Extraction, Separation and Application of Lignin from Oil Palm Empty Fruit Bunch for Linerboard Coating

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ABSTRACT

This work aimed at developing a novel bio-based coating for the corrugated packaging using the lignin from oil palm empty fruit bunch (OPEFB) as a raw material. Lignin was recovered by the acidification of a soda OPEFB's black liquor with four pH conditions (5, 4, 3, and 2) varied. The recovery mass of lignin increased with a decrease of pH of the black liquor. TGA showed that the chemical compositions of the lignin did not influence by the pH of black liquor. However, the microstructure of the lignin was degraded progressively when the pH of liquor reduced as was pointed out by FTIR analysis. Thus the pH-5 lignin fraction was selected for the development of coatings so as to avoid the losing of feature from the drastic degradation. OPEFB's lignin-based coatings were prepared by mixing of oxidized starch solution and 5% lignin (w/v of the solution) with the addition of three different stabilizers at 1–5% (w/w of the lignin). An increase in viscosity and stability of the developed coatings was found with the addition of stabilizers. The coatings with 1–3% arabic gum and with 4–5% carrageenan provided great water resistance of the coated linerboards as the commercial wax coating. Ring crush and bursting indexes (RCI and BI) of the coated linerboards was not affected ($p \geq 0.05$) by the addition of stabilizers. The coatings with 1% arabic gum and with 1% guar gum did not reduce ($p \geq 0.05$) the tensile index (TI) of the coated linerboards. Only for the coating containing 1% arabic gum provided overall of the coating characteristics and the coated linerboard properties as good as the commercial wax. This coating treatment was selected for the further development. The effect of lignin content on the performance of the developed coating was investigated. Different contents (1, 3, 5, 7 and 9%) of lignin were mixed with the oxidized starch solution and 1% arabic gum for producing the coatings. A greater ($p<0.05$) water resistance of the coated linerboards was found when the content of lignin increased, however at >5%, it was not significant ($p \geq 0.05$). All the RCI, BI and TI of the coated linerboards were not altered ($p \geq 0.05$) by the addition of lignin. It can be suggested that the optimal content of lignin for the preparation of coating is 5%. OPEFB's lignin derivatives were synthesized by the reactions of lignin and vegetable (palm and soybean) oils at the proportions of 1:1 and 1:2. The formation of lignin derivatives was confirmed by FTIR analysis. OPEFB's lignin derivative-based coatings were prepared by mixing of 5% lignin derivatives, oxidized starch solution and 1% arabic gum. The viscosity of the lignin derivative-based coatings was quite close to that of the commercial wax. A superior ($p < 0.05$) water resistance of the coated linerboards was found when the lignin derivative-based coatings were applied, comparing with the commercial wax coating. Increasing the oil dosage for the synthesis did not lead the coatings obtained to provide a greater water resistance of the coated linerboards ($p \geq 0.05$). All the RCI, BI and TI of the linerboards were not affected ($p \geq 0.05$) by the applying of lignin derivative-based coatings, as the same with the coating of commercial wax.

Keywords: Black liquor; Coating; Derivative; Linerboard; OPEFB's lignin; Stabilizer; Water resistance

ชื่อวิทยานิพนธ์ การสกัด การแยก และการประยุกต์ใช้สารลิกนินจากทลายปาล์มเปล่าสำหรับเคลือบกระดาษปะผิวลูกฟูก
ผู้เขียน นายดนุพงค์ นาราภักดีสกุล
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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อพัฒนาสารเคลือบผิวสำหรับบรรจุภัณฑ์กระดาษลูกฟูกโดยใช้ลิกนินที่ได้จากทลายปาล์มเปล่าเป็นสารเคลือบหลัก เริ่มต้นด้วยการปรับค่า pH ของน้ำต้มเยื่อกระดาษด้วยกรดเพื่อแยกลิกนิน โดยแปรค่า pH ที่ระดับ 5 4 3 และ 2 ตามลำดับ จากผลการทดลองพบว่า ร้อยละผลผลิตของลิกนินที่แยกได้มีปริมาณเพิ่มขึ้นเมื่อระดับค่า pH ของน้ำต้มเยื่อลดลง ค่า pH ของน้ำต้มเยื่อไม่มีผลต่อองค์ประกอบทางเคมีของลิกนินที่ได้ อย่างไรก็ตาม ผลจากการวิเคราะห์ด้วยเทคนิค FTIR แสดงให้เห็นว่า โครงสร้างทางเคมีของลิกนินเกิดการเสื่อมสภาพมากขึ้นเมื่อค่า pH ของน้ำต้มเยื่อลดลง ดังนั้นจึงเลือกลิกนินที่ได้จากการแยกที่สภาวะค่า pH 5 เพื่อใช้ในการเตรียมสารเคลือบ ทั้งนี้เพื่อหลีกเลี่ยงการเสื่อมสภาพที่มากเกินไปซึ่งอาจจะทำให้ลิกนินสูญเสียคุณสมบัติได้ จากนั้นทำการเตรียมสารเคลือบผิวจากลิกนินโดยการผสมลิกนินในปริมาณร้อยละ 5 เข้ากับสารละลายสตาร์ชออกซิไดซ์ และเติมสารช่วยเพิ่มความคงตัวในปริมาณร้อย 1 ถึง 5 ของลิกนิน โดยสารช่วยเพิ่มความคงตัวที่ใช้ในการทดลองนี้มี 3 ชนิด ได้แก่ อาราบิกกัม คาราจีแนน และกัวร์กัม จากผลการทดลองพบว่า การเติมสารช่วยเพิ่มความคงตัวทำให้ความหนืดและความคงตัวของสารเคลือบเพิ่มขึ้น กระดาษปะผิวลูกฟูกที่เคลือบด้วยสารเคลือบที่เติมอาราบิกกัมในปริมาณร้อยละ 1 ถึง 3 และกัวร์กัมในปริมาณร้อยละ 4 ถึง 5 มีค่าความต้านทานน้ำที่ดีเทียบเท่ากับการเคลือบด้วยสารเคลือบเชิงการค้า การเติมสารช่วยเพิ่มความคงตัวลงในสารเคลือบไม่ส่งผลต่อค่าบ่งชี้ความต้านทานต่อแรงกดอัด (RCI) และค่าบ่งชี้ความต้านทานต่อแรงดันทะลุ (BI) ของกระดาษ สารเคลือบที่เติมอาราบิกกัมและกัวร์กัมในปริมาณร้อยละ 1 ไม่ทำให้ค่าบงชี้ความต้านทานต่อแรงดึง (TI) ของกระดาษที่เคลือบลดลง สารเคลือบที่เติมอาราบิกกัมในปริมาณร้อยละ 1 เป็นเพียงสูตรเดียวที่มีประสิทธิภาพดีเทียบเท่ากับแว็กซ์เชิงการค้าทั้งในแง่ของลักษณะของสารเคลือบและสมบัติของกระดาษที่เคลือบ ดั้งนั้นจึงได้เลือกสารเคลือบสูตรนี้สำหรับการพัฒนาต่อไป จากนั้นทำการศึกษาผลของปริมาณลิกนินต่อประสิทธิภาพของสารเคลือบที่เตรียมได้ โดยการผสมลิกนินที่ปริมาณต่าง ๆกันเข้ากับสารละลายสตาร์ชออกซิไดซ์ และเติมอาราบิกกัมในปริมาณร้อยละ 1 เป็นสารช่วยเพิ่มความคงตัว โดยแปรปริมาณลิกนินที่ร้อยละ 1 3 5 7 และ 9 ตามลำดับ จากผลการทดลองพบว่า เมื่อ

ปริมาณลิกนินที่เติมเพิ่มขึ้น ความสามารถในการต้านทานน้ำของกระดาษที่เคลือบเพิ่มขึ้น อย่างไรก็ตาม ไม่พบความแตกต่างอย่างมีนัยสำคัญที่ปริมาณการเติมมากกว่าร้อยละ 5 การเติมลิกนินในทุกๆปริมาณไม่ส่งผลต่อค่า RCI BI และ TI ของกระดาษ จากผลที่ได้แสดงให้เห็นว่า การเติมลิกนินในปริมาณร้อยละ 5 มีความเหมาะสมสำหรับใช้ในการเตรียมสารเคลือบ จากนั้นทำการเตรียมอนุพันธ์ลิกนินโดยการสังเคราะห์ลิกนินกับน้ำมันพืชในอัตราส่วนต่างๆกัน ได้แก่ 1 ต่อ 1 และ 1 ต่อ 2 ตามลำดับ การเกิดอนุพันธ์ลิกนินสามารถยืนยันได้จากการวิเคราะห์ด้วยเทคนิค FTIR ทำการเตรียมสารเคลือบโดยผสมอนุพันธ์ลิกนินที่เตรียมได้ในปริมาณร้อยละ 5 เข้ากับสารละลายสตาร์ชออกซิไดซ์ และเติมอาราบิกกัมในปริมาณร้อยละ 1 เป็นสารช่วยเพิ่มความคงตัว จากผลการทดลองพบว่า ความหนืดของสารเคลือบที่เตรียมได้มีค่าใกล้เคียงกับแว็กซ์เชิงการค้า กระดาษที่เคลือบด้วยสารเคลือบจากอนุพันธ์ลิกนินมีค่าความต้านทานน้ำดีกว่ากระดาษที่เคลือบด้วยแว็กซ์เชิงการค้า การเพิ่มปริมาณน้ำมันในการสังเคราะห์อนุพันธ์ลิกนินไม่มีผลในการช่วยเพิ่มประสิทธิภาพในการต้านทานน้ำของสารเคลือบที่เตรียมได้ การเคลือบด้วยสารเคลือบจากอนุพันธ์ลิกนินไม่ส่งผลให้ค่า RCI BI และ TI ของกระดาษเปลี่ยนแปลง เช่นเดียวกับการเคลือบด้วยแว็กซ์เชิงการค้า

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Danupong Narapakdeesakul

CONTENTS

CONTENTS (continued)

CONTENTS (continued)

CONTENTS (continued)

Page

CONTENTS (continued)

CONTENTS (continued)

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Corrugated board has been used as a packaging material for at least 100 years. It is the most used type of package for packaging and distributing a wide variety of commodities ranging from fruits and vegetables, consumer products, to industrial items [1]. Worldwide demand for corrugated board has been increasing rapidly in the last decade [2]. Due to the advantages that are lightweight and inexpensive, with high strength-to-weight ratio, corrugated containers are considered as the leading choice of the transport packaging. It has been proposed that more than two thirds of the world's retail commodities are packed and transported in corrugated packaging [3]. Corrugated board is made from sustainable natural resources which are readily recovered and recycled more than other packaging substrates such as plastic, glass, metal and composite material [4]. In addition, it is a substrate that can be custom designed and provides excellent merchandising appeals though printing on the box panels [5].

The fact that the moisture has a strong influence on the strength of paper materials is well known [6]. The hydrophilic nature of its composition of cellulose, paperboards are prone to absorb water vapor from the environment, especially when stored under high humidity conditions. Absorption of moisture reduces physical and mechanical strength of the paper materials [7]. Thus the coating is considered necessary in improving the barriers against moisture of the paper packaging so as to maintain their strength for the great performance [8]. Petroleum-based polymers, such as polyethylene (PE), polyethylene tarephthalate (PET), and especially the wax, are the main sources of coatings used in paper industry. They can be applied as thin top coatings to render the paper surface more water resistant [9]. An increase in demand of their uses results in an increase in oil consumption [10]. Furthermore, these materials are limited in the extent that they can be separated, recycled, or composted after use [11]. Environment concerns over these coating materials have promoted research in the area of alternative materials. The challenge is to fine new materials or new uses of existing natural materials with regard to both functional properties and biodegradability. From that reason, biopolymers obtained from agricultural production become a major focus of interest because they are perfectly biodegradable and therefore perfectly safe for the environment [12,13].

Oil palm (*Elaeis guineensis* Jacq.) is a native of West Africa. From its home, the oil palm has spread throughout the tropics and is now grow in 16 or more countries for its oil-producing fruit [14,15]. However, the major center of production is in South East Asia (SEA) with Malaysia, Indonesia and Thailand, which produce about 80% of world’s palm oil [16]. Oil palm was introduced to Thailand in 1968, and now become one of the major agricultural crops of the southern region [17]. The palm oil industry plays an important role in enhancing the economic welfare of the population and in the economic development of the country [16]. As the climatic conditions in the south are suitable for palm trees, the oil palm plantation area has expanded ever since [18]. In 2010, the oil palm plantations in Thailand increased to 4.4×10^6 Rais (about 1.7×10^6 acres) and a large number of fresh fruit bunches (FFB) were harvested approximately about 8.2×10^6 tons [19].

Palm oil production generates a large scale of solid residues including cellulosic fibers, shells and oil palm empty fruit bunches (OPEFB) [20]. Normally, palm oil industry dispose about 1.1 tons of OPEFB per every ton of oil produced [21]. Although some OPEFB residues are currently used in the preparation of fertilizers or as mulching material, a major proportion is left in mill premises itself. When left in field, these wastes create great environmental problems [22,23]. Hence palm oil producing countries have focused to generate value out of these wastes which till date is considered to be challenging. The sustainable, non-hazardous, non-carcinogenic, eco-friendly, biodegradable product developed from these cellulosic wastes will surely benefit the human kind across the globe in broad-spectrum [24].

Lignin, a composition in plants, is one of the most abundant natural non-carbohydrate organic substrate on the earth accounting for approximately 30% of the organic carbon in the biosphere [25,26]. It is a complex racemic aromatic hetero-polymer with a number of chemical groups such as aromatic rings, phenolic and aliphatic alcohol groups, and methoxy groups, joined together by both ether (C–O–C) and carbon-carbon (C–C) linkages [8]. The function of lignin in the plants is to provide rigidity and cohesion to the cell walls, to confer water impermeability to xylem vessels, and to form a physicochemical barrier against microbial attack [27]. Generally, the nature fibers consist of basic chemical building block of cellulose, hemicellulose, and lignin with varying proportions [28]. For the OPEFB, it contains about 40–50% cellulose, 20–30% hemicellulose and 20–30% lignin [29–31]. Lignin has the right chemistry to be used in making coatings because they have small particle size, are hydrophobic and have the ability to form stable mixtures [32].

As is described above, it is possible to use lignin from OPEFB residues for producing the coating for the corrugated containers so as enhancing their barriers against moisture. This approach is the right way to reduce and to generate economic value out of these agricultural wastes. If it is possible, this novel coating would become an interesting alternative for replacing the conventional petroleum-based coatings because it is perfectly biodegradable and therefore perfectly safe for the environment. Thus the study on the potential use of lignin from OPEFB for the production of linerboard coating becomes a focus of interest with great challenging.

1.2 OBJECTIVES

The objectives of this work were to prepare and characterize the lignin from oil palm empty fruit bunch (OPEFB), to develop the coatings based on the OPEFB's lignin and its derivatives, and to evaluate the performance of the developed coatings in terms of the coating characteristics and the coated linerboard properties in compare with the commercial wax.

The scope of this work was divided into 4 parts as follows:

Part I: Isolation and characterization of lignin from oil palm empty fruit bunch

In this part, the lignin was extracted from OPEFB using a soda pulping process. The lignin was recovered from OPEFB's black liquor though the acidification with sulfuric acid. Four pH conditions were varied. The recovery yields of all lignin fractions were calculated and the characteristics of them were also analyzed by FTIR and TGA. The optimal OPEFB's lignin fraction was selected for the preparation of linerboard coating in the next experiment.

Part II: A study on the effects of stabilizers on the performance of OPEFB's lignin-based coatings

In this part, the OPEFB's lignin-based coatings were prepared with the addition of various types and levels of stabilizers (arabic gum, carrageenan and guar gum). The performance of the developed coatings was compared with the commercial wax in terms of the coating characteristics and the coated linerboard properties.

Part III: A study on the effects lignin content on the performance of the OPEFB's lignin-based coatings

In this part, the OPEFB's lignin-based coatings were prepared with varying the content of lignin. The optimal condition (type and level) of the stabilizer from Part II was applied in this section. The coating characteristics and the coated linerboard properties were investigated. All the results provided by the developed coatings were compared with those from the commercial wax coating.

Part IV: Synthesis of OPEFB's lignin derivatives and the performance of the lignin derivative-based coatings

In this part, the OPEFB's lignin derivatives were synthesized by the reactions of OPEFB's lignin and vegetable oils (palm and soybean oils) at various proportions. The OPEFB's lignin derivative-based coatings were prepared. The optimal condition (type and level) of the stabilizer from Part II and the optimal content of lignin from Part III was applied in this section. The performance of the developed coatings was compared with the commercial wax in terms of the coating characteristics and the coated linerboard properties.

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CHAPTER 2

LITERATURE REVIEW

2.1 CORRUGATED PACKAGING

2.1.1 History

In 1856 two Englishmen, Edward C. Healey and Edward E. Allen, received the first patent on the corrugated paper. With a simple hand-driven machine, they produced a corrugated paper that was used for the sweatbands of hats. In 1871 the American Alberto L. Jones attached a flat sheet to the corrugated paper and patented the technique in which heat was used to corrugated paper. This product was used to protect fragile goods as bottles. Then in 1874 the American Oliver Long patented the concept of the strengthening corrugated paper by adding another facing. The first Swedish manufacturing of corrugated board was started in Malmö by Carl T. Norén in 1905. The improvement of the machines made it possible to produce corrugated board of higher quality and in the 1920's the boxes made of corrugated board started to complete with the ones made of wood [1,2].

2.1.2 General information

Corrugated board has been used as a packaging material for at least 100 years, as evidenced by a history on the evaluation of corrugating machines [3]. It is the most used type of package for packaging and distributing a wide variety of commodities ranging from fruits and vegetables, consumer products, to industrial items [4]. Worldwide demand for corrugated board has been increasing rapidly. Between 2006 and 2007, the corrugated production increased 4.5% with a production of 42,285 million square meters in 2007 [5]. This is due to its advantages that are lightweight and inexpensive, with high strength-to-weight ratio [6]. Corrugated board is made from sustainable natural resources which are readily recovered and recycled more than other packaging substrates such as plastic, glass, metal and composite material [7]. The corrugated board panels are sandwich structures consisting of two flat plates called liners which are separated by a sine wave shape fluted core referred to as the corrugating medium or the medium as illustrated in Figure 2.1 [5,8].

Corrugated boxes or corrugated containers (Figure 2.2) are the most prominent application of the corrugated board [8]. Due to their high strength-to-weight ratio, corrugated containers are considered as the leading choice of the transport packaging. It has been proposed that more than two thirds of the world's retail commodities are packed and transported in corrugated packaging [6]. The popularity of corrugated packaging is also due to the fact that it is practical, useful, economical, renewable and recyclable. In addition, it is a substrate that can be custom designed and provides excellent merchandising appeals though printing on the box panels [8].

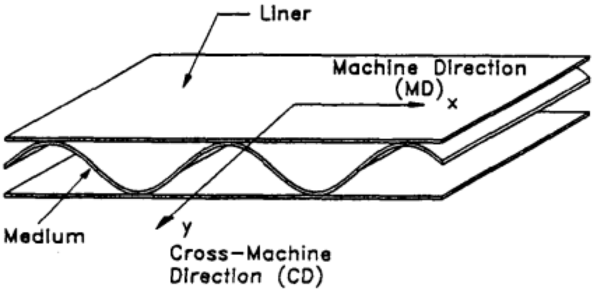


Figure 2.1 Basic geometry and component materials of corrugated board [5].

Figure 2.2 Photograph of the corrugated boxes [9].

2.1.3 Manufacturing

Corrugated board consists of one or several layers of the corrugating medium which is glued in between flat sheets of papers as seen in Figure 2.3.

The manufacturing processes can be roughly divided into two parts. First is the wet part where the medium is corrugated between two rolls and then glued onto the liners (Figure 2.4), and another one is the dry part where the heat is applied to dry the corrugated board [1].

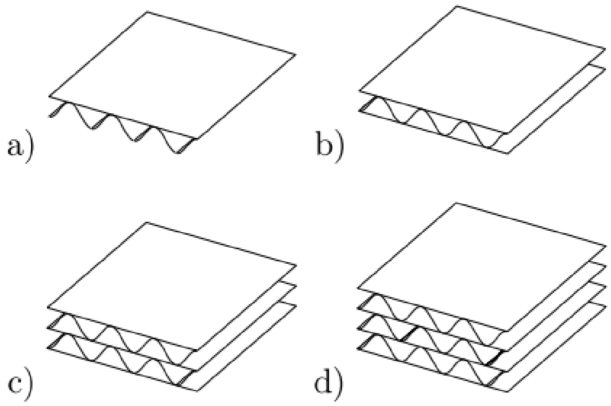


Figure 2.3 Different types of corrugated boards: a) Single face, b) Single wall, c) Double wall, d) Triple wall [1].

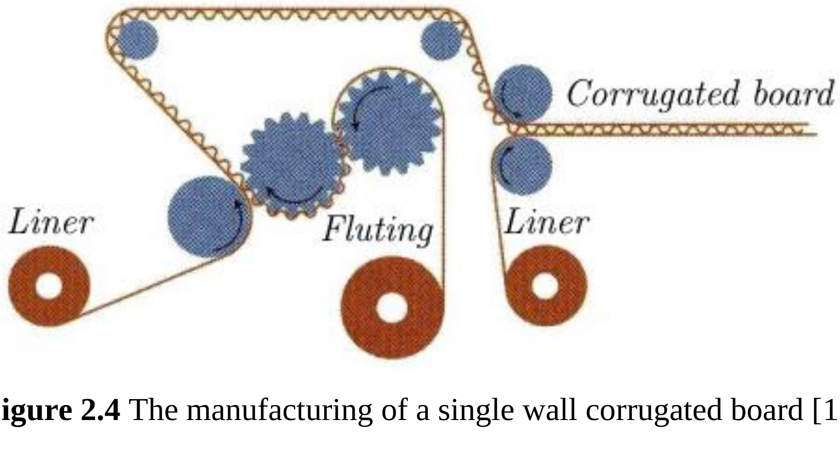


Figure 2.4 The manufacturing of a single wall corrugated board [1].

(a) Linerboard

The paperboard used for the liners is stiffness and strong so that a high bending stiffness of the combined board is achieved [5]. Most of the linerboards used for corrugated board are unbleached Kraft papers. The predominant raw materials used to manufacture linerboard are soft wood fibers [10]. Kraft linerboard used for corrugated manufacturing may have several grades depending on each manufacturer. Each paper grade is differed by its unique quality and noticeable appearance. Commonly, Kraft linerboard can be classified into three major grades as shown in Figure 2.5 [11].

(i) White linerboard

White linerboard (KS grade) is good for refrigeration and suitable for the need of high quality packaging as well as beautiful printing. It is normally used for packing frozen foods, flowers, fruit and electronic wares.

(ii) Golden yellow linerboard

Golden yellow linerboard (KA grade) is highlighted on the great strength of boxes. Due to its strength, KA grade linerboard is frequently used for a wide range of products.

(iii) Natural light brown linerboard

Natural light brown linerboard (KI grade) is normally used for medium weight products. The quality of KI grade linerboard is lower than the KA grade. Because of its light brown natural appearance, it presents an outstanding beautiful printing on top of an environmental friendly feel [11].

Figure 2.5 Major grades of Kraft linerboards; KS (left), KA (middle), KI (right) [11].

(b) Corrugating medium

The corrugating medium serves as a low density core within the sandwich structure to separate the linerboards, prevent the liners from sliding, and prohibit localized buckling [5]. The corrugating medium is normally manufactured from semi-chemical processes of hardwood. Hardwood pulps are used rather than softwoods because they cost less and contribute to the strength needed in corrugating medium [10]. A systemization of the medium was conducted according to name, marking, height, the wave differ in length (step), and the number of waves (Table 2.1). The properties of corrugated board directly depend on the properties of medium types [12].

(i) A-flute

Rough A-flute shows the reduced strength to pressure while the dynamic load perpendicular to the surface of the paperboard is larger. Furthermore, it shows greater strength towards bending and buckling, but only in the direction of wave. This flute type also exhibits a significant greater bursting strength than the B, C and E waves. However, it is seldom used at present.

(ii) B-flute

Fine B-flute shows good resistance to pressure and reduced strength to dynamic loads. There is a tendency of bending and buckling only in the direction of the wave, whereas the bending strength is larger vertically to the direction of the wave, which is not the case with rough waves. The B-flute provides a better printing surface and is more economical than the A-flute per unit area of board.

(iii) C-flute

Middle C-flute is intermediate in size between A and B-flutes, and also has the mechanical properties grouping together between them. It offers greater compression strength than B-flute, but may be crushed more easily. Generally, the A, B and C flutes are used for the production of tertiary packaging.

(iv) E-flute

Small E-flute offers greater compression strength compared to other types of corrugating flutes. On the other hand, this type of the fluting medium has the lowest resistance to bending and is used for making primary packaging [3,12,13].

Table 2.1 Flute types [12].

Flute type	Flute height (mm)	Flute/m length of the corrugated board	Glue consumption (g/m^2)
A	4.8	110	4.5–5.0
B	2.4	150	5.5–6.0
C	3.6	130	5.0–5.5
E	1.2	290	6.0–6.5
F, G, N	0.5–0.8	400–550	9.0–11.0

2.1.4 Properties and testing

The properties of papers and boards can be classified into several groups including chemical, physical, mechanical and optical properties. In this study, some properties have been focused and were tested in order to evaluate the performance of linerboards.

(a) Tensile strength

Tensile strength is a very useful property to describe the general strength of any materials. For paper, it is the maximum force per unit width that a paper strip can resist before breaking when applying the load in a direction parallel to the length of the strip.

For the tensile strength test, the test piece is stretched to the point where rupture occurs. The maximum tensile force the test piece can withstand before it breaks. From the tensile strength measured, the tensile index can be calculated using the following formula:

$$\text{Tensile index} = \text{tensile strength/basis weight}$$

Tensile index has primary used to describe the strength of pulps and to characterize the papers. The reason is that paper is an end product for which tensile strength is an important characteristic [14].

(b) Burst strength

Burst strength is the maximum pressure that the paper can resist without breaking with pressure applied perpendicular to the plane of the test piece. It is important for many packaging grade boards and especially container boards. Burst index of the materials can be calculated using the following formula:

Burst index = bursting strength/basis weight

Bursting strength is an old test for paper strength. It is a rapid and easy test to perform and does not require test piece cut exactly. Bursting strength somehow relates mathematically and physically to the tensile strength and elongation of paper.

The most common tester used for bursting strength measurements is the Mullen tester (Figure 2.6). A test piece placed over a circular elastic diaphragm is rigidly clamped at the periphery but free to bulge with the diaphragm. The hydraulic fluid pressure increases by pumping at a constant rate to bulge the diaphragm until the test piece ruptures. The bursting strength of the test piece is the maximum value of the applied hydraulic pressure [14].

Figure 2.6 A Mullen burst tester.

(c) Compression strength

The performance requirements of corrugated containers range from the need for advertising appeal to the mechanical strength for protecting the commodities. For corrugated boxes, the compression strength is generally considered to be the most prominent indicator of final box performance [15].

Top-to-bottom compression strength is one of the primary corrugated box end-use requirements, and is a performance metric often specified by the customers. The edgewise compression strength plays an important role in overall box compression performance [16].

McKee *et al.* [17] devised an equation which is known as the McKee's formula. It is used to predict top-to-bottom compression strength of corrugated boxes. The equation is as follows:

$$P = 5.78P_m(HZ)^{1/2}$$

Where, P = maximum top-to-bottom compressive force, N

P_m = edgewise compressive strength of board, N/m

H = board caliper, m

Z = container perimeter, m

From McKee's formula, it can be seen that there is a need for evaluating the edgewise compression resistance of the corrugated board. Intuitively, such a test should be well correlated with the test for compression strength of corrugated containers (the CD test for top-to-bottom and MD test for end-to-end compression). The test traditionally used for linking the edgewise compression strength of the fabricated corrugated paperboard to its paper components is the ring crush test [15].

