Effect of structural disparity of graphene-based materials on thermo-mechanical and surface properties of thermoplastic polyurethane nanocomposites

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ABSTRACT

Nanocomposites based on thermoplastic polyurethane (TPU) and graphene-based materials such as graphene oxide (GO) and reduced graphene oxide (RGO) was synthesized by in-situ solution polymerization technique. The effect of structural differences between GO and RGO in the thermo-mechanical and surface properties of TPU at ultralow concentration was the foremost aspiration of this work. TPU/GO nanocomposites exhibited superior mechanical properties compared to TPU/RGO nanocomposites at very low loading. With the incorporation of 0.10 wt% of GO, the resultant nanocomposite showed 280% increase in tensile strength and 410% increase in toughness. Interestingly, the elongation at break nanocomposite increased from 588% for pristine TPU to 1006% for TPU/GO-0.10. Property improvement of RGO filled nanocomposite was not so prominent as compared to GO filled nanocomposites. Thermal stability of the nanocomposites as examined by thermogravimetric analysis (TGA) depicted a 12 °C increase in thermal stability for 0.2 wt% GO filled nanocomposite whereas the same for RGO filled nanocomposite was only 6 °C. Contact angle study revealed that the RGO filled nanocomposites were becoming more hydrophobic whereas GO filled nanocomposites films showed the opposite trend.

1. Introduction

Polyurethane is an extremely versatile multi-block synthetic polymer having great industrial importance. Its versatility comes from a wide range of constituent monomeric materials which enable to tailor the properties according to the diversified demand of modern technologies like coatings, adhesives, fibers, foams, rubbers, thermoplastic elastomers and composites [1,2]. Thermoplastic polyurethane (TPU) is an important member of the polyurethane family and has a great technological interest. TPU carries both the properties of thermoplastics (easy processability) and elastomers (flexibility). Its tunable physical properties and melt processability makes it suitable for various applications. It can be used for those applications which demand high flexibility and elasticity [2]. However, the application of TPU containing a very low percent of hard segments is limited due to its low stiffness and strength [3]. Incorporation of nanofillers into the TPU matrix can eliminate this kind of limitations since, filler plays an important role in enhancing the physicochemical properties of polymers and therefore can be used for the development of new generation composite materials. Clay [4], nano silica [5,6], cellulose nanocrystal [7], carbon nanotubes [8], GO [9—14], RGO [15—17], graphene [18—21] can be used for this purpose. Among the various nanofillers employed for the fabrication of polymer nanocomposites, graphene and graphene-based materials such as graphene oxide (GO) and reduced graphene oxide (RGO) have drawn significant attention to the researchers and scientist owing to their unique combination of properties [22—26]. Polymer nanocomposites based on TPU and graphene-based materials have a great application opportunity in automobile body parts, flexible tubing, biomedical apparatus, paints, wire and cable coating etc [1].

Properties of polymer nanocomposites are largely dependent on the dispersion of nanofillers within the polymer matrix, filler-polymer compatibility and filler-polymer interaction [21]. These parameters are related to the structure of nanofillers that play a crucial role in determining its properties. Both GO and RGO is two-dimensional (2D) nanomaterials having exceptionally high tensile strength, tensile modulus and high surface area. GO contains a large

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number of oxygen-containing functional groups like hydroxyl, carbonyl, carboxyl, epoxy within the structure [27,28] which disrupt the conjugation of aromatic rings, making it electrically insulator [28]. On the contrary, RGO contains very few numbers of oxygen-containing functional groups [15,17,29] and it is electrically conductive. The conductivity comes from the restoration of conjugation due to the reduction of GO in a variety of ways [29]. A large number of oxygen-containing groups in GO is also responsible for the higher thickness of GO sheet compared to RGO. In GO, hydroxyl and epoxide groups mostly reside on its basal plane and the carboxyl groups at the edges. As a result, the basal plane of GO is less hydrophilic compared to its edge. This provides GO an amphiphilic character and helps to develop significant van der Waals interactions and sometimes covalent bonding with the polymer molecules, making it more compatible with organic polymers [30]. GO or RGO is able to provide astonishing property improvement at a very low loading by acting as a multifunctional crosslinker as well as a conventional reinforcing filler. Researchers and scientists working all over the world are curious to find out the hidden potential of these two 2D nanomaterials in enhancing the properties of TPU.

