

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

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ABSTRACT

Bio-polyols are important component in polyurethane industries. The preliminary studies into the synthesis of bio-polyol products (epoxy-polyol and epoxyl-polyurethanes) from *Jatropha curcas* were investigated. The reactions were followed by both Infrared and nuclear magnetic resonance. Infrared analysis was performed on a Nicolet 380 Fourier-transform infrared (FTIR) spectrophotometer using NaCl cells. ¹H-nuclear magnetic resonance (NMR) and ¹³C-NMR were obtained on a Bruker Avance 400 NMR spectrophotometer. Approximately 100mg sample was dissolved in 1 ml of deuterated chloroform. Physico-chemical characterisation of the samples for iodine value (IV), acid value (AV), saponification value (SV) and hydroxyl value (HV) were carried out by dissolving 0.25g of sample in appropriate medium and the various values determined titrimetrically. Thermal transitions of the products were studied by heating 5mg of the sample from 20 °C to 80 °C and then cooled to -50 °C on a differential scanning calorimeter (DSC). The preparation of epoxyl polyol and polyurethane 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 analysis shows the epoxy-polyurethane to be less stable compared to the epoxy-polyol.

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

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1. INTRODUCTION

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

Jatropha curcas is a shrub that grows in nearly all ecological zones in Nigeria. The plant is relatively drought resistant. In Nigeria the plant is used variously as shade for various crops, and also planted along water ways to reduce erosion. *Jatropha* seeds are also used as a laxative against constipation. The seed contain about 55% oil [10] with fatty acid composition of Palmitic acid (19.5%); Stearic acid (6.8%); Oleic acid (41.3%) and linoleic acid (31.4%). The presence of high percentage of unsaturated fatty acids in *Jatropha curcas* oil makes it very suitable for functionalization to produce modified oils. The presence of some anti-nutritional factors such as toxic phorbol esters and stearic acid render *Jatropha oil* as unfit for edible purposes. This implies that like other oilseeds, soybean, cottonseed, castor oil, linseed, rapeseed etc [11] which has been functionalised to yield polymerizable polymers or as industrial feedstocks in the preparation of diversified industrial products, *Jatropha curcas* seed oils may also be exploited in these regards. A particular advantage of the *Jatropha curcas* oil is that unlike the popular oilseeds, *Jatropha curcas* is not a food crop and it is not competing with existing food crops for the production of industrial products. In Nigeria, 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 was 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 self-reliance in industrial materials.

2. MATERIAL AND METHODS

Seeds of *Jatropha curcas* used in this work were obtained from a local farm in Ado-Ekiti., Nigeria. The seeds were air dried, ground to powder form and stored in an air tight container till further use. Soxhlet extractor was used to extract the oil using petroleum ether (b.p 60 °C – 80 °C) as solvent. Hydrogen peroxide 30%, Formic acid (99.7%), Toluylene 2,4-diisocyanate (TDI), were used as obtained from Merck (Darmstadt, Germany), while Dibutylindilaurate (DBTL) was obtained from Fluka (Seelze, Germany).

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

Jatropha curcas oil (20 grams, 0.023mole) was charged into a three necked round bottom flask equipped with a dropping funnel, magnetic stirrer and cold water condenser. To the mixture 2.5g of formic acid in one portion was added and the mixture stirred to homogeneity. The flask was immersed in a cold water bath (10-15 °C) and 40g of 30% hydrogen peroxide added drop wise 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 11.6M 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 45 °C to obtain the *Jatropha curcas* epoxy-polyol.

2.2 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 55-60 °C. TDI also dissolved in toluene along with 0.1ml of DBTL was now added drop wise into the reaction mixture over 30 min. The extent of loading of TDI is presented in Table 1.

