CELULOSIC NANOFIBER KENAF BAST USING SUPERCRITICAL CO_2 TECHNIQUE AS REINFORCEMENT IN NANOCOMPOSITE FOR PREMIUM PACKAGING APPLICATIONS

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by

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
B	Bleached
BC	Bacterial Cellulose
CNC	Cellulose Nanocrystals
CNF	Cellulose Nanofiber
DSC	Differential Scanning Calorimetry
DTG	Derivative thermogravimetric
FT-IR	Fourier Transform-Infrared Spectroscopy
MFC	Microfibrillated Cellulose
PLA	Polylactic Acid
SC-CO_2	Supercritical Carbon Dioxide
SFE	Supercritical Fluid Extraction
SEM	Scanning Electron Microscopy
TCF	Totally Chlorine Free
TEM	Transmission Electron Microscopy
TGA	Thermogravimetry Analysis
UB	Unbleached
XRD	X-Ray Diffraction

LIST OF SYMBOLS

%	Percentage
°C	Degree celcius
μm	Micrometer
cm	Centimeter
G	Giga
g	Gram
h	Hour
J	Joule
k	Kilo
kg	Kilogram
M	Molar
m	Meter
mg	Miligram
mm	Milimeter
min	Minutes
nm	Nanometer
MPa	Mega pascal
T_{onset}	Onset decomposition temperature
T_{max}	Decomposition temperature

GENTIAN NANO SELULOSA KULIT KENAF MENGGUNAKAN TEKNIK SUPERKRITIKAL CO_2 SEBAGAI PENGUAT DALAM NANOKOMPOSIT UNTUK APLIKASI PEMBUNGKUSAN PREMIUM

ABSTRAK

Kajian ini menyelidik ciri-ciri fungsi gentian nano selulosa (CNF) yang diekstrak melalui kaedah peluntur bebas klorin (TCF) diikuti dengan proses rawatan superkritikal karbon dioksida (SC-CO_2) yang mesra alam. Hasil spektrum FT-IR memberikan kesan penyingkiran lignin gentian kenaf yang efektif sebagai hasil rawatan. Gambar SEM menunjukkan bahawa bahagian amorfus seperti hemiselulosa dan lignin disingkirkan dan permukaan gentian menjadi licin setelah rawatan alkali dan pemutihan. Defibrilasi gentian dengan teknik SC-CO_2 dapat membantu hidrolisis asid ringan dan homogenisasi tekanan tinggi untuk mengasingkan CNF dengan sifat peningkatan. Ukuran zarah menunjukkan bahawa CNF yang diekstrak dengan SC-CO_2 mempunyai diameter dalam lingkungan 18-51 nm dan potensi zeta -31 mV berbanding CNF tanpa SC-CO_2. CNF yang diperoleh disahkan menggunakan analisis TEM, FTIR dan nombor kappa membuktikan delignifikasi dan defibrilasi berlaku. Analisis XRD menunjukkan bahawa kehabluran gentian ditingkatkan setelah setiap rawatan. Seterusnya, penghasilan CNF SC-CO_2 diperkuat biopolymer PLA dihasilkan melalui kaedah penuangan pelarut. Kesan penambahan CNF (1, 3 dan 5 % berat) dikaji setelah penambahannya ke dalam matriks PLA. Sifat mekanikal meningkat apabila kandungan CNF meningkat. Penemuan ini dibuktikan dengan analisis morfologi dengan SEM dan AFM yang menunjukkan penyebaran CNF yang baik di dalam nanokomposit. Kajian haba nanokomposit menunjukkan sedikit peningkatan setelah penambahan CNF. Ujian ketelapan dan sudut kontak menunjukkan penambahan CNF

meningkatkan hidrofilik sampel. Penghasilan CNF melalui kaedah gabungan menunjukkan sifat yang lebih baik daripada yang dihasilkan dari kaedah konvensional dan nanokomposit yang dihasilkan dalam kajian ini dapat disesuaikan untuk potensi aplikasi pembungkusan premium.

CELLULOSIC NANOFIBER KENAF BAST USING SUPERCRITICAL CO_2 TECHNIQUE AS REINFORCEMENT IN NANOCOMPOSITE FOR PREMIUM PACKAGING APPLICATIONS

ABSTRACT

This study investigates the characteristic functional properties of cellulose nanofibers (CNF) from kenaf fiber extracted via a total chlorine-free (TCF) bleaching method followed by an eco-friendly supercritical carbon dioxide (SC-CO_2) treatment process. The FTIR spectra result gave remarkable effective delignification of the kenaf fiber as the treatment progressed. SEM images showed that amorphous portions like hemicellulose and lignin were eliminated and smoother fiber surface after the alkali and bleaching treatment, respectively. The fiber defibrillation by SC-CO_2 technique can assist mild acid hydrolysis and high-pressure homogenization to isolate the CNF with enhance properties. Particle size showed that the extracted SC-CO_2 CNF has a diameter in the range of 18-51 nm and zeta potential of -31 mV compared to non-SC-CO_2 CNF. The obtained CNF was verified using TEM, FTIR and kappa number analysis to approve the delignification and defibrillation occurred. XRD analysis revealed that the crystallinity of the fiber was enhanced after each treatment. Next, the production of SC-CO_2 CNF reinforced in PLA biopolymer were fabricated using the solvent casting method. The effect of CNF loading (1, 3 and 5 wt. %) was studied upon its addition within the PLA matrix. The mechanical properties had increased as the CNF concentration increased. This finding proved by the morphological analysis with SEM and AFM which displayed good dispersion of CNF within the nanocomposites. The thermal studies of the nanocomposites showed slight improvement after the addition of CNF. The wettability test and contact angle shown the addition of CNF

increases the hydrophilicity of the sample. The production of CNF through combine methods showed enhanced properties to those produced from conventional methods and the fabricated nanocomposite in this study was adaptable for potential premium packaging application.

