# DEVELOPMENT OF UNSATURATED POLYESTER HYBRID COMPOSITES FILLED WITH EMPTY FRUIT BUNCH AND OIL PALM ASH

**NOORUL LINDA SURAYA BTE MUSTAHIL**

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**by**


## NOORUL LINDA SURAYA BTE MUSTAHIL


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## LIST OF ABBREVIATIONS

| | |
|---|---|
| ANOVA | Analysis of Variance |
| ASTM | American Society for Testing and Materials |
| DP | Degree of Polymerization |
| DTG | Derivative Thermogravimetric Analysis |
| EDX | Energy Dispersive X-ray |
| FT-IR | Fourier Transform Infra-Red |
| LVL | Laminated Veneer Lumber |
| MEKP | Methyl Ethyl Ketone Peroxide |
| OPA | Oil Palm Ash |
| OPEFB | Oil Palm Empty Fruit Bunch |
| PE | Polyethylene |
| PP | Polypropylene |
| SADT | Self Accelerating Decomposition Temperature |
| SEM | Scanning Electron Microscopy |
| TGA | Thermogravimetric Analysis |
| UV | Ultraviolet |
| XRD | X-Ray Diffraction |

# LIST OF SYMBOLS

| | |
|---|---|
| A | Area |
| Cr | Crystallinity |
| D | Diameter |
| H | Hour |
| W | Weight |
| GPa | Giga Pascal |
| kPa | Kilo Pascal |
| MPa | Mega Pascal |
| KBr | Potassium Bromide |
| $g/cm^3$ | Gram per cubic centimeter |
| g/ml | Gram per milliliter |
| $kJ/m^2$ | Kilojoule per square metre |
| $m^2/g$ | Meter square per gram |
| $cm^{-1}$ | Reciprocal centimeter |
| θ | Theta |
| ° | Degree |
| cP | Centipoise |

| | |
|---|---|
| Wt% | Weight percent |
| % | Percent |
| °C | Degree celcius |
| α | Significance level in ANOVA |
| m | Meter |
| µm | Micrometer |
| mm | Millimeter |
| ß | Beta |
| ρ | Density |

**PEMBANGUNAN KOMPOSIT HIBRID POLIESTER TAK TEPU TERISI DENGAN TANDAN KOSONG BUAH KELAPA SAWIT DAN ABU KELAPA SAWIT**


## ABSTRAK

Tandan kosong buah kelapa sawit dan abu kelapa sawit dilaporkan sebagai antara sisa kelapa sawit yang banyak dibuang. Kerja penyelidikan ini bertujuan untuk membangunkan komposit hibrid poliester tak tepu terisi dengan pengisi OPEFB dan OPA yang bertindak sebagai alternatif yang berdaya maju kepada komposit polimer sedia ada. Kelebihan komposit hibrid adalah salah satu jenis penguat / pengisi terlibat boleh melengkapkan dengan apa yang kurang dalam penguat / pengisi lain. Dalam kajian ini, OPEFB dan OPA pengisi telah dicampurkan bersama ke dalam resin poliester tak tepu dengan berbeza nisbah pengisi OPEFB kepada OPA (0:100, 20:80, 40:60, 60:40, 80:20 and 100:0) dan berbeza saiz pengisi (60 jaringan, 100 jaringan and 200 jaringan). Sifat-sifat kedua-dua pengisi pada mulanya dicirikan oleh spektroskopi inframerah (FT-IR), analisis taburan saiz zarah, serakan tenaga X-ray spektroskopi (EDX), X-ray pembelauan sinar (XRD), termo analisis gravimetrik (TGA) dan mikroskop elektron pengimbas (SEM). Komposit hibrid poliester tak tepu terisi dengan OPEFB dan OPA telah ditekan sejuk dan keras di bawah suhu bilik dengan penambahan metil etil keton peroksida (MEKP) sebagai ejen pengeras. Sifat-sifat fizikal, mekanikal, haba, morfologi dan dipercepatkan cuaca kemudiannya dianalisa. Sifat-sifat fizikal komposit menunjukkan bahawa penggabungan silika dalam OPA pengisi membantu dalam pemadatan antara pengisi dan resin, oleh itu, meningkatkan ketumpatan dan mengurangkan ruang kosong pada komposit yang terhasil. Komposit dengan lebih nisbah OPEFB kepada OPA menunjukkan peratusan

tertinggi penyerapan air kerana sifat hidrofilik bahan selulosanya. Keputusan yang diperolehi juga menunjukkan bahawa saiz dan nisbah pengisi yang berbeza memberikan kesan penting terhadap sifat mekanik komposit hibrid pengisi yang dihasilkan. Tegangan, pembengkokan dan impak sifat-sifat komposit meningkat dengan ketara dengan saiz pengisi yang lebih kecil dan kebanyakannya dengan penggabungan 20:80 dan 40:60 daripada nisbah pengisi OPEFB kepada OPA. SEM mikrograf menunjukkan pengisi terbenam kukuh dengan resin menjelaskan sebab kekuatan impak tinggi bagi 200 jaringan dengan (40:60) nisbah pengisi OPEFB kepada OPA komposit poliester tak tepu. Sifat haba komposit dengan lebih nisbah OPA memperlihatkan kestabilan haba yang lebih baik dan suhu degradasi tinggi berbanding komposit dengan lebih nisbah OPEFB. Ikatan yang kuat dan interaksi yang baik antara pengisi OPEFB dan OPA terutama pada saiz pengisi yang lebih kecil membantu melambatkan penguraian komposit ketika proses pembakaran. Sifat dipercepatkan cuaca komposit hibrid terisi OPEFB dan OPA mempamerkan kurang perubahan terhadap sifat-sifat mekanik komposit kecuali pada lebih nisbah OPEFB. Ia mungkin disebabkan oleh degradasi selulosa selepas terdedah kepada UV dan penembusan kelembapan dalam takung cuaca. Penemuan ini mencadangkan bahawa penghibridan dengan nisbah pengisi OPEFB dan OPA yang betul boleh membawa kepada sifat fizikal, mekanikal, haba dan cuaca komposit hibrid yang lebih baik.

