Properties of Polyvinyl Alcohol Composite Film Reinforced with Nanocellulose Isolated from Coconut Husks Fiber

by

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LIST OF ABBREVIATIONS

TEMPO	2,2,6,6-tetramethylpiperidinyl-1-oxyl
AFM	Atomic Force Microscopy
BBD	Box-Behnken Design
CO_2	Carbon dioxide
CNCs	Cellulose Nanocrytals
ClO_2	Chlorine Dioxide
DDLS	Dielectrophoretic Dynamic Light Scattering
DMF	Dimethylformamide
DLS	Dynamic Light Scattering
etc	Et Cetera
FTIR	Fourier Transform Infrared Spectroscopy
Tg	Glass Transition Temperature
HCl	Hydrochloric Acid
-OH	Hydroxyl Group
MARDI	Malaysian Agricultural Research and Development Institute
Tm	Melting Point
CH_4	Methane
MCC	Microcrystalline Cellulose
MFC	Microfibrillated Cellulose
HNO_3	Nitric Acid
O_2	Oxygen
PLA	Polylactic Acid
PVOH	Polyvinyl alcohol
KOH	Potassium Hydroxide
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
SANS	Small Angle Neutron Scattering
$NaClO_2$	Sodium Chlorite
NaOH	Sodium Hydroxide
H_2SO_4	Sulphuric Acid
TEM	Transmission Electron Microscopy
H_2O	Water

LIST OF SYMBOLS

α	Alpha
~	Approximately
^{o}C	Degree Celsius
^{o}C/min	Degree Celsius per minute
%E	Elongation at break
GPa	Giga pascal
g	Gram
h	Hour
kWh	Kilo watt hour
kV	Kilovolt
L	Litter
µm	Micrometer
mA	Milliampere
mg	Milligram
mL	Milliliter
mL/min	Milliliter per minute
mm/min	Millimeter per min
mmol	Millimole
m^2/g	Millisqure per gram
min	Minute
ng	nanogram
nm	Nanometer
cm^{-1}	Per centimeter
min^{-1}	Per minute
%	Percent
±	Plus minus
rpm	Rotation per minute
s	Second
ϴ	Theta
v:v	Volume to volume
w/v	Weight per volume
w/w%	Weight per weight percent
wt%	Weight percent

Sifat - Sifat Filem Komposit Polivinil Alkohol Diperkuat dengan Nanoselulosa Terpencil dari Sabut Sekam Kelapa

ABSTRAK

Sekam kelapa adalah sisa industri pertanian yang terdapat dalam jumlah banyak di beberapa negara, termasuk Malaysia. Penyelidikan ini menggunakan sisa sekam kelapa sebagai sumber selulosa untuk mendapatkan nanohablur selulosa (CNCs) melalui proses hidrolisis asid. Reka bentuk box-behnken (BBD) berdasarkan kaedah gerak balas permukaan (RSM) telah digunakan untuk mengkaji kesan kepekatan asid sulfurik, suhu tindak balas dan masa tindak balas terhadap hasil CNCs dan model regresi telah ditentukan antara hasil tiga faktor ini. Hasil kajian menunjukkan bahawa hasil CNCs adalah 44.84%, di bawah keadaan optimum dari kepekatan asid sulfurik adalah 64.61%, suhu tindak balas adalah 44.6 °C dan masa tindak balas adalah 58.54 min. CNCs menunjukkan morfologi berbentuk jarum, penghabluran yang tinggi (63.5%), purata panjang (L) adalah 92.84 nm, diameter (D) adalah 7.90 nm, dan nisbah aspek yang tinggi (L/D) sebanyak 12. Kesan menggabungkan CNCs dari sekam kelapa kepada kekuatan tegangan, terma dan kesusutan berat polivinil alkohol (PVOH) untuk membentuk filem nanokomposit biodegradasi telah dinilai. Filem nanokomposit PVOH/CNCs dengan kandungan CNCs yang berbeza (1, 3, 5, 7 dan 9% mengikut berat) telah disediakan dengan kaedah tuangan larutan. Indeks penghabluran, kekuatan tegangan, kestabilan terma (TS), dari nanokomposit telah diukur. Jika dibandingkan dengan filem PVOH (0), kekuatan tegangan nanokomposit meningkat dengan ketara, sebanyak 35.7%. Berdasarkan analisis termogravimetri, penggabungan CNCs ke dalam PVOH telah meningkatkan kestabilan terma filem nanokomposit. Kemampuan biodegradasi filem nanokomposit PVOH/CNCs juga telah diukur selepas filem-filem tersebut didedahkan dengan kaedah penimbusan tanah selama 10 minggu. Penambahan CNCs ke dalam matriks PVOH telah memberi peningkatan kepada kesusutan berat filem nanokomposit dan PVOH (9) telah menunjukkan kesusutan berat badan tertinggi (23.1%) berbanding dengan kandungan CNCs yang lain. Tanah yang telah diperolehi dari permukaan PVOH/CNCs telah dipencilkan menggunakan teknik pencairan bersiri. Kemudian, keupayaan mikroorganisma untuk mendegradasi plastik telah disiasat oleh fermentasi keadaan pepejal (SSF) dan fermentasi keadaan cecair (LSF). Bakteria terpencil (D1, D2, D3, D4 dan D5) telah dikultur dalam media garam mineral yang mengandungi serbuk filem PVOH/CNCs. Bakteria D1 menunjukkan tindak balas pertumbuhan tertinggi (0.254) pada media. Kulat S1 telah menyumbang kepada kesusutan berat filem nanokomposit PVOH/CNCs sebanyak 3.13% setelah 14 hari pemeliharaan. Analisis molekul melalui tindak balas berantai polimerase dan penjujukan DNA telah menunjukkan bahawa bakteria D1 adalah *Citrobacter freundii* sp. dan kulat S1 ialah *Aspergillus japonicas* sp. dengan masing-masing mempunyai 99% dan 100% persamaan. Kebaharuan kajian ini mendapati *Aspergillus japonicas* sp. dan *Citrobacter freundii* sp. adalah laporan pertama bagi kulat dan bakteria strain untuk PVOH/CNCs terpencil yang dijumpai di dalam tanah. Oleh itu, kulat dan bakteria yang telah dipencilkan dari tanah mempunyai keupayaan untuk mendegradasi filem nanokomposit PVOH/CNCs.

