PROPERTIES OF *Leucaena leucocephala* Lam. BARK AS LIGNIN ADHESIVE AND PARTICLEBOARD

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FACULTY OF SCIENCE AND NATURAL RESOURCES
UNIVERSITI MALAYSIA SABAH
2023

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DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

FACULTY OF SCIENCE AND NATURAL RESOURCES
UNIVERSITI MALAYSIA SABAH
2023

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS

JUDUL : **SIFAT-SIFAT KULIT *Leucaena leucocephala* SEBAGAI PELEKAT LIGNIN DAN PAPAN PARTIKEL**

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DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, equations, summaries, and references, which have been duly acknowledged.

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FIELD : **INDUSTRIAL CHEMISTRY**

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ACKNOWLEDGEMENT

Allah SWT has given me permission to complete this dissertation, and I am thankful for it.

This appreciation goes to the Ministry of Higher Education (KPT) and University Malaysia Sabah (UMS) for sponsoring the scholarship and funding my research project through the SLAI and UMS Great funds.

Thank you to the administration of University Malaysia Sabah, UMS Postgraduate Center, Postgraduate Coordinator of the Faculty of Science and Natural Resources, library staff, all academic and support staff of the Faculty of Science and Natural Resources (FSSA) and the Faculty of Tropical Forestry (FPT) who are directly involved and indirectly in providing energy resources and facilities during the research project.

Thank you so much for the support and encouragement given by the main supervisor, Assoc. Prof. Dr. Jahimin Asik and co-supervisor, Assoc. Prof. Dr. Mohd Sani Sarjadi. Not forgetting the laboratory assistants (Mr Airin Termin, Mr Rizan Gulam Hussein, Mr David Kungin, Mr Azli Sulid, Mr Seliman Rajion, Mr Erwan Silin, Madam Nermalawati Nazri, Madam Valenah Lawrence, Mr Rozaidi Hassan, Mr Ahmad Dasuki Kopong, Mr. Taipin Gadoit, Madam Juliana and Madam Lyana. Thank you for your help and support.

This honor is also dedicated to my late father, Mr. Md Salim Bin Ahmad (Al-fatihah). To my spirit booster Meriam Binti Omar (mother), Wan Zaimah Wan Mohamad (mother-in-law), Mohamed Azhari (spouse), Alia Maisarah, Bahiyah Masturina, Camelia Marissa (daughters), and my other siblings. May ALLAH bless them all. Amen.

Rafidah Bt Md Salim
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ABSTRACT

Bark from trees is considered a worthless raw material. However, this resource could be economically beneficial if utilized efficiently due to its rich chemical compounds. Employing bark particles without mixing other fibres minimised formaldehyde emissions from the particleboards meanwhile lignin extracted from bark used as an adhesive in bark particleboard can maximize the use of biomass waste, be cost effective, and be environmentally friendly. Utilizing appropriate particle sizes could improve the physical and mechanical qualities bark particleboard. In this study, *Leucaena leucocephala* stem bark that was eleven years old was examined for its chemical composition and usage. The chemical compositions (extractive, cellulose, and lignin) were analysis using FTIR spectroscopy. In the second section, the properties of particleboards made from coarse (2.5 to 12.0 mm), medium (1.0 to 2.5 mm), and fine (0.2 to 1.0 mm) *Leucaena leucocephala* bark particles bonded with urea formaldehyde adhesives were evaluated and in the final stage, lignin extracted from bark was used as an adhesive in bark particleboard at different particle sizes. The results found that the bark of *L. leucocephala* has a pH value of 6.04 and that the solubility of the bark in 1% NaOH alkali is the highest (41.36%) compared to the solubility in hot water (14.45%) and cold water (14.36%), while the chemical composition of the bark of *L. leucocephala* was ash (15.76%); extractives (8.39%); cellulose (29.19%) and lignin (38.24%). Results from FTIR analysis revealed that aromatic functional groups were mainly found in the extractive, while water, carbonyl and ether were the dominant groups in cellulose, and methyl, methylene, carbonyl, and carboxyl groups were enriched in lignin. The varying particle sizes had a significant impact on bark particleboard bonded with Urea formaldehyde (UF) adhesives which fine particles (0.2 to 1.0 mm) offered excellent physical properties for moisture content and dimensional stability, while coarse particles possessed good mechanical properties such as density, modulus of elasticity (MOE), modulus of rupture (MOR), and internal bonding (IB). The findings showed that lignin adhesive particleboard works more consistently than UF adhesive particleboard in an air-dry environment, but UF adhesive particleboard exhibits better resistance to water in wet situations. Compared to UF adhesive particleboard, lignin adhesive particleboard is more elastic and ruptures. The thickness swelling decreases in air-dry conditions, but it increases in wet situations as the particle size increases. Bark particleboard has superior strength when the particles used in its production are finer. In MOE, MOR, and IB, fine particles fared best.

