Tunable EMI shielding effectiveness using new exotic carbon: Polymer composites

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ABSTRACT

β-Naphthalene sulfonic acid (β-NSA) doped polyaniline (PANI) composites having different carbon fillers such as MWCNTs, carbon fiber (CF), reduced graphene oxide (rGO) have been prepared by chemical oxidative polymerization route. SEM images demonstrate that β-NSA leads to the formation of the tubular structure with incorporated MWCNT, CF and rGO. TGA studies show the improvement in thermal stability of the composites. Shielding effectiveness were calculated using S-parameters obtained from the Vector Network Analyzer (VNA) in 8.2–12.4 GHz frequency range. The maximum shielding effectiveness achieved for PANI composites along with MWCNT, CF, rGO was 37, 31 and 39 dB respectively.

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1. Introduction

The tremendous boom of electronic gadgets utilizing wi-fi and bluetooth technology such as cell phone, tablet, laptop, smart television etc. as well as accelerated growth of transient power resources gave birth to electromagnetic interference (EMI), which causes most undesirable consequences in terms of electromagnetic radiation pollution in the modern society [1, 2]. In order to minimize radiation pollution to create a safer and healthier environment, it is critical demand of present time to develop some new materials, which have better absorption characteristics in the microwave frequency range [3]. Thus, selective frequency radiation shield are playing an important role for the proper operation of electronic devices in all industrial as well as strategic sectors. Recently, electromagnetic interference (EMI) shielding in microwave range has become the most important concern for the researchers. Therefore, they develop lightweight, portable, flexible, corrosion resistant, cost effective and easy to process EMI shielding materials to protect sensitive circuits and to defend the workspace and environment from unwanted radiation coming from electronic equipment [4–8].

To mitigate the EMI shielding problem, In the last few decades, polymer carbon composites have been extensively explored for various applications in different fields, e.g., composites with different carbon forms such as carbon fiber, multiwalled carbon nanotubes (MWCNT) [9], reduced graphene oxide (rGO) [10, 11] and carbon black have been synthesized using in-situ polymerization in the presence of specific dopants/surfactants [12]. Dopants play a crucial role in designing shape, size as well as physical properties of polymers. It has been recently shown that promising shielding performance could be achieved with composites comprising of an electrically conducting polymer matrix filled with conducting, magnetic and dielectric materials such as CNT-polymer composites, nickel ceramic composites etc. However, high filler contents are required from 10 to 15% for fibers and 30% for spheres to reach a percolation level leading to microwave losses. These materials are generally compared to each other with respect to their imaginary part of permittivity ($\varepsilon''$) or loss tangent ($\varepsilon''/\varepsilon'$). For years, carbon nanotubes (CNTs) have been used as reinforcement material in polymer matrices to enhance the mechanical and electrical properties of the latter [13–15]. Although, CNTs have received much attention as they impart insulating polymers with high electrical and EMI shielding properties, their further application is hampered due to the cost, impurities because of catalyst, intrinsic bundling and aggregation. To enhance the properties of conducting polymer
for developing EMI shielding material, intensive efforts have been made on polymer carbon composites using graphite and carbon black [16–18].

This manuscript discusses the synthesis of MWCNT, EG and CF filled in polyaniline (PANI) tube core-shell structure useful for microwave absorption. The selection of the different materials to synthesize the present composites has been based on systematic experimental efforts as well as the associated properties of these compounds to fabricate the desired material with all required property for EMI shielding in a single composite.