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113 **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

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115 **2.3 Characterisation**

116 Structural elucidation of JCO, JCEP and JCEPU was carried out by Fourier transform
 117 infrared (FTIR), proton and carbon 13 nuclear magnetic resonance (^1H NMR and ^{13}C NMR)
 118 spectroscopic techniques. FTIR of the samples were done on Nicolet 380 FTIR (Thermo
 119 Electron Corporation, Madison, USA) using NaCl cell. ^1H and ^{13}C NMR spectra were
 120 recorded on a Bruker Avance 400 (Bruker Instruments, Inc. Karlsruhe, Germany) Fourier
 121 transform spectrometer operating at 400.6MHz. The gated decoupling pulse sequence was
 122 used with the following parameters; number of scans, 256; acquisition time 1.366s; pulse
 123 width 10.3 μs . Free induction decay FID was transformed and zero filled to 300k to give
 124 digital resolution of 2Hz/point. Thermal analysis was carried out by DSC 822^e (Mettler Toledo
 125 GmBH, Giessen, Germany) in Nitrogen atmosphere. Hydroxyl value (HV), iodine value (IV),
 126 saponification value (SV), specific gravity (SG), viscosity and refractive index (RI) were
 127 determined according to standard procedure (DFG, 1994) (13).

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129 **2.4 Evaluation of film characteristics**

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

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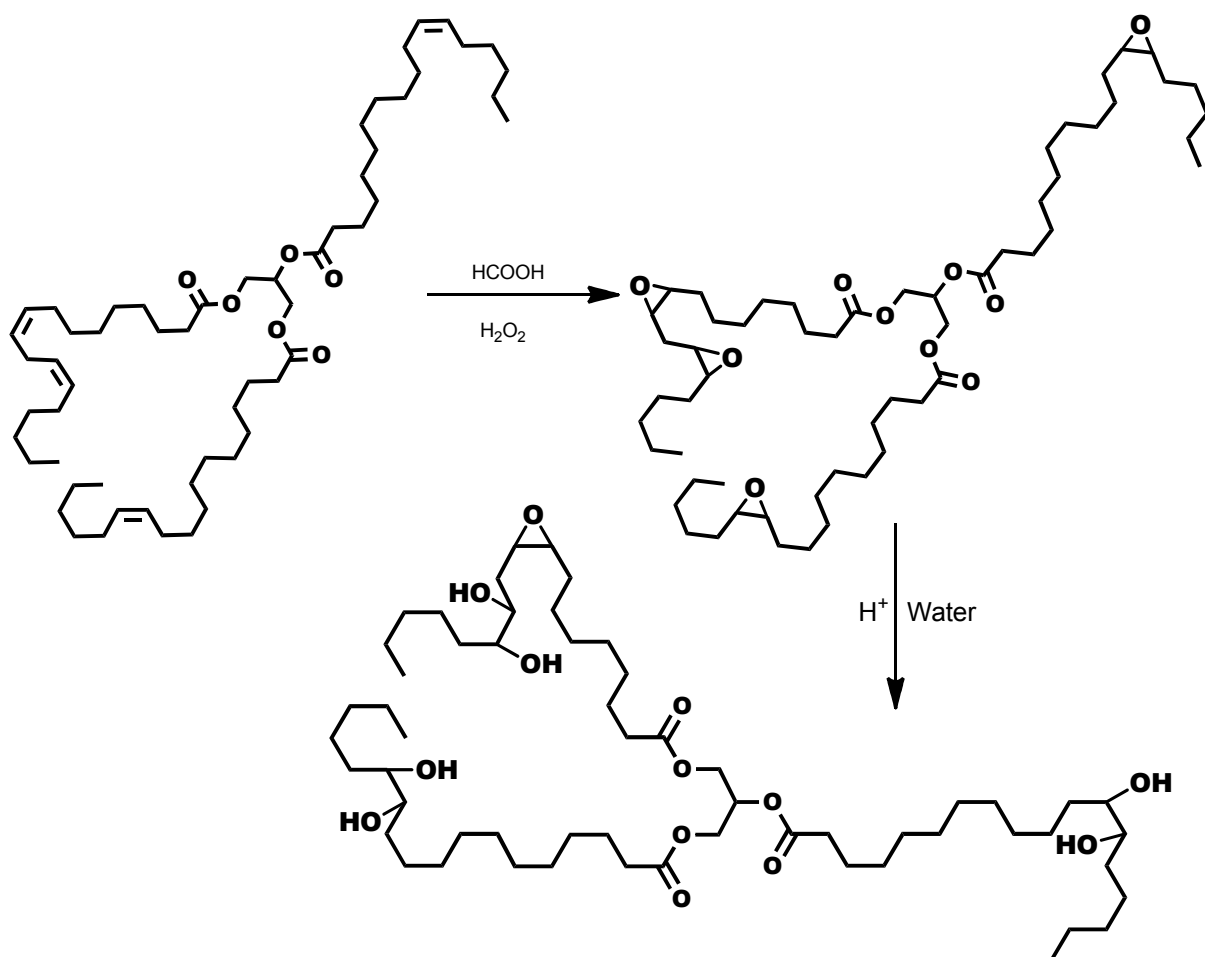
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143 3. RESULTS AND DISCUSSION

