A Kinetic Study of Certain Vegetable Oil Based Polyurethane

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Abstract- Vegetable oil polyol derived hyper-branched polyurethanes (PUs) polymer were synthesized by polycondensation method, using dibutyltin dilaurate as a catalyst. The resulting polyol and polyurethanes were characterized by Fourier Transform Spectroscopy (FT-IR), Proton Nuclear Resonance Spectroscopy (^{1}H NMR) and ^{13}C Nuclear Resonance Spectroscopy (^{13}C NMR). The effect of cross-linking on the polyols and chain extender density of polyurethane (PUs) molecular weight is determined by the Gel Permeation Chromatography (GPC). The isothermal behavior of the synthesized polyurethanes was studied by thermogravimetric analysis (TGA) under nitrogen atmosphere and the results were compared with the corresponding molecular weight. A details of thermal degradation studies of polyurethane (TICP) has been carried out to ascertain its thermal stability. The thermal curve has been discussed in order to determine their mode of decomposition, activation energy (Ea) can be calculated by Coats and Redfern, Murray and White , Doyel's , Freeman- Carrol's method. And the thermodynamic parameters such as, activation of enthalpy (ΔH), free energy change (ΔG), entropy change (ΔS) have been used to determined by Freeman-Carrol's method. The results indicates that the prepared polyurethanes have high thermal stability.

Keywords- Thermal Degradation, Activation Energy, Vegetable Oils, Cross-Linking, Polyurethanes

I. INTRODUCTION

In recent years, with advances in material science, the need for environment-friendly substituted raw materials for preparing polymers has been increasing drastically. A lot of investigations have been carried out on polymer materials based on renewable resources. The main target has been the preparation of polyol from plant sources. These sources are easily available, economical and are also friendly to the environment [1]. Bio-based materials, that are commonly used as starting material for polyurethanes include cellulose, starch, natural oil, and sugar [2-5]. The most promising among these are vegetable oils .[5] The six common fatty acids are palmitic (C 16 : 0), stearic (C 18 : 0), oleic (C 18 : 1), linoleic (C 18 : 2), linolienic (C 18 : 3), and recinoliec (C 18 : 1 OH)acids (in this notation, the first number represents the number of carbon atoms, the second number represents the number of C-C double bonds, and OH represents hydroxyl groups in fatty acid) [5-6]. The reactive sites are ester bonds, C=C, and the hydroxyl group which exist in some oils. All the vegetable oils have been studied in details towards the preparation of polyols and polyurethanes.[7-10].

In this paper, we report on the development of polyols by the oxirane ring opening technique. The oxirane ring opening is a significant class of organic equilibrium exchange reactions in which one epoxy ring is opened by another fatty acid moiety. In the epoxidation of vegetable oils, the triglyceride reacts with methanoic acid and is followed by the addition of peroxide. There are several aspects to be considered such as, the type of polyol preparation, the carboxyl to epoxy mole ratio and the temperature, all of which have an influence on the progress of the reaction. The recinoleic fatty acid is obtained directly via saponification of castor oil that is by treatment of the oil with an alkali in the presence of HCl as a neutralizing agent. A variety of vegetable oils are prepared to polyols, such as, castor oil fatty acid (CaOFA) was used to ring- opening to epoxy groups in epoxidised mahua oil (EIO). The present communication deals with the effect of the ring-opening duration of newly synthesized polyurethane (PUs) such as TICP derived from ICOL. Their structures and functionalities are characterized by the FT- IR,^{1}H NMR, ^{13}C NMR and the viscosity of the polyols is characterized by Rheometry. We also look at the synthetic and thermal degradation properties of newly synthesized polyurethanes (PUs) such as TICP derived from ICOL. The Freeman-Carroll's methods have been applied for the calculation of kinetic parameters from the thermogravimetry (TGA) curve. The thermal degradation curve has been discussed in order to determine their mode of decomposition, apparent activation energy, activation of enthalpy, free energy change and entropy change.

II. EXPERIMENTAL

A. Materials

Vegetable oils such as, mahua oil (approximately six oxirane rings per triglyceride) were purchased from local sources, Magnesium sulfate ($MgSO_4$), hydrogen peroxide, methyl ethyl ketone (MEK), toluene diisocyanate (TDI) and ethyl ether were purchased from Fisher Scientific Company (Fair Lawn, NJ). Hydrochloric acid, sodium hydroxide, sodium bicarbonate, formic acid and dibutyltin dilaurate (DBTDL) were obtained from Sigma-Aldrich (Milwaukee, WI). All materials were used without further purification.

