Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 13 Issue 06, June - 2024

Bio-lignin Based Adhesives Ecofriendly Synthesis for Wood Applications

Reward Paradza, Eubert Mahofa
Department of Chemical and Process Systems Engineering, School of Engineering and Technology,
Harare Institute of Technology, Harare, Zimbabwe

Abstract
The increasing global demand for fossil fuels, especially in developing countries, poses a significant threat to petroleum resource availability in the coming years. The depletion of petroleum resources is inevitable. Since 2009, Zimbabwe has been spending an average of $50 million annually on adhesive imports, according to ZIMSTATS. This highlights the need for the chemical industry to seek alternative raw materials. Formaldehyde-based adhesives are non-biodegradable, carcinogenic, petroleum-derived, and pose environmental concerns during their production and use. This study investigates a hot-water extracted lignin-based resin as an alternative. Various lignin resins were prepared and tested for bond strength to evaluate their functionality. The resins were hydrolysed in alkaline conditions to enhance surface interactions, before adding lignin. Lignin was used to substitute phenol in the adhesives at levels of 10%, 30%, and 50%, resulting in shear strength values of 0.334 kPa, 0.456 kPa, and 0.591 kPa, respectively. The results indicated that substituting phenol with up to 50% lignin in adhesive resins caused minimal changes in the shear strength properties of the wood composites.
***Keywords*: Lignin, formaldehyde, renewable, phenol, resins**

INTRODUCTION

An adhesive is a material used to hold two surfaces together. It must wet the surfaces, adhere to them, develop strength after application, and remain stable over time. Petroleum-derived synthetic resins, especially formaldehyde-based resins like melamine-urea-formaldehyde, are extensively used for bonding and binding purposes in various industries such as paper, packaging, construction, and aerospace. However, formaldehyde-based adhesives are non-biodegradable and petroleum-derived, raising environmental concerns. Although adhesives made from these resins possess high glue strength and water resistance, the release of formaldehyde, particularly from the breakdown of UF-resins in wood composites, poses significant health risks, as formaldehyde is carcinogenic to humans. According to a material safety data sheet (MSDS) from Science Lab (Fatemeh, 2017), formaldehyde has been categorized as a carcinogenic and toxic material, with an acute oral toxicity (LD50) of 100 mg/kg in rats. Beyond health concerns, the extensive use of petroleum-derived synthetic resins is unsustainable due to the inevitable depletion of fuel reserves and increasing pressure on petroleum resources. Consequently, there is an urgent need to develop adhesives based on ecological and bio-renewable resources. These new adhesives should be environmentally friendly, safer for human use, economical (preferably independent of oil prices), sustainable, and possess mechanical properties comparable to those of PF resins. One promising alternative investigated in this study is a hot-water extracted lignin-based resin. Natural adhesives are commonly used for bonding paper, foil, and light wood (Rodríguez, 2016). Lignin is abundant in plants and is an unwanted by-product of the pulping process for papermaking and bio-ethanol production. The organic structure of lignin is similar to that of phenol, enabling its substitution in phenol-formaldehyde resins. Lignin is composed of highly cross-linked phenolic C6C3 units connected by a series of carbon-oxygen (ether) and carbon-carbon linkages. This natural phenolic structure makes lignin an attractive potential replacement for phenol. However, the complex structure of lignin alone cannot fully meet the desired adhesive properties. Chemical modifications, including phenylation, methylation, and demethylation, can enhance its properties. This research aims to produce a lignin-based adhesive that can potentially replace phenol-formaldehyde resins.

Materials and methods

Several experiments are to be carried out which will result in production of a functional adhesive. Different samples were created which differed in amount of lignin used to substitute phenol in resin samples. Groundnut shells, which were obtained from Mbare market, were dulled; the grain and the shells were separated. The waste was to be used as the source of lignin. The waste shells were initially washed with distilled water to remove all the dust and sand particles. After washing, the shells were dried in an oven for 2hours at 100^0C. The experimental yield was the calculated.

Delignification of groundnut shells

Groundnut shells are crushed to a size range between 5-25mm. The powder is placed in a round bottomed flask. Sodium hydroxide solution is added to the flask prior to heating. The mixture is heated to 100^0C and maintained at temperature 100 $\pm5^0$C. After heating for 4hours, the suspended pulp fibres are separated from the black liquor. The liquor is precipitated with 50% sulphuric acid. The precipitated is washed with acidified water with a pH of 2.

