



## Physical Properties and Curing Characterization of Bio-based Phenol Formaldehyde Resins

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### ABSTRACT

An understanding of the curing mechanism of Phenol Formaldehyde (PF) resole resins as it relates to its physical properties provides an insight into the overall quality and durability of glue line in particleboard. From the foregoing therefore, the curing characterization of the Bio-phenol Formaldehyde (BPF) resole resin was studied by Differential Scanning Calorimetry. The result showed that the activation energy of the cure PF resin decreases with increasing percentage BPF replacement by weight. Also, the thermal curing kinetics of the BPF resole resins indicated that at low bio-phenol replacement of 25 and 50 wt%, the curing temperatures were lower than that of the commercial and laboratory synthesized pure PF resins. However, BPF resin at 75 % substitution, displayed a higher curing temperature than the commercial and laboratory synthesized pure PF resins. These results shows that the presence of bio-oil in BPF resins could play two adverse roles in the process of curing depending on the amount of bio-oil in the BPF resins.

**Keywords:** Synthesis, Bio-phenol, formaldehyde, resins, *Detarium senegalense*, Thermal curing

### Introduction

Phenol-formaldehyde (PF) resins are widely used as an adhesive in the wood products industry for the manufacture of particleboard and other composite products because of its high strength and moisture resistance (Shiraishi *et al.*, 1993; Wang *et al.*, 2009). Phenol, the most costly chemical raw material for the manufacturing of PF resins, is primarily produced from petroleum-derived benzene by the cumene process developed by Hock and Lang (1944). Dwindling of petroleum resources as well as increasing demands for petroleum by developing economies, political and environmental concerns over fossil-based resources has necessitated the interest in exploring and developing alternative renewable resources for both energy and chemical production (Russel *et al.*, 1985).

The lignocellulosic biomass used as precursor in the production of bio-phenol is *Detarium senegalense*, a lesser-utilized tropical hardwood species in Nigeria, composed of lignin, an amorphous micromolecule, which comprises of three phenyl-propanols macromolecule that is, p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, that can be decomposed into the oligomeric and monomeric phenolic compounds through thermochemical technology such as direct liquefaction (Kleinert and Barth, 2009; Wang *et al.*, 2009). 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.

Among the properties that will qualify wood bark as a potential raw material in the developing bio-refinery and chemical industries are the percentage bark



composition as well as the percentage variation of bark within and between species. Ten (10) tropical hard wood species was studied for variation in their barks percentages within trees of the same species and those of different species, *D. senegalense* performed best (Ogunwusi, 2013).

Thermosetting adhesives (phenolic resins) are usually monitored by exothermic or endothermic behaviour during gelling and hardening (chemical curing) using suitable test methods. Differential Scanning Calorimetry (DSC) analysis is a useful tool to test chemical curing. DSC has the advantage of being based on the same assumption as the heat equation, which is the proportionality between the rate of heat generation and the rate of reaction. Many studies have reported the curing characterization of phenol produced from forestry residue (Zhao, 2010; Cheng, 2011). However, their focus was essentially on softwood bark because of its composition of both guaiacyl and syringyl units derived from trans-coniferyl and trans-sinapyl alcohols. Notwithstanding, it has been established that the weight percentage of lignin, cellulose, and hemicellulose in any type of biomass as well as the composition of syringyl, guaiacyl and p-hydroxyphenyl is affected by several factors among which are: Geographical location, Soil type, Climatic Conditions, Plant Species, pH level, Soil Nutrients and the Age of Plant (Vassilev *et al.*, 2010). Incorporating phenolic components obtained from tree bark into the PF resin as partial replacement for Petroleum-based phenol, can add significant complexity to the resin structure and affect the reactivity and performance of the resulting resins. Therefore, a better fundamental understanding of the impact of such phenol components on the curing properties of the bio-based PF resins is highly necessary.

