SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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EXTRACTION OF NANOCELLULOSE FROM SUGARCANE BAGASSE USING DIFFERENT ACIDS AND ITS EFFECTS ON POLY(LACTIC ACID)

By

GAN IVY

Supervisor: Prof. Dr. Chow Wen Shyang

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **"Extraction of nanocellulose from sugarcane bagasse using different acids and its effects on poly(lactic acid)"**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this any other examining body or university.

Name of Student   : Gan Ivy   Signature   :

Date   : 1 June 2017

Witness by

Supervisor   : Prof. Dr. Chow Wen Shyang   Signature   :

Date   : 1 June 2017

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LIST OF ABBREVIATIONS

$\Delta Hf°$	Endothermic Enthalpy of 100% Crystallized PLA
ΔH_m	Endorthermic Enthalpy of Samples
CNC	Cellulose Nanocrystal
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetry
FTIR	Fourier Transform Infrared Analysis
HBr	Hydrobromic Acid
HCl	Hydrochloric Acid
H_2SO_4	Sulphuric Acid
H_3PO_4	Phosphoric Acid
LOI	Lateral Order Index
P-CNC	Phosphoric Acid Derived Cellulose Nanocrystal
pKa	Acid Dissociation Constant
PCL	Polycaprolactone
PHB	Poly (3-hydroxybutyrate)
PGA	Polyglycolic Acid
PET	Polyethylene Terephthalate
PLA	Poly(Lactic Acid)
SBF	Sugarcane Bagasse Fiber
SB-MCC	Sugarcane Bagasse Microcrystalline Cellulose
S-CNC	Sulphuric Acid Derived Cellulose Nanocrystal
T	Transmittance
T_d	Degradation Temperature

T_g	Glass Transition Temperature
TGA	Thermogravimetry Analysis
T_m	Melting Temperature
T_{max}	Temperature Of Maximum Decomposition
T_{onset}	Onset Of Thermal Decomposition
w	Weight percentage of PLA
Xc	Degree Of Crystallinity
XPS	X-Ray Photoelectron Spectroscopy

LIST OF SYMBOLS

cm^3	cubic centimetre
cm^{-1}	per centimetre
eV	electron volt
g	gram
g^{-1}	per gram
h	hour
J	joule
kg	kilometre
kPa	kilopascal
L	liter
M	molar
mg	milligram
min	minute
mL	milliliter
mm	millimetre
mm^2	square millimetre
m^3	cubic metre
mol	mole
mol^{-1}	per mole
MPa	megapascal
mV	millivolt
N	newton
nm	nanometre

rpm   revolutions per minute

μm   micrometre

°C   degrees Celsius

°F   degrees Fahrenheit

%   percent

PENYARIAN SELULOSA NANO DARIPADA HAMPAS TEBU DENGAN ASID BERBEZA DAN KESANNYA KE ATAS POLI(ASID LAKTIK)

ABSTRAK

Penggunaan sisa hampas tebu sebagai sumber untuk penyarian kristal selulosa nano (CNC) akan mengurangkan bahan buangan alam sekitar. Hidrolisis dengan asid kuat seperti asid sulfurik (H_2SO_4) adalah kaedah biasa untuk menghasilkan CNC tetapi sifat cas negatif sulfat pada permukaan CNC akan mengurangkan sifat terma dan menyebabkan keserasian yang lemah dengan poli(asid laktik) (PLA). Tujuan kajian ini adalah menggunakan asid ringan, iaitu asid fosforik (H_3PO_4) untuk menghasilkan ciri-ciri CNCs yang mempunyai sifat terma yang baik dan mempunyai keserasian yang bagus dengan PLA. CNCs diekstrak daripada hampas tebu melalui rawatan alkali diikuti dengan hidrolisis asid. CNCs kemudiannya dicampurkan ke dalam matriks PLA untuk menghasilkan komposit nano dengan kaedah penuangan larutan. Ciri-ciri permukaan dan sifat terma CNCs yang diperolehi dari acid yang berbeza dan komposit nano PLA/CNC telah ditentukan. Spektroskopi fotoelektron sinar-X (XPS) menunjukkan bahawa S-CNC (yang diperolehi dari hidrolisis H_2SO_4) mempunyai nisbah karbon/oksigen (C/O) yang lebih tinggi daripada P-CNC (yang diperolehi dari hidrolisis H_3PO_4). Saiz zarah P-CNC adalah lebih kecil daripada S-CNC, walaubagaimanapun, keupayaan zeta S-CNC adalah lebih tinggi daripada P-CNC. Spektroskopi infra-merah jelmaan Fourier (FTIR) menunjukkan bahawa PLA/P-CNC-10 memberikan keserasian yang lebih baik berbanding dengan komposit nano PLA/S-CNC-10. Darjah penghabluran (*Xc*) PLA/P-CNC-10 adalah lebih tinggi daripada PLA/S-CNC-10. Analisis Termogravimetri (TGA) menunjukkan bahawa P-CNC dapat meningkatkan kestabilan terma komposit nano PLA/P-CNC-10.

