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Properties of Lignin from Oil Palm Empty Fruit Bunch and Its Application for Plywood Adhesive

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Abstract

Lignin from lignocellulosic biomass is a potential biopolymer for wood adhesive. The aims of this study were to characterize lignin isolated from the black liquor of oil palm empty fruit bunch fiber pretreated with steam explosion in alkaline conditions and to examine the bond quality of aqueous polymer isocyanate (API) adhesive prepared from lignin, natural rubber latex (NRL), and polyvinyl alcohol (PVA) as base polymers with isocyanate crosslinkers. Lignin was precipitated from the black liquor by adding hydrochloric acid; then the precipitate was separated by filtration, thoroughly washed with water up to pH 2 and pH 5, and dried. The isolated lignin was characterized by ultimate analysis, UV spectroscopy, FT-IR spectroscopy, and thermal analysis. Three-layer plywood samples were prepared, and the bond strengths of the plywood samples were determined in dry conditions and after cyclic boiling. The lignin isolates with different pH values did not have significantly different chemical and thermal properties. Both lignin isolates had similar C, H, and O contents, identical functional groups in the FTIR spectra, similar absorption in the UV spectra, and high decomposition temperatures. The base polymers composition that could produce API adhesive for exterior applications was NRL/PVA/lignin (4/4/2). The use of more lignin in the adhesive formulation decreased the bond strength of the plywood.

Abstrak

Sifat lignin dari tandan kosong kelapa sawit dan aplikasinya sebagai perekat kayu lapis. Lignin dari biomassa lignoselulosa merupakan biopolimer potensial untuk perekat kayu. Tujuan penelitian ini adalah untuk mengenali sifat lignin yang diisolasi dari lindi hitam sisa pretreatment *steam explosion* alkalis serat tandan kosong kelapa sawit, dan untuk menguji daya rekat perekat *aqueous polymer isocyanatae* (API) yang dibuat dari lignin, lateks karet alam (LKA) dan polivinil alkohol (PVA) sebagai polimer dasar dengan senyawa isosianat sebagai *crosslinker*. Lignin diendapkan dari lindi hitam dengan menambahkan asam klorida, setelah itu endapan dipisahkan dari larutan dengan penyaringan, dicuci dengan air sampai pH 2 dan pH 5, dan dikeringkan. Isolat lignin dikarakterisasi dengan analisis ultimat, spektroskopi UV, spektroskopi FT-IR, dan analisis termal. Kayu lapis (tiga lapisan) dibuat dari vinir kayu meranti (depan dan belakang) dan sengon (tengah) dan keteguhan rekatnya diuji pada kondisi kering dan setelah melalui perebusan berulang. Isolat lignin dengan pH yang berbeda tidak memberikan pengaruh nyata terhadap sifat kimia dan sifat termalnya. Kedua isolat lignin mempunyai kadar C, H, dan O yang mirip, gugus fungsi yang identik pada spektra FTIR, serapan yang mirip pada spektra UV, dan suhu dekomposisi yang tinggi. Komposisi polimer dasar yang dapat menghasilkan perekat API untuk aplikasi eksterior adalah LKA/PVA/lignin (4/4/2). Penggunaan lignin yang lebih banyak menurunkan keteguhan rekat kayu lapis.

Keywords: adhesive, lignin, natural rubber latex, oil palm empty fruit bunch, plywood

1. Introduction

Lignin is the second largest biomass available after cellulose, which is rich in phenolic compounds. Lignin can be obtained by direct isolation from plants or by

acid precipitation from the black liquor produced as a byproduct during chemical pulping or pretreatment of lignocellulosic biomass using alkaline solutions. The utilization of black liquor or lignin is still limited. In the pulp industry, black liquor is usually used as fuel for

boilers. Lignin's properties usually vary due to differences in raw materials and the process of isolation.

Wood adhesive has a large influence on the price of wood panels because it can constitute as much as 32% of the total manufacturing cost of the panels [1]. Formaldehyde-bearing adhesives, such as urea formaldehyde (UF), phenol formaldehyde (PF), melamine formaldehyde (MF), and phenol resorcinol formaldehyde (PRF), are the most widely used wood adhesives, probably due to their low prices. The global market of wood panels is very concerned about environmental issues, such as formaldehyde emissions; the market demands products that have very low or no formaldehyde emissions.

