

**CHARACTERIZING NANOFIBRILLATED
CELLULOSE FROM OIL PALM EMPTY FRUIT
BUNCH AND ITS INFLUENCE AS
REINFORCEMENT AGENT IN EPOXY BASED
NANOBIOCOMPOSITE**

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**UNIVERSITI SAINS MALAYSIA
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By

IREANA YUSRA BINTI ABDUL FATAH

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
ASTM	American Society for Testing and Materials
CNC	Cellulose nanocrystal
CNF	Cellulose nanofibrils
DGEBA	Diglycidyl ether of bisphenol-A
DP	Degree of polymerization
DSC	Differential Scanning Calorimetric
DTG	Derivative thermogram
EFB	Empty Fruit Bunch
FD	Freeze drying
FDT	Final degradation temperature
FFB	Fresh fruit bunches
FT-IR	Fourier Transform Infrared
GPa	Giga Pascal
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulfuric acid
HCl	Hydrochloric acid
HPH	High pressure homogenizer
HSMD	High shear mechanical disperser
HUIS	High intensity ultrasonication
IDT	Initial degradation temperature
LM	Light Microscopy
MFC	Microfibrillated cellulose

MgSO ₄	Magnesium sulphate
MPa	Mega Pascal
MPOB	Malaysian Palm Oil Board
NaOH	Sodium hydroxide
NaSiO ₃	Sodium silicate
NBKP	Northern Bleached Kraft Pulp
NCC	Nanocrystalline cellulose
NFC	Nanofibrillated cellulose
OD	Oven drying
OH	Hydroxyl
OPEFB	Oil palm empty fruit bunch
OPF	Oil palm frond
OPT	Oil palm trunk
PPF	Pressed fruit fiber
POME	Palm oil mill effluent
SCD	Supercritical drying
SD	Spray drying
SEM	Scanning Electron Microscope
SEM-EDX	Scanning Electron Microscope coupled with energy dispersive X-ray
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
TPS	Thermoplastic starch
UT	Ultra Turrax
XRD	X-ray diffraction

LIST OF SYMBOLS

cm	Centimeter
°C	Degree Celsius
T _g	Glass transition temperature
g	Gram
Hz	Hertz
Kg	Kilogram
kHz	Kilohertz
KJ	Kilojoules
kV	Kilovolts
T _{max}	Maximum degradation temperature
m	Meter
µm	Micrometer
mm	Millimeter
nm	Nanometer
N	Newton
Phr	Parts by weight
%	Percentage
θ	Theta
V	Volume
W	Watt
Wt	Weight

LIST OF PUBLICATIONS

	Publications	Page
Appendix 1.1	Abdul Khalil H.P.S., Bhat A.H., Ireana Yusra A.F. (2012). Green composites from sustainable cellulose nanofibrils: A review. <i>Carbohydrate Polymers</i> , 87, 963– 979	201
Appendix 1.2	Ireana Yusra A. Fatah, Abdul Khalil H. P. S., Md. Sohrab Hossain, Astimar A. Aziz, Yalda Davoudpour, Rudi Dungani and Aamir Bhat. (2014). Exploration of a Chemo-Mechanical Technique for the Isolation of Nanofibrillated Cellulosic Fiber from Oil Palm Empty Fruit Bunch as a Reinforcing Agent in Composites Materials. <i>Polymers</i> , 6, 2611-2624	202
Appendix 1.3	Abdul Khalil, H. P. S., Ireana Yusra, A. F., Bhat, A. H. and Jawaid, M. (2010). Cell wall ultrastructure, anatomy, lignin distribution, and chemical composition of Malaysian cultivated kenaf fiber. <i>Industrial Crops and Product</i> , 31, 113–121.	203
Appendix 1.4	Abdul Khalil, H.P.S., Bhat, I., Ireana Yusra, A.F., Sanusi, Z.A. & Hezri, A.A. (2011). Broad perspective of palm oil for non-food applications for sustainable tomorrow. In: <i>Palm Oil: Nutrition, Uses and Impact</i> , Nova Science Publishers, 129-158.	204

**MENCIRIKAN SELULOSA NANOFIBRIL DARIPADA TANDAN KOSONG
BUAH KELAPA SAWIT DAN PENGARUHNYA SEBAGAI AGEN
PENGUAT DALAM BIONANOKOMPOSIT BERASASKAN EPOKSI**

ABSTRAK

Tujuan kajian ini adalah untuk menentukan pengaruh hidrolisis asid sulfurik, penguraian mekanikal dan penghomogenan bertekanan tinggi sebagai proses kimia-mekanikal berkesan untuk pengasingan selulosa nanofibril (NFC) berkualiti daripada gentian tandan kosong buah kelapa sawit (OPEFB). Kumpulan berfungsi dan penghabluran gentian telah dijalankan oleh spektroskopi Fourier inframerah (FT-IR) dan pembelauan sinar-X (XRD). Morfologi dan kestabilan haba telah disiasat menggunakan mikroskop pengimbas elektron (SEM), mikroskop penghantaran elektron (TEM) dan analisis termogravimetri (TGA), kalorimetri pengimbasan berbeza (DSC). Keputusan FT-IR menunjukkan bahawa lignin dan hemiselulosa telah dikeluarkan secara berkesan daripada selulosa yang diekstrak dan nanofibril. Analisis XRD menunjukkan bahawa peratusan penghabluran telah meningkat daripada gentian mentah kepada selulosa mikrofibril (MFC), tetapi penurunan bagi NFC adalah disebabkan oleh penceraian ikatan hidrogen. Saiz diameter NFC yang diperolehi adalah dalam lingkungan 5 hingga 10 nm. Analisis TGA menunjukkan bahawa NFC mempunyai kestabilan haba yang tinggi. Hasil kajian ini menunjukkan bahawa gabungan hidrolisis asid sulfurik, penguraian mekanikal dan penghomogenan bertekanan tinggi telah terbukti sebagai proses kimia-mekanikal berkesan untuk mengasingkan gentian nanoselulosa daripada gentian selulosa tumbuhan. Sebahagian lain daripada kajian ini adalah pembangunan bod bionanocomposit berasaskan epoksi. Objektifnya adalah untuk mengkaji dan menganalisis kesan penguat dan penyebaran bagi NFC yang diisi dalam peratusan

