Formulation of an Environmentally Friendly Adhesive for Wood

M. N. Mohamad Ibrahim,*[1] A. Md. Ghani,[1] N. Zakaria,[1] S. Shuib,[2] C. S. Sipaut[1]

Summary: Malaysia has over 4 million hectares of oil palm plantations that yield large amounts of empty fruit bunches (EFB) generated from palm oil milling operations. These forms of lignocellulosic residue pose an environmental hazard if their disposal is not managed in a systematic manner. One of the useful elements extracted from these EFBs is lignin. The general purpose of this study is to explore the potential uses of lignin extracted from soda black liquor (paper and pulping waste) derived from oil palm empty fruit bunches (EFB) in the formulation of a more environmentally friendly wood adhesive. In this work, the potential for replacing phenol with lignin in phenol formaldehyde resin formulation is examined. The quantity of phenol was reduced by synthesizing the resin at a lignin to phenol ratio of 1:1. The physical and chemical properties of lignin phenol formaldehyde resin (LPF) and commercial phenol formaldehyde resin (CPF) were then compared. The infrared spectrum revealed similarities in the functional groups of both LPF and CPF resins. Tensile strength comparisons between both resins revealed that the LPF resin had a higher bonding strength (11.60 MPa more in term of allowable maximum load). In addition, the kinematics viscosity test showed that the LPF resin had lower kinematic viscosity than the CPF resin after 21 days of storage. Finally, the scanning electron microscope images for both resins showed similarities in terms of penetration into wood vessels.

Keywords: black liquor; lignin phenol formaldehyde resin; oil palm empty fruit bunch; scanning electron microscopy; strength

Introduction

The *Elaesis guineenis* or commonly known as the oil palm was introduced to various parts of the tropics for its oil producing fruit. It is estimated that over 4 million hectares of land is currently under oil palm cultivation in Malaysia.[1] Besides producing palm oil, the oil palm industry also generates massive amount of lignocellulosic residues such as trunks, fronds and empty fruit bunches (EFB). This residue poses a serious environmental threat if their disposal is not effectively managed.[2] EFB has long been recognized as a potential alternative raw material for the paper and pulp industry.[3–5] The pulping process of EFB is uniquely idiosyncratic as it not only produces paper but also a by-product known as black liquor from which lignin can be extracted. Lignin is a biopolymer that is found in 20-30% of perennial land growing plants.[6,7]

Lignin is an amorphous polyphenolic material derived from the enzyme-mediated dehydrogenate polymerization of three major phenylpropanoid monomers, namely, conifery, sinapyl and p-coumaryl alcohol.[8] Its structural elements are linked by carbon-carbon and ether bonds to form a tri-dimensional network that are linked to hemicelluloses polysaccharides inside the cell wall.[9] Lignin is usually insoluble in all solvents and can only be degraded by either physical or chemical pulping processes at

---

[1] School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia
Fax: (+604-6574854); E-mail: mnm@usm.my

[2] School of Mechanical Engineering, USM Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia

high-temperatures and pressures. The delignification reactions involve the cleaving of non-phenolic ß-O-4 and phenolic α-O-4 linkages and their subsequent release from the polysaccharide.[10,11]

The existence of a variety of functional groups enables lignin to undergo a large number of modifications. For instance, both the aliphatic and aromatic hydroxyl groups are found in abundance and are potential reactive sites. Besides this, the structural similarity of lignin to phenol makes it a viable substitute of phenol in wood adhesive resin. Currently, there is a great variety of adhesives in use in the wood industry. Among the most prominent wood adhesives in use are formaldehyde-based condensation resins. These resins are formed by the reaction of formaldehyde with various chemicals such as urea, melamine, phenol or resorcinol or a combination of these substances and phenol formaldehyde (PF) based resin is the most common type[12] of resin utilized in the production of wood articles. With the increasing use of composite materials such as strand board, flake board and composite lumber, the demand for adhesive has also witnessed a concomitant increase. These adhesives are easily available today, but the scarcity of petroleum products could affect their future cost and the availability of these petroleum based adhesives.[13] Concerns about the effect of spiraling oil prices on the wood adhesives industry have also spawned initiatives to formulate bio-based wood adhesives.

The objective of this study is to explore the potential of substituting phenol partly with lignin derived from the pulping waste of empty fruit bunch. In order to ascertain its viability as a substitute product, various tests have been conducted on this environmentally friendly and potentially inexpensive wood adhesive.