Properties of Polyvinyl Alcohol Composite Film Reinforced with Nanocellulose Isolated from Coconut Husks Fiber

ABSTRACT

Coconut husks is an agro-industrial waste available in large quantities in several countries, including Malaysia. This research utilizes the waste of coconut husks as a source of cellulose to obtain cellulose nanocrystals (CNCs) via acid hydrolysis process. The box-behnken design (BBD) based on the response surface methodology (RSM) was applied to study the effects of sulphuric acid concentration, reaction temperature and reaction time on the yield of CNCs and the regression model was established between the yield and three factors. The results showed that the yield of the CNCs was 44.84%, under the optimum conditions of 64.61% of sulphuric acid concentration, 44.6 °C of reaction temperature and 58.54 min of reaction time. The CNCs presented a needle-shaped morphology, high crystallinity (63.5%), average length (L) of 92.84 nm, diameter (D) of 7.90 nm, and high aspect ratio (L/D) of 12. The effect of incorporating CNCs from coconut husks into the tensile strength, thermal and weight loss of polyvinyl alcohol (PVOH) to form biodegradable nanocomposites film were evaluated. PVOH/CNCs nanocomposite films with different CNCs contents (1, 3, 5, 7 and 9% by wt) were prepared by solution casting method. The crystallinity index, tensile strength, thermal stability (TS), of the nanocomposites were measured. When compared to PVOH (0) film, the tensile strength of the nanocomposites improved significantly, by 35.7%. Based on the thermogravimetric analysis, the incorporation of CNCs into PVOH had improved the thermal stability of nanocomposite films. The biodegradability of PVOH/CNCs nanocomposites film was also measured after the films were introduced to the soil burial method for 10 weeks. The addition of CNCs into PVOH matrix had enhanced the weight loss of nanocomposite films and PVOH (9) showed the highest weight loss (23.1%) compared to the other contents of CNCs. The soil obtained on the surface of PVOH/CNCs were isolated using serial dilution technique. Then, the potential microorganisms of degrading plastic were investigated by solid state fermentation (SSF) and liquid state fermentation (LSF). The isolates bacterial (D1, D2, D3, D4 and D5) were cultured in mineral salt medium broth containing PVOH/CNCs film powder. The bacterial D1 showed the highest growth response (0.254) in broth media. The fungal S1 had contributed to the weight reduction weight of PVOH/CNCs nanocomposite film by 3.13% after 14 days of cultivation. The molecular analysis through polymerase chain reaction and DNA sequencing indicated that the bacterial D1 is *Citrobacter freundii* sp. and fungal S1 is *Aspergillus japonicas* sp. with 99% and 100% similarities, respectively. The novelty of the study found *Aspergillus japonicas* sp. and *Citrobacter freundii* sp. were the first reported as fungal and bacterial strain of PVOH/CNCs degrader found in the soil. Therefore, the fungi and bacteria isolated from soil have the capability in degrading PVOH/CNCs nanocomposite films.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

Plastic is a naturally recalcitrant polymer, once it enters the environment, it will remain there for many years. Accumulation of plastic as wastes in the environment poses a serious problem and causes an ecological threat. Annually, more than 350 million tons of plastics are produced in the world (Haghighi et al., 2021). According to the article appread in The Edge Malaysia Weekly on 17 February 2019, they stated that Malaysia is the top world's top dump site for plastic waste which is about 157, 299 from January to June 2018. Besides, it is estimated that 85% of trash in the oceans is made of plastics and most of them are disposable items.

The growing interest in environmentally friendly materials has motivated academic and industrial research in the development and use of biodegradable polymers for applications in which synthetic polymers or mineral fillers have been traditionally used. Toward this end, several biodegradable polymers have been modified to attempt to be competitive with petroleum based polymers with respect to performance and cost.

Poly(vinyl alcohol) (PVOH) is the largest synthetic water-soluble polymer produced in the world (Ramaraj, 2006). PVOH is biodegradable under aerobic and anaerobic conditions (Ben Halima, 2016; Matsumura et al., 1999). PVOH is widely used in the textile, adhesive, cosmetic, food, drug, paper, and packaging industries. The main functional uses of PVOH include filtration, catalysis, membranes, optics, drug release, enzyme mobilization, and tissue engineering, among others (Ahmed et al., 2020; Ebadi et al., 2021; Hari Gopi et al., 2019). It is one of the few semicrystalline polymers soluble in water and has good interfacial characteristics and mechanical properties, due to being a hydroxylated polymer capable of forming both intra-and intermolecular hydrogen bonds (Chou & Tsai, 2021; Wang et al., 2020).

PVOH has excellent film-forming properties and causes no toxic effects in the human body for it is biocompatible (Ruiz et al., 2021). Films made from PVOH are transparent, have good chemical and thermal stability, and good mechanical strength, biodegradable and do not represent a threat to the environment (Cazón et al., 2020). However, the highly hydrophilic nature of these films which renders polyvinyl alcohol (PVOH) as a poor barrier to water; critically limits wider application of this polymer and PVOH-based composites. In addition, its thermal stability, despite being considered good (initial temperature of degradation ~200°C), may be improved (Kobayashi et al., 2005). Taking into account the limitations of films made of PVOH, the natural polymer such as cellulose as a filler have a potential to improve the the properties of composite the film.

Cellulose is the most abundant natural polymers and renewable resource on the earth. They are biodegradable, renewable and low cost. However, cellulose have certain drawbacks such as high moisture absorption and low mechanical properties. One way to improve the properties of and greatly enhance their commercial potential is to incorporate nanosized reinforcement to produce cellulose nanoparticle (CNPs), cellulose nanowhiskers (CNWs) and cellulose nanocrystals (CNCs) (Neto et al., 2012; Silvério, Flauzino Neto, & Pasquini, 2013).

