# Dielectric properties of epoxy based composites containing graphite, graphite oxide and thermally exfoliated graphene oxide

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# Abstract

The discovery of graphene and subsequent development of graphene-based nanocomposites in different matrices including that in polymer is an important addition in the area of nanoscience and technology. This work deals with the studies on the dielectric properties of the nanocomposites of graphite, graphite oxide (GO) and thermally exfoliated graphene oxide (TEGO) in epoxy matrix. GO was synthesized using modified Hummers method which on heat treatment at ~300  $^{\circ}$ C resulted into formation of graphene oxide termed as TEGO. The synthesized GO and TEGO were characterized using scanning electron microscope, energy dispersive X-ray, Fourier transform infrared spectrophotometer, Raman spectrometer, X-ray diffractometer, UV-Vis spectrometer, CHNSO analyzer, surface area analyzer, and dc electrical conductivity. Composites using graphite powder (GP), GO and TEGO individually were prepared in epoxy resin. The dielectric (dielectric permittivity, dielectric loss tangent) properties of composites were studied in frequency range of 8 - 12 GHz. Dielectric tangent loss (tan $\delta_{\epsilon}$ ) vary from 0.02 for GP to 0.35 for TEGO. The effect of addition of GP to GO and TEGO composite on dielectric properties was investigated. The order of tan $\delta_{\epsilon}$ values of composites is: TEGO > GP-TEGO > GP-GO> GO >GP. TEGO composite showed significant dielectric loss among the reported composites. The results thus indicate TEGO as filler for epoxy based composites to afford specific dielectric properties, especially as an alternative of much more expensive carbon nanotubes. Copyright © 2018 VBRI Press.

Keywords: Graphite oxide, thermally exfoliated graphene oxide, epoxy, composite, dielectric loss.

#### Introduction

Graphite is the most stable, crystalline form of carbon with layered, planar structure and C-atoms are arranged in a honeycomb lattice in each layer. Graphene, single layered form of graphite, has been considered the 'mother of all carbon forms' as a building block. Graphene research has developed at a very rapid pace during the last several years. High-purity and near-pristine graphene are usually prepared by the physical routes such as mechanical exfoliation, epitaxial growth and vapor deposition process [1-3]. However, large-scale production of graphene sheets at low cost is still a challenge. A chemical route for the bulk production of graphene via graphene oxide is more favoured by chemists but there are more defects on graphene sheets prepared by this route. Nevertheless, graphene produced by this method, is convenient to cast into various structures or to integrate with other materials to prepare novel nanocomposites.

Graphene, a novel two-dimensional carbon material has triggered enormous interest due to its many

extraordinary properties [4] such as high carrier mobility[5], mechanical stiffness [6,7] and intriguing electromagnetic response [8-10]. The unique electrical properties of graphene enable the development of advanced materials for microwave attenuation and electromagnetic interference (EMI) shielding. The microwave absorption of a composite material is usually believed to depend on relative complex permittivity and permeability, impedance mismatch condition, intrinsic characteristics of filler and electric conductivity of the composites [11]. It is expected that large aspect ratio and high intrinsic electric conductivity could render graphene or graphene-based materials very promising as a new type of strong and lightweight EM wave absorption materials [9, 10, 12-14]. However, the study finds out that the maximum reflection loss of sole Graphene is only -6.9 dB, because its good electric conductivity becomes a disadvantageous factor according to the impedance match mechanism [15]. Chemically reduced graphene in low loading (~3 vol%) in a polymer matrix is reported to show

high microwave absorbing capacity [16]. On the other hand graphene-epoxy composites with 15 wt% of graphene loading exhibited high EMI shielding effectiveness ~21dB over X-band [17]. Zhang et al have demonstrated the broadband and tunable highperformance microwave absorption property of an ultralight and highly compressible graphene foam [18]. Graphene/polyaniline nanorod arravs showed improved EM absorption properties in comparison graphene [19]. RGO/CuS/PVDF composites to synthesized using a simple hot-press by Zhang et al exhibited high values of reflection loss [20]. Graphite flakes has also been explored for microwave absorption and reported to produce significant return loss [21]. Hence, the analysis of electromagnetic properties of composites based on graphite and graphene or thermally reduced graphene oxide in polymers matrices are very popular topic in material sciences.

