CHARACTERISATION OF CELLULOSE NANOCRYSTALS FROM OIL PALM FRONDS FOR CARBOXYMETHYL CELLULOSE BIO-NANOCOMPOSITES

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by

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LIST OF ABBREVIATIONS

BNC	Bacterial Nanocellulose
CA	Cellulose Acetate
CAB	Cellulose Acetate Butyrate
CAP	Cellulose Acetate Phthalate
CMC	Carboxymethyl Cellulose
CMF	Cellulose Microfibrils
CNC	Cellulose Nanocrystals
CNF	Cellulose Nanofibrils
CNW	Cellulose Nanowhiskers
DP	Degree of Polymerisation
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric
FT-IR	Fourier Transform Infrared Spectroscopy
EAB	Elongation at Break
EC	Ethyl Cellulose
EFB	Empty Fruit Bunches
FESEM	Field Emission Scanning Electron Microscopy
HEC	Hydroxyethyl Cellulose

HPC	Hydroxypropyl Cellulose
HPMC	Hydroxypropylmethyl Cellulose
HPMCP	Hydroxypropylmethyl Cellulose Phthalate
MC	Methyl Cellulose
MFC	Microfibrillated cellulose
MPOB	Malaysian Palm Oil Board
NaCMC	Sodium Carboxymethyl Cellulose
NCC	Nanocrystalline cellulose
NFC	Nanofibrillated cellulose
OPF	Oil Palm Fronds
OPT	Oil palm Trunks
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TPS	Thermoplastic Starch
XRD	X-Ray Diffraction

LIST OF SYMBOLS

%	Percentage
w/w	Weight per weight
v/v	Volume per volume
°C	Degree Celsius
L	Litre
N	Newton
g	Gram
MPa	Mega pascal
cm	Centimetre
nm	Nanometre
h	Hour
min	Minute
µ	micro

PENCIRIAN NANOKRISTAL SELULOSA DARIPADA PELEPAH KELAPA SAWIT UNTUK BIO-NANOKOMPOSIT KARBOKSIMETIL SELULOSA

ABSTRAK

Nanokristal selulosa (CNC) telah dihasilkan daripada pelepah kelapa sawit (OPF) untuk menghasilkan bio-komposit karboksimetil selulosa (CMC) - nanokristal selulosa. Kajian asas pada bahagian atas, tengah dan bawah bahagian pelepah kelapa sawit telah dijalankan dan berdasarkan imej pengmbas mikroskop elektron (SEM), ia menunjukkan bahawa bahagian bawah OPF mempunyai peratusan berkas vaskular yang lebih tinggi berbanding bahagian tengah dan bahagian atas. Ia telah disokong oleh keputusan analisis kimia yang menunjukkan bahawa bahagian bawah OPF mempunyai kandungan α-selulosa tertinggi. Seterusnya, bahagian atas, tengah dan bawah OPF digunakan untuk menghasilkan CNC dengan menggunakan rawatan kimo-mekanikal. Bahan kimia seperti natrium klorit, asid asetik, kalium hidroksida dan asid sulfurik digunakan untuk menulenkan selulosa dan diikuti dengan rawatan mekanikal termasuk homogenisasi dan sonikasi untuk menghasilkan kadar sebaran CNC yang baik. Analisis pembelauan sinar-X (XRD) menunjukkan bahawa CNC dari bahagian atas OPF mempunyai indeks penghabluran yang tertinggi. Ia menunjukkan bahawa rawatan asid hidrolisis berjaya menghidrolisis struktur amorfos di dalam OPF dan mengekalkan struktur kristal. Ampaian CNC dari bahagian bawah OPF mempunyai zeta potential tertinggi, menunjukkan bahawa ia lebih stabil berbanding bahagian atas dan tengah. Bahagian atas OPF digunakan selanjutnya untuk menyiasat kesan kepekatan asid dan masa hidrolisis pada sifat CNC. Tiga kepekatan asid sulfurik (58 %, 60 %, 64 %) dan masa hidrolisis (45 min, 60 min, 75 min) telah digunakan semasa

rawatan kimo-mekanikal. Variasi dalam hasil CNC menunjukkan bahawa ia sangat bergantung kepada keadaan hidrolisis asid. CNC yang dihidrolisis dengan 60 % H_2SO_4 selama 45 minit menunjukkan indeks penghabluran tertinggi (70.1%). Spektrum Fourier transformasian inframerah (FTIR) menunjukkan pola yang serupa untuk semua sampel yang menunjukkan bahawa keadaan hidrolisis asid yang berbeza tidak mengubah struktur kimia CNC. Berdasarkan pencirian keseluruhan, hidrolisis asid (60 %, 45 min) didapati sesuai untuk menghasilkan OPF CNC dan berjaya menghidrolisis struktur amorfos tanpa merosakkan struktur kristal. OPF CNC yang dihidrolisis dengan 60 % H_2SO_4 selama 45 minit dimasukkan ke dalam matriks CMC untuk menghasilkan bio-nanokomposit CMC-CNC. Asid sitrik telah ditambahkan sebagai ejen paut silang untuk mengurangkan sifat hidrofilik bio-nanokomposit. Sifat-sifat mekanikal menunjukkan bahawa penambahan 3% OPF CNC dalam matrik CMC berjaya meningkatkan kekuatan tegangan dan Young’s modulus. Penambahan CNC dalam peratusan yang lebih tinggi mengakibatkan pengurangan sifat-sifat mekanik, yang disebabkan oleh aglomerasi CNC dalam bio-nanokomposit. Ia disokong oleh imej SEM yang menunjukkan penyebaran CNC yang tidak sekata dan pembentukan ketulan besar dalam bio-nanokomposit. Ujian kelembapan menunjukkan bahawa penggabungan OPF CNC telah meningkatkan sudut sentuhan. Sementara itu, ujian pengekalan air menunjukkan bahawa peratusan air yang disimpan dalam bio-nanokomposit adalah berkadar langsung dengan peratusan penambahan CNC. CMC-CNC9 mempunyai kapasiti pengekalan air tertinggi kerana kehadiran kandungan CNC yang lebih tinggi yang boleh menghasilkan ikatan hidrogen daripada molekul air.

