Lubricant properties of the polyol from the seed oil of *Lonchocarpus sericeus*

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ABSTRACT

Oil was extracted from the seed of the *Lonchocarpus sericeus* using hexane in a soxhlet extractor. The oil was characterized and used for the synthesis of polyol via epoxy ring opening reaction with 2-ethylhexanol. The structural characterization of the polyol was confirmed using FTIR and ^{1}HNMR. The GC analysis of the oil of *L. sericeus* revealed C18:3 and C18:1 fatty acid as the dominant fatty acids present in the oil. The polyol had hydroxyl value of 182.10 ± 0.20 mg KOH/g, a copper strip corrosion value of 1A and a flash point of 280.00 ± 1.20^{o}C. The synthesis and lubricant properties exhibited by the polyol suggested that the seed oil of *L. sericeus* can be chemically modified and employed as a starting material for lubricant production.

Keywords: Epoxidation, fatty acids, *Lonchocarpus sericeus*, lubricant, polyol

INTRODUCTION

Unsaturated fatty compounds have found new applications as renewable raw materials as the use of renewable resources in industrial application is of great importance to the oleochemical industry (Kirk-Othmer 1996). These compounds can be functionalized at the C-C double bond by electrophilic addition reactions to give oleochemicals potentially new and interesting properties. Vegetable oil, for example, has been found to be a renewable resource for industrial applications that can be used as base stock for the production of environmentally friendly and rapidly biodegradable lubricants (Ghazali and others 2006). Vegetable oil normally consists of a triglyceride mixture of fatty acids with the individual fatty acids characterized by the number of carbon atoms in the hydrocarbon chain, ranging generally from C8 to C22 and additionally by the number of double bonds (unsaturated bonds) in the chain.

Lubricants are a substance used to reduce friction between moving surfaces. They may also serve the function of transporting foreign particles and of distributing heat. Typically, lubricants are 90% composed of a base oil (most often petroleum fractions, called mineral oils) with the remaining 10% being additives (Bartels and others 2003). Vegetable oils or synthetic liquids such as hydrogenated polyolefins, esters, silicones, fluorocarbons and many others are sometimes used as base oils. Additives deliver reduced friction and wear, increased viscosity, improved viscosity index, and resistance to corrosion and oxidation (Boughton and Horvath 2004). In addition to industrial applications, lubricants are used for many other purposes which include bio-medical applications on humans (e.g. lubricants for artificial joints), ultrasound examinations, internal examinations for males and females, and the use of personal lubricants for sexual purposes.

However, the application of vegetable oils as a lubricant is limited due to their low oxidation stability and high melting point, which is due to the â-carbon in the glycerol molecule and the unsaturation or double bonds in the acyls of the fatty acids (Kaya and others 2009). Chemical modification of vegetable oils by addition reactions to the double bonds constitutes a promising way of improving the property and quality of vegetable oil (Wagner and others 2001, Birova and others 2002). This modification can be achieved by introducing a different functional group to the unsaturation or double bonds in the acyls of the fatty acids.

Polyols are compounds containing more than one hydroxyl group (OH). Each hydroxyl is attached to separate carbon atoms of an aliphatic skeleton. Polymeric polyols are mainly used as reactants to make other polymers. They have several applications such as in the production of polyurethanes, lubricants, fibers, foam insulators, adhesives and protective coatings (John and others 2002, Narine and others 2007). The low-temperature behavior, stability, evaporation tendencies, ageing resistance, and compatibility with technical materials present polyols of vegetable oils as promising lubricants (Sharma and others 2006, Marchetti and Errazu 2008).

The *Lonchocarpus sericeus* is a shrub or small tree that can grow from 10 to 16 meters high. It flowers with dense hanging racemes of purple flowers, mainly when leafless, which makes it perfect for display purposes. It is frequently planted in villages as a shade-tree and in gardens and commentaries. The wood is clear yellow, sometimes marbled, with heart-wood and olive-green. The bark strips easily and is a good source of fiber. The flowers have a marked smell similar to vanilla. The fruit and seeds, however, are considered to be violently poisonous (Burkill 1994). The seed of this plant is often discarded as waste in Nigeria and there is no specific use for either the seed or oil from the plant. This present work evaluated the properties of polyol synthesized from the seed oil of *L. sericeus* by epoxy ring opening reaction with 2-ethylhexanol.