CHAPTER 1

INTRODUCTION

1.1 Overview

Nanotechnology can be defined as any usable unit or material that is 1-100 nm (nanometer) in size. Their application can be seen in every sector of life, from biological drugs to skincare products used every day, due to their high surface area (Moniri et al., 2017; Nasir et al., 2017). By increasing the surface to volume ratio, moving to the nano stage improves the nanoparticle's chemical or biological activity, optical, magnetic, and other physical properties. Nanocellulose materials can be isolated via chemicals and mechanical processes or the combination of both. Different process produce different types of nanocellulose such as cellulose nanofiber (CNF), cellulose nanocrystals (CNC) and bacterial cellulose (BC) (Abitbol et al., 2016; Huang et al., 2016; Nasir et al., 2017).

In addition, the isolation of cellulose nanofiber from kenaf was found to be considered as its higher cellulose content and excellent in mechanical properties (Hamidon et al., 2018; Kian et al., 2019; Pandey et al., 2015).The production demand of kenaf is growing globally due to the rapidly growing rate and alternative ways to avoid deforestation. The usage of the cellulose material specifically in nanosize has gained enormous attention among researchers due to its biodegradability, renewability, high tensile and flexural strength, large surface area, smaller size, non-toxic, etc. (Abdul Khalil et al., 2020; Jauhari et al., 2015; Ramesh, 2018).

Nanocellulose fiber is widely used in functional composites as a reinforcing agent including in thermoplastic and thermosetting polymers (Zimmermann et al., 2016). Generally, cellulosic fibers give strength, while polymers (also called the

matrix) add dimensional stability and transfer the shear stress between fibers. As a result, it creates a strong product that can be conveniently optimized for a wide range of applications.

Natural fibers reinforced polymer composites are often preferred due to their biodegradable existence. Each day, environmental protection agencies establish new and strict regulations, but researchers and manufacturers recognize natural fibers as an appealing option compared to glass fibers. Even though there are new and strict regulations established by environmental protection agencies, due to their incompatibility, there were many concerns reported on using natural fibers as reinforcement in polymer composites. Therefore, modification of the surface of the natural fibers by extracting their highly crystalline and rigid nanoparticles is required to overcome the problem.

The properties of CNF depend on the variety and severity of the treatment besides the preliminary method of cellulose extraction. Delignification and mercerization processes were among the approaches used by many researchers (Abu-Thabit et al., 2020; Gurunathan et al., 2015; Putrino et al., 2020; Sanyang et al., 2016). These processes can be used to extract the amorphous structure of fibers, such as hemicellulose and lignin, that separates the fibers into smaller fibrils known as cellulose microfibrils (Ilyas et al., 2018). Mild acid hydrolysis and high-pressure homogenization were the common methods used for isolating nanocellulose and it also have been showing good results with high mechanical and thermal properties (Fatah et al., 2014; Henschen et al., 2019; Li et al., 2020; Pacaphol & Aht-Ong, 2017). However, this method still can be improved to produce nanocellulose with enhance properties.

In the other hand, supercritical carbon dioxide (SC-CO_2) is a green method of producing nanocellulose by separating materials using carbon dioxide (CO_2) as a supercritical solvent (Daza Serna et al., 2016). Without excessive usage of organic solvent, CO_2 is non-toxic, non-flammable, odourless, inert and inexpensive, as well as the critical temperature and pressure are low (31 °C and 7.4 MPa). Previously, SC-CO_2 has been extensively used as organic solvents in food processing, pharmaceutical industries, coating technologies (Chan et al., 2017). Furthermore, SC-CO_2 was used for oil extraction and alternative way for Soxhlet extraction to remove lignin, hemicellulose and limited study on defibrillation process for cellulose nanofiber (CNF) isolation (Kong et al., 2020; Sodeifian et al., 2017).

There is a dearth number of research information using cellulose nanofiber isolated by SC-CO_2 technique. The application of SC-CO_2 on nanocellulose extraction has drawn attention as a potential environmentally friendly method (Cho et al., 2013; François et al., 2020; Zimmermann et al., 2018). SC-CO_2 was a novel attempt to assist the extraction of nanocellulose fiber using variation of pressure (30-50 MPa). In order to produce homogenize and stable suspension of CNF for reinforcement in nanocomposites, therefore, it is necessary to study the effect of pressure on SC-CO_2 technique to assist mild acid hydrolysis and high-pressure homogenization for high quality CNF isolation. This nanocellulose then incorporate in PLA film for potential premium packaging applications. There are no studies that reported on the combined method of SC-CO_2 method, mild acid hydrolysis and high-pressure homogenization on isolating CNF. Therefore, the effectiveness of this method on kenaf bast need to be explored.

1.2 Problem Statement

Petroleum-based plastics have been commonly used as main packaging materials. This is primarily due to inexpensiveness, suitable manufacturing, high aesthetic efficiency and outstanding physicochemical properties. However, non-biodegradable synthetic polymers in the natural environment cause serious environmental problems and have increased global concerns in this regard. Nowadays, it is recognized that edible/biodegradable films derived from biopolymers are capable, at least partially, to replace synthetic plastic materials (Shabanpour et al., 2018). As a thermoplastic biopolymer, polylactic acid (PLA) alone has some drawbacks, such as brittle, low thermal properties and low toughness, which restrict its applications. To overcome this problem, cellulose nanofiber from kenaf fiber was introduced to reinforce and enhance the properties of nanocomposite by reducing the brittleness and increase the toughness and thermal properties for premium packaging application.

Meanwhile, conventional methods for nanocellulose isolation (e.g. acid hydrolysis, ultrasonic, steam explosion) suffer from some disadvantages, such as poor thermal stability and crystallinity, as well as low dispersibility. To resolve the aforementioned issues, this area requires exploring new technologies. By isolating with the combined method of supercritical carbon dioxide assisted by mild acid hydrolysis and high-pressure homogenization, this advancement can lead to producing pure and better stability of nanocellulose materials and this will facilitate the development of different packaging industries.

The use of organic solvent can pose the environmental concern such as atmospheric and land toxicity. Hence, by introducing SC-CO_2 technique, the CO_2 in supercritical is a green solvent that can be easily achieved at low temperature and pressure. Sustainable and environmentally safe method by integrating SC-CO_2

technology on isolating nanocellulose can lead to the development of high quality and high properties of cellulosic nanofibers to reinforce in biocomposites. Compared to conventional methods, the incorporation of cellulose nanofibers generated from the combination of chemo-mechanical method will increase crystallinity and thermal stability as well as lowering the size of CNF production that would help in the improvement of the mechanical properties particularly in packaging applications. Hence, this study is designed to explore the new green technique on producing better CNF isolation on morphological, mechanical, physical and thermal properties of bionanocomposites for premium packaging applications.