ABSTRAK

SIFAT-SIFAT KULIT Leucaena leucocephala Lam. SEBAGAI PELEKAT LIGNIN DAN PAPAN PARTIKEL

Kulit kayu dari pokok dianggap sebagai bahan mentah yang tidak bernilai. Walau bagaimanapun, sumber ini boleh memberi manfaat dari segi ekonomi jika digunakan dengan cekap kerana kaya dengan sebatian kimianya. Menggunakan partikel kulit kayu tanpa mencampurkan gentian lain meminimumkan pelepasan formaldehid daripada papan partikel manakala lignin yang diekstrak daripada kulit kayu digunakan sebagai pelekat dalam papan partikel kulit kayu boleh memaksimumkan penggunaan sisa biojisim, menjimatkan kos dan mesra alam. Menggunakan saiz partikel yang sesuai boleh meningkatkan kualiti fizikal dan mekanikal papan partikel kulit kayu. Dalam kajian ini, kulit batang Leucaena leucocephala yang berumur sebelas tahun telah diperiksa komposisi kimia dan penggunaannya. Komponen kimia (ekstraktif, selulosa, dan lignin) dianalisis menggunakan spektroskopi FTIR. Dalam bahagian kedua, sifat-sifat papan partikel yang diperbuat daripada partikel kulit Leucaena leucocephala yang kasar (2.5 hingga 12.0 mm), sederhana (1.0 hingga 2.5 mm), dan halus (0.2 hingga 1.0 mm) yang diikat dengan pelekat urea formaldehid telah dinilai dan pada peringkat akhir, lignin diekstrak daripada kulit kayu digunakan sebagai pelekat dalam papan partikel kulit kayu pada saiz partikel yang berbeza. Hasil kajian mendapati kulit kayu L. leucocephala mempunyai nilai pH 6.04 dan keterlarutan kulit dalam 1% alkali $NaOH$ (41.36%) adalah paling tinggi berbanding keterlarutan dalam air panas (14.45%) dan air sejuk (14.36%), manakala komposisi kimia kulit kayu L. leucocephala ialah abu (15.76%); ekstraktif (8.39%); selulosa (29.19%) dan lignin (38.24%). Keputusan daripada analisis FTIR mendedahkan bahawa kumpulan berfungsi aromatik terutamanya ditemui dalam ekstraktif, manakala air, karbonil dan eter adalah kumpulan dominan dalam selulosa, dan kumpulan metil, metilena, karbonil, dan karboksil kaya dalam lignin. Saiz partikel yang berbeza-beza memberi kesan yang ketara ke atas papan partikel kulit kayu yang diikat dengan pelekat urea formaldehid (UF) yang mana partikel halus (0.2 hingga 1.0 mm) menawarkan sifat fizikal yang sangat baik untuk kandungan lembapan dan kestabilan dimensi, manakala partikel kasar mempunyai sifat mekanikal yang baik seperti ketumpatan, modulus keanjalan (MOE), modulus pecah (MOR), dan ikatan dalaman (IB). Penemuan menunjukkan bahawa papan partikel pelekat lignin berfungsi lebih konsisten daripada papan partikel pelekat UF dalam persekitaran kering udara, tetapi papan partikel UF mempamerkan kerintangan yang lebih baik terhadap air dalam keadaan basah. Berbanding dengan papan partikel pelekat UF, papan partikel pelekat lignin lebih elastik dan pecah. Bengkak ketebalan berkurangan dalam keadaan kering udara, tetapi ia meningkat dalam keadaan basah apabila saiz partikel bertambah. Papan partikel kulit kayu mempunyai kekuatan yang unggul apabila partikel kulit yang digunakan dalam pengeluarannya lebih halus. Dalam MOE, MOR dan IB, partikel halus adalah yang terbaik.

