Original Research Article

Bench scale production of enhanced phenol-formaldehyde (PLGF) adhesive: Effect of lignin-gluten modification

Abstract

Phenol–formaldehyde (PF) adhesive was successfully modified using lignin from palm fruit empty bunches and gluten from wheat four. The polymerization reaction was carried out under basic medium. 90% substitution of the phenol component of the Phenol–formaldehyde adhesives was achieved. Also 80% substitution for formaldehyde was also achieved. The mixture of 10:70:20 of phenol, lignin and formaldehyde under basic medium gelled at relatively low time (131min), with viscosity768.2mPa.s, free formaldehyde value of 0.12% and solid content of 66.83%. The gel time was found to be a function of formaldehyde-phenol ratio; however introduction of lignin also affected the gel time positively. Further modification using gluten further lowered the gel time and free formaldehyde to 95min and 0.08%. Also, there was remarkable improvement on the solid content from 66.83 to 74.32%. Hence, modification of Phenol–formaldehyde resol using lignin and gluten can improve the resol quality.

Keywords: Resol, phenol, formaldehyde, lignin, gluten

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Introduction

Massive growth and development in the construction industry has led to very high demand for phenolic resins (Jędrzejczak et al.,2021). By 2019, the value of phenolic resin industries globally was estimated at a whopping sum of $19.31 billion(Isa et al.,2022).Phenolic resin synthesized from phenol and formaldehyde continues to dominate the resin industry, over a century after its development, due to its versatile properties and performance in a wide variety of applications. The production and commercial applications of this phenolic resin spread out to the whole world after its first production in Germany in the year 1909 (Sarika et a.,2020).Some of the properties of the phenolic resin that keeps its value very high include the following ;excellent mechanical properties, flame retardancy, flexibility, low cost, high thermal stability, water and chemical resistance. These properties have made it a good choice of material for applications in aerospace industry, as adhesive in particleboard manufacturing units (Xu,Y et al., 2019). However, despite the popularity and widespread acceptance of phenol formaldehyde resin, in recent years there have been significant drives towards replacing fully or partially the raw material for the synthetic process of phenol-formaldehyde resin production There are three main motivation for such replacement: (1) moving towards a more sustainable bio-sources of raw material(Asim, et al.,2018) (2) Improving health and safety during manufacturing and end use (Xu,Y et al., 2019). (3) Enhancing the performance characteristics of the resin (Asim, et al.,2018). These motivations are based on the fact that the raw materials for PF resin are all petroleum based. These raw materials are fast depleting and are non-renewable, to add more desired properties to the resin adhesive. The most outstandingly is the need for a more environmental friendly process in production and use. Globally, un-combined monomeric formaldehyde (free-formaldehyde) that escapes into the environment is a silent killer (Brandacher et al.,2006). In the atmosphere,

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formaldehyde usually breaks down quickly to create formic acid and carbon monoxide, both are harmful substances. Exposure to formaldehyde can make animals sick, affect their ability to breed and reduce their life spans. In Human beings, formaldehyde causes myeloid leukemia and rare cancers, including cancers of the paranasal sinuses, nasal cavity and nasopharynx according to the report of International Agency for Research on Cancer (IARC) in 2011. Phenol-formaldehyde resins (PFR)(widely used in glues, paints, coatings, wood preservatives, adhesives of plywood and particleboard production etc) production, curing and ageing are among the major source of free-formaldehyde exposure to the environment(Brandacher et al.,2006). Presently, PFR has global annual production of >12 million tons (Leikauf,2020). Reduction in percentage of formaldehyde and finding a replacement for fossil or petroleum based phenol will greatly enhance the eco-friendliness of this resin by reducing the free formaldehyde and making the phenol absorbable into the environment without adverse effect. This is the broad objective of this proposed work. Commercial grade phenol will be boughtfrom the market;lignin will be obtained from oil palm empty fruit bunches while gluten will be extracted from wheat flour. Bench scale formation of phenol-formaldehyde resin will be conducted. Systematically based on ratio, attempt would be made to replace formaldehyde and enhance the mechanical properties with lignin and gluten (as filler). The production process will be accessed based on gel time and viscosity and free-formaldehyde values.At the end, the possibility of replacing between 80- 90% formaldehyde while still maintaining the resin desirable characteristics would be accessed and reported as the conclusion

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Materials and methods

The materials for this research were locally sourced from Awka and its environ. The lignin wasobtained from oil palm empty fruit bunch(OPEFB).The phenol was sourced from a local

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market in Ifite, Awka Anambra state. The formaldehyde was sourced from a nearby market (Ekeawka).The wheat flour was sourced from first market ifiteAwka.

