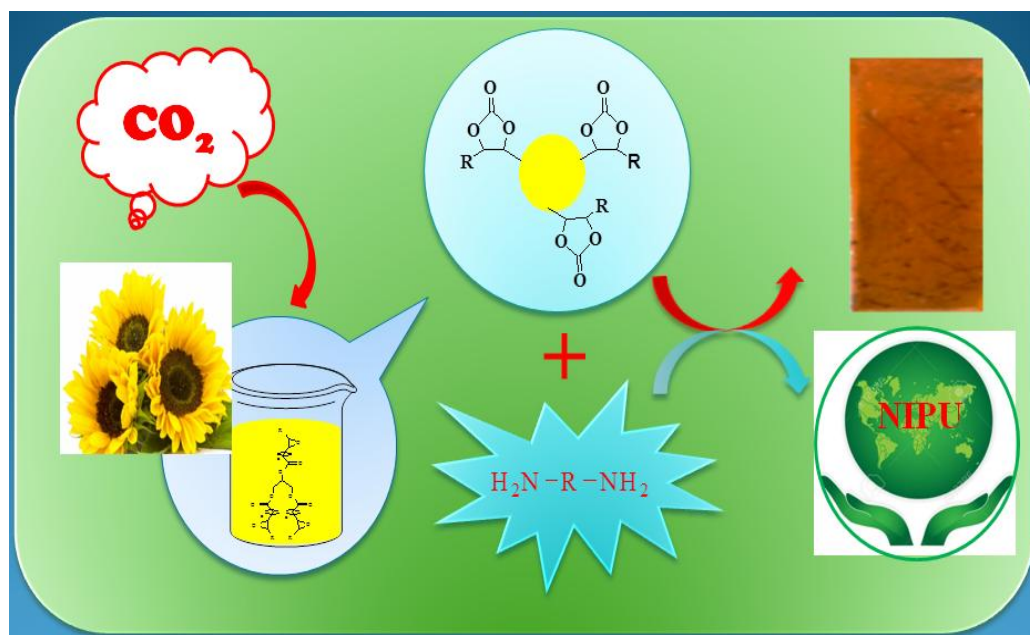# Chapter 2

Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties

Bio-based non-isocyanate polyurethanes are synthesized from carbonated sunflower and found to be suitable for coating applications

2.1 Introduction

Currently the sixth most extensively used polymer, with an annual worldwide production of around 16 million tons, polyurethanes (PUs) possess a significant group of polymer materials [1]. PUs have wide applications in versatile fields like adhesives, tissue engineering, surface coatings, elastomers, electro-mechanical devices like actuators, transducers and sensors, and biomedical equipments such as heart valves, contact lenses, blood bags, renal dialyzers and blood oxygenators [2–6]. Generally, PUs are obtained by the polyaddition reaction between a diol and a diisocyanate which are petroleum dependent [7]. From environmental and economic viewpoints, the development of greener chemical routes to substitute the petro-based precursors is becoming a very essential topic of research in recent years. Following this vision, synthesis of polymers from renewable resources like vegetable oils has attracted tremendous attention in the recent years because of their low cost, worldwide availability, environment-friendly nature and also due to diminution of petroleum resources [8–10].

Literature survey reveals that in the synthesis PUs, various vegetable oils *viz* castor, linseed, canola and jatropha oil based polyols are extensively used as a precursor. These vegetable oil-based PUs with versatile and comparative thermo-mechanical properties are considered as good substitutes to petroleum-based products [11–14]. Generally, all the vegetable oils have C=C double bonds and esters, necessary for obtaining numerous bio-based polyols which are functionalizable through various synthetic routes like ozonolysis [15], hydroformylation [16,17], epoxidation followed by oxirane ring opening [18,19], trans-esterification [20,21], and more recently investigated olefin metathesis [22,23] and thiol-ene reactions [24]. However, even though there has

This part of the thesis is published in

Doley, S. and Dolui, S. K. Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties. *European Polymer Journal*, 102:161-168, 2018.

been a huge emergence of several promising vegetable based polyols, the use of isocyanates remains a main problem to overcome. Isocyanates are highly toxic and volatile materials made from toxic phosgenation of diamine and long term exposure can cause several harmful health effects. According to annexure XVII of the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), some isocyanates are recognized as carcinogens, mutagens or toxic, and methylenediphenyl diisocyanate (MDI) should be no more than 0.10 wt % in a constituent of mixtures [25]. Therefore, in order to fulfill the green chemistry rule and as a response to concerns about health and safety, an alternative innovative synthetic route needs to be developed for the substitution of isocyanates in the synthesis of PUs from renewable resources.

Recently, Jayakannan and Deepa have synthesized isocyanate- and phosgene-free aliphatic PU *via* transurethane polycondensation by using different amines and alcohols [26]. Other most studied approaches are AB type self condensation [27] and aminolysis of cyclic carbonates [28–33]. Among these routes, the step-growth polyaddition of diamines with dicyclocarbonates leading to non-isocyanate polyurethanes (NIPUs) is the most attractive one from the environmental and economic view-point. This cyclic carbonate is obtained by the slow coupling of CO_2 with epoxides which is a known source of global warming. CO_2 is used as a feedstock to make materials with a low carbon footprint [34–37]. The cyclic carbonates are non-toxic, biodegradable and can be used as solvents with high boiling and flash points. PUs prepared by this route contain additional hydroxyl groups that forms hydrogen bonds with the urethane carbonyl group resulting in superior resistance to organic solvents, higher stiffness and higher water uptake [29,32,38,39].

Although cyclic carbonates are commonly synthesized from petro-based molecules like poly(propylene glycol), polyethylene glycol and bisphenol A diglycidyl ether, lately carbonated vegetable oils (triglycerides) [40,41] are being progressively used as raw materials for NIPUs [29–34]. For the first time, Tamami and coworkers synthesized soybean oil based cyclic carbonates (CSBO) by using 5 mol% of tetra-n-butylammonium bromide (TBABr) with respect to epoxy as a catalyst under atmospheric pressure at 110 °C in 70 h of reaction time [40]. The authors also showed that CSBO simply reacted with various amines to get the respective NIPUs at 60 °C. Bähr and Mulhaupt demonstrated that TBABr with silica-supported 4-pyrrolidinopyridinium

iodide (3.5 g per 100 g/epoxidized soybean oil (ESBO)/ linseed oil (ELO)) improves the carbonation kinetics at CO_2 pressures of 10 bar and 30 bar, and temperature of 140 °C for 40 h [41]. They found that carbonation formation was influenced by pressure and the catalyst type.

In this study, we used sunflower oil as a raw material for the synthesis of NIPUs. We first examined the effect of time during the carbonation process by using TBABr (3.5 g per 100 g epoxy) at 120 °C and 50 bar CO_2 pressure. Consequently, we also investigated the influence of the amine/cyclic carbonate molar ratio and curing agent on the thermal, mechanical and chemical properties of the prepared NIPUs.

2.2 Experimental

2.2.1 Materials

Sunflower oil was obtained from local market (molar mass = 876 g mol^{-1}). CO_2 (Assam air products, Guwahati, 99.99% pure) was used as received. Hydrogen peroxide (H_2O_2) (50%) and formic acid (HCOOH) (85%) were obtained from Merck. Sigma Aldrich supplied TBABr, ethylene diamine (EDA), diethyltriamine (DETA) and isophorone diamine (IPDA).

2.2.2 Preparation of epoxidized sunflower oil (ESFO)

The epoxidation of sunflower oil was performed in the presence of a mixture of HCOOH and H_2O_2, which was added drop-wise through fitting arrangements in a 250 ml three necked round bottom (RB) flask. The reaction mixture was continuously stirred with a mechanical stirrer at 60 °C. The molar ratio of C=C bond of the oil: HCOOH: H_2O_2 was taken as 1:0.5:1.7. The obtained mixture was cooled down and washed repeatedly with distilled water and $NaHCO_3$ solution until pH became neutral. The oil part was separated and dried over anhydrous Na_2SO_4. The yield was around 90-93% with epoxy value 0.40 mol/100 g. The epoxy equivalent value of the prepared epoxidized oil was calculated by standard test method.

