EXTRACTION AND CHARACTERISATION OF CELLULOSE FROM MERBAU (*Intsia bijuga*)

NUR AMIRA BINTI MAMAT RAZALI

MASTER OF SCIENCE (PHYSICS)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

2014

EXTRACTION AND CHARACTERISATION OF CELLULOSE FROM MERBAU (*Intsia bijuga*)

NUR AMIRA BINTI MAMAT RAZALI

Thesis Submitted to the Centre for Graduate Studies, Universiti Pertahanan Nasional Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science (Physics)

December 2014

ABSTRACT

Extractions of natural cellulosic material from Merbau (*Intsia bijuga*) were prepared at atmospheric pressure. The samples of celluloses produced were named as untreated material (RAW), post delignification cellulose (PDC), acid-bleached cellulose (ACBC), alkali-bleached cellulose (ALBC) and alkali-treated cellulose (ATC). Untreated material (RAW) is a sample which did not undergoes any chemical treatment. Dried wood samples were delignified in acetic acid/hydrogen peroxide media with addition of 5% sulfuric acid (H_2SO_4). The product produced of this stage was named as post delignification cellulose (PDC). The delignified cellulose was divided into two parts. It was then bleached separately in acid and alkali media. The produced samples were assigned as acid-bleached cellulose (ACBC) and alkali-bleached cellulose (ALBC) respectively. Finally, the alkali-bleached cellulose was treated with 17.5% sodium hydroxide (NaOH), this produced cellulose was named as alkali-treated cellulose (ATC). The spectroscopic characterizations of celluloses samples show that untreated material (RAW), post delignification cellulose (PDC), acid-bleached cellulose (ACBC), alkali-bleached cellulose (ALBC) have native cellulose (cellulose I) structure dominated by monoclinic (I_β) phase with $z < 1$. However, the alkali-treated cellulose (ATC) has totally changed the cellulose structure I to cellulose structure II. In XRD studies, in was found that crystallinity index was higher in acid-bleached cellulose (ACBC) (82.4%) followed by alkali-bleached cellulose (ALBC) (78.8%), alkali-treated cellulose (ATC) (77.9%), post delignification cellulose (PDC) (76.1%) and untreated material (RAW) (57.2%). The highest crystallinity (ACBC) give the smaller average of crystallite size (1.5368 nm) followed by ALBC = 2.0491 nm, ATC = 3.7755 nm, PDC = 8.1934 nm, and RAW = 9.6052 nm. In FTIR analysis also supported the results from the XRD analysis which indicated that RAW, PDC, ACBC and ALBC samples are cellulose I with the visible peak appeared in all sample at 1317 cm^{-1} and ATC is cellulose II with the existence of peak at 1315 cm^{-1}. The unique sets of characteristic of cellulose will accelerate fundamental and applied research and development of cellulose material for a number of industrial applications.

