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Thermal Kinetics and Post Curing Thermal Stability of Bio-Based Phenol Formaldehyde Resins for Its Potential in Particleboard Production

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Abstract

The thermal degradation kinetics and post curing behavior of phenol-formaldehyde and Bio-phenol formaldehyde (BPF) resole resins were investigated with thermogravimetry analysis at four different heating rates (5, 10, 15 and 20°C/min) from 25 to 700°C. The curing reaction for all the resole resins proved to be approximately 1st order, and the activation energies of the BPF resins at 25 wt% and 50 wt% bio-phenol replacements were 132.2 kJ/mol and 131.6 kJ/mol. These were comparable to that of the laboratory synthesized pure PF resin 131.0 kJ/mol but also remarkably lower than the commercial PF resin (138.1 kJ/mol) respectively. The result of the thermal degradation kinetics showed that the post-curing thermal stability of the 25 and 50 wt% BPF resins were similar to that of the commercial and laboratory synthesized pure PF resin but, that of 75 wt% differed from the commercial or laboratory synthesized PF resin.

Keywords: Thermogravimetric analysis (TGA), curing kinetics, Activation energy, phenol-formaldehyde resole resin, Bio-Phenol Formaldehyde resole resin (BPF)

1. Introduction

Phenol, being the most costly chemical raw material for the manufacturing of Phenol Formaldehyde PF resins, a thermosetting resins classified as exterior adhesive because of its resistance to water, weathering, and high temperature in the cured glue line. 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 for the production of bio-phenol precursor is *Detarium senegalense* which is composed of lignin, an amorphous micromolecule comprising of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked together by condensed linkages and ether linkages. This macromolecule can be decomposed/de-graded into the oligomeric and monomeric phenolic compounds through thermochemical technology such as direct liquefaction (Kleinert, et al., 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.

D. senegalense is a lesser-utilized tropical hardwood species in Nigeria and among the properties that will qualify bark of wood as a potential raw material in the developing bio refinery and chemical industries are the percentage of the bark they contain and the extent of within and between species variation in bark percentages. 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 are usually monitored by exothermic or endothermic behaviour during gelling and hardening. Modifications of PF resins with renewable phenol from barks and other additives to improve the reactivity of PF resins has necessitated studying the post curing thermal stability of PF resin at higher temperature. Thermal analysis and testing of polymers and lifecycle is a powerful means of measuring physical properties, transitions, ageing processes, the effect of additives and the influence of diverse production conditions on materials.

It is essential that the properties of polymers, raw materials and finished products are well understood as they are integral to enhancing the performance of materials to meet specifications for the desired end-use, and within the remit of product failure analysis

Thermal analysis is therefore, a powerful technique for studying the kinetics in relations to the physicochemical processes. Thermogravimetric analysis TGA is a technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme. In this definition, a controlled temperature program means heating or cooling the sample at some predetermined and defined rate. TGA is a common technique for characterizing polymer thermal degradation behavior (Shulman 1996 and Chetan et al., 1997). Kinetic studies during the thermal degradation process have been used to acquire fundamental understanding of the structural changes in phenolic resins (Chen et al., 2008). Depending on whether a single or multiple-heating rate is used, the technique used to obtain the kinetic parameters is differential or an integral method (Popescu 1996; Vyazovkin et al., 2011). Multiple heating rates method gives more reliable results than the single heating rate method with smaller experimental errors (Cetic and Ozmen 2002). "Model-free" isoconversional method is a widely adopted technique for deriving relevant kinetic parameters using thermogravimetric (TG) and Differential Thermogravimetric (DTG) curves measured at different heating rates of mass change per-pre-selected temperature interval that makes no presumption about the reaction function and reaction order (Vyazovkin 2001; Orfao 2002; Vyazovkin et al., 2011). Thermogravimetric data can be presented in two ways. The TG curve is a plot of the mass against time or temperature, with the mass loss on the ordinate plotted downward and mass gains plotted upward relative to a baseline. Alternatively, data can be presented as a Derivative Thermogravimetric (DTG) curve, which is a plot of the rate of change of mass (m) with respect to time (t) or temperature (T) against time or temperature. (Rao et al., 1998; Lee et al., 2003).