B. Synthesis of vegetable oil

1) Synthesis of the Epoxidized Vegetable Oils

Epoxidized vegetable oils with different epoxy groups were made as per the method previously reported. [1] Briefly, mahua oil and formic acid (the molar ratio of these two is 1:4.12) were charged into a 500 mL flask at 50 °C. The content were vigorously stirred. Then, hydrogen peroxide (50%, the molar ratio of hydrogen peroxide to double bonds in triglyceride is 1.8:1) was added slowly using a syringe over a period of 4 hours. The reaction was allowed to continue at 50 °C for another 4 hours. Then, sodium bicarbonate was added to neutralize the solution and diethyl ether was added. This resulted in two layers. The organic layer was washed with distilled water until the solution became neutral. Epoxidized mahua oil (EIO) was obtained after drying with $MgSO_4$ and filtering. The organic solvent was removed by a rotary evaporator. The product that resulted was left to dry in a vacuum oven overnight.

2) Synthesis of functionalized fatty acid

Castor oil was saponified into fatty acid by heating with sodium hydroxide at 70 – 80 °C. Then, in order to neutralize the solution, hydrochloric acid was slowly added. Finally, the organic layer was washed with water and purified. It was then dried over $MgSO_4$ and filtered. The result was CaOFA, a clear light brownish fatty acid, while most of the fatty acids in vegetable oil are linolenic acids, linoleic acids and oleic acids.

3) Synthesis of Polyols

The polyols were prepared by ring–opening reactions between epoxidized oils and CaOFA fatty acid. The polyol were identified as mahua-castor oil polyol (ICOL). The CaOFA and epoxidized oil (EIO) were mixed and kept at 150 °C – 180 °C in dry N_2 atmosphere. After the 6 hours, a yellowish viscous liquid was obtained.

4) Synthesis of polyurethane

The synthesized polyol ICOL was made to react with 0.5% excess of toluene diisocyanate (TDI) to prepare (TICP) polyurethane. Ethyl methyl ketone (MEK) was used as a solvent under 70°C at N_2 atmosphere. The same procedure was followed to prepare other polyurethanes such as, TICP. The polymers thus obtained were kept in to vacuum evaporation for 48hrs. The final polymer of 75% solid content was obtained.

C. Characterizations

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 and ^{13}C NMR spectroscopic analyses of the monomers of polyol and cross-linker CaOFA fatty acid. The prepared polyols and CaOFA fatty acid molecular weight distribution were measured using a Varian PL-gel permeation chromatography (GPC) 50 plus equipped with a differential refractive index (DRI)/viscometer which is a combined detector. The reference material tetrahydrofuran (THF) was used as an elutent and the flow rate was fixed at 1.00 mL min[1].The viscosity of prepared polyols were determined using U/S portable rheometer at 25°C. The thermogravimetric

analysis (TGA) was performed on a NETZSCH TG 209 apparatus using 5 mg samples. This was done within the temperature range of 100–600 °C under an argon atmosphere, at a heating rate of 10 °C/min.

III. RESULTS AND DISCUSSION

### A. Fourier Transform Infrared Spectroscopy

The FT-IR was used to investigate the structure and functionalities of the prepared epoxy of vegetable oils and CaOFA. The measurement of FT-IR was carried out in attenuated total reflectance mode using a thermoset scientific nicolet 6700 spectrometer. IR spectra were obtained at 4 cm^{-1} resolution between standard wave number ranging from 400 to 4000 cm^{-1}. [1]

Fig. 1(a) shows the FT-IR spectra of the epoxidised EIO. The FT-IR spectra shows that the presence of epoxy group at 843 cm^{-1} respective epoxy oils. Fig. 1(c). shows, the broad peak between 3600 to 2500 cm^{-1}, which was assigned to overlapped signal from the -OH stretching of the hydroxyl and the carboxylic groups of fatty acid CaOFA. The peak at 843 cm^{-1} could not be seen any more for the fatty acids because most of the epoxy groups were reduced during the ring opening step [2-3]. Fig 1(b), shows that the intensity of epoxy group at 843 cm^{-1} vanished while the CaOFA of fatty acid units facilitated the ring opening of all the epoxy oils. The reaction of carboxyl to epoxy group ratio were increased because of which most of epoxy groups were ring- opened by hydroxylated fatty acid CaOFA. The –OH group is intrinsically present in CaOFA fatty acid recinoliec acid moiety is shown the fig. 1(c). On the other hand, the ICOL polyol of all the –OH groups and the presence of broad peak at 3498 cm^{-1}, shows the -OH group of CaOFA overlapped with all the epoxy vegetable oils. [4]

