Structural Characterization of Cure Bio-based Phenol Formaldehyde Wood Adhesive

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

Article Information

Original Research Article

ABSTRACT

Bio-phenol formaldehyde (BPF) resole resins were characterized by liquid-state ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy. The liquid ^{13}C NMR analysis indicated that the condensation reactions between the bark phenolic compounds and the formaldehyde occurred during the synthesis of the resins. Methylene ether bridges in the resins were more pronounced in the BPF resin when compared to the PF resin system. The liquid-state ^{13}C NMR study revealed significant differences in the resins structures induced by the inclusion of bark-phenolic components. The bark-phenolic components favored the formation of *para-ortho* methylene linkages in the BPF resins and also enhanced the cure rate of the BPF resin system.

Keywords: Bio-phenol formaldehyde resole resins; ^{13}C nmr; methylene ether bridges.

1. 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 [1,2]. Phenol, the most costly chemical raw material for the manufacturing of PF resins, is primarily produced from petroleum-derived benzene by the cumene process [3] developed by Hock and Lang.

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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 [4].

The lignocellulosic biomass used as precursor in the production of bio-phenol in this study 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 [2,5]. In this regard, *Detarium senegealens* biomass can be a potential source of bio-phenolic compounds to replace petroleum-based phenol in the production of PF resins; owing to the high percentage bark abundance within trees of the same species and those of different species [6].

The curing behavior of PF resin, studied by the use of Differential Scanning Calorimeter is fundamental to optimizing the hot press temperature as well as improving the physical and mechanical properties of the particleboards produced from the resin. In general, curing of PF resin could be influenced by the interaction between the resin and phenolic bark component. Those effects are multiplied and complicated as a result of the complex composition and structure of wood as well as bark composition. Many studies have reported the curing and structural characterization of forestry residue [7,8] but 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 also 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 [9] among which are: Geographical location , soil type, climatic conditions, plant species, pH level, soil nutrients and age of plant species. Also, the unraveled complexity of the structure of lignin which is dependent on its source among other factors is equally significant.

Incorporating phenolic-bark components into the PF resin synthesis, as partial replacement for petroleum-based phenol, can add significant complexity to the resin structure and affect the reactivity and stoichiometry of the resins, Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR) is an advanced analytical technique that probes and give complete and reliable information on the chemical structures present in the cured bio-phenol formaldehyde resin obtained from *D. senegalense*, allowing the identification of several functional groups and its quantitative determination.The aim of this study therefore, is to probe the network structure and position of linkages between the cured system of the commercial PF and bio-phenol formaldehyde phenol rings of the cured resin using ^{13}C NMR spectroscopy techniques.

2. EXPERIMENTAL PROCEDURES

2.1 Materials and Methods

2.1.1 Bark collection and sample preparation

Bark of *D. senegalense* was obtained from Aiyegun sawmill, new Garage, Ibadan Nigeria. Reliable information from the sawmillers was that the log was collected from Onigambari reserve. Onigambari Forest Reserve is located on latitude 70.25°N and 7.55°E and longitude 3.53°N and 3.9°E within the low land semideciduous forest belt of Nigeria and covers a total land area of 17,984ha. The air-dried 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 105°C 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. The liquefaction of the hammer-mill *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 [7] was followed to obtaining the bio-phenol fraction.

2.2 Synthesis of BPF Resole Resins Using the Phenol Bark Component of *Detarium senegalense* Bark

2.2.1 Methods

Bio-phenol formaldehyde resole resin was synthesized using bark phenolic compound from

D. senegalense (forest biomass) via the solvolysis liquefaction method, the bio-oil obtained, was successfully incorporated into the synthesis of bio-phenol formaldehyde (BPF) resins up to 75 percent replacement by weight substitution for petroleum-based phenol.

The resin synthesis were carried out in a laboratory glass reactor equipped with a stirrer, a thermometer, and a reflux condenser. The mixture of phenol and 37% aqueous formaldehyde was heated up to a temperature of 45°C, and then the catalyst, a 10% sodium hydroxide solution as was added. After the components were heated to 90°C over a period of 30 min, the temperature was kept at 90°C for 60 min. The experiment was repeated for 25%, 50% and 75% phenol replacement.

2.3 Commercial PF Resins

In order to understand how the bark phenolic compounds affect the resulting resin properties, a conventional commercial pure phenol formaldehyde is used as control for the study.