ABSTRAK

Pengestrakan bahan selulosa semulajadi dari Merbau (*Intsia bijuga*) telah dilakukan pada tekanan atmosfera. Sampel selulosa yang terhasil dinamakan sebagai bahan yang tidak dirawat (RAW), selulosa selepas penyahlignin (PDC), selulosa terluntur-asid (ACBC) , selulosa terluntur-alkali (ALBC) dan selulosa terawat-alkali (ATC). Bahan yang tidak dirawat (RAW) adalah sampel yang tidak menjalani sebarang rawatan kimia. Sampel kayu kering telah dinyahlingin dalam asetik asid / hidrogen peroksida media dengan penambahan 5% asid sulfurik (H2SO4). Produk yang dihasilkan daripada peringkat ini dinamakan sebagai selulosa selepas penyahlignin (PDC). Selulosa dinyahlignin telah dibahagikan kepada dua bahagian. Ia kemudiannya dilunturkan secara berasingan dalam media berasid dan beralkali. Sampel yang dihasilkan masing-masing telah dinamakan sebagai selulosa terluntur-asid (ACBC) dan selulosa terluntur-alkali (ALBC). Akhir sekali, selulosa terluntur-alkali telah dirawat dengan 17.5% natrium hidroksida (NaOH) yang menghasilkan selulosa dinamakan sebagai selulosa terawat-alkali (ATC) . Pencirian spektroskopi daripada sampel selulosa menunjukkan bahawa bahan yang tidak dirawat (RAW), selulosa selepas penyahlignin (PDC), selulosa terluntur-asid (ACBC), selulosa terluntur-alkali (ALBC) mempunyai struktur selulosa asli (selulosa I) yang di dominasi oleh fasa monoklinik (I_{β}) dengan $z < 1$. Walau bagaimanapun, selulosa terawat-alkali (ATC) telah mengubah struktur selulosa I kepada struktur selulosa II. Dalam kajian XRD, didapati bahawa indeks penghabluran adalah lebih tinggi dalam selulosa terluntur-asid (ACBC) (82.4%) diikuti oleh selulosa terluntur- alkali- (ALBC) (78.8%) , selulosa dirawat- alkali (ATC) (77.9%), selepas dinyahlignin selulosa (PDC) (76.1%) dan bahan yang tidak dirawat (RAW) (57.2%). Penghabluran tertinggi (ACBC) memberikan purata saiz kristal yang lebih kecil (1.5368 nm) diikuti oleh ALBC = 2.0491 nm , ATC = 3.7755 nm, PDC = 8.1934 nm, dan RAW = 9.6052 nm. Analisis FTIR juga menyokong keputusan daripada analisis XRD yang menyatakan bahawa RAW, PDC, ACBC dan ALBC merupakan struktur selulosa I dengan kehadiran puncak dilihat pada jalur 1317 cm^{-1} dan ATC adalah selulosa II dengan kemunculan puncak pada jalur 1315 cm^{-1}. Dengan adanya ciri-ciri selulosa yang unik ini akan meningkatkan asas penyelidikan dan dapat memperluaskan lagi aplikasi bahan selulosa dalam industri.

ACKNOWLEDGMENTS

A major research project like this is never the work of anyone alone. The contributions of many different people, in their different ways, have made this possible. I would like to extend my appreciation especially to the following.

At first I would like to thank and appreciate my supervisor Prof. Dr. Fauziah binti Haji Abdul Aziz, for making this research possible. Her supports, guidance, advice throughout the research project, as well as her pain-staking effort in proof reading the drafts, are greatly appreciated. Indeed, without her guidance, I would not be able to put the topic together.

I would like to extend my sincere thanks to my co-supervisor, Prof. Datin Dr. Saadah binti Abdul Rahman, a great supervisor who gives me chances to use the facilities at University of Malaya. Without her helps I could not completed my research.

Special thanks to UPNM X-ray Research Group members for helping me towards the accomplishment of this research. I would also thanks to Faculty of Science and Defence Technology (FSTP) and Centre for Graduate Studies (PPS) for their great administrative assistance.

And last but not least, I would like to appreciate to all my beloved husband, Mr. Mohammad Shukri bin Mat Yassim, my siblings, my friends and especially to my late mother and my late father whom I owe a big debt of gratitude to them for their full support during my entire life.

APPROVAL

This thesis was submitted to the Senate of Universiti Pertahanan Nasional Malaysia and has been accepted as fulfillment of the requirements for the degree of Master of Science (Physics). The members of the Supervisory Committee were as follows.

Fauziah binti Haji Abdul Aziz
Professor Dr.
Centre for Defence Foundation Studies
Universiti Pertahanan Nasional Malaysia (UPNM)
Main supervisor

Saadah binti Abdul Rahman
Professor Datin Dr.
Faculty of Science and Technology
University of Malaya (UM)
Co-supervisor

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

DECLARATION OF THESIS

Author's full name	: Nur Amira binti Mamat Razali
Date of birth	: 10 January 1987
Title	: Extraction and characterisation of cellulose from Merbau (*Intsia bijuga*)
Academic session	: 2011/2012 – 2014/2015

I declare that this thesis is classified as:

☐	**CONFIDENTIAL**	(Contains confidential information under the official Secret Act 1972)*
☐	**RESTRICTED**	(Contains restricted information as specified by the organization where research was done)*
■	**OPEN ACCESS**	I agree that my thesis to be published as online open access (full text)

I acknowledge that Universiti Pertahanan Nasional Malaysia reserves the right as follow

1. The thesis is the property of Universiti Pertahanan Nasional Malaysia.
2. The library of Universiti Pertahanan Nasional Malaysia has the right to make copies for the purpose of research only.
3. The library has the right to make copies of the copies of the thesis for academic exchange.