The Fourier transformed infrared spectra of fig. 1(f) and 1(g). demonstrates that polyurethane TICP polymer are on the oxygen atoms of the carbonyl (C=O), ether and ester group (C-O-C) and amine functional groups (C-N and N-H) are absorbed at 1750-1710 cm^{-1}, 1300-1000 cm^{-1} and 1550 – 1500 cm^{-1},. After the poly condensation reaction, it was noticed that the spectra of polyurethane, the C=O stretching had three peaks due to free or non-hydrogen-bonded - the C=O peak observed at 1727-1735 cm^{-1}, the disordered hydrogen- bonded C=O symmetrical stretching at 1718-1721 cm^{-1} and the vibrational stretching frequency observed at 1703-1704 cm^{-1} respectively. It is also significant to note that the N-H group in polyurethane can develop hard segment to hard segment disordered Hydrogen bonding with the oxygen of carbonyl groups.[5,12] Such strong -H bonding acts as a physical crosslink and this leads to the restriction of the segmental motion of the polymer chain. The observed N-H bending vibrations at 1598 cm^{-1}, C-O-C stretching absorption band corresponding to linkage between -OH and -NCO groups to form urethane bond in the range 1057-1130 cm^{-1} also provides strong evidence for the formation of polyurethanes. The peaks corresponding to the absorption of NH, C=O and C-O were observed at 3314 cm^{-1}, 1707 cm[-1](non-hydrogen bonded), 1643 cm^{-1} (hydrogen bonded) and 1225 cm^{-1}, respectively. This indicates the new synthesized product having urethane (-NHCOO) group.
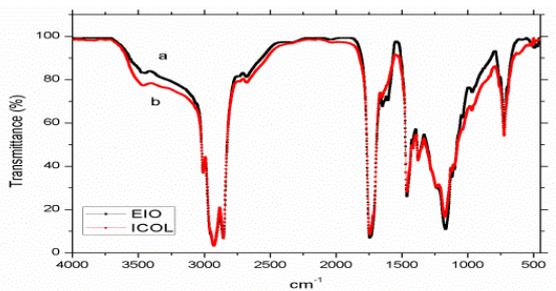
(a) & (b)
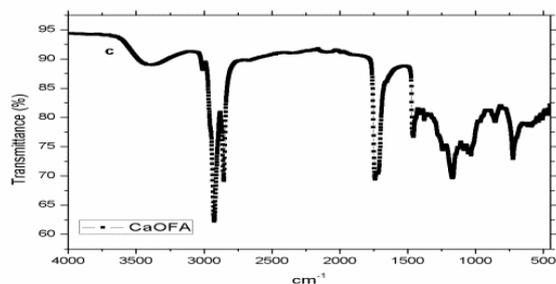
(c)
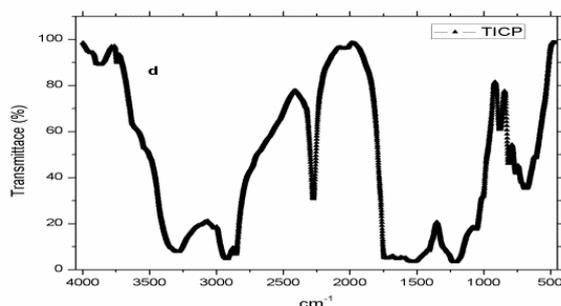
(d)

Figure 1. (a) epoxidised oil and (b) polyol, (c) CaOFA Fatty Acid, (d) TICP

B. Nuclear magnetic resonance spectrometry (^1H NMR & ^{13}C NMR)

The proton NMR of the polyols were prepared from epoxidised EIO oils, ring opened by CaOFA. In the ring opening reaction, the polyols were synthesized from epoxidised oils and were prepared by using the solvent/catalyst free method. Fig. 2(a) shows the 1H NMR spectra of CaOFA fatty acid, with the peak intensity increasing at δ = 5.3–5.4 ppm corresponding to carbon-carbon double bond in CaOFA, the terminal -CH3 and internal long chain protons of -CH2C- signal at δ = 0.89 ppm and δ = 1.63 ppm. [4-6].The peaks for –OH protons of recinoliec acid moieties of CaOFA appeared at 3.56 ppm.

The prepared ICOL are shown in fig.2 (b). The chemical shift value observed at δ = 2.21 ppm corresponds to the –CH2COO- proton. After the reduction reaction, the epoxy peak at δ = 2.22 – 2.65 ppm disappeared. The chemical shifts value of the methylene proton of recinoeic acid (carbon-carbon double bond) signal shifted to 3.73 ppm. The intensity of the proton of C=C present in ICOL were slightly brought down,