CHARACTERISATION OF CELLULOSE NANOCRYSTALS FROM OIL PALM FRONDS FOR CARBOXYMETHYL CELLULOSE BIO-NANOCOMPOSITES

ABSTRACT

Cellulose nanocrystals (CNC) were produced from oil palm fronds (OPF) to produce carboxymethyl cellulose (CMC)-cellulose nanocrystals bio-nanocomposite. A fundamental study on top, middle and bottom parts of raw oil palm fronds was conducted and based on the scanning electron microscope (SEM) images, it showed that the bottom part of OPF had greater percentage of vascular bundles compared to middle and top parts. It was further supported by chemical analysis that showed bottom part of OPF had the highest α-cellulose content. The top, middle and bottom parts of OPF were further utilised to produce CNC by applying chemo-mechanical treatment. Chemicals such as sodium chlorite, acetic acid, potassium hydroxide and sulphuric acid were used to purify the cellulose and followed by mechanical treatments including homogenizing and sonication to provide good dispersion of CNC suspension. The x-ray diffraction (XRD) analysis showed that the CNC from top part of OPF had the highest crystallinity index. It inferred that the acid hydrolysis treatment managed to hydrolyse the amorphous region in top part of OPF and preserved the crystalline region. The CNC suspension from the bottom part of OPF had the highest zeta potential, indicating a more stable suspension compared to top and middle parts. The top part of OPF was further utilised to investigate the effect of acid concentration and hydrolysis time on properties of CNC. Three sulphuric acid concentrations (58 %, 60 %, 64 %) and hydrolysis time (45 min, 60 min, 75 min) were used during the chemo-mechanical treatment. The variations in yield suggested that it was highly dependent on the acid hydrolysis condition. The CNC hydrolysed with 60 % H_2SO_4 for 45 min showed the highest crystallinity index (70.1%). The Fourier transform infrared (FTIR) spectra showed similar patterns for all samples indicating that different acid hydrolysis conditions did not change the chemical structure of the CNC. Based on the overall characterisation, the acid hydrolysis (60 %, 45 min) was found suitable for the isolation of OPF that managed to hydrolyse the amorphous region of CNC without destructing the crystalline structure. The OPF CNC hydrolysed with 60 % H_2SO_4 for 45 min was incorporated in the CMC matrix to produce CMC-CNC bio-nanocomposites. Citric acid was added as a crosslinker to reduce the hydrophilicity of bio-nanocomposite. The mechanical properties showed that incorporation of 3% of OPF CNC in the CMC matrix managed to improve the tensile strength and Young’s modulus. Higher percentage of CNC incorporation resulted in reduction of the mechanical properties, which was attributed to the agglomeration of CNC in the bio-nanocomposites. It was supported by SEM images that showed uneven dispersion of CNC and formation of big lumps in the bio-nanocomposites. The wettability test showed that incorporation of OPF CNC had increased the contact angle. Meanwhile, water retention test showed that the percentage of water retained in the bio-nanocomposites was proportional to the percentage of CNC addition. The CMC-CNC9 had the highest water retention capacity due to the presence of greater CNC content that could bind with hydrogens from water molecules.

1 CHAPTER ONE: INTRODUCTION

1.1 Research Background

Malaysia is one of the major producers and exporters of palm oil in the world. In conjunction with that, it produces a large amount of oil palm biomass namely fronds, empty fruit bunches, trunks, and mesocarp fibres which was reported to be 70 million tons in 2016. The oil palm fronds (OPF) were reported to be the largest biomass generated in the oil palm plantation which was 47% out of the total oil palm biomass wastes (MPOB, 2017). The current practice of disposing OPF has caused environmental pollution since it was not properly managed. Major parts of OPF was left in the plantation area for the purpose of nutrient recycling. Some parts of the OPF were also used for ruminants' feed. However, there were still some parts of the OPF that was left unused and attracted microorganisms that finally caused air pollution. One of the ways to counter the environmental problem is by utilising the OPF as a starting material for the production of fibre-based products (Mat Rasat et al., 2014).

Several applications of the oil palm biomass were introduced in renewable energy source, furniture products, electricity generation and pulp and paper production (Loh, 2017; Abdullah et al. 2015; Suhaily et al. 2012 & Rafidah et al. 2017). Since OPF is highly fibrous in nature with a cellulose content of approximately 65%, it has high potential to be used as a starting material for cellulose nanocrystals (CNC) as it will give high CNC yield with improved properties depending on the isolation treatment (Dungani et al. 2017). The CNC can be isolated by using different methods namely chemical, mechanical, chemo-mechanical and enzymatic treatment based on its desired final properties. The method of production will determine the category of the nanocellulose based on the treatment subjected to the fibres (Borjesson & Westman, 2015).