Aqueous polymer isocyanate (API) adhesive is a type of adhesive without formaldehyde emissions. API adhesive mainly consists of water soluble polymers and emulsions, such as polyvinyl alcohol (PVA) and polystyrene-co-butadiene rubber (SBR) latex, with isocyanate compounds (pMDI and dibutyl-phthalate 30%) as crosslinking agents [2]. By changing the base polymers or the amount of crosslinking agents, a wide range of API adhesives can be formulated with various physical properties [3]. API adhesives have good adhesive properties at ambient temperatures and excellent resistance to warm/boiling water, are environmentally friendly, and are widely used in the timber-processing industry [4]. According to Taki *et al.* [1], tensile strength of birch wood bonded with API adhesive and tested at different temperatures (-100 to 200 °C) ranged from 3 to 15 MPa. Hongjiu *et al.* [3] reported that rosewood specimens glued by API adhesive and tested at room temperature had compression shear strength ranging from 9 to 15 MPa, while those tested with warm and boiling water ranged from 6 to 9 MPa and from 4 to 5.8 MPa, respectively.

There are some renewable resources which have potential to be used as wood adhesives, including API adhesive, lignin from black liquor, and natural rubber latex (NRL). Lignin has long been studied as a substitute for the phenolic compound in PF and PRF adhesives. Natural rubber is produced from the sap of *Hevea brasiliensis*. It has long been known as a biological resource that can be used as an adhesive. However, it is characteristically low in adhesion and cohesion, has poor resistance to stress and heat, and only fair resistance to moisture. It does have an excellent resistance to organisms, and it can make an instant bond with a relatively low pressure [5]. It is also quite cheap and abundantly available in Indonesia.

So far, black liquor is only burned to produce energy for the boilers in pulp and paper plants [6]. The utilization of lignin from black liquor becomes more important due to the possibility of using lignocellulosic biomass for

ethanol production [7,8]. The first step in converting lignocellulosic material to ethanol is a pretreatment that should remove as much lignin as possible. Therefore, utilizing the lignin, such as for adhesives, will give added value to the material [9].

Previous studies show the success of lignin isolated from black liquor as formaldehyde-bearing adhesives, such as PF and PRF. The lignin is used as substitute for PF [10-13] or PRF [14-16]. It also can be used as a total replacement of the toxic phenol compound used to make lignin formaldehyde [17]. Patents on the use of lignin from black liquor as a substitute for PF are published by Kambanis *et al.* [18] and Sudan [19]. So far there is no report on the use of lignin as a substitute for the base resin in API adhesive. Stephanou and Pizzi [20] use pMDI in the preparation of lignin phenol formaldehyde for a faster curing process of the adhesive.

The objectives of this research were to characterize the lignin obtained from the black liquor of alkaline pretreatment of oil palm empty fruit bunch (OPEFB) fiber and to study the formulation of API adhesive using NRL and lignin as base resins as well as their bonding strength as plywood adhesives.

2. Methods

Materials. Black liquor was obtained from the Research Center for Chemistry, Indonesian Institute of Sciences, Serpong, Tangerang Selatan, which resulted from the pretreatment of OPEFB using steam explosion with alkaline (NaOH), having a total solid content of 4.6-5.1%. Natural rubber latex was purchased from Balai Penelitian Perkebunan Sembawa, South Sumatera. The concentrated latex (61-62% total solid content) was diluted with water to 50 and 60% total solid content. The PVA, purchased from a local market in Bogor, was dissolved in warm water to reach 15% total solid content. The isocyanate crosslinking agent and other chemicals were purchased from domestic chemical suppliers in Bogor and Jakarta. Veneers of meranti (*Shorea sp.*) and albizzia (*Paraserianthes falcataria*) used for the preparation of plywood were obtained from East Kalimantan and West Java, respectively.