1.3 Research Objectives

The present research embarks on the following objectives:

1) To study the effects of different pressure on SC-CO_2 on the isolation of cellulose fiber.
2) To analyze the morphological, chemical and thermal properties of SC-CO_2 isolated cellulosic nanofiber.
3) To evaluate the morphological, physical, thermal and tensile strength properties of cellulose nanofibers reinforced PLA biocomposites for premium packaging applications.

1.4 Novelty of Study

This research focuses on the production of cellulose nanofiber (CNF) made from kenaf bast and their effect on bionanocomposites properties. The novelty of this research is to study the defibrillation effect of SC-CO_2 towards the CNF isolation. The new isolation method of CNF using the combined method of supercritical carbon

dioxide (SC-CO_2) assisted by mild acid hydrolysis and high-pressure homogenization method can enhance the quality of CNF production.

The uniqueness of this study relies on the effect of pressure during SC-CO_2 on the CNF isolation. The kenaf bast pulp was first prepared via pre-treatment involving pulping and bleaching sequences. The bleached pulp was then undergoes SC-CO_2 and further process by mild acid hydrolysis and high-pressure homogenization for the complete CNF isolation. On the SC-CO_2 process, this study applied various parameter of pressures and the defibrillation of cellulose fiber helps to open the fiber surface area for easier CNF isolation. Next, the CNF was incorporated in PLA nanocomposites and characterized with different loading of SC-CO_2 CNF. The CNF is used as the reinforcement in PLA resulted in the improvement of bionanocomposites properties that potentially used for premium packaging applications.

1.5 Outline of Thesis Structure

Chapter 1: Introduction of the research study, which concentrated on introducing the background and objectives of the research, problem statement, challenges and gaps, and also novelty and scope of this study.

Chapter 2 - Explained on literature surveys of kenaf bast fibers, polymer, supercritical fluid extraction, production processes of nanocellulose. It also covered detail scientific information about bionanocomposites and their packaging application.

Chapter 3 - Justification on the applied materials, chemicals and also the method of production of nanocellulose and bionanocomposites and the testing that has been done.

Chapter 4 – Discussed the results and discussion for morphological, physical, mechanical and thermal properties of isolated cellulose nanofiber and the reinforced in biocomposites.

Chapter 5 - Concludes the finalize discussions and proposed recommendations for further research proposals.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Lignocellulosic fiber is a complex system that comprises cellulose, lignin, hemicellulose, ash and extractives. The cellulose fibrils were constructed in a soft matrix embedded within lignin and hemicellulose (Fatah et al., 2014; K. Spence et al., 2011). To date, the extraction of cellulose material has been the focus of the researchers to develop new advanced material for specific applications. Nanocellulose is one of the advanced materials and has been widely applied as reinforcement in the composite system due to its high availability, low cost, nano-scale size, lightweight, renewability and unique morphology (Joseph et al., 2020; Oksman et al., 2016).

Nanocellulose can be divided into three types which are cellulose nanofiber (CNF), cellulose nanocrystals (CNC) and bacterial cellulose (BC). Each type of nanocellulose was produced via different isolation techniques including mechanical (high-pressure homogenization, cryocrushing, ultrasonification, grinding, etc.), chemical (acid hydrolysis, alkali treatment, etc.) or biological techniques (enzymatic hydrolysis). Meanwhile, supercritical carbon dioxide (SC-CO_2) is one of the extraction techniques commonly used for oil extraction (Louaer et al., 2019), decaffeination (Ilgaz et al., 2018; Zabot, 2019), sterilization (Omar et al., 2017), aerogel production (Ciftci et al., 2017), etc. To date, this method was known to have the capability to assist nanocellulose production of acid hydrolysis and the high-pressure homogenization method (Bogdanovic et al., 2016; Neves et al., 2019). These combined methods are expected able to improve the CNF production as reinforcement in biocomposites with higher properties especially for film production, cosmetics, medical and other outdoor

applications. All these bionanocomposite productions and applications will be discussed in more detail in this chapter.

2.2 Lignocellulosic Material

Lignocellulose is a composite biological material and the main component of cell walls in trees, shrubs and grasses. Chemically, lignocellulosic materials are composed of organic and inorganic components. Among the organic components, carbohydrate polymers (cellulose and hemicellulose) and aromatic polymers (lignin) are the main components, while pectin and protein account for a small part. Inorganic components include water, salt and other minerals (H. P. S. Abdul Khalil et al., 2019). The chemical composition of lignocellulosic fibers depends on many factors, including plant age, growing location and plant type. Fibers are composed of different amounts of organic and inorganic components. The components are connected through a large number of non-covalent and covalent interactions, thus forming a highly complex structure (Gazzotti et al., 2019; Nasir et al., 2017; Usmani et al., 2017).

Generally, according to the source, natural fibers can be divided into three categories: plant fibers, animal fibers and mineral fibers. Plant fibers are called vegetable fibers or cellulose fibers since they are mainly composed of cellulose. Besides, the plant fibers can be classified into bast, fruits, seeds, wood (hardwood and softwood), leaves, and stems (Jonoobi et al., 2015). Figure 2.1 shows the classification according to the source of natural fibers (Ekundayo & Adejuyigbe, 2019).

Cellulose is the world's largest abundant organic biopolymer material and exists as the main structural component of plants, animals and other microbial cells. In plant-based materials, the main source of cellulose separation can be classified as wood or non-wood and natural cellulose fibers. Depending on the source of cellulose,

cell wall components in plants have a strengthening effect, and their structure may change greatly. Cellulose is a semicrystalline polysaccharide macromolecule made up of D-anhydroglucose ($C_6H_{11}O_5$) linear chain units connected by β-(1-4)-glycosidic bonds. The most basic important factor structure of all plant cell walls is cellulose (Figure 2.2), which has high stability and strength properties (George & Sabapathi, 2015).