because of the oxirane ring opened by recinoliec acid of CaOFA, reached a peak at δ = 5.39 ppm. The recinoliec acid –OH group overlapped with newly formed –OH peak, the corresponding peak was at δ = 5.56 ppm. [6] On the other hand, the peak intensity at δ = 3.5 – 3.6 ppm decreased, indicating the complete reduction of triglyceride. This resulted in the formation of primary –OH groups backbone which appeared at δ = 5.56 ppm. Thus, it can be concluded that ICOL was successfully prepared and confirmed. [7-8].
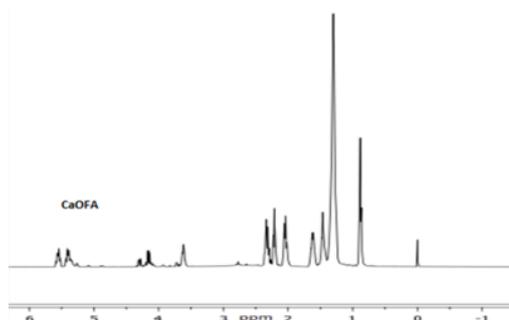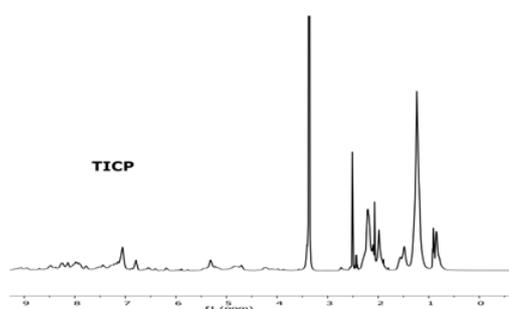

(a)
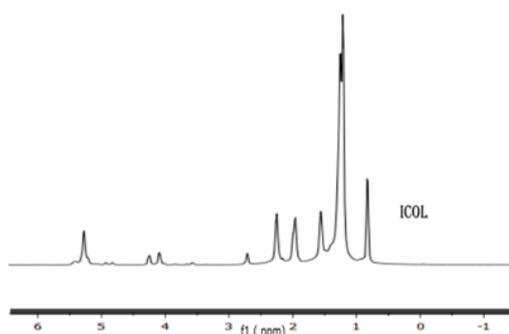
(b)
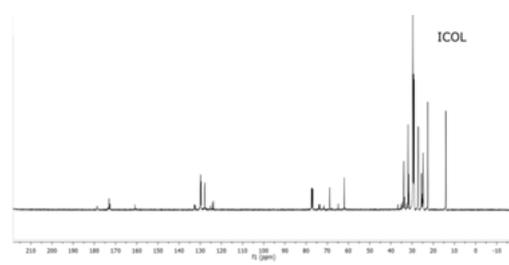
(c)

(d)

Figure 2. (a) ^1H specra of CaOFA fatty acid , (b) ^1H specra of ICOL , (c) ^{13}C specra of ICOL Polyol, (d) ^1H specra of TICP Pus

The ^{13}C NMR spectra of polyol ICOL were shown in fig. 2 (c). The chemical shifts value of –COOC- were observed at δ=172 ppm and δ=74 ppm. The corresponding methylene (carbon-carbon double bond) peak appeared at δ=131 ppm, and the terminal and long chain carbon of polyol gives signal at δ=14.0 ppm. After the ring opening of the oxirane ring, the signals obtained at δ=71 ppm, δ=34 ppm and δ=27 ppm correspond to C-C-C=C-C respectively. Finally, after the reduction reaction, recinoleic acid of CaOFA hydroxyl (-OH) group overlaps with newly formed –OH group, the obtained peak was at δ=74 ppm, and the corresponding –C-O-CO-CH$_2$- peak at δ=67 longer observed.[9,10]. Thus, it can be once again concluded & confirmed that ICOL were successfully prepared.

The polyols of ICOL react with diisocyanats namely TDI shown in the fig.2 (d). After the polycondensation reaction, the intensity of the polyol peak 5.31 ppm decreased, and the new signal of urethane (-NH) was shown at (TICP) 8.53 ppm and 8.24 ppm, and other peaks observed at 7.0-7.10 ppm, while the -CH$_3$ peak was individually observed at 3.80 ppm designated to the protons of CH$_2$OCO. This supports the synthesis of polyurethane the polyols (ICOL). The other peaks observed were assigned to C=C proton as 5.26 ppm respectively.

C. Gel permeation Chromatography

The GPC curve of polyol ICOL and CaOFA fatty acid were shown in the fig.3. The reaction of carboxyl to epoxy group ratio increases (C. Zhang et al.), the epoxy group were totally ring opened by CaOFA.[10-13] From GPC curve, comparison of CaOFA fatty acid with ICOL, the polyol retention peaks were shifted to longer retention time and became broadend, which indicates that the molecular weight of the polyol increased. On the other hand, the obtained second peak shifted to shorter retention time. Considering there is another one –OH group in CaOFA, which the number was almost identical with carboxyl. It is deduced that the –OH group in CaOFA, as well as newly formed –OH in epoxies, were also involved in the ring opening reaction and possibly connected with EIO molecules, causing the increasing molecular weight [14]. The molecular weight of polyol and polyurethane values are displayed in table 1. This can be explained as all the epoxidised vegetable oils have been fully ring opened by CaOFA fatty acid. The result of this is more connections of polyols and less olegomerization. This can be conclude the polyurethanes TICP were successfully prepared from ICOL.

