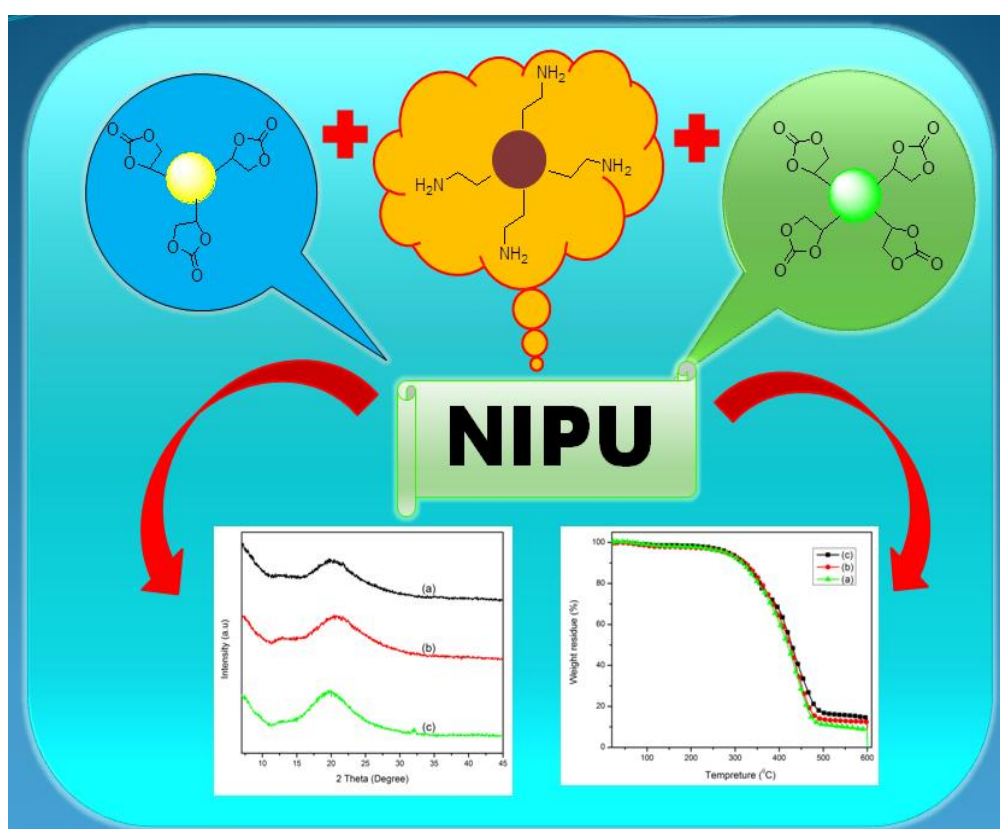


Chapter 5

A non-isocyanate approach towards the synthesis of polyurethane with high performance: Blending of cyclic carbonate based on soybean oil and glycerol



Carbonated soybean oil and glycerol based highly branched cyclic carbonates are used as precursor for synthesis of NIPU with suitable tensile strength

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5.1 Introduction

The utilization of renewable raw material for the polymer synthesis has seen an increasing awareness in both academic and industries as a substitute to petro-based polymers because of the shrinking of fossil resources and concerns about the environment [1–4]. Along with the various types of renewable resources, vegetable oils have gained more consideration owing to their inexpensive, green and globally available [5–8]. Vegetable oils are applied in the preparation of a variety of polymer such as polyester, polyurethane and epoxy etc. by different chemical modifications of triglyceride and C=C bonds present on it [9–11].

Polyurethanes (PUs), with a global market of 16 million tons per year, are the most significant group of polymers with a wide range of application like coatings, adhesives, sensors, bio-medical device and foams [12–15]. Commonly PUs are prepared from isocyanate and polyols *via* polyaddition reaction. Nowadays, various bio-based polyols are used to make partially bio-based PUs. Although there is a promising development in the production of bio-based PUs, the use of highly toxic isocyanate remains an important problem to suppress [16,17]. From this perspective, the most promising alternate way is the treating of five-membered cyclic carbonate with amines, resulting in non-isocyanate polyurethane (NIPU) with hydroxyls groups on the polymeric network, a non-toxic and secure substitute to isocyanate and phosgene-based PUs [18–20]. Additionally, the main advantage of this routes is that these cyclic carbonates can be readily synthesized by utilizing the greenhouse gas, CO₂ and epoxides [21–23]. PU synthesized through this isocyanate-free method from vegetable oil have been comprehensively studied by many research groups [24–29]. However, due to the lower reactivity and primary amine and amide towards the cyclic carbonate and the

This part of the thesis has been communicated

Doley, S. and Dolui S. K. Blending of cyclic carbonate based on soybean oil and glycerol: A non-isocyanate approach towards the synthesis of polyurethane with high performance. (*Communicated*)

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flexible nature of vegetable oils, the NIPUs exhibit low mechanical properties. It is required to develop catalysts and molecular structures having upto six- or seven-membered rings to increase the reactivity of cyclic carbonates. Moreover, the cyclic carbonates based on rigid structures like terpene, lignin and syringaresinol, and also by cross-linking NIPU with epoxy resin, and ketonic resin etc. (also known as hybrid NIPU (HNIPU)) have been used to compete with the traditional PUs [20,30–33].