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LIST OF ABBREVIATIONS

SO_2	-	Sulphur dioxide
FT-IR	-	Fourier Transform Infrared Spectroscopy
NH_4CL	-	Ammonium chloride
NaOH	-	Sodium hydroxide
C-O	-	Carbonyl group
COOH	-	Carboxylic acid functional group
$-CH_3$	-	Methyl
$-CH_2$	-	Methylene
-OH	-	A hydroxyl group
DP	-	Degree of polymerization
(a.u.)	-	Arbitrary unit
cps	-	Centipoise
ρ	-	Density
µm	-	Micrometre
nm	-	Nanometre
$p<0.01$	-	Probability less than 0.01
$p<0.05$	-	Probability less than 0.05
kg/m^3	-	Kilogram per cubic metre
kg/m^2	-	Kilogram force per square metre
N/mm^2	-	Newton per square millimetre
MPa	-	Megapascal
R	-	Replicate
DS	-	Dimensional swelling
MOR	-	Modulus of elasticity

MOE	-	Modulus of rupture
IB	-	Internal bonding
TS	-	Thickness swelling
WA	-	Water absorption
MC	-	Moisture content
UF	-	Urea formaldehyde
PF	-	Phenol formaldehyde
ASTM	-	American Society for Testing and Materials
DPPH	-	2,2-diphenyl-1-picryl-hydrazyl-hydrate
VOC	-	Volatile organic compound

CHAPTER 1

INTRODUCTION

1.1 Introduction

Leucaena leucocephala is a species of flowering tree in the pea family Fabaceae (Drumond & Ribaski, 2010; Bhavani & Prasad, 2012). It is commonly known by various names, including white leadtree, jumbay, and wild tamarind (Dias *et al*., 2020). *Leucaena leucocephala* is native to Central America but has been widely introduced and naturalized in tropical and subtropical regions around the world (Ramirez-Bahena *et al*., 2020). *Leucaena leucocephala* has two main subspecies, *L. leucocephala* subspecies *leucocephala*, known as "common leucaena" or "koa haole," and *L. leucocephala* subspecies *glabrata*, known as "giant leucaena." Common Leucaena is a small bushy shrub that forms a lot of seeds, because of which it can spread easily and is considered invasive (Rahman *et al*., 2020). Giant leucaena, on the other hand, is a tree with large branches. It produces much less seeds and is not considered invasive (Bageel *et al*., 2020). Giant Leucaena can grow to become big trees of up to ~20 m in height, or it can be grown as a legume fodder by maintaining the plants as dwarf bushes through repeated harvest of foliage, up to ten times a year (Ishihara *et al*., 2018).

Leucaena leucocephala is a fast-growing tree species that can be cultivated in Malaysia and other tropical and subtropical regions (Ishihara *et al*., 2018). It has potential as an alternative resource for the furniture and panel board industries due to a shortage of rubberwood (Rahman *et al*., 2020). Leucaena trees have shown good growth performance, and their wood is suitable for the manufacture of wood composites (Hiwale, 2015). In addition to its use as a raw material, *L. leucocephala* is also a leguminous fodder-fuel-fertilizer adding tree/shrub that can be grown in poor soils under low and medium rainfall (Bageel *et al.*, 2020). It can be intercropped with other field crops and fruit trees, making it suitable for agroforestry (Nehdi *et al.,* 2014). *Leucaena leucocephala* oil extracted from its seeds has high vitamin E activity and can be used in cosmetic or pharmaceutical preparations (Drumond & Ribaski, 2010). *Leucaena leucocephala* has multiple uses, including as a raw material for industries, a fodder crop, and a source of oil with potential applications in cosmetics and pharmaceuticals.

Leucaena leucocephala bark has various uses. It is considered a potential biomass energy source (Rasat *et al.*, 2016). The bark can be used for vegetation recovery projects in degraded areas (Dias *et al.*, 2020). Additionally, the bark contains mimosine, a toxic non-protein amino acid, which can be quantified under different environmental conditions to manage and prevent toxicity (Honda & Borthakur, 2019). The bark can also be used for rapid multiplication and genetic improvement of individual clones of *L. leucocephala* (Drumond & Ribaski, 2010).

Leucaena leucocephala bark is also potentially used in agroecosystems for animal nutrition and health due to the presence of secondary metabolites such as flavonoids, alkaloids, reducing carbohydrates, and tannins (Dago Duenas *et al.*, 2020). It can also be used for phytoremediation of heavy metal-polluted and degraded sites, as it has characteristics that can lower the cost of regeneration and facilitate phytoextraction and nitrogen fixation (Ssenku *et al.*, 2017). In addition, *L. leucocephala* bark shows promise as a raw material for the manufacture of wood composites, such as particleboards, due to its growth performance and usability in meeting board requirements (Rahman *et al.*, 2020). Furthermore, *L. leucocephala* bark has potential as a biomass energy source, with different portions and particle sizes influencing its properties, including calorific value (Rasat *et al.*, 2016). The bark is also the least acidic and has high solubility, making it a potential carbohydrate resource, although its chemical composition may influence rapid combustion during pyrolysis (Salim *et al.*, 2019).

