



Synthesis and Characterization of Oil-Modified Alkyd Resin from Epoxidized Neem Oil

I. R. Jack¹, A. U. Anya^{2*}, and O. F. Osagie¹

¹Department of Chemistry, Rivers State University of Science and Technology (RSUST), Port Harcourt, Nigeria.

²National Research Institute for Chemical Technology (NARICT), Zaria, Kaduna State, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACSJ/2016/26431

Editor(s):

(1) T. P. West, Department of Chemistry, Texas A&M University-Commerce, USA.

Reviewers:

(1) Nikesh B. Samarth, Institute of Chemical Technology, Mumbai, India.

(2) Rachna Jain, Research and Development, Tata Steel limited, India.

(3) Rajarshi Nareshkumar Patel, Sardar Patel University Affiliated institute, APMS, India.

(4) C. O. Akintayo, University of Ado Ekiti, Ado-Ekiti 4418, Nigeria.

Complete Peer review History: <http://sciencedomain.org/review-history/15257>

Original Research Article

Received 17th April 2016

Accepted 8th June 2016

Published 2nd July 2016

ABSTRACT

The aim and objective of this work is to synthesize a greener alkyd resin by substituting petroleum based epoxides in alkyd resin modification. Chemical transformation of the existing functional group present in neem oil via epoxidation, epoxy functionality was inserted and used as substitute to petroleum based epoxide. Epoxidization of neem oil was carried out with per-acetic generated in-situ at 50°C. Alkyd resin with oil-length of 64.5% was synthesized from the epoxidized neem oil ENO. Polyesterification reaction of the oil was carried out using glycerol and phthalic anhydride at 250°C to synthesize epoxidized neem oil alkyd resin ENOMAR. The resin where cured using methyl ethyl ketone peroxide MEKP and 12% cobalt naphthalate in toluene; this was applied uniformly on a different glass plate substrate and heated in an oven at 80°C and 120°C respectively at different time intervals. Films properties such as drying time, set to touch time and chemical resistance of the resins were determined. Minimum drying and set to touch time was recorded at 15 and 9 hrs at 120°C for 120 mins, while minimum value of 17 and 11 hrs was also recorded at 80°C for 120 min. Chemical resistance of the resin show good resistance in 10% HCl and distilled water. The resin also shows relatively good resistance in 1% NaCl and a poor result in

*Corresponding author: E-mail: anyauzo023@gmail.com

1% NaOH. Infrared analysis result of the resin shows broad and sharp peaks at 1732 cm^{-1} , 2928 cm^{-1} and 3465 cm^{-1} . Assessments of the properties show that epoxidized neem oil modified alkyd resin *ENOMAR* has film properties that are characteristic of good alkyd resins.

Keywords: Alkyd resin; chemical resistance; drying properties; infrared analysis.

1. INTRODUCTION

Alkyd resins are polyester that is derived from the polymerization reaction of polyhydric alcohol and poly-functional acid or polybasic acid modified with fatty acid or their triglyceride [1]. Alkyd resin was also defined by [2] as the products of poly-condensation reaction between polybasic acid and polyhydric alcohol modified with fatty acid or drying oil. Presently, alkyd resins are typically manufactured from acid anhydrides such as phthalic anhydride with polyols like glycerine and are modified with unsaturated fatty acids to give them air drying properties. About 60-70% of an alkyd resin constituents are made-up of biologically derived or biodegradable raw materials and the rest are non biodegradable [3]. Resins can either be produced with drying oil or chemically modified non-drying oils and are referred to as oil-modified alkyd resins and contribute to about 70% to the conventional binders used in surface coating. Some vegetable oil have the tendency to dry or form films in their natural form, this characteristic is directly related to their fatty acid composition and is an inherent characteristic of vegetable oil with high percentage of unsaturated fatty acid, thus such vegetable oil are referred to as drying oil. Non-drying vegetable oil such as neem seed oil that has low percentage of un-saturation, can be utilized for alkyd resin synthesis by incorporation of a suitable functional group like epoxide in the vegetable oil backbone through chemical reaction to transform. It has been reported by [4] that fatty acids from vegetable oil contained suitable functionalities in their backbone such as esters, triple and double bonds either conjugated or non-Conjugated and other functional groups that undergoes several chemical modifications. The functional group transformation of un-saturated bonds in non-drying oil to epoxide via epoxidation can be carried out; this will add value to it by changing the drying characteristic of the resin synthesized from it and enhance its use as alkyd resin feedstock. Epoxidation of neem oil was carried out with per-acetic acid formed in-situ according to a method reported in the literature by [5,6] and [7]. Epoxides functionality undergo curing

