

# DEVELOPMENT OF A BIOBASE - LUBRICANT FROM LOCUST BEAN SEED OIL

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**ABSTRACT:** his project is based on the modification of locust bean seed (*parkiabiglobosa*) oil to soothe its use as a biobased resin. This bio-resin was used to produce lubricant as a case study of its reactive ability. The locust bean seed oil was extracted by solvent contact and epoxidized using hydrogen peroxide . The epoxidised oil was analysed for the viscosity, iodine and oxirane values. The viscosity was determined at different temperatures for the purpose of use as a bio-lubricant. The oxirane values were determined at varying quantities of hydrogen peroxide. The effect of temperature and quantity of peroxide on iodine values was also analysed. The modification was successful because epoxidized locust bean seed oil (ELBSO) maintained high viscosity at high amount of peroxide.

**KEYWORDS:** Bio-resin, oxirane value, lubricant, locust bean, epoxidation.



## INTRODUCTION

Bio-based polymers are gaining overwhelming interest and recognition worldwide due to the health, safety, and environmental concerns over the conventional synthetic polymers, and the legislation against their usage. In both domestic and industrial applications, alternative materials with comparable properties are being sought. These bio-based polymers are renewable, biodegradable, and environmentally friendly<sup>[1]</sup>. There is an increasing demand for environmentally friendly lubricants particularly in areas where contact with water, food, or people is unavoidable. In such applications, emission of components of such lubricants into the environment is unavoidable. This is especially a problem for activities in sensitive environments such as marine and forestry. A solution to avoid extensive soil and water pollution is the use of environmentally friendly lubricants. Mineral oil based product that are currently in use are not biodegradable and they contaminate the environmental or become a disposal problem. Bio-based lubricants are important materials used to reduce friction between moving and stationary surfaces of engines and other machinery in order to reduce wear and dissipate heat on those surfaces and to provide other benefits such as corrosion protection<sup>[2]</sup>. Utilization of renewable raw materials in unsaturated polymer resins, UPRs and composites is becoming a feasible approach to reducing environmental impact and supporting sustainability efforts, while simultaneously creating value and building competitive advantage. Chemical tools for conversion of renewable resources into polyester resins have existed for several decades. For example, the alkyd resin industry utilizes those tools to effectively incorporate fatty acids, vegetable oils, rosin, and glycerol into their resins. Fatty acids, like tall oil fatty acids, and drying oils, such as tung oil and linseed oil, have been used frequently as renewable resource components of alkyd based paints and coatings.

Unlike UPRs, alkyd resins have lower reactivity and cannot be used in traditional composites applications. However, similar chemistry tools can be used to incorporate renewable raw materials into UPRs and composites. Fatty acids, vegetable oils, and their derivatives, which historically represented key components that distinguished alkyds from other polyester resins, have been used with UPRs in the composites industry merely as additives, such as mold release agents, and surface profile enhancers in sheet molding compounds (SMC). Only recently have these renewable components found their use for the synthesis of UPRs. Initially, academic researchers utilized synthetic pathways to convert inexpensive and readily available vegetable oils into an array of useful intermediates for UPR synthesis. These conversions were accomplished through transesterification, epoxidation, ozonolysis, hydroxymethylation, maleinization and cycloaddition reactions of plant oil triglycerides and their derivatives. However, despite the availability of chemical tools, no commercially available “green” UPRs appeared in the market until 2003. The first industrially available biobased UPR contained approximately 18% total bio-content derived from the combination of soybean oil and corn derived ethanol. This UPR was designed primarily for compression molding applications, in particular for the preparation of SMC molded parts for agricultural equipment, such as combines and tractors. Direct comparison of the resin’s liquid properties and mechanical properties of molded SMC parts showed similar properties to 100% petroleum-based resin counterpart. Since its introduction to the market, interest in “green” UPRs and composites has grown considerably and new opportunities in composites markets opened up. Because the first “green” resin could not be formulated to meet performance requirements for all composites applications, new generations of renewably resourced UPRs were needed to satisfy the demand. Diminishing petroleum reserves, crude oil price escalation, and rapid advances in white biotechnology changed raw material markets to a point where renewable raw materials and bioproducts can effectively compete with petrochemical analogues.<sup>[3]</sup> Now we are in an age of increasing oil prices, global warming and other environmental problems (e.g. waste) the change from fossil feedstock to renewable resources can considerably contribute to a sustainable development in the future. Especially plant derived fats and oils bear a large potential for the substitution of currently used petrochemicals, since monomers, fine chemicals and polymers can be derived from these resources in a straightforward fashion. The synthesis of monomers as well as polymers from plant fats and oils has already found some industrial application and recent developments in this field offer promising new opportunities. The plant oils cannot be used on their own in composite application unless they are suitably functionalized in order to add cross-linkable sites to the fatty acids of the triglyceride. The purpose of this is to cure the resin to completion upon heating with the addition of peroxide. Some of the available bio-based resins from plant oils are acrylatedepoxidized soybean oil (AESO), maleinatedepoxidized soybean oil (MAESO), methacrylated soybean oil (MSO), and methacrylic anhydride modified soybean oil (MMSO). These renewable resins have good mechanical properties that are comparable to those of petrochemical-based resins. The locust bean seed has a percentage oil content of 27 percent making it a more viable source of oil for development of resin.<sup>[5]</sup>