Leucaena leucocephala bark has been studied for its physicochemical properties such as pH, swelling capacity, and viscosities at different temperatures (Anupam *et al.*, 2015). The bark gum is slightly soluble in water and practically insoluble in ethanol, acetone, and chloroform. It swells to about 5 times its original weight in water. The gum exhibits pseudo plastic and thixotropic flow patterns, making it suitable for use as a disintegrant in tablet formulation and as a hydrogel in modified release dosage forms (Pendyala, & Chandrasekhar, 2010). It also has potential as suspending and emulsifying agents. The bark has been used to produce biochar through slow pyrolysis, resulting in a biochar with high stability and carbon sequestration potential (Anupam *et al*., 2015).

Bark particleboard is a type of particleboard made from bark waste which is a potential solution for using the bark waste produced by the forest industry. Previous research has shown the technical feasibility of making particleboards from black spruce bark residues bonded with urea formaldehyde resin (Shi & Wen, 2011). Another study investigated the effects of pressing temperature on the mechanical and physical properties of binderless bark particleboard made from Gelam bark waste. The results showed that increasing the pressing temperature improved the mechanical properties and decreased the physical properties (Blanchet *et al*., 2008). Additionally, low-density binderless bark particleboards were produced using Gelam wood bark. The physical properties of these particleboards met the requirements for density, moisture content, and thickness swelling, making them suitable for use in certain applications (Blanchet *et al*., 2000). Overall, bark particleboard offers a potential solution for utilizing bark waste and has shown promise in terms of its technical feasibility and physical properties.

Bark particle sizes vary depending on the study. In one study, wood particles were found to be longer and thinner than bark particles, while bark particles were more spherical in shape (Rezaei & Sokhansanj, 2018). Another study analyzed the acoustic properties of bark-based panels and found that particle size influenced the sound absorption coefficient values, with fine-grained particles showing better results (Tudor *et al.,* 2021). A study on pine bark substrates found that particle size affected the cation exchange capacity (CEC), with CEC increasing as particle size decreased (Altland *et al*., 2014). Additionally, a study on the comminution of bark planks found that the major fractions of ground bark particles were larger particles, with a small percentage of particles under 0.5 mm and a larger percentage of particles over 4 mm (Tudor *et al*., 2020). Finally, a study on mulberry bark powder preparation mentioned that the particle size of the powder was 100-150 micrometers (Yuqing & Huayu, 2015). The comminution of softwood bark, including larch, Scots pine, and spruce, has been examined for potential use in bark-based composites, with the 4-shaft shredder identified as the most appropriate tool for crushing bark planks (Tudor *et al*., 2020).

Lignin is a polyphenolic compound found in plant tissues, especially wood and bark (Neiva *et al.,* 2020). Lignin from different tree barks, such as Norway spruce, eucalyptus, mimosa, and blackwood acacia, have been characterized. The lignin from eucalyptus bark is enriched in syringyl units and β-ether linkages (Schuler *et al*., 2019). Hydrothermal liquefaction of beech wood bark and Kraft lignin from pine wood can produce monocyclic compounds like catechol, which has potential as a valuable product for chemicals (Dou *et al*., 2018). Willow bark lignin is predominantly composed of guaiacyl units and is more condensed in bark compared to other tissues (Watanabe *et al*., 2018). Hydrothermal treatment of bark can be used to separate lignin, with a yield of up to 65% from Japanese cedar bark (Deb *et al*., 2021). The lignin content in wood and bark varies among different species, and the ratio of wood lignin to bark lignin may correspond to timber quality.

Lignin extracted from bark has been explored as a potential substitute for phenol in adhesive resins (Khan *et al*., 2004). Various studies have investigated the synthesis of formaldehyde-free bioresin adhesives using lignin extracted from softwood bark (Sain *et al*., 2021). Additionally, a fast-reacting procyanidin-type condensed tannin derived from pine bark has been shown to be an effective adhesive for wood particleboard (Santiago-Medina *et al*., 2016). Tannins extracted from different wood barks, such as Aleppo pine and spruce, have been evaluated for their adhesive properties (Bertaud *et al*., 2012). Furthermore, lignin, a by-product of the pulping industry, has been used as a substitute for phenol in modified phenol-formaldehyde resins for plywood production (Dunky, 2021).

