Original Research Article

COMPARATIVE ANALYSIS OF POLYESTERIFICATION REACTION ON CRUDE AND EPOXIDIZED NEEM OIL-MODIFIED ALKYD RESIN

ABSTRACT

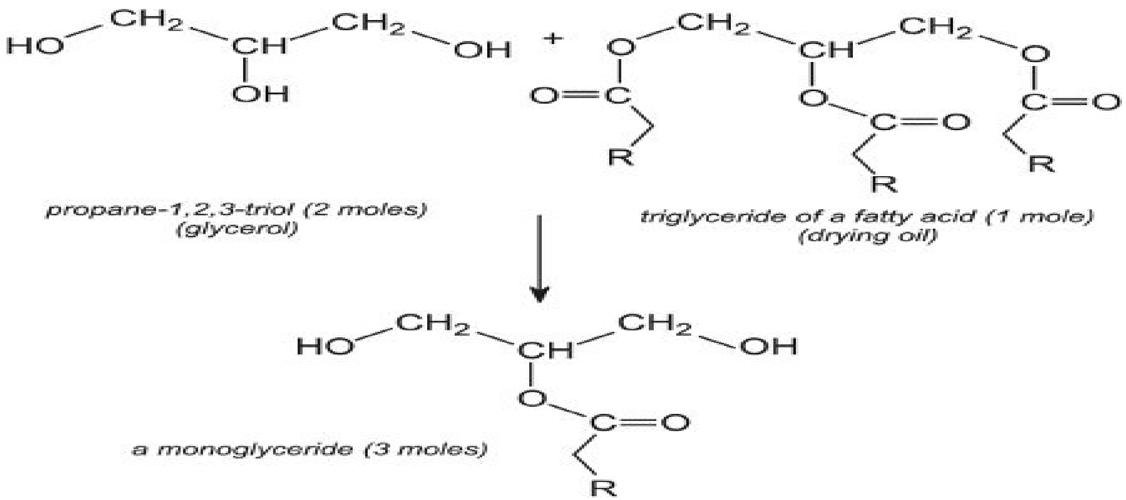
A portion of neem oil was epoxidized using per-acid generated in-situ. Polyesterification of crude neem oil (CNO) and epoxidized neem oil (ENO) was carried out using glycerol and phthalic anhydride to synthesize two different alkyd resins; crude neem oil modified alkyd resin (CNOMAR) and epoxidized neem oil modified alkyd resin (ENOMAR) with oil length of 64.5% each. Setting reaction temperature at 250°C, sample were withdrawn from the reaction mixture at interval of 30mins for a period of 150mins to determine the drop in acid value and was use to obtain a relationship with the degree of polymerization (D_P) and extent of esterification (P_A) for both resins. Minimum acid values of 13.01mgKOH/g and 16.09mgKOH/g were recorded after a reaction period of 150mins for (ENOMAR) and (CNOMAR) respectively. Maxima value of 4.000, (75.0%) and 3.647, (72.6%) were recorded after 150mins as average degree of polymerization (D_P) and percentage extent of esterification ($\%P_A$) for (ENOMAR) and (CNOMAR) respectively. Statistical analysis using ANOVA table to compare the degree of polymerization between (ENOMAR) and (CNOMAR) gave F_V=0.372 and F_C= 5.530. The result of polyesterification (P_A) and degree polymerization reaction (D_P) for both resins reveals that (ENOMAR) has faster rate of polymerization compared to (CNOMAR).

Keyword; Alkyd resin; Extent of esterification; Degree of polymerization and Polyesterification

