

Newly developed Epoxy-polyol and Epoxy-polyurethane from renewable resources

Akintayo C.O^a, Akintayo E.T^b., Ziegler Thomas^c and Babalola B. M.^a

a – Chemistry Department, Federal University Oye Ekiti, Ekiti State, Nigeria

b – Ekiti State University, Ado Ekiti, Ekiti State, Nigeria

c – Institute of Organic Chemistry, Auf der Morgenstelle 18, Universitat, Tübingen, 72076 Tübingen. Germany.

fkintayo@yahoo.co.uk

ABSTRACT

The focus of this work was to make preliminary studies into the synthesis of bio-based derived products, (epoxy-polyol and epoxy-polyurethanes) from *Synthesis and Performance of Novel Hydrogels Coatings for Implantable Glucose Sensors*. Spectral (IR, ¹H NMR and ¹³C NMR) , physico-chemical and thermal analysis of these products were performed using standard methods. The preparation of these products from *Jatropha curcas* oil was smooth and efficient. Results of film and solubility properties revealed that coatings of *Jatropha curcas* epoxy-polyurethanes performed better with increased loading of Toluylene 2, 4-diisocyanate (TDI) up to 2wt% while their solvent resistance decreased beyond a TDI loading of 1.2wt%. DSC shows the epoxy-polyurethane to be less stable compared to the epoxy-polyol.

27 Keywords: Synthesis, Epoxy-polyol, epoxy-polyurethane, *Jatropha curcas* oil

28

29

30 INTRODUCTION

31 Petroleum derived polyols have been widely used in the manufacturing of polyurethane
32 foams. However recently there has been an increased interest in the use of renewable
33 resources in the manufacturing of polymers such as polyurethanes. This has led to research
34 into developing natural oil based polyols that are suitable as full or partial replacements for
35 petroleum derived polyols in polymers such as polyurethanes (1, 2, 3). The mechanical
36 strength, excellent abrasion resistance, toughness, low temperature flexibility, chemical and
37 corrosion resistance of polyurethane has made them viable material in coating industries (4).
38 Many synthetic pathways using different renewable resources such as Sorbitol (5) and the
39 preparation of segmented polyurethane including sunflower and safflower, but mainly castor
40 and soybean oils have also been investigated (6). Usually hydroxyl groups have been
41 introduced into vegetable oils through a two-step synthesis involving the epoxidation of
42 unsaturated sites with formic acid and hydrogen peroxide, followed by epoxy ring opening (7,
43 8). Depending on the reaction conditions, polyols with high OH functionality (complete
44 reaction) or epoxy-polyol esters with remaining epoxy groups (partial conversion) are
45 obtained (7). The epoxy-polyol esters are in particular very interesting because of their better
46 oxidative stability (9).

47 *Jatropha curcas* is a bush that grows in nearly all ecological zones in Nigeria. The seeds
48 contain about 55% oil with fatty acid composition that mirrors that of most conventional plant
49 oils (10). This implies that like other oilseeds, soybean, cottonseed, castor oil, linseed,
50 rapeseed etc (11) which has been functionalised to yield polymerizable polymers or as
51 industrial feedstocks in the preparation of diversified industrial products, *Jatropha curcas*
52 seed oils may also be exploited in these regards. A particular advantage of the *Jatropha curcas*
53 oil is that unlike the popular oilseeds, *Jatropha curcas* is not a food crop and its not
54 competing with existing food crops for the production of industrial products. In Nigeria,
55 vegetable oil dependent industries rely mostly on imported oils like linseed and soybean oil

which are expensive because the locally available oils like palm oil, palm kernel oil, groundnut and coconut oils are in short supply (12). The present effort is aimed at modifying the triglyceride chain of *Jatropha curcas* oil to produce epoxy-polyol which are later used to synthesize polyurethane. Such effort is in consonance with Nigerian policy for development strategies that are in line with her natural resources endowment and also geared towards eventual self sufficiency in industrial materials.

Materials

Seeds of *Jatropha curcas* (obtained from a local farm in Ado-Ekiti., Nigeria) were air dried, ground to powder form and were subjected to oil extraction in a Soxhlet apparatus using Petroleum ether (b.p $60^{\circ}\text{C} - 80^{\circ}\text{C}$) as solvent. Hydrogen peroxide 30%, Formic acid (99.7%), Toluylene 2,4-diisocyanate (TDI), were used as obtained from Merck (Darmstadt, Germany), while Dibutyltin dilaurate (DBTL) was obtained from Fluka (Seelze, Germany).

