EXTRACTION OF NANOCELLULOSE AND CHARACTERIZATION OF MIGRATION BEHAVIOUR FOR POLY(LACTIC ACID)/ NANOCELLULOSE/ SILVER NANOCOMPOSITE

by

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LIST OF ABBREVIATIONS

Ag	Silver
AgNPs	Silver Nanoparticles
ASTM	American Society of Testing and Materials
BNC	Bacterial Nanocellulose
CNC	Cellulose Nanocrystal
CNF	Nanofibrillated Cellulose
CMC	Carboxymethyl Cellulose
CrI	Crystallinity Index
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetry
EFTEM	Energy Filtered Transmission Microscope
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Analysis
H_2SO_4	Sulphuric Acid
H_3PO_4	Phosphoric Acid
NaOH	Sodium Hydroxide
PCNC	Phosphoric Acid Derived Cellulose Nanocrystal
PCL	Polycaprolactone
PHB	Poly (3-hydroxybutyrate)
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PGA	Polyglycolic Acid
PET	Polyethylene Terephthalate
PLA	Poly(Lactic Acid)
PVA	Poly(Vinyl Alcohol)

SBF	Sugarcane Bagasse Fiber
SCB	Sugarcane Bagasse
SB-MCC	Sugarcane Bagasse Microcrystalline Cellulose
TiO_2	Titanium Dioxide
$UO_2(CH_3COO)_2$	Uranyl Acetate
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
ZnO	Zin Oxide

LIST OF SYMBOLS

ΔHf°	Endothermic Enthalpy of 100% Crystallized PLA
ΔH_m	Endothermic Enthalpy of Samples
Xc	Degree of Crystallinity
M	Molar Concentration (mol/dm^3)
I	Intensity
w	Weight Percentage (wt %)

PENGEKSTRAKAN SELULOSA NANO DAN PENCIRIAN TINGKAH LAKU PENGHIJRAHAN UNTUK KOMPOSIT NANO POLI(ASID LAKTIK)/ SELULOSA NANO/ PERAK

ABSTRAK

Objektif kajian ini adalah untuk mengkaji kesan kepekatan asid fosforik (H_3PO_4) terhadap sifat selulosa nano (PCNC), dan mengkaji kesan PCNC terhadap sifat-sifat nanokomposit poli(asid laktik) PLA serta tingkah laku penghijrahan perak (Ag) dari nanokomposit PLA /PCNC /Ag. Tiga kepekatan H_3PO_4 yang berbeza telah digunakan (iaitu, 5M, 8M dan 11M) untuk ekstrak PCNC daripada sisa hampas tebu. Sifat PCNC ditentukan dengan menggunakan mikroskop elektron penghantaran (TEM), spektroskopi infra-merah jelmaan Fourier (FTIR), pembelauan sinar-X (XRD) dan spektroskopi fotoelektron sinar-X (XPS). Keputusan TEM menunjukkan bahawa nisbah aspek PCNC telah dikurangkan apabila kepekatan H_3PO_4 meningkat. Nisbah aspek PCNC yang diasingkan oleh 5M H3PO4 ialah 45 dan dikurangkan menjadi 39 apabila H3PO4 meningkat kepada 8M. Interaksi di antara PCNC adalah disebabkan oleh kewujudan ikatan P-O-P (dibuktikan dengan FTIR dan XPS). Keputusan XRD menunjukkan bahawa kepekatan H_3PO_4 yang meningkat akan meninggikan indeks penghabluran PCNC. Indeks kristalografi dan saiz hablur PCNC meningkat dari 61.7 ke 69.0 dan 3.68 hingga 5.36 apabila kepekatan asid meningkat dari 5M ke 11M. Kesan PCNC terhadap sifat mekanik dan terma pada nanokomposit PLA telah ditentukan dengan menggunakan ujian tegangan dan kalorimetri pengimbasan pembezaan (DSC). Modulus dan kekuatan tegangan PLA meningkat dengan penambahan PCNC sintesis daripada 5M $H_3PO_{4.}$ Darjah penghabluran PLA telah menunjukkan kenaikan tertinggi iaitu kira-kira 51% oleh penanmbahan PCNC disintesis meggunakan 5M H_3PO_4. Ujian penghijrahan keseluruhan dan spesifik PLA

/ PCNC / Ag dijalankan dengan menggunakan Spektrometri jisim plasma berinduktif (ICP-MS) dan spektrometri pancaran optikal plasma berinduktif (ICP-OES). Kajian penghijrahan menunjukkan tiada nanokomposit PLA yang melebihi had pengijrahan keseluruhan (60 mg kg^{-1}) dan had penghijrahan spesifik (0.05 mg kg^{-1}). Walau bagaimanapun, PCNC didapati boleh bertindak sebagai pembawa untuk Ag dari nanokomposit PLA dan tindakan ini akan mempengaruhi sifat penghijrahan zarah nano Ag.

EXTRACTION OF NANOCELLULOSE AND CHARACTERIZATION OF MIGRATION BEHAVIOUR FOR POLY(LACTIC ACID)/ NANOCELLULOSE/ SILVER NANOCOMPOSITE

ABSTRACT

The objectives of this research is to study the effect of concentration of phosphoric acid (H_3PO_4) on the properties of cellulose nanocrystal (PCNC), examine the effect of PCNC on the properties of poly(lactic acid) PLA nanocomposites as well as the migration behaviour of silver (Ag) from PLA/PCNC/Ag nanocomposites . Three different concentrations of H_3PO_4 were utilized (i.e., 5M, 8M and 11M) to extract PCNC from sugarcane bagasse. The properties of the PCNC were determined by Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). TEM results showed that the aspect ratio of PCNC was reduced as the increasing concentration of the H_3PO_4. The aspect ratio of PCNC isolated by 5M H_3PO_4 was 45 and reduced to 39 when the H_3PO_4 was increased to 8M. The self-interaction of PCNC was induced by the P-O-P linkages (evidenced from FTIR and XPS results). XRD results showed that increased H_3PO_4 concentration increased the crystallinity index of the PCNC. The crystallinity index and crystal size of the PCNC was increased from 61.7 to 69.0 and 3.68 to 5.36 respectively, when the acid concentration was increased from 5M to 11M. The effect of PCNC on mechanical and thermal properties on the PLA nanocomposites was determined by using tensile test and Differential Scanning Calorimetry (DSC). The tensile modulus and strength of PLA was slightly increased by incorporation of PCNC (synthesized using 5M H_3PO_4). The degree of crystallinity of PLA shows highest increment which was about 51% by the addition of PCNC isolated from 5M H_3PO_4. The overall and

