ISOLATION AND CHARACTERIZATION OF CELLULOSE NANOCRYSTALS FROM OIL PALM TRUNK

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ISOLATION AND CHARACTERIZATION OF CELLULOSE NANOCRYSTALS FROM OIL PALM TRUNK

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LIST OF ABBREVIATIONS

CNC	Cellulose nanocrystals
CNW	Cellulose nanowhiskers
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetric
EFB	Empty fruit bunch
FTIR	Fourier transform infrared
MCC	Microcrystalline cellulose
MDF	Medium density fiberboard
MPOB	Malaysian Palm Oil Board
NCC	Nanocrystalline cellulose
NFC	Nanofibrillated cellulose
OPF	Oil palm frond
OPT	Oil palm trunk
PVA	Polyvinyl alcohol
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
XRD	X-Ray Diffraction

PENGASINGAN DAN PENCIRIAN SELULOSA NANOKRISTAL DARIPADA BATANG KELAPA SAWIT

ABSTRAK

Kajian ini bertujuan untuk mengkaji sifat-sifat selulosa nanokristal (CNC) yang diekstrak daripada batang pokok kelapa sawit (*Elaeis guineensis*) (OPT). Enam jenis CNC diekstrak daripada OPT dengan menggunakan dua kaedah yang berbeza. Empat jenis CNC yang diperolehi daripada OPT secara keseluruhan iaitu nanokristal yang terhasil daripada bahan asal tanpa rawatan dan rawatan air panas serta daripada parenkima dan berkas vaskular OPT melalui kimo-mekanikal diikuti hidrolisis dengan asid sulfurik. Dua jenis nanokristal selulosa lagi diperolehi melalui pra-hidrolisis dan tanpa pra-hidrolisis air disediakan melalui pemulpaan soda diikuti pelunturan ozon dan dihidrolisis dengan asid hidroklorik. Sifat-sifat fizikal, dan kimia, sifat-sifat termal dan indeks penghabluran nanokristal selulosa yang masing-masing ditentukan menggunakan pengimbas mikroskop electron (SEM), penghantaran elektron mikroskop (TEM), potensi zeta dan penganalis unsur, Fourier transformasi inframerah (FTIR), analisis termal gravimetrik (TGA) dan analisis pembelauan sinar-X (XRD). Keputusan menunjukkan gentian individu berbentuk partikel rod dengan purata diameter dan panjang bersaiz nano terhasil bagi semua selulosa nanokristal. Spektra FTIR memaparkan puncak yang mewakili lignin dan hemiselulosa hilang selepas rawatan kimia dan pemulpaan selain menunjukkan bahawa kedua-dua komponen tersebut hilang sepenuhnya daripada sampel selepas hidrolisis asid dijalankan. Termogravimetrik pula memaparkan bahawa kestabilan termal bagi semua bahan meningkat selepas hidrolisis asid dilakukan. Lengkungan TGA menunjukkan kedua-dua nanokristal selulosa daripada parenkima dan berkas vaskular OPT memiliki kestabilan termal yang baik tetapi nilai kestabilan termal bagi parenkima selulosa

nanokristal adalah lebih tinggi daripada berkas vascular. Walaupun kandungan sulfur memberi kestabilan ampaian kepada CNC, tetapi, ianya memberi kesan kepada hasil dan suhu permulaan degradasi CNCs yang diasingkan menggunakan asid sulfuric disebabakan cas negative oelg kumpulan sulfat. Analisis XRD menunjukkan bahawa berlaku peningkatan penghabluran selepas proses hidrolisis asid menerangkan sifat semula jadi penghabluran nanokristal terasing untuk semua sampel. Pengasingan selulosa nanokristal dengan pemulpaan soda dan pelunturan ozon diikuti hidrolisis asid hidroklorik mempamerkan nilai penghabluran tertinggi iaitu 75% walaupun kemerosotan selulosa berlaku ketika pelunturan ozon dijalankan. Pengasingan selulosa nanokristal menggunakan pemulpaan soda diikuti pelunturan ozon dan hidrolisis asid hidroklorik menunjukkan peningkatan ciri-ciri dari segi dimensi, termal dan penghabluran berbanding pengasingan selulosa nanokristal menggunakan asid sulfurik. Seterusnya, kajian dijalankan untuk menghasilkan filem bio-nanokomposit yang berpotensi digunakan sebagai pembalut luka. Selulosa nanokristal terasing yang dipilih digabungkan dengan polivinil alkohol (PVA) melalui teknik ‘solvent casting’. Filem PVA diperkuat dengan beberapa kandungan selulosa nanokristal (0, 1, 3, dan 5%) dibuat dan diuji sifat fizikal dan mekanikalnya. Keputusan ujian memaparkan keserasian yang amat baik antara matriks (PVA) dan penguat (CNC) yang bertanggungjawab meningkatkan sifat mekanikal filem PVA/CNC. Keseimbangan termal meningkat selaras dengan penambahan CNC ke dalam matriks PVA. Berdasarkan spektra FTIR dan analisis XRD, penambahan CNC tidak menunjukkan sebarang kesan terhadap penghabluran matriks PVA. Keputusan menunjukkan sifat-sifat mekanikal, fizikal dan termal yang baik bagi PVA/ CNC bio-nanokomposit.

ISOLATION AND CHARACTERIZATION OF CELLULOSE NANOCRYSTALS FROM OIL PALM TRUNK

ABSTRACT

This study investigated the properties of cellulose nanocrystal (CNC) isolated from oil palm trunk (*Elaeis guineensis*) (OPT). Six types of CNCs were extracted from OPT using two different methods. Four types of CNCs were derived from the OPT as a whole that is CNCs from raw and water treated and also from separated parenchyma and vascular bundle of OPT using chemo-mechanical followed by sulfuric acid hydrolysis. Two more types of CNC with and without water pre-hydrolysis were prepared by soda pulping followed by ozone bleaching and hydrolyzed with hydrochloric acid. Physical and chemical properties, thermal behaviour, and also crystallinity index of all obtained CNCs were determined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), zeta potential, elemental analyzer, fourier transform infrared (FTIR), thermogravimetric analysis (TGA) and X-ray diffraction (XRD), respectively. The results showed individual fiber of rod-shape particle with a nano-sized average diameter and length in all cellulose nanocrystals produced. The FTIR spectra indicated that the peaks attributed to lignin and hemicelluloses were absent after chemical and pulping treatment and seems that both components were completely removed from the samples after acid hydrolysis. Thermogravimetric analysis displayed that the thermal stability in all materials increased after acid hydrolysis. The TGA curves showed that both cellulose nanocrystals from parenchyma and vascular bundle have good thermal stability with higher values observed for parenchyma compared with vascular bundle cellulose nanocrystals. Even though sulfur content giving a stable CNC suspensions, however,

