CHARACTERIZATION OF LIGNOCELLULOSIC FILM MADE OF UNBLEACHED PULP SOLUTIONS AND CELLULOSE NANOWHISKER FROM OIL PALM EMPTY FRUIT BUNCH

NAJIEHA BINTI NORAZLI

UNIVERSITI SAINS MALAYSIA

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by

NAJIEHA BINTI NORAZLI

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LIST OF SYMBOLS

θ (theta)	Angle of Rotation
β (beta)	Beta Decay Constant
cm	Centimetre
α (alpha)	Coefficient of Thermal Expansion
CI	Crystallinity Index
°C Degree Celsius	Degree Celsius
°C/min	Degree Celsius per minute
GPa	Gigapascal
g	Gram
kDa	Kilodalton
MPa	Megapascal
mm	Micrometer
mw	Milliwatts
%	Percentage
m^2	Meter square
mL	Millilitres
min	Minutes
Mg/°C	Milligram per celcius

LIST OF ABBREVIATIONS

BNC	Bacterial Nanocellulose
$C_{14}H_8O_2$	Anthraquinone
C_2H_5OH	Ethanol
C_7H_8	Toluene
CA	Contact Angle
CH_3COOH	Acetic Acid Glacial
CI	Crystallinity Index
CMC	Carboxymethyl cellulose
CNF	Cellulose nanofiber
CNT	Cellulose nanotubes
CNW	Cellulose nanowhiskers
CPO	Crude palm oil
DMAc	N-N Dimethylacetamide
DP	Dissolving Pulp
DSC	Differential Scanning Calorimetry
EAB	Elongation at Break
FFB	Fresh Fruit Bunches
FTIR	Fourier Transform Infrared Spectroscopy
FTIR-ATR	Fourier Transform Infrared-Attenuated Total Reflectance
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric Acid
HCl	Hydrochloric Acid
HS	Hestrin-Schramm
KI	Potassium Iodide
KOH	Potassium Hydroxide
LiCl	Lithium Chloride
MCC	Microcrystalline Cellulose
$MgSO_4$	Magnesium sulphate
MWCNT	Multi-walled cellulose nanotubes
$NaClO_2$	Sodium chlorite
NaOH	Sodium Hydroxide

OPEFB	Oil Palm Empty Fruit Bunch
OPF	Oil palm fronds
OPT	Oil Palm Trunk
PKS	Palm Kernel Shell
PMF	Palm mesocarp fiber
SEM	Scanning Electron Microscopy
SWCNT	Single-walled cellulose nanotubes
TCF	Total Chlorine free
TEM	Transmission Electron Microscopy.
TGA	Thermogravimetric Analysis
TS	Tensile Strength
XRD	X-ray Diffraction
YM	Young Modulus

PENCIRIAN FILEM LIGNOSELULOSA DIPERBUAT DARIPADA LARUTAN PULPA TIDAK TERLUNTUR DAN SELULOSA NANOWISKER DARIPADA TANDAN BUAH KOSONG KELAPA SAWIT

ABSTRAK

Kajian mengenai bio-nanokomposit menggunakan bahan hijau mampan daripada sisa biojisim sedang mendapat perhatian di seluruh dunia. Biojisim lignoselulosa dalam bentuk bahan tumbuhan menawarkan sumber boleh diperbaharui yang banyak dalam menggantikan sumber fosil tradisional. Dalam kajian ini, filem biojisim lignoselulosa disediakan secara langsung daripada larutan pulp tandan buah kosong kelapa sawit (OPEFB) dalam DMAc/LiCl tanpa penambahan bahan pembentuk filem tambahan yang diinkorporasikan dengan 1%, 3%, dan 5% melalui kaedah pengecoran pelarut menggunakan pelbagai jenis OPEFB CNW yang diasingkan menggunakan pelbagai jenis rawatan penanggulan lignin yang berbeza dan kemudian dicor ke dalam filem. Sifat mekanikal, sifat morfologi, sifat termal, dan kumpulan fungsional serta kesan penambahan OPEFB CNW ke dalam filem bio-nanokomposit kemudian dinilai dengan spektroskopi inframerah (FTIR), sudut sentuhan, analisis mekanikal, difraksi sinar-X (XRD), mikroskopi elektron imbasan (SEM), termogravimetri (TGA) dan kalorimeter pembezaan pengimbasan (DSC). Filem separa-tembus cahaya dengan warna kekuningan diperoleh disebabkan oleh kehadiran lignin. Hasil kajian menunjukkan kebolehserasian yang baik antara bahan lignoselulosa dan CNW yang bertanggungjawab terhadap peningkatan sifat mekanikal filem. Ini juga mengakibatkan hidrofilisiti filem yang kurang apabila pembebanan pengisi meningkat dan tiada perbezaan besar antara kesan dua jenis CNW yang

digunakan. Spektra analisis FTIR menunjukkan corak yang serupa dengan hanya berbeza dalam ketajaman dan pelebaran puncak. Tiada perubahan dalam komposisi kimia antara kedua-dua jenis delignifikasi itu. Bagi analisis XRD, penggabungan kedua-dua jenis sampel CNW tidak menunjukkan kesan terhadap kristaliniti filem lignoselulosa. Walau bagaimanapun, kristaliniti berkurang apabila pembebanan pengisi meningkat. Kebolehstabilan termal berkurang dengan penggabungan kedua-dua CNW ke dalam filem lignoselulosa. Kajian ini akan memberi pemahaman tentang kesan penggabungan CNW dan kesan rawatan penanggulan lignin yang berbeza dalam mengasingkan CNW terhadap prestasi filem lignoselulosa.