In this work, five-membered cyclic carbonate prepared from soybean oil and glycerol derived hydroxyl-terminated highly branched polyester is used as prospective reagents for the synthesis of NIPU. Highly branched polymers exhibits a variety of unique properties like lower viscosity, soluble in most of the organic solvents and have a lot of functional end groups that can be tailored. As a consequence of their distinctive properties, these are suitable for many applications like coatings, adhesives, composites and medical applications [34–36]. In the present study, hydroxyl-terminated highly branched polyester (HHPE) is synthesized by the reaction between glycerol and 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) *via* A₃+B₃ polymerization reaction which is further utilized to obtain five-membered highly branched cyclic carbonates (CHPE). Here CHPE is used as a novel precursor for the synthesis NIPU. Therefore, to improve the properties of vegetable oil-based NIPU, carbonated soybean oil (CSBO) is blended with CHPE to get bio-based NIPU with high performance. Accordingly, the influence of HHPE on the properties of the NIPU was observed.

5.2 Experimental

5.2.1 Materials

Soybean oil was obtained from the local market. Bisphenol A (Research-lab fine chem industries, Mumbai) was recrystallized from toluene before use. (bis-MPA) (Alfa Aesar), poly(amido amine) (Kumud Enterprise, Kharagpur, West Bengal, India) and epichlorohydrin (Sisco Research Laboratories Pvt. Ltd., India) were used for this work.

5.2.2 Preparation of carbonated soybean oil (CSBO)

As a precursor for CSBO, epoxidized soybean oil (ESBO) was first synthesized. For this purpose, soybean oil and formic acid (HCOOH) were put in a three-necked (RB) flask equipped with a mechanical stirrer and thermometer by taking a C=C bond of the

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oil: HCOOH: H₂O₂ molar ratio of 1.0: 0.5: 1.7. After reaching 60 °C, H₂O₂ was added gradually through a dropping funnel to it and maintained for 5 h. The product, once cooled, was washed continually with water and NaHCO₃ solution till pH 7. The resulting organic layer was collected and dried with anhydrous Na₂SO₄. The epoxy equivalent weight (EEW) of ESBO was found to be 355±4 g/eq.

CSBO was prepared by the reaction between CO₂ (50 bar) and ESBO at 120 °C for 12 h by using 10% (w/w) tetra-n-butylammonium bromide (TBABr) as the catalyst in a high-pressure reactor. After the desired time, the resulting viscous product was collected.

5.2.3 Preparation of hydroxyl-terminated highly branched polyester (HHPE)

HHPE was prepared by melt polycondensation reaction between bis-MPA and glycerol as the core. The esterification reaction was carried out in 1:10 mole ratio between glycerol and bis-MPA catalyzed by p-toluene sulfonic acid (p-TSA) (0.06 wt% with respect to bis-MPA) in a three-necked RB flask. The RB flask was placed in an oil bath and provided with a N₂ inlet and a mechanical stirrer, and steadily heated upto 145 °C. After the reactants were melted, the temperature was kept at 145 °C for about 3 h. The resulting HHPE was washed with NaCl solution (10%) and water and kept at 60 °C to dry it. Finally, the product was collected with yield 92-95% and degree of branching (DB) was found to be 0.42 with hydroxyl end groups [37,38].

5.2.4 Preparation of highly branched cyclic carbonates (CHPE)

CHPE was prepared by the reaction of highly branched epoxy with CO₂ by using TBABr as the catalyst. Initially, the highly branched epoxy (EHPE) was prepared by the reaction of bisphenol A and epichlorohydrin (1:2 equivalents compared to OH group) with HPPE (10, 20, and 30 wt% compared to bisphenol A). Typically, 10 g bisphenol A, 16.22 g epichlorohydrin and 3 g HHPE (30% with respect to bisphenol A) were put in a three-necked RB flask equipped with a water condenser, a thermometer and continued to stir magnetically at 100 °C. After 4 h, the reaction was cooled down to 60 °C and 5 N NaOH aq. solution (equivalent to OH groups) was added dropwise to the system. The reaction was carried out for an additional 3 h [39]. The organic phase was isolated out and washed with 10% NaCl aq. solution and finally distilled water. The resulting epoxy

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was collected and dried at 60 °C and coded as EHPE1. Similarly, the epoxies with 20 and 10 wt% of HHPE were also prepared and encoded as EHPE2 and EHPE3 respectively.

From this resulting epoxy, CHPE was synthesized as follows: EHPE and 10% (w/w) TBABr as a catalyst are dissolved in dimethylformamide (DMF) and charged into a high-pressure reactor. Then, 50 bar of CO₂ pressure was introduced to the system which is then maintained at 80 °C for 12 h. The resulting carbonate was precipitated out by adding water and the organic phase was separated and kept at 60 °C for 24 h to dry it. The cyclic carbonate obtained from EHPE1, EHPE2, and EHPE3 were assigned as a CHPE1, CHPE2, and CHPE3 respectively.