it was affecting the yield and the onset temperature of the CNCs isolated using sulfuric acid due to the negative charged of sulfate group. The XRD analysis showed that crystallinity increased after acid hydrolysis indicating the crystalline nature of the isolated nanocrystals for all samples. Cellulose nanocrystals isolated using ozone bleaching and hydrochloric acid hydrolysis showing the highest crystallinity that is 75 % even though cellulose degradation occurs in the ozone bleaching stage. Cellulose nanocrystals isolated using soda pulping followed by ozone bleaching and hydrolyzed with hydrochloric acid showed greater properties in terms of dimensions, thermal and crystallinity as compared to the cellulose nanocrystals isolated using chemo-mechanical followed by sulfuric acid hydrolysis. Further works were carried out to produce bio-nanocomposite films. The chosen cellulose nanocrystals were incorporated with polyvinyl alcohol (PVA) with solvent casting technique. The PVA films reinforced with several cellulose nanocrystals contents (0, 1, 3, and 5 wt %) were casted and were evaluated for their mechanical and physical properties. The result displayed excellent compatibility between matrix (PVA) and reinforcement (CNC) which is responsible for the increasing in mechanical properties of PVA/CNC films. Thermal stability increased with the incorporation of the CNC into PVA matrix. From the FTIR spectra and XRD analysis, the incorporation of CNC did not have an effect on the crystallinity of the PVA matrix. The results showed a good mechanical, physical and thermal properties of the PVA/CNC bio-nanocomposite films.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Utilization of oil palm trunk that produces 19.4 million tons of dry weight annually (MPOB, 2015) motivates the researchers to turn this bio-fibers into valuable sustainability products. One of the solutions to tackle the problem of oil palm trunk being left to rot in the plantation field is by converting them into value- added products to be used potentially in the furniture, cattle feedstock and others. As lignocellulosic materials with an abundance of tiny structural entities known as cellulose fibrils, oil palm trunk can provide a sustainable source for isolation of cellulose microfibers and nanofibers. These nano fibers can be isolated from the cellulosic plants either by chemical, mechanical and enzymatic process. The nanofibers isolated were called differently based on their process of production. Cellulose nanofibril or nanofibrillated cellulose (NFC) were produced using mild chemical or enzymatic fiber treatment followed by mechanical treatment while cellulose nanowhiskers or cellulose nanocrystals (CNC) were isolated using a strong acid hydrolysis.

Isolation of CNC from cellulosic plants involved two stages where the first stage is a pre-treatment of the fibers to remove the matrix substances particularly lignin, hemicelluloses and others. The second stage is controlled acid hydrolysis, which remove the amorphous domains of the cellulose polymer and leaving the crystalline part of the fibrils (Brinchi et al., 2013).

Pre-treatment of the cellulosic plants is a necessary preparation to produce the cellulose nanocrystals to depolymerize and solubilize the lignin, hemicelluloses, and other non-cellulosic substances. Pulping and bleaching processes usually served for

this purposes where the chemicals have been involved such as sodium hydroxide (pulping) and bleaching agents (oxygen, sodium hypochlorite and ozone) (Eichhorn, 2010; Brinchi et al., 2013). However, the use of sodium hypochlorite is considered harmful and not environmentally friendly. Thus, in this study an approach of using more environmentally method of soda pulping and ozone bleaching in a pre-treatment process to obtain high purity of cellulose microfibers also been conducted.

The cellulose nanocrystals were isolated from oil palm trunk fibers using two approaches that are by chemo-mechanical treatment and sulfuric acid hydrolysis and secondly, soda pulping and ozone bleaching followed by hydrochloric acid hydrolysis. The first approach consumes a lot of chemicals and uses a more concentrated acid. Therefore, in order to reduce chemicals consumption, the second approach have been proposed. Since this is the first study as there is no study as to our knowledge reported that isolating the cellulose nanocrystals from oil palm trunk, both approaches have been compared for their yield, chemical and physical, thermal properties and also crystallinity.

The study reported to use oil palm trunk as raw materials to produce cellulose nanocrystals is very limited. The motivation is to convert this biomass into a cellulose particularly cellulose nanocrystals, owing to its cellulosic nature and as carbohydrates reserve compel this study to be conducted. A few studies (Fahma et al., 2010; Mohamad Haafiz et al., 2013) have been reported using other parts of oil palm tree particularly empty fruit bunch (EFB) to isolate the nanocellulose from this biomass waste. However, studies on the isolation of cellulose nanocrystals from oil palm trunk have not been yet reported. Therefore, this study is done to provide data on the first cellulose nanocrystals isolated from oil palm trunk.

In order for the value-added utilization of cellulose nanocrystals from oil palm trunk, the cellulose nanocrystals obtained have been used to develop bio-nanocomposite films. The selected isolated and characterized cellulose nanocrystals from oil palm trunk were later incorporated with the polyvinyl alcohol (PVA) to form a PVA/CNC bio-nanocomposite films. Polyvinyl alcohol has been chosen due to its easy process ability and biocompatible (Lee et al., 2009). The hydroxyl group on the hydrolyzed PVA are expected to interact with the hydrophilic surfaces of CNCs, leading to strong hydrogen bonding and improved the mechanical properties of the PVA/CNC films. Therefore, PVA/CNC bio-nanocomposite films have been fabricated to study their mechanical behavior.

1.2 Problem statement

Owing to the annual availability of the oil palm biomass particularly oil palm trunk and the continuous supply of the waste as resources, the utilization of the trunks into a value-added product gaining much attention from the researchers. The goals are to use the waste resources which contributing to the environmental pollution to produce green products. Therefore, isolation of cellulose nanocrystals from oil palm trunk has been proposed to widen the utilization of oil palm trunk.

In this study, two approaches have been used to isolate the cellulose nanocrystals from oil palm trunk. The first approach is via chemo-mechanical treatment followed by sulfuric acid hydrolysis. The second approach is via soda pulping and ozone bleaching followed by hydrochloric acid hydrolysis. In the first approach, sodium hypochlorite being used as one of the bleaching agents to remove the lignin. In addition, when using sulfuric acid the cellulose nanocrystals obtained had a low yield and low thermal stability but good stable suspensions. Therefore, in

the second approach, an environmentally friendly method have been conducted in removing the lignin with high purity of cellulose. Using hydrochloric acid will enhance the thermal stability of the cellulose nanocrystals but giving a poor dispersion stability. The cellulose nanocrystals obtained will be comparable for their properties in term of yield, thermal stability and crystallinity.