CHARACTERIZATION OF LIGNOCELLULOSIC FILM MADE OF UNBLEACHED PULP SOLUTIONS AND CELLULOSE NANOWHISKER FROM OIL PALM EMPTY FRUIT BUNCH

ABSTRACT

Studies of bio-nanocomposites using sustainable green materials from biomass waste are presently gain the attention worldwide. Lignocellulosic biomass in the form of plant materials offers the most abundant renewable resource in replacing traditional fossil resources. In the present study, lignocellulosic biomass films were prepared directly from oil palm empty fruit bunch OPEFB pulp solutions in DMAc/LiCl without additional film-forming additives incorporated with 1%, 3%, and 5% via solvent casting method using various types of OPEFB CNW isolated using different types of delignification treatment and then casted into films. Mechanical behaviour, morphological properties, thermal properties, and functionality groups and the effect of adding the OPEFB CNW into the bio-nanocomposites films were then evaluated by infrared spectroscopy (FTIR), contact angle, mechanical analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric (TGA) and differential scanning calorimeter (DSC). The semi-transparent film with a yellowish colour was obtained due to the presence of lignin. The results showed good compatibility of lignocellulosic material and CNW which is responsible for the increasing in mechanical properties of the film. This also led to less hydrophilicity of the film as the filler loading increasing and no big difference between the effects of two types of CNW used. FTIR analysis spectra show a similar pattern with only different in the intense and broadening of the peaks. No chemical composition changes between those two delignification. For XRD analysis, the incorporation of both types of CNW sample did not show effect on the crystallinity of the lignocellulosic film. However, the crystallinity decreases as the filler loading increase. Thermal stability decreased with the incorporation of both CNW into lignocellulosic film. This study will provide understanding in the effect of incorporating CNW and effect of different delignification treatment isolating CNW on the lignocellulosic film performance.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Polymeric materials are being used in more and more industrial goods (Polyexcel, 2019). This is mostly because they are inexpensive and because their thermal and mechanical properties can be controlled. But a lot of these goods are made to be thrown away quickly. This has caused concern in many parts of society because they are hard to break down in the environment and take up a lot of space, where they stay for years until they break down completely (Geyer, 2020). Natural biopolymer films have attracted a lot of interest in recent years because of their excellent transparency, mechanical strength, and desired thermal stability (Ghanbarzadeh et al., 2011; Hua et al., 2022). Biodegradable polymer such as lignocellulosic material could be used instead in this case. Lignocellulosic biomass is a mixture of cellulose, hemicelluloses, lignin, and extractives. It is one of the oldest materials and is still used extensively in industry (Renneckar & Zhou, 2009). On the basis of lignocellulosic biomass, numerous innovative materials have been created, including wood plastic composite (Guo et al., 2010), biomass-based carbon (Pilon & Lavoie, 2013), wood ceramics (Hirose et al., 2002), semi-conducting materials (Trey et al., 2012), and aerogels (Lu et al., 2012). However, because lignocellulosic biomass has complex structural and chemical mechanisms, it is still very difficult to directly convert it into useful components.

The oil palm empty fruit bunches (OPEFB) are a type of lignocellulosic material that is generated as a by-product of the palm oil industry (Noah, 2022). Despite their potential, their utilization has been limited (Nyawi, n.d). The OPEFB utilization of as a natural fiber to produce reinforced composites has been on the rise. In the year 2021, Malaysia, recognized as one of the leading global producers of palm oil (Dirkes et al., 2021; Hariz et al., 2023; Parveez et al., 2023). This production resulted in the generation of 22-23, million tons OPEFB as biomass waste (Anuar et al., 2019; Padzil et al., 2020). Due to their high cellulose content (ranging from 42-65% by mass), OPEFB fibers possess the potential to serve as viable source materials for sustainable polymer. However, cellulose also has numerous drawbacks, including poor thermal stability and low barrier efficacy, which significantly restrict its use (Ghaderi et al., 2014). With the development of nanotechnology, there are many different cellulose extraction methods that have been developed over the years, particularly in terms of delignification and bleaching, and several studies on these materials have been published (Bhat et al., 2019; Haldar & Purkait, 2020; Huang et al., 2020; Kale et al., 2018; Melikoğlu et al., 2019; Mokhena & John, 2020; Nagarajan et al., 2021; Norazli et al., 2023; Rana et al., 2021). This material has continued to attract more and more research worldwide toward an understanding of the different aspects involved in producing effective, sustainable, and high-value products such as CNW. The process of extracting CNW from lignocellulosic plants comprises of different phases. OPEFB has a complex and waxy structure; therefore, an efficient extraction process is required. The initial stage involves a pre-treatment of the fiber to eliminate matrix substances, specifically lignin, hemicellulose, and other related compounds. The subsequent step involves the regulated application of acid hydrolysis, aimed at eliminating the amorphous regions of the cellulose polymer, thereby retaining the crystalline parts that make the fibrils (Fatema et al., 2022; Jiang et al., 2021; Lee et al., 2014; Mishra et al., 2019).

The lignin, hemicellulose, and other non-cellulosic substances need to be depolymerized and removed before the CNW is synthesized. This is done by pre-treating the cellulosic plants. Most of the time, chemicals like sodium hydroxide are used in the pulping process. Whereas sodium hypochlorite was commonly used in the bleaching process (Aridi et al., 2021; Suali et al., 2022; Susi et al., 2022). The use of sodium hypochlorite, on the other hand, is thought to be dangerous and bad for the environment (Sharma et al., 2020). Therefore, in this study, an attempt was made to get high-purity CNW by using a delignification way that is better for the environment as part of a pre-treatment process. A large amount of chemicals, water and energy are used during the delignification process. For this reason, it is extremely important for economic and ecological aspect to develop eco-friendlier bleaching technology that eliminates the need for heat energy and process water of the bleaching of this lignocellulosic biomass. The CNW has been extracted from OPEFB using two different delignification methods, which are acidified chlorite delignification and total chlorine free delignification. Then, followed by acid hydrolysis.

