



Newly Developed Epoxy-Polyol and Epoxy-Polyurethane From Renewable Resources

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Authors' contributions:

The work was carried out in collaboration between all authors. Author COA designed the study, carried out the syntheses and evaluates the coating characteristics. Authors ETA and ZT did the spectroscopic analyses. Author COA managed the draft of the manuscript until published. Author BMB managed the literature searches. All authors read and approved the final manuscript.

Research Article

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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 epoxy-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 epoxy-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

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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.

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 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 feed stocks 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* 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. MATERIALS 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 Dibutyltin dilaurate (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 curcase* poxy-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.

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

2.3 Characterisation

Structural elucidation of JCO, JCEP and JCEPU was carried out by Fourier transform infrared (FTIR), proton and carbon 13 nuclear magnetic resonance (¹H NMR and ¹³C NMR) spectroscopic techniques. FTIR of the samples were done on Nicolet 380 FTIR (Thermo Electron 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^e (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) [13].

2.4 Evaluation of Film Characteristics

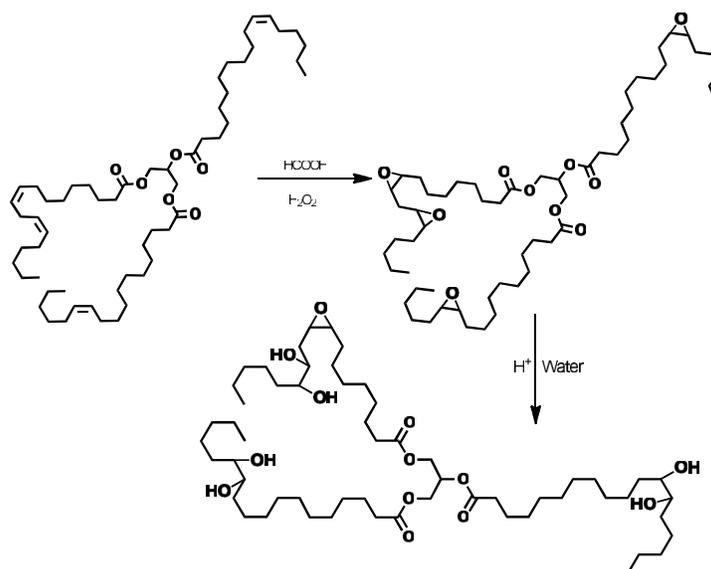
Samples of UJCO were thinned with toluene to brushable consistency. The solutions prepared were applied by brush on clean, mild steel panels of 15cm x 15cm for evaluating drying time, tin panels of the size 15cm x 15cm for flexibility and adhesion, scratch hardness and impact resistance and glass panels of the size 15cm x 15cm 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 various tests. The film characteristics were determined according to Indian standard specification [14,15].

3. RESULTS AND DISCUSSION

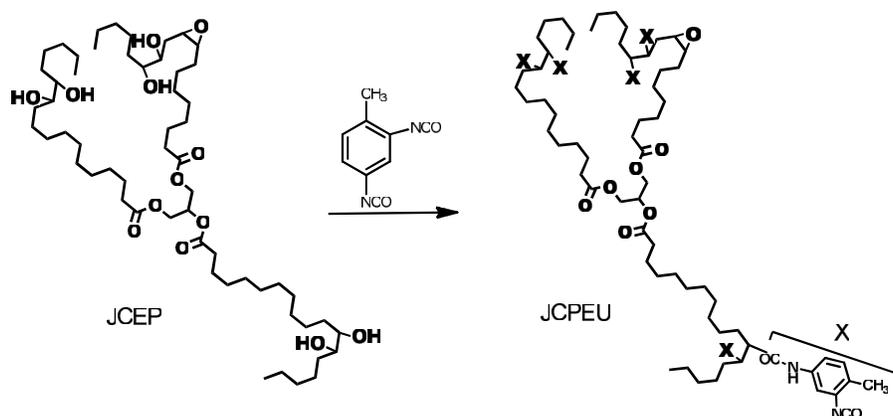
Preliminary work was carried out to determine the optimal conditions for epoxidation of *Jatropha curcas* oil and further hydrolysis of the epoxidised oil to epoxy polyol. Results revealed that epoxidation of *Jatropha curcas* oil was almost complete after 5hr using 2.5g of 85% formic acid in excess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

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

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



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



Scheme 2. Synthesis of *Jatropha curcas* epoxy polyurethane (JCEPU)

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 4.1-4.2ppm for the four methylene proton in glycerol centre and another peak at 5.25ppm for the methine proton of glycerol. The peaks at 5.3-5.5ppm arise from protons on the carbon double bonds (CH=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 HC=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 CH₂-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 that is 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 (Fig.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.