rendah (kurang daripada 1%: 0%, 0.25%, 0.5% dan 0.75% NFC) dalam bahan matrik. Keputusan yang diperolehi dibandingkan dengan epoxy tulen yang disediakan, 0% NFC (kawalan). Pencirian sifat morfologi, fizikal, mekanikal dan haba bagi bionanokomposit telah dinilai sewajarnya. Melalui imej mikroskop cahaya (LM) dan mikrograf TEM yang diperhatikan, keputusan mempamerkan bahawa NFC yang diisi 0.25% dan 0.5% tersebar secara seragam di dalam matrik epoksi dan secara rawak di seluruh sampel, sementara NFC yang diisi 0.75% menunjukkan taburan dan penyebaran yang lemah. Nilai penyerapan air meningkat dengan peningkatan dalam NFC terisi berbanding epoksi tulen. Ujian mekanikal menunjukkan bahawa sifat-sifat tegangan dan lenturan bionanokomposit menyamai pola yang sama di mana mereka meningkat dengan peningkatan peratusan NFC yang diisi dari 0 hingga 0.75%. Manakala bagi pemanjangan pada tahap maksimum, nilainya menurun dengan peningkatan NFC yang diisi manakala epoksi tulen (0%) menunjukkan nilai yang paling tinggi. Kekuatan impak bionanokomposit diperkuat NFC yang rendah berbanding epoksi tulen adalah disebabkan oleh ciri-ciri impak gentian semula jadi yang rendah. Walau bagaimanapun, dengan peningkatan peratusan NFC yang diisi, kekuatan impak menunjukkan perubahan peningkatan yang disebabkan oleh sifat unik NFC. Analisis terma (TGA dan DSC) menunjukkan bahawa kehadiran NFC walaupun pada peratusan yang rendah dan dengan peningkatan jumlah NFC membawa kepada peningkatan dalam kestabilan haba bagi bionanokomposit. Oleh itu, melalui pencirian penguat NFC bionanokomposit berasaskan epoksi, keputusan yang diperolehi telah menunjukkan bahawa penguat NFC terisi yang rendah (di bawah 1%) mempengaruhi sifat resin epoksi dan menunjukkan peningkatan terhadap bionanokomposit tersebut.

CHARACTERIZING NANOFIBRILLATED CELLULOSE FROM OIL PALM EMPTY FRUIT BUNCH AND ITS INFLUENCE AS REINFORCEMENT AGENT IN EPOXY BASED NANOBIOCOMPOSITE

ABSTRACT

The aim of the present study was to determine the influence of sulfuric acid hydrolysis, mechanical disintegration and high pressure homogenization as an effective chemo-mechanical process for the isolation of quality nanofibrillated cellulose (NFC) from oil palm empty fruit bunch (OPEFB) fibers. The functional groups and the crystallinity of all fibers were carried out by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD), respectively. The morphology and thermal stability were investigated by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Thermogravimetric analysis (TGA), Differential scanning calorimetric (DSC), respectively. The FTIR results showed that lignin and hemicellulose were removed effectively from the extracted cellulose and nanofibrils. XRD analysis revealed that the percentage of crystallinity was increased from raw to microfibrillated cellulose (MFC), but the decreased for NFC was due to a breakdown of the hydrogen bond. The diameter size of the NFC determined was within 5 to 10 nm. The TGA analysis showed that the isolated NFC had high thermal stability. The finding of present study reveals that combination of sulfuric acid hydrolysis, mechanical disintegration and high pressure homogenization had proven to be an effective chemo-mechanical process to isolate cellulose nanofibers from cellulosic plant fiber. Another part of this present study was the development of epoxy based nanobiocomposite board. The objective was to investigate and analyze the reinforcing effect and dispersion of low percentage NFC loading (less than 1 %: 0%, 0.25%, 0.5% and 0.75% NFC) in the matrix material.

The results obtained were compared with the prepared neat epoxy, 0% NFC (control). The characterizations including morphological, physical, mechanical and thermal properties of the nanobiocomposite were evaluated accordingly. In light microscopy (LM) images and TEM micrographs observation, the results illustrated that 0.25% and 0.5% NFC loading are homogeneously dispersed in the epoxy matrix and randomly distributed throughout the sample, while the 0.75% NFC loading showed poor distribution and dispersion. The water absorption value increased with the increase in the NFC loading as compared to the neat epoxy. Mechanical testing showed that tensile and flexural properties of nanobiocomposite had posed a similar trend/pattern where they increased with increasing NFC loading percentage from 0 to 0.75%. While for the elongation at break, the value decreased with increasing NFC loading where neat epoxy (0%) showed the highest value. Low impact strength of NFC reinforced nanobiocomposite as compared to the neat epoxy was due to the low impact properties of the natural fiber. However, by increasing the NFC loading percentage, the impact strength showed incremental change due to unique properties of NFC. Thermal analysis (TGA and DSC) indicated that incorporation of NFC even at low percentage and with increasing NFC amount led to increase in thermal stability of nanobiocomposite. Therefore, from NFC reinforced epoxy based nanobiocomposite characterization, the results obtained had indicated that low NFC reinforced loading (below 1%) influenced the resin epoxy properties and showed improvement to the nanobiocomposite.

CHAPTER 1

INTRODUCTION

1.1 Introduction and Research Background

Palm oil producer are generating large amount of oil palm biomass waste in the form of empty fruit bunches and fruit shells, arising serious environmental impacts (Fahma et al., 2010). Malaysia alone has been reported to produce oil palm biomass around 40 million tons annually including 280,000 tons empty fruit bunches, which represent cheap, plentiful and enthusiastically available source of lignocellulosic biomass (Jonoobi et al., 2011b; Turunawarasua et al., 2013). Moreover, the cellulose content in oil palm empty fruit bunch (OPEFB) is 44.4% along with 30.9% hemicellulose and 14.2% lignin (Fahma et al., 2010). This very large generation of OPEFB and its high cellulose content have attracted a great deal of research interest to produce nanocellulose for use as a reinforcing agent in composites materials.

