

**CHARACTERIZATION AND PROPERTIES OF
CARBOXYMETHYL CELLULOSES – OIL PALM
EMPTY FRUIT BUNCH HEMICELLULOSES
BLEND AND NANOCOMPOSITE FILMS**

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BLEND AND NANOCOMPOSITE FILMS**

by

NADHILAH BINTI MUHAMMAD RAZAK

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In the name of Allah, The Most Gracious and The Most Merciful.

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LIST OF ABBREVIATIONS

CMC	Carboymethyl Celluloses
DP	Degree of polymerization
DSC	Diffential scanning calorimetry
FT-IR	Fourier transform infrared spectroscopy
HCL	Hydrochloric acid
MW	Molecular weight
MMT	Montmorillonite
NaCl ₂	Sodium hypochlorite
OPEFB	Oil Palm Empty Fruit Bunch
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
WVP	Water Vapor Permeation
XRD	X-ray diffraction

LIST OF SYMBOLS

μm	Micrometer
cm	Centimeter
mm	Millimeter
kg	Kilogram
g	Gram
ml	Milliliter
min	Minutes
$^{\circ}C$	Centigrade degree
T_g	Glass transition temperature
T_m	Melting temperature
θ	Diffraction angle
λ	X-ray wavelength (\AA)
$\%WL$	Weight loss percentage
T_{max}	Maximum Temperature

**PENCIRIAN DAN SIFAT FILEM ADUNAN DAN NANOKOMPOSIT
METILSELLULOSA – HEMISELLULOSA TANDAN KOSONG
BUAH KELAPA SAWIT**

ABSTRAK

Dalam kajian ini, hemiselulosa berjaya diekstrak daripada tandan kosong buah kelapa sawit. Hemiselulosa dihasilkan melalui teknik pengekstrakan alkali-etanol. Hemiselulosa kemudian dicampur dengan karboksimetil selulosa (CMC) pada jumlah yang berbeza (20, 40, 60, dan 80 % berat) dengan menggunakan kaedah penuangan larutan bagi menghasilkan filem hemiselulosa-karboksimetil selulosa (H-CMC). Montmorillonite (MMT) dengan 2 % ditambah untuk meningkatkan sifat-sifat filem tersebut. Kesan nisbah campuran dan kesan penambahan MMT pada sifat fizik-kimia, mekanikal, haba dan halangan filem nanokomposit berjaya dianalisis dan dicirikan. Filem-filem tersebut dicirikan dengan menggunakan mikroskop imbasan elektron (SEM), spektroskopi infra-merah transformasi Fourier (FTIR), pembalau sinar-X (X-RD), kalorimetri pengimbasan kebezaan (DSC), analisa thermogravimetri (TGA), kekuatan regangan, berat molekul, kebolehtelapan wap air, sudut hubungan dan analisa penguraian bio. Analisis FTIR mendedahkan puncak kumpulan karbonil yang mewakili peningkatan intensiti dengan penambahan hemiselulosa untuk semua filem campuran H-CMC. Analisis haba pula menunjukkan suhu lebur telah berubah kepada suhu yang lebih tinggi daripada 258.34 °C hingga 260.14 °C pada 80% kandungan hemiselulosa berbanding filem CMC tulen. Pemerhatian SEM menunjukkan permukaan seragam dan licin bagi filem campuran sehingga tambahan kandungan 40 % hemiselulosa dimuat sebelum permukaan menjadi kasar pada 80 % kandungan hemiselulosa. Pemanjangan takat putus filem hemiselulosa meningkat

sebanyak 14.30 % dengan penambahan hemiselulosa. Namun begitu kekuatan tegangan filem H-CMC20 menurun sebanyak 56 % apabila kemasukan hemiselulosa sebanyak 80 % berbanding filem CMC. Berbanding dengan filem-filem campuran H-CMC, filem nanokomposit H-CMC-MMT menunjukkan kekuatan regangan yang sangat baik iaitu 29.6 MPa, 15.2 % lebih tinggi daripada filem campuran. Filem nanokomposit menunjukkan peningkatan kekuatan tegangan, disebabkan oleh ikatan hidrogen yang kuat dan interaksi elektrostatik antara CMC dan MMT. Selain itu, filem nanokomposit mempamerkan perilaku haba dan kebolehtelapan wap air yang tinggi. Kajian ini menunjukkan filem nanokomposit boleh digunakan dalam pelbagai bidang aplikasi dalam salutan dan pembungkusan industri.

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CELLULOSES - OIL PALM EMPTY FRUIT BUNCH HEMICELLULOSES
BLEND AND NANOCOMPOSITE FILM**

