



CHARACTERIZATION AND PERFORMANCE EVALUATION OF BIO-BASED PHENOL FORMALDEHYDE RESINS FROM *Detarium senegalense* J.F. Gmel BARK

¹Olayiwola Y.B, ²Fasina O, ³Oluyeye A.O, ³Lajide L and ⁴Olayiwola V.A.

¹Federal College of Forestry, Ibadan, Nigeria. ²Auburn University, Alabama, U.S.A

³Federal University of Technology, Akure, Nigeria. ⁴Forestry Research Institute of Nigeria.

Email: yetundebolarinwa@yahoo.com, Phone: 07034545446, 07031088599.

ABSTRACT

This study explores production of bio-phenolic compounds from bark of *Detarium senegalense* (forest biomass) via the solvolysis liquefaction method, which was aimed at substituting the petroleum-based phenol with the bio-phenolic compounds and subsequently producing high quality liquefied bio-based phenol formaldehyde resins (LBPF) resole. The bio-oil obtained from the direct solvolysis liquefaction of *D. senegalense* bark, was successfully incorporated into the synthesis bio-oil phenol formaldehyde (LBPF) resins up to 75 percent replacement by weight substitution for phenol. The result of physical and mechanical properties of the LBPF resol resins indicated that it had higher molecular weights, higher polydispersity indices and shorter gel time(s) than the laboratory synthesized and commercial PF resin without the bark components. The experimental LBPFs were applied as adhesives in the production of laboratory scale particle boards, then the tensile strengths was evaluated. Internal bond strengths of LBPF resins up to 75 percent replacement by weight exceeded or were still comparable to those of the commercial PF resin. Also, the tensile strengths of the bonded panels with the LBPF resins up to a high value of 75 percent replacement by weight of F/P ratio exceeded or were comparable to that of the commercial PF resin adhesive.

Conclusively, all the LBPF resin-bonded particle board panels gave comparable tensile strengths to those of the conventional PF adhesive.

Keywords: Synthesis, Liquefied bio-phenol formaldehyde resins, Solvolysis liquefaction, *Detarium senegalense* bark, Particle Board.

Introduction

Worldwide, there has been growing concerns about ways to efficiently utilize forest trees, residues and underutilized tree species. Efficient utilization of these resources will reduce the burden of overdependence on conventional trees species used for lumber and structural applications. Wood composite engineering makes this possible. (Kreibich; 1984.)



Composite panels which include particleboard, oriented strand board, plywood, laminated veneer lumber (LVL) have become more desirable and attractive to use because they combine material properties in ways not found in natural designed materials such as lumber. Common adhesives used for binding wood materials in the composites industry include phenol formaldehyde (PF), urea formaldehyde (UF), diphenylmethane diisocyanate (MDI) and melamine urea-formaldehyde (MUF).

Phenol-formaldehyde (PF) resins are widely used as adhesives (Amen-Chen, *et al.*, 2002 (a), 2002 (b) Alma, *et al.*, 2006; Wang, *et al.*, 2009 (a)). In the wood products industry for the manufacture of plywood, oriented strand board (OSB), particleboard, fiberboard, other composite products, and molded products (Alma, 1996, 1997; Shiraishi, *et al.*, 1993) because of its high strength and moisture resistance. Phenol as the most costly chemical raw material for the synthesis of PF resins is primarily produced from petroleum-derived benzene by the cumene process developed by Hock. *et al.*, 1944. Depleting petroleum resources combined with increasing demands for petroleum by developing economies as well as political and environmental concerns over fossil-based resources has intensified the interest in researching and developing alternative renewable resources for both energy and chemical production. (Russel, *et al.*, 1985).