Epoxidation and hydroxylation of *Jatropha curcas* oil (JCO)

To 0.023mole of JCO in a three necked round bottom flask equipped with a dropping funnel, magnetic stirrer and cold water condenser, was added 2.5g of formic acid in one portion and mixture stirred to homogeneity. The flask was immersed in a cold water bath ($10-15^{\circ}\text{C}$) and 40g of 30% hydrogen peroxide added dropwisely into the reaction mixture while stirring. After complete addition of hydrogen peroxide, the temperature was raised to 50°C . Reaction was allowed to continue for another 5hr. Then the mixture was allowed to cool and 25ml of distilled water added. Then 2.5ml of concentrated HCl was added and temperature of the whole mixture increased gradually to 80°C . Reaction was allowed to continue for another 5hr. Progress of the reaction in the latter stage was monitored by determining the hydroxyl value. On completion of reaction, the product was extracted into ether and the ethereal layer was washed with aqueous sodium carbonate, followed by distilled water and sodium chloride

solution. The ether layer was then dried over anhydrous sodium sulphate and ether was removed over rotary evaporator at 45⁰C to obtain the *Jatropha curcas* epoxy-polyol.

Synthesis of *Jatropha curcas* oil Epoxy-Polyurethane (JCEPU)

20g of *Jatropha curcas* epoxy-polyol (JCEP) prepared was dissolved in toluene in a three necked round bottom flask fitted with a nitrogen inlet tube, a thermometer and mechanical stirrer. Temperature of the reaction mixture was maintained at 55-60⁰C. TDI also dissolved in toluene along with 0.1ml of DBTL was now added dropwisely into the reaction mixture over 30 min. The extent of loading of TDI is presented in Table 1.

Table 1:- Data for the feed composition of JCEP and TDI

Sample Code	Amount of JCEP(g)	Amount of TDI (g)
JCEPU-1	20	1.0
JCEPU-1.2	20	1.2
JCEPU-1.5	20	1.5
JCEPU-2.0	20	2.0

Characterisation

Structural elucidation of JCO, JCEP and JCEPU was carried out by FTIR, ¹HNMR and ¹³C NMR spectroscopic techniques. FTIR of the samples were done on Nicolet 380 FTIR (Thermo Electro Corporation, Madison, USA) using NaCl cell. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 (Bruker Instruments, Inc. Karlsruhe, Germany) Fourier transform spectrometer operating at 400.6MHz. The gated decoupling pulse sequence was used with the following parameters; number of scans, 256; acquisition time 1.366s; pulse

width 10.3 μ s. Free induction decay FID was transformed and zero filled to 300k to give digital resolution of 2Hz/point. Thermal analysis was carried out by DSC 822 $^{\circ}$ (Mettler Toledo GmbH, Giessen, Germany) in Nitrogen atmosphere. Hydroxyl value (HV), iodine value (IV), saponification value (SV), specific gravity (SG), viscosity and refractive index (RI) were determined according to standard procedure (DFG, 1994) (13).