MATERIALS AND METHODS

Materials

The mature seeds of the *Lonchocarpus sericeus* were collected from the trees grown at the garden of the University of Ibadan in Oyo State, Nigeria. They were identified at the herbarium unit of the Botany Department of the University of Ibadan. Formic acid (100%), hydrogen peroxide (30%), and 2-ethylhexanol were purchased from Merck (Darmstadt, Germany). All solvents and chemicals used in this study were of analytical grade and were purchased from S.D. Fine Chemicals, Mumbai.

Physicochemical analysis of *Lonchocarpus sericeus*

Oil from the dried seeds of the *L. sericeus* were extracted with *n*-hexane for 10 hours using soxhlet extractor (Adewuyi and others 2009). The oil was analyzed for iodine value, saponification value, and free fatty acid content by methods described by the Association of Official Analytical Chemists (AOAC 1994). The percentage Oxirane value of the epoxidised *L. sericeus* seed oil was determined by AOCS method (AOCS 1997a).

Fatty acid composition of *Lonchocarpus sericeus*

Fatty acid methyl esters of the oil were prepared by refluxing the samples at 70°C for 3 hours in 2% sulphuric acid in methanol. The esters were extracted into ethyl acetate, washed free of acid, and passed over anhydrous sodium sulphate. The ethyl acetate extracts were further concentrated using a rotary evaporator. The fatty acid composition was analyzed using an Agilent 6890 N series gas chromatography equipped with a flame ionization detector (FID) on a split injector. A fused silica capillary column (DB-225, 30 x 0.32 m i.d., J & W Scientifics, USA) was used with the injector and detector temperature maintained at 230°C and 250°C, respectively. The oven temperature was programmed to 160°C for 2 minutes and finally increased to 230°C at 4°C/min. The carrier gas was nitrogen at a flow rate of 1.5 mL/min. The area percentages were recorded with a standard Chemstation Data System.

Epoxidation of the oil of *Lonchocarpus sericeus*

The epoxidation was carried out in 150-mL three-necked round-bottom flask equipped with a thermometer sensor and a mechanical stirrer. The whole apparatus was kept in an oil bath to maintain the desired temperatures. 0.0482 mol of the methyl esters and 0.106 mol of 100% formic acid were placed in the flask and cooled to a temperature of 15°C while stirring. 0.407 mol of hydrogen peroxide was added, drop-wise, with continuous stirring for about 30 minutes. The temperature was later raised to 70°C and maintained at this temperature for 3 hours. After the formation of epoxide, the mixture was cooled to room temperature and the epoxidised oil was extracted with ethyl acetate, washed with water until free of acid, and passed over sodium sulfate. This was later concentrated using a rotary evaporator. The equation of reaction is shown in Figures 1A and B.

$$H_2O_2 + HCOOH \longrightarrow HCOOOH + H_2O$$

Figure 1A. Formation of peroxyacid (Rangarajan and others 1995, Okieimen and others 2002)

Figure 1B. Epoxidation (Rangarajan and others 1995, Okieimen and others 2002)

Synthesis of polyol from the epoxidised oil of *Lonchocarpus sericeus*

Polyol was synthesized from the epoxidised oil of the *L. sericeus* by oxirane ring opening using 2-ethylhaxanol in the presence of tetrafluoroboric acid as catalyst (1 % by weight of 2-ethylhexanol and epoxidised oil). The molar ratio of the epoxyl group to the OH group was 1:10. Alcohol and catalyst were placed in a 500 ml three-neck flask equipped with a refluxing column, a mechanical stirrer, and a thermometer. The flask was heated using an oil bath. Epoxidised oil was then added to the mixture of the alcohol and the catalyst. The reaction mixture was kept at 80°C for 3 hours. After cooling to room temperature, ammonia (30% in water) was added to neutralize the catalyst. The reaction mixture was washed with water several times and passed over sodium sulphate. The resulting product was later concentrated using a rotary evaporator. The equation of reaction is shown in Figure 1C.

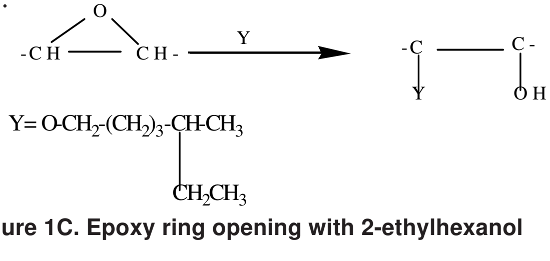

Figure 1C. Epoxy ring opening with 2-ethylhexanol

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the oil and polyol were recorded using a Perkin Elmer FTIR system spectrum BX LR64912C. The samples were spread over NaCl cells, and their spectra were recorded in the range of 4000-400 cm^{-1}.

