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Enhanced electromagnetic interference shielding effectiveness of carbon-based conducting polymer nanocomposites

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Abstract. Carbon is always a fascinating material, the allotropes of carbon family like fullerenes, graphite, graphene, carbon nanotubes and various fillers that improve the Electromagnetic interference (EMI) shielding is of large interest in various frequency band. In the present work, initially Multiwalled Carbon Nanotubes (MWCNT) and Graphene (GNS) were functionalized to improve the interaction of conducting polymer. Polyaniline (PANI)/(MWCNT) and Polyaniline (PANI)/(GNS) were synthesized by in situ oxidative polymerization method and then characterized by SEM analysis. The electrical conductivity of the nanocomposites increases with increase in weight percent of CNT or GNS as compared to pure polyaniline. The carbon based conducting polymer nanocomposites showed semiconducting nature with enhanced EMI shielding effectiveness. The EMI Shielding effectiveness (SE) of carbon based conducting polymer nanocomposites increases with increase in weight percent of CNT or GNS. For both the nanocomposites PANI/MWCNT and PANI/GNS absorption is the mechanism which is dominant which can be used as an Electromagnetic Interference Shielding material.

1. Introduction

The rising requirement of high standard of electronic and communication devices in various fields of military, industry, and commercial applications led to compactness of electronic devices and systems this increases the complexity of the circuit. This offers a new kind of challenge that makes us to make a lot of efforts to come up with, that is the electromagnetic radiation. These electromagnetic radiations interfere and may harm the system, which is called electromagnetic (EM) pollution. Electromagnetic Interference is a severe basis of concern as it affects the activity of a device or transmission channel. The progress of a range of materials for electromagnetic interference (EMI) shielding applications has been initiated by the scientific and research communities to overcome this problem. For this several materials, such as metals, carbon derivatives and polymer nanocomposites, have been extensively explored recently. Polymer based nanocomposite shielding materials are beneficial over the usual metal based shielding owing to its low density, corrosion resistivity and simple processability [1]. The tunable dielectric and magnetic attributes, light weightless and low cost of conducting polymer-based composites gained the huge importance as EMI shielding materials. The properties can promote additional modification by varying nature of dopant, by merging comonomers or by controlling reaction conditions. Among the conducting polymer PANI has special status due to its non-redox doping property, superior environmental steadiness and economical practicability [2]. Now, a day polymer research is exploring the synergetic outcome of nano reinforcement in improving the range of properties of polymers. Carbon derivatives, among various nano reinforcement, shows a potential substitute for reinforcing polymers due to its exceptional mechanical properties, heat



resistance, low density, high aspect ratio and high surface area. The properties of carbon derivatives based nanocomposites robustly depend on the dispersal state of carbon derivatives in polymer matrix and on the interfacial interface between carbon derivatives and polymer [3, 4]. In aerospace and automotive where a weight reduction is extremely crucial matter, CNT and GNS are in recent times being considered as capable flawless nanoscale filler due to their properties in polymer composites. CNTs have fascinated due to their unique structural and electronic properties. CNTs hold diameter dependent specific surface area that offers existing surface area for interface when incorporated into the polymer which modulates the matrix properties in considerable way [5, 6]. The thinnest two-dimensional material discovered so far is Graphene. It is a 2 dimensional carbon nanomaterial with a shape of honeycomb lattice. It is consisting of carbon atoms in sp^2 hybrid orbital [7]. Graphene shows extremely good mechanical stiffness and chemical stability. The large specific surface area, low density high electrical conductivity and exceptional electromagnetic interference shielding effectiveness made the material more attractive [8]. Fayzan et al performed Electromagnetic Interference shielding measurements of PVC/PANI/GNP composites in range of frequency 10 MHz – 20 GHz and found to be ~ 51 dB [9]. Ji-Hwan et al synthesized G-PDMS composites by three-roll milling method and EMI Shielding Effectiveness of composite was 25 dB in frequency range 1.0–3.0 GHz [10]. Zhikang et al produce a Graphene/Polyurathene (PUG) sponge through a two-step hydrothermal reductive chemical reaction with an excellent EMI shielding effectiveness of 33 dB [11]. However, in the present work we studied the morphology, electrical conductivity and Electromagnetic Interference shielding effectiveness of PANI/MWCNT as well as PANI/ GNS nanocomposites in Ku band.

2. Experimental

2.1. Materials

The chemicals purchased were of Analytical Reagent grade, Aniline ($C_6H_5NH_2$), sulphuric acid (H_2SO_4), nitric acid (HNO_3) and ammonium persulfate [$(NH_4)_2S_2O_8$] were obtained from Merck Limited., India. From NPL, New Delhi (India), Graphite flakes and CNTs were made accessible. Distillation of Aniline was done under reduced pressure and kept below $4^\circ C$. In every synthesis process distilled water were used.

