



Novel green nano composites films fabricated by indigenously synthesized graphene oxide and chitosan



Younus H. Khan^{a,b}, Atif Islam^{a,*}, Afsheen Sarwar^a, Nafisa Gull^a, Shahzad M. Khan^a, Muhammad A. Munawar^a, Saba Zia^a, Aneela Sabir^a, Muhammad Shafiq^a, Tahir Jamil^a

^a Department of Polymer Engineering and Technology, University of the Punjab, Lahore, Pakistan

^b Department of Angewandte Chemie, Hochschule Reutlingen University, Germany

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ABSTRACT

Graphene oxide (GO) was indigenously synthesized from graphite using standard Hummers method. Chitosan-graphene oxide green composite films were fabricated by mixing aqueous solution of chitosan and GO using dilute acetic acid as a solvent for chitosan. Chitosan of different viscosity and calculated molecular weight was used keeping amount of GO constant in each composite film. The structural properties, thermal stability and mechanical properties of the composite films were investigated using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and tensile test. FTIR studies revealed the successful synthesis of GO from graphite powder and it was confirmed that homogenous blending of chitosan and GO was promising due to oxygenated functional groups on the surface of GO. XRD indicated effective conversion of graphite to GO as its strong peak observed at 11.06° as compared to pristine graphite which appeared at 26° . Moreover, mechanical analysis confirmed the effect of molecular weight on the mechanical properties of chitosan-GO composites showing that higher molecular weight chitosan composite (GOCC-1000) showed best strength (higher than 3 GPa) compared to other composite films. Thermal stability of GOCC-1000 was enhanced for which residual content increased up to 56% as compared to the thermal stability of GOCC-200 whose residue was restricted to only 24%. The morphological analysis of the composites sheets by SEM was smooth having dense structure and showed excellent interaction, miscibility, compatibility and dispersion of GO with chitosan. The prepared composite films find their applications as biomaterials in different biomedical fields.

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1. Introduction

Chitosan, a biodegradable natural biopolymer, has become important choice for the researchers for growth and development along with the environmental care of producing biodegradable products (Yang, Tu, Li, Shang, & Tao, 2007; Tang, Du, Hu, Shi, & Kennedy, 2010). Biopolymer based green composites are known to be 'green' when they are biodegradable at the end of their service life, renewable, environment friendly and sustainable in every way. Generally, chitosan (a green biopolymer) finds its wide applications in the areas of membranes, tissue engineering, drug delivery, wound dressing, packaging materials etc. due to its exceptional biocompatibility, water treatment, bone substitutes, biosensors, artificial skin, non-toxicity, antimicrobial activities and biodegrad-

ability (Singh et al., 2013; Islam, Yasin, Bano, & Riaz, 2012; Ma et al., 2010; Islam, Riaz, & Yasin 2013; Pan, Wu, Bao, & Li, 2011; Islam & Yasin 2012). It numbers second most abundance in natural biopolymers on the earth after cellulose and have attracted much attentions due to low cost, low immunogenicity (Hu et al., 2011; Liu et al., 2012) and is a natural green adsorbent containing hydroxyl, amino and carbonyl groups (Chen et al., 2014). It is a linear cationic (adsorbs easily on negative charge surface) amino polysaccharide having various reactive sites for grafting, ionic interactions, insoluble ionic complexes with a variety of water soluble anionic polymers and adsorption for metal ions (Liu et al., 2012; Qu, Wirsén, & Albertsson, 2000; Gorochoveva, Naderi, Dedinaite, & Makuška, 2005; Ding et al., 2004; Abou-Aiad, Abd-El-Nour, Hakim & Elsabee, 2006). In addition, chitosan behaves as a stimulus responsive polymer whose solubility can be tailored by change the pH value (Bao et al., 2011). The characteristic properties of chitosan are affected by its molecular weight and degree of de-acetylation (DDA). DDA can be lowered by re-acetylation and molecular weight can be reduced

* Corresponding author.

E-mail address: dratifislam@gmail.com (A. Islam).