Generally, cellulose exists in the form of ordered microfibrils and enclosed with hemicellulose and lignin (Moran et al. 2008). It is made up of high molecular weight homopolymer of β-D-glucopyranosyl repeating units linked by 1, 4-glycosidic linkages (Rowell et al. 2005). Cellulose is available in two forms which are cellulose type I (native cellulose from plants) and cellulose type II (regenerated cellulose from chemical treatment) (Eichhorn et al. 2010). Meanwhile, the CNC are physically in the form of rod-like shape and possesses a dimension less than 100 nm. The length and width of CNC varies depending on the cellulose source and method of isolation (Habibi et al. 2010).

The process of isolating CNC varies depended on the desired properties. The most common way to isolate CNC is by using acid hydrolysis treatment. Generally, the process of isolating CNC was done in two stages. The first stage was aimed to remove hemicellulose and lignin while acid hydrolysis was conducted to remove the amorphous structure of the cellulose polymer and preserve the crystalline region of the fibrils (Brinchi et al. 2013). Acid hydrolysis treatment was frequently used to isolate CNC because it causes breakdown of the fibres into rod-like fragments. Few types of acids were found suitable for CNC isolation such as sulphuric acid, hydrochloric acid, formic acid and phosphoric acid. Among all of the resultant CNC, the CNC produced from sulphuric acid hydrolysis are stable in aqueous suspension due to the presence of sulphate groups on their surfaces (Dufresne, 2013). Therefore, sulphuric acid was chosen for the acid hydrolysis treatment in this study to prevent agglomeration of CNC when it was further used for bio-nanocomposite application.

The parameters that should be monitored during acid hydrolysis are the concentration of acid, time of hydrolysis, temperature during hydrolysis and acid to cellulose ratio. The optimum sulphuric acid hydrolysis used to isolate cellulose microfibers from oil palm empty fruit bunches (EFB) was 64% acid concentration and 1 hour of hydrolysis time (Fahma et al. 2010). The hydrolysis condition differs according to the nature of raw materials. Thus, it is crucial to find the right condition for the isolation of CNC as it would determine the final properties of the nanocrystals.

Previous work done by Mohaiyyiddin et al. (2016) isolated nanocellulose from oil palm fronds by using 64 % v/v sulphuric acid for 45 min and resulted in having crystallinity index of 57.7 %. Meanwhile Sauhrab et al. (2016) applied retting treatment on oil palm fronds followed by ball milling and acid hydrolysis to obtain cellulose nanocrystals. To date, there is no study reported on the production of CNC from different parts of OPF by chemo-mechanical treatment. The method was chosen considering its efficiency to isolate CNC without causing total destruction of the cellulose crystalline structure. This study was conducted to provide data on properties of CNC obtained from different parts of OPF. Different treatment conditions were introduced in order to find the optimum condition that could result in CNC with good thermal, crystallinity and morphology. The CNC sample that had good crystallinity and thermal properties were further utilised for the production of skin tissue repair material.

Since CNC obtained from top part of OPF showed high crystallinity index, it was further utilised for the production of bio-nanocomposites. The CNC with the highest crystallinity index and thermal properties was selected to be incorporated with carboxymethyl cellulose (CMC) to form CMC-CNC bio-nanocomposites. The CMC was chosen due to its transparency, good film-forming ability, non-toxicity, biocompatible with wide range of polymers and biodegradable property (Li et al. 2016). However, due to its high hydrophilicity, citric acid was incorporated to the mixture to crosslink with the free hydroxyl groups in order to make it less hydrophilic and improve its water retention properties (Rivero et al., 2010). The CNC in the bio-nanocomposite acts as the reinforcement to the film to improve its mechanical properties.

1.1 Problem Statements

With regards to the availability of oil palm fronds as the largest contributor of oil palm biomass, works have been conducted to utilise oil palm frond as a starting material to produce value-added products. It has gained much interest rather than leaving it unexploited in the plantation area. The aim is to reduce the environmental pollution and at the same time contributes in the production of high-valued product. Therefore, the production of cellulose nanocrystals from oil palm fronds was proposed to counter the current issue regarding dumping of oil palm fronds.

Mechanical treatment was associated with high energy consumption and damage of cellulose crystalline structure during isolation treatment. While strong acid hydrolysis resulted in partial degradation of cellulose and caused reduction in crystallinity index. Therefore, a proper acid hydrolysis condition is essential to isolate cellulose nanocrystals from oil palm fronds. The isolation of cellulose nanocrystals from different parts of oil palm fronds was conducted by chemo-mechanical treatment. The top, middle and bottom parts of oil palm fronds were investigated to determine the effect of anatomical structure of oil palm fronds on the properties of cellulose nanocrystals. A thorough study was conducted on acid hydrolysis condition for the isolation of OPF CNC that was aimed to result in higher yield, crystallinity index and better thermal stability.

One of the problems associated with the conventional skin tissue repair material is the usage of cotton gauze that stick to the wounded area upon drying. This would cause pain when it was removed from the skin. Hence, a better material that could provide moist environment during the healing process is required in order to absorb the abscess from the body and easier to remove. Therefore, the usage of bio-polymer was found suitable for this application and could solve the problem associated with the conventional material.

1.2 Objectives

The objectives of the study are:

1) To determine the effect of anatomical structure of raw materials on the properties of cellulose nanocrystals isolated by chemo-mechanical treatment.
2) To characterise cellulose nanocrystals isolated from top, middle and bottom parts of oil palm fronds by using one condition of chemo-mechanical treatment.
3) To determine the optimum sulphuric acid hydrolysis condition to isolate cellulose nanocrystals from oil palm fronds.
4) To investigate the effect of cellulose nanocrystals from top part of oil palm frond as a reinforcement in the production of carboxymethyl cellulose-cellulose nanocrystals bio-nanocomposites.
5) To determine the effectiveness of oil palm fronds cellulose nanocrystals and citric acid addition on the properties of bio-nanocomposites.