Cellulose, a ubiquitous organic compound, is a common structural component in most of the plant's cell wall. The cellulose is considered nearly inexhaustible source of raw material due to increasing demand for the green biocompatible products (Abdul Khalil et al., 2012a; Jawaid et al., 2014). The excellent mechanical properties, remarkable reinforcing capability, low density, thermal stability, and environmental benefits of cellulose have attracted scientist's interest in utilizing cellulosic fibers to develop environmentally friendly composite materials. Over the years, numerous research have been conducted on the isolation of nanocellulose from various cellulosic plant sources, such as oil palm biomass (Fahma et al., 2010, 2011;

Nazir et al., 2013), kenaf (Jonoobi et al., 2011a; Chan et al., 2012), wood pulp (Siddiqui et al., 2011), rice straw (Lu and Hsieh, 2012), bamboo (Yu et al., 2012), and flax (Qua et al., 2011).

The term microfibrillated cellulose (MFC) is applied to those fibril aggregates with a diameter between 30 and 100 nm and of several micrometers in length. However, MFC can also be considered as nanofibrillated cellulose (NFC), as the definition of NFC is a size <100 nm in one dimension (Jonoobi et al., 2011a,b). Nanocellulose extracted from plant, agricultural/forest crops or residues can be categorized in two main subcategories, nanofibrillated cellulose (NFC) and nanocrystalline cellulose (NCC), based on the structure, condition, isolation method and cellulosic source. NFC consists of alternating crystalline and amorphous domains are long, flexible, entangled network with a diameter of approximately 1–100 nm (Brinchi et al., 2013). While NCC exhibits a relatively low aspect ratio of straight crystalline rod-like shapes with typical diameter of 2–20 nm and the length varies between 100 and 500 nm. The particles are highly crystalline, accumulated around 54% and 88% (Abdul Khalil et al., 2012a, Abdul Khalil et al., 2014).

There are various methods for preparing nanocellulosic fibers from cellulose fibers including chemical, mechanical and chemo-mechanical treatment processes (Abdul Khalil et al., 2012a, 2014; Ireana Yusra et al., 2014). Acid hydrolysis has been extensively studied to isolate nanofibers from different cellulosic sources (Fahma et al., 2010; Qua et al., 2011; Brinchi et al., 2013). It is being reported that hydrolytic conditions, such as temperature, acid-to pulp ratio, reaction time and acid type, have a remarkable influence on the surface charge and dimensions of the nanocellulose

fibers. Sulfuric acid (H₂SO₄) and hydrochloric acid (HCl) are commonly used in the acid hydrolysis process for NCC production to remove the amorphous regions (Qua et al., 2011; Brinchi et al., 2013). However, sulfuric acid provides a highly stable aqueous suspension with the introduction of sulfate groups on the surface of crystallites (Jonoobi et al., 2011a; Qua et al., 2011).

Nowadays, high pressure homogenizers (HPH) have been extensively used to isolate cellulose nanofibers from various lignocellulosic sources (Abdul Khalil et al., 2012a, 2014). The HPH has been viewed as an efficient method for refining the fiber through high pressure. The HPH alone is not sufficient to fibrillate cellulose into nano-sizes, requires pre-treatment and combination of further mechanical treatment to reduce the fiber size, and prevents from stacking the small orifice of HPH (Lasseguette et al., 2008; Siro et al., 2011; Jonoobi et al., 2011a,b).

The study on cellulosic nanofibers as a reinforcing agent in nanobiocomposites had started two decades ago (Dufresne et al., 2000; Eichhorn et al., 2010). Theoretically, the utilization of cellulose nanofibers as reinforcement in nanobiocomposite is basically due to the potentially high stiffness of the cellulose crystal. High crystallinity from hierarchical structure in plant can be break down into individualized nanofibers that will result in lowering the amorphous material amount. Since the plant fibers are hierarchically fibrous in nature, fibrous material in the form of nanowhiskers or nanofibrils is feasible to be isolate, whereas therefore due to their aspect ratio (length/diameter) and reinforcing capabilities are believe potentially suitable for the nanobiocomposite materials (Abdul Khalil et al., 2012a).

In this new field, the researchers with nanotechnological bent of mind are interested in nanocellulose reinforced polymer nanobiocomposites fiber because of the unique promising properties and great advantages. The cellulose nanocomposite materials is more favourable as compared to conventional composites due to the superior mechanical, thermal and barrier properties at low reinforcement loading, transparency, recyclability and lightweight of the cellulose nanocomposite (Abdul Khalil et al., 2012a,b). In addition, the nanocellulose reinforced polymer nanocomposites with high flexibility, considerable improvement in their properties and allows biodegradability in nature is expected to enhance far beyond the possibilities of the micro-size components and as well as the conventional composite (Voronova et al., 2012). Therefore, this could also lead to environmentally compatible and high-performance components and end-products.

1.2 Problem statement

Some researchers have reported similar methods in preparing MFC to those introduced by Turbak et al. (1983) (Nakagaito and Yano, 2005; Andresen et al., 2006; Stenstad et al., 2008). However, the obtained materials are quite inhomogeneous and as for the microfibrils appearance consideration, they contain large residual fiber fragments and fibril bundles (Kaushik, 2011). Therefore, this research work was conducted to explore and develop new technique/method for NFC isolation through combination of chemical and mechanical treatment well known as chemo-mechanical process using acid hydrolysis, high shear mechanical dispersion and high pressure homogenizer. It is also expected to produce better fibrillation and properties from this combination process as compared to other previous research.

Nanocellulose, including NFC and NCC structure form, can be isolated from a variety source of lignocelluloses material including plant, agricultural/forest crops or residues and some bacterial. Although acid hydrolysis, high shear mechanical dispersion and high pressure homogenization have been utilized to produce nanocellulose fiber and viewed as effective with the combination of other cellulosic fiber processing methods, there are very few studies that have considered preparing nanofibrillated cellulose from OPEFB with the combination method of sulfuric acid hydrolysis and high pressure homogenization as a chemo-mechanical process (Fahma et al., 2010; Jonoobi et al., 2011a,b; Ferrer et al., 2012; Nazir et al., 2013; Haafiz et al., 2013, 2014). Furthermore, research and comprehensive detail on the study, characterization and properties of nanofibrillated cellulose (NFC) from this abundant agro-waste OPEFB fiber were lacking and less available (Jonoobi et al., 2011b; Ferrer et al., 2012).