Ability to analyze the structure and network formation of these resins with modern instrumental techniques increases our understanding of these phenomena transitions, ageing processes, the effect of additives and the influence of diverse production conditions on materials there by allows for better product quality control.

2. Experimental

2.1. Synthesis of BPF Resole Resins Using the Phenol Bark Component of *Detarium Senegalense* Bark

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.

2.2. 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.

2.3. Curing Characterization:

The thermal curing properties of the resins were evaluated with a Differential Scanning Calorimetry TA DSC-Q200, TA Instruments, Auburn University, Alabama, USA) under (50-60) ml/min N₂ at four different heating rates (5, 10, 15 and 20 °C/min) between 120 °C and 200 °C in a sealed Aluminum crucible

2.4. Post Curing Thermal Stability of the PF Resins Using Thermal Gravimetric Analyzer (TGA)

The phenol formaldehyde resins and the bio-based phenol formaldehyde resins, that were previously cured in an oven at 80 °C for 24 hours using DSC technique. The cured resins were ground into fine powders that were able to pass through a 100 mesh screen. About 10 mg of each cured resin sample was placed on a platinum pan and heated from 25 °C to 700 °C at the rate of 10 °C /min under N₂ atmosphere using a thermal gravimetric analyzer (TGA-Q500, TA Instruments, Auburn University; Al. USA). For the removal of moisture from the resins, they were mounted in a vacuum-dried oven at 40°C for 48h.

2.5. Curing Kinetics Mechanisms for the PF and BPF Resins

The non-isothermal DSC methods have been widely used for investigating the curing kinetics of thermosetting phenolic resins (Park et al., 1999; Want et al., 2005; Gabilondo et al., 2007; Wang et al., 2009; Cheng et al., 2011; Zhao et al., 2011; and Homaira, Siddiqui, 2013). The results from a single heating rate of (10 °C/min) may be inconsistent (Park et al., 1999; and Vázquez et al., 2002). The multiple-heating rate method was employed with four different heating rates varying between 5 °C/min and 20 °C/min (Table 2). By assuming that the cure reaction

pathway does not change with the heating rate, the curing kinetic parameters of the curing reaction of the resins were calculated using Kissinger equation. (Kissinger, 1957). The equation written as:

$$\ln \left(\frac{\beta}{T_p^2} \right) = \ln \frac{AK}{E_a} + \frac{1}{T} \left(\frac{E_a}{R} \right) \quad (1)$$

Where, T_p is the maximum exothermic temperature in the DSC profile, E_a is the activation energy (kJ/mol), and R is the gas constant ($= 8.314 \text{ J/mol/K}$). The activation energy (E_a) and reaction order (n) was calculated from the slope of the regression line of plots of $\ln (\beta/T_p^2)$ vs. $1/T_p$, respectively. The working plots are shown in Figure 2, and the calculated results presented in Table 3. The curing reaction for all the resole resins is approximately 1st order ($n = 0.94-0.95$)

2.6. Kinetic Analysis of the PF Resins and Bio-Based PF Resins Thermal Degradation Process Using Kissinger Equation

The nth-order and autocatalytic kinetics are the two reaction mechanisms used to describe curing reactions. They can be expressed as follows. For nth order kinetics,

The rate of the solid-state reaction is given by

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

K is the rate constant α – it is the fraction of reaction, or extent of reaction, $f(\alpha)$ is the differential form of the reaction model.

The extent of reaction is determined by

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (3)$$

Where:

m_i is the initial mass of the reaction.

m_t is the mass at time t .

m_f is the final mass at the end of the reaction.

The rate constant k , largely depends on temperature and it is the most important parameter as is directly related to activation energy and pre-exponential factor by the Arrhenius Equation which is as follows:

$$K = Ae^{-E_a/RT} \quad (4)$$

E_a is the activation energy, A is the pre-exponential factor, T is the absolute Temperature and R is the gas constant.