The edgewise compression strength of the corrugated board can be predicted by the formula [18] below:

$$P_m = 1.25[\Sigma RC_f \times t_f + \Sigma RC_1]$$

Where, P_m = edgewise compressive strength of board, N/m

RC_f = ring crush value of flute, N

RC_l = ring crush value of liner, N

t_f = appropriate take-up factor of the flute

Ring crush testing has a strong historical footing and has been the default test for evaluating paper compression strength for the industry [16]. For the ring crush test, the test piece is formed into the shape of a short cylinder by inserting it into an annular groove of the specimen holder (Figure 2.7). The cylinder is loaded axially until the test piece fails [14].

Figure 2.7 Ring crush test for measuring the resistance of paper to the compression force.

(d) Water resistance

Because water facilitates the bonding of the hydrophilic pulp fibers to form paper, moisture has a strong influence on the mechanical properties of paper. Many methods are available for testing the water resistance of paper. The Cobb test is widely used and has been adopted as an internal standard. It measures the amount of water absorbed by the sample during a certain time in gram per square meter. This test is used primarily as an indicator of the water resistance of paper [14,19].

A simple Cobb tester is show in Figure 2.8. The Cobb test amounts to selling on side of the paper sample to a rubber mat by means of a cylindrical ring clamped over the upper surface of the sample. The cylindrical ring has an inside area of 100 cm^2 and a height of 2.5 cm. The aqueous liquid is poured into the ring to a depth of 1cm, and the liquid is poured off at 10 seconds before the end of a specified time interval. The sample is removed and blotted with a standardized blotting paper. Exactly at the end of the present time interval, a second blotting paper is put on top of the first and a 10 kg roller is passed over the three sheets to extract the free water. The weight increase in the paper sample is taken to be the amount of liquid absorbed in the present time interval [20].

Contact angle measurement between the water drop and the surface of paper has also been used as an indication of the water resistance. When a droplet is placed on a surface, the contact angle is the angle formed between the outer edge of the liquid droplet and the solid surface. If the contact angle is 0°, the liquid completely wets a solid surface. A contact angle greater than 90° implies that the surface is resistant to wetting by the liquid. The contact angle of a water drop increases as the paper surface becomes more hydrophobic and conversely decreases as the surface becomes more hydrophilic. The illustration of the contact angle of hydrophilic and hydrophobic surfaces is shown in Figure 2.9 [21].

Figure 2.8 A Cobb sizing tester.

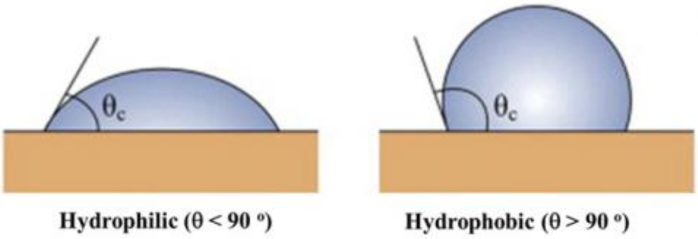


Figure 2.9 Illustration of the contact angle of hydrophilic and hydrophobic surfaces [21].

2.2 COATING FOR PAPER PACKAGING

2.2.1 General information

Paper is an important medium for communication, education, artistic products, packaging, sanitary and technical applications. Paper products make our daily lives easier. Paper and paperboard are often used as packaging materials with good strength, flexibility, and low cost [22]. Paperboard is the basis of the corrugated fiberboard that is the most widely used distribution container material representing more than 80% of the volume of all paper-based packaging materials. Paperboard offers high compressive strength and good flexibility for package production. However, due to the hydrophilic nature of its composition of cellulose, paperboards are prone to absorb water vapor from the environment, especially when stored under high humidity conditions. Absorption of moisture reduces physical and mechanical strength of the paperboards, causing corruption of boxes during storage and distribution [23]. Therefore, the coating or surface sizing is considered necessary in improving the moisture and water barriers of the paperboards so as to maintain their strength for the effective uses [24].

2.2.2 Wax coating

Wax coating enhances the hydrophobicity of paper or board substrates. Wax impregnation means that the wax penetrates into the fiber structure to give a matte surface. A glossy, hydrophobic surface can be formed through rapid cooling of the hot-melted wax using a chill roll, in which case the wax freezes and thus remains on the surface. Incorporation of wax in barrier dispersions is one way to enhance the water resistance of such coatings [25]. In recent years, natural waxes such as candelilla, carnauba or beeswax have received some interest. These waxes can be applied as thin top coatings to render the surface more water resistant or to protect the underlying moisture-sensitive coating. The main disadvantage with wax treatment involves difficulties associated with recycling since separation of wax from the fibrous material includes both large costs and severe processing problems [26].

2.2.3 Environmental concerns about coating

Surface treatment of paperboard for the improvement of functionality especially the barrier against moisture has been dominated by lamination with low-cost, readily available plastic materials over the last decade. More recently, the development of synthetic polymer dispersions has increased their attractiveness for use in the coating of board [27]. For example, wax emulsions and polyurethane- or styrene-based copolymers are typical hydrophobic sizing agents that are applied in molten form to the surface of paperboard and for improvement of the moisture and water barrier properties. Other synthetic polymers and modifiers, such as rubber derivatives, vinyl copolymers, polyamides, polyesters, and butadiene-styrene copolymers, are also developed. These coating treatments provide the surface with a hydrophobic nature and thus preventing wetting of the paperboard. [28,29].

The synthetic polymer materials are limited in the extent that they can be separated, recycled, or composted after use. Environment concerns over the use of these synthetic coatings have promoted research in the area of alternative materials. The challenge is to fine new materials or new uses of existing natural materials that are competitive with plastics with regard to both biodegradability and functional properties [27]. Biopolymers obtained from agricultural production and biodegradable synthetic polymers become a focus of interesting to use as barrier coatings on paper packaging materials. They are perfectly biodegradable and therefore perfectly safe for the environment [29,30].

2.2.4 Bio-based and biodegradable coatings

In recent years, environmental aspects have become the subject of greater attention, and considerable work and effort has been put into the replacement of fossil-based raw materials with environmentally friendly, biodegradable or recyclable materials from natural sources. Natural polymers have been the focus of much research because of interest in their potential use as biodegradable coatings for packaging. They originated from naturally renewable resources offer favorable environment advantages of biodegradability compared to conventional petroleum-based polymers. Biodegradable synthetic polymers are also focused with the same purpose. Several studies have been undertaken to investigate the potential of biodegradable polymers for coating applications.

(a) Poly(vinyl alcohol) (PVOH) and derivatives

PVOH is a water-soluble synthetic polymer with good film-forming properties. The hydrophilic character of PVOH, however, means that the material offers a poor barrier against water vapor, and that the permeability increases with increasing RH. In contrast, PVOH films are practically impermeable to gases such as O_2, N_2 and CO_2 and are resistant to oils, grease, and organic solvents [28]. PVOH is prepared from the radical polymerization of vinyl acetate that gives poly(vinyl acetate) in a first step. Hydrolysis of the product, catalyzed by NaOH, then gives PVOH. The degree of hydrolysis can be controlled to reach different grades of PVOH regarding water solubility and adhesive properties [27].

PVOH has been used in the paper industry for long time. In recent years, some novel substituted products have reached the market. Novel modification of PVOH includes the incorporation of silanol groups (Figure 2.10), available as Kuraray R-polymers (Kuraray Europe GmbH, Frankfurt am Main, Germany). The high reactivity of the silanol groups can give rise to cross-linking with inorganic materials such as alumina present on paper surfaces, leading to gel formation and the formation of a film on the surface which exhibit good barrier properties against oil and improved water resistance compared to conventional PVOH [27].

PVOH is readily degraded in waste water–activated sludge through enzymatic oxidation followed by hydrolysis, resulting in chain cleavage. The material can also be recycled or combusted to carbon dioxide and water [31]. Chemically modified PVOH (Kuraray R-polymers and Exceval TM) has a biodegradability of >90% measured by the Zahn–Wellens test and >70% measured by the method OECD 301 A, according to the manufacturer [27].

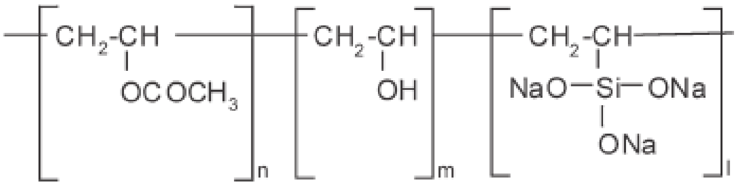


Figure 2.10 PVOH modified with silanol groups [27].

(b) Poly(lactic acid) (PLA)

Lactic acid is produced by fermentation of natural carbohydrates, e.g. maize cassava, wheat or waste products from the agricultural or food industries. PLA (Figure 2.11) is a thermoplastic, biodegradable polymer produced synthetically by polymerization of lactic acid monomers or cyclic lactide dimers. Lactic acid contains an asymmetrical carbon atom giving rise to the two optically active, L and D isomers. Lactide dimers are formed by the condensation of two lactic acid molecules, resulting in L-, D- or LD (meso) lactide. Commercial quantities of PLA for packaging applications are produced through ring-opening polymerization of lactide because this reaction favors the formation of higher-molecular-weight PLA [32].

PLA can be used for paper and board coatings, for use as drinking cups and containers [32]. The major drawback with PLA is its insolubility in water, thus making it less attractive for use in industrial dispersion coating for paperboard. PLA shows moderate moisture barrier properties but results in poor oxygen barrier. The increased surface hydrophobicity of board coated with PLA has been demonstrated through a tremendous decrease in the water absorptiveness. Recycling of PLA can be carried out by simply hydrolysis through water action [23].

PLA coated paperboard biodegrades rapidly upon composting. This process can be catalyzed by enzymes, or by the activity of bacteria or fungi. PLA has been shown to be fully biodegradable according to the 90% criteria. PLA is FDA approved and is on the EU positive list [27,33].

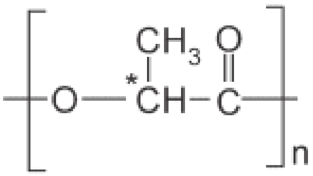


Figure 2.11 Poly(lactic acid) [35].

(c) Chitosan

Chitosan, a natural polysaccharide, is derived by deacetylation of chitin (Figure 2.12), the second most abundant naturally occurring biopolymer after cellulose. Chitosan is an edible and biodegradable material that has attracted notable interest in the packaging area Chitosan has been documented to possess film-forming properties for use as edible and biodegradable films or coatings [35].

Chitosan films have moderate water vapor permeability (WVP) and could be used to increase the storage life of fresh produce and foodstuffs with higher water activity values. Chitosan exhibits excellent oxygen-barrier properties due its high crystallinity and the hydrogen bonds between the molecular chains. Moreover, chitosan is a good barrier against grease. These properties make chitosan an attractive polymer for the barrier coating of cellulose-based materials for packaging purposes [35,36].

Chitosan is readily compatible with paper and is one of the most interesting polysaccharide coating materials for paper and paperboard. Bordenave *et al.* [37] evaluated the barrier properties against moisture and the liquid water sensitivity of chitosan-coated papers. They showed that the chitosan coating led to a significant decrease of the paper moisture transfer but the surface hydrophilicity remained high. Although chitosan-coated materials exhibited good moisture barrier properties, it is not sufficient for food applications. Chitosan can be degraded rapidly by the action of bacteria [27].

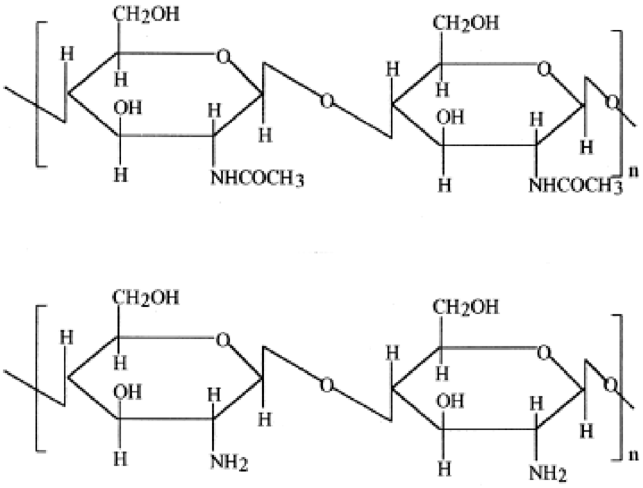


Figure 2.12 Structures of chitin and chitosan [38].

(d) Whey protein

Whey is a by-product from the cheese-making process and is thus widely available. Once considered as merely a waste product, whey has gained interest in recent years due to its high protein content. The main component of whey is β-lactoglobulin, but the proteins α-lactalbumin, immunoglobulin(s) and bovine serum albumin are also included as are some specific polypeptides in a complex mixture [27].

Whey protein is already known as an excellent barrier to oxygen, aroma, and oil and can be used as a coating material for improving the oxygen barrier property of packaging [39]. Compared to currently-used sizing agents, whey protein may have some advantages. It forms an intact water-insoluble film out of aqueous solution, due to the formation of intermolecular disulfide bonds after heat denaturation. Thus, such a whey protein film has a cross-linked structure [35].

Some studies have considered whey proteins as coatings on paper. Han and Krochta [40] reported that the whey protein coating increased the water-vapor-barrier property of pulp paper. The water vapor permeability (WVP) decreased by 44.8% compared to the uncoated paper after whey protein isolate (WPI) coating with 10 g/m^2. Chan and Krochta [41] reported a significant reduction in oxygen permeability for paperboard coated with denatured and undenatured WPI. Gällstedt *et al.* [42] showed that WPI and whey protein concentrate (WPC) enhanced the strength and toughness of the paper. Conversely, Han and Krochta [43] reported that whey protein coating decreased the tensile strength of the paper, because the coated paper structure has smaller interaction force between fibers because of coating interference.

(e) Zein

Zein is a group of proteins present in corn and is commercially available as a by-product from the corn wet milling industry [27]. Corn zein protein coatings are used as oxygen, moisture, and grease barriers for nuts, candies, and other foods. Corn zein films and coatings have relative insolubility in water, and they form strong, glossy films resistant to grease and oxygen permeation [35].

Trezza and Vergano [44] measured the grease resistance of corn zein-coated paper with respect to coating level, plasticizer addition, and time exposure. As coating level increased, uniformity of the coating also increased. Coating uniformity and quality are necessary for good grease resistance. Zein-coated papers were as effective grease barriers as were polyethylene laminates used for quick-service restaurant sandwich packaging. These results showed the potential for fully compostable paper-based wraps and boxes for the food service industry. Furthermore, they also found that coating of paper with corn zein has also led to a reduction in water vapor (WVTR) and oxygen transmission rate (OTR), but demonstrated the need for high coat weights and uniform coating layers.

Parris *et al.* [45] found that Kraft paper coated with corn zein isolate (composition 80–85% protein, 15–20% lipid and <0.25% starch) showed significant improvement in grease resistance and water vapor barrier properties. The zein-lipid coating could be easily separated from the Kraft paper, using enzymatic hydrolysis, thus providing advantageous properties with respect to repulping and recycling as compared to wax-treated paper.

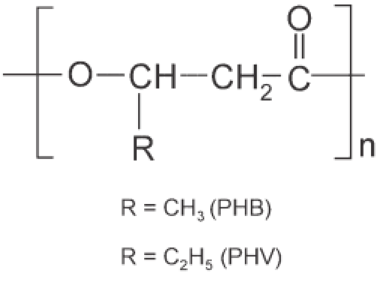
(f) Polyhydroxyalkanoates (PHAs)

PHAs are biopolymers produced by microorganisms for energy or for carbon reserves. Examples are polyhydroxybutyrate (PHB) and poly(hydroxybutyrate-co-valerate) (PHB/V) (Figure 2.13). These polymers are insoluble in water. PHB forms highly crystalline films which are thus stiff and very brittle, whereas films from copolymers containing the longer alkyl chain of HV give films with excellent toughness and strength [27,46].

PHAs possess excellent film-forming and coating properties and are water resistant due to their high hydrophobicity. PHB-coated paperboard has been used for packaging of ready meals, while PHB/V-coated board has been used for dry products, dairy products and beverages. The drawbacks with PHAs are poor gas barrier properties and high production costs [47].

Krook *et al.* [48] investigated the creasability of PHB/V compression molded onto paperboard. The PHB/V coating showed no evidence of cracks, and the delamination was observed to decrease with increased molding temperature due to improved paperboard-coating adhesion.

Paper coated with PHB and PHB/V has been demonstrated to biodegrade rapidly. The biodegradation mechanism of these bacterially produced polyesters involves hydrolysis in water followed by chain scission [27].



$$\left[-O-\underset{\underset{R}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}- \right]_n$$

Figure 2.13 PHA monomer [46].

(g) Oxidized starch

Starch is a naturally abundant plant polymer with the function of which is to serve the plant with carbohydrates. The starch consists of α-D-anhydroglucose units built up of the components of amylose and amylopectin [27]. Amylose has historically been regarded as linear with the glucose units linked together by α-1,4-glucosidic bonds. Amylopectin is a highly branched molecule in which the branches are bound to the main chain through α-1,6-glucosidic linkages [49] (Figure 2.14). Starch in its native form exists as semi-crystalline granules which vary in size and shape depending on the plant source [27].

Starch has been a subject of academic and industrial interest for many decades because it is a renewable, biodegradable, abundantly available and cheap resource [50]. For oxidized starches (Figure 2.15), they attracted much significance and are widely used, e.g. in paper, textile, laundry finishing and food industries, to provide surface sizing and coating properties because of their low viscosity, high stability, high transparency, excellent film-forming and binding properties [51–55]. Oxidized starch is commonly prepared by reacting starch with an oxidant under controlled temperature and pH. Many oxidizing reagents, i.e. periodate, chromic acid, permanganate, nitrogen dioxide and sodium hypochlorite have been used to oxidize starches [52,56]. During the oxidation reaction, the starch is extensively depolymerized and the hydroxyl groups on the ring carbons are oxidized to aldehyde and carboxyl groups resulting in change of the physical and chemical properties [50,53,57].

Ahn and Ahn [58] treated the outside of single-wall corrugated boards with oxidized starch solution and then used them for making the corrugated boxes. They found an increase in the compression strength of the boxes which was directly depended on the concentration of solution used.

Jonhed *et al.* [59] applied the oxidized hydrophobized potato starch solution to the liner and board. They found that the water absorption of coated papers in terms of Cobb_{60} values was reduced, comparing with the uncoated ones. However, the sized papers showed a reduction in water contact angle.

Lipponen *et al.* [60] sized the papers with the solution of oxidized potato starch. The results show that after sizing, the oil absorption of papers was reduced while their internal strength seemed to be increased.

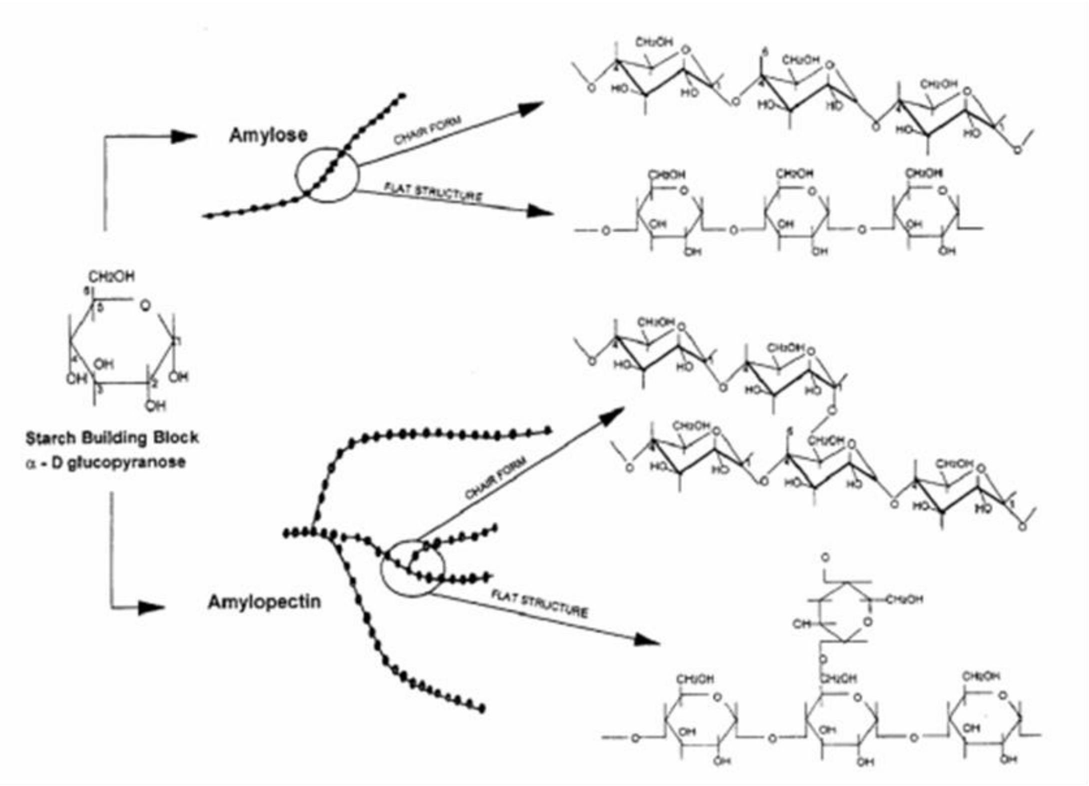


Figure 2.14 Amylose and amylopectin in starch granule [61].

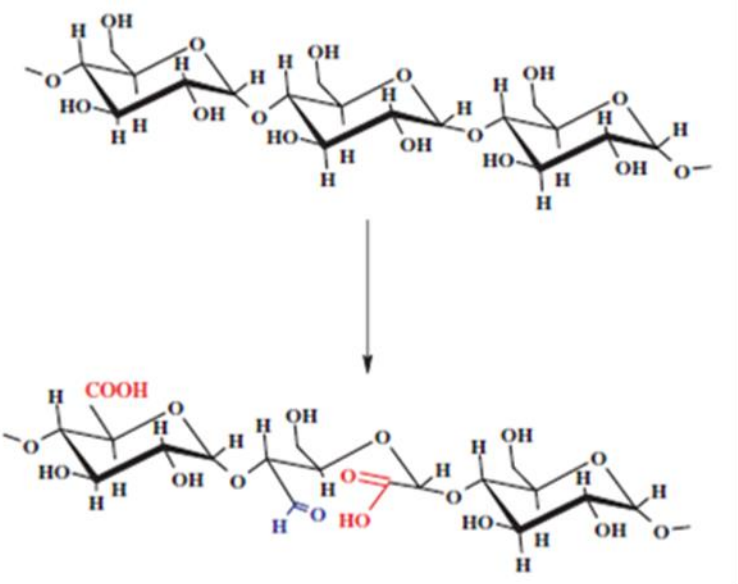


Figure 2.15 Schematic representation of starch oxidation [62].

2.3 LIGNIN

2.3.1 General information

Lignin is one of the most abundant natural non-carbohydrate organic substrate on the earth, accounting for approximately 30% of the organic carbon in the biosphere [63–65]. The importance of lignin in plants should be considered from different aspects, i.e. it is crucial for structure integrity of the cell wall and stiffness and strength of the stem [65–67]. From the nutritional point of view, lignin has always been blamed as an important barrier to polysaccharide utilization [68]. In addition, lignin waterproofs the cell wall, enabling transport of water and solute through the vascular system, and plays a role in protecting plants against pathogens [69].

2.3.2 Chemistry

Lignins are complex racemic aromatic heteropolymers with the substituents connected by both ether (C–O–C) and carbon-carbon (C–C) linkages (Figure 2.16). It is derived mainly from three hydroxycinnamyl alcohol monomers differing in their degree of methoxylation: p-coumaryl alcohol (p-hydroxyphenyl propanol), coniferyl alcohol (guaiacyl propanol) and sinapyl alcohol (syringyl propanol) (Figure 2.17) [70,71]. The lignin content of softwoods ranges from about 25–35%, which is greater than the lignin content of hardwoods, 18–25%. Softwood lignin is made up of approximately 80% coniferyl, 14% p-coumaryl and 6% sinapyl alcohols. In contrast, hardwood lignin is composed of 56% coniferyl, 4% p-coumaryl and 40% sinapyl alcohols [65,70]. Grass lignin is rich in p-coumaryl units. Figure 2.18 depicts some of the common linkages found in softwood. The abundance of these types of linkages is summarized in Table 2.2. The dominant linkage in softwood lignin is the β–*O*–4 linkage [72,73]. This linkage is often modeled by guaiacylglycerol-β-guaiacylether dimers (Figure 2.19).

Sarkanen and Ludwig [73] classified lignin into two groups, namely guaiacyl and guaiactyl-syringyl lignin. Most of the gymnosperm lignins are typical guaiacyl lignins, although they contain small amounts (<1.5%) of syringyl units and a rather lower proportion of p-hydroxyphenyl units. Both dicotyledon and grass lignin are true guaiacyl-syringyl lignins. The syringyl content of woody angiosperm lignins varies between 20 and 60% [74].

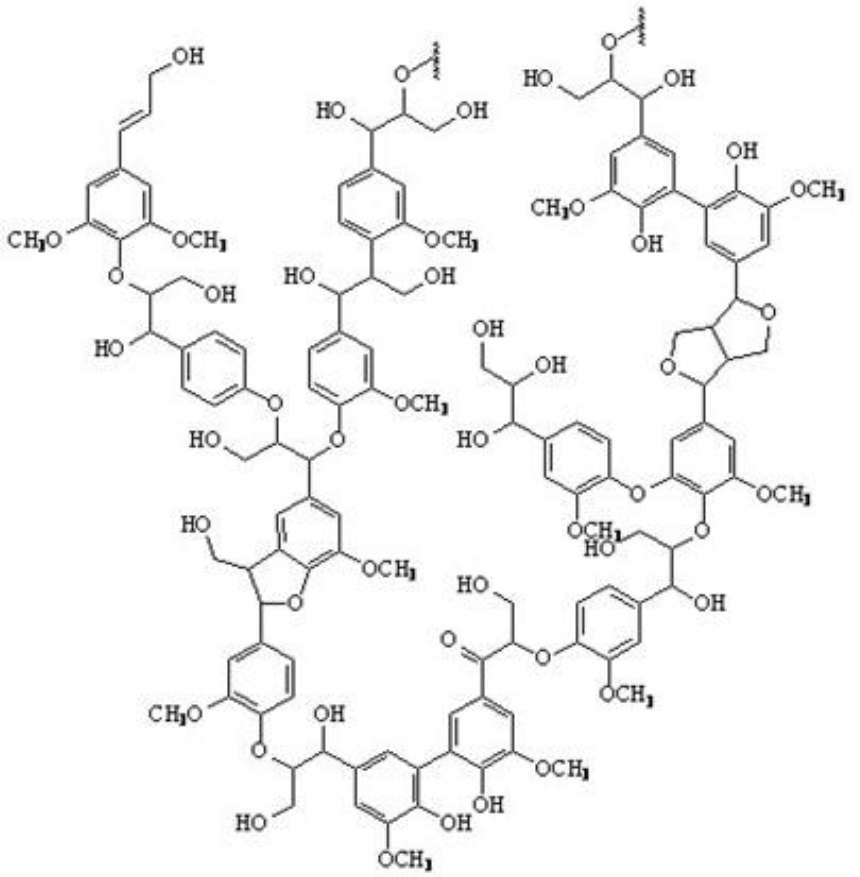


Figure 2.16 Chemical structure of lignin [65].