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145 Preliminary work was carried out to determine the optimal conditions for epoxidation of
146 *Jatropha curcas* oil and further hydrolysis of the epoxidised oil to epoxy polyol. Results
147 revealed that epoxidation of *Jatropha curcas* oil was almost complete after 5hr using 2.5g of
148 85% formic acid in excess hydrogen peroxide. Subsequent hydrolysis of some of the oxirane
149 rings in the epoxidised *Jatropha curcas* oil to hydroxyl was indicated by the hydroxyl value
150 which increased with reaction time and temperature. The optimal hydrolysis condition was
151 achieved at a reaction time of 5hr and a temperature of 80 °C by hydrolysing with 2.5ml of
152 Conc HCl. The samples produced at these optimal conditions were subsequently used for
153 the rest of the experiment.

154 Akintayo [16] reported earlier the fatty acid composition of *Jatropha curcas* oil as C16:0
155 (19.5%); C18:0 (6.8%), C18:1 (41.3%) and C18:2 (31.4%). The epoxidation of such an oil
156 containing one and two double bonds to yield mono and di-epoxies and the hydroxylation as
157 well as the reaction of the JCEP with TDI to produce epoxy-polyurethane are described
158 structurally in schemes 1 and 2



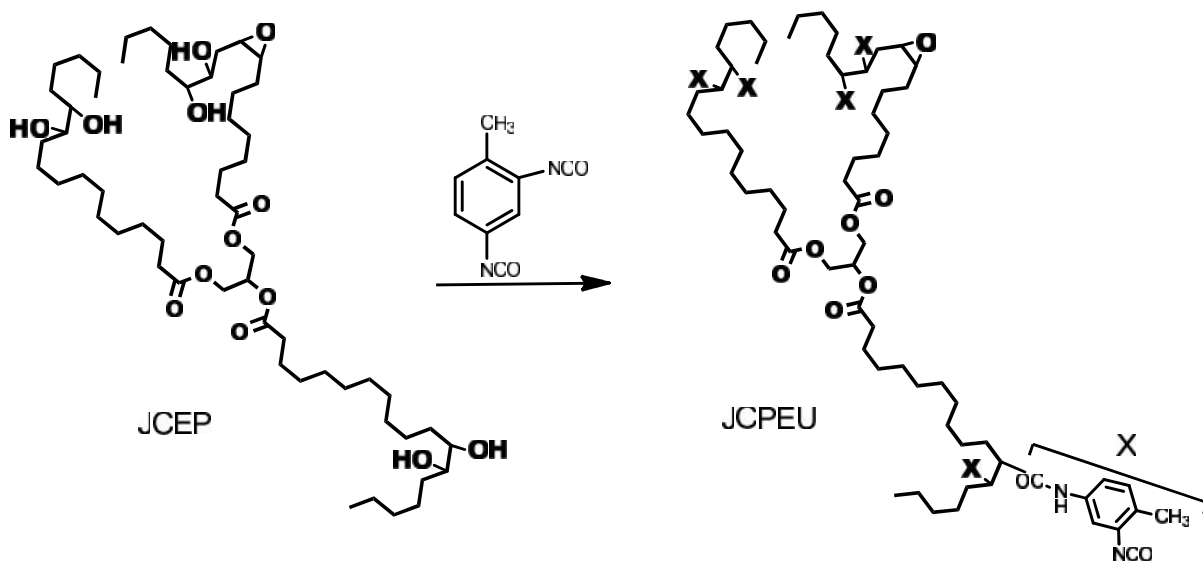
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Scheme 1: Epoxidation and hydroxylation of *Jatropha curcas* oil