By rearranging and integrating equation (3)

We obtain

$$g(\alpha) = k/t \quad (5)$$

where $g(\alpha)$ is the integral form of the kinetic model and t is the time.

From equation (3) and (4)

$$g(\alpha) = Ae^{-E_a/RT} / t \quad (6)$$

Taking logarithm and rearranging the terms, the following equation is obtained:

$$-\ln(t) = \ln(A) - \ln(g(\alpha)) - \frac{E_a}{RT} \quad (7)$$

Since the value of $\ln(g(\alpha))$ is very small as compared to $\ln(A)$, it can be neglected and the value of E_a and A can be obtained from the plot of $-\ln(t)$ against $1/T$.

The value of E_a and A as obtained will be corresponding to the specific value of α and the time related to that α value.

In solid state decomposition reaction, the rate of reaction, using Equations (3) and (4) can be written in the following form:

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT} f(\alpha) \quad (8)$$

The Kissinger method is based on the study of the rate equation at the maximum reaction rate in non-isothermal system. At the maximum reaction rate, $d^2\alpha/dt^2$ is equal to zero and thus the following is obtained:

$$\frac{d^2\alpha}{dt^2} = \left(\frac{E_a\beta}{RT_m^2} + Af^n(\alpha_m) e^{-E_a/RT_m} \right) \left(\frac{d\alpha}{dt} \right)_m = 0 \quad (9)$$

This can be re-written as:

$$d(\alpha/dt) dt = A \exp(-E_a/R/T) (E_a/R/T^2) (1-\alpha)^n dT/dt - n(1-\alpha)^{(n-1)} A \exp$$

$$(-E_a/R/T) d\alpha/dt$$

By further assuming $n(1-\alpha)^{(n-1)} = 0$

a number close to unit, and $dT/dt = \beta$ (heating rate) is a constant. Kissinger reached T_m is the temperature at which the maximum reaction rate is observed, and α_m is the fraction reached at the maximum reaction rate. Taking logarithm and re-arranging, β

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{-AR}{E_a} f^n(\alpha_m)\right) - \frac{E_a}{RT_m} \quad (10)$$

For the first-order reaction $f'(\alpha) = -1$ and Eq. 9 becomes

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{Ea}\right) - \frac{Ea}{RT_m} \quad (11)$$

3. Results and Discussion

The Kissinger plot thus says that for a given DSC curve with the heating rate, β , one observes the maximum reaction rate at the peak temperature T_m : for a set of DSC Curves with different heating rates, one can plot the quantity of $\ln(\beta/T_m^2)$ against $1/T_m$ to obtain the Kissinger plot. From the slope of the Kissinger plot, the Activation Energy Ea is obtained; also, from the intercept, one obtains the pre-exponential factor A as well.

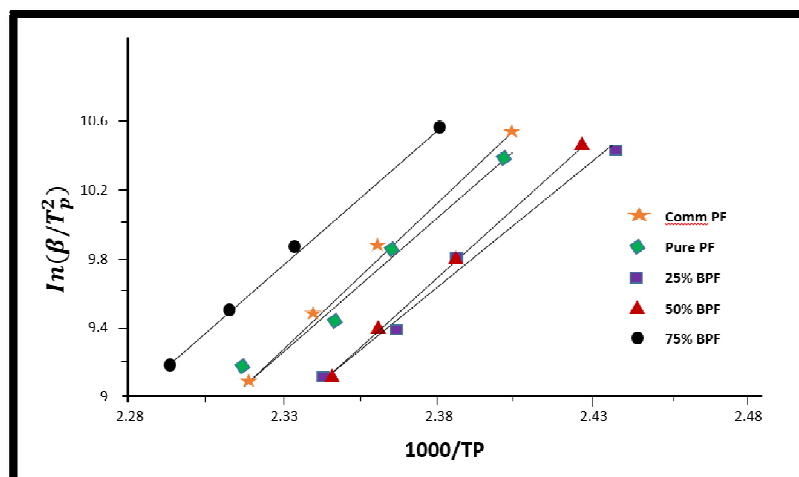


Figure 1: Curing Kinetic Parameters for the Resins as Calculated by the Kissinger Equation (Kissinger, 1957)