# DEVELOPMENT OF UNSATURATED POLYESTER HYBRID COMPOSITES FILLED WITH EMPTY FRUIT BUNCH AND OIL PALM ASH

## ABSTRACT

Oil Palm Empty Fruit Bunch (OPEFB) and Oil Palm Ash (OPA) were reported as among highly dumped oil palm waste. This research work aims to develop hybrid unsaturated polyester composites filled with OPEFB and OPA filler which emerges as a viable alternative to the existing polymer composites. Advantage of hybrid composite is one type of reinforcement/filler involved could complement with what are lacking in the other reinforcement/filler. In this study, OPEFB and OPA filler were mixed together into unsaturated polyester resin with different OPEFB to OPA filler ratio (0:100, 20:80, 40:60, 60:40, 80:20 and 100:0) and different filler sizes (60 mesh, 100 mesh and 200 mesh). The properties of both fillers were first characterized by Fourier Transform Infrared spectroscopy (FT-IR), particle size distribution analysis, Energy Dispersive X-Ray spectroscopy (EDX), X-Ray Diffraction (XRD), Thermo Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). The hybrid unsaturated polyester composites filled with OPEFB and OPA were cold pressed and cured under room temperature with the addition of methyl ethyl ketone peroxide (MEKP) as a curing agent. The physical, mechanical, thermal, morphological and accelerated weathering properties were then analyzed. Physical properties of composites showed that the incorporation of silica in OPA filler help in compaction between filler and resin, thus, increased the density and reduced the void content of composites produced. Composite with more OPEFB to OPA ratio showed highest percentage of water absorption due to the hydrophilic nature of its cellulosic materials. The results obtained also showed that different filler size and filler ratio gives a significant effect towards mechanical properties of hybrid filled composites produced. Tensile, flexural and impact properties of composites significantly improved with smaller size of fillers and mostly with incorporation of 20:80 and 40:60 of OPEFB to OPA filler ratio. The SEM micrograph showed strong embedded fillers with resin explained the reason of high impact strength of 200 mesh size with (40:60) OPEFB to OPA filler ratio unsaturated polyester composite. Thermal properties of composites with more OPA ratio showed better thermal stability and high degradation temperature as compared to composites with more OPEFB ratio. Strong bonding and good interaction between OPEFB and OPA fillers especially in a smaller size filler helps in delaying the decomposition of composites in burning process. Accelerated weathering properties of hybrid filled of OPEFB and OPA composites exhibited less change towards mechanical properties except for composites with more OPEFB ratio. It might be due to the degradation of cellulose after exposed to UV and moisture penetration in weathering chamber. This finding suggests that with better hybridization ratio of OPEFB and OPA filler can lead to better physical, mechanical, thermal and weathering properties of hybrid composites produced.

# CHAPTER 1

# INTRODUCTION

## 1.1 General Background

Environmental issues such as pollution, climate change, global warming, deforestation, industrial waste and etc, are no more a blame game and a small issues. Rapid modernization technologies which starting from household demand tills the engineering and manufacturing industry led to major environmental issues. The environment has suffered tremendously since the advent of industrialization. Mass production and the rise of factories with abundant dump waste led to the wide ranging of environmental damaged. With numerous environmental consequences, people began to realized and adopt a number of sustainability trends to overcome the effects of this industrialization.

Solid wastes are growing in volume and toxicity. There are numerous solid wastes in this entire world which includes landfills, incinerators and etc. Solid wastes nowadays are different from wastes in past few decades. In this modern era, wastes contain more materials that non-degradable, synthetic and toxic. Oil palm mill also face huge challenge in order to manage their waste. According to Hassan and Abdu (2015), Malaysia is one of the largest producer of palm oil with around 41% of the total world supply in the year 2009– 2010. This rapid production and exportation subsequently leading annually to millions of tonnes of oil palm wastes.

Wastes minimization, wastes processing and wastes recycling are among the ultimate goal of waste management. For each bunch of the fresh palm fruit, approximately 21% of palm oil, 6-7% of palm kernels, 14-15% of palm fibers, 6-7% of palm shells and 23% of empty fruit bunches can be obtained (Rahman et al., 2014). Oil palm industry in Malaysia has generated an average of 53 million tonnes of yield every year and every 1 kg of palm oil produced would yield approximately 4 kg of dry oil palm biomass. This amount is anticipated to rise annually and estimated will be risen to 100 million dry tonnes of solid biomass by the year 2020 (Umar et al., 2014).