Urea-formaldehyde adhesives are commonly used in the production of wood-based panels due to their high reactivity, good performance, and low cost (Santos *et al*., 2014). These adhesives can improve the strength, density, and wear resistance of panel materials, achieving anti-fouling and anti-scratch effects (Korai *et al.*, 2014). They also can reduce formaldehyde emissions, meeting national standards and exceeding the quality of imported products (da Silva *et al.*, 2019). The use of modifiers in urea-formaldehyde adhesives can further enhance the veneer strength of finished product plates, reduce costs, and decrease formaldehyde release (de Carvalho *et al.,* 2021). Overall, urea-formaldehyde adhesives have a wide range of applications in the wood processing and production industry, providing good product properties, simple preparation processes, and low costs (Sernek *et al.*, 2020). However, urea-formaldehyde adhesives have several disadvantages. They can release formaldehyde, which is toxic and harmful to human health. Some urea-formaldehyde adhesives may have high formaldehyde release amounts, leading to pollution and environmental concerns (He, 2017).

Bark particleboard is a type of particleboard made from bark waste. It can be produced using different temperatures and pressures, which affect its mechanical and physical properties. Increasing the pressing temperature generally improves the mechanical properties, such as modulus of rupture and modulus of elasticity, while decreasing the physical properties, such as thickness swelling and water absorption (Christy *et al.,* 2021). However, the mechanical strength of bark particleboard is generally lower than that of commercial wood particleboards (Lakreb *et al.,* 2018). Low-density binderless bark particleboards can also be produced using a hot-pressing method at low temperature and pressure. These particleboards meet the requirements for density, moisture content, and thickness swelling, but may have cracks and delamination issues (Christy *et al.,* 2020). Bark particleboards can also be used as internal layers in three-layered particleboards, which meet the requirements for modulus of rupture, modulus of elasticity, internal adhesion, thickness swelling, water absorption, moisture content, and density (de Campos *et al.*, 2014).

Bark particleboard offers several benefits. Impregnating wood particles with bark extractives improves decay resistance and thickness swelling of the particleboard (Nemli *et al.,* 2006). The mechanical properties of particleboard made from bark may decrease with increasing bark content, but the Janka hardness remains unaffected (Yemele *et al.*, 2008). Particleboard made from 50% black spruce bark shows higher modulus of elasticity, modulus of rupture, and internal bond compared to the control (Yemele *et al.*, 2008). It is technically feasible to make particleboard from black spruce bark residues bonded with urea formaldehyde resin, meeting indoor performance requirements (Blanchet *et al.*, 2000). Hot-water treatment of bark affects the physical and chemical properties, decreasing hydrophilic characteristics and the amount of condensable polyphenols (Claude *et al.*, 2008). The thickness swelling of particleboard made from hot-water-treated bark may be higher than that made from untreated bark.

Bark particleboard has some drawbacks in terms of its physical and mechanical properties. An excessive bark content in the particleboard can negatively affect its strength properties and dimensional stability (Yemele *et al.,* 2008). Additionally, the use of hot water extracted bark particles in particleboard production can have detrimental effects on the physical and mechanical properties of the boards (Yemele *et al.*, 2008). However, impregnating wood particles with bark extractives can improve the decay resistance and thickness swelling of the particleboard (Nemli *et al.*, 2006). Despite these drawbacks, it is technically feasible to make particleboard from bark residues that meets the indoor performance requirements for wood particleboards (Blanchet *et al.,* 2000).

Demethylation of lignin involves the removal of methyl groups from the lignin structure, resulting in an increase in phenolic hydroxyl groups and reactivity (Venkatesagowda, 2019; Venkatesagowda & Dekker, 2021; Sawamura *et al.*, 2017). This can be achieved through chemical, enzymatic, or biological methods. Enzymes called O-demethylases have been identified as potential catalysts for lignin demethylation, with bacteria and fungi being capable of demethylating lignin and lignin-related compounds (Hu *et al.*, 2014). Chemical reagents such as hydroiodic acid and iodocyclohexane have also been used to efficiently demethylate lignin, leading to increased phenolic-OH levels and improved properties. Thiol-mediated demethylation is another approach that has been explored to increase the reactivity of lignin. Overall, demethylation of lignin is a promising strategy to enhance its functionality and expand its potential applications in various industries.

Demethylation of lignin using sodium sulfite has been investigated in several studies. Konduri & Fatehi (2015) modified hardwood kraft lignin with formaldehyde