As one of the important derivatives of cellulose, cellulose nanocrystals (CNCs) has great potential in energy storage (Yarbrough et al., 2017), biomedicine (Trache et al., 2017), environmental remediation and other aspects (Pui et al., 2018), because of its excellent mechanical properties, good thermal stability, high biodegradability and other properties

(Thomas et al., 2018). As reported by Ardanuy & Claramunt, (2011), highly crystalline CNCs can be obtained, typically of diameter about 2–20 nm and length of 100–600 nm, by the removal of amorphous part of cellulose. In the world of materials science, CNCs have become desirable for the scientists and researchers due to their high aspect, high surface area, exceptional modulus and tensile strength (150 & 10 GPa) respectively (Adriana et al., 2005). CNCs have been isolated from agro-industrial biomass, marine animals and microorganisms (Nasir et al., 2017). Lignocellulosic biomass is one of the sources from agro-industrial have a potential resources to obtain the cellulose.

Malaysia, like most developing countries, is facing an increase in the generation of waste and accompanying problems associated with waste disposal (Lina, 2004). According to Department of Statistics Malaysia in 2020, they reported that scheduled wastes generated in 2019 was 4.0 million tonnes. As such, waste generation has increased by 3% annually which has alarmed the waste managers. The national average of 1.3 kg/capita is expected to be increasing linearly, reaching 2.23 kg/capita by 2024 (Mohamad et al., 2009). Approximately 30,000 tons of municipal solid wastes are generated daily, covering 83% of the country's waste generation, including agrowastes. Globally, 998 million tonnes of agricultural waste is produced per year and in Malaysia, 1.2 million tonnes of agricultural waste is disposed of into landfills annually (Agamuthu, 2009). It is estimated that 15% of the total waste generated in Asia is agrowaste, with agricultural waste generation in Malaysia at approximately 0.122 (kg/cap/day) in 2009 which is projected to reach 0.210(kg/cap/day) by 2025 (Agamuthu, 2009). Clearly, the way to limit the impact on the environment is by reducing the amount of waste that is generated, or the waste must be recycled, composted or reused. Therefore, The production of CNCs obtained by agricultural crops residue allows a significant reduction both in the volume of waste accumulated in the environment and in the extraction of raw materials.

In Malaysia, coconut (*Cocos nucifera*) was considered as one of the most important crops. Development of coconut product was very well-known from the past decades (Basu et al., 2015). It has been developed for food and beverage (e.g. coconut oil and coconut milk) (Lamaming, Hashim, Peng, et al., 2015; Rodsamran & Sothornvit, 2018). Total acreage of coconut plantations was 85,000 ha in 2019. Coconut waste is a copious agricultural waste and it also composes part of kitchen waste. The waste is generated from different parts of the coconut head, namely the husk, kernel and meat (inner part). The large amount of coconut waste will retain at the land fill for long time due to the high durability of coconut husks and caused the increasing number of landfill in Malaysia. According to Gunasekaran et al. (2012), coconut husks is a serious waste disposal issue for environment as it occupies around 60% of the domestic waste volume that are being leaving in environment.

From the viewpoint of waste management, utilization of coconut husk with higher efficiency was considered as an important key for sustainable development. In the past, such types of agro-waste have been utilised as animal feed or organic fertilizer or are otherwise allowed to decay naturally in fields, discarded or burnt, whereas current practices are on-farm, burning, burial, stockpiling and landfilling (Agamuthu, 2009). Despite its reuse as animal feed/ supplement, there is a potential alternative to reduce the agricultural waste in which the extracted cellulose in nanosized dimension can be incorporated into polymer composites (Nascimento et al., 2016).

CNCs can be acted as the reinforcing component in order to provide the significant improvement on mechanical properties and thermal stability. The use of CNCs from coconut husk as a reinforcement part in composite was investigated by many research groups (Chen & Chouw, 2018; Obada et al., 2020; Srinivasababu, 2017). Mechanical properties of the composites can be enhanced by the existence of coconut fiber. Also, it was notable that coconut fiber in composite can lead to the enhancement in thermal stability as reported by Jang et al. (2012).

There are many methods to prepare CNCs, such as acid method (Shamskar et al., 2016), mechanical method (S. Singh et al., 2018), oxidation method and enzymatic hydrolysis (Chen, Deng, Shen, & Jia, 2018). Sulphuric acid hydrolysis is usually preferred technique to prepare CNCs, it allows disintegration of amorphous regions by introducing negative charges to nanoparticle surfaces, resulting into formation of stable nanocrystal suspensions (Beck-candanedo et al., 2005). Wulandari et al. (2016) prepared CNCs by acid hydrolysis technique and found that the CNCs of higher crystallinity and needle like shape morphology were obtained.

Alternative strategies to reduce accumulation of plastic wastes have been initiated and implemented from a different aspect including from microbiological view point. Utilization of biopolymers (environmental friendly) is an alternative for partial replacement of conventional plastics (Abdul Khalil et al., 2016; La China et al., 2018). Polyhydroxyalkanoates (PHAs), poly(e-caprolactone) (PCL), and poly(l-lactide) (PLA) and polyvinyl alcohol (PVOH) have been developed as biologically recyclable green polymers (Munir et al., 2018). Besides manufacturing degradable plastics, microbial biodegradation of plastic has been obtaining much attention of many scientists worldwide. Many promising works on searching potential microbes and modification of environmental condition to increase the degradation rate of plastic have been reported. Emadian et al. (2017) and Harrison et al. (2018) reported that *Bacillus weihenstephanensis* sp., *Bacillus* sp., *Staphylococcus* sp., *Streptocococcus* sp. and *Diplococcus* sp. isolated from garbage soil shows their ability to degrade polymer. While

Rajandas et al. (2012) identifies some gram negatives *Pseudomonas fluorescens* sp., *Pseudomonas aeruginosa* sp., and *Acinetobacter ursingii* sp. isolated from plastic contaminated soil could also degrade polymer.