Previous researchers stated that in the early cultivation, it was a common practice to dispose oil palm waste by uncontrolled tipping or dumping, an operation which waste is spread over the estates ground or tipped to fill in low economic value open dumps without taking care of the surrounding environment nor considering any precautions to compact and prohibit the spreading of contaminants into the underlying waterways (Ismail et al., 2015). However presently, palm oil industry has utilized the left-over yield to generate energy and electricity. The left over yields are collected at palm oil processing plants and burned at 800-1000 °C (Ooi et al., 2014). This energy generation sufficient to provide the energy required for a palm processing plant that uses around 750kWh of energy and can help to reduce the use of fossil fuels (Foo and Hameed, 2009).

## 1.2 Problem Statement

Researchers have investigated many researches in utilizing back the oil palm wastes and to date, there are so many researches invented focusing on the value added of it. Oil Palm Empty Fruit Bunch (OPEFB) and Oil Palm Ash (OPA) are among the main oil palm wastes which suitable to be used as reinforcement or filler in polymer composites (Hassan et al., 2010). A review from Mohammed et al. (2015) stated that OPEFB fiber can be used as reinforcement with synthetic polymers as well as biodegradable or bioresin including thermoplastics and thermosets. Industries have been established to tailor the OPEFB fiber composites mostly in conventional composites such as medium density board. For OPA on other hand, Bhat and Abdul Khalil (2011) explored the utilization of OPA in polypropylene composites. The incorporation of OPA increased the impact strength as compared to polypropylene alone.

Most work on hybrid composites reported either consisting both mineral fillers (Sudheera et al., 2014), one natural filler comprising with one synthetic fibers (Zhang et al., 2011) or both mineral fillers but only based in thermoplastic resin (Leong et al., 2004). Various studies were done on the reinforcement of thermoplastic resin matrix such as low-density polyethylene (LDPE) with carbon black and OPEFB (Choh et al., 2016), polyamide66 (PA66) and polytetrafluoroethylene (PTFE) with mineral fillers such as silicon carbide (SiC) and alumina (Rudresh et al., 2016).

However, there are lack of research focusing on OPEFB and OPA as filler in thermoset resin especially in unsaturated polyester resin. Several attempts of OPEFB reinforced/filled polymer composites are having low water resistant due to the hydrophilic properties of OPEFB cellulosic nature (Hassan et al., 2010). On the other hand, some of OPA filled polymer composites also have some drawbacks in terms of brittleness and according to Ibrahim et al. (2012), OPA fillers incorporated with unsaturated polyester resin have lower elasticity and the brittleness of composites produced led to lower tensile strength.

Hence, this research work aims to develop a good performance of hybrid unsaturated polyester composites filled OPEFB and OPA. Hybrid is defined as two or more components which one component can compliment with what is lacking in another one to form a good combination product (Saba et al., 2016). In this research, a combination of OPEFB and OPA filler in an unsaturated polyester resin could give added advantages towards the properties of composite produced. Besides, this research will maximize the utilization of oil palm waste and promising cleaner environment.

## 1.3 Objectives

The main objectives of this research are as follow:

- To produce and characterize the potential of OPEFB and OPA as a filler in hybrid composites.

- To study the effect of different filler ratios of OPEFB and OPA towards the physical, mechanical, thermal, morphological and weathering properties of OPEFB and OPA filled unsaturated polyester hybrid composites.

- To evaluate the effect of various sizes of OPEFB and OPA as filler towards the physical, mechanical, thermal, morphological and weathering properties of OPEFB and OPA filled unsaturated polyester hybrid composites.

## 1.4 Organization of thesis

This thesis has been divided into 5 respective chapters:

Chapter 1: Introduction; provides a brief overview on research background, problem statement and objectives of research.

Chapter 2: Literature review; focused on literature surveys of past research on polymer bicomposites, OPEFB and OPA fundamental studies, hybrid filler and hybrid biocomposites.

Chapter 3: Materials and methods; explain on materials used for this research and experimental method of processing technique used to analyze the characterization of OPEFB and OPA fillers, technique of biocomposites production and also standard method used in testing and analysis of hybrid biocomposites.

Chapter 4: Results and discussion; provide the outcome of research such as the characterization and analysis of OPEFB and OPA fillers, physical, mechanical, thermal, morphological and weathering properties of hybrid unsaturated polyester composites filled OPEFB and OPA.

Chapter 5: Conclusions and recommendation; summarize of overall conclusions and recommendation for future work of this research.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Natural Fiber/Filler Polymer Composites

Natural fiber/filler polymer composites are now inevitable in development of many 'green' and sustainable industry such as automotive, manufacturing and construction industry. Researchers over the globe are seriously looking at natural fibres as alternatives to replace synthetic fibres/fillers. Natural fiber/filler polymer composites are defined as biocomposite materials when one of its phases either matrix (polymer) or reinforcement (fiber/filler) comes from natural source (Abdul Khalil et al., 2015; Azman et al., 2010).

The individual materials that build up composites are called constituents. Most composites have two constituent materials: a binder or matrix, and reinforcement. The reinforcement is usually much stronger and stiffer than the matrix, and gives the composite its good properties (Jawaid and Abdul Khalil, 2011). The matrix holds the reinforcements in an orderly pattern. The reinforcements are usually discontinuous, thus, the matrix also helps to transfer load among the reinforcements (Rijswik et al., 2001). Continuous attention on this natural composites either in research field or industrial sector are merely because of the good properties and superior advantages of natural fibers/fillers over synthetic fibers/fillers in term of its comparable mechanical and physical properties, low cost, less abrasive, and many more advantages (Abdul Khalil et al., 2012a).

