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Synthesis of lignin-based phenol-formaldehyde adhesive - A sustainable alternative to petrochemical

Nguyen Thi Nhu Y[1], Nguyen Thi Yen Nhi[1], Tran Thi Minh Thu[1], Nguyen Thi Ven[2], Tran Nguyen Phuong Lan[2] and Luong Huynh Vu Thanh[2*]

[1]*Can Tho University of Technology, Viet Nam*

[2]*Can Tho University, Viet Nam*

*Correspondence: Luong Huynh Vu Thanh (email: lhvthanh@ctu.edu.vn)

ABSTRACT

This study is to investigate the capability of producing lignin-based phenol-formaldehyde adhesive (LBPFA) with lignin derived from coir pith collected in the Mekong Delta, Viet Nam. The LBPFA synthetic process underwent non chemical modifications to minimize petrochemicals and energy. Effective factors as reaction time, reaction temperature and various lignin contents of phenol substitution were examined. Physical, chemical and thermal properties containing formaldehyde content, viscosity, solid content, Fourier transformed infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), tensile strength, tensile modulus and tensile strain were conducted. LBPFA was successfully synthesized at various levels of lignin contents substituting for phenol. The LBPFA's parameters were in accordance with GB/T14372-2006 standard. The optimum reaction time, reaction temperature and lignin replacement content for LBPFA synthesis process were identified at 180 minutes, 90°C and 40% wt/wt, respectively. The LBPFA showed the highest dry and wet tensile strengths of 14.42 MPa and 7.66 MPa on wooden boards compared to corresponding figures of commercial resin with 2.98 MPa and 0 MPa, respectively. For plywood, bending strength shown in LBPFA and commercial adhesive were 15.97 MPa and 20.16 MPa, respectively.

1. INTRODUCTION

Coir pith is a common agricultural by-product in Mekong Delta especially in Ben Tre province. Due to low value, coir pith was not utilized completely, which resulted in polluted air and water environment at coconut fiber processing areas (Luong et al., 2017; Nguyen et al., 2018). Lignin is one of the main components of plants, acting as a natural adhesive polymer in plant cell walls, increasing mechanical strength and waterproofing. Lignin is a heterogeneous polymer containing several function groups: hydroxyl, phenolic and

ester groups. Its physical and chemical properties are highly dependent on biomass sources, locations and extraction methods (Mansori et al., 2006; Duval et al., 2014).

Poly (phenol-formaldehyde) resins are being used in about one-tenth of all plywood and particle board industries. The outstanding performance of phenolic resins are high strength, long-term mechanical and thermal stability, low toxicity, low formaldehyde content, high water resistance, low phenolic swelling, excellent electrical and thermal insulation. The drawback of these resin is that it is toxic due to

using phenol, ingredients depending on petrochemical resources, high manufacturing cost, hardening more slowly than the amino plastic (Wang et al., 2009; Zakaria et al., 2015).

Fluctuations in oil price caused by over-explored natural resources and concerns about chronic exposure to phenol of workers during the manufacturing process have been the main reasons boosting many researchers studying on replacing phenol by biomass during the last three decades (Mainka et al., 2015). Many studies showed that lignin formula has capability to replace phenol in producing Phenol-Formaldehyde Resin (Cetin et al., 2003; Tejado et al., 2007; Hemmila et al., 2013; Norgren et al., 2013; Yang et al., 2015). This method is not only reducing toxicity but also decreasing manufacturing cost and environmental pollution (Derek, 2008). Lignin was used to replace phenol in manufacturing phenol formaldehyde adhesive in many researches: lignin could be used as an alternative (10-100%) in the production of phenol-formaldehyde or epoxy resins (Tejado et al., 2007). In detail, phenol formaldehyde adhesive was synthesized from organosolv pine lignin (Wang et al., 2009), biorefinery technical lignin (Liitia et al., 2014). These processes successfully synthesized phenolic colloids by substituting 5-50% lignin with different sources for phenol. However, designed processes were divided into several stages which were time-consuming, used ure as a stabilizer and the quality of adhesive and its durability have not been assessed yet (Mainka et al., 2015).

Lignin is accounted for 28.58% (wt/wt) coir pith with soda extracting method. Coir pith lignin has molecular mass of 27.6 kDa which is much greater than that figure of lignin from hardwood, softwood and grass, so the content of phenolic hydroxyl group in coir pith lignin is also greater. This proves coir pith lignin having potential applications in chemical synthesis and producing phenolic resins (Nguyen et al., 2017).