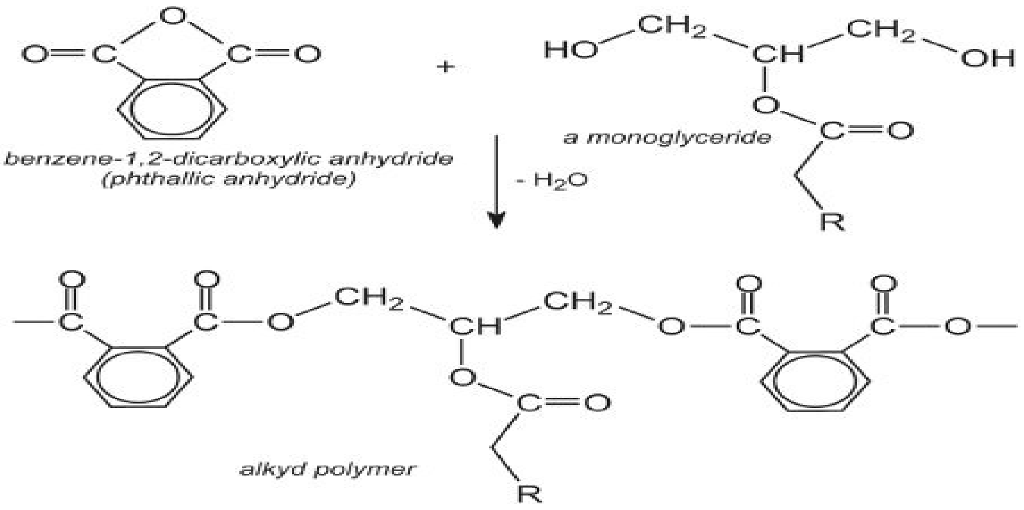
1. INTRODUCTION

Alkyd resins are tough resinous polyester polymer prepared by condensation polymerization of polyhydric alcohol and poly-functional acid or polybasic acid modified with fatty acid or their triglyceride. Many researchers have made an attempt to define alkyd resin over the years. (Bobalek et al. 1964) defines alkyd resin as the reaction product of polyhydric alcohol and poly-functional acid modified by fatty acid or their triglyceride. (Ikhuoria et al 2004) also define alkyd resin as products of poly-condensation reaction between polybasic acid and polyhydric alcohol modified with fatty acid or drying oil, while (Lanson 1985) define alkyd resin as unsaturated polyesters, in which the un-saturation is located at chain ends instead of within the polymer chain. It is estimated that alkyd resins contribute about 70% to the conventional binders used in surface coating today. Surface coatings composition is basically made up of the binder (alkyd resin), pigments and solvents (Wicks et al., 1992) and act mostly as a protective and decorative agent on the surface of the substrate applied. Alkyd resin is known to be the most versatile resin forming reaction. In fact, no other resinous polymer lends itself to greater internal variation or to more useful modification by physical or chemical blending with other polymers (Panda, 2000). Several seed oils have also been used in the synthesis of different polymeric resins like polyester, epoxy, polyurethane, polyamide etc (Aigbodion and Pillai, 2001). The fatty acids from vegetable oil contain suitable functionalities in their backbone such as esters, triple and double bonds either conjugated or non-Conjugated (Larock et al., 2009) and other functional groups that can undergo several chemical modifications. There are two most important methods used in alkyd resin synthesis notably fatty acid and glycerides (alcoholysis) process. Fatty acid process is used when high performance alkyds are needed and this is achieved because the composition of the resulting resin can be more precisely controlled during preparation. The glycerides process is used to prepare more economical alkyd resins, where the end product quality control is not as paramount. This two methods involve a two steps process namely alcoholysis and trans-esterification reaction as shown in scheme 1 and 2 below. The objective of this work is aimed at determining and comparing the extent of esterification (P_A) and degree of polymerization (D_P) between epoxidized neem oil modified alkyd resin (ENOMAR) and crude neem oil modified alkyd resin (CNOMAR). (Aigbodion & Okiemen 1996), studied the kinetics of poly-esterification reaction of rubber seed oil.

SCHEMATIC ROUTE OF ALKYD RESIN FORMATION



(scheme. 1) schematic route of mono-glyceride formation (alcoholysis)



(scheme.2) Schematic route of alkyd resin formation (Poly-esterification reaction)

2. MATERIALS AND METHODS

2.1 Materials

The neem seed was obtained and extracted in national research institute for chemical technology (NARICT) Zaria, Kaduna State. Technical grade reagents of hydrogen peroxide, wijs, solution, acetic acid, carbon tetrachloride, sulphuric acid (98%), sodium thiosulphate, potassium iodate, phthalic anhydride, glycerol, styrene, zinc oxide, nitrogen gas and other reagents were all of analytical grade from (BDH). The glassware and equipment used were 500ml three neck round bottom flask, dean and stark flask, water bath, glass plates, mechanical stirrer, thermometer, reflux condenser, heating mantle, dropping funnel and FTIR-8400S SHIMADZU.

2.2 Methodology

The pretreatment of neem seed was carried out by first de-shelling and isolating the seed, this was followed by washing and drying the seed before extraction using cool press method to obtain crude neem oil (CNO). The following method was adopted in the epoxidation process of crude neem oil (CNO). About 300g of (CNO) was introduced into 500ml three necked round bottom flask fitted with reflux condenser and mechanical stirrer and placed in a water bath. The temperature was regulated to 40^{o}C and the flask allowed to stand for 5min while stirring at constant speed of 500rpm before adding about 0.1% (v/w) concentrated sulphuric acid to oil weight. In a separate flask (conical flask); solution of per-acetic acid was prepared by mixing 14.82g of acetic acid and 118.98g of hydrogen peroxide. This solution was added drop-wise to the heated neem oil at a constant rate over a period of one hour. The temperature was raised to 55^{o}C while still stirring at 500rpm for fine dispersion. This was allowed to stand for 6hrs while maintaining constant temperature of 55^{o}C and stirring speed of 500rpm. During the reaction period, oxirine oxygen content test (OOC) was periodically carried out using AOCS Cd 9-57 test method to ascertain the degree of epoxidation. After having about 85% of (OOC) test, the reaction was quenched and the mixture transferred to a separating funnel where it was allowed to stand for 24hr. The epoxidized neem oil (ENO) was separated by decanting off the aqueous phase.