Since preparation of TEGO and its hybrid with graphite and graphite oxide and their dielectric properties in microwave region is not much reported as of now, this paper is focused on exploration of the dielectric properties of GP, GO and TEGO/epoxy composites in microwave region (8-12 GHz). The effect of adding GP to GO and TEGO composite on dielectric properties was also investigated. There are very few reports on this research theme to the best of our knowledge. For the elementary study, it is worth to study new and unexplored composite systems for dielectric properties that can broaden further research on this subject and becomes our major incentive for this work.

## Experimental

#### Materials

Graphite powder (mesh size 50 micron), sulfuric acid (assay, 98.0%), phosphoric acid (assay, 85%), sodium nitrate (99% GR), potassium permanganate (99% GR), hydrogen peroxide (30%). All chemicals were procured from Merck, India and used directly without further purification to synthesize graphite oxide. Epoxy resin was used as matrix for composite preparation. Epoxy resin (Synpol Epoxy 450X) was supplied by M/s Synpol Products Pvt. Ltd., India.

## Preparation of graphite oxide and TEGO

GO was synthesized from GP using modified Hummer's method [22]. In brief, 6 g of sodium nitrate were mixed into 230 ml of conc. sulphuric acid and phosphoric acid (9:1 weight ratio) under constant stirring followed by the addition of 10.0 g of graphite. After 4 h, 30 g of KMnO<sub>4</sub> was added gradually to the above solution while keeping the temperature below 20°C. The mixture was stirred at ~  $35^{\circ}$ C for 48 h and the resulting solution was diluted by adding 460 ml of water under vigorous stirring. To ensure the completion of reaction with KMnO<sub>4</sub>, the suspension was further treated with 5 ml H<sub>2</sub>O<sub>2</sub> solution (30%). The resulting mixture was filtered and residue of GO was washed repeatedly with HCl and H<sub>2</sub>O, followed by drying, GO was thus obtained. The graphite oxide was thermally exfoliated at  $\sim$ 300 °C in air to obtain low density black powder of TEGO.

### Preparation of epoxy composite

The calculated amount (wt%) of GP- 10%, GO-10%, TEGO-10%, physically mixed GP -10% and GO-10% termed as [GP-GO-20%] and GP-10% and TEGO-10% termed as [GP-TEGO-20%] was dispersed individually into epoxy resin and the mixture was blended by a shear mixer to make a homogeneous blend, followed by adding a curing agent. Finally, the mixture was poured into the mold and cured at room temperature. Cured composite sheet was carefully removed from the mould and used for measurement of EM properties.

## Characterization

Scanning Electron Microscope (SEM, Carl Zeiss SMT Ltd, EVO-MA 15) equipped with an energy dispersion X-ray spectroscope (EDX, INCA Energy 250 Microanalysis System) was used to analyze the surface morphology at operating voltage of 20 kV. EDX analysis was performed to analyse their chemical constituents.