The incorporation of nanocellulose into composite materials and nanocomposite films has received a lot of research attention (Ren et al., 2019; Wu et al., 2012). Bio-composites films that are renewable and green in nature were developed using cellulose, starch, and lignin in a room temperature ionic liquid (Wu et al., 2009), as well as from wood hydrolysate that is rich in polysaccharides (Zhu et al., 2011). Films composed of synthetic wood composites, which were isolated cellulose, hemicelluloses, and lignin, were fabricated using a solvent of room temperature ionic liquid (Simmons et al., 2011). More excitingly, raw lignocellulosic biomass solutions have been successfully used to create composite fibers (Chen et al., 2014). The findings of these studies indicate the feasibility of converting untreated lignocellulosic biomass into valuable products through direct dissolution in appropriate solvents.

Based on the above works, the integration application of lignocellulosic biomass fiber and CNW arouses our further interest. To the best of our knowledge, no study on renewable lignocellulosic film directly from OPEFB fibre has been found in the literature. Therefore, this study aimed to explore the feasibility of producing new eco-friendly, sustainable, and biodegradable films from untreated lignocellulosic biomass utilizing DMAc/LiCl as a solvent, without any supplementary film-forming agents with the addition of CNW added as a reinforcement. The physicochemical, thermal, and mechanical properties of the films that were produced were analyzed.

1.2 Problem statement

Petroleum polymers are used in a wide range of essential products to society's basic needs especially in plastic packaging application. Traditional petroleum-based plastic packaging is strong, versatile, and durable but not biodegradable. The non-biodegradable nature of synthetic polymers makes them a permanent waste thus led to many environmental pollution (Evode et al., 2021). Due to the many environmental concerns caused by synthetic materials made from petroleum polymer, the development of biodegradable material has considerably increased. Malaysia is abundant with OPEFB with high cellulose content, the cheapest natural lignocellulosic fibre with excellent properties. It could replace the use of petroleum polymer. Therefore, the development of lignocellulosic film from these material is a great interest. However, cellulose also has some disadvantages, such as low barrier performance, poor thermal stability, which largely limit its application in packaging (Ghaderi et al., 2014). With the development of nanotechnology, CNW can be prepared via physical methods, chemical methods and biosynthesis methods, which improve the mechanical properties, barrier properties and optical properties of cellulose based products. The most widely used approach to get rid of lignin as a first step was acidified sodium chlorite delignification. The employment of totally chlorine-free techniques, such as deep eutectic solvents, ionic liquids, and hydrogen peroxide solutions, is part of current methods. However, lignin, hemicellulose, and cellulose are organized in a complex hierarchical microstructure, depending on the natural lignocellulosic supply, creating a refractory nature against chemicals and microbial treatments. To create value-added goods utilizing either of the methods, effective separation of these components is essential. The aim of the current research was to create an efficient method for separating pure cellulose and CNW from OPEFB using acid hydrolysis. Different delignification techniques, acidified $NaClO_2$ delignification and total chlorine-free (TCF) delignification have been used. To the best of our knowledge no study has been reported on comparing the different pretreatment before isolation of CNW and their use in lignocellulosic nanocomposites preparation. Several investigations, including FTIR, XRD, SEM, DSC, and TGA, have been used to thoroughly evaluate their impact on the physicochemical characteristics and thermal stability of the derived CNWs and lignocellulosic film produced.

1.3 Objectives

The present research embarks on the following objectives:

1) To investigate the effect of different types of delignification technique on physical, chemical, and thermal properties of CNW produced.
2) To characterize and compare the effect of different filler loading amount on physical, mechanical, morphological, and thermal properties of the lignocellulosic nanocomposite film.

1.4 Significant of research

A renewable bio-macromolecule called CNW is primarily derived from lignocellulosic materials utilizing a variety of techniques. CNW was successfully isolated from an OPEFB in the current study. Furthermore, several prior studies to manufacture CNW have been conducted without fully addressing the question of the effect of different pretreatments on the final properties of the derived CNW from lignocellulosic material. The present work is trying to figure out how the main two delignification processes affect the properties of CNW made from lignocellulosic material. It was shown that OPEFB is a major source of CNW, and that the way lignocellulosic material is used affects the CNW's physical, chemical, and thermal properties in a significant way. Then, the fabricated CNW was used to produce lignocellulosic films. Earlier studies report that lignocellulosic film from different source such as bagasse, flax, wood fiber, ramie, rice husks, wheat, barley, oats, kapok, areca, banana, bamboo, hemp, jute, kenaf, palm, pineapple, sisal, and cotton have also been used as reinforcement (Afzal et al., 2021; Sanjay et al., 2016). So, this research expected that to be able to fabricate a lignocellulosic film directly from OPEFB with the addition of CNW and study its physical, mechanical, and thermal properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Lignocellulosic Nanocomposites

2.1.1 Lignocellulosic Material

Lignocellulosic materials are organic materials primarily composed of cellulose, hemicellulose, and lignin. Cellulose is a type of organic compound that belongs to the group of polysaccharides. It is a polymer that consists of many glucose units linked together by β (1→4) glycosidic bonds. Cellulose is the main component of plant cell walls, and it gives them strength and rigidity (Gupta et al., 2019). Cellulose is known for its high tensile strength, low weight, and biodegradability (Xu et al., 2019; Wang et al., 2021). It is also transparent, which makes it suitable for certain applications. Hemicellulose is a branched polymer composed of various sugar monomers (Qaseem et al., 2021). Unlike cellulose, hemicellulose is more heterogeneous in its structure. Hemicellulose contributes to the flexibility of plant cell walls. It has a lower tensile strength compared to cellulose but plays a crucial role in binding cellulose fibres together (Rao et al., 2023). Lignin is a complex, irregular polymer composed of phenolic compounds. It provides rigidity to plant cell walls and acts as a natural adhesive. Lignin is known for its high resistance to decomposition and its ability to withstand harsh environmental conditions. It has a complex structure with aromatic rings, contributing to its strength (Glasser, 2019).