2. MATERIALS AND METHODS

2.1. Materials

Alkali lignin particles with size range of some tens to hundreds micrometer and average molecular weight of 27.6 kDa were extracted and purified from coir pith in Mekong Delta, Viet Nam according to a previously reported method (Nguyen et al., 2018). Other chemicals: NaOH (96%), H_2SO_4 (95-98%), HCl (36-38%), HCHO (37-40%), C_6H_5OH and $NH_2OH.HCl$ (98.5%) purchased from Xilong

Scientific, China and distilled water obtained from Chemical engineering laboratory were used.

2.2. Preparation of lignin-based phenol-formaldehyde adhesive (LBPFA) solutions

The general process of producing LBPFA and identifying its characterizations were briefly shown in Fig. 1. The extracted lignin was used to replace phenolic group in synthesis of LBPFA. In Fig.2, the procedure of LBPFA synthesis was presented in detail. Firstly, LBPFA was prepared by replacing phenolic ingredient with different amounts of lignin (10, 20, 30, 40, 50 % wt/wt). The weight ratios of formaldehyde to phenol (including both phenol and lignin) and of phenol to NaOH were constantly kept at 4:3 (wt/wt) (equaling to 1.53:1.0 in molar ratio) and 10:3 (wt/wt), respectively, for all trials. Then, lignin was dissolved in NaOH 1M solution inside a three-necked flask, temperature was gradually increased to 70^0C with continuous stirring using plastic coated magnets so that lignin could be completely dissolved. Adding adequate volume of formaldehyde (37%), adjusting pH in the range of 10-12 by NaOH 0.5M were the following steps. Increasing temperature to T^0C during t time (minutes) (T and t are the surveyed parameters – Table 1) was next controlled. After that, the system was cool to room temperature and the final product was collected.
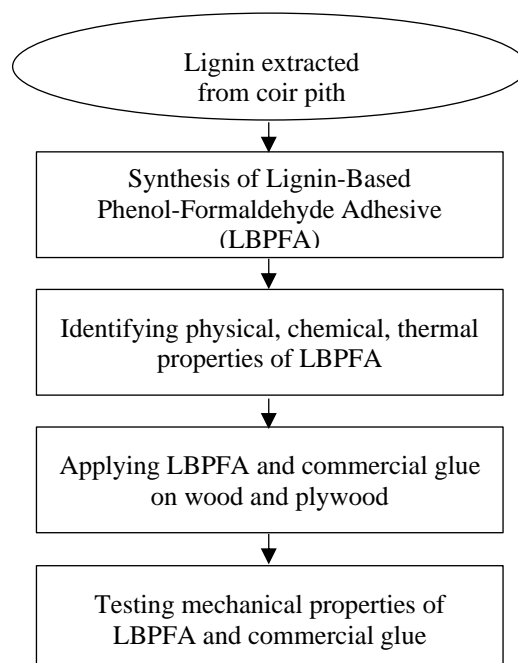
Lignin extracted
from coir pith

↓

Synthesis of Lignin-Based
Phenol-Formaldehyde Adhesive
(LBPFA)

↓

Identifying physical, chemical, thermal
properties of LBPFA

↓

Applying LBPFA and commercial glue
on wood and plywood

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Testing mechanical properties of
LBPFA and commercial glue

Fig. 1. Process of producing and identifying LBPFA's characterizations
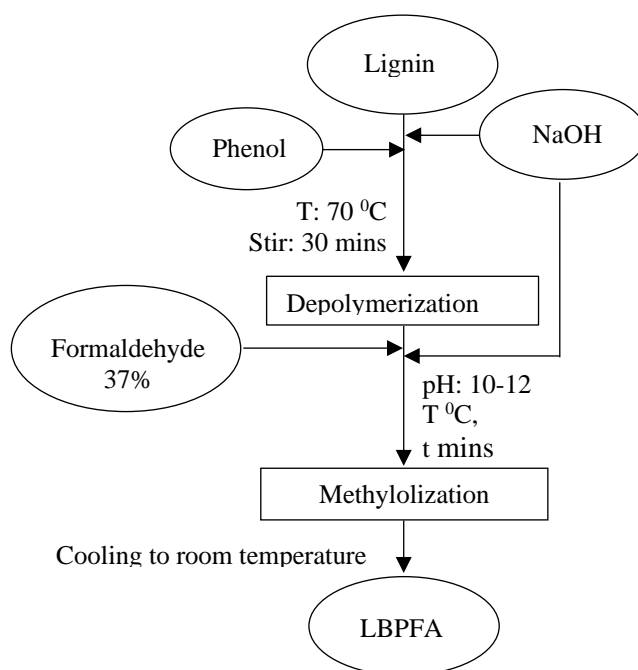
Fig. 2. Synthesis of lignin-based phenol-formaldehyde adhesive process