## 2.2 Constituents of Composites

Composites are combinations of materials differing in composition, where the individual constituents retain their separate identities. These separate constituents act together to give the necessary mechanical strength or stiffness to the composite part. Composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk properties significantly different from those of any of the constituents. Matrix phase is the primary phase having a continuous character (Satyanarayana et.al, 2009). Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. Dispersed (reinforcing) phase is embedded in the matrix in a discontinuous form as secondary phase. Dispersed phase is usually stronger than the matrix, therefore, it is sometimes called reinforcing phase.

### 2.2.1 Thermoset-based matrix (Unsaturated polyester resin)

Matrix is a main component in polymer composites systems which act as a glue to hold the fibres/fillers together. It is divided into two major groups known as thermoplastic and thermoset resin (Abdul Khalil and Rozman, 2004). According to Li and Strachan, (2015), polymers properties depend on the chemistry of their constituent monomers and how these monomers combine with each other into the polymer architecture or molecular structure. Important classes include linear chain, branched, and networked polymers. Thermoplastic resins become soft when heated, and may be shaped or molded while in a heated semi-fluid state and become rigid when cooled. They are often supplied as granules and heated to permit fabrication by methods such as molding or extrusion (Pascault et al., 2002). Thermoset resins, on the other hand, are material that hardens when heated and cannot be remolded and it usually liquids in their initial form. Thermoset resins are normally cured by the use of catalyst, heat or a combination of the two (Bobade et al., 2016).

In thermoset polymers, the liquid resins are converted into hard brittle solids by chemical cross-linking which leads to the formation of a tightly bound three-dimensional network of polymer chains. The main characteristic that distinguishes thermoset is the irreversibility of the solidification process that takes place as a result of chemical reaction. This chemical reaction is typically polymerization reaction that leads to a macroscopic network molecule. The starting point is a group of small molecules in the liquid state. These small molecules start reacting with each other step by step, forming increasingly larger molecules that branch out like a tree. Eventually the branches of different 'trees' start merging with each other, forming a network or 'cross linked' structure. Ultimately, all the 'trees' end up linked into one giant network (Dholakiya, 2012). The polymer thus formed will have a permanent shape defined by the shape of the container at the time the network was formed. This polymer is insoluble as a result of its three-dimensional network structure (Hale, 2002).

Unsaturated polyester resin is a thermoset capable of being cured from a liquid to a solid state when subjected to appropriate conditions. According to Dholakiya (2012), unsaturated polyester resins have been used remarkably since 1930 for wide range of applications. A whole range of polyesters is made from different acids, glycols and monomers, all having varying properties. There are two types of polyester resins used as a standard laminating system in the composites industry (Bobade et al., 2016). Orthophtalic polyester resin is the standard economic resin is now becoming the preferred material in the marine industry, where its superior water resistance is desirable (Ray and Rout, 2005). An idealized chemical structure of unsaturated polyester is shown in Figure 2.1.

Unsaturated polyesters are extremely versatile in properties and applications and have been popular thermoset used as the polymer matrix in composites. They are widely produced industrially as they possess many advantages compared to other thermosetting resins including room temperature cure capability, good mechanical properties and transparency. Curing of unsaturated polyester is due to a polymerization reaction that causes cross linking among individual linear polymer chains. In contrast to other thermosetting resins, no by-product is formed during the curing reaction; hence resins can be molded and laminated at low pressure and temperature (Kargarzadeh et al., 2015; Aziz et al., 2005).

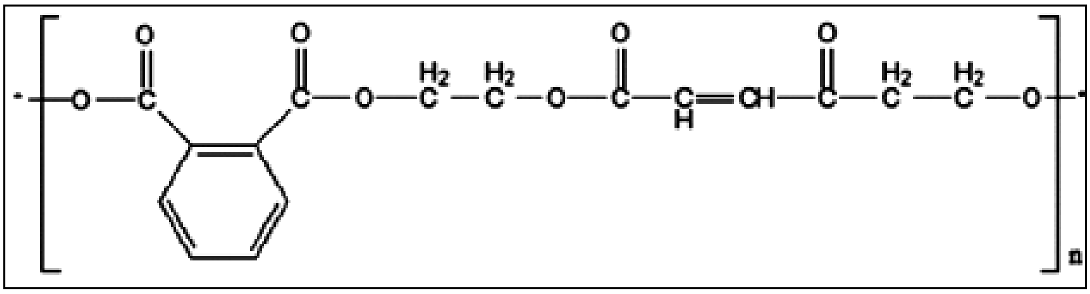

**Figure 2.1**: Idealized chemical structure of a typical unsaturated polyester resin (Kargarzadeh et al., 2015)

### 2.2.2 Reinforcement (Filler and characteristics of biofiller)

Filler particles can be defined as variety of solid organic or inorganic particulate materials which physically could be in irregular, circular, fibrous or plate-like in shape. It is commonly used in reasonably high volume loadings in plastics and according to Knock and Glenn, (1951), fillers were first added to resins in the early 1950's and act as enhancer properties of plastic materials. Filler particles used in polymer composites mainly due to few properties advantages of it such as behave isotropically as compared to long fibers, improved strength, decrease thermal expansion, reduce the water absorption and minimise polymerisation shrinkage in composites (Abdul Khalil et al., 2015). Besides, fillers have been used extensively because of few advantages such as easy processibility (simple mixing and dispersion process), higher possibility in modify its appearance (opacity, color and texture) and also easier to control and alter density of composites if it is in filler form rather than long fiber form (Gonzalez et al., 2002). However, the level of improvement or changing depends significantly upon type, size and shape, composition and surface of the fillers (Tebtiang & Venables, 1999).

