EXTRACTION AND CHARACTERIZATION OF NANOCELLULOSE FROM RUBBER WOOD

by

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THESIS DECLARATION

I hereby declare that the work embodied in this Report is the result of the original research and has not been submitted for a higher degree to any universities or institutions.

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I certify that the report of this final year project entitled "Extraction and Characterization of Nanocellulose from Rubber Wood" by Soo Choy Yoke, E13A318 has been examined and all correction recommended by examiners have been done for the degree of Bachelor of Applied Science (Materials Technology), Faculty of Earth Science, University Malaysia Kelantan.

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LIST OF ABBREVIATIONS

BMIMCI	1-Butyl-3-methylimidazolium chloride
CI	Crystallinity Index
CNC	Cellulose nanocrystal
CNF	Cellulose nanofibril
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetry
EMIMCI	1-Ethyl-3-methylimidazolium chloride
FE-SEM	Field emission-scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
gt	Gauche-trans
IL	Ionic liquid
TAPPI	Technical Association of the Pulp and Paper Industry
tg	Trans-gauche
XRD	X-ray diffraction
USDA	United States Department of Agriculture

LIST OF SYMBOLS

K	Correction factor
λ	Wavenumber
β	Corrected angular width in radians
α	Alpha
GPa	Gigapascal
wt %	Weight percentage
θ	Diffraction angle

ABSTRACT

Rubber wood (*hevea brasiliensis*) sawdust is one of the agricultural waste that have potential in the production of renewable resource such as cellulose and nanocellulose. Utilization of ionic liquids (ILs) as solvents for cellulose processing has been growing exponentially because of the unique physiochemical properties and potential to be eco-friendly. In the present study, 1-buty-3-methylimidazolium (BMIMCl) was used as a solvent to convert cellulose into nanocellulose. The process is done in two steps, there are by isolating α-cellulose from rubber wood through a series of chemical treatments (alkali treatment and bleaching) and converting cellulose into nanocellulose with BMIMCl. The objectives of this study were to determine the effectiveness of BMIMCl to convert cellulose into nanocellulose and to study the properties of BMIMCl treated cellulose. To determine how effective IL treatment is, it was compared to the untreated cellulose. In term of chemical and structural properties, thermal properties and morphological of BMIMCl treated cellulose were characterized through the FTIR, XRD, TGA and FESEM respectively. It is noteworthy that crystallinity and crystallite size of cellulose decreased after IL treatment. In addition, the thermal stability of BMIMCl treated cellulose decreased and the pyrolysis residues increased. The results showed that most crystalline structure of cellulose was destroyed to amorphous structure, and the remained crystalline structure of cellulose was converted to cellulose II from cellulose I in extracted α-cellulose. The more amorphous structure of BMIMCl treated cellulose resulting in a decrease in thermal stability. BMIMCl was effective used to convert cellulose into more amorphous structure. Results from this work may be potentially applied in various fields such as textile, drug delivery and enzyme hydrolysis for bio-energy production.

ABSTRAK

Habuk kayu getah (*hevea brasiliensis*) adalah salah satu daripada sisa buangan pertanian yang berpotensi dalam penghasilan sumber yang boleh diperbaharui seperti selulosa dan nanoselulosa. Penggunaan cecair ionik (ILs) sebagai pelarut untuk pemprosesan selulosa telah berkembang dengan pesat disebabkan sifat-sifat fisiokimia yang unik dan lebih mesra alam. Dalam kajian ini, 1-buty-3-methylimidazolium (BMIMCl) telah digunakan sebagai pelarut untuk menghasilkan nanoselulosa daripada selulosa. Proses pembuatan dilakukan dengan dua tahap iaitu isolasi α-selulosa dari getah kayu melalui serangkaian rawatan kimia (perlakuan alkali dan pemucatan) dan menukar menjadi nanoselulosa menggunakan BMIMCl. Nanoselulosa telah diisolasi dari kayu getah dengan tujuan untuk mengetahui keberkesanan BMIMCl untuk menukar selulosa ke nanoselulosa dan untuk mempelajari sifat-sifatnya. Untuk menentukan keberkesanan rawatan cecair ionik, ia dibandingkan dengan selulosa yang tidak dirawat. Dari segi sifat kimia dan struktur, sifat terma dan morfologi selulosa selepas rawatan BMIMCl telah disifatkan masing-masing melalui FTIR, XRD, TGA dan FESEM. Pengurangan hablur dan saiz kristalit dalam nanoselulosa telah diperhatikan selepas rawatan cecair ionik. Kestabilan haba semakin menurun dan sisa pirolisis meningkat. Hasil ini menunjukkan kebanyakkan struktur kristal selulosa telah dimusnahkan dan menukar kepada struktur amorfus, manakala baki struktur kristal selulosa telah menukar menjadi selulosa II dari selulosa I dalam α-selulosa. Struktur yang lebih amorfus bagi selulosa selepas rawatan BMIMCl mengakibatkan penurunan dalam kestabilan terma. Hasil kajian ini berpotensi digunakan dalam pelbagai bidang seperti tekstil, penyampaian ubat dan hidrolisis enzim untuk pengeluaran bio-tenaga.

CHAPTER 1

INTRODUCTION

1.1 General Background

In the 21st century, the increasing of environmental crisis caused by non-renewable material has pushed towards the development of new types of green bio-based, green and degradable materials from natural sources for applications in which synthetic polymers or inorganic fillers are traditionally used. In this context, intensive study has been devoted to cellulose, and especially to cellulose which has revealed to be an interesting model filler in various matrices known as cellulose nanocrystals (CNCs) (Moura *et al*.,2011). Given their renewable character, cellulose-containing materials have been proposed as sustainable alternatives to petroleum-based feedstock.

A lignocellulosic material contains 35–50% cellulose, up to 35% hemicelluloses, 5–30% lignin as well as a few percent of extractives. Agriculture residues are important lignocellulosic material (Jiang *et al*., 2011). The use of residual biomass as feedstock for the production of high performance materials, enables a possible commercial application in view to generate value-added products from agro industrial waste. Rubber tree is one of the main agricultural products that exist, it being the most produced latex in the Malaysia. Rubber wood sawdust is an important agricultural waste that can be easily found in some states of Malaysia (Kamphunthong *et al*., 2012).

As an agricultural plant, the rubber tree *(Hevea brasiliensis*) has become one of the major crops that contributes to economic growth of Malaysia. The rubber wood is a type of wood that consist abundant lignocellulosic materials in Malaysia. Rubber tree is a major industrial crop grown in Southeast Asia with an estimated plantation area of 1.8 million ha (20% of global plantation) in Malaysia alone (Alhasan *et al.*, 2010). This type of wood is used mainly in the production of furniture and a large amount of sawdust is produced as industrial waste. This natural waste bio-resource can become a potential raw material for the production of nanocellulose due to its high cellulose content.

In general, cellulose is a fibrous, tough, water-insoluble substance that plays an essential role in maintaining the structure of plant cell walls. Cellulose is characterized as a natural high molecular weight linear homopolymer constituted of repeating *β-D*-glucopyranosyl units joined by 1–4 glycosidic linkages in a variety of arrangements. Cellulose, an important structural component of plants have received much attention because of the emerging potential associated with nanomaterials and nanotechnology (Bettaieb *et al.*, 2015). The crystalline structure of native cellulose corresponds to the polymorph known as cellulose I. However, if dissolved and regenerated from a solution, it most often crystallized in a thermodynamically more stable crystalline form, called cellulose II (Azubuike *et al.*,2012). Cellulose II nanoparticles also classified as one type of nanocellulose.

Nanocellulose has many unique characteristics such as lightweight, low density, high surface area, high aspect ratio and even modifiable surface properties due to the reactive OH functional groups. Furthermore, evaluation of its biodegradable properties in aqueous environment has been conducted according to the OECD standard. In fact, biodegradation rate of nanocellulose is much faster than that of their macroscopic counterpart, whereas other type of carbon-based nanomaterials such as fullerenes and carbon nanotubes are not providing any biodegradation property (Brinchi *et al*., 2013). The main reason of fast biodegradation rate is attributed to its natural structure which derived from and constitute for the macroscopic cellulose. Synthesizing regenerated nanocellulose from lignocellulosic materials is very useful in various applications such as a potential use as excipients in the pharmaceutical industry.

In this work, rubber wood sawdust used as an alternative feedstock to produce nanocellulose. Research on the nanocellulose isolation using acid hydrolysis has been reported by a few researchers (Brinchi *et al*., 2013; Jiang & Hsieh, 2013). However, no studies could be found yet on the conversion of the cellulose to nanocellulose isolated from rubber wood using ionic liquid. Therefore, this study introduce a relatively new green chemistry approach for the preparation of nanocellulose using 1-butyl-3-methylimidazolium chloride (BMIMCl) as solvent. Ionic liquid (IL) is suggested to perform as a reaction medium for the solvolysis or dissolution of cellulose to disrupt the hydrogen bonding in the present study. The aim of this study is convert cellulose isolated from rubber wood sawdust to nanocellulose using ionic liquid. The properties of nanocelluloses extracted from rubber wood were evaluated and compared.

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1.2 Problem Statement

The increasing number of agriculture waste is a serious problem towards the environment. This is because development of agriculture sector creates numerous amount of agriculture waste. Rubber wood sawdust is one of the abundant agricultural waste in Malaysia. Nanocelluloses are expected can be prepared from natural industrial waste derived from rubber wood sawdust. Utilizing rubber wood sawdust as a source for nanocellulose production will tackle the problem of rubber wood waste being left out in the field or burned and contribute to the economy by turning it into valuable products. Besides that, this will also conserve energy and reduce waste because the products are considered as sustainable green materials.

Acid hydrolysis is by far the most popular method for nanocellulose production known for its effectiveness, since last decades. However, this method is not recommended because it usually requires relatively harsh conditions such as extreme acidic condition and often using hazardous chemicals such as concentrated acids and alkaline and hence, is not environmental friendly. Furthermore, acid hydrolysis might be contributed to serious environmental threats due to the acid recovery and reuse issues once discharged into the effluent streams (Harmsen *et al*., 2010; Lee, Hamid & Zain, 2014; Sun & Cheng, 2002).

In the limelight of this issue, the demand for the implementation of “green” processes for cellulose processing is getting more considerable attentions. The use of ILs for cellulose processing is suggested to be a green technology with their non-toxic and non-harsh characters under mild conditions because ILs are able to recyclable and reusable, thereby effectively reduced solvent consumption. ILs are capable to solubilize cellulose by causing the disruption to the hydrogen bonding network of cellulose (Wang *et al*.,2011). Therefore, ILs can be employed as substitution to the traditional volatile organic solvents and conventional acids in the production of nanocellulose. Besides that, atmospheric solvent loss and flammability hazard can be minimized via the application of ILs because they have low vapour pressure and better thermal stability. Moreover, they are ease of recovering and the ability to recycle and reusable contribute to the lower operating cost of the catalytic process (Tan *et al*., 2015). In overall, the substitution of acids by ILs can act as an environmentally friendly approach to synthesis the nanocellulose.