ABSTRACT

In this study, hemicelluloses were successfully extracted from oil palm empty fruit bunch. Hemicelluloses produced through alkali-ethanol extraction technique. The hemicelluloses then blended with carboxymethyl cellulose (CMC) at various hemicelluloses loading (20, 40, 60, and 80 wt %) by using solution casting method to produce hemicelluloses-carboxymethyl cellulose (H-CMC) blend films. Montmorillonite (MMT) with 2 % was added to enhance the properties of the (H-CMC-MMT) nanocomposite films. The effect of blending ratio and the effect of MMT loading on the physico-chemical, mechanical, thermal and barrier properties of nanocomposite films were successfully analyzed and characterized. The films were characterized by mean of scanning electron microscopy (SEM), fourier transform infrared spectroscopy analysis (FTIR), X-ray diffraction (X-RD), differential scanning calorimetry (DSC), thermogravimetry (TGA), tensile strength, molecular weight, water vapor permeability, contact angle and biodegradability analysis. FTIR analysis revealed the peak of carbonyl group that representing hemicellulose intensity increases with additional of hemicelluloses for all H-CMC blend films. Thermal analysis shows the melting temperature was shifted to higher temperature from 258.34 °C to 260.14 °C by 1.8 % of high loading hemicelluloses at 80 % compared to pure CMC films. SEM observation revealed uniform and smooth surface of H-CMC blend films up to 40 % hemicelluloses loading before the roughness occurred at 80 % hemicelluloses loading. The elongation at break of

hemicelluloses blend films increased by 14.30 %, however the tensile strength of the hemicelluloses blend films decreased by 56 % when 80 % hemicelluloses loading was used compared to CMC films. Compared to the blend films, the nanocomposite films shows excellent tensile strength of films by (29.6 MPa), which was 15.2 % higher than the blend film. The nanocomposite films enhanced the tensile strength due to the effect of the strong hydrogen bonding and electrostatic interaction between CMC and MMT. In addition, the nanocomposite films had high thermal behavior and low water vapor permeability. These observations suggest that the blend film can be uses in area of application in the coating and packaging industry.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Plastic can be found elsewhere and it has been revolutionized the way we live and had become an essential in our daily life. The plastic pollution ends up in streams, oceans, open spaces and resulting in the death of millions of animals. It is impractical and costly to recycle plastics. Low recycling rates and the sharp rise in petroleum price are also a great concern. Therefore, demand for biodegradable plastic is growing as an alternative to reduce the dependency on petroleum based plastic and to generate new green material which can exhibit great economic impact and in the same time the material considered as environmental friendliness.

Recently most of the plastic and polymer materials for packaging purpose available today are based on petroleum sources. Due to the pollution and disposable problems generated from petroleum based plastic, the production of biodegradable plastic obtained from renewable raw materials have becomes an important trend. This trend included in the production of biodegradable film from starch (Bhat et al., 2013), pectin (Fang et al., 2000), natural polymer (celluloses, hemicelluloses, lignin) and chitosan (Fishman et al., 1994). In 2013 forecast analysts reported by Helmut Kaiser Consultancy (2013) predicted that the biodegradable plastic market will experience significant growth approximately 25 - 30 % of total plastic market by 2020. Research studies also give more attention to reduce the environmental impact

of plastic waste through the production of biodegradable based polymer films derived from natural sources, since these can be applied in medical and food industries (Valdes et al., 2014, Hansen & Placket., 2008 and Mooney, 2009).

Biodegradable polymer are classified into three groups which are originated from natural sources also known as biomass, through chemical synthesis on renewable monomers and by bacteria. Biomass from natural sources can be a huge impact and solutions to overcome the environmental issues. Examples of biomass used in biodegradable polymer include corn, sugarcane, tapioca and other forms of lignocellulosic materials such as kenaf, bamboo and oil palm biomass including oil palm trunk, oil palm frond as well as oil palm empty fruit bunch. Among all these biomass materials, oil palm empty fruit bunches (OPEFB) has shown to be promising with wide area of applications.

Since Malaysia generates a lot of OPEFB as Malaysia is the second largest palm oil producer in the world. Surplus of this raw material become an environmental problem and contribute to growing landfilled. Therefore biodegradable plastic from OPEFB able to generate huge value since it is renewable, abundant and inexpensive raw material. OPEFB can be an effective management of waste as its offer an alternative to petrochemical based plastic film.

Chemically OPEFB composed of 33 % cellulose, 23 % of hemicellulose and lignin 25 % (Bardant et al., 2012). Due to its huge available and has fairly high hemicellulose contents, OPEFB appears to be a potential value added product in

order to produce biodegradable plastic in order to utilize the large amount of waste and reduce the environmental impacts (Yang et al. 2006).

Hemicelluloses is one of the popular biodegradable polymers due to its good flexibility, biodegradability, good gas permeability and highly branched and has wide applications in the packaging and biomedical (Coma, 2013; Walker, 2006 and Gáspár et al., 2005). Previous studies have shown that hemicelluloses are hydrophilic in nature and have poor strength properties from different raw material which are barley, cotton stalk and maize bran (Hansen and Plackett, 2008). In the review paper, the author highlight that many source of hemicelluloses are not yet relatively exploited.

Hemicelluloses have been commercially used as sweetening agents, thickeners and emulsifiers in food. So far the non-food utilization of hemicelluloses has been very limited. Hemicelluloses can be categorized as polymer with low molecular weight compared to cellulose. Hence, hemicelluloses can be used commercially for the preparation of polymeric materials for packaging. Moreover, films and coatings based on hemicellulose are shown to be good in oxygen barriers. However, it has some limitations such as low strength, hydrophilicity, poor water vapor/gas barrier properties and undesirable thermal stability, making hemicelluloses unsuitable for certain applications (Zhong et al., 2013). Recent study for utilization hemicelluloses-based biodegradable film shows good oxygen barrier but have brittle characteristic, poor mechanical behavior and water sensitivity which are the main key problem in packaging industry (Huq et al., 2012).

