

Conclusion and future scopes

Highlights

In this chapter, an effort is made to summarize the entire work of the thesis. The conclusions and most importantly the future direction of the reported works are also highlighted.

7.1. Summary and conclusions

The thesis is devoted to the development of castor oil based hyperbranched polyurethane (HPU) and its graphene based nanocomposites for prospective applications as smart materials. The works compiled in the thesis reveal a couple of fascinating observations, achievements and prospects for future works. The effect of incorporation of different nanomaterials such as graphene oxide (GO), reduced graphene oxide (RGO) and RGO based nanohybrids on the properties of HPU nanocomposites was comprehensively investigated. The thesis is divided into seven chapters. The first chapter describes a general introduction and brief review on the polymer, especially polyurethane (PU) and its graphene based nanocomposites. The chapter mainly addresses the importance, preparation and characterization techniques, properties and applications of PU and their nanocomposites. The scopes, objectives and plans of the present work are also mentioned at the end of this chapter.

The second chapter of the thesis describes the synthesis of HPU by an $A_2 + B_3$ approach using castor oil or its monoglyceride as a biobased B_3 moiety with other conventional reactants. It also deals with characterization and property evaluation of the synthesized HPU. The synthesized HPU exhibited good mechanical, thermal and dielectric properties with excellent chemical resistant towards various chemical media. Results showed that monoglyceride based HPU is superior in properties than direct castor oil based one.

Again, an effort was made for the fabrication of different HPU nanocomposites with various types of graphene based nanomaterials to address the cutting-edge demands of smart materials. These works are presented in four consecutive chapters namely Chapter 3, 4, 5 and 6. The third chapter deals with fabrication, characterization and property evaluation of graphene based HPU nanocomposites. This chapter contains three sub-chapters, where, the first sub-chapter demonstrates the preparation, characterization and property evaluation of GO and RGO. Second sub-chapter deals with the fabrication of HPU/GO nanocomposite and its properties evaluation. The last subchapter demonstrates fabrication of a tough RGO based HPU *in situ* nanocomposites using RGO and functionalized RGO as reactive chain extenders as well as nanoreinforcing materials. All the nanocomposites showed good shape memory behavior and mechanical properties. HPU/functionalized RGO nanocomposite demonstrated superior shape memory effect, electrical conductivity and mechanical properties than others prepared nanocomposites.

The spectrum of HPU nanocomposites was further expanded by the incorporation of the iron oxide/RGO nanohybrid. The works on these nanocomposites are described in fourth chapter. Incorporation of this nanohybrid results in rapid and repeatable self-healing abilities of the nanocomposite under exposure of MW and direct sunlight. In addition, the fabricated nanocomposite exhibited good thermal and mechanical properties with excellent shape-recovery under the same stimuli.

Furthermore, an antimicrobial smart HPU nanocomposite was fabricated using sulfur nanoparticle decorated RGO nanohybrid. The works on these nanocomposites are included in fifth chapter. The nanocomposite showed a profound microbial inhibitory effect against *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans*. The nanocomposite also demonstrated good mechanical and thermal properties with multistimuli responsive shape memory and self-healing attributes.

The sixth chapter describes sunlight-induced self-cleanable HPU/TiO₂-RGO nanocomposite with multistimuli responsive shape memory and self-healing attributes. These properties of the nanocomposite can be tuned by judicious choice of amount and composition of TiO₂-RGO nanohybrid. The presence of an adequate amount of RGO (0.5–1 wt%) in the nanocomposite helps in rapid and efficient healing, whereas a relatively high amount of TiO₂ nanoparticles (5–10 wt%) aids in achieving good self-cleaning properties. Thus, from the present work following conclusions can be briefed.

- (i) Castor oil and its monoglyceride can be used as branch generating units with other conventional reactants to generate the hyperbranched structure of PU.
- (ii) RGO and RGO based nanohybrids can be used as reactive chain extenders as well as nanoreinforcing agents to effectively improve the thermal and mechanical properties of the pristine HPU. Most importantly, elongation at break of the nanocomposite can also be improved over the pristine HPU by the same due to the formation of covalent and non-covalent bonds between nanomaterials and polymeric chains.
- (iii) Excellent shape memory behavior under different stimuli such as thermal, MW, sunlight, etc. can be achieved by incorporation of RGO and RGO based nanohybrids in HPU.
- (iv) The study conferred that iron oxide-RGO nanohybrid amongst other studied nanohybrid offers a better self-healing ability to HPU nanocomposite along with excellent shape memory behavior.
- (v) Antimicrobial smart HPU nanocomposite can be obtained by incorporating sulfur nanoparticle decorated RGO nanohybrid in HPU.

(vi) The study also revealed that self-cleaning surface can be achieved by incorporation of TiO₂-RGO nanohybrid in HPU.

7.2. Future directions

The thesis presented a comprehensive and systematic study on smart HPU nanocomposites. Although, these studies pave the way for a number of prospective applications as smart materials, a couple of pertinent windows still open to be delved into. Some of these scopes are highlighted below.