Development of new materials and green processes are driven by the goals to achieve green chemistry, sustainability and eco-efficiency. To date, environmental concerns have gained considerable attention and cannot be neglected. Therefore, the establishment of recycle-based and sustainable communities is becoming increasingly important. A strong driving force is initiated toward the exploitations of nanocellulose as a promising renewable, sustainable and biodegradable material into the synthetic development of environmental friendly and biocompatible products (Lin *et al*., 2014).

1.3 Objectives

The objectives for this study are:

1. To extract cellulose from rubber wood sawdust.
2. To study the effectiveness of BMIMCl to convert cellulose to nanocellulose.
3. To characterize the thermal properties and morphological properties of nanocellulose obtained from the extraction of rubber wood.

1.4 Scope of Research

In this study, in order to extract the cellulose from the lignocellulosic waste, the rubber wood sawdust is used. Rubber wood is chosen due to its availability in Malaysia which is easy get in the market. The rubber wood is highly potential to produce cellulose. This study is conducted using soxhlet extraction and ionic liquid solvent. Regenerated cellulose is prepared successfully in BMIMCl through dissolution and regeneration approaches. The resultant nanocellulose that regenerated from IL was then further isolated by washing to remove the residual IL. Nanocellulose was allowed to freeze dry prior performing characterizations.

Then, multiple characterization techniques were used to characterize the BMIMCl treated celluloses in terms of morphological, physical, chemical, structural and thermal properties. The crystallinity and phase structure of cellulosic samples were characterized by XRD and chemical functional groups was investigated by FTIR. Moreover, the FESEM was used to illustrate the morphology of the BMIMCL treated sample. Besides that, thermal decomposition behavior of cellulosic samples were determined by TGA.

CHAPTER 2

LITERATURE REVIEW

2.1 Lignocellulosic Natural Fiber

Lignocellulose is a combination of lignin, hemicellulose and cellulose which compacted to form lignocellulose biomass (Ng *et al.*, 2015). Wood is a renewable source for cellulose, lignin, hemicelluloses and extractives. A lignocellulosic material contains 35–50% cellulose, up to 35% hemicelluloses 5–30% lignin as well as a few percent of extractives and utilize in more environmentally friendly way has been a very active research area during the recent years (Mäki-Arvela *et al*., 2010). The isolation of nanocellulose from wood sources is less popular compared to non-wood sources. This is partly due to the higher amount of lignin (~ 20 wt %) in wood compared to non-wood materials (2–3 wt % lignin), which has to be removed from the fibers (Kamphunthong *et al.*, 2012). Due to the wood resources consist of higher amount of lignin compared to other types of biomass, it make more recalcitrant and resistant than the other feedstock in cellulose separation step (Lee *et al*., 2014). However, lignocellulosic resources remains the most important raw material source of cellulose (Wang *et al*., 2011). Therefore, with appropriate methods, production of nanocellulose from the lignocellulosic wood resource is possible. Rubber wood is one of the popular lignocellulosic nature tropical wood in the Malaysia.

2.2 Rubber Wood

In Southeast Asia, rubber wood is a type of wood taken from rubber tree. It is valued for its dense grain, minimal shrinkage, attractive colour, and acceptance of different finishes. This wood is used mainly in the production of furniture, and a large amount of sawdust is produced as industrial waste (Kamphunthong *et al*., 2012). Rubber wood is lignocellulosic nature, composed of flexible cellulose fibers assembled in an amorphous matrix of lignin and hemicellulose. Chemical compositions of this wood show that its main components are cellulose (∼30–50% by weight), hemicellulose (∼19–45% by weight), and lignin (∼15–35% by weight). The cellulose fiber of rubber wood is a non-branched polymer of (1→4) *β-O*-glucopyranose linkages between glucose units (Mahdavi *et al*., 2011**)**. The composition of rubber wood powder determined by the USDA's method in the previous study is shown in Table 2.1 (Petchpradab *et al*., 2009).

The other major components of rubber wood are hemicelluloses and lignin. Hemicellulose is a branched multiple polysaccharide polymer composed of different types of sugars including glucose, xylose, galactose, arabinose, and mannose. Lignin is a highly crosslinked phenolic polymer. Both hemicellulose and lignin are amorphous polymers, whereas cellulose is a semicrystalline polymer. There are two types of linkages between carbohydrate groups and lignin. One is an ester-type bond between the hydroxyl of lignin and the carboxyl of uronic acid in hemicellulose (Sheltami *et al*., 2012).

In the present investigation, rubber wood has been used for the production of microcrystalline cellulose and nanocellulose. Rubber wood fibers generally have a high elastic modulus of about 10 GPa. However, by use an appropriate isolation method to extract the nanofibers from rubber sawdust, crystalline cellulose or cellulose nanofibers with a modulus comparable to commercial E-glass fiber (~ 100 GPa) can be obtained. These cellulose nanofibers have great potential for use as reinforcements in biocomposites for construction, automotives, and furniture because of their high strength, recyclability, and environmental sustainability (Kamphunthong *et al*., 2012)

Table 2.1: Chemical composition of rubber wood (Petchpradab *et al*., 2009)

Composition of rubber wood	**Percentage based on dry weight (%)**
Hemicellulose and cell wall	29%
Lignin	28%
Cellulose	39%
Ash	4%

2.3 Cellulose

Cellulose, an organic component from the primary cell wall of green plants with the formula $(C_6H_{10}O_5)n$, is the most common organic compound on earth (Li *et al.*, 2009). In general, cellulose is a fibrous, tough, water-insoluble substance that plays an essential role in maintaining the structure of plant cell walls. The most common cellulose is name as alpha-cellulose consists of 100% of cellulose. Cellulose is a long polymer chain which builds up by the condensation of basic unit called beta-glucose related to next glucose unit together by β-1,4 glycosidic bond linkage, as shown in Figure 2.1. Each glucose unit is oriented 180 ° to its neighbours. The cellulose content differs for different plant species. Cotton has the highest content of cellulose (90~99 %), wood (40~50 %), jute (60~70 %) and flax fibers (~80 %) are all main sources of cellulose (Aboody, 2013).

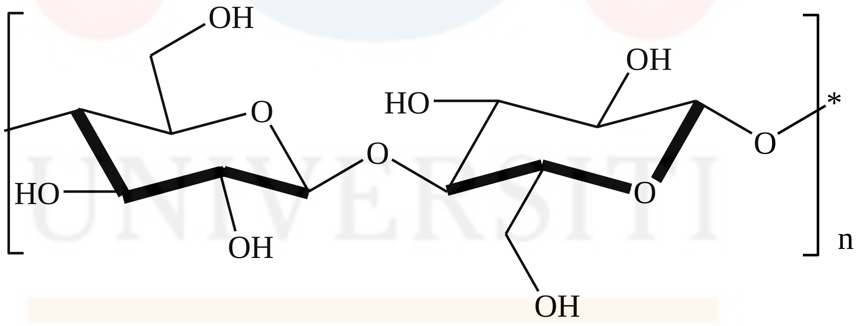

Figure 2.1: Structure of cellulose (O'Sullivan,1997)

In nature, the cellulose molecular chains are biosynthesized and self-assembled into microfibrils, which are composed of crystalline domains and amorphous. Crystalline cellulose are strong and inaccessible structural elements. As against, amorphous cellulose consists of disordered structure with chain segments that having the length as short as the order of one cellobiose unit. Amorphous regions are weak and accessible places of the fibrils which held by van der Waals forces (Ioelovich, 2016). Cellulose chains are packed in an ordered manner to form compact microfibrils, which are stabilized by both inter-molecular and intramolecular hydrogen bonding. Each cellulose chain has two ends, one with an original C4-OH group is called the non-reducing end and the other with an original C1-OH is called the reducing end (Aboody, 2013).Within the cellulose fibrils there are regions where the cellulose chains are arranged in a highly ordered structure called crystallites and regions that are disordered called amorphous. It is these crystalline regions that are extracted, resulting in nanocellulose (Brinchi *et al.,*2013).

In the crystalline regions, cellulose chains are tightly packed together in crystallites, which are stabilized by a strong and very complex intra- and intermolecular hydrogen-bond network. The hydrogen-bonding network and molecular orientation in cellulose can vary widely, which can give rise to cellulose polymorphs or allomorphs, depending on the respective source, method of extraction, or treatment. In the crystalline regions the inter- and intra-molecular interactions networks and the molecular orientations can vary, giving rise to cellulose polymorphs or allomorphs (Moon *et al*., 2011). Generally, cellulose displays six interconvertible polymorphs, namely, I, II, III_I, III_{II}, IV_I, and IV_{II}, with the possibility of conversion from one to another (Habibi *et al*., 2009).

Native cellulose has been thought to have one crystal structure, cellulose I, but occurs in two suballomorphs designated I_α and I_β, coexisting in variable portions depending on the origin of the cellulose (Habibi *et al*., 2009). While cellulose I_α consists of triclinic unit cells, the I_β allomorph which is predominant in higher plants exhibits a monoclinic type of unit cells (Khalil *et al*., 2012). Cellulose I (α and β) has sheets stacked in a “parallel-up” fashion, and the hydroxyl methyl groups are oriented in a *tg* conformation so that their O6 atom points toward the O2 hydroxyl groups of the neighboring residue, which engenders a second inter-residue hydrogen bond. During conversion of cellulose I to cellulose II, the hydroxyl groups rotate from the *tg* to the *gt* conformation, which explicitly requires a change in the hydrogen-bond network (Habibi *et al*., 2009).

At present, it seems generally accepted that cellulose II consists of antiparallel chains, opposed to the parallel arrangement of the glucan chains in cellulose I (Lennholm & Iversen, 1995).The chains in cellulose II are in an antiparallel arrangement yielding a more stable structure, which makes it preferable for various textiles and paper materials (Habibi *et al*., 2009). Cellulose II has been rarely found in nature (e.g. in the marine algae Halicystis), but it can be produced artificially from cellulose I by regeneration or mercerization (Besseuille & Bulone, 2008). The regeneration process involves dissolution of the cellulose in a specific solvent (e.g. N-methylmorpholine-N-oxide), while in the mercerization process the cellulose is only swollen in aqueous sodium hydroxide (Khalil *et al*., 2012). The interconversion of the polymorphs of cellulose is shown in Figure 2.2 (O’Sullivan, 1997).