A great deal of previous research into modifying hemicelluloses film by Chen et al. (2015) positively improving the mechanical properties. This phenomenon was surprisingly supported by Kirsi et al., (2012) where elongation at break of films increased, and Young's modulus decreased with increasing sorbitol content as a crosslinker. Hemicelluloses from barley husk can form flexible films without plasticizer and demonstrate strong tensile strength with stress at break of 50 MPa (Höije et al., 2005). However, it was very hygroscopic and the resulting films were brittle. Therefore, in a follow-up study, Coma (2013), offers new technique to increase the mechanical properties of hemicellulose performance by blending or mixing with hemicellulose and commercial cellulose. A significant analysis and discussion on the subject was presented by Hartman, et al. (2006) from a physical blend of hemicellulose with alginate or Carboxymethyl Cellulose (CMC) which able to show dramatically strengthen the tensile strength. Considering all of this evidence, it seems that hemicelluloses blend with commercial cellulose will give a promising result. This suggest hemicelluloses incorporation with CMC will be predicted as a desirable application films for packaging. To increase the barrier properties, addition of CMC to be proven to decreased the water vapor permeability (K_w) of films (Averous et al., 2004). Hence, the addition of CMC expected to improve mechanical properties significantly.

CMC was reported to be used as biodegradable polymer due to its ability to form a transparent and flexible film. CMC has proven no harmful effects on human health, and is used as highly effective additive to improve the quality of products (Ma et al., 2008). CMC has high stability against moisture as it contain hydrophobic polysaccharide backbone and hydrophilic carbonyl group which shows amphiphilic

character (Zhang et al., 2013; Bertuzi et al., 2007 and Hartman et al., 2005). CMC shows excellent form of smooth and transparent free standing film with efficient barrier to oxygen and carbon dioxide (Ghanbarzadeh, 2011 and Edlunt et al., 2010). CMC has relatively good strength and stiffness compared to other biodegradable polymer, it has been widely commercialized used.

Nevertheless, pure 100 % CMC film shows poor mechanical strength (Paunonen, 2013). Continuous effort has been carried out to further enhance the mechanical properties of the blend CMC film. Almasi et al., (2010) studied the blend of CMC and citric acid as a crosslinker. Even with using glycerol as plasticizer, the mechanical is not improved. To exhibit considerable improvement in mechanical, thermal, optical, physical properties and fire retardancy, the film were incorporate with at low filler contents by incorporating montmorillonite as reinforcement filler (Chen et al., 2015).

Montmorillonite (MMT) has been the commonly used layered silicate. MMT is nanoclay that has been used to produce nanocomposite films and the addition of montmorillonite provides excellent liquid/moisture resistance (Ali and Ahmad, 2012). Moreover, due to low molecular weight and non-crystalline properties, hemicelluloses are easy to access and susceptible to hydrolysis. Therefore, addition of montmorillonite clay has great potential in producing nanocomposites which possess a reduced flammability and other superior physical properties (Chen et al., 2015 and Berta et al., 2006). As montmorillonite, belongs to the family of 2:1 phyllosilicate, it is capable of forming a stable suspension in water and also promotes dispersion of this inorganic crystalline layer in water soluble

polymers (Chen et al., 2015). The main problem faced during the nanocomposite preparation is the tendency of the nanoparticles to be in stack form. Therefore, only low levels of MMT are needed to be added in order to enhance the properties of hemicelluloses film.

To the best of our knowledge, little information study has been reported on the incorporation of MMT into hemicelluloses, one of it was incorporated MMT with hemicellulose from bamboo. The result showed that MMT able to enhanced the mechanical properties and improved other properties such included thermal, barrier and flame resistance has been studied by Chen et al., (2015). This formed the basis to undertake the current study to develop better materials with enhanced ductility, strength, thermal stability and biodegradability. Previous studies have shown that MMT used as reinforcement fillers able to produce film composites with balanced properties which are face difficult to obtain without incorporating filler. Therefore, it would be interesting to understand whether CMC embedded in hemicelluloses with MMT would result in better nanocomposites with a balance of properties in terms of tensile, thermal and biodegradability properties. Therefore this current work provide a better understanding on physic-chemical, structural and mechanical properties of hemicellulose film obtained from oil palm empty fruit bunch.

1.2 Problem Statement

Lignocellulose which consists of celluloses, lignin and hemicelluloses get an attention to produce a biodegradable film. However, when hemicelluloses from OPEFB was used, its exhibits poor performance because of its brittleness, and hydrophilic in nature. To overcome this problem, blend CMC with hemicelluloses can form a strong and flexible film (Hartman et al., 2006). It is expected that incorporation of MMT nanofiller enhanced the tensile properties and thermal stability of hemicelluloses (Chen et al., 2015). Therefore, addition of the fillers can be promising to improve the nanocomposites for applications where high strength/stiffness and ductility are required.

1.3 Research Objectives

The objective of this current study is as followed:

- 1) To study about the effect of blending ratio of hemicelluloses/CMC blend films on the physico-chemical, tensile strength, thermal and barrier properties
- 2) To evaluate the effect of 2 % MMT loading on physical, tensile strength, thermal and barrier properties of hemicelluloses/CMC nanocomposite films

CHAPTER 2

LITERATURE REVIEW

2.0 Oil palm tree

The oil palm (*Elaeis guineensis*) originated in the tropical rain forest region of West Africa. Oil Palm is a monocotyledonous crop and the trees may grow up to twenty to thirty meter and more in height. The trunks of young and mature trees are wrapped in fronds which give them a rather rough appearance and it will not formed until three years (Verheye, 2010). The older trees have smoother trunks. Oil palm tree will start bearing fruits after 30 months of field planting and will continue to be productive for the next 20 to 30 years; thus ensuring a consistent supply of oils. Figure 2.1 shows oil palm fruit each ripe bunch is commonly known as Fresh Fruit Bunch (FFB) (Corley and Tinker, 2016).