1.3 Significant of Research and Justifications

This research was expected to provide a new insight on the potential of oil palm fronds fibre to be utilised in high end applications such as in biomedical field. The application in this work was aimed to be used as reinforcement for bio-nanocomposites from carboxymethyl cellulose. Some of the justifications include:

i. The availability of oil palm fronds throughout the year made it suitable to substitute existing source of fibre. Since the current practice of disposing oil palm fronds was not environmentally friendly, the utilisation of this material will contribute to save the environment and reduce its abundance.

ii. Acid hydrolysis treatment using strong acid was able to isolate cellulose nanocrystals effectively. However, the treatment conditions had major effects in order to produce cellulose nanocrystals with improved properties. Therefore, the right parameters should be chosen during the manufacturing process considering that the origin and types of raw materials would give different cellulose nanocrystals properties.

iii. Outstanding properties of cellulose nanocrystals had been widely discussed in various field of research. Since it was biocompatible, cellulose nanocrystals can be mixed with various types of polymers. In order to reduce dependency on petroleum-based polymers, carboxymethyl cellulose was chosen to be used as the matrix while cellulose nanocrystals acted as the reinforcement for bio-nanocomposites. Both materials were hydrophilic in nature, but the addition of citric acid would improve its physical properties and provide a potential of this bio-nanocomposite to be used as skin tissue repair material. In addition, the CMC is biodegradable, biocompatible, non-toxic and easily available. Therefore, it could be beneficial for bio-medical industry to substitute the conventional wound gauze with this bio-nanocomposites.

2 CHAPTER TWO: LITERATURE REVIEW

2.1 Oil Palm

2.1.1 Introduction of Oil Palm

Oil palm is cultivated in most of the tropical areas in the world and has become one of the foremost industrial crops. The oil palm (*Elaeis guineensis Jacq*.) is a non-woody plant and possesses distinctive properties from hardwood and softwood. It originates from Africa and categorised under family of *Aracaceae* that possesses monocotyledonous characteristics (Corley & Tinker, 2015). The matured oil palm tree generally height up to 20 to 30 m and covered with feather-like shape leaves (Edem, 2002). Every part of oil palm tree can be used for diverse purposes. For instance, the edible oil is extracted from ripe oil palm fruits. The oil palm fruits, normally reddish in colour grow in bulky bunches and each weigh at about 10–40 kg. The oil extracted from the pulp is edible and normally used for cooking while the oil extracted from the kernel (palm kernel oil) is used primarily in soap-manufacturing (Handerson & Osborn 2000).

With regards to huge oil palm plantation in Malaysia, the supply of oil palm biomass is 7 times the availability of natural timber (MPOB, 2017). Generally, after 3 years of planting, oil palm fruit is harvested, and its maximum yield is achieved in the 12–13th year of its age. The yield continues to drop until it reaches the end of the 25th year (Abdullah & Sulaiman, 2013). In the case of replantation, massive amount of oil palm trunks was cut and left in the plantation area. The OPT contains moisture content of approximately 70% fresh weight. Therefore, the freshly cut trunks cannot be burnt in the plantation. The trunks normally would take between five to six years to naturally decompose (Kosugi et al. 2009). Thus, leaving the trunks in the plantation would only cause harm as it obstructs the replantation process and harbours insects which would harm the new trees.

As of December 2016, the total oil palm plantation area in Malaysia was reported to be 5.74 million hectares with 0.5 million hectares increment from the previous year (MPOB, 2017). Table 2.1 summarized the oil palm planted area by state in Malaysia. We can see that half of the oil palm plantation was contributed by Sabah and Sarawak while the other half was found in peninsular Malaysia. An increase in the oil palm plantation is directly proportional to the increment of oil palm biomass wastes. Therefore, other than concerning about the oil production, managing oil palm wastes should also be considered very important to not cause environmental pollution.

Oil palm contributes extensively to country’s economic growth of Southeast Asia especially Malaysia, which depends profoundly on the palm oil sector (Handerson & Osborn, 2000). A previous study by Sulaiman et al. (2012) reported that the average yearly production of palm oil in Malaysia will exceed 15.4 million tons in the period year of 2016-2020 due to notable and constant growth of the palm oil in the global market over four decades.

Table 2.1 Oil palm planted area by state as at December 2016 (hectares)

State	Mature	%	Immature	%	Total	%
Johor	678,508	91	67,122	9	745,630	13
Kedah	82,727	94.2	5,059	5.8	87,786	1.5
Kelantan	112,449	72.3	43,009	27.7	155,458	2.7
Melaka	51,178	91.1	4,971	8.9	56,149	1
Negeri Sembilan	154,388	86.3	24,570	13.7	178,958	3.1
Pahang	630,612	86.1	101,440	13.9	732,052	12.8
Perak	353,417	88.8	44,491	11.2	397,908	6.9
Perlis	603	92.5	49	7.5	652	0
Pulau Pinang	13,413	94.9	722	5.1	14,135	0.2
Selangor	127,595	91.9	11,236	8.1	138,831	2.4
Terengganu	144,497	84	27,446	16	171,943	3
Peninsular Malaysia	2,349,387	87.7	330,115	12.3	2,679,502	46.7
Sabah	1,383,109	89.1	168,605	10.9	1,551,714	27
Sarawak	1,268,942	84.2	237,827	15.8	1,506,769	26.3
East Malaysia	2,652,051	86.7	406,432	13.3	3,058,483	53.3
Total	5,001,438	87.2	736,547	12.8	5,737,985	100

Source: MPOB, 2016

2.1.2 Oil Palm Biomass

Oil palm biomass can be obtained throughout the year during harvesting and pruning of oil palm tree. Oil palm biomass are found in the form of fronds, empty fruit bunches, trunks, mesocarp fibre, palm kernel shell and palm oil mill effluent. It was reported that more than one hundred million tonnes of residues annually produced by the oil palm industry. For one hectare of oil palm plantation, the biomass residues generated was about 22 tonnes per year (Tau et al., 2007). The availability of the oil palm biomass in Malaysia is summarized in Table 2.2.