Lignin isolation from black liquor. This process aimed to separate the lignin from the black liquor. The black liquor was run through a filter paper to separate the insoluble materials from the liquor. Hydrochloric acid (2N) was then added into the black liquor with continuous stirring until the pH of the black liquor solution reached 2 to precipitate the lignin. The lignin suspension was kept for eight hours to complete the precipitation. The precipitate was then separated by vacuum filtration, washed twice with distilled water, and dried at 45 °C for 24 hours. Some precipitates were washed several times with distilled water until the pH of

the precipitates reached 5. The yield of lignin was determined using the formula shown in Equation 1.

$$\text{Yield of lignin} = \frac{\text{dry weight of isolated lignin}}{\text{dry weight of black liquor}} \times 100\% \quad (1)$$

Lignin content. The lignin content was determined according to NREL LAP 003 [21] for klason lignin or acid insoluble lignin (AIL) and NREL LAP 004 [22] for acid soluble lignin (ASL).

Ash content of lignin. The ash content of the lignin was determined gravimetrically by heating the lignin in a muffle furnace at 800 °C until it reached a constant weight.

Ultimate analysis. The black liquor and the lignin isolates were also analyzed for their ultimate content, including carbon (C), hydrogen (H), nitrogen (N), and sulfur (S), using an ultimate analyzer (CHNSO LECO CHN-2000). The content of oxygen (O) was calculated by subtracting 100 from the total of C, H, N, and S content. The protein content was calculated as $N (\%) \times 6.25$. The average of the double bond equivalent (DBE) was calculated based on the elemental composition, $C_aH_bO_cS_d$, using formula shown in Equation 2 [23].

$$DBE = C - \frac{H}{2} + \frac{N}{2} + 1 \quad (2)$$

Functional group analysis using FT-IR. Five mg of lignin was ground and impregnated in 200 mg of dried potassium bromide (KBr) to make a KBr plate, then analyzed using FT-IR in the range of 4000-400 cm^{-1} .

UV analysis. The UV absorbance property of lignin was analyzed using an UV-Vis Spectrophotometer (Hitachi U-2001) by comparing the absorbance of lignin in a dioxane-water solution and in an alkaline solution. Seven mg of lignin was dissolved in five mL of a dioxane and water mixture (9:1, v/v), and the same amount of lignin was dissolved in NaOH with a pH of 12. Both solutions were diluted with distilled water up to 50 times, and then the absorbance was measured in the wavelength range of 200-400 nm.

Thermal analysis. Thermal analysis was conducted using a Simultaneous Thermal Analyzer (PerkinElmer STA 6000), which can serve as TGA and DSC, so that it can generate both the TGA and DSC curves. Approximately 35 mg of a lignin sample was heated from room temperature up to 800 °C (10 °C/minute) in a nitrogen gas medium. The glass transition temperatures (T_g) were the midpoints of the temperature ranges at which changes in the heat capacity occurred.

Formulation of adhesives. There were several base polymer compositions prepared in the adhesive

formulation as shown in Table 1. The lignin used in the adhesive formulations was lignin isolate pH 2 because the characterization of the lignin showed that there were no significant differences in the chemical and thermal characteristics of lignin isolate pH 2 and lignin isolate pH 5, and the isolation process of lignin pH 2 was simpler than that of lignin pH 5. The base polymers were prepared from a mixture of NRL (solid content 50 and 60%) and lignin solution (25% lignin pH 2 in 5% NH_4OH) and a mixture of NRL, PVA, and a lignin solution (25% lignin pH 2 in 5% NH_4OH). The isocyanate crosslinking agent was added at the level of 15% of the weight of the base polymers.

Preparation and testing of plywood samples. The adhesives were spread on the surface of red meranti (*Shorea sp.*) veneers (250 x 120 x 1.5 mm) as face and back veneers at a glue spread rate of 300 g/m^2 double glue line (DGL). The veneers were put together with albizzia (*Paraserianthe falcataria*) veneer (250 x 120 x 2.1 mm) as the core veneer. The veneers with adhesives were cold pressed at 14 MPa for 24 hours. The plywood samples produced were conditioned at room temperature for about two weeks, then they were measured for their bond strength in dry conditions and after a cyclic boiling test [24], using a Shimadzu Universal Testing Machine. Eight test pieces were prepared for each replication of treatment. Four pieces were used for testing in dry conditions, and the four others were used in the cyclic boiling test. For the cyclic boiling test, the test pieces were immersed in boiling water for four hours