3.1. Thermal Stability Characterization of PF and BPF Resins

The thermal stability of the non-volatile contents of the BPF and PF resole resins were evaluated by TGA technique. Figure 2 shows the TG-DTG results of the resole resins between 25 °C and 700 °C. The decomposition temperatures and mass loss values of the thermal events, and mass residue at 700 °C are listed in Table 1. As shown in Figure 2, all the PF resins present similar thermal decomposition patterns, showing three major thermal event. From the table, the first thermal event for the commercial PF resin was observed at temperature range between 70 and 300 °C, and 7 % mass loss was recorded. The second thermal event was observed at temperature range between 365 and 500 °C, and a 7 % mass loss was recorded. The last thermal event was detected at temperature range between 500 and 650 °C and the overall mass loss of 12 % was obtained. Also, for the laboratory synthesized pure PF resin, the first thermal event was observed at temperature range between 71 and 300 °C, and 8 % mass loss was recorded. The second thermal event was obtained at temperature range between 305 and 500 °C with a mass loss of 5 %. The last thermal event was detected at temperature range between 500 and 649 °C and the overall mass loss of 11 % was obtained. With 25wt% BPF resin, three decomposition events also took place. The first event ranges between 150 and 300 °C leading to 5 % mass loss. The second event ranges between 300 and 460 °C, leading to 8 % mass loss; and the third event ranges between 460 and 650 °C leading to the overall mass loss of 15 %. For the 50 wt% BPF resin, three decomposition events were also recorded. The first event ranges between 150 and 300 °C leading to 6 % mass loss, the second event ranges between 300 and 430 °C leading to 9 % mass loss; and the third event ranges between 430 and 650 °C leading to the overall mass loss of 18 %.

However, 75 wt% BPF, degradation processes occurred at higher temperatures, i.e.; the first thermal event was observed between 150 and 300 °C, leading to 7 % mass loss, the second thermal event, between 300 and 600 °C leading to the main loss region, (41 % mass loss) and the third event was obtained, between 600 and 690 °C leading to 9 % mass loss. Also, from Table 4, the residual carbon contents at 700 °C were 73, 71, 68, 65 and 42 % for the commercial PF resin; laboratory synthesized pure PF resin, 25 wt% BPF, 50 wt% BPF and 75 wt% BPF resins, respectively.

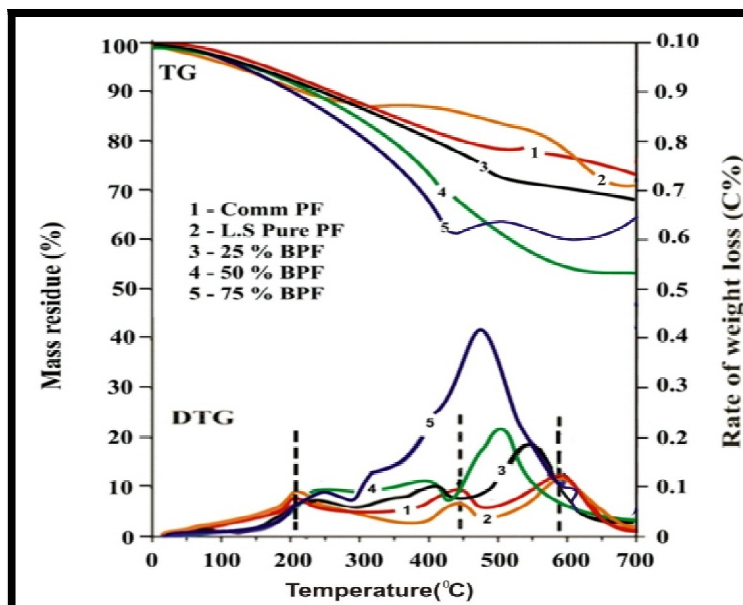


Figure 2: Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) profiles of the resins

