Original Article

Synthesizing of oil palm empty fruit bunch lignin derivatives and potential use for production of linerboard coating

Danupong Narapakdeesakul, Waranyou Sridach, and Thawien Wittaya*

Department of Material Product Technology, Faculty of Agro-Industry, Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand.

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Abstract

This work describes the synthesis of oil palm empty fruit bunch (OPEFB) lignin derivatives and their performance for the production of linerboard coating. OPEFB lignin derivatives were synthesized by the reactions of OPEFB lignin and soy bean oil with two proportions (OPEFB lignin: soy bean oil at 1:1 and 1:2). The formation of the derivatives was confirmed by FTIR analysis. OPEFB 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 lignin derivative-based coatings had low viscosity similar to commercial wax. OPEFB lignin derivative-coated linerboards had a better (p<0.05) water resistance than the linerboard coated with commercial wax. However, an inverse trend was found for the contact angle. The results showed that increasing the soy bean oil content for synthesizing did not affect the water resistance of coated linerboards (p>0.05). The mechanical properties, including ring crush, tensile and bursting strength of linerboards coated with OPEFB lignin derivatives and commercial wax were not different (p>0.05). The results point out that the OPEFB lignin derivatives had a performance suitable for use as linerboard coating. It provided a better water resistance of the coated linerboards, and was also more environmental friendly.

Keywords: coating, OPEFB lignin, lignin derivative, linerboard, water resistance

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 paper is very sensitive to the moisture; hence the coatings are necessary in enhancing the moisture resistivity of the 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 and they cause serious environmental problems. Therefore, the materials derived from renewable resources and agricultural wastes have become a focus of interest to use as an alternative for coating production (Lim et al., 2004; Rodriguez et al., 2007).

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 (Chavaparit et al., 2006). In 2010, the oil palm plantations in Thailand increased to 4.4×10^6 rai (about 1.7×10^6 acres) and a large quantity of fresh fruit bunches (FFB) was harvested approximately 8.2×10^6 tons (Phitthayapinant and Nissapa, 2010). Many factories in the southern region 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 (Ibrahim and Chuah, 2004). OPEFB solid wastes contain high moisture content because of the stream used for sterilization, hence they are not suitable as fuel. Nowadays, OPEFB solid wastes have become a 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 mushrooms.

Previous literature has described that the OPEFB contains lignin as the component approximately about 25% (Jeffries, 1994; Boerjan et al., 2003). 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 mixtures (Park et al., 2008). Hence it is possible to use the lignin as a coating material for enhancing the water resistance of papers. This approach is a way to reduce the OPEFB wastes in the oil palm industries and also to increase their economic value. Furthermore, lignin is more environmentally friendly than 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 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 (Narapakdeesakul et al., 2113). 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 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 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).

2. Methodology

2.1 Raw materials

Oil palm empty fruit bunches (OPEFB) were supplied by the Virgin Vegetable Oil Co., Ltd., Songkha, Thailand. The linerboards (KS170) and the commercial wax (WR390) were obtained from Thai Containers Songkha (1994) Co., Ltd., Songkha, 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.

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 hours. 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 hours. 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 hours. 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 hours. 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.

2.3 Synthesis of lignin derivatives

The procedure for synthesizing the lignin derivatives was modified from Anstonson et al. (2008). OPEFB 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 hours 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.

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 as % transmittance in a frequency range of 400-4000 cm⁻¹.

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 hours at the rate of 10 cycles per hour. After
Coating preparation and linerboard coating procedures

The OPEFB lignin derivative-based coatings were prepared by mixing of 3% oxidized starch solution (as a coating medium) and OPEFB 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 seconds, and then immediately applied to the linerboards by using a twin-rolls coating machine. The coating density was controlled at 0.64±0.07 g/m². 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 hours before testing.

2.6 Coating preparation and linerboard coating procedures

Testing of coated linerboard properties

FTIR analysis of OPEFB's lignin derivatives

A decrease in transmittances of two absorption bands starting materials are shown in Figure 1. Most absorption bands of both lignin derivatives presented the same intensities as those of the naïve (unmodified) lignin (Table 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 2). A decrease 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. This would be indicate that OPEFB’s lignin derivative structures had been altered in the forms of C=O.
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 above, the structures of OPEFB lignin derivatives were changed by the increase in ester linkages and the reduction in methyl groups compared with the unmodified lignin. Thus, the reaction of OPEFB lignin and soybean oil forming lignin-soybean oil derivative can be modeled (Figure 2). Methoxy groups (OCH$_3$) in the lignin structure are described as the most active sites for the chemical modification (Antonsson et al., 2008). 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