Forest/agricultural biomass or residues are lignocellulosic materials containing about 10-35 wt% lignin, 35-45 wt% cellulose and 15-35 wt% hemicelluloses (Gani and Naruse, 2007; Bridgwater and Peacocke, 2000; S'anchez, 2009; USDA Forest Service Research Note, 1971). Lignin is the second most abundant polymer found in nature and a major waste product of the paper industry (50 million tons produced per year). Lignin is an amorphous macromolecule comprised of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked together by condensed linkages (such as, α -1, β -5, 5-5 and β -1 linkages) and ether linkages (such as., 5-O-4, α -O-4 and β -O-4). This macromolecule can be decomposed/de-graded into the oligomeric and monomeric phenolic compounds through thermochemical technologies such as hydrolysis, pyrolysis and direct liquefaction (Kleinert, *et al.*, 2009; Wang. *et al.*, 2009; Liu and Zhang, 2008; Bridgwater, 2004; Amen-Chen, *et al.*, 2002). In this regard, lignocellulosic biomass can be a potential source of bio-phenolic compounds to replace petroleum-based phenol in the production of PF resins.

Detarium senegalense is one of the lesser-utilized tree species that is presently finding its way to our timber market as a potential valuable wood for various end uses. Among the properties that will qualify the bark of a wood as a potential raw material in the developing biorefinery and tannin industries are the percentage of the bark they contain and the extent of within and between species variation in bark percentages.

Among ten (10) tropical hard wood species studied for variation of their barks percentages within trees of the same species and those of different species, *D. senegalense* performed best (Ogunwusi, 2013). When bark percentages are too low, its use for production of bark chemicals



may not be economical (Ogunwusi, 2013; Harkin and Rowe, 1971). However, if the woods are only to be sawn and used for planks production, the lower the percentage of bark in the species the better. High bark percentage reduces the volume of usable wood and adds to the transportation cost. Therefore high bark percentage in *D. Senegalense* is an advantage since the interest is to explore it for chemical production. This has necessitated this study whose broad objective was to utilize the bark components from *D. senegalense* as a partial substitute for petroleum-based phenol with a high bio-oil substitution ratio (> 50 wt%); to formulate LBPF, and to obtain a desirable resin performance which includes higher adhesive strength for particle board production and lower thermal curing temperatures during curing of the resins for minimal energy input purposes.

MATERIALS AND METHOD

Materials

The solvents and chemicals used in this study were distilled water, ACS reagent-grade ethanol, acetone, Solid phenol crystal, sodium hydroxide solution, formaldehyde, Commercial PF resin. (All obtained from Fisher Scientific, Fair Lawn NJ) The biomass used in this study was bark of *Detarium senegalense* obtained from a local sawmill in Ibadan. Reliable information from the sawmilling was that the log was collected from Onigambari reserve. Onigambari Forest Reserve is located on latitude 70 25' and 70 55'N and longitude 30 53' and 30 9'E within the low land semi-deciduous forest belt of Nigeria and covers a total land area of 17,984ha.

Method

The bark samples of *D. senegalense* was hammer milled (New Holland grinder model 358, New Holland, PA) with 3.175-mm (1/8 in.) sieve size for particle reduction. It was then oven dried at 105⁰C for 2hrs. Elemental composition of carbon, hydrogen, nitrogen, and sulfur in the *D. senegalense* samples were analyzed with a CHNS Flash Elemental Analyzer 1112 series and using helium as a carrier gas also the compositional analysis for its contents of cellulose, hemicelluloses and lignin test were done in accordance to the TAPPI test method T249cm-85 (for cellulose and hemi-cellulose).

Preparation of phenolic bio-oil from woody biomass by direct liquefaction

The liquefaction of the hammer-milled *D. senegalense* bark was carried out in a 1000 mL stainless steel autoclave reactor equipped with a stirrer and a water-cooling coil. Liquefaction procedure of Chen. *et al.*, (2011) was followed



