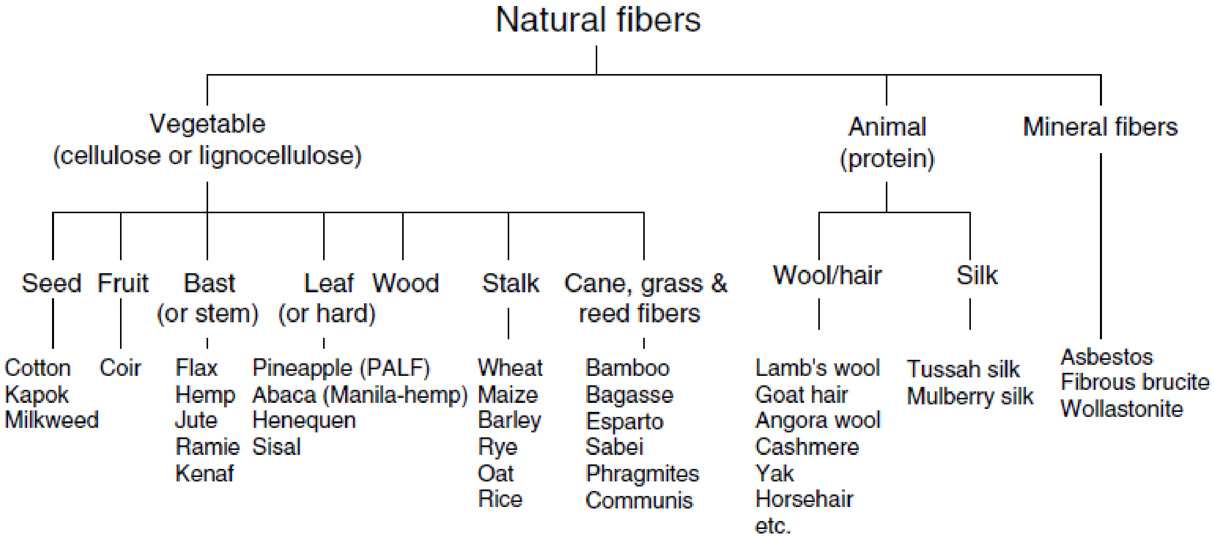


Figure 2.11: Classification of natural fibres (Bismarck et al., 2005)

2.4.2 Main Components of Natural Fibres

Natural fibres (vegetable fibres/plant fibres) consist of cellulose, hemicelluloses, lignin, pectin, wax and moisture. The main components of natural fibres are shown in

Figure 2.12. Each of plant components has different characteristic from one another. General characteristic of each natural fibres main component is shown in **Table 2.3**.

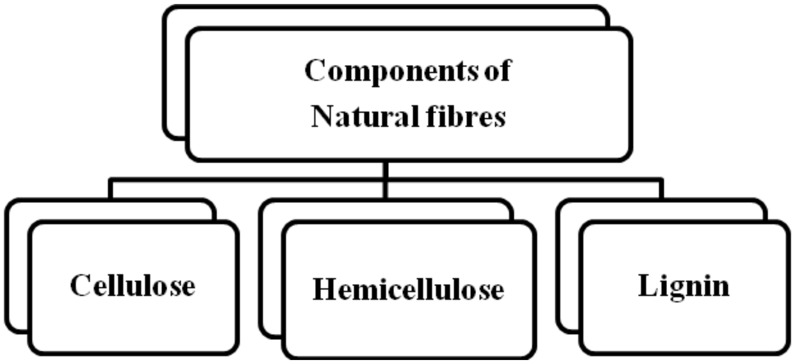


Figure 2.12 : Main components of natural fibres

Table 2.3 : General characteristic of each natural fibre components

Component	**Composition (%)**	**Material Behaviour**	**Hydrophilic/ Hydrophobic**
Cellulose	44-50	Crystalline	Hydrophilic
Lignin	20-25	Amorphous	Hydprophobic
Hemicellulose	20-30	Amorphous	Hydrophilic

The percentage of cellulose, lignin and hemicelluloses and other components in the natural fibres varied depends on the species, age, origin, and environment of cultivation. **Table 2.4** shows the composition of different natural fibres (Mohanty et al., 2000, Alvarez & Vázquez, 2009).

