

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

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**UNIVERSITI PERTAHANAN  
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**NUR AMIRA BINTI MAMAT RAZALI**

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## 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 ( $I_\beta$ ) phase with  $z < 1$ . However, the alkali-treated cellulose (ATC) has totally changed the cellulose structure I to cellulose structure II. In XRD studies, it 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  $1317\text{ cm}^{-1}$  and ATC is cellulose II with the existence of peak at  $1315\text{ cm}^{-1}$ . 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 dinyahlignin dalam asetik asid / hidrogen peroksida media dengan penambahan 5% asid sulfurik ( $H_2SO_4$ ). 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 ( $I_\beta$ ) 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  $1317\text{ cm}^{-1}$  dan ATC adalah selulosa II dengan kemunculan puncak pada jalur  $1315\text{ cm}^{-1}$ . Dengan adanya ciri-ciri selulosa yang unik ini akan meningkatkan asas penyelidikan dan dapat memperluaskan lagi aplikasi bahan selulosa dalam industri.

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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.

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## 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<br>Microscopy |
| FTIR      | Fourier Transform Infrared Spectroscopy        |
| RAMAN     | RAMAN spectroscopy                             |
| XRD       | X-ray diffraction                              |
| FWHM      | Full width half maximum                        |
| $\theta$  | Angle of x-ray diffraction                     |
| $\lambda$ | 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 ( $\pm 40$ ) 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 microfibrils, 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 ( $\text{CH}_3\text{COOH}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as delignification media with the addition of a little concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) 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 D-anhydroglucose units joined together by  $\beta$ -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  $1.5 \times 10^{12}$

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*)**

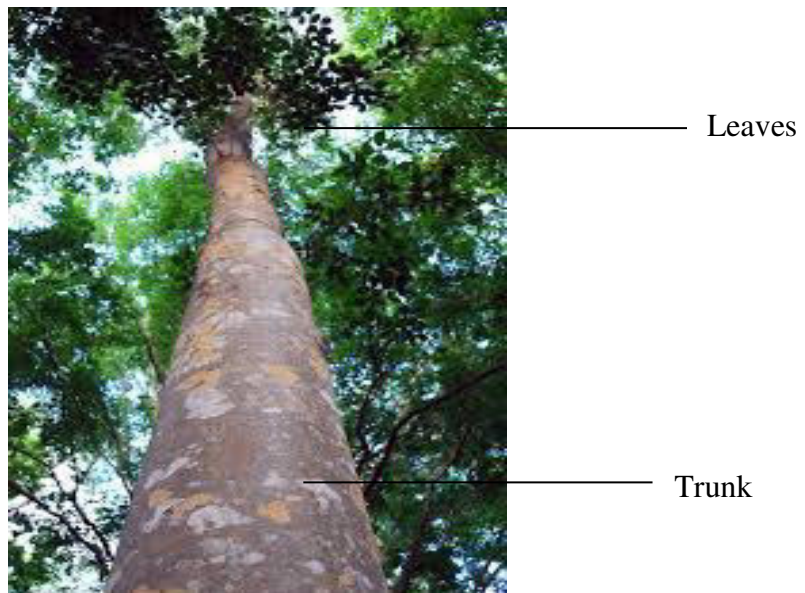
The genus *Intsia* is an Old World tree genus and originates from East Africa (introduced), through tropical Asia to the tropical islands of the Pacific Ocean, and northern Australia. *Intsia bijuga* is the most widely distributed species, widespread in East Africa (Zanzibar), where it was introduced 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 diameter at breast height (dbh) more than 45 cm, with an estimated volume of 5.1 million m<sup>3</sup>. 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/>)**