2.2.2 Preparation of carbonated sunflower oil (CSFO)

CSFO was synthesized by reacting CO_2 with ESFO under 50 bar CO_2 at 120 °C for 12 h in a reactor by using the TBABr catalyst (3.5 mol% with respect to ESFO).

After completion of the reaction, CO_2 pressure was discharged and the resulting cyclic carbonate oil was collected. The conversion obtained was 86%. The conversion of ESFO into CSFO was determined by integration of peaks related to the epoxy protons in ^1H NMR spectra of ESFO in the **Fig. 2.3**. The carbonate equivalent weight (CEW) was found to be 380 g/eq. The CEW was calculated from the % of conversion epoxy group into cyclic carbonates.

2.2.3 Preparation of NIPUs

NIPUs were synthesized in a 100 ml one necked round bottom (RB) flask by reacting CSFO (5 gm) with EDA at molar ratios of 1:0.75, 1:1 and 1:2 at 80 °C for 2-4 h without using any catalyst or solvent. The viscous product was poured into a Teflon sheet and kept at 90 ^0C for 2 days and then at 140 °C for 1 h to achieve fully cured coatings. Similar method was followed to synthesize DETA and IPDA based NIPUs at different molar ratio.

2.2.4 Characterizations

2.2.4.1 Fourier transform infrared (FT-IR) spectroscopy analysis

FT-IR is a well-known technique for determination of the functional groups contain in material. The analysis of FT-IR spectra in the lower frequency finger print region can give information about the degree of polymerization and the substituent's effect on the electronic behavior of the polymer chain.

A Nicolet Impact 410 FT-IR spectrometer was used to record the FT-IR spectra of the specimens equipped with a KBr plate. The spectra were reported in wavenumber (cm^{-1}) as a function of transmittance intensity in percentage.

2.2.4.2 Nuclear magnetic resonance (^1H and ^{13}C NMR) spectrometer

NMR is one of the main spectroscopy techniques which is used to extract electronic, chemical and structural information about the molecules. This system differentiates different atoms within a molecules or collection of molecules of the same type. ^1H and ^{13}C NMR spectra were acquired by a Jeol FT-NMR spectrometer (400 MHz). As an internal standard tetramethylsilane (TMS) is used and deuterated chloroform ($CDCl_3$) servers as the solvent. The chemical shift values were given in parts per million (ppm).

2.2.4.3 Scanning electron microscopy (SEM)

SEM is an electron microscope that acquires high-resolution imaging of sample surfaces. The SEM uses a high energy beam of electrons that interacts with the atoms of the samples generating a signal that gives the samples surface topography, composition, phase domain size and number of phases, etc. The morphology of the prepared film was observed by a JSM-6390LV, JEOL, Japan modeled SEM instrument. A surface coating of platinum was applied for analysis.

2.2.4.4 Gloss

Gloss is an optical property characterized by the angular distribution of light scattered from a surface which suggests how surface of a sample reflects light in a mirror like direction. The light reflected back by the specimen is measured by passing light through the samples at a specified angle.

The gloss of the prepared polymer films were evaluated by mini gloss meter (S.C. Dey & Co., Kolkata) by placing the gloss meter over the polymer films casted on glass slides at an incident angle of 60º.

2.2.4.5 Tensile strength and elongation at break

Tensile strength is the maximum stress of a material that can withstand while stretched before failure and elongation at break is the deformation of a body under applied stress. Tensile property of the NIPUs film was examined using a universal testing machine (UTM, Zwick, Z010) with 40 mm gauge length and 10 kN load cell. The expansion rate was 5 mm min^{-1}. For each NIPU, three samples were prepared and tested to obtain an average value. The samples dimensions were 60 mm in length, 0.4 mm in thickness and 10 mm in width.

2.2.4.6 Scratch hardness

The scratch hardness test was conducted to understand the scratch resistance of the polymer. The scratch hardness tester (Sheen instrument Ltd., UK) was used to conduct the scratch hardness test on the specimens.

2.2.4.7 Thermogravimetric analysis (TGA)

TGA is most helpful method to calculate the weight loss of a sample associated

with a transition under inert or air atmosphere. It record % of weight loss as a function of temperature graphically in x-y chart and the graph obtained is called a thermogram.

To examine the thermal stability of the films, TGA was conducted on a Shimazdu TGA 50 thermal analyzer with 10 °C min^{-1} heating rate between 25-600 °C in a nitrogen atmosphere.

2.2.4.8 Chemical resistance

To examine the influence of the chemical environment on the specimens, their resistance of towards water, HCl (10%, aq), and NaOH (2%, aq) was carried out. A tiny piece of the cured films was put in each of the above mentioned solution at room temperature. After 21 days, the films were taken out of the solution and dried till a stable mass was attained. The following notations were used to describe their state: Excellent = no weight loss; Good = loss of gloss or partially loss; Fair = blistering or mostly loss; Poor = film removed.

2.2.4.9 Anticorrosive property

The anticorrosive behavior of the prepared films were determined on SP-150 Biologic electrochemical workstation at constant temperature of 25 °C by using three electrode cells namely a platinum electrode, a calomel electrode, and a coated panel as the counter, reference, and working electrode respectively. The measurements were performed in 3.5% NaCl solution at room temperature. The surface area of the coated panels was 1 cm^2.

2.2.4.10 Epoxy value

Epoxy equivalent weight (EEW) of a polymer is defined as the number of moles of epoxy groups per g of the polymer. This value is measured by refluxing the resin with 10 ml, 2 N HCl in 20 ml of ethanol for duration of 90 min. Then, the resulting mixture was titrated with 0.5 N NaOH. The amount of NaOH required for neutralization (T ml) and for blank treatment without the samples was evaluated (B ml). The following equation was used to calculate the epoxy equivalent weight.

$$EEW = \frac{\text{Weight of the sample (gm)} * 1000}{(\text{Blank} - \text{Sample}) * \text{Normality}}$$