1.3 Objectives

The objectives of the study are:

1) To produce and characterize cellulose nanocrystals from oil palm trunk using chemo-mechanical treatment and sulfuric acid hydrolysis.
2) To study the properties of parenchyma and vascular bundle of oil palm trunk and their isolated cellulose nanocrystals using chemo-mechanical treatment and sulfuric acid hydrolysis.
3) To isolate and investigate the properties of cellulose nanocrystals isolated from oil palm trunk using soda pulping and ozone bleaching via hydrochloric acid hydrolysis.
4) To produce and study the properties of cellulose nanocrystals reinforced polyvinyl alcohol bio-nanocomposite films

1.4 Novelty

The novelty of the research lies in the contribution of the research data findings dealing with oil palm trunk and cellulose nanocrystals. The oil palm industry is contributing to the waste management problems. Therefore, researchers tend to find the solution for converting the biomass into something valuable and contribute to the growth of Malaysia's economy. Oil palm trunk mainly use in the

furniture making industry and production of the board including MDF. Recently, study on the isolation of cellulose based particularly in nanocellulose fibers gaining much attention. To the best our knowledge, isolating the nanocellulose in the type of cellulose nanocrystals from oil palm trunk has not been reported yet. Thus, this is a pioneer work to provide the data of cellulose nanocrystals isolated from oil palm trunk and we can claim that our research is the first to study the isolation of the cellulose nanocrystals from oil palm trunk.

1.5 Thesis organization

In this thesis, it consists of nine chapters. In the first chapter, it is an introduction of the background study, problem statement, objectives and the novelty of the study. Chapter two contains a review of published literature relating to this subject. The literature review was used to guide the reader to understand the study regarding its design, methods, analysis and expected trends.

Chapter 3 covered the information of the materials and chemicals that had been used during the study. It also described in details on the experimental methods from the preparation of the samples to the process of producing cellulose nanocrystals. It also entails various analysis to characterize the samples including FTIR, SEM, TEM, TGA, XRD, DSC and other chemical composition analysis.

In Chapter 4, properties of parenchyma and the vascular bundle of oil palm trunk were investigated. Study on the properties of the cellulose nanocrystals isolated from oil palm trunk cellulose microfibers is discussed in detailed in Chapter 5. In Chapter 6, the study provides more details study on the properties of cellulose nanocrystals isolated from separated parenchyma and the vascular bundle of oil palm trunk. In Chapter 7, an attempt to isolate cellulose nanocrystals using environmental friendly

method has been carried out. Soda pulping and ozone bleaching followed by hydrochloric acid hydrolysis were proposed to carry out the isolation process. The properties of cellulose nanocrystals produced by this method were compared to the cellulose nanocrystals produced by other method mentioned in Chapter 5.

In Chapter 8, production of bio-nanocomposites film from the mixture of PVA and cellulose nanocrystals produced in this study were made. This chapter also discussed the properties of the produced film and its potential to be used in the wound dressing. Finally, Chapter 9 summarized the conclusion of all the findings from this study. Also, recommendation and suggested future works were also mentioned in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 The oil palm

2.1.1 Oil palm and its availability in Malaysia

Oil palm (*Elaeis guineensis*) is one of the routines and principal crops in Malaysia. Malaysia and Indonesia are the two leading countries in producing and exporting palm oil which account 85% of world palm oil production (Abdullah and Sulaiman, 2013). The oil palm (Fig. 2.1) industry contributed to the impressive economic growth and paved the way for Malaysia to succeed in the palm oil industry. The factors contributing to this achievement include the perfect conditions for the oil palm cultivation, an adept refining and milling technologies, efficient research and development, and effective and sufficient management skills in dealing with palm oil industry (Abdullah and Sulaiman, 2013).

Fig. 2.1 Oil palm

By the year 2000, with a value of 10.8 million tons half of the world palm oil production was contributed by Malaysia, and the production values keep increasing

until now. According to Sulaiman et al. (2011), for the period year for 2016-2020, Malaysia will pass the 15.4 million tons for the average annual production of palm oil due to the remarkable and constant growth in the global market over four decades. As of December 2014, the plantation of oil palm in Malaysia covers an area of 5.39 million hectares (Malaysian Palm Oil Board, 2015), as shown in Table 2.1.

Table 2.1: Oil palm planted area and output in Malaysia

	Jan–Nov 2014	Jan–Nov 2015	Change	Change (%)
Planted area (ha)	5,392,235	-	-	-
Production (tons)				
Crude palm oil	18,302,152	18,561,320	259,168	1.42
Crude palm kernel oil	2,102,352	2,099,063	–3 289	–0.16
Closing Stocks (tons)				
Palm oil	1,892,717	2,277,636	384,919	20.34
Palm kernel oil	4,551,554	4,571,660	20,106	0.44

Source: Malaysian Palm Oil Board (2015)

2.1.2 Oil palm biomass

The oil palm industry has always been related to the environment due to the uses of massive land for the plantation. It has been estimated that about 50–70 tons of biomass residues can be produced in one hectare of oil palm cultivation area. With the value, oil palm industry is contributing to a large quantity of biomass waste in Malaysia with 85.5 % from more than 70 million tons biomass generated as shown in Fig. 2.2 (Shuit et al., 2009; Hassan and Shirai, 2003). The solid biomass residue that created from the blooming of oil palm industries contributed to the major disposal problem which led to the environmental issue. The solid biomass residue produced are

in the form of oil palm trunk (OPT), empty fruit bunches (EFB), oil palm fronds (OPF), palm shells, palm pressed fibers (PPF), and palm oil mill effluent (POME).