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

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

177 The structures of the JCEP and JCEPU were confirmed by NMR analyses. The ^1H NMR
178 spectra of the JCO, JCEP and JCEPU are presented in Figure 2, The ^1H NMR of JCO is
179 similar to other vegetable oils showing characteristic signals at $4.1\text{--}4.2\text{ppm}$ for the four
180 methylene proton in glycerol centre and another peak at 5.25ppm for the methine proton of
181 glycerol. The peaks at $5.3\text{--}5.5\text{ppm}$ arise from protons on the carbon double bonds ($\text{CH}=\text{CH}$).
182 The peaks in the region $2.7\text{--}2.8\text{ppm}$ correspond to methylene groups surrounded by single
183 bonded atoms. ^1H NMR of JCEP show the characteristic glycerol methylene and methine at
184 5.26 and $4.1\text{--}4.2\text{ppm}$ respectively but only residual $\text{HC}=\text{CH}$ at $5.3\text{--}5.5\text{ppm}$. However, there is
185 the appearance of new peaks in the region $2.9\text{--}3.2\text{ppm}$ indicating the presence of epoxy
186 protons. The peak at 1.5ppm correspond to the methylene group next to epoxy band

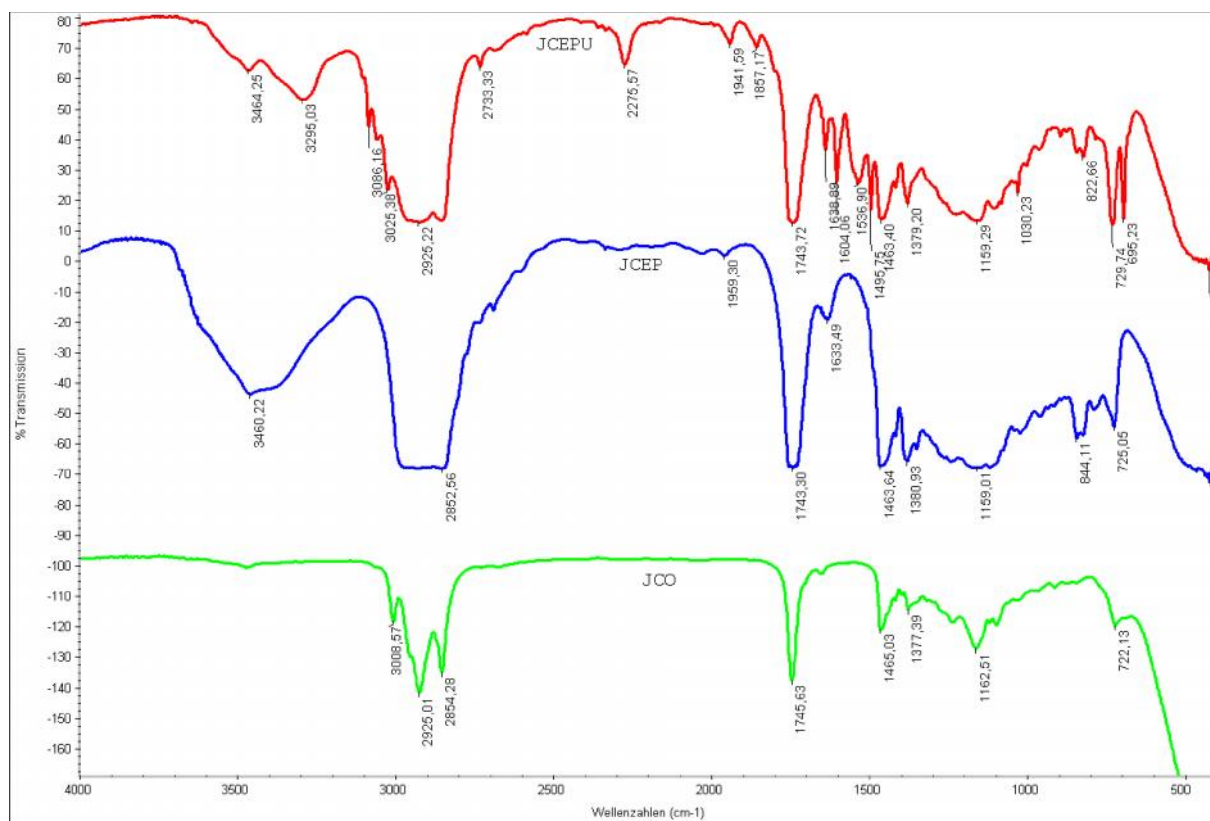
187 $\text{CH}_2\text{-COC-}$ and another peak at around 1.7ppm corresponding to methylene group
188 sandwiched between two epoxy groups. There is also the appearance of peaks between
189 $3.4\text{--}3.5$ for methine proton bearing the OH group that is CH-OH