2.3 Results and discussion

2.3.1 Spectroscopic (FT-IR and NMR) studies

2.3.1.1 Conversion of ESFO to CSFO

The reaction of ESFO with CO_2 was conducted in a high-pressure reactor (**Fig. 2.1**) at 120 °C and 50 bar by using TBABr as organo-catalyst for 12 h (**Scheme 2.1**). The halide ion (Br^-) opens up the epoxy groups, generate an alkoxide ion which attacks the CO_2 to give cyclic carbonate ring (**Scheme 2.2**). The successful conversion of epoxide (ESFO) into cyclic carbonate (CSFO) group is established by spectroscopies analyses. The band at 1746 cm^{-1} is due to the ester group of the oil (**Fig. 2.2a**). The formation of cyclic carbonate oil is confirmed by the disappearance of the peak at 830 cm^{-1} corresponding to the epoxy group in **Fig. 2.2a** and the simultaneous emergence of a new band at 1803 cm^{-1} in **Fig. 2.2b** due to C=O carbonyl stretching of the cyclic carbonate.
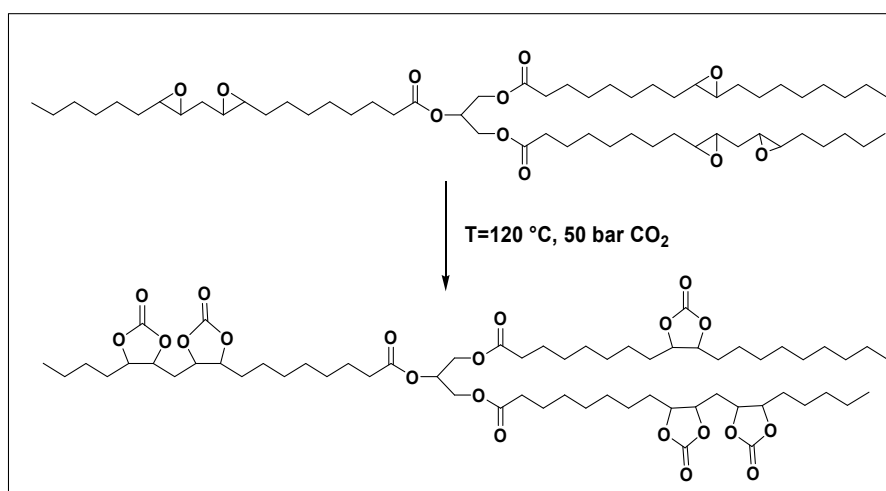
Scheme 2.1: Reaction of oxirane with CO_2 to form five-membered cyclic carbonate.
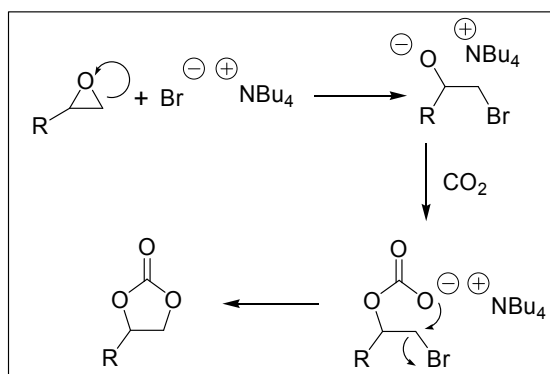
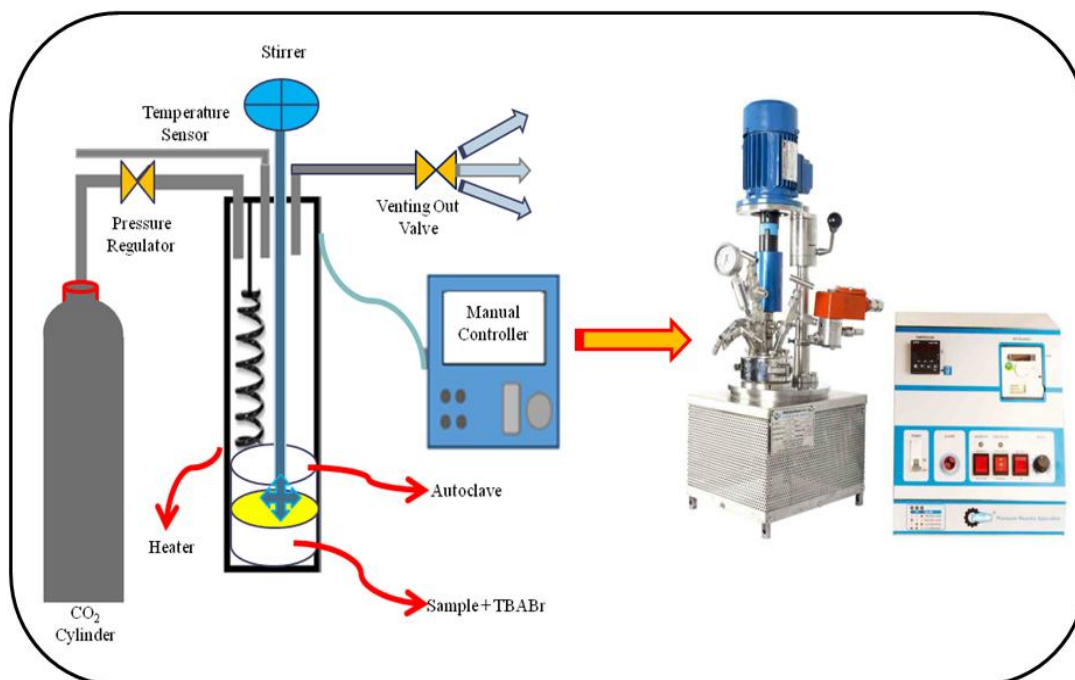**Scheme 2.2:** Plausible mechanism of formation of cyclic carbonate by TBABr as the catalyst.

Fig. 2.1: Schematic representation of high-pressure autoclave reactor used to conduct the carbonation reaction.
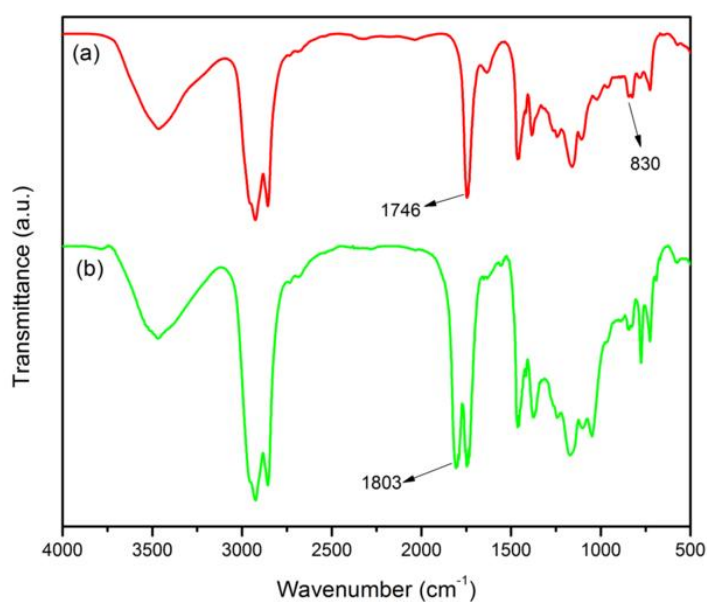

Fig. 2.2: FT-IR spectra of (a) ESFO and (b) CSFO.

Again, the formation of CSFO is established by ^{1}H NMR studies. The disappearance of peaks at 2.80-3.20 ppm is attributed to the C-H in the α-position of epoxy group (**Fig. 2.3**, time = 0 h) and appearance of a new peak at 4.6 ppm (**Fig. 2.3**, time = 12 h) is ascribed to the C-H in the α-position of cyclic carbonate group. **Fig. 2.3**

also displays the kinetics of epoxy conversions at 120 °C and 50 bar CO_2 for 12 h. It is seen that as the reaction time increases, the intensity of peak due to ESFO decreases. By taking the group (one proton, -CH of the triglyceride group) at 5.16 ppm as reference, the integration are normalized and the % of conversion is calculated. After 12 h, 86% conversion of epoxy groups into cyclic carbonate was obtained as shown in **Fig. 2.4**.
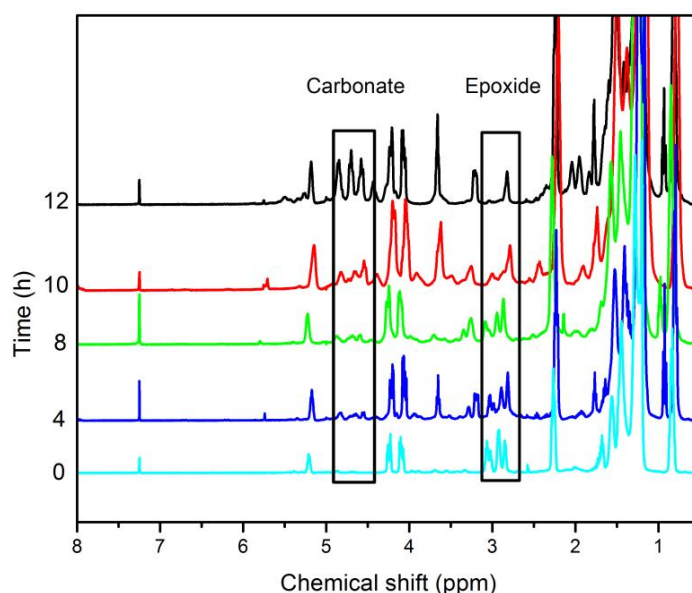