The transformation of the cellulose structure from native cellulose I into cellulose II is possible after alkali treatment or mercerization (Borysiak & Doczekalska, 2005). If cellulose I or II is exposed to ammonia or various amines, cellulose III is formed upon removal of the swelling agent. The resulting form of cellulose III depends on whether the starting form is I or II, giving rise to cellulose III_I or III_{II}. Their diffraction patterns are similar except for the meridional intensities. Furthermore, either of these forms III_I or III_{II} reverts to its parent structure if placed in a high temperature and humid environment. While polymorphs IV_I and IV_{II} may be prepared by heating cellulose III_I or III_{II}, respectively, up to 260 °C in glycerol. In a like manner to the case of cellulose III, these two forms can revert to the parent structures I or II (Habibi *et al*., 2009).

The properties of cellulose including good mechanical properties, low density, and biodegradability depend on the type of cellulose present. In both processes, a final re-crystallization step leads to the final cellulose II, which is thermodynamically more stable than the cellulose I allomorph (Khalil *et al*., 2012). However, the cellulose I form that has the highest strength (Borysiak & Doczekalska, 2005). According previous research, cellulose type I shows the best mechanical properties (Mandal & Chakrabarty, 2011).

Since the first discovery and isolation of cellulose by Anselme Payen in 1838, extensive studies on its physical and chemical aspects have been conducted to expand the niche regarding its promising structural features, biosynthesis and assembly as well as various processing techniques indeed (Habibi *et al*., 2010). Nowadays, the breakthrough on “nanocellulose” has triggered the subsequent interests in research by scientists and researchers from all over the world on nanocellulose and made it as an important component in many practical applications.

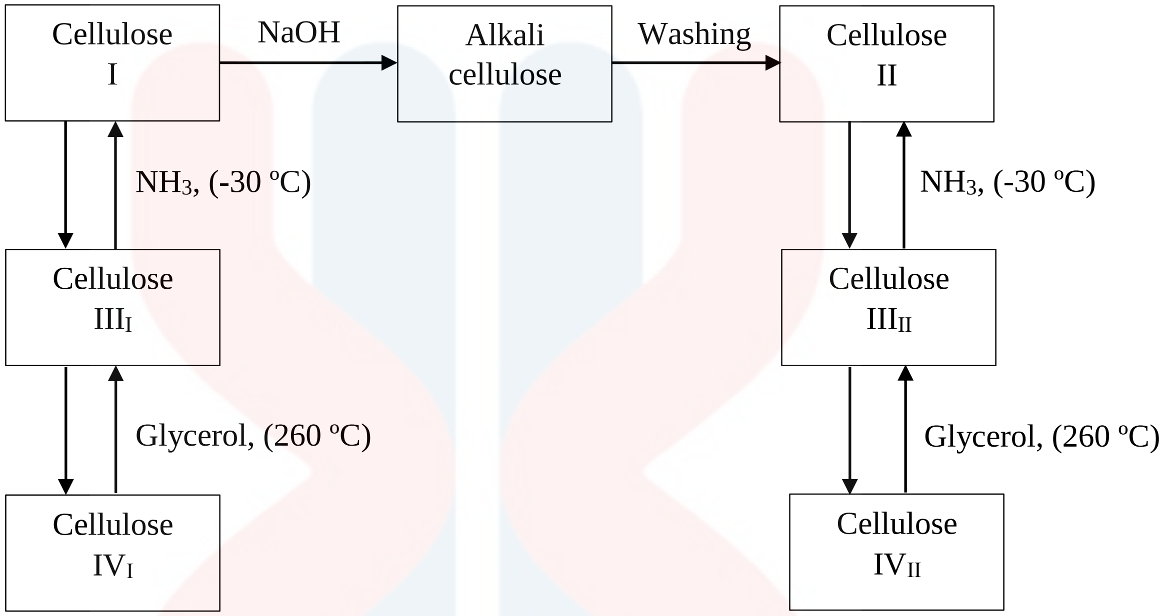

Figure 2.2: Interconversion of the polymorphs of cellulose (O'Sullivan,1997)

2.4 Extraction of Cellulose

The extraction of cellulose from the natural resources is varied according to the different research. Traditionally, cellulose is extracted from wood through the Kraft pulping process, which involves the semi-chemical degradation of the lignin or hemicellulose matrix by treatment with solutions of sodium hydroxide and sodium sulfide at high temperatures and pressures (Wang *et al*., 2011). Besides that, a protocol based on acidified sodium chlorite is frequently applied to delignify woody materials as an initial step in the extraction of cellulose (Loader *et al*., 1997). Apart from that, a modified protocol for cellulose purification based on the simultaneous delignification and removal of non-cellulosic polysaccharides (NCPs) using an acetic acid: nitric acid mixture (Brendel *et al*.,2000).

In this study, cellulose isolated from the lignocellulosic material by sequential removal of wax, lignin and hemicellulose following the method of TAPPI test method T204. According to the previous research, pure cellulose was isolated from rice straw (Calrose variety) by a three-step process of 2:1 v/v toluene/ethanol extraction, acidified $NaClO_2$ dissolution of lignin (1.4%, 70 ºC, 5 h) and alkaline dissolution of hemicellulose and silica (5% KOH, 90 ºC for 2 h) to a 36% yield (Lu & Hsieh, 2012).

2.5 Nanocellulose

Nanocellulose generally refers to the cellulose structure that exists in nanometer scale, precisely range from 1 to 100 nm for at least one of its dimensions (length, width or diameter).On the basis of their dimensions, functions, and preparation methods, which in turn depend mainly on the cellulosic source and on the processing condition (Brinchi *et al.*, 2013). Nevertheless, the nomenclature for nanocellulose has not yet standardize and this presents ambiguities in the naming of cellulose particles with dimensions in nanometer range (Klemm *et al*., 2011). There are two general types of nanocelluloses are recognized, namely cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). These two nanocelluloses can be distinguished by their different production processes and structures. CNFs having a high aspect ratio in both amorphous and crystalline regions (Khalil *et al.*, 2014). However, CNCs is the whisker form of nanocellulose and generally refer to the crystals with nanometer in the cellulose.

Properties of nanocelluloses are usually affected by the source of cellulose and also by their isolation method. Usually, CNCs are prepared by strong acid hydrolysis (for example: 64% sulfuric acid) of cellulose to remove amorphous regions, to obtain needle-like morphologies with 10-20 nm in diameter and several hundred nanometers in length. On the other hand, CNFs are prepared by TEMPO-mediated oxidation, mechanical methods, or enzymatic hydrolysis to obtain long flexible fiber networks with a fibril diameter similar to or larger than CNCs depending on the degrees of fibrillation (Oun & Rhim, 2016). The optimum content of cellulose and possible formation of nanocellulose are important issues to address in order to form an ideal nanoscale cellulose with desired properties.

CNCs are endowed with several characteristics which make them unique. They are high surface area, unique optical properties, high crystallinity, exceptional mechanical properties with high stiffness and Young's modulus up to 134 GPa as well as high tensile strength (up to 7.5 GPa), together with the biodegradability and renewability of cellulose (Tan *et al*., 2015). This has made this intermediate a precious green alternative to materials, construction, packaging, automobile, transportation, and biomedical fields. Nanocellulose created a revolution in biobased materials for diverse applications (Lee *et al*., 2014). Among the potential applications for nanocellulose may be mentioned are paper and paperboard products, bionanocomposites in foods, cosmetics, medical, optical devices, pharmaceuticals, chemicals with dispersion and emulsion and oil recovery. Besides that, nano-size cellulosic materials is also a good candidate for the preparation of polymer nanocomposites (Souza *et al*., 2010).

According to the research by Boldizar *et al.* (1987), nanocellulose had been use as reinforcement for various polymer including polypropylene, polystyrene and high density polyethylene. Compared to inorganic fillers, the prime advantage of propagating nanocellulose includes their renewable, low cost, low density, and nonabrasive nature, which allows them to formulate bio-based nanocomposites with easy process ability (De Mesquita *et al*., 2010). Because of having well dispersed nano-sized particles in the composites, they exhibit remarkably improved mechanical, thermal, and physicochemical properties with very low levels of reinforcement (usually less than 5 %) and have a little impact on the optical property when compared to pure polymers or conventional composites (Souza *et al*., 2010). This is proved that the nanocomposites had significantly higher mechanical properties than conventional composite even at such low nanocellulose loading.

Furthermore, it is a well-known fact that nanocellulose has inherent renewability, sustainability as well as biodegradability and biocompatibility. Biodegradability of nanocellulose has been evaluated according to OECD standard 301B (Organization for Economic Co-operation and Development) at where cellulose nanoparticles were degraded in aqueous environment much faster than that its corresponding macroscopic structure (Brinchi *et al*., 2013). On the other hand, other carbon-based nanomaterials such as fullerenes and carbon nanotubes are non-biodegradable at all. Therefore, nanocellulose can be applied as environmental friendly material such as biodegradable plastic to replace the dependence on petrochemical-based products.

Apart from that, the regenerated nanocellulose with the cellulose II polymorph have some preferable properties over cellulose I polymorph. Besides applications in smart materials, such as electro-activepaper (EAPap), sensors and actuators. Uses such as the recently introduced new filler/binder for solid dosage forms, and have been recommended as a second-generation multifunctional direct compression excipient, affording the manufacture of rapidly disintegrating tablets (Azubuike *et al*.,2012; Han *et al*.,2013). Many scientists and researchers believed that improvement of hydrophilicity with excellent biocompatibility as well as their biodegradability properties would broaden the interest of nanocellulose as a promising smart and green material in the field of composite, packaging as well as biomedical applications.

Preparation of nanocellulose from agricultural residues is one of the promising strategies for eliminating the cost of landfill disposal associated with using synthetic polymers (De Mesquita *et al*., 2010). Many researchers have been extensively studied the preparation and extraction of nanocellulose from several agricultural sources such as wheat straw and soy hulls (Alemdar & Sain, 2008), hemp (Luzi *et al*., 2014), marinebiomass (Bettaieb *et al.*, 2015), cotton linter (Morais *et al*., 2013), coconut husk fibers (Rosa *et al*.,2010) and bamboo residues (Abe & Yano,2010) etc. In this study, we use the rubber wood sawdust as the agricultural waste for the preparation the nanocellulose. Nanocellulose is fabricated with the aim to provide an environmental friendly materials as an alternative to plastics materials.