EXTRACTION OF NANOCELLULOSE FROM SUGARCANE BAGASSE USING DIFFERENT ACIDS AND ITS EFFECTS ON POLY(LACTIC ACID)

ABSTRACT

The usage of abundant sugarcane bagasse as a source for the extraction of cellulose nanocrystals (CNC) would reduce waste in the environment. Strong acid hydrolysis by sulphuric acid (H_2SO_4) was a common method to produce CNC but the negative charged sulphate group on the surface of CNC had reduced the thermal properties and caused poor compatibility with poly(lactic acid) (PLA). This present study is to determine the feasibility of utilizing mild acid, phosphoric acid (H_3PO_4) to produce better thermal properties of CNCs and improved its compatibility with PLA. In this study, CNCs was extracted from sugarcane bagasse through alkaline treatment followed by acid hydrolysis. The obtained CNCs were then incorporated in PLA matrix to produce nanocomposite by solution casting method. The surface characteristics and thermal properties of different acid derived CNCs and the PLA/CNC nanocomposite were determined. The X-ray Photoelectron Spectroscopy (XPS) result showed that S-CNC (CNC by H_2SO_4 hydrolysis) was having slightly higher oxygen/carbon (O/C) ratio than P-CNC (CNC by H_3PO_4 hydrolysis). The particle size of P-CNC was smaller than S-CNC, however, the zeta potential of S-CNC is higher than P-CNC. The Fourier Transform Infra-Red Spectroscopy (FTIR) result indicated that PLA/P-CNC-10 gave better compatibility compared to PLA/S-CNC-10 nanocomposites. The degree of crystallinity (Xc) of PLA/P-CNC-10 is higher than the PLA/S-CNC-10. Thermogravimetric Analysis (TGA) results indicate that P-CNC could increase the thermal stability of PLA/P-CNC-10 nanocomposites.

CHAPTER 1

INTRODUCTION

1.1   Background

For last few years, the industrial and academic researchers were began to pay attention on the development of green polymers that can be obtained from the natural sources due to the growing recognition on the environmental issues caused by the large quantities of plastic wastes. Thus, the polymers with properties of biocompatible and biodegradable properties attracted more interest respect to non-degradable petroleum based polymers. The development of green polymers as environment friendly materials could eventually diminish accumulated plastic waste and greenhouse gas emissions (Luzi et al., 2016). Moreover, the increasing of necessity to protect the environment had causes increment on the utilization of environmentally friendly products. The usage of natural fibers as an essential source of raw materials in production processes is very important for developing countries which having enormous agriculture production. In comparison to others agricultural corps, sugarcane is one of the agriculture crops that have high volumes of production and having huge quantities of residues. The capability to utilize agricultural residues wisely in biocomposites field had promoted them in non- food application this great effort had created another economy pathway for the agricultural sector (Oliveira et al., 2016).

The concern about taking care of environment from pollutions had caused numerous efforts have been taken to establish biodegradables polymers and composites. Among all the biodegradable aliphatic polyesters, polycaprolactone (PCL), poly (3-hydroxybutyrate) (PHB), polyglycolic acid (PGA) and polylactic acid (PLA) are now

involving in commercial applications with the addition of bio-based materials (Abdulkhani et al., 2014). The Poly(lactic acid) (PLA) have been studied for many decades but only getting attention lately as potential environmental friendly biodegradable plastic because it could be easily obtained as it able to be generated from renewable resources (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 (Song et al., 2014). Beside its bio-based character, the high transparency and good melt-processability had also caused PLA was getting considerable interest for the development of green polymer. Moreover, extensive studies had been conducted regard PLA was due to its favourable mechanical properties which is comparable to poly (ethylene terephthalate) (PET). However, the major drawbacks for PLA were its brittleness, expensive production cost and low thermal stability which prohibited them to be used in some application (Kiziltas et al., 2016). The limitation of PLA to be used in certain application can be improved by incorporation of biodegradable fillers such as cellulose. By the aid of cellulose, both of the thermal and mechanical properties of PLA could be enhanced and eventually optimizing the cost performance of this green material (Frone et al., 2013).

Recently, cellulose nanocrystals (CNC) have been researched for the topic as a promising nanoreinforcement in the biodegradable polymers which can be enhanced the properties of the biomaterial especially in the applications for food packaging (Luzi et al., 2016). The cellulose is the source where CNCs can be extracted from and this cellulose can be defined as a natural biopolymer that embedded in the plant cell wall including sugarcane bagasse, cotton, flax, jute and so on (Mandal & Chakrabarty, 2011). The term nanocellulose can be used to describe the cellulose crystal or fiber that contain at least single dimension within nanometer size range. Generally, there are three

different types of nanocellulose which are bacterial cellulose (BC), cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) or cellulose nanowhiskers (CNWs). These nanaocellulose can be categorized depend on their morphology of crystalline regions and degree of crystallinity. Apart from that, the great influence of nanocellulose in the economy could be evidenced from the growing number for the patents or any publications regards on the cellulose nanoparticles. Most of the studies in the previous time were mainly focus on the preparation and characterization of nanocellulose. Nowadays, the studied on the nanocellulose had been move on to the topic regards on the development of nanocellulose in nanocomposite. This difference denoted that development of the nanocellulose had been move towards the industrialization. The excellent intrinsic properties of nanocellulose such as high aspect ratio, dimensions in nanoscale, low density and satisfying mechanical properties had promote them to become cost effective bio-based products (Xu et al., 2016). Nevertheless, there are some obstacles for their application as their dominant hydrophilic characteristic had limited their compatibility with hydrophobic polymer matrices (Lizundia et al., 2016).

The incorporation of CNC into biodegradable PLA matrix could produce a wholly organic bionanocomposite and this combination resulted enhancement in the nucleation effects, foam formation and even the barrier properties of PLA (Lizundia et al., 2016). According to Mericer et al. (2016), outstanding gas barrier properties of PLA nanocomposites could be achieved when the cellulose was used to produce this nanocomposite. They have found out that the ability of cellulose to form a dense interfibrillar networks via hydrogen bonding and high degree of crystallinity of cellulose had made PLA to have good gas barrier properties. Therefore, the incorporation of cellulose into PLA to produce PLA nanocomposites had eventually enhanced the properties of PLA and also overcome the limitations of PLA without

sacrificing the biodegradability and biocompatibility of PLA (Luzi et al., 2016). Besides having biodegradabe properties, the reasons for PLA/CNC composites have getting high concern were due to their properties of fire resistance, low density, non-abrasiveness and safe to be used. However, the shortcoming of this composite was due to the incompatibly of both CNC with PLA, moisture absorption and low thermal stability of cellulose (Abdulkhani et al., 2014).