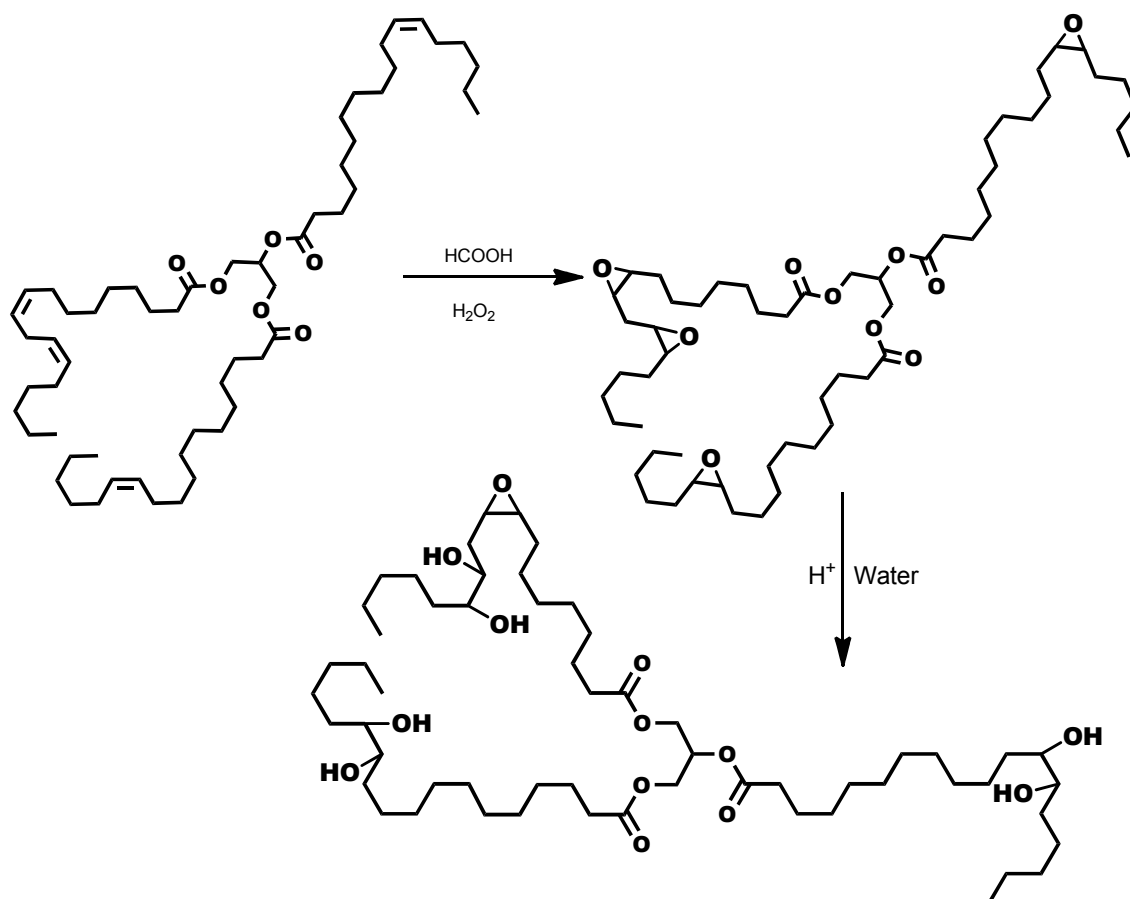
Evaluation of Film Characteristics

Samples of UJCO were thinned with toluene to brushable consistency. The solutions prepared were applied by brush on clean, mild steel panels of 15cmx15cm for evaluating drying time, tin panels of the size 15cmx15cm for flexibility and adhesion, scratch hardness and impact resistance and glass panels of the size 15cmx15cm for water, alkali and solvent resistances. All coated panels were air dried for 48hr and sides protected by dipping them into molten wax before carrying out the above tests. The film characteristics were determined according to Indian standard specification (14, 15).

118

119 RESULTS AND DISCUSSION

120 We reported earlier (16) the fatty acid composition of *Jatropha curcas* oil as C16:0 (19.5%);
 121 C18:0 (6.8%), C18:1 (41.3%) and C18:2 (31.4%). The epoxidation of such an oil containing
 122 one and two double bonds to yield mono and di-epoxies and the hydroxylation as well as the
 123 reaction of the JCEP with TDI to produce epoxy-polyurethane are described structurally in
 124 schemes 1 and 2

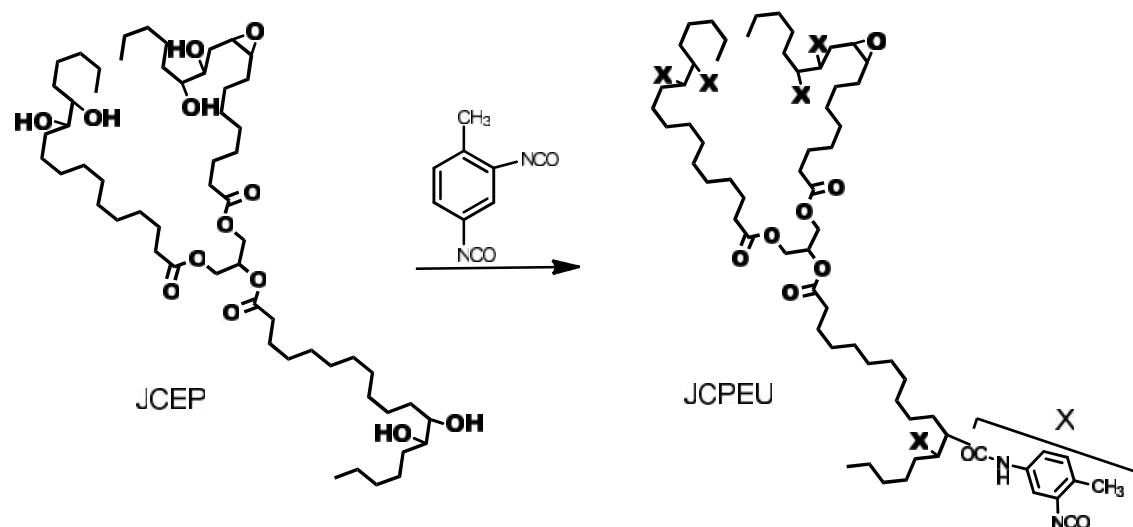


125

126

127 Scheme 1: Epoxidation and hydroxylation of *Jatropha curcas* oil

128



Scheme 2: Synthesis of *Jatropha curcas* epoxypolyurethane (JCEPU)

