Dielectric, AC conductivity and electromagnetic interference shielding behavior of graphite oxide/polyvinylpyrrolidone composites

B. Shruthi¹ · B. J. Madhu²

Received: 27 September 2019 / Accepted: 26 February 2020 / Published online: 2 March 2020
© Springer Nature Switzerland AG 2020

Abstract

Graphite oxide (GrO) was prepared using graphite powder by Hummers technique. GrO was characterized by X-ray diffraction analysis and the scanning electron microscopy analysis. Frequency dependence of the dielectric constant (ϵ'), a.c. conductivity (σ_{ac}) and electromagnetic interference (EMI) shielding effectiveness (SE) studies have been carried out on the pure polyvinylpyrrolidone (PVP) and GrO/PVP composites. Addition of GrO into PVP polymer matrix is found to enhance the ϵ' , σ_{ac} and SE. The ϵ' of GrO/PVP composites was found to reduce with an increase in the frequency. The σ_{ac} of GrO/PVP composites was enhanced with an increase in the frequency. Highest value 46.02 dB of EMI SE at 50 Hz was obtained in the 50 Hz–5 MHz frequency range. The SE of GrO/PVP composites was found to reduce with an increase in the frequency. The GrO/PVP composites were proven to be a promising highly efficient lightweight substance for the absorbing of EM waves at low frequencies.

Keywords Graphite oxide · Composites · Dielectric behavior · Electrical conductivity · EMI shielding

1 Introduction

Electromagnetic radiation such as those emanating from cellular phones, computer circuit, and electric overhead power lines tends to interfere with electronic equipments [1]. The electromagnetic (EM) interference shielding is required to guard electronic tools from EM interference. The highest common cause of EMI is electrostatic discharge. To shield an EM interference, substantial quantity of research has been devoted to the fabrication of the flexible polymer composites [2, 3]. Behavior of the polymer composites are controlled by the nature and concentration of its filler and base materials and also the degree of interaction among them. Generally, polymeric materials do not possess required electrical, dielectric or magnetic properties and are also transparent to EM radiations. By selecting appropriate fillers, the composite can be tailored to have desired characteristics. Polymer composites with

graphite based fillers have been studied extensively for EMI shielding in the recent past [4]. Recently, graphite oxide material has attracted much attention due to its excellent properties. Graphite oxide (GrO) typically preserves the layer structure of the graphite, but the layers are buckled. GrO has attracted major interest as a lightweight nanofiller for polymer composites. Graphite oxide-polymer composites show excellent properties as compared to the neat polymer [5, 6].

In the present work, GrO was synthesized from graphite powder by Hummers technique. The GrO was mixed with polyvinylpyrrolidone (PVP) polymer to form GrO/PVP composites. Investigations of structural and frequency dependence of ϵ' , σ_{ac} and EMI shielding effectiveness (SE) studies of GrO/PVP composites have been carried out in the frequency region 50 Hz–5 MHz.

✉ B. J. Madhu, bjmadhu@gmail.com | ¹Department of Chemistry, Dr. Ambedkar Institute of Technology, Bangalore 560 056, India. ²Post Graduate Department of Physics, Government Science College, Chitradurga 577 501, India.

2 Experimental

Chemicals and reagents used in the preparation were of analytical grade. AR grade Graphite powder (assay 98.5%) was used in the synthesis of the GrO. The GrO sample was synthesized using graphite powder by a Hummers technique [7, 8]. In the present studies, 2 g of Graphite powder and 1 g of sodium nitrate (NaNO_3) were systematically mixed and placed into 96 ml of concentrated H_2SO_4 (98%) contained with an ice bath. With continuous stirring using magnetic stirrer, 6 g of KMnO_4 was poured slowly to the mixture. The temperature of this mixture was maintained below 20°C . Resultant mixture was taken outside from the ice bath, then mixture was stirred at a temperature of 35°C in water bath for 16 h. At the end of the reaction, mixture turns into a pasty form with a brown colour. About 150 ml of water was poured into the paste. Due to the inclusion of water, concentrated H_2SO_4 medium discharges huge quantity of heat; hence to control the temperature less than 50°C , water was poured continuously.