During fibrillation, besides the high energy consumption from the HPH process as it increases with the increasing number of cycles (Zhang et al., 2012), cleaning and disassembling the long fibrils that often clog the system, mostly at the in-line valves, was detected to be main drawback of the homogenization process. Hence, researchers have introduced and combined some chemical, biological and mechanical pre-treatments such as alkaline-acid pre-treatment, enzyme pre-treatment, refining, cryo-crushing, high intensity ultrasonication, high shear mechanical disperser, microfluidizer and etc. before homogenization process which helps to overcome these drawbacks (Pan et al.,2013; Abdul Khalil et al., 2012a, 2014). In this particular study, the function of sulfuric acid pre-treatment is to reduce the cellulose fiber size and slow the sediment from fast settle down by good

dispersion in the HPH inlet. Whereas, the high shear mechanical dispersion was done to liberate the treated MFC and reduce the energy consumption of HPH machine.

Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are two strong acids commonly used in acid hydrolysis processes at high concentration for the NCC production to remove the amorphous regions (Qua et al., 2011; Brinchi et al., 2013). Nevertheless, sulfuric acid hydrolysis can also be conducted as a pre-treatment process of the cellulosic fiber, with the hypothesis that the utilization of low acid concentrations in the sulfuric acid hydrolysis process might fibrillate the micro-size cellulose (microfibrillate cellulose) fiber, since the acid to fiber ratio, acid concentration and treatment time plays an effective role on fibrillation and the properties of the cellulosic fiber. From the literature, there is no chemical treatment approach that was carried out using sulfuric acid hydrolysis at low concentration for a safety environment concern (Nazir et al., 2013; Lidia et al., 2014).

So, sulfuric acid has been preferred and widely used in the hydrolysis as compared to the hydrochloric acid due to its ability on providing a highly stable electrostatic aqueous suspension with the introduction of sulfate groups on NFC surface (Jonoobi et al., 2011a,b; Qua et al., 2011). Regarding the agglomeration that can occur in either during NFC drying process (irreversible agglomeration) or during mixing with hydrophobic matrix is a challenge for the hydrophilic and polar nature of cellulosic fiber (Eyholzer et al., 2010). In order to fix this matter, it is believed that NFC suspension treated with sulfuric acid can form a better distribution, dispersion as well as good chemical bonding and compatibility with the hydrophobic polymer matrix in the nanobiocomposites development.

The development of nanobiocomposites which related with nanocellulose as reinforcement material derived from renewable sources is currently an interesting research area. Upon the promising properties of nanobiocomposites, scientists believe that high potential applications from nanocellulose fiber can be utilized as extremely strong and transparent films in various diverse areas. Currently, nanocellulose is produce to manufacture the nanobiocomposites in a form of strong film, thin film for food packaging, quality paper, thin component in bio-medical, electric and electronic device, as coating material and etc. (Fukuzumi et al., 2009; Spence et al., 2010a,b; Kelley et al., 2010; Bhattacharya et al., 2012; Mathew et al., 2012; Ferrer et al., 2012; Kolakovic et al., 2012a,b; Yousefi et al., 2013; Wang et al., 2013).

Unfortunately, there is no research focused on the development and properties of OPEFB-NFC epoxy based nanobiocomposites board as a component for the automobile, packaging and especially in the automotive and bio-medical industry etc (Abdollah et al., 2008; Joshua et al., 2012; Masoodi et al., 2012; Cross et al., 2013; Farhan et al., 2014; Lani et al., 2014; Lee et al., 2014). In this study of nanobiocomposites, NFC from OPEFB was used as reinforcement in epoxy matrix to produce nanobiocomposite board at low reinforcement loading, below or less than 1 wt%. The experiment was done using very low reinforcement loading to study the properties and reinforcement effect of OPEFB-NFC epoxy based nanobiocomposites board.

1.3 Scope of the Present Work

The scope of this present study is to produce nanofibrillated cellulose (NFC) fiber from oil palm empty fruit bunch (OPEFB) using sulfuric acid hydrolysis, high shear mechanical disintegration and high pressure homogenization as a chemo-mechanical process. Low concentration of sulfuric acid was used to hydrolyze the cellulose fiber prior to facilitate the high pressure homogenization process. Subsequently, microfibrillate cellulose fiber (MFC) can be homogenized using HPH to produce nanofibrillated cellulose. Several analytical characterization methods, including transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR) and thermogravimetry analyses (TGA) were employed to determine characteristic morphological, chemical and thermal properties of NFC fiber.

The isolation of NFC from OPEFB fibers which is easily and abundantly available in Malaysia, can thus be utilized as a reinforcing material in the nanobiocomposites. The literature review on NFC epoxy based nanobiocomposite indicated that until now, no study/work has been done on the production of epoxy based nanobiocomposites board reinforced NFC fibers (Abdollah et al., 2008; Joshua et al., 2012; Masoodi et al., 2012; Cross et al., 2013; Farhan et al., 2014; Lani et al., 2014; Lee et al., 2014). This new and novel approach of NFC epoxy based nanobiocomposite at low percentage loading are expected to gain remarkable and competitive improvements in the physical, mechanical and thermal properties as compared to high loading percentage nanobiocomposites. The components of NFC

epoxy based nanobiocomposite especially in automotive, aerospace and biomedical sectors have been well-known to develop future prospect industries.

The research aim is to explore through example, the recent development state in the field of nanofibrillated cellulose and cellulose nanobiocomposite research and application. As clearly known, natural product, cellulose itself is also considered as polymers, had an impressive and promising future potential for the basic information together with great scale production in various applications.