Table 1. Examined parameters: replacing lignin content on phenol (% wt/wt), time and temperature reactions

% Lignin	Time (minutes)	Temperature (^{0}C)
0	60	80
20	90	90
30	120	100
40	150	
50	180	

2.3. Determination of LBPFA's characterizations

2.3.1. Formaldehyde content

Titration method was applied based on the reaction of formaldehyde with hydroxylamine hydrochloride NH$_2$OH.HCl to form HCl according to ISO 9397: 1997 standard.

2.3.2. Viscosity

The viscosity was measured by the handheld viscometer TMVM 1, SKF at Biotechnology Research and Development Institute, Can Tho University.

2.3.3. Thermal properties

Thermal stability of coir pith lignin-based adhesive was tested by DSC differential heat measurement method with NETZSCH TG209 F3 at College of Engineering Technology, Can Tho University. The

heating rate was 10°C.minute^{-1} from room temperature to 200°C in a nitrogen atmosphere with a flow rate of 10 mL.minute^{-1}. Samples were dried at 50°C for 24 hours and stored in desiccator before conducting the analysis.

2.3.4. FT-IR analysis of LBPFA

The specific bondings of synthetic LBPFA were analyzed by Nicolet 6700 FT-IR Thermo Scientific at the number of waves from 4000 to 500 cm^{-1} at College of Natural Sciences, Can Tho University.

2.3.5. Solid content

Solid content was determined by drying samples at 105°C for 4 hours in Memmert UF260.

2.3.1. Mechanical properties

The Panstone P-100 PCD hot press was used to press samples, the machine has 2 components: the hydraulic unit for adjusting pressure and the resistance for regulating the heat.

Mechanical measurements including tensile strength, tensile modulus, tensile strain and bending strength of the samples were tested by Zwick/Roell BDO-FB050TN.

2.4. Preparation of lap shear samples

Tests were carried out for each type of natural timber and artificial plywood with both coir pith lignin- based phenol-formaldehyde adhesive

(LBPFA) and a popular commercial adhesive (X'traseal x'bond construction adhesive). Each adhesive was applied on 5 samples in correspondence with one type of wood Melaleuca timber and artificial plywood which were purchased at A Dat carpenter workshop at Can Tho city for all tests. Samples' surface and moisture were firstly pretreated to improve the adhering process. Next, preparation of 0.15 g of each adhesive formulation was applied on the area of 25 mm x 25 mm at the end section of melaleuca timber and plywood samples (100 mm x 25mm x 7mm). Then, two pieces of wood were stuck by hand and put them into the hot-pressing machine (Panstone P-100 PCD) with pressing temperature, the time and the pressure at 100 ^{0}C, 3 minutes and 1 MPa, respectively. Finally, the samples were taken out and stored at room temperature for 3 days to stabilize before conducting mechanical tests.
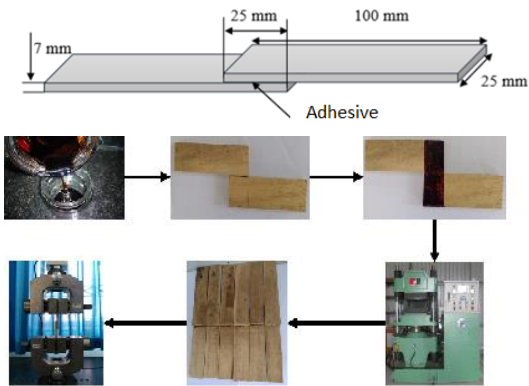