5.2.5 Synthesis of NIPUs

NIPUs were prepared by the reaction of a mixture of CSBO and CHEP (50% with respect to CSBO) with polyamidoamine (equivalent wt% with respect to total resin) at 70-75 °C for 4 h using tetrahydrofuran as a solvent in an RB flask. The resulting viscous product was poured into a Teflon sheet and kept at about 90 °C for 24 h and finally at 125-130 °C for 2 h to obtain fully cured films. The NIPUs synthesized by using CHPE1, CHPE2 and CHPE3 are encoded as NIPU1, NIPU2 and NIPU3 respectively.

Table 5.1: Composition of reactants used in various NIPU synthesis.

Reactants (g)	Sample name		
	NIPU1	NIPU2	NIPU3
CSBO	2	2	2
CHPE1	1	-	-
CHPE2	-	1	-
CHPE3	-	-	1
Polyamidoamine	3	3	3

5.2.6 Characterizations

The instruments used for characterization including FT-IR, NMR (using d₆-DMSO as a solvent), TGA, UTM and scratch hardness tester are mentioned in section

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2.2.4 of Chapter 2, and the one used for XRD analysis is described in section 3.2.6 of Chapter 3. The chemical resistance of the prepared films was examined by dipping small parts of the cured film in different solutions. The epoxy equivalent weight (EEW) of ESBO was calculated by using the method as mentioned in section 2.2.4.10 of Chapter 2.

5.3 Results and discussion

5.3.1 Spectroscopic (FT-IR and NMR) studies

5.3.1.1 Synthesis and Characterization of CSBO and CHPE

The conversion of epoxy groups to cyclic carbonate groups was performed in a high-pressure reactor and its formation was established by FT-IR study. In the FT-IR spectrum of ESBO (**Fig. 5.1a**), the peak for epoxy groups at 832 cm^{-1} disappears upon the reaction of ESBO with CO_2 and a new signal appears at 1806 cm^{-1} corresponds to the cyclic carbonate groups (**Fig. 5.1b**).

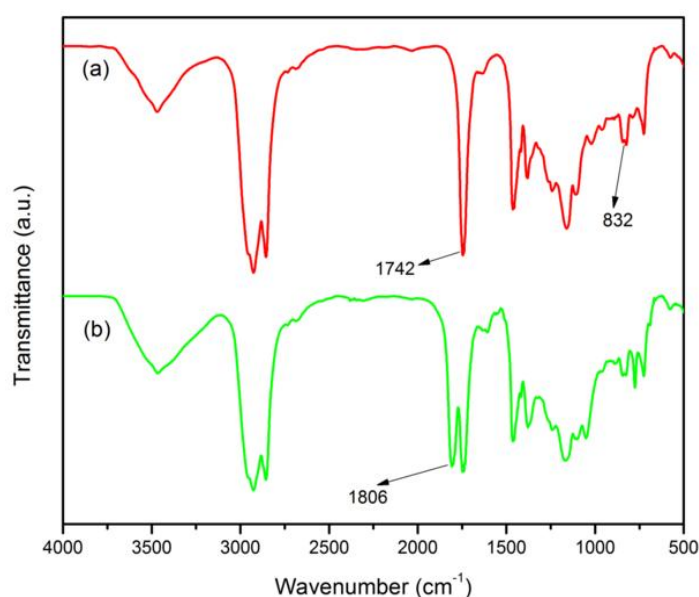
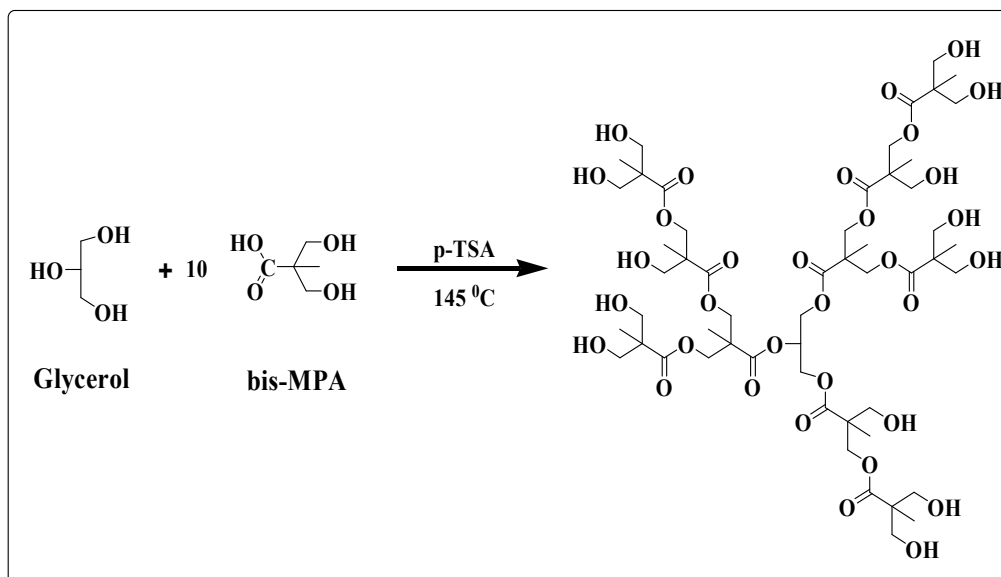


Fig. 5.1: FT-IR spectra of (a) ESBO and (b) CSBO.