After diluting with 240 ml of water, about 5 ml of 30% H_2O_2 was incorporated to the blend, and colour of the resultant solution changed to splendid yellow alongside foaming. After constant mixing for 2 h, the blend was filtered and washed with 10% HCl solution, water (de-ionized), and an ethanol (anhydrous) to evacuate other ions. Resultant graphite oxide was dried. Stabilization of GrO was attained by washing GrO with HCl and de-ionized water to eliminate the suspended residual metallic ions.

PVP (5 g) was dissolved in 100 ml of de-ionized water to create 5% solution. Resultant solution was mixed

systematically with the synthesized 0.5 g of graphite oxide to make GrO/PVP composites. Composite was dried and crushed into fine powder form.

Structure of the neat graphite powder and graphite oxide was analyzed using XRD analysis technique using the Bruker AXS-D8 advance diffractometer. Surface morphology of the graphite oxide was observed using SEM (JEOL Model JSM—6390LV SEM). Dielectric studies, ac conductivity analysis and EM shielding investigations on the GrO/PVP composites have been carried out utilizing the impedance analyzer instrument, HIOKI 3532-50 LCR HiTESTER. Measurements were made on the composite samples, which are in the compressed circular pellet form.

3 Results and discussion

3.1 X-ray diffraction and microstructural analysis

Figure 1 shows the XRD pattern of the neat graphite and GrO samples. The diffraction peaks observed at 26.6° , 43.45° and 54.8° in the Fig. 1a corresponds to graphite [PCPDF card # 41-1487]. Peak observed at 10.41° in the Fig. 1b is due to graphite oxide. Observed peak is broader and less intense than seen for the corresponding pristine graphite, as oxidation of graphite caused a larger change in crystalline phase and structure of graphite layers [9]. SEM image of the GrO is shown in the Fig. 2. From the figure, it can be observed that graphite oxide has layered structure.

Fig. 1 XRD pattern of **a** graphite and **b** graphite oxide (GrO)

Fig. 2 SEM micrograph of graphite oxide

Fig. 3 Frequency dependence of dielectric constant of pure PVP and GrO/PVP composites

3.2 Dielectric and a.c. conductivity studies

Variation of ϵ' with the frequency of pure PVP and GrO/PVP samples at the room temperature is shown in the Fig. 3. It can be seen that the ϵ' values of the GrO/PVP composites are substantially greater than that of the pure PVP. The ϵ' of the GrO/PVP composites is found to reduce with an increase in the frequency. It is the normal dielectric performance exhibited by the materials [10–15]. From Fig. 3, it can be noticed that ϵ' initially drops suddenly with rise in frequency however beyond 10 kHz remains reasonably constant. It is well known that, when the dielectric sample is exposed to ac electric field, the shift of ions, charges and alignment of the dipole moments tries to follow the direction of an

applied electric field. However, switching of the dislocation and alignments with the fast reversal of an electric field turn out to be more difficult at larger frequencies. When an applied frequency increases, ionic and also orientation sources of polarizability reduces and lastly vanish due to an inertia of ions and molecules. Thus, amongst the three kinds of polarizability, the electronic polarizability which includes electrons only survives up to high frequencies [16]. As the frequency of the applied electric field rises, various polarization influences filters out, as a consequence, the net polarization of the sample reduces, which in turn leads to the reduction in the value of dielectric constant.

The ac conductivity analysis of pure PVP and GrO/PVP composites was carried out at room temperature. Figure 4 represents the frequency dependence of σ_{ac} for pure PVP and GrO/PVP composites revealing increasing tendency in the ac conductivity with increase in the frequency, which is owed to an enhanced density of charge carriers for electrical conduction. Further, ac conductivity of the GrO/PVP composites is found to be much larger than that of the pure PVP sample. Normally, GrO is much less conductive than graphite, with an electrical conductivity that depends on the content of oxygen. The GrO retains the layer structure of graphite but it has much larger and less regular interplanar spacing [17]. It has been established that electrical conductivity and optical properties of the GrO dramatically depends on the level of oxidation [18]. In the present studies, observed enhanced ac conductivity of the GrO/PVP composites may be ascribed to the lower level of oxidation of the GrO and synergetic effect between the two components [18].