reaction with polybasic acid and other chemicals used in resin modification, this produce tough and chemically resistance coatings. The curing process takes place either between the epoxide molecules themselves or by the reaction between the epoxy group and other reactive molecules with or without the help of the catalyst [8]. The aim of this work is to synthesize a greener alkyd resin by substituting petroleum based epoxides through chemical transformation of the existing functional group present in neem oil via epoxidation. The drying process of alkyd resin takes place when atmospheric oxygen oxidizes the unsaturated bond present in the fatty acid.

2. MATERIALS AND METHODS

2.1 Materials

The neem seed oil was obtained, pretreated and extracted in national research institute for chemical technology (NARICT) Zaria, Nigeria. Nitrogen gas and analytical grade reagents of hydrogen peroxide (30%), acetic acid, wijs solution prepared by dissolving 16.2 g iodine monochloride in 1 litre of glacial acetic acid, carbon tetrachloride, sulphuric acid (98%), sodium thiosulphate, potassium iodate, phthalic anhydride, glycerol, styrene, sodium hydroxide and other reagents were all 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 FTIR-8400S SHIMADZU. Characterization of neem oil was carried out using American oil chemical society (AOCS) test methods. Table 2 depicts the result obtained from it characterization.

2.2 Methodology

2.2.1 Epoxidation of neem oil

About 300 g of neem oil was introduced into 500 ml three necked round bottom flask fitted with reflux condenser and mechanical stirrer and placed in a water bath. The temperature was

Table 1. Percentage composition of fatty acids in some vegetable oil

Veg oil	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Other	%US	%S
Rapsed [9]	4.1-6.1	1.2-2.0	57.5-68.9	16.0-23.9	5.5-11.3	-----	-----	-----
Soy bean [10]	10.57	4.09	22.98	54.51	7.23	0.62	84.72	14.66
Rubber seed [11]	8.78	6.15	38.96	42.12	2.38	0.90	83.70	15.61
Cotton seed [12]	24.40	2.20	17.20	55.00	0.30	1.20	72.20	26.60
Jatropha [13]	14.1-15.3	3.7-9.8	34.3-45.8	29.0-44.2	0.0-0.3	-----	-----	-----
Neem [14]	16-34	6-24	25-58	6-17	-----	-----	-----	-----

%US= Percentage un-saturation,
%S= Percentage saturation

regulated to 40°C and the flask allow to stand for 5mins while stirring at constant speed of 500 rpm 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 14.82 g of acetic acid and 118.98 g of hydrogen peroxide. This solution was added drop wise to the heated neem oil at a constant rate for a period of one hour. The temperature was raised to 55°C while still stirring at 500 rpm for fine dispersion. This was allowed to stand for 6hrs while maintaining constant temperature of 55°C and stirring speed of 500 rpm. 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 transferred to a separating funnel where it was allowed to stand for 24 hrs. The epoxidized neem oil ENO was separated by decanting off the aqueous phase. The OOC is calculated as follows

$$\%OOC = (TV \times N \times 1.60) / (Wt \text{ of sample}) \quad (1)$$

TV = Titra value of hydrogen bromide

N = Normality of Hydrogen bromide

Weight of sample = weight of oil sample

Table 2. Physicochemical properties of neem seed oil

Properties	Values
Specific gravity	0.912
Colour	Dark brown
Physical state	liquid
Acid value	16.83 mgKOH/g
Saponification value	173.06 mgKOH/g
Iodine value	84.69 cg/g
Peroxide value	1.42 mg/g

2.3 Synthesis of Alkyd Resin from Epoxidized Neem Oil ENO

Alkyd resin having oil-length of 64.5% was prepared from the epoxidized neem oil ENO. This was synthesized using two stage process namely alcoholysis followed by polyesterification process. Table 4 shows the percentage composition of ENOMAR.

Table 3. Characteristic properties of epoxidized neem oil ENO

Properties	ENO
Iodine value (Cg/g)	12.73
Oxirane content (%)	85.00
Specific gravity	0.959
Colour	yellow brown

Table 4. 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

2.3.1 Alkyd resin synthesis

2.3.1.1 Stage 1; alcoholysis

Monoglycerides were first prepared by reacting 300 g of ENO with 70 g of glycerol and 0.2% NaOH (w/w) in a reactor equipped with reflux condenser, mechanical stirrer arrangement and nitrogen in-let [15]. This was allowed to stir for 30 min at agitation speed of 800 rpm at room temperature in order to achieve good mixture. The oil was then heated to 250°C with agitation speed of 700 rpm in the presence of N₂ with sparging rate of about 0.05ft³/sec. The reaction continued until a sample of the reaction mixture

became soluble in one to three 1:3 volumes of anhydrous methanol and was cooled to 140°C.