Extraction of lignin

The oil palm empty fruit bunch (OPEFB) (Fig 1) was washed until clear and clean bunch fibres were obtained. The fibres were sun dried for 72 hours and thereafter dried using to bench scale laboratory drying oven. The fibres were then ground to reduce the particle size to about75µm using a mechanical grinder. This is pertinent toimprove the efficiency of lignin extraction.5g of fine OPFEB was introduced into35ml of 1.0M NaOH solution in a beaker and placed in a water bath at 100°C for 4 hours. The resultant solution was passed through a strainer, to recover theproducts.The lignin (black liquor) was separated from the cellulose and hemicellulose and stored under ambient temperature.

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Fig 1: Oil pam empty bunches for lignin extraction

Preparation of gluten

Gluten was prepared from wheat flour by gently washing the dough under a stream of running water. This removes the bulk of the soluble and particulate matter to leave a proteinaceous mass that retains its cohesiveness on stretching. In the process, 25g of wheat flour was mixed with 15 g of water. The solution was kneaded until stretchy dough was obtained. The dough was gently washed under running water for 30 minutes, where the starch content of the wheat flour was washed away, leaving behind, the stretchy material (gluten).

Preparationofunmodified P-F Adhesives

The unmodified P-F adhensive was prepared as a control to access the quality enhancements after modification.Phenol and formaldehyde were reacted in a beaker in the molar ratio of 9:1. 2ml of 0.5M NaOH solution was added into the beaker containing the PF resin and the mixture was placed in a water bath at 100°C until the resin became viscous. The experiment was repeated for molar ratios of 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8 and 1:9 and the resultant resin were characterized based on gel time,viscosity and the free formaldehyde.

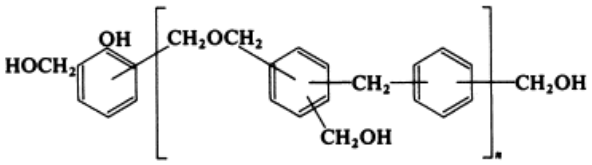

Fig 2 P-F resol resulting from P-F reaction under basic medium

Preparation of lignin - phenol formaldehyde (L-PF) resol

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P-F modification was targeted at reducing the percentage of formaldehyde and also enhancing or retaining the resin quality. L-PF adhesives were prepared by addition lignin into phenol-formaldehyde resin.The phenol was kept at a constant weight of 1g (based on the outcome of P-F study above)and reacted with varied weight of formaldehyde and lignin in ratio of 1:8, 2:7, 3:6, 4:5, 5:4, 6:3, 7:3, 8:1. Each sample was placed in a water bath at 100°C until the resin became gelled. The resultant resinswere characterized.

Preparation of phenol-formaldehyde-lignin and gluten (P-F-L-G)

The addition of Protein polymers in adhesives serve two purposes, they are good viscosity enhancers and can also work as receptors or cross-links to **improve adhesion properties.**Phenol, formaldehyde and lignin were reacted in a beaker in the molar ratio of 1:1:7 (based on the result from P-F-L) and reacted with 2ml of 0.5MNaOH solution in the beaker under controlled temperatures (100°C).Varied weight of gluten (plant based protein) ranging from 2g, 4g, 6g and 8g was added as soon as the reaction began. The mixture was monitored place until the resin became viscous.

Resol characterization

Gel time

The adhesive samples in the beaker were placed in a water bath (at 100°C) and stirred. The of time for gel formation was monitored and recorded.

Fourier Transform Infrared (FT-IR) Spectroscopy test

FT-IR spectra of both samples were performed in a Perkin Elmer model Spectrum V10 instrument. Each spectrum was recorded in a frequency range of 400–4000cm−1 using

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potassium bromide (KBr) disc. The KBr was previously oven-dried at 300°C to reduce the interference of water.