Experimental Part

Material

The oil palm empty fruit bunches (EFB) raw material in this study was supplied by Sabutek (M) Sdn. Bhd., Teluk Intan, Malaysia, a local company specializing in the recycling of EFB. Black liquor derived from the EFBs was supplied by the School of Technological Industry, Universiti Sains Malaysia (USM).

Extraction of Lignin

The pH of the obtained black liquor was 12.45 while its density was 1.02 g/cm^3. The soda lignin was then precipitated from concentrated black liquor by acidifying it to pH 2 using 20% sulphuric acid. The precipitate was filtered and washed with 20% sulphuric acid adjusted pH 2 water. Finally, the soda lignin was dried in a vacuum oven at a temperature of 55 °C for 24 hours prior to further analysis.[14]

Preparation of Adhesive

Lignin-phenol-formaldehyde (LPF) resin was prepared in two stages. The first stage involved the preparation of lignin-phenol adduct (LP) while the second step comprised the preparation of lignin-phenol-formaldehyde resin. In the first stage, 28.0 g dry lignin and 28.0 g phenol were mixed in a beaker. The mixture was stirred at 40 °C for one hour to obtain a homogenous mass of lignin-phenol adduct. In the second stage, 23.28 g of LP adduct, 20.27 g of formaldehyde solution, 10 g of methanol and excessive phenol (in order to obtain the desired phenol: lignin ratio) were mixed in a three-neck round bottom flask and heated. When the temperature attained 80 °C, 1.16 g of sodium hydroxide which was dissolved in 10 g of distilled water was added to the mixture. The heating process was allowed to continue for 4 hours.[15]

Adhesive Analyses

The Perkin Elmer model System 2000 Fourier Transfer Infrared (FT-IR) was used to analyze functional groups present in both the LPF and CPF resins.

Apart from this, all samples underwent the close contact joint or adhesive tensile strength tests in accordance with ASTM D897 specifications.[16] The same procedures were used to compare the adhesive strength of LPF resin with CPF resin. Wood samples measuring 100 mm x 25 mm x 10 mm were used as substrates for tensile testing. During the procedure, adhesive was applied on both sides of interface within a 50 mm x 25 mm area. The glued samples were pressed in a hot pressing machine at 160 °C for 20 minutes. Subsequently, the tensile strength of the samples were analyzed using Instron machine model 5582 UTM at a crosshead speed of 6 mm/min.

As for resin penetration into wood structure, the samples were analyzed using Scanning Electron Microscope (SEM) model Leosupra 50VP FESEM.

Finally, a capillary viscometer model Micro-Ubbelohde Viscometer with three tubes i.e capillary tube, venting tube and filling tube, was used to measure the viscosity of the resins. The procedure involved channeling the resin into the filling tube and allowing it to flow down to the bottom of the viscometer. The resin was then sucked up through the capillary tube by applying vacuum pressure at the venting tube. The duration taken for the sample to fall down to the bottom of the capillary tube was recorded after the suctioning process was stopped. The viscosity of both resins was determined on the seventh day of every week over a 3-week period.

Results and Discussion

Figure 1 depicts the infrared (IR) spectra of the lignin-phenol adduct, LPF and CPF resins. The absorption bands in the 3300 cm^{-1} region for lignin-phenol adduct,

