### LIST ABBREVIATIONS AND SYMBOLS USED

AF-CNT	Amine-functionalized carbon nanotube
AF-GO	Amine-functionalized graphene oxide
APTMS	(3-Aminopropyl)trimethoxysilane
ATPEG	3-aminopropyl-terminated poly (ethylene glycol)
BDA	1,4-butane diamine
bis-MPA	2,2-Bis(hydroxyl methyl)-propionic acid
C1	One-carbon building block
cm	Centimeter
CCLAY	Cyclic carbonate functionalized of clay
CDCl <sub>3</sub>	Deuterated chloroform
CHPE	Highly branched cyclic carbonates
CL	Cyclic limonene dicarbonate
CNT	Carbon nanotubes
CO <sub>2</sub>	Carbon dioxide
Corr. rate	Corrosion rate
CSBO	Carbonated soybean oil
CSFO	Carbonated sunflower oil
CTAN	Carbonated tannic acid
DA10	Decane diamine
DB	Degree of branching
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DBTDL	Dibutyltin dilaurate
DADI	Dianisidine diisocyanate
DADO	1,12- dodecane diamine
DETA	Diethylenetriamine
DETDC	Diethyltin dicaprylate
DI	Distilled water
DMC	Dimethyl carbonate
$H_2O_2$	Hydrogen peroxide
ECO	Epoxidized castor oil
EJO	Epoxidized jatropha oil

EEW	Epoxy equivalent weight
ELO	Epoxidized linseed oil
EO-TMPGC	Ethoxylated trimethylolpropane polyglycidylether
EEP	Ethyl 3-ethoxypropionate
ESO	Epoxidized soybean oil
ESS	Epoxidized sucrose soyate
ETAN	Epoxidized tannic acid
FT-IR	Fourier transform infrared spectroscopy
GO	Graphene oxide
GPTMS	3-Glycidoxypropyl trimethoxy silane
$H_2SO_4$	Sulphuric acid
HC1	Hydrochloric acid
НСООН	Formic acid
HDI	Hexamethylene diisocyanate
HHPE	Hydroxyl terminated highly branched polyester
HMDA	1,6-hexamethylene diamine
H-NIPU	Hybrid NIPU
HUM	Hydroxyurethane modifier
HV	Hydroxyl value
IV	Iodine value
I <sub>corr</sub>	Corrosion current density
IPDA	Isophorone diamine
IPDI	Isophorone diisocyanate
kg	Kilogram
KMnO <sub>4</sub>	Potassium permanganate
MA	Maleic anhydride
MDI	Methylene diphenyl diisocyanate
MHz	Mega hertz
MPa	Mega Pascal
MPDI	1, 3 Phenylene diisocyanate
mg	Milligram
MC	Montmorillonite nanoclay
mL	Milliliter

MWCNT	Multi walled carbon nanotube
mmpy	millimetres per year
mv	millivolt
Na <sub>2</sub> SO <sub>4</sub>	Sodium sulfate
NaHCO <sub>3</sub>	Sodium bicarbonate
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NIPUs	Non-isocyanate polyurethanes
NMR	Nuclear magnetic resonance
PA	Phthalic anhydride
PHU	Poly(hydroxyurethane)
p-TSA	P-toluene sulfonic acid
ppm	Parts per million
REACH	Registration, Evaluation, Authorisation and Restriction Of Chemical
ROP	Ring opening polymerization
RB flask	Round bottom flask
SEM	Scanning electron microscopy
SWCNTs	Single walled nanotubes
SYR	Syringaresinol
T <sub>d</sub>	Degradation temperatures,
Tg	Glass transition temperatures
TBABr	Tetrabutylammonium bromide
TBD	Triazabicyclodecene
TDI	Toluene diisocyanate
TEA	Triethylamine
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMPGC	Trimethylolpropane polyglycidylether
TMS	Tetramethyl silane
TREN	Tris(2-aminoethyl)amine
UTM	Universal testing machine
XRD	X-ray diffraction
ZnO	Zinc oxide
μm	Micro meter