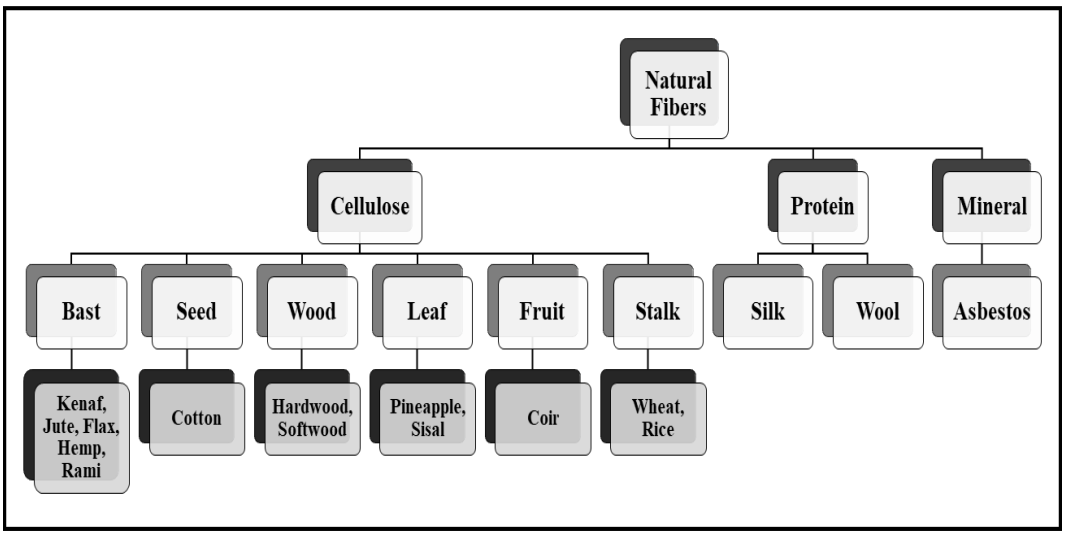

Figure 2.1: Classification of natural fibers (Ekundayo & Adejuyigbe, 2019)

The repeating unit of the cellulose chain is called dimeric cellobiose. These cellulose molecules form a straight, long, almost fully extended chain, and the cellobiose rotates 180° relative to each other along the main axis. The long cellulose chain is called α-cellulose, and the length of the β-1,4-glucan chain depends on the source of cellulose. The quality of celluloid substances is related to the degree of polymerization of cellulose molecules (Usmani et al., 2017).

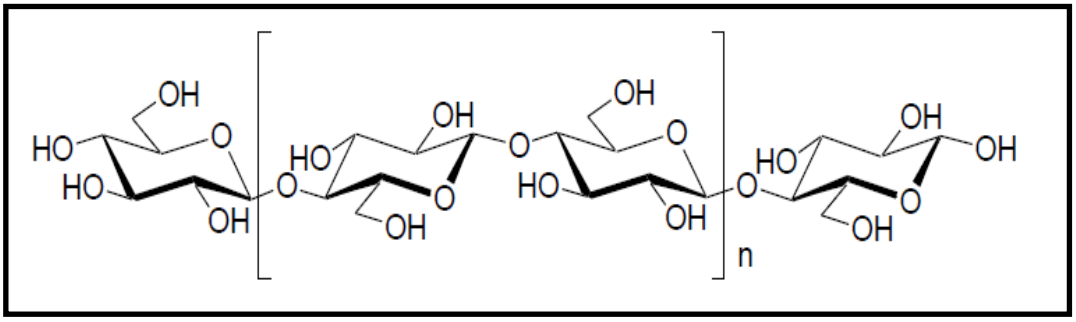

Figure 2.2: The chemical structure of cellulose (George & Sabapathi, 2015)

The cellulose content in the fiber usually affects the utilization rate, output and quality of the fiber for different reasons. For example, fibers with high cellulose content are more suitable for use in the textile and papermaking fields, while fibers with high hemicellulose content can be used to produce ethanol and other fermentation products because hemicellulose is prone to hydrolysis (Chandel et al., 2013; Sundarraj & Ranganathan, 2018).

Cellulose is usually selected as the source of the reinforcement material because it is biodegradable, renewable, low toxicity, inexpensive, and biocompatible with synthetic polymers, fillers and other biopolymers. Although cellulose fibers have good properties, including low cost, biodegradability, high mechanical strength, renewability, comparatively high density, etc., its still have some shortcomings such as hydrophilicity and difficulty to disperse in the hydrophobic matrix and high in water absorption (Ioelovich, 2017). Various types of improvements can be applied to solve the issues of cellulose fibers, such as acetylation, silylation and the addition of surfactants (Daud & Lee, 2017; Oladele et al., 2020).

Cellulose is arranged in all plants in a cellular hierarchical system (Figure 2.3) as the structural unit. The cell wall is made up in the form of a continuous network throughout the plant. In general, plant cell walls are composed of cellulose microfibrils, which are bound by an amorphous matrix of hemicellulose and lignin.

The microstructure of plant cell walls comprises the primary, secondary walls and middle lamella. The layers are different from each other in terms of chemical composition and structure, which will subsequently affect the characteristics, production, utility and value of the fiber in various applications (Siqueira et al., 2017; Uquiche et al., 2015).