2.4 Liquid State ^{13}C NMR Measurement

Liquid State ^{13}C NMR spectra were recorded using a Unity 400 spectrometer. The spectra were recorded under the following conditions: a pulse angle of 60 degrees (8.3 ms), a relaxation delay of 10 s and with gated Waltz-16 ^{1}H decoupling during the acquisition period. About 400 scans were accumulated for each spectrum. Some samples were dissolved directly in deuterated water, while other samples were freeze-dried first, and then dissolved in deuterated water for NMR tests. ^{13}C chemical shifts were measured with respect to tetramethylsilane (TMS) as the internal standard.

3. RESULTS AND DISCUSSION

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 1. 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 result is collaborated with the findings of [2,7] where the addition of a small amount of bio-phenol materials in PF resin (e.g. 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 as similarly observed by several authors [2,7]. These results suggested 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.

3.1 Chemical Shift and Assignment of Structural Compounds for PF and BPF Resins

The result showing the chemical shift and assignment of structural compounds for the PF and BPF resins when characterized using ^{13}C NMR are displayed in (Figs. 1 to 4) and the chemical shifts and signal assignment is listed on Table 2. The chemical shift between 166 -168 ppm was assigned to the carbonyl groups. Chemical shifts between 153.3 -163.9 ppm was assigned to C-OH on the phenolic rings. The chemical shifts between 153.5 -157.2 ppm was assigned to alkylated phenoxyl, in ortho position. The chemical shift between 158.0 -159.5 ppm was assigned to alkylated phenoxyl, in para position. The chemical shift at 146.51 ppm was assigned to C4 in etherified guaiacyl unit in *β*-5' of the liquefied *D. senegalense* bark. The chemical shift of 145.25 ppm was assigned to C4 in non-etherified guaiacyl unit of the liquefied *D. senegalense* bark. The chemical shifts between 134 -135 ppm was assigned to C1 in etherified guaiacyl and syringyl unit of the liquefied *D. senegalense* bark**.** The chemical shifts of 129.0 - 130.4 ppm were assigned to substituted para aromatic carbons of phenol. Chemical shift of 63.1- 64.7 ppm was assigned to para methylol. The chemical shifts between 48.7 -50 ppm was assigned to methoxyl groups. The chemical shifts between 39.1 -41 ppm was assigned to para-para methylene linkage. The chemical shifts between 34.6 -35.0 ppm was assigned to ortho-para methylene linkage. The chemical shifts between 29.3 - 30.9 ppm was assigned to methylene linkage between phenol and tannin-B ring while chemical shifts between 23.9 - 24.9 ppm was assigned to methylene linkage between phenol and tannin-A ring.

3.2 Structural Compositional Characterisation of the Commercial Pure PF Resins

From Fig. 1 the chemical shifts between 153.5 and 163.9 ppm assigned to phenoxyl carbons and the chemical shifts of para alkylated phenolic groups between 158.0 and 159.5 ppm, showed higher intensity than those of chemical shifts of ortho alkylated phenolic groups between 153.5 and 157.2 ppm in both resins. The chemical shift at 48.7 ppm was observed in both resin and was due to the methanol (CH_3OH) in the formaldehyde solution as a stabilizer. The methanol could also be formed during the resin synthesis from the Cannizzaro reaction of formaldehyde [10]. The chemical shift at 81.7 ppm relating to the unreacted formaldehyde was observed in both resins. The small chemical shifts around 86 and 87 ppm belonged to formaldehyde oligomers in the resins. The result was consistent with previously published research of [11,12,13].

The peaks between 114 and 116 ppm for unsubstituted ortho aromatic carbons of phenol and the peaks between 120 and 124 ppm for the unsubstituted para aromatic carbons of phenol were observed in both resins. The peaks between 60.4 and 64.7 ppm represented the methylol groups (Ph-CH_2OH), with the ortho link between 60.4 and 62.8 ppm and para link between 63.1 and 64.7 ppm were also observed in both resins.

Table 1. 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	25 wt% BPF	50 wt% BPF	75 wt% BPF
Onset Temp.(°C)	143.5	133.0	132.5	149.5
Peak Temp. (°C)	150.0	144.5	145.8	157.0
End Temp. (°C)	161.5	157.2	157.5	166.2