Table 2.4 : Composition of Different Natural Fibres

Natural Fibre	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pectin (%)	Wax (%)
Kenaf	31-39	15-19	21.5	-	-
Jute	61-71.5	12-13	13.6-20.4	0.2	0.5
Flax	71	2.2	18.6-20.6	2.3	1.7
Sisal	67-68	8-11	10-14.2	10	2
Hemp	70.2-74.4	3.7-5.7	17.9-22.4	0.9	0.8
Ramie	68.6-76.2	0.6-0.7	13.1-16.7	1.9	0.3
Henequen	77.6	13.1	4-8	-	-
Cotton	82.7	-	5.7	-	0.6

2.4.2.1 Cellulose

Cellulose is the main component of the cell wall and is one of the few natural compounds that maintain the same structure regardless of its source is wood, flax, hemp or other plants. Cellulose is made up from glucose units built into a long un-branched linear polymer. The simplicity of cellulose structure made the molecules easily packed into crystalline regions (Erik , 2007). The function of cellulose is to impart strength and rigidity to plants (Wong & Shanks, 2009). **Figure 2.13** shows the structure of cellulose.

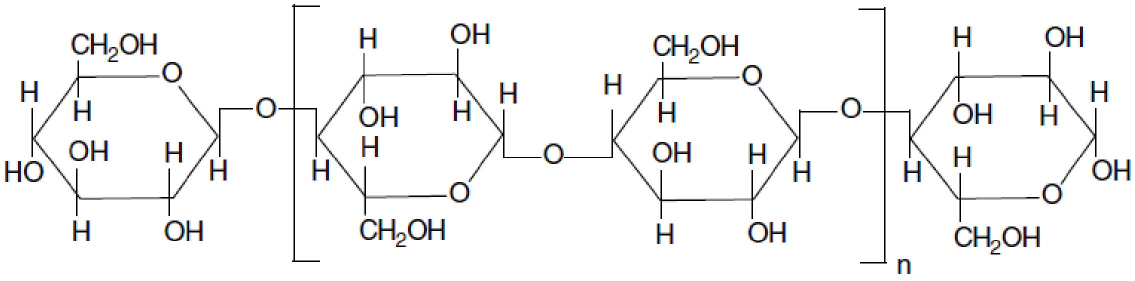


Figure 2.13 : Structure of cellulose (Mohanty et al.,2005)

2.4.2.2 Lignin

Lignin is a component that acts as a structural support material in plants by binding the other components together. Lignin is found between cellulose and hemicelluloses and on the walls of cells. In addition to providing support and structure, lignin also helps its parent plant to channel water to the entire part of the plant. The more lignin a plant has, the woodier it becomes; lignin provides the shape and form of stalks, twigs, and tree trunks. The exact chemical structure of lignin has not been established, but it is found that lignin contains high carbon and low hydrogen content. This suggests that lignin is highly unsaturated or aromatic in nature. The possible structure of lignin is shown in **Figure 2.14**.