1.4 Objectives of the Study

The objectives of this present research work are:

1. To optimize the chemical treatment and investigate the effect of acid pretreatment on the treated microfibrillated cellulose fiber through different acid concentration and hydrolysis time parameters
2. To develop and isolate the nanofibrillated cellulose fibers from oil palm empty fruit bunch by chemo-mechanical treatment process and study its characteristics (viz. morphology, chemical, crystallinity and thermal properties)
3. To evaluate the morphology, mechanical, physical and thermal properties of oil palm empty fruit bunch-nanofibrillated cellulose epoxy based nanobiocomposite at different low percentage reinforcement loading

1.5 Organization of Thesis

This thesis comprises of five respective chapters which are as follows:

Chapter 1- Covers the introduction and research background, including problem statement of major challenges, aim and scope together with objectives of the study.

Chapter 2- Focused on literature review of various aspects of the nanofibrillated cellulose from OPEFB as reinforcing material and the NFC epoxy based nanobiocomposites development and application. It also covered detail relevant scientific information related to the overall research study.

Chapter 3- State the materials and explains overall methodology framework of the study from the NFC isolation process to the nanobiocomposites development and including the characterization properties of each stage.

Chapter 4- Demonstrate the output results and discuss the research finding on morphology, crystallinity, mechanical, physical, chemical and thermal properties of the nanofibrillated cellulose and its nanobiocomposites.

Chapter 5- Consist of overall conclusions and recommendation for further future research study.

CHAPTER 2

LITERATURE REVIEW

2.1 Oil Palm

Oil palm tree, species of *Elaeis guineensis* belongs to the Palmacea family, originated from West Africa tropical forests is one of the most valuable and important commercial crop for worldwide mostly in Malaysia, Thailand and Indonesia country. Generally, oil palm tree (Figure 2.1) has age of 25 years old average perennial life span which accumulates measurement around \approx 45–65 cm in diameter and 7–13 m in height from the ground level. This agricultural crop is produced in 42 countries worldwide. Although the origin of oil palm tree is native to Africa, but Malaysia was acknowledged as the first country in terms of processing and large scale planting (Abdul Khalil et al., 2011).

Malaysia accumulates approximately 50% of the world's oil production therefore known as the world's largest oil producer and exporter. Oil palm has been the world's leading important fruit crop for almost 20 years where its production has nearly doubled in the last decade (Abdul Khalil et al., 2011, 2012a). In 2011, the plantations around the globe is not less than 16 million hectares where it covers overall around 5 million hectares in Malaysia. This counted amount of land area plantation generates a huge value number of dry weight biomass, including empty fruit bunches, trunks, fronds and other biomass fraction produced annually (Abdul Khalil et al., 2011).



Figure 2.1: Oil palm tree

2.1.1 Oil Palm Biomass

Biomass is a collective suitable standard name for all organic substance derived from plants and other living organisms that has not been preserve to form carbon materials. Whereas the oil palm biomass is a lignocellulosic residue referring to the agricultural waste mainly from oil palm which left in the plantation field. This oil palm biomass typically contains 50% cellulose, 25% hemicellulose and 25% lignin in their cell wall (Ronald, 2013).

In Malaysia, other than around 23 million metric tons yield of processed fresh fruit bunches (including palm kernel cake, crude palm oil and palm kernel oil) produced in 2011, 6.7 million metric tons of empty fruit bunch (EFB) (Figure 2.2), 13.0 million metric tons of oil palm trunk, 47.7 million metric tons oil palm frond, 7.1 million metric tons of pressed fruit fiber, 3.0 million metric tons of palm oil mill

effluent and 4.0 million metric tons of kernel shells were generated as biomass fractions from residue of oil palm. In the production flow, most of these biomass fractions had been collected with the crude palm oil during harvesting at the palm oil mill. As these resources are included in the production supply chain, therefore this situation allows saving the transportation cost. Apart from these, only oil palm biomass (OPF and OPT) will need to be processed on site and obtained from the oil palm plantation field (Ronald, 2013).



Figure 2.2: Oil palm empty fruit bunch (OPEFB)

Malaysia alone had produced about 70 million tons of oil palm biomass during 2006. Ratnasingam et al. (2011) had reported that the main oil palm biomass includes EFB, OPT and OPF accounts for 10%, 5% and 70% respectively from the total oil palm biomass produced where the total oil palm biomass produced annually around 89% were used as fertilizer, fuel and mulch. From these figures, large quantity of waste products especially in OPF and OPT during the replanting process occur due to the

increase in oil palm agricultural estate. Therefore, the oil palm industries in Malaysia had generated massive quantities of agricultural waste and will eventually create significant environmental problems with its presence at the cultivated area (Ronald, 2013). In spite of this huge production, oil from the palm oil comprises only a small fraction compared to the total biomass produced by the oil palm plantation. As such, the oil palm industry must take advantage/opportunity by utilizing it at the best possible manner and prepare to overcome the situation (Abdul Khalil et al., 2012a).

Presently, oil palm by-products are not proficiently utilized, where the enormous growth of oil palm plantation has generated large amounts of waste, creating tribulations in replanting operations and remarkable environmental concern. Therefore, the biomass fibers consumption towards proper economic utilization will be beneficial in creating value added products and solving the disposal problem. The oil palm sector produces large amount of biomass which constitutes agricultural lignocellulosic waste product during the milling processes, replanting and pruning when left in the field. This large number of unutilized by-product from oil palm tree can cause severe environmental and real estate problems (Abdul Khalil et al., 2011).

Intensive research and development (R&D) efforts in the Malaysian oil palm industry through large quantities of abundant oil palm biomass have currently come out with establish applications in several commercially possible bio-based products. These lignocellulosic materials from oil palm biomass can be utilized through biological, chemical and physical innovations for great value-added products. To remain competitive, constant latest innovation aspect which include products, services and processes are important in making the biomass supply chain as to

continue promoting the new market and economies especially in those far countryside areas. Consequently, Malaysia will remain beyond and on top of its competitors (Abdul Khalil et al., 2011).