Table 2. Assignment of chemical shift for commercial and BPF resin

| Chemical Shifts (ppm)	Assignment
166-168	Carbonyl C=O
153.5-163.9	phenoxyl carbons
153.5-157.2	phenoxy, alkylated in ortho position
158.0-159.5	phenoxy, alkylated in para position
146.51	C4 in etherified guaiacyl unit in β-5
145.25	C4 in non-etherified guaiacyl unit
134-135	C1 in etherified guaiacyl and syringyl unit
129.0-130.4	substituted para aromatic carbons of phenol
126.0-128.1	substituted ortho aromatic carbons of phenol
120.0-124.0	unsubstituted para aromatic carbons of phenol
114.0-116.6	unsubstituted ortho aromatic carbon of phenol
110-130	guaiacyl unit
86	C- β in β-O-4'
86-93.7	formaldehyde oligomers, Ph-CH2OCH2OH
81.7	unreacted formaldehyde in the resins
69.0-73.0	phenolic methylene ether bridges
63.1-64.7	para methylol
60.4-62.8	ortho methylol
54.3	methoxyl groups
48.7-50	methanol
39.1-41	para-para methylene linkage
34.6-35.0	ortho-para methylene linkage
29.3-29.6	ortho-ortho methylene linkage
29.3-30.9	methylene linkage between phenol and tannin-ring
28.8~29.1, 23.9~24.9	methylene linkage between phenol and tannin-ring
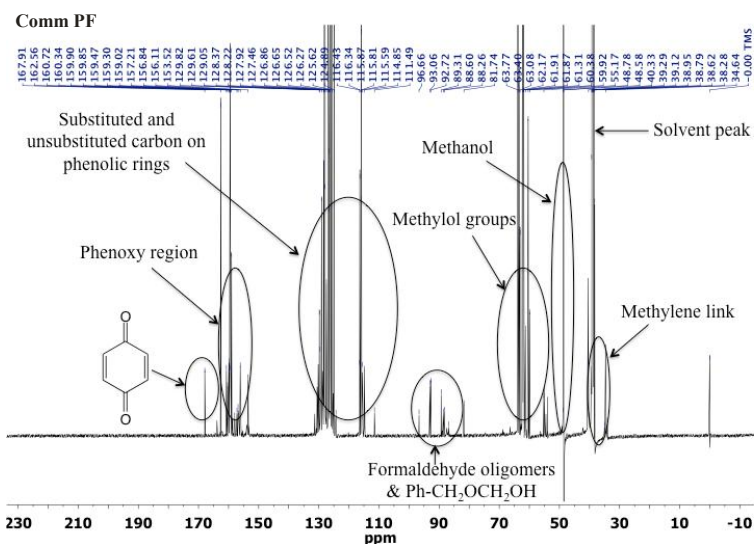
Fig. 1. Liquid-state ¹³C NMR spectrum of the commercial PF resin
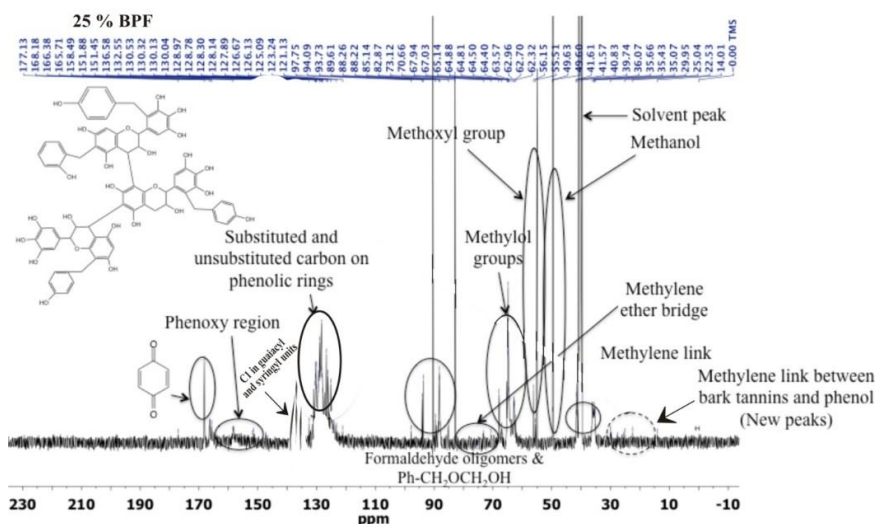

