Synthesis and Characterization of Biodegradable Jatropha Oil Based Polyurethanes Using Modified Sesame Oil as Cross-Linker Containing Different NCO Groups with Improved Thermal Stability

VENKATESH DESAPPAN and JAISANKAR VISWANATHAN*,

PG & Research Department of Chemistry, Presidency College (Autonomous), Chennai-600005, India

*Corresponding author: Fax: +91 44 28510732; E-mail: vjaisankar@gmail.com; venkatesh.d91@gmail.com

In this work, the modified S-diol were prepared from sesame oil to produce polyol. The thermal responsive vegetable oil-based polyurethane was prepared by polycondensation method. The different diisocyanate react with jatropha-sesame oil polyol to produce higher density with molecular weight of polyurethanes structure and functionality were characterized by Fourier transform spectroscopy, proton nuclear resonance spectroscopy and gel permeation chromatography. The thermal analysis was carried with TG analysis. The kinetic and thermodynamic parameters was calculated by TGA decomposition temperature and compared with PU-1, PU-2 and PU-3. Furthermore, the corresponding decomposition temperature of polyurethanes activation energy were calculated by Coats-Redfern, Sharp-Wentworth and Freeman-Carols methods, and it is investigated with lifetime of polyurethanes. Depending on the physically observed NH and C=O linkages of polyurethane matrix, which enhancing the hard and soft segment to improve their chain mobility. The success of the investigated polyurethanes, the corresponding estimated enthalpy, entropy and pre-exponential factors are much closer with toluene and phenyl based polyurethane matrix.

Keywords: Polyurethane, Thermal stability, Modified sesame diol.

INTRODUCTION

Most of the environmental dependence bio-based and renewable sources are used to produce variable materials and it can be using various applications, such as energy storage and conversion, biomedical, adhesives, coatings and nanocomposites, *etc*. These bio-based products prepared from various renewable resources such as, vegetable oils, peptides, cellulose and starch. In recent years, most of the bio-based new products were prepared from vegetable oils or plant oils, because of sample availability and the relatively low cost in nature. Vegetables or plant oils represent a renewable resource that can be used as reliable starting material to access new products with a wide array of structural and functional variations. The sample availability and the relatively low cost, make plant oils an industrially attractive raw material for the plastics industry [1-5]. On the other hand, a large demand of naturally occurring plant oils and fatty acids, many industries to manufacture bio-based functionalized polymers and polymeric materials [6-10]. Several

triglycerides of vegetable oils should be chemically modified to prepare polyols, and it can be used to synthesize polyurethanes and polyesters, among others and it has been the focus with many studies. The exception to lesquerella and castor oils, other vegetable oils do not contain hydroxyl groups, and it is chemically modified to introduce hydroxyl groups into their structure to produce polyols. The different chemical synthesis method is used to prepare functionalized polyols production, such as: (1) epoxidation and oxirane ring-opening [9]; (2) hydroformylation and hydrogenation [10,11]; (3) ozonolysis [12]; (4) thiol-enecoupling [13]; and (5) transesterification/amidation. In general, today it is possible for the researchers to chemically modify and transform the triglyceride into the reactive group *via* epoxidation, epoxidation and metathesis of double bond, and transesterification. However, oxirane ring content of linseed and soybean oils, presently it is used in appropriate curing agents in order to produce bio-based epoxies system with satisfactory properties [14-19].

Using this view, Desappan and Viswanathan [19] reported sesame and peanut oil with the crosslinker castor oil diol and Kessler *et al.* [20] reported a castor and soybean oil based polyurethane to produce good thermal and mechanical stability and it's used with various biomedical applications. In this paper, a vegetable oil-based polyols are synthesized form reaction between epoxidized jatropha oils with modified sesame oil diol and it enhances the higher polymeric matric network with different diisocyantes. Three different diisocyanates are used to prepare bio-based polyurethanes, such as hexamethylene diisocyanate, 2,4′-toluene diisocyanate and 4,4′-methylene diphenyl diisocyanate. The prepared polyurethanes functionality were characterized by FT-IR and ^{1}H NMR while the molecular weight of