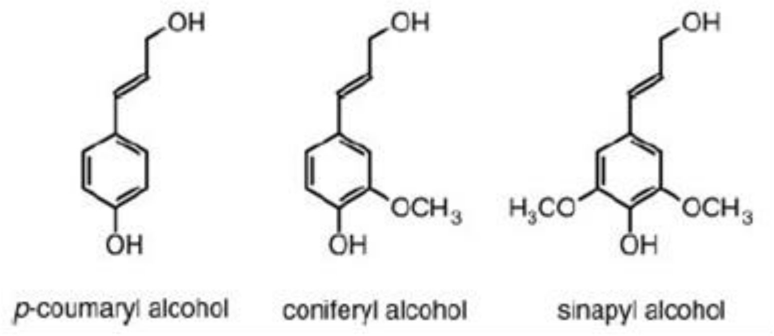


Figure 2.17 Major monolignols found in natural plant lignin [71].

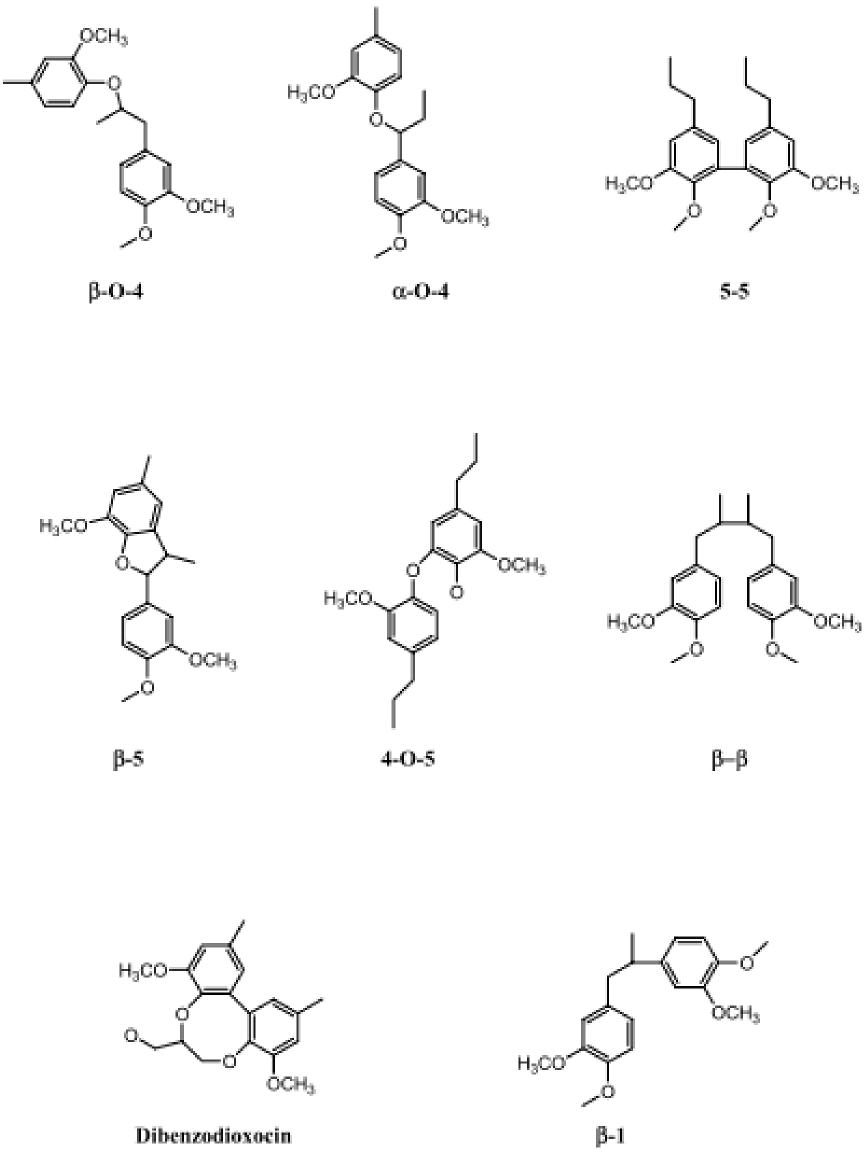


Figure 2.18 Common linkages between phenylpropane units in lignin [75].

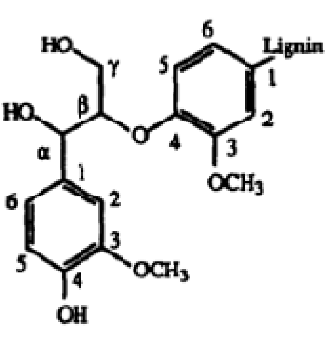


Figure 2.19 β-aryl ether lignin model [70].

Table 2.2 Proportions of different types of linkages connecting the phenylpropane units in softwood lignin [75].

Linkage type	Dimer structure	Percentage (%)
β–*O*–4	Phenylpropane β-aryl ether	45–50
α–*O*–4	Phenylpropane α-aryl ether	6–8
β–5	Phenylcoumaran	9–12
5–5	Biphenyl and dibenzodioxocin	18–25
4–*O*–5	Diaryl ether	4–8
β–1	1,2-Diaryl propane	7–10
β–β	β-β-Linked structures	3

2.3.3 Preparation

In general, lignin is isolated by wood pulping in order to use the fiber in paper applications. There are several methods used for removing lignin, but the most common used in industrial scale is Kraft pulping which produces strong pulps suitable for the production of corrugated board, liner board and paper bags. The Kraft process utilizes a solution of sodium hydroxide and sodium sulfide to treat wood chips at an elevated temperature around 170ºC. The phenolic groups are susceptible to ionization in alkaline conditions by extraction of the phenolic proton, causing the lignin chains to become soluble. Lignin produced by the Kraft pulping process is known as Kraft lignin.

A second historically important pulping process, though currently much less prevalent than Kraft pulping, is the sulfite process. In this process wood reacts with sulfur dioxide and hydrogen sulfite, causing sulfonic acid groups to be attached to the lignin backbone, thereby making the lignin water soluble. Lignin produced by the sulfite pulping process is known as lignosulfonate [76].

Other wood pulping processes have been developed, though they are not usually used on an industrial scale like Kraft or sulfite pulping. “Organosolv” lignin is produced by pulping wood in organic solvents with catalysts in both acidic and alkaline conditions. This process is claimed to be less polluting than Kraft or sulfite pulping due to the absence of sulfur compounds [77,78].

Caustic soda (NaOH) is one of the original chemical delignifying agents for lignocellulose material. The pulping process with pure NaOH solution is called soda pulping. It can be applied to a wide variety of lignocellulosics, especially to hardwoods and herbaceous material but has limited delignification ability compare to Kraft method [79]. The soda pulping is the simple process widely used in the laboratory scale for the scientific study. The delignification by soda pulping was found in many literatures [80–84].

In black liquor, free phenolic and carboxylic groups of the dissolved lignin are deprotonized. Although it might be possible to extract some lignin from the liquor by less polar solvents such as dichloromethane or ethyl acetate, this would yield very small amounts of lignin. The precipitation of lignin by acidification of the black liquor and protonation of the lignin functional groups is a more efficient way for isolating lignin. This can be done by carbon dioxide or different kind of mineral acids such as sulfuric acid, both give the same product in equal yields. Both sulfuric acid and carbon dioxide result in residual liquor possible to regenerate in the recovery system [85]. Several studies used sulfuric acid for recovering lignin from the black liquors [86–90].

The size of the lignin molecules is also possible to separate different fractions by stepwise precipitation of lignin between different pH-intervals [91]. To separate inorganic salts and other contaminants from the precipitated lignin, a washing step can be conducted by making slurry of the precipitated lignin in diluted mineral acid [85].

2.3.4 Utilizations for material applications

(a) Polymer blends

The development of biodegradable materials and materials from renewable sources, such as polyesters, polylactides, and polysaccharides, is in great demand. However, such polymers generally show poor mechanical, thermal properties and prohibitive cost which prevent their large commercial utilization. As a result of these limitations, research efforts have concentrated to modify these polymers by producing biodegradable polymers by bending with lignin [92].

Feldman *et al.* [93] formulated the blends of unplasticized poly(vinyl chloride) (PVC) and organosolv lignin. The results indicated that lignin could replace up to 20% of the copolymer. At this level of displacement, the mechanical properties of the new composites compared with those of the pure PVC. This suggested a proton donor/proton acceptor interaction between lignin and PVC chains.

Kubo *et al.* [94] blended organosolv lignin with poly(ethylene oxide) (PEO) over a range of blend compositions. They found that the organosolv lignin displayed better plastic behavior compared with kraft lignin and the corresponding PEO blends were described to possess good thermoforming properties.

Pucciariello *et al.* [95] prepared the blends of steam-explosion lignin and poly(ε-caprolactone) (PCL) with the technique of high energy ball milling. Their results showed that the addition of lignin stabilized the PCL against UV radiation and increased the modulus of the blends. However, the presence of lignin decreased the tensile strength and the elongation at break because of the poor compatibility between lignin and PCL.

Mousavioun *et al.* [96] investigated the thermal properties and miscibility of poly(hydroxybutyrate) (PHB) and soda lignin blends. Their results suggested compatibility for the blends containing up to 40 wt% soda lignin. The FTIR analysis shows that the miscibility of the blends is associated with the hydrogen bonding between the reactive functional groups in lignin with the carbonyl groups of PHB (Figure 2.20).

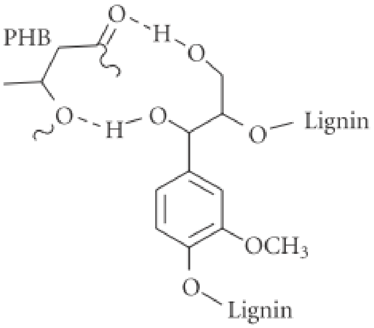


Figure 2.20 Hydrogen bonding interactions between soda lignin and PHB [96].

(b) Wood adhesives

Adhesives are required in many wood processing industries such as particleboard, wood panels, fiberboard, and plywood. Among the various adhesives used for the production of these materials, phenol formaldehyde (PF) resin is the most common type of adhesive. These adhesives are in adequately supply today, but the scarcity of petroleum products could affect the future cost and availability of these petroleum-based adhesives [97].

Hage *et al.* [97] mixed wood panel adhesive based on glyoxylated organosolv lignin and mimosa tannin mixtures for interior-grade applications. Two different formulations (glyoxalated lignin/tannin = 50/50 and 60/40) prepared with miscanthus organosolv lignin and mimosa tannins were analyzed. They found that the 50/50 formulation does not satisfy the internal bonding (IB) strength required, but the 60/40 formulation gives a good result and satisfies the relevant requirements of standard specifications for interior type wood particleboard.

Khan *et al.* [98] prepared lignin-phenol-formaldehyde (LPF) in two stages. The first stage involved the preparation of lignin-phenol (LP), while the second step comprised the preparation of lignin-phenol-formaldehyde resin. The objective of their study was to replace as much phenol as possible with lignin. They found that the maximum lignin to phenol ratio was found to be 30%.

Pizzi [99] developed a promising technology based on premethylolated lignin in the presence of small amounts of a synthetic phenol-formaldehyde (PF) resin and polymeric 4,4-diphenyl methane diisocyanate (PMDI). The proportion of premethylolated lignin used is 65 wt% of the total adhesive, the balance being made up of 10–15% PF resin and of 20–25% PMDI. This adhesive presses at very fast speed, well within the fastest range used today industrially.

(c) Corrosion inhibitors

Corrosion is an electrochemical process that takes place at the surface of a metal substrate when exposed to the atmosphere and other corrosive environment, causing the metal to deteriorate. As environmental constraints continue to limit the use of many types of corrosion inhibitors, lignin presents a green alternative to using synthetic organic corrosion inhibitors that are mostly expensive and toxic [100].

Akbarzadeh *et al.* [100] have shown that the soda and kraft lignin from the empty fruit bunch of palm oil was an excellent corrosion inhibitor of mild steel in NaCl at alkaline pH that was evaluated via electrochemical and weight-loss techniques.

Ren *et al.* [101] developed the lignin terpolymer by grafting copolymerization of both dimethyl diallyl ammonium chloride and acrylamide onto the lignin recovered from straw black liquor. The lignin terpolymer provided an inhibition of 95% against the corrosion of mild steel in 10% HCl.

(d) Surface coatings

Lignin and derivatives have the right chemistry to be used in making coating because they have small particle, are hydrophobic and have ability to form stable mixtures [88]. Many studies have focused on the uses and the modifications of lignin for a wide range of utilizations in the material coatings.

Park *et al.* [102] mixed the lignin extracted from sugarcane bagasse partially with phenol formaldehyde (PF) resin and then applied to the cardboards. Water absorption tests show that the lignin-PF resins are effective water barrier coatings for cardboard substrates. However, lignin-PF resin resulted in a negative charge which would contribute to the reduction in the contact angle.

Adcock *et al.* [103] synthesized poly[lignin-*g*-(1-phenylethylene)] graft co-polymers using free-radical graft polymerization. Maple wood filler was coated with the copolymers and used as the reinforcement for polystyrene composites. They reported that the copolymer coating decreases swelling in the composite, the partial molar volume of the imbibed water, and the dimensional change in the solid.

Chen *et al.* [104] developed the graft copolymers of Kraft lignin and 1-ethenylbenzene for wood coating. They found that the coating of graft copolymers change the contact angle of water on wood surface from 50 to 110°. Furthermore, lap shear strengths increase 56%, from 1826 to 2840 kPa, when the wood is coated with a graft copolymer containing 51.7% lignin.

Antonsson *et al.* [63] produced a new hydrophobic lignin-derivative from the reaction of Kraft lignin and linseed oil. They found that the filter paper treated with lignin-linseed oil derivative exhibited a wide contact angle while that of the filter paper treated with lignin was not measurable.

2.4 OIL PALM EMPTY FRUIT BUNCH

2.4.1 Introduction

Oil palm (*Elaeis guineensis* Jacq.) (Figure 2.21) is a native of West Africa. From its home, the oil palm has spread throughout the tropics and is now grow in 16 or more countries for its oil-producing fruit [105–107]. However, the major center of production is in South East Asia (SEA) with Malaysia, Indonesia and Thailand, which produce about 80% of world’s palm oil in 2001[108]. In Thailand, the oil palm was introduced in 1968, and become one of the major agro-industries in the south [109]. The palm oil industry plays an important role in the economic development of the country and in enhancing the economic welfare of the population [108]. In 2010, the oil palm plantations in Thailand increased to 4.4×10^6 Rais (about 1.7×10^6 acres) and a large quantity of fresh fruit bunches (FFB) were harvested approximately about 8.2×10^6 tons [110]. A photograph of FFB is illustrated in Figure 2.21. Palm oil occupies 70% of the Thai vegetable oil market, and is estimated to be worth 40,000 million Baht per annum and has known an average annual growth rate of 15% during the last decade. As the climatic conditions in the south are suitable for palm trees, the oil palm plantation area has expanded ever since [111]. Palm oil production generates large amount of solid residues that are fibers, shells and empty fruit bunches. For every 100 tons of fresh fruit bunches entered to the oil extraction processes, about 25 tons of oil palm empty fruit bunches (OPEFB) as solid wastes will be produced.

Figure 2.21 Photographs of oil palm tree (left) and fresh fruit bunch (right) [106].

2.4.2 Chemistry

All the nature fibers consist of basic chemical building block of cellulose, hemicellulose, and lignin with varying proportions. Other components such as pectins and waxes are also present in minor quantities in the fibrous materials [112]. Generally, the OPEFB contains about 40–50% cellulose, 20–30% hemicellulose, 20–30% lignin and 10–15% moisture content [113–115]. Abdul Khalil *et al.* [116] revealed that OPEFB contain highest composition of hemicellulose compared to coir, pineapple, banana, and even soft and hardwood fibers. Lignin which is also responsible for tough and stiffness properties of the fiber was lower than coir fibers, but still higher than other fibers. In addition, the OPEFB contains minor components of arabinose, xylose, mannose, galactose, silica, copper, calcium, manganese, iron, and sodium. Law *et al.* [106] found that OPEFB fiber contains about 1.5–2.5% of ash with carbon (45–50%) and oxygen (44–48%) as main constituents following the silica of about 5–6% and others.

2.4.3 Problems and Challenges

In general, palm oil industry has to dispose about 1.1 ton of OPEFB per every ton of oil produced [117]. Some quantity of this cellulosic material is currently used in the preparation of fertilizers or as mulching material [118]. However, a major proportion is left in mill premises itself. When left in field, these waste materials create great environmental problems [106,119]. A view of OPEFB wastes piled up for disposal in a palm oil mill is shown in Figure 2.22. Furthermore, these wastes also result in forfeiture of substantial economic value, which would have been induced by their suitable applications. Hence, palm oil producing countries, in particular, can generate revenue out of this waste product which till date is considered to be challenging. The sustainable, non-hazardous, non-carcinogenic, eco-friendly, biodegradable product developed from these cellulosic wastes will surely benefit the human kind across the globe in broad-spectrums [112].

Figure 2.22 View of OPEFB wastes piled up in a palm oil mill premise [119].

2.5 DISPERSION SYSTEM

2.5.1 General information

The primary purpose of dispersion is to break down particle aggregates and agglomerates to distribute these particles evenly throughout a medium. Usually the medium is a liquid or a solid polymeric material that is deformable during processing. Ideally, a good dispersion consist chiefly of primary particles, with only a minimum of loose aggregates and agglomerates [120].

2.5.2 Dispersion stabilization

The stage of great importance in the dispersion process is the stabilization of the dispersion. This ensures that the separation of the particles has been reached, and also that the particles are homogeneously distributed in the medium. If the dispersion has not been stabilized, flocculation may occur as a result of clumping together of the particles. Flocculation is generally a reversible process. Flocculates typically break down when shear is applied and will form again when the shear is removed. Where the dispersion is not stabilized, the use of stabilizers or polymeric dispersants can be considered. Such additives may be used directly during dispersion manufacture [120].

(a) Charge Stabilization

Dispersions may become stable through two generally accepted mechanisms: charge stabilization and steric or entropic stabilization. Charge stabilization is due to repulsive electrostatic interactions, which are the result of a charged electrical double layer surrounding the particles [121] as shown in Figure 2.23. The charged electrical double layer developed around the particles extends well into the liquid medium, and since all the particles are surrounded by the same charge (positive or negative), they repel each other when they come into close proximity [120].

(b) Steric stabilization

Steric stabilization is due to steric hindrance resulting from the adsorbed dispersing agent, the chains of which become solvated in the liquid medium, thus creating an effective steric barrier that prevents the other particles from approaching too close. This phenomenon is also called entropic stabilization, because as the coated particles approach each other, the solvated chains of the adsorbed dispersant lose some of their degrees of freedom, resulting in a decrease in entropy. Such lowering in entropy gives rise to repulsive forces, which keep the particles away from each other. This type of steric or entropic stabilization is also represented in Figure 2.23 [120]. Steric stabilization has long been found in colloidal particle system [122].

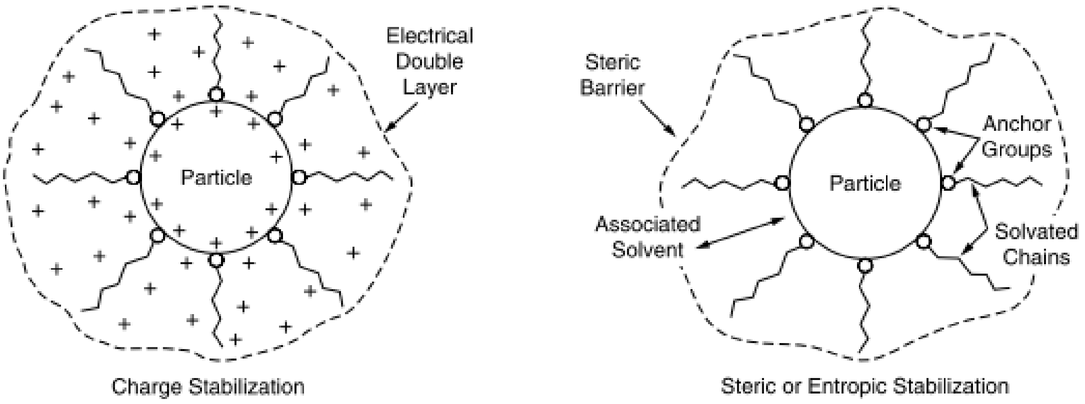


Figure 2.23 Charge and steric stabilizations [120].

2.5.3 Stabilizer

Stabilizers are thermodynamically unfavorable systems that tend to break down over time due to a variety of physicochemical mechanisms, including gravitation, flocculation, coalescence and Ostwald ripening [123–125]. Gravitational separation is one of the most common forms of instability in emulsions and dispersions, and may take the form of either “creaming” or “sedimentation” depending on the relative densities if the dispersed and continuous phases. Creaming is the upward movement of droplets due to the fact that they have a lower density than the surrounding liquid, whereas sedimentation is the downward movement of droplets due to the fact that they have a higher density than the surrounding liquid. It is possible to form emulsions or dispersions that are kinetically stable for a reasonable period of time by including know as surfactants, which are often called dispersing agents, emulsifiers, foaming agents, stabilizers, etc., depending on their performance activities and their effect on the final product. A useful distinction can be made in terms of stability. Emulsifiers are surface-active molecules that adsorb to the surface of freshly formed droplets during homogenization, forming a protective layer that prevents the droplets from aggregating, and must confer short-term stability [123,125], whereas stabilizers stabilize the system by retarding or preventing droplet movement through their modification of the rheological properties of the aqueous dispersion medium, and must confer long-term stability [124].

(a) Arabic gum

Arabic gum (acacia gum) is prepared from an exudate from the stems and branches of sub-Saharan *Acacia senegal* and *Acacia seyal* (Leguminosae) trees and produced naturally as large nodules during a process called gummosis to seal wounds in the bark of the tree. It is a less consistent material than other hydrocolloids [126].

Arabic gum is a complex and variable mixture of arabinogalactan oligosaccharides, polysaccharides and glycoproteins. Depending on the source, the glycan components contain a greater proportion of L-arabinose relative to D-galactose (*Acacia seyal*) or D-galactose relative to L-arabinose (*Acacia senegal*). Arabic gum consists of a mixture of lower molecular weight polysaccharide as the major component and higher molecular weight hydroxyproline-rich glycoprotein as the minor component but varies significantly with sources [127].

As a stabilizer, arabic gum is widely used in the drinks industry to stabilize flavors and essential oils, for example in soft drink concentrates. The simultaneous presence of hydrophilic carbohydrate and hydrophobic protein enables its emulsification and stabilization properties [128]. The arabic gum glycoprotein possesses a flexible but compact conformation. It is readily soluble to give relatively low viscosity newtonian solutions even at high concentrations [129].

(b) Carrageenan

Carrageenan is a collective term for polysaccharides prepared by alkaline extraction of red seaweed (*Rhodophycae*), mostly of genus *Chondrus*, *Eucheuma*, *Gigartina* and *Iridaea*. Different seaweeds produce different carrageenans [130].

Carrageenans are linear polymers of about 25,000 galactose derivatives with regular but imprecise structures, dependent on the source and extraction conditions. *k*-carrageenan is produced by alkaline elimination from μ-carrageenan isolated mostly from the tropical seaweed *Kappaphycus alvarezii* [131], whereas *i*-carrageenan is produced by alkaline elimination from *v*-carrageenan isolated mostly from the Philippines seaweed *Eucheuma denticulatum* [132].

Carrageenans are used mainly for thickening, suspending and gelling. *k*- and *i*-carrageenans form thermoreversible gels on cooling in the presence of appropriate counter ions. They are also used as a binder in cooked meats, to firm sausages and as a thickener in toothpaste and puddings [133].

(c) Guar gum

Guar gum (also called guaran) is extracted from the seed of the leguminous shrub *Cyamopsis tetragonoloba*, where it acts as a food and water store.

Guar gum is a galactomannana consisting of a (1→4)-linked β-D-mannopyranose backbone with branchpoints from their 6-positions linked to α-D-galactose (1→6-linked-α-D-galactopyranose). It is made up of non-ionic polydisperse rod-shaped polymers consisting of molecules made up of about 10,000 residues. Higher galactose substitution also increases the stiffness but reduces the overall extensibility and radius of gyration of the isolated chains [134].

Guar gum is an economical thickener and stabilizer. It hydrates fairly rapidly in cold water to give highly viscous pseudoplastic solutions of generally greater low-shear viscosity when compared with other hydrocolloids. Guar gum does not form gels but does show good stability to freeze-thaw cycles. It shows high low-shear viscosity but is strongly shear-thinning and is not affected by ionic strength or pH. Guar gum retards ice crystal growth non-specifically by slowing mass transfer across solid/liquid interface [135].

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CHAPTER 3

RECOVERY, CHARACTERISTICS AND POTENTIAL USE AS LINERBOARD COATING MATERIAL OF LIGNIN FROM OIL PALM EMPTY FRUIT BUNCH'S BLACK LIQUOR

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ABSTRACT: The present work aimed at recovering the lignin from the black liquor of oil palm empty fruit bunch (OPEFB) and the potential use of OPEFB's lignin for the production of linerboard coating. The influence of the pHs (5, 4, 3, and 2) of black liquor on the recovery mass and on the characteristics of OPEFB's lignin was studied. The recovered mass of lignin increased with the decreasing of the pH of black liquor. The alteration of the pH did not influence on the chemical components of the recovered lignin. However, it was observed that lignin progressively degraded when a lower pH was adjusted. The lignin recovered at pH-5 was selected for the preparation of coatings so as to avoid its feature losing from the drastic degradation. The OPEFB's lignin-based coatings were prepared by mixing of 3% oxidized starch solution and various contents of lignin (1, 3, 5, 7 and 9% w/v). It was observed that the lignin-based coatings had lower viscosity than the commercial wax. The water absorption of coated linerboards decreased ($p<0.05$) when the content of lignin increased from 1–5%. However, this decreasing was not significant ($p\geq0.05$) when the lignin content was higher than 5%. The mechanical properties of the linerboards coated with lignin-based coatings were similar to those with the commercial wax coating. This study indicates that the OPEFB's lignin-based coatings can be used as an alternative agent for the production of linerboard coating.

Keywords: Oil palm empty fruit bunch; Black liquor; Lignin; Linerboard; coating; Water resistance

3.1 INTRODUCTION

The corrugated box is the most popular paper packaging for transportation for a wide range of products. It is effective, lightweight and cost-effective. The structure of corrugated board consists of the linerboard and the corrugated medium. The fact that the moisture has a strong influence on the strength of paper materials is well known. Water molecules permeating into a paper structure can attach to the OH sites in a basic cellulose unit that causes reducing the strength of the paper [1]. Thus the coatings are considered necessary to improve barriers against moisture of paper packaging so as to maintain its strength. Synthetic polymers, such as polyethylene (PE) and wax, have been used as the main sources of coating in the paper industry [2,3]. Because these polymers are based on crude oil, an increase in demand for their use results in an increase in oil consumption. Moreover, they are not degradable in the normal environment; this causes serious environmental problems. Therefore, materials based on renewable resources and agricultural wastes have become a major focus of interest for use as an alternative for the production of coating [4,5].

Oil palm has become one of the major industrial crops of Thailand. The palm oil industry plays a key role in enhancing the economic welfare of the local population and in the economic development of the country [6]. Many companies in the southern region have been operating in palm oil production with the main goal of domestic consumption. Palm oil production generates a large scale of solid residues, especially oil palm empty fruit bunches (OPEFB). The OPEFBs present difficulties for use as a fuel because they contain high moisture content. In addition, eliminating them is costly in terms of transportation and energy consumption. Although there are some uses of OPEFB residues, such as a fertilizer for oil plantation and as material for growing mushrooms, no a large scale uses has been made of them. Today the OPEFB wastes have become a major problem for the oil palm industry, one that needs to be solved urgently.

Previous studies found that the OPEFB consists of lignin as approximately 25% of the composition [7,8]. Lignin is a three-dimensional polyphonic macromolecule which has a very complex structure. It is composed of many subunits, such as phenols, aromatic rings and methoxy groups, joined together with both C–C and C–O–C linkages. Lignin has the right chemistry – small particle size, hydrophobic behavior, and ability to form stable mixtures – suitable for the production of coating [9].