190 The ^1H NMR of the JCEPU shows the disappearance of CH-OH at around $3.4\text{--}3.5\text{ppm}$ and
191 the appearance of the new peaks for the aromatic protons of TDI between $7.2\text{--}7.4\text{ppm}$. The
192 presence of the peaks at $2.9\text{--}3.2\text{ppm}$ in the JCEPU confirms the presence of epoxy group
193 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 -NH at 138ppm.

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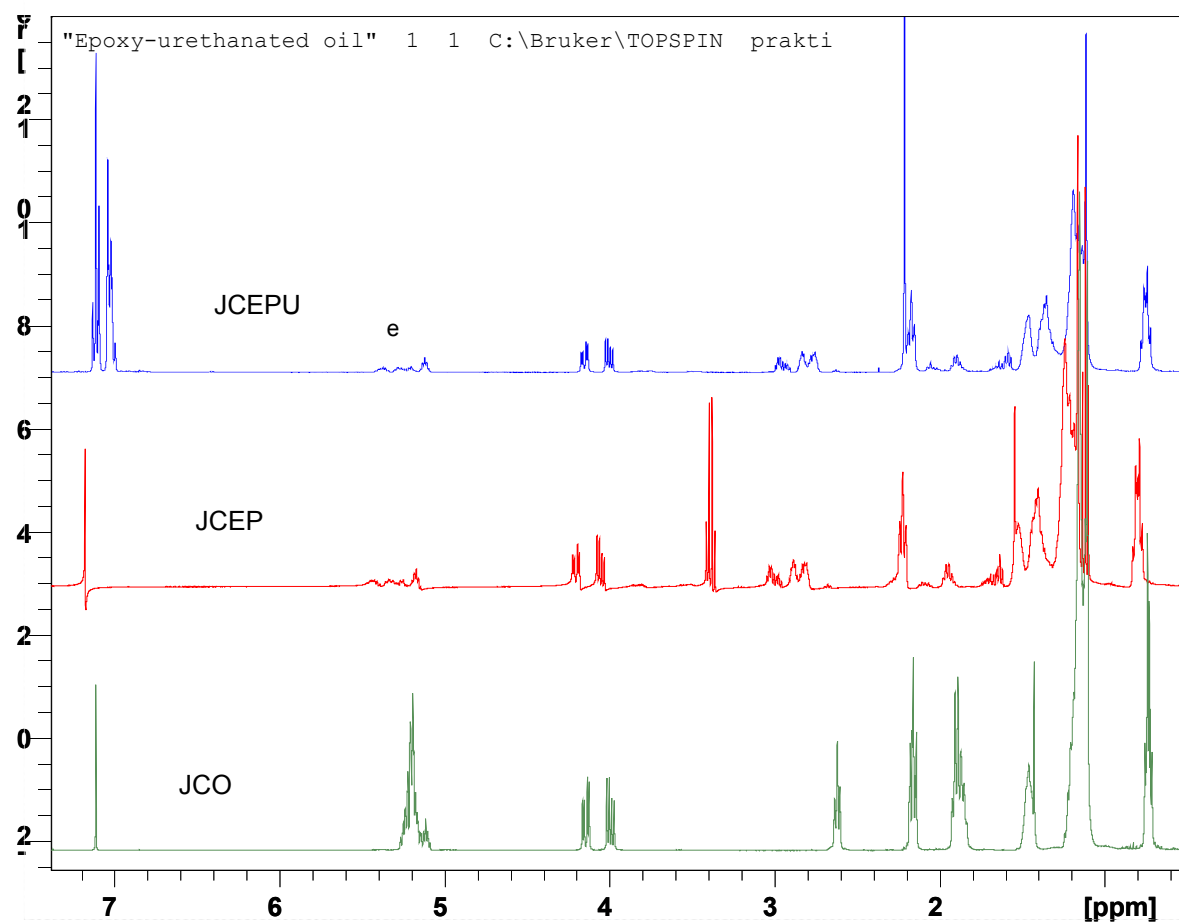
201 **Figure 1: Infrared spectra of JCO, JCEP and JCEPU**