2.6 Isolation of Nanocellulose

Nanocellulose can be extracted by various methods. There are different mechanical and chemical methods that can be used for preparation of nanocellulose from lignocellulosic biomass (Chirayil *et al*., 2014). According to the research by Khalil *et al*. (2014), nanocellulose can be produce using some techniques such as refining, homogenization, grinding, cryocrushing, and acid hydrolysis. High-pressure homogenization is one of the mechanical processes which can be used for the production of nanocellulose. Beside homogenization, refining, cryocrushing, grinding, which are similar to homogenizer, can also be considered as other mechanical approaches to reduce the size of cellulosic fibers from micro- to nanoscale. However, this production route is normally associated with high energy consumption for fiber delamination (Khalil *et al*., 2014). Chemical methods such as acid hydrolysis, alkaline-acid pretreatment, and oxidation pretreatment before mechanical processes can decrease the energy consumption (Chirayil *et al*., 2014).Therefore, the chemical treatment become the most popular way to isolate cellulose from the natural sources.

Among the several methods for preparing cellulose nanostructures, the acid hydrolysis is the most well-known and widely used. This process breaks the disordered and amorphous parts of the cellulose, releasing single and well-defined crystals. This event is supported by the fact that the crystalline regions are insoluble in acids under conditions in which they are employed (Silvério *et al*.,2013).

Acid hydrolysis generally is using either sulphuric acid (H_2SO_4), hydrochloric acid (HCl) or a combination of these two acids at various concentrations (Khalil *et al*., 2014). According to the previous research, the CNCs are prepared by strong acid hydrolysis of cellulose to remove amorphous regions, to obtain needle-like morphologies with 10–20 nm in diameter and several hundred nanometers in length (Oun & Rhim, 2016). The isolation of CNCs from natural resources usually occurs in two stages. The first stage is a pre-treatment of the source material. For wood and plants it involves the complete or partial removal of matrix materials such as hemicelluloses and lignin. The second one is a controlled chemical treatment to remove the amorphous regions of the cellulose (Brinchi *et al.*, 2013). Under controlled conditions, acid hydrolysis allows removal of the amorphous regions of cellulose fibres whilst keeping the crystalline domains intact in the form of crystalline nanoparticles (Nuruddin *et al.*, 2011).

However, the concentrated acid used in acid hydrolysis is toxic, hazardous, and corrosive (Lee *et al.*, 2014). The use of these toxic chemicals and the intensive processing conditions involved in the chemical isolation procedure pose environmental hazards in the air and water (Wang *et al*, 2011). Therefore, efficient utilization of renewable resource with no hazards emission such as ionic liquid is necessary.

2.7 Ionic Liquid

Since Swatloski *et al*. first reported that ionic liquid BMIMCl could dissolve cellulose without any pretreatment, ionic liquids have attracted the attention of the scientific community. Ionic liquids (ILs), which are also referred to as room temperature ionic liquids, room temperature molten salts (RTILs) or organic ionic liquids. All of these refer to an ionic system which takes on a liquid state at the room temperature or slightly warmer. ILs are molten salts with glass transition or melting temperatures below 100 ºC. They are salts composed of organic nitrogen inorganic cations and inorganic anions (Feng & Chen, 2008). Recently, ILs that being considered as green solvents have been successfully used to dissolve and process lignocellulosic materials without derivatization

(Shamsuri & Abdullah, 2010). ILs offer a potentially clean method for carrying out isolation of nanocellulose from the natural cellulose source materials.

Contrary to ILs, most salts or ionic compounds have high melting points because the electrostatic interactions that hold the compounds together are very strong. A good example to be presented is that sodium chloride (NaCl) with high melting point of 801 ºC and it exists as solid at room temperature. The strong coulomb attraction between cations and anions give rise to the formation of strong and stable crystal lattice structure. However, this phenomenon is not favorable for ILs due to the sufficiently distortion to the ordered ions structure that required for lower melting temperature of ILs.

In contrast to traditional volatile organic compounds, ILs have many attractive properties, including good chemical and thermal stability, non-flammability, immeasurable low vapor pressure, and recyclability (Tan *et al.*, 2015). ILs have optimized the compound characteristics such as a broader selection of anion and cation combinations, lower hydrophobicity, lower viscosity, enhanced electrochemical stability and the higher reaction rates which may lead to greater amount of output (Feng & Chen, 2008). ILs are capable of dissolving complex macromolecules and polymeric materials such as lignocellulose with high efficiency. ILs have gained much attention and became favorite research matter among various groups of scientists due to their above-mentioned interesting and unique features.

The most attractive characteristic of ILs is the adjustability of its physical, chemical and even biological properties by independent modification of the cation and anion (Jiang *et al.*, 2011). ILs can be hydrophilic and hydrophobic depending on the structures of cations and anions. The anion seems more important in determining the water miscibility of ILs (Zhao, Xia & Ma, 2005). Apart from that, ILs could be recycled up to three times compared to acid and alkaline isolation methods (Brinchi *et al*., 2013). Although the relatively high price of ILs prohibits their wide-scale application in the industry, their effective recover and large-scale production could avert this problem (Wang *et al*., 2011).

ILs have been investigated to act as a powerful solvent for cellulose dissolution and hydrolysis owing to their excellent solvency properties and process benefits. In 2002, Swatloski and his co-workers were the pioneer to discover that cellulose could be dissolved in high concentrations (up to 10 wt % cellulose) by heating (at around 100 °C) without derivatization using BMIMCl and the regenerated cellulose was less crystalline (Swatloski, Spear, Holbrey, & Rogers, 2002). Indeed, this experimental work presented a breakthrough for innovative new approaches about the cellulose dissolution which led to a development of a novel cellulose solvent. Since then, utilization of ILs for biomass processing has been growing exponentially and ILs were discovered to be effective in cellulose dissolution, as a reaction medium for functionalization and chemical reactions, to form cellulose composite materials and to produce cellulose films, fibers or beads (Wang *et al*., 2012).

IL treatment may constitute a versatile strategy for modification of the properties of cellulose powders, through physical dissolution under relatively mild conditions, in order to increase its industrial use and fulfill the various demands for functionality of different cellulosic products (Sun *et al*. 2011). ILs provide for versatile modification of the cellulose II powders (Azubuike *et al*., 2012). IL is capable of disrupting the hydrogen bonds by forming another hydrogen bond between anion of IL with cellulose (sugar hydroxyl protons) in 1: 1 ratio. This will break up the cellulose hydrogen bonded structure, thus decreasing the compactness of cellulose and making it more amorphous and susceptible to depolymerization process. Ionic liquid can dissolve both carbohydrates and lignin, which disrupt the intricate network of noncovalent interactions between these polymers. This treatment can reduce lignin content and cellulose crystallinity (Han *et al*., 2013).

The cations of ILs are often featuring an aromatic or cyclic structure and long alkyl chain. Common cations are alkylimidazolium, alkylpyridinium and quaternary ammonium based. Whereas the anions of ILs can be varied from chloride, formate, acetate, bromide, tetrafluoroborate, hexafluorophosphate or methanesulfonate (Gericke, Fardim, & Heinze, 2012). In fact, various combinations of cations and anions will contribute to the variety types of ILs.

Interestingly, ILs containing halide anions, especially anions, are particularly effective for solvation of cellulose. It has been reported that cellulose has a solubility of 10 wt % by conventional heating in BMIMCl while with a greater solubility of up to 25 wt % achieved by microwave heating (Rinaldi & Dwiatmoko, 2012). The greater capability of chloride anions based ILs to dissolve a high amount of cellulose are attributed to their high chloride concentration in ILs to disrupt and extensively break down the hydrogen bonding in cellulose, without caused derivatization (Cao *et al*., 2009).

This study will be concentrated on nanocellulos isolation that obtain from rubber wood and the nanocellulose isolation process was carried out in ionic liquid system. The ionic liquid that used in this research is BMIMCl. The chemical structure of BMIMCl ionic liquid as shown in Figure 2.3. BMIMCl is known to exhibit high viscosity of 11,000

MPa and melting point at 65 °C. The relatively high melting point and viscosity of BMIMCl caused dissolution of cellulose occurred at relatively higher temperature (often above 80 ºC) (Wang *et al*., 2012). BMIMCl, which is a good solvent for cellulose, exhibits relatively moderate toxicity compared to that of EMIMCl (Mäki-Arvela *et al*., 2010).

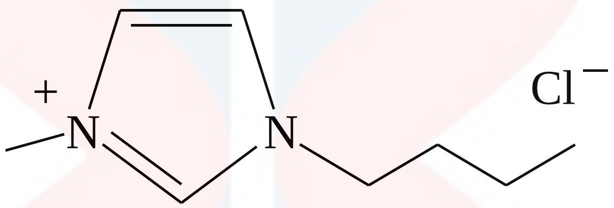

Figure 2.3: Chemical structure of BMIMCl (Islam *et al*., 2015)

CHAPTER 3

MATERIALS AND METHOD

3.1 Materials

In this study, the rubber wood sawdust were used as the raw material in this study. The raw material was collected from Kelantan, Malaysia. Chemicals that involved were ethanol, toluene, acetone, acetic acid (CH_3COOH), sodium chlorite ($NaClO_2$), sodium hydroxide (NaOH) and 1-butyl-3-methylimidazolium chloride (BMIMCl).

3.2 Methods

3.2.1 Sample preparation

The material that used for the study was rubber wood sawdust which collected from Jeli, Kelantan (Figure 3.1). The rubber wood sawdust were dried under the sun for 7 h to minimize the moisture content. Next, the raw material needed to be further dried in an oven for another 24 h under 60 ºC to prevent moisture (Mandal & Chakrabarty, 2011). After that, the rubber sawdust was turned into powder by passing through a 70-mesh stainless steel sieve.

Figure 3.1: Rubber wood sawdust

3.2.2 Preparation of free extractives sample

The isolation of cellulose was done following the procedure of Oksman *et al.*(2011) with a slight modification. About 10 g of rubber wood sawdust was weighed. Then, the sample was mixed with ethanol and toluene in the ratio 2:1 for 6 h at 150 ºC. Extractive of the rubber wood sawdust were removed by Soxhlet apparatus as described in TAPPI test method T204. The soxhlet apparatus setup as shown in Figure 3.2. The process was stopped after 6 h which the colour of solvent was changed from yellow or green colour into clear solvent in the timber. Then, the mixture was allowed to cool, which were then washed with distilled water and acetone. After that, the samples were dried at oven under 50 ºC for 24 h to remove traces of residual solvents and the solid in powder form were collected. The powder sample was known as free extractives sample and use for next process.