The Fourier transform infrared (FTIR) spectra were recorded in KBr with a resolution of 2 cm<sup>-1</sup> and scan range of 400-4000 cm<sup>-1</sup>by using ATR-FTIR spectrophotometer, Agilent; Model: 660. Raman spectra of the powder samples were recorded on an Avalon Raman microscope R3-532 using a TEGOn ion laser  $(\lambda = 532 \text{ nm})$  in the range of 1100–2000 cm<sup>-1</sup>. The structural characterization of the samples was carried out by the powder X-ray diffractometer (Philips X'Pert Pro diffractometer) using CuK $\alpha$  ( $\lambda = 0.154$  nm) radiation source operated at the voltage of 40kV and current of 30mA over the scattering angle ranging from  $2\Theta = 5 - 80^{\circ}$  with a step size of  $0.05^{\circ}$ /min. UV-Vis absorption spectra were recorded with a Perkin Elmer, Lambda 35 spectrometer. Elemental analysis was carried out with a CHNSO Elemental Analyzer, EA 2400, Perkin Elmer. N2 adsorptiondesorption isotherms were measured at 77 K on a Micromeritics, ASAP-2020. The surface area was calculated from the Brunauer-Emmett-Teller method (BET). DC electrical conductivity of these materials was measured at room temperature by Hall Effect method using Hall Effect measurement system, model HMS-3000. Vector network analyzer (VNA. model Hewlett-Packard 8510) was used to obtain S-parameters of the samples in the 8-12 GHz range at room temperature. EM parameters (complex permittivity) of the composites were calculated from the measured of **S**-parameters Nicolson-Ross values using algorithm [23].





Fig. 1. SEM images of (a) GO (b) TEGO.

#### **Results and discussion**

#### Physiochemical characterization

The SEM micrographs of synthesized GO and TEGO are given in **Fig. 1** (a) and (b). From the Figure, it can be observed that GO has layered structure, which are stacked and get separated from each other, folded and wrinkled after thermal exfoliation of GO.

GO and TEGO has been subjected to EDX analysis in order to study and identify the elemental composition. The EDX spectra shown in **Fig. 2(a) and (b)** (**supplementary information**) indicated the presence of C and O in both GO and TEGO; however, the peak intensity of O get decreased in TEGO indicating the removal of surface oxygen functional groups resulting into the partial reduction of GO after thermal treatment of GO.



Fig. 3. FTIR spectra of GO and TEGO.

Fig. 3 shows the FT-IR transmittance spectra of GO and TEGO. The spectrum of GO shows the presence of C–O (v (alkoxy)) at 1045 cm<sup>-1</sup>, C–O–C (v (epoxy)) at 1224 cm<sup>-1</sup>, and C=O in carboxylic acid and carbonyl moieties (v (carbonyl)) at 1732 cm<sup>-1</sup>, C–OH (1402 cm<sup>-1</sup>), C=C at 1620 cm<sup>-1</sup> is attributed to skeletal vibrations of unoxidized graphitic domains. The broad band at 3408  $cm^{-1}$  could be due to the O-H stretching mode [24]. The presence of these oxygen-containing functional groups reveals that the graphite has been oxidized. After thermal exfoliation of GO, the peak intensities of  $C=O(1732 \text{ cm}^{-1})$ , C-OH (1402 cm<sup>-1</sup>), and epoxy (1224 cm<sup>-1</sup>) groups get reduced and the absorbance bands at C-O of alkoxy groups (1045 cm<sup>-1</sup>), had completely vanished and peak at 1577 cm<sup>-1</sup> found to be more pronounced indicating the thermal reduction of GO to TEGO.

Fig. 4 (supplementary information) shows the Raman spectrum of GO and TEGO. Both the spectra show the existence of the D and G bands. For GO and TEGO peaks of D band observed at 1364 and 1380 cm<sup>-1</sup> and G band at 1596 and 1604 cm<sup>-1</sup> respectively. D band response can be attributed to either defects or to the breakdown of translational symmetry, while G band is related to the first-order scattering of the  $E_{2g}$  mode of sp<sup>2</sup> domain of graphite. Moreover, the intensity ratio of the D and G band  $(I_D/I_G)$  is a useful indicator to evaluate the ordered and disordered crystal structures of graphitic materials [25, 26]. The value of  $I_D/I_G$  is 0.80 and 0.56 for GO and TEGO respectively indicating the reduction in size of the in-plane sp<sup>2</sup> domains in GO, due to the extensive oxidation, confirm the successful oxidation of graphite.