Synthesis of BPF resole resins using DS derived bio-oil

Synthesis of the bio-based adhesive was carried out by loading 294.12 g of phenol and 588.24 g of formaldehyde (from formalin) into a 500 ml round bottom flask equipped with refluxing condenser. The content of the flask was homogenized for about 15min using a magnetic stirrer. The flask was immersed in a glycerol oil bath. The temperature of the oil bath was maintained at 80° C. 117.65 g of 50 % NaOH (w/w) was added at 15 min interval. Following each addition of sodium hydroxide the temperature was decreased by a 10°C. The reaction was terminated by rapidly cooling the mixture to 25° C after 90 minutes. The experiment was repeated for 25 %, 50 %, 75 % and 100 % phenol replacement. The weight in gram of Formaldehyde, Phenol and Sodium Hydroxide at each percentage level of oil- phenol replacement were calculated by the formula.

$$\text{Mixing Ratio} = A \times \frac{F}{F+P+NaOH} \quad (\text{Gardziella et al, 2000}) \dots\dots\dots \text{Equation 1}$$

Where: **A** is the formulation in 1000 ml standard solution, **F** is Formaldehyde, **P** is Phenol and **NaOH** is Sodium Hydroxide. The addition of formaldehyde, phenol and Sodium hydroxide (that is **F + P + NaOH**) is in the ratio of **2: 1: 0.4**

The weight in gram calculated for each ingredient was used in the formulation of 1000 ml solution

Lab PF and commercial PF resins

In order to understand how the bark phenolic compounds affect the resulting resin properties, a laboratory made control PF resin (lab PF) without bark components was prepared by following exactly the same reaction steps used for the synthesis of bio-based PF resins (**Table 1**).The conventional commercial phenol formaldehyde is used as control for the study.

Characterization of bio-based PF resins

pH, viscosity, solids content, gel time, of the bio-based PF resins

pH values of the resins were measured at 25°C. The viscosity of the resins was measured using a Brookfield rotary viscometer with spindle 3 at 25°C. Solids content measurement was according to (ASTMD3529:2003).Gel time was measured by charging 1g of resin into a 16-mm wide test tube and heating the test tube in an oil bath at 120±1°C. An average value of three replicate measurements was reported.

Molecular characteristics: Weight average molecular weight (Mw), number average molecular weight (Mn) and polydispersity index (Mw/Mn) of the extractives were measured by a Matrix-Assisted Laser Desorption/Ionization-Time-of-Flight/Time-of-Flight spectrometer (MALDITOF/TOF), Biosystems, Eng. Dept. Auburn Uni. AL. USA.



Preparation/ production of Experimental wood particleboard

Mixing of the ingredient

To prepare each panel of 750 kg/m³ density, prepared *Gmelina arborea* sawdust were weighed using the formula

$$\text{Density}(\text{gcm}^3) = \frac{\text{mass}(\text{g})}{\text{volume}(\text{cm}^3)} \dots\dots\dots\text{Equation (2)}$$

$$\text{Volume} = \frac{(250\text{mm} \times 350 \text{ mm} \times 12.5 \text{ mm})}{1,000} = 1093.75 \text{ cm}^3$$

$$0.75 = \frac{\text{mass}}{1093.75}$$

Therefore, Mass = 820.31g.

Eight hundred and twenty grams (820.31 g) by weight of the sawdust were further oven dried to obtain the weight on oven-dried basis; which was 805.5grammes. The resin used was calculated based on the oven-dried weight of the sawdust (10% by weight of the saw-dust) other additives were: Ammonium chloride, NH₄Cl (Hardener) 2% of the weight of the oil, Water 0.4% of the weight of the oil. These additives together with the saw-dust (weighed on oven-dried basis); were blended together thoroughly in mixing container to ascertain even distribution of adhesive on the particles.

Mat formation

After blending, the randomly oriented sawdust was carefully felted into the 250 mm x 350 mm X 12.5mm mould to form the mat.

Hot pressing/trimming of the board and conditioning

The mat was then hot pressed using a Wabash Hydraulic Press (Model 150-25-2TMAC, Wabash Metal Products Company, Inc.) Auburn university; into a target thickness of 12.7 mm (1/2 in.) guided by two rectangular steel stops. The boards were first pressed at 138 °C (280 F) to a maximum pressure of 65,500 kPa (9500 psi) for 2 min. The pressure was then gradually released resulting in a total press cycle time of 7 min. After hot pressing, all boards were cooled at room temperature followed by trimming the rough edges of one after the other. Similar method was used to produce all the boards for the study.