Figure 2.1: Oil palm tree (left), fresh fruit bunch (centre) and empty fruit bunch (right) (Law et al., 2007).

Oil palm as shows in Figure 2.2, grows well in the tropical climate and ideal growing conditions includes adequate rainfall over 2000 mm per year spread evenly through the year, adequate sunshine over 2000 h per annum and moderately high temperature of 25-33°C. Many countries keen to grow oil palm but unfortunately experience a few months of drought during each year and this severely affect the yield of the palm.



Figure 2.2 : Oil Palm Tree (*Elaies guineensis*)

According to the Integrated Taxonomy Information System (ITIS), the oil palm taxonomy is presented as Table 2.1.

Table 2.1: Oil palm Taxonomy

Type	Specific Name
Kingdom	Plantae
Sub-kingdom	Tracheobionta
Division	Angiospermae
Class	Monocotyledons
Sub-class	Arecidae
Order	Arecales
Family	Arecaceae
Genus	Elaeis
Species	<i>Elaeisguineensis</i> Jacq
Common name	African oil palm

Source: Erwinsyah, 2008

2.1 Oil palm history

In Malaysia, the first plantations were established and operated by British plantation owners, Scotsman William Sime and English banker Henry Darby, known as Sime Darby as an ornamental plant (Basiron *et al.* 2000). Sime Darby Plantation operations in Malaysia have a total land bank of 343,938 ha with oil palm planted area of 303,329 ha of which 83 % is mature. In 1917, the first commercial planting took place in Tennamaran Estate in Selangor, laying the foundations for the vast oil palm plantations and the palm oil industry in Malaysia (Sime Darby, 2017). The plantation has driven economic growth in Malaysia, create job to people and helped eradicate the poverty rate from 50 per cent of population when Malaysia achieved Independence in 1957 to less than five per cent today. Developments in Malaysia become more rapid, especially after 1960, when the replanting of old rubber estates with oil palms was stimulated by FELDA's smallholder schemes (Fold and Whitfield, 2012). Some plantations have already been replanted for third time (Basiron, 2005).

2.2 Current View of Oil Palm in Malaysia

Malaysia is the second largest producer in palm oil industry with total exports of palm oil and palm oil products reached 14.7 million tonnes in 2010 contributing 4500 million (USD) income to the country (Bazmi *et al.*, 2011). Accompanying the production of 1 kg of palm oil, approximately 4 kg of dry biomass are produced. One third of this biomass is OPEFB and the rest are fronds and oil palm trunks (Maitah *et al.*, 2016).

Annually, 19.8 million tons of OPEFB was produced in Malaysia (Daud and Law, 2010). The oil palm trees that were felled to the ground being shredded and left for biodegradation process which known as nutrient recycling process (Wan Asma et al., 2010). This process however took long time for this biomass to decay. Besides, direct burning of OPEFB causes environmental problems and surplus OPEFB land-filled will creating pollution and economic problems (Kong et al., 2014; Geng, 2013 Rahman et al., 2007).

Oil palm plantation has seen rapid development in Malaysia (Cheng et al., 2018). Malaysia is one of the top producers of palm oil in the world, with a total area of 50,000 km² of oil palm plantations (Chiew et al., 2013). In 2017, there are 49.9 million tons of oil palm empty fruit bunch (OPEFB) are produced in Malaysia (MPOB, 2017). By the year 2050, global food consumption demands for vegetable oil are estimated to reach 217 million tons and 37 % of the demands are estimated to come from palm oil (Byerlee et al., 2016). The main product from oil palm fruits is crude palm oil (CPO) and palm kernel oil (PKO) (Budidarsono et al., 2013).

Reported from Malaysia Palm Oil Council (2017), the cultivation of oil palm in Malaysia increasing with years as shown in Figure 2.3. However, a decline in 2016 reflective of the shortage of palm oil was due to El Nino, down seven per cent from 18.6 million tonnes in 2015 and the lowest annual level since 2010 (Malay Mail Online, 2017). Palm oil production declined by 13 % drought induced by the El Nino phenomenon in 2015, leading to an 8 % decline in palm oil exports. An El Nino weather effect across Southeast Asia, cause production to decrease the oil palm's

fresh fruit yields and lowering output in Malaysia and Indonesia, which produce about 90 percent of global palm oil.