Table 2.2 Annual availability of oil palm biomass by type

Biomass type	Site of production	Annual availability	
		Per ha (tonnes of dry biomass)	National total (m tonnes of dry biomass)
Fronds	Plantation	9.6	46.4
Trunks	Plantation	3.0	14.4
Empty fruit bunch	Mill	1.4	6.7
Palm kernel shell	Mill	0.8	4.1
Mesocarp fiber	Mill	1.4	6.9

Source: National Biomass Strategy 2020: New wealth creation for Malaysia's biomass industry (Version 2.0, 2013)

Usually, these biomasses were left to rot in the plantation or incinerated but this kind of practice eventually led to the emission of greenhouse gases such as aerosol particles, carbon dioxide, carbon monoxide, volatile organic compounds, organic halogen compounds (Yamada et al. 2010). Therefore, numerous researches were carried out in order to tackle this problem by utilizing the materials as a substitute to wood/non-wood fibre. Basically, oil palm biomass has good potential to be converted to numerous value-added products which can be clustered into bio-based chemical, direct fuel for power generation, material and biofuel (Sunarta et al. 2011). Based on Table 2.2, OPF is the largest contributor of oil palm biomass in Malaysia, followed by OPT, mesocarp fibres, EFB, and palm kernel shell. Its abundance throughout the year should be exploited to form value added products to be commercialised in the industry. Therefore, OPF is chosen to be used as a starting material in this work, considering their availability and promising properties.

2.1.3 Availability of Oil Palm Fronds

Oil palm frond is one of the by-products from cultivation of oil palm trees. They are available in the oil palm plantations when the palms are pruned or during the fruit harvesting throughout the year. The generation of fibrous waste materials resulting from the harvesting of oil palm fruits in Malaysia and Indonesia particularly increases due to rapid development of oil palm industry since 1990s (Dahlan, 2000). Figure 2.1 showed the oil palm fronds of a matured oil palm tree.

In the early years, the OPF and OPT were burned in the plantation area but due to environmental concern, it was banned in the 1990s. Therefore, the OPF and OPT are currently left on the ground which act as soil fertilizer. They retain moisture and return organic matter into the soil as can be seen in Figure 2.2 (Lim et al. 2012). Apart from providing nutrient for the soil, the OPF can be processed into pulp and refined for the ruminant roughage for goats and cattles. Besides, it also has potential to be used for balance diet pellet for fattening beef cattle (Sulaiman et al. 2012).

However, the fronds cannot be stacked with more than two layers around the tree because it could attract destructive insects in the palm plantations (Prasertsan et al. 1996). This kind of practice helps soil conservation, as well as controlling the erosion of the soil (Abu Hassan et al. 1994).

Figure 2.1: Oil palm fronds of a matured tree

Since the OPF was left to decompose in the plantation area, a notable number of research were carried out around Malaysia and Indonesia to investigate the nutritional value and economic accountability of the OPF for ruminants. These researches were aimed to improve self-reliance in meat and dairy production (Wan Zahari et al. 2003).

Figure 2.2: Current view of cut oil palm fronds in the plantation area.

These organic natural fibres also draw attention for researches on various usages in many structural and non-structural applications. These fibres are renewable, abundant, cheap, non-abrasive and easy to handle which make it suitable to be used as a substitution to wood resources.

2.1.4 Morphology of oil palm fronds

The OPF fibres contained vascular bundles of different sizes that are broadly imbedded in parenchymatous ground tissue. Every vascular bundle is made up of a fibrous sheath, fibres, parenchymatous tissues, phloem vessels. Xylem and phloem tissues are distinctive with one another. Phloem is divided into two separate areas in each bundle while protoxylem and metaxylem were separated by a layer of parenchyma cells (Mhd Ramle et al. 2012). The SEM image in Figure 2.3 showed the cross-sectional view of raw oil palm frond. According to previous study, within the stem and leaves, proto and metaxylem vessels are separated by at least one layer of live parenchyma cells, which form a living barrier to possible transfer of gas bubbles between proto and metaxylem vessels (Tomlinson et al. 2001).