Fig. 3. Illustration of the lap shear strength specimen

2.5. Determination of mechanical properties

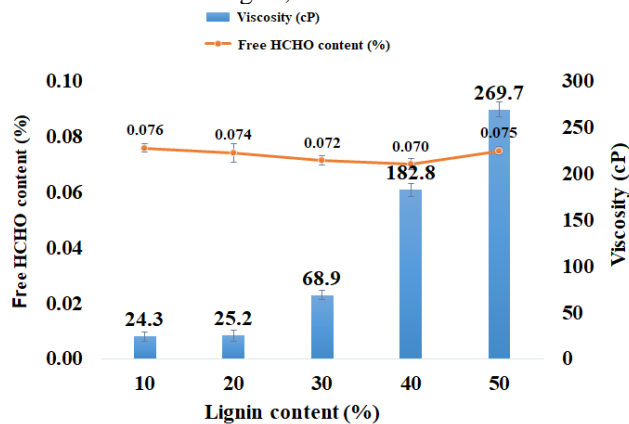The ASTM D5868-01 and ASTM D3434 standards were applied for dry and wet tensile strengths, respectively. Generally, the samples were submerged in boiling water in 4 hours, then were dried at 65±3ºC for 20 hours. After that these samples were submerged again in hot water for the next 4 hours before mechanical properties were checked. In the case of plywood, bending strength was mostly conducted by TCVN 7756-6:2007 standard.

3. RESULTS AND DISCUSSION

3.1. Effect of substituted lignin content on viscosity and free formaldehyde content

the lignin content of 10 and 20%, hovering at 25 cP and rapidly increased at those of 30, 40 and 50% at 68.9, 182.8 and 239.7 cP, respectively. These viscosities changed at the same conditions (time, temperature, and catalyst) indicated the ability to create resin differently. This can explain that the reactions are more effective when the amount of appropriate catalyst is sufficient to dissolve lignin and PF in certain synthesis environment.

The impact of free formaldehyde content versus lignin content was also illustrated. The lowest free formaldehyde content got the minimum at 40% replacing lignin. This could explain the catalyst amount was insufficient at the higher replacing level (50%). Combination of the capability of forming resin and the free formaldehyde content in Fig. 4, 40% lignin was selected as an optimal condition for following surveys. However, the goal of study is examination to replace phenol by lignin as much as possible and resin performance applied on wood board. Therefore, chosen values that meet the standard GB /T 14732-2006 for the next surveys were 30 - 50% lignin.

Fig. 4. Effect of lignin content to viscosity and free HCHO content

Effect of the lignin content is shown in Fig. 4. The viscosities of solutions increased proportionally according to the growth of lignin content on phenol. In fact, the viscosities changed almost negligibly at

3.2. Effect of temperature on adhesive forming capability

Temperature had a great influence on the reaction rate. Fig.5 showed that when temperature was 80^0C the solution presented a low viscosity of 31 cP and high free formaldehyde content. However, the viscosity increased slightly to 69 cP and rapidly to 198 cP as the temperature of reaction was 90^0C and 100^0C, respectively. In the meantime, free formaldehyde contents at these two temperatures

was mostly the same, 0.072% and 0.068%, respectively. It is known that low or high viscosity can be a drawback to perform the adhesive to wood boards. Besides, low free formaldehyde represented for high replacement of phenolic groups to the structure of the resin. However, the adhesive was partly solidified after these exothermic reactions ended at the reaction temperature of 100 ^0C. This could be explained by appearance of overheating or adhesive temperature reaching the glass transition temperature of lignin (Tg: 115.6^0C) or both of them. Therefore, 90^0C was selected as the optimal temperature for the synthesis process and following experiments.
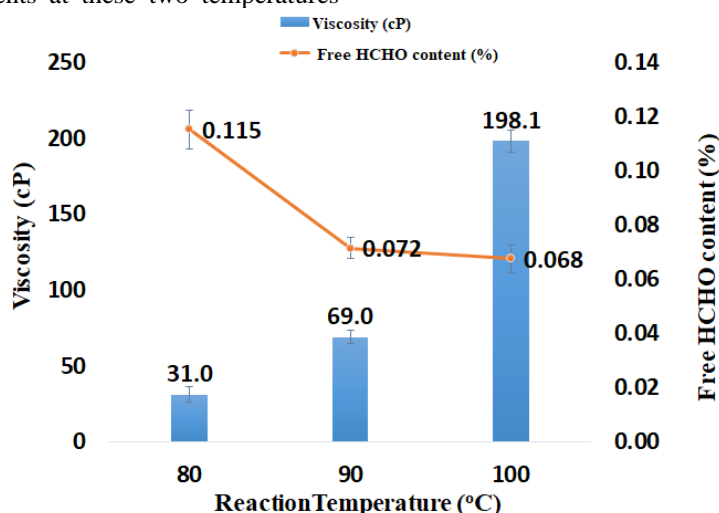

Fig. 5. Effect of temperature on LBPFA forming capability

3.3. Effect of reaction time on resin forming process

The cross-linking reaction time always accounts for a high number of total reaction time. The total reaction time for the LBPFA synthetic process consists of resolution, creating methylol groups on the benzene ring of lignin and phenol molecules, and condensation reaction (splitting water, creating methylene bonds). It is considered that a short run-time is not enough to create cross linkages. However, a long run-time leads to bonding reactions being increasingly tightened together and the solution becoming hard.