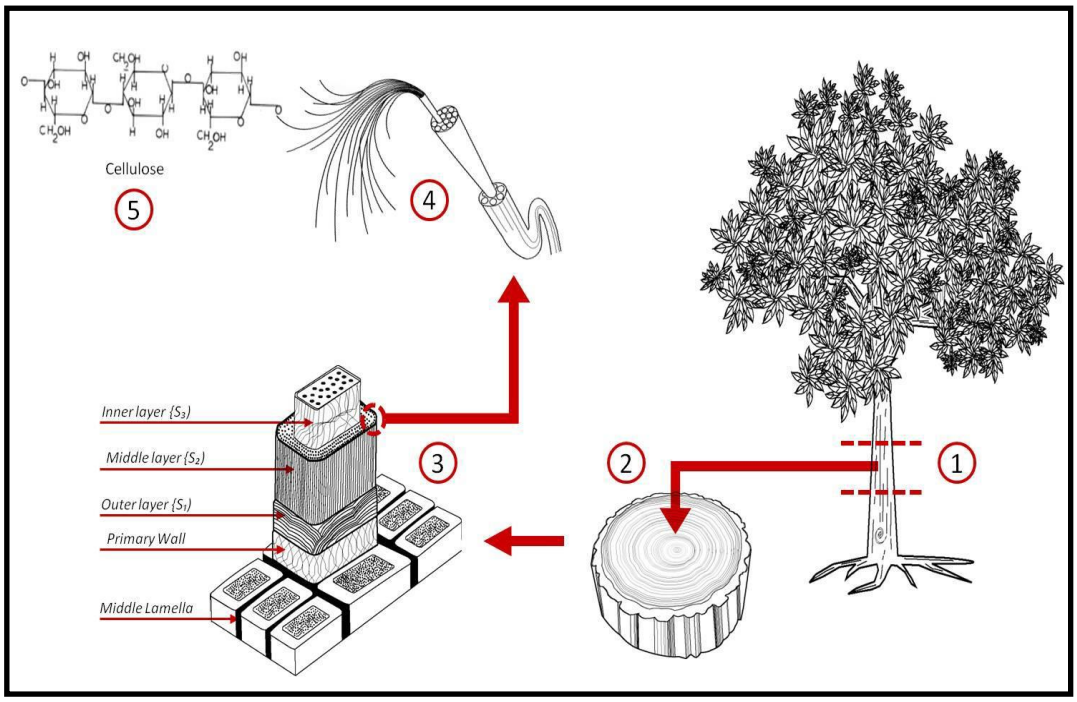

Figure 2.3: Schematic drawing of cellulose hierarchical structure (Abdul Khalil et al., 2014)

There are some features and a clear impact on the mechanical properties of the orientation of cellulose microfibrils arranged in the cell walls, where it varies depending on different plant species and the cell wall layer. Its fibrillar form of structure and the massive quantities of hydrogen bonds, caused the cellulose to have a high tensile strength that can bear the load (Saurabh et al., 2016).

Besides, lignin is a three-dimensional complex polymer, which is composed of propyl-phenol groups linked together by ethers and C-C bonds (Zhang et al., 2017).

Furthermore, it is the second most enriched present in lignocellulosic biomass after cellulose. By holding them together, rigidity and strength can be provided to the fiber. In better terms, in addition to hardening cellulose fibers, lignin can also act as a sealant to protect it from biological attack.

Hemicellulose is an amorphous, low-molecular-weight and heterogeneous polysaccharide that is connected to the lignin and cellulose in the cell wall of plant fibers and is composed of xylans, xyloglucan, mannan and glucomannan (Pauly et al., 2013). Hemicellulose acts as a compatibilizer to form an interface between hydrophilic cellulose and hydrophobic lignin. Depending on various sources, hemicellulose and lignin usually account for 20-40 %, 15-25 % of the chemical composition of cellulose fibers. The chemical composition of certain natural fibers is tabulated in Table 2.1 (Komuraiah et al., 2014).

Table 2.1: Chemical composition of some natural fibers (Komuraiah et al., 2014)

Type of fibers	**Cellulose (%)**	**Lignin (%)**	**Hemicellulose (%)**
Abaca	62.5	12	21
Alfa	45.4	14.9	38.5
Bagasse	37	22	21
Banana	62.5	7.5	12.5
Bamboo	34.5	26	20.5
Coir	46	45	0.3
Cotton	89	0.75	4
Flax	70.5	2.5	16.5
Henequen	60	8	28
Jute	67	9	16
Kenaf	53.5	17	21
Ramie	72	0.8	14
Sisal	60	8	11.5

The morphological structure of the overall system of cellulosic fiber is represented in Figure 2.4, which begins with the linkages of cellulose molecule chains

merging to form elementary fibrils, which then plug into larger units called microfibrils, which are then assembled into fibers. Thus, the smallest element that can be extracted from the cell wall structure is called microfibril. Microcrystalline cellulose (MCC), microfiber cellulose (MFC), cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), cellulose whiskers (CW) can be obtained naturally or organically from plant cellulose.

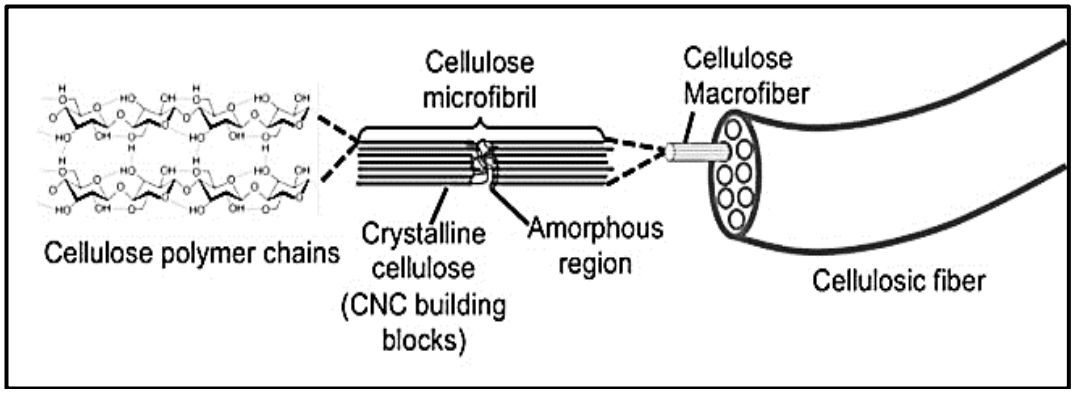

Figure 2.4: Schematic drawing of cellulose organization hierarchical structure, from fibers to cellulose molecule chains (Gumrah Dumanli, 2016)

2.3 Kenaf

The natural fiber used in this study is kenaf bast fiber which is a strong fiber with desirable properties such as recyclability, high toughness, high mechanical properties, and improved energy recovery. Nowadays, kenaf has attracted the attention of many researchers and scientists in the industry of composites for its bast and core fiber as it is very suitable as a reinforcing material or filler (Rizal et al., 2021; Sabaruddin & Paridah, 2018).