polyurethane and polyols were analyzed by GPC. The T_g values of polyurethanes are characterized by DSC analysis and the thermal studies of the prepared polyurethanes were analyzed by TGA. From the obtained thermograms, different decomposition and degradation temperatures were identified to calculate kinetic parameters. The kinetic parameters are calculated using various models such as Coat-Redfern, Freeman-Carols and Sharp-Wentworth method. Depending on the chain extender (diisocyanates), the physical properties of the prepared polyurethanes are different, meanwhile, thermal stability will have to determine the kinetic and lifetime of the biodegradable polyurethanes (Fig. 1).
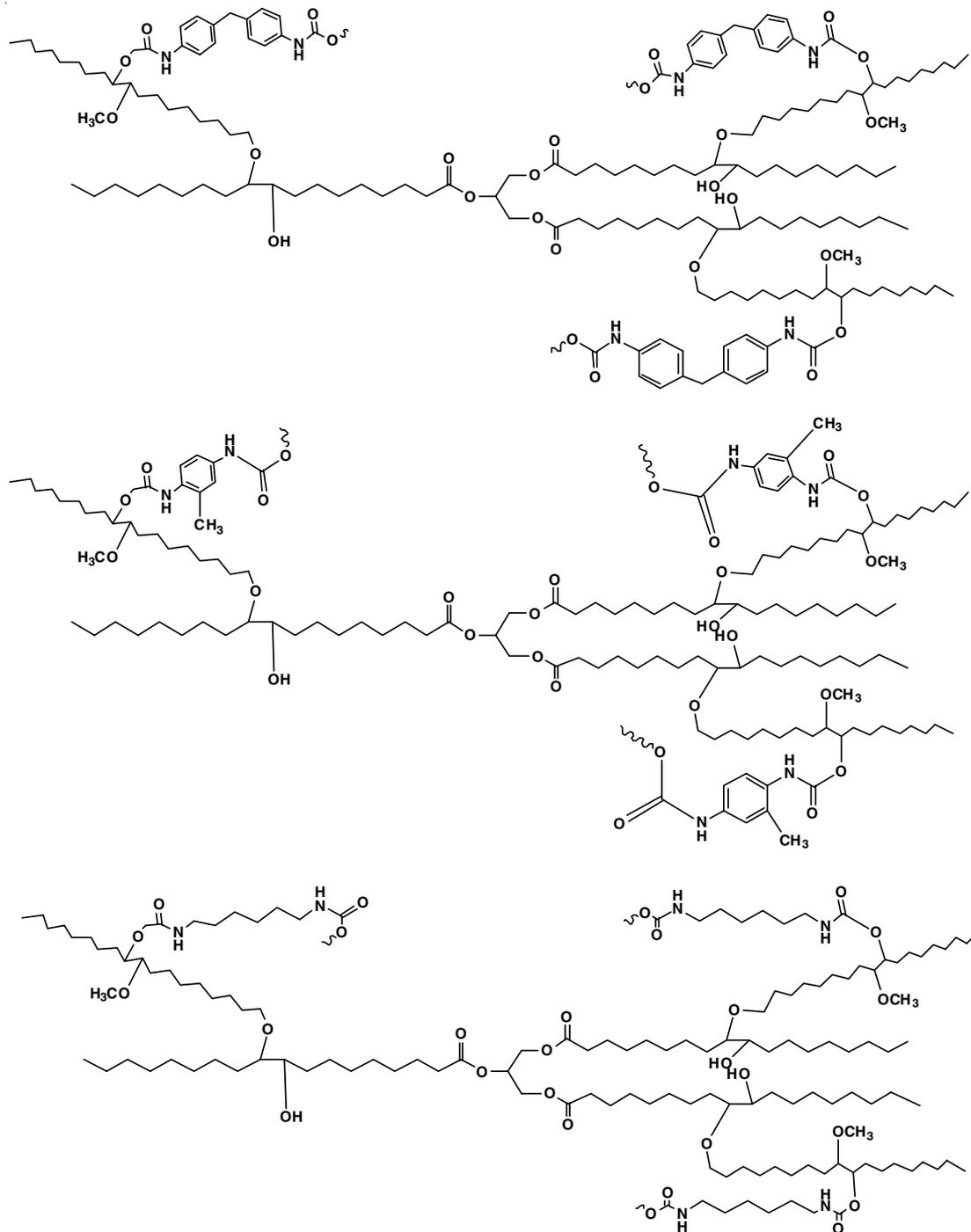

Fig. 1. Structures of PU-1, PU-2 and PU-3

EXPERIMENTAL

Vegetable oils such as sesame and peanut (approximately six oxirane rings per triglyceride) were purchased from a local source. Magnesium sulfate, hydrogen peroxide, methyl ethyl ketone, hexamethylene diisocyanate, 2,4′-toluene diisocyante, 4,4′-methelenebiphenyldiisocyanate and ethyl ether were purchased from Fisher Scientific Company (Fair Lawn, NJ). Sodium hydroxide, sodium bicarbonate, formic acid and dibutyltin dilaurate were obtained from Sigma-Aldrich (Milwaukee: USA). All the solvents and materials were used without further purification.

Synthesis of epoxidized vegetable oils: The epoxidized vegetable oils were prepared with a reported procedure. Briefly, the molar ratios of vegetable oil (sesame oil) and formic acid is 1:4.12, and charged into 500 mL round bottom flask at 50 ℃ under vigorous stirring. Then, 50 % molar ratio of H_2O_2 was added slowly over 4 h period (double bonds in triglyceride is 1.8:1) and the reaction was continued at 50 ℃ for another 4 h. Then, $NaHCO_3$ was added to reaction mixture and diethyl ether was added, which resulted in two layers. The organic layers were washed with distilled water until the solution became neutral. The solution was then dried using anhydrous $MgSO_4$ and filtered. The organic solvent is removed by rotary evaporator and the product was dried in a vacuum oven overnight. The same procedure was followed for the synthesis of epoxidized jatropha oil.