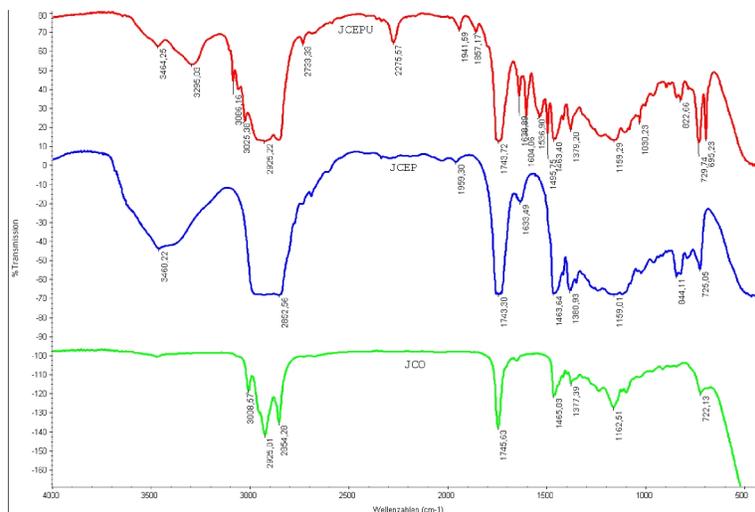


Fig. 1. Infrared spectra of JCO, JCEP and JCEPU

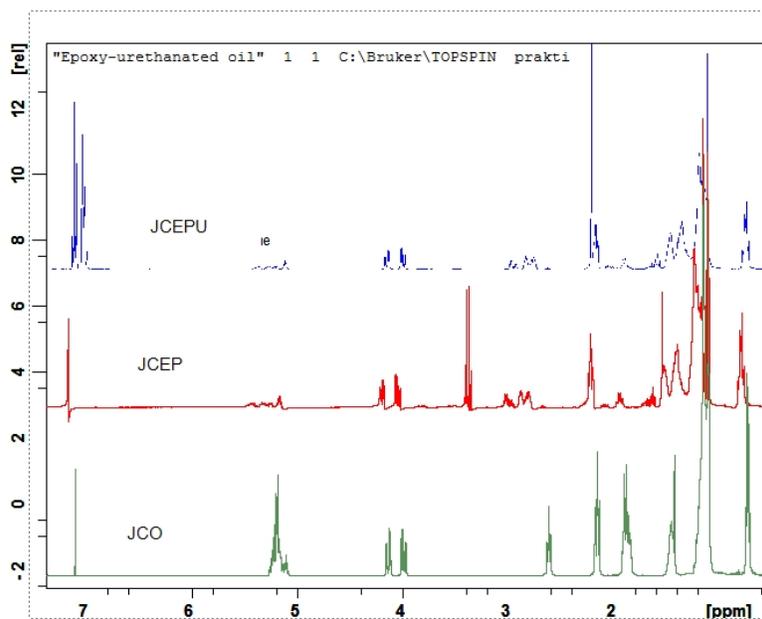


Fig. 2. Proton NMR of JCO, JCEP and JCEPU

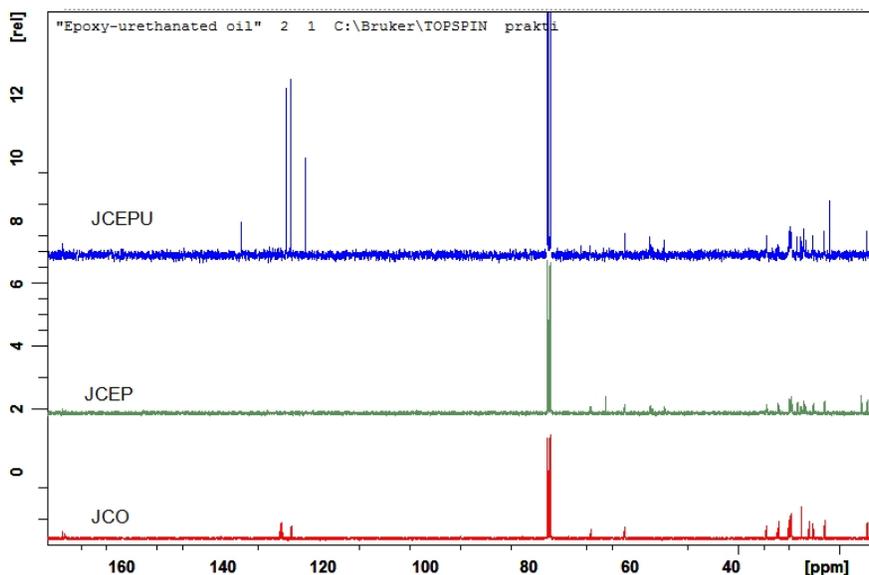


Fig. 3. Carbon 13 NMR of JCO, JCEP and JCEPU

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.

Table 2. 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

3.2 Film Properties of JCEPU's

The drying time of the JCEPU's decreased as the loading of TDI increased (Table 3). 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]

Table 3. Coating Properties of *Jatropha curcas* Epoxy polyurethanes (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 Fig. 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.

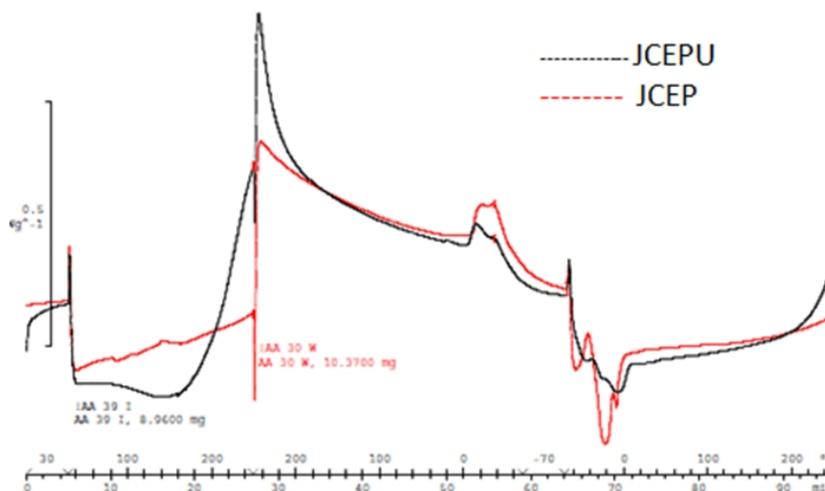


Fig. 4. DSC thermograms of epoxy-polyol and epoxy-polyurethane

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COMPETING INTERESTS

Authors declare that there are no competing interests.

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