Chapter 7

CONCLUSION

&

FUTURE SCOPE

7. 1 Conclusion:

Polyurethane (PU) is a significant polymeric material in our daily life with a wide range of applications. PUs are normally prepared by polyaddition reaction of diisocyanate (aliphatic or aromatic) with long chain polyols and low molecular weight polyol as chain extenders (e.g. ethylene glycol) in a two-step method. However, the use of diisocyanates is the main drawback in the traditional method due to its high moisture sensitivity and toxicity. As a solution to the reduction of petro-based resources and to fulfill the green chemistry regulation, recently, the PU research has concentrated on the substitution of polyols and isocyanates by renewable resources *via* non-isocyanate routes (also known as non-isocyanate polyurethane (NIPU)).

From the standpoint of green and sustainable chemistry, non-isocyanate based PUs is prepared by using sunflower and soybean oil, tannic acid, glycerol and CO_2 as sustainable materials. The first step is the epoxidation of vegetable oil and tannic acid. Subsequently, it is functionalized into five-membered cyclic carbonates by coupling with CO_2. The cyclic carbonates are treated with different amines to get NIPUs. Various nano-fillers such as graphene, multi walled carbon nanotubes and clay have been incorporated into the polymer matrix to improve the physical properties of the NIPUs. In this method, instead of using toxic isocyanates we have utilized the major green house gas CO_2 to synthesize NIPU.

The important outcomes of our study are summarized as follows:

Chapter 1: Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties

- The coupling CO_2 with epoxidized sunflower oil (ESFO) was carried out (P = 50 bar, T = 120 °C) by using tetra-n-butylammonium bromide as catalyst to make the cyclic carbonate sunflower oil (CSFO).
- The percentage of formation of CSFO groups from ESFO was achieved 86% in 12 h.
- NIPU prepared at 1:1 mole ratio (CSFO/amine) exhibited the highest mechanical properties thermal stability, and anticorrosion properties with respect to other mole ratios namely 1:0.75 and 1:2.

- In conclusion, the sunflower oil based NIPUs can be used as non-toxic bio-based materials for the coating purposes.

Chapter 2: *In situ* development of bio-based polyurethane-*blended*-epoxy hybrid materials and its nanocomposites with modified graphene oxide via non-isocyanate route

- The nanocompcoites of sunflower oil based NIPU blending with 30% epoxy were prepared by incorporating different wt% of amine functionalized graphene oxide (AF-GO).
- The nanocomposites with high 1 wt% AF-GOs exhibited impressive tensile strength (12.5 MP), thermal stability (upto 312 °C (5 wt% loss)) and chemical resistance in comparison to pristine HNIPU30.
- The property of the hybrid HNIPU30 was improved due to the strong covalent and hydrogen bonding interactions of AF-GO with the polymer networks.

Chapter 3: Development of sunflower oil based non-isocyanate polyurethane/multi walled carbon nanotube composites with improved physico-chemical properties

- Sunflower oil based NIPU/ amine functionalized multi walled carbon nanotubes (AF-CNTs) nanocomposite were prepared.
- The nanocomposites of sunflower oil based NIPU with 1.5% AF-CNTs demonstrated a tensile strength upto 8.92 MPa and thermally stable upto 310 ºC (5% wt loss) with1.5% AF-CNTs loading.

Chapter 4: A non-isocyanate approach towards the synthesis of polyurethane with high performance: Blending of cyclic carbonate based on soybean oil and glycerol

- Soybean oil based five-membered cyclic carbonates (CSBO) were obtained by reaction of CO_2 with epoxidized soybean oil (P = 50 bar, T = 120 °C) catalyzed by tetra-n-butylammonium bromide.

- Glycerol based hydroxyl terminated highly branched polyester (HHPE) were synthesized by melt polycondensation reaction between bis(hydroxymethyl)propionic acid (bis-MPA) and glycerol as the core.

- A series of glycerol derived highly branched epoxies were prepared from HHPE which are converted into highly branched cyclic carbonate (CHPE). Subsequently, the CSBO was blended with CHPE and cured by polyamidoamine.

- The prepared NIPUs displayed tensile strength upto 10.1 MPa and thermal stability upto 283 ºC (5% wt loss).

Chapter 5: Synthesis of tannic acid based polyurethane through non-isocyanate route and effect of organically modified clay on its physico-chemical behavior

- Tannic acid based five-membered cyclic carbonates (CTAN) were obtained by reacting CO_2 with epoxidized tannic acid (ETAN) (75 °C, 50 bar).
- Then tannic acid based non-isocyanate polyurethane (NPT) was prepared by the reaction of CTAN with polyamido amine.
- Finally, nanocomposites of the NPT were prepared with organically modified clay (CCLAY). The nanocomposites with 1.5 wt% CCALY loading exhibited impressive tensile strength (8.8 MPa), and thermally stable upto 267 ºC (10% wt loss).

Comparison of properties of the NIPU prepared from various sources:

System	Tensile strength (MPa)	Thermal stability (Temp @ 5% wt loss (°C)
(i) Sunflower oil based NIPU(IPDA)	5.2	280
(ii) Sunflower oil based hybrid NIPU with 1 wt% AF-GO	12.5	312
(iii) NIPU with 1.5 wt% AF-CNT)	8.92	310
(iv) Blend of soybean oil and glycerol based cyclic carbonate	10.1	283
(v) Tannic acid with 1.5 wt% CCLAY	8.8	267[a]

([a] *stands for temperature at 10 % wt loss*)

- ✓ *Without nano-filler*, NIPU synthesized from the blending of cyclic carbonated soybean oil with glycerol based cyclic carbonate exhibited the highest tensile strength (**system iv**).
- ✓ *With nano-filler*, NIPU prepared from the sunflower oil based hybrid NIPU nanocomposites with 1 wt% AF-GO displayed best tensile strength and thermal stability (**system ii**).

7.2 Future Scope

Although a large number of works have been done on bio-based NIPUs, the bio-based NIPUs suffer from poor mechanical performance due to lower reactivity between cyclic carbonates and amines that prevents them from various industrial applications. Therefore, still there are many scopes in this field need to improve. The future scopes on the basis of present research studies are:

- Development of catalyst to get high conversion of cyclic carbonates at short time and, low temperature and pressure condition.
- Utilization of CO_2 to synthesize six, seven and eight membered reactive cyclic carbonates as precursor for non-isocyanate polyurethane.
- Development of CO_2 derived bio-based polycarbonate.
- Development of fully bio-based hybrid NIPU with improved mechanical properties.