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Utilizing Lignin from Malaysian Bamboo (*Semantan*) as Partial Replacement of Phenol in Phenol Formaldehyde (PF) Adhesives: Physico-Mechanical Characteristic of Sustainable and Environmental-Friendly Adhesives

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This work focused on utilization of lignin from Malaysian bamboo species locally known as Semantan (*Gigantochloa scortechinii*) extracted via soda pulping method as partial replacement for phenol during the synthesis of phenol formaldehyde (PF) adhesives. Chemical characterization using spectroscopic method and analysis of thermal properties was carried out. Physico-mechanical characteristic of adhesives (pH, density, solid content), gelation time, dynamic viscosity and lap shear strength of adhesives were also studied. Scanning electron microscopy (SEM) was used to observed the morphology of the cured adhesives. Thermal study showed that addition of lignin during the adhesives synthesis led to reduction of thermal resistance and lowering the carbon residue at elevated temperature. Spectroscopic analysis indicated high degree of similarity in terms of chemical nature for both PF (control) and lignin phenol formaldehyde (LPF). Mechanical characterization performed based on dry lap shear strength indicated that LPF yield satisfactory results, a good indication that synthesis of adhesives with lignin with bamboo lignin as partial replacement for phenol is possible and can provide more economical and sustainable alternative to phenol derived from petrochemicals.

Keywords: Malaysian bamboo, lignin, phenol formaldehyde, *Gigantochloa scortechinii*, sustainable adhesives

I. INTRODUCTION

Decreasing supply of some fossil fuel fractions and increasing awareness of human impact on the environments have led to strong interest in the consumption of sustainable resources. To be able to maintain a high standard of living in ever increasing population and decreasing resources availability, today's society must be prepared to an economy based on sustainability in terms of energy, raw materials and processes. Currently, attention is focused on biomass specifically on lignocellulosic material as renewable source of

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*Corresponding author's e-mail: syaifulosman84@gmail.com chemicals. The major components of lignocellulosic materials are carbohydrate polymers (cellulose and hemicelluloses) and aromatic polymers (lignin and tannin).

Formulation of adhesive is highly dependent on chemicals derived from petroleum. Adhesives are crucial in wood processing industries such as plywood, fiber-board and particleboard. As the petroleum-based is getting scarce, this could negatively affect the production of the commonly used adhesives. Commonly used adhesives in wood industry include phenol formaldehyde (PF), urea formaldehyde (UF) and melamine urea formaldehyde (MUF). Phenol formaldehyde (PF) is more favorable as results of its water and weather resistivity that make it suitable for exterior applications. PF in particular is more widely used in industry due to its resistance to weather and humidity. As fossil fuel continues to be depleted and the price expected to soar again soon, cost of petrochemicals derived from fossil fuels will also increase. High price of phenol may inhibit the use of PF for broader applications. To date, several studies focused on replacing phenol by lignin from various sources (Jin et al. 2010; Zhang, Ma, Xu, et al. 2013; Zhang, Ma, Wang, et al. 2013; Stücker et al. 2016; Khan & Ashraf 2006) had been carried out and available in the literature. Figure 1 presents three main types of lignin.