TABLE I.   GELPERMEATION CHROMATOGRAPHY VALUE OF ICOL, CAOFA AND TICP

Sample Code	Viscosity (Pa s) at 25°C	Number average molecular weight (Mn)	Weight average molecular weight (Mw)	PDI
Polyols /ICOL	0.58	1085	1353	1.24
Fatty Acid/CaOFA	2.2	485	492	1.02
Polyurethane/TICP		1185	3020	1.74

PDI - polydispersity index

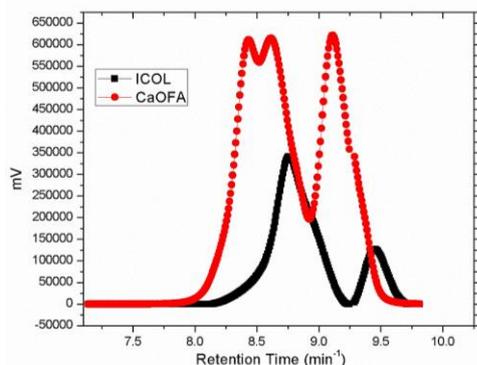Figure 3.   GPC curve of ICOL polyol and CaOFA fatty acid.

D. Rheometry analysis

The viscosity of prepared polyols were determined by using R/S portal rheometer at 25 ^{o}C for the shear rate varying from 1 to 100 s $^{-1}$. The polyols ICOL and CaOFA fatty acid plots (variation of shear stress against shear rate and viscosity against shear rate) shown in the Fig.4(a) and 4(b). However,

the fig 4(a) shows, linear dependence of shear rate on shear stress. The power law method had a flow behaviour index n<1, the obtained bio- polyols were 'n' value decreases and 'K' value increased shown in table.2. In other hand, Under a constant shear rate, viscosity will generally remain almost constant, Thus, the fig. 4(b) shows apparent viscosity of a pseudoplastic substance increases with the decreasing their shear rate, and increase in the molecular mobility of all polyol chains (due to epoxy group were ring opened by cross- linker CaOFA fatty acid), because of increases –OH group and C=C intrinsically present in recinoliec fatty acid moity. [15]The corresponding polwer law model indicates that the bio-polyols have higher molecular weight and they exhibits the Pseudoplastic non-Newtonian behaviour. [16-17]

TABLE II.   POWER LAW METHOD OF POLYOLS AND CAOFA FATTY ACID FLOW RATE.

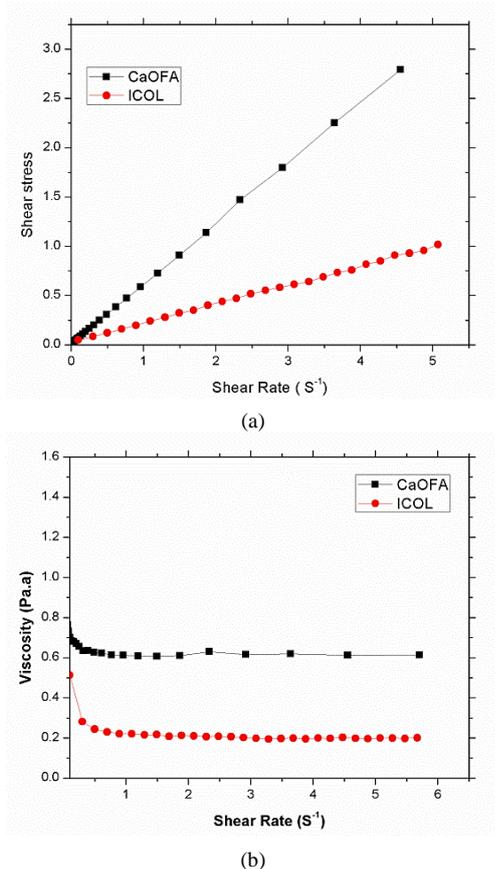| Sample code	K (pa s)	n(-1)	R^2
CaOFA	1.239	0.4855	0.6513
ICOL	1.011	0.2027	0.999

(a)

(b)

Figure 4.   (a). shear stress vs shear rate plots of polyol and CaOFA fatty acid, (b). Shear rate vs Viscosity plots of polyols and CaOFA fatty acid.