Particleboards evaluation

The particleboards were trimmed to 250 mm x 350 mm x 12.5mm. The boards were tested according to the standard of A208.1 (ANSI/A208.1, 1999) - Standard test methods for evaluating properties of wood-base fibre and particle panel materials). Internal bond strength (IB), thickness swell (TS), Water absorption (WA). Internal bonding strength test was performed on Zwick Roell Universal Testing Machine at the Centre for bio-products and renewable energy (Auburn University, USA); the crosshead speed was 1.3mm/min. The average values based on a minimum of 3 replicates were reported. The experimental design that was adopted was a Completely Randomized Design. Follow-up test was conducted with the use of Least Significant Difference Test (LSD). This was done to compare the mean

RESULTS AND DISCUSSION

Table 1: Formulation in 1000ml Standard Solution (A)

| | Replacement by Weight (g) | | | |
|-------------------------|---------------------------|-----------|-----------|----------|
| | LAB LBPF | 25 % LBPF | 50 % LBPF | 75% LBPF |
| Comm. Phenol (P) | 294.1 | 220.59 | 147.06 | 73.53 |
| Bio-oil | 0.00 | 73.53 | 147.06 | 220.59 |
| Formaldehyde (F) | 588.24 | 588.24 | 588.24 | 588.24 |
| NoaH | 117.65 | 117.65 | 117.65 | 117.65 |

Table 1 shows the formulation of the bio-phenol formaldehyde resin at various percentages replacement by weight. The mixing ratio given in equation 1 was used in the calculation.



Table 2: The result of the physical properties of LBPF resole resin.

| | pH | Solids content (%) | Viscosity at 25°C (cP) | Gel time at 120 °C (s) | Mn (Da) | Mw (Da) | Mw/Mn |
|----------|-------|--------------------|------------------------|------------------------|--------------------|--------------------|-------|
| 25% LBPF | 11.68 | 47.90 | 800 | 58 | 3.82×10^2 | 7.76×10^2 | 2.03 |
| 50% LBPF | 11.88 | 48.24 | 700 | 61 | 3.07×10^2 | 8.72×10^2 | 2.84 |
| 75% LBPF | 11.84 | 46.44 | 450 | 65 | 3.63×10^2 | 9.43×10^2 | 2.60 |
| Lab PF | 11.93 | 48.87 | 25 | 173 | 2.59×10^2 | 3.27×10^2 | 1.25 |
| Com PF | 11.16 | 59.00 | 200 | 172 | 2.12×10^2 | 3.86×10^2 | 1.82 |

(Lab PF: Laboratory made PF resin; Com PF: Commercial PF resin; LBPF: Liquefied Bark Phenol Formaldehyde resin, Weight average molecular weight (Mw), Number average molecular weight (Mn) and Polydispersity index (Mw/Mn))

The properties of the synthesized resins are shown in **Table 2**. The pH values for the liquefied bark-PF resins and the lab PF resin were similar. The solids content of the LBPFs were lower than the solids content of the commercial PF resin (59.00%), but was higher than the solids content of the lab PF resin (48.87%). It is known that commercial PF resins for particleboards production contain significant amounts of urea. This is why it has a very high solids content.

Even though the same synthesis procedure was followed, the LBPF resins had higher viscosities, higher molecular weights (Mw and Mn) and higher polydispersity indices (Mw/Mn) than the lab and commercial PF resin. This could be the result of the presence of some larger molecular compounds, that is, degraded bark components in the liquefied bark fraction. The low viscosity, low Mw and low polydispersity index of the lab PF resin (25 cp) indicated that this resin had a low degree of polymerization, which also explained why its solids content was lower than those of liquefied bark-PF resins.