specific migration test of PLA/PCNC/Ag was performed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), respectively. The migration studies show none of the PLA nanocomposites were exceeding overall migration limit (60 mg kg^{-1}) and specific migration limit (0.05 mg kg^{-1}). Nonetheless, it was found that the PCNC can acts as carrier for Ag from the PLA nanocomposites and this influencing the migration behaviour of the Ag nanoparticle.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The huge consumption of fossil fuel-derived plastic material has created consistent waste production issues that cause environmental pollution (Han et al., 2018). Variety of plastic source that contaminate environment had been reported. These including the disposal of municipal wastewater effluent, sewage sludge landfill and plastic mulch from agricultural activities and these improper ways of disposal had actually created major concern regarding soil pollution (Chae & An, 2018). Besides, there are accounts of unintentional contamination of soils with plastic fragments had causes these plastics being carried into streams, rivers or sea with rain water and flood events. In consequently, ocean pollution occurred and the ingestion of this plastic debris had eventually causes the suffering and death of the marine animal (Thompson et al., 2009; Stafford & Jones, 2019).

In 2015, the global plastic market reached 322 M tons, and approximately 49 M tons of plastics are utilized for packaging purposes. Owing to the inappropriate disposal and nonbiodegradability of these petroleum plastics, 4.8–12.7 M tons of plastics ended up in ocean in the year of 2010, and more than 30% of the plastic waste was land-filled in the year 2014. Consequently, the recycling of plastic has become an encouraging option to abate the accumulation of plastic waste in our environment (Ingrao et al., 2017) For instances, similar grades PET bottles can be recycled and reprocessing to polyester fibre, plastic crates and bins can be manufactured from recovered HDPE milk bottles (Hopewell et al., 2009), rigid PVC can be recycled as inner reinforcement layer in pipes, profiles production whereas flexible PVC can be recycled into powder in which can be used as a filler in the floor covering production (Al-Salem et al., 2009).

However, this recycling system does not work on food packaging systems because of the contamination of organic substances that is found on the food packaging plastics .Hence, food packaging producers should not only consider the factor of maintaining the effectiveness of the quality of food but also the environmental impact with regards to the disposal of packaging materials (Ingrao et al., 2017). For this reason, biopolymers in which can be defined as polymers originated from renewable biological resources have received widespread attention due to their biodegradability, and its ability to replace the fossil fuel-based plastic materials and address the waste disposal problem (Rhim et al., 2013).

Today, the development of green packaging materials that able to provide satisfactory impact on consumer health was considering an intensive research topic. According to Thompson et al. (2009), the approach of biomonitoring which measuring concentration contaminants in human tissues had shown that chemicals used in manufacturing plastics possess potential unfavourable effect on human health effect. Several chemical components within conventional plastic material such as Bisphenol A (BPA), polybrominated diphenyl ethers (PBDE), phthalates are released from plastic products and having known negative effects on human health, affecting the endocrine system (Talsness et al., 2009). Since green packaging materials can be produced from biopolymer which their feedstock may be natural polymers that will not causes any harmful damage to the human health, thus there was a need on the utilization of biopolymers for packaging material (Khalil et al., 2017).

Biopolymers can be divided into four categories: [i] polymers that have D-glycopyranoside as their building block or repeating unit (e.g., starches, cellulosic and ligno-cellulosic); [ii] polymers acquired through microbial sources (e.g., polyhydroxyalkanoates (PHAs) that include the polymer of poly(hydroxybutyrate) (PHB) and polyglycolic acid (PGA)); [iii] polymers that are chemically synthesized from agroresources (e.g., polylactic acid (PLA)) and [iv] polymers that are chemically synthesized from fossil fuel resources (e.g., polycaprolactones (PCLs) and poly (butylene succinate adipate) (PBAT)) (Souza & Fernando, 2016; Elsawy et al.,2017). Among all these biopolymers, poly(lactic acid) PLA has been employed for packaging purpose attributable to its good mechanical, superior transparency and ease of processing. In this regard, poly(lactic acid) PLA had become an attractive biopolymers with many short-term or disposable application, such as disposable cutlery (plates, cups and lids) and film packaging. Moreover, PLA also has been approved by the US Food and Drug Administration (FDA) as food contact substances therefore PLA can be widely used in both rigid and flexible food packaging applications (Arrieta et al., 2013). The bio-based character of PLA would contribute to the diminution of ecological impacts correlating with the extensive utilization of conventional plastics derived from non-renewable fuel sources (Lizundia et al., 2016). The building block of PLA which is lactic acid monomer was 100% generated from renewable sources and can be obtained through the fermentation of agricultural products such as maize, wheat, wood residues or other biomass (Song et al., 2014). Therefore, its production can help control the ever-increasing depletion rate of fossil fuel resources (Elsawy et al., 2017).

Furthermore, PLA can be recognized as the biopolymers that having greatest potential for the development of green polymer in food packaging due to its high transparency, good melt-processability and biocompatibility. Despite that, thermal properties, toughness, water and gas barrier properties of PLA are inferior to those conventional petroleum based polymers (Fortunati et al., 2012a). In particularly, the water vapour and gas barrier properties were considered a critical factor when come to food packaging application. The poor oxygen and water vapour barrier properties of PLA can cause oxidative rancidity (Robertson, 2016) and the existence of the water vapour promotes the formation of molds and bacterial growth (Criado et al., 2019). Therefore, the need to extend the shelf life of packaged food has oriented research towards innovative solutions by the incorporation of biodegradable fillers such as cellulose. By the aid of cellulose, both of the thermal and barrier properties of PLA could be enhanced and eventually optimizing the cost performance of this green material (Frone et al., 2013; Criado et al., 2019).

There are numerous agriculture residues available to extract cellulose and sugarcane bagasse is considered as an important raw material as it can provide important commercial economic benefit. The costing of collection as well as transportation for sugarcane bagasse is usually much lower than the other agriculture residues. Nevertheless, the emerging of innovations in sugar processing had reduced the energy consumption for sugar manufacture. This indicates that there are more sugarcane bagasse is available to utilize as lignocellulosic feedstock (de Oliveira et al., 2016). Besides that, the utilization of this agriculture waste can reduced the risk of spontaneous combustion which caused environmental pollutions when there were many remaining are stockpiled during the energy generation in sugar production. Therefore, utilizing sugarcane bagasse as a source of extraction CNC can add to this inexpensive biomass source (Mandal & Chakrabarty, 2011).