The infra red spectra of the JCO, JCEP and JCEPU are presented in figure 1. The JCEP spectra reveals the disappearance of the vinylic protons at 3008cm^{-1} and the appearance of a broad hydroxyl band at 3460cm^{-1} as well as the presence of epoxy band at 844cm^{-1} . These support the structure of JCEP in scheme 1. On reacting the JCEP with TDI to prepare the JCEPU, the IR spectra of the JCEPU showed only a residue OH band at 3464cm^{-1} indicating that most of the $-\text{OH}$ have reacted. However there is the appearance of NH stretching vibration band at 3295cm^{-1} . The TDI aromatic ring in JCEPU gave rise to characteristic peaks at 3086cm^{-1} for aromatic $=\text{C}-\text{H}$ stretching, 1604 , 1536 , 1495 , 1463cm^{-1} for the skeletal ring breathing. Free NCO of TDI was indicated by the peak at 2275cm^{-1} . The epoxy band also remained and indicated by the band at 822cm^{-1} . These bands support the structure of IV in scheme 2.

The structures of the JCEP and JCEPU were confirmed by NMR analyses. The ^1H NMR spectra of the JCO, JCEP and JCEPU are presented in fig 2, The ^1H NMR of JCO is similar to other vegetable oils showing characteristic signals at $4.1-4.2\text{ppm}$ for the four methylene proton in glycerol centre and another peak at 5.25ppm for the methine proton of glycerol. The peaks at $5.3-5.5\text{ppm}$ arise from protons on the carbon double bonds ($\text{CH}=\text{CH}$). The peaks in

the region 2.7-2.8ppm correspond to methylene groups surrounded by single bonded atoms. ^1H NMR of JCEP show the characteristic glycerol methylene and methine at 5.26 and 4.1-4.2ppm respectively but only residual $\text{HC}=\text{CH}$ at 5.3-5.5ppm. However there is the appearance of new peaks in the region 2.9-3.2ppm indicating the presence of epoxy protons. The peak at 1.5ppm correspond to the methylene group next to epoxy band $\text{CH}_2\text{-COC-}$ and another peak at around 1.7ppm corresponding to methylene group sandwiched between two epoxy groups. There is also the appearance of peaks between 3.4-3.5 for methine proton bearing the OH group i.e CH-OH . The ^1H NMR of the JCEPU shows the disappearance of CH-OH at around 3.4-3.5ppm and the appearance of the new peaks for the aromatic protons of TDI between 7.2-7.4ppm. The presence of the peaks at 2.9-3.2ppm in the JCEPU confirms the presence of epoxy group still in the JCEPU. The carbon-13 NMR (figure 3) of the samples further confirms the structures suggested in schemes 1 and 2. JCEP shows the characteristic epoxy carbon at between 56-57ppm and C-OH at 66ppm. While the C-OH peak at 66ppm disappeared in JCEPU, there was the appearance of C=C in the ring of TDI at 125-128ppm as well as methine carbon of TDI bonded to $-\text{NH}$ at 138ppm.