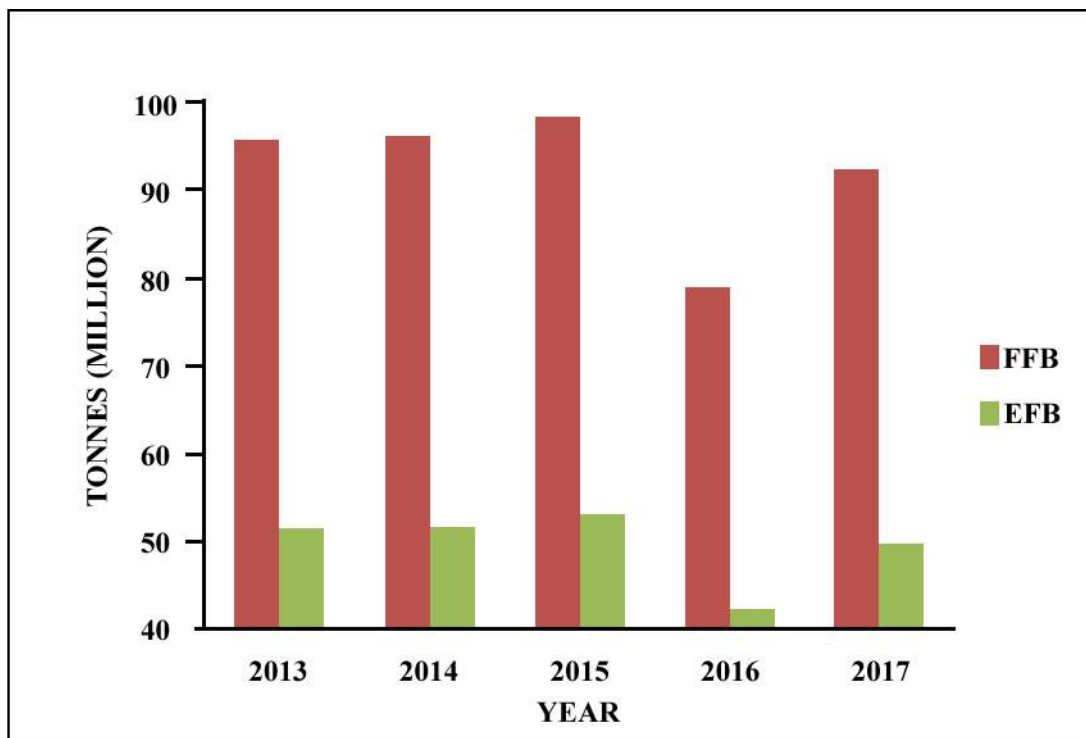


Figure 2.3 : Oil Palm Cultivation in Malaysia for Fresh Fruit Bunch (FFB) and Empty Fruit Bunch (EFB) (Malaysia Palm Oil Council, 2017)

Climate change and El Niño will continue to have major effects in this Southeast Asia, but is not yet predictable (Corley, 2016). However, as shown in Figure 2.3, the trend of higher production is expected to continue from 2017 forward since the demand for Malaysian palm oil continued to be driven by strong consumption in India, China, USA and ASEAN member-states (MPOB, 2017).

Moreover, world production of oils and fats stood at 206 million tonnes (World Oils & Fats Production, 2016) and of the 83 million tonnes of oils and fats traded worldwide during the year, palm oil and palm kernel oil accounted for 56 %

which proven the rapid expansion in world production of palm oil industry. Palm oil is a feedstock for food and biofuel (Saswattecha et al., 2016). According to Bakar et al, (2018) Malaysia is the second largest palm oil exports represent 37 % of the global palm oil trade after Indonesia. Palm oil has been met the global needs in international oils and fats markets.

The increasing share of the international of palm oils has naturally led to a steady buildup of scientific, technical and trade data and information. Many palm oil producing countries have established dedicated organizations and research institutes that generate data and information to add to the body of knowledge on oil palm cultivation, palm oil processing, and applications. It would be impossible to include the voluminous body of existing and new information as a space constraint necessitates the coverage to be selectively confined to describing only the essential aspects of the palm oil industry (Basiron et al. 2000).

The plantation of oil palm area has been increasing, resulting in substantial biomass residue within the harvesting sites. The solid oil palm biomass residue consisting of the empty fruit bunch (OPEFB), oil palm frond (OPF) and oil palm trunk (OPT) which were generated during the extraction of palm oil from the fresh fruit bunches. OPEFB however, have not been totally utilized due to the wet, bulky, and voluminous, which are unfavorable properties for transportation and handling.

These materials were left by the millers to rot at the palm mill and plantation which then cause environmental problem such as such as acidification

and eutrophication (Saswattecha et al. 2016). Besides, oil palm biomass agriculture industrial wastes are discarded, burned and neglected.

Moreover, Wood et al., (2017) discovered that soil bacterial diversity was highest on oil palm plantations. Research finding by Li et al., (2018) also pointing towards the relation exposure soil bacterial pollutants in urban soil and their potential risks to human health due to poor handling of waste.

2.3 Oil Palm Biomass and Its Utilization

Currently oil palm biomass is converted into various types of value-added products via several conversion technologies that are readily available and has potential commercial value added. Wood fiber of palm oil waste can be obtained from midrib or stem, trunk, empty fruit bunches, and oil palm shells. Figure 2.4 shows oil palm biomass in industry since 1990.