All these materials are abundant in nature and are derived from various sources such as wood, agricultural residues, and different types of biomasses (Okolie et al., 2021). Lignocellulosic materials are widely used in various industries, including biofuel production, paper manufacturing and the production of composite materials (Baghaei

& Skrifvars, 2020; Strnad & Zemljič, 2023; Uusi et al., 2021)The following table provides a list of some common lignocellulosic materials derived from natural fibers, highlighting their sources and primary applications.

Table 2.1 Common lignocellulosic materials derived from natural fibers, highlighting their sources and primary applications.

Lignocellulosic Material	**Source**	**Primary Applications**
Straw	Wheat, rice, barley	Biofuel (Sharma, 2020), packaging (Sain, 2020), construction materials (Cascone et al., 2019; Walker et al., 2020)
Bamboo	Bamboo plants	Construction (Correal, 2020; Manandhar et al., 2019; Shu et al., 2020), textiles (Rocky & Thompson, 2020), biofuel (Aizuddin et al., 2023)
Bagasse	Sugarcane	Biofuel (Huang, 2020), paper and pulp production (Adegustias et al., 2019), biodegradable packaging materials (Gond & Gupta, 2020), biocomposites (Józó et al., 2022)
Hemp fibers	Hemp plant	Textiles (Muzyczek, 2020), biocomposites (Dahal et al., 2022)

Flax fibers	Flax plant	Biocomposites (Li, 2022b; More, 2022), paper (Egamberdiev et al., 2022)
Kenaf fibers	Kenaf plant	Biocomposites (Tholibon et al., 2019), automotive interiors (Sreenivas et al., 2020), insulation materials (Umair et al., 2020)
Jute fibers	Jute plant	Biocomposites, packaging materials (Reddy et al., 2021; Shahinur et al., 2022)
Corn stover	Corn plants	Biofuel (Alavijeh & Karimi, 2019), biodegradable plastics (Guo et al., 2021; Xu et al., 2020)
Cotton stalks	Cotton plants	Biofuel (Uyan et al., 2020),composite materials (Jawahar et al., 2023)
Rice husks	Rice plants	Building materials(Jittin et al., 2020), biofuel (Sharma, 2020), silica production (Nawaz et al., 2022)
Coconut coir	Coconut husks	Mats, ropes, brushes, geotextiles, soil erosion control, biocomposites (Goyat et al., 2022; Jeetah & Jaffur, 2022)
Sisal fibers	Agave sisalana plant	Ropes (Basak et al., 2023), biocomposites (Naveen et al., 2019)

Switchgrass	Switchgrass	Biofuel (Larnaudie et al., 2022), , biodegradable plastics (Somleva et al., 2008)
Miscanthus	Miscanthus grass	Biofuel (Turner et al., 2021), paper (Danielewicz & Surma-Ślusarska, 2019), biodegradable plastics (Wu et al., 2020), insulation materials (Witzleben, 2022)

2.1.2 Nanocomposites

Nanocomposites are materials that incorporate nanoscale reinforcements into a matrix material, resulting in enhanced properties compared to the base matrix. The term "nanocomposite" typically refers to materials where at least one dimension of the reinforcing phase is in the nanometer scale (typically less than 100 nanometers) (Okamoto, 2023)These materials have unique properties such as improved electrical, mechanical, thermal, and magnetic properties, making them versatile and suitable for various applications in fields like avionics, biomedical, automotive, construction, and more (Gavali et al., 2023).

Nanocomposites can be synthesized using different methods, and their properties can be tailored by regulating factors like size, shape, and synthesis conditions (Sreevidya et al., 2023).Polymer nanocomposites have gained significant attention in the past two decades due to their nanoscopic nature and immense internal interfacial area, leading to improved multifunctional properties. These nanocomposites have found applications in areas such as gas barrier films, flame retardant products, and loadbearing applications (Hafeez, 2022). Different types of nanocomposites exist, including polymer-based and non-polymer-based, each with their own unique characteristics and applications (Okamoto, 2023).

The matrix material is the continuous phase that surrounds and binds the nanoscale reinforcements. Common matrix materials include polymers (polymer nanocomposites), metals (metal matrix nanocomposites), ceramics (ceramic matrix nanocomposites), and more. The nanoscale reinforcements can be nanoparticles, nanotubes, nanofibers, or other nanostructures (Thangadurai et al., 2022). Nanocomposites represent a rapidly evolving field of materials science, with ongoing research focused on optimizing their properties and expanding their range of applications. The ability to tailor materials at the nanoscale opens new possibilities for developing advanced materials with superior performance characteristics.

2.1.3 Properties of Lignocellulosic Nanocomposites Film

Lignocellulosic nanocomposite films, which are films composed of lignocellulosic materials (such as cellulose, hemicellulose, and lignin) reinforced with nanomaterials, exhibit a combination of properties that make them attractive for various applications. Lignocellulosic nanocomposites film exhibits some good properties like mechanical properties (tensile strength, modulus), thermal properties, barrier properties (gas and moisture), and other unique characteristics. Lignocellulosic materials are often biodegradable, and the addition of nanomaterials does not necessarily compromise this property (Imlimthan et al., 2021; Olivares et al., 2023). It can be derived from renewable resources, contributing to the sustainability of the nanocomposite film (Sahay, 2022).

The mechanical properties of films are crucial for determining their performance and suitability for specific applications. Nanocomposite films often show improved tensile strength compared to films made solely from lignocellulosic materials (Alias et al., 2021). Tensile strength is a fundamental mechanical property that indicates the film's resistance to stretching or deformation under tension (Shu et al., 2018; Zhang et al., 2019). Other than that, incorporating nanomaterials can enhance the stiffness of the film and improve resistance to cracking or breaking due to the presence of nano reinforcements (Alias et al., 2021). Greater stiffness and lower deformation under stress is crucial in applications where dimensional stability is essential.