Nuclear magnetic resonance spectroscopy (NMR)

^{1}HNMR spectra of the oil and polyol were obtained using a 300 MHZ Brucker NMR spectrophotometer in $CDCL_3$ containing some amount of TMS as internal standard.

Properties of polyol from *Lonchocarpus sericeus*

A copper corrosion test was carried out using the method described by the standard method of the American Society for Testing and Materials (ASTM) (2004). The four-ball weld load test of the polyol was estimated following the ASTM method (2010a). Viscosity was determined as described by the standard method of the ASTM (1998). The oxidative stability was determined using the standard test for oxidation stability of steam turbine oils by rotating pressure vessel as described by the ASTM (2002), while the hydroxyl value of the polyol was established as described by the standard method of AOCS (1997c). Density was determined using the Anton Paar density meter (DMA 450M model) as described by the ASTM 4052 (2009). The flash point was evaluated using the AOCS modified method for closed cup flash point determination (1997b). Emulsion stability was evaluated using the Scavini apparatus equipped with a tachometer, speed variator, and thermostated heater according to ASTM D 1401 (2010b) while pour point was determined using the ASTM D 5949 method (2010c).

RESULTS AND DISCUSSION

Physicochemical analysis and fatty acid composition of *Lonchocarpus sericeus* seed oil

Table 1 presents the physicochemical characterization of *L. sericeus* seed oil. The percentage oil content of the seed of *L. sericeus* was found to be 28.00 ± 0.50 %. The free fatty acid was 1.61±0.10 %. The color of the oil was light green, while the iodine value was found to be 166.88±0.80 g iodine/100g. The oil was liquid at room temperature with a saponification value of 195.20±0.50 mgKOH/g. The dominant fatty acid found in the oil were C18:1 (27.80 ± 0.20 %) and C18:3 (26.30 ± 0.20 %) as shown in Table 2. C24:0 was found as 4.60 ± 0.10 % while C22:0 was 13.90 ± 0.40 %.

Table 1. Physicochemical characterization of the oils from *L. sericeus*

Parameter	*L. sericeus*
Oil yield (%)	28.00 ± 0.50
Colour	Light green
Free fatty acid (%)	1.61±0.10
Iodine value(g iodine/100g)	166.88±0.80
State at room temperature	Liquid
Saponification value(mgKOH/g)	195.20±0.50

Values are mean ± standard deviation of triplicate determinations

Table 2. Fatty acid compositions (wt%) of *L. sericeus* seed oils

Fatty acids	*L. sericeus*
16:0	7.50 ± 0.10
18:0	4.30 ± 0.10
18:1	27.80 ± 0.20
18:2	11.30 ± 0.50
18:3	26.30 ± 0.20
20:0	1.60 ± 0.50
20:1	2.30 ± 0.10
22:0	13.90 ± 0.40
22:1	0.40 ± 0.20
24:0	4.60 ± 0.10
Unsaturated	68.10 ± 0.30
Saturated	31.90 ± 0.40

Values are mean ± standard deviation of duplicate determinations

Epoxidation and hydroxylation of *Lonchocarpus sericeus* seed oil

The presence of an unsaturated functional group was confirmed in the seed oil of *L. sericeus* by FTIR and ^{1}HNMR as shown in Figures 2A, 2B, and 3. The unsaturation of the fatty acid was found to be 68.10 ± 0.30 %, as shown in Table 2. The epoxidation reaction was characterized by two main reactions involving the formation of peroxoacid (peroxoformic acid) and formation of epoxides. The first step is the acid-catalyzed formation of peroxoformic acid from formic acid, while the second step is the uncatalyzed epoxidation of the *L. sericeus* seed oil with the peroxoformic acid. The percentage Oxirane oxygen content of the epoxidised *L. sericeus* seed oil was found to be 5.10 ± 0.40 %. The FTIR spectra of the oil and polyol are shown in Figures 2A and B. The C-H stretching of C=C-H in the oil, which suggests the presence of unsaturated functional groups, was detected at 3010 cm^{-1}. The unsaturated peak disappeared in the polyol indicating that the unsaturated bonds have been modified. Bands were noticed at 1736 and 730 cm^{-1}, which could be accounted for as being the C=O stretching frequency of ester. The peak at 2930 cm^{-1} was also found in the spectra, which may be attributed to the C-H stretching of $–CH_{3.}$ The peak at 3452 could be accounted for as being the vibrational frequency of the OH functional group suggesting the formation of the polyol.