2.3 Synthesis of Alkyd Resin from the Epoxidized Neem Oil (ENO) and Crude Neem Oil (CNO).

Two different resins were prepared from the epoxidized and crude neem oil with each having an oil length of 64.5%. This was synthesized using two stage process namely alcoholysis followed by polyesterification process. Table 1 and 2 below shows the percentage composition of *(ENOMAR)* and *(CNOMAR)* constituents.

Table 1: The Percentage Composition of (ENOMAR) Constituents

Raw materials	Weight (gram)	Weight (%)
(ENO)	300	64.5
Phthalic Anhydride	95	20.4
Glycerol	70	15.1
Total	465	100

Table 2: The Percentage Composition of (CNOMAR) Constituents

Raw materials	Weight (gram)	Weight (%)
(ENO)	300	64.5
Phthalic Anhydride	95	20.4
Glycerol	70	15.1
Total	465	100

2.4 Procedure for alkyd resin synthesis

Stage 1 (alcoholysis):

In this stage, two separate monoglycerides were first prepared from (ENO) and (CNO) one after the other by reacting 300g of each oil with 70g of glycerol and 0.2% NaOH (w/w) in a reactor equipped with reflux condenser and mechanical stirrer arrangement and nitrogen in-let (scheme 1). This was allowed to stir for 30mins at agitation speed of 800rpm at room temperature in order to help achieve good mixture. The oil was then heated to 250°C with agitation speed of (700 rpm) and N_2 (nitrogen) with sparging rate of about ($0.05ft^3$/sec). The reaction continued until a sample of the reaction mixture became soluble in one to three (1:3) volumes of anhydrous methanol. After completing the alcoholysis, the reaction mixture was cooled to 140˚C.

Stage 2 (trans-esterification)

In the second stage, 95g of phthalic anhydride was added each to the monoglyceride mixture formed from (ENO) and (CNO) produced from the alcoholysis process. The temperature was increased between to 250˚C and maintain at that temperature, while the sparging rate of the N_2 was increased to ($0.1 ft^3/sec$). Aliquots were withdrawn periodically from the reaction mixture at intervals of 30, 60, 90, 120, 150mins to determine the drop in acid value using titrimetric method. The reaction was quenched when the acid value dropped to 12.54mgKOH/g and 15.89mgKOH/g respectively for epoxidized and crude neem oil modified alkyd resins. The acid value of in-process samples taken at intervals were determined by titrating with a 0.1M KOH solution to the phenolphthalein end point after dissolution in a mixture of toluene and ethanol (1:1) (Bobalek et al., 1964). This was used to estimate the average degree of polymerization (Dp) and extent of esterification reaction (P_A) (Bobalek et al., 1964), (Odian., 2004) and (Fried., 2003). See equations below.

$$D_P = (1 — P_A)^{-1} \ldots\ldots\ldots\ldots\ldots \text{Eq (1)}$$

$$P_A = (C_O — C_t) / C_O \ldots\ldots\ldots\ldots \text{Eq (2)}$$

Where P_A = extent of esterification reaction

D_P = Average degree of polymerization

C_t = Acid value after time (t) of reaction

C_O= Initial acid value

Acid Value Determination

$$\text{Acid value} = M \times Tv \times 56.1 / W \ldots\ldots\ldots\ldots \text{Eq(3)}$$

Where M= Concentration of potassium hydroxide (KOH)

Tv= Titre value of KOH

W= Weight of oil in gram and 56.1g is the molar mass of KOH

From equation (1) and (2), the average degree of polymerization (D_P) and the extent of esterification reaction (P_A) for crude neem oil-modified alkyd resin (CNOMAR) *and* epoxidized neem oil modified alkyd resin (ENOMAR) are calculated, while equation (2) is use to estimate the acid values of each aliquot sample.

3.0 RESULTS AND DISCUSSIONS

The alkyd resins were synthesized using two stage processes; the first stage is the alcoholysis process involving the reaction between glycerol and triglyceride from (ENO) and (CNO) which results to the formation of mixtures of mono or di-glyceride compound depending on percentage composition of the reactants and extent of the alcoholysis reaction as shown in scheme 1. The second stage then followed, which is the trans-esterification reaction process involving the reaction between the glyceride mixtures with phthalic anhydride to form a polyester polymer known to be alkyd resin as shown in scheme 2. The results of (D_p), (P_A) and acid value for both resins with reaction time are shown in tables 3, 4, 5 and 6. The average degree of polymerization (D_P) which is defined as the average number of units per polymer chain was determined using acid values obtained at different time interval (Eq 1). The average degree of polymerization (D_P) values of *(CNOMAR)* and *(ENOMAR)* are shown in tables 3 and 4. A plot of $1/(1-P_A)$ versus time of reaction is linear and this behavior was generally observe in poly-esterification reaction (Odion.,2004). The results show that the average degree of polymerization (D_P) of *(ENOMAR)* and *(CNOMAR)* increases with increase in reaction time. Maxima values of 4.00 and 3.65 after reaction period of 150min were obtained as degree of polymerization (D_P) for *(ENOMAR)* and *(CNOMAR)* respectively. The tables 5 and 6 also show that the extent of esterification reaction (P_A) or percentage conversion ($\%P_A$) between *(ENOMAR)* and *(CNOMAR)* increase with increase in reaction time. Maxima value of 75.0% and 72.6% were obtained as percentage extent of esterification reaction ($\%P_A$) for *(ENOMAR)* and *(CNOMAR)* respectively. It can be inferred that the presence of epoxides functional group in neem oil may have positively affected the average degree of polymerization (D_P) and extent of esterification reaction ($\%P_A$). As depicted in tables 5 and 6, the (D_P) and ($\%P_A$) values of the epoxidized neem oil-modified alkyd resin *(ENOMAR)* are higher than those of neem oil-modified alkyd resin *(CNOMAR)*.