1.2 Problem Statement

Sugarcane bagasse (SCB) is a residue produced in large quantities every year by the sugar and alcohol industries, adequate use of the SCB gives an added value for this material and a solution for the removal of this abundant waste. 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. It was found the more the content of acid sulphate groups in crystal, the lower the thermal degradation temperature could have been. Besides that, CNC obtained from acid hydrolysis will be incorporate into PLA to produce PLA/CNC nanocomposite in this studies. In fact, hydroxyl groups in the cellulose eventually give hydrophilic properties to cellulose and this hydrophilic characteristic caused poor compatibility in the term of interfacial adhesion between hydrophilic CNC and hydrophobic PLA. Therefore, using different strength of acids to synthesis CNC may consider an approach to improve the thermal stability and compatibility of the CNC. The outcomes of this project will demonstrate not only the

potential of CNC with enhanced thermal stability but also better dispersibility of cellulose nanocrystal in PLA/CNC nanocomposites.

1.3 Objectives

This research is aim to study and develop cellulose nanocrystal (CNC) reinforced polylactic acid (PLA) nanocomposites primarily via solution casting method. In order to accomplish this main objective, this project was divided into two specific objectives:

1. To investigate the feasibility of using mild acid, phosphoric acid (H_3PO_4) to synthesis CNC with better thermal properties.

2. To improve compatibility, dispersibility and thermal stability of PLA/CNC nanocomposite.

1.4 Thesis Structure

This thesis consists of 5 chapters.

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

Chapter 2 contains literature review of thesis, which presents background literature on the general information about polylactic acid; an overview on the cellulose nanocrystal, isolation of CNC by acid hydrolysis; and a comprehensive literature review of PLA/CNC nanocomposites.

Chapter 3 represents the material approaches and research methodology of the project. This chapter will provide 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 nanocellulose composites will be

discussed in this chapter. The characterization method of cellulose nanocrystals and PLA composites will be given in this chapter.

Chapter 4 shows the results discussion of the thesis. Elaboration on the problems and the explanation will be included in this chapter.

Chapter 5 denotes 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

In this study, CNCs were fabricated utilizing two different types of acid which are sulphuric acid and phosphoric acid using the cellulose extracted from sugarcane bagasse. The procedure that used to extract cellulose from the sugarcane bagasse was reported by Brinchi et al. (2013) which involving the raw material preparation, delignification and bleaching process. The concentration of acid that used to hydrolyse the cellulose into nanocellulose was based on previous researches done by (Dhar et al., 2016). The concentration of sulphuric acid used to prepare the nanocellulose was 6 M (fiber to liquor ratio of 1:20) whereas concentration of phosphoric acid was 11 M (fiber to liquor ratio of 1:20). The influence of acid types on the morphology of CNCs, crystallinity, hydrophilic characteristics, thermal and dispersibility in PLA were studied in details.

CHAPTER 2

LITERATURE REVIEW

2.1   Polylactic acid (PLA)

Poly (lactic acid) (PLA) was discovered by Carothers at Du Pont in 1932. At first, only low molecular weight PLA was able to produce. Further work by DuPont resulted in higher-molecular weight product and patented in 1954 (Jamshidian et al., 2010). Even until today, PLA is one of the most studied polymeric materials because of their potential contribution in terms of reduced fossil-fuel dependence. Thus, the feasibility of procuring PLA from renewable plant resources makes it an attractive biopolymer for its study (Robles et al., 2015). The monomer of this polymer is lactic acid and can be obtained through the fermentation of maize or other sustainable agricultural raw resources (Abdulkhani et al., 2014). Besides that, lactides are stereoisomers in which L-lactic acid and D-lactic acid are the two optically active stereoisomers of lactic acid (*S* and *R* in absolute configuration, respectively) as shown in Figure 2.1. The pure L-lactic acid or D-lactic acid, or mixtures of both components are needed for the synthesis of PLA. The stereoisomers of lactic acid can be named by two different name which are d-lactic acid and l- lactic acid or can be known as D (-) lactic acid and L (+) lactic acid. For the small letters case, d- lactic acid and l-lactic acid, were applied to denote the direction of rotation of plane by polarized light and does not give any information regards their molecular configuration. However, the upper case, D (-) lactic acid and L (+) lactic acid were used in modern terminology and direction of rotation by polarized light was replaced by using the symbols (-) and (+) (Lockwood et al., 1965).
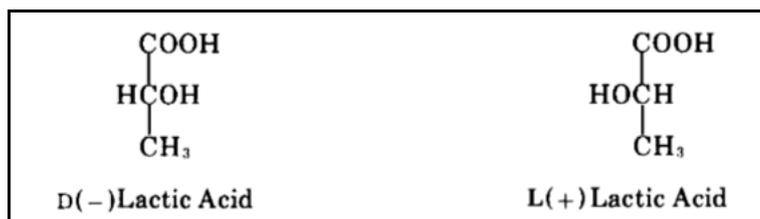
Figure 2.1: The stereoisomers of lactic acid (Lockwood et al., 1965).

Besides having L-lactic acid and D-lactic acid, there are also another structures of lactic acid existed which termed as Racemic DL-lactic acid. The DL-lactic acid contains both L- lactic acid and D-lactic acid in equimolar. The main difference of DL-lactic acid from the L- and D-lactic was their synthesis process. The DL-lactic acid can be only synthesis via chemical method whereas L- and D-lactic acid can be manufactured through fermentation process. The various structure of lactic acid was shown in Figure 2.2 (Masutani & Kimura, 2014).
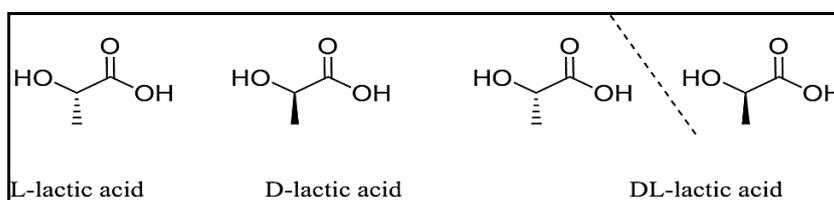
Figure 2.2: Different structures of lactic acid (Masutani & Kimura, 2014).