Table 1. Composition of the Base Polymers

Formula	NRL ^a	PVA ^b	Lignin ^c
A1	100	-	0
A2	80	-	20
A3	60	-	40
A4	50	-	50
A5	40	-	60
B1	100	-	0
B2	80	-	20
B3	60	-	40
B4	50	-	50
B5	40	-	60
C1	50	50	0
C2	40	40	20
C3	30	30	40
C4	25	25	50
C5	20	20	60

^a Total solid 50% (Formulas A & C), 60% (Formula B)

^b Total solid 15%

^c Total solid 25% (lignin in 5% NH_4OH)

then were dried at 60 °C for 20 hours. After that, the test pieces were again immersed in boiling water for four hours and then immersed in water at room temperature to cool down. The bond strength measurement test was conducted in wet conditions. Shear strength was determined at the maximum load.

3. Results and Discussion

Lignin yield and chemical compositions. The yield of lignin obtained from the black liquor of OPEFB pretreated with steam explosion in alkaline conditions reached as much as 62.45-65.28%. Analysis of AIL and ASL shows that the isolation of lignin from the black liquor in this experiment was successfully conducted and produced lignin isolates with a total lignin content higher than 95%. This amount is much higher than lignin content in the black liquor (55.33%).

The ash content of the black liquor and the lignin isolated from the black liquor of the alkaline pretreatment of the EFB fiber are shown in Table 2. The table shows that the ash content in the lignin isolates (<1%) is much lower than that of the black liquor (44%). A high ash content in the black liquor was probably due to some inorganic compounds, such as sodium, used in the pretreatment as well as some dirt from the raw material. These compounds, especially the sodium, were removed after the lignin precipitation using hydrochloric acid and followed by the separation of the lignin precipitates from the black liquor solution. The ash content of the two lignin isolates was higher than that of the kraft and soda pulping of the EFB, which was 0.14 and 0.55%, respectively [25].

Ultimate analysis (Table 2) shows that the carbon, hydrogen, oxygen, nitrogen, and sulfur contents of the isolated lignin were higher than those of the black liquor. This was also due to the removal of non-lignin compounds, such as sugar, wax, lipids, and other inorganic compounds, especially sodium, during the isolation of the lignin. Nitrogen was detected either in the black liquor or in the two lignin isolates. Zhao *et al.* [26] suggested that the nitrogen was part of the protein-lignin complex that formed during the delignification process. The percentage of nitrogen in the lignin isolates was higher than that in the black liquor. This supports the above suggestion that the nitrogen was bound tightly to lignin molecules as a protein-lignin complex and cannot be separated during lignin isolation. The sulfur contents in the black liquor and the two lignin isolates were very low ($\leq 0.15\%$) and might result from contamination during collection of the black liquor or during the isolation of lignin.

Based on the results of the ultimate analysis, empirical formulas of lignin can be deduced. The percentage of carbon, hydrogen, and oxygen in the two lignin isolates

Table 2. Ash, Elemental, Protein, and Lignin Content of Black Liquor, Lignin Isolate pH 2, and Lignin Isolate pH 5

Analysis Parameters	Black Liquor	Lignin Isolate pH 2	Lignin Isolate pH 5
Ash Content (%)	40.40	0.99	0.82
Ultimate Analysis (%):			
Carbon	22.76	50.48	50.71
Hydrogen	5.16	6.55	6.59
Oxygen	31.27	41.02	40.98
Nitrogen	0.33	0.81	0.75
Sulfur	0.15	0.08	0.15
Protein (%)	2.06	5.06	4.69
DBE		3.05	3.04
Lignin (%):			
AIL	51.23	93.43	93.67
ASL	4.1	1.81	1.88

led to the empirical formulas of $C_9H_{13.91}O_{5.49}$ and $C_9H_{13.93}O_{5.46}$ for the lignin isolates pH 2 and pH 5, respectively. The DBE, which indicates the degree of lignin condensation and the content of aromatic ring structures in the lignin molecules, could be also determined based on the elemental content of the lignin. The DBEs of the two lignin isolates were almost the same, which means that there was no effect of the lignin precipitate washings on the degree of lignin condensation and aromatic ring structure content of the lignin. The DBEs of the two lignin isolates obtained in this experiment were lower than those of the kraft and soda lignin of the EFB (4.679 and 3.727, respectively) [25] as well as the kraft, soda anthraquinone, and organosolve lignin reported by Mansouri *et al.* [6].