The LBPF resins had the shortest gel time when compared to the lab and commercial PF resins. The shorter gel time does not mean that LBPF resins have faster cure rates than the PF resins. Empirically, gel time can sometimes give indications about resin cure rates but conclusions should not be drawn on gel time alone. Phenolic resin gelation can sometimes be a physical phenomenon (reversible gelation) instead of a chemical one (irreversible gelation).

Table 3. The properties of particleboards made using LBPFs resin adhesives

| Properties | PF's and LBPF'S replacement by weight (%) | | | | |
|---------------------------------|---|-----------|-------------|-------------|-------------|
| | Comm PF | Lab PF | 25% LBPF | 50% LBPF | 75% LBPF |
| Density (g cm ⁻³) | 0.740 | 0.736 | 0.744 | 0.745 | 0.748 |
| Internal bonding strength (MPa) | 0.45 | 0.58 | 0.59 | 0.52 | 0.44 |
| Thickness swelling 72hrs (%) | 25.35 | 17.84 | 21.61 | 19.86 | 26.01 |
| Water absorption 72hrs (%) | 7.36 | 6.96 | 6.83 | 6.72 | 7.27 |

Table 4. The property requirements, as specified by the American National standard for Particleboard A208.1 (ANSI/A208.1, 1999), for M-2 grades of particleboard products.

| Grade ^a | MOR (MPa) | MOE (MPa) | Internal Bonding (Mpa) | Hardness (N) | Linear expansion Max. avg (%) | Screwholding (N) | | Formaldehyde maximum emission (ppm) |
|--------------------|--------------|--------------|------------------------------|-----------------|--|---------------------|------|--|
| | | | | | | Face | Edge | |
| M-2 | 14.5 | 2225 | 0.45 | 2225 | 0.35 | 1000 | 900 | 0.30 |

