CHAPTER 8

Conclusion and Future Scopes

Highlight

The present chapter summarizes the findings of the current investigation in a concise manner. Results of the study are briefed in a chapter wise manner and concluding remarks are drawn based on the findings. The chapter also tries to depict future directions of the present study, which may be conducted for further exploration in the field of environmental benign hyperbranched polyurethane nanocomposites and their applications.

8.1. Summary and conclusion

The thesis elucidates development of eco-friendly hyperbranched polyurethane nanocomposites for various applications. The thesis is divided into eight chapters. The first chapter delineates a concise account on polyurethane (PU), PU based nanocomposites (PUNC), their preparation, characterization, property evaluation and applications. Special emphasis has been given on bio-based, biodegradable and sustainable PU systems. This chapter reveals the scope and opportunities for the development of novel PUNC for different applications. Objectives and plans of work for the present investigation were set in relevance to the importance of the proposed research.

The second chapter describes synthesis, characterization and property evaluation of hyperbranched PU with environment friendly attributes. A hyperbranched poly(urea urethane) (HPUU) system was developed using dihydroxyamine compound as the branch generating moiety by following an A_2+CB_2 synthetic approach. The work shows a polymeric material with high mechanical, thermal and chemical properties. Biodegradability test revealed profound biodegradability by *Pseudomonas aeruginosa*. The chapter also elaborates synthesis, characterization and property evaluation of tannic acid based, low VOC containing, biodegradable waterborne hyperbranched polyurethane (WHPU), which exhibited moderate performance with excellent biological properties such as hemocompatibility and profound biodegradability. The findings of the chapter mandate WHPU as the more acceptable material compared to HPUU from the perspective of environmental issues.

The third chapter corroborates modification of tannic acid based WHPU in order to improve its performance. A combined system of glycerol based hyperbranched epoxy and vegetable oil based poly(amido amine) was used as modifier. The modified system was cross-linked by using ultra-sonication and heat energy. This chapter deals with the evaluation of various properties, which showed excellent improvement in mechanical properties, thermal stability and better chemical and water resistance compared to the neat polymer. Biodegradation study showed bio-disposability of the modified system. The work showed the way to develop environmentally benign WHPU as a high performing material by incorporating a reactive modifier into the polymer network.

Considering the cutting-edge demand to develop material with multifunctional properties, fourth chapter presents *in situ* and *ex situ* fabrication of tannic acid based WHPU nanocomposites by incorporating various weight percentages of carbon dot (CD). The chapter describes a facile preparation of CD by using corms of *Colocasia esculenta* as raw material. Nanomaterial and fabricated nanocomposite were characterized by using different techniques and properties were evaluated. The nanocomposite films demonstrated excellent optical properties, which could be used as anti-counterfeit material. These nanocomposite films were found to be biocompatible for *in vitro* adhesion, proliferation and differentiation of MG63 osteoblast cells with good cell viability. This indicates suitability of CD included WHPU for bio-medical application. The chapter further enlightens an insight on photo-catalytic activity of the nanocomposite system by performing solar driven hydrogen peroxide production.

The fifth chapter is an extension of Chapter 4, which deals with in depth biological study of modified WHPU/CD nanocomposite system. The chapter describes covalent functionalization of CD with four different peptides, *viz.* SVVYGLR, PRGDSGYRGDS, IPP and CGGKVGKACCVPTKLSPISVLYK and consequent fabrication of WHPU system by using these bio-nanohybrids. This polymeric bio-nanocomposite was blended with 10% of gelatin and examined as a non-invasive delivery vehicle. *In vitro* and *in vivo* biological assessment revealed aptness of peptide functionalized WHPU/CD nanocomposite for accelerated bone tissue engineering application.