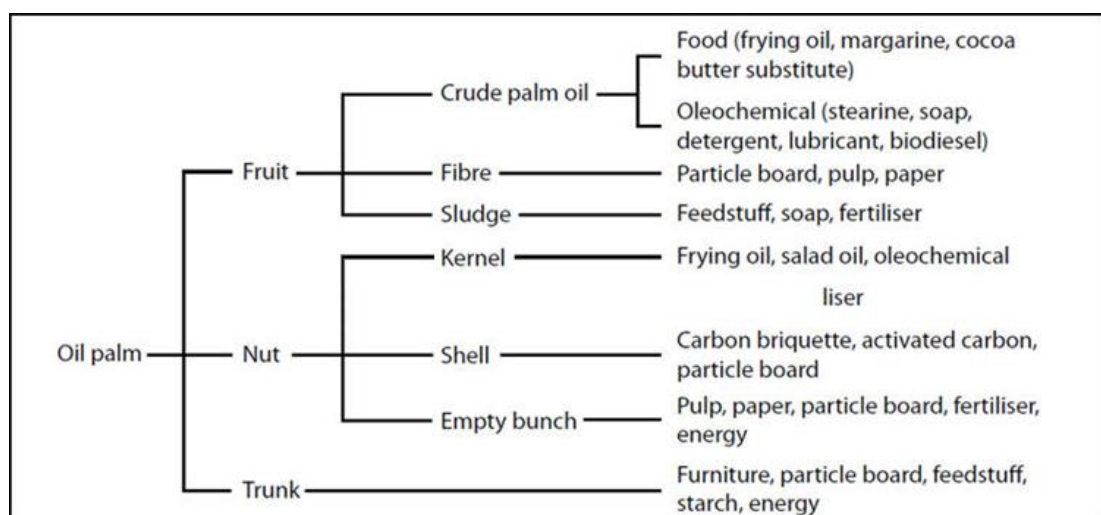


Figure 2.4: Uses of oil palm biomass in industry (Fairhurst and Mutert, 1999)

Leaving the trunk and fronds in the field without further processing will physically hinder the process of planting new crops as the stem can take about five years to decompose completely. Method to improve the technique of replanting program or looking for another possibility to improve the utilization of oil palm biomass (Erwinsyah, 2008). Alternatively, by converting the oil palm biomass into others valuable products because agro-wastes from the oil palm industry such as oil palm trunks (OPT), oil palm fronds (OPF), and empty fruits bunches (OPEFB) have attracted attention as potential sources for new value added materials for the composite industry.

In addition, Palm Oil Research Institute of Malaysia (PORIM) that published in 1979 by Act of Parliament has doing research, conference and workshop for the oil palm industries. Utilization of palm oil as a whole is recommended considering the innovation aspect.

Utilization of palm OPEFB as a whole attracts interest because of its biodegradability, abundance, low cost and renewable material (Hassan and Badri, 2016; Rayung et al., 2014). OPEFB as shown in Figure 2.5 is a fibrous strands surrounded by vascular fibre and enormous source of OPEFB had become environmental issues including fouling and pests. Figure 2.5 shows surplus of OPEFB were land-filled which can lead to environmental pollution and economic problems (Kong et al., 2014).

A number of researchers and research groups have already identified the possibilities for Oil Palm Empty Fruit Bunch (OPEFB) has been used for the application as flooring panels, processed to be a composite board (Indonesian Institute of Science (2001), high Density Fibreboard (HDF), paper (Wanrosli et al., 2007), biogas production (biodiesel) (Chavalparit et al., 2018) and fillers (Akasah et al., 2018). Besides, there is a commercial research on vanilla flavor from OPEFB (Zulkarnain et al., 2018).



Figure 2.5: Oil Palm Empty Fruit Bunch

Use of byproduct can increase financial viability of OPEFB and can also be pointed out that there is a need for an increased multidisciplinary research approach opportunity (Chavalparit et al., 2018). The chemical, physical and mechanical properties of lignocellulosic OPEFB indicate that these materials are similar to film and they may be suitable as raw materials for future film packaging (Abdul Khalil et al., 2008).

OPEFB used in wood industry as reinforcement of polymer-based composite (Hassan & Badri,2016). Composite films are formed by combining two or more materials to produce a film. Biocomposites are composite material, which are materials formed by a matrix (resin) and a reinforcement of natural fibres (usually derived from plants or cellulose). Biocomposites are the combination of natural fibers (biofibers) such as wood fibers (hardwood and softwood) or non - wood fibers (e.g., wheat, kenaf, hemp, jute, sisal, and flax) with polymer matrices from both of the renewable and non-renewable resources. The biofibers are one of the major components of biocomposites. The fibrous material derived from the tree, plant, or shrub sources is defined as biofiber. The natural/biofiber composites are emerging as a viable alternative to glass fiber composites, particularly in automotive, packaging, building, and consumer product industries, and becoming one of the fastest growing additives for thermoplastics (Mohanty et al., 2005). The majority of biocomposites are currently used in packaging industries, where increasing environmental awareness and the depletion of fossil fuel resources are providing the drivers for development of new renewable products (Fowler et al., 2007).

The matrix is generally a thermoplastic or thermosetting polymer in which filler are embedded to form a composite. The matrix preferably should be strong, that is contributes to the overall strength of the composites (Askeland Donald et al., 2011). The matrix plays a major role in the tensile load carrying capacity of a composite structure.

2.4 Lignocellulosic

The majority of natural fibers that have been investigated for composite reinforcement are lignocellulosic materials, or those derived from plants. The strengths of plant fibers have long been recognized and utilized. Roping, textiles, tools, and even housing materials are just some of the past and present applications that take advantage of the unique mechanical properties of plant fibers.

In addition to their good mechanical properties, there are several other advantageous qualities that plant fibers have over traditional composite fiber reinforcements. Cell walls of plants consist mainly of three organic compounds: cellulose, hemicellulose and lignin. Most of the low-value biomass is termed lignocellulosic which hemicelluloses are one of the three structural molecules in plants along with cellulose and lignin and are found abundantly in agricultural wastes (Fortunati 2016; Garcia Maria, 2016; Salmen, 2015). Table 2.2 shows the structure and chemical composition of celluloses, hemicelluloses and lignin in cell walls of plants.