UV spectroscopy analysis. The analysis of UV spectroscopy was conducted in two different solutions, neutral solution (dioxane-water) and alkaline solution (NaOH pH 12), because phenolics tend to ionize in an alkaline solution [23]. Results of the analysis (Figure 1) show that in a neutral medium (dioxane-water) the two lignin isolates had strong absorbance at 240 nm, while the black liquor showed low absorbance. In this medium, lignin isolate pH 2 did not show any absorbance at 280 nm, while lignin isolate pH 5 showed weak absorbance. The UV absorbance intensities of the two lignin isolates were lower than those from kraft and soda pulping of OPEFB [25]. In the alkaline medium (NaOH pH 12), there was a weak UV absorption of the black liquor at 200 nm, strong absorption of the two lignin isolates at 210 nm, and weak UV absorption of the two lignin isolates at 280 nm. The two lignin isolates showed similar UV absorption intensities. These intensities were similar to those of soda lignin of OPEFB but lower than those of kraft lignin of OPEFB [25]. Lignin's UV absorbance correlates with the amount

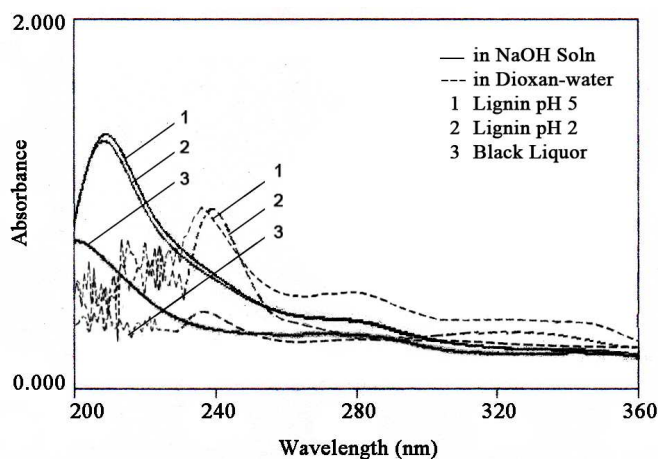


Figure 1. UV Spectra of Black Liquor and Lignin Isolates

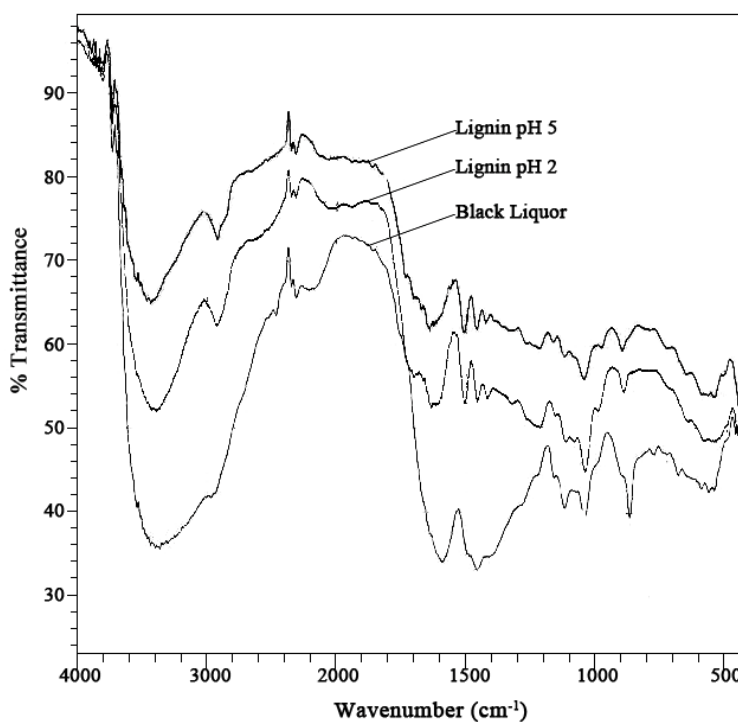


Figure 2. FT-IR Spectra of Black Liquor, Lignin Isolate pH 2, and Lignin Isolate pH 5

of phenolic hydroxyl group in the lignin. The more phenolic hydroxyl group, the higher the UV absorbance intensity.