by acidic de-polymerization (Berger et al., 2004). Crosslinking, graft copolymerization, complexation, chemical modifications and blending are performed to improve the mechanical properties of chitosan (Diaconu et al., 2010; El-Hefian, Nasef, & Yahaya, 2014; Mir, Yasin, Halley, Siddiqi, & Nicholson, 2011) which also lies within the nanoparticles inclusion. The use of nano-fillers such as carbon nanotubes, clays, etc. have already proven and an effective way to deal with the issues. Carbon nanotubes are the best solution as a reinforcing agents but have a limited use on industrial scale due to expensive synthesis steps and poor dispersibility (Yang et al., 2007). Recently, a mono layered carbon atoms (closely arranged in honeycomb) known as graphene has attracted the researchers since its discovery in 2004 due to its two dimensional structure with specific magnetism, unique mechanical, surface area, remarkable thermal, physical and electronic properties (Han, Yan, Chen, & Li, 2011; Geim & Novoselov, 2007; Kuilla et al., 2010; Li et al., 2014; Ye, Xie, Shi, Gao, & Ma, 2014). Its structure shows low chemical reactivity due to the absence of functional groups but GO, a derivative of graphene, possesses a range of oxygen functional groups and is mostly used in chemical functionalization (Anandhavelu & Thambidurai, 2013). In the past few years, graphene surface has been enriched with oxygen containing hydroxyl, carbonyl, carboxyl, and epoxy functional groups making its derivative (Karousis et al., 2011) and GO surface is highly negatively charged due to oxygenated functionalities that makes it hydrophilic (Bao et al., 2011). It can serve as a weak acid cation exchange resin due to ionizable carboxyl groups that can exchange with metal ions (Fan et al., 2012) and GO can easily disperse into some polar solvents which improve the interfacial interaction between GO and polar molecules and thus the mechanical properties of polar molecules can be increased (Li et al., 2014). Oxygenated groups in GO are covalently bonded either on basal planes or at the edges of the sheet. Generally, it is synthesized by modified Hummers method (Yadav & Ahmad, 2015) and can also be prepared by low cost chemical exfoliation of GO (Hegab, Wimalasiri, Ginic-Markovic, & Zou, 2015). Until now, much research work is being done on the modification of graphene and GO that show promising applications in the fields of adsorbents, chemical and biosensors, biomedical and mass spectrometry (Ye et al., 2014). Owing to both low cost and excellent mechanical properties, 2D graphene and GO sheets can be used as nanoscale filler for nanocomposite materials. GO/chitosan nanocomposites find their applications in orthopedic implants due to its biocompatibility and improved cellular behavior of bio inert surfaces (Ordikhani, Farani, Dehghani, Tamjid, & Simchi, 2015). Performance of biosensors has been improved by using graphene/GO nanocomposites that result in increment of electrical performance (Singh et al., 2013). Graphene based sheets are used in drug delivery as nano carriers (Zuo et al., 2013). Amino group of chitosan react with epoxy groups of GO through hydrogen bonding that improves mechanical properties (Han et al., 2011). Some studies reported chemical reaction between carboxyl functionalities of GO and amine groups of chitosan resulting in the formation of a strong chemical bond. However, these composites have some disadvantages like easy aggregation possibility and separation of composite is quite difficult when it is formed (Ding et al., 2015). Previous studies show that the tensile strength of composites compared to pristine biopolymer is improved as cellulose/GO composites whose mechanical properties are improved compared to pristine cellulose (Kumar & Koh, 2014). GO have been proved to exhibit better biocompatibility than reduced GO. Thus, GO is a promising nano filler for improving the properties of chitosan without disturbing its biocompatibility (Mazaheri, Akhavan, & Simchi, 2014). Some researchers reported microwave irradiation method to prepare chitosan modified graphene sheets which confirmed that chitosan is covalently bonded onto the graphene sheets by amide bonds (Hu et al., 2011). Ultra-low graphene loading in chitosan-based compos-

ite causes a dramatic increase in the wettability of chitosan (Bush, Thomas, Yu, & Koratkar, 2012).

Fabrication of novel transparent GO-chitosan nanocomposite films was reported by a simple and fully green method by mixing a suspension of GO in an aqueous solution of chitosan (Pan et al., 2011). According to our best of knowledge, no one has performed the effect of DDA and molecular weight of the chitosan on the properties of GO/chitosan nano composites. Here, we report simple green environmental favorable method for the preparation of GO/chitosan nano composites by casting a suspension of GO in aqueous solution of chitosan. Amount of GO is kept constant along with same quantity of chitosan with variable molecular weight, DDA and viscosity. These composite films were characterized using FTIR, XRD, SEM, TGA and tensile testing.

2. Experimental

2.1. Materials and chemicals

Chitosan with varying DDA (75–85%) was obtained from Germany and used as a matrix material. Natural graphite powder was purchased from Riedel deHäen Sigma-Aldrich, potassium permanganate (KMnO_4) was of analytical grade, sulfuric acid H_2SO_4 (98%) was purchased from BDH chemicals. Hydrogen peroxide (H_2O_2) was obtained from Merck chemicals, Germany (35% purity), sodium nitrate (NaNO_3) was purchased from Panreac, Spain, acetic acid (analytical grade) was purchased from Merck, Germany.

2.2. Synthesis of graphene oxide

GO was indigenously synthesized using Hummers and Offema method. 2 g of natural graphite powder was mixed with 1 g of NaNO_3 and 46 mL of H_2SO_4 in 500 mL beaker under magnetic stirring up to 20 min at 5 °C. Then, 6 g of KMnO_4 was introduced to the above mixture and temperature was kept 20 °C. After stirring for about 5 min, mixture was heated up to 35 °C for half an hour. Then, distilled water (92 mL) was inserted into the above mixture under continuous stirring. In the next step, 80 mL of water having temperature 60 °C along with H_2O_2 (3 wt.%) was added. The purpose of addition of H_2O_2 was the removal of remaining traces of KMnO_4 that was verified with the absence of bubbles present in the solution mixture. Centrifugation of the mixture was carried out for 45 min at 6500 rpm and the material obtained from centrifugation was put again into water in order to neutralize the pH up to 7. The resultant product was then freeze-dried and GO was obtained in the form of dark brown powder.

2.3. Fabrication of GO/chitosan composites

GO powder due to oxygenated functional groups present on its surface was easily dispersible in water. GO (0.05 g) was dispersed in 100 mL distilled water and into ultrasonic bath for about 1 h in a 250 mL beaker. Homogenous suspension having dark brown color was formed. Simultaneously, 2 g chitosan (DDA-Viscosity) (75–200, 85–600, 85–800, and 90–1000) was dissolved in 30 mL acetic acid in a separate 500 mL beaker and the mixture was kept overnight. It was followed by stirring for about 2 h at 60 °C. 0.05 mL tetraethylorthosilicate (TEOS) was added drop wise by dissolving it in 5 mL ethanol. After this, both chitosan solution and GO dispersion were mixed together under a constant stirring at 60 °C for about 4 h until the mixture became thick viscous liquid. The mixed solution was casted on plastic plates and dried under ambient conditions. The fabricated sheets were then removed carefully having approximately 0.16 mm thickness. The quantity of GO in all chitosan films was kept constant while different types of chitosan were used having different molecular weight and DDA. Various samples

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