TABLE III.   THE ACTIVATION ENERGY (ΔE) FOR THE THERMAL DECOMPOSITION OF THE POLYURETHANES ARE GIVEN

polymer	Temperature(^{o}C)	Activation energy (KJ)			
		M&W	C&R	Doyels	F&C
TICP	245 297 323 382 445	1458	633	134	47
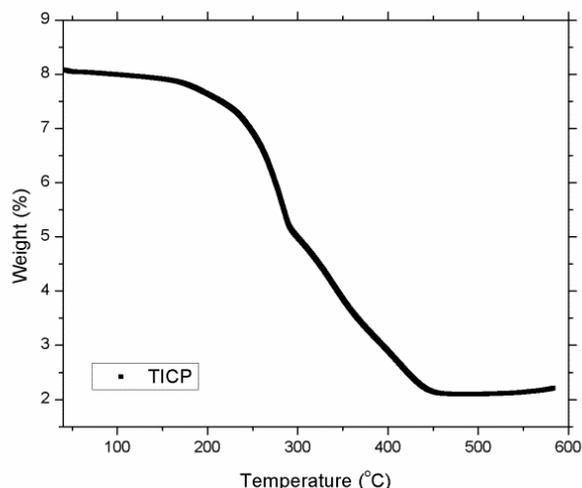
Figure 5.   TGA curve of TICP plot.

E. Thermogravimetry analysis

The thermal stability of TICP polyurethanes was evaluated by thermogravimetry analysis (TGA) by heating rate 10 ^{o}C min^{-1} under nitrogen atmosphere. The thermogravimetric analysis results are summarized in table 3. The TGA curve are illustrated in fig.5. respectively. In generally thermal stability of these PUs depends strongly on urethane groups per unit volume and an increase in the initial weight loss was observed as a result of the increase in the amount of urethane groups, on the other hand, it reveals that the increase of hard segment (NCO) in both the polymers.[18,19] This is due to the increase of the aliphatic moiety TDI and increase of intermolecular attractions between -NH and –CO through H- bonding, polar-polar interaction, etc., which makes the structure more compact. TGA curves of polyurethanes prepared from different polyols with different OH contents and TDI (TICP) are shown in Figure 3a. The corresponding TGA curves reveal two or three main degradation processes (Figure 3b). All polymers showed an initial weight loss. The first degradation of the PUs was started from 185 ^{o}C to 245 ^{o}C corresponding to 98% weight loss (average value.) that may be due to cleavage of urethane linkages, which dependence on the type of substituent present in the toluene diisocyanate and polyols (ICOL).