The effect of reaction time on viscosity and free HCHO content were presented in Fig. 6. The range of reaction time was set from 60 to 180 minutes. In Fig. 6(a), at the first 60-minute viscosity of the adhesive was unchanged at 31.10 cP at various lignin contents (30, 40 and 50%). Nevertheless,

when reaction time increased to 120 minutes, the viscosity of the adhesive with 30% lignin slightly rose to 32.81 cP while that of the adhesive with 40% and 50% lignin significantly increased to 89.64 cP and 136.02 cP. If the reaction was continually kept for 60 minutes more, the viscosity of the adhesive with 30% lignin moderately increased by 36.14 cP. In the meantime, for 40% and 50% lignin, the viscosity of the adhesive rocketed to 182.77 and 284.33 cP, respectively. The reason for a significant increase in the period of the last 60 minutes could be that cross-linking reactions considerably happened in the period of 60 to 120 minutes and the reactions mainly occurred in the period of 120 to 180 minutes. It was noticeable that with 50% lignin and run-time over 180 minutes, the adhesive became a thickened liquid and then solid. The appearance of LBPFA with synthetic conditions: 50% lignin, reaction temperature of 90°C and reaction time of 180 minutes and more than 180 minutes was illustrated

in Fig. 7. This is consistent with the theoretical basis given. Therefore, reaction time in range from 120 to 180 minutes was chosen as the appropriate time for the LBPFA synthetic process.

In contrast to viscosity, free formaldehyde content showed a reduction when reaction time increased showing in Fig. 6(b). When reaction time varied from 60 to 180 minutes, free formaldehyde content of the adhesive with 30, 40 and 50% lignin decreased from 0.120 to 0.082%, 0.250 to 0.073% and 0.270 to 0.082%, respectively. This result was completely consistent to the previous studies (Wang et al., 2009; Kalami et al., 2017).
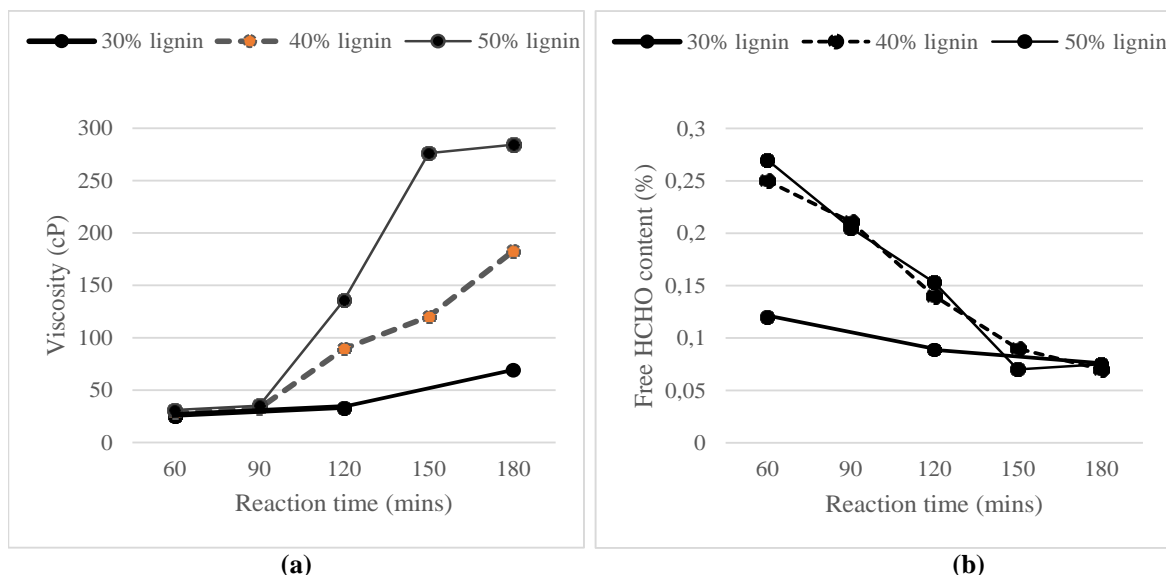