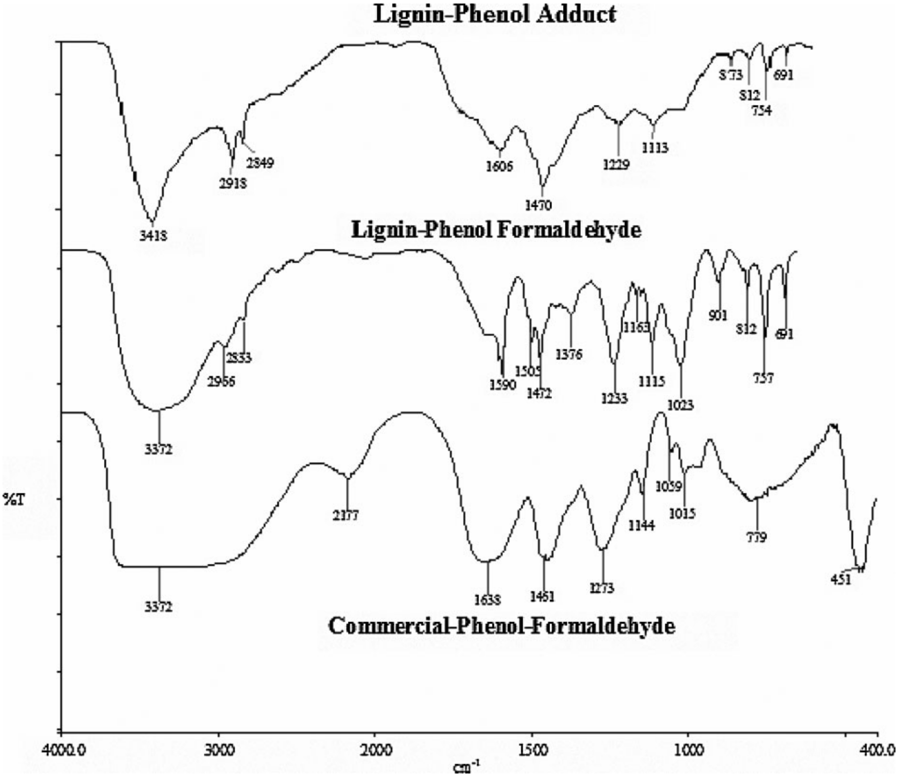

Figure 1.
Comparison of IR spectra of lignin-phenol adduct, LPF and CPF resins.

Table 1.
Tensile strength test using LPF resin as an adhesive.

Samples	Maximum load (N)	Ultimate Tensile Strength (MPa)	Elongation at break (%)
1	3823.50	15.39	1.84
2	2944.85	11.78	1.32
3	1866.08	7.51	0.33
Mean	2878.14	11.56	1.163

LPF and CPF resins reveal the presence of the OH functional group. In addition, the stretching vibrations of the aromatic compound for the lignin-phenol adduct, and the LPF and CPF resins are discernible within an adsorption band in the 1600 cm^{-1} to 1500 cm^{-1} region.

The bending vibration of a C-H asymmetry from methyl of aromatic group for CPF and LPF are respectively at the 1461 cm^{-1} frequency and 1472 cm^{-1} frequency. The frequency 1273 cm^{-1} for CPF and 1233 cm^{-1} for LPF indicate asymmetric stretching for phenolic C–C–OH. Besides this, the peak frequency of 1144 cm^{-1} for CPF is indicative of a C–O stretching vibration while the peak of frequency 1115 cm^{-1} shows the presence of ether aliphatic through asymmetric stretching vibration for C–O–C.[17]

Both the lignin-phenol adduct and the LPF resin have similar peaks at band 1470 cm^{-1} indicating the presence of a methylene bridge.[18] However, this band is not present in the CPF resin. Furthermore, two bands at 2900 and 2800 cm^{-1} in the lignin-phenol adduct and LPF spectra signify the presence of CH stretching. Finally, the confirmed presence of lignin in both the lignin-phenol adduct and LFP compounds is indicated by the CH stretching in syringyl and the presence of C–O primary alcohol at bands 1113 and 1115 cm^{-1} respectively.[18]

The tensile strength results for both CPF and LPF adhesive bonds were analysed in order to measure the bonding strength between the adhesive and the wood substrate. Table 1 and Table 2 show the results of the ultimate tensile strengths tests for LPF and CPF respectively. The mean value recorded was 11.56 MPa for LPF and 5.61 MPa for CPF. The results indicate that the adhesive strength of LPF on wood substrate was much stronger than that of CPF. It is also noted that the elongation at break for both samples are about 1%.

The ability of lignin phenol formaldehyde resin to bear additional loads before adhesive failure is attributable to the presence of lignin and phenol. In addition, the increased probability of strong bonds forming between the adhesive and wood substrate is facilitated by the structural similarity between lignin and phenol. Based on the image in Figure 2, it is evident that there is an even dispersion of LPF resin into the wood structure. Such uniform resin penetration into wood vessel pores helped further augment the strength of the wood structure.[19] In addition, the resin spread pattern between the two surface layers of wood is probably due to LPF's lower viscosity compared to CPF as shown in

Table 2.
Tensile strength test using CPF resin as an adhesive.