The scientific name of kenaf is *Hibiscus cannabinus*. The term of kenaf originated from Persian, which has short-day plantation, warm-season and annual herbaceous plants, with an average diameter of 67.6 microns (Arjmandi et al., 2021). It looks like bamboo and is closely related to cotton and jute. Some kenaf varieties can

be found in Malaysia. Different kenaf varieties can be distinguished according to their flower, leaf shape, stem and seed color, and adaptability under different environmental conditions. Kenaf type V36 is one of the kenaf varieties commonly grown in Malaysia because it is suitable for growing in the country's climatic conditions (Sri Aprilia et al., 2016). It can grow in hot and various environmental conditions. For example, even under moderate weather conditions, with a stem diameter of 25 to 51 mm, it can grow to more than 3 m in 3 months (Fiore et al., 2015). Kenaf can be grown in subtropical and tropical regions. From the perspective of energy consumption, 15 MJ of energy is used to produce 1 kg of kenaf compared to the production of 1 kg of glass fiber that requires 54 MJ (Saba et al., 2015).

Generally, Figure 2.5 presents the entire stalk of kenaf fiber that can be separated into the outer layer (bast) and the inner layer (core). Kenaf fiber is composed of darker, long bast about 35 wt. % and brighter, short core about 65 wt. % fibers (Saba et al., 2015). The cellulose content of bast fiber (55 %) is higher than core fiber (49 %) (Kudori et al., 2019), which makes bast fiber to be an excellent choice and great properties of nanocellulose for the preparation of hybrid biocomposites.

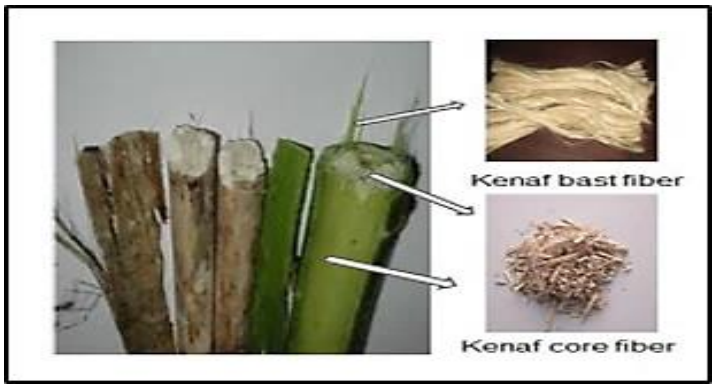

Figure 2.5: Kenaf plant and fiber parts (Birnin-Yauri et al., 2016)

Table 2.2 shows the chemical composition, physical properties and the comparison of kenaf bast and kenaf core. The outer fiber bark can be used to produce bast fiber, which has excellent tensile and flexural strength. These characteristics make bast fibers an ideal choice for the manufacture of various molded, extruded, woven and non-woven products.

Table 2.2: Physical properties of kenaf bast and core fibers (Akil et al., 2011)

Physical properties	**Core**	**Bast**
Fibril width, W (μm)	19.23	17.34
Fibril length, L (mm)	0.75	2.22
L/W	39	128
Lumen diameter (μm)	32	7.5
Lumen diameter (μm)	32	7.5

In order to increase the possibility of commercially available kenaf derivatives, Malaysia established the National Kenaf Research and Development Program to develop kenaf as a possible new industrial crop. Several groups of researchers reported varying chemical compositions of kenaf fibers that consist of cellulose (44.5-80 wt. %), hemicellulose (20.3-24 wt. %), lignin (5-21.5 wt. %) and less than 6 wt. % of ash and extractives. Table 2.3 summarizes the chemical composition of kenaf fibers collected from several studies.

Kenaf reinforced composites have been used for many applications such as automotive parts, absorbents, building materials, paper products and animal feeds (Birnin-Yauri et al., 2016; Saba et al., 2015; Sadrmanesh & Chen, 2019). These applications of kenaf fiber have been chosen as reinforcement in composites because of their biodegradability, low density, good mechanical properties and excellent damping characteristics (Dongre & Suryawanshi, 2021). Kenaf fiber reinforced in polypropylene composite material has been used by Toyota Motor Corporation for

interior components such as seatback panels and door trims. Moreover, Panasonic Electric Works used kenaf for structural wallboard for substituting plywood, which is commonly made from wood because of its lightweight composites (Qiushi Wang et al., 2018). Kenaf have been applied in many other applications such as construction (structural panels and buiding section), electrical and electronics (printed circuit boards and circuit components) and food packaging (wrapping films, containers, plastic carrier) (Sreenivas et al., 2020). The comparison of mechanical properties of some natural fibers is presented in Table 2.4.

Table 2.3: Chemical composition of kenaf fibers

Composition	α-cellulose (%)	Holocellulose (%)	Hemicellulose (%)	Lignin (%)	Extractive (%)	Ash (%)	References
Kenaf bast	44.4 – 63.5	73.2 - 86.8	17.6 - 21	9.3 - 21.1	2.7 - 5.5	0.6 - 5.9	Abdul Khalil et al., 2010; Jonoobi et al., 2015; Kian et al., 2019; Udohitinah & Oluwadare, 2011; Zhang et al., 2011)
Kenaf core	38.3 - 50.6	71.9 - 87.2	-	17.8 - 23.2	2.2 - 4.7	1.9 – 4.6	(Abdul Khalil et al., 2010; Udohitinah & Oluwadare, 2011)
Kenaf stem (Bast & Core)	44.5 - 80	74.3 - 87.7	20.3 - 24	5 - 21.5	1.7 - 6.4	2.4 – 5.1	(Abdul Khalil et al., 2010; Jonoobi et al., 2015; Ramesh, 2018; Sadrmanesh & Chen, 2019; Shakhes et al., 2011; Udohitinah & Oluwadare, 2011)
Hardwood	31 - 64	71 - 89	-	14 - 34	0.1 – 7.7	<1	(Abdul Khalil et al., 2010)
Softwood	30 - 60	60 - 80	-	21 - 37	0.2 – 8.5	<1	(Abdul Khalil et al., 2010)