The aim of this study therefore, is to investigate the relationship between the curing characterization of the BPF resins produced from *D. senegalense* bark using DSC technique, to establish the potential of the BPF resins in minimizing the heat energy input during hot pressing condition and also, for a better process development and to improving the quality of the final product relating to the structure of the polymer.

## Materials and Methods

### Bark collection and sample preparation

The bark of *Detarium senegalense* was obtained from Aiyegun sawmill, new Garage, Ibadan Nigeria. Reliable information from the sawmillers was that the log was collected from Gambari reserve. Gambari Forest Reserve is located on latitude 7°7' 60''N and longitude 3° 49'60'' E within the low land semideciduous forest belt of Nigeria and covers a total land area of 17,984ha (get a map.net) The air-dried bark samples of *D. senegalense* was hammer milled using 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 105°C for 2 hrs. Elemental composition of carbon, hydrogen, nitrogen, and sulfur in the *D. senegalense* samples were analyzed with a CHNS Flash Elemental Analyzer 1112 series. Compositional analysis for its contents of cellulose, hemicelluloses and lignin content were done in accordance with the TAPPI T249cm-85 (for cellulose and hemicellulose). 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 employed.



**Synthesis of bio-phenol formaldehyde resole resin using the phenol extracted from *Detarium senegalense* bark**

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 in accordance with Pilato (2010). Following the method prescribed by Abdelwahab and Nassar (2011), 117.65 g of 50 % NaOH (w/w) was added at 15 min interval. The addition of each quantity of sodium hydroxide caused a decrease of 10 °C. The resultant mixture was stirred and heated to 90–95 °C until the mixture became cloudy. After 90 minutes of reaction of the mixture, the experiment was terminated by rapidly cooling the mixture to 25 °C in

accordance with Pilato (2010). The experiment was repeated for 0 % (Laboratory synthesized pure PF with no bio-phenol substitution), 25 %, 50 % and 75 % bio-phenol replacement. The weight in gram of formaldehyde, phenol and sodium hydroxide at each percentage level of phenolic oil replacement was calculated using the formula developed by Gardziella *et al.* (2000).

$$\text{Mixing Ratio} = A \times \frac{F}{F + P + \text{NaOH}}$$

Where:

A= formulation in 1000 ml standard solution,  
 F= formaldehyde,  
 P= phenol and  
 NaOH= sodium hydroxide.

The addition of F,P and 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 (Table 1).

**Table 1:** Formulation of resin using P/F ratio 1:2

	Replacement by weight (g)			
	0 % BPF	25 % BPF	50 % BPF	75 % BPF
Comm. Phenol (P)	294.12	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
NaOH	117.65	117.65	117.65	117.65

**Determination of physical properties of PF resins pH, viscosity and gelation time and solid content of the PF resins**

pH values of the resins were measured by digital pH probe at 25 °C. An average of three measurements was taken and recorded for each BPF resins.

Viscosity measurements of the PF resoles resins were taken using Brookfield rotary

Viscometer Model DVE at 50 rpm and room temperature (25 °C) in accordance to recommendations by ISO-2555 for particleboard wood adhesives. An average of three measurements were taken and recorded for each BPF resins.



Gel time was measured by charging 1 g of resin into a 16 mm wide test tube and heating the test tube in an oil bath at  $120 \pm 1$  °C. Gel time was defined as the time period from the immersion of the test tube into the oil bath to the beginning of the resin gelation (resin forming a string when a glass rod was lifted from the resin). An average value of three replicate measurements was reported.

The solid contents of BPF resoles were determined in accordance to ASTM D4426-01 (2006). Around 1 g of each BPF sample was weighed on a glass dish, and heated in an oven at 125 °C for 105 minutes. Next, the BPF sample was placed in a desiccator for a period of 5-15 minutes and then weighed again to determine the weight percentage of the residues in relation to the original liquid BPF sample, that is, the non-volatile content

$$\% \text{ Solid content} = \frac{\text{weight of oven-dried adhesive}}{\text{weight of Adhesive}} \times 100$$

### Lab PF and commercial PF resins

In order to understand how the bark phenolic compounds affect the resulting resin properties, the 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. Both the lab PF and the conventional commercial phenol formaldehyde are used as control for the study.