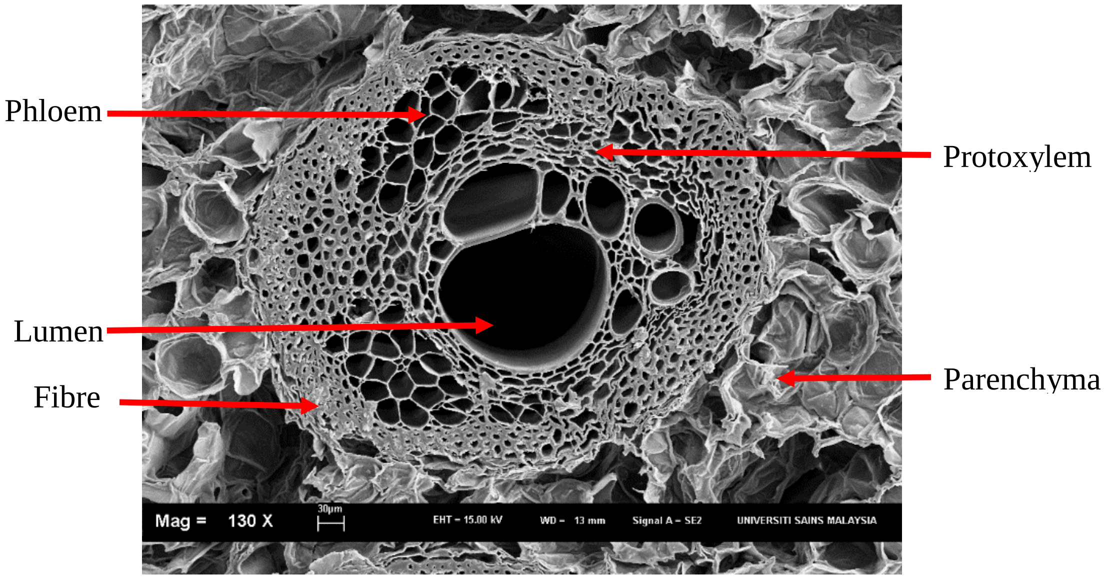

Figure 2.3: Anatomical structure of oil palm frond vascular bundle

2.1.5 Mechanical properties

Mechanical properties of fibre play an important role as it will determine the strength of materials. In the case of oil palm tree, variation in density for different parts of oil palm is attributed to its monocotyledonous nature. Meanwhile, the variations of density in OPF is observed to be affected by the morphological structure difference, number of fibrous bundles along the frond, and the movement of starch deposits in parenchyma cells. The mechanical properties of oil palm biomass are tabulated in Table 2.3, showing their tensile strength, Young's modulus and elongation at break. The data showed that the oil palm trunk possesses greatest mechanical strength followed by the OPF and EFB.

Table 2.3:Mechanical properties of oil palm fibres (Abdul Khalil et al. (2012)

Fibres	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Empty fruit bunch	50-400	0.57-9	2.5-18
Frond	20-200	2-8	3-16
Trunk	300-600	8-45	5-25

2.1.6 Physical properties

Physical properties of fibre that receives crucial concern are their fibre length, diameter, lumen diameter, cell wall dimension, and microfibril angle. However, these properties vary according to the species, origin, sources and maturity of the fibre itself (John & Thomas, 2008). Table 2.4 represents the physical properties of EFB, OPF and OPT fibre. There was a notable difference of fibre length and diameter for all samples but the lumen, density and fibril angle were comparable to one another.

Table 2.4:Physical properties of oil palm biomass fibre (Abdul Khalil et al. 2012)

Fibre	Fibre length (mm)	Fibre diameter (μm)	Lumen width (μm)	Density (g/cm^3)	Fibril angle (°)
Empty fruit bunch	0.89-1.42	8-30.0	8	0.7-1.55	46
Frond	0.59-1.59	11-19.7	8.20-11.66	0.6-1.2	40
Trunk	0.60-1.22	29.6-35.3	17.60	0.5-1.1	42

Researchers reported that OPF fibres are thicker and shorter in dimensions in comparison with OPT and EFB fibres. Thus, it managed to withstand collapse and does not contribute to interfibre bonding to the same extent (Reddy & Yang 2005). The structural characteristic of fibre will determine the performance of final products and their suitability to be used commercially. Other than that, the aspect ratio of fibre (length over width) is also an essential characteristic to be considered in order to fully utilise its maximum potential (Ververis et al. 2004). Thus, these individual fibre characteristics is crucial to be analysed when considering biomass materials to be used in multi-disciplinary applications as it will affect the final properties of the products.

2.1.7 Chemical composition of OPF

Cellulose, hemicellulose and lignin are mainly found in cell walls in the ratio of 4:3:3. However, this ratio differs according to sources of the fibre such as hardwood, softwood, non-wood and herbs (Chen, 2014). For instance, hardwood has greater amount of cellulose while leaves and wheat straw contains greater percentage of hemicellulose. Other than cellulose, hemicellulose and lignin, lignocellulosic materials also contain a small amount of compounds such as pectin and the ash. The major component of lignocellulosic material, cellulose is arranged regularly and gathered into bundles. This compact structure determines the framework of the cell wall (Mendu et al. 2011).

Cellulose structure is composed of glucose residues, with cellobiose as the basic coupling unit. Meanwhile hemicellulose is categorised as a heterogeneous polysaccharide that are formed through biosynthetic routes. Similar to cellulose, hemicellulose provide support to the cell wall with a degree of polymerization of 200 compared to cellulose ~10 000. The presence of hemicellulose and lignin in lignobiomass functions to provide strength to plant cell walls and protect the cellulose structure from enzymatic degradation (Suiter et al. 2010).

Hemicellulose is the second most abundant polymer after cellulose and mainly composed of hexoses (mannose, glucose, galactose), pentoses (xylose, arabinose), and acetylated sugars. It is a low-molecular weight polysaccharide, found in plant cell walls with cellulose and lignin (Song et al. 2008). Hemicellulose generally provides bonding between the cellulose and lignin and possesses great industrial potential from its physical, chemical and biological properties. Most of the hemicellulose fraction dissolves in water when it was treated with alkaline solution. However, hemicelluloses have limited solubility in cold alkaline solutions, but warm alkaline solutions could lead to its degradation. Hemicellulose is quite difficult to isolate due to the complex physical and chemical within the lignin-hemicellulose-cellulose structure of the plant material (Hoije et al. 2005).