Table 2.4: The comparison of mechanical properties of some natural fibers (Saba et al., 2015)

Types of fiber	Density (g/cm^3)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)
Kenaf	1.45	284 - 930	40 - 60	1.6 - 3.5
Jute	1.3	320 - 800	26.5	1.0 - 1.8
Sisal	1.5	363 - 700	9.4 - 22	2.0 - 7.0
Cotton	1.5 - 1.6	400	5.5 - 12	7.0 - 8.0
Hemp	1.47	270 - 900	70	1 - 3.5
Pineapple	1.56	170 - 1627	60 - 82	2.4
Flax	1.5	500 - 1500	27.6	2.7 – 3.2

2.4 Nanocellulose

Nowadays, scientists all around the world show their interest in nanocellulose as reinforcements or additives in a different polymer matrix to enhance the properties of the polymer. In general, the word "nanocellulose" refers to cellulose materials with nanometer in size on any one dimension of length or width. Nanocellulose is made up of any lignocellulose materials, such as plants, agricultural residues, as well as bacteria (Yu et al., 2021). Nanocellulose fibers are isolated from renewable materials, with biocompatibility, nanometer in size, biodegradability, lightweight and have high surface area. Nanocellulose has mechanical properties that are comparable to high-strength glass fibers or even higher than that. The fascinating properties make it enticing components for high-performance polymer nanocomposites. Incorporating nanocellulose into a polymer matrix can increase the mechanical properties of the resulting composite material and changes the failure mechanism to be better (Bangar & Whiteside, 2021).

To be precise, there are three types of nanocellulose known as (i) cellulose nanofiber (CNF) or nanofibrillated cellulose (NFC), (ii) cellulose nanocrystal (CNC) and also referred to as nanocrystalline cellulose (NCC) or cellulose nanowhiskers (CNW) and (iii) bacterial cellulose (BC). Different ways of nanoparticle extraction from cellulose sources resulting in particles with varied crystallinities, mechanical properties and surface chemistry (Abitbol et al., 2016; Huang et al., 2016). The image of different types of nanocellulose production by various extraction processes is shown in Figure 2.6. CNF and CNC are the most common, and they are made through a top-down process in which cellulose fibers are disintegrated into nanoscale fragments, while BC is made through a bottom-up process in which bacteria produce nanofibers from low molecular weight enzymes (Rajinipriya et al., 2018).

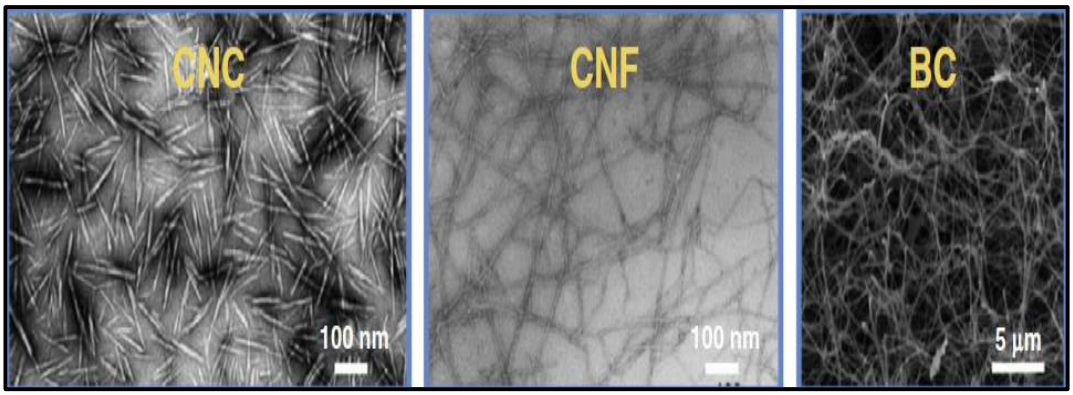

Figure 2.6: The image of nanocellulose from different extraction process (Abitbol et al., 2016)

In general, cellulose nanocrystal (CNC) has a lower aspect ratio (L/D, L = length, D = diameter) of straight crystalline rod-like shapes with standard diameters of 2-20 nm and lengths ranging from 100 to 500 nm (Börjesson & Westman, 2015). The particles are highly in crystallinity, with a crystalline content of between 54 and 88 percent (Budtova et al., 2020; Phanthong et al., 2018). However, the CNC has lacked amorphous regions and versatility. CNC was produced by chemical treatment method via acid hydrolysis from various cellulose sources (Saurabh, Mustapha, et al., 2016; Sofla et al., 2016). The amorphous regions of cellulose microfibrils are selectively hydrolyzed under certain conditions. When cellulose is exposed to pure acid hydrolysis, they are more prone to acid attack than the crystalline domains. As a result, these micro-fibrils decompose into shorter crystalline pieces with a high degree of crystallinity known as CNC. The shape of CNC produced from acid hydrolysis most likely resembles whiskers because of the tapering at the end of the crystals (Ilyas et al., 2018; Mondal, 2017; Lísias P. Novo et al., 2015).

In contrast to CNC, cellulose nanofiber (CNF) is a micrometer-long entangled fibril with a high aspect ratio that is made up of alternating amorphous and crystalline cellulose domains that are usually the products of further processed microfibrillated cellulose (MFC). The entanglement of long particles of approximately 1-100 nm in

size gives highly viscous suspension at relatively low concentrations usually below 1 wt. %. The extraction of CNF from cellulosic fibers can be achieved via three processes: (i) mechanical treatment (e.g., homogenization, ultrasonication, grinding, and milling), (ii) chemical treatments (e.g., TEMPO oxidation, acid hydrolysis), and (iii) combination of mechanical and chemical treatments (Buffiere et al., 2017; Chandra et al., 2016; Davoudpour et al., 2015; Fazeli et al., 2018; Ioelovich, 2017; Luo & Wang, 2017). The CNF can be produced via multiple mechanical shearing methods that are applied to the cellulosic fibers to release more or fewer CNF. The production route is usually associated with high energy consumption to break the inter-fibrillar hydrogen bonding of cellulose microfibers to release CNF (Nechyporchuk et al., 2016). Without pre-treatment, it is impossible to obtain a perfectly single homogeneous sample of the resulting material called microfibrillated cellulose during the mechanical defibrillation process.