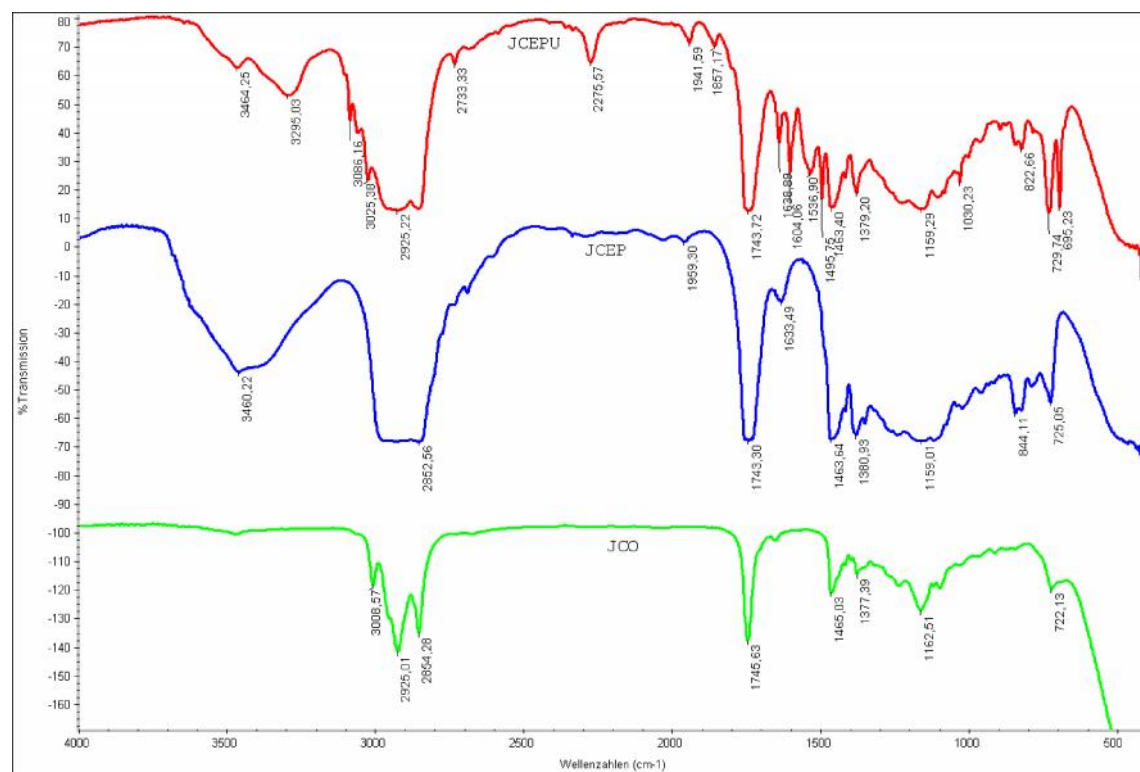


Fig 1: Infrared spectra of JCO, JCEP and JCEPU

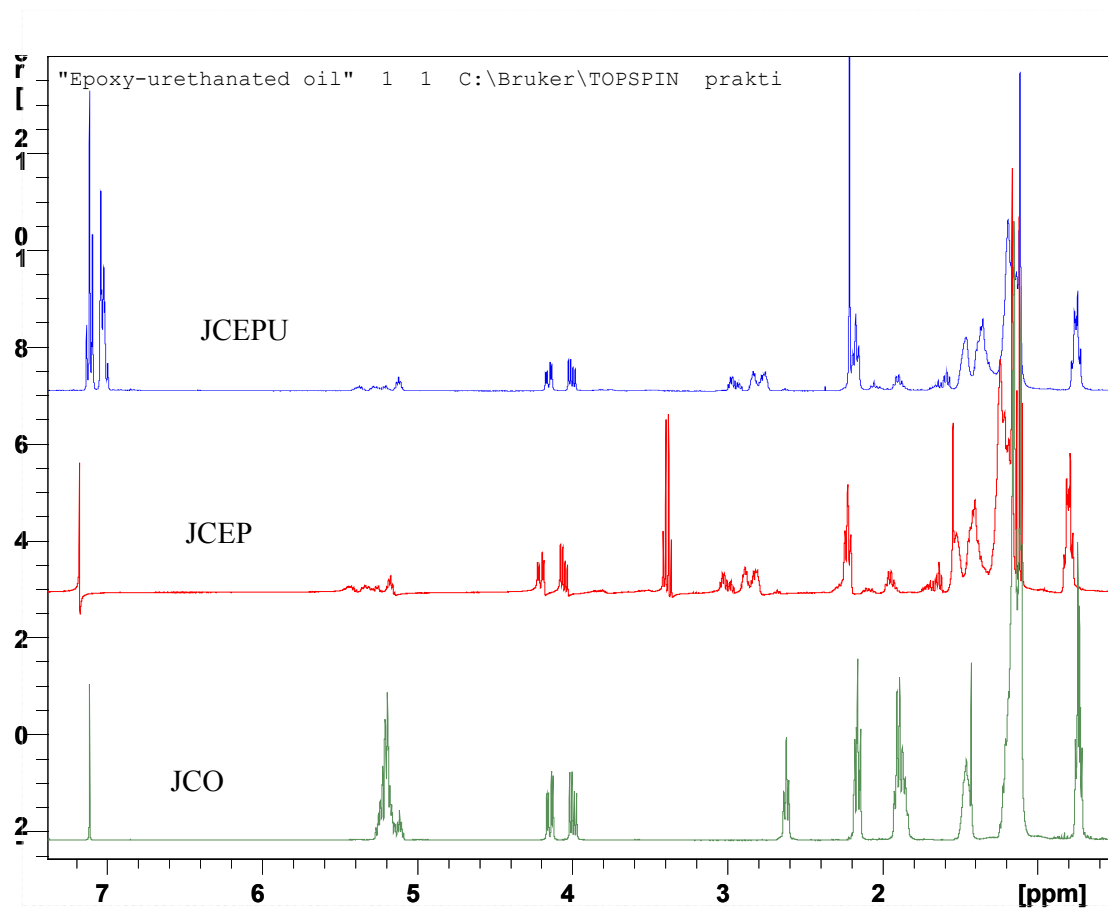


Fig 2: Proton NMR of JCO, JCEP and JCEPU

173

174

175

176

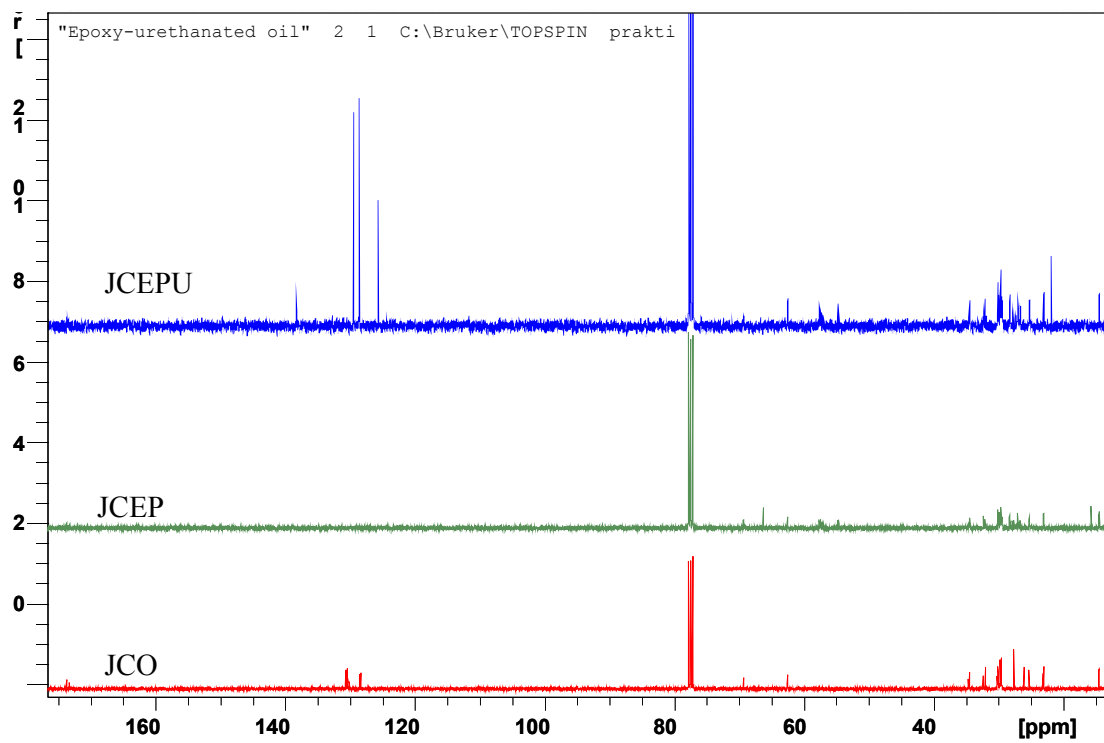


Fig 3: Carbon 13 NMR of JCO, JCEP and JCEPU

177

178

179

180

Physico-Chemical Properties of JCO, JCEP and JCEPU

Iodine and saponification values decreased in going from JCO to JCEP and then to the JCEPU's. The decrease in iodine value shows that in the course of the reaction, most of the unsaturated sites in the oil were consumed first to become epoxy ring which was then hydrolysed to yield hydroxyls that later reacted with the NCO of TDI to produce the epoxy-polyurethanes. The decrease in saponification value may be attributed to the increase in molar mass as the oil was being transformed to epoxy, hydroxyl and then urethane products. Hydroxyl value increased on hydroxylation. This was expected as –OH groups were introduced onto the triglyceride chain. The reaction of these OH with –NCO to yield the epoxy-polyurethane led to a decreased hydroxyl value in the epoxy-polyurethane sample. The increase in RI, SG and viscosity may be attributed to increase in molecular weight as the oil was transformed to epoxy-polyol and subsequently to epoxy-polyurethane. Apart from increase in molecular weight, intra-molecular hydrogen bonding also contributed to the increase in viscosity observed for the samples compared to the ordinary oil.

Film Properties of JCEPU's