### Curing Characterization

#### DSC measurement

A differential scanning calorimetry, DSC, (Mettler DSC 20) with a thermal analysis system (Mettler TA400) with STAR software was used. High-pressure steel sealed capsules that can withstand vapor pressure up to 10 MPa were used and dynamic scans were made under (50-60) ml/min N<sub>2</sub> at four different

heating rates (5, 10, 15 and 20 °C/min) between the scanning temperature ranged from 30 to 250°C.

#### Kinetic method

The activation energy at the peak point of DSC curve was obtained by standard method ASTM E698-79 (ASTM E698-18 2018). The relationship between activation energy and conversion during all the curing process was obtained according to the model-free kinetics, in which the activation energy at each conversion point was calculated by the Kissinger method (Kissinger 1957; He *et al.* 2001). A plot of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  was a straight line. The activation energy at conversion was obtained from the slope of the line.

### Results and Discussion

The result of the pH, percentage solid content, viscosity and gel were presented in Table 2. It was observed that 25 wt% BPF dropped the pH of the commercial and laboratory synthesized pure PF resins, and this was due to the acidic nature of the BPF resins. At 75 wt% BPF however, the pH raises again to alkalinity, because at this level the phenolic bio-oil has become dormant to the petroleum-based phenol due to steric hindrances and the final pH of the reaction is determined by the more potent phenol from petroleum source in the resin.

Nor Hafizah *et al.* (2012) reported similar pH of 12.7 for commercial phenol formaldehyde and less than pH of 10 for low and medium molecular weight PF. The pH of the LS and 25 to 75% phenolic lignin are similar to the commercial PF in this study (Table 2). Increase in acidity (pH) level would result in the increase of the resin's viscosity and consequently cause shortening of the gelation time. In addition, the pH of phenolic resin



(hydrogen ion concentration) has been reported to greatly affect the properties of finished composite products. Increase in the pH from 3.3 to 5 caused increase in the physical and mechanical properties of hardboard Fadl and Rakha, (1984); Pizzi (1993). However, damage to cellulose would occur when the acidity is much higher. Also, the increase in solid content of the BPF resins were caused by the incorporation of degraded lignin bark components in the resin based on the explanation given by Siddiqui (2013). The variation in their viscosities is due to the fact that viscosity increases with increase in the percentage replacement of bio-oil to phenol in the synthesized resin adhesive that was attributed to the larger molecular weights and complex molecular structures of the bio-phenolic compounds that constitute the bio-oil than those of phenol (Cheng *et al.*, 2011). Viscosity measurement of phenolic resins gives an indication to the advancement of the resin synthesis and the degree of its condensation reactions (Pilato, 2010; Kurt and Cil, 2012). Low resin viscosities or low degree of condensation reaction results in over-penetration of adhesive into the wood, resulting in starved glue-lines while too high viscosities result in low adhesive penetration

as well as poor mechanical interlocking of the adhesive into the wood (Dunky, 2003; Frihart, 2005).

The low viscosity, low weight average molecular weight and low poly dispersity index of the commercial PF resin indicated that this resin had a low degree of polymerization, which also explained why its solids content was higher than those of BPF resins.