Filled particulate composites consist of a matrix reinforced by a dispersed phase in form of filler particles. Filler particles reinforcement could be by ceramics, metallic or other particles of different sizes and shapes (Mishnaevsky, 2007). In last few decades, various kind of fillers have been used in plastic industries and the most commonly fillers used are calcium carbonate, mica, metal oxide, talc, magnesium carbonate, titanium dioxide and etc. Previous literature from few researchers on mineral fillers showed various properties of composites produced. Patnaik et al. (2009) studied on a comparative analysis of aluminum oxide ($Al_2O_3$) and silicon carbide (SiC) particles as filler materials in glass fiber polyester composites and found that the flexural properties, interlaminar shear strength, density and hardness were affected towards different types of mineral fillers used. Vincent et al. (2014) reported the addition of calcium carbonate/mica fillers resulted in higher tensile modulus compared to calcium carbonate/talc fillers in polypropylene composites.

Growing researches currently focus and directed more interest on the utilization of agricultural wastes as a substitution of fillers in composites industry. Utilization of different plants or their residues as filler in a synthetic polymer matrix has been a successful way to produce a new biocomposites filled with good and comparable various properties as mineral filled composites (Dungani et al., 2014). The natural agricultural waste and oil palm filler composites have several advantages in comparison with mineral fillers, including their low cost, low density, biodegradability and availability, ease of implementation and their specific properties (Abdul Khalil et al., 2012a). In addition, their high cellulose component makes them more biodegradable and recyclable.

According to Ewulonu and Igwe (2012), OPEFB filler loading was found to significantly improve the tensile properties of composites. Furthermore, the hardness of the composites was found to increase with increase in OPEFB loadings, and decrease in filler size. Hong et al. (2010) reported that carbon based fillers are good as conductive fillers due to its high thermal and electricity conductivity and also lower thermal expansion than metals. In other research on carbon black also stated that the addition of carbon black to polypropylene (PP) and polyethylene (PE) composites give an improvement in weathering resistance and also alter the dielectric properties of the composites (Dubey et al., 2014). Besides, Ooi et al., (2015) studied on potential of Oil Palm Ash (OPA) filler in natural rubber and found that OPA-filled natural rubber compounds showed better retention properties than unfilled natural rubber compound. Table 2.1 shows reported works on oil palm biomass as filler in biocomposites.

**Table 2.1**: Reported works on oil palm biomass as filler in biocomposites

| Biocomposites | References |
|---|---|
| Oil Palm Shell/Oil Palm Trunk Lumber | Dungani et al. (2013) |
| Oil Palm Ash/Epoxy | Abdul Khalil et al. (2013) |
| Oil Palm Empty Fruit Bunch/Polyethylene | Ewulonu and Igwe (2012) |
| Oil Palm Ash/Polyester | Ibrahim et al. (2012) |
| Oil Palm Ash/Polypropylene | Bhat and Khalil (2010) |
| Oil Palm Empty Fruit Bunch (carbon black)/Epoxy | Abdul Khalil et al. (2010b) |

## 2.3 Oil Palm Empty Fruit Bunch (OPEFB)

### 2.3.1 Availability, advantages and current trend

Oil palm industries generate abundant amount of biomass which in millions of tonnes per year (Rozman et al., 2005). The oil palm industry in Malaysia with its 6 million hectares of plantation produced over 11.9 million tonnes of oil and 100 million tonnes of biomass (Abdul Khalil et al., 2010c). Palm oil has now become the world largest source of edible oil with 38.5 million tonnes of the world total edible oils and fats production. Thus, oil palm has now become a major economic crop which triggered the expansion of plantation area in Malaysia and Indonesia.

Easy availability, abundantly available resource and futuristic road to ease the commercialization, a comprehensive review has been outlined on the research and development activities done to date on OPEFB fibers composite materials (Hassan et al., 2010). The sustainable, non-hazardous, non-carcinogenic, eco-friendly biodegradable product developed from these fibers will surely benefit the human kind across the globe in broad spectrum. In Malaysia, OPEFB is one of the biomass materials, which is a by-product from the palm oil industry, OPEFB are left behind after the fruit of the oil palm harvested for the oil refining process (Mohammed et al., 2015).

However, this 'waste' or by-product from the palm oil mills, which was once viewed as embarrassing liabilities are now viewed as co-products of increasing potential value due to continual effort of research and development on its applications. This will serve to promote a 'zero-waste' concept. OPEFB fibers have depicted a great potential in use as a reinforcing materials in a polymers. Numerous researches (Hassan et al., 2010) have been conducted over past decades related on

OPEFB in composite materials using different polymers such as polyester, polypropylene, poly (vinyl chloride) and polyurethane and phenol formaldehyde.