Methanolysis of epoxidized sesame oil: The synthesized epoxidized sesame oil was dissolved in methanol (molar ratios of epoxy to hydroxyl group of methnol was 1:10) and 0.01 wt. % of tetrafluoroboric acid added. Furthermore, the reaction carryout in a two-necked round-bottom flask equipped with a condenser and mechanical stirrer at 65 ℃ for 4 h under N_2 atmosphere.

Synthesis of 9-methoxy-octadec-9-ene-1,10-diol: S-diol was prepared according to the reported procedure [4,5]. Firstly, 100 mL of THF was added to $LiBH_4$ in a 1000 mL three-neck flask at 0 °C. Then, the addition of functionalized sesame oil 0.11 mol was dissolved in THF/methanol and then added to $LiBH_4$ suspension with mechanical stirring. The reaction was maintained at 0 ℃ for 10 h. The reaction mixture was poured into a 200 mL beaker with ice water, followed by addition of HCl, until the solution was clear. After the extraction with 30 mL of ethyl acetate, the organic layer was purified by washing with water, drying over $MgSO_4$ and filtering. Finally, the clear methoxy substituted sesame oil diol was obtained after removal of organic solvent using rotavapor and dried under vacuum. The yield of S-Diol was found to be ~ 78 %.

Synthesis of 9-hydroxy-10-(12-hydroxy-octadec-9-enyl-oxy)octadecanoic acid; 1-[10-hydroxy-9-(12-hydroxyhepta-dec-9-enyloxy)octadecanoyloxymethyl]-2-[10-hydroxy-9-(11-hydroxy-octadec-9-enyloxy)octadecanoyloxy]ethyl ester: The polyols were prepared by the ring-opening reaction as according to reported method [20]. The jatropha sesame oil polyols prepared from epoxidized oil were rings opened by modified sesame oil diol. Several aspects, sesame oil diol and epoxidized oil were mixed and kept at 65-75 ℃ in dry N_2 atmosphere. After 8 h, a brown-yellowish viscous liquid (JPOL) was obtained.

Synthesis of polyurethane: The synthesized polyol JPOL was reacted with 0.5 % excess of hexamethylene diisocyanate to prepare (PU-1) polyurethane. Methylethylketone used as a solvent under 70 ℃ at N_2 atmosphere. The same procedure was followed to prepare other polyurethane such as PU-2 (from toluene diisocyanate) and PU-3 from 4,4′-methylenediphenyl-diisocyanate)

Characterization: A variant spectrometer chemical structural studies were conducted using Bruker FTIR analyzer; ALPHA-Platinum FT-IR Spectrometer with ATR Platinum-Diamond sampling module. A Varian spectrometer (Palo Alto, CA) at 400 MHz was used to record the ^{1}H NMR spectra of the monomers of polyol and cross-linker S-diol. The prepared polyols and S-diol molecular weight distribution were measured using a Varian PL-gel permeation chromatography (GPC) 50 plus equipped with a differential refractive index (DRI)/visco-meter, which is a combined detector. The reference material tetrahydrofuran (THF) used as an eluent and the flow rate was fixed at 1.00 mL/min. Accurately weighed powder was taken into a pre-cleaned platinum pan, heated at a programmed rate of 10 ℃/min in the temperature range from 25 to 600 ℃ under nitrogen gas flow. The kinetics of thermal degradation studies has been discussed with synthetic and thermal degradation properties of a newly synthesized polymers derived from jatropha oil polyol and different chain extender of hexamethylene diisocyanate, 2,4′-toluene diisocyante, 4,4′-methelenebiphenyl diisocyanate. Thermal degradation curve analyzed in order to determine their mode of decomposition and the order of reaction. The methods employed are Coats-Redfern, Sharp-Wentworth and Freeman-Carroll methods have been applied for the calculation of activation energy and pre-exponential factor, frequency factor, free energy change, entropy change, enthalpy, apparent entropy, lifetime prediction and order of reaction calculated from Sharp-Wentworth and Freeman-Carroll′s methods.