Epoxides are well known commercially because of the many important reactions they undergo. Epoxidation of long chain olefins and unsaturated fatty acid is carried out on industrial scale<sup>[6]</sup> Fats and oil are renewable resources that can be enzymatically treated to produce materials that can other act as a replacement for materials derived from petroleum. Fatty epoxides are used directly as plasticizers that are compatible with polyvinyl chloride (PVC) resins and stabilizers for PVC to improve stability of polymer towards heat and UV-radiation.<sup>[7]</sup>

Due to the high reactivity of the oxidant ring, epoxide also acts as a raw material for variety of chemicals such as alcohols, alkanolamide, carboyl compounds, olefinic compounds and polyesters, polyurethanes and epoxyresins.

Epoxides with high oxirane and lower Iodine value are considered to be of better quality.<sup>[8]</sup> There are four known technologies to produce epoxides from olefinic type of molecules:

- Epoxidation with polycarboxylic acids (polycarboxylic acid e.g. ethanoic acid.)
- Epoxidation with organic and inorganic peroxides; this is the method considered for this work.
- Epoxidation with halo-hydrines; “halo” from halogens and hydrines are derivatives of hypohalous acid (HOX) e.g. hydrofluoric acid, HOCl.
- Epoxidation with molecular oxygen-Ozonolysis method; very expensive method.

Triglycerides are composed of three fatty acid chains joined together at the glycerol center. The fatty acids have various levels of saturation and unsaturation, and it is the unsaturated part that is functionalized to give the desired matrix which is used in composite manufacture. The triglyceride in the LBSO is cured with hydrogen peroxide. Many active sites from the triglycerides, such as double bonds, allylic carbons, and ester groups, can be used to introduce polymerizable groups.

**LOCUST BEAN SEED (PARKIA BIGLOBOSA)** The African locust bean tree, *Parkia biglobosa* is a perennial tree legume which belongs to the sub-family *Mimosoideae* and family *Leguminosae*. It grows in the savannah region of West Africa up to the southern edge of the Sahel zone 13°N (Campbell-Platt, 1980). These trees are not normally cultivated but can be seen in population of two or more in the savannah region of Nigeria (Schnell, 1957; Hopkins, 1983). The *Parkia* tree play vital ecological role in cycling of nutrients from deep soils, by holding the soil particles to prevent soil erosion with the aid of roots. The trees also provide shades for farmers (Campbell-Platt, 1980). *Parkia* tree is used as timber for making pestles, mortars, bows, hoe handles and seats (Hagos, 1962; Irvine, 1961). The trees of the *Parkia* species are usually and carefully preserved by the inhabitants of the area where they grow because they are valuable sources of reliable food, especially the seeds which serves as source of useful ingredients for consumption (Campbell- Pratt, 1980). It has been reported that the husks and pods are good food for livestock (Douglass et al., 1976;). The seeds are processed into a local product (Iru in Yoruba) used as soup ingredient. Percentage oil in African locust bean (*Parkia biglobosa*) is approximately 27% and its fatty acid composition is: palmitic (27.5%),

stearic (10.5%), oleic (14.5%), linoleic (44.5%) and linolenic (3.0%)<sup>[9]</sup>. It is a non-drying oil with iodine value of 94 mg iodine/g oil.