### 2.3.2 Properties of Oil Palm Empty Fruit Bunch (OPEFB)

The OPEFB is a good source of cellulose, hemicelluloses and lignin which are the main composition of lignocellulosic based polymer composites (Abdul Khalil et al., 2011b). The cell wall of lignocellulosic fibre (Figure 2.2) consists mainly of three layers which known as outer layer of the secondary wall (S1), main layer of the secondary wall (S2) and inner layer of the secondary wall (S3). The S2 layer is usually by far the thickest layer and dominates the properties of the fibres (Jayaraman, 2003; John and Thomas, 2008).

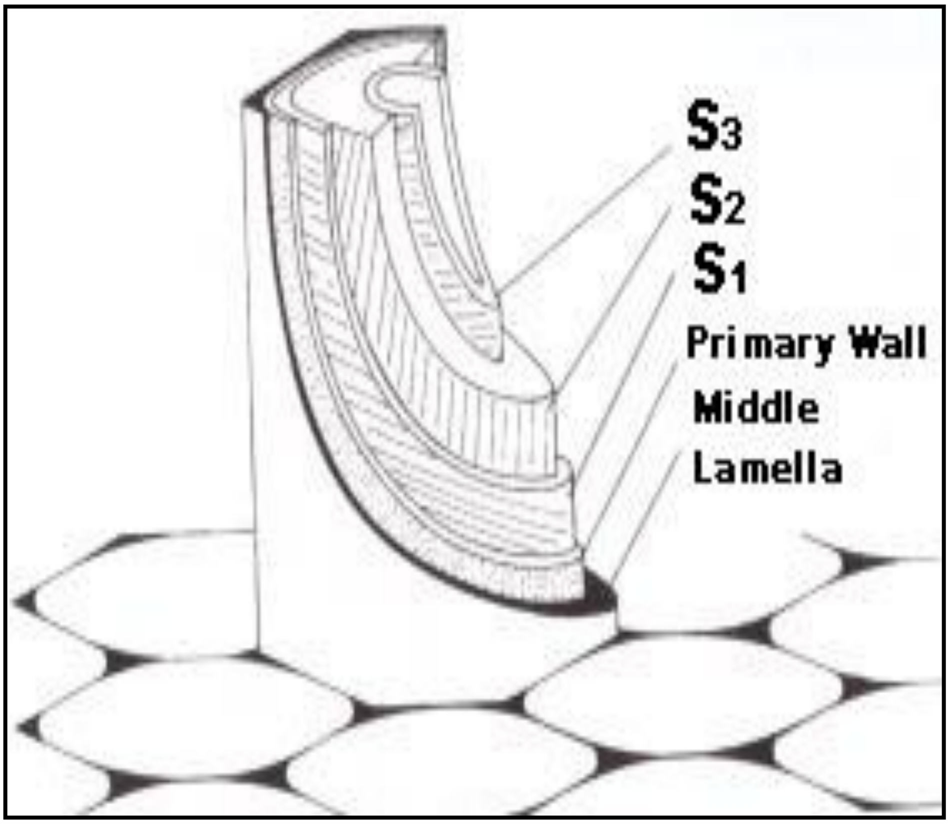


**Figure 2.2**: Cell wall structure of lignocellulosic fibres

(Khalil and Rozman, 2004)

Cell wall in all plant fibers contains cellulose, hemicellulose and lignin in varying amounts (Jayaraman, 2003). Cellulose attains its highest concentration in the S2 layer and according to John and Thomas (2008), the properties of fibres such as tensile strength, flexural strength and rigidity depends on the alignment of cellulose fibrils. The cellulosic fibrils run parallel to each other and form a crystalline structure in addition to some amorphous regions. The crystal and amorphous nature of OPEFB also contribute to major factor in determining the mechanical properties especially towards the modulus of composites produced. Abdul Khalil et al. (2006) reported that the OPEFB fibers are hard, tough and analogous as compared to other lignocellulosic fibers.

Aspect ratio of fibers which calculated as length per diameter has significant effect on final properties of composites. The OPEFB fibers are initially in the form of thread-like bundles and after processing physically it separate and available in long as well as in short length. Lengthwise, OPEFB fiber is between hardwood and softwood. Enhancement in aspect ratio by decreasing the diameter of the fiber could result in a better adhesion between fiber and matrix. Maintaining the fiber aspect ratio and geometry during processing of natural fiber polymer composite is vital. This is because the aspect ratio or the geometry of the fibers usually gets altered after undergo several process in producing a final composites (Joseph et al. 2005).

Chemical composition of fibers also plays an important role as its composition will affect the overall performance of the polymer composites produced. This chemical composition will contribute to not only mechanical properties of composites but somehow determined the water absorption behavior, thermal behavior and might also affect the durability of composites. Generally, the OPEFB fiber contains about 40–50% cellulose, 20–30% hemicellulose, and 20–30% lignin (Lani et al., 2014).

Cellulose is a natural polymer consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by β-1, 4-glycosidic linkage at C1 and C4 position. The degree of polymerization (DP) is around 10,000. Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose. Solid cellulose forms a microcrystalline structure with regions of high order, i.e. crystalline regions, and regions of low order, i.e. amorphous regions. Cellulose is resistant to strong alkali (17.5 wt %) but is easily hydrolyzed by acid to water-soluble sugars. Cellulose is relatively resistant to oxidizing agents (John and Thomas, 2008).