Besides having a good barrier properties, the food packaging also need to have antibacterial properties in order to prolong the freshness of the food. The spoilage of food had bring the contamination on food, making the food losing its colours, nutrition and promote the growing of pathogenic microbes, which food spoilage is the process of contamination of foods leading to loss of color, texture, and their nutritive value and permits growth of pathogenic microbes, which makes the food product became non-edible. Therefore, the utilization of antimicrobial agents in the prevention of food contamination recently is making a lot of scientific interest around the world and leading to extensive research on them. Today, nanotechnology application, particularly in the food sector, has been dominated by packaging materials. Nanomaterials such as silver nanoparticles (AgNPs) had been reported as a potential material that can be used to prevent the invasion of microbes into the food products through packaging (Su et al., 2017).

1.2 Problem Statement

Sugarcane bagasse (SCB) is a residue produced in large quantities every year by the sugar and alcohol industries (Mandal & Chakrabarty, 2011), adequate use of the SCB gives an added value for this material and a solution for the removal of this abundant waste (Martinez-Hernandez et al., 2017). The most dominant method for production of cellulose nanocrystals (CNC) from sugarcane bagasse was by using strong acid hydrolysis. Sulphuric acid is one of the most widely employed acid since its ability to provide certain degree of grafting of negative charged sulphate group onto the surface of CNC which can produce more stable aqueous nanocrystal suspensions. However, the presence of this sulphate groups in the crystals will tend to be diminish the thermostability of the crystals (Aguayo et al., 2018) due to the replacement of hydroxyl groups by sulphates which leads to the reduction of activation energy of the CNC (Chen et al., 2017). Mild acid such as phosphoric acid (H_3PO_4) could be employed for the extraction of CNC. CNC isolated from phosphoric acid displayed many potential advantages compared to the rest of the acids (Vanderfleet et al., 2017). The CNC isolated by phosphoric acid show excellent flame retardant properties due to the ability of the phosphate groups to enhance char forming that make the CNC to have self-extinguish properties (Ghanadpour et al., 2018). Besides that, reinforcing ability of CNC is comparable with the CNC isolated by sulfuric acid (Camarero Espinosa et al., 2013). The incorporation of CNC in the nanocomposite foam showed improvement for compressive strength in 90% strain and 170% in specific Young' modulus (Ghanadpour et al., 2018). Furthermore, the CNC not only imparts better thermal stabilities but also depicted as a promising biomedical materials that can be utilized as a bone scaffolding materials. There was study found that the CNC can actually promoting the growing of inorganic component of bone, hydroxyapatite. Thus, the outstanding flame retardancy, mechanical feature and formation of inorganic bone component of CNC have make CNC potentially applicable in variety of application (Ghanadpour et al., 2018;Vanderfleet et al., 2017). However, the suitable concentration of H_3PO_4 for the CNC extraction from sugarcane bagasse is still working out. Thus there is a need to determine the appropriate concentration H_3PO_4 in order to perform CNC isolation from sugarcane bagasse. Besides that, the incorporation of CNC into PLA had overcome the limitations of PLA without sacrificing the biodegradability of this green material by enhancing the properties of PLA such as thermal, mechanical and barrier properties (Luzi et al., 2016). Therefore, there is a need to have the incorporation of CNC in PLA in order to extent the application of PLA/CNC composites. Apart from that, the inferior of antimicrobial property in PLA/CNC provoke the need of introduction of nanomaterials into this nanocomposite. The utilization of AgNPs had getting concern due to their larger surface area-to-volume ratio, favoring interaction with microbial cells (de Azeredo, 2013). However, the study reported by Fortunati et al. (2013b) stated there was a high rate release of silver to food stimulant ethanol and was exceeding the upper limits of Ag migration (0.05 mg/L in water and 0.05 mg/kg in food) when PLA nanobiocomposites with modified cellulose was utilized. According to their studies, the PLA nanobiocomposites with 1 wt% and 5 wt% of modified cellulose in simulant ethanol 10% (v/v) had silver migration up to 0.061 and 0.087 mg/kg, respectively. Therefore, it is essential to study the appropriate amounts of silver nanoparticle on controlling the migration behavior of silver nanoparticles and produce nanocellulose that have better dispersibility in PLA/CNC biocomposites.

1.3 Objectives

This research is aim to study and develop CNC and silver nanoparticles reinforced PLA nanocomposites primarily via solution casting method. In order to accomplish this main objective, this project was divided into three specific objectives:

1. To study the effect of phosphoric acid on the properties of cellulose nanocrystals extrated from sugarcane bagasse.
2. To determine the effects of PCNC on the tensile and thermal properties of PLA nanocomposites.
3. To investigate the silver migration from PLA/PCNC/Ag nanocomposites.

1.4 Thesis structure

This thesis is consisted of five chapters.

Chapter 1 represented the introduction part of the thesis, which offered the background and problem statement of this research and an outline of the dissertation.

Chapter 2 contained literature review of thesis, which showed background literature on the general information about PLA; an overview on the CNC, sugarcane bagasse; and a comprehensive literature review of silver nanoparticles.

Chapter 3 represented the material approaches and research methodology of the project. This chapter contained a detailed explanation regards the source of chemical and chemicals. The complete methodology for the acid hydrolysis of the isolation of cellulose nanocrystals and fabrication of PLA/PCNC/Ag nanocomposites are discussed in this chapter. The characterization method of PCNC, PLA/PCNC and PLA/PCNC/Ag nanocomposites were given in this chapter.

Chapter 4 showed the results discussion of the thesis. Elaboration on the explanation was included in this chapter.

Chapter 5 denoted conclusion of the project. This chapter provide conclusion that based on the objectives of the projects and suggest recommendation for future studies.

1.5 Scope of study

The first stage of this study focuses on the isolation of CNC by phosphoric acid (H_3PO_4). The H_3PO_4 derived CNC will be named as PCNC in this study. The PCNC were extracted from sugarcane bagasse and fabricated utilizing three different concentrations of phosphoric acid which are 5M, 8M and 11M, respectively. The influence of H_3PO_4 concentration on the morphology, crystallinity and chemical properties of the PCNC were studied. In the second stage of study, the PLA/PCNC nanocomposites were prepared using solvent casting method. The effects of PCNC on the mechanical, thermal and morphological properties of PLA were investigated. PLA/PCNC/Ag and PLA/Ag nanocomposites were prepared in the final stage in order to determine the migration behaviour of silver from the nanocomposites.

1.6 Major Contribution of Study

This present study will be a great contribution to vast knowledge in the adequate use of the SCB by turning this abundant waste into a valuable material. The utilization of mild acid for isolation of PCNC can be more environmental friendly without scarify the reinforcing ability of the PCNC. The vital results from the migration study provide information regards potential interaction of PCNC and Ag.