Table 3: Shows Acid Value of Crude Neem Oil-Modified Alkyd Resin (CNOMAR) with their Corresponding Degree of Polymerization (D_P) and Reaction Time.

Initial acid value (C_O) = 58.69 mgKOH/g

Reaction time (mins)	Acid Value (mgKOH/g)	Degree of Polymerization (Dp)
30	50.50	1.162
60	44.88	1.308
90	28.05	2.092
120	22.44	2.615
150	16.09	3.647

Table 4: Shows Acid Values of Epoxidized Neem Oil-Modified Alkyd Resin (ENOMAR) with their Corresponding Degree of Polymerization (D_P) and Reaction Time.

Initial Acid Value is (C_O) = 51.94 mgKOH/g

Reaction time (mins)	Acid Value (mgKOH/g)	Degree of Polymerization (Dp)
30	43.06	1.206
60	27.82	1.867
90	20.10	2.583
120	17.82	2.915
150	13.01	4.000

Table 5: Values Showing Extent of Esterification Reaction (P_A), Percentage Extent of Esterification Reaction (%P_A) and Acid Value with reaction time for Epoxidized Neem Oil-Modified Alkyd Resin (ENOMAR).

Reaction time (mins)	Extent of esterification (P_A)	% extent of esterification (%P_A)	Acid value (mgKOH/g)
30	0.171	17.1	43.06
60	0.464	46.4	27.82
90	0.613	61.3	20.10
120	0.657	65.7	17.82
150	0.750	75.0	13.01

Table 6: Values Showing Extent of Esterification Reaction (P_A), Percentage Extent of Esterification Reaction (%P_A) and Acid Value with Reaction Time for Epoxidized Neem Oil-Modified Alkyd Resin (CNOMAR).

Reaction time (mins)	Extent of esterification (P_A)	% extent of esterification (%P_A)	Acid value (mgKOH/g)
30	0.140	14.0	50.50
60	0.235	23.5	44.88
90	0.522	52.2	28.05
120	0.618	61.8	22.44
150	0.726	72.6	16.09

3.1 Statistical Analysis

Table 7: ANOVA Table Comparing Degree of Polymerization (D_p) between (ENOMAR) and (CNOMAR)

Source	df	Sum of square (SS)	Mean square (MS)	F_v	F_c
Treatment	2-1 =1	0.265	0.265	0.237	5.530
Error sum of square (ESS)	10-2 = 8	8.930	1.116		
Total sum (TS)	9	9.200			

α=0.05, confidence limit (95%)

Tables 3 and 4 also shows decrease in acid values with increase in time for (ENOMAR) and (CNOMAR) during the polyesterification reaction. The decrease in acid values follows the usual polyesterification reaction where the rate of polymerization is synonymous with the rate of monomer consumption and product formation, hence polymers are formed by step-wise means while the monomer vanishes gradually. Minimum acid values of 13.01mgKOH/g and 16.09mgKOH/g were recorded for (ENOMAR) and (CNOMAR) respectively after reaction time of 150mins. The decrease in acid values as reaction progresses may be as a result of the reaction between the diabasic acid (phthalic anhydride) with the monoglyceride to form linear polyester (alkyd resin) as shown in scheme 2. This implies that as the reaction progresses, the phthalic anhydride which is highly acidic is gradually being consumed in the esterification reaction to form polyester, hence results to the reduction of acid value with reaction time as shown in tables 5 and 6 for both resins. Molecule of the phthalic anhydride reacts with hydroxyl functionality in monoglyceride and connects to form chain compound which is a complex branched network structure. Comparing the rate of consumption of phthalic anhydride between (ENOMAR) and (CNOMAR), results from tables 5 and 6 shows that throughout the period of reaction for both resins, the rate of monomer consumption is higher in (ENOMAR) compared to (CNOMAR). This is evidently seen from the acid values result obtained from aliquot sample of both resins, which shows less acid value for (ENOMAR) than (CNOMAR). This specific chemical behavior of (ENOMAR), is attributed to the presence of epoxides which has aids in easy consumption of the phthalic anhydride during the polyesterification reaction. Table 7 shows the statistical analysis of the resin comparing degree of polymerization (D_p) between (ENOMAR) and (CNOMAR). Assessments of the results indicate that there is a significant difference in their degree of polymerization (D_P).