Figure 3.2: The soxhlet apparatus setup

3.2.2 Preparation of holocellulose

The TAPPI method was used to prepare the holocellulose from the previously extractive-free rubber wood sawdust samples. First, 5 g of the free extractive powder was weighed and placed in a conical flask containing 100 ml distilled water, preheated to 70 ºC, after which 5 ml of acetic acid (CH_3COOH) and 1.5 g of sodium chlorite ($NaClO_2$) were added, and the samples were maintained at 70 ºC. During the heating process, the mixture in the conical flask was covered with small conical flask to prevent the strong odour of chemicals gas release from the mixture (Figure 3.3). After that, 5 ml of 10% CH_3COOH was added for 30 min and subsequently 1.5 g of $NaClO_2$ was added for another 30 min. This process was repeated for 4 times in 4 h and the mixtures were kept at 70 ºC. After 4 h, the covered conical flask was placed in the ice for the cooling process about 20 min (Figure 3.4). After cooling process, the solid was then filter and washed several times using cold distilled water and acetone to remove any excess of residual chemicals. Figure 3.5 shows the vacuum filtration setup. Then, the samples were dried in the oven at 50 ºC for 24 h. The powder samples known as holocellulose were collected and used for next process (Oksman *et al*., 2011).

Figure 3.3: The heating process

Figure 3.4: The cooling process about 20 min

Figure 3.5: The vacuum filtration about 15 min

3.2.3 Preparation of α- cellulose

The production of α-cellulose has been obtained by elimination of hemicellulose from the holocellulose sample. Briefly, about 2 g of sample and 15 ml of 17.5 % of NaOH were placed in a conical flask and stirred for 1 min. After that, 10 ml of 17.5 % of NaOH was added and stirred for 45 s. Ten milliliters of 17.5 % of NaOH was then slowly added into mixture again and stirred for 3 min. This step was repeated for 4 times in 10 min, the each addition was about 2.5 min. The mixture in conical flask was then covered and stirred for 30 min by using magnetic stirrer (Figure 3.6). Subsequently, 100 ml of distilled water was added and the mixture was stirred at room temperature for another 30 min. The precipitated material was then filtered using a Buchner funnel, washed thoroughly with 8.3 % of NaOH and cool distilled water as well as followed by soaking with 2 N of acetic acid. Lastly, the residue was dried in an oven at 50 ºC for 24 h. All these steps were allowed the elimination of hemicelluloses, while leaving the α-cellulose (Oksman *et al*.,2011).

Figure 3.6: The mixture was covered and stirred on magnetic plate

3.2.4 Ionic liquid treatment

Mass fraction of 2 % extracted cellulose was added in a beaker containing BMIMCl ionic solution and a magnetic stirrer. Then, the heterogeneous mixture was heated in an oil bath at 90 ºC under continuous vigorous stirring on a magnetic hot plate stirrer for 12 h, as shown in Figure 3.7. After 12 h, the mixture was allowed to cool at room temperature for 30 min (Tan *et al.*, 2015). The regenerated cellulose was then filtered and washed with distilled water (Figure 3.8). Generally, the washing process is necessarily repeated by increasing numbers of times until the off-white precipitate cellulose are achieved as shown in Figure 3.9. The whole procedures were repeated with the mass fraction of 5 % extracted cellulose and ionic liquid solution. Two different mass fraction of IL treatment as shown in Table 3.1. The regenerated cellulose precipitates were kept in -80 ºC freezer (Figure 3.10) for 24 h followed by freeze drying it for 24 h (Figure 3.11) to obtain nanocellulose in powder form. The regenerated cellulose samples must be in frozen state (Figure 3.12) before undergo the freeze drying process. Finally, the regenerated cellulose samples of the rubber wood were labeled IL 2 wt % and IL 5 wt % depending on the mass fraction. The overall procedures of nanocellulose isolation from rubber wood has been briefly mind-mapped in Figure 3.13.

Table 3.1: Cellulose and IL content in IL treatment.

Mass fraction	Total amount (cellulose)	Total amount (IL)
2 wt %	0.8 g	39.2 g
5 wt %	2.0 g	38.0 g

Figure 3.7: IL treatment apparatus setup

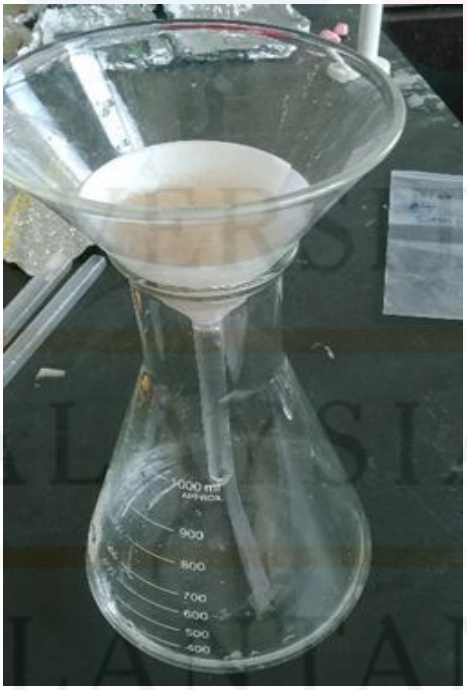

Figure 3.8: The filtering and washing process

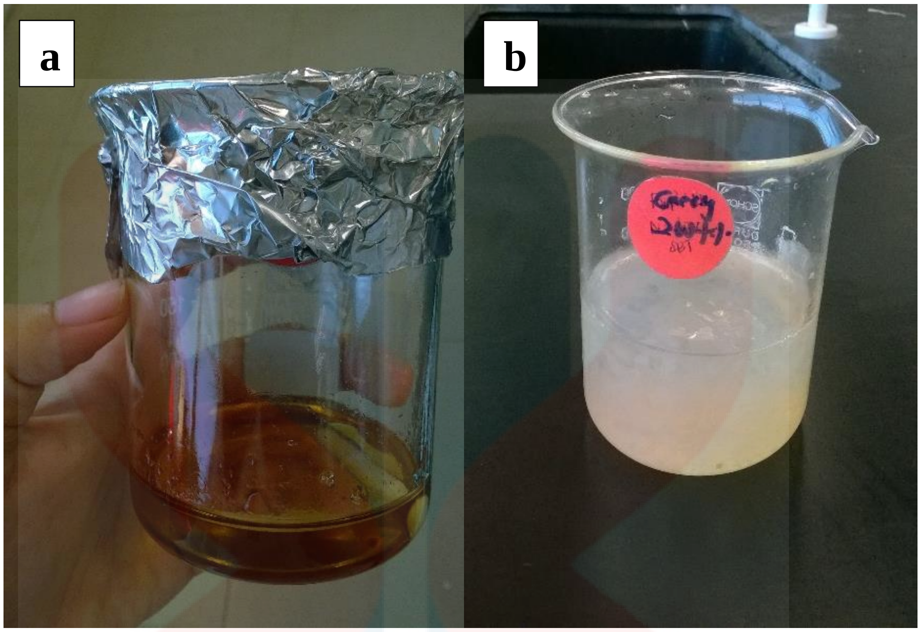

Figure 3.9: Nanocellulose precipitate (a) before and (b) after the washing process

Figure 3.10: The freezer at -80 °C

Figure 3.11: Freeze- drier

Figure 3.12: Nanocellulose sample in frozen state

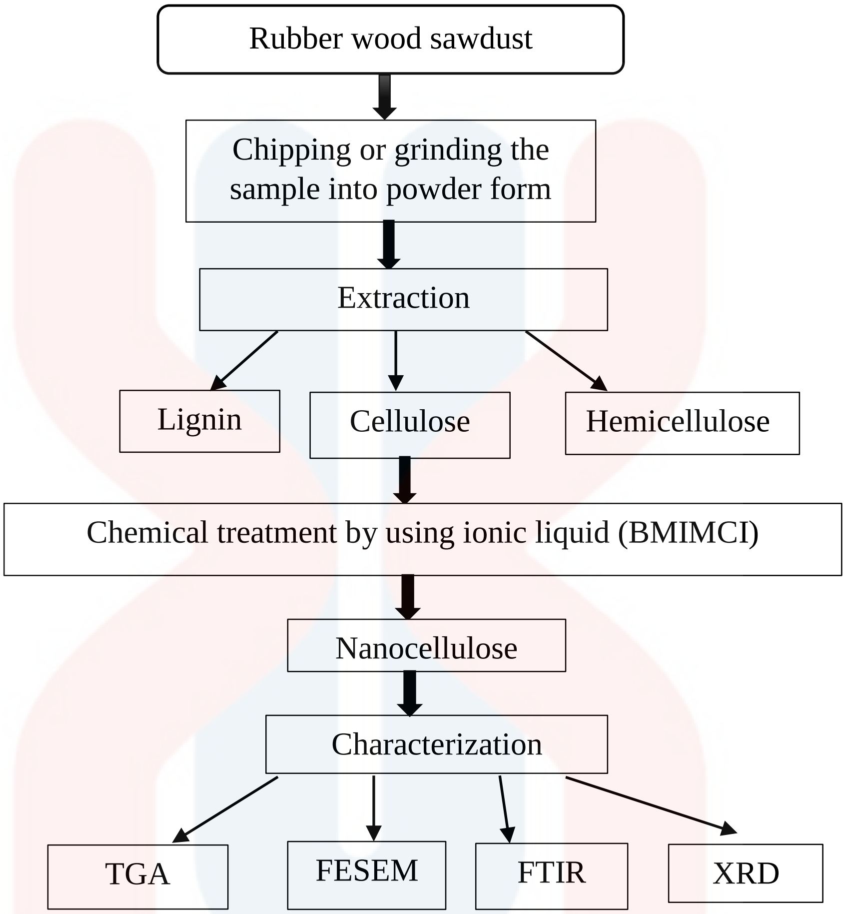

Figure 3.13: The flow chart for nanocellulose isolation process

3.3 CHARACTERIZATION

3.3.1 Field Emission Scanning Electron Microscopy (FESEM)

The morphology of samples were analyzed by JEOL (JSM-7800 F) FESEM at an accelerator voltage of 5 kV. The samples was coated with gold using sputter coater to avoid charging.

3.3.2 X-ray Diffraction (XRD)

The crystalline phase and crystallinity index of the samples were studied using an X-ray diffractometer (D2-Phaser Bruker XRD) equipped with a monochromatic CuKα radiation source ($\lambda = 0.154$ nm). The samples were scanned in the step-scan mode with a 2θ angle ranging from 5 º to 60 º with a step of 0.01 º and a rate of 1 º min^{-1} under room temperature. The operating voltage was 40 kV and the current was 40 mA.

In order to evaluate the crystallinity of the samples, the crystallinity index (CI) was determined based based on the reflected intensity data by using method of Segal *et al*. (1959):

$$\text{CI (\%)} = 100 \times (I_{200} - I_{\text{am}}) / I_{200}$$

where I_{002} is the maximum intensity for the crystalline portion in samples (i.e., cellulose) at about $2\theta = 22$ º and I_{am} is the intensity attributed to the amorphous portion of samples (i.e., hemicellulose and lignin) at $2\theta = 18$ º.