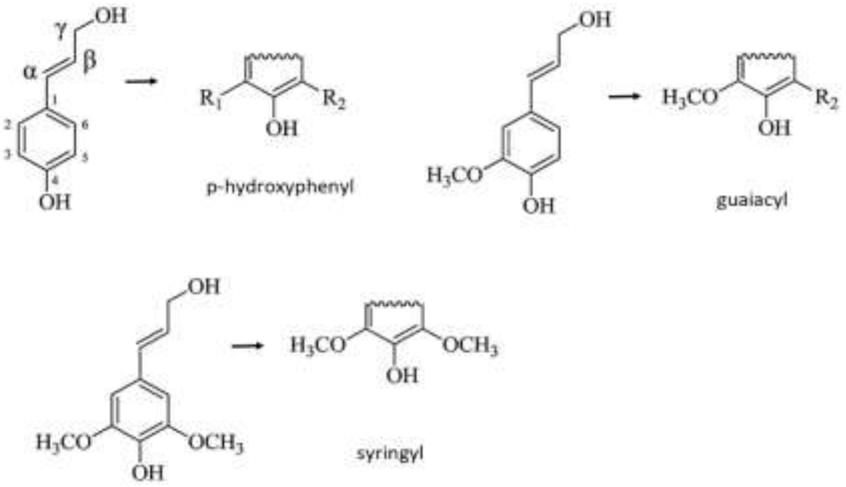

Figure 1. Lignin precursors and its corresponding structures in lignin polymers

In this study, lignin from *G. scortechinii* locally known as *Semantan* bamboo extracted via soda pulping method was used as partial replacement of phenol during the synthesis of adhesives. The properties of PF (control) and lignin phenol formaldehyde (LPF) will be measured and compared. Among the properties of adhesives studied were pH value, solid content, dynamic viscosity, thermal properties and spectroscopic analysis of adhesives. Mechanical strength of adhesives was also analyzed using lap shear strength tensile analysis.

II. MATERIALS AND METHODS

Bamboo species aged 3 were used. Outer skins were removed from the bamboo strips and bamboo strips were cut to smaller pieces prior to grinding process using Wiley grinder. Method of lignin isolation was performed according to steps illustrates in Figure 2.

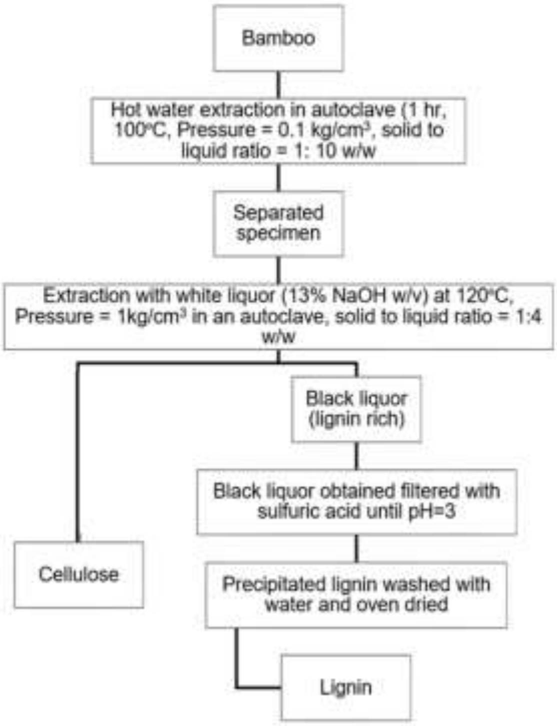

Figure 2. Methods of lignin extraction from bamboo

A. Synthesis of Adhesives

Phenol and formaldehyde were reacted in the ratio of F/P equivalent to 1.8. 40 gram of phenol, 12 g of 50% NaOH solution, 40 g of water were heated in three neck flask and heated to 84^{0}C while stirring with magnetic stirrer. 62.1 gram of formaldehyde (37%) were slowly added drop wisely into the reactor. The reaction was allowed to continue for 180 minutes at the temperature of 84^{0}C. After that the three-neck flask is quenched in cool water bath to stop the reaction. PF thermosetting resin was obtained. LPF was synthesized in the laboratory by varying ratio of lignin to phenol to 20%. Table 1 shows the analysis carried out in this paper. Viscosity of adhesive was measured from day one after synthesis up to 30 days. Determination of solid content was carried out by drying the adhesive specimen at 105°C for three hours. The sample was then cooled and reweighed.

Table 1. Analysis and related instruments carried out in this paper

Analysis	***Instruments***
pH	Mettler Toledo SevenEasy
Dynamic viscosity	Brookfield DV-I + Viscometer
Spectroscopic analysis	FT-IR NICOLET 6700
Thermal Gravimetric	PerkinElmer DSC 8000
Differential Scanning Calorimetry	Perkin Elmer DSC 7
Scanning Electron Microscopy	Hitachi 3400. Specimens spur coated with gold prior to analysis
Dry lap shear strength	Universal Testing Machine (UTM) Instron 5582

B. Preparation of Adhesive Lap Shear Specimens

Adhesive shear samples were prepared from two ply wood veneers. Adhesive spread was equivalent to $500g/m^2$. Veneer applied with glue the hot pressed at temperature of 160^{0}C for 6 minutes with uniform pressure. Then bonded veneers specimens are machined to produce specimens. The crosshead speed was equivalent to 1 mm/min. The analysis was carried out based on British Standard (BS) Standard 1204 for synthetic resins (Moubarik *et al.,* 2009).