Lignin is one of the amorphous structures in cell wall. It is made up of heteropolymer network of coniferyl, p-coumaryl, and sinapyl alcohol linked together by different bonding. Lignin acts as physical barrier of plant cell wall corresponding to its complex structure. It has a rigid structure, impermeable, insoluble in water, and resistant to oxidative stress and microbial attack. Apart from that, lignin also functions to provide toughness and stiffness to the fibres in order to protect the carbohydrates from physical and chemical damage (Saheb & Jog 1999). Hemicellulose and lignin are positioned next to each other thus formed a complex termed as lignocellulose (Goyal et al. 2006). In order to purify cellulose, it is crucial to remove the lignin in order to cause biomass swelling, increase the internal surface area, and increase accessibility of hydrolysis reaction (Doherty et al. 2011; Ebringerova et al. 2005).

Lignin is well known for its significant association with mechanical support for plant organs that enable them to grow in height (Boudet, 2000; Douglas, 1996). Lack of lignin in the plant cells will no longer allow plants to be upright (Zhong et al. 2000). However, lignin is usually not desirable for the production of many fibre-based products especially in the paper making process. As lignin naturally gives dark colour to the fibre, bleaching process or delignification took place in order to produce a white/bright colour paper. In this case, a lot of chemicals need to be used which resulted in an increase in their production cost. In the production of biocomposite, the presence of lignin causes an interference in chemical and physical bonding between materials presence in the formulation which would finally affect the mechanical and physical properties of the end product (Le Digabel & Averous, 2006). The chemical composition of selected oil palm biomass is tabulated in Table 2.5.

Table 2.5: Physical properties of oil palm biomass fibre (Hashim et al. 2011)

Parts of oil palm	Extractives	Chemical composition (%)		
		Holocellulose	Alpha cellulose	Lignin
Bark	10.0	77.82	18.87	21.85
Leaves	20.0	47.7	44.53	27.35
Fronds	3.5	83.13	47.76	20.15
Mid part of trunk	14.5	72.6	50.21	20.15
Core part of trunk	9.1	50.73	43.06	22.75

It can be seen that different parts of oil palm biomass possess different percentage of chemical composition, with OPT and OPF showing greater cellulose contents compared to other biomass. The chemical composition of OPF affects the properties and economic production of fibre-based materials. Abdul Khalil et al. (2008) reported that the cellulose content of OPF was 56.03%, which was higher than the cellulose content of other parts of oil palm tree. Similar finding was reported in previous research, indicating high percentage of cellulose in oil palm fronds (Sun & Cheng, 2002; Abdul Khalil & Rozman, 2004). Therefore, it has good potential to be used for the production of cellulose nanocrystals.

2.2 Lignocellulosic Material

Lignocellulosic comprised of three major components which are cellulose, hemicellulose and lignin. The content of these components differs based on the type of fibre as well as the origin, age and mode of extraction (Bledzki & Gasan, 1999). This oil palm biomass consists primarily of plant cell wall which composed of three main biopolymers namely; cellulose (~30- 50 % by weight), hemicellulose (~19-45 % by weight), lignin (~15-35 % by weight) and slight quantity of protein (Sauian et al., 2013). Cellulose, being the most abundant natural polymer in the world can be used for numerous applications due to its biodegradability, renewability and non-toxicity. Wood and cotton are among the major sources of cellulose. Cellulose can be derived from a wide range of sources such as hardwood and softwood, non-wood plants, seed fibres, bast fibres, bacteria, fungi, algae and marine animals (Varshney & Naithani, 2011). In comparison with hardwood and softwood, the non-wood plants receive high interest as a good source of cellulose due to their low lignin content. This in return requires less fibre delignification and the process of purifying the cellulose will be easier (Nechyporchuk et al., 2016).

2.3 Structural properties of Cellulose

Cellulose is signified as a well-organized structure of fibrillar elements composing cells. It is naturally fibrous, tough and water insoluble. Cellulose functions as a main role in upholding the plant cell wall structure (George & Sabapathi, 2015). The strong mechanical strength of cellulose is attributed to the presence of hydrogen bonds that significantly affect the microfibrillated structure and its hierarchical organization (Lindman et al. 2010). Figure 2.4 showed the division of cell wall structure.

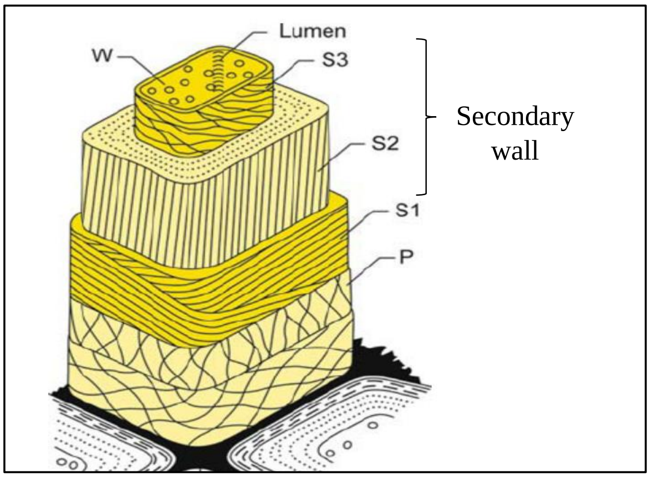

Figure 2.4: Cell wall structure of plant (Agarwal, 2006)

The lignocellulose wall comprised of several layers namely primary cell wall, secondary cell wall (inner, middle and outer layer), and the warty layer. The middle lamella functions as the binding agent for the adjacent cells due to the presence of lignin. The primary and secondary walls generally comprised of cellulose, hemicellulose and a matrix called pectin and lignin. Pectin exists in the primary wall while lignin is present in the secondary wall (Caffall & Mohnen, 2009). The microfibrils in the secondary wall are in the form of densely packed flat helix aligned in parallel direction. It contains most of the cellulose mass in fibre and possess a thickness that varies from 100 nm (cotton) to 300 nm (spruce wood). Meanwhile, a thin layer called warty layer is located at the inner surface of cell wall. The warty layer is mainly composed of hemicellulose and lignin (Klemm et al. 1998; Sjostrom, 1981). A detail illustration of cell wall components of plant is shown in Figure 2.5.