The drying time of the JCEPU's decreased as the loading of TDI increased. The curing of urethanes has been predicted to occur in three stages (17,18). A first stage called surface drying which occurs by solvent evaporation and a second and third stage curing which occurs through chemical reactions (19). Ahmad et al. (17) explained the mechanism of the second stage drying called dry to touch (DTT) as involving reaction of free –NCO group of the TDI with moisture to form amino group through primary addition. The amino group then reacts rapidly with another –NCO group present in another molecule leading to cross linking in the epoxy-polyurethane. The third stage drying called the dry to hard (DTH) is suggested to proceed slowly by auto-oxidation and occurs at the pendant fatty trimer chain of oil (18). The scratch hardness was estimated by the pencil hardness of the films. The hardness was

expressed in terms of the designation of the hardest pencil that failed to scratch the film. The results also revealed that scratch hardness also improved with loading of the TDI. All the films passed the impact resistance test. The increased loading of TDI in epoxy-polyurethanes means additional isocyanate moieties which provide extra cross linking sites. With more crosslink, the impact resistance is expected to improve. All samples passed the flexibility and adhesion test. This is likely to be due to the presence of epoxy groups in the sample. Epoxy is known to improve oxidative stability as well as flexibility and adhesion of samples by acting as plasticisers (7, 8, 20).