The second step degradation of the PUs was observed in the range of 250 ^{o}C to 297 ^{o}C corresponding to 88% weight loss. The thermal degradation exerted in the second step may be observed due to the breakdown of aliphatic alkyl group of fatty acid.[19] The third step thermal degradation reported in the temperature range 300 ^{o}C to 323 ^{o}C and weight loss in the range of 60 to 64 % and the major weight losses between 330°C and 445°C at 13% are due to complete decomposition of cross-linker (CaOFA) this is due to sluggish amongst both PUs formulations may be presence of -OH groups in recinoliec moiety of ICOL polyol. From the primary thermograms obtained for the polyurethanes, by plotting the percent weight loss against temperature activation energy can be calculated.The temperature at which major decomposition started was noted as the initial decomposition temperature. The order and energy of activation for the major decomposition reaction steps were calculated by Murray and white, Coats and Redferm, Doyle's The activation energies were calculated graphically from the equation after introducing the appropriate approximations assuming the correct order of the reactions which is determined from Freeman and Carrol 's method.[20]
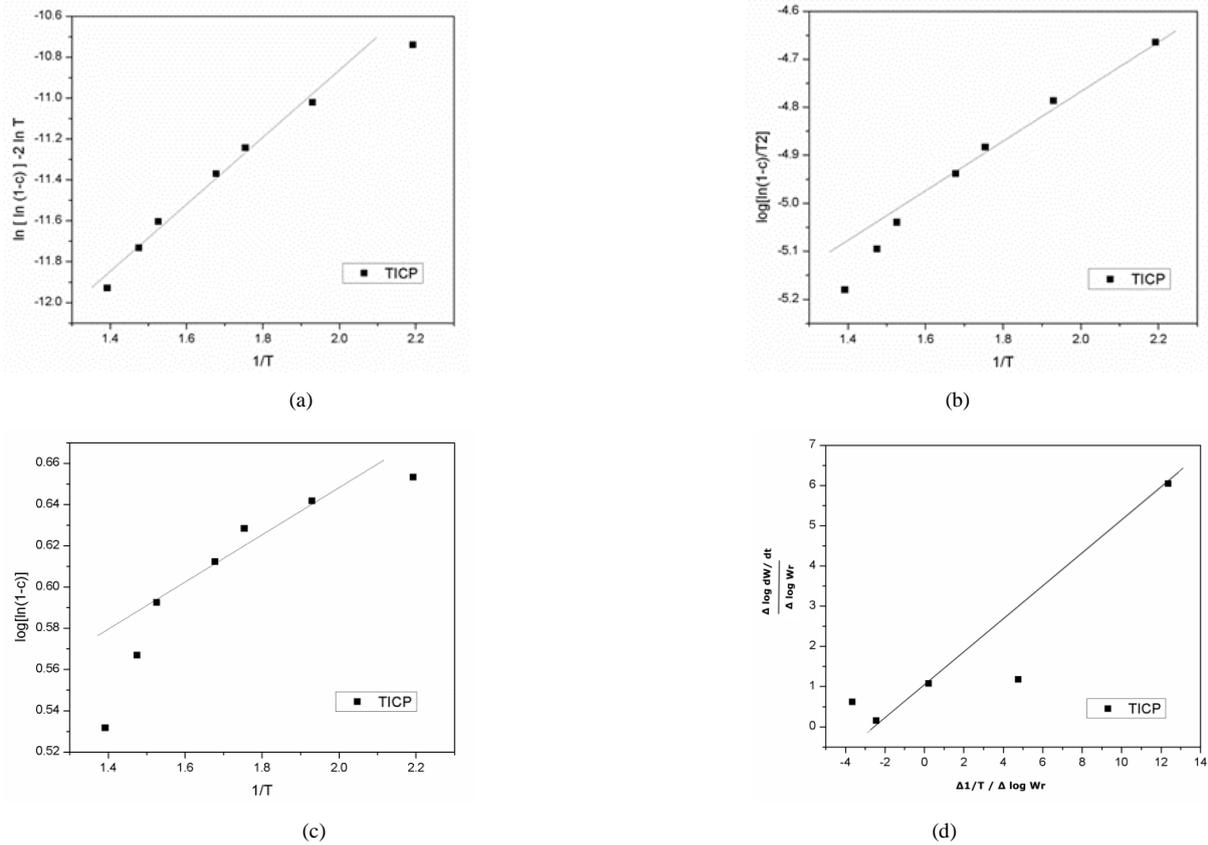
(a)

(b)

(c)

(d)

Figure 6.   (a). M&W curve of TICP plot, (b). C&R curve of TICP plot, (c). Doyels curve of TICP plot, (d). F & C curve of TICP plot

Activation energy can be calculated using the following approximation methods.

The Arrhenius equation can be given as,

$$\frac{dc}{dt} = Ae^{-E/Rt} \ (1 - C)^n \tag{1}$$

a. Murray and white:

$$\int_{T_0}^{T} e^{-E^*/RT} \ \simeq \left(\frac{RT^2}{E}\right) e^{-E^*/RT} \tag{2}$$

Plots, ln [ln (1-C)] -2lnT vs. 1/T for (n=1)

b. Coats and Redfern:

$$\int_{T_0}^{T} e^{\frac{-E^*}{RT}} \, dt \ \simeq (RT^2) \left[1 - 2\frac{RT}{E}\right] e^{\frac{-E^*}{RT}} \tag{3}$$

Plots, $\log \frac{[\ln(1-C)]}{T^2}$ vs. 1/T for (n=1)

c. Doyle:

$$\text{Log } R/E \int_{T_0}^{T} e^{-E^*/RT} \, dT \ \simeq -2.315 - 0.4567(E/RT) \tag{4}$$

For $20 \geq E/RT \geq 60$

Plots, log [ln (1-C)] vs. 1/T for n=1

The straight- line equation derived by Freeman and Carrol's, which is in the form of

$$\frac{\Delta \log dW/dt}{\Delta \log Wr} = n - \frac{E}{2.303 \ R} - \frac{\Delta 1/T}{\Delta \log Wr} \tag{5}$$

where:

dW/dt = rate of change of weight with time

W_r = Weight loss at completion of the reaction

W = Fraction of weight loss at time "t".

E = Energy of activation

n = order of reaction

From the slope we obtained energy of activation and intercept on y axis as order of the reaction (n = 0)

Freeman and carroll's method is plots of,

$$A = \frac{\Delta \log(dw/dt)}{\Delta \log Wr} \qquad \text{vs.} \qquad B = \frac{\Delta 1/T}{\Delta \log Wr}$$

For the purpose of this plot dW and dW_r can be determined directly from the thermogram in term of the no. of division. The activation energy calculation from TG curves of the polyurethanes.