III. RESULTS AND DISCUSSIONS

A. pH and Solid Content Analysis of PF and LPF

Table 2 shows the pH value and solid content of PF and LPF. For PF, the pH and solid content value was equivalent to 10.6 and 43.9% respectively whereas for LPF was equivalent to 10.9 and 39.6% respectively. pH is an important property as inappropriate pH can affect the viscosity, shelf and working life and curing properties of the adhesives. On the other hand, solid content is an important parameter since it can influence the behavior of adhesives during the applications and the performance of the bonded assembly.

Table.2. pH value and solid content result of PF and LPF

Sample	pH	Solid content
PF	10.6 (0.05)	43.9 (1.32)
LPF	10.9 (0.02)	39.6 (0.37)

Values in parentheses indicated standard deviation

B. Dynamic Viscosity Determination of Adhesives

Table 3 and Figure 3 shows the dynamic viscosity result of PF and LPF recorded from day one after synthesis up to 30 days. However, for LPF the measurement was halted after 24 days as the adhesives becomes too viscous and no longer measurable. Analysis indicated that the addition of lignin for phenol replacement within the adhesive system caused the viscosity to accelerate faster over time compared to pure PF (control). From the industry point of view, this might be unfavorable as high viscosity gain within the short period will results in shorter storage time before the adhesive becomes no longer workable.

Table 3. Viscosity (cP) evolution of PF (control) and LPF for 30 days at 10 days interval

Sample	Initial viscosity	10 days	20 days	30 days
PF	2.7	2.7	6.2	9.6
LPF	16.3	85.6	270.0	1432.0 (24 days)

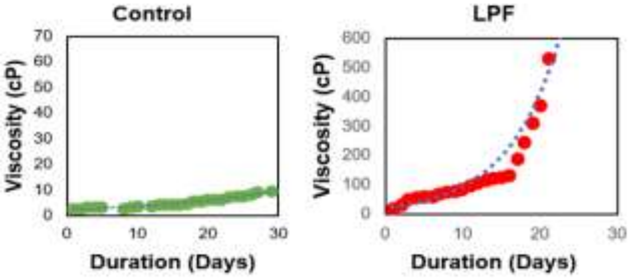

Figure 3. Graphical representation of dynamic viscosity of PF and LPF recorded within 30 days

C. Adhesive Gelation Time Analysis

Time required for adhesive to change from liquid to highly viscous gel that is no longer workable is known as gelation time. Figure 4 shows the gelation time for PF (control) and LPF. For pure PF used as control, the average gelation time was equivalent to 1715 seconds.

The gelation time for LPF decreased more than half to only 497 seconds, indicating rapid gelation time as a result of additional lignin into the adhesive system. Faster crosslinking rate due to higher level interaction between lignin and phenol to form LPF condensates is the main factor that contributes to faster rate of gelation time compared to PF.

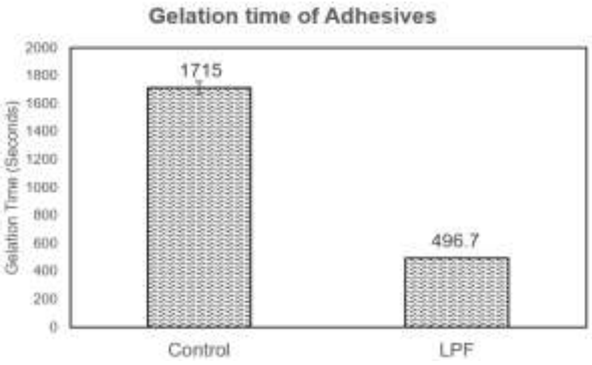

Figure 4. Gelation time of adhesives (seconds)

D. ATR-FTIR Analysis of Adhesives

Figure 5 shows the FTIR spectra of pure PF (control) LPF within the fingerprint region. From the results of ATR-FTIR spectra, it is obvious that functional groups that exists in PF and LPF are almost identical, indicating a high degree of resemblance in terms of chemical nature of two adhesives. At around 3300 cm^{-1}, the absorption band can be attributed to the existence of OH functional groups. Absorption at around 1638 cm^{-1} to 1500 cm^{-1} can be attributed to stretching vibrations of aromatic compound can be seen for both PF and LPF.