Samples	Maximum load (N)	Ultimate Tensile Strength (MPa)	Elongation at break (%)
1	2536.78	5.15	0.53
2	2269.43	4.55	1.45
3	2930.61	7.15	2.28
Mean	2578.94	5.61	1.42

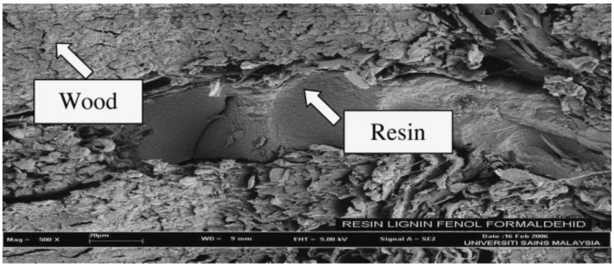

Figure 2.
SEM image for LPF resin penetration effect in wood vessel.

Table 3.
Results for viscosity test for LPF and CPF resins at different storage times.

Days	LPF resins (cSt)		CPF resins(cSt)	
	25 °C	29 °C	25 °C	29 °C
7	0.9656	0.8204	6.1781	5.7156
14	0.9908	0.8612	9.9864	8.6264
21	0.9746	0.8756	9.9884	9.1148

Table 3. This helps further solidify wood bonding.[20] Figure 3 depicts wood samples adhered with CPF resin. The bonds formed are not strong as indicated by the clear presence of fissures.

Table 3 shows the kinematics viscosity of LPF and CPF resins. The data indicates that LPF resin consistently generated lower values compared to CPF resin after being stored for three weeks. The results also indicate that the kinematics viscosity for both resins increased with the elapse of time. Overall, the densities of LPF and CPF were 1.088 g/cm^3 and 1.196 g/cm^3 respectively. Since increases in viscosity is directly proportional to its density, it is not surprising that the CPF resin generated higher viscosity values as this resin has a higher density than LPF. However, high density will hinder resin movement and cause resin to freeze rapidly when exposed to air.[21] The lower viscosity of the LPF resin is attributable to the abundant presence of both aliphatic and aromatic hydroxyl groups in lignin. This consequently increases the ionization of the phenolic hydroxyl group in LPF thus increasing intermolecular ionic repulsion among molecules. The existence of these forces between the molecules therefore account for the lower viscosity of the LPF resin when compared to the CPF resin.[22]

Apart from this, different temperatures generate different viscosity readings for both resins. At 29 °C, both resins share a lower viscosity reading compared to that at 25 °C. This is because viscosity decreases as temperature increases since the cohesive force between fluid molecules decreases as kinetic force increases.[23] As the tendency of resin to become viscous hinders the resin handling process on the substrate, especially on plywood,[24,25] the low kinematics viscosity of LPF resin is a preferable advantage as this would confer the resin a longer shelf life or storage time.

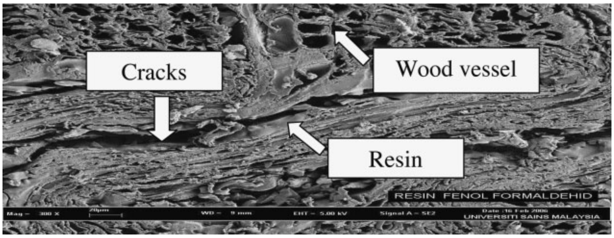

Figure 3.
SEM image for CPF resin penetration effect in wood vessel.

Conclusion

This research has successfully formulated a lignin-phenol-formaldehyde (LPF) resin as an alternative to existing commercial phenol-formaldehyde based (CPF) resin. Physical and chemical properties comparisons between LPF and CPF resins had been presented. FT-IR spectra reveal that the LPF resin possesses similar chemical characteristics with CPF resin. Viscosity test, tensile strength test and SEM analysis all indicate that the LPF resin performs better as a more environmentally friendly low cost wood adhesive. The study noted that up to 50% of phenol in commercial-phenol-formaldehyde (CPF) resin can be substituted by lignin in the production of lignin-phenol-formaldehyde (LPF) resin. Besides, LPF resin can be stored for a longer period of time compared to CPF resin due to its lower viscosity. This research project constitutes a two-pronged approach designed to overcome the problems related to the disposal of pulping waste in the form of black liquor as well as to recycle an agro- based industrial effluent into a valuable product. With increasing demands for EFB as an alternative material for pulp and paper production, producing wood adhesive from EFB lignin may be a viable commercial enterprise in future.