2.2. Synthesis of Graphene Nanosheets (GNS) and Functionalization of CNT and GNS

By using Hummers method graphite oxide (GO) were synthesized by means of graphite flakes. The exfoliations of graphene oxide were done to prepare graphene nanosheets (GNS) [12]. For surface alteration, functionalization of nanofillers is an effective way to develop the interfacial contact and bonding; it also helps to achieve the regular dispersal of CNTs and GNS [5]. The CNTs and GNS (filler) have restricted surface functional groups on their surface for building the chemical contact with polymer. Hence, CNTs and GNS were functionalized by acid treatment. For the functionalization of CNTs, the solution of 6 mole of sulfuric acid and 6 mole of nitric acid in 3:1 ratio were kept on magnetic stirrer for 30 minutes. In the stirred solution, CNTs were added and then solution was sonicated for 4 hours at $40^\circ C$. once the sonication is over the solution were centrifuge, so that the CNTs settled down. CNTs were filtered, washed with distilled water and dried to get functionalized CNTs [13]. Similarly, the procedure for the functionalization of GNS was followed and is reported in our earlier work [14].

2.3. Synthesis of PANI/CNT and PANI/GNS composites

An in-situ chemical oxidative polymerization method was used to synthesize PANI/CNTs composites. The weight percent of CNTs to aniline was varied from 1%, 3% and 5%. The solutions of 0.2 mole of sulfuric acid in 50 ml of distilled water were prepared. The solution was equally divided in 2 parts. In one part 0.2 mole aniline and functionalized CNTs were added and the mixed solution was ultrasonicated for 30 minute. Later on, mixture was kept for stirring for 5 hrs. To another part 0.2 mole ammonium persulfate was mixed.

To the stirring monomer, solution of APS was added drop by drop. The whole assembly was kept at low temperature to get the more yield. When the reactant completely added to the solution, greenish tint color was obtained and later it turns violet. After 6 to 7 hrs the black precipitate was obtained. The black precipitate were kept for about 15 hours and diluted with distilled water. The solution were filtered and washed until the filtrate became colorless. lastly, black precipitate was washed with ethanol and dried out for the night in oven at 80 °C [13, 15]. Similarly, the complete procedure is repeated for PANI/GNS synthesis. The synthesis were conducted and reported in our earlier work [16].

3. Results and discussion

3.1. Morphology

The surface morphology of PANI / MWCNT and PANI/ GNS composites were studied by SEM is shown in the figure 1. The micrograph of multi-walled carbon nanotubes shows that the diameter of nanotubes varies from 50-100 nm and length is few microns as shown in figure 1(b). The figure 1(c) micrograph shows that the MWCNTs were well dispersed in the composite. There was a homogeneous coating of polyaniline on MWCNTs indicating the good interface between nanotubes and polyaniline and shows interweaved fibrous arrangement with the diameter in the range of numerous tens of nanometer and length up to several micrometers. These networks give rise to conductive pass ways and lead to highly conductivity. The functionalized in figure 1(d) GNS is observed as a lustrous, glossy and crumpled sheet. Also in the figure 1(e) SEM images of PANI/GNS composites, it is observed that a large amount of GNS surface was covered with a evenly thin polyaniline layer and few regions of surface of GNS were deposited with polyaniline.

