Superior electromagnetic interference shielding effectiveness and electro-mechanical properties of EMA-IRGO nanocomposites through the *in-situ* reduction of GO from melt blended EMA-GO composites

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ABSTRACT

Fabrication of high-performance electromagnetic interference shielding efficient polymer-graphene nanocomposite is very challenging approach against electromagnetic pollution. Present work emphasizes on the preparation of *in-situ* reduced graphene oxide (IRGO) through *in-situ* melt blending of ethylene methyl acrylate (EMA) and graphene oxide (GO) to achieve enhanced shielding efficiency (SE) with controlled electro-mechanical properties of the composites. It involves the reduction mechanism of graphene oxide (GO) within polymer matrices, where efficacy highly influenced by methodologies, polymer chemistry as well as the processing parameters. 5 wt% IRGO loaded nanocomposite showed most improved shielding effectiveness (~30 dB) over the frequency range of 8.2–12.4 GHz whereas beyond this loading (7 wt%) the re-aggregation of the IRGO platelets cannot be ruled out due to high surface energy of the GO. High abundance of GO in polymer matrix can form better conducting pathways but due to lack of dispersion, the stress transfer during mechanical workout become inferior than other GO loaded composites. This hybrid nanocomposite fashioned 3D conductive network through segregated architecture in the matrix to commit lower conductive percolation with remarkable mechanical strength for its structural integrity. We believe this promising strategy of developing single step EMA-*in-situ* RGO (EIRGO) nanocomposites with enhanced shielding efficiency and amendable electro-mechanical properties can endorse large-scale production for techno-commercial applications.

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1. Introduction

Rapid procreation and implementation of electronic appliances and telecommunication technology emerges a new hazard known as electromagnetic interferences (EMI) which affect human life, electronic devices and medical instruments [1–5]. EMI shielding refers to the reflection and/or adsorption of electromagnetic radiation in wave form by a material which shields against the penetration of incident radiation. The high frequency electromagnetic waves, viz. radio waves from cellular phones incline to interfere with electronic devices. High performance flexible EMI shielding materials have utmost importance in civil and military applications [6–10]. Metals have the most significant shielding properties for

these purposes. But the main demerit lies on its corrosiveness, poor flexibility, high specific gravity, low chemical stability, low shaping capability and poor lasting tenure. Besides metals, some ceramic materials also exhibited superior radiation absorbing phenomenon. In this field ferrites are a common name [9,11–19]. These can be a very effective alternative for microwave attenuation and shielding applications because of their magnetic as well dielectric characters. Some ceramics having temperature mechanical property are also emerging star in this aspect, such as Si_3N_4 and SiC [20]. These features are well established when SiC has been boosted by fibers. Such materials are called fiber reinforced SiC or more precisely; ceramic matrix composites (CMC). These varieties can possess multi-scale tunable microstructure and tailorable fabrication methods [14,21]. In that context, polymer based shieling materials come ahead of technology. Especially, conducting polymers or conducting particles impregnated electro-conductive hybrid composites play a crucial role to commercially viable EMI shielding

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materials development [22]. Polymer composites having shielding effectiveness of 20 dB is required to provide uninterrupted functioning of the concerned object for commercial viability [8,23–25]. Incorporation of higher amount atomically thin graphene layer in polymer composite reflects an improved EMI SE because of their high aspect ratio, specific surface area, electrical conductivity with improved mechanical strength and carrier mobility due to long-range π-conjugation than other carbonaceous fillers [26–32]. High amount of filler loading affects both the processability and productivity. Segregated structure of graphene achieved high electrical conductivity at very low percolation by the formation of effective conductive network through the interfaces of polymer granules [33–35]. Pang et al. demonstrated that segregated network architecture of graphene enable to show very high conductivity of 0.04 Sm^{-1} at 0.6 vol% loading in UHMWPE composite [36]. Zhan et al. prepared graphene-natural rubber composite with high conductivity of 0.03 Sm^{-1} with improved mechanical strength of 23.3 MPa at 1.78 vol% graphene content through segregated morphology in latex [28]. Yan et al. also represents a very facile method to prepare *in-situ* thermally reduced graphene/UHMWPE composite of 28.3–32.4 dB EMI SE at very low percolation of 0.66 vol% due to segregation of RGO [37]. Although segregated structure enhances the conductivity and EMI SE of the composites at very low filler loading than the homogeneously dispersed one but it reduces the mechanical property by obstructing the diffusion of polymer chains through the matrix, which directly affects in commercial applications [38–42].