There were 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 high expensive manufacturing costs and it was found that this synthetic route cannot obtain high purity lactic acid but 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).

Today, there are two types of synthesis route for the production PLA polymers. PLA can be obtained either by having lactic acid undergone direct condensation (route 1) or through ring opening process via the cyclic intermediate dimer (lactide) (route 2) as shown in Figure 2.3. The direct condensation method was a long time reaction and in order to obtain high molecular weight polymer, this process was conducted in a severe conditions in which having reaction at high temperature at the range of 180–200°C and low pressure while the ring opening process can afford a high-molecular-weight PLA with narrow molecular weight distribution at relatively mild reaction conditions (low temperature of 130°C and short reaction times) (Hamdan & Sonomoto, 2011).
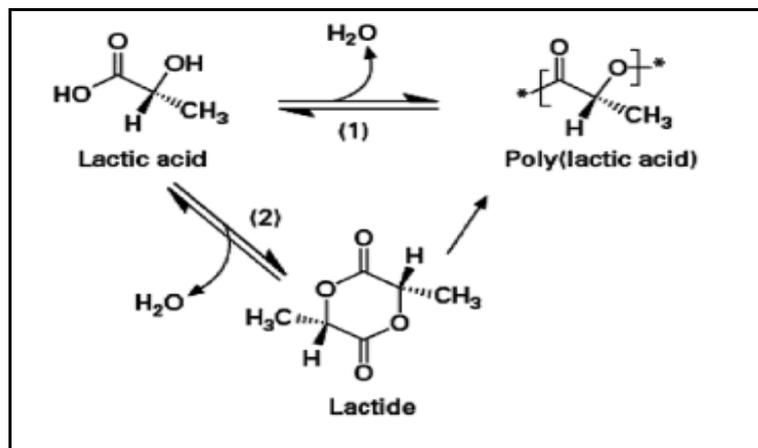
Figure 2.3: Polymerization routes to PLA (Hamdan & Sonomoto, 2011).

Apart from that, the bio-based character of poly (lactic acid) would commit to the diminution of environmental impact correlated with the extensive use of traditional plastics generated based on petrochemical resources (Lizundia et al., 2016). The PLA production was consider as eco-friendly process because carbon dioxide was consumed during its production process. The life cycle production of PLA begins with starch was

being extracted from plants such as corn. During the photosynthesis process, the corn plant will consume all the free energy which origins from the solar energy (Avinc & Khoddami, 2009). The basic stoichiometric equation for photosynthesis is shown as Figure 2.4.
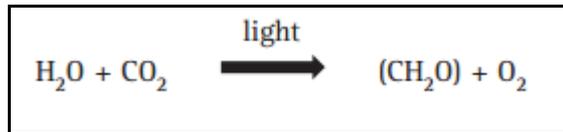
Figure 2.4: Basic stoichiometric equation for photosynthesis (Vink et al., 2007).

In this equation, (CH_2O) denotes carbohydrate, such as starch or sucrose. The carbon dioxide consumed by the corn plant for starch formation is then finally contributed to the construction of PLA polymer chains. Therefore, the benefit of PLA production compared to other commercial polymers is the ability of the reduction of carbon dioxide (CO_2) emission (Vink et al., 2007). The overall production of lactic acid from corn was shown in Figure 2.5.
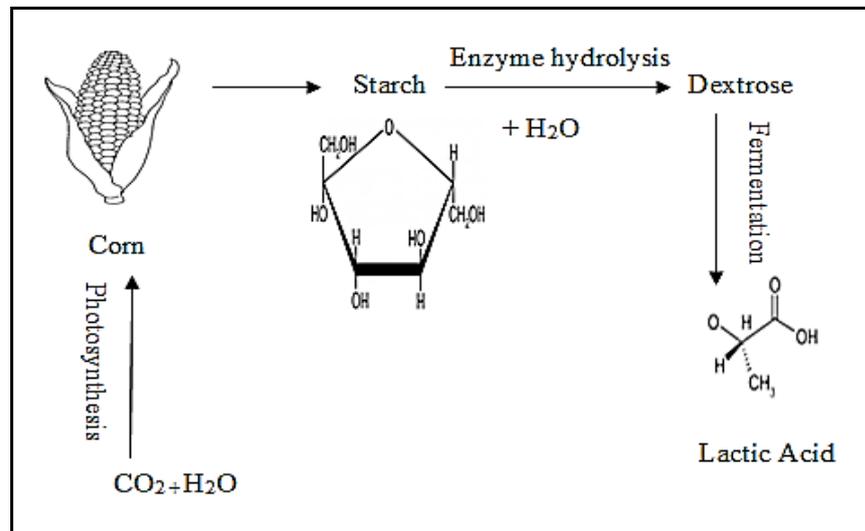
Figure 2.5: Production of lactic acid from renewable resources such as corn (Avinc & Khoddami, 2009).

Therefore, PLA can be consider as green material and its production can be considered as critical contributor to global warming as its manufacturing process was able to reduce the emission of carbon dioxide. During the corn growing, the carbon dioxide is harnessed from the environment and this suggested that PLA was also having a good potential to reduce the environmental pollutions compared to other commercial polymers (Vink et al., 2007).

