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 Setting reaction temperature at 250°C, sample were withdrawn from the reaction mixture at interval of 30 min for a period of 150 min to determine the drop in acid value and was use to obtain a relationship with the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 150 min for (ENOMAR) and (CNOMAR) respectively. Maxima value of 4.000, (75.0%) and 3.647, (72.6%) were recorded after 150 min 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

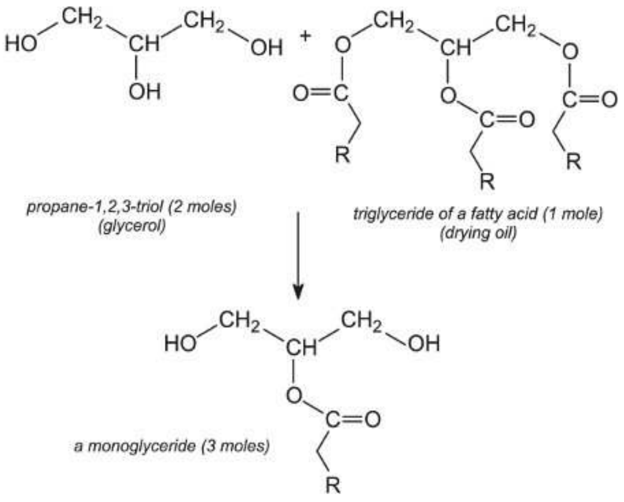
Alkyd resins are tough resinous polyester polymer prepared by condensation polymerization of polyhydric alcohol and poly-functional acid or polybasic acid modified with fatty acid or their triglyceride. Many researchers have made an attempt to define alkyd resin over the years. (Bobalek et al. 1964) 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 been used in the synthesis of different polymeric resins like polyester, epoxy, polyurethane, polyamide etc (Aigbodion and Pillai, 2001). Non-edible oilseeds such as neem (azadirachta indica), jatropha(jatropha curca), karanja(pongomia pinnate), Hura crepitan etc, can be use as a feedstock oil in alkyd resin synthesis. The fatty acid profile of jatropha (jatropha curca) and Hura crepitan was reported by (Odetoye et al 2010) and (Oyekunle and Omode 2008) respectively. In this work, neem seed oil a non-drying oil was utilized in synthesizing alkyd resin with an improve polymerization rate. Neem trees are evergreen plant that grows in tropical and semi tropical region and belong to the mohagony family (meliacease). They contain about 25%-45% oil on dry matter basis with it fatty acids profile seen in Table 1. The trees are abundant in northern part of Nigeria and it seed oil readily available, as such can be utilize as a feedstock in synthesizing alkyd resin in Nigeria. Chemical modification of neem oil existing functional group via epoxidation will improve the performance quality of an alkyd resin synthesized thereof. The use of (ENO) against (CNO) as a feedstock in synthesizing alkyd resin enhances the polyesterification rate and its performance quality.

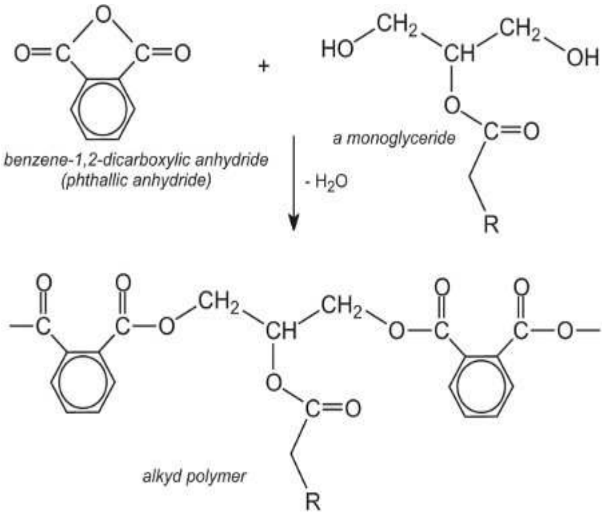
Table 1. Average fatty acid composition in crude Neem seed oil (Kaushik . N and Vir. S,2000).

FATTY ACID	SYSTEMATIC NAME	FORMULA	COMPOSITION RANGE
Linoleic	Cis-9, cis-12- Octadecedianoic	$C_{18}H_{32}O_2$	6-16%
Oleic	Cis -9-octadecenoic	$C_{18}H_{34}O_2$	25-54%
Palmitoleic	Cis-9-hexadecenoic	$C_{16}H_{30}O_2$	?
Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$	16-33%
Stearic	Octadecanoic	$C_{18}H_{36}O_2$	9-24%
Linolenic	Cis-6,cis-9,cis-12-octadecatrienoic	$C_{18}H_{30}O_2$	?