Modification of lignin

Methylation stage

Lignin powder (30 parts by mass, 96% solid) was slowly added to 50 parts water while sodium hydroxide solution (30%) was added periodically to maintain the pH of the solution between 12 and 12.5 for better dissolution of the lignin powder, which was also facilitated by vigorous stirring with an overhead

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 13 Issue 06, June - 2024

Preparation of adhesive samples

i. Preparation of Synthetic Resin Without Lignin (Control)
First, 20.48 grams of phenol (0.246 moles) were placed in a glass beaker. Approximately 22 grams of distilled water were then added. Immediately following the addition of the distilled water, about 36 grams of formalin were added dropwise. The mixture was heated to 80-85°C for 30 minutes. After this initial heating, 1.20 grams of aqueous sodium hydroxide were added to the mixture. The entire mixture was then heated for an additional 4 hours.

ii. Preparation of Synthetic Resin with 10% Lignin Substitution
3.28 grams of lignin cake were added to a glass beaker, followed by 28.8 grams of phenol. Approximately 20 grams of distilled water were then added. Immediately after, 37.8 grams of formalin were added dropwise. The mixture was heated at 80°C for 30 minutes, and then 1.16 grams of aqueous sodium hydroxide were added. The mixture was subsequently heated for an additional 4 hours.

Table 1 Percent substitution of lignin in prepared resin

sample no.	% sub	Mass of phenol(g)	Mass of lignin(g)
A	0	22.48	0
B	10	28.8	3.2
C	30	7.24	16.89
D	50	11.64	11.64

$$\text{Percentage Substitution} = \frac{mass\ of\ lignin\ used\ in\ grams}{mass\ of\ lignin\ used(g) + mass\ of\ phenol\ used\ (g)}$$

iii. Preparation of Synthetic Resin with 30% Lignin Substitution

7.24 grams of lignin cake were added to a glass beaker, followed by 16.89 grams of phenol. Approximately 20 grams of distilled water were then added. Immediately after, 37.8 grams of formalin were added dropwise. The mixture was heated at 80°C for 30 minutes, and then 1.16 grams of aqueous sodium hydroxide were added. The mixture was subsequently heated for an additional 4 hours.

iv.

v. Preparation of Synthetic Resin with 50% Lignin Substitution
To prepare the mixture, 11.64 grams of lignin cake were added to a glass beaker, followed by 11.64 grams of phenol. Approximately 20 grams of distilled water were then added. Immediately after adding the distilled water, approximately 37.8 grams of formalin were added dropwise. The mixture was heated at 80°C for 30 minutes, and then 1.16 grams of aqueous sodium hydroxide were added. The mixture was subsequently heated for an additional 4 hours.

Characterization of adhesives
Determination of viscosity
Viscosity has been used as the main parameter to monitor the synthesis of the adhesives. One hour after completion of the addition of all reactive chemicals the first sample for the viscosity determination was extracted from the flask and performed. A pipette tip was used to transfer 3-4ml of the respective adhesive into a beaker for testing.

Moisture content analysis and curing of wood samples
Aim: To determine the effect of filer addition on solid and moisture content
Procedure
1. The weight of the wood samples was taken
2. Wood samples were taken and placed in an oven at 120^0C for 2 hours
3. The weight of the wood samples was recorded after drying and the percentage of moisture and solid content were measured using the equations below

$$\%solid\ content = \frac{final\ mass\ of\ sample}{initial\ mass\ of\ sample}\ X\ 100$$

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 13 Issue 06, June - 2024

$$\%moisture\ \ content\ = \frac{initial\ mass\ of\ sample - final\ mass\ of\ sample}{initial\ mass\ of\ sample} X\ 100$$

Evaluation of bond strength
Samples of wood adhesives were prepared which are different, so to test for effectiveness of prepared samples, bond strength of adhesives on wood samples were tested using tensile machine

Procedure
1. Three wood samples were taken and were cleaned with sand paper in preparation for spreading different adhesive sample on each wood sample