![Figure 1. FTIR spectras of the starting materials and the OPEFB lignin derivatives obtained from the reactions with 1:1 (LSO1) and 1:2 (LSO2) proportions of lignin to soybean oil](image)

Table 1. Fundamental FTIR absorption bands of OPEFB lignin and its derivatives

<table>
<thead>
<tr>
<th>Wave number (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3410 (s)</td>
<td>Al. and Ar. O-H stretching</td>
</tr>
<tr>
<td>2926 (m)</td>
<td>Al. C-H stretching</td>
</tr>
<tr>
<td>1630 (w)</td>
<td>Ar. C=C stretching</td>
</tr>
<tr>
<td>1614 (m)</td>
<td>Ar. C=C skeletal vibration</td>
</tr>
<tr>
<td>1330 (w)</td>
<td>Ar. C-H in phase deformation (syringyl lignin)</td>
</tr>
<tr>
<td>1042 (m)</td>
<td>Ar. C-H in phase deformation (guaiacyl lignin)</td>
</tr>
<tr>
<td>896 (m)</td>
<td>Ar. C-H out of phase stretching</td>
</tr>
</tbody>
</table>

s = strong, m = middle, w = weak (signal strength)
Al. = aliphatic, Ar. = aromatic (compound types)
The FTIR bands were reported in accordance with the other literature (Colom et al., 2003; Ibrahim et al., 2011; Liu et al., 2011; Toledano et al., 2012; Yang et al., 2007).

Table 2. The changes in intensities of important FTIR bands of the OPEFB lignin derivatives.

<table>
<thead>
<tr>
<th>Wave number (cm$^{-1}$)</th>
<th>Lignin Transmittance (%)</th>
<th>LSO1 Transmittance (%)</th>
<th>LSO2 Transmittance (%)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1722</td>
<td>N/A</td>
<td>84.6</td>
<td>82.1</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>1516</td>
<td>63.4</td>
<td>69.6</td>
<td>77.7</td>
<td>CH$_3$ sym. bending</td>
</tr>
<tr>
<td>1462</td>
<td>62.4</td>
<td>67.3</td>
<td>75.1</td>
<td>CH$_3$ anti-sym. bending</td>
</tr>
<tr>
<td>1426</td>
<td>65.4</td>
<td>71.0</td>
<td>78.4</td>
<td>CH$_3$ anti-sym. bending</td>
</tr>
<tr>
<td>1377</td>
<td>67.3</td>
<td>71.3</td>
<td>N/A</td>
<td>CH$_3$ sym. umbrella type vibration</td>
</tr>
<tr>
<td>1214</td>
<td>59.8</td>
<td>46.3</td>
<td>44.2</td>
<td>C-O stretching (ester)</td>
</tr>
<tr>
<td>1159</td>
<td>41.0</td>
<td>46.4</td>
<td>53.1</td>
<td>CH$_3$ perpendicular rocking</td>
</tr>
</tbody>
</table>

N/A = not available (the peaks were not observed.)
The FTIR bands were reported according to the other literature (Azadfallah et al., 2008; Colom et al., 2003; Ibrahim et al., 2011; Liu et al., 2007; Liu et al., 2011; Singh, 2008).
linkages would be formed. When the oil content increased, this reaction was furthered because more nonpolar chains were created and could react with the lignin effectively.

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 obtained from the reaction of lignin and soybean oil at the ratios of 1:1 and 1:2, respectively (Table 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.

3.3 Coating viscosity

The viscosity of OPEFB lignin derivative-based, OPEFB’s lignin-based and commercial wax coatings were determined (Table 4). The viscosity of OPEFB’s lignin- and OPEFB lignin derivative-based coatings was quite close to commercial wax coating (Table 4). By the reason of, their containing 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

Table 3. The remaining oil content in the OPEFB lignin derivatives

<table>
<thead>
<tr>
<th>Oil content (% w.)</th>
<th>LSO1</th>
<th>LSO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.43±0.02%</td>
<td></td>
<td>0.50±0.01%</td>
</tr>
</tbody>
</table>

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.