Hemicellulose differs from cellulose in three aspects. Firstly, they contain several different sugar units whereas cellulose contains only 1, 4-β-D-glucopyranose units. Secondly, they exhibit a considerable degree of chain branching containing pendant side groups giving rise to its non-crystalline nature, whereas cellulose is a linear polymer. Thirdly, DP of hemicellulose is around 50–300, whereas that of native cellulose is 10–100 times higher than that of hemicellulose. Hemicellulose forms the supportive matrix for cellulose microfibrils. Hemicellulose is very hydrophilic, soluble in alkali, and easily hydrolyzed in acids (John and Thomas, 2008). The term “holocellulose” is used to describe the total carbohydrate content of fibres. In addition to holocellulose, plants materials contain an amorphous, highly-polymerized substance called lignin (Chen, 2014).

Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents. They are totally insoluble in most solvents and cannot be broken down to monomeric units. Lignin is totally amorphous and hydrophobic in nature. It is the compound that gives rigidity to the plants. It is thought to be a complex, three-dimensional copolymer of aliphatic and aromatic constituents with very high molecular weight (John and Anandjiwala, 2008).

## 2.4 Oil Palm Ash (OPA)

### 2.4.1 Availability, advantages and current trend

Waste from palm oil industry has been increasing annually. Despite the alternative of generating energy and electricity by burning oil palm waste, oil palm ash (OPA) which is a by-product of it is still accumulating as a problematic dump waste. According to Zarina et al. (2013), the palm oil waste was produced 4 million tons/years in Malaysia only. Futhermore, oil palm ash is rarely used and it may add to the future environmental problems (Kroehong et al. 2011).

Realizing the serious environmental problem might occur in future, many researchers started to explore and study the potential of oil palm ash. The conversion of biowaste from palm oil to oil palm ash (OPA) is an alternative method to utilize this biowaste in a socio-economic way. A developing research by the invention of wide range of potential oil palm ash product has received stern encourages and considerations worldwide.

This abundantly available throwaway waste from the fired-boiler furnaces has currently emerged to be an ideal adsorbent in the wastewater treatment and also as air purifier in cleaning of atmosphere contaminants (Foo and Hameed, 2009). In addition as reported previously by Kroehong et al. (2011), oil palm ash has an excellent pozzolanic reaction and can be used as a supplementary material to produce high strength concrete. Increasing attention and researches in utilizing oil palm ash as reinforcement or filler in polymer composite also give a brighter future to face this throwaway waste (Abdul Khalil et al. 2012b). Incorporation of oil palm ash with polymer resin give a significant improvement towards strength, thermal and durability properties of polymer composites (Bhat and Abdul Khalil, 2011).

### 2.4.2 Properties of Oil Palm Ash (OPA)

Oil palm ash is characterized by a spongy and porous structure in nature, of which its main components are in the angular and irregular form,with a sizable fraction showing cellular textures (Bhat and Abdul Khalil, 2011).. The chemical elements of oil palm ash are found to be silicon dioxide, aluminium oxide, iron oxide, calcium oxide, magnesium oxide, sodium oxide, potassium oxide and sulfur trioxide (Foo and Hameed, 2009).

An essential observation is that the OPA contained a high weight percentage of silicon (Si), which was 25.43 wt%. Other elemental components included potassium, magnesium, calcium, chlorine and aluminium. Due to high weight percentages of oxygen (49.85 wt %), it can be assumed that silicon, magnesium, aluminium, calcium and potassium may exist in oxide form. Silica or silicon dioxide ($SiO_2$) is perhaps the most essential substance found in the OPA. Researchers report that OPA contains up to 40% silica. Silica is the name given to a group of minerals composed from two most abundant elements which is silicon and oxygen. It is commonly in the crystalline state and rarely in an amorphous state. It is composed of one atom of silicon and two atoms of oxygen resulting in the chemical formula $SiO_2$.

Beside silica, other chemical components detected were potassium oxide, calcium oxide, magnesium oxide and aluminium oxide (Abdul Khalil et al. 2011a).

## 2.5 Hybrid Reinforced/Filled Composites

Hybrid composites are defined as the system in which one kind of reinforcing material is incorporated in a mixture of different matrices, or two or more reinforcing and filling materials are present in a single matrix or both approaches are combined (Saba et al., 2014). Recently, different hybrid filled composites have been explored and studied by numerous researchers. Rudresh et al. (2016) presently studied on the hybrid effect of micro fillers on the mechanical behavior of polyamide66 and polytetrafluoroethylene blend. They reported the tensile strength, flexural strength and modulus were effectively improved due to the hybrid effect of micro fillers. Zhang et al. (2011) studied on polypropylene hybrid composites filled by wood flour and short glass fiber and they stated that the hybrid composites produced was superior to enhance the tensile, flexural, and impact properties of composites. They also reported that hybrid composites had an excellent moisture resistance and low water absorption.