The thermal stability properties of lignocellulosic nanocomposite films are crucial considerations for their performance in various applications, especially when exposed to elevated temperatures (Petrushenko et al., 2015). These properties can be influenced by factors such as the type and proportion of lignocellulosic materials (Akinyi & Iroh, 2023), the presence of nanoparticles (Goikuria et al., 2017), and the overall composite formulation (Raju et al., 2023). Nanocomposites may exhibit enhanced thermal stability, making them suitable for applications where heat resistance is important. Higher thermal decomposition temperatures indicate better thermal stability and suggest that the material can withstand higher temperatures before significant degradation occurs (Dhakal et al., 2023; Presniakov et al., 2014). Depending on the type of nanomaterials used, the thermal conductivity of the film also can be improved. Understanding the thermal conductivity of lignocellulosic nanocomposites is essential for applications where heat dissipation or insulation properties are important.

Barrier properties in nanocomposite films refer to their ability to impede the permeation of gases, liquids, or other substances. Achieving effective barrier properties is crucial in applications such as packaging, where the prevention of moisture, oxygen, and other contaminants from penetrating the material is essential (Hemavathi et al., 2023). Nanocomposite films leverage nanomaterials, such as nanoparticles, to enhance these barrier properties. Nanocomposite films may have improved barrier properties against gases such as oxygen and carbon dioxide, making them suitable for packaging applications. Enhanced resistance to water vapor transmission can be crucial in certain applications. Nanoparticles, such as layered silicate nanoclays or graphene, can be incorporated to enhance the resistance of nanocomposite films to water vapor transmission (Khanzada et al., 2023). The nanofillers act as physical barriers, hindering the movement of water molecules.

Lignocellulosic nanocomposite films represent a promising area of research and development, combining the advantages of lignocellulosic materials with the unique properties offered by nanomaterials. Ongoing research is focused on optimizing processing methods, understanding the interactions between components, and expanding the range of applications for these films.

2.1.4 Potential Applications of Lignocellulosic Nanocomposites Film

Lignocellulosic nanocomposites have an extensive range of potential uses in several industries attributed to their remarkable combination of features, such as biodegradability, renewability, and enhanced mechanical strength (Raza et al., 2022; Ulaganathan et al., 2022). In food packaging, lignocellulosic nanocomposite films can be used as barrier materials to prevent the permeation of gases (e.g., oxygen, carbon dioxide) and moisture, enhancing the shelf life of packaged food (Tanpichai et al., 2023). Other than that, the biodegradable nature of lignocellulosic materials makes them suitable for environmentally friendly packaging solutions (Li, 2022a; Raghuvanshi et al., 2023).

Nanocomposites film also have potential in biomedical engineering (John et al., 2020). Lignocellulosic nanocomposites can be explored for the development of biodegradable implants and medical devices (Karki et al., 2021) and can be engineered for controlled drug release, making them suitable for drug delivery applications (Khan et al., 2023).

2.2 Lignocellulosic Material from Oil Palm Empty Fruit Bunch (OPEFB)

2.2.1 OPEFB

Oil palm (*Elaeis guineensis)* originated in West Africa and was traditionally valued for its various uses. Today, the production of oil palm has expanded extensively, especially in South America and Asia (Nigam & Pandey, 2009; Paterson et al., 2009; Yaap et al., 2011). Due to its heliophytic characteristics, this plant is currently being commercially cultivated in Indonesia, Malaysia, Thailand, and Colombia (Foster et al., 2017). Oil palm was initially brought into Malaysia throughout the nineteenth century for ornamental reasons (Mohammed et al., 2011). Over time, oil palm cultivation has become a significant agricultural product in Malaysia (Kamardin, 2023; (Yan, 2017). According to the MPOB (2023), in 2022, the Malaysian oil palm sector experienced an improvement compared to 2021, with increase in the production and export of crude palm oil (CPO) (MPOB, 2023). The extraction CPO and the extensive development of oil palm cultivating have resulted in severe environmental issues in Malaysia, despite their socioeconomic (Poludasu, 2023) and technological significance (Naidu & Moorthy, 2021).

The oil palm industry in Malaysia is the second largest in the world and produces large waste every day (Amran, 2023). The oil palm waste products are classified into two main categories: oil mill waste and plantation-based solid waste, based on its source of origin. The waste materials created from plantations include oil palm fronds (OPF) and oil palm trunks (OPT), which together make up more than 50% of all solid trash produced by the sector (Abdullah & Sulaiman, 2013). On the other hand, the remaining portion is obtained from the processing of fresh fruit bunches (FFB) in palm oil mills. This includes OPEFB, palm kernel shell (PKS), and palm mesocarp fibers (PMF) (Abdullah & Sulaiman, 2013).

OPEFB biomass refers to the plant material derived from the empty fruit bunches of oil palm trees. These empty fruit bunches are generated as a byproduct of the palm oil extraction process. Usually, OPEFB disposed of and burnt at the palm oil mill. Hence, it is essential to transform the OPEFB to preserve the environment by reducing greenhouse gas emissions and ensuring the sustainability of the oil palm industry. The nation would undeniably reap advantages from the transformation of this waste into valuable commodities. There is a growing demand among researchers to regulate the utilization of OPEFB, particularly in the context of industrial conversion. By utilizing all fractions obtained from the OPEFB as the primary material, it is anticipated that the increasing value of OPEFB will be optimized, hence minimizing the waste generated during the production of fuels and other commercially valuable chemical products (Ramé, 2018; Tahir et al., 2021).