A few appealing things about PLA are biocompatibility, processability, renewability and having lesser energy consumption (Rasal, 2010). Firstly, PLA can be produced from sustainable agricultural sources which can cut down the dependency on fossil fuel as well as alleviate the crisis of energy. Water and carbon dioxide which are non-toxic are the degradation products of PLA and this making PLA can be used as a biomaterial for biomedial applications such as clips and sutures. Furthermore, in comparing with biomaterials such as poly(hydroxyalkanoates) (PHAs) and poly(ethylene glycol) (PEG) , the good thermal processability of PLA had make it can be processes by various type of processing method such as extrusion, film casting and fiber spinning process (Rhim et al., 2006). Because of the biodegradable and biocompatible characteristics of PLA, these properties had made it an adequate applicant in the application of fresh food packaging or short shelf-life products such as blister package, overwrap and lamination films (Fortunati et al., 2012).

Overall, it was found that the properties of PLA were almost similar with polystyrene (PS) as it is having a low value for elongation at break about 2-5% and high Young's Modulus which is approximately 3 GPa. The weakness of PLA is that it cannot be used in applications that exceed 60°C due to its low heat distortion temperature (HDT) (Spinella et al., 2015). In order to overcome the weakness of this polymer, the

PLA matrices can be introduced by nanoscale particles which can accomplish synergetic effect (Lizundia et al., 2016).

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. 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).

Cellulose is a macromolecular chains and 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 polymer chains (inter-chain hydrogen bonding). The existence of this hydrogen bonding would influence the main physical properties of cellulosic structures and also the swelling and solvency properties of the cellulose (Zhang et al., 2013).

Besides that, 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 this number can ranged from hundreds to tens of thousands. 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 as depicted in Figure 2.6 (Chen et al., 2014).
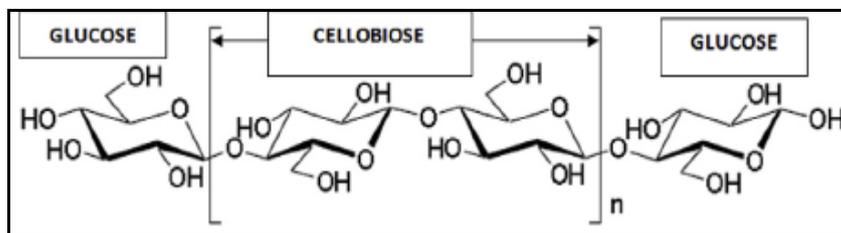
Figure 2.6: Chemical structure of cellulose showing cellobiose repeat unit (Ng et al., 2015).

By referring Figure 2.7, 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).
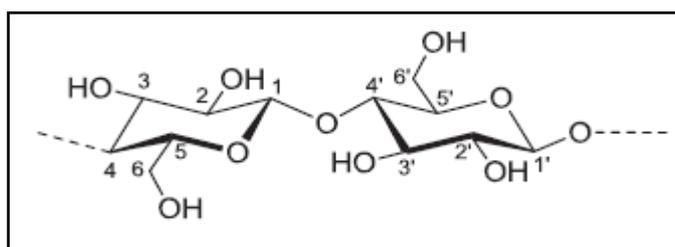
Figure 2.7: Schematic representation of cellulose structure (Kang et al., 2015).

The cellulose chains are packed tightly in crystallites region by complex and strong intra- and inter molecular hydrogen bond network. The different orientation of molecular and hydrogen-bonding network in the cellulose had gave rises to the cellulose polymorphs There are several types of interconvertible polymorphic forms of cellulose which namely I, II, III, IV and V. Cellulose I and cellulose II are the most common cellulose polymorphs found in nature (Habibi et al., 2010).

Cellulose I can be named as native cellulose and represented the crystalline cellulose. For cellulose II, it can be term as regenerated cellulose (Siqueira et al., 2010). The invariably cellulose II can be obtained by having alkaline treatment on native cellulose as this process can make the cellulose I transform into cellulose II (Kroon-Batenburg and Kroon, 1997).

Among the cellulose polymorphs, the cellulose I was having two suballomorphs which termed Iα and Iβ. Both of these suballomorphs was having parallel cellulose chains with different hydrogen bonding and resulted different type of crystalline structure. However, the structure for the cellulose II was arranged in antiparallel (Wei and McDonald, 2016). The good arrangement of cellulose chain in cellulose I make it having the best mechanical properties and the extra hydrogen bond per glucose residue in cellulose II had made these allomorphs having the most thermodynamically stable properties (Wulandari et al, 2016).

The basic structural component of cellulose is made up of cellulose microfibril and it was formed during the process of biosynthesis. Throughout the biosynthesis, the individual cellulose chains assembled together to form elementary fibrils via the intermolecular hydrogen bonding and the Van de Waals forces that involves oxygen and hydroxyl group. After that, the aggregation of these elementary fibrils will cause the