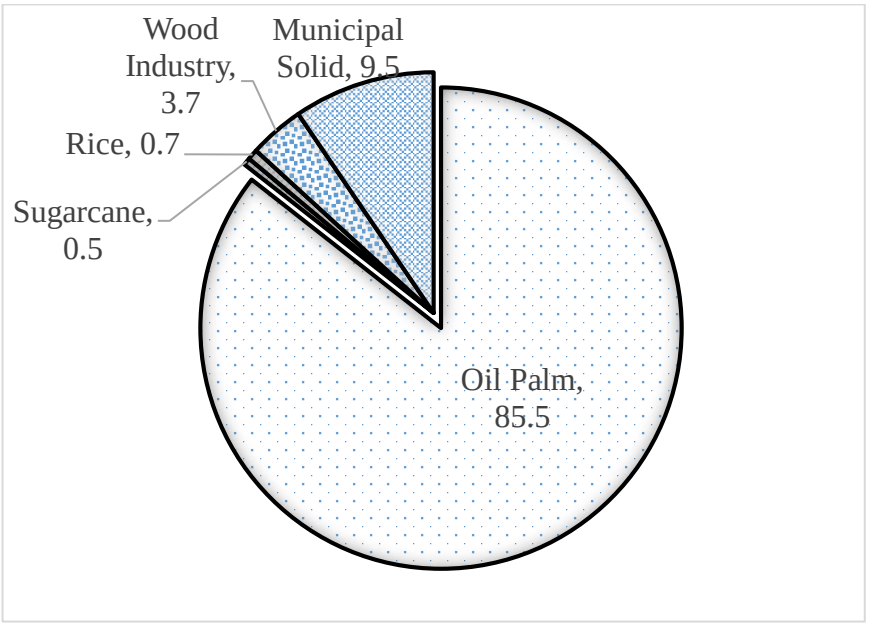

Fig. 2.2: Biomass produced from different industries in Malaysia (Hassan and Shirai, 2007)

Table 2.2 present the dry weight of potential oil palm biomass availability in the year of 2014. Mulch, energy, effluent treatment sludge, organic fertilizer derived from empty fruit bunches shells and are among the byproducts collected from these waste. The biomass waste can be processed to produce bio-oil, paper-making pulp, and plywood and saw wood, medium density fiberboards, and a blockboard. The palm fibers can be used as fillers in thermoplastic and thermoset composite for furniture and automobile components. Another attractive way is to convert this biomass into a solid fuel called biomass briquette. Empty fruit bunches in the form of powder and fiber were compressed together with palm kernel at high temperature and pressure using screw extrusion technology to produce briquettes (Husain et al., 2002). Some also

using EFB and palm kernel shells as a peat by mixing it with goat or poultry manure and other food crops (Abdullah and Sulaiman, 2013).

Table 2.2: The dry weight of potential oil palm biomass available in Malaysia in 2014

Sources of oil palm biomass	Amount (dry weight)
OPF (from pruning activity)	47.06 million tons
OPF (from replanting activity)	3.66 million tons
OPT (based on 5% replanting rate)	38.48 million trunks
	19.37 million tons
From the 434 palm oil mills operating at total capacity of 94.92 million tons of FFB,	7.31 million tons
~ Estimated EFB = 22% x 94.92 x 35% million tons	
Mesocarp fibers	7.69 million tons
Palm kernel shells	5.22 million tons
POME generated from per tons of FFB is about 67%.	63.60 million tons (million m^3)

Source: Malaysian Palm Oil Board (2015)

The oil palm fronds can be processed into pulp and refined for the ruminant roughage for cattle and goats. Besides that, balance diet pellet for fattening beef cattle can be created from the oil palm frond (Sulaiman et al., 2011). The conversion of biochemical products for instances bio-ethanol, fatty acids, and waxes could be achieved through biotechnology. The residual materials also was used in cultivating mushrooms.

The oil palm ash generated from the combustion of oil palm fiber and the shell could be utilized as an absorbent to remove the toxic gasses such as nitrogen oxide and sulfur oxide. This kind of technologies that converted the oil palm biomass into a wider application can be found in the growing Asian and African countries where oil palm plantations was an important financial resource (Basiron and Simeh, 2005).

With the depletion of fossil fuel, research to produce biofuels and bio refinery from oil palm trunk gained an attention from a various researchers (Kosugi et al., 2010; Prawitwong et al., 2012; Eom et al., 2015). The oil palm trunk containing 80 % of sap in felled trunks which consist of diverse free sugar that is suitable for the production of bioethanol. Saw-wood, plywood and lumber are the types of wood that also can be produced from the trunks. Usually, the plywood and lumber can be used as a core in the blackboards manufacturing while the saw-wood is mainly used for furniture making.

Due to one of its drawback that is low density, the trunks is not suitable for building materials. However, Sulaiman et al. (2011) reported that the oil palm trunk plywood strength was comparable with the commercial plywood. Besides, the addition of a chemical binder to the oil palm trunk particle boards to enhance and improve the properties of the board can be produced. Also, a mixture of oil palm trunk with EFB and palm fibers can be converted into energy in the forms of briquettes by combustion (Sumathi et al., 2008; Sulaiman et al., 2012). Table 2.3 summarized some of the utilization of oil palm biomass in the past years.

Table 2.3: Utilization of oil palm biomass

Materials	Use	References/Researcher
Oil palm trunk (OPT)	Binderless particle board/Particle board	Hashim et al., 2010a, 2010b, 2011 Sulaiman et al., 2009; Lamaming et al., 2012, 2013; Jumhuri et al., 2014
	Medium density fiber board	Zawawi et al., 2014
	Bioethanol	Yamada et al., 2009; Murai et al., 2009; Murai and Kondo, 2011; Kosugi et al., 2010
	Biobutanol	Komonkiat and Cheirsilp, 2013
	Parenchyma and vascular bundle	Mhd Ramle et al., 2012; Prawitwong et al., 2012; Abe et al., 2013
	Cellulose and hemicellulose	Runcang Sun et al., 2009
Empty fruit bunch (EFB)	Cellulose/NCC/NCF	Jonoobi et al., 2010; Fahma et al., 2010; Rohaizu and Wan Rosli, 2013; Haafiz et al., 2013, 2014; Al-Dulaimi et al., 2015
	Ethanol/bioethanol	Piarpuzán et al., 2011; Sudiyani et al., 2012; Tan et al., 2013, 2016
	Activated carbon	Hidayu et al., 2013;Lee et al.,2014
Oil palm frond (OPF)	Bioethanol	Srimachai et al., 2015; Kumneadklang et al., 2015; Abdullah et al., 2016
	Composite panel	Khalid et al., 2015;
	Activated carbon	Salman and Hameed, 2010; Salman, 2014

2.1.3 Properties of oil palm trunk

As a non-wood lignocellulosic material, the oil palm trunk consists of vascular bundle and parenchyma as ground tissue. The oil palm trees are available after the replanting process commenced which is 25 years of its life span. When measured 1.5 meters above the ground level, the length of the felled trees was reported in the range between 7 - 13 m with a diameter of 45 - 65 cm (Koh et al., 1999; Husin et al., 2000). The oil palm is classified as a monocotyledon, thus it does not contain growth rings cambium, secondary growth, sapwood and heartwood ray cells, knots or branches Therefore, the growth and increase in diameter of the trunks solely depend on the overall cell division and enlargement in the parenchymatous ground tissues, combined with the enlargement of the fibers of the vascular bundles (Killmann and Lim, 1985; Erwinsyah, 2008).