Soda pulping is one of the most frequently used methods for the delignification of agricultural residues. During the pulping processes, the lignin is separated from the raw material in the form of solid dissolving in the solvent. The color of this admixture is dark brown and it is called black liquor. Conventionally, the lignin has been recovered from black liquor through precipitation with the mineral acids such as hydrochloric and sulfuric acids. Koljonen *et al.* [10] and Mussatto *et al.* [11] noted that the recovery yield of lignin increases with a decreasing of the pH of black liquor. They also show that the lignin is clearly recovered when the pH of the liquor is adjusted to lower than 6.

In the present study, the black liquor was obtained by a soda pulping process using oil palm empty fruit bunch (OPEFB) as the raw material. Four pH values (5, 4, 3 and 2) were adjusted to the black liquor for lignin precipitation by the addition of sulfuric acid. The characteristics of each lignin fraction were analyzed with FTIR and TGA techniques. The OPEFB's lignin recovered at optimum pH was selected for the preparation of linerboard coatings. The OPEFB's lignin-based coatings were prepared by varying the contents of the lignin (1, 3, 5, 7 and 9%). The viscosity of the coatings was measured. The properties of coated linerboards (water absorption, surface contact angle, ring crush, tensile and bursting strength) were also investigated. The properties of the linerboards coated with OPEFB's lignin-based coating and commercial wax coating was also compared.

3.2 MATERIALS AND METHODS

3.2.1 Materials

Oil palm empty fruit bunches (OPEFB) were supplied by Virgin Vegetable Oil Co., Ltd., Songkhla, Thailand. The linerboards (KS170) and the commercial wax (WR390) were obtained from Thai Containers Songkhla (1994) Co., Ltd., Songkhla, Thailand. Arabic gum was purchased from Merck KGaA, Darmstadt, Germany.

Oxidized starch was supplied by Siam Modified Starch Co., Ltd., Pathumthani, Thailand. Other chemicals were purchased from S.V. Medico Co. Ltd, Songkla, Thailand.

3.2.2 Lignin preparation

Palm fruit bunches were cleaned with water at least 5 times before being chopped into small pieces, and then dried in a hot air oven for at least 72 h. A suspension of chopped OPEFB and 20% NaOH solution (1:15 w/v) was cooked at 170°C for 120 min in a rotary digester (Model RDB-D352, from Nanasiam Intertrade Co., Ltd.). Black liquor obtained from cooking was kept in an ambient temperature for 48 h. 4M sulfuric acid was dripped into the liquors until the pH was reduced to the specific values (varied at 5, 4, 3 and 2 for each batch) to precipitate lignin from the liquid (performed under an airflow to remove the odorous compounds given off during precipitation). After 24 h the lignin sediment was separated from the aqueous with no.4 filter papers (Whatman™), and then washed thrice with clean water. The lignin was dried in a vacuum oven at 70°C for 48 h to evaporate the solution remaining in it. After that, the lignin was mashed in a mortar and sieved through a 200 mesh strainer, and stored in an ambient temperature in the absence of daylight.

3.2.3 Calculation of lignin extraction yields

The recovery yield of each lignin fraction obtained from the different pH separations was computed as follows:

$$\%\text{ lignin yield} = (W_1/W_2) \times 100$$

where W_1 is the weight of recovered lignin and W_2 is the weight of OPEFB used for the extraction.

3.2.4 Fourier transform infrared spectrophotometry (FTIR)

FTIR analysis was performed on the lignin fractions by an infrared spectrometer (model Equinox 55, from Bruker Corporation, Germany). The KBr pellet technique was used for preparing samples. Each spectrum was recorded in a frequency range of 400-4000 cm^{-1}.

3.2.5 Thermogravimetric analysis (TGA)

The thermal behavior of lignin fractions was studied by using a thermogravimetric analyzer (model TGA7, from Perkin Elmer Inc., USA). Scans were recorded from 50 to 850°C with a heating rate of 10°C/min under a nitrogen atmosphere.

3.2.6 Coating preparation and procedures for coating linerboards

Lignin-based coating was prepared by the mixing of 3% oxidized starch solution (as the coating medium) and lignin powder (varying at 1, 3, 5, 7 and 9% w/v of the starch solution) with the addition of 1% arabic gum (w/w of lignin) as the stabilizer. The mixture was homogenized at 10,000 rpm for 60 s, and immediately applied to the linerboards by using a twin-roll coating machine. All coated linerboards were dried at 150°C for 1 min and conditioned at 50% RH in an ambient temperature for at least 48 h before testing.

3.2.7 Measuring of coating viscosity

The viscosity of the coating was measured using a Brookfield Viscometer (Model DV-II, from Brookfield Engineering Laboratory, USA). Thus 120 mL of coating was poured into a 140 ml beaker and then measured with the viscometer using a S62 spindle at the speed of 200 rpm. The viscosity was recorded as centipoise (cP) at 1 min after the measuring tool was started.

3.2.8 Testing of physical properties of linerboards

(a) Water absorption

The Cobb test method was performed in accord with TAPPI T441. A suitable size (about 5 in. × 5 in.) of the specimen was affixed to the test kit. Then 100 mL of water was poured over the sample and was then poured off after 45 s. After that the specimen was immediately covered with blotting paper and was rolled with a roller to remove the excess of water. The water absorption (WA) was reported in the form of the weight gain per water-contact area of the specimen (g/m^2).

(b) Contact angle measurement

A contact-angle measuring tool (Model OCA 15 EC, from Data Physics Instruments GmbH, Germany) was used to measure the contact angle of a drop of water on the surface of specimen. An angle of water drop was recorded at 1 s after dripping.

3.2.9 Testing of mechanical properties of linerboards

(a) Ring crush and tensile tests

The ring crush and tension properties of the coated linerboards were investigated with a Universal Testing Machine (Model LR30K, from LLOYD Instrument Co., Ltd., UK). A tensile test was performed in accord with TAPPI T494. A specimen (15 cm × 1.5 cm) was set in the clamps (the distance between clamps was fixed at 10 cm), and then the tension force was applied to the specimen with a strain rate of 15 mm/min. A ring crush test was also performed in accord with TAPPI T818. A specimen (6 in. × 0.5 in.) was set in a circular block, and then compressive force was applied via the plate to the center of specimen at a rate of 0.5 in./min. To avoid the effect of different thicknesses, the maximum loads recorded in both tests were divided with the basic weight of the tested paper, and reported as the ring crush index (RCI) and tensile index (TI).

(b) Burst test

The bursting strength of the coated linerboards was determined using a Mullen Bursting Tester (Model GT-7013-AD, from GOTECH Testing Machines Inc., Taiwan). A specimen (at least 4 in. × 4 in. in dimension) was inserted between the clamp ring and diaphragm plate, and then 100 psi of pneumatic pressure was applied to the specimen until it ruptured. To avoid the effects of different thicknesses, the bursting strength recorded was divided by the basic weight of the specimen and reported as the bursting index (BI).

3.2.10 Statistical analysis

All the properties of the coated linerboards were investigated using at least six replicates of the samples. The means and standard deviations were calculated and reported. The analysis of variance (ANOVA) was performed using Duncan's Multiple Range Test (DMRT) to determine the significant differences between the coating treatments. All significant values were expressed at 95% confidence level.

3.3 RESULTS AND DISCUSSION

3.3.1 Recovery of lignin from OPEFB's black liquor

The recovery yields of lignin fractions obtained from different pH precipitations are shown in Table 3.1. It was found that the recovered mass increased when the pH of the liquor was adjusted to lower values. Basically, lignin is highly soluble in an alkaline medium but its solubility decreases when the pH of the liquor is reduced [11]. The results demonstrate that when the pH of the liquors was reduced (from 5 to 2) through acidification, the solubility of the OPEFB's lignin was decreased leading to more precipitation. Thus, the recovered mass of the OPEFB's lignin was increased. A similar trend was reported by Mussatto *et al.* [11] and Sun *et al.* [12] who found that the recovery yields of lignin increased with reducing the pH of the liquors.

In addition, the color of the black liquor was altered when a lower pH was applied. It was observed that the color of the liquors changed from dark brown to pale yellow when the pH of the liquor was reduced from 5 to 2 (Figure 3.1). The dark color of the liquor is derived from the chromopholic groups in the lignin structure such as quinones, carbonyl groups, carboxylic acids, hydroperoxy radicals and phenolic hydroxyl groups, which are all soluble in an alkaline medium [11,13]. Furthermore, it was found that at a lower pH of the liquor, more lignin was precipitated leading to changes in the color of liquor and making it lighter. This phenomenon supported that the recovered mass of lignin increases with a reduction of the pH of the liquor.

Table 3.1 The yields of lignin recovered from different pH conditions of black liquors.

pH	Lignin yields (% dry wt. of OPEFB)
2	15.54±0.20 [a]
3	15.05±0.28 [b]
4	14.67±0.22 [b]
5	14.05±0.17 [c]

Means with different letters are significantly different ($P<0.05$).

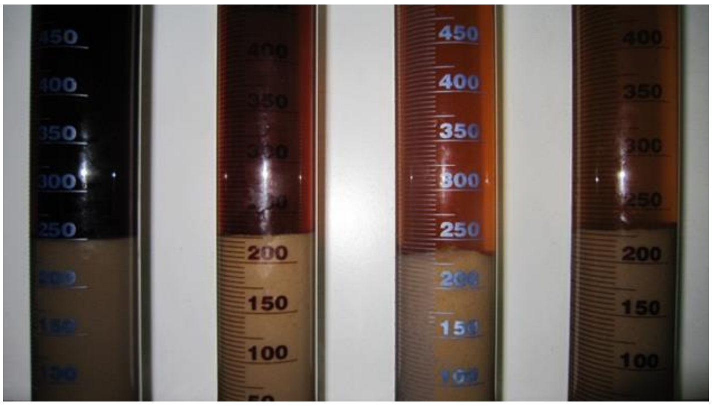

Figure 3.1 The physical characteristics of the black liquor at different pHs (5, 4, 3 and 2 from left to right).

3.3.2 FTIR analysis of lignin fractions

The FTIR spectras of the lignin fractions are shown in Figure 3.2. All absorption bands are reported to be in accord with previous studies [14–16]. In the regions of all lignin fractions, the bands with same intensity appeared excepting at a peak at ~1708 cm^{-1}. A wide absorption band appeared in a range of 3430–3415 cm^{-1} that can be attributed to aromatic and aliphatic O–H groups. A clear shoulder of the band at ~2920 cm^{-1} represented the C–H stretching vibration of methyl groups. The C–H bending of the vibration in methoxy groups was pointed out by a small peak appearing at ~2850 cm^{-1}. An absorption band found at ~1600 cm^{-1} indicated the aromatic skeletal vibration in aromatic rings. The vibration of syringyl ring breathing with C–O stretching was observed at ~1330 cm^{-1}. A clear band found at ~1330 cm^{-1} was attributed to the aromatic C–H deformation of the syringyl units. A strong band at ~1040 cm^{-1} was attributed to the aromatic C–H in the plane deformation of guaiacyl lignin.

A band of carbonyl stretching vibration of the lignin appeared at ~1708 cm^{-1}. The lignin fractions showed an increase in intensity of this band depending on the acidity of the liquor. This can be explained by the mechanism of acid-catalyzed hydrolysis. Lignin is composed of up to 14 different bond types. The major bonds are ether linkages with the most frequency is β–*O*–4 bond (Figure 3.3). Under an acidic condition, the predominant degradation of lignin is done through the acidolysis of β–*O*–4 linkages which generate Hibbert’s ketones and phenolic end groups (Figure 3.4) [17]. This mechanism is furthered when the acidity is greater. When the liquor was adjusted to lower acidity, the lignin fractions were progressively recovered in the form of Hibbert’s ketone. Actually, the structure of ketone consists of carbonyl functional group. For this reason, the lignin fractions showed an increase in the intensity of the carbonyl absorption band as a direct correlation to precipitation acidity.

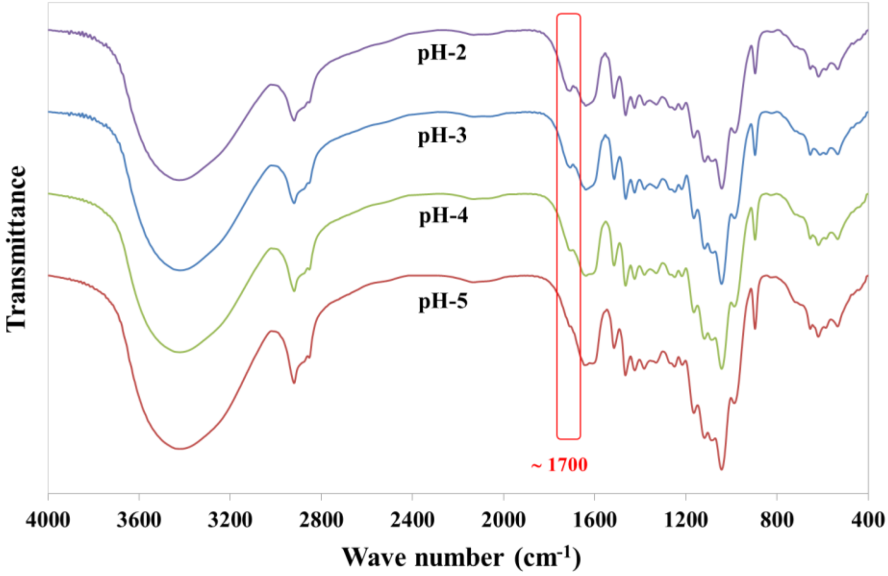

Figure 3.2 FTIR spectras of lignin fractions obtained from the black liquors at different pH conditions.

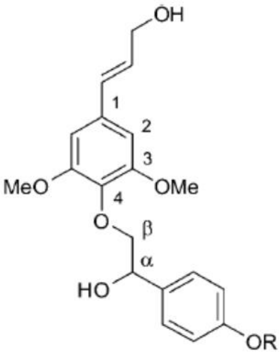

Figure 3.3 Fragment of lignin with β–*O*–4 ether bond [17].

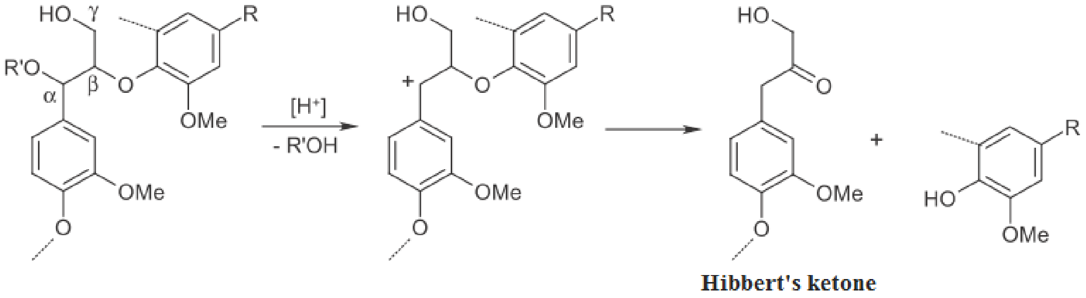

Figure 3.4 Cleavage of β–*O*–4 linkage in lignin by acidolysis and main products from the reaction [18].

3.3.3 TGA analysis of lignin fractions

The TGA curves of the lignin fractions are shown in Figure 3.5. The results demonstrate that all lignin fractions exhibited similar thermograms. Lignin degradation is a complex mechanism, and covers a wide range of temperature. The major decomposition appeared in a range of 275–325°C with a maximum weight loss (about 35%) at 300°C. This can be attributed to the degradation of the hemicellulose and cellulose attached to the structure of lignin. Ibrahim *et al*. [14] have noted the same trend and that the soda lignin extracted from OPEFB mainly degraded at temperatures between 300–310°C. At above 350°C, the mass loss rate of lignin fractions was very slow. The degradation in the region up to 400°C was due to the fission of methyl-aryl ether bonds. Aromatic structures were decomposed at above 400°C though the cleavage of the C–C bonds of the rings. Methoxy groups were cracked at about 400–600°C. Further heating to above 600°C led to the cracking of the C–O–C and C=O bonds.

Lignin fractions had yields of approximately 30% at combustion of 850°C. This remaining mass was the nonvolatile solids which are associated with the formation of highly condensed aromatic structures. It indicates that the lignin has high thermal stability. A minor shift of the curve pointed that the pH-2 lignin slightly tolerated thermal degradation more than other fractions. This may be because the strong acidolysis of lignin produced a large number of small molecules that was very stable at high temperature.

From the results it can be seen that the soda lignin extracted from the OPEFB in this study are in the form of lignocellulosic material with a cellulose component of about 35%. The pH of liquor does not evidently influence the composition of the lignin recovered from OPEFB.

The thermal degradation of the lignin in this study was reported in accord with previous studies [14,19–22].

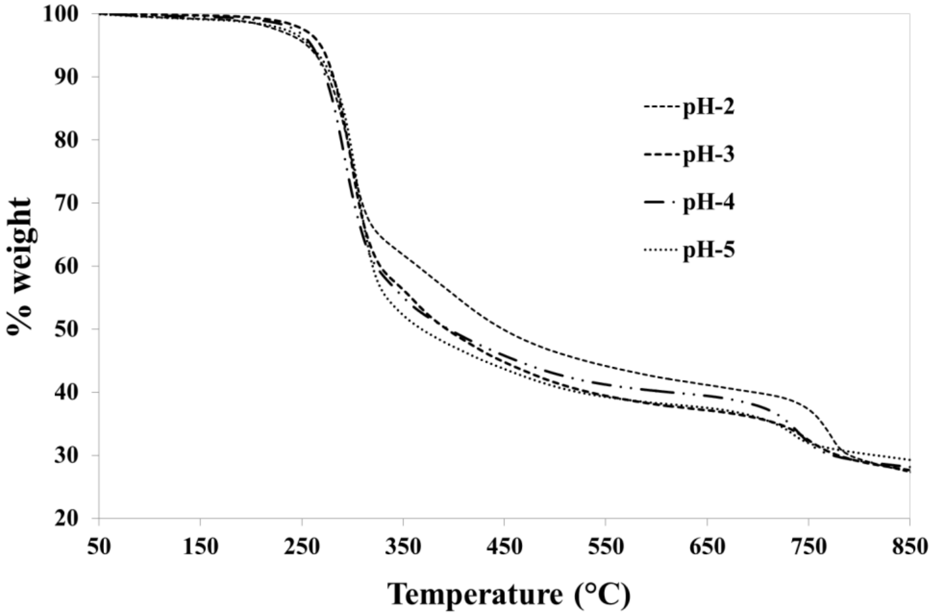

Figure 3.5 TGA thermograms of lignin fractions obtained from the black liquors at different pH conditions.

3.3.4 Selective lignin fraction for preparation of lignin-based coatings

According to the results discussed above, the lignin recovered at pH-5 was selected for the production of lignin-based coating. Although pH-5 condition gave the lowest yield of lignin compared to other conditions, it provided the lowest acidolysis degradation of lignin. A higher degradation of lignin might downgrade the properties of lignin. In addition, the chemical component of the lignin recovered at pH-5 condition is not different with other fractions.

3.3.5 Viscosity of lignin-based coatings

A minor increase in the viscosity of the lignin-based coatings was found with an increase in the content of lignin (Table 3.2). When the total solid content in the coatings increased, the rheology of the coatings was modified to a thicker condition. An empirical relationship between viscosity and the volume fraction of the solid has been proposed [23,24]. They show the same tendency whereby the viscosity of dispersions increases with the increasing volume fraction of the solids.

The characteristic of low viscosity is preferred as a feature of good coating. Coating with too high a viscosity may provide an uneven surface which is not desired in paper applications [25]. As was observed, the lignin-based coatings showed low viscosity compared to the commercial wax coating which is technically desirable. Furthermore, their similar rheology to the commercial wax coating offers advantages in terms of technical application in industrial uses.

Table 3.2 The viscosity of the OPEFB's lignin-based coatings containing various lignin contents.

Lignin contents (w/v of starch solution)					
1%	3%	5%	7%	9%	Wax
22.9	23.0	23.0	23.2	23.4	22.9

The viscosity is expressed as centipoise (cP).

3.3.6 Water absorption of coated linerboards

The fact that the influence of moisture has a strong influence on the mechanical properties of paper is well known. Molecules of water permeating into a paper structure will bond with the OH sites of the cellulose units. This can reduce the strength of paper though interfering of the inter-fiber bonding [1,25]. For that reason, the coatings have been considered necessary to enhance the moisture barrier of papers so as to maintain their strength.

The water absorption of the linerboards coated with lignin-based coatings containing various lignin contents is shown in Figure 3.6. It was found that the absorption values of the linerboards coated with lignin-based coatings were significantly ($p<0.05$) lower than those of uncoated papers. Moreover, a further decrease in water absorption of coated linerboards was found with an increase of the lignin contents. The hydrophobic characteristics of lignin have been assumed as a major factor in improving the water resistivity of coated linerboards. Basically, the structure of lignin comprises of some nonpolar units, such as phenols and benzene rings, which are hydrophobic. This causes improved water resistance of coated linerboards, and this became clearer when the lignin contents increased. Another factor that is considered in enhancing the water barrier is the physical changes of the coated paper surfaces. After the coating process, lignin particles are retained on the paper surfaces and attached to the cellulosic fibers. Hence the surface area of the fibers that water could penetrate through was reduced [25]. This mechanism causes enhancing the water resistivity of coated linerboards, and was greater when the lignin contents increased. However, a decrease in the water absorption of coated linerboards was not significant ($p \geq 0.05$) when more than 5% of lignin content was added to the coatings.

According to the results, it can be suggested that a suitable minimal content of lignin for the production of lignin-based coating is 5%. This condition provides good water resistivity of coated linerboards similar to the commercial wax coating.

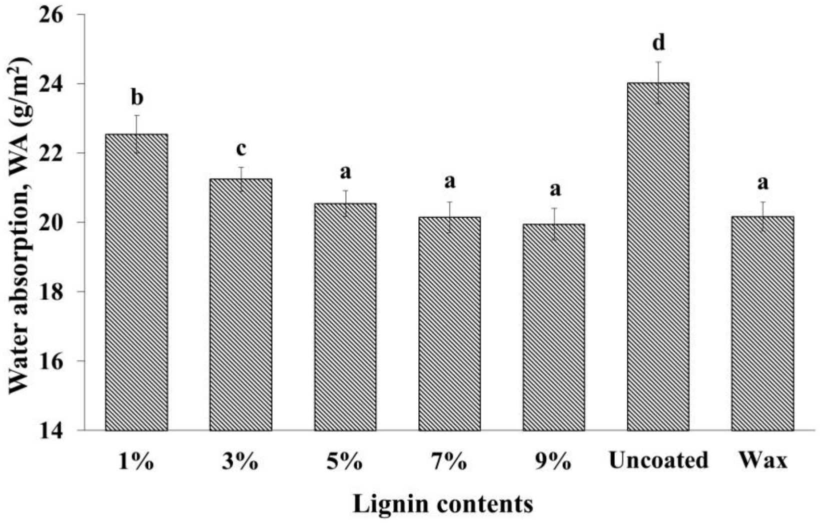

Figure 3.6 The water absorption of the linerboards coated with the OPEFB's lignin-based coatings containing various lignin contents. Means with different letters are significantly different ($P<0.05$).

3.3.7 Surface contact angle of coated linerboards

Technically, a material with high water resistivity should show a wide contact angle of water drop on the surface. Surprisingly, we found some unusual outcomes in this study. Although the lignin-based coatings really improved the water resistance of the coated linerboards, their coated surfaces did not show higher contact angles

(Figure 3.7). On the contrary, a slight decrease was found with an increase in the lignin contents. A cellulosic composition in the lignin was considered to be the main determinant to explain these uncommon results. Hemicellulose and cellulose units comprise many OH groups which make them have a high water-holding capacity. Regarding the TGA results shown previously, the OPEFB's lignin prepared in this study contains about 35% of cellulosic composition (including hemicellulose and cellulose). Thus when the lignin-based coatings were applied, this composition played a key role in the reduction of surface contact angles through their ability to absorb and hold water. A reduction was shown with significant differences ($p<0.05$), compared to the uncoated papers, when the lignin contents increased up to >5%. This was because the greater amount of hemicellulose and cellulose as a direct correlation to the lignin contents.

To evaluate the water resistance of the paper, the test of water absorption is accepted much more than that of contact angle. A water absorption value can indicate the resistivity to the permeation of water molecules through the structure of paper, whereas the contact angle shows the resistivity to water of the paper surface only [25]. Thus it can be demonstrated that the OPEFB's lignin-based coatings prepared in this study show potentiality in enhancing the moisture barrier of linerboards.

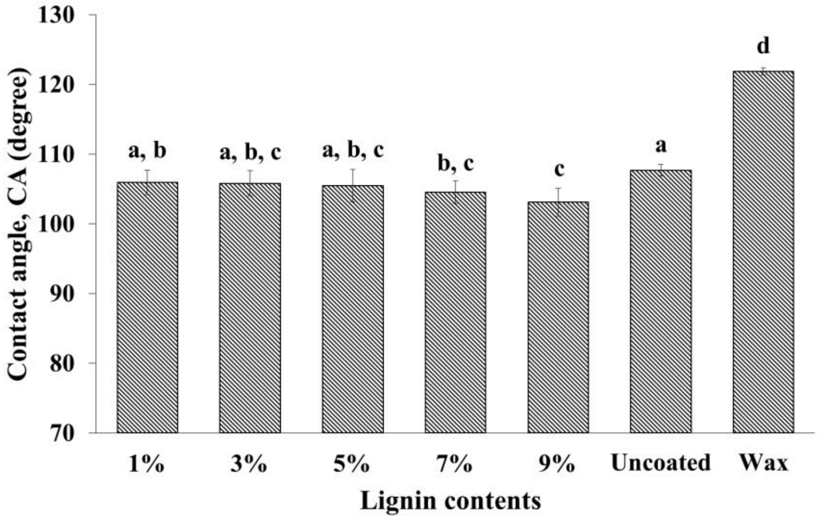

Figure 3.7 Surface contact angle of the linerboards coated with the OPEFB's lignin-based coatings containing various lignin contents. Means with different letters are significantly different ($P<0.05$).

3.3.8 Mechanical properties of coated linerboards

A tensile test has been used to evaluate the resistivity to tension force of paper materials. The tensile strength of paper is dependent on the strength and length of fibers, and especially the inter-fiber bonding strength [26].

As the results show in Figure 3.8, it was found that the lignin contents did not significantly ($p \geq 0.05$) influence the tensile index of coated linerboards. Normally, the effects of solid fillers in coating would result in a reduction in tensile strength of the coated papers. Because the fillers have remained in the spaces of paper structure after the coating processes, they might interfere the bonding between the fibers. However, the solid additives (lignin and oxidized starch) used in this study have large particle sizes. They had difficulty in penetrating the paper structures and this caused them to be retained on the paper surfaces only. Thus they did not result in a reduction in the tensile index of coated linerboards [25].

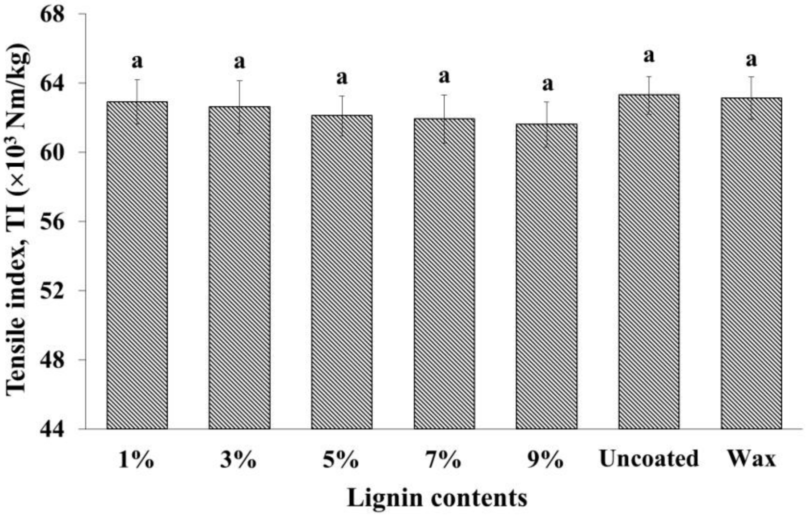

Figure 3.8 Tensile index of the linerboards coated with the OPEFB's lignin-based coatings containing various lignin contents. Means with different letters are significantly different ($P<0.05$).