The performance of hybrid composites is a weighed sum of the individual components. Even though natural filler composites have been established, but their potential for use in more widely applications still limited due to some decreasing in some properties even certain properties was improved. For that reason, studies on producing hybrid composites which are produced from a combination of several types of reinforcers with polymers will be useful in order to improve the physical and mechanical properties of composites. This is because each reinforcer has its own good characteristic which can cover other reinforcers defects (Babaei et al., 2014;

Saba et al., 2014). In other research, Sudheera et al. (2014) have studied on the enhanced mechanical and wear performance of epoxy/glass composites with potassium titanate whisker/graphite hybrid fillers and found that mechanical properties of epoxy/glass/ composites were improved with addition of small percentage of graphite as filler. Addition of potassium titanate whisker alone has deteriorated strength properties of epoxy/glass composites whereas in combination with graphite, strength properties considerably improved.

Previous researches reported few main factors that influenced the properties of hybrid composites such as size, shape, and distribution of filler particles in the polymer matrix (Safwan et al., 2013). Reduction in size of filler attributed to numerous unique characteristics such as greater surface area to volume ratio, more flexibility in surface functionalities and consequently resulted in superior mechanical performance of composites (Saba et al., 2014; Sreekanth et al., 2011). Safwan et al. (2013) mentioned that many previous researches were done between two different fillers which reinforced in thermoplastic resin. For instance, some worked on palm kernel shell and nanosilica in polypropylene (Safwan et al., 2013), wood flour and short glass fiber in polypropylene (Zhang et al., 2011) and mineral fillers in polypropylene (Leong et al., 2004). To date, so many researches on hybrid composites reported. However, so little work has been done on incorporating fillers which both are from natural agricultural and oil palm waste fillers in thermoset resin. Most work on hybrid composites reported either consisting both mineral fillers, one natural fillers another one synthetic fibers, both mineral fillers based in thermoplastic resin and etc. This limited research on hybrid filled composites initiate this research on development of hybrid OPEFB and OPA filled unsaturated polyester composite. Table 2.2 shows reported works on hybrid filled biocomposites.

**Table 2.2**: Reported works on hybrid filled biocomposites

| Biocomposites | References |
|---|---|
| Mineral fillers/ Polyamide | Rudresh et al. (2016) |
| Mineral fillers/Epoxy | Sudheera et al. (2014) |
| Palm kernel shell & nanosilica/Polypropylene | Safwan et al. (2013) |
| Wood flour & short glass/Polypropylene | Zhang et al. (2011) |
| Mineral Fillers/Polypropylene | Leong et al. (2004) |

## 2.6 Potential Applications

Impressive properties such as biodegradability and high specific properties of natural fillers and fibers gaining continuous interests from many kind of industries to substitute the usage of glass and man-made filler and fibers with this sustainability sources. Environmental awareness also leads to high rate of research and innovations on natural resources. In the past decades, composites materials have been utilized to solve technological problems for a long time and in the 1960s these materials start capturing the attention of industries with the introduction of biomass-based composites. Multiple applications of natural filler and fibre composites such as in automotive, packaging, sporting goods, furniture, home appliances, building construction, and medical equipment were developed (Figure 2.5) (Abdul Khalil et al., 2015; Kolybaba et al., 2003).

Oil palm biomass is seen as promising sustainable raw material for the manufacturing of natural fibre reinforced/filled composites for different applications. Earlier it was converted into yarn, string, ropes, floor mats, bags, floor and wall coverings, and different handicrafts industries and to date, there were so many advances applications that utilized oil palm biomass as a value added sources. Abundant wastes from palm oil plantation contributed to this evolution where most of researches explored more on this dump wastes problem by producing many prototypes that utilized back oil palm biomass. Oil palm biocomposite products are divided into conventional and advanced biocomposites. Various types of value-added products such as medium-density panels block board (Laemsak and Okuma, 2000), LVL (Noorbaini, 2009), mineral-bonded particleboard (Chew and Ong, 1985), plywood, chipboard (Sulaiman et al., 2008), thermoset and thermoplastic composites, nanobiocomposites (Abdul Khalil and Bhat, 2010a), and pulp and paper manufacturing (Shuit et al., 2009).

Palm oil mill processed ripe fruit bunches and then the fruits are removed and the fruits processed to extract edible industrial mesocarp and seed oil. The Oil Palm Empty Fruit Bunch (OPEFB) and Oil Palm Ash (OPA) and unusable residues from oil extraction are used as fuel. Most of them typically disposed in landfills. According to Abdul Khalil et al. (2015), there are many uses of potential value-added products made from oil palm biomass such as construction materials. The OPEFB can also be used as a major component of specialized construction materials. Significant research studies have been conducted on the development of new construction materials using OPEFB. For instance, the production of new plywood by layering between OPEFB and OPT has been developed. Other researchers such as Zaidon et al. (2007) and Deraman et al. (1999) studied mixing EFB and rubber wood into a particleboard. In recent years studies have been undertaken to utilize the considerable quantities of OPA as the value added resources from oil palm wastes. According to Zarina et al. (2013), OPA has potential applications as fire resistance panel or as fire resistant coatings. The OPA was also found has a suitable absorption capacity to remove dye from aqueous solutions (Darus et al., 2009). Besides, OPA also has been found to be a suitable replacement for up to 20% of Portland cement in concrete (Sata et al., 2004). Current growing researches on OPA in polymer composites could possibly open-up the road of more commercialization of this filler and thus, reduce the oil palm wastes problem.


**Figure 2.3**: Biocomposite products in various applications
(Abdul Khalil et al., 2015)