According to the literature, there are a number of studies reported regarding the enhancement of PVOH/CNCs nanocomposite film properties using different loadings of CNCs. However, to the best of our knowledge, there is lack of studies reported on the biodegradability properties of PVOH/CNCs nanocomposite films. Therefore, the aim of the present study is to characterize the properties PVOH/CNCs nanocomposite films with different CNCs content using solution casting method. In this study, coconut husks is used as the raw material for the isolation of CNCs through acid hydrolysis. The effect of different of CNCs contents on the morphological, tensile, thermal and biodegradation properties of PVOH/CNCs nanocomposite films are investigated.

1.2 Problem statement

High production of coconut milk and coconut water in Malaysia especially in coastal area has become a problem because the coconut husks are disposed freely in the field or wasted as agro-waste (Chandrahasa & Rajamane, 2014). Jabatan Pengurusan Sisa Pepejal Negara (JPSPN) stated that, all the non-recyclable waste will transfer to the landfill, and the landfill problem will cause environment and human health issue to Malaysia. In year 2012, Peninsular Malaysia is generated 25000 ton of waste and about forty 7 % of the waste is organic waste. Only 5 % of the waste had been recycled. According to Gunasekaran et al. (2012), coconut husks is a serious waste disposal issue for environment as it occupies around 60% of the domestic waste volume that are being leaving in environment. Therefore, by reusing the coconut husks, it can reduce the waste capacity of landfill and also the environment pollution in Malaysia.

The coconut husks are one of the lignocellulosic biomasses that contain cellulose, hemicellulose and lignin. Coconut husks contain higher cellulose content (about 38-39%) compared to the other agro-waste produce such as coir stover, kenaf fibres and wheat straw. The abundant source of coconut husks and its high cellulose content make it an ideal source for the isolation of CNCs.

There are many methods to prepare CNCs, such as acid method (Shamskar et al., 2016), mechanical method (S. Singh et al., 2018), oxidation method and enzymatic hydrolysis (Chen, Deng, Shen, & Jia, 2018). Sulphuric acid hydrolysis is usually preferred technique to prepare CNCs, it allows disintegration of amorphous regions by introducing negative charges to nanoparticle surfaces, resulting into formation of stable nanocrystal suspensions (Beck-candanedo et al., 2005). Besides, acid method also considered as easiest method compared to oxidation method and enzymatic hydrolysis.

In this study, the approach have been used to isolate the cellulose nanocrystals from coconut husks via sulfuric acid hydrolysis. In addition, when using sulfuric acid the cellulose nanocrystals obtained, certain condition parameters gave the low yield of CNCs. Therefore, in this study the cellulose nanocrystals obtained is determined using different parameters condition of sulphuric acid and study for their properties in term of yield. The effect of pretreatment and isolation process also would change the properties of raw cellulose coconut husks, treated coconut husks and CNCs in terms crystallinity, morpholgy and thermal stability.

PVOH can be used as polymer matrix as it is a synthetic water-soluble polymer (Qiu & Netravali, 2016). However, the neat polymer of PVOH has lower thermal, tensile strength and flexibility properties. Therefore, the different CNCs contents can be introduced into PVOH composites for the purpose of reinforcement in order to study the desired compatibility between nanofillers and polymer matrix.

PVOH also can act as biodegradable matrix under aerobic and anaerobic conditions (Singh et al., 2018). It has excellent film-forming properties and causes no toxic effects in the human body. A lot of researches have been done on the biodegradability of nanocomposite film by determining the weight loss, mechanical and morphological analysis. A few researchers reported that *Bacillus weihenstephanensis* sp., *Bacillus* sp., *Staphylococcus* sp., *Streptocococcus* sp. and *Diplococcus* sp. isolated from garbage soil shows their ability to degrade polymer. However, there are lack of explore on the identification of degrading microorganisms on the PVOH/CNCs nanocomposite film. Hence, this study also done in determining the degrading microorganisms that lead to the biodegradability of nanocomposite films.

1.3 Objectives

The key objectives of this study was to prepare and characterize the PVOH/CNCs nanocomposite film using different CNCs contents. The specific objectives of this study were listed as below:

i To characterize the extraction of CNCs from coconut husks via acid hydrolysis method at an optimal condition.

ii To study the effect of CNCs contents on the properties of PVOH/CNCs nanocomposite films.

iii To evaluate the biodegradability of PVOH/CNCs nanocomposite films and identify the degrading microorganism involved in biodegradation process of PVOH/CNCs nanocomposite films.

1.4 Research scope

In this research, CNCs was isolated from coconut husks fiber via sulphuric acid hydrolysis. The coconut husks fiber undorgone pre-treatment processes which were alkaline pre-treatment and bleaching pre-treatment. The optimization of reaction time, reaction temperature and sulphuric acid concentration were optimized using one factor at a time (OFAT) and proceed with box-behnken design (BBD) in response surface methodology (RSM). The physical, morphological and thermal properties of the raw coconut husks fiber, treated coconut husks fiber and CNCs were studied. The development of nanocomposite films have been done by incorporating CNCs into PVOH using different CNCs contents. The nanocomposite films were subjected to mechanical, morphological, physical and thermal analysis to evaluate the changes of nanocomposite films in different content of CNCs. Finally, the biodegradability of the nanocomposite films was tested using soil burial test. The biodegradability for nanocomposite films were determined by weight loss and mechanical properties of nanocomposite films. Isolation of potential degrading microorganisms for nanocomposite films done by serial dilution method. The 10^5 and 10^7 of microorganism were used for streak plate method. The fungi and bacteria that grew in the potato dextrose agar (PDA) plate were used to determine the potential fungi and bacteria strain involved in plastic degrader. The efficiency of potential degrading microorganism were evaluated using solid state fermentation (SSF) for fungi strain and liquid state fermentation (LSF) for bacterial strain. For SSF method, M9 minimal salt agar were used to determine the weight loss of PVOH/CNCs nanocomposite film after incubated for 14 days while for LSF method used M9 minimal salts to determine the optical density value (OD) of the growth bacteria. UV-Vis spectrophotometer were used to determine the OD value. Identification of potential degrading microorganisms for nanocomposite films were performed using polymerase chain reaction (PCR) methods and phylogenetic tree showed the scientific name for the unknown microorganism.