Table 4. The viscosity of coatings

<table>
<thead>
<tr>
<th>Coating treatments</th>
<th>Lignin</th>
<th>LSO1</th>
<th>LSO2</th>
<th>Wax</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>23.0±0.2a</td>
<td>22.7±0.1a</td>
<td>22.6±0.1a</td>
<td>22.9±0.2a</td>
</tr>
</tbody>
</table>

The viscosity is expressed as centipoise (cP). LSO1 and LSO2 were the coatings based on the OPEFB lignin derivatives synthesized by the reactions with 1:1 and 1:2 proportions of lignin to soybean oil, respectively. Means with different letters are significantly different (p<0.05).
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. According to the results, it can be observed that the viscosity of OPEFB lignin derivative-based coatings was close to that of the commercial wax coating. These indicate the advantages in terms of coating procedures of the industrial processes used. Furthermore, the derivative-based coatings have low viscosity, which is desired for good coating. Technically, the coating with too high viscosity may provide uneven paper surfaces and poor paper properties (Narapakdeesakul et al., 2013).

3.4 Water absorption of coated linerboards

The moisture is a variant that greatly influences the mechanical properties of papers. As the moisture is absorbed, the water molecules can bond with the OH sites of cellulosics and hence reduce the inter-bonding between the fibers. This causes a reduction in paper strength (Haslach, 2000). Consequently, the coatings are considered necessary in enhancing the moisture resistivity of the papers so as to maintain their strength.

Figure 3 demonstrates the water absorption of the linerboards coated with the OPEFB lignin-based coatings in comparison with other coated linerboards. Obviously, the OPEFB lignin derivative-coated linerboards had greater (p<0.05) water resistance than the others. The enhancement of water resistance of the coated linerboards resulted from the several 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 is also attached to the fibers. Thus the surface areas of fibers that the water could penetrate through were reduced (Narapakdeesakul et al., 2013).

Chemical modification (Figure 2) improved the hydrophobicity of lignin derivatives. This was because of 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. (2011). 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 an increase in the degree of alkyl chain substitution. Increasing the oil content for synthesizing did not lead the OPEFB lignin derivative to show a better performance. The water resistance of the linerboards coated with both derivatives was not significantly different (p>0.05). This suggests that improving the hydrophobicity of lignin requires not much content of soy bean oil.

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 lignin- and OPEFB 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 4). The effect of oxidized starch has been assumed to be the cause of these unusual results. Amylose and amylopectin as the starch components are highly hydrophilic (Schenck and Hebeda, 1992). 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 show, the linerboards coated with OPEFB 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 giving the derivatives to a greater hydrophobicity, which was directly dependent on the oil quantity used for the synthesis. Antonsson et al. (2008) 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 it highly hydrophobic (Khawaldia et al., 2010).

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 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.

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 (Rabinovitch, 2003).

OPEFB lignin- and OPEFB lignin derivative-based coatings did not have an impact on the tensile strength of the coated linerboards, as well as the commercial wax. The tensile index of all linerboards was not significantly (p≥0.05) different as seen in Figure 5. In general, the solid substrates can penetrate and be retained in the paper structures through the swelling of fibers during the coating processes. They may reduce the bonding strength between fibers and result in a reduction of tensile strength of the paper (Han and Krotchta, 2001). 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.

3.7 Ring crush and bursting properties of coated linerboards

The 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 the burst test has been widely used to evaluate the rupture resistance of the paper when a perpendicular force acts on the surface (Rhim et al., 2006).

As shown in Figures 6 and 7, respectively, applying the OPEFB lignin- and OPEFB lignin derivative-based coatings did not significantly (p≥0.05) alter the ring crush and bursting indexes of the coated linerboards, as well as the

![Figure 5. Tensile index of the linerboards coated with different coating treatments. Lignin = the OPEFB lignin-based coating, LSO1 and LSO2 = the coatings based on the OPEFB 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 significant differences between means (p<0.05).](image)

![Figure 6. Ring crush index of the linerboards coated with different coating treatments. Lignin = the OPEFB lignin-based coating, LSO1 and LSO2 = the coatings based on the OPEFB 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 significant differences between means (p<0.05).](image)
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 (Narapakdeesakul et al., 2013). Rhim et al. (2006) reported the same trend that the applications of the coatings with the protein coating materials did not influence 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 (Narapakdeesakul et al., 2013).

4. Conclusions

OPEFB lignin derivative-based coating had a very satisfactory performance for the production of linerboard coating. It provided better water resistance of coated linerboards than the OPEFB lignin-based and commercial wax coatings. Moreover, using of OPEFB lignin derivative-based coating did not downgrade the strength of coated linerboards. The results indicate that the OPEFB 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 through reducing the demand of them as the starting materials in the wax manufacturing.

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References