CHAPTER 2

LITERATURE REVIEW

2.1 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) has been employed for packaging purposes attributable to the ability of this aliphatic polyester to be derived from renewable agricultural resources in the way that its monomer can be generated by the fermentation of agricultural resources (Tiimob et al., 2018). Apart from that, the bio-based character of PLA would commit to the diminution of ecological impacts correlating with the extensive utilization of conventional plastics derived from non-renewable fuel sources (Lizundia et al., 2016). The PLA production was consider as eco-friendly process because carbon dioxide was consumed during its production process as shown in Figure 2.1.

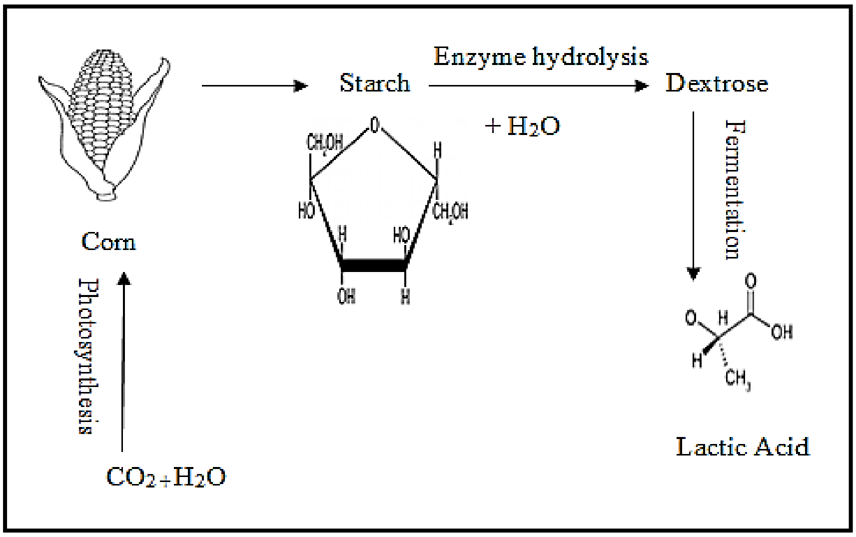

Figure 2.1: Production of lactic acid from renewable resources such as corn (Avinc & Khoddami, 2010).

The life cycle production of PLA begins with starch that is extracted from plants such as corn. During the growth of the corn, the carbon dioxide (CO_2) is harnessed from the environment for the purpose of photosynthesis. Throughout the photosynthesis process, consumption of free energy originated from solar energy and CO_2 will take place in corn plant for the sake of conversion of glucose into starch, and all this contributed in chain building for PLA. Therefore, the benefit of PLA production compared with other commercial polymers is the ability to reduce of CO_2 emission (Vink et al., 2007). According to the report studied by Reddy et al. (2013), the life cycle analysis for polypropylene or polystyrene plastics were having carbon footprint of approximately 2.0 kg carbon dioxide equivalents per kg of plastic (from cradle to factory gate). These carbon dioxide emissions are about 4 times higher than the carbon dioxide emission from PLA resin. Besides that, Shen (2011) had determined the difference in environmental impacts of PET and PLA plastics by performing simple life cycle assessments. Through his studies, he had found that both PET had emitted more carbon than PLA which is 3000 tons and 0.97 tons respectively. Gruber (2001) compared the net carbon dioxide emission cradle-to-grave basis of PLA with polystyrene cups and the PET bottles. He stated that the net emission of PLA was still the lower compared to the polystyrene cups and PET bottles and suggested PLA was having potential to have reduction greater than 50% in CO_2emissions relative to conventional plastics.

The building block for PLA is lactic acid and it can be obtained through the fermentation of maize or other sustainable agricultural raw resources (Abdulkhani et al., 2014). A few appealing things about PLA are biocompatibility, processability, renewability and having less energy consumption during the production of PLA (Rasal et al., 2010). In comparison with biopolymers such as poly(hydroxyalkanoates) (PHAs) and poly(ethylene glycol) (PEG), the good thermal processability of PLA means it can be manufactured through various processing methods such as extrusion, film casting and fiber spinning (Rhim et al., 2006). Because of the biodegradable and biocompatible characteristics of PLA, it received the approval from Food and Drug Administration (FDA) in the applications of food contact and became an adequate applicant in the application of packaging for fresh food or short service life goods which include overwrapping, lamination filming and blister packaging (Ingrao et al., 2017). Biocompatibility is consider as important characteristic in food packaging as there is a potential risk to human health associated with the type of materials used in food packaging. All applications of materials in food industry must be estimated for safety of use (Mitura & Zarzycki, 2018). Therefore, the biocompatible PLA which are non-toxic, non-cancerogenic, non-mutagenic, non-allergenic, and free from contaminants were suitable candidate in food packaging (Ahmed & Varshney, 2009).

Besides that, lactides are stereoisomers in which L-lactic acid and D-lactic acid are the two optically active stereoisomers of lactic acid as shown in Figure 2.2. The pure L-lactic acid or D-lactic acid, or mixtures of both components are needed for the synthesis of PLA. There are two various methods that can used to obtain lactic acid. These building blocks of PLA can be obtained either by chemical synthesis which using petrochemical feedstock or carbohydrate fermentation. However, the main route to produce lactic acid was by fermentation because chemical synthesis route was having major limitation by having expensive manufacturing costs and it was found that this synthetic route cannot obtain high purity lactic acid instead having optically inactive mixtures of L- and D-lactic acid. In contrast, the fermentation route can produce high purity lactic acid by having L isomer acid as product. The ability to manufacture high purity of L-lactic acid was important as it can provide ultimate property in the lactic acid derived polymers (Hamad et al., 2015).

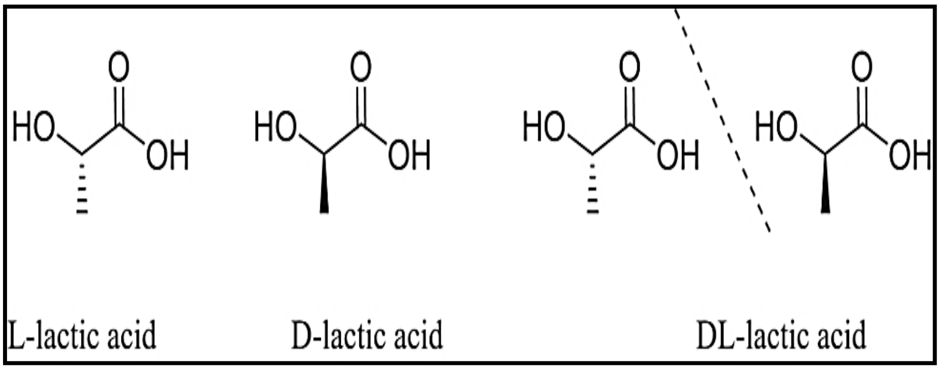

Figure 2.2: Different structures of lactic acid (Masutani & Kimura, 2014).