CHAPTER 2 : LITERATURE REVIEW

2.1 Main Sources of Cellulose

Plants are the potential main sources of cellulose because they are abundant and relatively cheap. The main source of cellulose is wood pulp and cotton fibers. Large-scale industrial infrastructures are presently available for their harvesting, processing, and extraction. A wide variety of other plant materials such as husks, jute, ramie, sisal, flax, hemp, etc are also well known sources for cellulose production. Other cellulose-producing plants include water plants, grasses, and some parts of plants such as leaves, stem, fruit, etc. Agricultural wastes such as wheat and rice straw, sugarcane bagasse, sawdust, cotton stables, etc are also used for the production of cellulose (Saini et al., 2015).

2.1.1 Lignocellulosic Biomass

Owing to the over consuming of petroleum resources and increasing demand of fossil-based fuels and chemical, it is necessary to develop renewable resources to produce biofuels and biochemical for economical and sustainable development (Clark, 2019). Lignocellulosic biomass industry has become green, possible alternative of fossil resources in order to compensate the increasing trend of world’s demand for petroleum usage (Raud et al., 2019; Refaat, 2012) . Besides, lignocellulosic biomass is regarded as an abundant carbon-neutral renewable source whose increased usage can help reduce carbon dioxide (CO_2) emissions and environmental pollution (Isikgora & Becer, 2015).

This type of biomass is the most abundantly available biopolymer in nature. It is estimated that the worldwide production of lignocellulosic biomass is about 1.3 × 10 metric tons per annum (Ganesh, 2012; Khairul Islam et al., 2019; Metzger & Hüttermann, 2009). The lignocellulosic resources included agricultural residues (palm trunk and empty fruit bunch, corncobs, wheat straw, sugarcane bagasse, corn stover, coconut husks, wheat rice, and empty fruit bunches); forest residues (hardwood and softwood); energy crops (switch grass); food wastes; municipal and industrial wastes (waste paper and demolition wood) (Bano & Negi, 2017; Chirat et al., 2010; Costa et al., 2013; Haghighi Mood et al., 2013; Limayem & Ricke, 2012; Lu et al., 2013; Thambiraj & Shankaran, 2017).

The high availability of biomass has appeared to be one of the most potential resources of transportation fuels and chemicals platform. Transformation of cheaper biomass into value-added product by the mean of converting "carbon source" into "carbon sink" indicates that carbon can be fully utilized before it would be released into the atmosphere (Jiménez & Chávez, 1988; Melero et al., 2012; Ng et al., 2012). Reconstruction of low cost lignocellulosic materials to products with superior functions presents a feasible option for improvement of energy security and greenhouse emissions reduction. With the availability of biomass, it is believed that this technology is capable of turning negative cost of biomass (plant waste) into positive-earning materials.

Lignocellulose is a class of biomass that comprises three major components which are cellulose, hemicellulose, and lignin. A typical lignocellulosic biomass consists of 50% cellulose, 25% hemicellulose, 20% lignin, and 5% other minor components (Demesa et al., 2020; Guo et al., 2012; Haghighi Mood et al., 2013; Metzger & Hüttermann, 2009). Figure 2.1 shows the chemical structures of the three main lignocellulosic components.

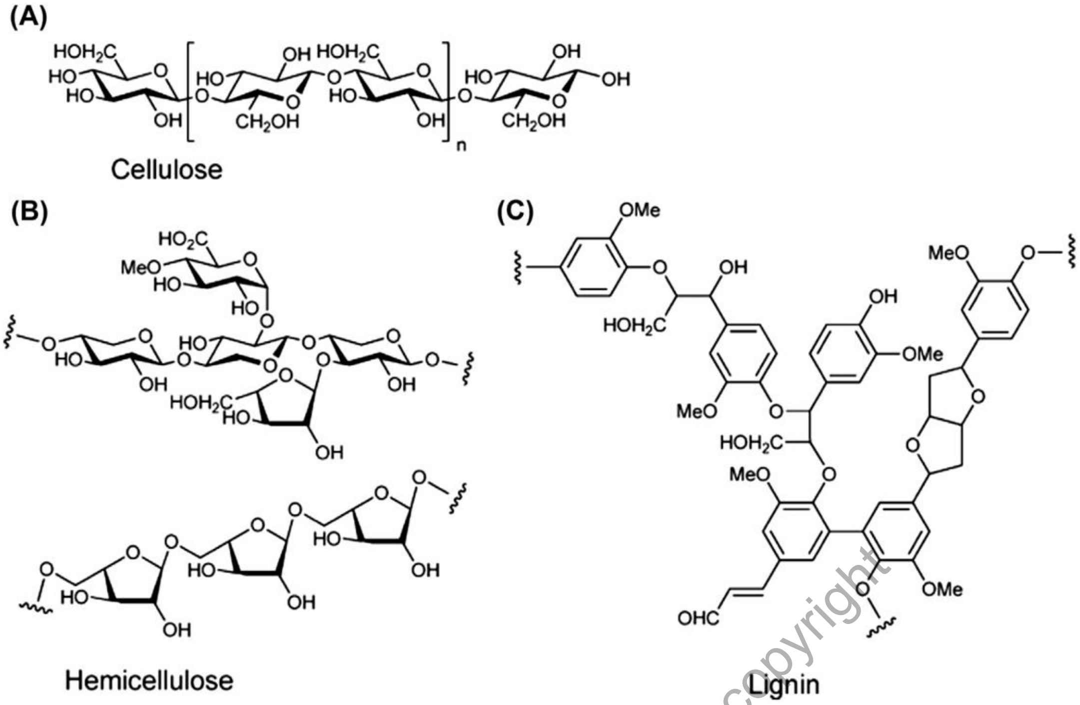

Figure 2.1 Chemical structures of (A) cellulose, (B) hemicellulose, and (C) lignin (Demesa et al., 2020)

Cellulose is a water-insoluble polymer composed of glucose linked by β-1,4-glycosidic bonds. Cellulose forms robust crystal structures due to the inter- and intramolecular hydrogen bonds. The nature of β-1,4-glycosidic bonds between the glucose molecules allows the polymer to arrange in long straight chains. This arrangement together with the even distribution of the hydroxides on both sides of the monomers enables hydrogen bonds to be formed between the cellulose molecules, which in turn results in a compound insoluble in water, but it absorbs 8% - 14% of water under normal atmospheric conditions (Guo et al., 2012; Harmsen et al., 2010). While its structure provides both mechanical and chemical stability, cellulose is further protected from degradation by its proximity to a sheath of matrix polymers including lignin and hemicelluloses.