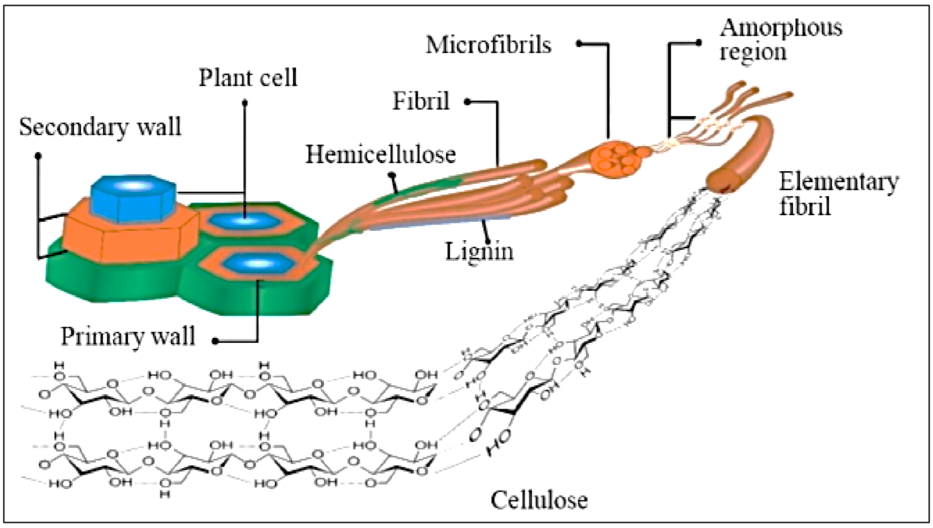

Figure 2.5: The components in plant cell wall (Habibi et al. 2006)

Generally, cellulose are divided in two major types, which are cellulose type I (native cellulose-originated from plants in its natural form) and cellulose type II (regenerated from cellulose I by applying chemical treatment). Cellulose is categorized as a semi crystalline polymer that contains ordered(crystalline) and disordered(amorphous) regions within the microfibrils. The innate degree of crystallinity for cellulose is normally in the range of 40-70% which is highly depending on the cellulose source and the treatment to isolate cellulose (Wertz et al., 2010). The degree of polymerization (DP) for cellulose also varies according to the type and source of cellulose. For instance, the DP of cellulose is approximately 10 000 in native wood, 20 000 in cotton, and about 200-500 in regenerated cellulose depending on the method of purification (Fengel & Wegener, 1983). Cellulose, the most abundant biopolymer in the world is a linear polysaccharide that is found mainly in plants. It is a high molecular weight homopolymer made of β-1,4-linked glucopyranose units. Each glucopyranose unit has three hydroxyl groups. These highly reactive hydroxyl groups contribute to the hydrophilicity, biodegradability and chirality of cellulose (Klemm et al. 2005). The chemical structure of cellulose is shown in Figure 2.6.

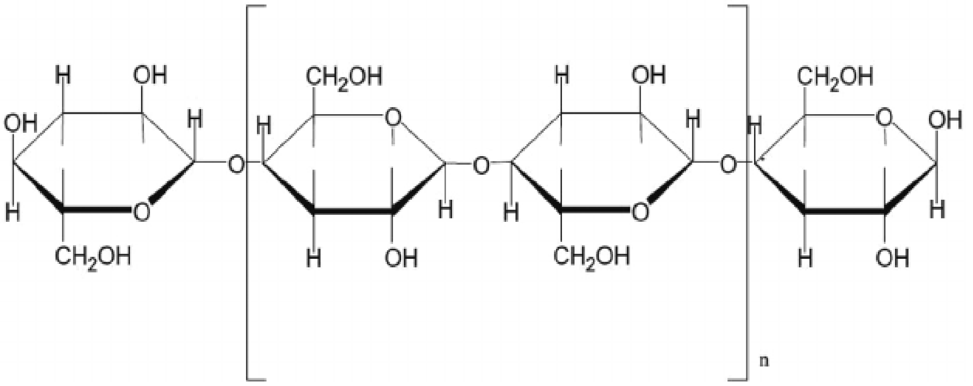

Figure 2.6: Chemical structure of cellulose (Thakur et al., 2014)

2.4 Isolation method of cellulose

Cellulose nanocrystals can be produced by chemical, mechanical, chemo-mechanical and enzymatic treatment. The methods of cellulose extraction will result in various types of nanocellulose depending on the desired properties and the suitability of the fibres (Kargarzadeh et al. 2012).

2.4.1 Chemical treatment

The process of isolating cellulose by chemical treatment is associated with the utilization of chemicals to extract and purify the cellulose. Normally, acid hydrolysis treatment using organic acid was employed and the cellulose obtained from this method is categorized as cellulose nanocrystals (Saxena & Brown, 2005).