RESULTS AND DISCUSSION

Thermogravimetric analysis: Thermogravimetry analysis of synthesized polymers (PU-1, PU-2 and PU-3) stability was evaluated by the TGA curve, 20 ℃/min heating rate under N_2 atmosphere. Fig. 2a shows the corresponding degradation of polymer with different isocyanate contents. The hard and soft segment of PU-1 was slightly reduced when compared with PU-2. In the chain extender of PU-1 connected with hexamethylene diisocyanate and PU-2 are toluene diisocyanate, respectively [1-4]. The degradation temperature of PU-1, PU-2 and PU-3 initial weight loss was increased when the number of urethane groups increased in the polymeric chain. In extent of hard, soft and segmental motion of PU-2 and PU-3 are closer with varying chain extender are used. From thermogram, five different weight loss were identified and the values are listed in Table-1. The comparative studies of PU-1 to PU-3 hard segment relatively increases, depending on diisocyanate linkage between polyol [5]. This is due to the intermolecular attraction between amine and carbonyl groups of the polymeric chain in it. The respective NCO linkage within the polymer chain increased the intermolecular interaction through hydrogen bonding, polar-polar interaction, *etc*. The respective thermograms of PU-1, PU-2 and PU-3 were synthesized from jatropha-sesame
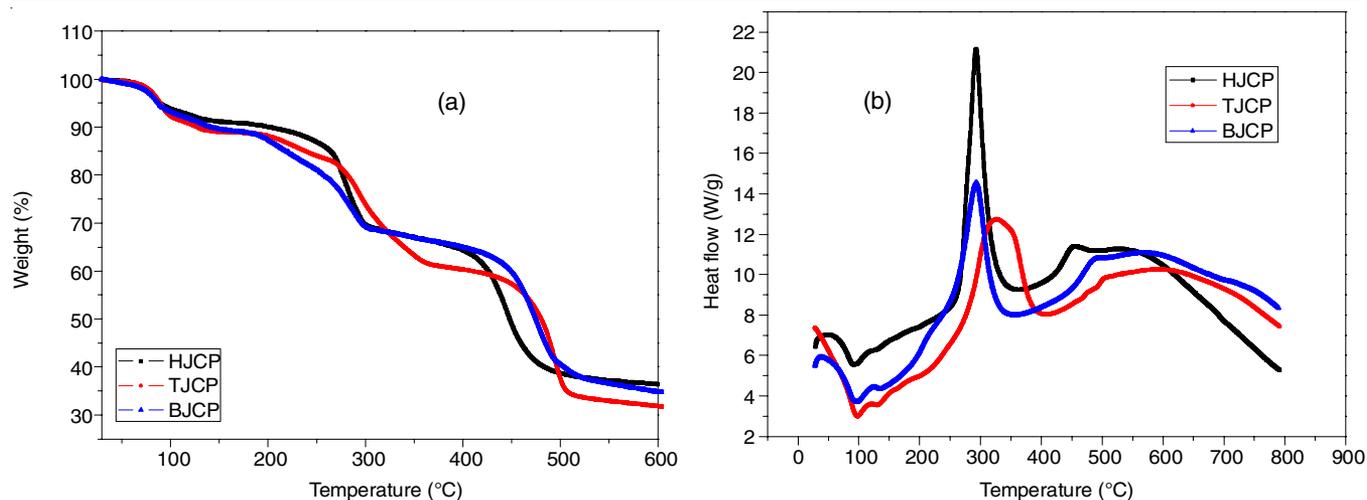
Fig. 2. (a) Thermal curves of PU-1, PU-2 and PU-3 plot, (b) DSC curves of PU-1, PU-2, and PU-3 plot

TABLE-1
KINETIC PARAMETERS CALCULATED FROM FREEMAN-CAROLS AND SHARP-WENTWORTH METHOD

Samples	A (s⁻¹)	ΔS (kcal/mol)	ΔH (kcal/mol)	ΔG (kcal/mol)	Z	S*	n	t_f
			Freeman-Carols method					
PU-1	7.269×10^2	24.01	-657.69	-1967	7.01	3.14	2	3.07×10^{-3}
PU-2	2.397×10^2	27.86	-543.55	-1601	5.96	1.12	3	6.59×10^{-2}
PU-3	4.703×10^3	10.20	-612.49	-1034	9.70	4.49	3	2.3×10^{-3}
			Sharp-Wentworth method					
PU-1	2.988×10^3	21.02	-549.60	-2321	9.01	3.43	3	8.98×10^{-3}
PU-2	4.485×10^3	24.92	-686.56	-2154	6.88	1.30	3	9.18×10^{-4}
PU-3	7.516×10^2	17.68	-559.15	-2334	6.17	5.11	3	3.73×10^{-4}

A = Pre-exponential factor, ΔS = Entropy, ΔH = Enthalpy, ΔG = Free energy change, Z = Frequency factor, S= Apparent entropy, n = Order of reaction (Decomposition).

polyol with a different hydroxyl group and three different diisocyanates (HMDI, TDI and MDI) are shown in Fig. 2a.

Initially, the first degradation of PU-1, PU-2 and PU-3 was observed in the temperature range of 189-230, 195-254 and 193-238 °C correspond to 92 % average weight loss, which might be due to urethane cleavage of polyurethanes [6-9]. Then the next corresponding 86 % weight loss was observed in the degradation temperature range at 280-302, 285-300 and 278-310 °C, respectively. The respective second degradation observed for the breakdown of S-diol fatty acid (alkyl moiety). Further, the 3rd stage degradation was noted in 60 % weight loss in the temperature range at 380-410, 388-416 and 366-401 °C; and the temperature ranges at 440-467, 458-478 and 456-481 °C were assigned to 4th degradation, which was happened to 32-39 % weight loss. Finally, the obtained major weight loss 6 to 17% is corresponded to the temperature at 498-520, 501-534 and 506-543 °C, respectively, which resulted in complete degradation process of S-diol. This happens due to their modified sesame diol to extend Pus chain, and it is sluggish in nature [10-12]. So, the obtained degradation temperature is used to calculate the activation energy of PU-1, PU-2 and PU-3, the respective major decomposition was noted. On the other hand, initial decomposition which major temperature was used to determine the energy of activation were calculated by Coats-Redfern, Freeman-Carols and Sharp-Wentworth methods. Using the thermal stability of polyurethanes, kinetic parameters