Hemicellulose is a two-dimensional heteropolysaccharide comprised of pentoses and hexoses with short branched side connections (Guo et al., 2012; Liu, 2010). Hemicellulose contains different sugar monomers, such as xylose, mannose, galactose, glucose, rhamnose, and arabinose. Xylose is the predominant sugar monomer found in hemicellulose. Xylan has been described as the most common type of polymers belonging to the hemicellulose family of polysaccharides (Harmsen et al., 2010). Hemicellulose also contains acetyl groups attached to the polymer chain. The composition and structure of hemicellulose vary depending on the source and the method used for extraction. Relative to cellulose, hemicelluloses have lower molecular weights and a lower degree of polymerization, and they thus break down more easily and are soluble in alkaline solutions.

Lignin is an amorphous three-dimensional polymer having phenylpropane units as the main building blocks. The phenylpropane units form a complex and cross-linked aromatic structure (Guo et al., 2012; Harmsen et al., 2010). The phenylpropanoid units are primarily methoxylated phenyl propylene alcohols connected by various types of linkages that include carbon–oxygen–carbon or ether (β-0-4 and α-0-4) and carbon–carbon (C-C) linkages, with the β-0-4 interunit linkages being the most abundant in lignin (Guo et al., 2012; Liu, 2010). The most commonly encountered alcohols in lignin are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Guo et al., 2012). Lignin is insoluble in water and has a high molecular weight. It has a higher energy content than cellulose or hemicelluloses and contains highly reactive groups (Varanasi et al., 2013). The aromatic ring structure of lignin provides distinctive functional sources when depolymerized (Liu, 2010). Lignin is chemically attached to cellulose and hemicellulose in its native state, where it functions as a strengthening material by helping to resist compressional forces (Nascimento et al., 2016).

These polysaccharides are associated with each other in a heteromatrix to different degrees and varying composition depending on the type of biomass, species of plant, and even source of the biomass (Himmel et al., 2007). Table 2.1 shows the chemical composition of biomass for different types of agriculture, industrial, and forestry wastes.

Table 2.1 Chemical composition of agricultural residues and wastes (Kumar et al., 2009; Pedersen & Meyer, 2010)

Type of biomass	Lignocellulosic substrate	Cellulose (%)	Hemicellulose (wt%)	Lignin (wt%)
Agricultural waste	Corncorbs	35 - 45	35	15
	Wheat straw	30	50	15
	Barley straw	33 - 40	20 - 35	8 - 17
Energy crops	Empty fruit bunch	41	24	21.2
	Switch grass	37 - 45	31.4	12
Forestry waste	Hardwood stems	40 - 55	24 - 40	18 – 25
	Softwood stems	45 - 50	25 - 30	25 – 35
Industrial waste	Waste papers from chemical pulps	60 - 70	10 - 20	5 - 10

The relative abundance of cellulose, hemicellulose and lignin is the key factor in determining the feedstock suitability for nanocellulose production (Islam et al., 2017). Generally, a biomass pretreatment step is necessary to ensure the separation of cellulose component from tight bond of polymeric constituents (cellulose, hemicellulose, and lignin) in lignocellulosic biomass (Tarchouna et al., 2019). The main intention of this fractionation treatment is to increase the accessibility of cellulose fiber to chemical attack prior to mild hydrolysis of isolated cellulose, by cleaving the ether bond between glucose chain in order to produce nanosize cellulose intermediate (Cabiac et al., 2011; Peng et al., 2011).

In higher plants, cellulose plays an essential role like reinforce element in the cell wall, generally together with lignin and hemicellulose. These three polymers are closely associated making up lignocellulosic biomass. Actually, the lignocellulosic structure can be regarded as a bio-nanocomposite, which results from a unique interplay between nano-scale domains of cellulose, hemicellulose and lignin (Ng et al., 2015). The relative content of cellulose and lignin in lignocellulosic biomass varies among species. From a technological point of view, lignin contents in the biomass is the important parameters to produce a pure cellulose pulp. Indeed lignin is the hardest chemical component to take away from lignocellulosic biomass. Table 2.2 shows the lignin and cellulose contents in several types of biomass that can be used to extract the cellulose in the fibers.

Table 2.2 Cellulose and lignin contents in several types of biomass (Ng et al., 2015)

Type of biomass	Cellulose, wt%	Lignin, wt%
Algae	20 - 40	-
Corn corbs	35 - 45	10
Coir Stover	33	14
Rice straw	36	12 - 14
Kenaf fibres	36	18
Switchgrass	37 - 45	18
Coconut husks	38 - 39	46 - 53

2.1.2 Coconut husks fiber

Among the sources, lignocellulosic agroindustrial byproducts are the most promising because of their low cost and availability. Examples include sugarcane bagasse (Li et al., 2012; Mandal & Chakrabarty, 2014) corn straw (Huntley et al., 2015), sisal (Rodrigues et al., 2015), pineapple leaves (Deepa et al., 2015), cotton linter (Morais et al., 2013), banana pseudostem (Pereira et al., 2014), banana peel, and coconut husk (Fahma et al., 2011; Nascimento et al., 2016; Rosa et al., 2012). However, the profit ability of new biobased industries highly depends on integrating biomass conversion processes to produce a range of fuels, power, materials and chemicals.