Most of the earlier research work related to TPU and graphene-based materials was focused on enhancing properties of composites at a relatively higher loading of GO or RGO [12,15,17] which actually add extra cost to the final product. Further, all the works highlight either the effect of GO or RGO or their modified materials for the enhancement of some specific physical or chemical properties. There is no literature on the effect of structural disparity of GO and RGO on physical properties of TPU at ultra low loading. Sadasivuni et al. [12] reported the effect of GO and 4, 4'-methylene diphenyl diisocyanate (MDI) modified GO on the dielectric and rheological properties of thermoplastic polyurethane. Filler concentration was varied from 0 to 3 wt% and found better properties for modified GO filled polyurethane nanocomposites at higher loading. Pokharel et al. [9] demonstrated an improvement of 40.5% in tensile strength and 19% in the elasticity of TPU with the addition of 1 wt% of GO. In another report, they explored the effect of hard segment length and GO percent on the thermal and mechanical properties of TPU/GO nanocomposites. For TPU having longer hard segment length, tensile strength increased by 7 folds and tensile modulus increased by 5 folds with the addition of 4 wt% of GO [10]. Wang et al. [31] reported significant improvement in tensile strength (239%) and storage modulus (202%) of polyurethane with the addition of 2 wt% graphene nanosheets. Thakur et al. [16] reported considerable increment in tensile strength (290%), tensile modulus (11 folds), elongation at break (40%) and toughness (4 folds) of castor oil based hyperbranched polyurethane by incorporating 2 wt% of RGO. Very few researchers have scrutinized the effect of this 2D materials at very low levels (≤ 0.20 wt %). Liao et al. [19] observed enhanced thermal, mechanical, electrical and rheological properties of polyurethane acrylates at ultralow percolation concentration (0.15 wt %). Furthermore, the surface properties of TPU/GO and TPU/RGO nanocomposites has not been explored by any researchers till now and the effect of structural differences between GO and RGO on the properties of their nanocomposites with TPU still remains in its infancy.

The present work was an attempt to investigate the effect of the structural difference of GO and RGO on thermal, mechanical and surface properties of polyether-based TPU for the first time. Further, most of the earlier works emphasized the effect of either GO or RGO on the properties of TPU at relatively higher loading (usually more than 1 wt %) whereas, the present study utilized ultralow percent (≤ 0.20 wt %) of graphene-based materials which will ultimately reduce the cost of the final products. TPU/GO and TPU/RGO nanocomposites were synthesized by in-situ solution polymerization technique and the resultant materials were characterized by X-ray diffraction spectroscopy (XRD), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and contact angle analysis.

2. Experimental

2.1. Chemicals

Poly (tetramethylene ether) glycol (PTMEG, $M_n = 2000$), 4,4'-methylene diphenyl diisocyanate (MDI) and natural graphite flakes (cat #332461) having a particle size ~150 μm were purchased from Sigma-Aldrich, Germany. 1,4-butanediol (1,4-BD), N, N-dimethyl formamide (DMF), dibutyltindilaurate (DBTL), sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and diethyl ether were purchased from Hi Media Laboratories Pvt. Ltd., India. AR grade potassium permanganate ($KMnO_4$), phosphoric acid (H_3PO_4), 30% hydrogen peroxide (H_2O_2) and hydrazine monohydrate were purchased from Rankem India. Ethanol was procured from Merck India. Polyether polyol, PTMEG was dried in a vacuum oven at 60 °C for 24 h. Both 1,4-butanediol (1,4-BD) and DMF were dried over 4 Å molecular sieves for 24 h before use. All other chemicals were used as received.

2.2. Synthesis of graphene oxide (GO)

GO was synthesized by one-pot sonication assisted mechano-chemical approach as reported in our previous work [27]. Briefly, 1 g graphite flake was added to a 9:1 mixture of concentrated H_2SO_4 and H_3PO_4 (126:14 ml), contained in a 500 ml beaker. The beaker was placed in a bath sonicator (LABMAN LMUC-4), operated at 100 W and 40 ± 3 kHz. 6 g $KMnO_4$ was added slowly, with constant stirring (250—300 rpm) to control the exothermic reaction. During this time sonication was turned off to minimize the temperature rise. After complete addition of $KMnO_4$, sonication was turned on and the temperature was set at 70 °C. Within an hour $KMnO_4$ was dissolved completely [32] and the reaction temperature reached to 70 °C. The combined effect of stirring and ultrasonication was continued for 3 h at 70 °C temperature. The mass was then cooled to room temperature and poured into ~200 ml ice and treated with 3 ml of 30% H_2O_2 to reduce the residual $KMnO_4$. The impurities were removed by passing the mixture through 150-μm standard testing sieve. The resulting solution mixture was centrifuged (REMI R-24) at 10,000 rpm for 30 min followed by washing the residue with 30% HCl and then several number of washing with distilled water until the pH of the supernatant liquid become ~7. The material was dispersed in water, ultrasonicated for 30 min at 400 W with the help of an ultrasonic processor (UP400S Hielscher Ultrasonics GmbH, Germany) to get GO dispersion and then freeze dried (iLShinBioBase, Korea) at −50 °C for 48 h to get the fluffy GO.

2.3. Synthesis of reduced graphene oxide (RGO)

Reduced graphene oxide (RGO) was synthesized by chemical reduction of GO using hydrazine hydrate as reducing agent as discussed elsewhere [33]. Briefly, 300 mg GO powder was taken in a 500 ml round-bottomed (RB) flask and stirred in a magnetic stirrer until an inhomogeneous yellow-brown dispersion resulted. The dispersion was sonicated in an ultrasonic bath cleaner (100 W) for 2 h to get homogeneous GO dispersion. 3 ml hydrazine hydrate was added and continued the reaction for 24 h at 100 °C in an oil bath with water cooled condenser fitted with the RB flask. RGO