2.3.1.2 Stage 2; polyesterification via transesterification

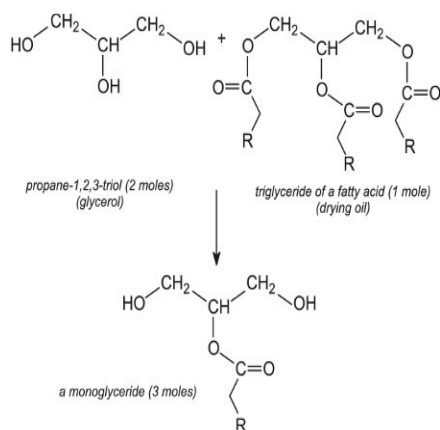
95 g of phthalic anhydride was added to the monoglyceride mixture formed from ENO produced from the alcoholysis process. The temperature was increased to 250°C and maintained at that temperature, while the sparging rate of the N₂ was increased to 0.1ft³/sec. Aliquots were withdrawn periodically from the reaction mixture to determine the drop in acid value using titrimetric method. The reaction was quenched when the acid value dropped to 12.54 mgKOH/g. The acid value of in-process samples were determined by titrating with a 0.1 M KOH solution to the phenolphthalein end point after dissolution in a mixture of toluene and ethanol 1:1.

2.4 Alcoholysis and Polyesterification Reaction Involve in Alkyd Resin Synthesis

In the alcoholysis process, epoxidized neem oil fatty acid triglyceride reacts with glycerol forming a monoglyceride. This was followed by polyesterification reaction involving phthalic anhydride with the monoglyceride to form a polyester alkyd resin as shown in Figs. 1 and 2.

3. RESULTS

Physicochemical properties of the synthesized epoxidized neem oil modified alkyd resin ENOMAR are presented in Table 5. An acid value of 12.54 mgKOH/g was obtained after reacting for 150 mins.



The performance properties of ENOMAR under different chemical environment are given in Table 8. In each case, equal amount of the cure film was dipped into the solvent and allowed for 6hrs. After which the film is dried and the weight loss measured. Increase in weight loss shows less resistance of the resin to the respective solvent and vice versa.

Table 5. Characteristics properties of the alkyd resins synthesized

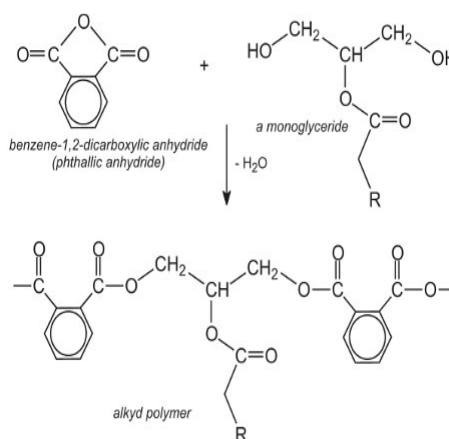
Properties	ENOMAR
Acid value (mgKOH/g)	12.54
Iodine value (Cg/g)	21.15
Refractive index	1.49
Specific gravity	0.984
Colour	Dark brown

Table 6. Drying and set to touch time of ENOMAR at 80°C

Time in oven (min)	ENOMAR drying time (hour)	ENOMAR set to touch (hour)
30	36	18
60	24	15
90	19	14
120	17	11

Table 7. Drying and set to touch time of ENOMAR at 120°C

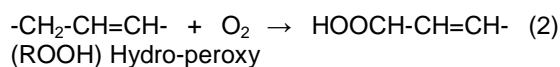
Time in oven (min)	ENOMAR drying time (hours)	ENOMAR set to touch (hours)
30	32	12
60	22	11
90	16	10
120	15	9