SIGNATURE

870110-03-5474

IC/PASSPORT NO.

Date: 26/5/2015

SIGNATURE OF SUPERVISOR

PROF. DR. FAUZIAH BINTI HJ. ABDUL AZIZ
Jabatan Fizik
Pusat Asasi Pertahanan
Universiti Pertahanan Nasional Malaysia

NAME OF SUPERVISOR

Date: 26/5/2015

Note: *If the thesis is CONFIDENTAL OR RESTRICTED, please attach the letter from the organization stating the period and reasons for confidentiality and restriction.

TABLE OF CONTENTS

LIST OF FIGURE

LIST OF TABLE

LIST OF PHOTO

LIST OF ABBREVIATIONS AND SIMBOLS

RAW	Untreated material
ACBC	Acid-bleached cellulose
ALBC	Alkali-bleached cellulose
DPC	After delignification process cellulose
ATC	Alkali-treated cellulose
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
RAMAN	RAMAN spectroscopy
XRD	X-ray diffraction
FWHM	Full width half maximum
θ	Angle of x-ray diffraction
λ	wavelength
d	Spacing between two planes
X_C	Crystallinity
D_{002}	Crystallite size
z	z-function

CHAPTER 1

INTRODUCTION

1.1 General Introduction

This study was conducted to examine the potentials of natural cellulose or native cellulose from Merbau (*Intsia bijuga*) as cellulose nano-composites. Merbau (*Intsia bijuga*) wood was chosen as a raw material in this research as it is categorised as natural bioresources heavy hardwood (HHW) and easily found in Peninsular Malaysia. Merbau is a very attractive wood; with its distinct growth ring, the tree can grow up to 30 (±40) m tall and the bark has a deep colour (yellow-orange to red-brown) (Oyen, 1886). It is a very good general-purpose timber because of its favourable physical and mechanical properties, combined with high natural durability and attractive appearance. Due to its characteristics, it becomes the main material for furniture industry in Malaysia. The physical characteristics of cellulose microfibres, size and degree of crystallinity of wood, and chemical treatment to the wood, can affect the production of any cellulose nanocrystal (CNC) (Raili Ponni et al., 2012). Peroxyacetic method is where cellulose is isolated at atmospheric pressure using a chlorine-free delignification.

This method uses a mixture of glacial acetic acid (CH_3COOH) and hydrogen peroxide (H_2O_2) as delignification media with the addition of a little concentrated sulfuric acid (H_2SO_4) to act as a catalyst (Long Khama et al., 2003). This method was chosen because it is a simple process using basic equipment and can be carried out in laboratory. It is also environmentally friendly as acetic acid in liquid waste can be recycled using simple distillation methods. To produce lignin-free cellulose and hemicellulose, the cellulose obtained will be bleached with hydrogen peroxide in both acidic and alkaline media. The cellulose is also treated with a strong alkali. The untreated material (RAW), post delignification cellulose (DPC), acid-bleached cellulose (ACBC), alkali-bleached cellulose (ALBC) and alkali-treated cellulose (ATC), are all characterised for suitability as part of nano-composite materials.

1.2 Cellulose

Cellulose and lignocellulose have great potential in the production of nanomaterials because they are abundant, renewable, have nanofibril structure, and can be made multifunctional and self-assemble into distinct architectures (Mohieldin, Zainudin, Paridah, & Ainun, 2011). As early as 1838, the term “cellulose” was first used by the French chemist Anselme Payen, when he revealed that after refinement of various plant tissues with an acid-ammonia treatment, then followed by an extraction in water, alcohol, and ether, a constant fibrous material remains. He determined the molecular formula to be $(C_6H_{10}O_5)_n$ and observed the isomerism of its structure with starch. Since then, it has been generally accepted that cellulose is a linear polymer consisting of Danhydroglucose units joined together by β-1,4-glycosidic linkages (Soykeabkaew, 2007). Cellulose from plant cell walls is the world's most abundant renewable resource. There is approximately 1.5 trillion tonnes of cellulose grown annually worldwide. Lignocellulose (wood) from tree is 38-50% cellulose, 23-32% hemicellulose and 15-25% lignin (Wegner & Jones, 2006). The use of lignocellulosic fibres derived from sustainable, annually renewable resources as a reinforcing phase in polymeric matrix composites, provides constructive environmental benefits with respect to biodegradability and the energetic cost of production. Research has shown that by adding an ounce of crystal (of cellulose) to a pound of plastic, the strength of the plastic can be increased by factor of 3000 (Postek et al., 2008).