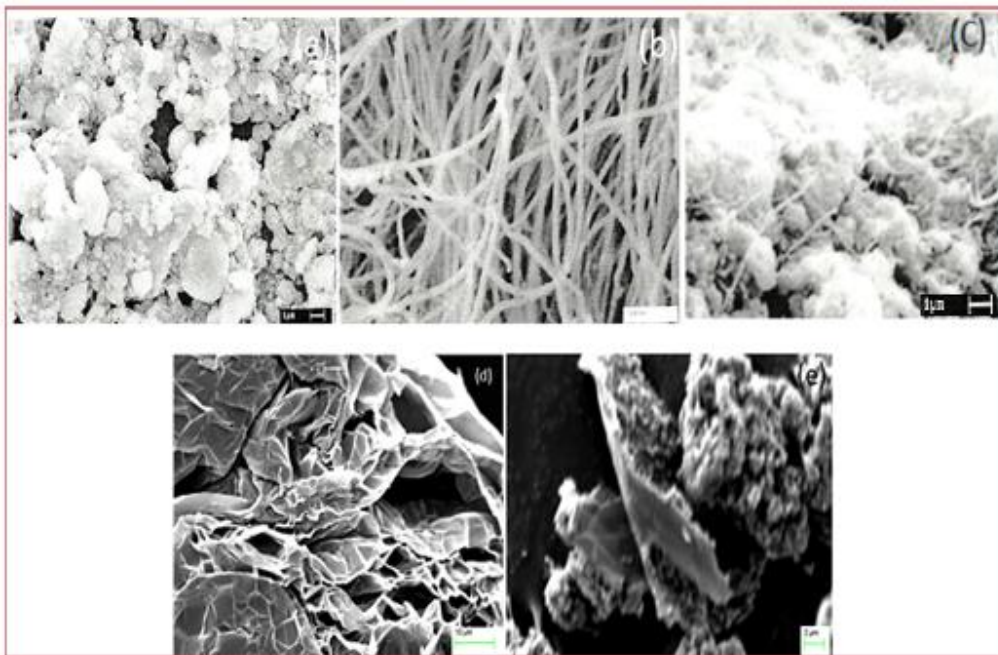
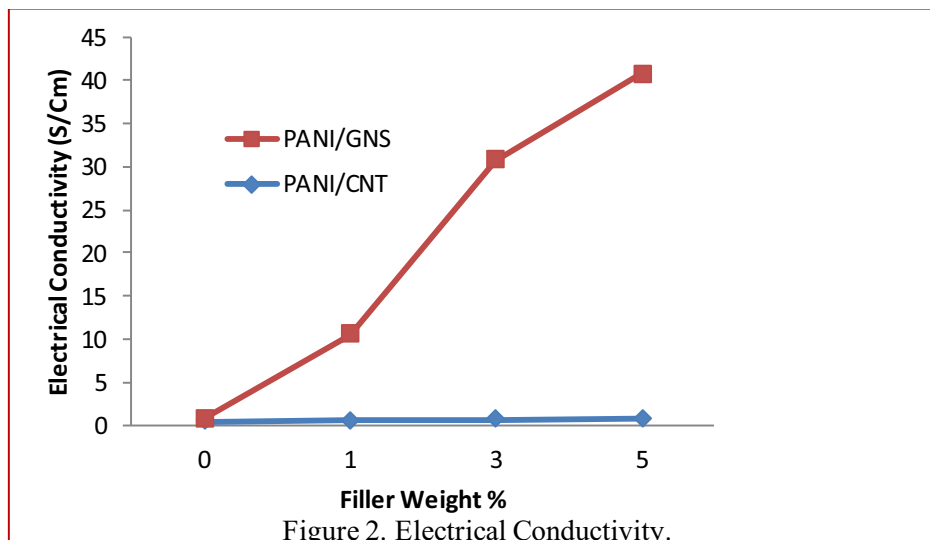


Figure1. SEM images (a) Pure PANI, (b) Functionalized MWCNT, (c) PANI/MWCNT, (d) Functionalized GNS, (e) PANI/GNS

3.2. Electrical conductivity

Basically, electrical conductivity level of carbon derivative is determined by sp^2 hybridization or graphitization as graphite is sp^2 hybridized and good conductors. The extremely conductive nano forms of carbon (MWCNT, SWCNT, GNS, etc) with high specific surface area confirmed as most admirable additives of carbon in performance of a range of devices [17]. The deviation of electrical conductivity of nanocomposites with increasing filler content was studied using four probe electrical conductivity meter. The round shaped pellets of synthesized nanocomposites were prepared at room temperature. Both the PANI/MWCNT as well as PANI/GNS nanocomposites composites showed improvement in electrical conductivity as compared to polyaniline. It is clearly observed that with the increasing the weight percent of carbon derivatives (MWCNT and GNS) electrical conductivity is also increases, the growth was found to be linear, these result also shows that high concentration of carbon derivatives gives superior network for electrical conduction [7]. The significant improvement of electrical conductivity enriches the lightweight PANI/MWCNT and PANI/GNS with high-quality electromagnetic interference (EMI) shielding efficiency.



3.3.

Electromagnetic Interference Shielding Effectiveness

Electromagnetic interference shielding effectiveness (SE) is the reduction of electromagnetic (EM) waves by shielding material [18]. The total shielding effectiveness (SE_T) of an EMI shielding material is the contribution of three mechanisms, shielding effectiveness due to reflection (SE_R), shielding effectiveness due to absorption (SE_A), and shielding effectiveness due to multiple-internal reflections (SE_M). The absorption being primary mechanism and reflection is secondary mechanism [19, 20]. The schematic representation of Electromagnetic Interference shielding mechanism is shown in figure 4. SE_M mechanism can be neglected if SE_A is greater than 10 dB.