Malaysia as nominated the world's foremost palm oil-producing country has initiated upon the industry as well as trade to flourish and grow rapidly. Hence, researches are working on extensive variety of by-products that led to the continuous R&D development efforts in making the downstream manufacturing turns to strong and establish industry (Abdul Khalil et al., 2011). Nevertheless, oil palm biomass fibers have potential and excellent specific properties as outstanding reinforcing agent used in the matrix as an alternative material for pulp and paper, hybrid composites and bio-composites industries (Abdul Khalil et al., 2012a). In conjunction, long-lasting and perennial in nature of tremendously available oil palm biomass supply are strong commercial assets to tap these new markets avenue (Ronald, 2013).

2.1.2 Oil Palm Empty Fruit Bunch Fibers (EFB) and Cell Wall Ultrastructure

Oil palm empty fruit bunch (EFB) is an abundant agricultural biomass where the source comes from oil palm tree by-product. The EFB is the empty bunch that is left behind and obtained after the oil palm fruit had been removed in the oil extraction process during harvesting. Fresh EFB accumulates around 12.4 million tons per year are regularly discharged from palm oil refineries where some quantity of this is used as fuel, while the rest is left unexploited (Abdul Khalil et al., 2011, 2012a).

The EFB fibers also known as lignocellulosic fibers consist of high cellulose content and certain amount of organic compound such as hemicellulose and lignin. The schematic drawing of cell wall ultrastructure and cellulose organization hierarchical structure of oil palm tree are shown in Figure 2.3. The existence of amorphous and crystalline regions is shown in lateral fiber structure. This high in cellulose content properties of EFB represents quality as potential natural fiber resource.

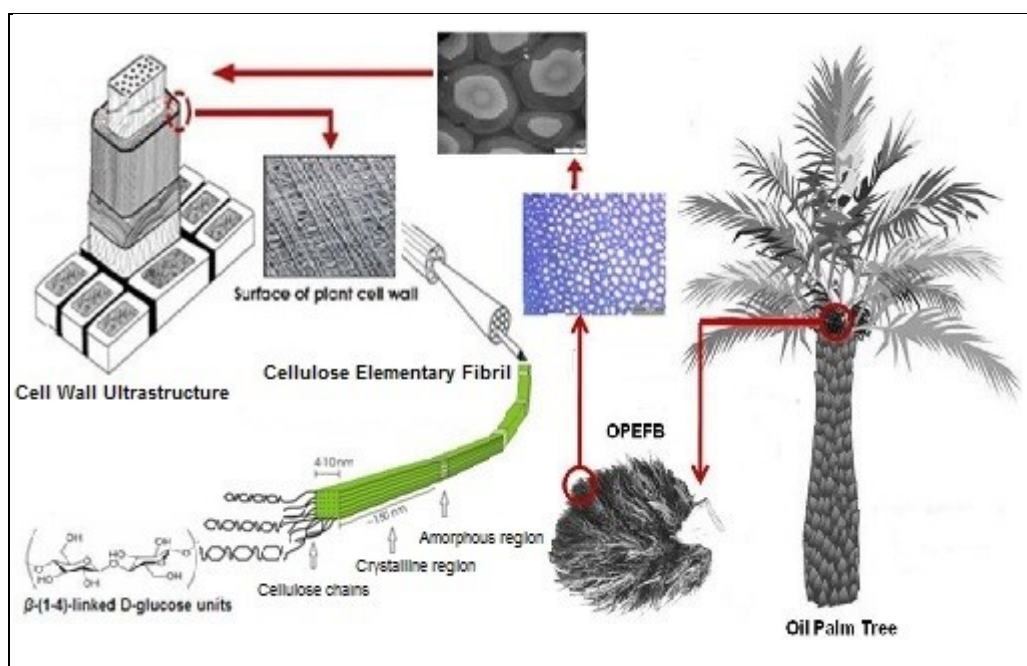


Figure 2.3: Schematic drawing of cell wall ultrastructure and cellulose organization hierarchical structure of oil palm tree (Kolakovic et al., 2012; Abdul Khalil et al., 2011)

Unfortunately, the applications using EFB fiber does not widely explore as compare to the total biomass productions. The main constituents in oil palm EFB fiber usually fluctuate depending on certain condition such as testing methods, environment, weather effect, plant age and soil condition. Furthermore, Abdul Khalil et al. (2011, 2012a) revealed that hemicellulose content is highest in oil palm EFB fiber as compared to banana stem, wood, pineapple leaf and coir fibers.

Many research and studies have been conducted regarding oil palm EFB fibers as an effective reinforcement in thermoplastics and thermosetting materials (Abdul Khalil et al., 2012a,b). These reveal that potential EFB fibers are suitable for composite development such as in hybrid composite board, medium density fiberboard, particleboard, pulp and paper and even nanocomposites. Currently, great amount of oil palm biomass are disposed off or burned to produce oil palm ash at the oil palm plantation mills. Thus, exploring the beneficial and practical oil palm biomass utilization as reinforcement in natural fiber based composites and nanocomposites will help to reduce the environmental problems issue as associated with the oil palm wastes disposal in industry (Abdul Khalil et al., 2012a,b).

2.2 Cellulose

Cellulose is the largest abundant organic biopolymer substance in the world and existing as main structural component in plants, animals and other microorganism cells. In plant-based materials, main sources of cellulose isolation can be classified to wood / non-wood and natural cellulosic fibers. Cotton is categorized under natural cellulose because it consisted almost entirely of glucose residues. Depending on the cellulose source, the cell wall constituent in plants has a reinforcing role and its structure can vary considerably (Abdul Khalil et al., 2012a). The production of cellulose around the world is estimated to be over 7.5×10^{10} tons annually (Abdul Khalil et al., 2014).

Cellulose consists of D-anhydroglucose ($C_6H_{11}O_5$) linear chain units that linked by β -(1-4)-glycosidic bonds is defined as semicrystalline polysaccharide macromolecule.

Cellulose is known as basic most important component structure in all plant cell wall corresponding to the high stability and strength properties. The cellulose amount in fibers usually can affect the fiber utilization, production and quality at different reasons. For instance, fiber that has high cellulose amount are more appropriate to be used in textile and paper field while fiber that has high hemicellulose amount can be used to produce ethanol and other fermentation product because hemicellulose are easy to be hydrolysed (Reddy and Yang, 2005).