Fig. 5.2 represents the FT-IR spectra of the synthesized HHPE, EHPE1 and CHPE1. In FT-IR spectrum of HHPE (**Fig. 5.2a**), after the polycondensation reaction between the OH group of glycerol and COOH groups of bis-MPA (**Scheme 5.1**), a characteristic signal at 1734 cm^{-1} is formed which is attributed to the stretching vibration of C=O of ester. It confirms the formation of highly branched ester. The broad peaks at

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around 3430, 2930, 2850 and 1465 cm^{-1} are ascribed to the OH group, CH_3 , CH_2 and C-O stretching vibrations respectively. The signals at 1228, 1132 and 756 cm^{-1} belong to the C-O and -OH out-of-plane bending respectively.



Scheme 5.1: Synthesis of HHPE from glycerol and bis-MPA.

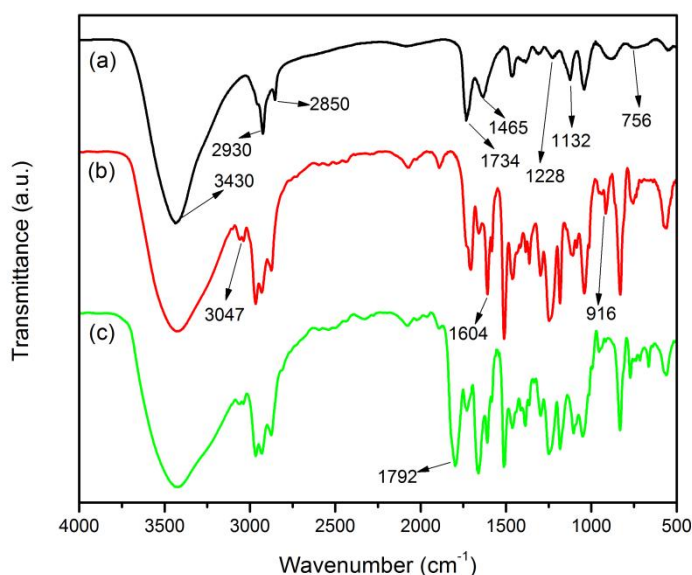


Fig. 5.2: FT-IR spectra of (a) HHPE (b) EHPE1 and (c) CHPE1.

In the ^1H NMR spectra of HHPE (**Fig. 5.3a**), the chemical shift values around $\delta = 3.2\text{--}3.6$ and $3.9\text{--}4.0$ ppm are due to protons attached to free hydroxyl groups ($\text{CH}_2\text{-OH}$ (e, f)) and protons attached to ester ($\text{CH}_2\text{-O-C=O}$ and CH-O-C=O (a, b, c)) respectively. The

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peaks at $\delta = 0.98$ - 1.14 and $\delta = 4.6$ are attributed to $-\text{CH}_3$ of bis-MPA moieties (d) and hydroxyl group (OH).

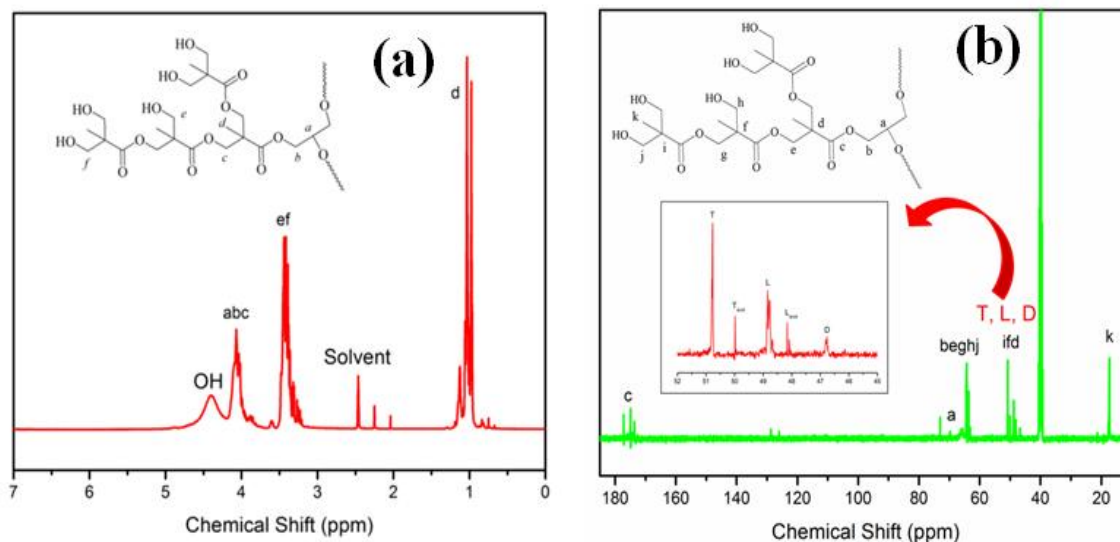


Fig. 5.3: (a) ^1H and (b) ^{13}C NMR spectra of HHPE.

In the ^{13}C NMR spectra of HHPE (**Fig. 5.3b**), the peak at $\delta = 17$ ppm corresponds to $-\text{CH}_3$ of the bis-MPA unit (k). The signals for methylene carbons (CH_2 (b, e, g, h, j)) and carbonyl of ester groups ($-\text{O}-\text{C}=\text{O}$ (c)) are observed at $\delta = 63$ - 67 ppm and 173 - 177 ppm respectively. The structural units formed due to the esterification reaction of glycerol and bis-MPA in the HHPE is shown in **Fig. 5.4**.