Wide variety of commercial methods have already been implied to prepare polymer-RGO composites like chemical or thermal reduction, microwave assisted reduction of graphene oxide followed by the incorporation of nano-filler into polymer matrices by solution compounding, melt blending and *in-situ* reduction during processing to get improved EM properties, thermal stability, mechanical strength and chemical resistance [15,43–53]. Thermal reduction of graphene oxide is much more favorable than the chemical method for large scale production because of its easiness in fabrication and environmentally friendly approach but they showed low electrical conductivities due to uneven distribution of RGO within polymer [54–60]. Dispersion of single-layered graphene in the polymer matrices by melt-blending is a daunting approach. Some works have been reported on master-batch melt blending technique to prepare composites of increased thermal, mechanical properties with enhanced glass transition temperature [61–64]. Yan et al. fabricated polymer-RGO composites for high performance EMI SE by applying very high pressure of 350 MPa than the conventional pressure [65]. To the best of our knowledge, no one yet reported preparation of polymer *in-situ* RGO (Polymer-IRGO) composite by single-step melt blending method to achieve improved electromechanical (EM) properties with enhanced EMI SE at very low percolation threshold.

In this contribution, we accentuate on the preparation of EIRGO nanocomposite by one step melt blending method and fine-tuned the dispersion to get improved EM properties, thermal properties with effective SE. Presence of polar groups in EMA assists strong interaction with nanofiller surfaces via hydrogen bonding. Excellent ageing and weather resistant, high processing temperature (160 °C - 230 °C of maximum 310 °C) draws a great attention to choose EMA for single step melt blending to fabricate polymer-IRGO composite [66]. Very high strength to weight ratio along with low density balance the disadvantage of improved mechanical strength by segregated structure obtained in the conventional method. The work focused on detailed analysis of reduction mechanism, evaluation of structure-property relationship of IRGO in EMA matrices to optimize the properties of filled composites. Aim of this work includes incorporation of GO (prepared by

Marcano et al. method) in EMA at an elevated temperature of ~210 °C by single step melt blending to fabricate EIRGO nanocomposites with adjustable EM, thermal properties and improved EMI SE for commercial applications, by applying conventional pressure during molding [67].

2. Experimental

2.1. Materials

Ethylene methyl acrylate (EMA), Elvaloy® 1330 (30% methyl acrylate), having melt flow index (at 190 °C/2.16 Kg) of 3.0 g/10 min (ASTM D 1238) was purchased from DuPont, India. Graphite Flakes (98% pure) was procured from Loba Chemie, India. Other reagents and solvents were obtained as analytical grades products. Potassium permanganate ($KMnO_4$, crystalline form, > 99%), H_3PO_4 (>99%), H_2SO_4 (96%) and H_2O_2 (30%) were obtained from Merck, Germany.

2.2. Fabrication of ethylne methyl acrylate in-situ reduced graphene oxide (EIRGO) nanocomposite

The synthesis of graphene oxide was done by the following method developed by Marcano et al. In a typical procedure natural graphite flake and potassium permanganate was mixed in 1:6 and added it to a precooled sulfuric acid and phosphoric acid (9:1) mixture. The solution was heated at 50 °C for 20 h in an oil bath. After adding water and 30% hydrogen peroxide the dark purple slurry of excess permanganate was destroyed and the mixture became yellow. The mixture was washed with distilled water to maintain pH ~6–7 and dried in vacuum oven at 80 °C for 15 h to get graphene oxide (GO). Different amount of graphene oxide (1, 3, 5 and 7 wt% with respect to base polymer) were added separately to EMA in Brabender Plasticorder internal mixer (PLE-330, attached with cam rotor, having torque measuring range of 200 Nm and speed range from 0.2 to 150 min^{-1}) to prepare EIRGO nanocomposites with variable loadings of nano-filler. All compositions were melt-blended for 20 min at 210 °C with rotor speed of 70 rpm to split nano-layers for achieve higher level of dispersion (Scheme 1). After mixing all products were passed through two roll mill to prepare compounded sheets at room temperature. The sheets were molded in a hydraulic press (Moore press, United Kingdom) at 200 °C for 15 min under 5 MPa pressure with average thickness ~5.0 mm.

2.3. Characterizations

Chemical structure of graphite flakes, GO and EIRGO, EGO composites were carried out on Perkin Elmer FTIR spectrometer (model-Spectrum-2, Singapore) in ATR mode. X-ray diffractions of EMA and IRGO composites with variable loading was performed in X'Pert PRO diffractometer (PANalytical B.V., The Netherlands) at a scanning rate 0.005°/s. Raman spectra of graphite, GO and RGO were recorded in Trivista 555 spectrograph (Princeton Instruments). Morphological characterizations of EIRGO composites were conducted in FESEM (Field Emission Scanning Electron Microscope, MERLIN with tungsten filament; Carl ZEISS, SMT, Germany), HRTEM (JEOL, Japan, tilt angle 24°, operated at 200 kV, filament LaB_6) and an intermittent contact mode AFM (Atomic Force Microscopy, Agilent 5500 Scanning Probe Microscope). Tensile properties of the composites and unfilled EMA were carried out in Universal tensile testing machine (Hounsfield H10 KS) at room temperature. All the dumb-bell shaped specimens were tested according to specifications of ASTM D412 and ASTM D624 with constant crosshead speed of 500 mm min^{-1}. All results were