The crystallite size of each sample perpendicular to the (200) planes, *w* (nm), was calculated by the Scherrer equation (Scherrer,1918):

$$w = \frac{K\lambda}{\beta \cos\theta}$$

where θ is the diffraction angle, K= 0.94 (correction factor), λ = 0.154 nm and β is the corrected angular width in radians at half maximum intensity of the (200) peak.

3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra for cellulosic samples were recorded on a FTIR instrument (Nicolet iZ10 FT-IR Microscope) in the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. FITR technique was used to study the different functional groups of extracted cellulose from rubber wood sawdust, and evaluated structural variations of cellulose before and after ionic liquid treatment.

3.3.4 Thermogravimetric Analysis (TGA)

The thermal stability of the different samples was determined by TGA measurements performed using a Mettler Toledo thermogravimetric analyser (TGA/DSC). Approximately 7 mg of each sample was transferred into the alumina crucible with a pinhole and followed by heating from room temperature to 550 ºC at a heating rate of 10 K min^{-1}. All measurements were performed under a nitrogen atmosphere with a gas flow rate of 20 cm^3 min^{-1} in order to prevent any premature thermoxidative degradation. TGA curves expressed the weight-loss rate as a function of time.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Chemical and structural properties of untreated and BMIMCl treated cellulose

In order to study the effectiveness of ionic liquid to convert cellulose into nanocellulose, studies on the chemical and structural characteristics of the cellulosic samples are essential. The structural changes of cellulosic samples were analyzed by FTIR spectroscopy in the region of 400-4000 cm^{-1}, which is commonly used to study the fine structural characteristics of cellulose (Ang *et al*., 2012). FTIR spectroscopy show some useful information related to the change of hydrogen bonding during crystal transformation (Oh *et al*., 2005). The aim of using FTIR in present study is to measure the changes of the structure of the regenerated cellulose obtained after IL treatment.

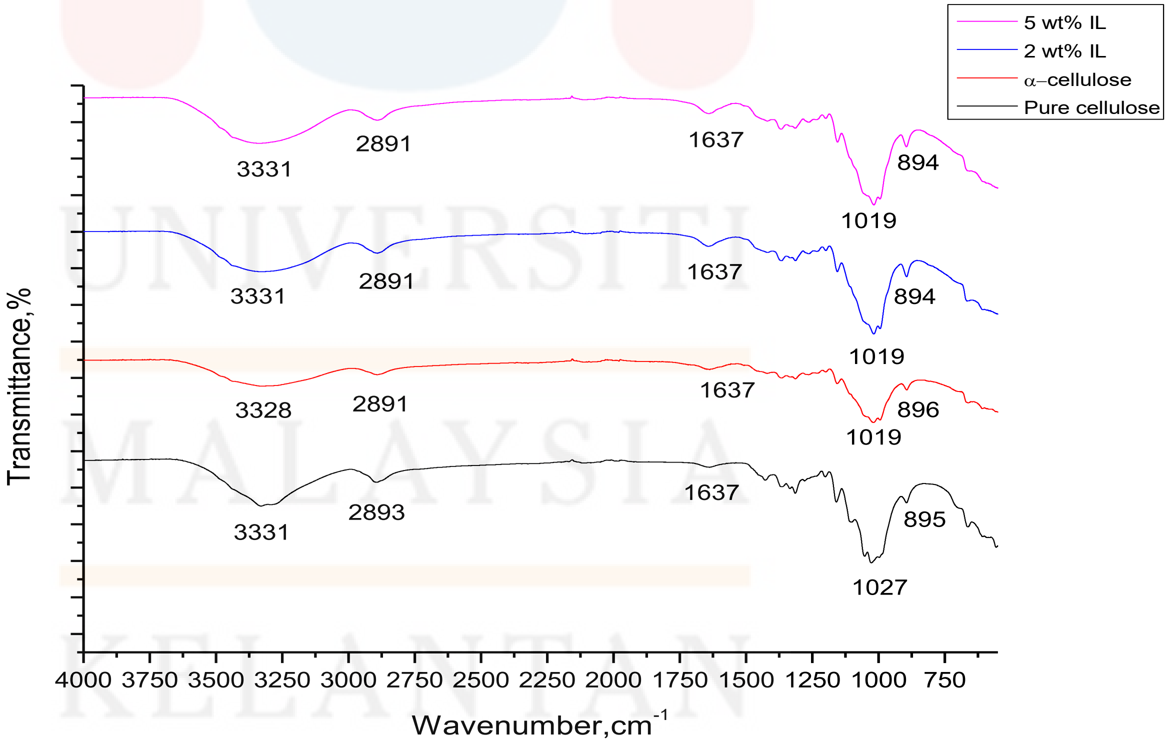

Figure 4.1: FTIR spectra of all cellulosic samples

Figure 4.1 illustrated that FTIR spectra of commercial pure cellulose, extracted *α*-cellulose and chemically treated celluloses of the rubber wood. The chemical treated cellulose was treated with BMIMCI at 2 wt % and 5 wt % . Evidently, the bands in the four spectra are rather similar, indicating the similar structure of the cellulosic samples either with or without IL treatment. All the cellulosic samples show the almost identical basic structure which indicated no changes in the functional groups. However, a slight difference can be detected in the infracted spectra in term of different absorbance value and shapes of bands and also their location.

Table 4.1: Group frequency of cellulosic samples (Ang *et al*., 2012; Liu & Chen, 2006)

Group frequency, wavenumber, cm^{-1}	Origin	Assignment
800-950	C-H	C-H deformation vibration in cellulose
1000-1200	C-O	C-O stretching vibration in cellulose
1500-1700	C=C	Aromatic C=C bending in lignin
1635-1640	O-H	O-H of water absorbed from cellulose
2850-2950	C-H	C-H stretching in cellulose-rich material
2995-4000	O-H	Free and hydrogen-bonded OH stretching

Table 4.1 shows the group frequency of absorption bands of the cellulosic samples and their assignments. Spectra of all the cellulosic samples show the strongest absorption band at 1019 cm^{-1}. This band corresponds to the stretching vibration of the C-O-C pyranose ring (antisymmetric in phase ring) of cellulose molecules (Mandal & Chakrabarty, 2011). The peak near 3331 cm^{-1}, which was observed in all spectra, is

attributed to characteristic hydrogen bond O-H stretching vibrations due to the presence of water. Cellulose is a linear polymeric compound has some important functional group within the cellulose units. The absorption around 2891 cm^{-1} observed in the four spectra which indicates the aliphatic saturated C-H stretching associated with methylene groups in cellulose. Moreover, the O-H bending of absorbed water bound to the cellulose structure gave rise to peak at 1637 cm^{-1}. Besides that, the absorption bands are clearly observed around 895 cm^{-1} corresponding to β-glycosidic linkages. In addition, the absence of peaks of IL (BMIMCI) in the spectra implied the complete removal of IL during the washing process (Han *et al*., 2013).

Compare between four spectrums, there were small differences of absorbances in spectrum of regenerated cellulose. The absorption from O-H stretching vibration shifted from 3328 cm^{-1} in spectrum of extracted α-cellulose to 3331 cm^{-1} in spectrum for 2 wt % and 5 wt % regenerated cellulose. This indicates the content of free hydroxyl group without cross-linking to form hydrogen bonds increased in regenerated cellulose nanoparticles (Zhang *et al*., 2005; Lan *et al*., 2011). Figure 4.1 shows that the band of extracted α-cellulose at 896 cm^{-1} shifted to 894 cm^{-1} for 2 wt % and 5 wt % treated cellulose. It was reported that the 896 cm^{-1} wavenumber can be assigned to the β-glucosidic linkage for the cellulose I structure and 894 cm^{-1} wavenumber to the cellulose II structure (Gwon *et al.*,2010). This change was due to the rotation of glucose residue around the glucosidic bond (Ray and Sarkar 2001).

The peak around 896 cm^{-1} was assigned to C-O-C stretching at β-1-4-glycosidic linkages, increased in intensity in the amorphous samples, compared to the other samples. The increase in the intensity of the peak around 896 cm^{-1} for 2 wt % and 5wt % regenerated cellulose compared to untreated cellulose as shown in Figure 4.1 indicates the structure of cellulose become more amorphous after the IL treatment. The intensity around 896 cm^{-1} band is very sensitive to the amount of crystalline versus amorphous structure of cellulose. The higher intensity of this band reflects higher amounts of disordered structure. Since disorder is expected by the different arrangement caused by changes in angles around *β*-glycosidic linkages and in hydrogen bond rearrangement thus, this band is assigned to deformation modes of COC, CCO, CCH and stretching vibrations in which motions of C5 and C6 atoms are strongly involved (Ciolacu & Popa, 2011; Proniewicz *et al*.,2001).

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X-ray diffraction measurements were performed on commercial pure cellulose, extracted α-cellulose, 2 wt % and 5 wt % IL treated cellulose, is shown in Figure 4.2. From Figure 4.2, it can be observed that the XRD show major intensity peak located at a 2θ value of around 22 °, which is related to the crystalline structure of cellulose for all samples, whilst the amorphous background is characterized by the low diffracted intensity at a 2θ value of around 12 ° to 16 ° (Segal *et al.*, 1959).