Acknowledgements: The authors would like to express their appreciations to Universiti Sains Malaysia and the Malaysian Ministry of Higher Education for the financial support of this project through a research grant (203/PKIMIA/671028). The authors also would like to thank Sabutek (M) Sdn. Bhd. for supplying the EFB long fiber and the School of Industrial Technology, Universiti Sains Malaysia for supplying black liquor used in this study.

[1] Malaysian Palm Oil Board Home Page, http://www.mpob.gov.my (accessed 8/2/2008).
[2] Sabutek (M) Sdn. Bhd. Home Page, http://www.sabutek.com.my (accessed 18/04/2005).
[3] S. Akamatsu, Y. Kobayashi, H. Kamishima, K. B. Hassan, M. N. Mohamad Yusof, M. Husin, Hassan, *Cellul. Chem. Technol.* **1987**, *21*, 191–197.
[4] K. C. Khoo, T. W. Lee, *Appita Journal* **1991**, *44*(6), 385–388.
[5] W. R. Wan Daud, K. N. Law, J. J. Valade, *Cellul. Chem. Technol.* **1998**, *32*(1), 133–143.
[6] K. V. Sarkanen, C. H. Ludwig, "*Lignin-Occurrence, Formation, Structure and Reactions*", Wiley Interscience, New York **1971**.
[7] W. G. Glasser, S. S. Kelly, in "*Encylopedia of Polymer Science and Engineering*", Vol. *8*, 2nd ed., N. M., Bikales, C. G., Overberger, G. Menges, Eds., Wiley Interscience, New York **1987**, p. 795.
[8] Y. L. Stephen, W. D. Carlton, "*Method in Lignin Chemistry*", 1st ed., Springer-Verlag, Berlin Heidelberg, Germany **1992**.
[9] R. C. Sun, J. Thomkinson, B. James, *Polym. Degrad. Stab.* **1999**, *68*, 195–200.
[10] G. Gellerstedt, E. L. Lindfors, *Holzforchung* **1983**, *38*(3), 151–158.
[11] B. D. Groot, J. E. G. V. Dam, R. P. V. D. Zwan, K. V. Riet, *Holzforchung* **2000**, *48*, 207–214.
[12] M. R. Roger, in "*Kimia Kayu Padu*", Edisi Kedua terjemahan Suhaimi Muhammed dan Halimahton Haji Mansor, 2nd ed., Percetakan Dewan Bahasa dan Pustaka, Kuala Lumpur **1994**.
[13] Wikipedia Home Page, www.wikipedia.org/wiki phenol formaldehyde resin (accessed on 23/6/2005).
[14] M. N. Mohamad Ibrahim, S. B. Chuah, W. D. Wan Rosli, *AJTSD*, **2004**, *21*, 57–61.
[15] A. K. Muzaffar, M. A. Sayed, P. M. Ved, *Int. J. Adhes. Adhes.* **2004**, *24*, 485–493.
[16] V. P. Alphonsus, "*Adhesion and Adhesives Technology, An Introduction*", Hanser Publisher, New York **1997**, p. 35–39.
[17] P. Y. Bruice, "*Organic Chemistry*", 3rd ed., Pearson Education International, New Jersey **2001**, p. 497–510.
[18] M. A. Khan, S. M. Ashraf, V. P. Malhotra, *J. Appl. Poly. Sc.* **2004**, *92*, 3514–3523.
[19] S. C. Nihat, O. Nilgul, *Int. J. Adhes. Adhes* **2002**, *22*, 477–480.
[20] W. Gindl, T. Schoberl, G. Jeronimidis, *Int. J. Adhes. Adhes* **2004**, *24*, 487–495.
[21] G. T. Tsoumis, "*Science and Technology of Wood: Structure, Properties and Utilization*", von Nostrand Reinhold, New York **1991**, p. 36–37.
[22] T. Seller, Jr., R. A. Haupt, *Ind. Eng. Chem. Res.* **1994**, *33*, 693–697.
[23] L. Robert, "*Polymer Chemistry, Revised Edition-A Teaching Package for Pre-Collage Teachers*", National Science Teachers Association, Wilson Boulevard **1995**, p. 145–156.
[24] S. J. Terry, "*Plywood and Adhesive Technology*", Marcel Deckker Inc., New York **1985**, p. 132–140.
[25] A. K. Shawkataly, H. Rokiah, "*Komposit Panel Berasaskan Sumber Kayu*", Penerbit Universiti Sains Malaysia, Pulau Pinang **2004**, p. 232–237.