Fig. 2.3: ^{1}H NMR spectra for the kinetics of ESFO conversion at 120 °C and 50 bar CO_2.
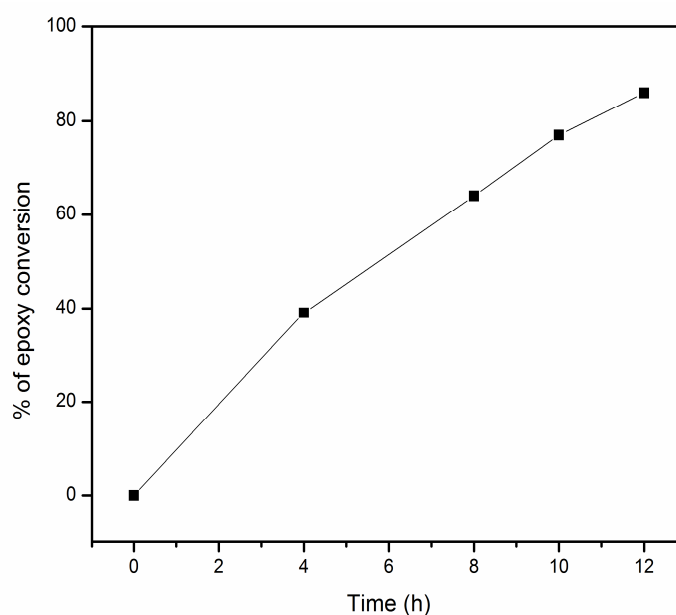

F**ig. 2.4:** Kinetics of carbonation of ESFO at 120 °C and 50 bar CO_2 pressure.

Furthermore, ^{13}C NMR spectra also confirm the formation of epoxy and cyclic carbonate groups. The peaks of epoxy groups are found at 54.4 and 57.1 ppm (**Fig. 2.5a**), and the peaks for carbonates are located at 79.5, 82.1, and 153.9 ppm (**Fig. 2.5b**).
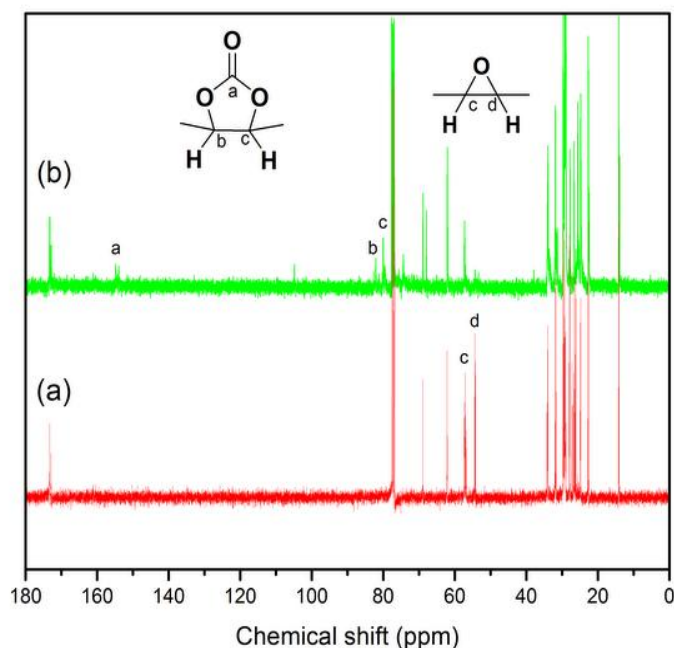

Fig. 2.5: ^{13}C NMR spectra of (a) ESFO and (b) CSFO.

2.3.1.2 Formation of NIPU

A series of NIPUs were prepared by reacting CSFO with various diamines such as EDA, DETA and IPDA at different CSFO/amine molar ratios. The formation of NIPU is confirmed by ^{1}H NMR and FT-IR studies. The ^{1}H NMR spectrum of the NIPU obtained from the reaction between CSFO and EDA at molar ratio 1:1 is shown in **Fig. 2.6**. New peaks at 3.5-3.6, 3.20 and 2.80 ppm reveal the formation of primary and secondary (h and i) hydroxyl group (produced along with urethane group), and urethane linkage (j and k) respectively. The peak at 2.1 is due to the amide groups (a) resulting from the aminolysis of ester groups of the oil (**Scheme 2.3a**).

By using FT-IR studies, we confirmed the formation of NIPU and examined the effect of various CSFO/amine molar ratios and molecular structure of curing agents (EDA, DETA and IPDA). Overall, in all the FT-IR spectra of NIPUs (**Fig. 2.7-2.9**), the peak appearing at 3300-3440 cm^{-1} is due to N-H and O-H stretching from hydroxyl and urethane groups. The intense peak around 1746 cm^{-1} is due to C=O stretching vibration

and the band at 1803 cm^{-1} is corresponding to the unreacted cyclic carbonate carbonyl. The peaks at 1710, 1654, 1540, 1250 and 1100 cm^{-1} are attributed to urethane groups, amide group resulting from the aminolysis of the triglyceride of the oil, N-H deformation of urethane group, C-N or C-O (in ester groups) and C-O-C stretching vibration respectively.
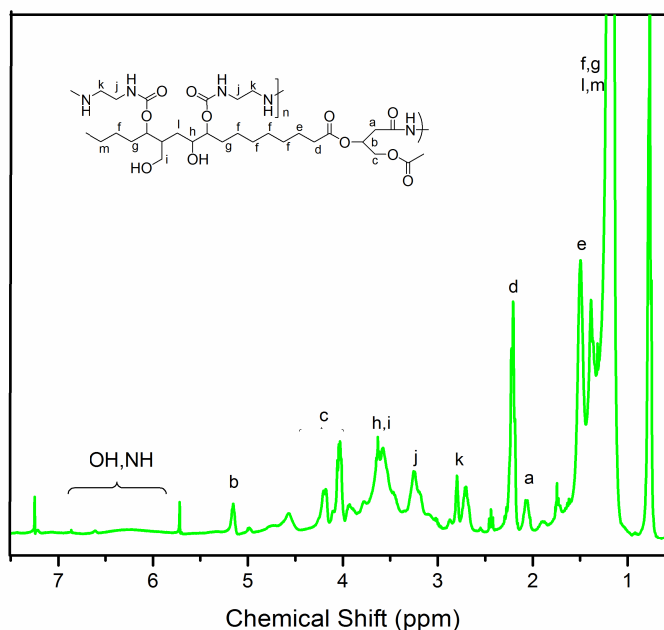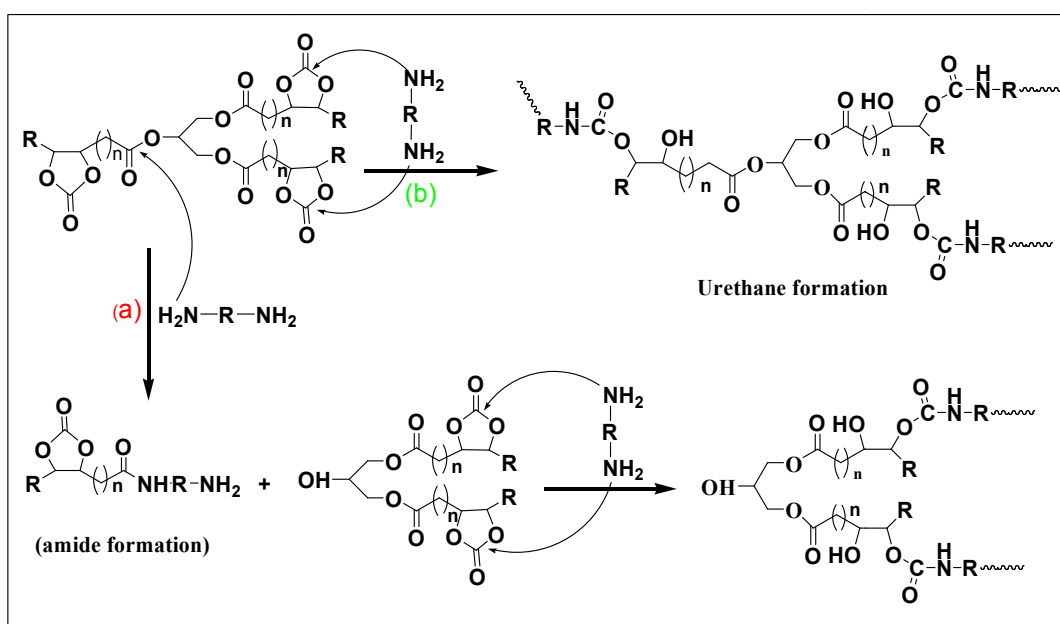

Fig. 2.6: ^{1}H NMR spectrum of EDA based NIPU at 1:1 at 80 °C.