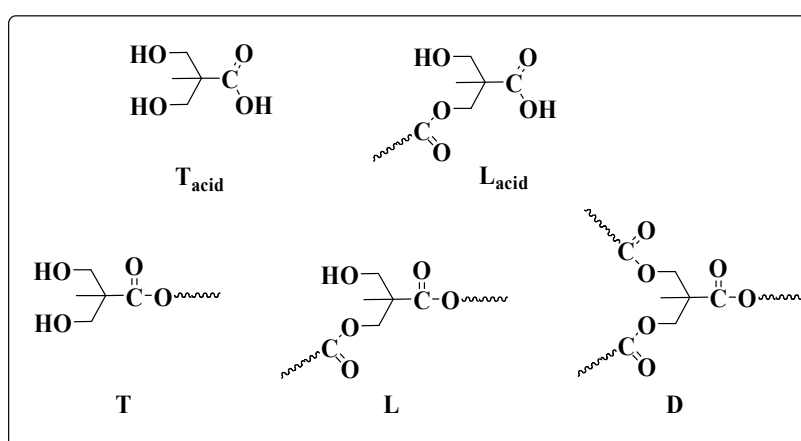


Fig. 5.4: T, D, and L units found in HPPE along with their acid-functional units.

The signal for the dendritic (D) linear (L) and terminal (T) repeating units of quaternary carbon of bis-MPA are found at around $\delta = 46.7$, 48.7 and 50.7 ppm

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respectively [40]. The peaks at around $\delta = 48.2$ and 49.8 ppm are attributed to the linear acid (L_{acid}) and terminal acid (T_{acid}) units. Here the degree of branching (DB) is calculated from the intensities of D, L and T units in the ^{13}C NMR spectrum by using by Frchet method i.e., $DB = (D + T) / (D + L + T)$ [41]. The DB of the HHPE was found to be 0.42 from the intensity of these peaks.

The highly branched epoxy was synthesized by the reaction of synthesized HHPE with a mixture of bisphenol A and epichlorohydrin *via in situ*. Owing to the higher acidic nature of phenolic proton of bisphenol A, it first reacts with epichlorohydrin to give bisphenol A diglycidylether in the presence of base and then the prepared bisphenol A diglycidylether reacts with HHPE to give highly branched epoxy resin in the reaction mixture [39]. The formation of highly branched epoxy is confirmed by FT-IR and NMR studies. In the FT-IR spectrum (**Fig. 5.2b**), the peak at 916 cm^{-1} due to asymmetric vibration of epoxy ring confirms the formation EHPE1. The bands at 3047 and 1604 cm^{-1} appears because of C-H and C=C stretching vibrations in the aromatic ring of bisphenol A. The 1H NMR spectrum of epoxy is presented in **Fig. 5.5**. In the 1H NMR spectrum, a new signal at $\delta = 2.75\text{-}3.20$ appears corresponding to the oxirane protons confirming the formation of epoxy. The peak at $\delta = 6.81$ (i) and 7.23 (h,) ppm are due to phenyl protons related to the bisphenol A.

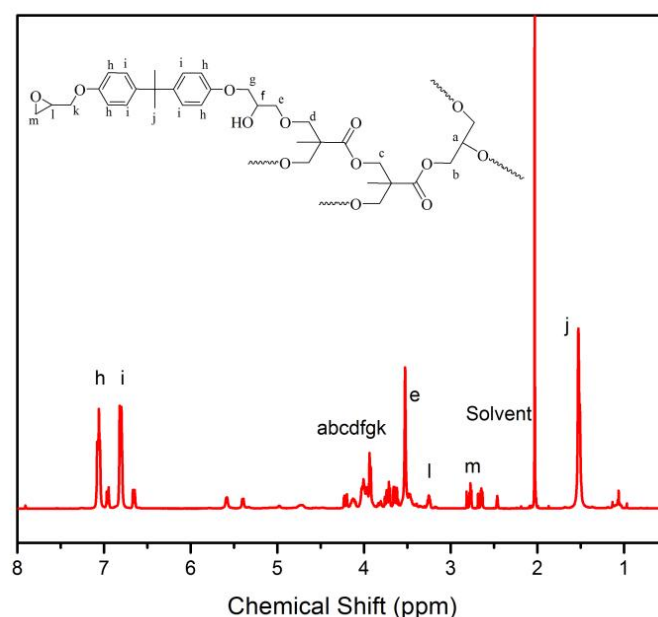


Fig. 5.5: 1H NMR spectrum of EHPE1.