Based on the main properties of this biopolymer, cellulose and its derivatives are important to replace petroleum based materials and often used in pharmaceutical due to their availability, low toxicity, biodegradability and renewable chemical resource in nature. As known, cellulose fibers also have relatively low elasticity than synthetic fibers and a comparatively high density, as well as better electricity and heat conductor. In addition, cellulose fibers are vulnerable to be damage by acidic condition but on the other hand have good resistance to bases (Abdul Khalil et al., 2010). Knowledge and understanding on cellulose properties is important and necessary for the successful of further production processes.

2.2.1 Structure of Cellulose

Chemically, cellulose structure is constructing from a linear polymer composed by cellulose monomers, D-anhydroglucose ($C_6H_{11}O_5$) units that linked together through β -(1-4)-glycosidic bonds to form the repeating units of the cellulose chain named dimer cellobiose (Figure 2.4). These cellulose molecules form a long straight, almost fully extended chain, where cellobiose are rotated 180° relative to each other along

the main axis. Long cellulose chain is known as α -cellulose where the β -1, 4 glucan chains length depends on the cellulose source. The quality of celluloid substance has connection with the degree of polymerization cellulose molecules (Maya Jacob and Sabu, 2008).

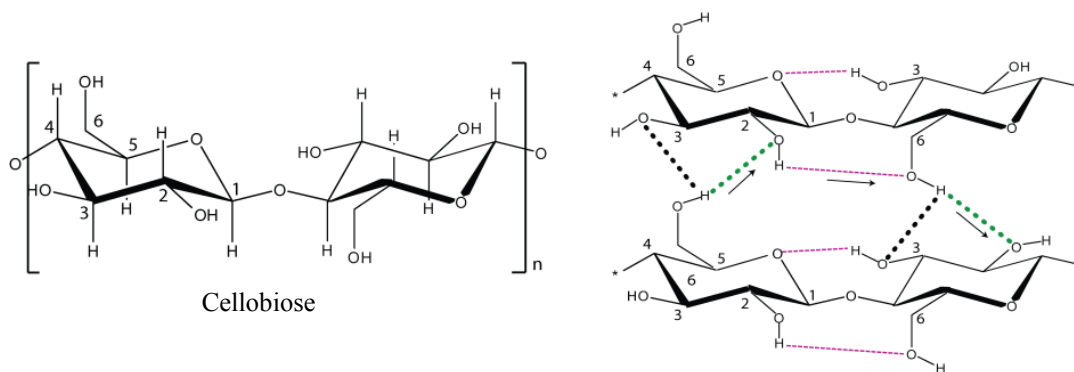


Figure 2.4: Molecular structure of cellobiose as repeating unit of cellulose polymer and formation of the intra-chain (red dashed line) and inter-chain (black and green dashed lines) hydrogen bonding (Nishiyama et al., 2008; Visakh and Thomas, 2010)

Cellulose from glucose molecules ($C_6H_{12}O_6$) is monosaccharide that produces through photosynthesis process from carbon dioxide. Intra- and intermolecular hydrogen bonds in glucose units are structured from the three free hydroxyl groups positioning at C_6 for the primary hydroxyl groups while C_2 and C_3 for the secondary hydroxyl groups (Brinchi et al., 2013). These hydrogen bonds chained together to create highly ordered three-dimensional crystal structures that hold the network providing the strength, stiffness, and structural stability in a plant.

Several glucan chains of cellulose assemble and merge to form into a single microfibril, that consist of two structure components which are the highly ordered region, crystalline domain and low order para-crystalline region, amorphous domain. Naturally occurring cellulose I, known as native cellulose has a thermodynamically meta-stable structure that can be transformed to either cellulose II, III or IV. In

nature, cellulose I occur in two crystalline sub-allomorphs, cellulose I- α (a triclinic unit cell structure), and cellulose I- β (a monoclinic unit cell structure) which predominantly in higher plants. Cellulose I crystalline structure is distinguishable from regenerated cellulose II structure by the hydrogen bond and chain patterns (Sehaqui et al., 2012).

Cellulose II, rarely found in nature can be artificially regenerated or mercerized from cellulose I. The regeneration process involves dissolution of the cellulose in a specific solvent while in the mercerization process the cellulose is soak in aqueous sodium hydroxide. In both processes, a final re-crystallization step leads to the final cellulose II, which more thermodynamically stable than cellulose I allomorph. Apart from these structures, there are further allomorphs of cellulose known, namely cellulose III and cellulose IV (Abdul Khalil et al., 2012a). Meanwhile treating the cellulose I with liquid ammonia followed by washing with alcohol will produce cellulose III. As for cellulose IV, it is formed upon treatment of the other modified cellulose in a suitable liquid under pressure at high temperature (Klemm et al., 2009).

Cellulose is relatively resistant to oxidizing agents and strong alkali; however it will easily form water-soluble sugars by acid hydrolysis reaction (John and Anandjiwala, 2008). During hydrolysis in acidic environment, the glucan chains are preferably cut in the amorphous domains. The resulting microfibril fragments are called whiskers due to their typical slender, rod-like shape. The single microfibrils then pack to larger bundles (fibril bundles, fibril agglomerates), hold together by the matrix substances (hemicelluloses, lignin and pectin). In a cellular hierarchical structure, cellulose is organized as the skeletal component in all plants.

Individual cellulose chain originally assemblies to form fiber cell wall do not occurred alone as individual molecule in nature. The cell wall was structured in dynamic and continuous network form throughout the whole plant body. Generally, the plant cell wall consists of cellulose microfibrils which are bounded by amorphous matrix of lignin and hemicelluloses. Plant cell wall microstructure includes middle lamella, primary and secondary walls. These layers differ from one another in terms of structure and chemical composition which later influences the fiber value, properties, production and utility in various applications (Sonia and Priya, 2013).