## METHODOLOGY

The locust bean seeds (*parkiabioglobosa*) undergoes the following pretreatments: sorting, cooking, peeling, drying, grinding followed by the extraction process.

The Extraction process was carried out by solvent extraction using the soxhlet extractor.

Epoxidation of locust bean seed oil (LBSO) was performed according to the method of Cheng and Rayson (2004). In this experiment 100g of oil was mixed with 1ml of NaOH solution in 500ml flask. The flask was allowed to attain equilibrium at a reaction temperature in thermostat bath. The mixture was stirred for 30min at a controlled rate so that the oil in the mixture was finely dispersed. The reaction was monitored by withdrawing aliquots of the reaction mixture at various time intervals into 100ml of cold water in a separating funnel. The oil was dried and concentrated in a vacuo and analyzed for iodine value. The conversions of the double bonds were calculated as:

$$X = [IV_0 - IV] / IV_0$$

X = Fraction of conversion

IV<sub>0</sub> = Initial Iodine value

The experiment was repeated for 2ml, 3ml, 4ml and 5ml hydrogen peroxide volumes; in each case maintaining the same mass of oil and volume of NaOH solution. After which their Iodine values (oxirane values) are determined to show levels of modification. Epoxidation was carried out at various temperatures (30°C, 40°C, 50°C, 60°C, 70°C) and at each stage the viscosity was determined.

**Viscosity measurement** was determined using a Cannon-Fenske viscometer and circulatory bath with temperature control. Viscosity was calculated using the ASTM method (ASTM, 1997)<sup>(4)</sup>. The sample was sucked into it and then immersed into the circulatory bath set at 30°C. The time of flow of the sample from the upper mark to the lower mark of the viscometer was recorded using a stop watch. The experiment was repeated thrice and the average flow time recorded. This was carried out for all modified samples at different temperatures (30°C, 40°C, 50°C, 60°C, 70°C). The efflux time for 60% sucrose solution was equally determined and recorded and the result obtained was used as the standard for the determination of the constants. The viscosity of the samples was calculated using the formula below;

$$\text{Viscosity } (\eta) = K \ell T$$

K = Instrument constant

ℓ = density of sample

T= Efflux time (sec)

**DETERMINATION OF IODINE VALUE** The iodine value of oil is the number of grammes of iodine which can be absorbed by 100g of the oil. It is the measure of the proportion of unsaturated acids present in the oil. In Dam's method, a reagent containing bromine, pyridine, concentrated sulfuric acid and glacial acetic acid was used. The standard procedure outline in Association of official analytical chemists (AOAC) was followed. To determine the iodine equivalent of the blank, 5ml of tetrachloromethane was pipeted in a conical flask and 5ml of dam's iodine was added from the buirette. It was corked and placed in a dark cupboard for 10min, it was then removed and 5ml of 10% KI (potassium iodide) solution was added, followed by 20ml distilled water. This was mixed thoroughly and titrated in the same flask with 0.0025N  $\text{Na}_2\text{S}_2\text{O}_3$  (Sodium thiosulphate). A 1% starch solution was used as indicator (1ml) towards the end of the titration. The end point was reached when the blue color was discharged. This procedure was repeated for the test samples but 5ml of 0.5% sample oil was used in place of tetrachloromethane. Dam's iodine was prepared by dissolving 8.2ml pyridine and 6ml concentrated  $\text{H}_2\text{SO}_4$  20ml glacial acetic acid which was added to a solution of 2.6ml bromine in 20ml acetic acid and made up to 1000ml with glacial acetic acid.