(a)   **(b)**

Fig. 6. Effect of reaction time on (a) viscosity and (b) free HCHO content

Fig. 7. Appearance of LBPFA at different reaction time: (a) 180 minutes and (b) more than 180 minutes

3.4. Adhesive parameters

Basic physical properties of lignin including free formaldehyde content, solid content, pH and viscosity were presented in Table 2. In fact, for free HCHO content the longer reaction time is the lower free HCHO content is. Moreover, when the percentage of lignin increased and reaction time kept long, solid content straightly increased from 38.44% to 53.38%. Similar to free HCHO content, pH of the LBPFA slightly decreased by less than 1 unit and the value of pH of the adhesive was moderately controlled. In terms of viscosity, the value of this parameter also increased straightly like solid content, but the gap was significant. In detail, viscosity of the adhesive at reaction time of 180 minutes was 68.9, 182.8 and 284.3 cP with lignin replacement of 30, 40 and 50%, respectively. Through experimental results, the adhesive's parameters met the GB/T 14372 – 2006 standard.

Table 2. Parameters of coir pith LBPFA at synthesis temperature of 90⁰C

Lignin content, %	Reaction time, minutes	Free HCHO content, %	Solid content, %	pH	Viscosity, cP
GB/T 14372		*≤ 0.3*	*≥ 35*	*≥ 7*	*≥ 60*
30	180	0.072	38.44	11.03	68.9
40	120	0.140	39.11	10.95	89.60
	150	0.090	41.55	10.17	120.1
	180	0.070	48.33	10.15	182.8
50	120	0.153	41.52	11.05	136.0
	150	0.070	52.47	10.21	276.2
	180	0.075	53.38	10.02	284.3

3.5. Chemical properties

FTIR of the LBPFA was shown in Fig.8 and typical peaks of the adhesive were presented in Table 3. In fact, the peak of O-H bonding was observed at wavenumber of 3410.10 cm^{-1}. Wavenumbers of 1587.41 and 1457.16 cm^{-1} were reported as bondings of aromatic rings in lignin. Besides, Ar-CH$_2$OH bondings were observed at wavenumber of 1203.48 and 1105.33 cm^{-1}. The peaks at 998.27 and 751.41 cm^{-1} were bondings of Ar-C-H. These peaks were also presented in the previous study of Wang (Wang et al., 2009).
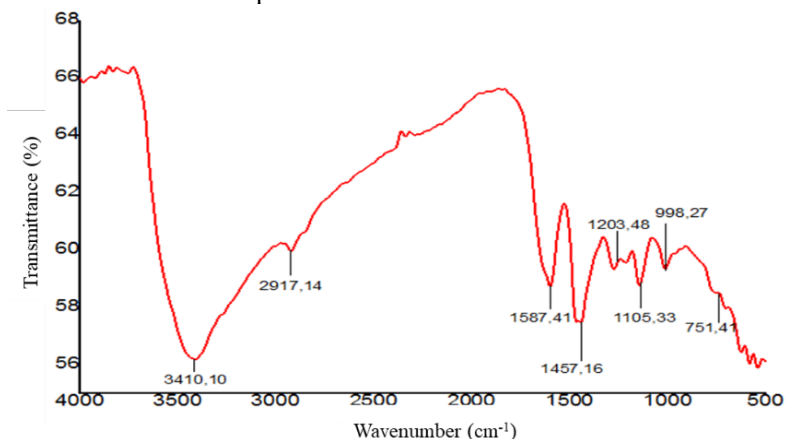

Fig. 8. FT-IR spectra of coir pith LBPFA

Table 3. FT-IR bands assignment in LBPFA

Wavenumber (cm^{-1})	Wavenumber of the LBPFA (cm^{-1})	Functional Group	Wavenumber(cm^{-1}) (Wang et al., 2009)
3440-3350	3410.10	O-H (phenolic OH and aliphatic OH)	3350
3981-2887	2917.14	C-H (CH$_3$ and CH$_2$)	3020; 2960
1600-1450	1587.41; 1457.16	Aromatic rings	1600; 1500; 1450
1260-1100	1203.48; 1105.33	Ar-CH$_2$OH	1100
1000-690	998.27; 751.41	Ar-C-H	-