They all presented a similar weight loss profile with the first step appearing at around 8% weight loss, since the TICP have the same amount of urethane groups. In Fig.5. are calculated from the slope of isothermal curves and distance between iso-conversional are given in Table.3. If the isothermals are fairly parallel, the activation energy does not appreciably change with temperature. However, Fig.5. Illustrates irregular spacing (nonparallel) between isothermals, demonstrating the complexity of the process. The average values of activation energy calculated by the Murray – White, Coats-Redfern, Doyels & Freeman-Carrol's method. All of the plots have a linear dependence, so their smaller the activation energy demonstrates that TICP can be decomposed from chain extender (TDI), while a high activation energy indicates that TICP is encapsulated in TDI.

The average values of activation energies at different iso-conversional points are calculated to be ±47 kJ.mol^{-1}, the estimated values are plotted and compared with those calculated using Freeman and carrol's method. From fig.6. (d) it is quite clear that activation energy passes through a minimum value at 50%. Fig. 6(a) shown, activation energy obtained through M&W method is varied within ±1458 kJ.mol^{-1} of the average value, while, the fluctuations in activation energy is much higher in those values obtained according to freman and carrol's procedure. This large difference between the activation energy reflected the complex nature of the degradation process, which can be observed by the decrease of the activation energy with increasing conversion.

Based on these results we suppose that the different kinetics degradation observed in our study is related to the different chemical structure of the mahua –polyol, i. e., the presence of cross-linker CaOFA and epoxy groups, we observe an excellent fit for the main part of the exotherm corresponding to more than 70% of the surface. It remains small discrepancies due to imperfect baseline definition. Table.3. indicates that the molar enthalpy (from F & C method) of urethane formation from secondary hydroxyl groups and aromatic isocyanates is 13.19 kJ mol^{-1}. The free energy of activation (ΔG) -2817 kJ mol^{-1}, which illustrates that the polymerisation process of TICP is a non-spontaneous one. The enthalphy (ΔH) of activation is -4857 kJ mol^{-1}, which is larger different to the activation energy calculated by the Freeman-Carrol's method. From those results, we can consider that, for TDI, polyurethanes have equal molar enthalpy of reaction at lower than 298 K. The reaction rates are sufficiently slow to allow efficient mixing during a few minutes without significant extent of reaction.

and tolune diisocyanate. The –OH functionality of the polyols and CaOFA functionalities were confirmed by FT-IR spectrometer. The varying environments of the hydroxyl group (-OH) in fatty acid chain and after the reduction reaction, ICOL of polyols C=C proton intensity slightly reduced, when the oxirane ring was opened by CaOFA - that this leads to each polyol structure was again confirmed by ^{1}H and ^{13}C NMR spectrum. After the poly-condensation reaction, the intensity of polyol peak decreased, and the new signal of urethane (NH) was identified and their structures were confirmed by ^{1}H spectrum. Furthermore, the carboxyl to epoxy groups increasing their cross-linking density of polyol moiety and molar ratio of NCO/OH group, that the results reveals to polyurethane successfully synthesixed by polyols.

From the GPC, the shorter and longer retention time of ICOL chromatogram peaks reveals that their molecular weight has increased. The rheometry analysis shows the cross- linker CaOFA fatty acid reacts with epoxy group, number of -OH group increased in ICOL polyols, due to CaOFA of the viscosity decreases with an increase in decreasing shear rate. The segmental ratios have a significant effect on the thermal properties of both polyurethanes. This is due to the increase of the aromatic moiety TDI and increase of intermolecular attractions between -NH and –CO through H- bonding, polar-polar interaction and etc., which makes the structure more compact. The activation energy of mainly tends to increases with increasing heat rate. The average value of activation energy obtained from M&W, C&R, Doyel's and F&C method was 1458 kJ mol^{-1}, 633 kJ mol^{-1}, 134 kJ mol^{-1} and 47 kJ mol^{-1} respectively. Which was larger different to the enthalpy of activation (-4857 kJ mol^{-1}). The entropy of activation was 13.19 kJ mol^{-1} K^{-1} and the free energy of activation was -2817 kJ mol^{-1}. The study of the polymerisation of TICP provides a novel method to study the interaction mechanism between TDI and polyol (ICOL) thermo-responsive encapsulated material. Which can be confirmed by Freeman and Carrol's method.

TABLE IV.   THE KINETIC PARAMETERS FROM FREEMAN AND CAROLL'S METHOD

Polymer	ΔS (Kcalmol^{-1})	ΔH (Kcalmol^{-1})	ΔG(Kcalmol^{-1})
TICP	13.19	-4857	-2817

IV.   IV. CONCLUSION

Thermo-responsive TICP polyurethane successfully prepared from Madhuca longifolia (Mahua oil) based polyol

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