The ring crush strength of paperboard has been estimated with the aim of evaluating the compressive strength of corrugated boxes. The bursting strength indicates the resistance to rupture of the paper when a perpendicular force acts on the surface [25,27]. The ring crush and bursting indexes of the linerboards coated with the lignin-based coatings containing lignin at various contents are shown in Figure 3.9 and 3.10, respectively. The results show that the lignin contents did not significantly ($p \geq 0.05$) influence the ring crush and bursting indexes of coated linerboards. Technically, both tests directly correlate to the deformation of the microstructure of the papers. The ring crush strength is related to compressive deformation whereas the bursting strength is associated with the breaking of the fibers. Hence the addition of lignin, including oxidized starch, did not evidently affect the ring crush and bursting index of coated linerboards. Rhim *et al.* [27] reported the same findings that the ring crush strength of coated paperboards was not altered when the coatings with biopolymer additives was applied. Moreover, the addition of fillers did not influence the bursting index of coated linerboards as noted by Narapakdesakul *et al*. [25].

From the results, it can be indicated that the use of OPEFB's lignin as a coating material did not reduce the strength of coated linerboards like the use of commercial wax.

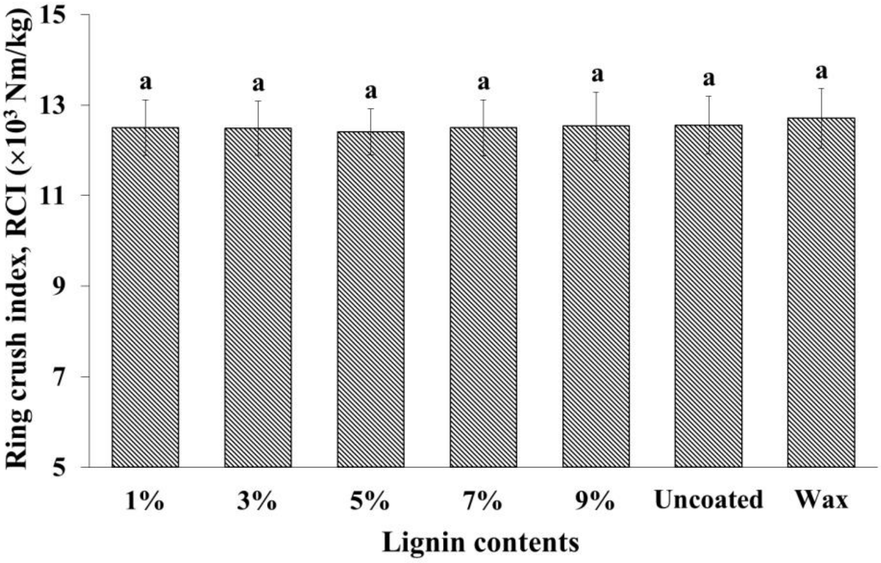

Figure 3.9 Ring crush index of the linerboards coated with the OPEFB's lignin-based coatings containing various lignin contents. Means with different letters are significantly different ($P<0.05$).

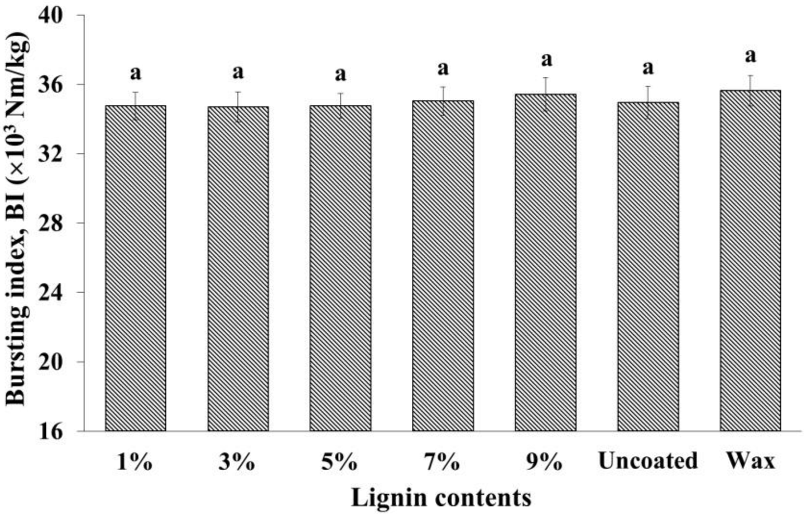

Figure 3.10 Bursting index of the linerboards coated with the OPEFB's lignin-based coatings containing various lignin contents. Means with different letters are significantly different ($P<0.05$).

3.4 CONCLUSIONS

The pH is a variable that influences the recovery of OPEFB's lignin from black liquor. Reducing the pH of the liquor resulted in an increase in the recovery of the mass of lignin. Altering the pH of black liquor would affect the chemical structure but did not result in changes of the components of the recovered lignin. OPEFB's lignin has the potential to be used as an alternative agent for linerboard coating applications. The OPEFB's lignin-based coating can improve the water barriers and also maintain the strength of the coated linerboards like the commercial wax coating.

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CHAPTER 4

DEVELOPMENT OF OIL PALM EMPTY FRUIT BUNCHES' LIGNIN FOR PRODUCTION OF LINERBOARD COATING: EFFECT OF SELECTED STABILEZERS ON COATING CHARACTERISTICS AND COATED LINERBOARD PROPERTIES

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ABSTRACT: Linerboard coating, using lignin extracted from oil palm empty fruit bunches (OPEFB) was prepared by mixing 5% w/v lignin into oxidized starch solution. The effect of the type (arabic gum, carrageenan and guar gum) and concentration (1–5% w/w of lignin) of stabilizers on the coating characteristics and properties of coated linerboard was investigated. The viscosity and stability of lignin-based coatings were improved with the addition of stabilizers. Lignin-based coatings containing arabic gum were found to be more stable than carrageenan and guar gum, even though they had meager viscosity. The linerboards coated with lignin-based coatings consisting of 1–3% of arabic gum and 4–5% of carrageenan provided lower water absorption than others. These conditions showed similar water absorption to linerboards coated with commercial wax coating. The type and concentration of stabilizers in this study did not affect the ring crush and bursting index of coated linerboards, and had little effect on the tensile index when a higher concentration (>1%) of stabilizers was applied. The results showed that the addition of 1% arabic gum into lignin-based coating provided good coating characteristics and properties of this coated linerboard were similar to commercial wax coating. This study indicates that OPEFB's lignin can be exploited for the production of coating for linerboard as an alternative to commercial wax coating.

Keywords: Coating; Lignin; Linerboard; Oil palm empty fruit bunch; Stabilizer

4.1 INTRODUCTION

Packaging is enclosing which has four key functions: containment; protection; convenience; and communication. Packaging is mainly intended to contain and to protect the material it contains so that goods can be safety and conveniently transported, stored and retailed for consumer use. The remaining function of packaging is communication, which includes the dissemination of information through instructions for preparation and storage, marketing of the brand through the inclusion of logos, and utility or convenience of use [1]. Paper is one of the most important packaging materials. Paper and cardboard have been used as both primary and secondary packaging for a wide range of foods for many years. Furthermore, corrugated box is the most popular and cost-effective packaging method for the transportation of manufactured goods [2].

Paper is manufactured from renewable raw materials and offers the advantage of being both recyclable and biodegradable. However, because of paper's poor barrier properties and high sensitivity to moisture, the use of barrier coating is important and necessary to improve its properties [3,4]. Generally, paper is coated with non-degradable polymer coating materials such as polyethylene (PE), polyethylene tarephthalate (PET) and synthetic wax. This process is done to provide barrier properties and increase the shelf-life of the packaged products. However, these materials have accumulated as solid wastes after disposal. Manufacturing them generates environmental problems, so materials based on agricultural wastes are being considered as an alternative source for the production of coating [4–6].

Oil palm is one of the major agro-industries in the South of Thailand, and palm oil makes up 70% of the Thai vegetable oil market [7,8]. Palm oil production generates large amounts of processed residues such as fibers, shells and empty fruit bunches. For every 100 tons of fresh fruit bunches (FFB) processed, approximately 20 tons of nut shells, 7 tons of fibers, and 25 tons of oil palm empty fruit bunches (OPEFB) will be produced [9,10]. Many companies operate refineries extracting crude palm oil in the 9 provinces of the southern region of Thailand. In 2010, the oil palm plantations covered 4,417,373 Rais (about 1,746,491 acres), and 8,223,135 tons of fresh fruit bunches were harvested which approximated to 2,057,834 tons of

OPEFBs [11]. Normally, the OPEFBs are residues of processes that result in a high moisture content because of the steam used for sterilization; this makes them unsuitable for fuel. In addition, it presents particular difficulties in terms of its transportation and incineration. For these reasons, OPEFB have become the major component of all solid waste from palm oil industries [12,13].

Previous studies suggest that the composition of OPEFB consist of approximately 20–30% lignin. Lignins are complex racemic aromatic heteropolymers with the substituents connected by both ether (C–O–C) and carbon-carbon (C–C) linkages. [14,15]. Lignins have the right chemistry to be used in the making of coating because they have small particle size, are hydrophobic and have the ability to form stable mixtures [16]. These reasons suggest it is possible to use lignin as material for the production of lignin-based coating which is more environmentally friendly than the other coatings based on synthesized polymers. Furthermore, this is a suitable way to reduce OPEFB solid wastes from oil palm industries, and to use localized agricultural wastes productively.

Lignin was mixed with a coating medium (starch solution) for imparting coating paper properties (binding between itself and between binder and paper), and similar synthetic coatings. However, the stability of the lignin and coating medium was poor. Hence, the objective of this work was to develop coating based on OPEFB's lignin (with oxidized starch as the medium) for application in paper and linerboard. The study dealt with the effects of the type and concentration of selected stabilizers (arabic gum, carrageenan and guar gum) on the coating characteristics, including viscosity and stability. The properties of the coated linerboards, including water absorption, contact angle, ring crush strength, tensile strength and bursting strength, were also studied.

4.2 EXPERIMENTAL PROCEDURES

4.2.1 Materials

The oil palm empty fruit bunches (OPEFB) were supplied by the Virgin Vegetable Oil Co., Ltd., Songkhla, Thailand. The used linerboards (KS170) and commercial wax (WR390) were obtained from Thai Containers Songkhla (1994) Co., Ltd., Songkhla, Thailand. The oxidized starch was supplied by the Siam Modified Starch Co., Ltd., Pathumthani, Thailand. The stabilizers (arabic gum, *k*-carrageenan and guar gum) were purchased from Merck KGaA, Darmstadt, Germany.

4.2.2 Preparation of lignin from OPEFB

Palm fruit bunches were washed with clean water 3–5 times, chopped into small pieces and then dried in a hot air oven for at least 72 h. The moisture content of the dried OPEFBs was about 15%. Next, a suspension (1:15 w/v of chopped palm fruit bunch in 20% NaOH solution) was prepared at 170°C for 120 min in a rotary digester (Model RDB-D352, from Nanasiam Intertrade Co., Ltd.). After that the OPEFB pulp was separated from the black liquor with a strainer, and the liquid obtained was stored in an ambient temperature for the next experiment. The soluble lignin in the black liquor was precipitated with drops of 4M sulfuric acid until the pH level of the liquid was reduced to 5 (this procedure was performed using an airflow to remove the odorous compounds given off during precipitation).

The colloid obtained was then stored in an ambient temperature for 24 h. After that the precipitated lignin was filtered through a Whatman™ no.4 filter paper, and then washed thrice with clean water. The solution remaining in the precipitated lignin was evaporated in a vacuum oven at 70°C for 48 h. The dried lignin was ground in a mortar and sieved with a 200 mesh strainer, and then stored in an ambient temperature in the absence of daylight.

4.2.3 Coating preparation and procedures for coating linerboard

Generally, starches have been used for coating paper to provide smooth surfaces, and to improve paper properties such as capacity to take print and other optical properties. Chantaramee *et al.* [17] reported that the coating of oxidized starch provided good properties of coated linerboards, such as water resistivity and printing properties more than other starches.

For this present study, all the lignin-based coatings were prepared using oxidized starch solution as the coating medium. The starch solution was prepared by adding 3% oxidized starch to filtered water, and stirring at 80°C until it was completely gelatinized. Then 5% lignin powder by w/v of starch solution was added. The stabilizers (arabic gum, carrageenan and guar gum) at various concentrations (1, 2, 3, 4 and 5% w/w of lignin) were also added in this way. Next the mixed suspensions were homogenized at 10,000 rpm for 60 s, and then immediately applied to the linerboards by using a twin-rolls coating machine. The coated linerboards were dried at 150°C for 1 min and conditioned at 50% RH in an ambient temperature for at least 48 h before testing.

4.2.4 Coating characteristics

(a) Viscosity

The viscosity of the coatings was determined using a Brookfield Viscometer (Model DV-II, from Brookfield Engineering Laboratory, USA). A 120 ml of prepared coating was filled into a 140 ml beaker and then the process was performed using a S62 spindle at the speed of 200 rpm. The viscosity of each sample was recorded 1 min after the measuring tool was started.

(b) Stability

The stability of the lignin-based coatings prepared was observed by a method adopted from Drakos and Kiosseogou [18]. After homogenization, 100 ml of coating was used to fill a 100 ml cylinder and stored in an ambient temperature for observation. The level of the colloid phase was noted at 1, 2, 3, 4, 6 and 24 hours after storage in accordance with the cylinder’s scale (in the range of 0–100); a high scale indicated good stability.

4.2.5 Coated linerboard properties

(a) Physical properties

(i) Water absorption

The Cobb test method was performed in accord with TAPPI T441. The water absorption of the coated linerboards was estimated by weight analysis; all specimens were weighed both before and after testing. Specimens of a suitable size (about 5 in. × 5 in.) were placed under the cylinder of the apparatus, and a 100 ml of water was then poured over the sample. After a specified time (45 s), the water was poured off, and the specimen was immediately covered with standard blotting paper and rolled with a couch roller to remove the excess of water. The total time that the specimen was in direct contact with the water was 60 s. The weight gain of the test piece was calculated and given as the water absorption (WA) in g/m^2 in accord with the standard method.

(ii) Contact angle measurement

The contact angle of a liquid drop on the surfaces of the specimens was measured with the contact angle measuring instrument (Model OCA 15 EC, from Data Physics Instruments GmbH, Germany) at 1 s after dripping took place.

(b) Mechanical properties

(i) Ring crush and tensile testing

The ring crush and tension properties of the coated linerboards were investigated with a Universal Testing Machine (Model LR30K, from LLOYD Instrument Co., Ltd., UK). The tensile testing was performed in accord with TAPPI T494. All specimens were cut into 15 cm. × 1.5 cm. pieces. The distance between clamps was fixed at 10 cm, and the strain rate was set at 15 mm./min. The ring crush of the samples was determined in accord with TAPPI T818. Each specimen (6×0.5 in^2 in dimension) was set into a circular block, and then compressive force was applied to the specimen's center via the plate at the rate of 0.5 in./min. The maximum loads in both tests were recorded as the tensile index (TI) and ring crush index (RCI) by dividing with the basic weight of the paper tested so as to avoid the effect of different thicknesses.

(ii) Burst testing

The contact angle of a liquid drop on the surfaces of the specimens was measured with the contact angle measuring instrument (Model OCA 15 EC, from Data Physics Instruments GmbH, Germany) at 1 second after dripping took place.

4.2.6 Statistical analysis

Analysis of variance (ANOVA) was performed using Duncan’s multiple range test (DMRT) to determine the significant differences between means of all the properties tested. All significant values were expressed at 95% confidence level.

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of type and concentration of stabilizers on coating characteristics

The viscosity of the prepared coatings is presented in Table 4.1. It can be clearly seen that the coating viscosity tended to increase with an increase of the stabilizers. This was due to the change in rheology of the lignin-based coatings, as the stabilizers have a high ability to absorb and hold water. As they swell, they provide less free volume of gyration which impedes their ability to rotate themselves in water [19]. This phenomenon causes an increase in the viscosity of lignin-based coatings, and is more evident when the stabilizer is highly concentrated. The same trend in our results was observed in other studies which reported that viscosity of the mixtures was increased when the concentration of the stabilizers increased [19–21].

When the same concentration of stabilizers was compared, it was found that the addition of guar gum as a stabilizer gave higher viscosity than the addition of carrageenan and arabic gum, respectively. This is due to the different specific characteristics of each stabilizer, such as chemical structure, molecular weight and their conformation. These cause different swelling behaviors in an aqueous environment that affects the volume of gyration. Baranowska *et al.* [22] reported that the addition of guar gum as a stabilizer provided more viscous potato starch suspensions than the addition of *k*-carrageenan and arabic gum, respectively. This shows the same trend for stabilizers in terms of viscosity as in our study. In addition, the results pointed out that lignin-based coatings prepared with a low addition of arabic gum had viscosity similar to commercial wax coating (23.1 cP).

Table 4.1 The viscosity of lignin-based coatings contained various types and concentrations of stabilizers.

Type of stabilizers	% stabilizers (w/w of lignin)				
	1%	2%	3%	4%	5%
Arabic gum	23.1	23.1	23.2	23.4	23.5
Carrageenan	24.9	25.7	26.8	28.8	30.4
Guar gum	28.6	34.7	41.2	52.5	59.1

Viscosity unit is centipoise (cP)

The effects of the type and concentration of stabilizers on the stability of lignin-based coatings is shown in Table 4.2. The results show that the phase separation of all the lignin-based coatings was not noticed during 0–3 h of storage. Furthermore, it was found that the lignin-based coatings containing guar gum as a stabilizer showed greater stability than those containing arabic gum and carrageenan, respectively. The addition of stabilizers increases the thickening of suspensions that causes an increase in their stability. Lee and Wagner [23] showed that the shear thickening phenomenon induced dramatic changes in a suspension's microstructure, such as particle aggregation, which results in poor fluid and coating qualities. This might explain why high viscosity coating results in good stability. However, not only did the viscosity affect the coating stability, the emulsifying property of added substrates also influenced.

Emulsifiers are widely use in food applications; they confer shot-term stability [24]. The key molecular characteristic of an emulsifier is that it is amphiphilic in nature, the hydrophobic part of the molecule prefers a non-polar environment while the hydrophilic part prefers an aqueous (polar) environment [25]. Generally, proteins are the main emulsifiers while the polysaccharides act as stabilizers. Although arabic gum is a polysaccharide, its structure contains proteinaceous material covalently attached to the polysaccharide part [26]. Therefore, arabic gum not only enhances the viscosity of the aqueous medium through their thickening and steric stabilizing like most other polysaccharide gums, but it also forms a thick macromolecular layer around the nonpolar part resulting in good steric stability [27]. For these reasons, it is clear that the coatings that consist of arabic gum are more stable than carrageenan even though they have less viscosity. Although all the lignin-based coatings prepared in this study did not provide long stability like commercial wax, but it is ineffective to use. In the paper industry, a coating has to be used a few times after preparation.

Table 4.2 The stabilizers at different storage times of lignin-based coatings contained various types and concentrations of stabilizers**.**

Stabilizers		Storage times (h)					
Type	Concentration	1	2	3	4	6	24
Arabic gum	1%	N	N	N	51	42	29
	2%	N	N	N	51	41	29
	3%	N	N	N	51	41	29
	4%	N	N	N	49	40	29
	5%	N	N	N	49	40	29
Carrageenan	1%	N	N	N	47	42	29
	2%	N	N	N	45	40	27
	3%	N	N	N	40	39	26
	4%	N	N	N	40	39	26
	5%	N	N	N	40	40	26
Guar gum	1%	N	N	N	65	57	35
	2%	N	N	N	66	59	34
	3%	N	N	N	68	61	32
	4%	N	N	N	N	64	36
	5%	N	N	N	N	N	38

[a] The stability values were presented as percentages of colloid phase level in accordance with the cylinder's scales (0–100); a high scale indicated good stability.

[b] N = no phase separation.

4.3.2 Effect of type and concentration of stabilizers on water absorption of coated linerboards

The water absorption of linerboards coated with lignin-based coatings containing various types and concentrations of stabilizers is presented in Figure 4.1. The water absorption of linerboards coated with lignin-based coatings that contained stabilizers was significantly lower than the linerboards coated with lignin-based coating without stabilizers (not shown in the figure) and uncoated linerboards. The effects of stabilizers on water absorption of coated linerboards were assessed. It was found that the linerboards coated with lignin-based coatings containing arabic gum and carrageenan as the stabilizers showed significantly ($p<0.05$) higher water resistance than the linerboards coated with lignin-based coatings containing guar gum (Figure 4.1). The linerboards coated with lignin-based coatings that contained 1–3% of arabic gum and commercial wax coating did not show different levels of water absorption ($p\geq0.05$). When the concentration of arabic gum was increased up to 4 and 5%, higher water absorption of the coated linerboards was shown. However, an inverse trend was observed when carrageenan was used as a stabilizer.

In the previous discussion, in the technical sense the addition of stabilizers caused stabilizing the dispersed lignin particles in the aqueous phase through the stabilizing and emulsifying effects described. The water resistivity of coated linerboards was attributed mainly to the specific characteristics and contents of the lignin retained on the paper surfaces through its hydrophobic behavior. When the stability of the lignin-based coatings was improved, the lignin was better dispersed in the suspension and distributed better on the coated surfaces. Thus, the coated linerboards showed greater water resistivity. What is more, the water barrier property was involved with the physical change of the coated paper surfaces. The lignin particles that remained on the paper surfaces were attached together with cellulosic fibers, so the surface area of the water that was directly contacted to the fibers was reduced. Han and Krochta [28] and Rhim *et al.* [29] noted that water can be absorbed by a cellulose structure. Therefore, lower water contact area causes reduced absorption through the cellulosic structure. This phenomenon was more evident for the stable lignin-based coatings due to the greater lignin retention on the linerboard surfaces. However, the lignin-based coatings containing guar gum provided poor water resistivity for coated linerboards even though they had excellent stability. This could be because the viscosity of the lignin-based coatings was too high when guar gum was added. Their ability to flow and distribute on paper surfaces during the coating procedure was not good; hence uneven surfaces appeared and resulted in high water absorption.

The results showed that the specific characteristics of stabilizers clearly impacted on the water absorption of coated linerboards. At low concentrations (1–3%) of stabilizers, the water absorption of linerboards coated with lignin-based coatings containing arabic gum showed higher water resistance than did others coated with lignin-based coatings containing carrageenan. The emulsifying property of arabic gum gives it better mixing stability than carrageenan, thus a higher water resistivity of coated linerboards using arabic gum was shown. However, an inverse trend was seen when the concentration of stabilizers increased up to 4 and 5%. At these concentrations, the lignin-based coatings containing arabic gum provided higher water absorption of coated linerboards than those containing carrageenan. This was because too much arabic gum caused agglomeration of itself instead of stabilizing the lignin particles. The agglomerates caused weak areas of the linerboard surfaces whereby the water could easily permeate. When carrageenan is added as a stabilizer, this mechanism is diminished. The addition of carrageenan provided high coating viscosity that intercepted the molecular mobility both of itself and the lignin particles. It would thus, prevent the self-agglomeration of carrageenan and stabilize the lignin as well. The factors meant that the lignin-based coatings containing arabic gum provided higher water absorption of coated linerboards than others containing carrageenan when the concentrations increased to 4 and 5%.

According to the results (data not shown), the water absorption of linerboards coated with starch solution and uncoated linerboards was not different ($P \geq 0.05$). It is clear that the improvement of water resistivity of coated linerboards can be attributed to lignin, not to the effect of oxidized starch.

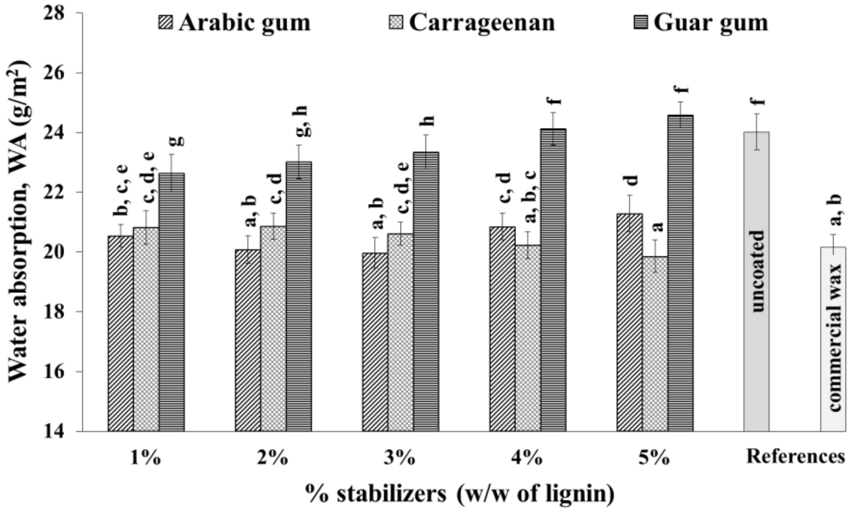

Figure 4.1 The water absorption of linerboards coated with lignin-based coatings containing various types and concentrations of stabilizers. Mean values with different letters are significantly different ($p<0.05$).

4.3.3 Effect of type and concentration of stabilizers on surface contact angle of coated linerboards

The results of the measurement of the surface contact angle of linerboards coated with the lignin-based coatings containing various types and concentrations of stabilizer are shown in Figure 4.2. It was found that the surface contact angle of linerboards coated with oxidized starch solution (data not shown) was lower than that of the uncoated linerboards. This reduction of the contact angle is due to the water absorption of oxidized starch. The starch granules consist of amylose and amylopectin which are highly hydrophilic [30,31]. When lignin was added to the oxidized starch solution, it provided an increase in the surface contact angle of coated linerboards (and was close to uncoated linerboards). It may be suggested that the lignin presented hydrophobic characteristics through its specific structural composition such as aromatic rings and phenolic groups [16,32].

The effect of stabilizers on the surface contact angle of coated linerboards was established. It was found that increasing the stabilizer concentrations from 1–5% in the lignin-based coatings yielded an increase in the surface contact angle of coated linerboards. However, lignin-based coatings containing arabic gum as the stabilizer showed an inverse trend (Figure 4.2). This was mainly due to the influence of the characteristics of arabic gum; the polysaccharide structure of arabic gum contains hydrophilic proteinaceous material as described in previous results. This caused a reduction of the hydrophobic behavior of coated paper surfaces when a higher concentration (>1%) was applied. Rhim *et al.* [29] reported that the surface contact angle of paperboard coated with soy protein isolate was lower than that of uncoated paperboard. This result indicates that the reduction of the surface contact angle of linerboards coated with lignin-based coatings containing arabic gum as the stabilizer was due to the hydrophilic nature of the protein component. In contrast, the results show that the linerboards coated with commercial wax provided a superior surface contact angle. This was due to its high hydrophobicity which can be attributed to the high content in esters of long-chain fatty alcohols and acids, as well as long-chain alkenes [33,34]. Generally, the surface contact angle of the substrate surface is directly related to water absorption as the high contact angle of the surface gives good water resistivity. However, in this present study the water absorption of coated linerboard was not related to the contact angle due to the different features as discussed in previous results.