Solid content(SC)

Approximately one grams of the sample was poured into a pre-weighed dish. Dish with sample was weighed and recorded. The dish was placed in an oven with temperature set at 105°C and the specimen was dried for 3 hours. The dish was removed from oven, weighed again and recorded as dry specimen plus tare dish weight (3). The SC was calculated according to EPA 1316 standard formula.

Free Formaldehyde

Formaldehyde reacts with sodium sulfite to form the sulfite addition products and liberates sodium hydroxide (NaOH) (Lubis et al.,2017), however, at room temperature, the methanol groups present also reacts to liberate NaOH. The process was titrated at 0degrees Celsius to minimize the reaction of the methanol groups.Sufficient quantity of crushed ice was prepared for experiment (two trays of cubes). 70cm³ of 1.0M Na_2SO_3 solution was placed into a beaker. The solution was stirred and approximately 100g of crushed ice and 2g of NaCl was added. 0°C was maintained during test, and the ice was added as necessary.10-15drops of thymolphthalein indicator was added to the chilled solution. 0.1M NaOH was added until the solution turned blue; then 0.1M NHCl was added until the colorless endpoint. On the analytical balance, the amount of resin indicated under the "*Resin Sample Size*" was weighed. About 1inch of resin was poured into a 5oz plastic cup. The gross weight of the cup, resin, and disposable pipette (with the narrow tip broken off) fitted with a small rubber bulb was determined. The desired amount of resin was pipetted out into the stirring, chilled solution (approximately 1.5 to 2g per pipette-

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full).The cup, resin, and pipette with the bulb was quickly reweighed. The resultant weight loss equal the grams of resin to be ingested. The solution was rapidly titrated with 0.1M NHCl to the colorless endpoint described. The test was repeated in triplicate and the percentage free-formaldehyde(%HCHO)was calculated using ISO 11402 standard formula 2019 (Wang,et al., X.

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Viscosity

The viscosity of the resins produced were measured using a Brookfield rotary viscometer with spindle at 20±2°C.The Brookfield viscometer rotates a disc or cylinder in a fluid sample and measures the torque needed to overcome the viscous resistance to the induced movement. This is done by rotating the spindle with an electric motor, through a beryllium-copper spring. Analytical estimation was done using ASTM D1084 (Zhang et a.,2021).

Result and discussion

Effect of formaldehyde content on the production of PF resol

The effect of the formaldehyde content on the formation time of the PF resol was studied at different percentages of formaldehyde. Figure 3 shows the impactformaldehyde percentages on the gel time. It is pertinent to note from Figure 3, that increase in percentage of formaldehyde reduced the formation time of PF resol. This is attributed to the facts that increase in formaldehyde increases the free formaldehyde which in turns decreases the gel time. Similar work was reported by Zhao et al., 2018.

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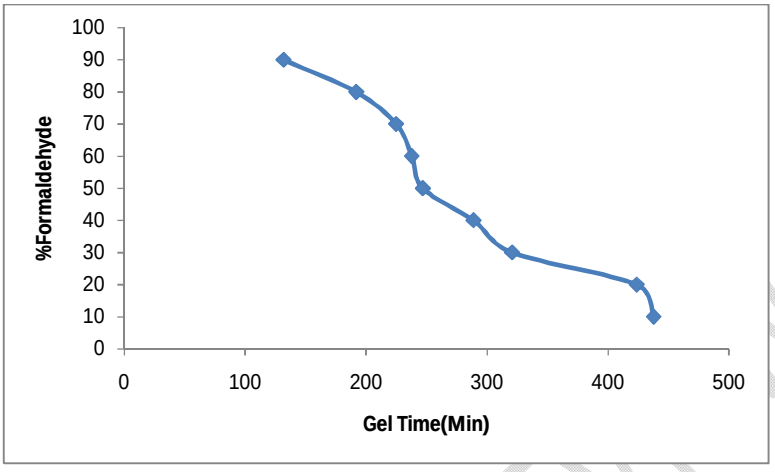