Scheme 2.3: Reaction of five-membered cyclic carbonate with amine to form (a) amide and (b) urethane.

More specifically, **Fig. 2.7** displays the FT-IR spectra of CSFO/EDA based NIPUs, prepared at various carbonate/amine molar ratios. Similar spectra were observed for DETA based NIPUs (**Fig. 2.8**). In the NIPU at 1:0.75 ratios, the presence of a shoulder peak on ester carbonyl at 1700 cm^{-1} indicates the formation of urethane along with a considerable amount of remaining cyclic carbonate. The band of amide at about 1643 cm^{-1} is hardly visible, demonstrating that aminolysis of the ester groups is not visible.
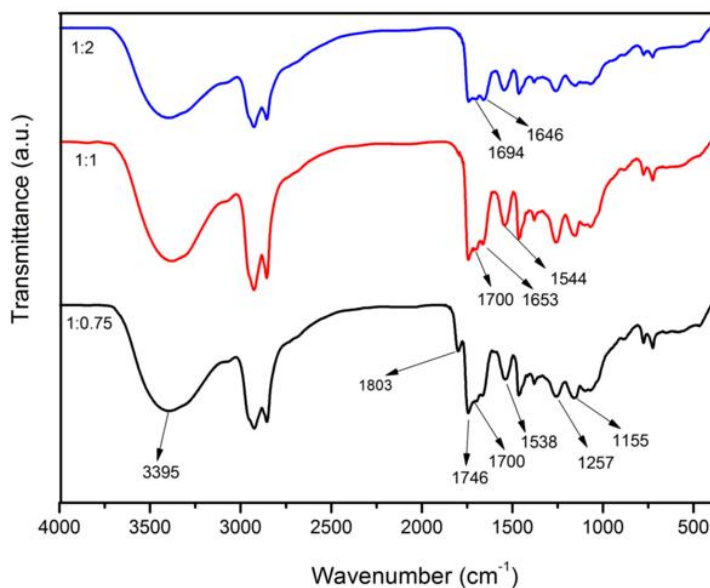

Fig. 2.7: FT-IR spectra of EDA based NIPUs at different carbonate to amine ratios.
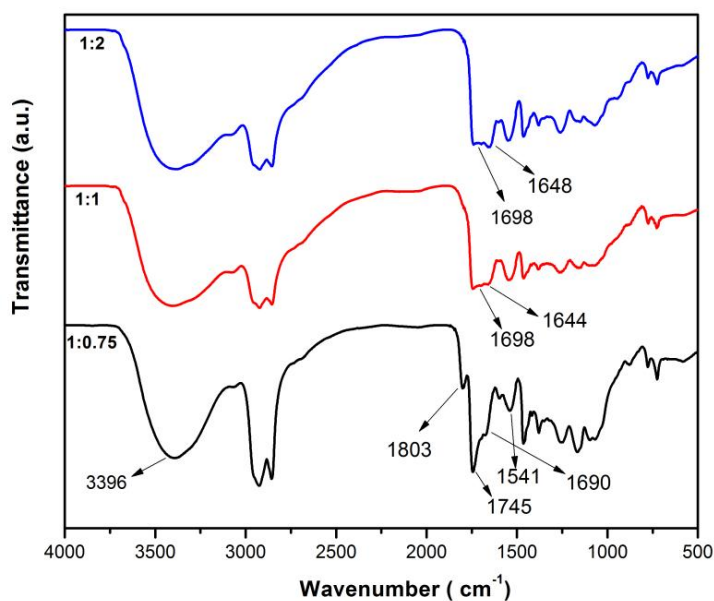

Fig. 2.8: FT-IR spectra of DETA-based NIPUs at different carbonate to amine ratios.

NIPU synthesized at 1:1 carbonate/amine ratio shows a strong shoulder peak of urethane and a very clear amide absorption band due to aminolysis of ester group **(Scheme 2.3a)**. At ratio 1:2, the amide absorption peak becomes as strong as the urethane peak. The band for ester group of the oil appears as a little shoulder on the urethane peak in comparison to carbonate/amine ratios at 1:0.75 and 1:1, suggesting that reaction of amine group with ester leading to the formation of amide group.
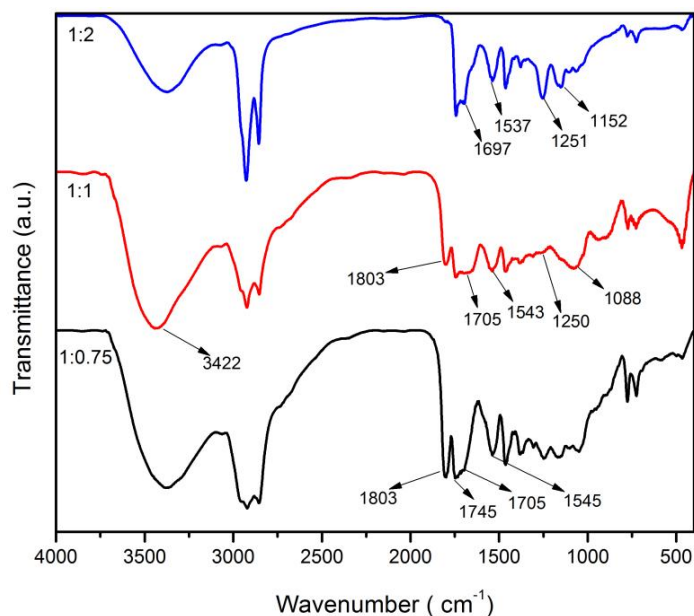

Fig. 2.9: FT-IR spectra of IPDA-based NIPUs at different carbonate to amine ratios.

However, in case of IPDA, which has two different reactivities of amine groups react slowly (The amine group at the primary C-atom is high reactive than the amine group bonding to the secondary C-atom). The conversion of cyclic carbonate into urethane groups was less than EDA and DETA and no aminolysis of ester groups was observed **(Fig. 2.9)**. This result is similar to the result previously reported by Boyer et al. [42].

2.3.2 Surface morphology (SEM) analysis

Fig. 2.10 shows the SEM micrograph of surface for cured pristine NIPU. Polar functional groups (e.g. hydroxyl and urethane etc.) present in the polymer matrix enable miscibility of the constituent *via* the strong electrostatic and hydrogen bonding interactions. In the micron scale, a homogeneous surface of the NIPU is found from the SEM analysis.
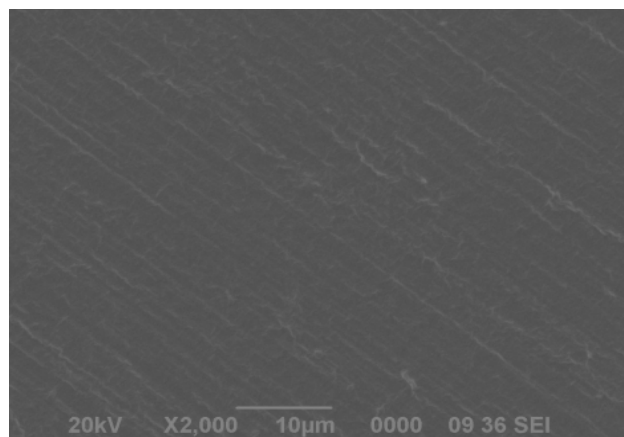
Fig. 2.10: SEM micrograph of EDA-based NIPU at 1:1 molar ratio.