Middle lamella acts as a matrix that separates individual cells and mainly consists of lignin. The primary wall is the very thin outer part of a cell wall (less than 1 μm) which mainly consists of amorphous hemicelluloses and lignin together with the present of some pectins, proteins and celluloses. The secondary wall consists of three layers; S1, S2 and S3, where most of the cellulose located in the thickest secondary wall, S2 layer. Furthermore secondary layer contributes to overall fiber properties where it composed of microfibrils. These microfibrils create an irregular pattern of crystalline and amorphous regions where the structure is not completely crystalline with the presence of less ordered amorphous domains. Cellulose diameter size, range in 5 to 30 nm is depends on the cellulose source (Akil et al., 2011).

The orientation of cellulose microfibrils (microfibril angles) organized in the cell walls have certain characteristic and a strong effect on the mechanical properties, where it differ depending on the cell wall layer and upon various plant type. For instance, low microfibril angles such as in S2 (with microfibril orientation nearly parallel to fiber axis) will increase modulus of elasticity, while high elongation at

break related to the large microfibril angles (Klemm et al., 2009). As a consequence of its fibrillar structure and the large amounts of hydrogen bonds, cellulose has a high tensile strength. It is therefore the structural element of a plant that bears the load in tensile mode (Abdul Khalil et al., 2012a).

The morphological structural hierarchy of plant starts from the linkages of cellulose molecule chain merges to form elementary fibrils, which plug into larger units called microfibrils, which are then in turn assembled into fibers (Abdul Khalil et al., 2014). Therefore microfibril is considered as the smallest entity that can be isolated from the cell wall structure. The diameter and length of these elementary fibrils are around 3-5 nm and up to few micrometers, respectively. The elementary fibrils are then aggregated to form bundles with diameters in a range of 5-30 nm and further microscopic cellulose fibers in several micron diameters. The scheme of cellulose hierarchical organization is shown in Figure 2.5. This hierarchy provides the plant fiber with high mechanical performance with characteristics such as tensile strength, resilience and stability as well as structural plasticity (Sehaqui et al., 2012).

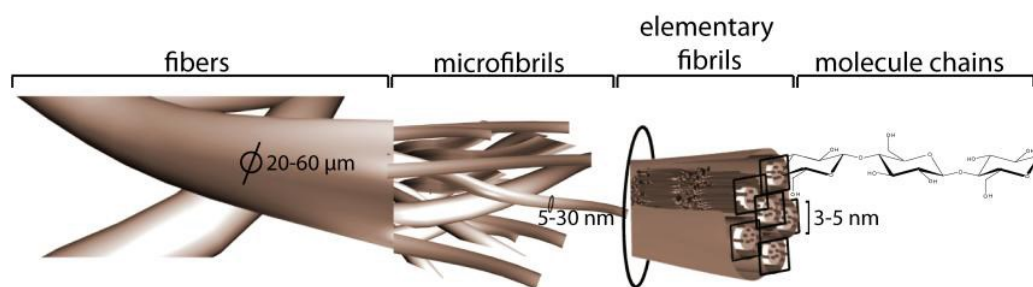


Figure 2.5: Schematic drawing of cellulose organization hierarchical structure, from fibers to cellulose molecule chains (Paakko et al., 2008)

2.2.2 Nanocellulose

Generally, ‘nanocellulose’ term is referring to cellulosic materials that at least one dimension is in the nanometer scale, nano-size cellulose. Nanocellulose can be extracted from various lignocelluloses material including plant, agricultural/forest crops or residues and some bacterial (Table 2.1). There are various methods for preparing nanocellulosic from cellulose plant fibers including chemical, mechanical and chemo-mechanical treatment process (Abdul Khalil et al., 2012a, 2014; Ireana Yusra et al., 2014). Acid hydrolysis as chemical treatment has been extensively studied to isolate nanocellulose from different cellulosic sources (Fahma et al., 2010; Qua et al., 2011; Brinchi et al., 2013).

Table 2.1: Various sources of nanocellulosic fibers (Abdul Khalil et al., 2012a)

Various sources (Nanocellulosic fibers)	References
Wood	Abe et al., 2007; Chen et al., 2011
Cotton	De Morais Teixeira et al., 2010
Potato tuber cells	Dufresne et al., 2000
Cladodes and spines from <i>Opuntia ficus-indica</i>	Malainine et al., 2003
Prickly pear fruits of <i>Opuntia ficus-indica</i>	Habibi et al., 2008
Lemon and maize	Rondeau-Mouro et al., 2003
Soybean	Wang and Sain, 2007a
Wheat straw and soy hulls	Alemdar and Sain, 2008
Hemp	Wang and Sain, 2007b
Coconut husk	Rosa et al., 2010
Branch-barks of mulberry	Li et al., 2009
Pineapple leaf	Cherian et al., 2010
Banana rachis	Zuluaga et al., 2009
Sisal	Morán et al., 2008
Pea hull	Chen et al., 2009
Sugar beet	Dinand et al., 1999; Dufresne et al., 1997
Oil Palm Empty Fruit Bunch	Fahma et al., 2010

Processes that often involve in the mechanical treatments were refining, grinding and cryo-crushing followed by a high pressure homogenization (HPH). Usually in most cases, the mechanically HPH process does not stand alone, when the pre-treatment was applied together with the HPH process, it is denoted as chemo-mechanical treatment process, a combination of chemical and mechanical treatment process (Pan et al., 2013; Ireana Yusra et al., 2014).

Recently, nanocellulose has attracted much attention during the past few years. The qualified characteristic for nanocellulose such as specific surface area and high aspect ratio, high strengthening and flexibility effect, good optical and thermal properties will find many applications in high technology and quality grade paper, nanocomposites, coating additives, food packaging, gas barriers and etc. (Belbekhouche et al., 2011; Moon et al., 2011). For instance, nanocellulose with functional hydroxyl groups also allows chemical modifications for further applications (Kaushik, 2011).

Incorporation of biodegradable, biocompatibility and non-toxicity nanocellulose as reinforcement material in the polymer matrix has proven to be an important strategy due to high mechanical performance and great properties in producing nanobiocomposites for biochemical and biomedical applications (Abdul Khalil et al., 2012a). These biodegradable nano-reinforcements also promise a great potential for novel green nanocomposite materials development in consideration to the environment awareness. Moreover, it has also shows potential in various nanotechnology applications including automotive, automobile and electronic devices industries (Abdul Khalil et al., 2014).