Figure 3: Effect of formaldehyde content on gel time

Effect of Phenol content on the production of PF resol

The influence of phenol content studied using different percentages of phenol is presented in Figure 4. The formation time of the resol increases with increase in the percentage of phenol. This trend results from the longer crosslink reaction needed at relatively low formaldehyde –phenol (F/P) ratio.The F/P ratio increase will result in gradual increase in the viscosity and solid content of the resin (Kotha&Khedkar, 2012).This can be attributed to the fact that formaldehyde and phenol engage in hydroxymethylation reaction at the ortho- and para- to the phenolic hydroxyl group, which in-turns leads to reduction in gel time. Hence, to achieve high F/P, the system needs to operate at reduced phenol value.(Khan et al.,2004) opined that this could be achieved by adding some bio additives such as lignin or tanin. However, increase in phenol value decreases the F/P value which results in increased gel time, which is not desirable in adhesive production. This effect is also supported using Table 1, showing clearly the variation of gel time with F/P values.

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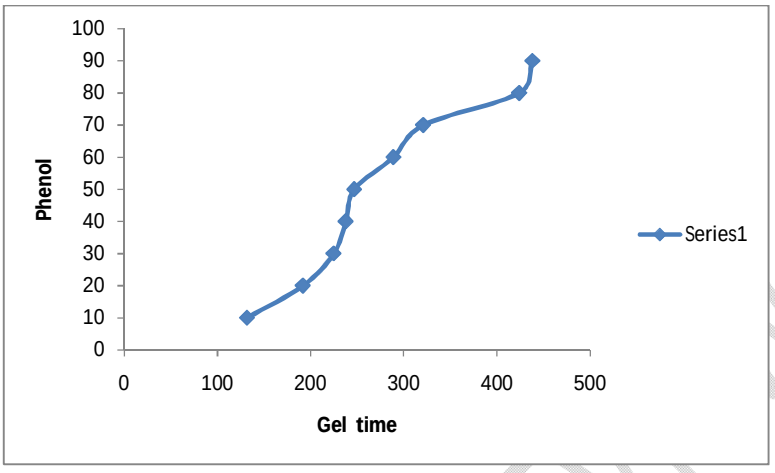

Figure 4 Effect of PF ratios on the gel time

Table 1:Effect of F/P ratio on the Gel Time

Formaldehyde (%)	Phenol (%)	F/P	Gel time (mins)
10	90	0.11	438
20	80	0.25	424
30	70	0.43	321
40	60	0.6	289
50	50	1	247
60	40	1.5	238
70	30	2.3	225
80	20	4	192
90	10	9	132

Table 1 also shows that the least formation time (gel time) was obtained at PF ratio of 1:9. The PF resol obtained at that ratio (1:9) were characterized for solid content, viscosity and free formaldehyde, while the present functional group were obtained using Fourier transform infrared spectroscopy(FTIR). Table 2, below presents the properties of the produced PF resol.

Table 2: Properties of PF resol

SC(%)	Viscosity(mPa.s)	Free formaldehyde(%)

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84.05	1103.5	0.38

From the table above, it was observed that the produced PF resol has high solid content of 84.05%. This solid content was observed to be high compared with most available works (Zhao et al.,2016). High solid content is desirable in adhesives. It influences the drying time, moisture effect and helps in providing more adhesive coverage on the material being bonded. The resol viscosity of 1103.5mPa.s was obtained which is within the standard viscosity for a standard conventional adhesive (El Mansouri et al.,2018).This high viscosity is due to the very high amount of solid content in the resin, it has been observed that increase in solid content equally increases the viscosity (Allegra, et a.,2019).The free formaldehyde (FF) was found to be 0.38%. This FF is above the allowable standard of 0.05% (Li, 2016). The resol with FF of 0.38% will pose adverse challenge on both human and environment due to high formaldehyde emission when used for wood work. Exposure of formaldehyde to human can lead to myeloid leukemia(Allegra, et a.,2019). Hence, though other properties of the produced resol meet the conventional standard, the PF resol needs modification in order to bring the FF to an acceptable standard.

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FTIR analysis of PF resol

The functional groups present in PF resin of F/P ratio 1:9 obtained using FTIR analysis of the FTIR pattern (spectra) in Fig 5 are presented in Table 2. The FTIR spectra of the recovered resolpresent 12 prominent peaks. The peaks assignment to the prominent peaks is shown in Table 2peaks within 3655- 3466cm-1 represent phenolic OH stretch, 3269.84 tensile vibration of –CH2 group was found at 3269.84cm-1.C-C aromatic ring stretch at1660.606cm-1,alkyl-phenol C-O stretch andsemicircle ring stretch at 1424.84 cm-1 and 1209.9cm-1 respectively.