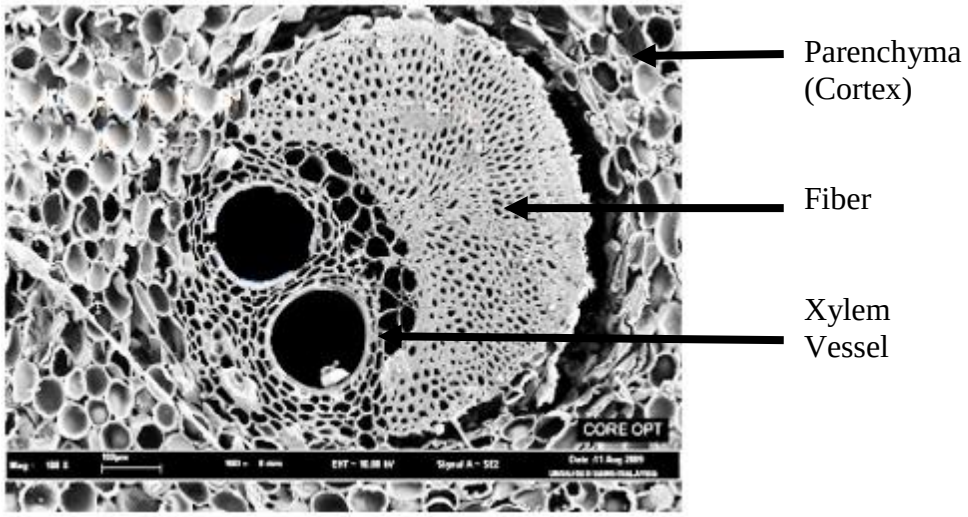

Fig. 2. 3: Anatomical structure of oil palm trunk (Hashim et al., 2012)

Fig. 2.3 exhibited a cross-section of the anatomical structure of oil palm trunk. The trunks are divided into three main zones which are cortex, periphery and central. The outer part of the trunk which was measured approximately 1.5 -3.5 cm in wide was covered by the narrow cortex. In this zone, vascular bundles and a vast amount of

numerous strands ground parenchyma having a narrow and random shaped fibrous strands can be found. Packed vascular bundles and small layers of parenchyma and filled up the periphery region of the oil palm trunk. The vascular bundle in this region is growing up in a sclerotic zone to provide the primary mechanical support for the palm. With 80 % of the total area of the trunk, the central regions mainly consist of vascular bundles (Killmann and Lim, 1985) and 70 % of parenchyma cortex tissue (Bakar et al., 2008). The vascular bundles that were ingrained in the thin-walled parenchymatous ground tissues are found to be larger in size and widely distributed. The size of the vascular bundles is likely to increase and found more distributed towards the core of the trunk.

The previous study on the length, width, and cell wall thickness of oil palm trunk fiber were measured with the length ranged from 1.02 mm to 1.97 mm. The fiber length tends to decrease from the peripheral zone towards the central region and the bottom towards the top. The width of the fiber ranged from 28.9 to 45.1 micron while the cell wall thickness ranged from 2.1 to 6.3 micron. However, only a little changes in cell wall thickness observed with the increase in height (Mohd. Noor et al., 1984).

The vascular bundle and parenchymatous tissue act as transporting and food storage organs respectively (Corley and Tinker, 2003). The vascular bundle in the outer part not only provides mechanical support but help in transporting water and nutrients (Corley and Tinker, 2003). The density of vascular bundles is found to be decreased gradually nearing the central zone and increased from the lower to the upper part of the oil palm (Lim and Khoo, 1986). The amount of vascular bundles also determines the density and mechanical properties of the oil palm trunk (Bakar et al., 2012; Darwis et al., 2013).

The vascular bundles were characterized as dense, fibrous and least hygroscopic. However, the vascular bundle is much less densely packed approaching the central zone where higher amount of storage tissue is located. The vascular bundle also composed of xylem, fibers, sieve tubes, vessels, axial parenchyma, protoxylem, stegmata and companion cells (Lim and Fujii, 1997; Sulaiman et al., 2012; Abe et al., 2013). According to Abe et al. (2013), the parenchyma cells are soft, spongy, and highly hygroscopic in nature. The living parenchyma cells store the food as carbohydrate, mostly in the form of sugars and starch. The ground parenchymatous tissue was consist of thin-walled spherical parenchyma cells, which is highly dense and thick in the core region as compared to the outer region.

The moisture content of the oil palm trunk is high, reaching up to 500 % while the density of the oil palm stems is in the range 0.24-0.53 g/cm^3. With the high moisture content and variation in density, processing the trunks may be difficult in the terms of drying and treatment processes of the stem (Lim and Gan, 2005; Balfas, 2008). Collapse, cupping, internal checks and wavy formations are among the defects that occurred during the drying process of oil palm trunk.

2.1.3(a) Chemical composition of oil palm trunk

The chemical components of oil palm trunk from various studies are tabulated in Table 2.4. Majority of plant consist of lignin, cellulose and hemicellulose which make up the biomass of trees and agricultural by-products. Cellulose and hemicellulose are made up of chains of sugars. Cellulose is made of linked glucose molecules strengthen the cell walls of most plants. Hemicellulose or polyose is a mixture of various monosaccharides namely glucose, xylose, mannose, galactose, arabinose, fructose and 4-0-methyl glucuronic acid. According to Widyorini et al.,

(2005), the mechanical strength of plant tissue was provided by cellulose while rigidity and stiffness was contributed by lignin. The cellulose content of the oil palm trunk is within the range of 29 % -50 % and the lignin was 20 % -25%. The value varies depending on the part of the trunk. The low lignin content (15.70% – 24. 51 %) is a positive attribute for pulp and paper-making industry (Abdul Khalil et al., 2008).