Coconut is one of the most important agriculture products in Malaysia. Coconuts are Malaysia's fourth largest industrial crop behind oil palm, rubber and rice with most of the plantations found in Sabah and Sarawak. According to Hoe (2019), Malaysian Agricultural Research and Development Institute (MARDI) reported that Malaysia is among the top 10 coconut producers in the world by produced the total acerage of coconut plantation in year 2016 is about 504, 722 tonnes/year. In terms of acerage, Sabah, Sarawak, Johor, Kelantan, Selangor and Perak are the major coconut planted states, whereby the area planted with coconut ranged between 9266-16 600 ha (Table 2.3).

Table 2.3 Major coconut producing states in Malaysia (Hoe, 2019)

State	Production (tonnes/year)	Planted area ('000 ha)	Average yield (tonnes/ha/year)
Selangor	99 674	9 281	10.74
Johor	95 677	11 751	8.14
Perak	87 890	9 266	9.49
Kelantan	68 890	9 326	7.39
Sabah	46 732	16 600	2.82
Sarawak	30 654	12 616	2.43
Pahang	29 781	6 135	4.85
Melaka	16 490	2 254	7.32
Terengganu	10 692	3 345	3.20
Negeri Sembilan	10 109	1 398	7.23
Kedah	6 689	2 273	2.94
Labuan	778	141	5.52
Perlis	472	183	2.58
Pulau Pinang	244	40	6.10
Total	**504 772**	**84 609**	**5.97**

Coconut is a very useful plant, the part that can use from coconut plant are roots, husks, stems, nuts, leaves and even other components from the trees (Chen & Chouw, 2018). Coconut Milk is produce by the coconut fruits and it is main target for food product in Malaysia. Coconut milk is the essential ingredient that most use in Malay dishes in Malaysia for example curry, and dessert (Alexander, 2006). When the coconut milk are collected, the shells and husks of coconut are dumped openly (Figure 2.2), thus produced high amount of coconut waste by increase the load for the land fill in Malaysia. MARDI reported that Malaysia now generate large amounts of coconut husks as it not correctly collected and disposed of, cause's environmental problems, reducing the useful lifetime of landfills or causing water pollution.

Figure 2.2 Coconut husks waste are dumped on landfill

Coconut fiber is a lignocellulosic material, characterized by high toughness and durability due to its high lignin content, when it compared with other natural fibers. Lignin, like cellulose and hemicelluloses, is a major component of plant materials and the most abundant form of aromatic carbon in the biosphere (Rosa et al., 2010; Xu et al., 2015). Coconut fibers can be extracted and used to manufacture several products, such as reinforced polymeric composites, reinforced cement and concrete, geotextile fabrics and screens, and wood-replacement fibreboards (Ardanuy & Claramunt, 2011; El Miri et al., 2015; Sun et al., 2014; Xie et al., 2018). Other alternatives for adding value and reducing the disposal issues of coconut husks involve the extraction the cellulose forming cellulose nanocrystals (Nascimento et al., 2016).

2.2 Structure and morphology of cellulose

Cellulose is one of the most important natural polymers produced in the biosphere, and it is considered the most abundant renewable polymer on Earth. This annual production is estimated to be over 7.5 x 10^{10} tons (Habibi et al., 2010) Cellulose is widely distributed in higher plants; consisting of up to 38 – 39 % cellulose in coconut husks fiber (Haldar et al., 2018). Furthermore, it is also distributed in annual crops, and even in several marine animals like tunicates, and to a lesser degree in algae, fungi, bacteria, invertebrates, and even amoeba (Siró & Plackett, 2010; Thakur & Thakur, 2014).

Figure 2.3 shows the cellulose consists of a linear homopolysaccharide composed of β-D-glucopyranose units linked together by β-1-4-linkages (Trache et al., 2016). The repeating unit is a dimer of glucose, known as cellobiose. Each monomer has three hydroxyl groups, and it is therefore obvious that three hydroxyl groups and their ability to form hydrogen bonds play a major role in directing the crystalline packing and also governing the physical properties of cellulose (Maya Jacob & Sabu, 2008).

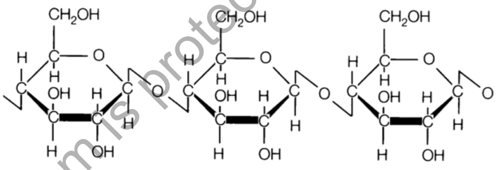

Figure 2.3 The molecular structure of cellulose (Trache et al., 2016)

The number of glucose units or the degree of polymerization (DP) is up to 20,000 units, but its value can vary among a wide range, and the value is around 10,000 in wood. In nature, cellulose does not occur as an isolated individual molecule, but it is found as assemblies of individual cellulose chain-forming fibres (Trache et al., 2016).

The morphological hierarchy is defined by elementary fibrils, which pack into larger units called microfibrils, which are in turn assembled into fibres (Habibi et al., 2010; Haldar &

Purkait, 2020). Within the cellulose fibrils, Figure 2.4 shows there are regions where the nanocellulose chains are arranged in a highly order structure-crystallites (called nanocrystalline cellulose) and regions that are disordered-amorphous-like (called nanofibrillated cellulose) (Collazo-bigliardi et al., 2018; Mahadi et al., 2015; Moon et al., 2011). Several types of cellulose indicate that cellulose have different polymorphs. The types of cellulose would be discussed in the next section.

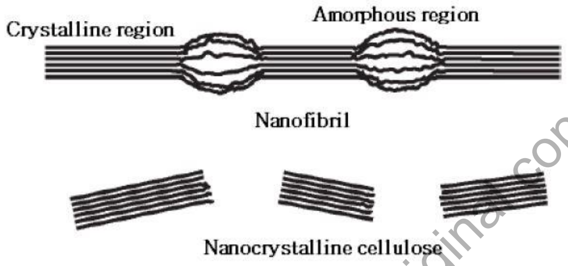

Figure 2.4 Crystalline and amorphous region of the cellulose (Mahadi et al., 2015).