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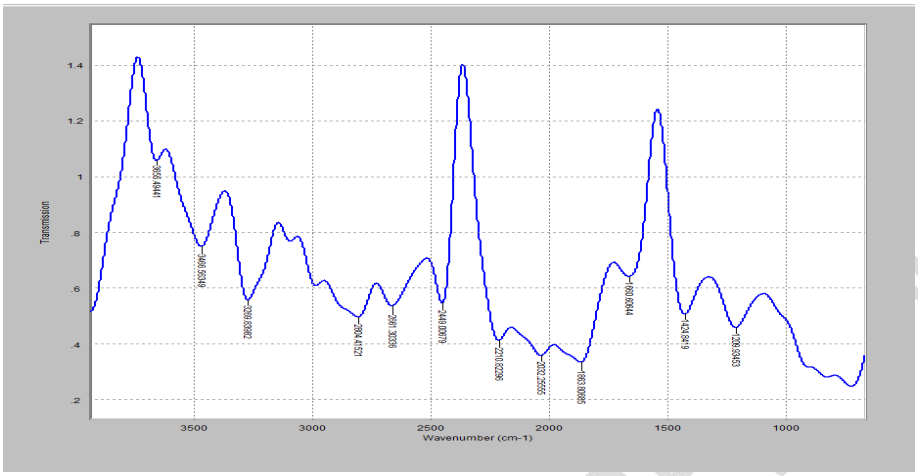

Figure 5: FTIR S Spectra of PF resol

Table 2: FTIR transmission and their peaks areas

Transmission	Wave number cm^{-1}	Functional group
48.60717	1209.9355	alkyl-phenol C-O stretch
79.95325	1424.842	Semicircle ring stretch
36.10268	1660.606	C-C aromatic ring stretch
325.426	2804.415- 2616	Aliphatic-CH2 asymmetric stretch
159.6944	3269.84	tensile vibration of –CH2
151.8069	3466.563	phenolic -OH stretch
11.78203	3655.494	phenolic -OH stretch

Modification of PF Resol

The PF resol was modified to improve its quality in terms of gel time and FF reduction. Lignin extracted from palm bunch was added in different percentages(10-90%), the phenol content were

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kept constant at 10% while the percentage of formaldehyde were varied as well (10-90%). The result obtained are presented in Table.3

Table 3: Effect of Lignin addition on the formation PF resin

Formaldehyde (%)	Lignin (%)	Phenol (%)	Gel time (min)
10	80	10	152
20	70	10	131
30	60	10	147
40	50	10	159
50	40	10	124
60	30	10	149
70	20	10	157
80	10	10	154

Table 3 shows the effect of PF modification using the bio-based lignin. From Table 3, it can be observed that the lignin-phenol-formaldehyde formulation significantly affected the formation time positively. There was general reduction in gel time. The highest gel time for PF without modification was 438min, while upon modification, the highest time observed was 152min. The best gel time of 124min was observed at 40-10-50 lignin-phenol- formaldehyde ratio. However, the formaldehyde level was still high; hence, the LPF combination with low formaldehyde (70-10-20%) and relatively low gel time (131min) were chosen over 40-10-50 resol. To ascertain the quality of the recovered LPF resol (modified resol), the resol was characterized and compared with the produced PF resin quality and other resins obtained from literature. The properties of the resins are presented in Table 4.