OPEFB biomass is recognized for its renewable and sustainable nature, making it a valuable resource for various applications. OPEFB biomass is produced in large quantities by the palm oil industry. Due to the continuous cultivation of oil palm trees for palm oil production, there is a consistent and abundant supply of OPEFB biomass. OPEFB biomass is considered renewable because it is a byproduct of the oil palm industry, which relies on the cultivation of oil palm trees. The cultivation process involves replanting, ensuring a continuous and sustainable supply of biomass.

Palm solid residues predominantly consist of lignocellulosic components, characterized by varying concentrations of lignin, cellulose, and hemicellulose (Megashah et al., 2018; Said et al., 2021). The composition can vary based on factors such as the age of the palm fruit bunches and the oil extraction process. Cellulose is a major component of OPEFB, constituting a significant portion of its fibrous structure. Cellulose is a linear polymer composed of glucose units linked by β-1,4-glycosidic bonds (Gupta et al., 2019). It provides strength to the cell walls. Hemicellulose is another important polysaccharide found in OPEFB. It is a branched polymer made up of various sugar monomers, including glucose, xylose, mannose, and others (Teerakulkittipong, 2021).

2.2.2 Utilization of OPEFB in Lignocellulosic Film

OPEFB-based films are films or sheets produced from the fibres of oil palm empty fruit bunches. These films exhibit a range of characteristics that make them suitable for various applications. Film production from OPEFB has been studied in several papers. The findings suggest that the addition of cellulose nanofiber from OPEFB in starch-based biopolymers can significantly improve the mechanical properties and water barrier properties, making them suitable for food packaging applications (Salehudin et al., 2013). Mohamad et al. (2012) fabricated cellulose acetate film from OPEFB and evaluated its biocompatibility for dental applications. Abdulrazik et al. (2022) developed a mathematical programming model to optimize transportation modes and processes for OPEFB-based bio-material production . Aditiawati et al. (2018) used enzymatic methods to isolate cellulose nanofibers (CNF) from OPEFB biomass and characterized their properties. Rozman et al. (1999) investigated the mechanical and water absorption properties of OPEFB-based composites with different thermoplastic matrices. These papers provide insights into various aspects of film production from OPEFB, including material characterization, process optimization, and property evaluation.

Utilizing OPEFB for film production presents both challenges and opportunities. OPEFB-based films have some advantages over petroleum-based plastics, such as biodegradability, renewability, and low cost. However, they also face some challenges, such as poor mechanical properties, high water sensitivity, and low compatibility between the fibres and the matrix. OPEFB fibres may have limitations in terms of mechanical strength compared to synthetic materials. OPEFB fibres can improve the tensile strength and modulus of the bioplastic composites, but they may also reduce the elongation at break. The optimal fibre content and the use of compatibilizers, such as epoxidized oils, can enhance the mechanical performance of the OPEFB-based films(Khalil et al., 2017; Yang et al., 2021). Other than that, converting OPEFB fibres into films can be a complex process, requiring specialized equipment and processing techniques. Continued research and development can lead to the refinement of processing methods, making them more efficient and cost-effective. As technology advances and awareness grows, OPEFB-based films have the potential to play a significant role in the sustainable materials landscape.

2.3 Cellulose Nanowhiskers (CNW): Extraction and Properties

2.3.1 Extraction Methods

Shifting from the utilization of OPEFB to the extraction of CNW, the focus shifts towards utilizing cellulose's properties for advanced applications. CNW extraction, a process aimed at obtaining highly crystalline cellulose structures, aligns with the sustainable utilization of natural resources. This is accomplished by eliminating the amorphous components of cellulose. CNW, CNF, and bacterial nanocelluloses (BNCs) are the three primary classifications that can be applied to nanocelluloses. These classifications are based on material sources and extraction methods. As a result of differences in the origin of the cellulose, the conditions under which it was extracted and processed, and the possibility of pre- or post-treatments, the extracted nanocelluloses exhibit a wide range of characteristics, including particle size, crystallinity, and shape. Figure 2.1 depicts the most typical technique of producing the CNW from various wastes derived from biomass. This approach involves reducing the size of natural cellulose. Mechanical hydrolysis, chemical hydrolysis, biological hydrolysis, and combination techniques are some examples of these types of processes (Chaka, 2022; Yu et al., 2021).