Fig. 2. Liquid-state ^{13C} NMR spectrum for 25 wt% bio-phenol formaldehyde

3.3 Structural Compositional Characterization of 25 wt% Bio-phenol Formaldehyde Resole Resin

The differences between the liquid-state ¹³C NMR spectra between of 25 wt % BPF resin and the commercial PF resin were observed clearly. The incorporation of phenolic-bark extracts in the formulation of the BPF resin introduced new peaks (Fig. 2).The appearance of the new chemical shifts between 29.3 and 30.9 ppm, 28.8 and 29.1 ppm, 23.8 and 24.9

ppm in the BPF resins could be attributed to the methylene groups between phenol and the tannin-B ring (29.3 and 30.9 ppm), and between phenol and the tannin-A ring (phloroglucinol ring, 28.8 and 29.1, 23.9 and 24.9 ppm) [14,15]; these peaks were not observed in the commercial and laboratory synthesized pure PF resins. These peaks provide evidence that the tannins components (both A ring and B ring) in the phenolic bio-oil extract reacted with the formaldehyde during the resin synthesis.
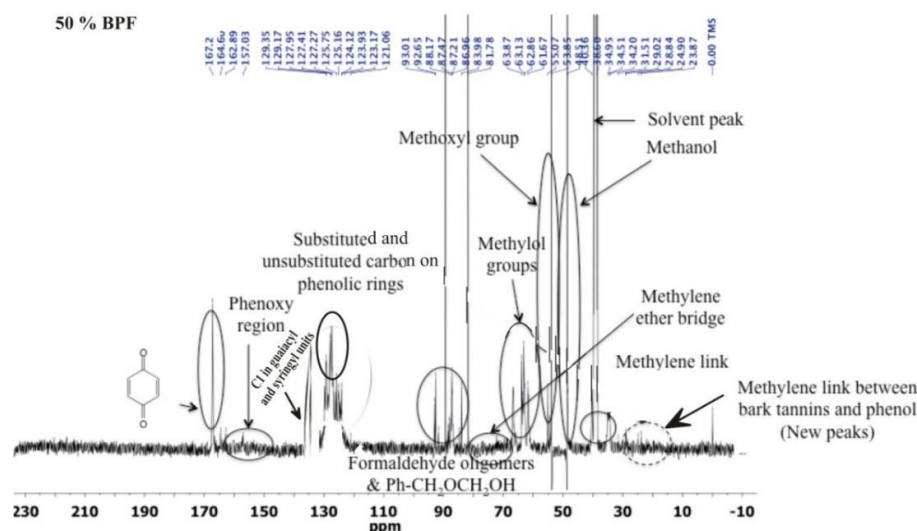
Fig. 3. Liquid-state ^{13}C NMR spectrum for 50 wt% bio-phenol formaldehyde

The DSC result in Table 1 shows the inclusion of bark phenolic component decreases and at the same time accelerated the curing temperature of the resin. The findings is corroborated with the previously published DSC research work of [8,16], that establishes that the introduction of phenolic-bark extractives to the PF resin synthesis affected the curing behavior and curing kinetics of the resulting BPF resin by acting as an accelerators in PF resins for plywood production due to their ability to minimize gelation and shorten press time. The BPF resins had faster curing rates than the commercial and laboratory synthesized pure PF resin. The reaction between the tannin components in the phenolic-bark extractives and formaldehyde could be one of the reasons for the acceleration of the curing rates of the BPF resins.

The intensities of the chemical shifts of the phenoxyl groups between 150 and 160 ppm for 25 wt% BPF resin is weaker than those of the commercial and laboratory synthesized pure PF resins. The intensity chemical shifts between 164 and 167 ppm represent carbonyl groups in BPF resin was stronger in 25 wt% BPF. The methoxyl group from the phenolic-bark components was clearly observed in the spectrum of the 25 wt% BPF resin at 55.5 ppm. The chemical shifts between 71 and 76 ppm also represented the C-α in the β-O-4' guaiacyl unit as well as the methylene ether bridges. The chemical shifts at 133 to 135 ppm were attributed to C$_1$ in guaiacyl and syringyl units.

3.4 Structural Compositional Characterization of the 50 wt% Bio-phenol Formaldehyde Resole Resin

The intensities of the chemical shifts between 60 and 65 ppm as well as between 35 and 37 ppm, were attributed to methylol groups and methylene group, respectively. It was weaker in the 50 wt% BPF resins Fig. 3. than in the commercial PF resins Fig. 1. that is with increasing bio-oil-phenol ratio to 50 wt% in the BPF resin, the intensities of these chemical shifts decreased, due to the fact that, as more bio-phenol was replaced by the petroleum-based phenol, less methylol groups and methylene groups were formed between phenols; indicating that the liquefied bark had retarded the reaction of phenol and formaldehyde probably due to steric hindrance [8,16]. The chemical shift at 174.83 ppm arose from the C=O group of the glucuronic acid indicating that it was esterified to lignin. The chemical shifts at 133 to 135 ppm attributed to C$_1$ in guaiacyl and syringyl units were stronger in 50 wt% BPF than in the 25 wt% BPF resins. The chemical shift at 55.5 ppm attributed to the methoxyl groups (-OCH3).