#### **LIST OF FIGURES**

#### **Chapter 1: General introduction**

Fig. 1.1: Different types of PUs and their applications	1.3
Fig. 1.2: Global production of PU and an estimated forecast till 2020	1.3
Fig. 1.3: Structure of different types of polyols	1.4
Fig. 1.4: Chemical structures of some essential isocyanates	1.5
Fig. 1.5: Different types of catalysts used for the aminolysis of cyclic	1.15
carbonate reaction	
Fig. 1.6: Some examples of utilization of CO <sub>2</sub> as a one-carbon (C1)	
building block in organic synthesis	
Fig. 1.7: Various types of renewable raw materials used in the plastic	
industry	
Fig. 1.8: Chemical structures of some fatty acids present in vegetable oils	1.20
Fig. 1.9: Chemical structure of tannic acid	1.26
Fig. 1.10: Schematic representation of (a) conventional composite, (b)	
intercalated composite and (c) exfoliated composite	

# Chapter 2: Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties

Fig. 2.1: Schematic representation of high-pressure autoclave reactor used	2.8
to conduct the carbonation reaction	
Fig. 2.2: FT-IR spectra of (a) ESFO and (b) CSFO	2.8
<b>Fig. 2.3:</b> <sup>1</sup> H-NMR spectra for the kinetics of ESFO conversion at 120 °C	2.9
and 50 bar CO <sub>2</sub> pressure	
Fig. 2.4: Kinetics of carbonation of ESFO at 120 $^{\circ}$ C and 50 bar CO <sub>2</sub>	2.9
Fig. 2.5: <sup>13</sup> C NMR spectra of (a) ESFO and (b) CSFO	2.10
Fig. 2.6: <sup>1</sup> H NMR spectrum of EDA based NIPU at 1:1 at 80 °C	2.11
Fig. 2.7: FT-IR spectra of EDA based NIPUs at different carbonate to amine	2.12
ratios	
Fig. 2.8: FT-IR spectra of DETA based NIPUs at different carbonate to	2.12
amine ratios	
Fig. 2.9: FT-IR spectra of IPDA-based NIPUs at different carbonate to	2.13

amine ratios

Fig. 2.10: SEM micrograph of EDA-based NIPU at 1:1 molar ratios	2.14
Fig. 2.11: TGA thermograms of (a) EDA at different carbonate/amine ratios	
(b) DETA 1:1 and IPDA 1:1 based NIPU	
Fig. 2.12: Bode plots (a) and Tafel plots (b) of CSFO cured with various	
diamines at 1:1 ratios	

Chapter 3: *In situ* development of bio-based polyurethane-*blended*-epoxy hybrid materials and its nanocomposites with modified graphene oxide via non-isocyanate route

Fig. 3.1: FT-IR spectra of (a) GO and (b) AF-GO	3.6
Fig. 3.2: FT-IR spectra of (a) epoxy resin (b) CSFO (c) HNIPU30 and (d)	3.6
HNC1.0	
Fig. 3.3: XRD patterns of (a) GO and (b) AF-GO	3.8
Fig. 3.4: XRD patterns of (a) HNIPU30, (b) HNC0.3 (c) HNC0.6 and (d)	3.8
HNC1.0.	
Fig. 3.5: SEM images of (a) HNIPU30 and (b) HNC1.0	3.9
Fig. 3.6: TEM micrographs of the nanocomposites (HNC1.0) at different	3.10
magnifications.	
Fig. 3.7: TGA thermograms of HNIPU30, HNC0.3, HNC0.6 and HNC1.0	3.12

### Chapter 4: Development of sunflower oil based non-isocyanate polyurethane/multi walled carbon nanotube composites with improved physico-chemical properties