PLA can be available in different molecular weight. However, only PLA with high molecular weight will be selected for use in the packaging industry. This is because high molecular weight PLA can provide a good mechanical property that was crucial in food packaging applications (Jamshidian et al., 2010). Gupta and Kumar (2007) also stated that the high molecular weight of PLA possess mechanical properties that are comparable to other commodity thermoplastics such as polystyrene and PET. There are two main PLA industrial manufacturers which are NatureWorks LLC and Corbion and both of these manufacturers were using ring opening polymerization to produce PLA. The ring opening polymerization with rapid reaction time and comparatively mild reaction conditions was able to yield PLA with high molecular weight while having smaller molecular weight distribution (Hamdan & Sonomoto, 2011).

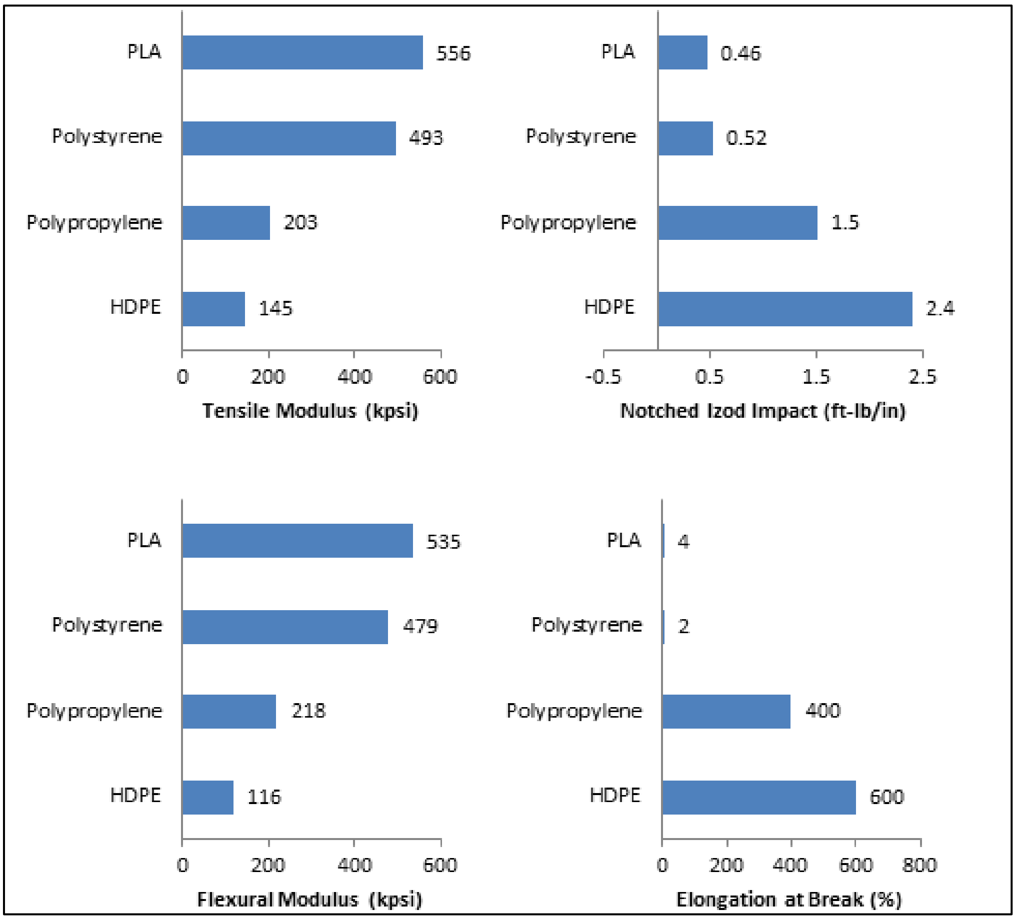

Figure 2.3: Comparison of the mechanical properties of PLA with some common plastic packaging material (adapted from Dorgan et al., 2000).

In addition, the unique properties of PLA are comparable to polyolefin and poly(ethylene terephthalate) PET and this allows them to be used in a broad range of applications. Overall, it was found that the properties of PLA were almost similar with polystyrene (PS) as it has low value for elongation at break about 2-5% and high Young’s Modulus which is approximately 3 GPa (Spinella et al., 2015) and the comparison of mechanical properties with others common plastic packaging material was shown in Figure 2.3. Despite that mechanical properties of PLA wad comparable to the conventional plastic packaging material, however the brittleness, thermal instability, low melt strength, high water vapour and oxygen permeability of PLA had limited their use as film in food packaging applications (Jabeen et al., 2015).

2.2 Cellulose

Cellulose represents biomaterial that is richly existed in the plant. During the photosynthesis process, all the trees and plants are utilizing water and carbon dioxide to synthesis cellulose in cellulosic fibers and embedded them in hemicellulose and lignin (Ng et al., 2015). Cellulose accounts for about 35%–50% of the total composition of natural fibers and plants produce about 75 billion tons of cellulose per year, making cellulose inexhaustible biopolymers (Feng et al., 2018).

Cellulose also can be referred as linear homopolymer. This homopolymer comprises of about (44.44%) carbon, (6.17%) hydrogen and (49.39%) oxygen. This composition of elements had gave rise to the chemical formula of $(C_6H_{10}O_5)n$; n, named as degree of polymerization (DP), denotes the number of repeating unit (glucose group) and the number of glucose units or the degree of polymerization (DP) is up to 20 000. Generally, the value of DP was greatly dependent on the source of extraction. When come to 20th century, it was discover that pure dehydrated repeating units of D-glucoses was presence in cellulose and this repeating unit can be considered as a dimer of glucose which called celloboise (Chen, 2014) as depicted in Figure 2.4. Cellobiose is recognized as a cellulose repeat unit within the cellulose in which having a rotation of 180^o towards each other (Candido et al., 2017).