were calculated and compared with the respective Freeman-Carols and Sharp-Wentworth methodm which was used to calculate the kinetic parameters of synthesized polymers (PU-1, PU-2, and PU-3).

However, the kinetic parameters such as enthalpy, entropy, pre-exponential factor, free energy, frequency factor and lifetime of polyurethanes calculated values are shown in Table-2. The activation energy cannot change with temperature when the isothermal curves are fairly parallel. However, the non-parallel irregular spacing are illustrated by isothermal conversion curve, Fig. 2a shows the obtained complexity of the process curve was obtained in thermogram. The different isoconversion points are used to calculate the average value of activation energy (Table-3) and the estimated values are plotted and compared with other models such as Freeman-Carols and Sharp-Wentworth. The obtained E_a values are quite clear with 40-60 % of minimum values. The difference between the Freeman-Carols and Coats-Redfern activation energy varied within 326 and 346, 141 and 150, 388 and 439 kJ/mol of the average value, but the Sharp-Wentworth model closed with the activation energy. However, the fluctuations in E_a is much higher in those values are obtained according to Freeman-Carols and Sharp-Wentworth models. These activation values indicated a decrease of E_a values with increasing conversion, due to the complex nature of the degradation process, while a large difference between the activation energy.

TABLE-2
ACTIVATION ENERGY OF POLYURETHANE CALCULATED
FROM DIFFERENT DECOMPOSITION TEMPERATURE

Polymers	Temp. (°C)	Activation energy (ΔE_a) (kJ/mol)		
		Coat's-Redfern	Freeman-Carroll	Sharp-Wentworth
PU-1	161 247 332 458 504	114.82	49.21	69.26
PU-2	187 256 339 472 517	117.37	80.19	54.96
PU-3	172 260 389 436 512	123.37	49.55	56.57

Thermal degradation kinetic parameters *viz.* activation energy (E_a), pre-exponential factor (A), frequency factor (Z), apparent entropy (S^*) and reaction order (n) were calculated using thermal curves. Kinetic constants of polyurethane (PU-1, PU-2 and PU-3) measured at heating rates of 5 to 20 °C/min indicates that at larger heating rates both the activation energy and the pre-exponential factor decreases. The approximate order of reaction was calculated using the one-step kinetic model of different decomposition. Freeman-Carols and Sharp-Wentworth methods are used to calculate enthalpy, entropy and free energy change and compared. The obtained values reveal that aromatic linked to polyurethane is closed with the polymer matrix and not for aliphatic linked polyurethane.

In present study, kinetic different degradation was observed and the corresponding estimated results show jatropha-sesame with TDI and MDI supposed to increase the molecular rigidity than HMDI with jatropha-sesame *i.e.*, the composition of modified S-diol ring opened with epoxidized jatropha oil. The corresponding exotherm reaction is the main part of the polymeric matrix with more than 65 % of the surface. Using modified sesame oil, diol improved the urethane formation and the molar enthalpy values of PU-1, PU-2 and PU-3 are given in Table-2. The estimated enthalpy results revealed very close with all the polyurethanes due to methoxy bonded sesame oil polyol which enhanced the polymer credibility and molar ratios of diisocyanate with a polyol. From these results, it could be considered that for HMDI, TDI and MDI, the three different polyurethanes have an equal molar enthalpy of reaction at lower < 298 K. The reaction rates are sufficiently slow to allow efficient mixing during a few minutes without the significant extent of reaction.

Lifetime prediction: The kinetic and thermal mechanism of the solid-state jatropha-sesame oil-based polyurethanes to increase the mobility of chain and chain extenders (HMDI, TDI and MDI) were studied. The formulated jatropha oil-based polyurethane with diisocyanate lifetime was estimated from apparent kinetic parameters. The estimated values are compared with PU-1, PU-2 and PU-3's major mass loss reaches 6, 5 and 4 wt. %, which revealed that the failure of chain mobility makes

more compact in nature. Following equations can be estimated for the lifetime of the polymer.