2. Experimental

2.1. Synthesis of carbon fiber-PANI, MWCNT-PANI and rGO – PANI composite

The chemical oxidative polymerization of aniline was carried out to prepare PANI composites. β-NSA was used as a dopant without an external template. A typical preparation process for PANI composite is as follows: 0.3 M solution of βNSA and calculated amount of MWCNT or was homogenized (ART MICRRA D8 rotating at 15000 rpm for 2 h) to obtain a uniform suspension containing RF particles. 0.1 M aniline has been added and stirring continued for another 1 h to form an emulsion. The aniline–β-NSA mixture containing filler particles were cooled in an ice bath for 2 h before oxidative polymerization. Finally, the oxidant APS (0.1 M) was added drop wise to the above solution keeping the temperature of the reactor at 0 °C with vigorous stirring for 10 h. The green polymer precipitates so obtained were treated with methanol in order to remove oligomers. The resulting precipitate was filtered and washed thoroughly till the filtrate became colorless and then dried at 60–65 °C in a vacuum oven for 24 h. Throughout the experiment, the molar ratio of aniline to β-NSA and APS was maintained at 1:3 and 1.0, respectively. However, the concentration of MWCNT, CF and rGO was chosen 1:1 with respect to monomer and compositions were abbreviated as PCNT, PCF, and PrGO, respectively. Schematic representation of incorporation of MWCNTs, CF and rGO into PANI matrix is shown in Fig. 1.

3. Results and discussion

3.1. SEM analysis

Scanning electron microscopy has been carried out for exploring the surface morphology PANI composites. Fig. 2 shows the SEM micrograph of MWCNT, CF, rGO, PMWCNT, PCF and PrGO. The average diameter and length of individual MWCNT used for composite material are 60 nm and 15 μm, respectively, as shown in Fig. 2 (A). Fig. 2(C) and (E) shows the pristine morphology of CF and rGO plates. Fig. 2(D) exhibits the homogenous distribution of MWCNTs throughout the PANI matrix. The estimated particle size of rGO has been found to be few micrometer as shown in Fig. 2(C). SEM image of PANI composites synthesized in the presence of β–NSA reveal an interesting morphology featuring formation of tube like structure. Densely packed tubes have a range of diameter and length of ~0.5–2 μm and up to 15 μm, respectively. SEM micrograph of PANI composites reveals that MWCNTs, CF and rGO are entrapped within the PANI matrix. Therefore, the length and the diameter of the tubes vary depending on the nature of the filler.

3.2. Structural analysis

Fig. 3 (a) shows the XRD patterns of rGO, MWCNT, CF, PANI, and PANI composites. PANI shows two broad peaks at 2θ = 19.795° (d = 4.481 Å) and 25.154° (d = 3.537 Å), which reveals its amorphous nature. The XRD patterns of MWCNT shows reflection peaks at 2θ values of 26.5° and 42.64° corresponding to (0 0 2) and (1 0 0) diffraction planes, respectively. The presence of rGO is confirmed by the broad peaks at 2θ = 26.44° (d = 3.368 Å), 2θ = 54.599° (d = 1.679 Å). The XRD patterns of CF shows two main peaks at 26° and 43.5° confirming the graphitic nature of CF. The peaks present in CF, MWCNT and rGO have also been observed in their respective PANI composite which indicate the incorporation of these particles in the PANI matrix.

3.3. TGA analysis

TGA of the PANI doped with β-NSA and PANI composites has been carried out in order to investigate the improvement in the thermal stability of PANI composite by the incorporation of fillers (rGO, MWCNT and CF). Fig. 4 shows the thermograms of CF, rGO, MWCNT and their respective PANI composites. Before TGA measurements, all the samples were kept in a vacuum oven at 100 °C for 5 h. Therefore, thermograms of the entire samples show no wt. loss before 120 °C due to absence of moisture. Thermograms of PANI and its composites show two major weight losses. In case of pristine PANI, the first weight loss observed at 230 °C is due to loss of dopant from the polymer matrix and the second major loss from 530 °C has been attributed to the destruction of polymeric backbone. The total weight loss in this case is ~99%. PANI doped with NSA is thermally stable up to 230 °C. Among the carbon fillers, CF shows the highest thermal stability as almost no wt. loss has been observed in CF. rGO shows the thermal stability upto 700 °C, afterward a small weight loss is observed. Good thermal stability is due to the thermal reduction of GO at 700 °C.