2.3.3 Mechanical properties

The mechanical properties of the cured films are given in **Table 2.1**. Cyclic carbonate was cured with various diamines at different carbonate/amine molar ratios to examine the influence of the amine functionality and its molecular structure on the mechanical properties of the NIPUs.

Table 2.1: Mechanical properties of NIPUs.

Sample	Tensile strength (MPa)	Elongation at break (%)	Scratch hardness (kg)
EDA-1:0.75	0.90 ± 0.50	145 ± 5	0.6 ± 0.2
EDA-1:1	4.10 ± 0.2	180 ± 4	3.4 ± 0.5
EDA-1:2	1.25 ± 0.4	187 ± 8	1.5 ± 0.2
DETA-1:0.75	0.85 ± 0.6	100 ± 4	1 ± 0.3
DETA-1:1	3.27 ± 0.4	228 ± 4	3 ± 0.2
DETA-1:2	1.00 ± 0.2	240 ± 7	1 ± 0.4
IPDA-1:0.75	1.30 ± 0.3	178 ± 3	1.7 ± 0.6
IPDA-1:1	5.20 ± 0.4	204 ± 5	4 ± 0.5
IPDA-1:2	n/a (too brittle)	n/a	3 ± 0.6

Mechanical properties of NIPUs are highly dependent on the structure of the curing agent, the cross-linking density and the hydrogen bonding between various functional groups like urethane, ester and hydroxyl groups present on the polymer network. The NIPUs at carbonate to amine ratio of 1:0.75 display low hardness and tensile strength, and high elongation for all samples due to incomplete cross-linking, less hydrogen bridging and residual cyclic carbonates, which act as plasticizers. The coatings prepared at carbonate to amine ratio 1:1 show less residual carbonate and high formation of urethanes group, resulting in higher cross-linking density, which is reflected in the highest hardness and tensile strength amongst all the ratios **(Scheme 2.3b)**. At carbonate to amine ratio of 1: 2, the excess amine reacts with ester groups present in the oil to form amides and produces a network with lower cross-linking density **(Scheme 2.3a)**. This results in lowering of hardness and tensile strength and the highest elongation at break. The NIPUs based on IPDA has higher strength than the aliphatic diamine owing to the availability of rigid cyclo-aliphatic moiety which imparts rigidity to the cured polymer network. The long chain DETA curing agent results in soft material with lesser hardness in contrast to the IPDA and short diamine EDA based systems.

2.3.4 Thermal properties

The thermal stability of the NIPUs film cured with EDA, DETA and IPDA at different carbonate/amine ratios was measured with TGA as shown in **Fig. 2.11**. **Table 2.2** shows the temperatures corresponding to weight loss at various levels. A slight decrease in mass between 0-150 °C is observed in all the samples owing to the vaporization of linked and residual water molecules.

From the table, it is seen that regarding the effect of the carbonate/amine ratios of the EDA based NIPUs, the NIPU prepared at 1:1 mol ratio displayed high thermal stability with respect to the other mol ratio. Regarding the effect of molecular structure of the curing agent, the NIPU based on IPDA 1:1 (5% wt loss at T = 280 °C) has greater thermal stability than EDA (5% wt loss at T = 271 °C) and DETA 1:1 (5% wt loss at T = 267 °C) based NIPU. The difference in the thermal stability of samples prepared based on EDA and DETA is not large.

Table 2.2: Thermal stability of NIPUs.

Sample	Temp @ 5% wt loss (°C)	Temp @ 25% wt loss (°C)	Temp @ 50% wt loss (°C)
EDA 1:0.75	262	323	363
EDA 1:1	271	346	390
EDA 1:2	266	328	387
DETA 1:1	267	331	372
IPDA 1:1	280	361	401

The cyclic diamine (IPDA) cured NIPUs shows higher thermal stability due to its rigid structure as compared to long chain carbon linkages present in the aliphatic diamines (EDA and DETA). In the case of aliphatic diamines, they possess more flexible polymeric network and therefore, rapid degradation of the chemical bonds occurs.
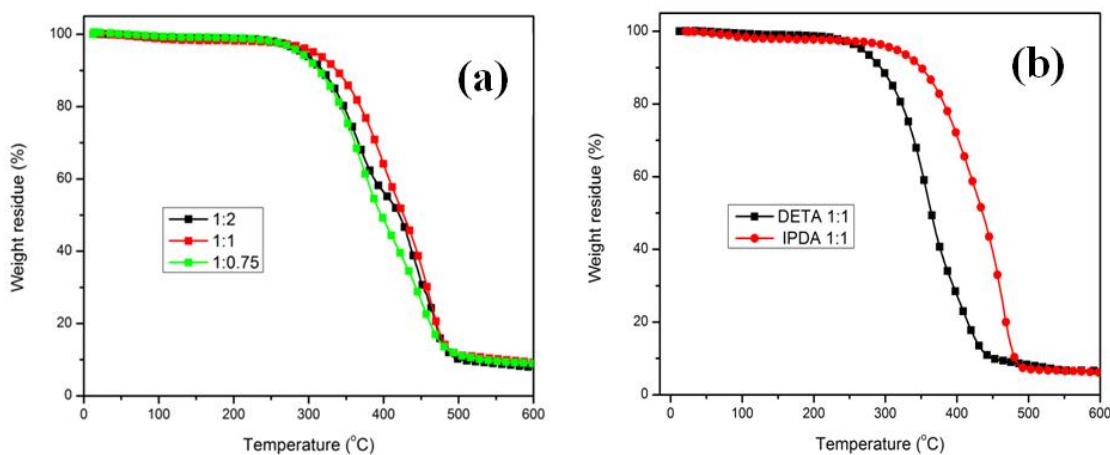

Fig. 2.11: TGA thermograms of (a) EDA at different carbonate/amine ratios (b) DETA 1:1 and IPDA 1:1 based NIPU.

2.3.5 Optical properties

The gloss of the cured NIPUs film was determined by using 60° glossometer. The values are found in the range of 82-101, 77-96 and 78-90 for NIPUs cured with IPDA, EDA and DETA respectively. These values suggest that the cured NIPUs film exhibit

superior dimensional stability and smooth surface morphology. The IPDA based NIPUs show the highest gloss followed by EDA and DETA based NIPUs owing to the presence of cyclic-aliphatic ring.

2.3.6 Chemical properties

All the prepared NIPUs were examined for their acid, alkali and water resistance by immersion method and the observations are given in **Table 2.3**. The samples prepared at carbonate to amine ratio of 1:1 show suitable resistance to acid (10% HCl) due to the presence of NIPU chains that has good hydrogen bridging between the urethane and hydroxyl groups. In the samples prepared at ratios of 1:0.75 and 1:2, the coatings are fairly resistant to the acid due to lower cross-linking density between urethane, hydroxyls and ester groups. In the case of alkali resistance, coatings based on IPDA have small resistance due to the effect of rigid cyclo-aliphatic structure. However, the coating with EDA and DETA are not so resistant to alkali due to saponification of the ester group.

Table 2.3: Chemical resistances of NIPUs.