FT-IR spectroscopy analysis. The FT-IR analysis was conducted to investigate the structural changes taking place before and after lignin isolation from the black liquor. The FT-IR spectra of the black liquor and the two lignin isolates are shown in Figure 2, while their corresponding assignments and bands are presented in Table 3. Figure 2 reveals that the two lignin isolates had similar functional groups, which are different from those in the black liquor. This means that washings of

lignin precipitates with distilled water did not change the lignin structure, while the isolation of lignin from the black liquor changed the structure. There are some other non-lignin components in the black liquor that might be bound to the lignin structure so that some specific functional groups of the lignin could not be observed in the spectra.

In general, lignin was identified by the presence of functional groups at bands $3450\text{--}3400\text{ cm}^{-1}$ for O-H stretching, $2940\text{--}2820\text{ cm}^{-1}$ for C-H stretching (methyl group), $1600\text{--}1505\text{ cm}^{-1}$ for aromatic ring, $1470\text{--}1460\text{ cm}^{-1}$ for C-H deformation (asymmetric in $-\text{CH}_3$ and

–CH₂), 1330-1325 cm⁻¹ for C-O stretching (syringil), ~1220 cm⁻¹ for phenolic OH and ethers in syringil and guaiacyl, 1085-1030 cm⁻¹ for aliphatic OH or ether, and 875-850 cm⁻¹ for C-H out of plane (aromatic). Both lignin isolates showed sorption at the above bands, while the black liquor showed sorption only at bands 3450-3400 cm⁻¹, 2940-2820 cm⁻¹, 1600-1505 cm⁻¹, 1470-1460 cm⁻¹, 1085-1030 cm⁻¹, and 875-850 cm⁻¹. The absence of bands at 1330-1325 cm⁻¹ and ~1220 cm⁻¹ in the black liquor indicated that the syringil and guaiacyl structures were not yet in their perfect forms.

Thermal analysis. Results of the TGA analysis (Fig. 3a) show that the black liquor started to decompose at a

lower temperature (100-200 °C) than did the two lignin isolates (200-400 °C). This was due to non-lignin components, such as extractives or carbohydrates, especially hemicelluloses, contained in the black liquor, which could be degraded at lower temperatures than lignin. Hemicelluloses were degraded at 200-300 °C, while lignin was at 300-450 °C [28]. Further decomposition of the black liquor was observed at 200 °C, which was due to lignin degradation. At 800 °C the percentage of the non-volatile residue of black liquor was higher (46.80%) than that of the lignin isolate pH 2 (36.79%) and the lignin isolate pH 5 (30.25%). This was probably due to the presence of a metal inorganic element, such as sodium, that was used in the

Table 3. FT-IR Absorption Bands and Assignments for Black Liquor, Lignin Isolate pH 2, and Lignin Isolate pH 5

Band Location (cm ⁻¹)				Assignments [23,26]
Black Liquor	Lignin pH 2	Lignin pH 5	Band (cm ⁻¹) [25,27]	
3396	3430	3398	3450-3400	O-H stretching (phenolic OH and aliphatic OH)
2966	2942	2920	2940-2820	C-H stretching (CH ₃ dan CH ₂)
	1703	1703	1715-1710	C=O stretching (unconjugated ketone, carbonyl, and ester groups)
1591	1635	1641	1605-1600	C-C stretching (aromatic ring)
	1508	1506	1515-1505	C-C stretching (aromatic ring)
1454	1460	1458	1470-1460	C-H deformation (asymmetric in –CH ₃ and –CH ₂)
	1421	1425	1430-1425	C-C stretching (aromatic ring) with C-H in-plane deformation
	1327	1328	1330-1325	C-O stretching (syringil)
	1220	1217	1220	C-O(H) + C-O(Ar) (phenolic OH and ether in syringil and guaiacyl)
1120	1118	1118	1115	Ar-CH in-plane deformation (syringil)
1043	1043	1041	1085-1030	C-O(H) and C-O(C) (first order aliphatic OH and ether)
867	894	896	875-850	C-H out of plane (aromatic ring)