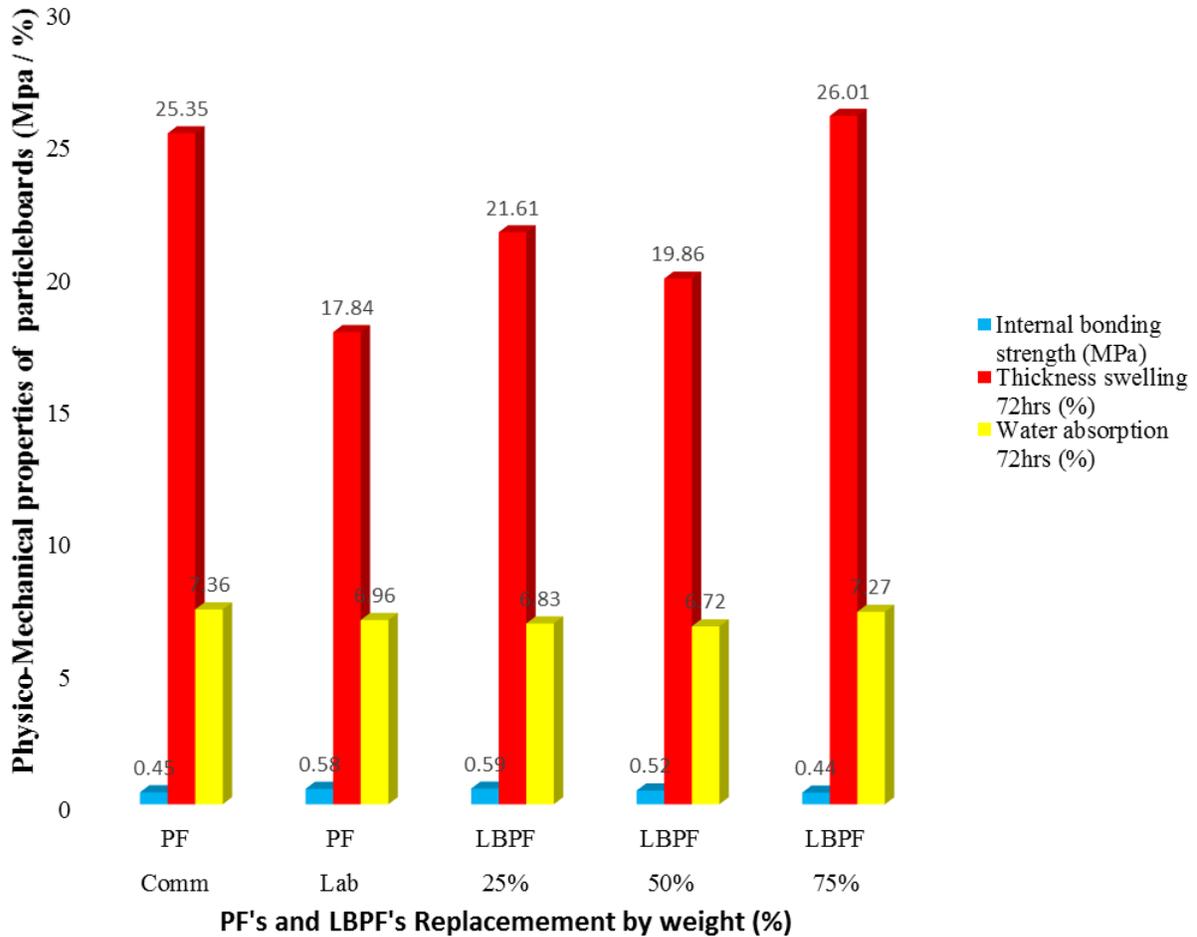


Figure 1. Properties of particleboard using LBPF Resins

The result of the physical and mechanical properties of the panels produced from the formulated LBPF resin was presented on **Table 3** above. The board density was 750Kg/m^3 .

The result of the Internal bonding strength on **Table 3 and Fig.1** above revealed that 75 % LBPF resin behaves in almost the same manner as the commercial which has internal bonding strength of 0.45, followed by 50 % LBPF replacement with the value of 0.52, this is followed by 25 % PPF replacement with value of 0.58. Laboratory made LBPF had the highest internal bonding strength value of 0.58; which is in line with the properties requirement for particleboard production as specified by the America National Standard for particle board. (**Table 4.**); also the work of Cheng, *et al.*, (2011) where they incorporate OLPF resin at 25 %, 50 % and 75 % PF replacement level, and the resultant resin were used as plywood binder where phenol replacement ratio up to 75 percent replacement by weight showed higher tensile strengths than that of conventional PF resin. Although the OLPF adhesives have better bond strengths and thermal stability than DLPF



adhesives, the DLPFs have lower free formaldehyde content and can be cured at a lower temperature.

Also the result of the analysis of variance for the internal bonding strength shows that there is significant difference among the adhesives formulations at different percentages, which suggest that the concentration of the adhesives at different formulation percentages has effect on the result obtained.

Also, from **Table 3** the mean values obtained for water absorption 72hrs for the LBPF formulated at different percentages it was observed that commercial (control) has the highest value of 7.36 followed closely by the lab made LBPF with value of 6.98, followed by 75 % LBPF replacement with value of 7.27. Twenty-five (25) % LBPF replacement has the next value of 6.83, followed by 50 % LBPF replacement had the least value for water absorption- 6.72. Consequently, analysis of variance conducted reveals that there is significant difference in the water absorption (72hrs) among the formulated adhesives at different percentages, which suggest that concentration of the formulation adhesives at different percentages has effect on the result obtained. This result may suggest that the hydrophilic nature of some compounds in the liquefied bark may be responsible for less water-resistant resins in comparison with the commercial resins. However, these hydrophilic compounds contribute or add cohesiveness to the resin as demonstrated in the IB results, which are quite high. It is possible that the hydrophilic compounds are cellulose-derivatives in their monomeric or oligomeric state.