Fig 1

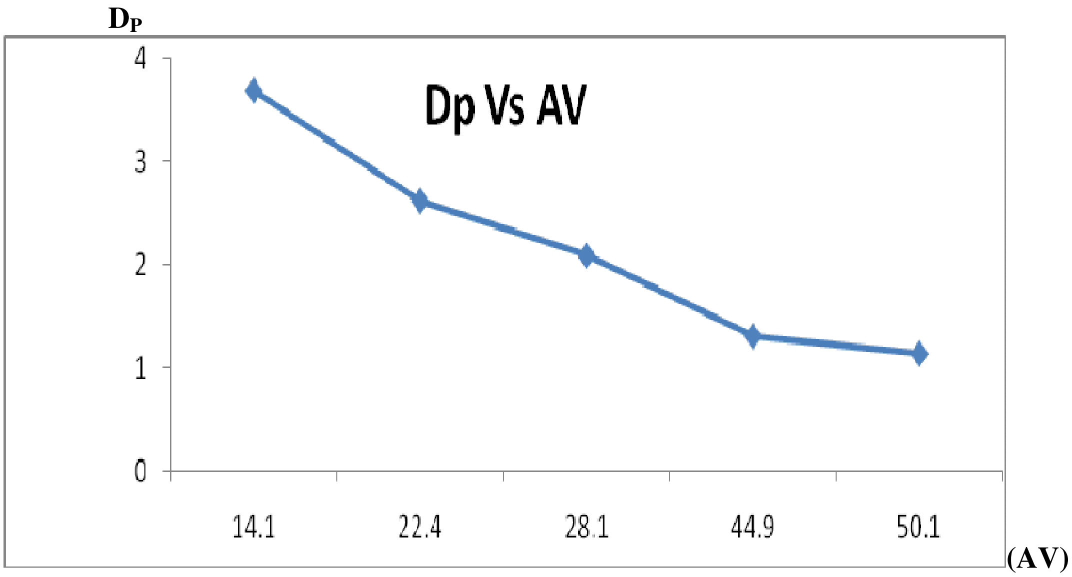


Fig I: Graph of Average Degree of Polymerization (D_p) Versus Acid Value (AV) for (CNOMAR)

Fig 2.

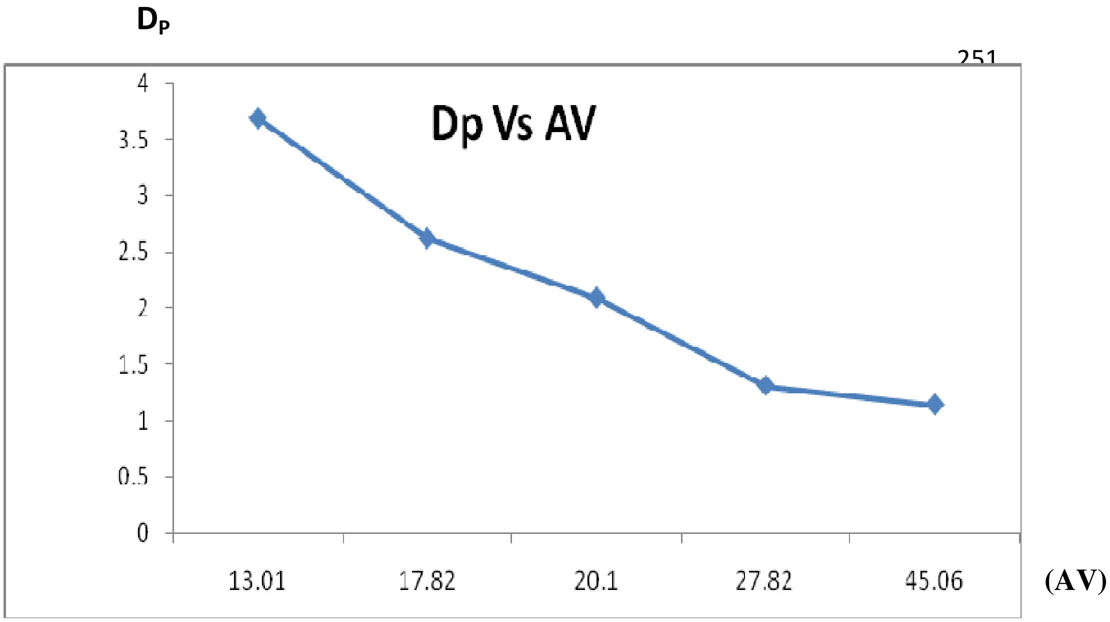


Fig 2: Graph of Average Degree of Polymerization (D_p) Versus Acid Value (AV) for (ENOMAR)