2.2.1 Polymorhps of cellulose

There are four different polymorphs of cellulose are known, including cellulose I, II, III, and IV. (KroonBatenburg and Kroon, 1997). Cellulose I and II are the most studied forms of cellulose. In living plants, the Natural cellulose is cellulose I; the most widespread crystalline form, which consists of an assembly succession of crystallites and disordered amorphous regions (Sauperl et al., 2009). The natural crystal is made up of metastable cellulose I with all cellulose strands in a highly ordered parallel arrangement (Revol and Goring, 1981). Two coexisting crystal phases, cellulose Iα and cellulose Iβ are contained in cellulose I. Phase Iα has a triclinic unit cell containing one chain, whereas cellulose Iβ is represented by a monoclinic unit cell containing two parallel chains (Nishiyama et al., 2002). Cellulose produced by bacteria and algae is enriched in Iα while cellulose of higher plants consists mainly of Iβ.

Cellulose in regenerated cellulose fibers (solubilisation and subsequent recrystallization) and mercerization (alkali treatment) is cellulose II. The conversion of cellulose I to cellulose II is irreversible, suggesting that cellulose I is metastable and cellulose II is stable. Chemically, cellulose II has higher chemical reactivity than cellulose I and can be made into excellent cellophane, so it is regarded as one of the most useful fibers and has broad applications in chemical industry (Liu and Hu, 2008). The crystal structure of cellulose I in native cellulose can be converted to that of cellulose II by mercerization (Ciacco et al., 2010; Dinand et al., 2002). During the process of mercerization, entire fibers are converted into a swollen state and the assembly and orientation of microfibrils are completely disrupted. The original parallel-chain crystal 2 structure of cellulose I changes to anti-parallel chains of cellulose II (Dinand et al., 2002). Since cellulose II involves chain folding (Langan et al., 1999), its structure is more difficult to unravel and the reverse transformation from cellulose II to cellulose I does not occur (Revol and Goring, 1981).

With various chemical treatments it is possible to produce the structures cellulose III and cellulose IV. Cellulose III_I and III_{II} can be formed from cellulose I and II, respectively, by treatment with liquid ammonia; the reaction is, however, reversible (Hayashi et al., 1973). Cellulose IV_I and IV_{II} can be obtained by heating cellulose III_I and III_{II}, respectively (O'sullvian, 1997). Besides, cellulose III and IV are amorphous cellulose as compared to cellulose I and II. Cellulose microcrystals or cellulose nanocrystals are produced by breaking down the cellulose fiber and isolating the crystalline regions (cellulose I and cellulose II only) (Habibi et al., 2010). They have been produced from different cellulose sources and observed by a variety of techniques with dimensions ranging from several nanometers to several micrometers (Satyamurthy et al., 2011).

2.2.2 Micro and nano cellulose

There is a wide range of cellulose particle types that are being studied for various commercial applications. The diversity of cellulose particle types depend on cellulose source and extraction processes. The nomenclature has not been standardized and some misunderstanding and ambiguities are present in the literature (Follain et al., 2013; Le Bras et al., 2015; Moon et al., 2011). A research done by Moon et al. (2011) reported that cellulose particles can be classify into two which were microcrystalline cellulose (CMCs) and nanocrystalline cellulose (CNCs). MCC also known as nanofibril cellulose (NFC) is a commercial available material used for applications in pharmaceutical and food industry and also as starting material to prepare CNCs in laboratories (Debiagi et al., 2019, 2020; Ilyas et al., 2017). The dimension of CNCs and CNCs are in the range of 10-50 µm and below 100nm, respectively (Mahadi et al., 2015; Mokhena, 2019). CNCs may be classified in three main subcategories. Herein, we follow the nomenclature used by Klemm et al. (2011), as stated in Table 2.4, they used the terms CNCs and microfibrillated cellulose (MFC).

Table 2.4 Types of nanocellulose (Klemm et al., 2011)

Types of nanocellulose	Synonyms	Typical source
Nanocrystalline cellulose, NCC	Cellulose nanocrystals, crystallites, whiskers, rod like cellulose microcrystals	Wood, cotton, hemp, flax, wheat straw, rice straw, coconut husks, mulberry bark, ramie, MCC
Microfibrillated cellulose, MFC	Microfibrillated cellulose, nanofibrils, microfibrils, nanofibrillated cellulose	Avicel, tunicin, algae, bacteria, wood, sugar beet, potato tuber, hemp, flax

The name MFC is widely used in scientific and commercial literature – it is commercially available (Klemm et al., 2011). MFC is generally produced by delamination of wood pulp by mechanical pressure before and/or after chemical or enzymatic treatment. The microfibrils, long and flexible, are around 20 nm wide, and several micrometres in length; they consist of alternative crystalline and amorphous domains. One of the main drawbacks to the MFC production has been the very high energy consumption amounting to over 25, 000 kWh per ton (Klemm et al., 2011), but more recently there has been a focus on energy-efficient production methods (Lindstrom, Ankerfors & Henriksson, 2007; Paako et al., 2007). We will no longer consider MFC because we focus our attention on CNCs. In fact, CNCs exhibits elongated crystalline rod-like shapes, and has very limited flexibility – as compared to MFC as it does not contain amorphous region.

2.2.3 Cellulose nanocrystals (CNCs)

CNCs is formed by rigid rod-like particles with widths and lengths of 5 - 70 nm and between 100 nm and several micrometres respectively. The particles are 100% cellulose and highly crystalline, between 54 and 88% (Chen et al., 2016; Moon et al., 2011). The aspect ratio, defined as the length to diameter ratio, spans a broad range. The variety of dimensions, morphologies, degree of crystallinity depends on the source of cellulosic material and conditions under which preparation is carried out as well as on the experimental technique used (Gupta & Raghav, 2019; Habibi et al., 2010).

The quality and quantity of produced CNCs significantly depends on the source material used and condition followed during the process of formation. A large number of different sources reported as potential sources for the formation of CNCs such as chinese silver grass, eucalyptus wood, wood saw dust (Kunaver et al., 2016), sugarcane bagasse (Sukyai et