The result of the mean thickness swelling 72hrs on **Table 3** also reveals that 75 % LBPF replacement has the highest value of 26.01, followed by commercial (control) which has value of 25.35; this is followed by 25 % LBPF resin replacement with values of 21.61. Fifty (50) % LBPF replacement has the least value of 19.86. The laboratory made LBPF had the least value of 17.84. The result of their analysis of variance reveals that there is significant difference among the adhesives formulated at different percentages that is the concentration of the adhesives at different formulation percentages has effect on the result obtained. It has been reported that higher thickness swelling is related to higher internal bonding of panels (Wu and Piao 1999). Since thickness swelling is the consequence of compression stress relief due to deformation of the mattress, moisture pick-up from the surroundings and from degradation of inter-particle bonding due to the combination of the processing temperature used and resin bonding quality

These suggested that such bark extractives could replace up to 75 % of phenol to make bark LBPF resins without significantly reducing the bond strength. Good strength of the bark extractive-PF resins 75 % replacements of phenol could be attributed to the catechol moiety of the tannins in the bark extractives (Sowunmi, *et al.*, 1996; Li, *et al.*, 2004). These preliminary results indicates that homogenous panel could be produced with 75 % LBPF replacement at this level, to yield the highest dry IB, attained one of the best water absorption and thickness swelling when compared with commercial produced under the same condition. Consequently its ability to savage the cost factor in phenol while maintaining a workable viscosity.



Conclusion and Recommendations

The LBPF resins made from *Detarium senegalense* bark have higher average molecular weights, higher polydispersity indices and shorter gel times than the lab and commercial PF resins. The viscosities of the LBPF resins were higher than the viscosity of the lab PF resin, but lower than the viscosity of the commercial PF resin. All these resins had similar bonding strengths. LBPF from *D. senegalense* are suitable to be used as an alternative to petroleum-based phenol in the formulation of bio-based phenolic resole resins for use as particleboard binder. The bio-based PF resins at 75 % bio-phenol replacement by weight had comparable bonding strength and curing performance to the commercial PF resins with good promises for industrial utilization.

It is therefore recommended that further research could be made in the area of bio-based PF resins improve performance of the bio-based PF resins in other to facilitate their future applications and commercialization. It would be worthwhile to explore barks from other lesser utilized tree species, single bark species and multiple bark species mixtures are worth to be investigated. Also, optimizing the formulation recipes and synthetic conditions for the bio-based PF resole resins to improve their performance will be of interest. Different molar ratios of the raw materials, various phenol substitution levels, and Liquefied bark from various liquefaction conditions, LBPFs from various extraction conditions, different cooking temperature and cooking time etc. should also be further researched. It would be of great importance to investigate free formaldehyde emission of the bio-based PF resole resins and conduct economic analysis and life cycle assessment on this novel green adhesive.

REFERENCES

- ANSI A 208.1-(1999) -American Nationals standard for Particleboard products.
- ASTM D103796a (standard test methods for evaluating properties of wood-base fiber and particle panel materials).
- ASTM D3529 / D3529M - 97(2003) Standard Test Method for Matrix Solids Content and Matrix Content of Composite Prepreg
- Amen-Chen C, Riedl B and Roy C. (2002 (a)): Softwood bark pyrolysis oil–PF resols–Part 2. Thermal analysis by DSC and TG. *Holzforschung*. 56: 273–280.
- Amen-Chen C, Riedl B, Wang X and Roy C. (2002) Softwood bark vacuum pyrolysis oil–PF resols for bonding OSB Panels. Part III. Use of propylene carbonate as resin cure accelerator. *Holzforschung* (b), 56: 281–288.
- Alma MN. (1996)Several acids-catalysed phenolation of wood and its applications to molding materials. Ph. D. Dissertation. Kyoto University. Kyoto, Japan.