formation of larger size microfibrils. Microfibrils can be defined as a fibrils that having diameter in the range of 5-50 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. The cellulose cell wall and the organization of microfibril are presented in Figure 2.8 (Siqueira et al., 2010).
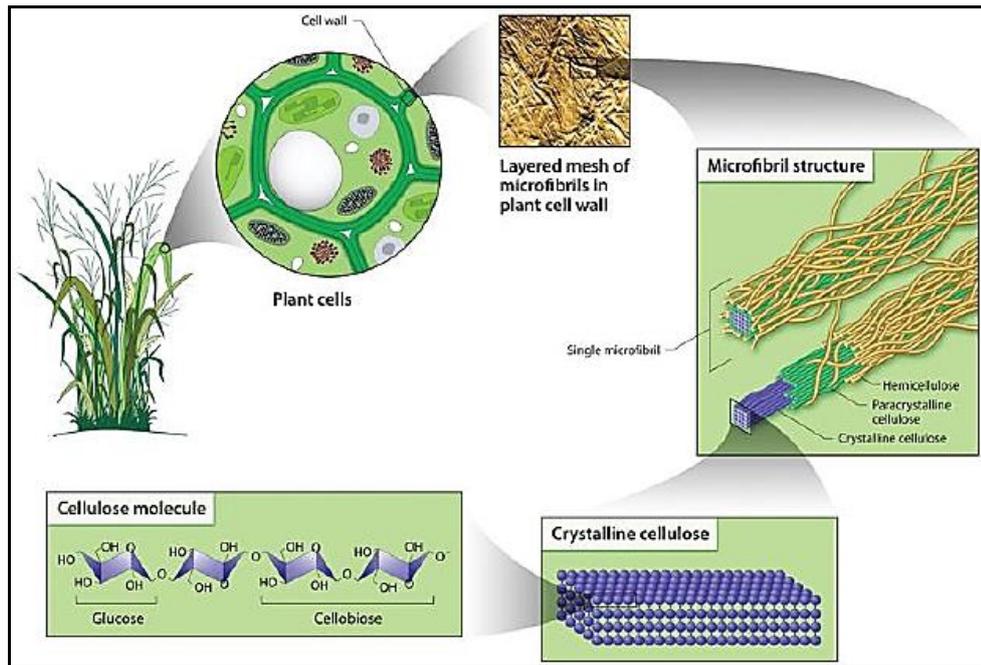
Figure 2.8: Scheme of the cellulose cell wall and microbial organization (Siqueira et al., 2010).

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 (Jonoobi et al., 2015). 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 (Dufresne, 2013).

2.3   Sugarcane Bagasse

Sugarcane is one of plants that having the most effective bioconversion that are good in capturing sunlight via photosynthesis. In comparison to the other agriculture crops, sugarcane was consider as main agricultural crops which having the highest production. The sugarcane stalk actually comprises of two different parts, an inner pith consisting majority of the sucrose and outer rind that contains lignocellulosic fibres. Due to their global availability throughout the year, the sugarcane had eventually serve as a crucial bioproduct feedstocks and responsible for producing most of the lignocellulosic biomass in the sector of agriculture in the world (Har et al., 2013). Global production of major agriculture waste was shown in the Table 2.1.

Table 2.1: Worldwide availability of major agricultural wastes (Sakar et al., 2012).

Agricultural wastes	Availability (million tons)
Wheat straw	354.34
Rice straw	731.3
Corn straw	128.02
Sugarcane bagasse	180.73

Sugarcane bagasse (SCB) can be obtained by extracting sucrose from the sugarcane plant and it was consider as a low cost lignocellulosic biomass. The extracting process creates an enormous volume of residue by having approximately 240 kg of bagasse with 50% humidity in one ton of sugarcane. In this bagasse, both crushed rind and pith fibers were found (Sidana & Farooq, 2014). There are total three types of polymers that made up this lignocellulosic biomass which are lignin, hemicellulose and cellulose. The chemical compositions of this bagasse consists of 43.6% of cellulose, 33.8% of hemicellulose, 18.1% of lignin, about 2.3% of ash and 0.8% of wax on a dry weight basis. However, the distribution of lignin, hemicellulose and cellulose within the cell walls are not uniform (Laopaiboon et al., 2009).

The main constituent of lignocellulosic biomass is made up of cellulose. The second most abundant component of lignocellulosic biomass was hemicellulose which having an amorphous and random structure. This hemicellulose is composed of different kinds of heteropolymers which including arabinoxylan, galactomannan, glucomannan, glucuronoxylan, xylan and xyloglucan. These heteropolymers can be categorized as 5-carbon and 6-carbon monosaccharide units, whereby 5-carbon monosaccharide units termed as pentoses (arabinose, xylose); 6-carbon monosaccharide units named as (glucose, galactose, mannose) and acetylated sugars. Besides that, the complex network of bonds form by hemicellulose imbedded in plant cell had actually supply structural strength by providing linkage for cellulose fibers to form microfibrils and cross-linking with lignin. Meanwhile, lignin can be described as a three-dimensional polymer that made up by phenylpropanoid units. The lignin in the bagasse can functions as a cellular adhesive that tend to offering stiffness to the cell wall, allowing plant tissue to have adequate compressive strength and protecting the plant against pathogens and insects. Furthermore, lignin is bound tightly to both

hemicellulose and it is insoluble in water. There are also phenylpropanoid monomeric units found within the lignin and these monomeric units are termed as guaiacyl (G), *p*-hydroxyphenyl (H) and syringyl (S) units (Isikgor & Becer, 2015).

The lignocellulose source was easily available and this make it can be hydrolysed by acid solution to get predominantly fermentable sugars, such as xylose, glucose and small amount of arabinose. These fermentable sugars are important for the manufacturing of bio-products (Laopaiboon et al., 2009; Ga´mez et al., 2006) and there were many studies and research had been reported to synthesis nanocellulose extracted from sugarcane bagasse. By using acid hydrolysis, the spherical form with rod-like shaped highly crystalline cellulose nanocrystals can be obtained. Basically, the biopolymers in lignocellulosic materials would be dehydrated and redistributed due the strong oxidizing agents behaviour of strong acids. The ability of utilizing sugarcane bagasse to produce highly crystalline cellulose particles had eventually added value to this inexpensive biomass source. Today, the usage of bagasse as raw material for the applications of industry had been studied and published. The industrial applications including the manufacturing of pulp and paper, generation of electricity and products based on fermentation. Recently, the novel composite regards the usage of biomass for processing had gained growing interest due to the renewable and ecological characteristic of this biomass (Mandal & Chakrabarty, 2011).