Finally, MWCNT shows a 25% weight loss which is attributed to the catalyst present in MWCNTs. However, when PANI was synthesized by the incorporation of CF in the reaction system along with the surfactant, the thermal stability of PANI-CF composite improved and reached 220 °C. The PANI composites show multi-step weight loss corresponding to the loss of different species. It has

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**Fig. 1.** Schematic representation exhibits the synthesis of PANI composites.
been observed that the thermal stability of the polymer composites is highly improved with the filler loading. This shows that, in-situ polymerization of aniline in the presence of carbon fillers leads to a more thermally stable conducting polymer.
3.4. Conductivity measurement: four probe method

The room temperature electrical conductivity of PANI composites is more than pristine PANI (Table 1). This is attributed to two reasons. Firstly, the all the exotic carbon forms (MWCNT, CF and rGO sheets) possess very good conductivity. Secondly, the conducting network is improved by filler loading resulting in enhancement of electrical conductivity of the composites. Most importantly, these samples show optimum value of conductivity which is desired for exhibiting good microwave shielding response [19–21].

3.5. Electromagnetic shielding measurement

EMI SE of PANI composites have been evaluated using equations given elsewhere [3]. In brief, the EMI Shielding effectiveness of a shield is measured as the logarithmic ratio of incoming power (Pi) to outgoing power (Pt) of radiation and expressed in decibels (dB). Mathematically, shielding effectiveness is a negative quantity as Pt is always less than Pi.

When a shield is activated using microwave radiation, phenomena namely transmission, reflection, and absorption can be observed [22,23]. Out of them, shielding effectiveness of a shield is shared by reflection as well as absorption and can be written as [24–26].

\[ SE_T (dB) = SE_R + SE_A = 10 \log \left( \frac{P_t}{P_i} \right) \]  

Table 1 gives the comparison of electrical conductivity and average EMI shielding effectiveness (SE) (averaged over 201 data points from 8.2 to 12.4 GHz) of the different composites. The value of EMI SE for PANI, PCF, PCNT and PrGO is 25.44, 35.77, 30.02 and 39.27, respectively as shown in Fig. 5. This total shielding is shared by both SE due to absorption and SE due to reflection as shown in Fig. 6. From Fig. 6 it is concluded that the total shielding effectiveness is conquered by absorption. But the shielding mechanism in PCF, PrGO and PCNT is quite different. In case of pristine PANI and PCF, the SE is mainly attributed to orientational and space charge polarization. The contribution to the orientational polarization is due to the presence of bound charges (dipoles). In conjugated polymers, two types of charged species are present, one polaron/bipolaron system that is mobile and free to move along the chain, others are bound charges (dipoles) which have only restricted mobility and account for strong polarization in the system [27]. When the frequency of the applied field is increased, the dipoles present in the system cannot reorient themselves fast enough to respond to the applied electric field and as a result, attenuation occurs. In the case of PCNT and PrGO: MWCNTs and rGO, both contain the defects which may construct localized states near to the Fermi level to increase the radiation attenuation [28]. The microstructure investigations show that the rGO contains clustered defects and residual bonds arising from oxidation process [29].

There are more oxygenic functional groups on the r-GOs which might increase the EM wave attenuation performance. Meanwhile, because of the least thickness and high electron mobility, rGO has higher specific surface area and higher hopping conductivity which induces strong polarization loss are conductance for the EM wave [28]. Therefore, PrGO shows the maximum SE among all the PANI composites. In brief, radiation attenuation in PANI composites are the result of complex phenomena like natural resonance, dipole relaxation, electronic polarization and its relaxation, polarization of polarons and bipolarons in the polymer matrix and their relaxation and certainly the unique structure of the shield. The schematic representation of the attenuation of EM wave is depicted in Fig. 7.

4. Conclusion

The CF, MWCNTs and rGO were successfully incorporated in the PANI using micro emulsion method. The SEM investigation confirms core–shell tubular structure of PANI and conformal coating of PANI on rGO, MWCNTs and CF. The core-shell tubular structure of PANI composites attributes the enhanced interfacial polarization and the effective anisotropy energy of the composite as a result of which more and more scattering occurs which leads to the high attenuation. Thus, the obtained results suggest that among the PANI composites rGO is the best candidate than MWCNTs and CF for microwave shielding with vast utility in radio frequency range.
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