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 transformations. There are two most important methods used in alkyd resin synthesis notably fatty acid and glyceride (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 glyceride process is used to prepare more economical alkyd resins, where the end product quality control is not as paramount. These two methods involve a two steps process namely alcoholysis and polyesterification 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 polyesterification reaction of rubber seed oil.

SCHEMATIC ROUTE OF ALKYD RESIN FORMATION





Scheme 1, Alcoholysis ***Scheme 2, Polyesterification***

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 (30%), wijs solution, acetic acid, carbon tetrachloride, sulphuric acid (98%), sodium thiosulphate, potassium iodate, phthalic anhydride, glycerol, styrene, sodium hydroxide, nitrogen gas and other reagents was obtained from BDH chemical limited. 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 and dropping funnel.

2.2 Methodology

Pretreatment of neem seed was carried out by first cracking the seed nut and isolating seed from the nut, this was followed by washing and drying of 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 5 min 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 peracetic 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. The mixture was allowed to stand for 6 hr while maintaining constant temperature of 55^{o}C and stirring speed of 500rpm. During the reaction period, oxirane oxygen content test (OOC) was periodically carried out using American oil chemist society (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 24 hr. 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. 300g of (ENO) and (CNO) each was used in preparing the two resins. The chemical additives used and its percentage compositions are the same as seen in Table 2.

Table 2: Percentage Composition of the alkyd resin Constituents

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

2.3.1 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 30 min 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 700rpm and N_2 sparging rate of about 0.05ft^3/sec. The reaction was 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 (polyesterification)

In the second stage, 95g of phthalic anhydride was added to each of the monoglyceride mixture formed from (ENO) and (CNO) in the alcoholysis process. The temperature was increased to 250˚C and was maintained at that temperature, while the sparging rate of the N_2 was increased to 0.1ft^3/sec. Aliquots were withdrawn periodically from the reaction mixture at intervals of 30, 60, 90, 120, 150 min 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), American oil chemist society (AOCS) Cd 3d-63. 2009) test method. This was used to estimate the average degree of polymerization (Dp) and extent of esterification reaction (P_A) (Energy conversion and management 2015) and (Process safety and environmental protection 2015). See equations below.

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

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

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

Acid value = M x Tv x 56.1/ W…………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 (3) was used 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 glyceride mixtures of mono or diglyceride compound depending on percentage composition of the reactants and extent of the alcoholysis reaction as shown in scheme 1. The second stage was followed, which is the polyesterification 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 polyesterification reaction (Odion.,2004). The effect of karawila seed oil on the degree of cross linkage in soybean oil modified alkyd resin was discussed by (Amarasinghe et al 2012). As the reaction time proceeds from 30-150 min, there is a cross linkage between phthalic anhydride and the fatty acid monoglyceride (scheme 2) resulting to gradual increase in D_P and P_A. This was evidently noticed by a drop in acid value as the reaction proceeds. The gradual decrease in acid value with time is an indication that phthalic anhydride (dibasic) is gradually being consumed during the polymerization process. 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 150 min were obtained as degree of polymerization (D_P) for *(ENOMAR)* and *(CNOMAR)* respectively. Tables 5 and 6 shows that the extent of esterification reaction (P_A) or it 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 ($\%P_A$) for *(ENOMAR)* and *(CNOMAR)* respectively. It can be inferred that the presence of epoxy 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 crude neem oil-modified alkyd resin *(CNOMAR)*.

Table 3: 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: 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 of 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 of 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 shows decrease in acid values with increase in reaction 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 150 min. The decrease in acid values as reaction progresses is as a result of the reaction between the dibasic 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 during the polyesterification reaction to form polyester, hence a drop in acid value with reaction time is observed as shown in tables 5 and 6 for both resins. Molecule of 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 epoxy functionality which has enhanced the consumption rate of phthalic anhydride during the polyesterification reaction. Table 7 depicts the statistical analysis of the resins, comparing the 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