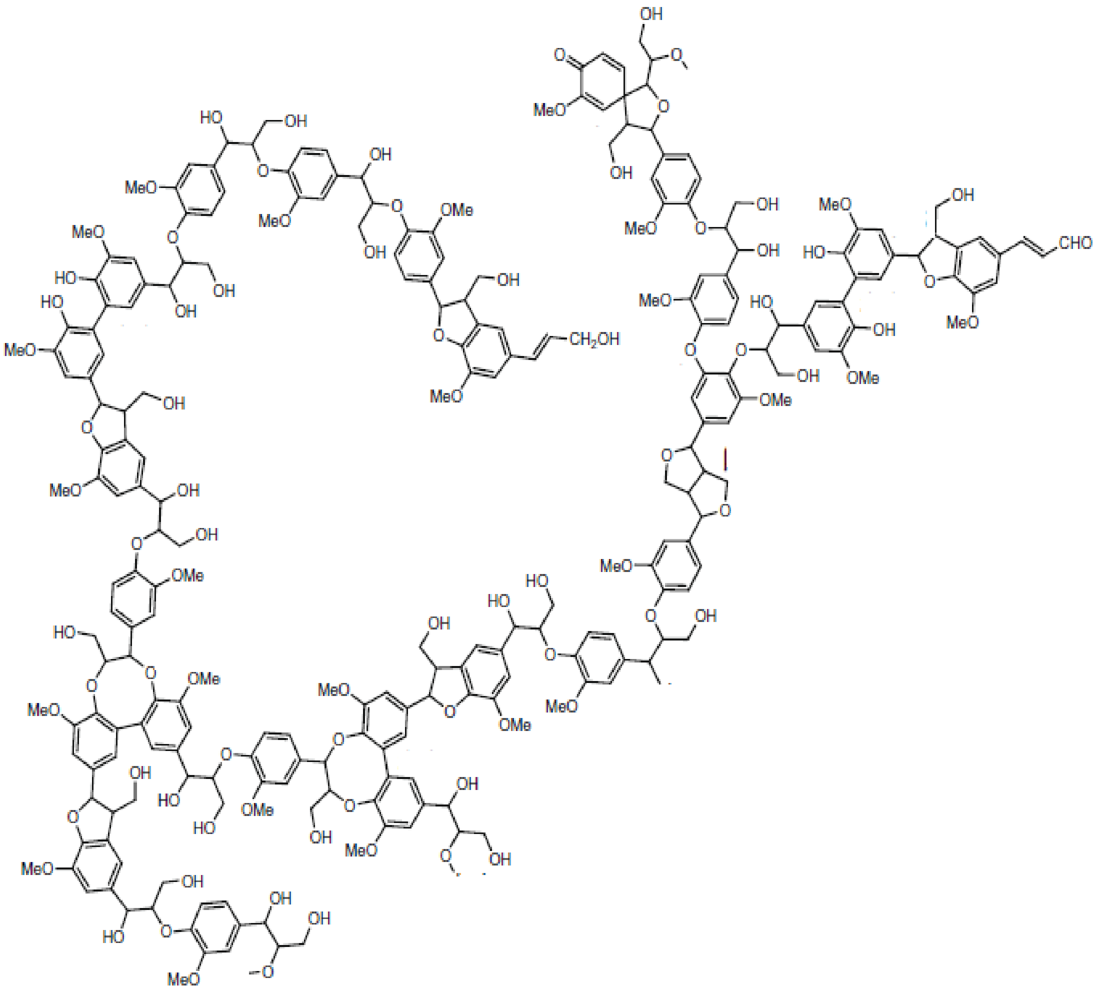


Figure 2.14 : Possible structure of lignin (Chen & Sarkanen, 2010)

2.4.2.3 Hemicellulose

Figure 2.15 shows a structure of hemicelluloses. Hemicellulose is an amorphous substance and consists of short chained isotropic polysaccharides. Hemicellulose is not a form of cellulose as the name would suggest (Wong & Shanks, 2009). Hemicellulose contains several monomers in the form of sugar units such as glucose, manose, xylose, galactose and arabinose and glicuronic acid. The monomers structure is shown in **Figure 2.16**.