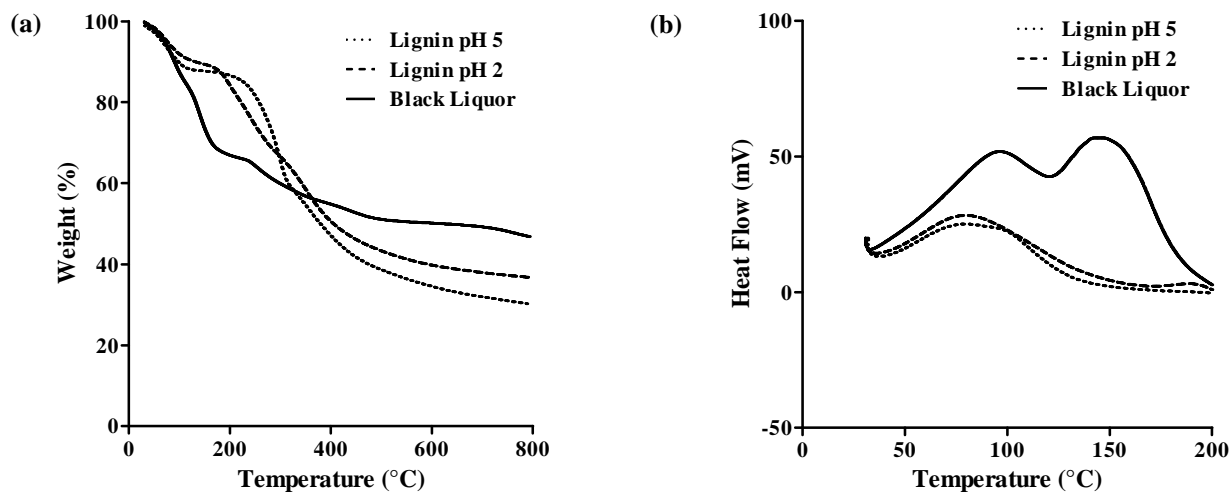


Figure 3. TGA (a) and DSC (b) Curves of Black Liquor, Lignin Isolate pH 2, and Lignin Isolate pH 5

pretreatment process in the black liquor. There was only small amount of sodium contained in the two lignin isolates, since most of the sodium was removed during the lignin isolation. The results of the TGA analysis also show that the lignin in the isolate pH 2 decomposed very quickly at temperatures between 200 and 400 °C, while the isolate pH 5 decomposed between 250 and 400 °C. Lignin isolate pH 5 was obtained by washing lignin isolate pH 2 several times in distilled water. This process might remove some organic and inorganic non-lignin materials, so the isolate pH 5 started to decompose at higher temperature due to the lower amount of organic non-lignin materials and ended with a lower percentage of non-volatile residue due to the lower amount of inorganic non-lignin materials, such as chlorine. The temperature ranges of the maximum rate of weight loss in this study were wider than those of soda, kraft, or ash-AQ lignin of OPEFB, which decomposed at temperatures between 300 and 400 °C [28,29]. This difference was probably due to differences in the degree of branching and condensation of the lignins as well as the molecular weights of the lignins.

The results of the DSC analysis showed that the glass transition temperatures (T_g) of the black liquor, lignin isolate pH 2, and lignin isolate pH 5 were 96.04, 79.94, and 79.16 °C, respectively. The T_g s of both the lignin isolates obtained in this experiment were slightly higher than those of the kraft or soda lignins of OPEFB, which were 67.47 and 71.64 °C, respectively [25], but much lower than those obtained from different raw materials

and processes, which can reach as high as 150-165 °C [29].