- (i) The self-healing and shape memory behaviors of such nanocomposites can be conducted using different other types of contact and noncontact stimuli such as infrared light, electricity, magnetic field, etc.
- (ii) The study on antimicrobial and self-cleaning properties can be carried out using various other microbes and model dirt, respectively. Also, these properties can be studied extensively and systematically.
- (iii) The theoretical study of such nanocomposites can be conducted to understand the reinforcing as well as the healing mechanism.
- (iv) The biomedical applications of the tough HPU nanocomposites can also be further studied.
- (v) Different quantum dot based HPU nanocomposites can be prepared to obtain fascinating optical properties. For this purpose, various quantum dot can be used such as CdSe, CdSe/ZnS, carbon dot, etc.
- (vi) Various other properties such as gas barrier, electromagnetic interference and photocatalytic properties of the nanocomposites can be carried out.

List of publications

In Journals

From thesis

- 1) **Thakur, S.**, & Karak, N. Alternative methods and nature-based reagents for the reduction of graphene oxide - a review, *Carbon* **94**, 224--242, 2015.
- 2) **Thakur, S.**, & Karak, N. Castor oil-based hyperbranched polyurethanes as advanced surface coating materials, *Prog. Org. Coats.* **76**, 157--164, 2013.
- 3) **Thakur, S.**, & Karak, N. Green reduction of graphene oxide by aqueous phytoextracts, *Carbon* **50**, 5331--5339, 2012.
- 4) **Thakur, S.**, & Karak, N. Bio-based tough hyperbranched polyurethane-graphene oxide nanocomposites as advanced shape memory materials, *RSC Adv.* **3**, 9476--9482, 2013.
- 5) **Thakur, S.**, & Karak, N. Ultratough, ductile, castor oil-based, hyperbranched, polyurethane nanocomposite using functionalized reduced graphene oxide, *ACS Sustainable Chem. Eng.* **2**, 1195--1202, 2014.
- 6) **Thakur, S.**, & Karak, N. Multi-stimuli responsive smart elastomeric hyperbranched polyurethane/reduced graphene oxide nanocomposites, *J. Mater. Chem. A* **2**, 14867--14875, 2014.
- 7) **Thakur, S.**, & Karak, N. One-step approach to prepare magnetic iron oxide/reduced graphene oxide nanohybrid for efficient organic and inorganic pollutants removal, *Mater. Chem. Phys.* **144** (3), 425--432, 2014.
- 8) **Thakur, S.**, & Karak, N. A tough, smart elastomeric bio-based hyperbranched polyurethane nanocomposite, *New J. Chem.* **39**, 2146--2154, 2015.
- 9) **Thakur, S.**, Das, G., Raul, P., & Karak, K. Green one-step approach to prepare sulfur/reduced graphene oxide nanohybrid for effective mercury ions removal, *J. Phys. Chem. C* **117** (15), 7636--7642, 2013.
- 10) **Thakur, S.**, Barua, S., & Karak, N. Self-healable castor oil based tough smart hyperbranched polyurethane nanocomposite with antimicrobial attributes, *RSC Adv.* **5**, 2167--2176, 2015.
- 11) **Thakur, S.**, & Karak, N. Tuning of sunlight-induced self-cleaning and self-healing attributes of an elastomeric nanocomposite by judicious compositional variation of the TiO₂-reduced graphene oxide nanohybrid, *J. Mater. Chem. A* **3**, 12334--12342, 2015.

- 12) **Thakur, S.**, Barua, S., & Karak, N. Reduced graphene oxide-metal oxide nanohybrid for efficient adsorption, photodegradation and photoinactivation of chemical and microbial contaminants, **Communicated**.

Other related publications

- 1) Barua, S., **Thakur, S.**, Aidew, L., Buragohain, A.K., Chattopadhyay, P. & Karak, N. One step preparation of a biocompatible, antimicrobial reduced graphene oxide–silver nanohybrid as a topical antimicrobial agent, *RSC Adv.* **4** (19), 9777--9783, 2014.
- 2) Talukdar, D., Das, G., **Thakur, S.**, Karak, N., Thakur, A.J. Copper nanoparticle decorated organically modified montmorillonite (OMMT): An efficient catalyst for the *N*-arylation of indoles and similar heterocycles, *Catal. Commun.* **59**, 238--243, 2015.
- 3) Ghosh, B., Gogoi, S., **Thakur, S.**, Karak, N., Bio-based waterborne polyurethane/carbon dot nanocomposite as a surface coating material, *Prog. Org. Coats.* **90**, 324--330, 2016.

In conferences

- 1) **Thakur, S.**, & Karak, N. Castor oil modified hyperbranched polyurethane as shape memory materials, National conference on chemistry, chemical technology and society (NCCCTS-11), Tezpur University, Tezpur, 11-12 November, 2011.
- 2) **Thakur, S.**, & Karak, N. One-step approach to prepare superparamagnetic iron oxide/reduced graphene oxide nanohybrid for efficient inorganic pollutants removal, 3rd International conference on advanced nanomaterials and nanotechnology (ICANN-13), IIT Guwahati, Guwahati, 1-3 December, 2013.
- 3) **Thakur, S.**, & Karak, N. Ultratough bio-based hyperbranched polyurethane/reduced graphene oxide nanocomposites, APA International Conference on Polymers: Vision & Innovations, IIT Delhi, Delhi, 19-21 February, 2014.
- 4) **Thakur, S.**, & Karak, N. Bio-based smart hyperbranched polyurethane nanocomposite with antimicrobial and repeatable self-healing attribute, 9th Polymer award function & national seminar on ‘Multifunctional Polymer Materials’ (POLY 2014), Viswa Bharati, Shantiniketan, 14-15 February, 2015. (**Awarded for best oral presentation**)