Fig. 4.1: FT-IR spectra of (a) f-CNT and (b) AF-CNT	4.5
Fig. 4.2: FT-IR spectra of (a) CSFO, (b) CNT0 and (c) CNT1	4.6
Fig. 4.3: XRD patterns of (a) MWCNT, (b) f-CNT, (c) AF-CNT (d) CNT0	4.7
and (e) CNT1	
Fig. 4.4: SEM micrographs of (a) CNT0 and (b) CNT1 nanocomposite films	4.8
Fig. 4.5: TGA curves of the nanocomposites with different wt% of AF-CNT	4.10

# Chapter 5: A non-isocyanate approach towards the synthesis of polyurethane with high performance: Blending of cyclic carbonate based on soybean oil and glycerol

Fig. 5.1: FT-IR spectra of (a) ESBO and (b) CSBO5.5

Fig. 5.2: FT-IR spectra of (a) HHPE (b) EHPE1 and (c) CHPE1	5.6
<b>Fig. 5.3:</b> (a) $^{1}$ H and (b) $^{13}$ C NMR spectra of HHPE	5.7
Fig. 5.4: T, D, and L units found in HPPE along with their acid-functional	
units	
<b>Fig. 5.5:</b> <sup>1</sup> H NMR spectrum of EHPE1	5.8
<b>Fig. 5.6:</b> <sup>1</sup> H NMR spectrum of CHPE1	5.9
Fig. 5.7: FT-IR spectra of (a) NIPU1 and (b) NIPU3.	5.11
Fig. 5.8: XRD patterns of (a) NIPU1 (b) NIPU2 and (b) NIPU3	5.11
Fig. 5.9: TGA thermograms of (a) NIPU1 (b) NIPU2 and (c) NIPU3	5.13

# Chapter 6: Synthesis of tannic acid based polyurethane through non-isocyanate route and effect of organically modified clay on its physico-chemical behavior

Fig. 6.1: FT-IR spectra of (a) ETAN and (b) CTAN	6.5
Fig. 6.2 FT-IR spectra of (a) Csilane and (b) CCLAY	6.7
Fig. 6.3: FT-IR spectra of (a) NPT and (b) NPTC0.5	6.8
Fig. 6.4: XRD curves of clays (a) pristine clay and (b) CCLAY	6.9
Fig. 6.5: XRD curves of clays (a) NPT and (b) NPTC1.0	6.9
Fig. 6.6: SEM micrographs of (a) NPT and (b) NPTC1.0	6.10
Fig. 6.7: TEM microphotograph of the NPTC1.0 nanocomposite at different	6.10
magnifications	
Fig. 6.8: TGA thermograms of (a) NPT, (b) NPTC0.5, (c) NPTC1.0 and (d)	
NPTC1.5	

#### LIST OF SCHEMES

#### **Chapter 1: General introduction**

Scheme 1.1: Two-step synthesis of procedure of traditional PU	1.6
Scheme 1.2: Synthetic approach to NIPU via polycondensation routes	1.7
Scheme 1.3: Synthetic approach to NIPU via different rearrangements	1.8
Scheme 1.4: Synthesis of [n]-PU by ROP of cyclic urethane or aziridine	1.9
Scheme 1.5: Aminolysis of cyclic carbonate to produce NIPUs	1.10
Scheme 1.6: Synthetic methodologies of five-membered cyclic carbonates	1.12
Scheme 1.7: Mechanism of NIPU formation via addition polymerization	1.14
Scheme 1.8: Schematic pathway of synthesis of alkyd resin from vegetable	1.21
oils	
Scheme 1.9: Synthetic pathway of epoxy resins from vegetable oils	1.23
Scheme 1.10: Synthetic pathway of polyetheramide from vegetable oils	1.24
Scheme 1.11: Synthetic pathway of polyols from vegetable oils	1.25

Chapter 2: Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties

	Scheme 2.1: Reaction of oxirane with CO <sub>2</sub> to form five-membered cyclic	2.7
	carbonate	
	Scheme 2.2: Plausible mechanism of formation of cyclic carbonate by	2.7
	TBABr as the catalyst	
	Scheme 2.3: Reaction of five-membered cyclic carbonate with amine to form	2.11
	(a) amide and (b) urethane	
_		
C	Chapter 3: In situ development of bio-based polyurethane-blended-epoxy	hybri