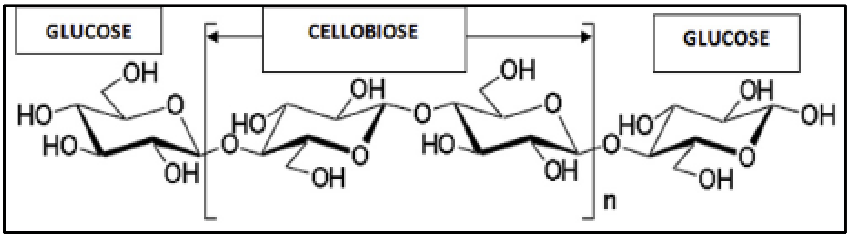

Figure 2.4: Chemical structure of cellulose showing cellobiose repeat unit (Ng et al., 2015).

Besides that, the molecules of cellulose can be known as linear syndiotactic polysaccharide, which comprising of D-glucose (a basic sugar) and β-D-anhydroglucopyranose units connected by *β*-(1， 4)-glycosidic bonds (Ng et al., 2015). The *β*-glucosidic bond plays an important role in linking the anhydroglucose units together at carbon atoms one and four as shown in the Figure 2.5.

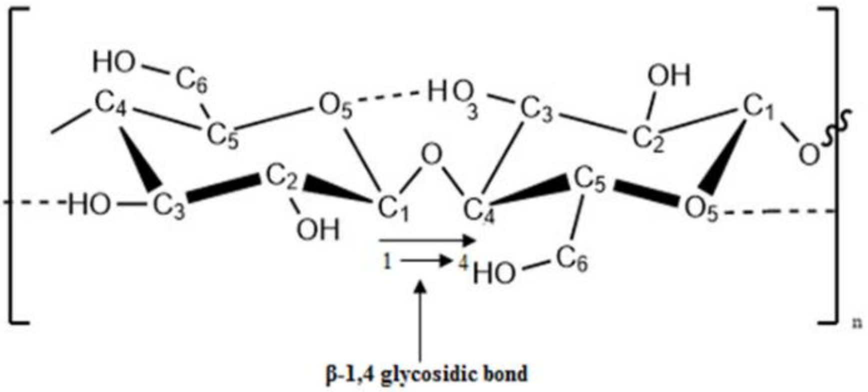

Figure 2.5: *β* -1,4 glycosidic bond of a cellulose unit (Sampath et al., 2016).

The presence of the *β*-(1, 4)-glucosidic bond had provide the ability for the macromolecular chains to align themselves straight and these arrangement allowed the hydroxyl groups at particular positions of the cellulose to form hydrogen bonds. There are 2 types of hydrogen bonding can be found in cellulose which are hydrogen bond within the molecules (intra-chain hydrogen bonding) and between the cellulose chains (inter-chain hydrogen bonding) (Zhang et al., 2013).

Moreover, these existences of this hydrogen bonds cause the cellulose to become insoluble in almost all of the solvents by the reason of considerable strength that is imparted by the bonds on the cellulose (Hoi & Martincigh, 2013). According to Bochek 2003, the dissolution of cellulose required breaking of at least all the interchain hydrogen bonding and the hydrogen bonds presence in cellulose were having energy up to 25.0 kJ and this high energy had strongly confines the range of solvent for cellulose which in turn making cellulose was hardly soluble in most of the solvents. Besides that, the cellulose can form thin and long fibrils by grouping about 100 cellulose chains together and these fibrils are made up of two parts which are amorphous and crystalline respectively (de Oliveira et al., 2016). The relationship between the crystalline and amorphous regions determines the degree of crystallinity and the dimensional characteristics of the crystalline domains (Leão et al., 2017). The degree of crystallinity of the cellulose can be considered as the ratio of amorphous cellulose to crystalline domains. Celluloses from different sources present different crystalline/amorphous regions ratio. Thus degree of crystallinity cellulose varies widely from species to species. For instance, the degree of crystallinity of cellulose derived from bacteria, cotton, and Valonia algae is about 75%, 40–45%, and 93%, respectively (Varshney & Naithani, 2011).The dimensional characteristics of the crystalline domain can be related to the dimensions of the microfibrils, varies widely from species to species. For example, algal and tunicate cellulose microfibrils, which are highly crystalline, can have nanocrystals up to several micrometers in length (Beck-Candanedo et al., 2005).

By referring Figure 2.6, there are three free hydroxyl groups with vary reactivity exist at each unit of anhydroglucose. It was found that both C-2 and C-3 were having secondary OH whereas C-6 position was having primary OH. By replacing these free OH groups for other chemical groups, for example acetyl, carboxymethyl and methyl, a diverse derivative compounds can be synthesized. The high economic value derivative compound converse from the cellulose has obtained high attention in the fields of sustainable chemistry as it allowed the development of environmental friendly technologies. The high purity of cellulose is required for the synthesis of cellulose derivatives and therefore reduction of the amount of lignin and hemicellulose to a minimum level is an important criteria that need to fulfil in order to synthesis a good properties cellulose derivatives (Candido et al.,2017).

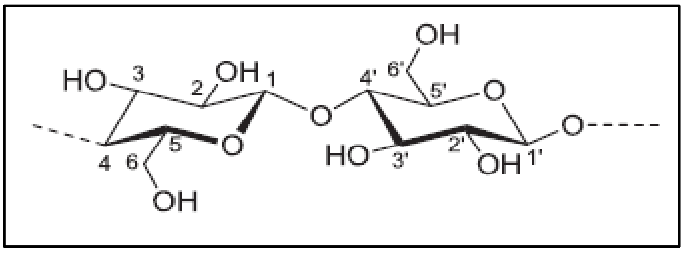

Figure 2.6: Schematic representation of cellulose structure (Kang et al., 2015).

Apart from that, cellulose chains are arranged in microfibrils or bundles of polysaccharide that are arranged in fibrils (bundles of microfibrils), which in turn make up the plant cell wall. This arrangement not only aids in the stability of plant structures but also suggests that cellulose is a biomaterial with high strength and other superior mechanical properties (Brigham, 2018). These cellulose microfibrils were formed during the process of biosynthesis. Throughout the biosynthesis, the individual cellulose chains will have aggregations to form a fibril, which is a long thread-like bundle of molecules laterally stabilized by intermolecular hydrogen bonds. After that, the aggregation of these elementary fibrils will cause the formation of larger size microfibrils. These microfibrils can be defined as a fibrils that having diameter in the range of 2-20 nm with some microns in length. Moreover, each microfibrils can be also referred as a string of cellulose crystals that connected along microfibril axis by the disorientated amorphous domains (Siqueira et al., 2010). The cellulose cell wall and the organization of microfibril are presented in Figure 2.7.