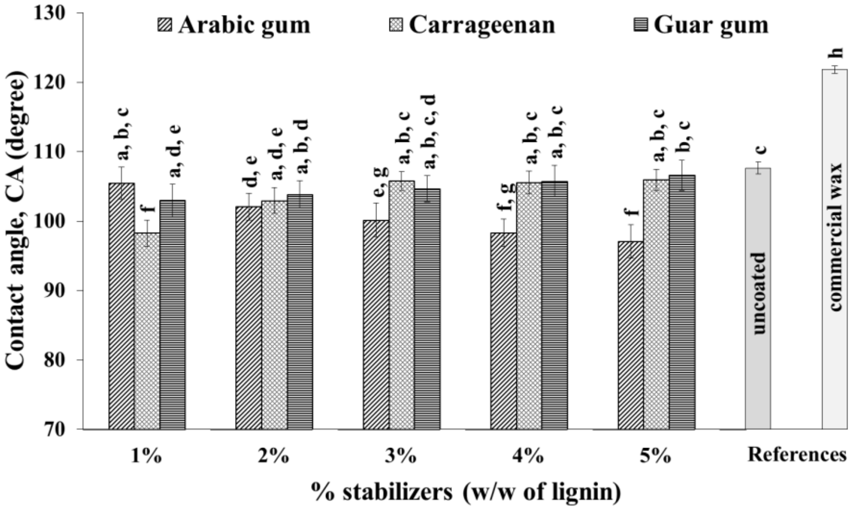

Figure 4.2 The surface contact angle of linerboards coated with lignin-based coatings containing various types and concentrations of stabilizers. Mean values with different letters are significantly different (p<0.05).

4.3.4 Effect of type and concentration of stabilizers on tensile strength of coated linerboards

The tensile index of linerboards coated with the lignin-based coatings containing different types and concentrations of stabilizers are shown in Figure 3.3. Tensile strength is a measure of the resistivity of materials under tension to breaking. This depends on the strength, length and surface area of fibers, and also the bonding strength between them [34,35]. The results demonstrate that the addition and increasing of the stabilizers in lignin-based coatings yielded a lower tensile index of the coated linerboards. This reduction in the tensile index of the coated linerboards was due to the interference of the coating materials on the fiber-to-fiber interaction. During the coating process, the coating swells the fibers and penetrates into spaces between them. After drying, the coating fillers remain between the fibers and this causes reduced interaction between them [29,36]. This phenomenon is more evident with an increasing of the concentration of stabilizer.

A reduction of the tensile strength of papers due to the use of coating materials was found in previous studies [5,26]. Han and Krochta [36] reported that the tensile strength of paper decreased when whey protein coating was applied. Rhim *et al.* [29] also noted that the tensile strength of paperboard coated with soy protein isolate was reduced by 37.5% compared with uncoated paperboard. According to the present study, the tensile index of linerboards coated with lignin-based coating without stabilizers and uncoated linerboards was not different ($P \geq 0.05$). It can be seen that the addition of lignin to the coatings did not affect the tensile index of coated linerboards. This may be because the large particle size of the lignin causes it to be retained on paper surfaces but not to fill the spaces between the fibers, hence it did not reduce the fiber-to-fiber interaction.

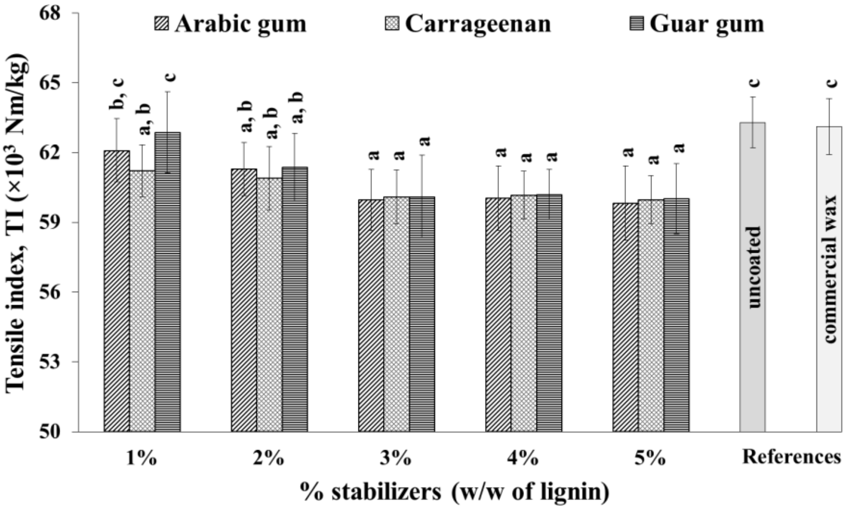

Figure 4.3 Tensile index of linerboards coated with lignin-based coatings containing various types and concentrations of stabilizers. Mean values with different letters are significantly different ($p<0.05$).

4.3.5 Effect of type and concentration of stabilizers on ring crush index of coated linerboards

Compressive strength is an important factor for corrugated boxes. A ring crush test is usually used as the standard method for testing linerboard and corrugated medium in order to evaluate the compression strength of corrugated box containers [29]. Figure 4.4 demonstrates the effect of stabilizers added to the lignin-based coatings on the ring crush index of coated linerboards. The results show that the type and concentration of the stabilizers used in this study did not affect the ring crush index of the coated linerboards. Normally, the stabilizers that permeate to and are retained in spaces between fibers may reduce the fiber-to-fiber interaction; this results in the poor mechanical properties of coated papers. However, this phenomenon has very little effect with respect to the ring crush test which is mainly involved with deformation in the microstructure of fibers. The solid fillers which filled the spaces between fibers caused an increase in the density of the paper surfaces, and also formed a strong matrix. This can improve the resistivity to the deformation of fibers. These reasons show how the undesirable effect from stabilizers is expiated, and the ring crush index was not lowered when the stabilizers were added. The results in this study are similar to the study of Rhim *et al.* [29] who reported that the application of biopolymer-based coating did not affect the ring crush properties of coated paper.

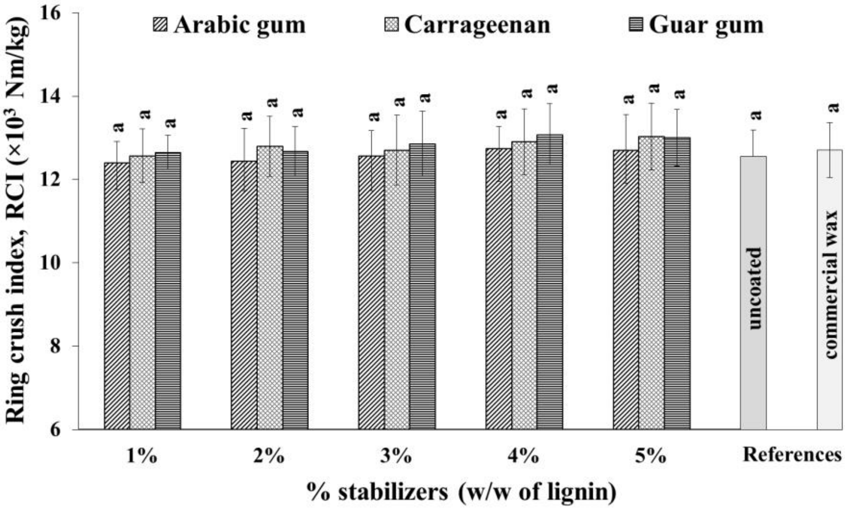

Figure 4.4 Ring crush index of linerboards coated with lignin-based coatings containing various types and concentrations of stabilizers. Mean values with different letters are significantly different ($p<0.05$).

4.3.6 Effect of type and concentration of stabilizers on bursting strength index of coated linerboards

Burst testing is the method use to estimate the usability and behavior of paper when perpendicular forces act on the surface. It can indicate the resistance to rupture of paper materials [29]. The effect of the type and concentration of stabilizers added to the lignin-based coatings on the bursting index of coated linerboards is shown in Figure 4.5. The results suggest that neither the type nor the concentration of the stabilizers selected for this study had any impact on the bursting index of the coated linerboards ($P\geq0.05$). However, it can be seen that the stabilizers added in lignin-based coatings had some effect as the results show a slight increase in the bursting index of the coated linerboards. Solid fillers, which are retained on the pores of the paper surfaces, increase the surface density and also form a strong continuous layer on the surfaces. This may improve the resistivity to breakdown of fibers when force is applied.

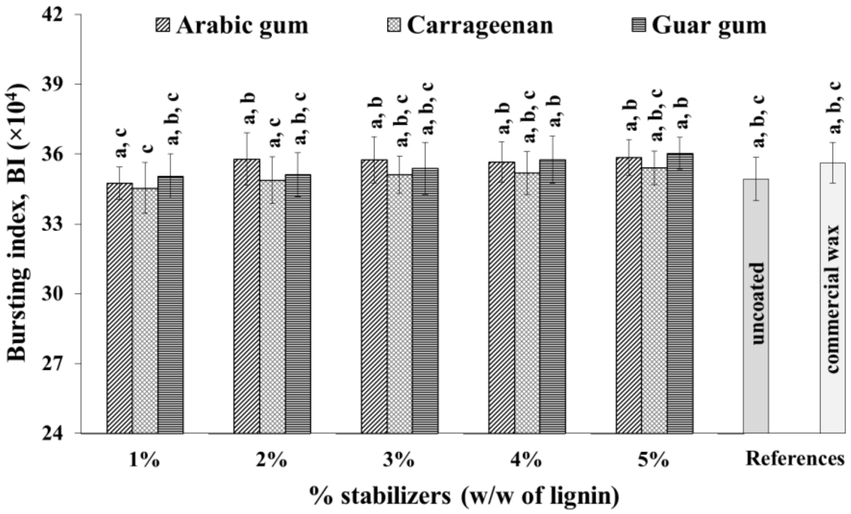

Figure 4.5 Bursting index of linerboards coated with lignin-based coatings containing various types and concentrations of stabilizers. Mean values with different letters are significantly different ($p<0.05$).

4.4 CONCLUSIONS

The addition of stabilizers affected the coating characteristics and end-use properties of coated linerboards. This mainly related to the specific characteristics and level of concentration of the stabilizer used. The optimum condition for the use of a stabilizer in lignin-based coating was when 1% arabic gum was added as the stabilizer. This state provided good coating characteristics and the coated linerboard properties were as good as commercial wax coating. It was also cost effective. This study suggests that the lignin extracted from OPEFB can be exploited as coating in the production of linerboard coating as an alternative to commercial wax.

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CHAPTER 5

NOVEL USE OF OIL PALM EMPTY FRUIT BUNCH'S LIGNIN DERIVATIVES FOR PRODUCTION OF LINERBOARD COATING

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ABSTRACT: Oil palm empty fruit bunch's (OPEFB) lignin derivatives were synthesized by the reaction of OPEFB's lignin and palm oil using the ratios of 1:1 and 1:2, respectively. The formation of lignin derivatives was confirmed by FTIR analysis. The OPEFB's lignin derivative-based coating was prepared by mixing 5% w/v lignin into oxidized starch solution containing 1% arabic gum as a stabilizer. It was found that the viscosity of the OPEFB's lignin derivative- based coatings was close to the commercial wax. The results showed that the linerboards coated with OPEFB's lignin derivative-based coatings had a superior water resistance than the linerboards coated with commercial wax. However, an inverse trend was found for the contact angle. It was observed that increasing the palm oil dosage for synthesizing did not affect the water resistance of coated linerboards ($p \geq 0.05$). The mechanical properties (ring crush test, tensile and bursting strength) of linerboards coated with OPEFB's lignin derivative-based coatings were similar to those with commercial wax coating. This study suggests that OPEFB's lignin derivatives have the potentiality for producing the good linerboard coating. It provided better water resistance of coated linerboards than the commercial wax coating, and was also more environmental friendly.

Keywords: Coating; Linerboards; Mechanical properties; OPEFB's lignin derivatives; Palm oil; Water resistance

5.1 INTRODUCTION

Paper is and has been one of the most important packaging materials used for a wide range of products for many years. It is manufactured from renewable raw materials and offers the advantages of being both recyclable and biodegradable. In addition, paper has been used as both primary and secondary packaging to contain and protect the manufactured goods so that they can be safe during transportation and storage before being sold to customers [1,2].

The corrugated box is the most popular paper packaging widely used for the transportation of manufactured goods because it is effective, lightweight and inexpensive. The structure of corrugated board consists of a corrugated medium attached with linerboard on both sides. It is well know that the paper materials are very sensitive to moisture, thus coatings are considered necessary to apply to the linerboard for improving the barrier properties of corrugated board [3,4]. Petroleum-based polymers, such as polyethylene (PE), polyethylene tarephthalate (PET) and wax, are the main sources of coatings used in paper industry. They can improve the moisture resistivity and maintain the strength of a corrugated box. However, these synthetic materials generate environmental problems during their manufacturing and they accumulate as a lot of solid waste after use. In recent years, many studies have focused on material based on renewable sources and agricultural wastes to use as alternatives for the production of coating [5,6].

Oil palm is one of the major industrial crops of the southern region of Thailand. The crude palm oil industry plays an important role in the economic development of the country and in enhancing the economic welfare of the population [7]. Many companies in the southern region are working on crude palm oil extraction and purification to produce oil palm for consumption. In 2010, the oil palm plantations increased to 4.4×10^6 Rais (about 1.7×10^6 acres) and the harvesting of fresh fruit bunches totaled approximately 8.2×10^6 tons [8]. Palm oil production generates large amounts of solid residues including cellulosic fibers, shells and oil palm empty fruit bunches (OPEFB). The sterilization of fresh fruit bunches with steam during the extraction processes is the cause of the high moisture content in OPEFB residues that makes them unsuitable as fuel. In addition, they present difficulties in disposal and are wasteful in terms of cost. Although some residues are utilized as fertilizer in the palm oil plantations, much is wasted by dumping in areas adjacent to the factories [7,9]. Nowadays, OPEFB solid wastes have become a major problem in the oil palm industry, and their potential is not used.

Previous researches show that OPEFB contains high amounts of lignin, approximately 25% [10,11]. Lignin, a three-dimensional polyphonic macromolecule of very complex structure, is one of the major components in plants. It consists of many subunits joined together with both C–C and C–O–C linkages. The function of lignin in nature is to provide rigidity and cohesion to the cell walls of materials, to confer water impermeability to xylem vessels, and to form a physicochemical barrier against microbial attack [12]. Lignin has the right chemistry – small particle size, hydrophobic behavior, and ability to form stable mixtures – suitable for the production of coating [13].

Previous results from our study [14] suggested that lignin-based coating, prepared from mixing OPEFB's lignin (5% w/v) and oxidized starch solution with the addition of 1% arabic gum as a stabilizer, provided as good coating characteristics and coated linerboard properties as commercial wax coating. However, the structure of lignin consists of many chemical groups, especially methoxy groups, which are possible sites for chemical modification. Thus, an improvement in the hydrophobicity of lignin is considered necessary for improving the efficiency of linerboard coating.

In this present study, the OPEFB's lignin-palm oil derivative was synthesized by the reaction of lignin from OPEFB and the palm oil. The study dealt with the effect of OPEFB's lignin derivatives-based coating on viscosity. The coated linerboard properties (water absorption, contact angle, ring crush strength, tensile strength and bursting strength) were also investigated.

5.2 EXPERIMENTAL PROCEDURES

5.2.1 Materials

Oil palm empty fruit bunches (OPEFB) were supplied by the Virgin Vegetable Oil Co., Ltd., Songkhla, Thailand. The linerboards (KS170) and the commercial wax (WR390) were obtained from Thai Containers Songkhla (1994) Co., Ltd., Songkhla, Thailand. Arabic gum (stabilizer) was purchased from Merck KGaA, Darmstadt, Germany. Oxidized starch was supplied by the Siam Modified Starch Co., Ltd., Pathumthani, Thailand.

5.2.2 Lignin preparation

Palm fruit bunches were washed with clean water 3–5 times, chopped into small pieces and then dried in a hot air oven for at least 72 hours. The moisture content of the dried OPEFBs was about 15%. Next, a suspension (1:15, w/v of chopped palm fruit bunch in 20% NaOH solution) was prepared at 170°C for 120 min in a rotary digester (Model RDB-D352, from Nanasiam Intertrade Co., Ltd.). After that the OPEFB pulp was separated from the black liquor with a strainer, and the liquid obtained was stored in an ambient temperature for the next experiment. The soluble lignin in the black liquor was precipitated with drops of 4M sulfuric acid until the pH level of the liquid was reduced to 5 (this procedure was performed using airflow to remove the odorous compounds given off during precipitation). The colloid obtained was then stored in an ambient temperature for 24 h. After that the precipitated lignin was filtered through a Whatman™ no.4 filter paper, and then washed thrice with clean water. The solution remaining in the precipitated lignin was evaporated in a vacuum oven at 70°C for 48 h. The dried lignin was ground in a mortar and sieved with a 200 mesh strainer, and then stored in an ambient temperature in the dark.

5.2.3 Synthesizing of lignin derivatives

OPEFB's lignin dissolved in acetone (3:30 g/ml) was combined with a mixture of palm oil and concentrated sulfuric acid (15:0.1 g/ml) at the ratios of 1:1 and 1:2 (w/w). Then, the mixture was stirred for 2.5 h over a nitrogen flow at 70°C in three neck round flask. After the reaction ended, the mixture was cooled to room temperature and washed in pentane to remove the excess of palm oil that did not react with lignin. The left-over pentane remaining in the derivative was evaporated in a vacuum oven for 48 h. After that, the derivative was mashed in a mortar and sieved through a 200 mesh strainer, and then stored in an ambient temperature in the dark.

5.2.4 Fourier transform infrared spectrophotometry (FTIR)

FTIR analysis was performed by an infrared spectrometer (Model Equinox 55, from Bruker Corporation, Germany). The KBr pellet technique was used for preparing the samples. Each spectrum was recorded in a frequency range of 400–4000 cm^{-1}.

5.2.5 Determination of crude oil content

Lignin derivatives (2 g) were weighed on the filter papers, placed in Soxhlet extractors, and then extracted with 150 ml of petroleum ether for 14 h at the rate of 10 cycles per hour. After extraction, petroleum ether remaining in the samples was evaporated on a rotary evaporator at 50°C. The samples were then dried at 100°C for 1 h, and the oil content was determined gravimetrically.

5.2.6 Preparation of coatings and procedures for coating linerboards

The OPEFB's lignin derivative-based coatings were prepared by the mixing of 3% oxidized starch solution (as a coating medium) and OPEFB's lignin derivative powder (5%, w/v of starch solution) with the addition of 1% arabic gum (w/w of derivative) as a stabilizer. The suspensions were homogenized at 10,000 rpm for 60 s, and then immediately applied to the linerboards by using a twin-roll coating machine. After coating, all coated linerboards were dried at 150°C for 1 min and conditioned at 50% RH in an ambient temperature for at least 48 h before testing.

5.2.7 Measuring of coating viscosity

A Brookfield Viscometer (Model DV-II, from Brookfield Engineering Laboratory, USA) was used to measure the viscosity of coatings. A coating (120 ml) was poured into a 140 ml beaker and then processed using a S62 spindle at the speed of 200 rpm. The viscosity was recorded as centipoise (cP) at 1 min after the measuring tool was started.

5.2.8 Coated linerboard properties

(a) Water absorption

The Cobb test method was performed according to TAPPI T441. A suitable size (about 5 in. × 5 in.) of specimen was fitted to the test kits, and then poured over the sample with 100 ml of water. After 45 s the water was poured off, and then the specimen was covered immediately with blotting paper and rolled with a roller to remove the excess of water. The water absorption (WA) was reported in the form of the weight gain per water-contact area of specimen (g/m^2).

(b) Contact angle measurement

The contact angle of a drop of water on the surface of specimen was measured with a contact-angle measuring tool (Model OCA 15 EC, from Data Physics Instruments GmbH, Germany). An angle of water drop was recorded at 1 s after dripping.

(c) Ring crush and tensile testing

The ring crush and tension properties of the coated linerboards were investigated with a Universal Testing Machine (Model LR30K, from LLOYD Instrument Co., Ltd., UK). A tensile test was performed according to TAPPI T494. A specimen (15 cm × 1.5 cm) was set in the clamps (the distance between clamps was fixed at 10 cm), and then the tension force was applied to the specimen using a strain rate at 15 mm/min. A ring crush test was also performed in accord with TAPPI T818. A specimen (6 in. × 0.5 in.) was set in a circular block, and then compressive force was applied to the specimen's center via the plate using the rate of 0.5 in./min. The maximum loads of both tests were recorded, and resulted as the tensile index (TI) and ring crush index (RCI) by dividing these with the basic weight of the paper tested so as to avoid the effect of different thicknesses.

(d) Burst test

A Mullen Bursting Tester (Model GT-7013-AD, from GOTECH Testing Machines Inc., Taiwan) was used to determine the bursting strength of the linerboards. The specimen (at least 4 in. × 4 in. in dimension) was inserted between the clamping ring and diaphragm plate, and then 100 psi of pneumatic pressure was applied to the specimen until it ruptured. To avoid the effect of different thicknesses, the bursting strength recorded was divided by the basic weight of specimen and reported as bursting index (BI).

5.2.9 Statistical analysis

All the properties of the coated linerboards were investigated using at least six replicates of the samples tested, and the means and standard deviations were calculated and reported. Analysis of variance (ANOVA) was performed using Duncan's Multiple Range Test (DMRT) to determine the significant differences between coating treatments. All significant values were expressed at 95% confidence level.

5.3 RESULTS AND DISCUSSION

5.3.1 FTIR analysis of lignin-palm oil derivative formation

OPEFB's lignin and OPEFB's lignin derivatives demonstrated generally similar intensities in the FTIR frequencies as shown in Figure 5.1. A wide absorption band appeared at 3415–3430 cm^{-1} that can be attributed to aromatic and aliphatic O–H groups. A clear shoulder of the band at ~2920 cm^{-1} can be assigned to the C–H stretching vibration of methyl groups. A small peak appeared at ~2850 cm^{-1} that was attributed to the C–H bending of vibration in methoxy groups. An absorption band found at ~1600 cm^{-1} was attributed to the aromatic skeletal vibration in aromatic rings. The vibration of syringyl ring breathing with C–O stretching appeared at ~1330 cm^{-1}. An obvious band appeared at ~1330 cm^{-1} and was attributed to the aromatic C–H deformation of syringyl units. A strong band at ~1040 cm^{-1} indicated the aromatic C–H in plane deformation of guaiacyl type lignin. The FTIR bands reported this way are in accord with previous studies [15–18].

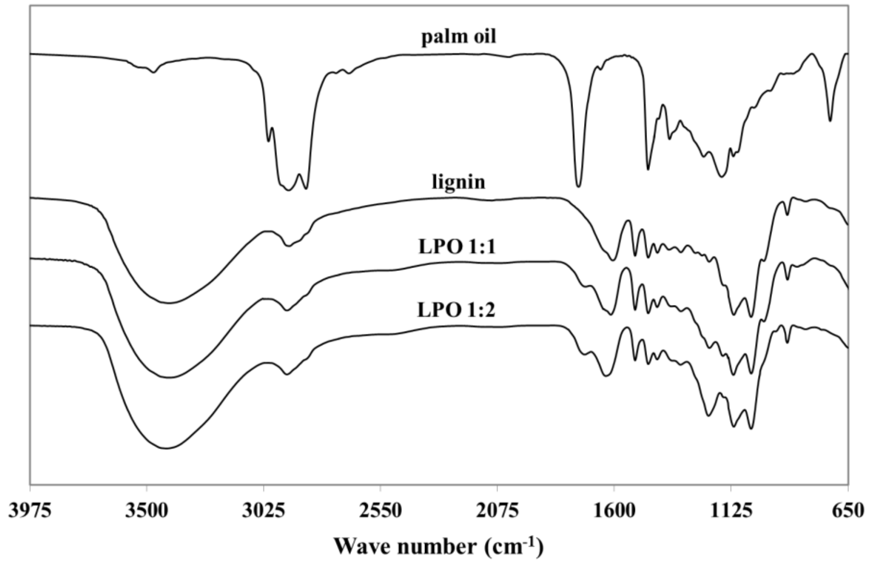

Figure 5.1 FTIR spectras of OPEFB's lignin and OPEFB's lignin derivatives (lignin:palm oil at 1:1 (LPO 1:1) and 1:2 (LPO 1:2)).

The synthesizing of lignin with palm oil caused the intensity of some frequencies of the synthetic derivatives to be altered as shown in Table 5.1. OPEFB's lignin derivatives showed a decrease in transmittances, compared to the unmodified lignin, at the frequencies of 1720 and 1215 cm^{-1} which was attributed to C=O stretching and C=O stretching (in ester) vibrations, respectively. A further decrease in transmittances of these bands was seen when the dose of palm oil used for synthesis was doubled. The reduction of transmittances indicated an increasing of these functional groups in the structures of OPEFB's lignin derivatives. It can be indicated that the structures of OPEFB's lignin derivatives have been changed in the forms of C=O and C=O increases which directly depended on oil palm dosages.

OPEFB's lignin derivatives showed an increase in transmittances of the methyl bands when compared to the unmodified lignin, and it was more evident for the derivative obtained from the reaction with double doses of oil (Table 5.1). The first band was found at 1515 cm^{-1} that was attributed to out-of-phase bending in symmetric vibration of CH_3. The bands of the two anti-symmetric vibration of CH_3 are presented at 1462 and 1425 cm^{-1}. An umbrella type vibration of CH_3 was correlated to the frequency at 1375 cm^{-1}. The vibration of perpendicular rocking of CH_3 was also presented at 1158 cm^{-1}. This increment of transmittances of methyl bands suggested that the synthesizing with palm oil caused a reduction in the methyl groups in the structure of lignin derivatives. It is clear that the synthesizing of OPEFB's lignin derivative using double oil doses showed a greater reduction of these functional groups. All FTIR characteristics reported this way are in accord with previous findings [20–23].

According to the FTIR analysis discussed previously, the main changes in the OPEFB's lignin structures after synthesis are in the form of increases in the ester bonds and the reduction of methyl functional groups. From this a possible reaction of lignin and palm oil which created the lignin-palm oil derivative can be modeled as shown in Figure 5.2. Under acid-catalyzed condition, the ester linkages in triglycerides are broken out generating the hydrocarbon chains with –C=O ending segments. Methoxy groups (OCH_3) are noted as the most active sites of lignin for chemical modification [24]. It can be demethylated (removing the CH_3) easily creating the –O sites which are sensitive to reacting. During synthesizing, the free –O of lignin created would react with the –C=O ending of hydrocarbon chains and then the lignin derivative with ester linkages would be formed. This reaction further occurred when the dose of palm oil was doubled because more hydrocarbon chains were generated and could react with the lignin effectively.

Table 5.1 Percentages of transmittance and the assignments of significant FTIR frequencies of OPEFB's lignin and OPEFB's lignin derivatives.

Infrared (cm^{-1})	Transmittances (%)			Assignments
	Lignin	LPO 1:1	LPO 1:2	
1720	N	84.3	81.7	C=O stretching
1515	63.4	69.8	78.1	CH_3 sym. bending (out of phase)
1462	62.4	67.6	75.8	CH_3 anti-sym. bending
1425	65.4	71.4	78.7	CH_3 anti-sym. bending
1375	67.3	72.0	N	CH_3 sym. umbrella type vibration
1215	59.8	45.8	43.4	C-O stretching (in ester)
1158	41.0	46.9	54.0	CH_3 perpendicular rocking

[a] The infrared assignments are accorded to the previous literatures [19–21].

[b] LPO 1:1 and LPO 1:2 = OPEFB's lignin derivatives synthesized by using lignin:palm oil at 1:1 and 1:2, respectively.