Chapter 3: *In situ* development of bio-based polyurethane-*blended*-epoxy hybrid materials and its nanocomposites with modified graphene oxide via non-isocyanate route

Scheme 3.1: Amine functionalization of GO	3.5
Scheme 3.2: Plausible interactions of AF-GO with the polymer matrix	3.11

Chapter 4: Development of sunflower oil based non-isocyanate polyurethane/multi walled carbon nanotube composites with improved physico-chemical properties

Scheme 4.1: Amine functionalization of MWCNT	4.5
Scheme 4.2: Plausible cross-linked structure of the CSFO/IPDA/AF-CNT	4.9
nanocomposites	

# Chapter 5: A non-isocyanate approach towards the synthesis of polyurethane with high performance: Blending of cyclic carbonate based on soybean oil and glycerol

Scheme 5.1: Synthesis of HHPE from glycerol and bis-MPA	5.6
Scheme 5.2: Mechanism of formation of cyclic carbonate by using TBABr	5.9
in DMF	
Scheme 5.3: Synthesis of EHPE and subsequent conversion of it into CHPE	5.10

### Chapter 6: Synthesis of tannic acid based polyurethane through non-isocyanate route and effect of organically modified clay on its physico-chemical behavior

Scheme 6.1: (a) Formation of ETAN and (b) its reaction with CO <sub>2</sub> to form	6.6
five-membered cyclic carbonate (CTAN)	
Scheme 6.2: Cyclic carbonate functionalized of clay (CCLAY)	6.7
Scheme 6.3: Reaction of CTAN and CCLAY with polyamidoamine to form	6.8
NPT and NPTC	

#### LIST OF TABLES

#### **Chapter 1: General introduction**

**Table 1:** Iodine value and fatty acid compositions of the various vegetable oils
 1.19

### Chapter 2: Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties

Table 2.1: Mechanical properties of NIPUs	2.14
Table 2.2: Thermal stability of NIPUs	2.16
Table 2.3: Chemical resistances of NIPUs	2.17
Table 2.4: Potentiodynamic polarization data of NIPU coatings in 3.5 wt%	2.18
NaCl solution	

# Chapter 3: *In situ* development of bio-based polyurethane-*blended*-epoxy hybrid materials and its nanocomposites with modified graphene oxide via non-isocyanate route

Table 3.1: Composition of the nanocomposites	3.4
<b>Table 3.2:</b> Performance of the HNIPU and its nanocomposites	3.11
Table 3.3: Thermal stability of nanocomposites	3.12
Table 3.4: Chemical resistance test for the nanocomposite films	3.13

### Chapter 4: Development of sunflower oil based non-isocyanate polyurethane/multi walled carbon nanotube composites with improved physico-chemical properties

Table 4.1: Composition of the nanocomposites	4.4
Table 4.2: Mechanical properties of the nanocomposites	4.9
Table 4.3: Thermal properties of the nanocomposites	4.10
Table 4.4: Chemical resistance tests for the nanocomposite films	4.11

### Chapter 5: A non-isocyanate approach towards the synthesis of polyurethane with high performance: Blending of cyclic carbonate based on soybean oil and glycerol

Table 5.1: Composition of reactant used in various NIPU synthesis	5.4
<b>Fable 5.2:</b> Mechanical properties of NIPUs	5.12
Table 5.3: Thermal stability of NIPUs	5.13

# Chapter 6: Synthesis of tannic acid based polyurethane through non-isocyanate route and effect of organically modified clay on its physico-chemical behavior

Table 6.1: Composition of the nanocomposites	6.4
Table 6.2: Mechanical properties of NPT and NPTC	6.11
Table 6.3: Thermal properties of NPT and its nanocomposites	6.12
Table 6.4: Chemical resistances of NPT and NPTC	6.13