XRD patterns of GO in **Fig. 5** show a distinct diffraction peak at  $10.80^{\circ}$  corresponding to  $\{001\}$  plane with an interlayer spacing of 0.87 nm and another peak at  $42.26^{\circ}$  attributed to the planes  $\{100\}$ . The distance between consecutive carbon layers increased for GO due to the introduction of oxygen functional groups to the carbon basal plane via chemical oxidation reaction and



Fig. 5. XRD spectra of GO and TEGO.

intercalated water molecules between layers. TEGO produced after thermal exfoliation of GO does not contain a diffraction peak at 10.80° which indicate the reduction of graphite oxide during thermal exfoliation. In addition a new broaden diffraction peak at 24.15° (d-spacing : 0.36 nm) correspond to {002}plane. The diffraction peaks at  $42.11^{\circ}$ ,  $49.13^{\circ}$ , and  $72.72^{\circ}$  observed in TEGO can be attributed to the hexagonal graphite structure planes  $\{100\}, \{004\}, \text{ and } \{110\}.$  These diffraction peaks are signature of the hexagonal graphite lattice of graphene material and in consistence with the reported results for reduced graphene oxide [27, 28]. The  $\{002\}$  and  $\{004\}$ peaks at  $2\theta = 24.15^{\circ}$  and  $49.1^{\circ}$  correspond to parallel graphene layers. The {100} and {110} diffraction peaks at  $2\theta = 42$ . 11° and 72.72° characterize the 2D in-plane symmetry along the graphene layers.

**Fig. 6 (supplementary information)** shows the UV-Vis absorption spectra of GO and TEGO. From the Figure, it is observed that GO shows maximum absorption peak at ~231 nm attributable to  $\pi$ - $\pi$ \* transition of the aromatic C=C bonds and shoulder peak at ~300 nm due to n- $\pi$ \* transitions of aromatic C=O bonds. Absorption peak around 230 nm is red-shifted to 270 nm in TEGO as illustrated in **Fig. 6**, which is consistent with the characters of reduced GO [**29**, **30**]. To evaluate the reduction level of TEGO, we determine its elemental (C, H and O) composition by elemental analysis and calculated the C/O atom ratio. The initial GO with a 1.1 C/O ratio can reach 4.9, when it was thermally treated at 300 °C (**Table 1 supplementary information**).

Room temperature dc conductivity values ( $\sigma$ ) of GO and TEGO were measured to be 1.0x10<sup>-3</sup> and 2.96 S/cm respectively. Result indicates that TEGO shows three orders higher conductivity than GO which further confirms the reduction of GO and the restoration of the sp<sup>2</sup> symmetry. The N<sub>2</sub> BET surface area of GO and TEGO was found to be 34.13 and 338.77m<sup>2</sup>/g with N<sub>2</sub> BJH desorption pore volume of 0.030 and 1.87 cc/g,

respectively. The increase in BET surface area indicates exfoliation of layers in TEGO.

#### Electromagnetic properties

The microwave absorption of epoxy composites were investigated by measuring the relative complex permittivity ( $\varepsilon = \varepsilon' - j\varepsilon''$ ) of the composite samples. The real part of effective permittivity  $\varepsilon'$  is a measure of the ability to store the external electromagnetic energy in the material, which is due to electric polarization effects and dielectric relaxation involving unpaired point defects, bound charges and polarized interfaces [**31-33**]. The imaginary part of effective permittivity  $\varepsilon''$  relates to ability of a material to dissipate the energy from an external electromagnetic field and convert it to heat, which is mainly due to the presence of free electrons in the material [**34**]. The relative complex permeability ( $\mu = \mu' - j\mu''$ ) of the epoxy composites are not shown here due to the non-magnetic nature of filler and epoxy.