$$\text{Iodine value (IV)} = (\text{blank titre value} - \text{test titre value}) \times 0.003175 \times 40 \times 100.$$

## RESULTS

Weight of seeds before extraction=1350g

Weight of seeds after extraction= 1248.7g

Weight of extracted oil=101.3g . Percentage oil yield=7.5%

Table 1; Viscosity of ELBSO at varying temperatures and quantity of  $\text{H}_2\text{O}_2$

Amount of $\text{H}_2\text{O}_2$	30°C	40°C	50°C	60°C	70°C
1ml	180	99	98	97.8	97
2ml	220	115	113.9	113.7	112.9
3ml	290	148	145	144	144
4ml	360	188	187	186.5	186.2
5ml	860	440	435	434.7	434.2

Table 2; Log of Viscosity at inverse temperatures in Kelvin ( $\text{K}^{-1}$ )

Amount of H <sub>2</sub> O <sub>2</sub>	3.3x10 <sup>-3</sup> K <sup>-1</sup>	3.2x10 <sup>-3</sup> K <sup>-1</sup>	3.1x10 <sup>-3</sup> K <sup>-1</sup>	3.0x10 <sup>-3</sup> K <sup>-1</sup>	2.9x10 <sup>-3</sup> K <sup>-1</sup>
1ml	2.25	1.996	1.991	1.990	1.987
2ml	2.342	2.061	2.057	2.056	2.053
3ml	2.462	2.170	2.161	2.158	2.158
4ml	2.556	2.274	2.272	2.271	2.269
5ml	2.934	2.643	2.638	2.638	2.637

Table 3; Iodine values (mg I<sub>2</sub>/g Oil) of ELBSO at varying temperatures and amount of H<sub>2</sub>O<sub>2</sub>

Amount of H <sub>2</sub> O <sub>2</sub>	30 <sup>0</sup> C	40 <sup>0</sup> C	50 <sup>0</sup> C	60 <sup>0</sup> C	70 <sup>0</sup> C
1ml	94.40	84.10	80.10	75.40	70.40
2ml	91.80	79.90	77.40	70.30	66.30
3ml	87.25	74.10	70.50	64.50	59.50
4ml	82.50	69.40	62.50	58.50	54.50
5ml	79.10	64.20	59.80	50.70	45.70