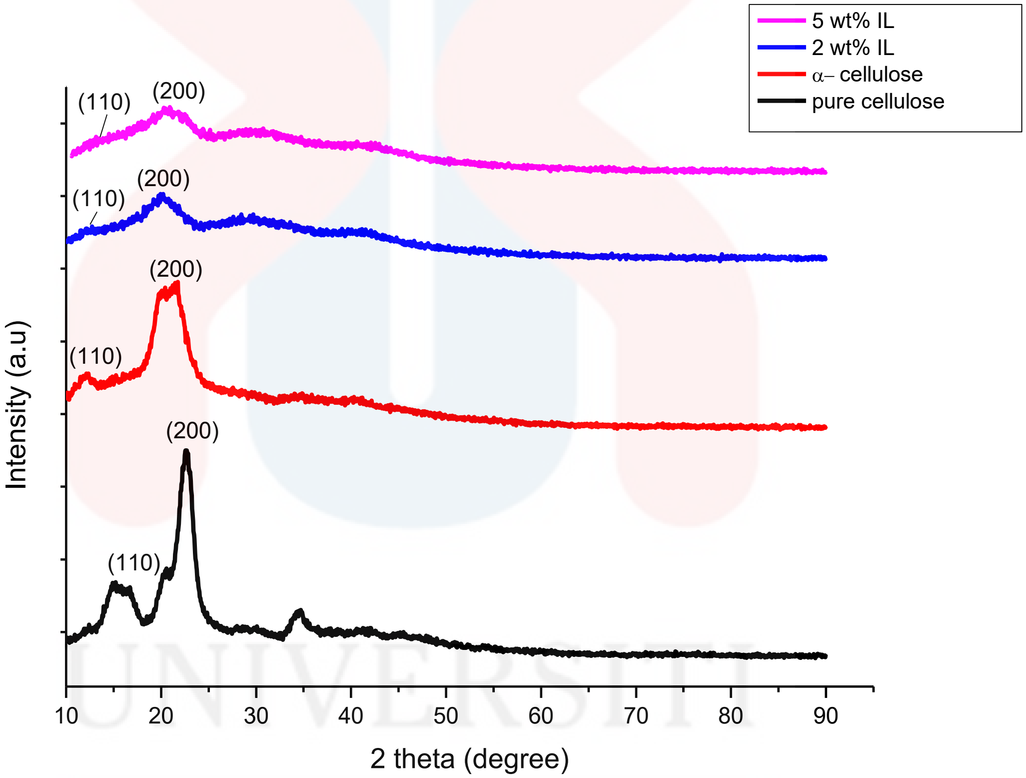

Figure 4.2: XRD pattern of all cellulosic samples

Results show that ionic liquid treated cellulose samples had broader diffraction peak compared to the untreated celluloses. In general, the broader diffraction peak indicated that more amorphous structure was present. Based on the diffraction pattern, the treated cellulose is more amorphous than the untreated cellulose. Besides that, the diffraction peak of 2 wt % IL treated cellulose shaper than 5 wt % IL treated cellulose. This implied that the 2 wt % treated cellulose consist highly crystallinity compared to 5 wt % treated cellulose. The diffraction peak also shift to the left after the BMIMCl treatment. The peaks are shifted towards lower diffraction angle suggest that lattice is expanded and related to the more amorphous structure.

Table 4.2 shows the peak positions and diffraction planes of the cellulosic samples. The extracted α-cellulose showed two well-defined diffraction peaks at 2θ = 14.3 º and 22.0 º, as the typical diffraction patterns of cellulose type I (Jin *et al*.,2011; Quan *et al*.,2009). However, two conspicuous broad peaks at 2θ = 12.1 º and 20.1 º were observed in the XRD patterns for 2 wt % regenerated cellulose, which were in accordance with the typical diffraction patterns of cellulose II, accompanying with lower crystallinity.

Table 4.2: Peak positions in x-ray diffractograms and diffraction planes of cellulosic samples

Samples	Diffraction angle 2θ (º)	
	(110)	(200)
MCC cellulose	16.9	22.7
α-cellulose	14.3	22.0
IL treated (2 wt %)	12.1	20.1
IL treated (5 wt %)	12.8	20.1

The peak at around 22 º (due to the 200 crystalline plane) present in the pure cellulose and extracted α- cellulose diffraction pattern are significantly weakened and shifted to 20.1 º (Table 4.2), indicating that there is minimal structural order in the cellulose after ionic liquid treatment (Lee *et al.*, 2009) and it likely due to the transformation from cellulose I to cellulose II (Sun *et al.*, 2009).

The crystallinity index (CI) is related to the strength and stiffness of fibers. The CI and the crystallite size for all samples were calculated from the XRD data and the results are tabulated in Table 4.3.

Table 4.3: Crystallinity indexes of cellulosic samples

Type of cellulose	Crystallinity index (%)	Crystallize size (nm)
MCC cellulose	72.69	4.61
α-cellulose	46.29	2.94
IL treated (2 wt %)	22.78	2.35
IL treated (5 wt %)	20.73	1.79

As shown in Table 4.3, the CI calculated from the IL treatment samples are significantly lower than either the untreated extracted cellulose or pure cellulose sample. High value of CI indicates an ordered compact molecular structure, which translates to dense particles; whereas lower value of CI implies a more disordered structure, resulting in a more amorphous powder. The similar decrease in CI values for reconstituted cellulose II powders was previously reported in the literatures (Han *et al.*, 2013; Jin *et al.*, 2012). Note that CI values for cellulose I and II cannot be directly compared, but in general comparable crystallinities of I and II should result in substantially lower CI values for cellulose II. Therefore, in the present case, with CI values for the regenerated cellulose being lower than the untreated and pure cellulose sample, the crystallinities of regenerated cellulose would be much lower. This demonstrated that the cellulose I is probably transformed into cellulose II after the BMIMCI treatment. Besides, the crystallite size of untreated pure cellulose and extracted cellulose calculated perpendicular to the (200) planes were 4.61 and 2.94 nm, while the 2 wt % and 5wt % regenerated cellulose had a crystallite size of 2.35 and 1.79 nm, respectively. The result shows the crystallite sizes of the BMIMCl treated celluloses smaller than the untreated extracted α-cellulose and pure cellulose. The reduced crystallite size of treated celluloses were likely because of the incomplete growing of crystallites after regeneration (Han *et al*.,2013; Gao, Shen &Lu, 2011).

XRD results suggested that CI of cellulose decreased after the IL treatment. These results indicate that transformation from cellulose I to cellulose II occurred after the IL treatment. The lower crystallinity regenerated cellulosic samples indicated that this interaction was not sufficient to completely reestablish the strong hydrogen bond network of original microcrystalline cellulose. Therefore, the cellulose treated with BMIMCl could only regain a lower crystallinity and reconstitute into nano-sized particles with cellulose II crystalline allomorph. This meant that, in the treatment process, IL gradually broke intermolecular and intramolecular hydrogen bond and destroyed the original crystalline form. This transformation from cellulose I to cellulose II because of the dissolution and regeneration in BMIMCl agrees with earlier findings (Han *et al*.,2013; Jin *et al*.,2012; Chen *et al*.,2012). Therefore, BMIMCl cannot only be used to extracted cellulose nanocrystals from lignocellulosic biomass, but also help converting cellulose I to cellulose II during the process.

4.2 Thermal properties of untreated and BMIMCl treated cellulose

Figure 4.3 shows the TGA curves of pure cellulose, extracted *α*-cellulose and BMIMCI treated cellulose samples for 2 wt % and 5 wt %. The small initial drops occurring below 100 ºC in all cases are corresponding to the evaporation of retained moisture loosely bound to the surfaces of cellulose (Mandal & Chakrabarty, 2011). This finding is in good accordance with the characteristic absorbance band of bending vibration of intermolecular bonded water interaction at 1640 cm^{-1} as observed in the FTIR spectra was reported in earlier section.

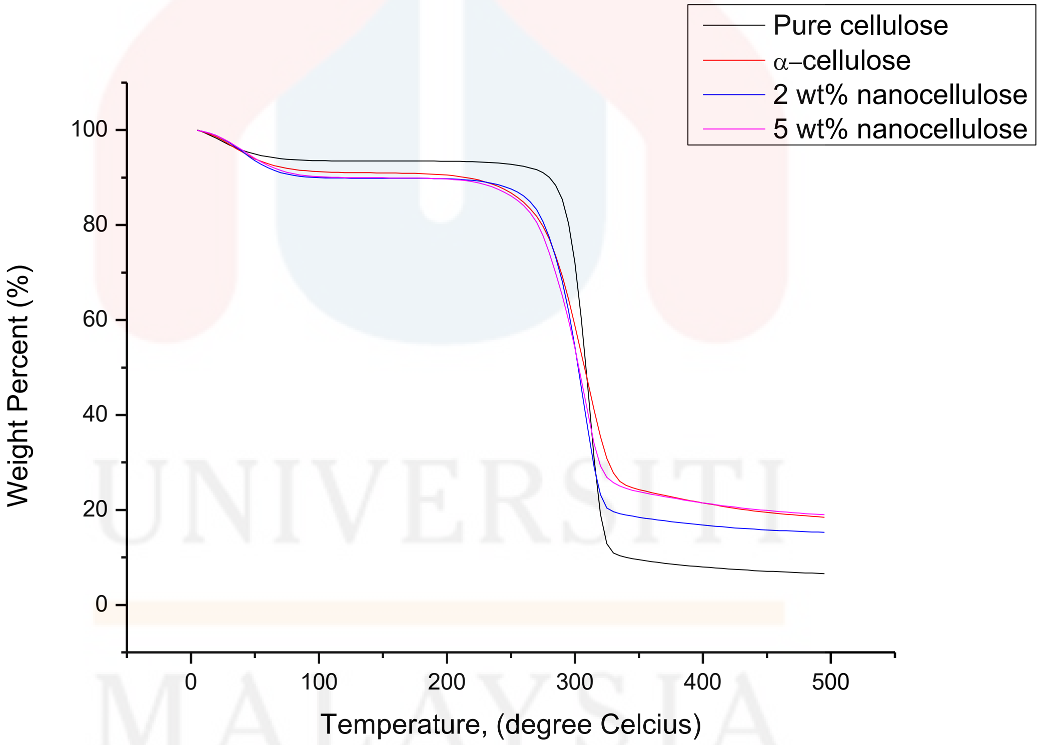

Figure 4.3: TG curves of all cellulosic samples

A single pronounced decomposition followed by slow weight loss was observed in all curves. As expected, the pure commercial cellulose starts to decompose at slightly higher temperature that is 276 ºC, compared to the regenerated cellulose samples for 2 wt % and 5 wt % which begin to decompose at 252 ºC and 250 ºC, respectively. These decreasing trends of decomposition temperature implied that the thermal stability of BMIMCl treated cellulose samples were lower than untreated cellulose. The reason of this decrement was probably due to the partial hydrolysis and degradation of macromolecular cellulose during ionic liquid treatment (Han *et al*.,2013).

The decomposition of all samples took place within a range of temperatures with single pyrolysis process as revealed by the DTG curve, as shown in Figure 4.4.