Figures 3A and 3B show the ^{1}HNMR spectra of the oil and polyol, respectively. The ethylene protons were observed only in the oil at 5.3 ppm confirming the unsaturation observed at 3010 cm^{-1} in the FTIR spectrum. The methane proton of the CH backbone of the â-glycerol carbon was observed at 4.4 ppm. The methyl groups of the esters in the oil and polyol were seen at 2.3 ppm and 1.9 ppm, respectively. The saturated methylene groups were observed at about 1.1-1.4 ppm, while terminal methyl groups exhibited a chemical shift between 0.5 and 1.0 ppm in the oil and polyol. The formation of polyol was confirmed by a signal at 2.8 ppm, which was assigned to the contribution from the hydroxyl functional groups.

Properties of polyol from *Lonchocarpus sericeus*

The hydroxyl value of the polyol from *L. sericeus* was determined to be 182.10 ± 0.20 mg KOH/g as presented in Table 3. The hydroxyl value is higher than what was reported for canola based polyol (152.4 ± 0.3 mg KOH/g), castor oil (165.2 ± 3.8 mg KOH/g), and in the range of that of soybean based polyol (Narine and others 2007). This is important in quality control and it gives an idea of the molecular weight and the functionality of the polyol, especially when it is to be used in the creation of other products such as in the case of polyurethane.

A copper strip corrosion test indicated some clues on the possibility of corrosion or corrosion tendency of