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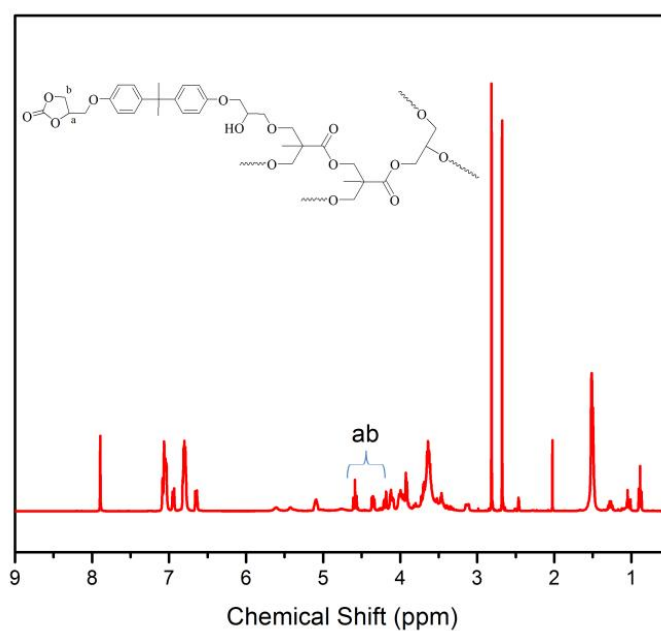
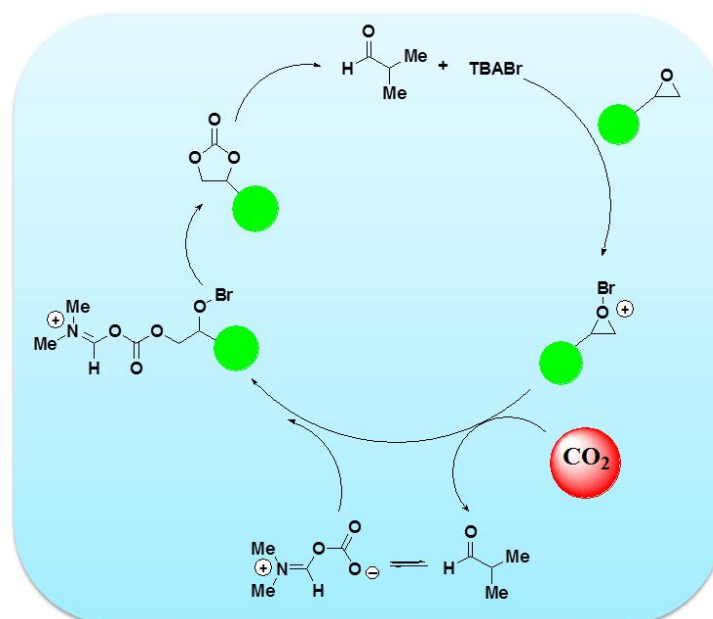


Fig. 5.6: ^1H NMR spectrum of CHPE1.

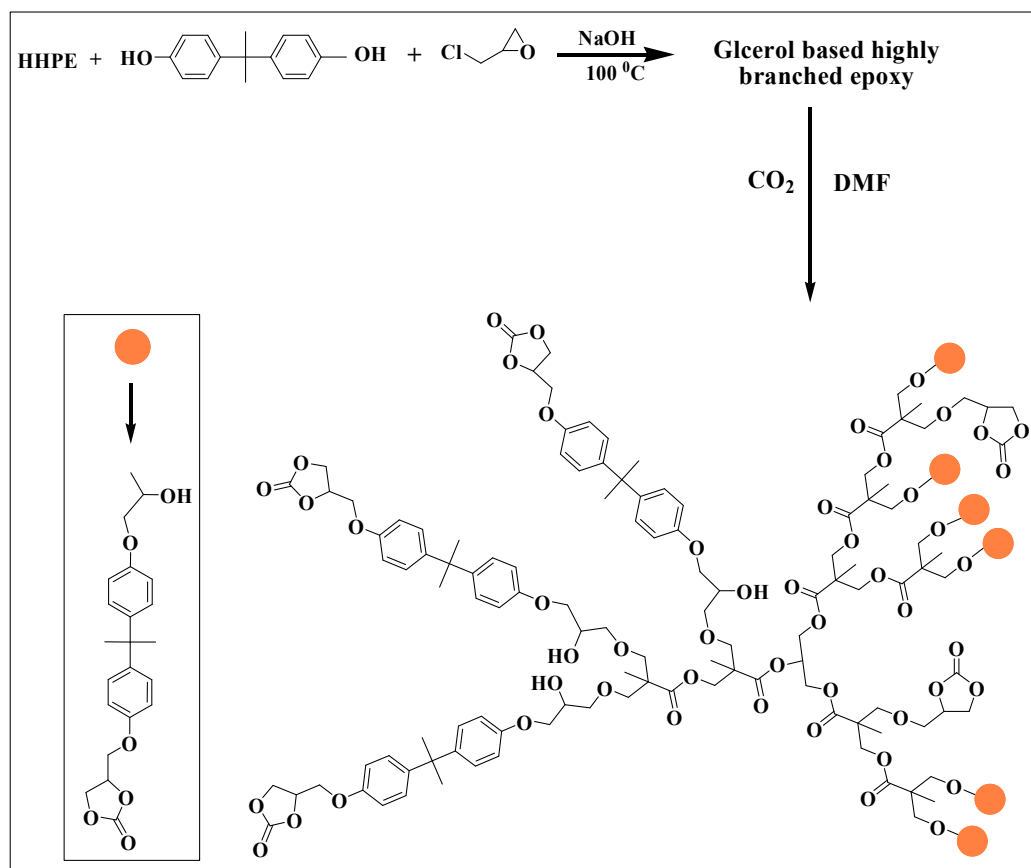


Scheme 5.2: Mechanism of formation of cyclic carbonate by using TBABr in DMF.