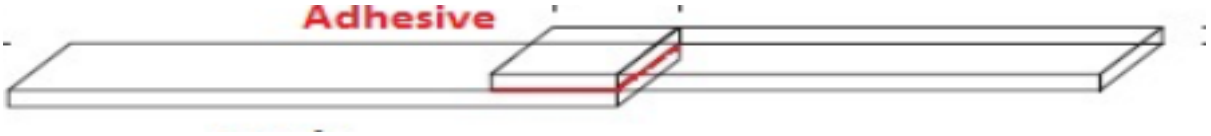

Figure 1 Lap joint on adhesives

2. On each side of wood sample, the adhesive solution was spread and the area was noted
3. The wood samples were hard-pressed with a load of 5kg for 2hours
4. The resultant specimen was then tested for bond strength using tensile testing machine
5. The wood samples are clamped to tensile and the highest force required for breaking was noted and recorded. The following equation was used to calculate

$$pressure(Mpa) = \frac{force\ x\ 1000(N)}{Area}$$

RESULTS AND DISCUSSION

Results for raw material characterisation

Table 2 Determination of Moisture content, ash content and volatile matter

Parameter	Mass
Mass of beaker and powdered groundnut shells before drying	44g
Mass of beaker and after drying	28g
Mass of sample	16g
Mass of water removed	0.61g
Percentage removed	3.79

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 13 Issue 06, June - 2024

Volatile matter and ash content testing

Volatile matter $= \frac{G-H}{mass\ of\ sample} = 72.39\%$

Ash content $= \frac{G-C}{mass\ of\ sample} = 4.21\%$

Where C- mass of crucible

G- Mass of crucible + sample after heating

H – Mass of crucible+ sample before heating

Analysis of results
The level of ash content is ansignificant parameter, which highlights the extent of purity of raw material before use. The high the level of ash content the lower the purity of the product. From the experimental determination of 4.21% ash content, a value of was obtained which falls within the expected range. An ash content level of less than 5% is usually expected.

Results for the Delignification process

Calculation of experimental yield based on chief raw material used (groundnut nutshell)

First run

Mass of powder ground nut shell used in grams = 240g

Mass of lignin cake produced in grams = 69.05g

Second run

Mass of powder ground nut shell used in grams = 240g

Mass of lignin cake produced in grams = 71.05.9g

Average mass of lignin produced = 70.05g

Experimental yield

$$= \frac{mass\ of\ product\ produced\ (Lignin)}{mass\ of\ chief\ raw\ material\ used\ (groundnut\ shell\ powder\ )}$$

$$= \frac{70.05g}{240g} = 28.0$$

Results for solid content, viscosity and pH values

Table 3 Determination of Moisture content, ash content and volatile matter

sample no.	Lignin % substitution	pH values	solid content%	Viscosity @ 26^0C	Densities
A	0	10.90	-	88.42	0.712
B	10	10.70	12.1	97.20	0.654
C	30	10.80	12.3	102.40	0.645
D	50	10.0	11.20	104.50	0.630

RESULTS ANALYSIS

The pH-value was determined at room temperature immediately after the resin was prepared. The alkalinity or acidity of solutions has a major effect on many adhesives' properties. The degree of acidity and alkalinity directly affects adhesive properties such as viscosity, aging stability of the liquid adhesive, and properties of the adhesive bond such as water resistance are highly pH dependent. The acidity (pH) of the adhesives was measured. 4 ml of each adhesive was dispensed into clean glass vials and stirred for 30 s. The pH values were measured at room temperature (25-26 °C) using a digital pH meter.

Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 13 Issue 06, June - 2024

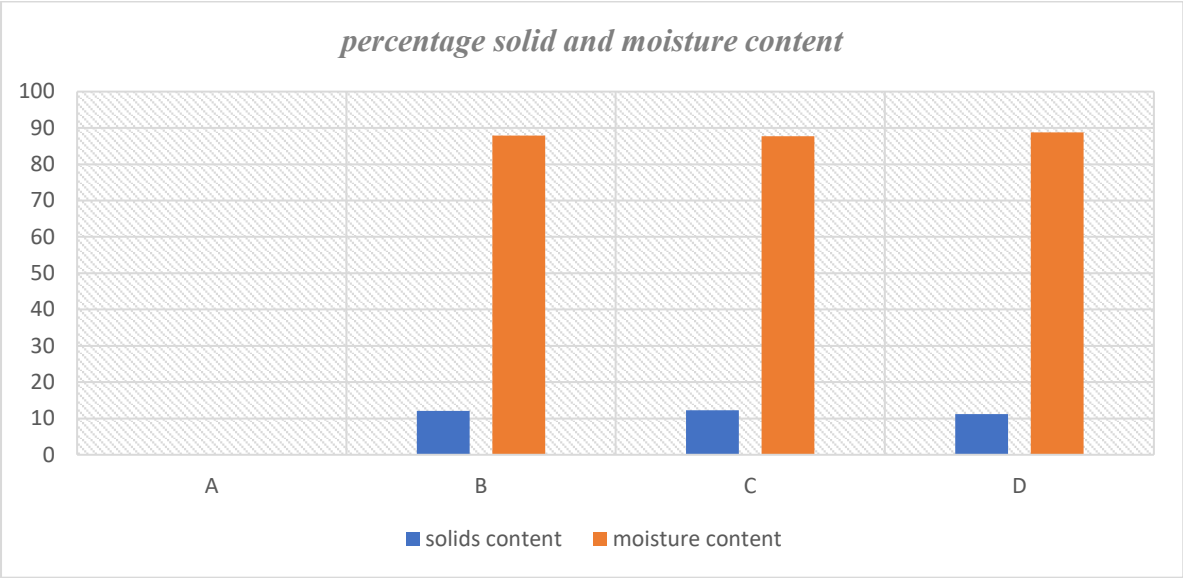

Figure 2 percent of solid and moisture content of samples

The level of moisture content is an important parameter when biodegradability of the adhesive product is to be considered. Adhesive samples with high moisture content are more prone to bacterial attack therefore; their shelf life is reduced. Storage of adhesives samples with low moisture content can be done with less bacteria attack. Sample D showed the minimum moisture content, which is preferred/expected range. With increase in pH as subsequent higher lignin percentage was used the higher the solids content. The higher the pH the greater the extent of hydrolysis. Low the solids contents are directly proportional to a drop in pH values. Level of solids content directly affects the adhesion properties of resins; appropriate solid content can improve the shear strength of the adhesive by preventing the penetration of adhesive into the veneer. Thus, allowing the adhesive to stay on the surface of the wood for effective bonding (Gao et al., 2012)

Table 4 Results analysis for adhesive strength

sample	area bonded(x $10^{-4}cm^2$)	force @ breaking(kN)	shear strength(kPa)
A	25	0.26	0.334
B	25	0.45	0.456
C	25	0.68	0.59
D	25	0.95	0.724

ANALYSIS OF RESULTS

The results above were obtained from tensile testing machine, sample D highest shear strength on specimen better than samples A, B and C. Sample D was reinforced with a higher percentage of lignin substitution. As sown by the graph above, increase in lignin percentage resulted in improved adhesive and bonding properties. These results show result show how lignin can be used as

