

Regular Article

Improved thermomechanical and electrical properties of reduced graphene oxide reinforced polyaniline – dodecylbenzenesulfonic acid/divinylbenzene nanocomposites

Abhishek K. Pathak^{a,b}, V. Kumar^c, Sushant Sharma^{a,b}, T. Yokozeki^c, S. R. Dhakate^{a,b,*}

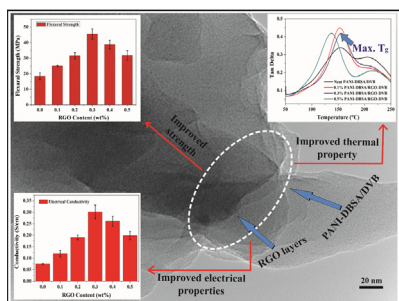
^aAdvanced Carbon Products and Metrology Section, Advanced Materials and Devices Metrology Division, CSIR-National Physical Laboratory, Dr K.S. Krishnan Marg, New Delhi 110012, India

^bAcademy of Scientific Innovation and Research (AcSIR), NPL, New Delhi, India

^cDepartment of Aeronautics and Astronautics, Graduate School of Engineering, The University of Tokyo, Tokyo, Japan



GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Various efforts are going on to improve the electrical properties of carbon fiber reinforced polymer (CFRP) composites. Conducting polymer is one the promising material to achieve the desired electrical properties of CFRP composites without compromising the mechanical properties as a lighting sticking material.

Experiments: In present study, in addition to conducting polymer polyaniline (PANI), another conducting phase reduced graphene oxide (RGO) was incorporated in PANI based system. The RGO was synthesized and incorporated in different weight (0–0.5 wt%) fraction in dodecylbenzenesulfonic acid (DBSA) doped PANI-divinylbenzene (DVB) polymer to get PANI-DBSA/DVB nanocomposite. The mechanical and interfacial interaction was analyzed by universal testing machine (UTM) and transmitted electron microscopy (TEM).

Findings: The addition of optimum 0.3 wt% RGO improved flexural strength and modulus of PANI-DBSA/RGO-DVB composite by 153% and 32% respectively over neat PANI-DBSA/DVB nanocomposite. The maximum electrical conductivity 0.301 S/cm, glass transition temperature (T_g) and thermal stability of nanocomposite realized at 0.3 wt% of RGO. Raman spectroscopy and HRTEM confirmed the improvement of interfacial bonding by H-bonding and π - π interaction. For the 1st time we are reporting RGO utilisation for the improvement of thermomechanical and electrical interfacial properties of PANI-DBSA/DVB nanocomposite for the structural applications.

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* Corresponding author at: Advanced Carbon Products and Metrology Section, Advanced Materials and Devices Metrology Division, CSIR-National Physical Laboratory, Dr K. S. Krishnan Marg, New Delhi 110012, India.

E-mail address: dhakate@nplindia.org (S.R. Dhakate).

1. Introduction

Carbon fiber reinforced polymer (CFRP) composites are used as structural material in various applications. Majorly, the epoxy polymer is used as a matrix for developing high strength CFRP composite as a structural material for aerospace applications [1–3]. But, one of the serious drawbacks associated with the epoxy based CFRP is their poor electrical conductivity, and this necessitates the addition of conducting material (copper mesh) to anticipate the major problem of light striking in aerospace application [4]. To mitigate the issue of epoxy based polymer composite, researchers are using conducting polymers as matrix precursors [5,6]. Conducting polymers discovery is a revolutionary finding in the branch of material sciences and engineering. It opens various promising areas in the field of material science, for example EMI shielding, electrical and thermal conductivity, microwave absorption, energy storage and self-healing composites [7–9]. Most commonly employed intrinsic conducting polymers are polyaniline (PANI), polythiophenes, poly(3,4-ethylenedioxythiophene) (PEDOT), polyphenylene sulfide (PPS) and poly(p-phenylene vinylene) (PPV) [10–15]. But, PANI is one of the widely used conducting polymer because of its ease of synthesis, unique electrochemical properties, low cost and environmental stability [16,17]. While in case of other conducting polymer, the stability and high cost of production bounds their use in structural applications. Electrically deposited PANI on silicon carbide surface can achieve the metal like conductivity [18] and PANI/single walled nanotube can serve as printable conductor for organic electronics device [19]. One of the most important uses of PANI is in the fabrication of conducting composite, which can be used in various structural as well as electrical applications [20–22]. Apart from this, dielectric properties and EMI shielding constitutes other attractive areas of PANI based composite [23,24]. However, on other hand, PANI has poor solubility in both melt and solution processing because of the rigid PANI chain structure. The poor solubility problem was solved by adding dopant which resulted in improved processability and miscibility [25]. Recently, Kumar et al [26–28] used PANI based matrix system in which PANI, dodecylbenzenesulfonic acid (DBSA), and divinylbenzene (DVB) used as conducting polymer, dopant and cross-linking monomer respectively. These PANI based composites by allowing modifications in their mechanical and electrical properties. Recently, many research groups have introduced carbon and metal nanoparticles to improve interfacial properties of PANI based composite [29–32]. In this direction, Chang et al. reported the improvement in electrical and mechanical properties of CFRP composite through synergistic effect of graphene oxide (GO) and PANI [21,33]. Petrovski and team have showed the synergistic effect of graphene and carbon nanotubes with PANI and reported the improved electrochemical performance of the nanocomposites [34]. Ashokan et al. demonstrated the enhancement in electrical conductivity of PANI/DBSA system by inclusion of CuO nanoparticles, and these composites can be further used for diode and solar device applications [35].