The BPF resins had the longest gel time when compared to the commercial and laboratory synthesized pure PF resins. However, the longer gel time is not an indication that the BPF resins cures at a slower rate than the commercial and laboratory synthesized pure PF resins as shown in Table 3. The commercial and laboratory synthesized pure PF resins had the highest peak temperature when compared to 25 and 50 wt% BPF resin, probably, the least reactive. Empirically, gel time can sometimes give indications about resin cure rates but conclusion cannot 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 2: Physical properties of BPF and PF resin**

Resin Formulation	<sup>a</sup> pH at 25°C	<sup>a</sup> Solid Content at 120°C	<sup>a</sup> Viscosity (cP)	<sup>a</sup> Gel Time (s)	<sup>b</sup> M <sub>n</sub> (Da)	<sup>b</sup> M <sub>w</sub> (Da)	<sup>(PD)</sup> <sup>b</sup> M <sub>w</sub> /M <sub>n</sub>
Comm PF	11.55	58.20	280	390	7.48x10 <sup>2</sup>	14.92x10 <sup>2</sup>	1.99
L.S Pure PF	11.28	50.00	200	380	6.70x10 <sup>2</sup>	14.40x10 <sup>2</sup>	2.14
25 % BPF	10.65	51.70	380	660	6.56x10 <sup>2</sup>	15.32x10 <sup>2</sup>	2.33
50 % BPF	11.20	52.80	420	540	6.88x10 <sup>2</sup>	15.75x10 <sup>2</sup>	2.28
75% BPF	11.37	54.40	640	410	7.32x10 <sup>2</sup>	17.46x10 <sup>2</sup>	2.38

<sup>a</sup>Each value represents an average of 3 samples; <sup>b</sup>Each value represents an average of 2 samples. (M<sub>w</sub>: weight average molecular weight, M<sub>n</sub>: number average molecular weight, Polydispersity index (PD): M<sub>w</sub>/M<sub>n</sub>)



A kinetic analysis of curing reactions for the BPF resin and PF resin starts with the activation energy ( $E_{698}$ ) calculated using ASTM E698-18 (2018), which treats the complex cure as single-step reactions of the first order. This method uses the activation energy at the peak point of DSC curves as the

apparent one of the curing reactions. The apparent activation energy is useful to compare the chemical reactivity of different reactions. The effect of phenolic bark on the activation energy of PF resin cure is summarized in Table 3.

**Table 3.** The Differential Scanning calorimetry (DSC) results of the main exothermic peak for the resins at heating rate of 10 °C/min.

Resin Formulation	Comm. PF Resin	LS. Pure PF Resin	25 wt% BPF	50 wt% BPF	75 wt% BPF
Onset Temp.(°C)	143.5	140.5	133.0	132.5	149.5
Peak Temp. (°C)	150.0	152.2	144.5	145.8	157.0
End Temp. (°C)	161.5	169.5	157.2	157.5	166.2