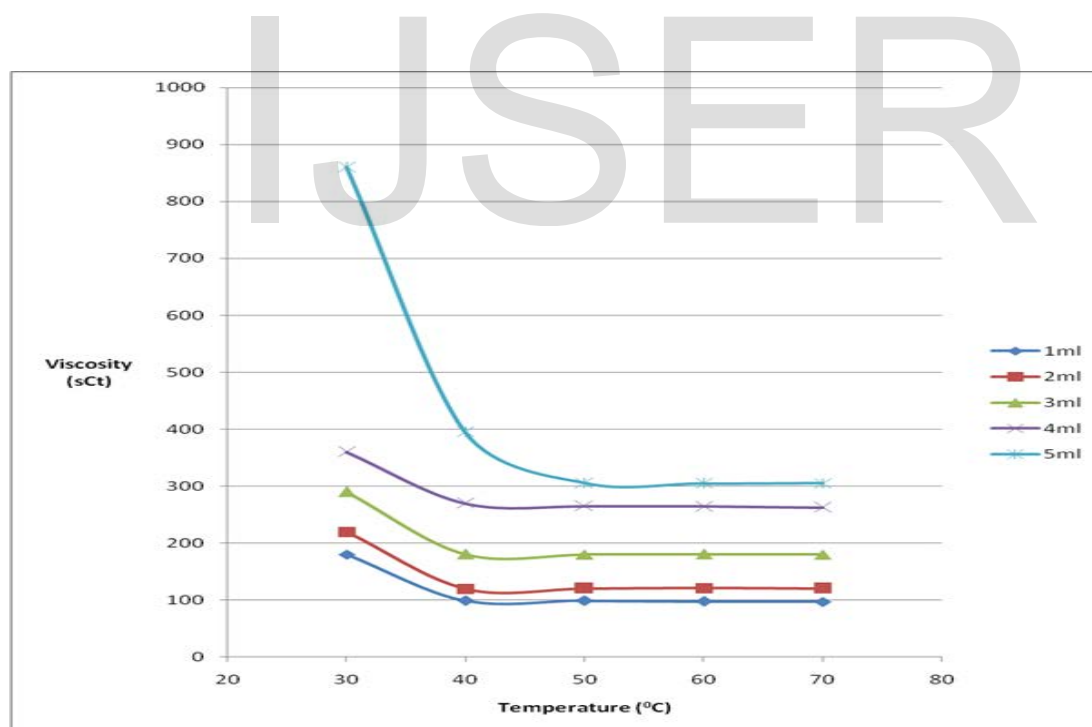


Fig. 1: Plot of viscosity against temperature

Fig. 1 shows the effect of temperature on the viscosity of epoxidized locust bean seed oil (ELBSO). The viscosity decreased to low values as temperature increases. The increase in temperature tends to increase molecular interchange and reduce attractive forces between

molecules. However in liquids the reduction in attractive forces is more significant than increases in molecular interchange and therefore viscosity decrease with increasing temperature<sup>(8)</sup>. Graphically, ELBSO obtained at 5ml H<sub>2</sub>O<sub>2</sub> exhibits the best viscosity stability as temperature varies between 30<sup>0</sup>C-70<sup>0</sup>C.

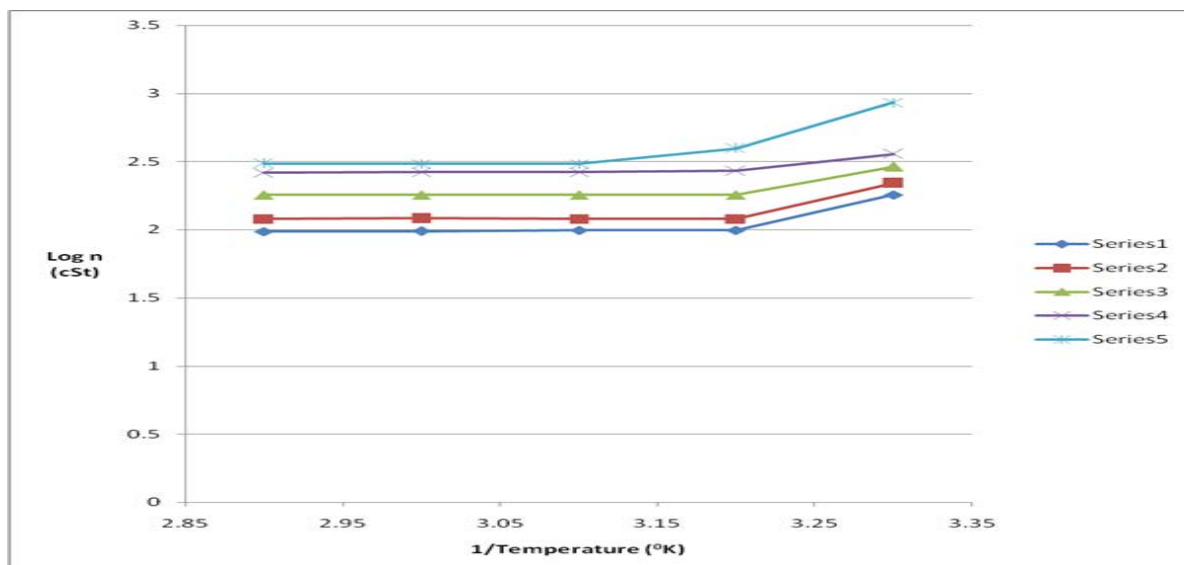


Fig. 2: Plot of log of viscosity against 1/T (K<sup>-1</sup>)

Fig.2 presents the Arrhenius plot of log of viscosity against 1/T. From the plot, the activation energies reflect the viscosity-temperature stability of ELBSO. Hence, ELBSO with the smallest and highest values of activation energy (E<sub>a</sub>) indicates the best and worst viscosity-temperature stability ELBSO respectively.