The sixth chapter reports synthesis of CD decorated hydroxyapatite (HAp) nanohybrid (CD@HAp) and consequent fabrication of WHPU nanocomposite by using this nanohybrid. Different bio-based and waste materials were used in the synthesis of the nanohybrid, which include corm of *Colocasia esculenta* as CD precursor and egg shell as HAp precursor. The synthesized nanohybrid and nanocomposites were characterized by using different analytical and spectroscopic techniques. Biological assessment of the nanohybrid and nanocomposite films demonstrated excellent cytocompatibility, cell proliferation and alkaline phosphatase activity with MG63 osteoblast cell line. Substantial improvement in the mechanical and thermal properties of the nanocomposite has also been perceived. The overall results endorse development of a sustainable nanocomposite with high load bearing ability and profound bioactivity.

The study also includes *in situ* fabrication of tannic acid based WHPU nanocomposite by using nickel ferrite ($NiFe_2O_4$) decorated reduced graphene oxide (rGO) nanohybrid ($NiFe_2O_4$@rGO), which has been reported in the seventh chapter. $NiFe_2O_4$@rGO nanohybrid was prepared through a hydrothermal method. The prepared nanohybrid and nanocomposite were characterized by using different spectroscopic and analytical techniques. Various properties of the nanocomposite were also evaluated. The nanocomposite exhibited excellent thermal stability and good mechanical properties compared to the neat system. The nanocomposite also exhibited outstanding multi-stimuli responsive shape memory behavior under sunlight, thermal and microwave (300 W) irradiation. The study showed that developed nanocomposite can be used as a high performing, non-contact triggered smart material for advanced shape memory application.

Thus, from the present work following conclusions can be briefed.

(a) The study shows that naturally available poly-hydroxyl compounds like tannic acid can be used in the synthesis of WHPU system. Utilization of such bio-based material is effective to address a cocktail of challenges ranging from sustainability to bio-disposability.

(b) The study confers effectiveness of hyperbranched epoxy and vegetable oil based poly(amido amine) as a combined modifier for WHPU. The study shows that incorporation of such reactive modifier into WHPU system could lift up its performance in a dramatic way.

(c) The study confirms suitability of CD as a nanomaterial to develop nanocomposite system for multidimensional utility. It can be concluded that inclusion of CD within WHPU matrix can enhance various properties, *viz.* mechanical, thermal, optical, biological and photo-catalytic significantly.

(d) The study ensures cytocompatibility of CD, specifically with MG63 cell line. Hence, it can be used in the fabrication of bio-materials used in bone tissue engineering applications. Further, study reveals the suitability of CD as a biocompatible nanomaterial to functionalize different biomolecules including peptides for various bio-medical applications.

(e) The study also shows the way to prepare nanohybrids of CD with other biologically active nanomaterial. In this regard, nanohybrid of CD@HAp has been studied. It has been found that WHPU/CD@HAp possesses better osteogenic activity than WHPU/HAp nanocomposite system. Such results endorse biological activity of CD.

(f) The study confers that $NiFe_2O_4$@rGO can be effectively used to fabricate WHPU nanocomposite with multi-stimuli responsive shape memory attributes. Incorporation of $NiFe_2O_4$@rGO enabled the polymer matrix to respond significantly under the stimuli of microwave and sunlight.

Thus, the work shows how different useful properties can be imparted to a single polymeric material by using nanotechnology based modification. The overall results demonstrated development of nanotechnology based multifunctional materials for multifaceted utility.

8.2. Future scopes

The thesis compiles a comprehensive study on eco-friendly polyurethane nanocomposites for potential applications. However, the work may establish a platform for future research, which would be quite relevant for the development of such materials. The present study may pave direction for future study under the following perspectives:

(a) Upgradation of the developed bio-based polymeric system with more than 50 wt% of renewable resource based material.

(b) Development of bio-based diisocyanate for the synthesis of polyurethane.

(c) Life cycle assessment study of the developed materials.

(d) Enhancement of light harvesting property of carbon dot by developing various nanohybrid systems.

(e) Utilization of carbon dot (and its nanohybrid) based polyurethane nanocomposites for opto-electronic and photo-catalytic applications.

List of Publications

Journal articles

(1) **Gogoi, S.**, & Karak, N. Biobased biodegradable waterborne hyperbranched polyurethane as an ecofriendly sustainable material, *ACS Sustainable Chem. Eng.* **2**, 2730--2738, 2014.