$$\frac{d\alpha}{dt} = A \exp \frac{E_a}{RT}(1-a)^n \tag{3}$$

$$t_f = \frac{1-0.0513}{A} \exp \frac{E_a}{RT}(n=1) \tag{4}$$

The estimated approximate E_a of PU-1, PU-2 and PU-3 3.07×10^{-3}, 6.59×10^{-2} and 2.3×10^{-3} (Freeman-Carols method) and 8.98×10^{-3}, 9.18×10^{-4} and 3.73×10^{-4} (Sharp-Wentworth method). Depending on the chain mobility of carbonyl and amine linkage chain extender (HMDI, TDI, MDI) in polymeric matrix, the carbonyl and amine linkage between the carbonyl and amine linkage of polymeric chain mobility, the corresponding thermal curve of mass loss give low energy of dissociation, so, it is easy to find out the lifetime of the polymers (Table-2). On the other hand, lifetime was strongly dependent on decreasing temperature and significant temperature increases from 20 to 650 °C. However, the physical state of the polyurethanes strongly depends on the polymeric chain mobility between the kinetics of degradation. Furthermore, the solid state of chain mobility will low than the molten state, thereby making the predictions even inaccurate for the solid state.

FTIR: The prepared S-diol and epoxy jatropha-oil based polyol functionality and structure were investigated by AT-IR and FT-IR. The FT-IR (Fig. 3) showed a epoxidized jatropha-
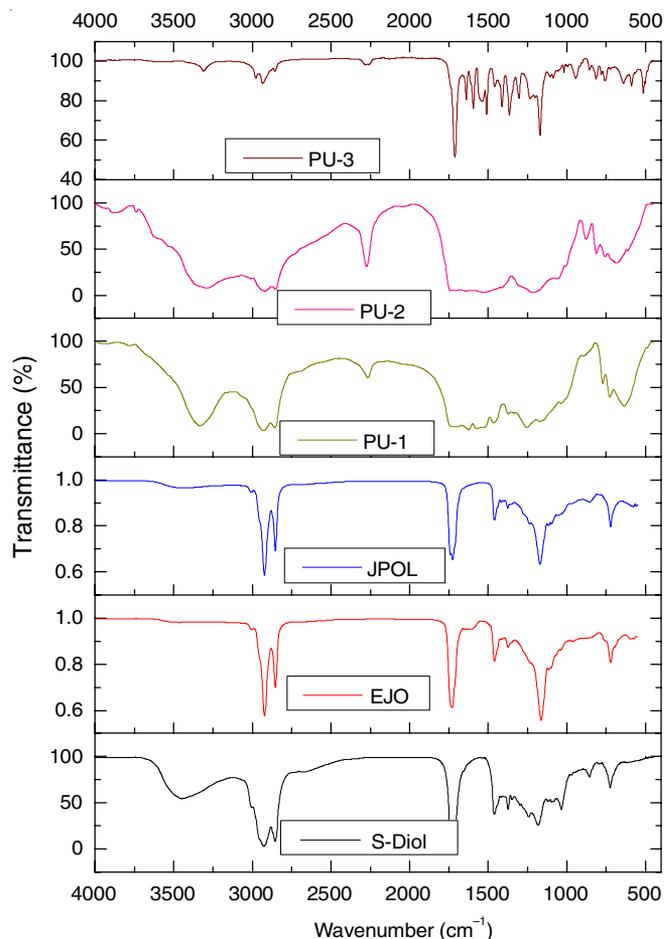

Fig. 3. FT-IR spectra of epoxidized EJO oil, JPOL polyol, sesame diol, PU-1, PU-2 and PU-3

oil. The FT-IR spectrum revealed that the presence of epoxy group at 843 cm^{-1}, respective epoxy oils [13-16,18]. The corresponding modified diol, the overlapped signal from the -OH stretching of hydroxyl group of modified sesame oil peak appeared at 3500-3000 cm^{-1}, then the intensity of epoxy group was reduced during the ring opening reaction using methanolysis [17,18].

In polyol, the ring opening reaction of epoxy groups was opened by modified sesame diol. The reaction of epoxy group ratio was increased, when the primary -OH group interacted with them. Secondary hydroxyl group was newly formed during the methanolysis reaction of epoxidized sesame oil. On the other hand, the prepared jatropha-sesame oil based polyol, the -OH broad peak appeared at 3378 cm^{-1}, which showed a overlapped signal of all the primary and secondary -OH groups of polyols [14-16].

The infrared spectra of polyurethane PU-1, PU-2 and PU-3 shows the oxygen atoms of carbonyl (>C=O), ether and ester group (C-O-C) and amine functional groups (C-N and N-H) absorbed at 1750-1710, 1300-1000 and 1550-1500 cm^{-1}. After polycondensation reaction, the >C=O stretching have three peaks due to free or non-hydrogen-bonded >C=O peak which was observed at 1735-1727 cm^{-1}, while disordered hydrogen-bonded >C=O symmetrical stretching at 1721-1718 cm^{-1} and the vibrational stretching frequency observed at 1703-1704 cm^{-1}, respectively.