Table4.; Energy of Activation of ELBSO

ELBSO Sample/ml (H <sub>2</sub> O <sub>2</sub> )	E <sub>a</sub> (Jmol <sup>-1</sup> )
1	-0.26
2	-1.14
3	-1.52
4	-1.87
5	-2.04

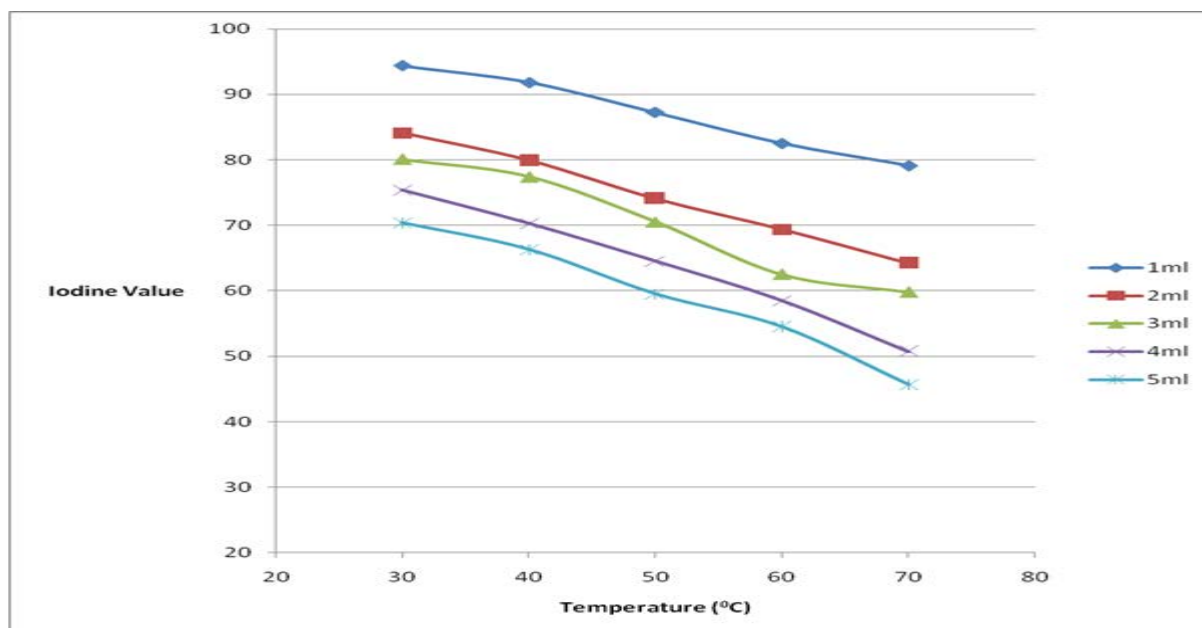


Fig.3: Plot of iodine value against temperature

The deviation from linearity which was observed in the figure above was considered due to epoxide degradation and the inner caging effect of the carboxyl (-COOH) group as the kinetic chain of epoxidation increases<sup>(9)</sup>. The above figure explains the reduction in iodine value with increasing quantity of peroxide and temperature.

Table 5: OXIRANE VALUES

Initial titre value (IV<sub>0</sub>):149.84

Quantity of H <sub>2</sub> O <sub>2</sub> (ml)	Iodine value (mg I <sub>2</sub> /g Oil)	X= {(IV <sub>0</sub> -IV)/IV <sub>0</sub> }
1	94.40	0.37
2	91.80	0.39
3	87.25	0.42
4	82.50	0.45
5	79.10	0.47

X denotes the Oxirane values. Oils with decreasing iodine values and increasing oxirane value are better used as bio-lubricants<sup>(7)</sup>.



## CONCLUSION

Bio-based lubricant have been successfully produced from locust bean seed oil with properties capable of replacing synthetic based lubricants. In conclusion, oil with lower iodine values and higher oxirane values are most suitable for use in bio-based lubricants. That is why the values obtained at all operation conditions for the oil containing 5ml of hydrogen peroxide are most preferable for use as a bio-based resin and as bio-lubricant considering its very high viscosity.

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