2.4   Cellulose Nanocrystal (CNC)

Cellulose nanocrystals (CNCs) 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 CNCs 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 (CNCs) (Habibi et al., 2010). 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).
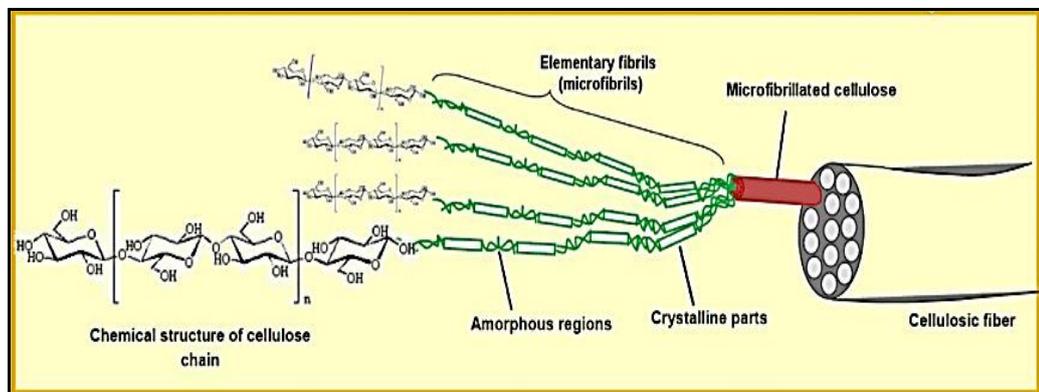
Figure 2.9: Part of cellulose fiber where the crystalline and non-crystalline regions are shown. Acid hydrolysis removes the non-crystalline regions and only crystalline parts will remain (CNC) (Lavoine et al., 2012).

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 most common acid that used for cellulose acid hydrolysis is strong inorganic acids which are H_2SO_4 and HCl. However, some weakness was discovered for the CNCs that had been isolated by these inorganic acids. It was found that CNCs isolated by the HCl was having limited dispersibility due to the low density surface charges and this had causes flocculation in aqueous suspensions. In contrast, CNCs isolated by H_2SO_4 was having a highly stable colloidal suspension due to the sulfonation of the CNC which promoting highly negative surface charge on the surface of CNC. However, sulfate groups ($-OSO_3-$) on the surface of the CNC were also tending to reduce the thermostability of the nanocrystals (Vasconcelos et al., 2017).

Nanocrystals are often termed as nanoparticles, nanofibers or whiskers however the most commonly used nomenclature was CNCs. The perfect native CNCs was having an estimated theoretical value of Young's modulus of 167.5 GPa which is even stronger than steel (Tashiro & Kobayashi, 1991), whereas the native CNCs obtained from cotton and tunicate was having elastic modulus up to 105 and 143 GPa respectively (Sturcova et al., 2005). Moreover, the CNC are found to have good ability to enhance toughness along with stiffness and strength via the interface interaction between CNCs-matrix and this made CNCs are more preferable to use as a load bearing constituents. This fact is well supported by the perfect crystalline structure of CNCs

which have crystallinities up to 65-95% which almost was having similar value to the theoretical modulus of a perfect crystal. Therefore, CNCs can be an ideal nano-reinforcement for either water soluble or water insoluble polymer matrices and eventually produce various types of reinforced composites (Ng et al., 2015).

2.5   PLA/CNC nanocomposites.

Polymer nanocomposites are fabricated by incorporated of nanofillers or nanometric particles into a polymer matrix. In this case, the cellulose nanocrystals (CNCs) will be introduced into Polylactic acid (PLA) matrix. With the incorporation of natural fiber CNCs into the biodegradale PLA, the waste disposal for lignocellulosic filled nanocomposite becomes much easier and more environment friendly as fully combustion for lignocellulosic filled composites only emitted water and carbon dioxide (Mandral & Chakrabarty, 2014).

Besides providing good disposal properties to PLA, the introduction of CNC can produce enhanced properties nanocomposites that can satisfy the requirement for both current technology and industrial applications (Lama et al., 2017). However, the low Heat Distortion Temperature (HDT) of PLA had limited its use to be applied as green replacement for the applications that required higher temperature. The blending of nanofillers with PLA was found to be useful to overcome the low HDT of PLA and this had made CNCs are gaining more attractions to be studied as promising nanofiller in biodegradable polymeric matrices (Spinella et al., 2015). Therefore, extensive studies regard the properties and structural of PLA/CNC had been conducted up to now and the reported studies was focus mainly on viscoelasticity and thermal behaviour of final properties of PLA/CNC composites that used in bio-applications and packaging material (Xu et al., 2016).

Despite the fact that thermal properties of PLA nanocomposites could be enhanced by incorporating CNC, the enhancement of the PLA/CNC nanocomposites still have to depend on the quality of CNC dispersion in the polymer matrix (Khoshkava & Kamal, 2013). CNC are excellent candidates for the fabrication of nanocomposite but they also cause high hydrophilicity challenges. The highly hydrophilicity was contributed by huge number of hydroxyl groups on the surface of fibers and this gave poor interfacial bonding between the fibers and the hydrophobic PLA matrix (Pickering et al., 2016).

In this sense, during the incorporation of CNC within the PLA matrix, the intramolecular and intermolecular hydrogen bonding between the adjacent cellulose chains tend to make the CNCs bundle together which restraint their functions as elements for reinforcing. Therefore, the hydrophilic nature of cellulose had causes ineffective transfer of CNC properties to the PLA matrix (Lizundia et al., 2016).

The structure and properties of the nanocomposites was affected by the interfacial interaction between fiber and polymer matrix and also the bonding of fiber-fiber within the network of cellulose. These interfacial interaction and fiber bonding were dependent on the surface properties of nanocellulose. In order to attain the transfer of remarkable mechanical properties of single fiber level of nanocellulose to the bulk nanocompoites, the hydrophilic nanocellulose need to be disperse well in the hydrophobic polymer matrices and the interface of fiber-matrix was also required to be optimized . Therefore, the surface properties of CNCs were playing an important role to determine the final properties of PLA/CNC nanocomposite (Oksman et al., 2016).