(2) **Gogoi, S.**, Barua, S., & Karak, N. Biodegradable and thermostable synthetic hyperbranched poly (urethane-urea)s as advanced surface coating materials, *Prog. Org. Coat.* **77**, 1418--1427, 2014.

(3) **Gogoi, S.**, Barua, S., & Karak, N. Cross-linking kinetics of hyperbranched epoxy cured hyperbranched polyurethane and optimization of reaction conversion by central composite design, *Chem. Eng. Sci.* **127**, 230--238, 2015.

(4) **Gogoi, S.**, & Karak, N. Bio-based high-performance waterborne hyperbranched polyurethane thermoset, *Polym. Adv. Technol.* **26**, 589--596, 2015.

(5) **Gogoi, S.**, Kumar, M., Mandal, B. B., & Karak, N. High performance luminescent thermosetting waterborne hyperbranched polyurethane/carbon quantum dot nanocomposite with in vitro cytocompatibility, *Compos. Sci. Technol.* **118**, 39--46, 2015.

(6) **Gogoi, S.**, Kumar, M., Mandal, B. B., & Karak, N. A renewable resource based carbon dot decorated hydroxyapatite nanohybrid and its fabrication with waterborne hyperbranched polyurethane for bone tissue engineering, *RSC Adv.* **6**, 26066--26076, 2016.

(7) Ghosh, B., **Gogoi, S.**, Thakur, S., & Karak, N. Bio-based waterborne polyurethane/carbon dot nanocomposite as a surface coating material, *Prog. Org. Coat.* **90**, 324--330, 2016.

(8) **Gogoi, S.**, Maji, S., Mishra, D., Devi, K.S.P., Maiti, T.K., & Karak, N. Nano-bio engineered carbon dot-peptide functionalized water dispersible hyperbranched polyurethane for bone tissue regeneration, *Macromol. Biosci.* DOI: 10.1002/mabi.201600271 (**In Press**).

(9) **Gogoi, S.**, & Karak, N. Solar driven hydrogen peroxide production using polymer supported carbon dot as heterogeneous catalyst, *Catal. Commun.* (**Communicated**).

(10) **Gogoi, S.**, & Karak, N. Biobased hyperbranched waterborne hyperbranched polyurethane/$NiFe_2O_4$@rGO nanocomposite with multi-stimuli responsive shape memory attributes, *RSC Adv.* **6**, 94815--94825, 2016.

(11) Gogoi, G., **Gogoi, S.**, & Karak, N. Dimer acid based waterborne hyperbranched poly(ester amide) as a sustainable material, *Polym. Degrad. Stab.* (**Communicated**).

<u>Patent</u>

Karak, N., Das, V.K., & **Gogoi, S.** Selective para-hydroxylation of substituted aromatic hydrocarbon by using metal free heterogeneous catalyst (Patent applied)

<u>Conference</u>

1. **S. Gogoi**, N. Karak, Biodegradable hyperbranched polyurethane, **SANICON 2014**, Defence Research Laboratory, Solmara, Tezpur, Assam, 16-17th December, 2014.
2. **S. Gogoi**, N. Karak, Bio-based waterborne hyperbranched polyurethane thermoset, **9th POLY-2014**, Viswa-Bharati, Shantiniketan, 14-15th February, 2015.
3. **S. Gogoi,** N. Karak, Renewable resource based biodegradable waterborne hyperbranched polyurethane, **2nd ASP-2015**, Indian Institute of Technology, Guwahati, 21-22nd January, 2015.
4. **S. Gogoi.,** N. Karak, Carbon dot included waterborne hyperbranched polyurethane as a multidimensional utility material, **CDCS-2015**, Tezpur Univesity, Tezpur, 23-24th November, 2015.
5. **S. Gogoi.,** N. Karak, Carbon dot: Perception as a sustainable nano-filler for polymeric material, **MRSI Symposium**, CSIR-NEIST, Jorhat, 18-20th February, 2016.