Table 2.4: Chemical composition of oil palm trunk

Chemical compositions (%)	Hashim et al., 2010		Lamaming et al., 2013	Abdul Khalil et al., 2008	Chin et al., 2011
	Mid part of trunk	Core part of trunk			
Extractives	14.50	9.10	12.2	5.35	Na
Holocellulose	72.60	50.73	69.80	73.06	78.5
Alpha-cellulose	50.21	43.06	59.9	41.02	47.5
Lignin	20.15	22.75	21.0	24.51	18.4
Ash	Na	Na	Na	2.2	1.69

* Na - Not available

Chemical composition varies in the plant and inside plant, from various parts of the same plant. The chemical composition will differ from plants as it was affected by the age of the plant, geographic locations, soil and weather conditions (Rowell, 2000; Murai et al., 2009). Height and zone also contribute to the variation in the chemical composition value (Sudin et al., 1987). Polysaccharides in oil palm trunk including the glucose were released from cellulose and hemicelluloses derived from various monosaccharides such as mannose, galactose, xylose, and arabinose. It was recorded by different researchers (Husin, 2000; Murai et al., 2009) that three main free sugars

namely glucose, sucrose, and fructose accumulated and distributed along the trunks particularly on the center part contributing in the higher proportion of free sugar.

Oil palm trunks contain large proportional of sap which includes an abundant amount of free sugars, saccharides, and polysaccharides. The sugar content reported, around 10 and 12 % on sugar composition (Okafor, 1975). The total sugar content of sap samples indicates that sucrose, glucose and fructose form as a primary free sugar with the glucose contributing to the highest constituent of sugar (Yamada et al., 2010; Kosugi et al., 2010). Another short chain of polysaccharides namely maltose, xylose, galactose, arabinose and inositol also present in a small quantity from a total amount of sugar inside the oil palm trunks. The total sugar content of the oil palm trunk may be different time to time. The differences may be influenced by age and species of the tree, soil, time of tapping and also the storage time to keep the oil palm trunk (Tomimura, 1992, Kosugi et al., 2010;Yamada et al., 2010).

2.2 Cellulose

Fibers contain cellulose, lignin, hemicellulose, and pectin that contribute to the properties of the fiber. Cellulose was first noted in 1838 (Dufresne et al., 2000) since it is the common materials of plant cell wall. Cellulose is mainly isolated from wood, but it also can be obtained from various sources of lignocellulosic materials. They also can be isolated from algae (*Valonia*), bacteria (*Gluconacetobacter xylinus*), and sea animals (tunicates). The structure of cellulose may differ as it influenced by the source of the cellulose. As a building material of long fibrous cells, cellulose is high in strength and stiffness.

The cellulose structure built by unbranched β (1→4) linked D-glucopyranosyl units of polymer chains. The intra- and intermolecular hydrogen bonds were formed by three hydroxyl groups. The primary hydroxyl group placed at C_6 whereas the secondary hydroxyl groups positioned at C_2 and C_3. Formation of highly ordered three-dimensional crystal structures was contributed by this hydrogen bonds (Eyholzer, 2010).

Cellulose is arranged in a hierarchical cellular structure. The wood cell walls (Fig. 2.4) are divided by a compound middle lamella, consisting of the middle lamella and the primary cell wall layer. The secondary cell wall layer consists of S1, S2, and S3 layer. The cellulose amount predominantly found in the S2 layer (Core et al. 1979, Fengel and Wegener, 1989). The nanosized fibrils, which biosynthesized from the cellulose molecules will combine to form nanosized cellulose microfibrils (McCann et al., 1990; 1992; Stamboulis et al., 2001; Wang et al., 2007).

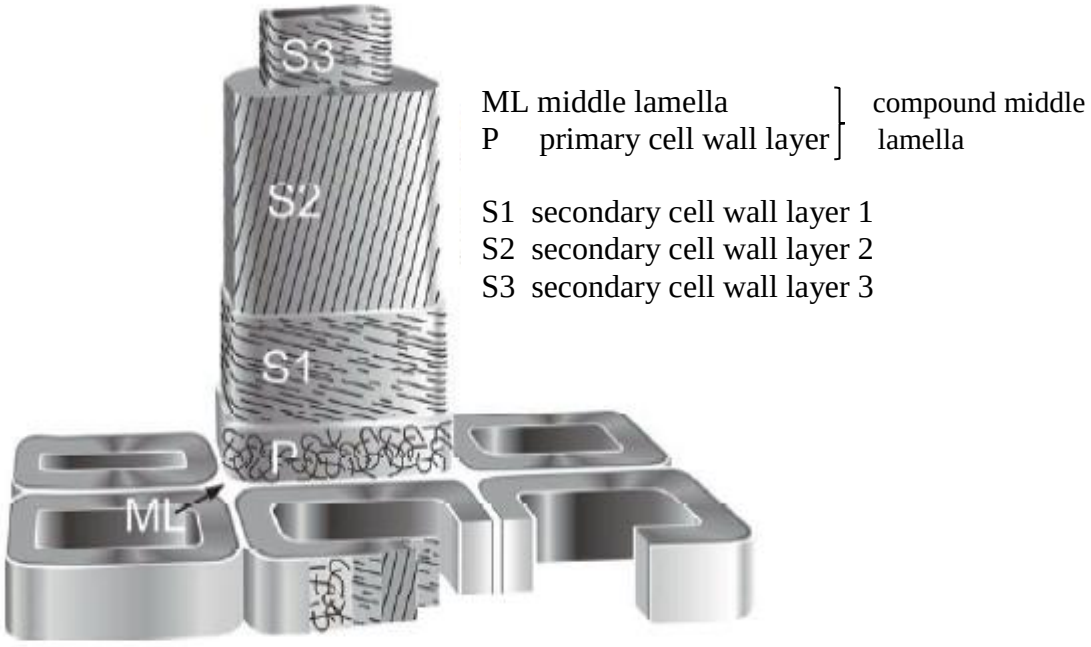

Fig.2.4 Structural design of cell wall (Eyholzer, 2010)

In early year, the term microfibril defined as the smallest entity that extracted from the cell wall structure. However, the real nano size of the fibrils that having a range from 3 to 30 nm (varies on the origin of the cellulose) does not indicated by the term. A highly ordered structure of single microfibrils was made from the assembling and merging of several cellulose synthases glucan chains. The single microfibrils are group to larger bundles that consists of fibril bundles agglomerates, bind by the matrix substances of lignin, hemicelluloses, and pectin (Abdul Khalil et al., 2012).

The microfibrils were also having a low order known as amorphous regions. In general, the fringed-fibrillar model is selected in Fig. 2.5 to portray the individual glucan chains that go through a random pattern of amorphous and crystalline domains of the single microfibrils (Fink et al. 1993; Klemm et al. 2005).