1.3 Problem statement of the research

Studies on sources of wood cellulose have long been conducted. Softwood in temperate countries has been used in studies and research in most international industries and universities but these researches have not stressed on the physical and mechanical properties of the wood. In the meantime, there are not many studies and works on hardwood from tropical countries such as Malaysia. Hence, this study has focused on a species of Malaysian wood, Merbau (*Intsia bijuga)* from Pahang. This study has elucidated the morphology and physical properties of the cellulose structure from Merbau (*Intsia bijuga*) due to its high crystallinity and strength as compared to softwood and non-woody celluloses. Cellulose nanocrystal applications in commercial production include cellulose nanopaper, artificial veins and bone scaffolding, as well as spray-dried cellulose nanofibrils for pharmaceutical recipients. This research is also vital in the development of a novel composite manufacturing process for ballistic and biomedical applications as well as drug carrier.

1.4 Motivation of the study

Study in micro or nanomaterial from forest product (wood) is experiencing rapid growth due to the following advantages over traditional reinforcing agents. Nanomaterials from forest products are: (1) renewable and environmentally friendly, (2) low in density, (3) low in cost, (4) non-abrasive, (5) safe fibre handling, and (6) high in specific properties. The demand for natural or wood fibre-plastic composites has enjoyed significant double-digit growth since the early 1990s in North America and Europe (Morton, 2003; Xu, 2008). The market in North America includes automotive, building, appliance and other applications. The automotive and construction market need low density reinforcement for engineering thermoplastics to have higher strength, higher modulus, and lower density materials. Purified cellulose from wood fibre is more thermally stable than other constituents, such as lignin and hemicellulose, so it has the potential to be used as a reinforcement of engineering thermoplastics (Xu, 2008). Hence, this study has focussed on a species of Malaysian wood, the Merbau (*Intsia bijuga*) from Pahang. This study has elucidated on the morphology and physical properties of the wood's cellulose structure.

1.5 The Purpose and objectives of this research

This research was deliberated to clarify the physical properties of natural cellulose extracted from Merbau (*Intsia bijuga*) as a probable source of cellulose Nanocrystal (CNC). CNC is a newly-appreciated class for nanomaterial (Postek et al., 2008). It is contrived by the hydrolysis process of natural cellulose from Merbau (*Intsia bijuga*).

The objectives of this research are:

1. To extract the cellulose from waste of Merbau (*Intsia bijuga*);
2. To study the morphology of cellulose samples of Merbau (*Intsia bijuga)*; and
3. To analyse the characterisation data of Merbau (*Intsia bijuga)* from X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy.

1.6 Structure of the dissertation

This dissertation consists of five chapters. The following is a summary of the chapters presented in this thesis:

Chapter 1 Introduction

This chapter introduces the background and motivation of this study and presents an overview of this thesis.

Chapter 2 Literature Review

This chapter provides a brief review of raw material of Merbau (*Intsia bijuga*), cellulose and methods of preparing and characterising of cellulose micro or nano fibre from previous works.

Chapter 3 Material and method

This chapter introduces the material used in this research. It also discusses on the preparation procedure of Merbau (*Intsia bijuga*). Then, it gives detailed descriptions of characterisation processes such as field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR), respectively.

Chapter 4 Result and discussion

This chapter describes the result of the preparation of cellulose and the details about the characterisation result. The different types of cellulose have different physical properties where they are different in structure, morphology and the functional group of the cellulose.

Chapter 5 Conclusion and recommendation

This chapter summarises the main conclusions of this dissertation and provides suggestions for future work which are required to further understand the behaviour of micro or nano cellulose.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of the next generation of materials, products, and processes. Biodegradable plastics and bio-based polymer products based on annually renewable agriculture and biomass feedstock can form the basis for a portfolio of sustainable, eco-efficiency product that can compete and capture markets currently dominated by products based exclusively on petroleum feedstock (Mohanty, Misra, & Drzal, 2002). In recent years, there is increasing interest in the development of biodegradable and plant derived composite material, which sometimes are referred to as “green” composites (Oudiani, Chaabouni, Msahli, & Sakli, 2011; Takagi & Asano, 2007).