Sample	HCl (10% aq.)	NaOH (2% aq.)	Water
EDA 1:0.75	Fair	Poor	Good
EDA 1:1	good	Fair	Good
EDA 1:2	Fair	Poor	Fair
DETA 1:0.75	Fair	Poor	Good
DETA 1:1	Good	Poor	Fair
DETA 1:2	Fair	Poor	Fair
IPDA 1:0.75	Good	Fair	Good
IPDA 1:1	Excellent	Fair	Good
IPDA 1:2	Good	Fair	Good

Excellent= No weight loss

The water resistance test shows a loss in gloss for all the prepared NIPUs coating owing to the presence of secondary hydroxyl that favours the hydrophilicity of the polymer network [43]. Samples prepared at 1:1 ratio has good resistance to water compared to the sample with ratio of 1:0.75 while 1:2 ratio shows poor resistance to water. At higher carbonate/amine ratio, the extra amine groups react with the ester group of oil to form amides and free hydroxyl groups with glyceride. As a result, there is an increase in the hydrophilicity of the polymeric matrix **(Scheme 2.3a)**. IPDA based coating displays improved resistance due to its cyclic-aliphatic nature, which make better compactness and contribute in shielding of the hydroxyl groups in comparison to the aliphatic amines EDA and DETA.

2.3.7 Anticorrosive property

To determine the anticorrosive performance of the NIPUs, potentio-dynamic polarization studies and electrochemical impedance spectroscopy (EIS) were used. The NIPU films were deposited as a layer on the metal substrate which acted as a barrier with good electrical resistance. Anticorrosive and EIS properties of the coated films were studied after exposing for 24 h in 3.5% (w/v) NaCl solution. The rate of diffusion of solution into coated films depends on branching and cross-linking density of polymeric network [43]. From **Table 2.4** and **Fig. 2.12a** and **b**, it is indicated that IPDA based NIPUs display the highest resistance and lowest corrosion rate due to its rigid structure. NIPU based DETA presents permeable and leaky film due to its long aliphatic chains resulting in low barrier properties. Because of this, DETA based NIPUs shows low corrosion protection. These results demonstrated that the prepared NIPUs coating are suitable barrier to the metal surface and IPDA based NIPU is the best coating amongst the prepared NIPUs.

Table 2.4: Potentiodynamic polarization data of NIPU coatings in 3.5 wt% NaCl solution.

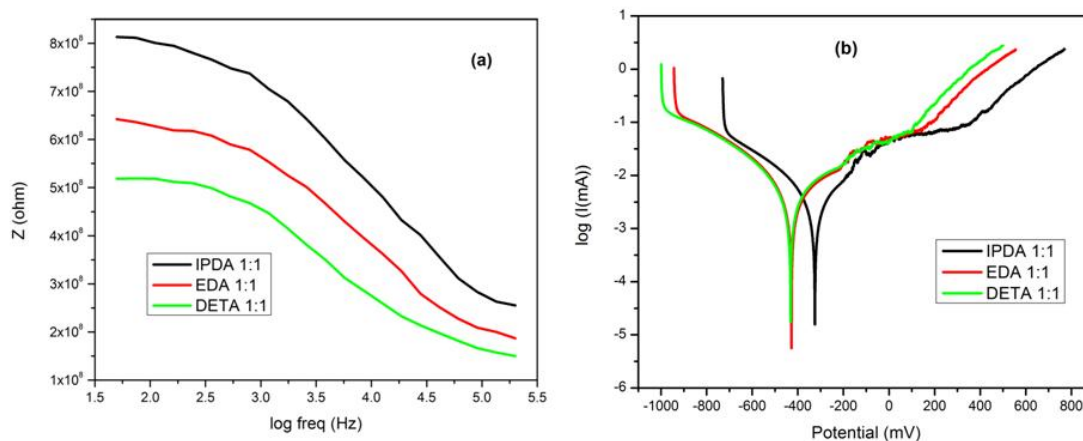| Sample	E (mv)	I_{corr} (µA)	Corr rate (mmpy)
IPDA 1:1	-325.825	1.695	0.0391504
EDA 1:1	-426.913	3.521	0.0818542
DETA 1:1	-435.651	3.828	0.0888991

Fig. 2.12: Bode plots (a) and Tafel plots (b) of CSFO cured with various diamines at 1:1 ratios.

2.4 Conclusion

The solvent-free reaction of ESFO with CO_2 was performed (P = 50 bar, T = 120 °C) by using TBABr as organo-catalyst to produce the cyclic carbonated oil with 86% conversion as a new monomer for NIPUs synthesis. The procedure used here provides a lot of benefits. The structure of diamine and different carbonate/amine molar ratios affected the properties of the NIPUs. Except for IPDA, other diamines produced amide groups along with the formation of urethanes group. The Different curing agents were used to establish the structure-properties relationships where we observed that stoichiometric ratio gave better results than others. In all the CSFO/amine based NIPUs, along with ester and urethane group, an amide group was also present due to the reaction of amine with glyceride except IPDA. With regard to the effect of the structure of curing agent on NIPU properties, IPDA based coating displayed the highest tensile strength (5.20 MPa), thermal stability up to 280 ^{0}C (5% weight loss), gloss, hardness, suitable chemical resistance and corrosion resistance (0.0391504 mmpy) than EDA, followed by DETA based coating. Meanwhile, the long chain aliphatic diamine, DETA based coating gave high elongation at break. On the whole, the results of the study suggest the sunflower oil based NIPU can be used as non-toxic bio-based material for coating purposes.

2.5 References

[1]   Kathalewar, M., Sabnis, A., and D'Mello, D. Isocyanate free polyurethanes from new CNSL based bis-cyclic carbonate and its application in coatings. *European Polymer Journal*, 57:99-108, 2014.

[2]   Diaconu, I. and Dorohoi, D. Properties of polyurethane thin films. *Journal of Optoelectronics and Advanced Materials*, 7(2):921-924, 2005.

[3]   Król, P. Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. *Progress in Materials Science*, 52(6):915-1015, 2007.

[4]   Pelrine, R. E., Kornbluh, R. D., and Joseph, J. P. Electrostriction of polymer dielectrics with compliant electrodes as a means of actuation. *Sensors and Actuators A: Physical*, 64(1):77-85, 1998.

[5]   Zdrahala, R. J. and Zdrahala, I. J. Biomedical applications of polyurethanes: A review of past promises, present realities, and a vibrant future. *Journal of Biomaterials Applications*, 14(1):67-90, 1999.

[6]   Santerre, J. P., Woodhouse, K., and Labow, R. S. Understanding the biodegradation of polyurethanes: From classical implants to tissue engineering materials. *Biomaterials*, 26(35):7457-7470, 2005.

[7]   Kong, X., Liu, G., and Curtis, J. M. Novel polyurethane produced from canola oil based poly(ether ester) polyols: Synthesis, characterization and properties. *European Polymer Journal*, 48(12):2097-2106, 2012.

[8]   Stemmelen, M., Lapinte, V., Habas, J. P., and Robin, J. J. Plant oil-based epoxy resins from fatty diamines and epoxidized vegetable oil. *European Polymer Journal*, 68:536-545, 2015.

[9]   Gogoi, P., Boruah, M., Sharma, S., and Dolui, S. K. Blends of epoxidized alkyd resins based on jatropha oil and the epoxidized oil cured with aqueous citric acid solution: A green technology approach. *ACS Sustainable Chemistry & Engineering*, 3(2):261-268, 2015.

[10]   Rix, E., Grau, E., Chollet, G., and Cramail, H. Synthesis of fatty acid-based non-isocyanate polyurethanes, NIPUs, in bulk and mini-emulsion. *European Polymer Journal*, 84:863-872, 2016.

[11]   Petrović, Z. S. and Petrovic´kansas, Z. S. Polymer reviews polyurethanes from

vegetable oils polyurethanes from vegetable oils. *Polymer Reviews*, 48(1):109-155, 2008.

[12] Lligadas, G., Ronda, J. C., Galià, M., Cá diz, V., and Domingo, M. Plant oils as platform chemicals for polyurethane synthesis: Current state-of-the-art. *Biomacromolecules*, 11(11): 2825-2835, 2010.

[13] Zlatani?, A., Lava, C., Zhang, W., and Petrovi?, Z. S. Effect of structure on properties of polyols and polyurethanes based on different vegetable oils. *Journal of Polymer Science Part B: Polymer Physics*, 42(5):809-819, 2004.