[c] N, the transmittance was not observed (peak may be overlapped with the side bands)

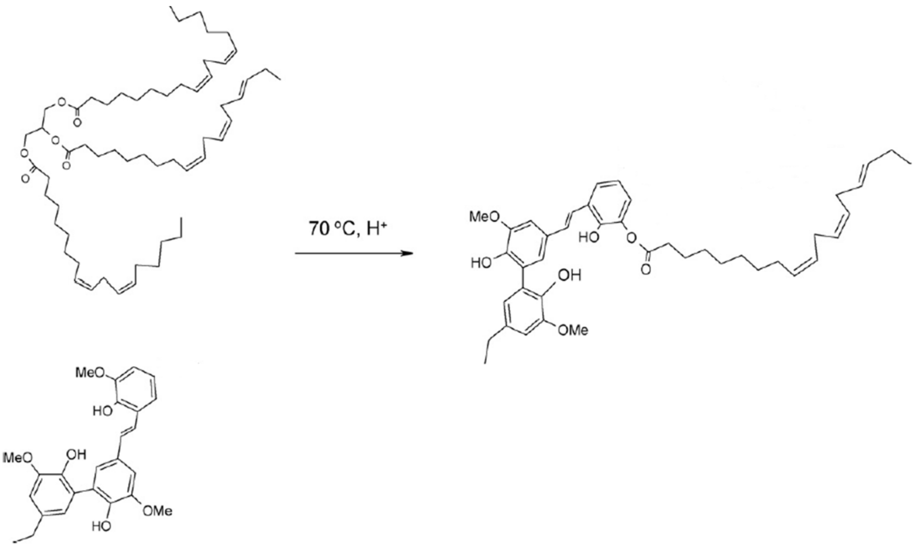

Figure 5.2 A possible reaction of lignin and triglyceride forming lignin derivatives.

5.3.2 Excess oil in OPEFB's lignin derivatives

An objective of this analysis was to investigate the excess (free) palm oil in the OPEFB's lignin derivatives. The results showed that the content of free palm oil remaining in OPEFB's lignin derivatives was very low. There were about 0.40% and 0.46% for the derivatives synthesized from the reaction of lignin and palm oil at the ratios of 1:1 and 1:2, respectively (Table 5.2). According to this analysis, it might be assumed that the properties of coated linerboards were not influenced by the excess oil but resulted from the intrinsic properties of OPEFB's lignin derivatives.

Table 5.2 Amount of crude fat remaining in the lignin derivatives.

Crude oil content (% dry wt.)	
LPO 1:1	LPO 1:2
0.40%	0.46%

LPO 1:1 and LPO 1:2 = OPEFB's lignin derivatives synthesized by using lignin: palm oil at 1:1 and 1:2, respectively.

5.3.3 Coating viscosity

The viscosity of OPEFB's lignin derivative-based, OPEFB's lignin-based and commercial wax coatings were measured (Table 5.3). The viscosity of OPEFB's lignin derivative-based and OPEFB's lignin-based coatings was quite close to that of commercial wax coating. Because they contain the same content in terms of solid additives (including lignin/or derivatives, oxidized starch and arabic gum), their rheology was similar. In addition, the chemical modification of lignin did not influence the viscosity of the coatings. This was because the characteristics of lignin and lignin derivatives were homologous; and the structures of the derivatives have minor differences that would not alter the rheology of coatings. The viscosity of OPEFB's lignin derivative-based coatings was approximately the same as the commercial wax coating. This suggests the usefulness, in terms of coating procedures, of the industrial processes used. Furthermore, they have low viscosity which is required for good coating; coating of too high viscosity might result in an uneven surface which is not wanted in paper applications [14].

Table 5.3 The viscosity of coatings.

Coating types			
Lignin	LPO 1:1	LPO 1:2	Commercial wax
23.0 cP	22.5 cP	22.3 cP	22.9 cP

Lignin = the lignin-based coating, LPO 1:1 and LPO 1:2 = OPEFB's lignin derivative-based coatings synthesized by using lignin: palm oil at 1:1 and 1:2, respectively.

5.3.4 Water absorption of coated linerboards

It is well known that moisture has a strong influence on the mechanical properties of paper. The water molecules permeating into a paper structure may become attached to three OH sites in a basic cellulose unit that causes a reduction in the internal strength of the paper [24]. Therefore, the coatings play an important role in enhancing the moisture resistivity of papers to maintain their strength for their effective use.

The water absorption of linerboards coated with OPEFB's lignin derivative-based coatings compared to other reference linerboards is shown in Figure 5.3. The results demonstrated that the linerboards coated with OPEFB's lignin derivative-based coatings had higher water resistance than the OPEFB's lignin, commercial wax coating and uncoated linerboards. Narapakdeesakul *et al.* [14] noted that the improvement in the water resistivity of OPEFB's lignin-coated linerboards was mainly brought about by the hydrophobic nature of lignin with respect to the functional groups, such as aromatic rings in its structure. Furthermore, it was correlated to the physical changes in coated paper surfaces. The lignin particles remaining on the paper surfaces have become attached together with cellulosic fibers. Hence the surface area of fibers that the water could penetrate through was reduced.

As the results shown, the superior water resistance of coated linerboards has been shown when OPEFB's lignin derivative-based coatings were used. Chemical modifications made in lignin using palm oil caused improvement in its hydrophobicity due to the nonpolar chains joining in its structure (Figure 5.2). Thus the linerboards coated with OPEFB’s lignin derivative-based coatings had lower water absorption than the other ones coated with OPEFB’s lignin-based and commercial wax coatings. The hydrophobic modification of coating material with nonpolar chains was found in the study of Havimo *et al.* [25]. They modified the structure of cellulose by attaching of alkyl chains. They found that the barrier against water vapor of the paperboard coated with modified cellulose was enhanced, depending on the degree of alkyl-chain substitution. The effect of nonpolar chains on the improvement of the water resistance of paperboard was also noted by Butkinaree *et al.* [26]. They concluded that the stearic acid, which contains long saturated chains in the structure, can be used to improve the water resistance of paperboard. When the stearic acid was added to the starch-based coating, the water absorption of coated paper was significantly decreased depending on the added concentrations.

The effect of synthesizing conditions (the ratios of OPEFB’s lignin and palm oil at 1:1 and 1:2) on the water absorption of coated linerboards was also compared. The results showed that increasing the palm oil dosage in the synthesizing process did not significantly enhance the water resistance of coated linerboards ($p \geq 0.05$). This might suggest that a small volume of oil palm is sufficient to improve the hydrophobicity of lignin.

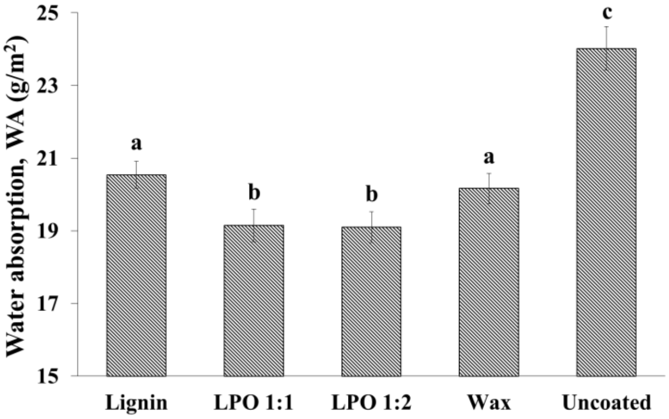

Figure 5.3 The water absorption of linerboards coated with different coatings. Lignin = the lignin-based coating, LPO 1:1 and LPO 1:2 = OPEFB's lignin derivative-based coatings synthesized by using lignin: palm oil at 1:1 and 1:2, respectively. Mean values with different letters are significantly different ($p<0.05$).

5.3.5 Surface contact angle of coated linerboards

In a technical sense, a material with high water resistance should show a wide contact angle of water drop on the surface. However, unusual outcomes were observed in this study. Although the linerboards coated with the OPEFB's lignin derivative-based and OPEFB's lignin-based coatings showed better water resistivity than the uncoated linerboards, the surface contact angles of them show an inverse trend (Figure 5.4). It should be noted that the oxidized starch used as the coating medium is the main determinant of contact angle reduction. The starch granules consist of amylose and amylopectin which are intensively hydrophilic [27]. Thus the addition of oxidized starch to the coatings provided sensitive paper surfaces that can absorb water easily, and then cause a reduction of the contact angles of the coated linerboards.

However, it was observed that the linerboards coated with OPEFB's lignin derivative-based coatings exhibited higher surface contact angles than the OPEFB's lignin-coated ones. This was more evident for the derivatives obtained from the reaction with high oil content. It was due to the hydrophobic improvement of lignin derivatives, from the attaching of nonpolar chains to their structures, which was furthered with increasing the palm oil dosages. Antonsson *et al.* [23] reported the same trend. The filter paper treated with lignin-linseed oil derivative presented a wide contact angle while that of the filter paper treated with lignin was not measurable (the water was completely absorbed by the filter paper). This indicates that the hydrophobicity of lignin was really improved by synthesizing with the oil. Not surprisingly, the linerboards coated with commercial wax coating showed superior contact angles. This is because the structure of synthetic wax coating contains high amounts of long-chain fatty alcohols, fatty acids and alkenes, which make its highly hydrophobic [28].

In the applications to paper, the results of water absorption are considered much more important for the estimation of water resistivity of the papers than the contact angle. A water absorption value can indicate the resistivity to the permeation of water molecules through the internal structure of paper, whereas the contact angle points to the resistivity to water of the paper surface only. Hence it can be concluded that the OPEFB’s lignin derivative-based coatings prepared in this study showed the potential for improving the water barrier property of linerboards more than that of commercial wax coating.

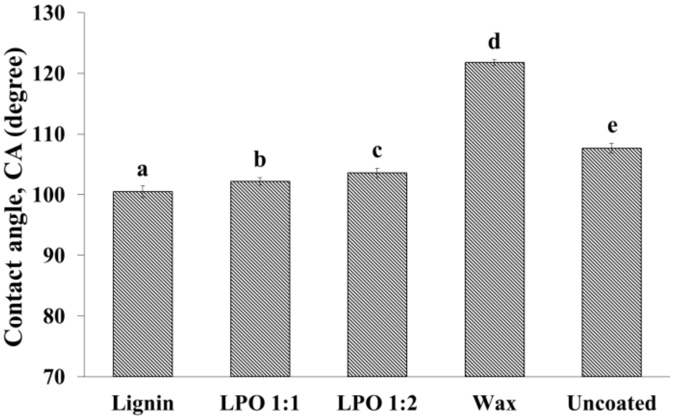

Figure 5.4 Surface contact angles of linerboards coated with different coatings. Lignin = the lignin-based coating, LPO 1:1 and LPO 1:2 = OPEFB's lignin derivative-based coatings synthesized by using lignin: palm oil at 1:1 and 1:2, respectively. Mean values with different letters are significantly different ($p<0.05$).

5.3.6 Mechanical properties of coated linerboards

The tensile index of the uncoated and coated linerboards with OPEFB's lignin derivative-based, OPEFB's lignin-based, and commercial wax coatings is shown in Figure 5.5. Technically, tensile testing is a measurement of the resistivity to the breaking of materials under the tension force. The tensile strength of paper is dependent on the strength, length, and surface area of fibers, and especially the fiber-to-fiber bonding strength [29]. According to the results, it was found that the coating treatments used did not significantly ($p\geq0.05$) affect the tensile index of coated linerboards. Generally, the solid fillers can be penetrated and retained in paper structures during the coating process. These may reduce the fiber-to-fiber interaction that causes the decreasing of the tensile strength of paper [30]. However, the main solid fillers, such as starch and lignin derivatives, used in this study have the large particle sizes that cause them to be retained only on the surfaces but do not allow penetration into the papers. Thus they did not interfere with the inter-fiber bonding and did not reduce the tensile index of the coated linerboards.

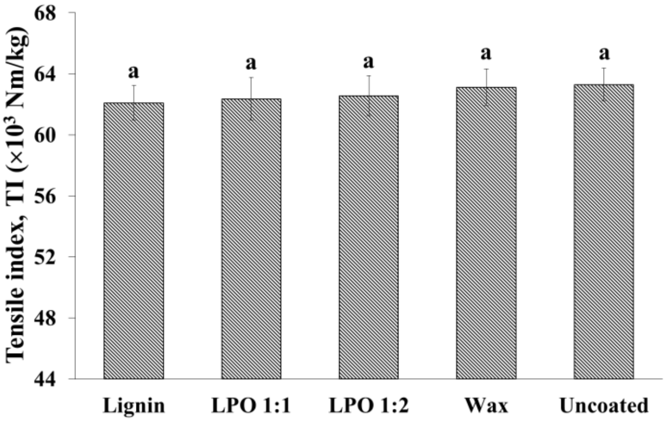

Figure 5.5 Tensile index of linerboards coated with different coatings. Lignin = the lignin-based coating, LPO 1:1 and LPO 1:2 = OPEFB's lignin derivative-based coatings synthesized by using lignin: palm oil at 1:1 and 1:2, respectively. Mean values with different letters are significantly different ($p<0.05$).

A ring crush test is the standard method for testing linerboards and corrugated mediums to evaluate the compressive strength of corrugated box. A burst test is used for estimating the behavior of paper when a perpendicular force acts on the surface, and it indicates the resistance to rupture [14,31]. The ring crush and bursting index of all coated linerboards are shown in Figure 5.6 and 5.7, respectively. The results showed that the coating treatments used did not significant ($p\geq0.05$) affect the ring crush and bursting index of coated linerboards. Basically, the ring crush and bursting tests are mainly involved with the deformation in the microstructure of papers. The ring crush test is correlated with compressive deformation whereas the burst test is associated with the breakdown of fibers. Hence the effect of solid fillers was not evident in reducing the ring crush and bursting index of coated linerboards. These results are in accord with other studies. Rhim *et al.* [31] reported that the application of biopolymer-based coating did not affect the ring crush index of coated paper. Our preliminary results [14] also show that the addition of fillers to lignin-based coatings did not reduce the bursting index of coated linerboards.

Our results indicate that the coating of OPEFB's lignin derivative did not downgrade the mechanical properties (strength) of coated linerboards. Hence it had a great potential for use as linerboards coating.

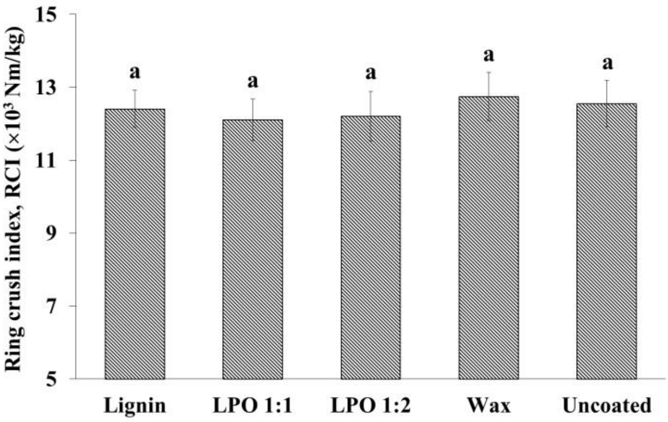

Figure 5.6 Ring crush index of linerboards coated with different coatings. Lignin = the lignin-based coating, LPO 1:1 and LPO 1:2 = OPEFB's lignin derivative-based coatings synthesized by using lignin: palm oil at 1:1 and 1:2, respectively. Mean values with different letters are significantly different ($p<0.05$).

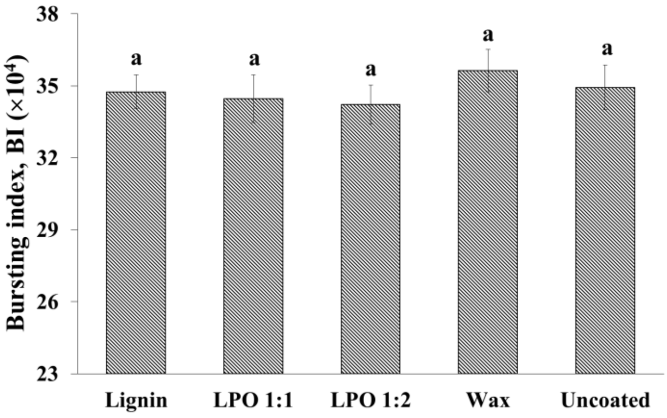

Figure 5.7 Bursting index of linerboards coated with different coatings. Lignin = the lignin-based coating, LPO 1:1 and LPO 1:2 = OPEFB's lignin derivative-based coatings synthesized by using lignin: palm oil at 1:1 and 1:2, respectively. Mean values with different letters are significantly different ($p<0.05$).

5.4 CONCLUSIONS

OPEFB's lignin derivative-based coating showed a high efficiency for paper coating applications. It provided superior water resistance of coated linerboards when compared with the OPEFB's lignin-based and commercial wax coatings. In addition, the use of OPEFB's lignin derivative-based coating did not downgrade the strength of coated linerboards the same as the OPEFB's lignin-based and commercial wax coatings. This study suggests that the OPEFB's lignin-palm oil derivative can be used as an alternative for the production of linerboards coating for the paper industry.

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CHAPTER 6

SYNTHESIZING OF OIL PALM EMPTY FRUIT BUNCH'S LIGNIN DERIVATIVES AND THEIR POTENTIAL USE FOR PRODUCTION OF LINERBOARD COATING

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ABSTRACT: This work describes the synthesis of oil palm empty fruit bunch (OPEFB)'s lignin derivatives and their performance for the production of linerboard coating. OPEFB's lignin derivatives were synthesized by the reactions of OPEFB's lignin and soy bean oil with two proportions (OPEFB's lignin:soy bean oil at 1:1 and 1:2). The derivative formation was confirmed by FTIR analysis. OPEFB's lignin derivative-based coatings were produced by mixing of oxidized starch solution and 5% lignin derivatives with the addition of 1% arabic gum (w/w of the derivatives) as the stabilizer. It was found that the OPEFB's lignin derivative-based coatings had low viscosity similarly to the commercial wax. OPEFB's lignin derivative-coated linerboards exhibited better ($p<0.05$) water resistance than the linerboard coated with commercial wax. However, an inverse trend was found for the contact angles. Increasing the soy bean oil content for synthesizing did not lead the lignin derivative to provide a better water resistance of the coated linerboards ($p \geq 0.05$). The mechanical properties, including ring crush, tensile and bursting strength of the linerboards coated with OPEFB's lignin derivatives and commercial wax were not different ($P \geq 0.05$). The results point out that the OPEFB's lignin derivative has a great performance for using as the linerboard coating material. It provides greater water resistance of the coated linerboards than the commercial wax coating.

Keywords: Coating; Linerboard; Mechanical properties; OPEFB's lignin derivative; Water resistance

6.1 INTRODUCTION

Corrugated box is one of the most popular packaging used for transporting a wide range of products. It is effective, lightweight and worthwhile in terms of manufacturing cost. Corrugated board structure consists of the corrugated medium and the linerboard. It has been known that the papers is very sensitive to the moisture, hence the coatings are necessary in enhancing the moisture resistivity of papers. Nowadays, the coatings used in the paper industry are the petroleum-based polymers such as polyethylene (PE) and wax. An increase in demand of their uses results in an increase in oil consumption. In addition, these synthetic materials are not degradable in normal environment which cause serious environmental problems. Therefore, the materials derived from renewable resources and agricultural wastes become a focus of interesting to use as an alternative for coating production [1,2].

Oil palm is one of the major industrial crops of the southern region of Thailand. The palm oil industry plays an important role in the economic development of the country and in enhancing the economic welfare of the population [3]. In 2010, the oil palm plantations in Thailand increased to 4.4×10^6 Rais (about 1.7×10^6 acres) and a large quantity of fresh fruit bunches (FFB) were harvested approximately about 8.2×10^6 tons [4]. Many factories in the southern have worked on palm oil production for the main goal in domestic consumption. For every FFB entered to the oil extraction processes, about 25% of oil palm empty fruit bunches (OPEFB) will be produced [5]. OPEFB solid wastes contain high moisture content because of the stream used for sterilization, hence they are not suitable as the fuel. Nowadays, OPEFB solid wastes become the major problem of the oil palm refineries. Although there is some usability of OPEFB, such as a fertilizer for oil plantation and a material for growing the mushrooms, a large scale has not been used.

Previous literatures describe that the OPEFB contains lignin as the component approximately about 25% [6,7]. Lignin is a complex aromatic heteropolymer which comprises a lot of subunits connected by C–C and C–O–C linkages. It presents the hydrophobic behavior and the ability to stabilize the mixtures [8]. Hence it is possible to use the lignin as a coating material for enhancing the water resistance of papers. This approach is the way to reduce the OPEFB wastes in the oil palm industries and also to increase their economic values. Furthermore, lignin is more environmentally friendly than the synthetic polymers because it is based on renewable resources and is degradable in the normal environment.

Preliminary, the lignin-based coating we prepared by mixing of oxidized solution and %5 w/v OPEFB's lignin with the addition of 1% arabic gum (w/w of lignin) as a stabilizer. It was found that the OPEFB's lignin based coating showed good coating characteristics and provided as good coated linerboard properties, as well as the commercial wax [9]. However, the lignin structure consists of the methoxy groups which are suitable for the chemical modification. Thus it is possible to improve the hydrophobicity of lignin by the structural modification for a better waterproof performance of the lignin-based coating.

The objective of this study was to develop the OPEFB's lignin derivative-based coating with a good waterproof performance for the linerboard coating. OPEFB's lignin-soy bean oil derivatives were synthesized by the reactions of OPEFB's lignin and soybean oil. The performance of OPEFB's lignin derivative-based coatings was compared with the commercial wax in terms of coating viscosity and coated linerboard properties (water absorption, contact angle, and ring crush, tensile and bursting strength).

6.2 METHODOLOGY

6.2.1 Materials

Oil palm empty fruit bunches (OPEFB) were supplied by the Virgin Vegetable Oil Co., Ltd., Songkhla, Thailand. The linerboards (KS170) and the commercial wax (WR390) were obtained from Thai Containers Songkhla (1994) Co., Ltd., Songkhla, Thailand. Arabic gum (stabilizer) was purchased from Merck KGaA, Darmstadt, Germany. Oxidized starch was supplied by the Siam Modified Starch Co., Ltd., Pathumthani, Thailand. Soybean oil (A-ngun™) was bought from the retail market. Other chemicals were purchased from S.V. Medico Co. Ltd, Songkla, Thailand.

6.2.2 Lignin preparation

Oil palm empty fruit bunches were washed with clean water 3–5 times, chopped into small pieces and then dried in a hot air oven for at least 72 h. A suspension of chopped OPEFB and 20% NaOH solution (1:15 w/v) was cooked at 170°C for 120 min in a rotary digester (Model RDB-D352, from Nanasiam Intertrade Co., Ltd.). After that, the liquid phase (black liquor) was separated through a strainer and then was stored in an ambient temperature for 24 h. For the lignin precipitation, 4M sulfuric acid was added to the liquor until the pH was reduced to 5 (this procedure was performed using airflow to remove the odorous compounds given off during precipitation). The liquor was then stored in an ambient temperature for 24 h. After that, the liquor was filtered through a filter paper to separate lignin sediment from an aqueous, and then the lignin was neutralized with clean water. The solution remaining in lignin was evaporated in a vacuum oven at 70°C for 48 h. The lignin was ground in a mortar, sieved through a 200 mesh strainer, and then stored in an ambient temperature in the absence of daylight.

6.2.3 Synthesizing of lignin derivatives

The procedure for synthesizing the linin derivatives was modified from Antonsson *et al.* [10]. OPEFB’s lignin dissolving in acetone (3:30 g/ml) was combined with a mixture of soybean oil and concentrated sulfuric acid (15:0.1 g/ml). The mixing proportions used were 1:1 and 1:2 w/w. The mixtures were stirred in three neck round flask at 70°C for 2.5 h under a nitrogen flow. After the reaction ended, the mixtures were cooled to room temperature and washed in pentane to remove the excess oil from the lignin derivatives. The derivatives obtained were then dried in a vacuum oven for 48 h to evaporate the excess pentane. After that, the derivatives was mashed in a mortar, sieved through a 200 mesh strainer, and stored in an ambient temperature in the absence of daylight.

6.2.4 FTIR analysis of lignin derivatives

FTIR analysis was performed to the lignin derivatives and starting materials using an infrared spectrometer (Model Equinox 55, from Bruker Corporation, Germany). The KBr pellet technique was used for preparing the samples. Each spectrum was recorded in a frequency range of 400–4000 cm^{-1}.

6.2.5 Oil content analysis

Soxhlet extraction method was used to evaluate the remaining oil content in the lignin derivatives. The derivatives (2 g) were weighed on the filter papers, placed in Soxhlet extractors, and then extracted with a 150 ml of petroleum ether for 14 h at the rate of 10 cycles per hour. After extraction, the samples were dried at 50°C on a rotary evaporator to remove the petroleum ether. The samples were then dried at 100°C for 1 h, and the oil content was calculated gravimetrically.

6.2.6 Coating preparation and linerboard coating procedures

The OPEFB's lignin derivative-based coatings were prepared by mixing of 3% oxidized starch solution (as a coating medium) and OPEFB's lignin derivative powder (5% w/v of starch solution) with the addition of 1% arabic gum (w/w of the derivative) as a stabilizer. The mixtures were homogenized at 10,000 rpm for 60 s, and then immediately applied to the linerboards by using a twin-rolls coating machine. All the coated linerboards were dried at 150°C for 1 min and conditioned at 50% RH in an ambient temperature for at least 48 h before testing.

6.2.7 Coating viscosity measurement

The viscosity of coatings was measured by a Brookfield Viscometer (Model DV-II, from Brookfield Engineering Laboratory, USA). A 120 ml coating was poured into a 140 ml beaker and then performed with the apparatus using a S62 spindle at the speed of 200 rpm. The viscosity was recorded as centipoise (cP) at 1 min after the apparatus was started.

6.2.8 Testing of coated linerboard properties

(a) Water absorption

Cobb test method was performed in accord with TAPPI T441. A specimen (5 in. × 5 in.) was fitted to the test kits, and then poured over it with a 100 ml of water. The water was poured off after 45 s, and then covered the specimen with the blotting paper and rolled immediately with a roller to remove the excess water. The water absorption (WA) value of specimen was calculated gravimetrically as weight gain per water contact area (g/m^2).

(b) Contact angle measurement

Surface contact angle of coated linerboards was measured using a contact angle measuring tool (Model OCA 15 EC, from Data Physics Instruments GmbH, Germany). A specimen was fitted to the tool and then the water was dripped on the specimen surface. An angle of the water drop was recorded at 1 s after dripping.

(c) Ring crush and tensile testing

Ring crush and tensile properties of the coated linerboards were investigated with a Universal Testing Machine (Model LR30K, from LLOYD Instrument Co., Ltd., UK). A tensile test was performed following TAPPI T494. A specimen (15 cm. × 1.5 cm.) was set in the clamps with the distance between clamps fixed at 10 cm. The tension force was applied to the specimen with a strain rate of 15 mm/min. For a ring crush test, TAPPI T818 was followed. A specimen (6 in. × 0.5 in.) was set in a circular block, and then the compressive force (0.5 in./min) was applied through the plate to the center of specimen. The results was reported as ring crush and tensile indexes (TI and BI) by dividing the maximum loads recorded with the basic weight of the papers so as to avoid the effect of different thicknesses.

(d) Burst testing

The bursting strength of the coated linerboards was determined using A Mullen Bursting Tester (Model GT-7013-AD, from GOTECH Testing Machines Inc., Taiwan). A specimen (4 in. × 4 in.) was inserted between the clamping ring and diaphragm plate, and then a 100 psi of pneumatic pressure was applied to the specimen until it ruptured. The bursting strength recorded was divided by the basic weight of specimen and reported as bursting index (BI) so as to avoid the effect of different thicknesses.

6.2.9 Statistical analysis

All the coated linerboard properties were investigated with at least eight replicates of the samples tested. Means with standard deviations were calculated and reported. Analysis of variance (ANOVA) with Duncan's Multiple Range Test (DMRT) was performed on the data obtained to assay the significant differences between coating treatments used. All significant values were expressed at 95% confidence level.