Bond strengths of adhesives. Bond strengths of adhesive used to prepare plywood samples were determined by measuring shear strength of the plywood specimens. Shear strength of the plywood samples adhered with adhesives produced in this experiment is shown in Table 4. The minimum shear strength required for plywood is 0.7 N/mm². Results of the dry test, which resembled interior applications, showed that all adhesive formulas used in plywood preparations could meet the standard for interior applications, except formula B5 (NRL 60% : Lignin = 40:60). The use of NRL with 50% total solid content in adhesive formulation gave a relatively higher bond strength than that of NRL with 60% total solid content, which might be due to the greater ease of spreading the glue in the former. It is interesting to note that the use of lignin in the base polymer formulation of API adhesives, for example in formula A4, resulted in a similar bonding performance as when PVA was used in the formulation (formula C1). This suggests that lignin can be used in the formulation of the base polymer of API adhesive, replacing PVA, for interior applications. Results of the cyclic boiling test, which resembled exterior applications, showed that several adhesive formulas could meet the standards for exterior applications, namely formulas B1, C1, and C2. The test also showed that lignin can be used as a base polymer in the API adhesive formulation at the level of 20% or less of the total weight of base

Table 4. Shear Strength of Plywood After the Dry and Cyclic Boiling Tests

Formula	NRL ^a	PVA ^b	Lignin ^c	Shear Strength (N/mm ²)	
				Dry Test	Cyclic Boiling Test
A1	100	-	0	1.52 ± 0.05	0.59 ± 0.06
A2	80	-	20	1.57 ± 0.22	0.45 ± 0.05
A3	60	-	40	2.07 ± 0.24	0.67 ± 0.29
A4	50	-	50	2.17 ± 0.35	0.44 ± 0.21
A5	40	-	60	1.54 ± 0.27	0.28 ± 0.08
B1	100	-	0	1.48 ± 0.03	0.70 ± 0.01
B2	80	-	20	1.28 ± 0.05	0.41 ± 0.04
B3	60	-	40	1.65 ± 0.12	0.56 ± 0.04
B4	50	-	50	0.93 ± 0.12	0.32 ± 0.14
B5	40	-	60	0.59 ± 0.15	0.20 ± 0.04
C1	50	50	0	2.24 ± 0.27	0.93 ± 0.14
C2	40	40	20	1.77 ± 0.08	0.80 ± 0.06
C3	30	30	40	1.30 ± 0.43	0.65 ± 0.05
C4	25	25	50	1.06 ± 0.14	0.56 ± 0.08
C5	20	20	60	1.19 ± 0.28	0.31 ± 0.04

^a Total solid content 50% (Formulas A & C), 60% (Formula B)

^b Total solid content 15%

^c Total solid content 25% (Lignin in 5% NH₄OH)

polymers that were composed of NRL/PVA/lignin (4/4/2). The addition of more lignin to the base polymer mixtures tended to decrease the bond strength of the adhesives. Bearing some hydroxyl groups in its structure, lignin was expected to be a substitute for the hydroxyl group provided by PVA, which would crosslink with the isocyanate. The crosslinking was performed as was expected in dry conditions but not after it was exposed to high temperatures and wet conditions, such in the cyclic boiling test. The T_g of the lignin isolate (79.94°C) was not very different than that of PVA (75-85 °C). Thus, the thermal properties of lignin were probably not the cause of the decreasing bonding performance. There might be some other factors, such as differences in the number of hydroxyl groups and the hydroxyl groups' configuration (aromatic and aliphatic) present in lignin and PVA, that caused the decrease in bonding performance of lignin substituted for the API adhesive after the cyclic boiling test. Therefore, it is important to conduct more comprehensive studies of the correlation between the chemical characteristics of lignin, especially the hydroxyl groups' configuration in lignin molecules and the crosslinking reaction formed in API adhesive.

4. Conclusions

Lignin isolated from steam explosion alkaline pretreatment of OPEFB has similar properties as that isolated through kraft and soda pulping of OPEFB. The lignin isolates from OPEFB with different pH values did not have significantly different chemical and thermal properties. Both lignin isolates had similar C, H, and O contents; identical functional groups in the FT-IR spectra; similar absorption in the UV spectra; and high decomposition temperatures. Lignin can be used as a component of base polymers for API adhesive. The base polymers composition that could produce an API adhesive for exterior applications is NRL/PVA/lignin (4/4/2). The use of more lignin in the adhesive formulation decreased the bond strength of the plywood. Further studies are needed in order to better understand the bonding mechanism between the base polymers used and the isocyanate crosslinker.

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