Table 2.2: Structure and chemical composition of celluloses, hemicelluloses and lignin in cell walls of plants.

Type	Cellulose	Hemicellulose	Lignin
Subunits	D-Pyran glucose units	D-Xylose, mannose, L-arabinose, galactose, glucuronic acid	Guaiacylpropane(G), syringylpropane (S)
Bonds between the subunits	β -1,4-Glycosidic bonds	β -1,4 Glycosidic bonds in main chains; β -1.2-, β -1.3-, β -1.6-glycosidic bonds in side chains	Various ether bonds and carbon-carbon bond, mainly “-O-4 ether bond
Polymerization	Several hundred to tens of thousands	Less than 200	4,000

OPEFB consist mainly of lignocellulosic compounds, namely cellulose, hemicellulose and lignin. Cellulose, in particular, constitutes about 37 % (dry weight) of the OPEFB, and is a compound with high value and can be exploited for the benefit of the palm oil industry (Rosnah et al., 2009). Fibers which are embedded in biopolymers (biocomposites) is really interesting due to its biodegradability and low environmental impacts which are really desired as compared to the petroleum based film. The interfacial behaviour (fibre/matrix) is really important as it affect the properties of the film (Le Duigou and Castro, 2017).

The natural fiber and traditional non biodegradable polymers based composites are gaining market demand in light of increasingly strict environmental regulations and eco-friendly biodegradable plastic are attracting the attention of many industries.

2.4.1 Celluloses

Celluloses are widely used since it is the most abundant natural biopolymer, complex carbohydrate and consist of long linear chain of sugar molecule. The chemical formula of the cellulose is $(C_6H_{10}O_5)_n$. Celluloses composed of D-glucose unit linked by beta 1,4 glycosidic bond. The monomer of cellulose is glucose and two glucose molecules build a cellobiose unit also known as anhydroglucose. It can be seen in Figure 2.6.

Hydroxyl group at C2, C3 and C6 position can undergo reaction with alcohol. Cellulose has strong tendency to form hydrogen bond. Intra-inter-bond which give the stiffness (Nishiyama et al., 2002). Celluloses contain both crystalline and amorphous structure. Human cannot digest celluloses unlike animal.

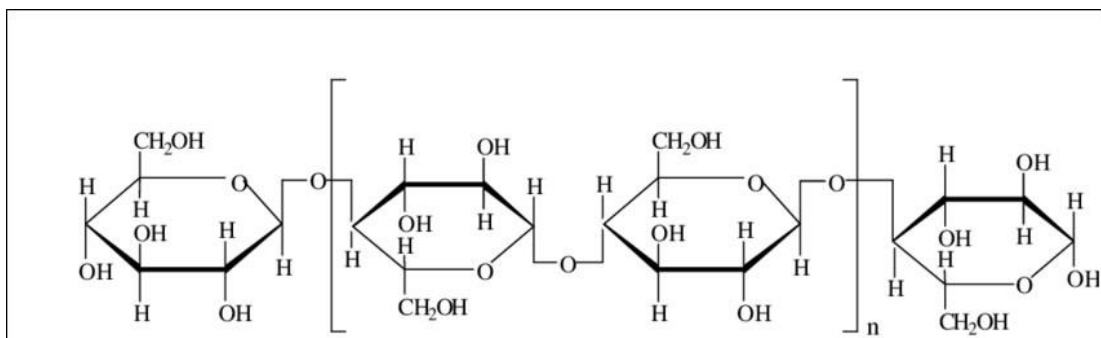


Figure 2.6 : Chemical Structure of Cellulose (Al-Mobarak et al., 2013)

Cellulose is a relatively hygroscopic biopolymer and it swells in water, it is insoluble. However, it is soluble in dilute acid solutions at high temperatures and dissolves in concentrated acids where hydrogen bonds can break however severe degradation by hydrolysis may occur. Alkaline solutions cause swelling of the cellulose also dissolution of some low molecular weight fractions of the cellulose (Krassig and Schurz, 2002).

Holocelluloses consist of celluloses and hemicelluloses. Holocellulose is made up of simple sugar such as D-glucose, D-mannose, D-xylose, L-arabinose, D-glucuronic acid and other sugars like L-rhamnose and D-fructose. These polymer are rich in hydroxyl groups that responsible for moisture sorption through hydrogen bonding (Haygreen and Bowyer 1996). Degree of polymerization of celluloses (DP) depends on its source, process and treatment (Hallac and Ragauskas, 2011). In industry, celluloses had been used in cotton (purest natural form of celluloses), pharmacy and cellophane. Cellophane obtained when a viscous celluloses react with sulfuric acid. It highly impermeable to dry gases and bacteria.

Cifriadi et al., (2017) studies the bioplastic production from celluloses of oil palm empty fruit bunch. Celluloses as a film need modification since it does not have plasticizing character. Biodegradable film from celluloses derivative has already been studied nano crystal, nano fibre celluloses and cellulose acetate.