A small chemical shift between 71 and 73 ppm, was obviously observed in the spectrum of 50 wt% BPF resins but not in the spectrum of the commercial PF and laboratory synthesized pure PF resins and it indicated the existence of the methylene ether bridges which confirmed that the structure of BPF had introduced steric hindrance. It could therefore be concluded that
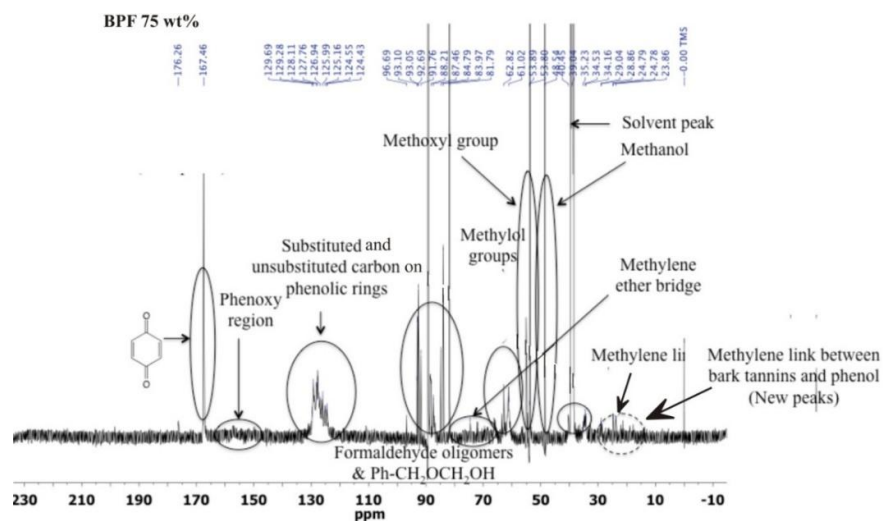
Fig. 4. Liquid-state ^{13}C NMR spectrum for 75 wt% bio-phenol formaldehyde BPF resins

the phenolic ring attached to the bark component during liquefaction were mostly at their ortho-position.

3.5 Structural Compositional Characterization of the 75 wt% Bio-phenol Formaldehyde Resole Resin

The spectrum for 75 wt% BPF resin is shown in Fig. 4. At this substitution level, the intensities of chemical shifts for the unsubstituted *para* carbons of phenol between 120 and 124 ppm were lower than those of the commercial pure PF resin. The chemical shifts between 115 and 116 ppm, which correspond to the unsubstituted *ortho* aromatic carbons of phenol, were absent. This suggest that the *ortho* aromatic carbons of phenol had completely reacted in the reaction of the bio-phenol with the formaldehyde. Similar observations have been reported by several authors [11,12] for PF resole resins, and the reason was that the ortho substitution was more favored by the addition of curing accelerators. It, therefore, suggests that BPF resins have the potential to speed up resin curing reaction (Table 1). The methoxyl group at 54.3 ppm from the BPF resins was clearly observed in 75 wt% BPF resins, and the intensity increased with the increasing amount of phenol replacement by weight in the resin synthesis.

The intensities of the chemical shifts between 150 and 160 ppm due to phenoxy groups which decreased in the spectra of 25 wt% and 50 wt% BPF resins when compared to the spectrum of commercial pure PF resin, were almost invisible in the spectrum of 75 wt% BPF resins. The

chemical shifts between 166 and 168 ppm, which represent carbonyl groups in BPF resins increased in intensity with the increasing level of phenol substitution. The carbonyl groups in the BPF resins may have originated from the bark extractives, or the oxidation of the phenolic rings or both.

The assignment of chemical shifts for the commercial and BPF resins in this study was therefore consistent with what had been observed by [11,14,17,18,19,20] as summarized in Table 2.

4. CONCLUSION

The liquid-state ^{13}C nuclear magnetic resonance (NMR) study revealed significant differences in the resins structures induced by the inclusion of bark-phenolic components. Methylene ether bridges, which were absent in the commercial and laboratory synthesized pure PF resins, were found in the BPF resins. The bark-phenolic components favoured the formation of *para-ortho* methylene linkages in the BPF resins. The BPF resins also showed a higher ratio of *para-para* and *ortho-para* methylene link ($-CH_2-$), a higher unsubstituted and substituted hydrogen ($-H/-CH_2OH$) ratio and a higher methylol/methylene ($-CH_2OH/-CH_2-$) ratio than the commercial and laboratory synthesized pure PF resins.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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