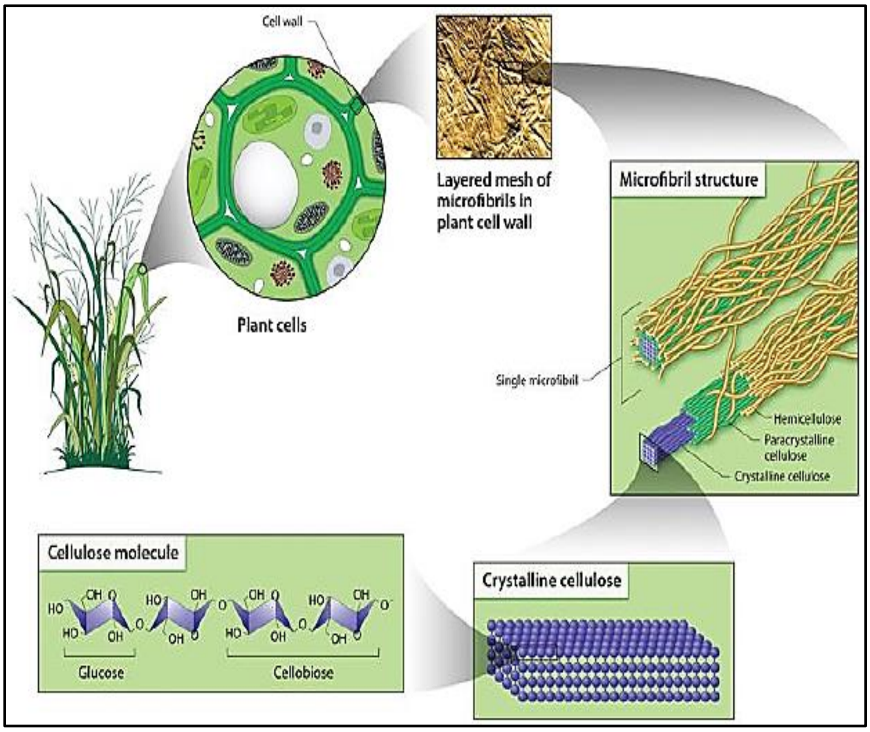

Figure 2.7: Scheme of the cellulose cell wall and microbial organization (Siqueira et al., 2010).

Apart from that, cellulose also can be used to produce various types of nanomaterials and these nanomaterials are often named as nanocellulose or cellulosic nanomaterials. This nanocellulose sometimes also termed as rods, whiskers, nanocrystals, nanofibers or nanofibrils with a condition that the cellulose crystal or fibre is having at least one dimension in the range of nanometer size. In 2011, a roadmap regard the development of international standards for nanocellulose by Technical Association of the Pulp and Paper Industry (TAPPI) and the abbreviations for different nanocellulose had been stated as following: cellulose microfibrils (CMFs), cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) (Börjesson & Westman, 2015). The cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) are having needlelike crystals which is having diameter in the range of 4-25 nm and length within the range of 100-1000 nm. Both of this CNFs and CNCs usually can be obtained by bleaching process (specifically for materials rich in lignin) and acid hydrolysis Besides that, at most of the time cellulose nanostructures have been utilized as reinforcing phases, but they may also be applied as matrices such as films for the applications of food packaging (Azeredo et al., 2017).

2.3 Nanocellulose

There are three types of nanocellulose that have been utilized for the application of cellulose-derived packaging which are cellulose nanocrystals (CNC), bacterial nanocellulose (BNC) and nanofibrillated cellulose (CNF) (Ferrer et al., 2017). Division of these nanocellulose depends on their size, synthesis method, function and source. CNC are the archetypal cellulose that has a low aspect ratio, with diameters of about 5 nm and length of 100-250 nm. The degree of crystallinity in CNC can be high and sometimes it can achieve 90% crystallinity. The CNC mostly can be synthesized by acid hydrolysis. CNF usually has a higher aspect ratio than CNC and tend to have a web-like structure. The diameter of CNF is usually in the range of 5-60 nm and its synthesis methods include grinding, high pressure homogenizing, high pressure microfluidization and high intensity ultrasonication. For the preparation method of BNC, it is normally synthesized by microorganisms including species of Gluconacetobacter, Komagataeibacter, Enterobacter, Rhodococcus and Sarcina bacterial genera are capable of producing nanoscale cellulose through fermentative processes (Jeremic et al., 2019) which results in highly crystalline cellulose with high degree of polymerization (Feng et al., 2018). The nanofibers of BNC are structures of around 100 μm in length and 100 nm in diameter (Stanisławska, 2016). However, this kind of synthesis method is usually very expensive (da Gama & Dourado, 2018). In comparison with CNF, CNC tend to offer better elongation properties because CNF is more susceptible to fiber agglomeration due to its larger aspect ratio which causes it to be more prone entanglements. The smaller size of CNC has less of an effect on the transparency and this could be one of the advantages for the application of food packaging in which transparency is one of the important criteria (Azeredo et al., 2017).

Besides that, large specific surface areas and the ability to form hydrogen bonds had makes nanocellulose able to form a dense network which is very hard for various molecules to pass through. This property is excellent for barrier applications, and this is what the packaging industry is looking for (Ferrer et al., 2017). The dense network structure of the nanofibrils within the nanocellulose contributes to its good oxygen barrier properties. Among those three types of nanocellulose, CNC has the highest degree of crystallinity due to their production method which involves the strong acid hydrolysis that is capable of hydrolysing disordered and amorphous cellulose. The remaining ordered crystalline region of cellulose will then be responsible for gas molecules barrier properties. The impermeable nature of cellulose crystalline regions had enhanced the effective flow path of the air, water vapour or gas molecules as shown in Figure 2.8. Despite the crystalline regions of cellulose being impermeable to most molecules, this characteristic enhances the effective flow path within the cellulose regardless of gas, air or water molecules. The extent of the tortuosity of nanocellulose for the reduction of the permeability of gas molecules through biocomposite films is a topic that worthy of further studies (Ferrer et al., 2017).