On the other hand, bacterial cellulose (BC) is particularly produced by microorganisms, with *Gluconacetobacter xylium* which is known as the most efficient amongst other cellulose producing microorganisms (*Agrobacterium*, *Acetobacter*, *Aerobacter*, *Achromobacter*, *Alcaligenes*, *Azobacter*, *Sarcina*, *Pseudomonas*, *Rhizobium* and *Salmonella*). BC is commonly used in biomedical applications as it is a pure, versatile material and highly compatible (Picheth et al., 2017). A different source of the plant may require pre-treatment to remove the lignin and hemicellulose content before the hydrolysis. It is synthesized as pure cellulose and can be characterized by an average diameter of 20-100 nm and micrometer length, entangles to form stable network structures (Abitbol et al., 2016). Jonoobi et al., (2015) reported that nanofibers from bacteria have been found to have widths between 9.7 and 12 nm.

Based on the top-down process of isolation, cellulosic source, structure and their condition, nanocellulose can be divided into two major subcategories: nanofibrillated cellulose (CNF) and nanocrystalline cellulose (CNC), which differ in morphology, diversity dimensions, degree of crystallinity, and functions (Abdul Khalil et al., 2014). Table 2.5 lists the differences between the above nanocellulose groups, which are simply defined by the different processes of isolation and scale and their abbreviations.

Table 2.5: Types of nanocellulose (Abdul Khalil et al., 2014b; Zimmermann et al., 2016)

Types of nanocellulose	**Synonyms**	**Abbreviations**	**Isolation Processes**	**Average size**
Nanofibrillated cellulose (CNF)	Nanofibrils, microfibrils, nanofibrillated cellulose, microfibrillated cellulose	CNF, NFC, MFC	Mechanical shearing, homogenization, enzymatic hydrolysis	Diameter: 5–60 nm Length: several micrometers
Cellulose nanocrystal (CNC)	Nanocrystalline cellulose (NCC), nanowhiskers, crystalline nanocellulose	CNC, NCC, CNW	Strong acid hydrolysis, sonication	Diameter: 5–70 nm Length: 100–250 nm (plant); 100 nm–several micrometers (tunicates, bacteria, algae)

Different isolation processes resulted in different nanocellulose types. Many types of natural fibers have been studied by various researchers as listed in Table 2.6. The combination processes of isolation are essential to produce the desired nanocellulose properties as a reinforcement material.

Table 2.6: The example of nanocellulose isolation from natural fibers via different methods from various studies

Fiber	Method	Nanocellulose Type	References
Kenaf bast	High-pressure homogenization	CNF	(Davoudpour et al., 2015)
Kenaf core	Acid hydrolysis	CNC	(Sabaruddin et al., 2020)
Empty fruit bunch	Steam explosion and nano grinding	CNF	(Supian et al., 2020)
Northern bleached softwood kraft	High shear grinding	CNF	(N. Saba et al., 2017)
Sugarcane bagasse	High-pressure Homogenization	CNF	(Saelee et al., 2016)
Pineapple leaf fibers	Acid hydrolysis and ball milling	CNF	(Ravindran et al., 2019)
Sugarcane bagasse	Acid hydrolysis	CNW	(Esmail et al., 2018)
Hardwood pulp	TEMPO oxidation	CNF	(Kafy et al., 2017)
Textile waste (cotton)	High-pressure Homogenization	CNF	(Rizal et al., 2021)
Oil palm front	Acid hydrolysis	MCC	(Owolabi et al., 2017)
Jute	Acid hydrolysis	CNF	(Ritesh Kumar et al., 2020)
Sugar palm fibers	Acid hydrolysis	CNC	(Ilyas et al., 2018)
Cotton	High-pressure Homogenization	CNF	(Yihong Wang et al., 2013)
Softwood pulp	High Shear Homogenization	CNF	(J. Zhao et al., 2013)
Pineapple leaf fibers	High-pressure Homogenization	CNF	(Mahardika et al., 2018)
Cotton	High-pressure Homogenization	CNF	(Chen et al., 2014)
Jute	Alkali treated	CNF	(Ritesh Kumar et al., 2020)
Bamboo	Acid hydrolysis	CNF	(Saurabh, Mustapha, et al., 2016)

Nanocellulose is usually utilized in composites systems as reinforcement. The reinforcement can be in the form of flakes, fibers, particles, and whiskers that are used to strengthen the composite materials. Fibers which have a long diameter and almost

oval appearance on the other side of their length are referred to as CNF. Meanwhile, whiskers that are denoted to as CNC have a smaller diameter and length than fibers, and particles may be smaller, oval, or have no actual form. A supporting component or particles in a composite provides stability and strength, helping it to function better. Furthermore, the reinforcement of nanocellulose materials like CNF and CNC can be incorporated in polymers to a desirable solution for designing and producing modern high-end nanocomposites for use in different areas of materials science with enhanced thermal resistance, rigidity, and corrosion resistance (Kalia et al., 2011; Yadav et al., 2021).

2.5 Production of Cellulose Nanofiber (CNF)

Nanocellulose specifically cellulose nanofiber (CNF) was preferable for its higher mechanical properties and it can be produced via various methods. The process of isolation usually starts with the extraction of fibers from the plant stems. The extraction of cellulose from those fibers can be done by the purification process involving chemical pre-treatments which consist of alkali extraction and bleaching. The hydroxyl groups of intramolecular and intermolecular hydrogen bonds are broken by this chemical procedure at the first stage and thus, it will help for the preparation of cellulose nanofibrils (Mahardika et al., 2018). Usually, CNF is produced by mechanical method while CNC is produced by chemical method. Some of the mechanism and methods of producing CNF and CNC is shown in Figure 2.7. The dimensions and morphologies of CNF can vary tremendously, depending on the degrees of defibrillation and the pre-treatment occupied. CNF consists of amorphous cellulose and less crystalline compared to CNC. Nowadays, various cellulosic fibers