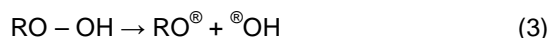
4. DISCUSSION

The percentage composition of the alkyd resin constituents are listed in Table 4, while Table 5 shows some of the physicochemical properties of the resin. The results of drying and set to touch time of ENOMAR after heating in an oven set at temperature of 80°C and 120°C at different time intervals are listed in Tables 6 and 7 respectively. Minimum drying and set to touch time was recorded at 17 and 11 hrs after heating for 120 mins at 80°C, while the time of 15 and 9hrs was recorded as the minimum drying and set to touch time after heating for 120 mins at 120°C. Increase in temperature from 80°C to 120°C reduces the drying time and enhances the curing rate of the alkyd resin synthesized. This is attributed to increase in cross-linkages of the polymeric compound initiated by heat. The results also show that increase in temperature from 80°C to 120°C reduces the drying time. The drying process is based on reaction between oxygen from the epoxy functional group and unsaturation present in the oil [16]. [17] and [18] as shown in equation 2 and 3. Table 8 shows the performance properties of the cured ENOMAR under different chemical environments. The result shows that ENOMAR are highly resistant to 10% hydrochloric acid solution and distilled water but shows relatively poor resistance in 1% sodium hydroxide solution. The poor resistance to alkaline solution by ENOMAR may be as a result of the presence of alkali hydrolysable group. The IR-spectra of

ENOMAR is shown in Fig. 1. In the IR spectrum, the small shoulder 3465.23 cm⁻¹, 3316.71 cm⁻¹ and 3205.80 cm⁻¹ correspond to free isolated hydroxyl (O-H) alcohol of the polymer. The strong broad band at 1732.13 cm⁻¹ indicate the presence of carbonyl group (C=O), while a medium band at 2928.04 cm⁻¹ correspond to the presence of olefins. The presence of several other bands are an indication of other functional group such ether, ester etc that comes as a result of ring opening of the epoxy group, thus culminating to side reactions. Ring opening of oxirane functional group during the process of synthesizing ENOMAR gives alkoxy and hydroxyl radicals. This radical are susceptible to other side reactions that form ester and ether. The drying process of alkyd resin takes place when unsaturated bonds present in fatty acids are oxidized by atmospheric oxygen to give hydro-peroxy groups as seen below.



Decomposition of hydro-peroxy give alkoxy and hydroxyl radicals



The alkoxy, hydroxyl radicals are susceptible to side reactions which results to ester and ether formation. These radicals are form after the epoxy ring opening, thus exposing it to other side reactions.

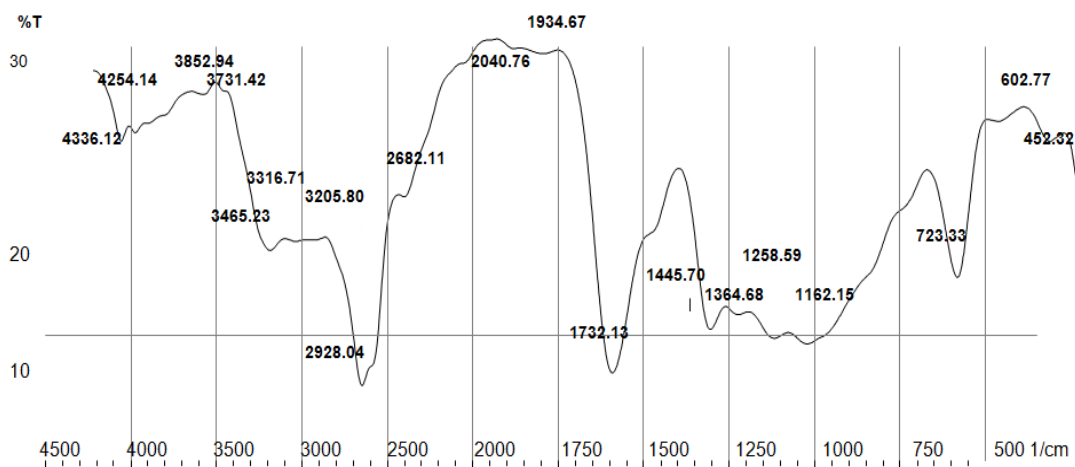


Fig. 1. Infrared spectra of ENOMAR

Table 8. Chemical resistance of ENOMAR in different chemical environments

Alkyd type	10% HCl	1% NaOH	10% NaCl	Distilled H ₂ O
ENOMAR	Very good	Fair	Very good	Very good