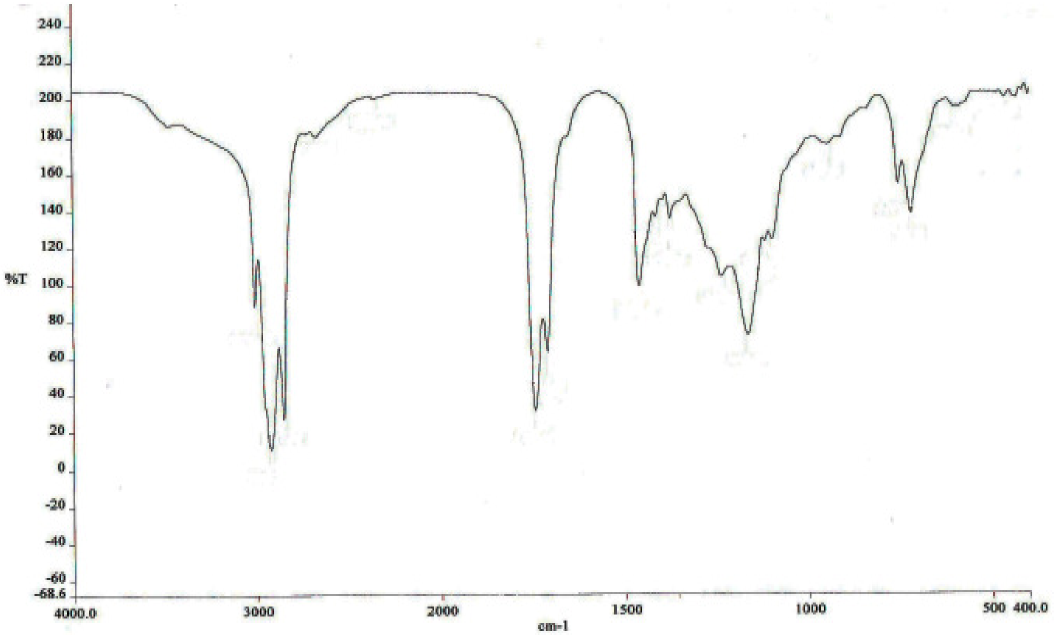

Figure 2A. FTIR spectra of the oil of *L. sericeus*

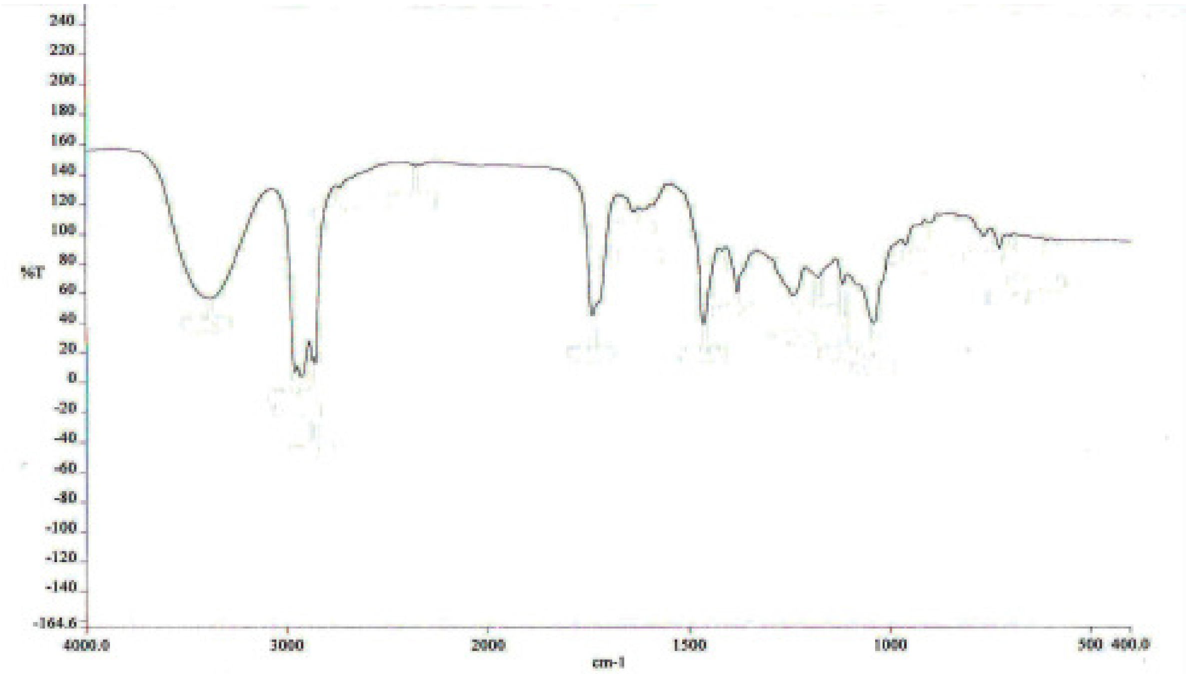

Figure 2B. FTIR spectra of the polyol of *L. sericeus*

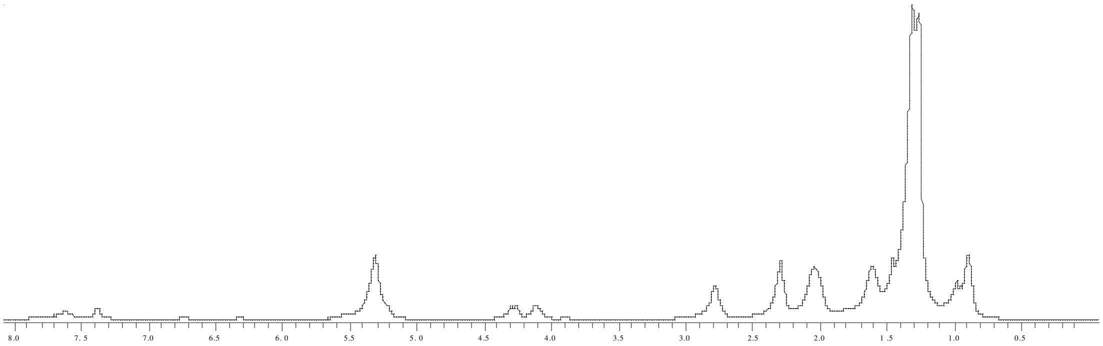

Figure 3A. ^{1}HNMR spectra of the oil of *L. sericeus*

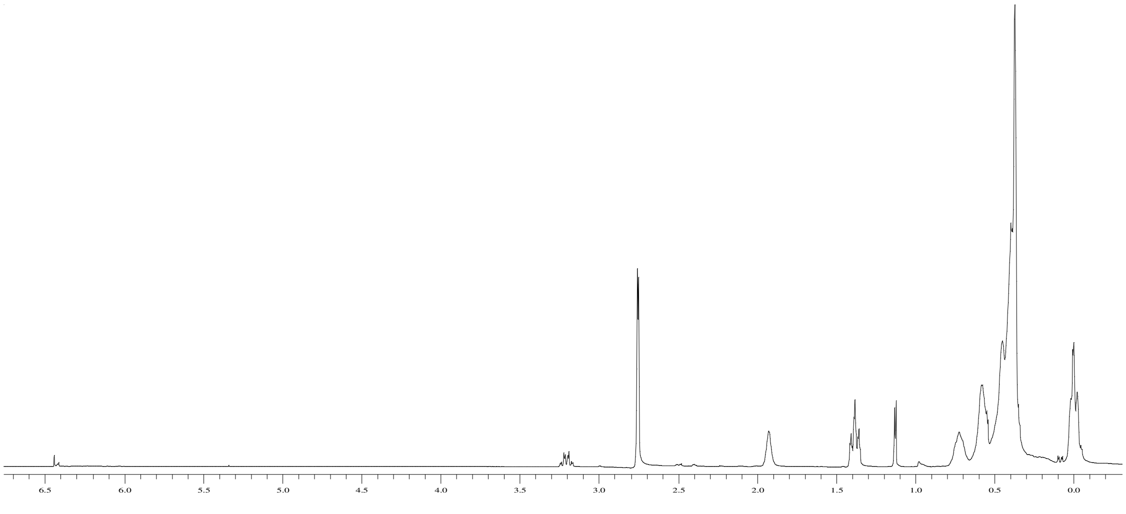

Figure 3B. ^{1}HNMR spectra of the polyol of *L. sericeus*

the polyol. The copper strip corrosion test of *L. sericeus* polyol gave a result of 1A indicating the stability of this polyol towards corrosion. This is also an indication that the oil of *L. sericeus* may be suitable as a feed stock for the production of lubricants since the 1A value reflects the ability of this polyol to withstand corroding conditions . The four-ball wear test was indicative of the relative wear-preventive properties of lubricating fluids in sliding contact under the prescribed test conditions. The value of the four-ball weld load test was found as 140.00 ± 0.00 Kg for the polyol of *L. sericeus*. The flash point was determined to be 280.00 ± 1.20°C; the flash point is the lowest temperature at which the polyol can vaporize to form an ignitable mixture in air, which helps in characterizing and classifying such products. A value of 221°C has been recommended by International Organization for Standardization (ISO) for Grade 32 oil, while the density was 0.857 g/m^3 (Rexnord 1998, BRHRTSG 2004). The flash point in the study was higher than the ISO specification, which indicated that *L. sericeus* polyol can be easily handled and transported since flammability will not be a serious issue; moreover, the use of such as a lubricating agent in high temperature systems will be an advantage. Part of ISO specifications also included a viscosity of 32 Cst at 40°C, and 5.4 Cst at 100°C. The viscosity in the present study was noticed to decrease as temperature increases