CHPE was synthesized by reacting EHPE with CO_2 at 50 bar and its formation is supported by spectroscopic analyses. Scheme 5.2 shows the mechanism of formation of glycerol based five-membered cyclic carbonates in DMF. In the FT-IR spectrum (Fig. 5.2c), as the EHPE1 reacts with CO_2 the characteristic peak of epoxy diminishes with the emergence of a new signal at 1796 cm^{-1} , which confirms the formation of five-

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membered cyclic carbonate. Similarly, in the ^1H NMR spectrum of CHPE1 (Fig. 5.6), the peak at $\delta = 4.30\text{--}4.60$ ppm (a, b) is due to the formation of cyclic carbonate. The whole conversion process of the formation of highly branched epoxy and cyclic carbonates is shown in Scheme 5.3.



Scheme 5.3: Synthesis of EHPE and subsequent conversion of it into CHPE.

5.3.1.2 Synthesis and characterization of NIPUs

A group of NIPUs were prepared by the reaction of a mixture of CSBO and CHPE with polyamidoamine and their formation was established by FT-IR analyses (Fig. 5.7). In the FT-IR spectrum of NIPU1 and NIPU3 (Fig. 5.7a and 5.7b), it is seen that the peak for cyclic carbonate in both CSBO and CHPE disappear after the reaction with polyamidoamine, simultaneously a new shoulder peak is observed at around 1705–1702 cm^{-1} . This affirms the formation of urethane group. Additionally, the peaks at 1250, 1558 and 1646 cm^{-1} are attributed to C-O stretching vibration, N-H deformation of urethane group, amide group from the aminolysis of ester group and polyamidoamine respectively.

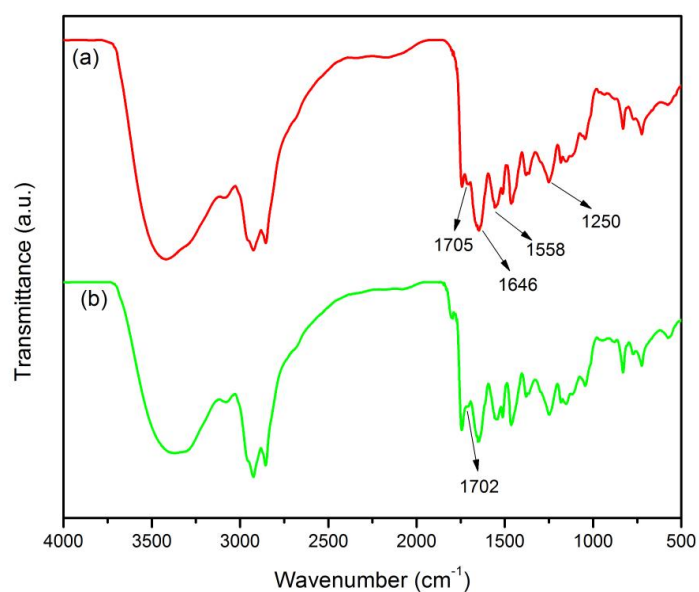


Fig. 5.7: FT-IR spectra of (a) NIPU1 and (b) NIPU3.

5.3.2 XRD analysis

Fig. 5.8 displays the XRD diffractograms of the pristine NIPU1, NIPU2 and NPU2.0. The XRD spectra shows a broad amorphous peak at $2\theta=20-24^\circ$ in all the samples. These broad peaks are ascribed to the amorphous structure of the prepared NIPU.

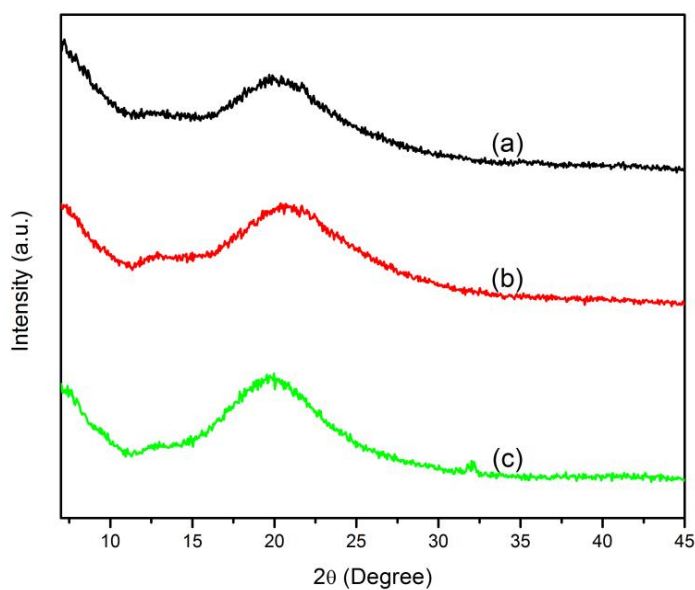


Fig. 5.8: XRD patterns of (a) NIPU1 (b) NIPU2 and (b) NIPU3.