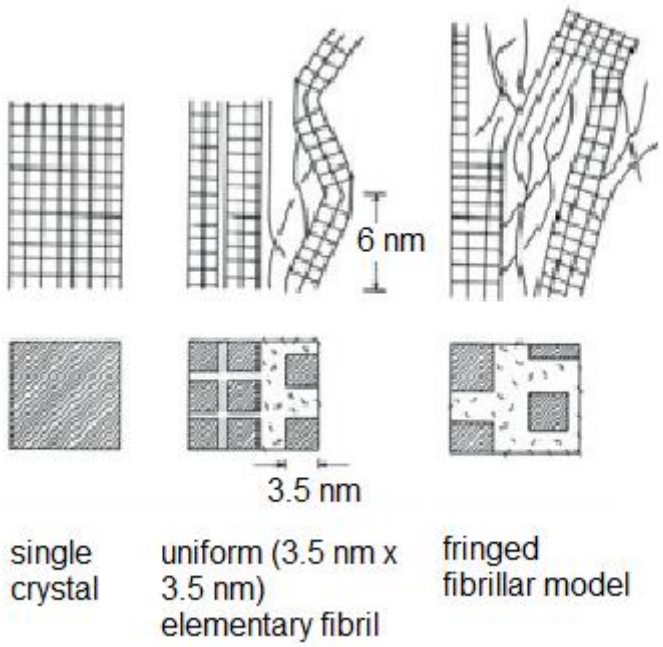

Fig. 2.5 Various models of the structure of single microfibrils (Fink et al., 1993)

According to Abdul Khalil et al., (2012), the cellulose microfibrils arranged in the cell walls having a particular orientation known as microfibril angles that will differ from the cell wall layer and varies from plant to plant. The orientation of the

microfibrils is presumably controlled by microtubules found in an aligned orientation to the microfibrils. This microfibrils orientation will affect the mechanical properties of the fibers in different plants. Klemm et al., (2005) stated that the low microfibril angles found in the S2 layer where the microfibril orientation nearly aligned to the axis of fiber. Low microfibril angle will have a high modulus of elasticity and the large angles give a higher elongation at break. A high tensile strength is due to the fibrillar structure, and the great number of hydrogen bonds found in cellulose. Thus, the load in tensile mode is supported by the structural element of a plant (Sjöström**,** 1993).

2.2.1 Cellulose nanofibers

Cellulose fibers are comprised of a bundle of individual cellulose fiber having a diameter in the range of 25-30 μm. This individual cellulose fiber is compose of bundles of microfibers, which were described as a fiber with a repeated cellulose chains with slight hemicellulose and lignin content, and having a diameter of 0.1 – 1 μm, with a minimum corresponding length of 5-50 μm (Chakraborty et al., 2006). The cell wall of an individual fiber consists of bundles of macro fibrils, which are strands of nanosized microfibrils. The molecular arrangements of the molecular of these fibrillar bundles are so narrow, that the reported average diameter of the bundle is about 10 nm (Wang et al., 2007). The microfibers compose of nanofibers, which has a diameter in the range of 10-70 nm and lengths of thousands of nanometers (McCann et al., 1990; 1992). These nanofibers are consists of cellulose chains bound by hydrogen bonding (Wang et al., 2007)

Cellulose nanofibers have higher surface area (more than 200 times) compared to the isolated softwood cellulose (Krieger, 1990) and possess higher capacity of

water-uptake, finer web-like network and higher crystallinity and tensile strength. These properties enabled the cellulose nanofibers potential to be used as reinforcement. It has been reported by Kroon-Batenburg et al. (1986) that the theoretical stiffness estimated to reach 130 GPa and up to 7 GPa in tensile strength. The cellulose nanofibers have a great energy absorbing capability compared to the synthetic fibers. It was also comparable to other materials including carbon fibers and glass fibers.

Aspect ratio is the length over a diameter of the fibers. The microfibers with aspect ratio more than 20 shows a good reinforcement in the structural application. Fig. 2.6 shown aspect ratio of the macro, micro and nano type of cellulose fibers. A combination of a suitable polymer matrix and the cellulose nanofibers to be used in high-quality specialty applications of bio-based composite as an effective reinforcement.

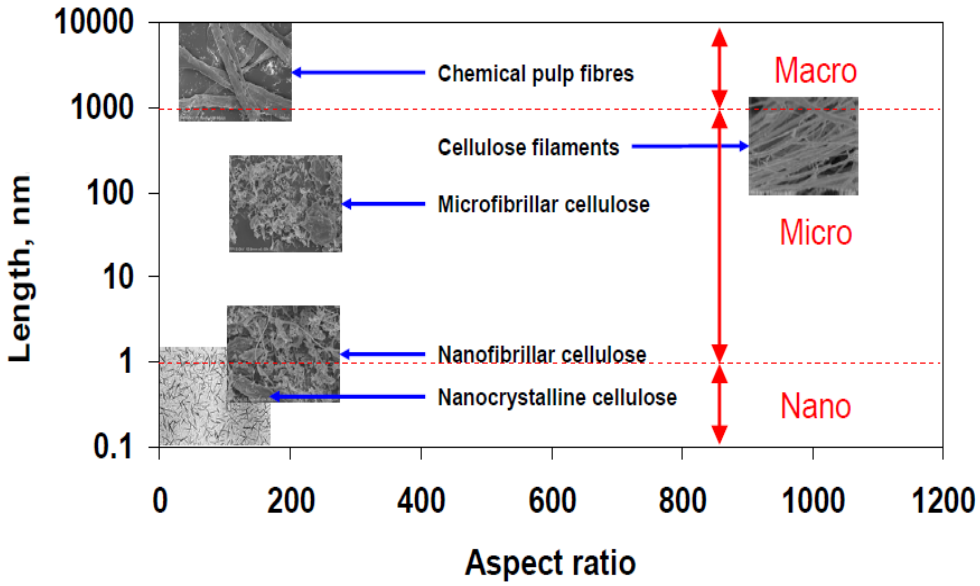

Fig. 2.6 Aspect ratio (length/diameter) of the cellulose fibers (Berry, 2010)

Nanocellulose is defined as the products extracted from native cellulose that mainly found in the plants, bacteria or even in animals (Klemm et al., 2010). The family of nanocellulose can be categorized into three types (Fig. 2.7). They are (1) cellulose nanocrystals (CNC), also designated as nanocrystalline cellulose (NCC), cellulose nanowhiskers, (CNW); (2) nanofibrillated cellulose (NFC) or cellulose nanofibrils (CNF), cellulose nanofibers, or microfibrillated cellulose (MFC); and (3) microbial cellulose or bacterial cellulose (BC) (Dufresne, 2012; Klemm et al., 2011).