[14] Hazmi, A. S. A., Aung, M. M., Abdullah, L. C., Salleh, M. Z., and Mahmood, M. H. Producing jatropha oil-based polyol via epoxidation and ring opening. *Industrial Crops and Products*, 50:563-567, 2013.

[15] Petrovic´, Z. S., Zhang, W., and Javni, I. Structure and properties of polyurethanes prepared from triglyceride polyols by ozonolysis. *Biomacromolecules*, 6(2):713-719, 2005

[16] Guo, A., Demydov, D., Zhang, W., and Petrovic, Z. S. Polyols and polyurethanes from hydroformylation of soybean oil. *Journal of Polymers and the Environment*, 10(1/2):49-52, 2002.

[17] Petrović, Z. S., Guo, A., Javni, I., Cvetković, I., and Hong, D. P. Polyurethane networks from polyols obtained by hydroformylation of soybean oil. *Polymer International*, 57(2):275-281, 2008.

[18] Dai, H., Yang, L., Lin, B., Wang, C., and Shi, G. Synthesis and characterization of the different soy-based polyols by ring opening of epoxidized soybean oil with methanol, 1,2-ethanediol and 1,2-propanediol. *Journal of the American Oil Chemists' Society*, 86(3):261-267, 2009.

[19] Caillol, S., Desroches, M., Boutevin, G., Loubat, C., Auvergne, R., and Boutevin, B. Synthesis of new polyester polyols from epoxidized vegetable oils and biobased acids. *European Journal of Lipid Science and Technology*, 114(12):1447-1459, 2012.

[20] Gryglewicz, S., Piechocki, W., and Gryglewicz, G. Preparation of polyol esters based on vegetable and animal fats. *Bioresource Technology*, 87(1):35-39, 2003.

[21] More, A. S., Maisonneuve, L., Lebarbé, T., Gadenne, B., Alfos, C., and Cramail, H. Vegetable-based building-blocks for the synthesis of thermoplastic renewable polyurethanes and polyesters. *European Journal of Lipid Science and Technology*,

115(1):61-75, 2013.

[22] Montero de Espinosa, L. and Meier, M. A. R. Plant oils: The perfect renewable resource for polymer science?! *European Polymer Journal*, 47(5):837-852, 2011.

[23] Desroches, M., Escouvois, M., Auvergne, R., Caillol, S., and Boutevin, B. From vegetable oils to polyurethanes: Synthetic routes to polyols and main industrial products. *Polymer Reviews*, 52(1):38-79, 2012.

[24] Desroches, M., Caillol, S., Lapinte, V., Auvergne, R., and Boutevin, B. Synthesis of biobased polyols by thiol-ene coupling from vegetable oils. *Macromolecules*, 44(8):2489-2500, 2011.

[25] Nohra, B., Candy, L., Blanco, J. F., Guerin, C., Raoul, Y., and Mouloungui, Z. From petrochemical polyurethanes to biobased polyhydroxyurethanes. *Macromolecules*, 46(10):3771-3792, 2013.

[26] Deepa, P. and Jayakannan, M. Solvent-free and nonisocyanate melt transurethane reaction for aliphatic polyurethanes and mechanistic aspects. *Journal of Polymer Science Part A: Polymer Chemistry*, 46(7):2445-2458, 2008.

[27] Palaskar, D. V., Boyer, A., Cloutet, E., Alfos, C., and Cramail, H. Synthesis of biobased polyurethane from oleic and ricinoleic acids as the renewable resources via the AB-type self-condensation approach. *Biomacromolecules*, 11(5):1202-1211, 2010.

[28] Maisonneuve, L., Lebarbé, T., Grau, E., and Cramail, H. Structure-properties relationship of fatty acid-based thermoplastics as synthetic polymer mimics. *Polymer Chemistry*, 4(22):5472, 2013.

[29] Maisonneuve, L., Lamarzelle, O., Rix, E., Grau, E., and Cramail, H. Isocyanate-free routes to polyurethanes and poly(hydroxy urethane)s. *Chemical Reviews*, 115(22):12407-12439, 2015.

[30] Foltran, S., Maisonneuve, L., Cloutet, E., Gadenne, B., Alfos, C., Tassaing, T., and Cramail, H. Solubility in CO_2 and swelling studies by in situ IR spectroscopy of vegetable-based epoxidized oils as polyurethane precursors. *Polymer Chemistry*, 3(2):525-532, 2012.

[31] Maisonneuve, L., More, A. S., Foltran, S., Alfos, C., Robert, F., Landais, Y., Tassaing, T., Grau, E., and Cramail, H. Novel green fatty acid-based bis-cyclic carbonates for the synthesis of isocyanate-free poly(hydroxyurethane amide)s. *RSC Advances*, 4(49):25795-25803, 2014.

[32] Maisonneuve, L., Wirotius, A. L., Alfos, C., Grau, E., and Cramail, H. Fatty acid-based (bis) 6-membered cyclic carbonates as efficient isocyanate free poly(hydroxyurethane) precursors. *Polymer Chemistry*, 5(21):6142-6147, 2014.

[33] Ochiai, B., Inoue, S., and Endo, T. One-pot non-isocyanate synthesis of polyurethanes from bisepoxide, carbon dioxide, and diamine. *Journal of Polymer Science Part A: Polymer Chemistry*, 43(24):6613-6618, 2005.

[34] Paddok, R. L. and Nguyen, S. T. Chemical CO_2 fixation: Cr(III) salen complexes as highly efficient catalysts for the coupling of CO_2 and epoxides. *Journal of American Chemical Society*, 123(46):11498-11499, 2001.

[35] North, M., Pasquale, R., and Young, C. Synthesis of cyclic carbonates from epoxides and CO_2. *Green Chemistry*, 12(9):1514, 2010.

[36] Jing, H. and Nguyen, S. T. $SnCl_4$-organic base: Highly efficient catalyst system for coupling reaction of CO_2 and epoxides. *Journal of Molecular Catalysis A: Chemical*, 261(1):12-15, 2007.

[37] Foltran, S., Alsarraf, J., Robert, F., Landais, Y., Cloutet, E., Cramail, H., and Tassaing, T. On the chemical fixation of supercritical carbon dioxide with epoxides catalyzed by ionic salts: an in situ FTIR and raman study. *Catalysis Science & Technology*, 3(4):1046, 2013.

[38] Bähr, M., Bitto, A., and Mülhaupt, R. Cyclic limonene dicarbonate as a new monomer for non-isocyanate oligo- and polyurethanes (NIPU) based upon terpenes. *Green Chemistry*, 14(5):1447, 2012.

[39] Javni, I., Hong, D. P., and Petrović, Z. S. Soy-based polyurethanes by nonisocyanate route. *Journal of Applied Polymer Science*, 108(6):3867-3875, 2008.

[40] Tamami, B., Sohn, S., and Wilkes, G. L. Incorporation of carbon dioxide into soybean oil and subsequent preparation and studies of nonisocyanate polyurethane networks. *Journal of Applied Polymer Science*, 92(2):883-891, 2004.

[41] Bähr, M. and Mülhaupt, R. Green chemistry linseed and soybean oil-based polyurethanes prepared via the non-isocyanate route and catalytic carbon dioxide conversion. 2012.

[42] Boyer, A., Cloutet, E., Tassaing, T., Gadenne, B., Alfos, C., and Cramail, H. Solubility in CO_2 and carbonation studies of epoxidized fatty acid diesters: towards novel precursors for polyurethane synthesis. *Green Chemistry*,

12(12):2205, 2010.

[43] Pathak, R., Kathalewar, M., Wazarkar, K., and Sabnis, A. Non-isocyanate polyurethane (NIPU) from tris-2-hydroxy ethyl isocyanurate modified fatty acid for coating applications. *Progress in Organic Coatings*, 89:160-169, 2015.