In PU-1, the polymer has aliphatic linked isocyanate groups while the others have aromatic linked diisocyanate groups. However, functional groups in the polymers *viz.*, amine, ether and ester groups were appeared at 1575, 1558, 1500 cm^{-1} respectively PU-1, PU-2 and PU-3. After the polycondensation reaction, the symmetrical stretching peak was observed at 1710, 1748, 1788 cm^{-1} (PU-1, PU-2 and PU-3) for disordered hydrogen bonded >C=O peak at 1720, 1729, 1735 (PU-1, PU-2 and PU-3) for the non-hydrogen bonded >C=O, respectively. The oxygen and carbonyl groups with disordered hydrogen bonding of soft-

hard and hard-hard developed the >N-H bonding in the polyurethane matrix. The segmental motion of polyurethane polymer was restricted by physical cross-links of strong hydrogen bonding. The observed peak at 1588, 1599 and 1609 cm^{-1} for PU-1, PU-2 and PU-3 were identified as the bending vibration of >N-H group. The linkage between hydroxyl and -NCO groups of urethanes stretching absorption band of corresponding ether group may appearred at 1034,1060 and 1090 cm^{-1} respectively PU-1, PU-2 and PU-3 and the peak at 1580, 1599 and 1593 cm^{-1} respectively PU-1, PU-2 and PU-3 for >N-H bending vibration.

NMR: The S-diol of ^{1}H NMR spectra (Fig. 4a) shows the corresponding secondary hydroxyl groups overlapped signal intensity individually which was observed at δ 3.8-4.6 ppm, and the methoxy group was identified at δ 2.6 - 3.1 ppm, respectively [19-21]. Internal and terminal protons signal were attributed to appear at δ 1.67 ppm and δ 0.90 ppm [18,20]. Fig. 4b shows the ^{1}H NMR spectra of prepared jatropha-sesame oil polyols, a chemical shift value of -O(O)C=CH$_2$ proton at δ 2.35 ppm. The disappeared peak of corresponding epoxy groups no longer shown after the reduction reaction, the signal at δ 2.15-2.70 ppm [11-15,17]. The shifted signal of methoxy proton of oleic acid moiety was detected at δ 3.58-3.61 ppm. During the ring opening reaction between epoxidized jatropha oil and modified sesame oil, the intensity of proton signals increased at δ 5.34-5.49 ppm. The overlapped signal at δ 5.5 ppm was observed for the newly formed hydroxyl group at polyol [11]. On the other hand, after the complete reduction of triglycerides indicates the signal at δ 4.44-4.58 ppm decreased. The primary signal at 5.5 ppm corresponding to the backbone of hydroxyl group. This lead to conclude that jatropha-sesame oil was successfully prepared [12,13].

^{1}H NMR spectra of polyurethanes (Fig. 4b) of jatropha-sesame oil polyol (JPOL) were reacted with three different diisocyantesand compared with the chemical shift values. Herewith the PU spectrum shows the intensity of polyol signals were decreased at δ 5.33 (PU-1), δ 5.44 (PU-2) and δ 5.56 (PU-3),
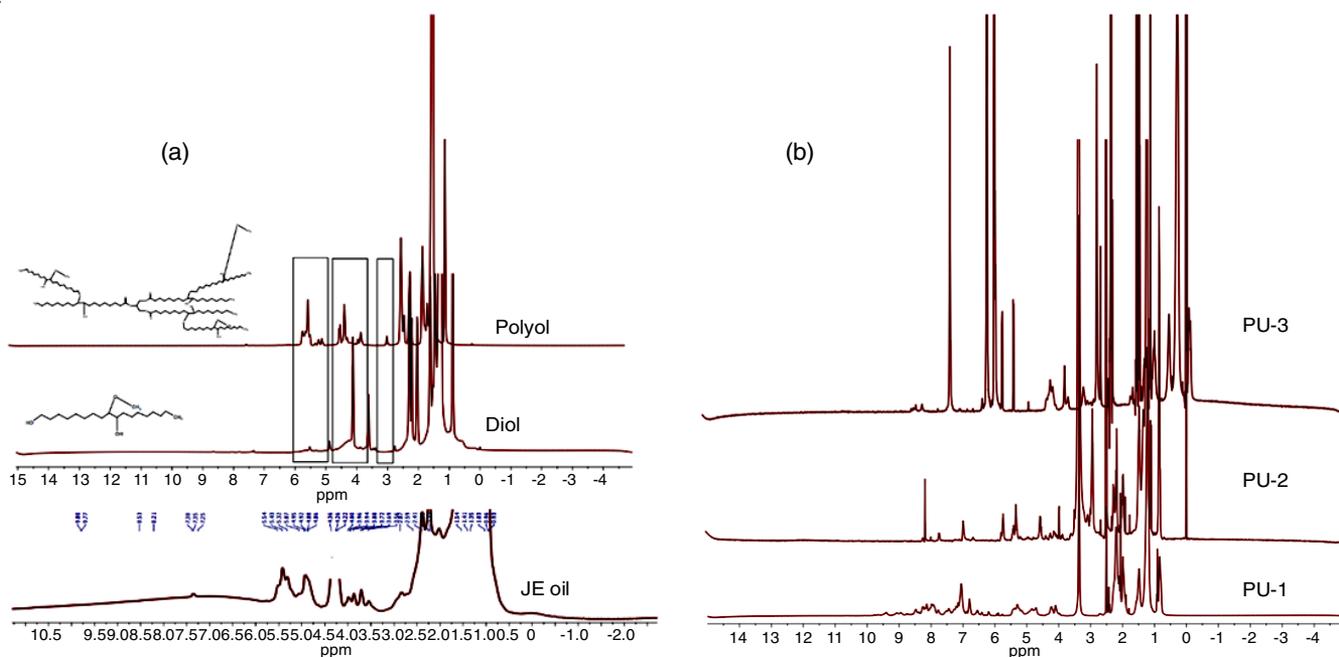