Absorption at around 1463-1472 cm^{-1} can be attributed to CH deformation mode in (CH_2) group.Khan & Ashraf (2006), mentioned that the appearance of this band in LPF indicated the presence of -CH_2 bridge within the system as presented in Figure 6. At around 1235 cm^{-1}, the absorption band can be attributed to C-O vibration from aromatic groups. Low intensity absorption band at around 1130 cm^{-1} can be attributed to the stretching vibration of ether linkages. Additionally, the peaks around 1013-1019 cm^{-1} attributed to the presence of C-O stretching vibration of aliphatic C-O (Ar) and methylol C-OH (Moubarik et al. 2013). Absorption band and its assignments in LPF are summarized in Table 4.

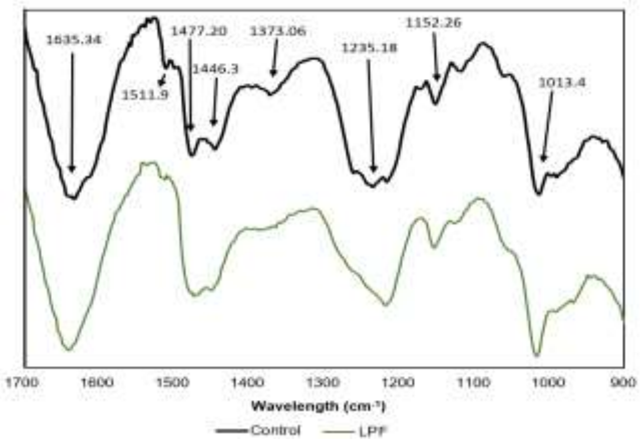

Figure 5. ATR-FTIR spectrum of pure PF (Control) and LPF within the fingerprint region

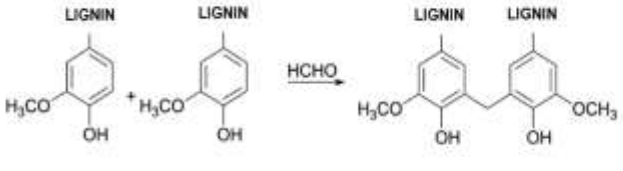

Figure 6. Crosslinking between lignin and formaldehyde

Table 4. Absorption band in LPF and its band assignments (Khan & Ashraf 2006; Moubarik et al. 2009; Hussin et al. 2017; Lee et al. 2015)

Wavelength (cm^{-1})	Assignments
3400-3300	OH stretching vibrations
2923	CH_2 asymmetric stretching peak
2842	CH_2 symmetric vibrations
1638 and 1500	C=C stretching vibration in benzene ring
1463-1472	CH deformation mode in CH_2 group (indicated -CH_2 bridge in the system)
1208-1235	C-O vibration from aromatic group for PF C-O stretching vibration in syringyl phenolic group for LPF
1130	Stretching vibration of ether linkages
1050	C-O stretching vibration of aliphatic C-OH
1013	Methylol group and presence of C-O stretching vibration of aliphatic C-OH and aliphatic C-O

E. Thermal Gravimetric Analysis

TGA curve reflected the weight loss of material associated to the temperature degradation whereas DTG curves shows the corresponding weight loss. In this study, TGA analysis was performed from room temperature up to 800°C in nitrogen gas filled environment. The result indicated that the remaining solid mass for both PF and LPF was equivalent to 73.4°C and 51.6°C respectively. Two distinct thermal event can be observed for PF, at around 203°C and 535°C. However, for LPF, decomposition behavior becomes more complex as a result of additional lignin within the adhesive system. TGA analysis also indicated that additional lignin lowered the thermal resistance and reduced the amount of carbon residue at elevated temperature. Table 5 compares the weight of charred residue of specimens (PF and LPF) at specific temperature.

Table 5. Weight of adhesive (%) charred residue at specific temperature

Samples	Temperature		
	450°C	600°C	800°C
PF (%)	93.7	80.1	73.4
LPF (%)	70.4	55.0	51.6

F. Differential Scanning Calorimetry (DSC) Analysis

Table 6. Onset temperature, peak temperature and curing rate of adhesives

Sample	Onset temperature (T_o) °C	Peak temperature (T_p) °C	$\Delta T = T_p - T_o$
PF	100.9	117.5	16.6
LPF	105.9	122.3	16.4

DSC analysis was carried out by heating the adhesive specimen from room temperature up to 250°C at heating rate of 10°C/min. Nitrogen gas was utilized at the flow rate of 20.0ml/min. For PF, onset temperature (T_o) was equivalent to 100.9°C, peak temperature (T_p) equivalent to 117.5°C and endset temperature was equivalent to 120.3°C whereas for LPF, the value was equivalent to 105.9°C, 122.3°C and 135.2°C respectively for T_o, T_p and endset temperature.