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5.3.3 Mechanical properties

The mechanical properties of the NIPUs are listed in **Table 5.2**. These NIPU materials exhibit acceptable mechanical behavior. NIPU1 (with 30wt% HHPE) exhibits a tensile strength of 7.2 MPa whereas, with NIPU3 (with 10 wt% of HHPE), the tensile strength is found to be 10.1 MPa. As the high content of HHPE, the rigidity of the polymeric chains decreases due to aliphatic polyester moiety. In case of NIPU3, due to the presence of more amount of bisphenol A as compared to NIPU1, the rigidity of the polymeric chains increases due to aromatic nature of bisphenol A as well as more dense polymer networks through covalent bond, hydrogen bonding and electrostatic interactions of the functional groups present in the polymer matrix. Consequently, the performance of the blend is increased.

Table 5.2: Mechanical properties of NIPUs.

Sample	Tensile strength (MPa)	Elongation at break (%)	Scratch hardness (kg)
NIPU1	7.2±0.2	97±4	4.5±0.3
NIPU2	8.1±0.2	84±2	5.3±0.2
NIPU3	10.1±0.3	80±2	5.8±0.2

5.3.4 Thermal properties

The thermal stability of NIPU materials was also measured by TGA and the degradation temperatures at different at weight losses are tabulated in **Table 5.3**. The prepared NIPUs exhibit good thermal stability (**Fig. 5.9**). It is clear from the **Table 5.3** that NIPU3 hybrid materials have superior thermal stabilities due to the highly cross-linked polymer matrix and more rigid aromatic nature of bisphenol A. The 5wt% loss of NIPU1 occurs at 275 °C whereas in case of NIPU2, the 5wt% loss occurs at 283 °C. The degradation occurring at around 280 °C is due to the degradation of urethane bond and amide bond of polyamidoamine whereas the degradation around 419-429 °C is due to the degradation of the aromatic moiety of bisphenol A.

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Table 5.3: Thermal stability of NIPUs.

Sample	Temp @ 5% wt loss (°C)	Temp @ 25% wt loss (°C)	Temp @ 50% wt loss (°C)
NIPU1	275	369	419
NIPU2	280	374	425
NIPU3	283	372	429

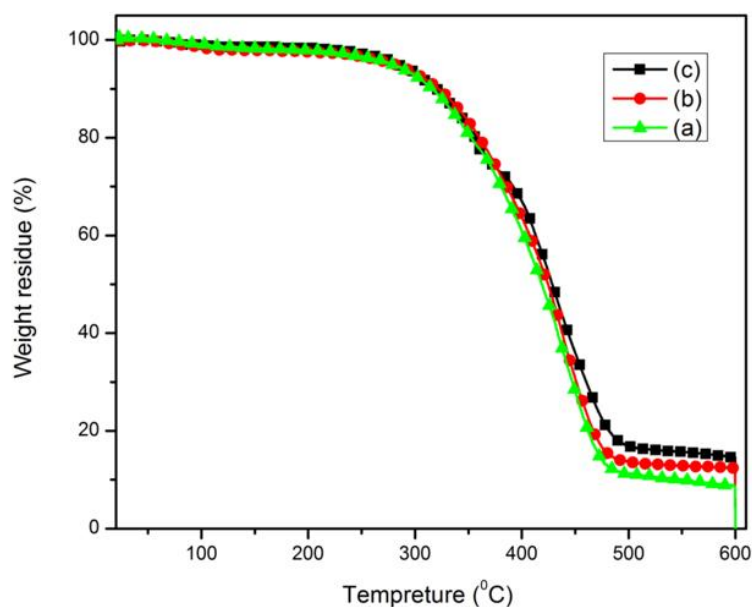


Fig. 5.9: TGA thermograms of (a) NIPU1 (b) NIPU2 and (c) NIPU3.

5.3.5 Chemical properties

The chemical resistance of prepared NIPUs was examined by dipping them in acid, alkali and water for 21 days and the outcomes are listed in **Table 5.4**. All the prepared NIPUs display satisfactory resistance to water and acid except alkali because of the more cross-linked polymeric chain *via* various interactions like hydrogen bonding and electrostatic interactions and also the presence of rigid bisphenol A diglycidyl ether as the terminal moieties. Due to the presence of hydrolyzable ester bonds in both CHPE and CSBO, the alkali resistances of these NIPUs are poor.

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Table 5.4: Chemical resistances of NIPU.

Sample	HCl (10% aq.)	NaOH (2% aq.)	Distilled Water
NIPU1	Good	Poor	Excellent
NIPU2	Good	Poor	Excellent
NIPU3	Excellent	Fair	Excellent

**Excellent= No weight loss*

5.4 Conclusion

We have presented a method for the preparation of bio-based PU from soybean oil and glycerol through a non-isocyanate and eco-friendly route. The urethane precursors, cyclic carbonates based on soybean oil and glycerol derived highly branched structures were synthesized by coupling of CO₂ with respective epoxy groups. The NIPU was synthesized by the reaction of CSBO and CHPE with polyamidoamine. Concerning the effect of HHPE, the NIPU3 showed high tensile strength and thermal stability. This is due to the increased rigidity of the polymeric chain and dense polymer network with an increase in the amount of bisphenol A. The prepared bio-based NIPUs exhibit high performances suitable for coating applications.

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