2.4.2 Hemicelluloses

The primary cell wall (P) is a thin layer, consisting of cellulose, hemicellulose, pectin, and protein completely embedded in lignin (Sjostrom, 2013). The hemicellulose present in fibers promotes swelling and leads to more bonding between fibers and improved strength properties. Hemicelluloses are one of the three structural molecules in plants along with cellulose and lignin and are found abundant in agricultural wastes (Saha, 2003). Contrary to cellulose, hemicelluloses polysaccharides have amorphous and branched structure which makes its solubility behavior distinctly different.

For instance hemicellulose can be separated from cellulose and plant cell walls by alkaline treatment. Therefore, Liu et al., (2017), had studied about hemicellulose from plant biomass to be used in medical and pharmaceutical application. Nevertheless, hemicelluloses were varying widely depending on the biomass sources (Zhou et al., 2018).

The most remarkable difference between hemicelluloses and cellulose is hemicelluloses has short branches consisted of various sugar monomers. The backbone of hemicelluloses structure has either a homopolymer or a heteropolymer with short branches connected by β -(1, 4)-glycosidic and β -(1, 3)-glycosidic bonds (Derrien et al., 2018). In Figure 2.7, the principal monomers of hemicelluloses can be viewed.

Hemicelluloses constitute about 25 % to 40 % of OPEFB and are a group of branched polysaccharide polymers (heteropolysaccharide) built of xylan, glucomannan, galactoglucomannan, arabinogalactan and galactan, with low molecular weight (Paavilainen 2002).

Figure 2.7 shows different monomer of hemicelluloses or known as heteropolymer of pentoses (xylose and arabinose) and hexoses (glucose, galactose, mannose) and sugar acids (acetic) (Sabiha-Hanim & Siti-Norsafurah, 2012). Various sources of hemicelluloses has been studied such as barley husks, aspen wood, oats, corn hulls, birchwood, grass, corncob and their derivatives. Hemicelluloses percentage from oil palm biomass is the second highest after celluloses percentage (Table 2.3).

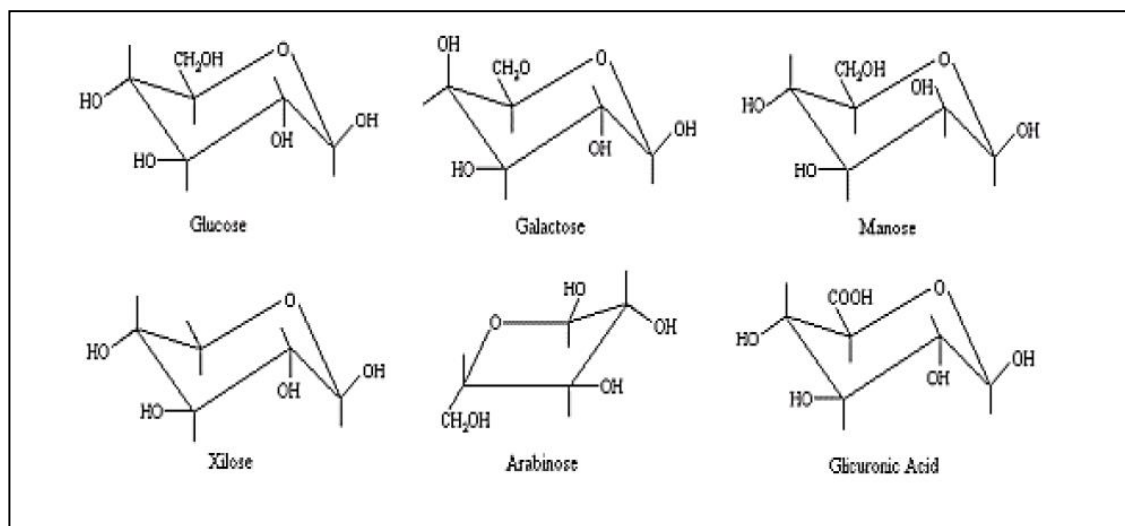


Figure 2.7: Monomers of hemicellulose (Stöcker et al., 2008)

Table 2.3 : Hemicelluloses percentage from oil palm biomass

Oil palm biomass	Hemicellulose (%)
Oil palm frond (OPF)	25 - 34 (Ariffin et al., 2006; Law and Jiang., 2001)
Oil palm trunks (OPT)	30 - 33 (Abdul Khalil et al., 2008)
Empty fruit bunches (OPEFB)	32 - 34 (Khalid et al., 2009; Ramli et al., 2002)

Hemicelluloses shows good barrier in food packaging to medical applications (Luckachan & Pillai, 2011; Hansen & Plackett, 2000) with great oxygen barriers and water resistance (Hansen & Plackett, 2008). The main group of hemicellulose in softwood is galactoglucomannan and in hardwood glucuronoxylan (Saha, 2003).

Hemicelluloses exist in amorphous form, these polymers are chemically not as stable as cellulose, and thus partly dissolve in both acid and alkaline pulping conditions (Gullichsen and Fogelholm, 2000). It is widely recognized that hemicelluloses, due to increased bonding within or between fibers, are beneficial for pulp and paper properties (Hannuksela et al. 2004). However, higher hemicelluloses content lead to a more porous surface of kraft fibers which also affect the water vapor permeability (Duchesne et al. 2001). Range of degree of polymerization (DP) hemicelluloses is 80 - 200 which is significantly related to thermal stabilization and can influence on structure and properties of packaging film (Karimi & Taherzadeh, 2016; Sudhakar et al., 2016; Shi et al., 2016; Li et al., 2015). Degree of polymerization is important because the electrophilic hydrogen atoms of water