Table 4: Properties of different compared resols

	SC (%)	Viscosity (mPa.s)	Free-formaldehyde (%)	References
PF	84.05	1103.5	0.38	This work
PF	76.6	658	0.19	Zhao et al.,2018

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LPF	66.83	768.2	0.12	This work
LPF	24.7	0.4	0.5	Kalami, 2017
PF	27.9	0.28	0.39	Kalami,2017
LPF	42.5	420	0.04	El Mansouri et al.,2018
LPF	41.3	330	0.03	El Mansouri et al.,2018

From the table above, it was observed that solid content (SC) was 66.83%. This value was observed to be high as well, though not up to the SC of PF resin but within the standard SC for conventional adhesives (50%) (Zhao et al.,2018). This reduction in SC also transcends to equivalent reduction in viscosity as the viscosity of the recovered resol reduced to 768. 2 mPa.s compared with most available works (Zhao et al., 2018). Introduction of lignin also yielded the desired effect. The reduction in formaldehyde usage was achieved which resulted in approximately 69% reduction in free formaldehyde. Comparing with most works cited, the LPF recovered is better than some presented (Table 4). However, El Mansouri et al., 2018 reported a lower FF than the one recovered from this work. The analysis of FTIR spectra of LPF resin (Fig 6) was also compared with the PF spectra(Fig 5) to ascertain the modification in the present functional groups due to addition of lignin.

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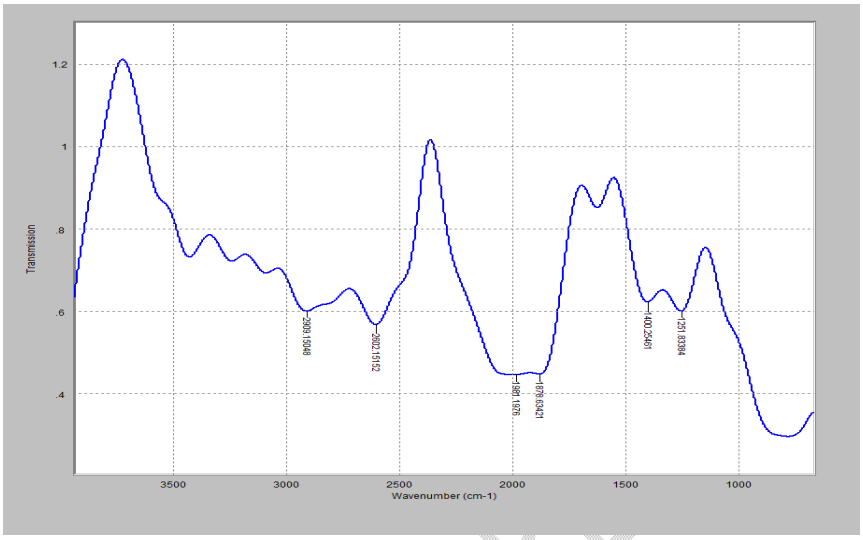

Fig 6: FTIR spectra of modified LPF

Reduction in number of prominent peaks was observed. 6 moderately broad peaks were obtained from the FTIR spectra of LPF resol. The peaks and their assign functional groups are shown in Table 5.

Table 5: **FTIR peaks for LPF and their functional groups**

Transmission	Wave number cm^{-1}	Functional group
0.6	2909.15048 - 2602.15152	in-plane and out-of-plane stretching of aliphatic -CH_2-
0.43	1961.1978- 1878.63421	C=O stretching
0.61	1400.25461	Presence of methylene bridges
0.6	1251.83384	In-plane vibration of C-O of

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phenolic group

4.4. Further modification of resol using gluten

Attempt was made to for further reduce theformaldehyde and possibly the FF using gluten and to observe the effect of this further modification on the gel time.Table 6 presents the resultobtained from this modification.The percentage of lignin, formaldehyde and phenol were maintained at 70, 20, and 10 while gluten was added in grams.

Table 6: Effect of gluten on modified LPF resols

Formaldehyde (%)	Phenol (%)	Lignin (%)	Gluten (g)	Gel time (min)
20	10	70	2	117
20	10	7 0	4	95
20	10	70	6	115
20	10	70	8	102

From table 6, addition of gluten further reduced the gel time.The best gel time was found to be at 95 minutes. The best resol obtained was characterized and presented in Table 7.

Table 7: Showing characterized resol

SC (%)	Viscosity (mPa.s)	Free formaldehyde (%)
74.32	169.7	0.08

From the Table 7, it was observed that gluten addition resulted to increase in the solid content of the resol. The viscosity was equally found to be within acceptable range of been greater than as cited from previous work (Kalami,2017).The free formaldehyde was equally found to be within acceptable range, the free formaldehyde at 0.08% is within the range of acceptable range.