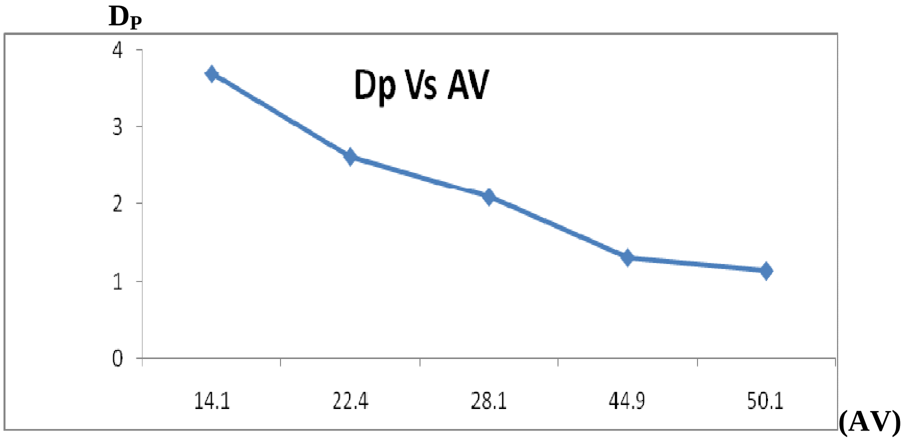
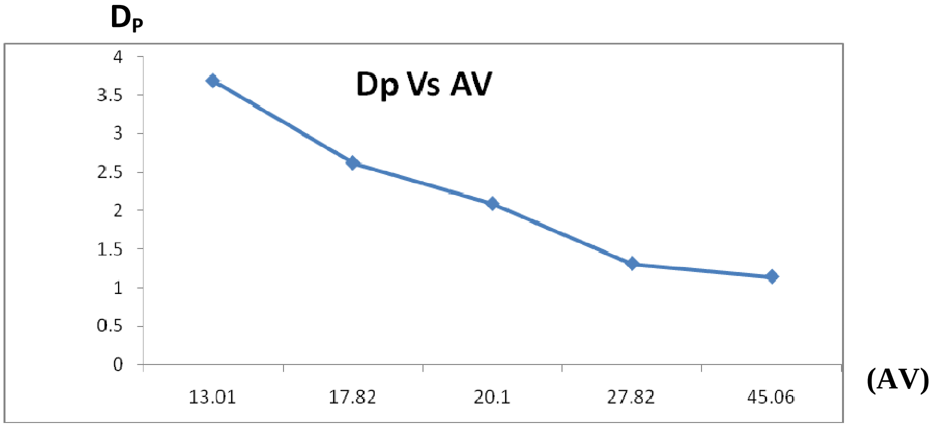


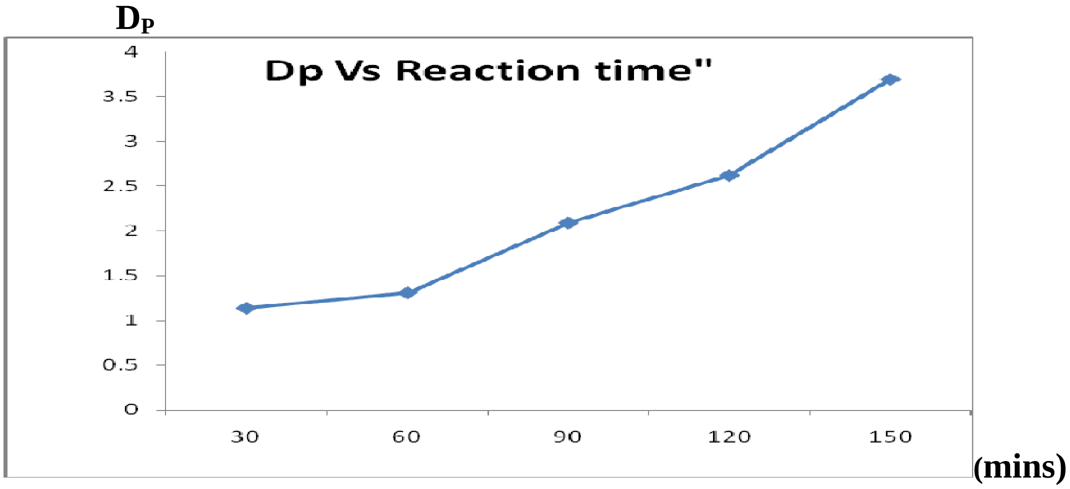
Fig I: Graph of Average Degree of Polymerization (D_p) Versus Acid Value (AV) for (CNOMAR)

Fig 2.