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207 **Figure 2: Proton NMR of JCO, JCEP and JCEPU**

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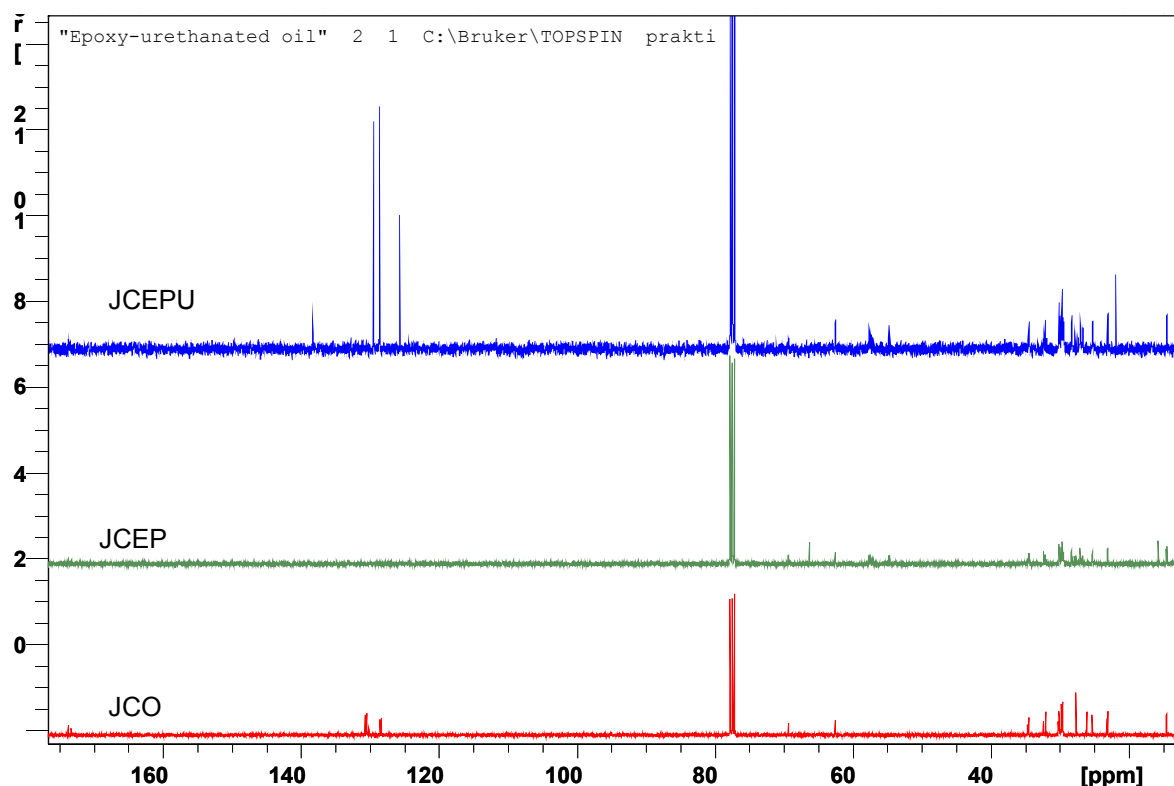


Figure 3: Carbon 13 NMR of JCO, JCEP and JCEPU

3.1 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 (Table 2). 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.