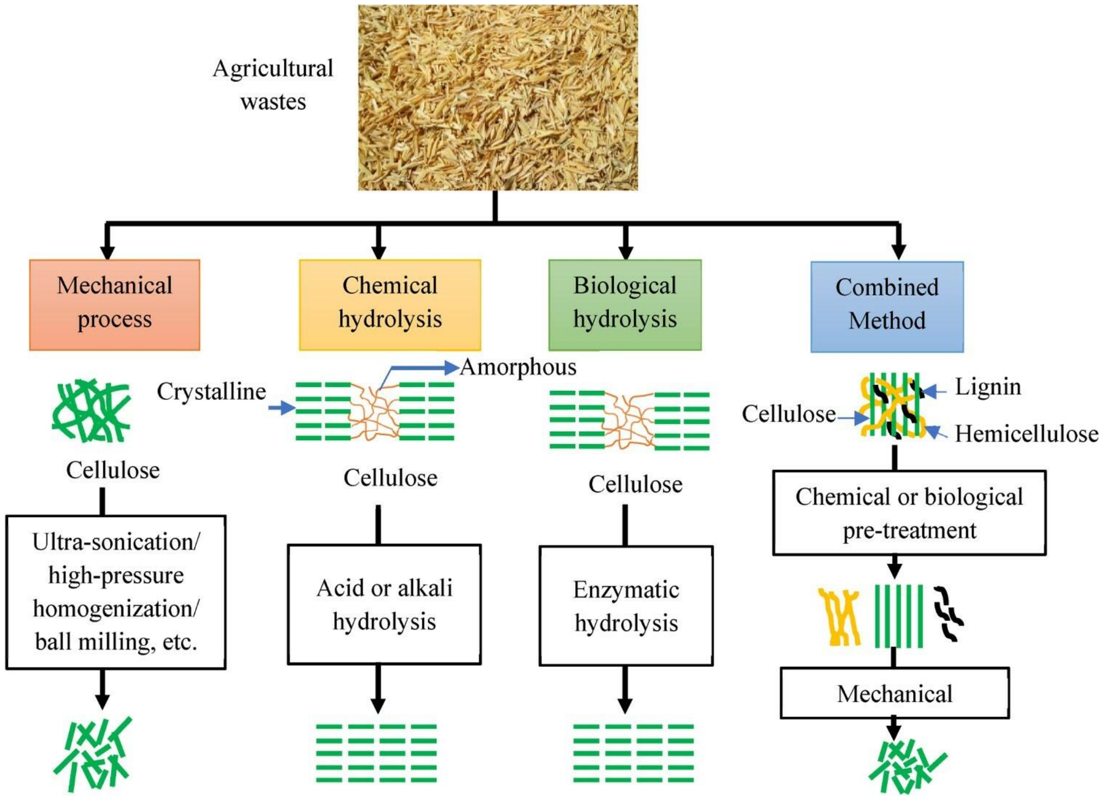

Figure 2.1 Schematic diagram of common CNW extraction methods from agricultural wastes: adapted from Chaka, 2022).

The cellulose sources will be subjected to high shear forces during the mechanical process of extracting CNW through grinding, ball milling, cryo-crushing, high-pressure homogenization, ultrasonication, and micro-fluidization (Kaur et al., 2021). The limited utilization of this technology can be attributed to its high energy consumption. Additionally, the mechanical processes involved in the process adversely damage the structure of cellulose, leading to a decrease in the level of crystallinity and purity of the extracted CNW (Cao et al., 2021; Phanthong et al., 2018). Chemical hydrolysis is another way. In this method, the solid parts of the cellulose stay together, but the amorphous part breaks down. It is one of the easy and inexpensive ways to get the CNW ready. But it has some problems, like being unstable at high temperatures because of sulfone groups on the surface of the recovered CNW, needing a lot of water and special reactors to separate acid or alkali from CNW, and having to neutralize waste solutions that are bad for the environment (Yu, 2021).

The third way is biological hydrolysis, or BNC. It is mostly fermented by gram-negative bacteria that are not harmful, like Acetobacters species, by making glucose chains and crystals. This process uses very little energy and doesn't use any harmful chemicals. It makes a material that works very well and is biocompatible, which meets the needs of green and sustainable growth (Jaiswal et al., 2021; Wang, 2020). But the BNC process is very sensitive to things like the culture medium, the type of bacteria, the concentration of the inoculum, the temperature, and the time of fermentation (Oviedo et al., 2021). The Hestrin-Schramm (HS) culture medium is often used (Costa et al., 2017), and it adds up to 30% of the total cost of making BNC, making the process expensive (Revin et al., 2018). Instead of D-glucose, some researchers used agro-industrial wastes as a source of carbon in low-cost fermentation media to get around the problem of high fermentation medium costs (Güzel & Akpınar, 2020; Kadier et al., 2021; Marestoni et al., 2021). BNC has different physical and chemical features and shapes depending on the bacteria that are used in different growing situations and for different purposes. The BNC isn't very productive or competitive on a large scale because it needs expensive and fine-grained culture medium ingredients and has strict timing and response conditions that must be met (Abol-Fotouh et al., 2020; Hussain et al., 2019).

The fourth way to extract CNW is called a combined method. This is when chemical or biological methods are mixed with physical methods to make nanocelluloses that can be used for different things (Lu et al., 2018; Squinca et al., 2020). To dissolve the hemicellulose, lignin, and pectin in this process, weak enzymes or alkaline acids will be used first. This is done before the mechanical process for extracting the CNF.

2.3.2 Properties of CNW

CNW has several properties that make it attractive for various applications. CNW are derived from cellulose, a renewable and biodegradable natural polymer making them have good biodegradability and sustainability properties. The biodegradability of CNW makes them environmentally friendly and suitable for use in sustainable and biodegradable materials. CNW have a high crystallinity and retain the crystalline structure of cellulose, typically ranging from 26.8% to 74% (Khattab et al., 2023; Tyshkunova et al., 2022). The crystalline structure imparts stiffness and mechanical strength to the CNW, making them valuable as reinforcing agents in various applications. For its morphology characteristic, CNW are nanoscale in size, typically with diameters in the range of a few nanometers and lengths in the range of several hundred nanometers. The nanoscale dimensions impart unique properties, including a high surface area, transparency, and potential for interaction with other materials at the nanoscale (Fan et al., 2022). The high aspect ratio contributes to the reinforcement properties of CNW when incorporated into composite materials, enhancing mechanical strength (Fan et al., 2022; Liu et al., 2019). CNW can be incorporated into different materials, such as polylactide-based copolymers (Khattab et al., 2023), cryogels (Tyshkunova et al., 2022), and edible films (Papadaki et al., 2022), to enhance their properties . The addition of CNW can improve the mechanical properties of materials, including tensile strength and Young's modulus. CNW can also enhance the thermal stability of materials (Li et al., 2022; Sucinda et al., 2020). Furthermore, CNW can reduce water vapor permeability, making them useful for applications requiring water barrier properties (Li et al., 2016; Sharon et al., 2016). Overall, CNW offer versatility and potential for use in various industries, including biomedical applications (Seddiqi et al., 2021), tissue engineering (Eshgh et al., 2022), nanocomposites (Eichhorn, 2011;

Kim et al., 2021; Liu et al., 2016), and packaging (Das et al., 2023; Eichhorn, 2011; Francisco et al., 2020).