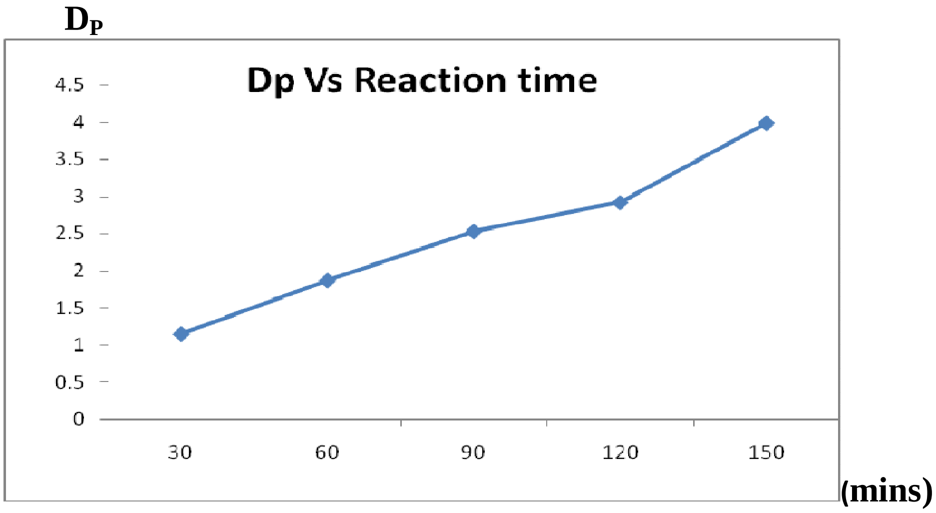
Graph of Average Degree of Polymerization (D_p) Versus Acid Value (AV) for (ENOMAR)

Fig 3,



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

Fig 4,



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

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 reveals that phthalic anhydride is being consumed and polyesterification reaction is much more in (ENOMAR). This is 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). 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 indicate that (ENOMAR) polymerizes faster than (CNOMAR).

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°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.

REFERENCE

Amarasinge.A.D, De silva.S.H, Premachandra.B.B, Prashantha.M.A (2012). Effect of karawila oil (momordica charantia) on synthesizing alkyd resins based on soybean (glycine mix). Progress in organic coatings. 74. 228-232.

American oil chemist society (AOCS) 2009. Official test method Cd 3d-63

Aigbodion, A. I. and C.K. Pillai. (2001). Synthesis and molecular weight characterization of rubber seed oil-modified alkyd resins. Journal of Applied Polymer Science (79); 2431-2438

Aigbodion,A.I, and Okieimen F.E (1996). Kinetics of the preparation of rubber seed oil alkyd. European Polymer Journal. 32(9); 1105-1108. PII: S0014-3057(96) 0053-5

Bobalek, E.G, Moor. E.R, Levy.S.S and Lee.C.C (1964). Some implication of gel point concept on the chemistry of alkyd resins. Journal of Applied Polymer Science. 8:625-657.

Clayton. A.M (1988) (Ed). Epoxy Resin Chemistry and technology, 2nd Ed, MarcelDecker, New York

Energy Conversion and Management. (2015) 106, 932-940

Fried. J.R. (2003). Polymer science and technology, 2nd Edn. Pearson Education Inc, New York, pp; 22-29. ISBN; 0-13-018168-4

Ikhuoria. E.U, Aigbodion.A.I and Okieimen .F.E (2004). Enhancing the quality of alkyd resins using methyl ester of rubber seed oil. Tropical Journal of Pharmaceutical Research. 3(1); 311-317

Kaushik . N and Vir. S(2000). Variation of fatty acid composition of neem seed. Biochemical society transaction volume 28(6)

Lanson, H.J (1985). Alkyd resins. In. Marks.H.F, Bikalas.N.M, Overberger.C.G and Menges (Eds). Encyclopedia of Polymer Science and Engineering. Vol 1. Wiley-Inter-science. New York. p.p; 50

Larock, R.C.and Lu.Y. (2009). Novel polymeric materials from vegetable oils and vinyl monomers; preparation, properties and applications. Chemsuschem2, 136-147

Odetoye.T.E, Ogunniyi.D.S, Olatunji.G.A (2010). Preparation and evaluation of jatropha curcas linneaus seed oil alkyd resins. Industrial crops products. 32, 225-230.

Odion, G.(2004). Principle of polymerization. 4th Edn. New York. John wiley and sons Inc, pp 39-56. ISBN; 0-417-27400-3

Oyekunle. J.A and Omode. A.A (2008).Chemical composition and fatty acid profile of lipid fraction selected from Nigerian indigenous oil seeds. International journal for food products. 11, 273-281

Panda, H.,(2000). Alkyd resins technology handbook; Asia pacific business press inc, AN ISO 9001;

Process Safety and Environmental Protection, (2015) 95, 126-135

Wicks, Z. W., Jones, F., and Pappas, S. P.,(1992). Organic Coatings: Science and Technology, Vol. 1, Film Formation Components and Appearance. New York. John Willey & Sons Inc. pp. 1-7.