Fig. 7 shows the frequency dependence of  $\varepsilon'$ (real part) and  $\varepsilon''$  (imaginary part) of  $\varepsilon$  in the range of 8-12 GHz for the composites. As observed from Fig. 7 the  $\varepsilon'$  values of GP- 10 % /epoxy composite, is ~3.9 and for GO-10 %/ epoxy composite and TEGO -10 %/ epoxy composite the values are ~3.4 and ~7.4 respectively. There is no variation in the  $\varepsilon'$  values of GP and GO composite whereas a slight decrease of  $\varepsilon'$  value of TEGO composite was observed in the studied frequency range. The effect of addition of GP to GO and TEGO on EM properties has also been studied. Results show that  $\varepsilon'$  value of GP-GO-20%/epoxy composite decreases from 5.2 to 5.1 and for GP-TEGO-20%/epoxy composite the  $\varepsilon'$ decreases from 9.3 to 8.7. The decrease of  $\varepsilon'$  of the composites as the increase of frequency may arise from the lags of induced charges in the material to follow the reversing electromagnetic filed in the high frequency range [35].



Fig. 7. Frequency dependence on real part of complex permittivity of GP-10%, GO-10%, TEGO-10%, GP-GO-20% and GP-TEGO-20% composites.



Fig. 8. Frequency dependence on imaginary part of complex permittivity of GP-10%, GO-10%, TEGO-10%, GP-GO-20% and GP-TEGO-20% composites.

Fig. 8 shows the imaginary part of effective permittivity of epoxy composites with different composition. The values of  $\varepsilon''$  are 0.1, 0.1, 2.7, 0.2 and 2.2, corresponding to of GP-10 %, GO-10 %, TEGO-10 %, GP-GO-20% and GP-TEGO-20% composites, respectively. For GP and GO composites the  $\varepsilon''$  values are very low, indicating very poor dielectric loss. We can also see that the values of  $\varepsilon''$  of TEGO-10%/epoxy composite are observed highest among all the studied samples. The addition of GP to GO and TEGO does not bring much change in  $\varepsilon''$  values of GO and TEGO composites. The relatively low  $\varepsilon''$  value is due to low conductivity of the composites [**34**].

**Fig. 9** shows dielectric loss tangent  $(\tan \delta_{\varepsilon})$  values of the composites.  $tan \delta_{\epsilon}$  is directly related to the attenuation factor to convert stored energy to the dissipative heat, and thus, microwave absorption performance improves as it increases. tan $\delta_{\varepsilon}$  values of GP-10 %, GO-10 %, TEGO-10%, GP-GO-20% and GP-TEGO-20% composites are 0.02, 0.03, 0.35, 0.05 and 0.2 respectively. It is evident that the  $tan \delta_{\epsilon}$  value of TEGO based composite (TEGO-10 %/epoxy or GP-TEGO-20%/epoxy) is about one order higher than the other composite systems. This is attributed to the defects and residual oxygen functional groups in TEGO which act as polarized centers and enhance orientation polarization. Besides, carbon atom and oxygen atom have different affinities to catch electrons, which result in electronic dipole polarization. More importantly, there exist many interfaces between TEGO and epoxy trigging interfacial polarization. Furthermore, the accumulation of free charges gives rise to the strong interfacial polarization and leads to the increase of EM wave absorption. TEGO can form local conductive network, which result into conversion EM wave into heat easily. Highly structured and porous nature of TEGO scatter EM wave efficiently.



Fig. 9. Frequency dependence on dielectric tangent loss of GP-10%, GO-10%, TEGO-10%, GP-GO-20% and GP-TEGO-20% composites.

#### Conclusion

In summary, GO was synthesized and thermally exfoliated to produce TEGO. Characterization results indicate the simultaneous exfoliation and partial reduction of GO during thermal exfoliation. Epoxy composites of GP, GO, TEGO, GP-GO and GP-TEGO were fabricated for the investigation of their effective dielectric permittivity, over the frequency range of 8 to 12 GHz. The order of  $tan \delta_{\epsilon}$  values of composites is: TEGO >GP-TEGO> GP-GO> GO >GP. Result shows that addition of GP to GO and TEGO does not change the effective dielectric permittivity significantly over the studied frequency range. Among all composite systems, TEGO-10%/epoxy composite showed significant dielectric loss and can be considered as an alternative of much more expensive carbon nanotubes based for composites specific microwave absorption applications.

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