3.6. Thermal properties

Differential scanning calorimetry analysis of LBPFA at the room temperature of 25°C to 180°C was shown in Fig. 9. A heat collecting tip from room temperature to 180°C was obtained. The peak of the cure was 115.6ºC, which was low compared to range of 130-180ºC reported by Pflugen (Pfungen, 2015). The low solidified temperature of the adhesive is caused by different sources of raw materials and refined or unrefined lignin. Additionally, only one peak was obtained in Fig. 9 showing the consistency in the LBPFA synthetic process. In case of being more than one peak in the cure, the reaction of lignin, phenol and formaldehyde was incompleted (Kalami et al., 2017).
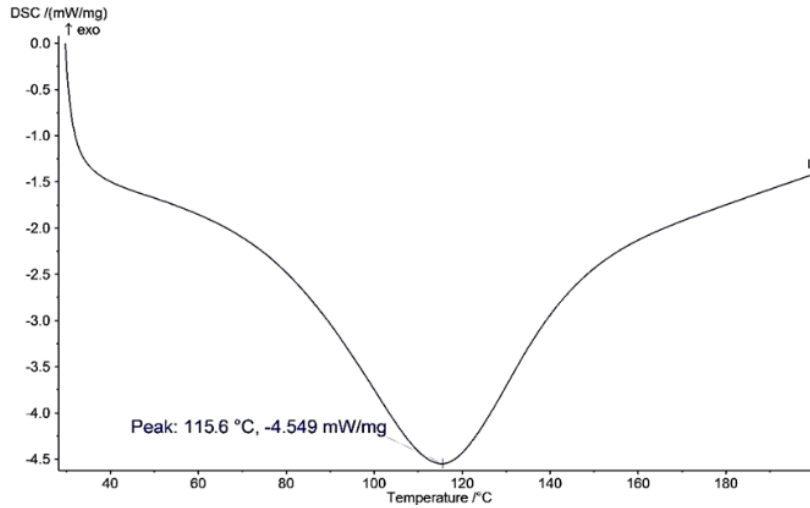
Fig. 9. DSC curve of coir pith LBPFA

3.7. Adhesive mechanical performance

Fig. 10 showed that tensile strength of LBPFA increased according to increasing the content of lignin in the range of 30- 40%. However, the tensile strength decreased as long as increasing lignin content to 50%. Both dry and wet tensile strengths respectively reached the peaks at 14.42 and 7.66 MPa as 40% replaced lignin content was used. Moreover, the viscosity of the adhesive with 40% lignin content was 185 cP, which was good for the bonding of two wood panel surfaces. The decrease in tensile strength as increasing lignin content to

50% would be caused by high viscosity and high solid content making it hard to evenly spread adhesive on the board surface. In this study, another common commercial glue being applied on construction and interior was also compared. The results showed that the glue's tensile strength was very low (2.28 MPa) and its waterproofing capacity was not compared to synthetic LBPFA.

Generally, the tensile strength of LBPFA was high and the value of dry tensile modulus was higher than that of the wet tensile modulus. The detailed results were shown in Fig. 11.
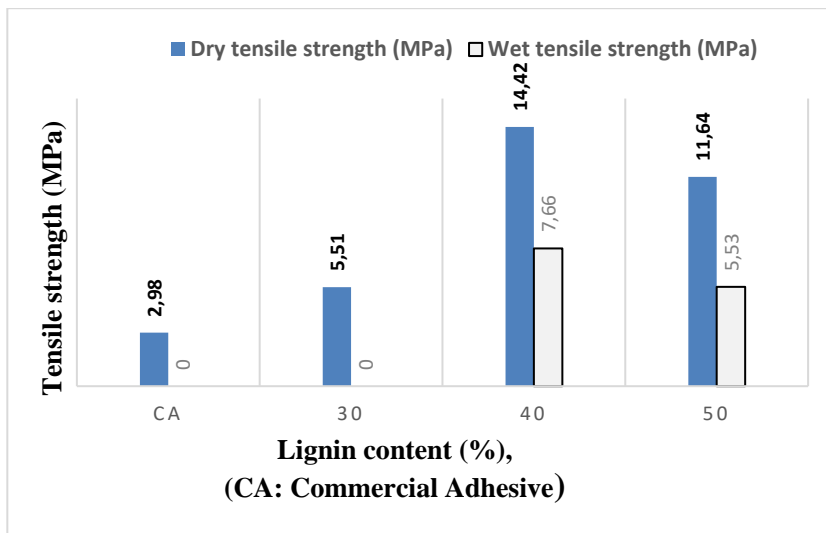