Conclusion

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The modification of phenol-formaldehyde resol was successfully carried out. The present modification reduced the phenolic content, formaldehyde content and the free formaldehyde. The gel time was a function of phenol content, and was also lowered by introduction of lignin. Further modification with gluten further reduced the free formaldehyde. Hence, it can be concluded that lignin and glutin modification is an effective means of reducing the percentage of phenol and formaldehyde needed for adhesive production.

References

Allegra, A., Spatari, G., Mattioli, S., Curti, S., Innao, V., Ettari, R., &Musolino, C. (2019). Formaldehyde exposure and acute myeloid leukemia: a review of the literature. *Medicina*, *55*(10), 638.

Asim, M., Saba, N., Jawaid, M., Nasir, M., Pervaiz, M., &Alothman, O. Y. (2018). A review on phenolic resin and its composites. *Current Analytical Chemistry*, *14*(3), 185-197.

Brandacher, G., Winkler, C., Schroecksnadel, K., Margreiter, R., & Fuchs, D. (2006). Antitumoral activity of interferon-γ involved in impaired immune function in cancer patients. *Current drug metabolism*, *7*(6), 599-612.

Isa, A., Nosbi, N., Che Ismail, M., MdAkil, H., Wan Ali, W. F. F., & Omar, M. F. (2022). A review on recycling of carbon fibres: methods to reinforce and expected fibre composite degradations. *Materials*, *15*(14), 4991.

Jędrzejczak, P., Collins, M. N., Jesionowski, T., &Klapiszewski, Ł. (2021). The role of lignin and lignin-based materials in sustainable construction–a comprehensive review. *International Journal of Biological Macromolecules*, *187*, 624-650.

Kalami, S., Arefmanesh, M., Master, E., &Nejad, M. (2017). Replacing 100% of phenol in phenolic adhesive formulations with lignin. *Journal of Applied Polymer Science*, *134*(30), 45124.

Kalami, S., Chen, N., Borazjani, H., &Nejad, M. (2018). Comparative analysis of different lignins as phenol replacement in phenolic adhesive formulations. *Industrial Crops and Products*, *125*, 520-528.

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UNDER PEER REVIEW

Khan, M. A., Ashraf, S. M., & Malhotra, V. P. (2004). Development and characterization of a wood adhesive using bagasse lignin. *International Journal of Adhesion and Adhesives*, *24*(6), 485-493.

Kotha, S., &Khedkar, P. (2012). Rongalite: a useful green reagent in organic synthesis. *Chemical Reviews*, *112*(3), 1650-1680.

Leikauf, G. D. (2020). Formaldehyde and other saturated aldehydes. *Environmental Toxicants: Human Exposures and Their Health Effects*, 555-626.

Li, C., Zhang, J., Yi, Z., Yang, H., Zhao, B., Zhang, W., & Li, J. (2016). Preparation and characterization of a novel environmentally friendly phenol–formaldehyde adhesive modified with tannin and urea. *International Journal of Adhesion and Adhesives*, *66*, 26-32.

Lubis, M. A. R., Park, B. D., & Lee, S. M. (2017). Modification of urea-formaldehyde resin adhesives with blocked isocyanates using sodium bisulfite. *International Journal of Adhesion and Adhesives*, *73*, 118-124.

Mahandra, H., Wu, C., &Ghahreman, A. (2021). Leaching characteristics and stability assessment of sequestered arsenic in flue dust based glass. *Chemosphere*, *276*, 130173.

Sarika, P. R., Nancarrow, P., Khansaheb, A., & Ibrahim, T. (2020). Bio-based alternatives to phenol and formaldehyde for the production of resins. *Polymers*, *12*(10), 2237.

Zhang, F., Zhang, L., Muhammad, Y., Cai, Z., Guo, X., Guo, Y., & Huang, K. (2021). Study on preparation and properties of new thermosetting epoxy asphalt. *Construction and Building Materials*, *311*, 125307.

Zhao, S., Wang, Z., Kang, H., Li, J., Zhang, S., Han, C., & Huang, A. (2018). Fully bio-based soybean adhesive in situ cross-linked by interactive network skeleton from plant oil-anchored fiber. *Industrial Crops and Products*, *122*, 366-374.

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