Key; Very good = >70%, Good = 60-69%, fair = 50-59%, Poor = < 50%

5. CONCLUSION

The aim and objective of this work is to synthesize a greener alkyd resin by substituting petroleum based epoxides that is used in alkyd resin modification. Through chemical transformation of the existing functional group present in neem oil via epoxidation, epoxy functionality was inserted and used as substitute to petroleum based epoxide. Assessments of the properties show that epoxidized neem oil modified alkyd resin *ENOMAR* has film property that is characteristic of a good alkyd resin. Alkyd resin with acid value of 12.54 mgKOH/g was synthesized from epoxidized neem oil after reaction period of 150 mins. The FTIR analysis result of the resin show characteristic of a good resin which buttresses that a good quality alkyd resin can be synthesized from epoxidized neem oil; a non edible vegetable oil with low unsaturation sourced locally. Assessments of the resin properties also reveals that epoxidized neem oil modified alkyd resin *ENOMAR* cures faster after being exposed at 120°C for 150 mins compare at 80°C for 150 mins. This is a typical characteristic property of a polymeric reaction which is often initiated by heat.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Bobalek EG, Moor ER, Levy SS, Lee CC. Some implication of gel point concept on the chemistry of alkyd resins. *Journal of Applied Polymer Science*. 1964;8:625-657.
- Ikhuoria EU, Aigbodion AI, Okieimen FE. Enhancing the quality of alkyd resins using methyl ester of rubber seed oil. *Tropical Journal of Pharmaceutical Research*. 2004;3(1):311-317.
- Hofland A. Alkyd resin down and out to alive and knocking. *Progress in Organic Coating*. 2012;73:274-282.
- Larock RC, Lu Y. Novel polymeric materials from vegetable oils and vinyl monomers; preparation, properties and applications. *ChemSusChem*. 2009;2:136-147.
- Mungroo R, Goud VV, Narayan NS, Dalai A K. Utilization of green seed canola oil for in situ epoxidation. *European Journal of Lipid Science and Technology*. 2011;113:768-774.
- Petrovic Z, Zlatanovic A, Lava CC, Sinadinovic-fiser S. Epoxidation of soybean oil in toluene with peroacetic and peroxyformic acids- Kinetic and side reactions. *European Journal of Lipid Science and Technology*. 2002;(104):293-299.
- Sinadinovic-Fise S, Jankovic M, Petrovic Z. Kinetics of in situ epoxidation of soybean oil in bulk, catalyzed by ion exchange resin. *Journal of American Oil Chemist Society (JAOC)*. 2001;(78):725-731.
- Bhatnagar MS. *Polymeric materials encyclopedia* CRC. Press, Inc; 1996.
- Milan P, Dubrarka S, Zvonko M, Sandra N, Jasminka, B, Dunja, M. Fatty acid composition in oil of recent rapeseed hybrids. *Agriculture Conspectus Scientific*. 2007;72(3):187-193.
- Earl G, Lawrance A, Caiping S, Tong W, Pamela J. *Bailey's industrial oil and fat products*, sixth edition, six volume set. Copyright John Wiley & Sons, Inc; 2005.
- Kittigowittana K, Wongsakul S, Krisdaphong P, Jimtaisong A, Saewan N. Fatty acid composition and biological activities of seed oil from rubber cultivar. *International Journal of Applied Research in Natural Products*. 2008;6(2):1-7.
- National cotton seed product association (NCPA). *Willow tree circle cordova*. TN38018; 2016.
- Azhari M, Faiz R, Yumus T, Mohd T, Yaw S. Reduction of free fatty acids in crude *Jatropha curcas* oil via an esterification. *International Journal of Engineering and Technology*. 2008;5(2):92-98.
- Kaushik N, Vir S. Variation of fatty acids composition of neem seed. *Biochemical Society Transaction Volume*. 2000;28(6).
- Aigbodion AI, Okieimen FE. An investigation of the utilization of African locust bean seed oil in preparation of alkyd

- resins. Nigeria. Ind. Crops Prod. 2001; 13:29-3.
16. Karakaya C. Synthesis of oil based hyper-branched resins and their modification with melamine formaldehyde resins in chemical engineering. Progress in Organic Coating. 2007;59(4):265-273.
17. Bat E. Synthesis and characterization of hyper-branched and air drying fatty acid based resins in chemical engineering. Ankara. METU. Progress in Organic Coatings. 2005;55(4):330–336.
18. Oyman ZO, Ming W, Linde R. Oxidation of drying oils containing non - conjugated and conjugated double bonds catalyzed by a cobalt catalyst. Progress in Organic Coatings. 2005;54(3):198204.

© 2016 Anya et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
<http://sciencedomain.org/review-history/15257>