2.6   Acid hydrolysis

Cellulose hydrolysis has been discovered by H. Braconnot since 1819 and remains as a topic of extensive research until now. In that time, H. Braconnot used concentrated sulphuric acid to treat wood and obtained sugars through acid hydrolysis process. From the industrial standpoint, acid hydrolysis of cellulose is an important technology and the information regards the main properties of cellulosic fibers (Taherzadeh & Karimi, 2007). Nowadays, it is common to have cellulose microfibrils to undergo acid hydrolysis as this process is very convenient in obtaining CNCs (Ng et al., 2015).

Cellulose microfibrilled are made up of interconnection of the cellulose chains in the highly ordered crystalline parts with the cellulose chains in the disordered amorphous parts. By subjecting acid to the cellulosic fibers, the degree of polymerisation (DP) will be reduced due to the breakage of the glucosidic linkages in the cellulose. At first, rapid degradation process will be occurred, however as the process proceeds, the degradation process slows down and eventually reaching a certain level of DP (Palme et al., 2015). Throughout the hydrolysis process, the acids only having very slow reaction with the crystalline parts and the degradation mainly happens in the amorphous part of the cellulose. The reaction of acid with the crystalline parts of cellulose at a slower rate or hindered was due to the crystalline structure had limit the accessible of both hydrogen ions and water molecules to reach the glycosidic bond in the crystalline region. Hence, this causes hydrolysis take place primarily in the amorphous regions of cellulose (Ogeda et al., 2012).

In addition, the main function of the acid in the acid hydrolysis process is to release hydronium ions (H^+) as shown in the Figure 2.10. This hydronium ion (H+) was

responsible for the hydrolytic cleavage of glucosidic bonds in cellulose chains. During the acid hydrolysis process, the hydronium ions (H^+) tend to have reaction with the oxygen on the glycosidic bonds that located in the middle of two anhydroglucose units. This reaction caused protonation of the oxygen and led to hydrolytic cleavage of glucosidic bonds in the amorphous regions. Thus, the nanofibril bundles with hierarchical structure were broken down and turn into crystalline nanocrystals at the end of this process (Siqueira et al., 2010; Ng et al., 2015).
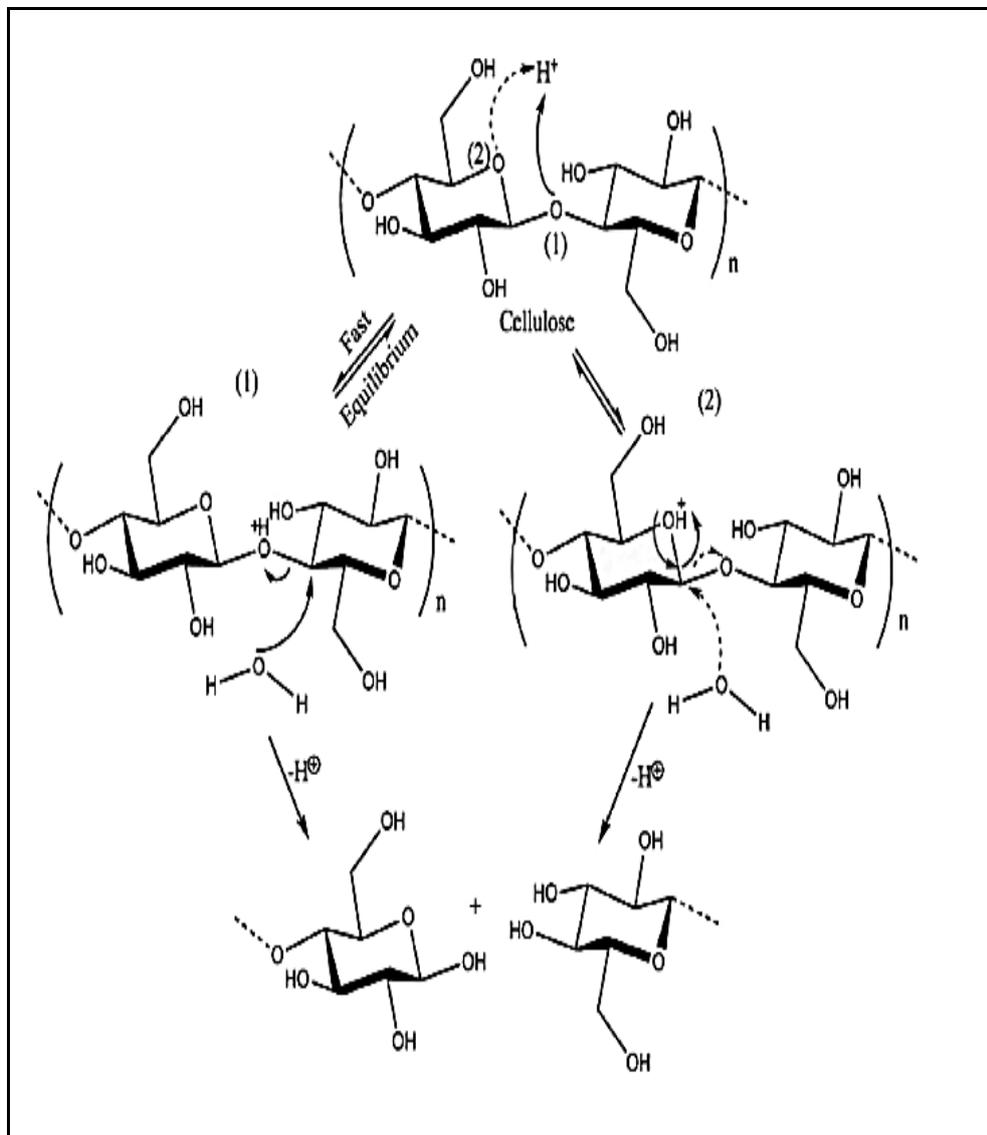
Figure 2.10: The mechanism for acid hydrolysis of cellulose (Ng et al., 2015).