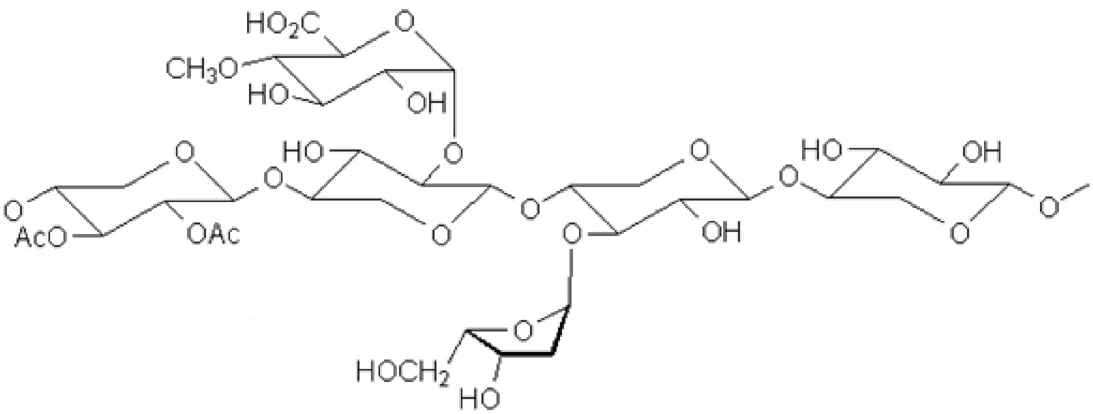
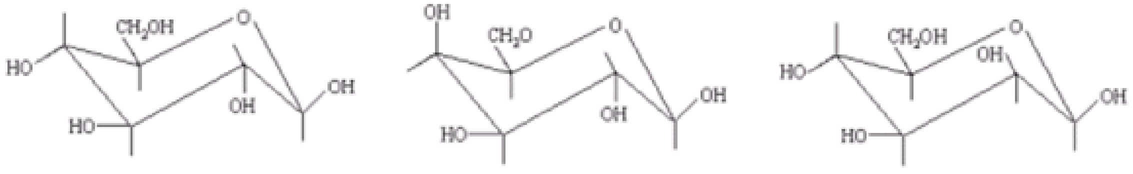
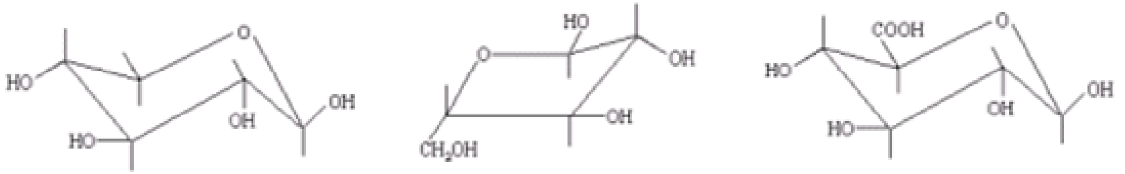


Figure 2.15 : Structure of Hemicellulose



Glucose **Galactose** **Manose**



Xilose **Arabinose** **Glicuronic Acid**

Figure 2.16 : Monomers of Hemicellulose

2.4.3 Disadvantages of natural fibres

The biggest problem with the use of natural fibres as filler or reinforcement in the polymer composite system is the incompatibilities between the matrix and the natural fibres (Kim et al., 2007; Hong et al., 2008). The incompatibility of the fibres and the matrix leads to the formation of a weak interface which results in poor mechanical properties of the composites (Habibi et al., 2008). The weak interactions between the fibre and the matrix lead to inferior mechanical properties due to the inefficient stress transfer from the matrix to the fibres (Wong & Shanks, 2009). Another problem associated with natural fibers is hydrophilic properties that cause it to absorb moisture from the environment. Moisture absorbing properties are not only contributing to the low mechanical properties, but it also causes dimensional instability that can cause failure during service cycle. Moisture absorbing properties are caused by the existence of many hydroxyl groups on the surface of natural fibers that enable it to make hydrogen bonds with water molecules.

2.4.4 Chemical Modifications/Chemical Treatments

Suitable selection of chemical treatments and compatibilizers are needed to improve the interaction and adhesion between the fibre and matrix phases. Many researchers have reported studies on chemical modifications/chemical treatments (Gassan & Bledzki, 1999; Li et al., 2007; Hong et al., 2008; Annie et al., 2008; Liu et al., 2009) and the use of compatibilisers (Othman et al., 2006; Salmah & Ismail, 2008; Santos et al., 2009) to improve the interaction between the matrix and natural fibres. Some chemical modification or chemical treatment could lead to less water absorption by the natural fibre reinforced composites (Abdul Khalil et al., 1997). The most popular chemical modifications are the use of compatibilizer, treatment with silane and acetylation (Liu et al., 2008; Durmuş et al., 2007; Kim et al., 2007; Xie et al., 2010)