In this study, it was found that partial replacement of phenol using bamboo lignin increased the curing temperature of the adhesive system. This is the result of increasing complexity of LPF compared to the molecular structure of PF. ΔT (T_p-T_o) or rate of curing for PF and LPF was equivalent to 16.6°C and 16.41°C respectively as shown in Table 6. Lower value of ΔT indicated higher rate of curing (Khan & Ashraf 2006) and this study revealed that ΔT of LPF is slightly lower than PF, similar to the trend observed by previous authors on lignin modified adhesives from various sources (Khan & Ashraf 2006; Ghorbani *et al.,* 2012; Abdelwahab & Nassar 2011). The finding correlates to the gelation time measurement, where lignin modified adhesives indicated faster gelation time compared to unmodified adhesives.

G. Morphology Analysis of Adhesives

Adhesive with favorable characteristics can be achieved by having good dispersion of lignin within the adhesive system. Morphology analysis of cured adhesives was carried out using Scanning Electron Microscopy (SEM) analysis (Figure 7). From the analysis, it can be observed that cured PF has more smooth and uniform surface as a result of high reactivity between phenol and formaldehyde. On the other hand, cured LPF also shows similar surface microstructure to cured PF without existence of rough surface that may negatively affect the bonding strength of LPF. This also indicates a good reactivity between Semantan lignin and formaldehyde at 20% lignin substitution.

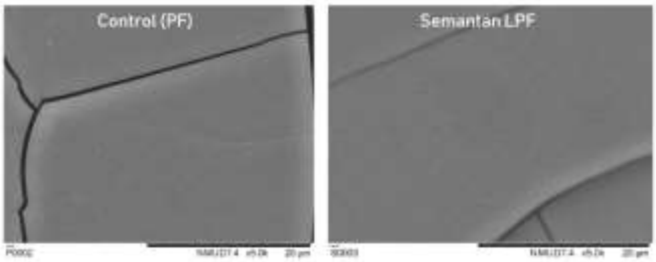

Figure 7. SEM images of PF and LPF (5K magnification)

H. Dry Lap Shear Strength of Adhesives

Mechanical strength of adhesives was characterized by lap shear method using Universal Testing Machine. Figure 8shows the average adhesive lap shear tensile strength for both PF and LPF. For PF, the average value was equivalent to 4.54 MPa whereas for LPF, the dry lap shear strength was slightly lower than PF at average value equivalent to 3.18 MPa and this gives us indication that partial replacement of phenol with lignin slightly reduce. Nevertheless, the lap shear strength of adhesive with partial lignin replacement of phenol at 20% has acceptable lap shear strength, surpassing the minimum dry strength requirement of relevant national standard (Jin *et al.,* 2010).

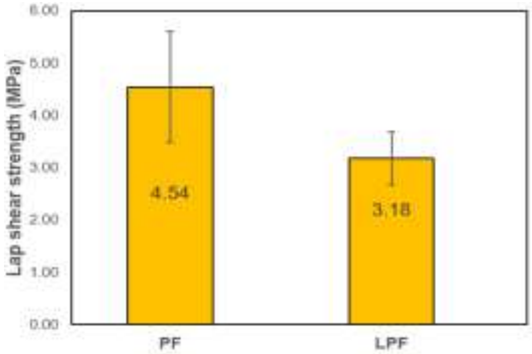

Figure 8. Dry lap shear strength of PF and LPF

IV. SUMMARY

In this study, partial replacement of phenol by bamboo lignin at 20% during the adhesive synthesis was carried out. From the study, it can be concluded that:

1. Both PF and LPF has high degree of similarity in terms of functional group that exist as indicated by the ATR-FTIR analysis.
2. Additional lignin within the adhesive system causes the viscosity to increase faster over time. LPF has shorter gelation time compared to PF that is due to faster crosslinking rate resulting from high level interaction between lignin and phenol to form LPF condensates.
3. Thermal analysis indicated that additional lignin lowered thermal resistance of adhesive and reduced the amount of carbon residue at elevated temperature.
4. Dry lap shear strength of LPF is slightly lower than PF, equivalent to 3.18 MPa compared to 4.54 MPa respectively.

V. ACKNOWLEDGMENT

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