Fig. 10. Tensile strength of CA and LBPFA

The results of bonding ability on artificial plywood between synthetic LBPFA and commercial glue were 15.97 MPa and 20.16 MPa, respectively. Both

showed high tensile strain-stress behaviors although tensile strain-stress of the commercial product was slightly higher than that of LBPFA. However, the

amount of LBPFA applied was low (200 g.m^{-2}), it was easy to use, evenly distributed on the board surface, only 0.36% error which indicated its uniform. LBPFA had good waterproofing ability. However, the process of pressing and treating the sample needs to use heat to create bonds better. In the case of commercial ones, a large amount of glue (400 g.m^{-2}) was required. In addition, commercial glue was too condensed to spread out evenly on the wood surface (about 0.58% error), no water resistance but there was no need to use heat once making press.
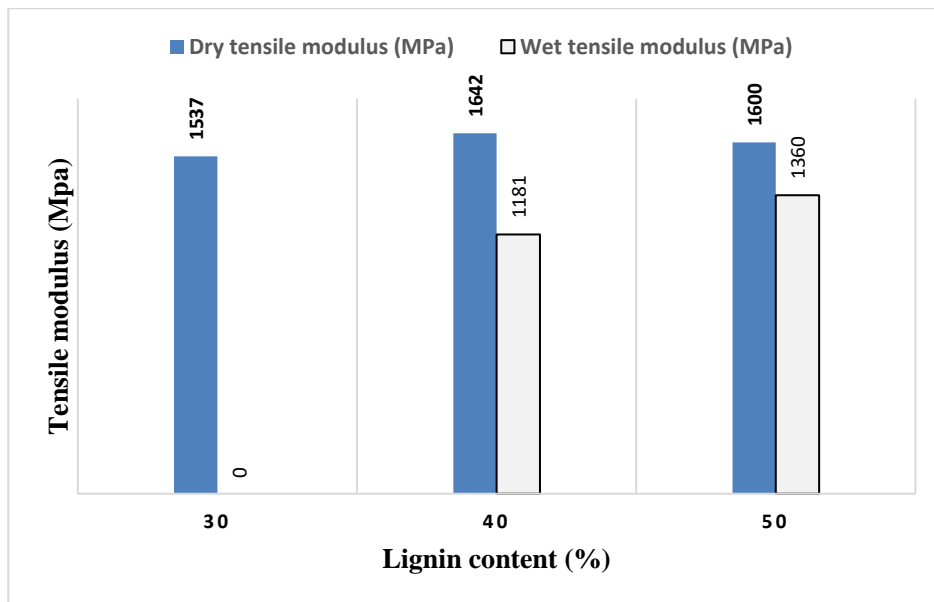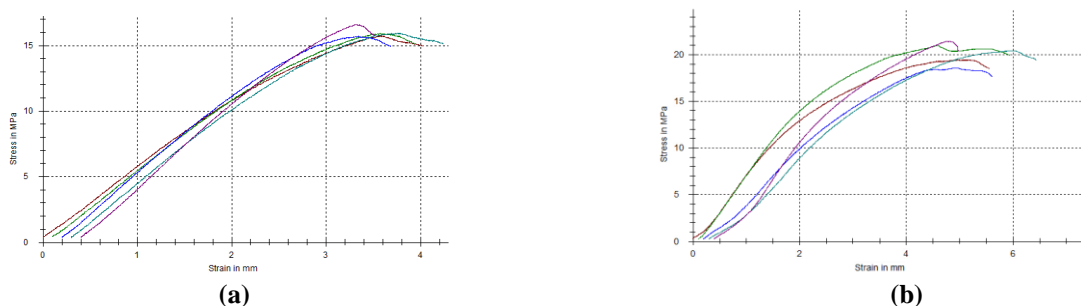

Fig. 11. Tensile modulus of LBPFA

Fig. 12. Tensile strain-stress behavior of (a) LBPFA and (b) commercial glue on artificial plywood

4. CONCLUSION

Resol-type LBPFA was successfully synthesized from coir pith lignin with the replacement of lignin on phenol in the range of 30%-50% total amount of phenol. The optimal conditions in the synthesis process: lignin content, reaction temperature, reaction time was 40% (wt/wt), 90 ^{0}C, 180 minutes, respectively. At the optimal conditions, the highest value of the tensile strength was 14.42 MPa. LBPFA was successfully applied on natural wood and artificial plywood and showed outstanding results compared to commercial ones.

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