DSC

The DSC thermograms of the JCEP and JCEPU are presented in figure 4. The thermograms are similar except for the broad exothermic peak observed for the epoxy-polyurethane between 140⁰C and 200⁰C centering at 160⁰C which is indicative of the melting of the resin. The results therefore show the epoxy-polyurethane to be less stable compared to the epoxy-polyol. This may be attributed to thermally less stable urethane linkages in the epoxy-polyurethane. The epoxy-polyol did not exhibit any glass transition (T_g) while the epoxy-polyurethane exhibited a glass transition at -20⁰C and this may be rationalised in terms of the stiffening effect of the appended aromatic moieties in the epoxy-polyurethane.

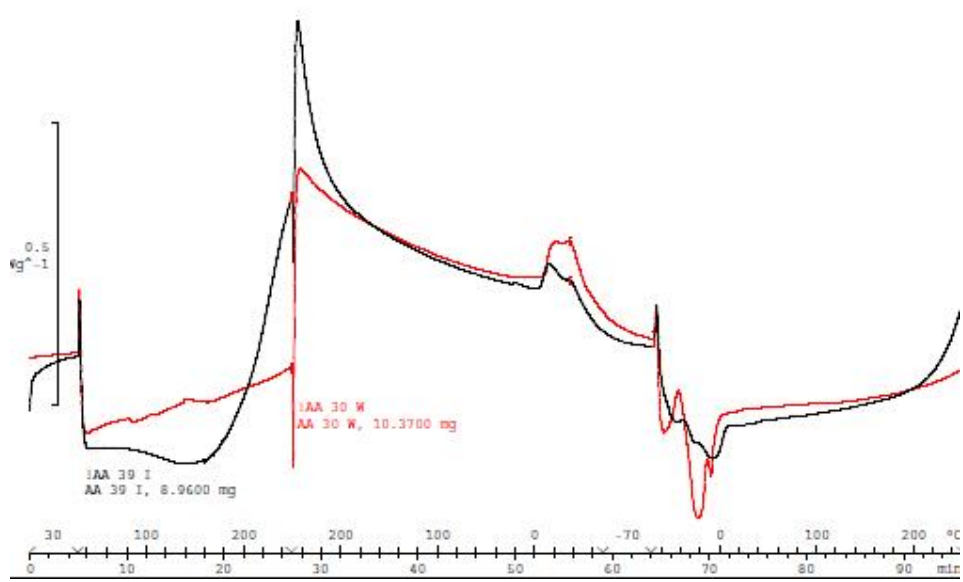
233

234

235

236

----- JCEPU
----- JCEP



237

238

Figure 4: DSC thermograms of epoxypolyol and epoxy urethane

239

240

Table 2.0: Physico-Chemical analysis of JCO, JCEP and JCEPU

Sample	IV(mgI ₂ /g)	HV(mgKOH/g)	SV(mgKOH/g)	RI	SG	Viscosity
JCO	105.2	1.15	198	1.468	0.9452	18.5
JCEP	6.5	15.8	107	1.482	1.0435	28.8
JCEPU-1	5.4	6.6	58	1.493	1.115	38.5
JCEPU-1.2	5.2	5.8	55.4	1.495	1.117	42.6
JCEPU-1.5	5.1	5.6	53.2	1.497	1.119	55.8
JCEPU-2.0	5.1	5.5	52.5	1.498	1.119	60.5

241

242

243

244 Table 3: Coating properties of *Jatropha curcas* Epoxypolyurethanes (JCEPU's)

	JCEPU-1.0	JCEPU-1.2	JCEPU-1.5	JCEPU-2.0
Surface drying (hr)	7	6	3	2
Hard dry (hr)	88	72	48	24
Scratch Hardness (Pencil Brand)	6B	4B	2B	2H
Impact resistance (1Kg load)	Pass	Pass	Pass	Pass
Flexibility and Adhesion (1/8" Mandrel)	Pass	Pass	Pass	Pass

245

246 Table 4: solvent resistance of *Jatropha curcas* Epoxypolyurethanes (JCEPU's)

	JCEPU-1.0	JCEPU-1.2	JCEPU-1.5	JCEPU-2.0
Water resistance	b	b	b	b
Xylene resistance	b	b	b	c
NaOH (2%) resistance	c	c	d	e
HCl (2%) resistance	c	c	d	e
NaCl (3.5wt%) resistance	c	c	c	d