- Alma MN (1997): The use of wheat straw-phenol condensation products as molded materials. *J Polym Eng.*, 17: 311–322.
- Alma MH, Basturk MA and Shiraishi N. (2006): Cocondensation of NaOH-catalyzed liquefied wood wastes, phenol, and formaldehyde for the production of resol-type adhesives. *Ind Eng Chem Res.*, 40: 5036–5039.
- Bridgwater AV, and Peacocke (GVC). Fast pyrolysis processes for biomass. *Renew Sust Energ Rev.*, 4(1): 1–73.
- Cheng S, D’cruz I, Wang M, Leitch M and Xu C. Highly efficient liquefaction of woody biomass in hot-compressed alcohol-water co-solvents. *Energy Fuel.* 2011, 24 (9): 4659–4667.
- Gani A and Naruse I (2007). Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. *Renew Energy.* 32(4): 649–661.
- Gardziella, A., Pilato, L and Knop, A. (2000): Phenolic resins: Chemistry, applications, standardization, safety, and ecology. (Springer Verlag).
- Harkin, J.M. and Rowe, J.W; (1971): Bark and its possible uses, Forest Research Note-091, 4 056-9 71, Forest Products Laboratory, Forest Service, U.S. Department of Agriculture
- Hock H, Lang S. *Ber Dtsch Chem* (1944) Ges. B77, p. 257.
- Kleinert M and Barth T (2008). Phenols form lignin, *Chem Eng Technol*, 31: 736-745.
- Kreibich R.E., (1984): Wood Adhesives: Present and Future (A. Pizzi, ed.), *Applied Polymer Symposium* 40, pp. 1-18.
- Li, K., Geng, X., Simonsen, J and Karchesy, J (2004). Novel wood adhesives from condensed tannins and polyethylenimine, *International journal of adhesion and adhesives*, 24, 327-333.
- Liu Z, and Zhang F. (2008) Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. *Energ Convers Manag.*, 49: 3498–3504.
- Ogunwusi, O; (2013): Properties of *Detarium senegalense*, a lesser used tropical timber growing in Nigeria
- Russell JA, and Riemath WF (1985): Method for making adhesive from biomass. US Patent 4 508 886, USA as represented by the United States Department of Energy.
- S'anchez C, (2008) Lignocellulosic residues: Biodegradation and bioconversion by fungi, *Biotechnology Advances.* doi:10.1016/j.biotechadv.11.001.
- Sowunmi, S., Ebewe, R.O., Conner, A.H.,and River, B.H. (1996), Fortified Mangrove TanninBased Plywood Adhesive, *Journal of applied polymer science*, 62, 577-584.
- Shiraishi N, Kajita H, and Norimoto M (1993): Recent research on wood and wood-based materials. *Elsevier Applied Science*, London and New York, p. 36.



TAPPI test method T249cm-85 -Carbohydrate Composition of Extractive-free Wood and Wood Pulp by Gas-liquid Chromatography-Technical Association of the Pulp & Paper Industry

Wang M, Xu C, Leitch M (2009): Liquefaction of cornstalk in hot-compressed phenol–water medium to phenolic feedstock for the synthesis of phenol–formaldehyde resin. *Bioresource Technol. (a)*, 100: 2305–2307.

Wu, Q. and C. Piao. (1999): Thickness swelling and its relationship to internal bond strength loss of commercial oriented strandboard. *Forest Products Journal* 49, 50-55

Hock H, Lang S. (1944) *Ber Dtsch Chem Ges.* B77, p. 257.

Russell JA, Riemath WF (1985). Method for making adhesive from biomass. US Patent 4 508 886, USA as represented by the United States Department of Energy.

Shiraishi N, Kajita H, Norimoto M. (1993), recent research on wood and wood-based materials. Elsevier Applied Science, London and New York. p. 36.

USDA Forest Service Research Note FPL-091 Bark and its possible uses. Revised 1971.

Available at <http://www.fpl.fs.fed.us/documnts/fplrn/fplrn091.pdf>.

Wang M, Xu C and Leitch M (2009). Liquefaction of cornstalk in hot-compressed phenol–water medium to phenolic feedstock for the synthesis of phenol–formaldehyde resin. *Bioresour Technol. (a)*, 100: 2305–2307.