Fig 3,

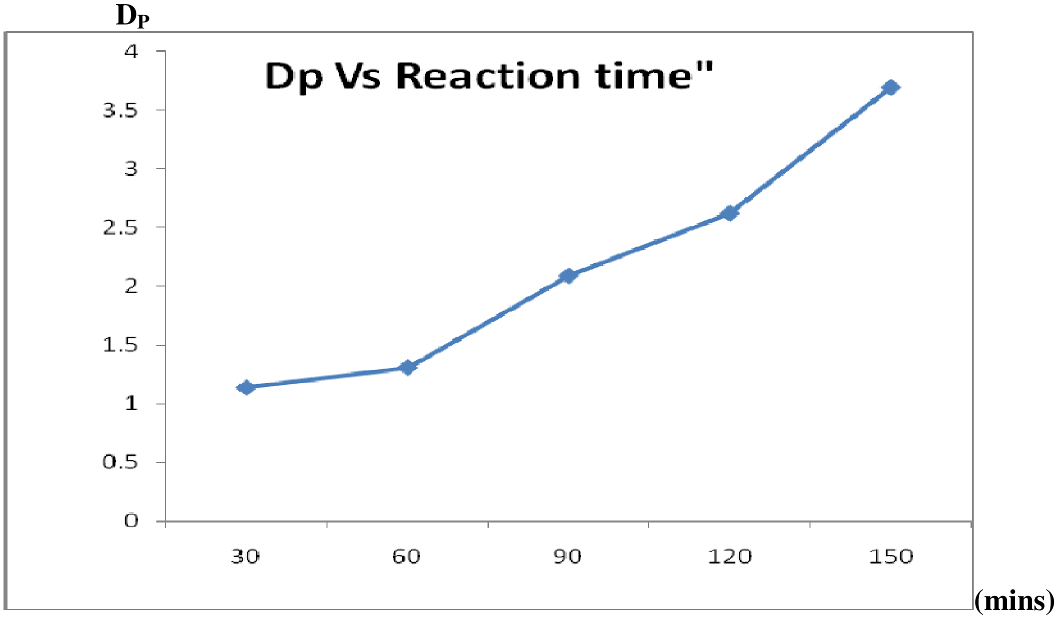


Fig 3: Graph of Average Degree of Polymerization (D_p) of (CNOMAR) Versus Reaction Time

Fig 4,

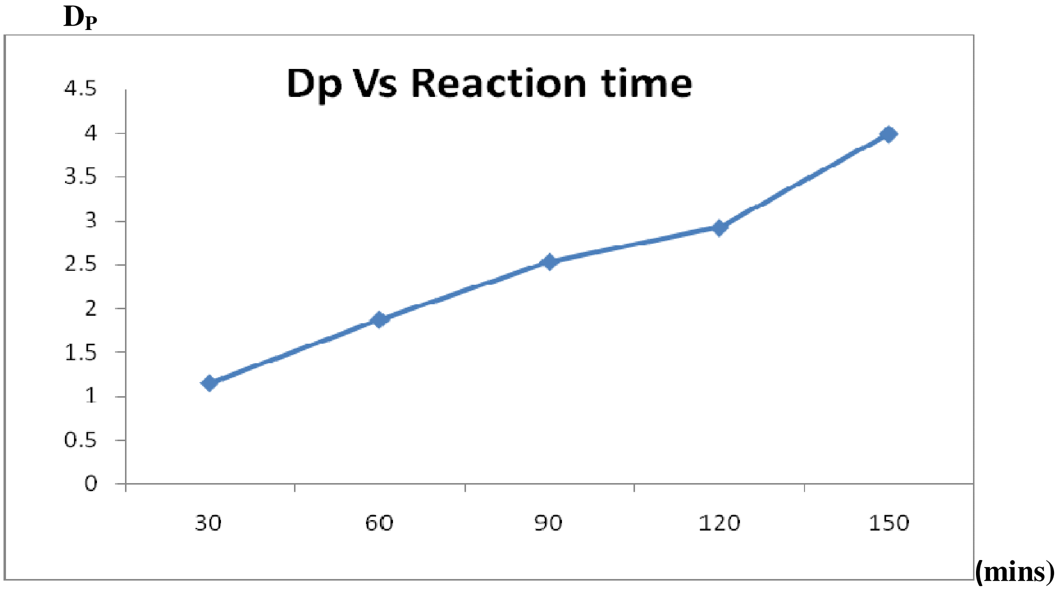


Fig 4: Graph of Average Degree of Polymerization (D_p) of (ENOMAR) Versus Reaction Time