6.3 RESULTS AND DISCUSSION

6.3.1 FTIR analysis of OPEFB's lignin-soybean oil derivatives

FTIR spectras of the OPEFB's lignin derivatives and starting materials are shown in Figure 6.1. Most absorption bands of both lignin derivatives presented the same intensities as those of the native (unmodified) lignin (Table 6.1), e. g., the bands of aliphatic and aromatic O–H stretching (3410 cm^{-1}), aliphatic C–H stretching (2926 cm^{-1}), and the aromatic bands of C=C stretching (1630 cm^{-1}), C=C skeletal vibration (1614 cm^{-1}), C–H in phase deformations (1330 and 1042 cm^{-1}) and C–H out of phase bending (896 cm^{-1}). However, an alteration in intensities was found in some bands (Table 6.2).

Table 6.1 Fundamental FTIR absorption bands of OPEFB’s lignin and its derivatives.

Wave number (cm^{-1})	Assignments
3410 (s)	Al. and Ar. O–H stretching
2926 (m)	Al. C–H stretching
1630 (w)	Ar. C=C stretching
1614 (m)	Ar. C=C skeletal vibration
1330 (w)	Ar. C–H in phase deformation (syringyl lignin)
1042 (m)	Ar. C–H in phase deformation (guaiacyl lignin)
896 (m)	Ar. C–H out of phase stretching

[a] s = strong, m = middle, w = weak (signal strength)

[b] Al. = aliphatic, Ar. = aromatic (compound types)

[c] The FTIR bands were reported in accordance with the other literatures [11–15].

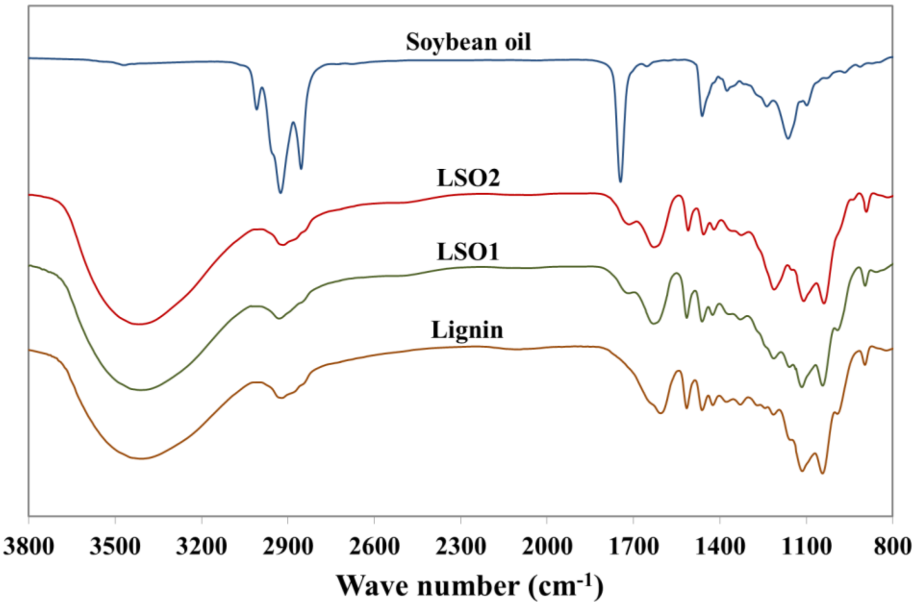

Figure 6.1 FTIR spectras of the starting materials and the OPEFB’s lignin derivatives obtaining from the reactions with 1:1 (LSO1) and 1:2 (LSO2) proportions of lignin to soybean oil**.**

An increase in transmittances of two absorption bands at 1722 and 1214 cm^{-1} was found for OPEFB’s lignin derivatives and was clearer for the derivative obtaining from the reaction with double oil content. These bands were attributed to C=O stretching and C–O stretching (in ester) vibrations, respectively. It can be indicated that OPEFB’s lignin derivative structures have been altered in the forms of C=O and C–O increases which were furthered with increasing the oil content.

The methyl (CH_3) vibration bands of the OPEFB’s lignin derivatives presented a decrease in transmittances compared with the native (unmodified) lignin and were clearer for the derivatives obtaining from the reaction with double oil content, namely, a band of out-of-phase bending in symmetric vibration (1516 cm^{-1}), two bands of anti-symmetric vibrations (1462 and 1426 cm^{-1}), an umbrella type vibration band (1377 cm^{-1}) and a band of perpendicular rocking vibration (1159 cm^{-1}). An increase in transmittances of these bands indicated a reduction of CH_3 functional groups in the derivative structures which was furthered with increasing the oil content.

As the FTIR results discussed, the structures of OPEFB’s lignin derivatives have been changed in the forms of the increasing in ester linkages and the reduction in methyl groups. Thus, a reaction of OPEFB’s lignin and soybean oil forming lignin-soybean oil derivative can be modeled (Figure 6.2). Methoxy groups (OCH_3) in the lignin structure are described as the most active sites for the chemical modification [10]. They can be demethylated easily and hence create the sensitive –O sites. Under acidic condition, the nonpolar chains with –C=O ending segments would be created through breaking the ester linkage of triglycerides. Consequently, the –O sites of lignin and the –C=O endings of hydrocarbons chain would bond together and then the lignin derivative with ester linkages would be formed. When the oil content increased, this reaction was furthered because nonpolar chains were more created and could react with the lignin effectively.

Table 6.2 The changes in intensities of important FTIR bands of the OPEFB's lignin derivatives.

Wave no. (cm^{-1})	Transmittances (%)			Assignments
	Lignin	LSO1	LSO2	
1722	N/A	84.6	82.1	C=O stretching
1516	63.4	69.6	77.7	CH_3 sym. bending
1462	62.4	67.3	75.1	CH_3 anti-sym. bending
1426	65.4	71.0	78.4	CH_3 anti-sym. bending
1377	67.3	71.3	N/A	CH_3 sym. umbrella type vibration
1214	59.8	46.3	44.2	C-O stretching (ester)
1159	41.0	46.4	53.1	CH_3 perpendicular rocking

[a] N/A = not available (the peaks were not observed.)

[b] The FTIR bands were reported according to the other literatures [11–13,16–17].

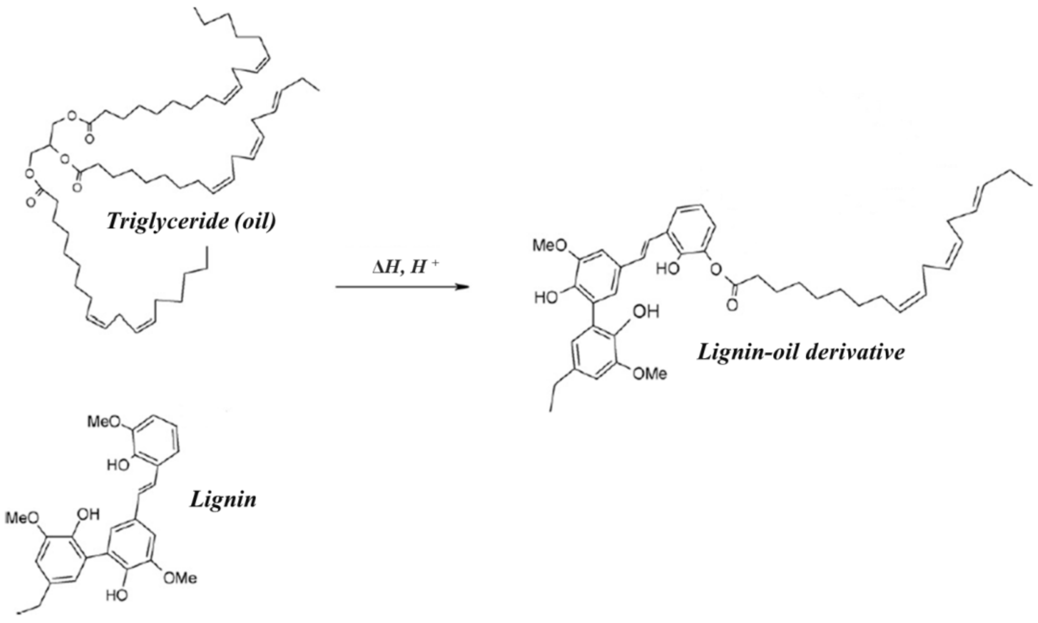

Figure 6.2 A possible formation of lignin-oil derivative.

6.3.2 Excess oil content of OPEFB’s lignin derivatives

The results showed that the content of free soy bean oil remaining in OPEFB’s lignin derivatives was very low. They found approximately about 0.43% and 0.50% in the derivatives obtaining from the reaction of lignin and soybean oil at the ratios of 1:1 and 1:2, respectively (Table 6.3). From this analysis, it can be confirmed that the enhancement of coated linerboard properties was not influenced by the high excess oil but resulted from the intrinsic features of the OPEFB’s lignin derivatives.

Table 6.3 The remaining oil content in the OPEFB’s lignin derivatives.

Crude oil content (% dry wt.)	
LSO1	LSO1
0.43%	0.50%

LSO1 and LSO2 were the OPEFB’s lignin derivatives synthesized by the reactions with 1:1 and 1:2 proportions of lignin to soybean oil, respectively.

6.3.3 Coating viscosity

The viscosity of OPEFB’s lignin derivative-based, OPEFB’s lignin-based and commercial wax coatings were measured (Table 6.4). The viscosity of OPEFB’s lignin- and OPEFB’s lignin derivative-based coatings was quite close to each other. By the reason of they contained the same solid contents, including lignin/or derivatives, oxidized starch and arabic gum, their rheology was similar. In addition, the characteristics of the lignin and its derivatives were also homologous; the structures of the derivatives have minor differences compared with the native (unmodified) lignin. Hence they would not alter the rheology of the coatings. It can be observed that the viscosity of OPEFB’s lignin derivative-based coatings was close to that of the commercial wax coating. These indicate the advantages in terms of can be applied with the same industrial processes. Furthermore, the derivative-based coatings have low viscosity which is desired for the good coating. Technically, the coating with too high viscosity may provide uneven paper surfaces and poor paper properties [19].

Table 6.4 The viscosity of coatings.

Coating treatments			
Lignin	LSO1	LSO2	Wax
23.0	22.7	22.6	22.9

[a] The viscosity is expressed as centipoise (cP).

[b] LSO1 and LSO2 were the coatings based on the OPEFB's lignin derivatives synthesized by the reactions with 1:1 and 1:2 proportions of lignin to soybean oil, respectively.

6.3.4 Water absorption of coated linerboards

The moisture is a variant that greatly influence on the mechanical properties of papers. As the moisture is absorbed, the water molecules can bond with the OH sites of celluloses and hence reduce the inter-bonding between the fibers. This causes reducing the paper strength [20]. Consequently, the coatings are considered necessary in enhancing the moisture resistivity of the papers so as to maintain their strength.

Figure 6.3 demonstrated the water absorption of the linerboards coated with the OPEFB's lignin-based coatings in compare with other coated linerboards. Obviously, the OPEFB's linin derivative-coated linerboards had greater ($P<0.05$) water resistance than the others. The enhancement of water resistance of the coated linerboards was resulted from the different factors. The hydrophobic feature of lignin has been assumed as the first determinant; lignin structure consists of some nonpolar functional groups especially the benzene rings. The physical changes of the coated linerboard surfaces are considered secondary. After coating processes, the lignin has been retained on the paper surfaces and also attached to the fibers. Thus the surface areas of fibers that the water could penetrate through were reduced [19].

Chemical modification (Figure 6.2) made the hydrophobicity of lignin derivatives improved. This was because the joining of nonpolar chains to their structures. Thus the lignin derivative-based coatings provided greater ($P<0.05$) water resistance of the coated linerboards than the unmodified lignin-based coating. The same trend that the nonpolar chain improved the hydrophobicity of the coating material was described by Havimo *et al.* [21]. They found that the coating of alkyl chain-modified cellulose could enhance the water vapor barrier of the coated paperboards and was more effective with increasing the degree of alkyl chain substitution.

Increasing the oil content for synthesizing did not lead the OPEFB’s lignin derivative to show a better performance. The water resistance of the linerboards coated with both derivatives was not significantly ($p \geq 0.05$) different. This suggests that improving the hydrophobicity of lignin requires not much content of soy bean oil.

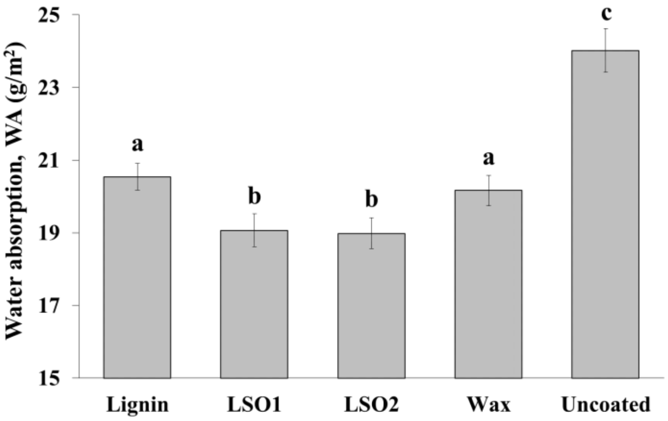

Figure 6.3 The water absorption of linerboards coated with different coatings. Lignin = the lignin-based coating, LSO1 and LSO2 = the coatings based on the OPEFB’s lignin derivatives synthesized by using the proportions of lignin to soy bean oil at 1:1 and 1:2, respectively. Different letters over the bars indicate the significant differences between means ($p<0.05$).

6.3.5 Water contact angle of coated linerboards

Basically, a wide contact angle of water drop should be shown on the surface with high water resistance. However, the present study found the surprising outcomes. Although the linerboards coated with OPEFB’s lignin- and OPEFB’s lignin derivative-based coatings showed greater ($P<0.05$) water resistance than the uncoated papers, their coated surfaces presented narrower ($P<0.05$) contact angles (Figure 6.4). The effect of oxidized starch has been assumed as the cause of these unusual results. Amylose and amylopectin as the starch components are highly hydrophilic [22]. The addition of oxidized starch to the coatings would provide sensitive paper surfaces that could absorb water easily. Thus the linerboards coated with the lignin- and derivative-based coatings exhibited a reduction in surface contact angles compared with the uncoated ones.

As the results shown, the linerboards coated with OPEFB’s lignin derivative-based coatings presented broader ($P<0.05$) contact angles than those coated with OPEFB’s lignin-based coating. This was due to the structural modification led the derivatives to a greater hydrophobicity which was directly dependent on the oil quantity used for the synthesis. Antonsson *et al.* [10] found that the filter paper treated with lignin-linseed oil derivative exhibited a wide contact angle while that of the filter paper treated with lignin was not measurable. This trend is the same as was found in our study, thus it is clear that the hydrophobicity of the lignin is really improved by the modification with the vegetable oils.

Not surprisingly, the superior contact angles were found on the surfaces of the linerboards with commercial wax coating. The structure of synthetic wax contains high amounts of long-chain fatty alcohols, fatty acids and alkenes, which make its highly hydrophobic [23].

Generally, the water absorption value is considered importantly to evaluate the water resistance of the paper much more that the water contact angle. The water absorption value indicates the resistivity to the permeation of water molecules through the internal structure of the paper whereas the contact angle represents the water resistance of the paper surface only. Thus it can be summarized that the OPEFB’s lignin derivative-based coatings was better than the commercial wax coating used in this study in terms of enhancing the water resistance of the coated linerboards.

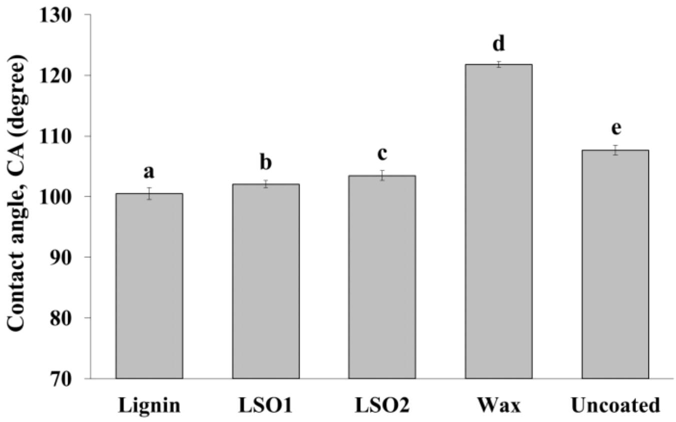

Figure 6.4 Water contact angle of linerboards coated with different coatings. Lignin = the lignin-based coating, LSO1 and LSO2 = the coatings based on the OPEFB's lignin derivatives synthesized by using the proportions of lignin to soy bean oil at 1:1 and 1:2, respectively. Different letters over the bars indicate the significant differences between means ($p<0.05$).

6.3.6 Tensile properties of coated linerboards

Tensile testing is a measurement of fracture resistivity of the materials under the tension force. The tensile strength of paper is dependent on the strength, length, and surface area of fibers, and especially the interfiber bonding strength [24].

OPEFB's lignin- and OPEFB's lignin derivative-based coatings did not impact the tensile strength of the coated linerboards, as well as the commercial wax. The tensile index of all linerboards was not significantly ($p\geq0.05$) different as seen in Figure 6.5. In general, the solid substrates can penetrate and be retained in the paper structures through the swelling of fibers during coating processes. They may reduce the bonding strength between fibers and result in a reduction of tensile strength of the paper [25]. However, due to the solid fillers used in this study (lignin, lignin derivatives and oxidized starch) have the large size of particles/or molecules, they could not penetrate into the paper structures and would be retained only on the surfaces only. Thus they did not reduce the interfiber bonding, and hence a reduction of tensile index of the coated linerboards was not found.

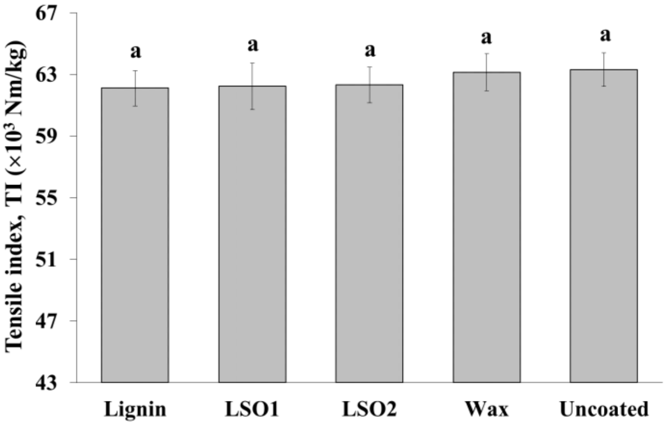

Figure 6.5 Tensile index of linerboards coated with different coatings. Lignin = the lignin-based coating, LSO1 and LSO2 = the coatings based on the OPEFB's lignin derivatives synthesized by using the proportions of lignin to soy bean oil at 1:1 and 1:2, respectively. Different letters over the bars indicate the significant differences between means ($p<0.05$).

6.3.7 Ring crush and bursting properties of coated linerboards

A ring crush test is the standard method for testing the compressive strength of the linerboards and corrugated mediums. It has been performed so as to evaluate the compressive resistance of the corrugated box. For a burst test, it has been widely used to evaluate the rupture resistance of the paper when a perpendicular force acts on the surface [26].

As shown in Figure 6.6 and 6.7, respectively, applying the OPEFB's lignin- and OPEFB's lignin derivative-based coatings did not significantly ($p\geq0.05$) alter the ring crush and bursting indexes of the coated linerboards, as well as the commercial wax coating. Technically, ring crush and burst strength evaluations are associated with the microstructure deformation of the papers. The ring crush test is correlated with the compressive deformation whereas the burst test is involved with the breakdown of fibers. Hence the effect of solid substrates was not much to cause any alteration of ring crush and bursting indexes of the coated linerboards [19]. Rhim *et al.* [26] reported the same trend that the applications of the coatings with the protein coating materials did not influence on the ring crush strength of the coated paperboards. Our preliminary study also showed that the solid fillers added to the lignin-based coatings did not affect the bursting strength of the coated linerboards [19].

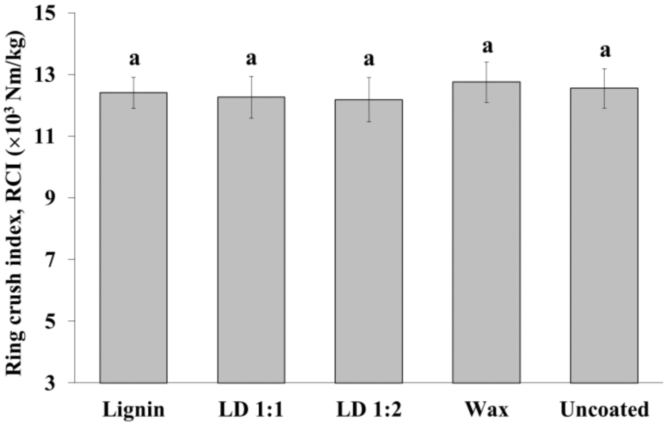

Figure 6.6 Ring crush index of linerboards coated with different coatings. Lignin = the lignin-based coating, LSO1 and LSO2 = the coatings based on the OPEFB's lignin derivatives synthesized by using the proportions of lignin to soy bean oil at 1:1 and 1:2, respectively. Different letters over the bars indicate the significant differences between means ($p<0.05$).

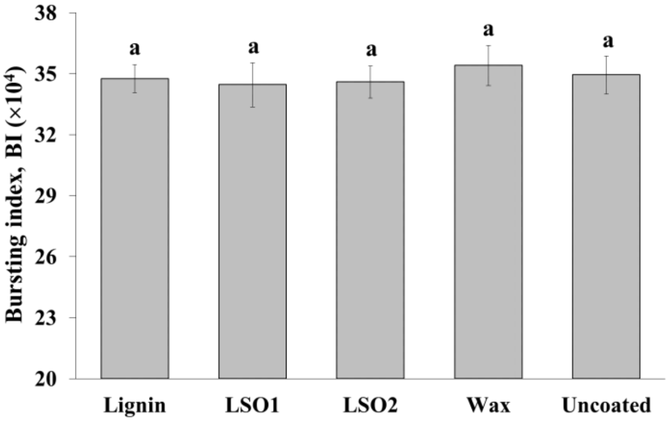

Figure 6.7 Bursting index of linerboards coated with different coatings. Lignin = the lignin-based coating, LSO1 and LSO2 = the coatings based on the OPEFB's lignin derivatives synthesized by using the proportions of lignin to soy bean oil at 1:1 and 1:2, respectively. Different letters over the bars indicate the significant differences between means ($p<0.05$).

6.4 CONCLUSIONS

OPEFB's lignin derivative-based coating has a great performance for the production of linerboard coating. It provided better water resistance of the coated linerboards than the OPEFB's lignin-based and commercial wax coatings. Furthermore, using of OPEFB's lignin derivative-based coating did not downgrade the strength of coated linerboards the same as the OPEFB's lignin-based commercial wax coatings. The results indicate that the OPEFB's lignin derivative can be utilized as an alternative resource to replace the synthetic wax for producing the linerboard coating. This novel approach is the way to conserve the petroleum resources though reducing the demand of them as the starting materials in the wax manufacturing.

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CHAPTER 7

SUMMARIZATION AND SUGGESTION

The objective of this work was to develop a novel bio-based coating for the corrugated packaging using the lignin from oil palm empty fruit bunch (OPEFB) as a raw material. The study dealt with the extraction and characterization of lignin from agricultural OPEFB residues, the synthesis of OPEFB's lignin derivatives, the production of both OPEFB's lignin- and OPEFB's lignin derivative-based coatings, and the evaluation of the performance of the developed coatings in terms of the coating characteristics and the coated linerboard properties, comparing with the commercial wax coating.

Lignin was extracted from OPEFB by using a soda pulping process. Four pH conditions (5, 4, 3 and 2) were adjusted to OPEFB's black liquor for recovering the soluble lignin through the acidification of sulfuric acid. It was found that the recovery mass of lignin increased with reducing the pH of the black liquor. As the pH of the liquor reduced, the lignin was progressively recovered in the form of Hibbert's ketone as was indicated by FTIR analysis. The pH of liquor did not influence on the chemical compositions of the lignin recovered as was carried out by TGA: all the lignin fractions exhibited similar thermograms. The lignin obtained from the pH-5 liquor was selected for the development of coatings so as to avoid the losing of feature from the drastic degradation.

OPEFB's lignin-based coatings were prepared by mixing 3% oxidized starch solution with 5% lignin (w/v of the solution). The effects of the type (arabic gum, carrageenan and guar gum) and concentration (1–5%, w/w of lignin) of stabilizers on the coating characteristics and properties of coated linerboard was investigated. An increase in viscosity and stability of the developed coatings was found with the addition of stabilizers. Lignin-based coatings with arabic gum were found to be more stable than those with carrageenan even though they had a lower viscosity. The coatings with 1–3% arabic gum and with 4–5% carrageenan provided great water resistance of the coated linerboards as the commercial wax coating. The stabilizers used in this study did not affect ($p \geq 0.05$) the ring crush and bursting indexes (RCI and BI) of the coated linerboards. The lignin-based coatings with 1% arabic gum and with 1% guar gum did not reduce ($p \geq 0.05$) the tensile index (TI) of the coated linerboards as the commercial wax. Only for the coating with 1% arabic gum provided overall of the properties of coated linerboards as good as the commercial wax in terms of the water resistance and the mechanical properties. It also had the viscosity close to the commercial wax. This coating treatment was selected for the further development.

The effect of lignin content on the performance of the OPEFB's lignin-based coatings was investigated. OPEFB's lignin-based coatings were prepared by mixing of 3% oxidized starch solution and various contents of lignin (1, 3, 5, 7 and 9%, w/v of the solution) with the addition of 1% arabic gum as the stabilizer. A minor increase in the viscosity of the lignin-based coatings was found with an increase in the content of lignin. However, it was still close to the commercial wax. An increase ($p < 0.05$) in water resistance of the coated linerboards was found with increasing the content of lignin, however at >5%, it was not significant ($p \geq 0.05$). All the RCI, BI and TI of the coated linerboards were not influenced ($p \geq 0.05$) by the addition of lignin. It can be suggested that the lignin content at 5% is suitable for the production of lignin-based coating and was therefore considered for developing further.

The hydrophobicity of the OPEFB's lignin was improved through chemical modification. OPEFB's lignin derivatives were synthesized by the reactions of lignin and vegetable (palm and soybean) oils at the proportions of 1:1 and 1:2. The formation of lignin derivatives through ester linking was confirmed by FTIR analysis. OPEFB's lignin derivative-based coatings were prepared by mixing of 3% oxidized starch solution and 5% lignin derivatives (w/v of the solution) with the addition of 1% arabic gum as the stabilizer. It was found that the viscosity of all the OPEFB's lignin derivative-based coatings was quite close to the commercial wax. The linerboards with lignin derivative-based coatings exhibited greater ($p < 0.05$) water resistance than those with commercial wax coating. Increasing the oil dosage for the synthesis did not lead the lignin-based coatings obtained to a better performance in enhancing the water resistance of the coated linerboards ($p \geq 0.05$). The lignin derivative-based coatings did not reduce ($p \geq 0.05$) the RCI, BI and TI of the coated linerboards as the commercial wax coating.

This work suggests that OPEFB's lignin has a great performance for using as an alternative source for the production of coating for the corrugated packaging. The extension of these outcomes to the industrial scale is possible and should be promoted. This approach will surely benefit in reducing the agricultural OPEFB residues, in saving the environment through its biodegradability, and in conserving the petroleum resources through reducing the demand in wax consumption.

It is well known that the primary function of the coating for corrugated packaging is to enhance its water resistance. To ensure this functionality, the performance as a water barrier of the coatings developed in this study should be further investigated. This can be performed through the tests such as water dynamic contact angle, water repellency and surface energy of the coated papers.

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Lists of Publications

Narapakdeesakul, D., Sridach, W. and Wittaya, T. 2013. Development of oil palm empty fruit bunches' lignin for production of linerboard coating: effect of selected stabilizers on coating characteristics and coated linerboard properties. Prog. Org. Coat., 76(2–3): 482–487.

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