247

248 b – not affected

249 c – loss of gloss

250 d – slight blistering

251 e – blistering

252 **Acknowledgement**

253 This work was funded by the International Foundation for Science (IFS) in conjunction with

254 the Organisation for the Prohibition of Chemical Weapons (OPCW), Grant No. F\4588-2 to

255 Akintayo C.O. We also appreciate the provision of some facilities by Prof. Thomas Ziegler of
256 the Institute of Organische Chemie, Universitat Tübingen, Tübingen, German
257

REFERENCES

1. Petrovic Z. S., Zhang W., Javni I. Structure and Properties of Polyurethanes Prepared from Triglyceride Polyols by Ozonolysis. *Biomacromolecules*. (2005); 6 (2):713–719
2. Petrović Z. S., Cevallos M. J., Javni I., Schaefer D. W., Ryan J. Soy-oil-based segmented polyurethanes. *Journal of Polymer Science Part B: Polymer Physics*. (2005); 43 (22): 3178–3190,
3. Velayutham T.S., Abd Majid W. H., Ahmad A. B, Gan Yik Kang,S.N. Synthesis and characterization of polyurethane coatings derived from polyols synthesized with glycerol, phthalic anhydride and oleic acid. *Progress in Organic Coatings*. (2009); 66 (4): 367–371
4. Ismail E. I, Motawie A. M, Sadek E. M. Synthesis and characterization of polyurethane coatings based on soybean oil–polyester polyols. *Egyptian Journal of Petroleum*. 2011; 20 (2): 1–8
5. Anand A., Kulkarni R. D., Gite V. V. Preparation and properties of eco-friendly two pack PU coatings based on renewable source (sorbitol) and its property improvement by nano ZnO *Progress in Organic Coatings*. 2012; 74 (4,): 764–767
6. Ferrer M. C. C , Babb D., Ryan A. J. Characterisation of polyurethane networks based on vegetable derived polyol. *Polymer*. 2008; 3279–3287
7. Monteavaro L.I, daSilva E.O., Costa A.O., Samios D., Gerbase A.F., Petzhold C.I. Polyurethane networks from formiated soy polyols: Synthesis and mechanical characterization. *JAOCS*. 2005; 82 (5) : 365-371
8. Guo A., Cho Y.J and Petrovic Z.S. Structure and properties of halogenated and non halogenated soy-based polyols. *J. Poly. Sci., Part A: Polym. Chem*. 2000; 38: 3900-3910
9. Hwang H.S and Erhan S.Z. Modification of epoxidised soybean oil from lubricant formulations with improved oxidative stability and lower pour point.

- 284 J. Am. Oil Chem. Soc. 2001; 78:1179-1184
- 285 10. Becker K and Maker P.S. *Jatropha curcas*: A potential source for tomorrow's oil and
286 biodiesel. *Lipid Technology*. 2008; 20(5): 104-107
- 287 11. Petrovic Z.S. Polyurethanes from vegetable oils. *Polymer Reviews*. 2008; 48(1): 109-
288 155
- 289 12. Okiemen F.E., Pavithram C. and Bakare I.O. Epoxidation and hydroxylation of rubber
290 seed oil: one pot multi-step reactions. *Eur.J.Lipid. Technol.* 2005; 107, pp 330-336
- 291 13. DFG, German Society for fat science, German standard Methods for the analysis of
292 fats and other lipids. Wissenschaftliche verlagsgesellschaft mbH, Stuttgart,
293 Germany. 1994.
- 294 14. Indian standard specifications (IS), 1968; 101: 38
- 295 15. Indian standard Specification (IS), 1981; 158: 8-9
- 296 16. Akintayo E.T. Characteristics and composition of *Parkia biglobbosa* and *Jatropha*
297 *curcas* oils and cakes. *Bioresources Tech.* 2004; 92: 307-310
- 298 17. Ahmad S., Ashraf S.M., Hasnat A., Yadar S. and Jamal A. *J.Appl.Polym.Sci.* 2001;
299 82: 1855-1865
- 300 18. Meneghetti S.M.P., Souza R.F.D., Monteiro A.L., Souza M.O.D. *Progress in Organic*
301 *Coatings*. 1988; 33: 219-224
- 302 19. Sharmin E., Ashraf S.M and Ahmad S. Synthesis, characterization, antibacterial and
303 corrosion protective properties of epoxies, epoxy-polyol and epoxy-polyurethane
304 coatings from linseed and *Pongamia glabra* seed oils. *Int.J.Biol.macro.* 2007; 40: 407-
305 422
- 306 20. Jarni I., Zhang W., Petrovic Z.S. *J.Appl.Polym.Sci.* 2003; 2912-2916.