One of the researches being carried out is on cellulose. Cellulose is a natural polysaccharide polymer. It is a sustainable polymer which is derived from natural fibre such as plant, algae, and bacteria and sometimes animal. From the current research study, cellulose is the most common organic polymer, representing about 1.5×10^{12}

tonnes of the total annual biomass production, and is considered as an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products (Klemm, Heublein, Fink, & Bohn, 2005).

2.2 Merbau (*Intsia bijuga*)

The genus Intsia is an Old World tree genus and originates from East Africa (introduced), through tropical Asia to the tropical islands of the Pacific Ocean, and northern Australia. *Intsia bijuga* is the most widely distributed species, widespread in East Africa (Zanzibar), where it was introduced in 1934 (World Agroforestry Centre, 2006) in the Indian Ocean Islands, India, Indochina, Malaysia, Micronesia and Northern Australia (Tong, Chen, Hewitt, & Affre, 2009). According to the Forestry Department of Peninsular Malaysia, using peninsula-wide forestry inventory data, there are 1.1 million Merbau trees with a diametre at breast height (dbh) more than 45 cm, with an estimated volume of 5.1 million m^3. Peninsular Malaysia has the highest Merbau log production of the three regions of the country by far (Tong et al., 2009).

The timber of Merbau (*Intsia bijuga*) species is classified as durable under exposed conditions. The classification is based on the standard graveyard tests of untreated specimens of dimension 50 mm x 50 mm x 600 mm conducted at the Forest Research Institute Malaysia (FRIM). Two such tests were conducted on the species *Intsia bijuga*. In the first series of such tests, the average service life for 14 test specimens was 5.5 years (Foxworthy & Woolley, 1930). In the second test, the average service life for 60 specimens was 6 years (Tong et al., 2009).

Intsia bijuga is very widespread in coastal regions of islands in the Indian and Pacific Oceans, including eastern Madagascar and the Seychelles. It has been planted near the sea-shore in Tanzania and in Mauritius. In tropical Asia, the wood is known as 'merbau'. Merbau is a very good general purpose timber. It is suitable for a wide range of purposes because of its favourable physical and mechanical properties. Merbau is used in construction work in house-building, especially for high-class exterior joinery such as for window and weather boarding. It is also used for furniture-making and waterworks construction.

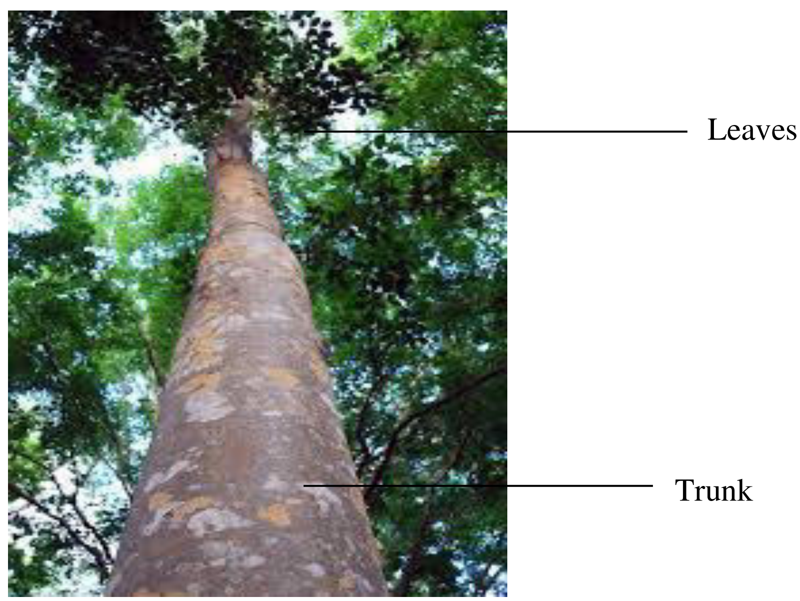

Photo 2.1: Merbau (*Intsia bijuga*) tree (http://www.balinghasai-farms.info/2012/08/23/intsia-bijuga/)