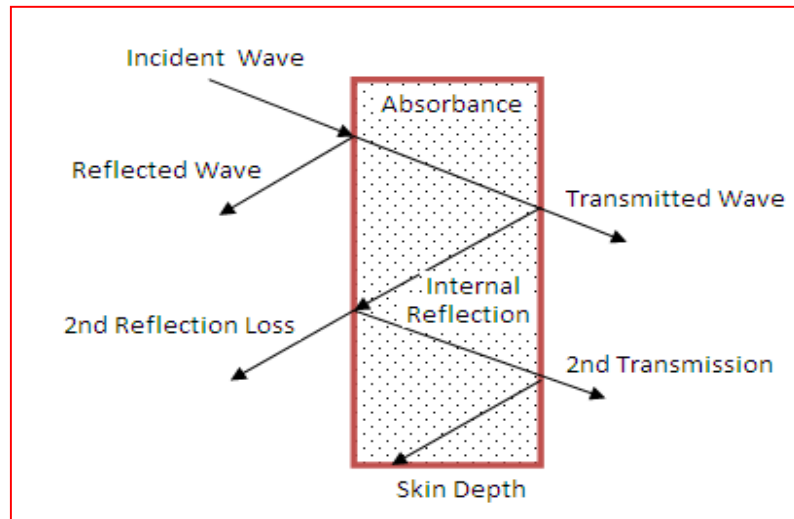


Figure 3. Schematic representation of EMI shielding mechanism.

SE measurements were done in the range of frequency 12 to 18 GHz i.e. Ku band. Figure 4 shows the total shielding effectiveness of nanocomposites PANI/MWCNT and PANI/GNS as a function of frequency with increasing filler contents. The experimental results were studied and observed that absorption mechanism is more dominating over reflection mechanism. The functional group on the functionalized filler makes composite more conductive which is responsible for the absorption dominance. The SE_T of nanocomposites reveals that, the total shielding effectiveness for all composition is almost linear with frequency. The total shielding effectiveness of nanocomposites is observed to be increasing by means of the addition of filler content. In both the kind of composites it was observed that the total shielding effectiveness is dominated by the absorption phenomena.

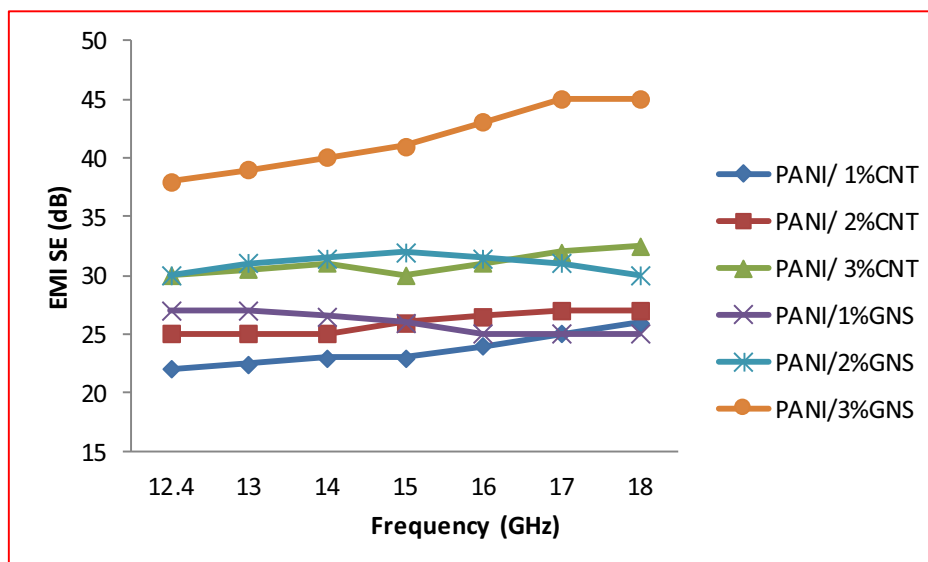


Figure 4. Total Electromagnetic Interference Shielding Effectiveness.

4. Conclusion

The nanosized fillers (MWCNT and GNS) are dispersed in polyaniline to reside in large number of sites in the polyaniline matrix and enhanced the electrical conductivity of the nanocomposites. The total electromagnetic interference shielding effectiveness (SE_T) of PANI/GNS was observed to be comparatively improved than PANI/MWCNTs nanocomposites. The required value of SE_T is 20 dB) for commercial applications. In both the nanocomposites obtained value of SE_T is greater than the essential EMI shielding effectiveness value. The results showed that absorption mechanism is dominated over other two mechanisms, signifying PANI/GNS and PANI/CNTs nanocomposites can be used as weightless electromagnetic interference shielding materials.

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