231 **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

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237 **3.2 Film properties of JCEPU's**

238 The drying time of the JCEPU's decreased as the loading of TDI increased (Table 3). The
 239 curing of urethanes has been predicted to occur in three stages [17, 18]. A first stage called
 240 surface drying which occurs by solvent evaporation and a second and third stage curing
 241 which occurs through chemical reactions [19]. Ahmad et al. [17] explained the mechanism of
 242 the second stage drying called dry to touch (DTT) as involving reaction of free –NCO group
 243 of the TDI with moisture to form amino group through primary addition. The amino group
 244 then reacts rapidly with another –NCO group present in another molecule leading to cross
 245 linking in the epoxy-polyurethane. The third stage drying called the dry to hard (DTH) is
 246 suggested to proceed slowly by auto-oxidation and occurs at the pendant fatty trimester
 247 chain of oil [18]. The scratch hardness was estimated by the pencil hardness of the films.
 248 The hardness was expressed in terms of the designation of the hardest pencil that failed to
 249 scratch the film. The results also revealed that scratch hardness also improved with loading
 250 of the TDI. All the films passed the impact resistance test. The increased loading of TDI in
 251 epoxy-polyurethanes means additional isocyanate moieties which provide extra cross linking
 252 sites. With more crosslink, the impact resistance is expected to improve. All samples passed
 253 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]

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

3.2 Differential scanning calorimetry (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 140 °C and 200 °C centring at 160 °C 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 -20 °C and this may be rationalised in terms of the stiffening effect of the appended aromatic moieties in the epoxy-polyurethane.

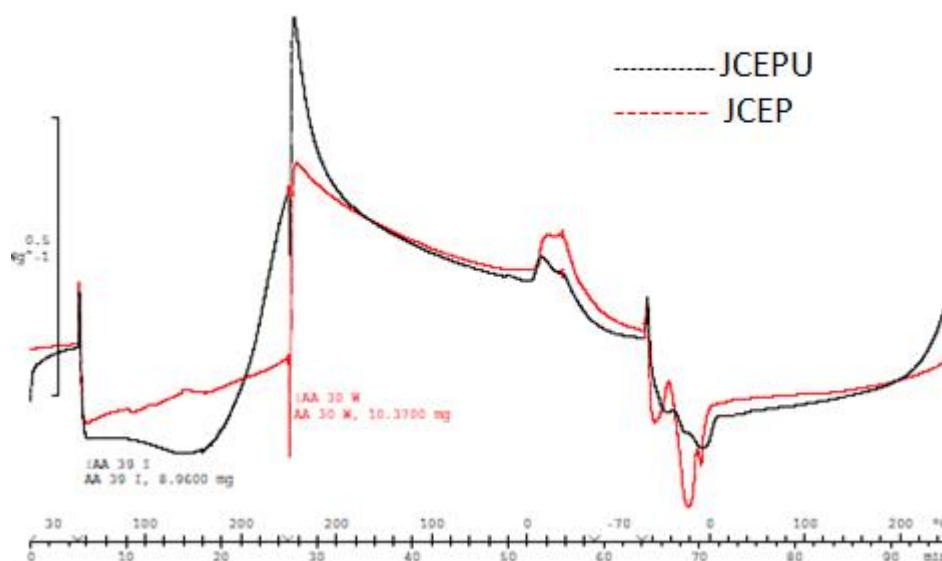


Figure 4: DSC thermograms of epoxy-polyol and epoxy-polyurethane

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