2.3.3 Application as Filler in Nanocomposites Film

Nanofiller refers to nanoparticles that are incorporated into a polymer matrix to enhance its mechanical, thermal, electrical, optical, and other characteristics (Amanda & Cesar, 2018). They play a crucial role in enhancing the properties of composite films. Nanofillers can have different shapes, sizes, and compositions, such as CNW, nanoclays, carbon nanotubes, graphene, and metal nanoparticles (Zulkefli et al., 2023).

Carbon nanotubes (CNT) are very thin carbon fibers that have a diameter in the nanometer range and a length in the micrometer range. CNT were first identified in 1991 by Iijima (1991). Since their discovery, these nanomaterials have found diverse applications (Yamabe et al., 1999). The composition of CNT is comprised of a rolled-up graphitic sheet, which is a two-dimensional arrangement of carbon atoms organized in a hexagonal lattice resembling a honeycomb structure (Guldi, 2010; Yamabe et al., 1999).The nanotubes can be categorized as either multi-walled (MWCNT) or single-walled (SWCNT) based on the method used for their manufacture (Machado et al., 2014; Yamabe et al., 1999), as illustrated in Figure 2.2. Multi-walled carbon nanotubes (MWCNTs) are composed of many cylindrical layers of graphene sheets stacked in a coaxial manner around a hollow core at the center. Conversely, SWCNT is composed of a solitary sheet of graphene that is wrapped into a continuous cylinder (Ma et al., 2010; Schadler, 2003). Besides its outstanding electrical and conductive characteristics, CNT also possesses remarkable mechanical qualities. They have an elastic modulus of around 1 terapascal (TPa) and can achieve a maximum tensile strength of 300 gigapascals (GPa) when free of defects (Guldi, 2010; Sui et al., 2002). The capabilities mentioned are attributed to the presence of a robust covalent connection between carbon atoms and their organization in cylindrical nanostructures (Maron et al., 2018).

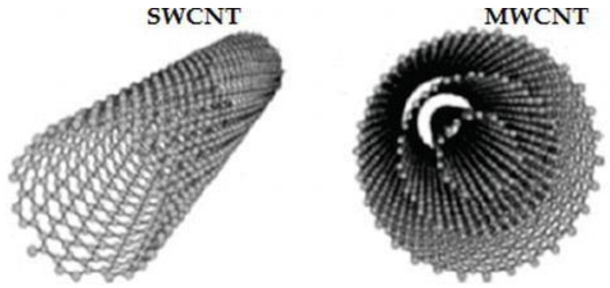

Figure 2.2 Representation of SWCNT and MWCNT(Machado et al., 2014)

Nanoclays are a type of nanomaterial derived from natural clay minerals that have been processed to achieve nanoscale dimensions. These materials are characterized by their extremely small particle size, often in the nanometer range, which imparts unique properties and performance benefits. The most commonly used nanoclays are derived from the modification of layered silicate minerals, such as montmorillonite, kaolinite, and halloysite (Kotal & Bhowmick, 2015; Schadler, 2003). The incorporation of nanoclays fillers into polymer matrices improves the hydrophilicity, hygroscopicity, thermal stability, and mechanical properties of the composite film (Nabiyev et al., 2021).

Biomass is becoming increasingly seen as a viable and sustainable option for generating energy and producing goods. Cellulose is a highly promising biomass resource. Through appropriate chemical and mechanical processes, it is feasible to generate fibrous materials with nanometer-scale dimensions in one or two directions from any naturally existing cellulose sources (Dufresne, 2017). Nanocellulose refers to materials that are generated from cellulose and have at least one dimension in the nanoscale range. This substance has been characterized as a novel bionanomaterial

(Dufresne, 2013). The acid hydrolysis method is used to isolate monocrystals of crystalline cellulosic areas (Nickerson & Habrle, 1947). The initial publication on the mechanical restructuration of cellulose fibers was released in 1983 through two companion papers (Lin et al., 2012). Nanocellulose-based materials possess a minimal carbon footprint and exhibit characteristics of sustainability, renewability, recyclability, and non-toxicity. Consequently, they hold the potential to serve as genuinely eco-friendly nanomaterials, offering numerous advantageous and unforeseen qualities. Figure 2.3 depicts a graphical representation of the crystalline arrangement of cellulose.

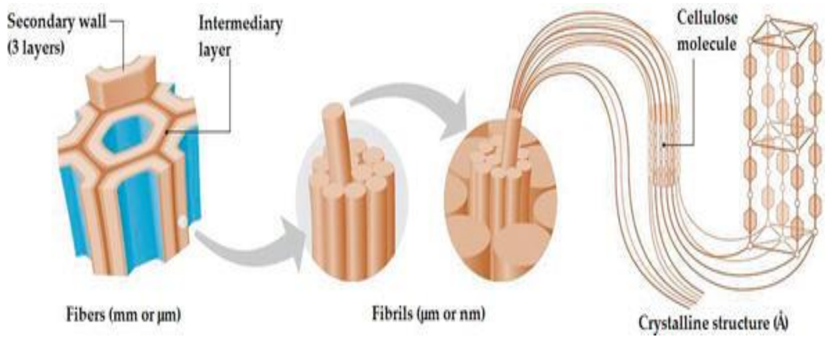

Figure 2.3 A graphical representation of the crystalline arrangement of cellulose.(Ben Azouz et al., 2012)

The synthesis of CNW from biomass is a two-step process where the initial delignification is crucial. Delignification removes lignin, exposing cellulose fibres for further processing. This step is foundational, ensuring the cellulose's purity and accessibility, essential for producing high-quality CNW. Following this, acid hydrolysis targets the cellulose, preserving its crystalline structure while eliminating amorphous regions, resulting in CNW. This sequence demonstrates the importance of delignification in transitioning from biomass to nanoscale cellulose, underscoring its role in creating materials with superior properties for diverse applications. Investigating the impact of delignification on CNW production is crucial for optimizing processes. Understanding how different delignification techniques affect CNW purity and