as this was found to be 32.62 ± 0.50 Cst at 25°C, 17.04 ± 0.20 Cst at 40°C and 3.00 ± 0.30 Cst at 100°C; these values suggest the flow of this polyol at the examined temperatures and the conditions at which they could be used. The density was also found to follow this trend by reducing as temperature increases just as the pour point was found to be 2.50 ± 0.20°C. The oxidative stability was found to be 85.00 ± 0.50 min with an iodine value of 0.30 ± 0.10 g iodine/100g while the emulsion stability was 9.00 ± 0.20 min. Apart from the ISO, other specifications have been recommended by various bodies such as the American Petroleum Institute (API) and the American Society for Testing and Material (ASTM).

Table 3. Lubricant properties of the polyol from *L. sericeus*

Parameter	L. sericeus
Iodine value (g iodine/100g)	0.30 ± 0.10
Hydroxyl value (mg KOH/g)	182.10 ± 0.20
Viscosity (25°C) (Cst)	32.62 ± 0.50
Viscosity (40°C) (Cst)	17.04 ± 0.20
Viscosity (100°) (Cst)	3.00 ± 0.30
Copper Strip Corrosion	1A
Pour point (°C)	2.50 ± 0.20
Oxidative Stability (min)	85.00 ± 0.50
Four ball test (Kg)	140.00 ± 0.00
Emulsion stability(min)	9.00 ± 0.20
Density (25°) (g/cm3)	0.993 ± 0.10
Density (40°) (g/cm3)	0.981 ± 0.10
Density (90°) (g/cm3)	0.929 ± 0.10
Flash point (°C)	280.00 ± 1.20

Values are mean + standard deviation of triplicate determinations

CONCLUSION

The lubricant properties of polyol synthesized from the seed oil of *Lonchocarpus sericeus* was studied. The structural characterization of the synthesized polyol was confirmed using FTIR and ^{1}HNMR. The properties such as copper strip corrosion test, hydroxyl value, flash point, viscosity and four-ball wear exhibited by the polyols in the present study showed that the seed oil of *L. sericeus* can be chemically modified and employed as a starting material for lubricant.

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