Fig. 4. [1]H spectra of epoxidized oil, JPOL and S-Diol (a) and PU-1, PU-2 and PU-3 polymer (b)

which is due to the polycondensation reaction between the isocyanate and polyol. The PU-1, PU-2 and PU-3 of urethane (>NH) signal attributed to increase the intensity and the corresponding signals at δ 8.33, δ 8.89 and δ 8.78 ppm, respectively. The chemical shift values of OCOCH₂ corresponding protons signal appeared at δ 3.56 (PU-1), δ 3.77 (PU-2), δ 3.66 (PU-3) and the other signal of O=C-NH protons were observed at δ 7.04 (PU-1), δ 7.78 (PU-2) and δ 7.89 (PU-3). The important signal of C-OCH₃ of crosslinker protons assigned to appear at δ 3.9 (PU-1), δ 4.1 (PU-2) and δ 4.5 (PU-3). These results revealed to that all the polyurethanes were successfully prepared [7,9-15,21-23].

Gel permeation chromatography: The molecular weight of jatropha-sesame polyol and PU-1, PU-2 and PU-3 were characterized by gel permeation chromatography. The prepared polyol has high PDI value and the results revealed that the modified sesame oil when reacted with epoxidized jatropha oil enhanced the molecule interaction and its density also increased (Table-3). The comparative studies of polyols with different isocyanate linked polyurethanes namely PU-1, PU-2 and PU-3 are shown in Fig. 5.

TABLE-3
DETERMINATION OF MOLECULAR WEIGHT OF MONOMER AND POLYMERS BY GEL PERMEATION CHROMATOGRAPHY

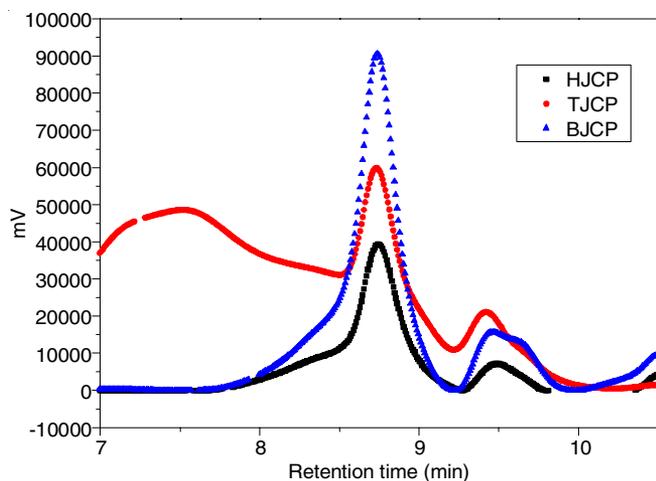| Sample	Viscosity (pa s) 25 °C	Number average molecular weight	Weight average molecular weight	Polydispersity index
Polyol				
JPOL	0.50	1327	2316	1.14
	0.58	940		
Polyurethane				
PU-1	–	1891	1927	1.83
PU-2	–	1459	2992	1.97
PU-3	–	1798	2875	1.88

Fig. 5. GPC curves of PU-1, PU-2 and PU-3 polymers

The GPC curves of PU-1, PU-2 and PU-3 retention peaks was also compared. The various hard-hard and soft-hard segments of polyurethane were improved and also their self-rigidity [24-26]. According to the isocyanate linkages in polyurethane, PU-1 has lower retention as compared to PU-2 and PU-3, which is due to the segmental motion of polyurethane which increased

their molecular rigidity and extended the solid-state property [4,6,13,27]. These results identified all the aromatic linked polyurethanes (PU-2 & PU-3) having higher stability in nature as compared to PU-1 [22-26,28-31].

Conclusion

The polyurethanes having higher crosslinking density and improved thermal stability are prepared using modified sesame oil. The prepared PU-1, PU-2 and PU-3 having activation energies are very closed, however, thermal stability of PU-1 is lower than the PU-2 and PU-3. Because of the presence of aromatic moiety in PU-2 and PU-3, which enhanced the molecular rigidity and compatibility. These results revealed that improving the segmental ratios due to the presence of modified sesame diol with higher functionality polyols. The estimated entropy values are compared with polyurethanes, the corresponding PU-2 and PU-3 varied with PU-1. This maybe due to the order of decomposition closed with each polymer.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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