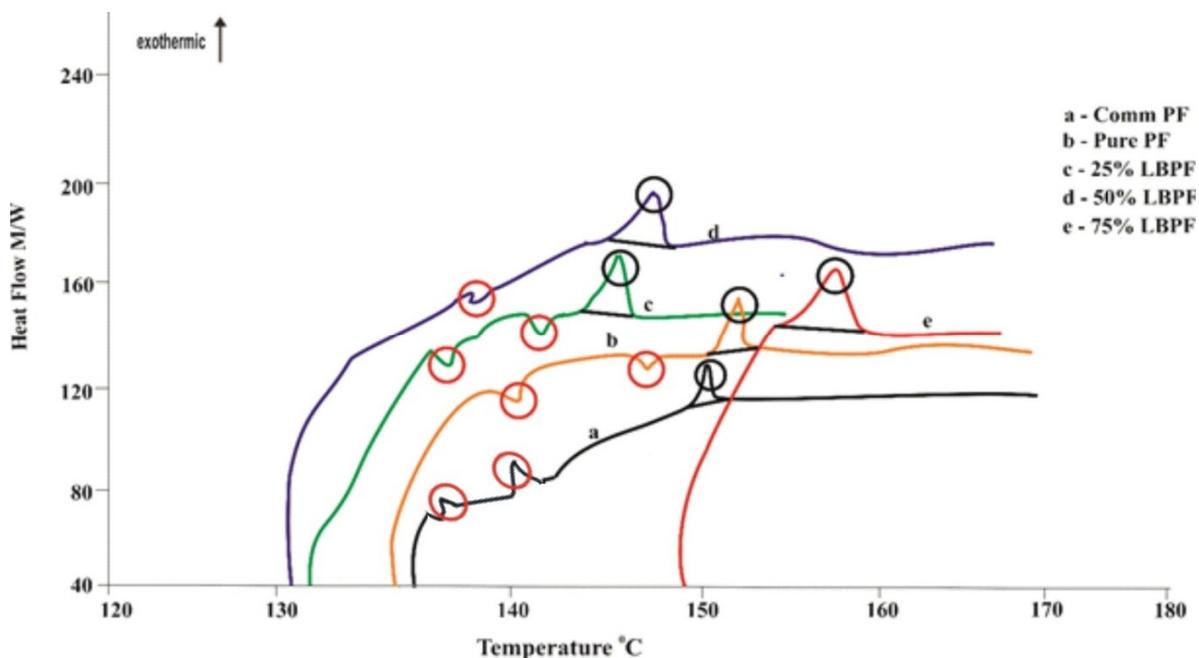


Figure 1: Differential Scanning calorimetry (DSC) profiles of resins at 10°C/min



From Figure 1, the DSC graph indicates the main exothermic peaks of the resins (denoted by the black circle). These peaks were attributed to the condensation of phenol or bio-phenol with methylol groups ( $-\text{CH}_2\text{OH}$ ) to form a methylene bridge and the condensation of two methylol groups to form dibenzyl ether bridges (Gabilondo *et al.*, 2007; Wang *et al.*, 2009; Cheng *et al.*, 2011). The DSC profiles for BPF resins displayed shoulder peaks between 135 and 142 °C, (denoted by red circle) and these might be due to the free formaldehyde present in the resin formulation (Wang *et al.*, 2009; Cheng *et al.*, 2011). Likewise, commercial and laboratory synthesized PF resin also exhibited two distinct shoulder peaks, (denoted by red circle) between 138.5 and 141.5°C. The first peak was attributed to condensation reaction of the resin to form methylene and ether bridges and the second peaks displayed at a higher temperature was due to the breakage of dimethylene ether linkages and re-condensation through the methylene bridges (Wang *et al.* 2009 and Cheng, 2011).

The DSC results of the main exothermic peaks for BPF and reference PF resole resins at a heating rate of 10 °C/min shown in Table 3, reveal that at low bio-phenol replacement level of 25 and 50 wt%, the curing temperatures were lower than that of the commercial and laboratory synthesized pure PF resins, which suggested that the presence of bio-oil could promote the curing reactions of the BPF resins. This observation corroborate the findings of Vázquez *et al.*, (2002), Khan and Ashraf (2007); and Wang *et al.*, and(2009) Cheng, (2011), where the addition of a small amount of bio-phenol materials in PF resin (tannin and lignin) reduced the curing temperature.

BPF resin at 75 % substitution, however, displayed a higher curing temperature than the

commercial and laboratory synthesized pure PF resins similarly to the observed data by Wang *et al.* (2009) and Cheng *et al.* (2011).

### Conclusion

The research provided fundamental information on the curing temperature of BPF resin using phenol precursor obtained from bark of *Detarium senegalense* by employing the Differential Scanning Calorimetry. 25 and 50 wt% bio-phenol replacement reduces the curing temperature of the BPF resins than the Commercial and Laboratory synthesized pure PF resins while 75wt% bio-phenol replacement increases the curing temperature when compared to that of Commercial and Laboratory synthesized pure PF resins. The variation of the pH values in the curing systems may be the most probable contribution, since the synthesis and curing reactions of PF resole resin are carried out in basic conditions, while wood bark contains acidic extractives which decreases the pH values in the BPF resin. These results suggested that the presence of bio-phenol in BPF resins could play two adverse roles in the process of curing depending on the amount of bio-phenol in the BPF resins.

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