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 13 Issue 06, June - 2024

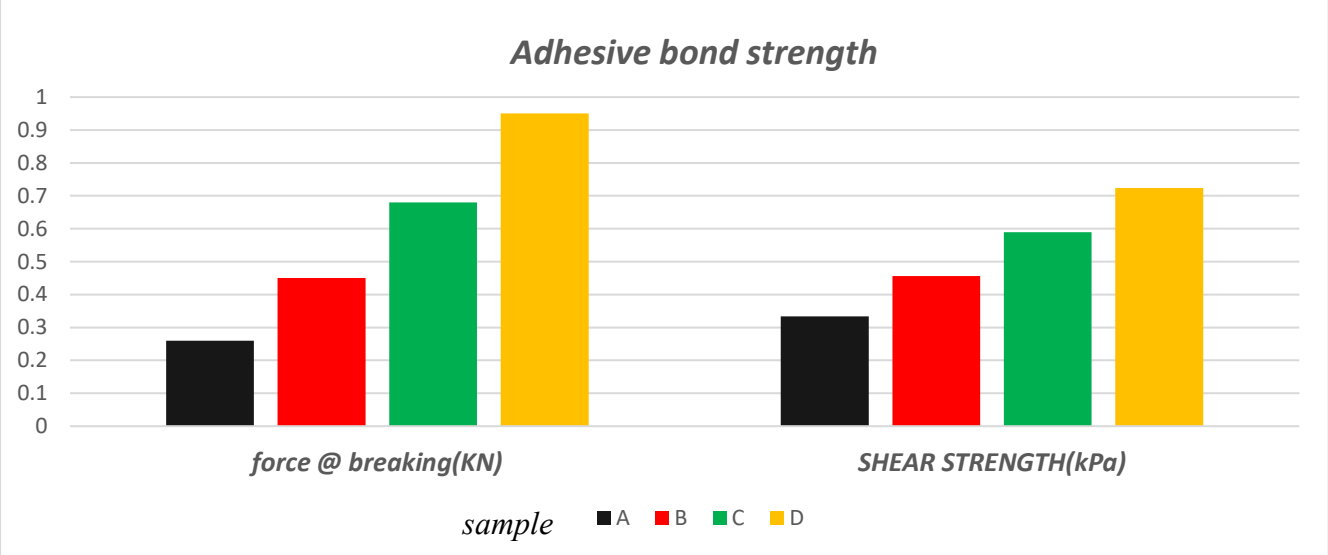

Figure 3 Change in shear strength as lignin percent substitution increases

ANALYSIS OF RESULTS

The results above were obtained from tensile testing machine, sample D highest shear strength on specimen better than samples A, B and C. Sample D was reinforced with a higher percentage of lignin substitution. As sown by the graph above, increase in lignin percentage resulted in improved adhesive and bonding properties. These results show result show how lignin can be used as substitute for pure phenol in adhesive resin formulation. However, there is need to find out to what extent does lignin substitution result in improved properties.

CONCLUSION

Lignin-based adhesives for wood applications were successfully prepared, demonstrating enhanced bonding properties, tensile strength, and water resistance. Three samples with different lignin substitution levels (10%, 30%, and 50%) were created to examine the effect of lignin content in the adhesive matrix. Tensile tests on wood samples revealed the impact of each lignin percentage on adhesive performance. Although further tests to explore additional substitution levels could not be conducted, this study has shown that with the proper technology, lignin adhesives can meet the accelerated water resistance standards required for wood products. The study concluded that increasing the pH led to higher solids content due to extended hydrolysis times. Higher solids content prevents the adhesive from penetrating wood samples, resulting in greater shear strength. However, while higher pH levels positively influence adhesive properties, they can also cause staining of wood samples. Therefore, lignin-based adhesives have the potential to replace synthetic adhesives currently used extensively in wood applications.

ACKNOWLEDGEMENTS

The authors are grateful to the Department of Chemical and Process Systems Engineering and the Department of polymer science and technology at the Harare Institute of Technology for provision equipment and facilities.

REFERENCES

Cothran, J.D. and Jing, F., Georgia-Pacific Chemicals LLC, 2017. Powdered lignin. U.S. Patent 9,610,706.
Fatemeh, F., 2017. Bio-Based Adhesives and Evaluation for Wood Composites Application. Polymers, 9(70), pp. 1-29.
Ghaffar, S.H. and Fan, M., 2014. Lignin in straw and its applications as an adhesive. International Journal of Adhesion and Adhesives, 48, pp.92-101.
Hemmil, V. A. K., 2017. Development of sustainable bio-adhesives for engineered wood panels. RSC Advances, 7(38604).
Lambuth, A.L., 2017, October. Protein adhesives for wood. In Wood Adhesives (pp. 17-46). Routledge.
Moubarik, A., Grimi, N., Boussetta, N. and Pizzi, A., 2013. Isolation and characterization of lignin from Moroccan sugar cane bagasse: Production of lignin–phenol-formaldehyde wood adhesive. Industrial crops and products, 45, pp.296-302.
Petrič, M. and Oven, P., 2015. Determination of wettability of wood and its significance in wood science and technology: a critical review. Reviews of adhesion and adhesives, 3(2), pp.121-187.
Pizzi, A., 2017, October. Lignin Formaldehyde Wood Adhesives. In Wood Adhesives (pp. 171-206). Routledge.
Rodríguez, M., Riisager, A., Kegnæs, S. & Shunmugavel, S., 2016. Lignin biomass conversion into chemicals and fuels. DTU Chemistry.
Sadare, O.O., 2015. Preparation, Characterization and Performance Evaluation of Nanocomposite SoyProtein/Carbon Nanotubes (Soy/CNTs) from Soy Protein Isolate (Doctoral dissertation).
Yelle, D.J. and Ralph, J., 2016. Characterizing phenol–formaldehyde adhesive cure chemistry within the wood cell wall. International Journal of Adhesion and Adhesives, 70, pp.26-36.
Zhang, Y., Wu, J.Q., Li, H., Yuan, T.Q., Wang, Y.Y. and Sun, R.C., 2017. Heat Treatment of Industrial Alkaline Lignin and its Potential Application as an Adhesive for Green Wood–Lignin Composites. ACS Sustainable Chemistry & Engineering, 5(8), pp.7269-727