Fig 5,

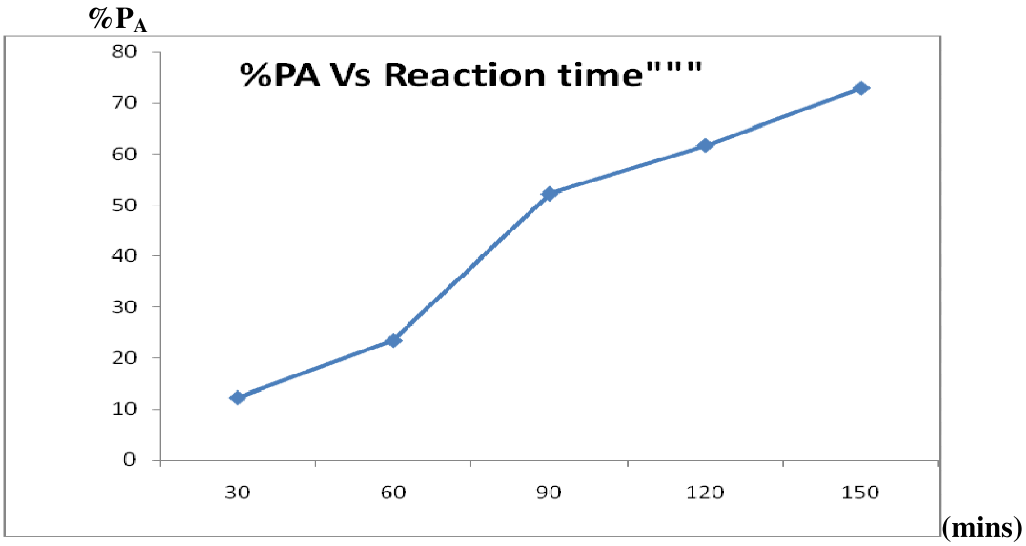


Fig 5: Graph of Percentage Extent of Esterification Reaction (%P_A) of (CNOMAR) Versus Reaction Time

Fig 6,

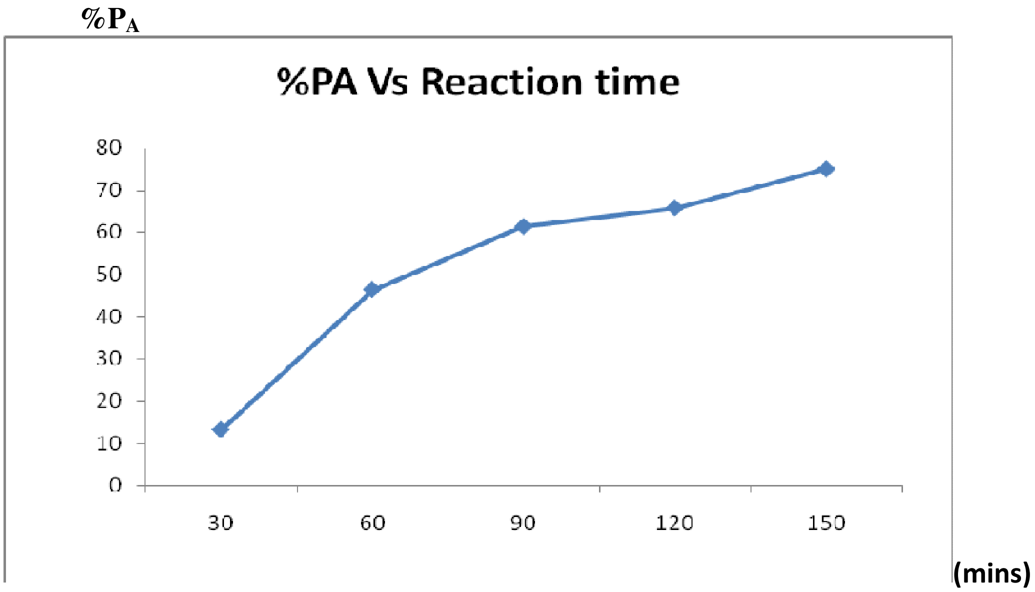


Fig 6: Graph of Percentage Extent of esterification Reaction (%P_A) of (ENOMAR) Versus Reaction Time.

Fig 7,

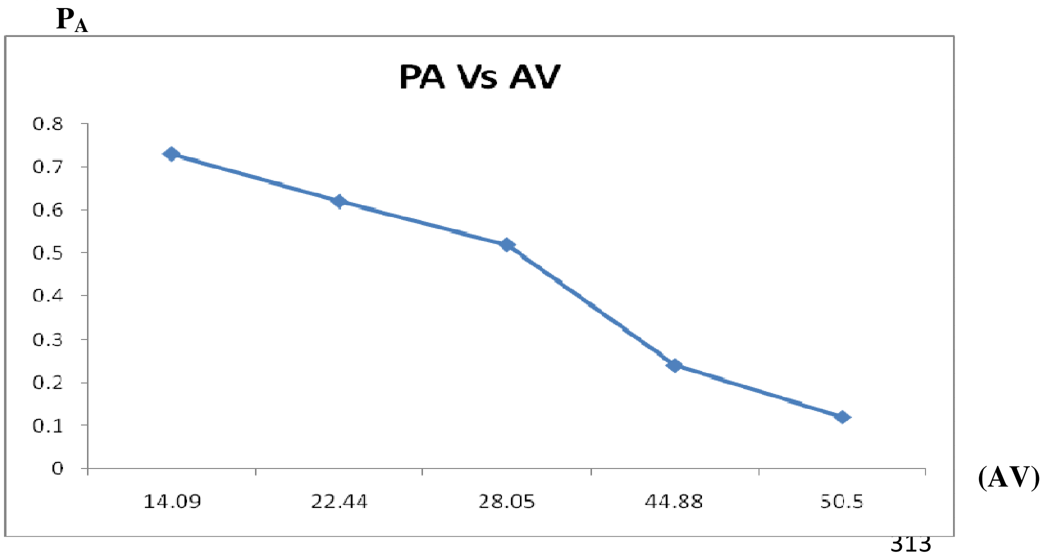


Fig 7: Graph of Extent of Esterification Reaction (P_A) Versus Acid Value (AV) for (CNOMAR**).**