Cellulose nanocrystals (CNC) also called as nanocrystalline celluloses (NCCs), or cellulose nanowhiskers (CNW), consist of rod-like cellulose crystals with width in the range of 5–70 nm and lengths between 100 nm to several micrometers (Klemm et al., 2010). They are produced using acid hydrolysis where the amorphous domains of a purified cellulose were removed and regularly followed by ultrasonic treatment (Klemm et al., 2011, Moon et al., 2011). In the acid hydrolysis process, the glucan chains were cleaved in the amorphous domains resulting in typical slender and rod-like shape microfibril fragments. Owing to their rod-like nature, these type of cellulose can form birefringent gels and liquid crystalline structures, reminiscent of spherulitic structures in polymers (Marchessault et al., 1959; Eichhorn, 2010).

Cellulose nanocrystals or nanowhiskers are not the same as nanofibrillar cellulose which was also referred as microfibrillar cellulose or microfibrillated cellulose. This type of cellulose is generated by means mechanical/chemical treatment or purely chemicals produces long nano-sized individualized fibrils. Originally, this cellulose was developed by Turbak et al. (1983) and should not be confused with cellulose nanocrystals or nanowhiskers.

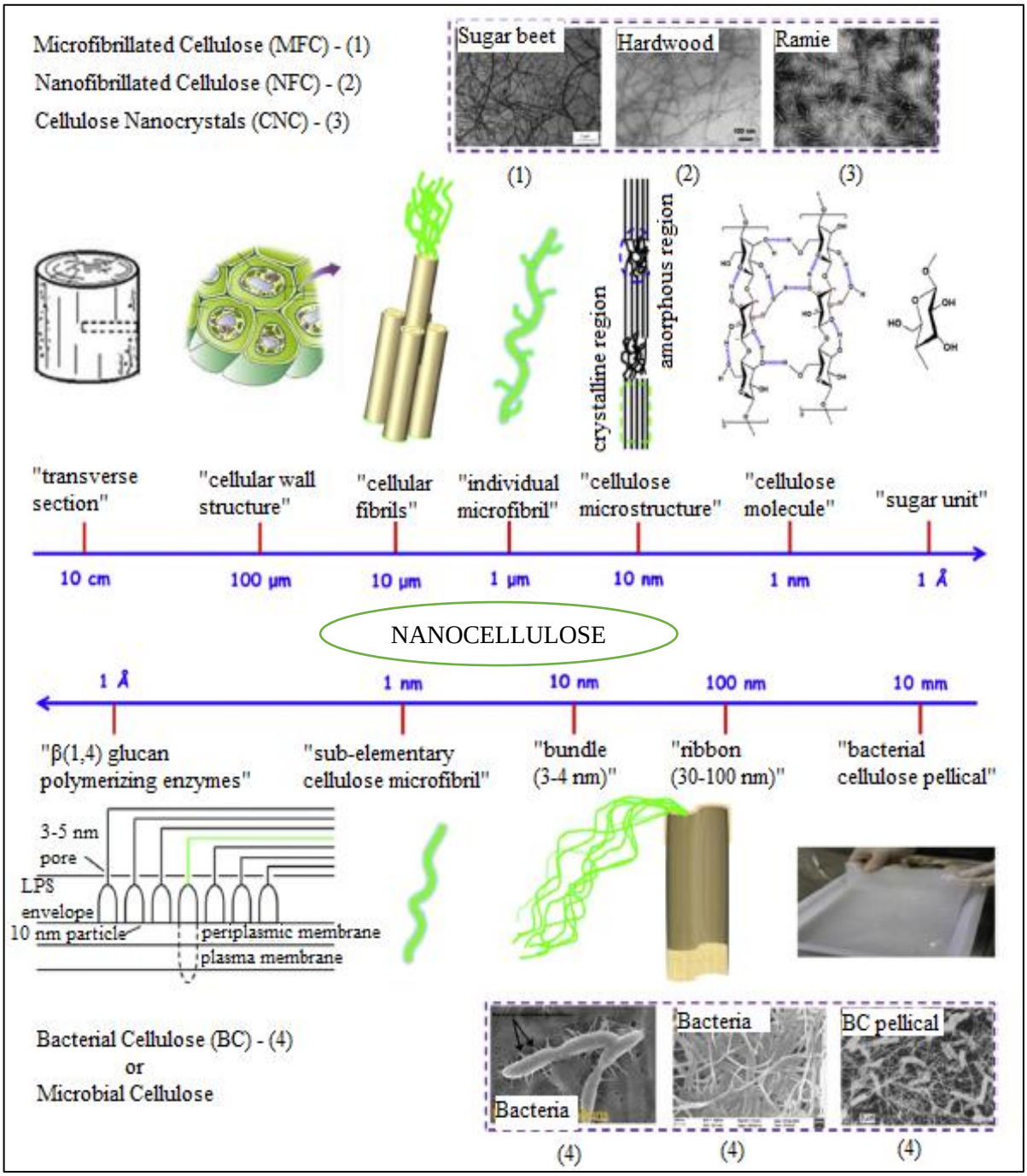

Fig. 2.7 Hierarchical structure of cellulose (adapted from Lin and Dufresne, 2014)

Cellulose nanocrystals is an inexpensive biomaterial having a good mechanical properties, high aspect ratio, high absorbency, biodegradable and sustainable resources (Brinchi et al., 2013), and also claim to be toxic free. Owing to their nano-scaled size, nanocellulose mainly cellulose nanocrystals possesses a variety of characteristics of traditional materials They include special geometrical dimensions and morphology, rheological properties, high specific surface area, crystallinity alignment and orientation, liquid crystalline behaviour, barrier properties, mechanical reinforcement, biocompatibility, and surface chemical reactivity. Properties of the nanocellulose can be categorized into three parts that are physical properties, surface chemistry and biological chemistry. Lin and Dufresne, (2014) covered in great details about the properties of the cellulose in the aforementioned topics.

2.2.2 Isolation of cellulose nanocrystals

In the past years, cellulose nanofibers were isolated from the cellulosic fibers of plants, animals, bacteria and even algae. Previously, wood was the primary source for cellulose extraction due to its high cellulose contents and availability (Beck-Candanedo et al., 2005). But the problem of deforestation and shortage of wood forced the worldwide researcher to look for other cellulose resources. Table 2.5 presented types of the nanocellulose extracted from various sources. Tunicate has been a favored for cellulose nanocrystals source owing to its high crystallinity and length (Terech, et al., 1999) but due to the limited availability and high harvesting cost, the use of it is restricted.

The production of cellulose nanocrystals (CNC) and microfibrillated cellulose (MFC) with the terminologies are displayed in Fig. 2.8. The isolation of the cellulose nanocrystals is a two-stage process. The first stage consists of pretreatments of the