2.4.4.1 Compatibilisers

The use of compatibilizers to improve the matrix-fibre interactions have been studied widely by a number of researchers (Kim et al., 2007; Lei et al., 2007; Ara**ú**jo et al., 2008; Li et al., 2007). Kim et al. (2007) has reported the use of maleic anhydride-grafted polypropylene (MAPP) significantly improved the properties of bio-flour-filled polypropylene composites. The use of maleic anhydride polyethylene (MAPE) as a compatibilizer has been reported by Liu et al. (Liu et al., 2008). Durmus et al. (2007) in their report, has studied the use of oxidized polyethylene as a compatibilizer to improve the interaction between the matrix and the filler.

2.4.4.2 Acetylation

Acetylation of natural fibres has been an active area of study to improve the resistance to moisture absorption of natural fibres (Li et al., 2007). Acetylation process replaces the hydroxyl groups of the natural fibres with acetyl group (Abdul Khalil et al., 1997). Acetic anhydride reacts with hydroxyl groups in the natural fibre cell wall to yield an acetylated fibre (Niska & Sain, 2008). Luz et al. (2008) in their work had reported the decreased of OH groups and the appearance of acetyl group when the natural fibre was modified with acetic anhydride. Tensile strength and tensile modulus of acetylated fibre were found to be greater than the unmodified fibre due to better resin wetting. Strong interface was observed between the acetylated fibres and the matrix as compared to the unmodified fibres system (Wong & Shanks, 2009). The schematic reaction of natural fibre acetylation is shown in **Figure 2.17.**

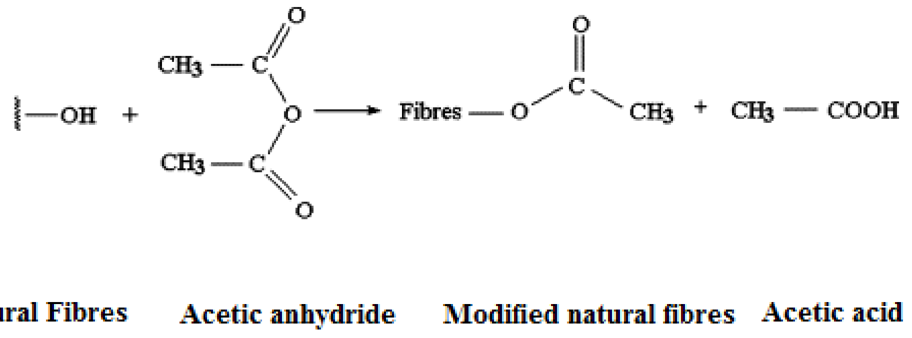


Figure 2.17 : Chemical reaction of acetic anhydride modification of natural fibres

2.4.4.3 Silane Treatment

Silanes are categorised as organic-inorganic coupling agent and were primarily introduced to the glass fibre-reinforced composites to improve the interfacial adhesion of the composites. However, they have been found also to be effective with natural fibres reinforced composites (Hong et al., 2008; Li et al., 2007). There are various types of silane coupling agents as shown in **Table 2.5**. Among all of the silanes used, aminosilane, especially ɣ-aminopropyltrimethoxysilane (ɣ-APS) have been widely used (Xie et al., 2010).

Table 2.5 : Various types of silane coupling agents (Xie et al., 2010)

Classification	**Main target Resin**
Aminosilane	Epoxy, Polyethylene, Butyl rubber
Vinylsilane	Polyethylene, Polypropylene, Polyacrylate
Mercaptosilane	Natural rubber
Methacrylsilane	Polyethylene, Polyester
Acryloxy	Polyester
Epoxysilane	Epoxy

In the presence of water, hydrolysable alkoxy group leads to the formation of silanol group. The silanol groups then reacts with the hydroxyl groups of the fibre, forming steady covalent bonds to the cell wall that are chemisorbed onto the fibres surface (Li et al., 2007). The schematic reaction between the fibres, silane and matrix is shown in **Figure 2.18**.