Fig 8,

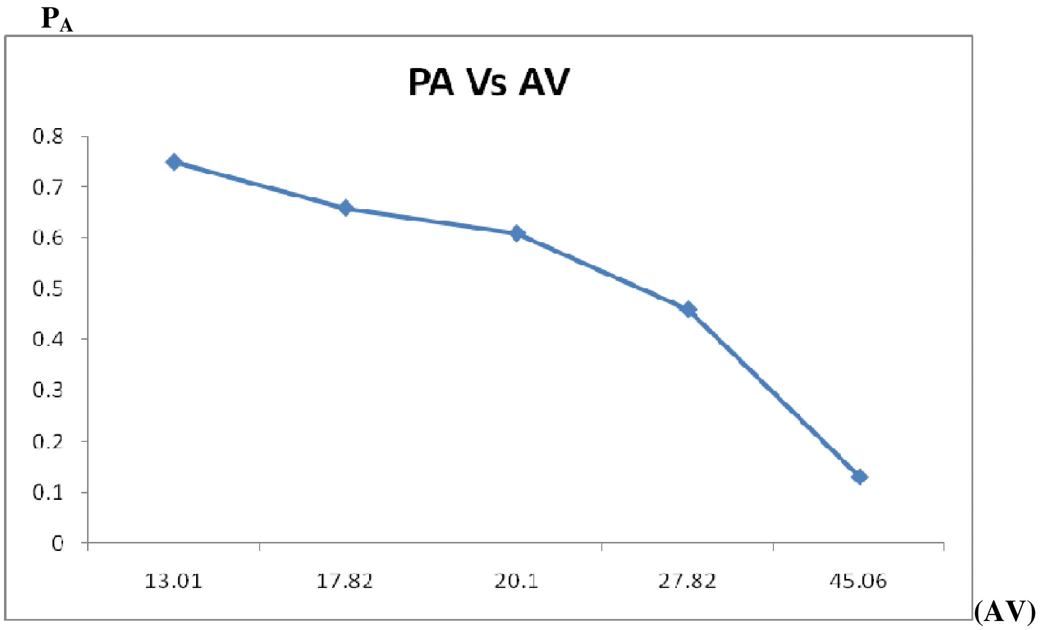


Fig 8: Graph of Extent of Esterification Reaction (P_A) Versus Acid Value (AV) for (ENOMAR**)**

Fig 1 and 2 are graphs showing the degree of polymerization (D_P) versus acid value (AV) for both (CNOMAR) and (ENOMAR) respectively. The result from both graphs shows that (D_P) increases as the acid value (AV) decreases. However, the decreasing effect of the acid value is more pronounced in

(ENOMAR) compared to (CNOMAR), which shows that more phthalic anhydride is being consumed and that polyesterification reaction is much more in (ENOMAR). Fig 3 and 4 represents the graphs of degree of polymerization (D_P) versus reaction time for (CNOMAR) and (ENOMAR). Both graphs also show increase in (D_P) with reaction time. Again, results show that (ENOMAR) polymerizes faster than (CNOMAR). While fig 5 and 6 are graphs of percentage conversion or percentage extent of esterification ($\%P_A$) versus reaction time for (CNOMAR) and (ENOMAR), which shows increase in ($\%P_A$) with reaction time for both resins, but it was observed that the increasing effect of ($\%P_A$) is more on (ENOMAR) and buttresses that percentage conversion rate of phthalic anhydride is higher in (ENOMAR) compared to (CNOMAR). Fig 7 and 8 is a graph showing the relationships between extent of esterification (P_A) versus acid value (AV) for (CNOMAR) and (ENOMAR) respectively. The results from the graphs show that the acid value (AV) decreases with increase in (P_A) and also show the decreasing rate of acid value (AV) in (ENOMAR) which is higher compare to (CNOMAR). This is also an indication that shows that the rate at which the monomer (phthalic anhydride) is consumed with time is higher in (ENOMAR) and that polyesterification reaction is faster in (ENOMAR).

4. CONCLUSION

Neem oil was epoxidized using per-acid generated in-situ. The epoxidized neem oil (ENO) and crude neem oil (CNO) was reacted separately with glycerol and phthalic anhydride at 250^{o}C to investigate the polyesterification reaction of both resins. Assessment of the results obtained from comparing the polyesterification reaction between (ENOMAR) and (CNOMAR) reveals that polymerization reaction was faster in epoxidized neem oil (ENO) compare to crude neem oil (CNO). This buttresses that epoxy functionality enhances polymerization, an attribute that contributes to curing tendencies of resins.

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