On the other hand, derivatives of GO have not been investigated as reinforcement in nanocomposites to a larger extent. The reduced graphene oxide (RGO) is an emerging nanomaterial because of easy synthesis, high surface area and electrical conductivity [36,37]. It is generally synthesized by high temperature thermal reduction of GO in inert atmosphere [38]. RGO has limited oxygen based functional groups, which make it a suitable candidate for development of composite with most of the polymers because of its ease of dispersion [39]. Also, it has a graphite-like structure which is responsible for electrical conductivity of polymer composites [40]. Recently, few research groups have used RGO with PANI polymer to improve its mechanical and electrical properties [20,41,42]. Liu et al. has reported the effects of RGO at different contents on mechanical

and electrochemical performance of RGO/carbon nanoparticles/PANI nanocomposites as well as on the RGO/CNT/PANI nanocomposites. He reported the improvement of 43% tensile strength in RGO/carbon nanoparticles/PANI nanocomposites compared to RGO/CNT/PANI nanocomposites with almost same electrochemical performance [41,42]. All the studies reported so far for RGO-PANI is deals with electrochemical properties of composite. There is no report on the mechanical and thermal properties of RGO incorporated PANI-DBSA/DVB polymer system which is the requisite properties for structural applications. Therefore, in the present study RGO incorporated PANI-DBSA/DVB nanocomposites are fabricated and their thermomechanical and electrical properties are studied. RGO was incorporated in different weight fractions in PANI-DBSA/DVB polymer system. The synergistic effect of RGO on mechanical, electrical and thermal properties of nanocomposites were investigated by different characterization techniques. Further, the effect of RGO reinforcement in nanocomposites were analyzed by using FTIR, Raman spectroscopy and correlated with morphology studied by electron microscopy (SEM and TEM).

2. Materials and experimental section

2.1. Materials

Commercially available graphite powder from Pure Carbon (from Pune, India) were used as a precursor for GO synthesis. Powder KMnO_4 (99% pure) and NaNO_3 (99.98% pure) from Thermo Fisher Scientific India Pvt. Ltd. used an oxidizing agent. The reaction solvent H_2SO_4 (98% v/v), ion removing solvent HCl (35% v/v) and reaction stopper agent H_2O_2 (30% v/v) were purchased from Thomas Baker Pvt. Ltd., Merck Specialties Pvt. Ltd. and RFCL Ltd. India respectively. The conducting polymer PANI and the dopant DBSA was provided by Regulus Co. Ltd., and Chemical Co. Inc., Tokyo, Japan respectively. The cross-linking agent DVB monomer was obtained from Sigma-Aldrich Co., St. Louis, USA. All the chemicals were used as they were procured.

2.2. Synthesis of graphene oxide and reduce graphene oxide

First, GO was synthesized by the chemical oxidation reaction using Hummer's method [43,44]. In this, mixture of commercial graphite powder (5 g) and NaNO_3 (2.5 g) in conc. H_2SO_4 (150 ml) was prepared. Oxidizing agent KMnO_4 (15 g) was added slowly to the reaction mixture with continuous stirring in the ice bath to control the highly exothermic reaction. After complete addition of KMnO_4 , the reaction mixture was stirred further for 24 h at 40 °C on magnetic stirrer and after that, temperature of reaction mixture was raised to 100 °C for 1 h while stirring. The reaction was cooled to room temperature, and 250 ml of distilled water was added. Finally, the reaction was stopped by adding 15 ml 30% H_2O_2 to the mixture. The acidic reaction mixture was diluted with 250 ml deionized water, and the solution was filtered. The filtered part was washed by 5% HCl solution five times to remove unreacted KMnO_4 and metal impurities. The filtered GO were dried in the oven at 80 °C for 24–30 h. The reduced graphene oxide was synthesized by heat treatment of GO at high temperature 750 °C in inert atmosphere for 15 min. Further, the temperature of furnace was raised to 1000 °C and reduction remains continued for 15 min at 1000 °C. RGO was collected after cooling the furnace to room temperature.

2.3. Preparation of RGO-PANI/DBSA-DVB nanocomposites

Initially, the desired amount of RGO was taken with a required volume of DVB, and this mixture was dispersed by ultra-sonication

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