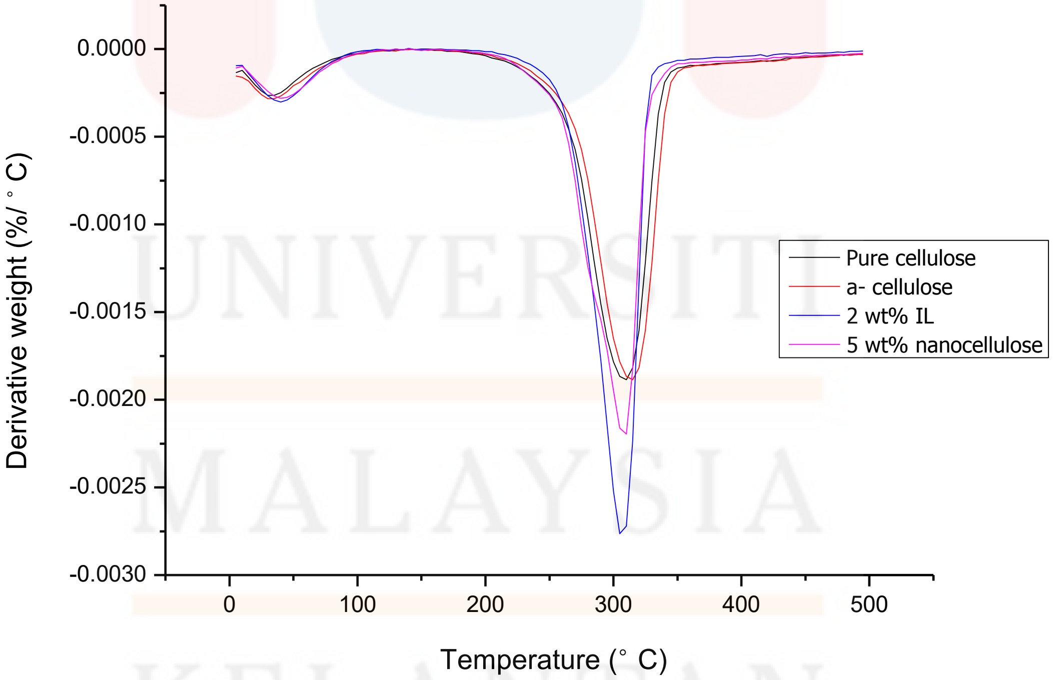

Figure 4.4: DTG curves of all cellulosic samples

The pyrolysis occurred ranging from 270 ºC to 370 ºC with T_{max} at 325 ºC, 323 ºC, 302 ^{o}C and 311 ^{o}C for extracted cellulose, pure cellulose, 2 wt % and 5wt % BMIMCl treated cellulose respectively. T_{max} values of IL treated cellulose samples were lower than the representative values for pure commercial cellulose and extracted α-cellulose from rubber wood. Similar phenomenon was reported previously (Chen,Wang & Liu, 2012). This demonstrated that the thermal stability of cellulose decreased after treated with BMIMCl, which was consistent with the observed decrease of crystallinity index of cellulose treated with IL. The decrease in thermal stability could be due to several reason. First, the adhesion of the anion group from the ionic liquid onto the surface of cellulose nanoparticles could have an effect on thermal behavior of cellulose (Han *et al*., 2013). Second, the high surface area of cellulose nanoparticles might be diminished their thermo-stability due to the increased exposure surface area to heat (Lu &Hsieh, 2010). This decreased thermal stability indicating that the decrease in molecular weight of the BMIMCI treated samples (Chen *et al*.,2012).

Although the BMIMCl treated celluloses had lower temperature for decomposition, the char yield (CY) at 550 ºC of ILtreated samples either 2 wt % or 5 wt % were greater than the pure cellulose and the extracted cellulose sample. Based on the result, the char residue of BMIMCl treated celluloses (15-19 %) was greater than untreated cellulose samples (13-14 %). The similar decreased pyrolysis residues of regenerated cellulose after ionic liquid treatment were reported by Luo *et al*., 2005. Pyrolysis residues are primarily indecomposable inorganic salts. The higher pyrolysis residues of regenerated cellulose indicated that more inorganic salts were involved into cellulose after treatment of

BMIMCl ionic liquid. This increase in char residue was promoted as the decomposition of free end chains took place at a lower temperature.

Therefore, the result demonstrated that after cellulose treated with BMIMCl, its thermal stability decreased, this was consistent with the decrease in molecular weight of cellulose after IL treatment. This phenomena can be explained by noting that cellulose is attracted by Cl^- during the treatment process in BMIMCl, and most of the hydrogen bonds and part of the molecular cellulose chain are degraded, resulting in a decrease in molecular weight and thermal stability (Han *et al*., 2013)

4.3 Morphological properties of the BMIMCl treated cellulose

The morphological investigation of cellulose after ionic liquid treatment was performed using FESEM observations. One example of a FESEM image of cellulose treated with 2 wt % BMIMCl ionic liquid is reported in Figure 4.5. The original appearance of the 2 wt % BMIMCL treated cellulose is shown in the image at three magnifications (60X, 5000X and 10000X). FESEM micrograph in Figure 4.5 (a) at 60X show surface layers of celluloses. Note the apparently rough surface of the cellulose at 5000X as shown in Figure 4.5 (b).

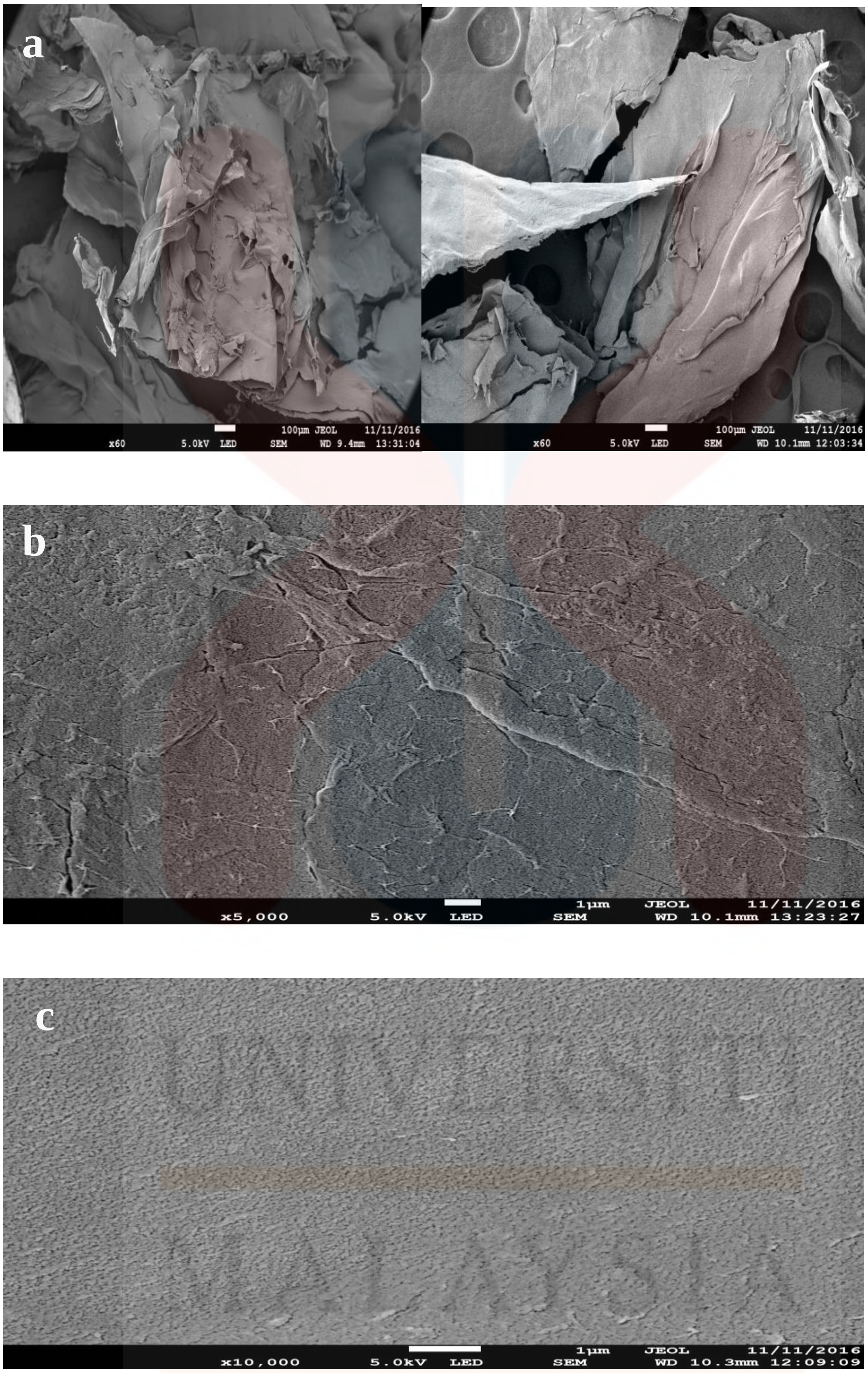

Figure 4.5: FESEM images of 2 wt% CNC sample at 60x (a), 5000x (b) and 10000x (c)

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The present work showed that cellulose can be successfully extracted from rubber wood sawdust. The structural and chemical properties show the BMIMCl treated celluloses more amorphous than the untreated celluloses due to the transformation in *β*-glucosidic linkages and the lower crystallinity. The cellulose treated with 2 wt % IL consist higher crystallinity compared to 5 wt % IL treated cellulose based on XRD. Besides that, the thermal properties of treated cellulose less stable than the untreated cellulose. The micrograph of BMIMCl treated cellulose showed the roughly surface layer. This findings proved that the transformation of crystal structure from cellulose I into cellulose II took place in BMIMCl treated cellulose. Therefore, BMIMCl is proved to be highly effective used to convert cellulose I to cellulose II. However, it was found less effective for conversion of cellulose into nanocellulose. The reduced crystallite size of BMIMCl treated celluloses were likely due to the incomplete growing of crystallites after regeneration. The properties of regenerated cellulose characterized in this study provided some fundamental information for the potential application in enzymatic reaction for bio-energy production and use as excipients in the pharmaceutical industry.

5.2 Recommendations for future work

In the present work, ILs have been utilized as the solvent for the conversion of cellulose into nanocellulose. The result show that BMIMCl treatment is less effective in production of nanocellulose from cellulose.

Therefore, there are several recommendations and suggestions should be noteworthy for future work as proposed below:

I. The combination for both chemical treatment and physical treatment could be said as a promising method which is more effectively used for conversion of cellulose into nanocellulose. For instance, combination for the high pressure homogenization (HPH) and the ILs treatment take more efficient in conversion of cellulose into nanocellulose compare to apply IL treatment solely.

II. The extraction process should be repeated over 10 times to make sure the lignin and the extractives can be totally removed to achieve the yielding for high purity of cellulose.

III. To investigate the influence of parameters such as reaction temperature, time, concentration in term of mass loading of MCC and different sonication treatments in the conversion from cellulose to nanocellulose. These factors need to be taken into consideration for further investigation due to the efficient for conversion and the properties of cellulose may be decide upon these parameters.

IV. The utilization of different anions-based ILs (e.g., sulfonate, phosphate, formate) and vary the cations (e.g., pyridinium) as well as different side chain (alkyl chain lengthI of alkylimidazolium cations (e.g., ethyl-) for conversion of cellulose into nanocellulose. The accessibility and price of ILs are important elements to be considered for their roles as solvents, so that the process is economically feasible.

V. FESEM micrograph need to compare with the untreated cellulose or the other results to provide more information about the morphological properties.

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