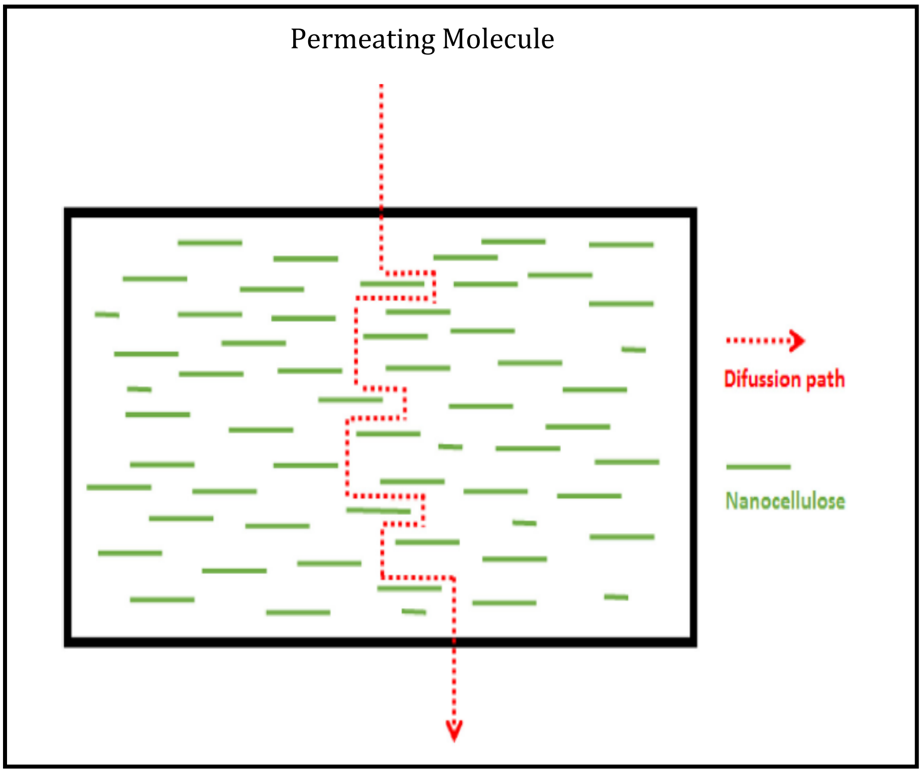

Figure 2.8: Schematic representation of increased diffusion path within the nanocellulose films (Ferrer et al., 2017) in which can be prepared from solvent casting of nanocellulose gels (Das et al., 2017).

The enhancement of barrier properties for nanocellulose composite that incorporated by nanocellulose could be explained by percolation theory in which sufficient amount of CNC must be incorporated and well dispersed within matrix in order to form a continuous structure that able to strengthen the properties of the composite. For instance, studies done by Abdollahi et al. (2013) had shown that composite made up alginate and CNC had shown reduction on water solubility and water vapour permeability by about 40% and 17%, respectively, upon increasing the loading of CNC to 10%. The impermeable nature of cellulose crystalline regions had lengthened the effective flow path of the air, water vapour or gas molecules. Generally, an optimum CNC content had been reported which was around 5 wt% and the strength of the polymer/ nanocellulose composite will be debilitated if the amount of CNC introduced was beyond the optimum value. This is because the OH groups on the surface of CNC will tend to have hydrogen bonding interactions, causing aggregations of CNC (Azeredo et al., 2017).

2.4 Cellulose Nanocrystal (CNC)

Cellulose nanocrystals (CNC) can be described as a stiff particles in rod-like shape that contain of cellulose segments in an almost perfect crystalline structure. Microfibrillated cellulose was the source where CNC can be obtained from. Generally, cellulose fiber consists of two different regions, highly ordered crystalline regions and some disordered regions (amorphous) in vary proportions. The nanocellulose with high degree of crystallinity can be extracted from the crystalline region of microfibrillated cellulose. The process of extraction can be achieved by appropriate combination of chemical, mechanical and enzyme treatments. This extraction process only involving the amorphous regions of cellulose microfibrils instead of crystalline regions as the disordered amorphous structure are more accessible to be attacked. Consequently, shorter and higher crystallinity of crystalline part will be obtained as the results of breaking down of microfibrils during the extraction process and the obtained products are generally known as cellulose nanocrystals (CNC) (George & Sabapathi, 2015). Besides that, the ratios of crystalline and amorphous domains in native cellulose fibers are dependent on type of plant species and growing conditions of the plant. For these reasons, different cellulose source could give different properties of cellulosic nanocrystals (García et al., 2016).

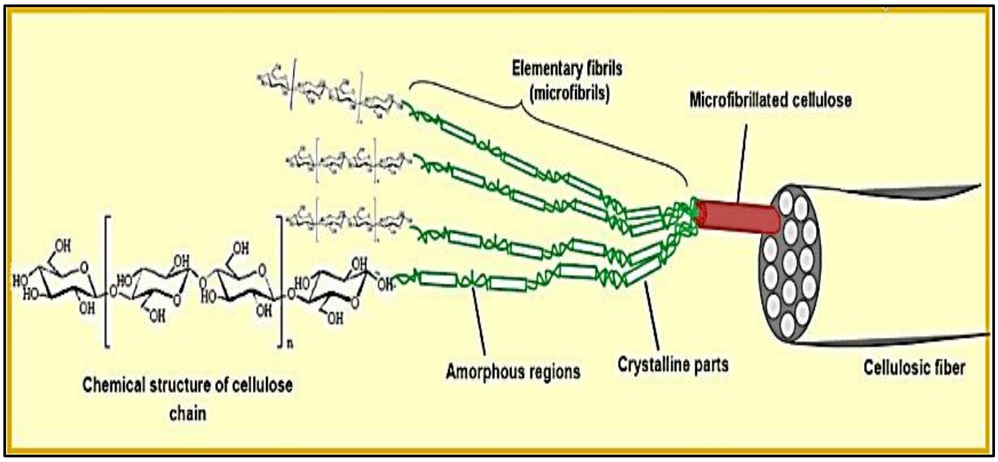

Figure 2.9**:** Part of cellulose fiber where the crystalline and non-crystalline regions are shown. Acid hydrolysis removes the non-crystalline regions and only crystalline parts will remain (CNC) (Lavoine et al., 2012).

CNC can be obtained by numerous approaches but strong acid hydrolysis represents the dominant method used to produce CNC. The acid hydrolysis method had been discovered since 1940s and this method persisted until today. Under controlled conditions, the acid hydrolysis process only manage to remove the susceptible amorphous regions and this resulted crystalline regions intact. Early research demonstrated utilizing 2.2 wt% of sulphuric acid only can obtain low yield of CNC and this reaction took a long period of time. Recent study discovered that using of approximately 65 wt% of sulphuric acid can generate a satisfying dispersing property CNC (Wang et al., 2012).

The CNCs was having high elastic modulus up to 145 GPa and the extraordinary modulus of CNC is resulted from the highly ordered crystal which is formed by orderly arrangement of cellulose chains into regular system stabilized by hydrogen bonding. Moreover, the CNC are found to have good ability to enhance toughness along with stiffness and strength via the interface interaction between