It is known that the degradation of phenolic resins has three steps: post-curing, thermal reforming and ring stripping (Khan and Ashraf, 2007; Cheng, 2011). From Figure 2, The first event of the commercial PF resin was observed in the range of 70 °C to 300 °C (7 % mass loss), which could be ascribed to the post-curing reactions of the resin (the removal of terminal groups and further crosslinking or condensation reactions); the second event was obtained from 365 °C to 500 °C (7 % mass loss), which could be attributed to the breaking down of the bridged methylene linkage; and the last event was detected in the range of 500 °C to 650 °C (the main mass loss region, 12 % mass loss) due to the breakdown of the ring network. Also for the laboratory synthesized pure PF resin, the first event was observed in the range of 150 °C to 300 °C (8 % mass loss), which could be ascribed to the post-curing reactions of the resin (the removal of terminal groups and further crosslinking or condensation reactions); the second event was obtained from 365 °C to 500 °C (5 % mass loss), which could be attributed to the breaking down of the bridged methylene linkage; and the last event was detected in the range of 500 °C to 650 °C (the main mass loss region, 11 % mass loss) due to the breakdown of the ring

Resin	T _{s1} /T _{p1} /T _{e1} (°C)	T _{s2} /T _{p2} /T _{e2} (°C)	T _{s3} /T _{p3} /T _{e3} (°C)	Mass Residue at 700 OC (%)
		Mass loss in parenthesis		
Comm PF	70/219/300 (7%)	365/448/500 (7%)	500/592/650 (12%)	73 (± 0.1)
Lab PF	71/220/300 (8%)	305/447/500 (5%)	500/593/649 (11%)	71 (± 0.5)
25 wt% BPF	150/220/300 (5%)	300/422/460 (8%)	460/551/650 (15%)	67 (±0.4)
50 wt% BPF	150/242/300 (6%)	300/390/430 (9%)	430/500/650 (18%)	65 (± 0.2)
75 wt% BPF	150/242/300 (7%)	300/463/600 (41%)	600/648/690 (9%)	42 (± 0.2)

Table 1: Thermal Stability Characterization of Resins Showing the Decomposition Temperatures and Mass Loss Values of the Thermal Events, and Mass Residue at 700 °C for the Resins

When the bio-oil substitution in the BPF resole resins was 50 wt% and lower, that is 25 %wt, the three decomposition ranges were 150 °C to 300 °C (around 5% mass loss), 300 °C to 460 °C (9 % mass loss), and 460 °C to 650 °C (the main mass loss region, i.e. 15 % mass loss for the 25 % BPF, and 18 % mass loss for the 50 % BPF). The ranges of the thermal events for 75 % BPF, however, were transferred to higher temperatures, i.e., 150 °C to 300 °C (7 % mass loss), 300 °C to 600 °C (the main loss region, 41 % mass loss) and 600 °C to 690 °C (9 % mass loss). As discussed previously in the DSC analysis, substituting phenol with bio-oil at a ratio higher than 50 wt% would lead to the synthesis of BPF resin whose properties are governed by the less reactive bio-oil. Therefore, the large mass loss (41 %) for the 75 % BPF resin at temperature ranges of 300 to 600 °C could be explained by the degradation of side chains present in the bio-oil molecules, and the breakdown of the methylene linkage, as was

similarly observed by Wang et. al (2009). From Table 1, the residual carbon contents at 700 °C were 73, 71 and 68, 65, 42 % for the commercial PF; laboratory synthesized pure PF and 25 wt% BPF, 50 wt% BPF, 75 wt% BPF resins, respectively. The decrease in the carbon residue for BPF resins at an increased bio-oil ratio was due to the loss of numerous side chains from the bio-oil molecules (Wang et al., 2009). BPF resins with up to 50 wt% bio-oil displayed comparable thermal resistance to the pure PF resole resin

4. Conclusions

The thermal stability and thermal degradation kinetics of the PF resins were significantly affected by the resin synthesis conditions. The inclusion of the bark phenolic compound in the PF resin synthesis affected the thermal degradation and overall mass loss of the resin at 75wt%

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