Fig. 4 Frequency dependence of AC conductivity of pure PVP and GrO/PVP composites

Fig. 5 Frequency dependence of shielding effectiveness of pure PVP and GrO/PVP composites

3.3 Electromagnetic shielding effectiveness

The EM interference shielding effectiveness (SE) is defined as the ratio of an incident power to the transmitted power and generally indicated in terms of decibels (dB) as below [2, 3];

$$SE = 10 \log \left(\frac{P_i}{P_t} \right) (dB) \quad (1)$$

The P_i is an incident power and P_t is the transmitted power. The total EM interference SE of a substance of thickness t is expressed as the aggregate of the SE due to reflection (SE_R) and SE due to absorption (SE_A),

$$SE = SE_R + SE_A \quad (2)$$

$$SE = 20 \log \left[\frac{\left(\frac{\sigma_{ac}}{\omega_H \epsilon_0 \mu_r} \right)^{\frac{1}{2}}}{4} \right] + 20 \log \left[\exp \left(\frac{t}{\delta} \right) \right] (dB) \quad (3)$$

where t is the thickness of the shielding substance, ϵ_0 is the permittivity of the free space, μ_r is magnetic permeability, ω_H is the angular frequency ($\omega_H = 2\pi f_H$) and δ is the skin depth ($\delta = (2/\omega_H \mu \sigma_{ac})^{1/2}$) known as the depth to which the EM radiation pierces in to the sample, while its intensity reduces to e^{-1} of its initial strength.

Shielding effectiveness (SE) was calculated using the Eq. (3). Frequency dependence of SE of pure PVP and GrO/PVP composites at room temperature is displayed in the Fig. 5. SE of the GrO/PVP is greater than that of the

corresponding pure PVP polymer. Drastic increase in the SE values of GrO/PVP composites in the studied frequency range is attributed to the higher ac conductivity of the GrO/PVP composites. Highest SE of 46.02 dB at 50 Hz was attained for the GrO/PVP composites in the studied frequency range. Hongtao Guan et al. and Li et al., shown that the substance can be employed for EMI shielding purpose in the low frequency range if the SE of the substance is larger than 5 dB and 15 dB respectively [19, 20]. Current GrO/PVP composites possess acceptable shielding effectiveness (~46.02 dB) in the lower frequency region at room temperature. SE of the GrO/PVP composites was found to reduce with increase in the frequency, indicating that the current composites are useful for the EM interference shielding at lower frequency region.

4 Conclusions

GrO was synthesized using graphite powder by Hummers method. GrO was characterized by XRD and SEM analyses. Frequency dependence of the dielectric constant, ac conductivity and SE of pure PVP and GrO/PVP composites were studied. Dielectric constant of the GrO/PVP composite was found to reduce with an increase in frequency. Further, the a.c. conductivity of the pure PVP and GrO/PVP composites was found to enhance with an increase in the frequency. Frequency dependence of EM interference SE was studied. The maximum value 46.02 dB of EMI shielding effectiveness at 50 Hz was obtained for GrO/PVP composites in the 50 Hz–5 MHz frequency range. The SE of GrO/PVP composites was found to reduce with an increase in the frequency. The present GrO/PVP composites are favorable highly efficient lightweight substance for the absorbing of EM waves at lower frequency regions.

Acknowledgements Authors wish to acknowledge the STIC, CUSAT, Cochin for SEM analysis.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Chung DDL (2000) Materials for electromagnetic interference shielding. *J Mater Eng Perform* 9:350–354
2. Madhu BJ, Ashwini ST, Shruthi B, Divyashree BS, Manjunath A, Jayanna HS (2014) Structural, dielectric and electromagnetic shielding properties of Ni–Cu nanoferrite/PVP composites. *Mater Sci Eng B* 186:1–6
3. Madhu BJ, Gurusiddesh M, Kiran T, Shruthi B, Jayanna HS (2016) Structural, dielectric, ac conductivity and electromagnetic

- shielding properties of polyaniline/Ni 0.5 Zn 0.5 Fe₂O₄ composites. *J Mater Sci* 27:7760–7766
4. Panwar V, Park J-O, Park S-H, Kumar S, Mehra RM (2010) Electrical, dielectric, and electromagnetic shielding properties of polypropylene-graphite composites. *J Appl Polym Sci* 115:1306–1314
 5. Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, Piner RD, Nguyen ST, Ruoff RS (2006) Graphene-based composite materials. *Nature* 442:282–286
 6. Ramanathan T, Abdala AA, Stankovich S, Dikin DA, Alonso MH, Piner RD, Adamson DH, Schniepp HC, Chen X, Ruoff RS, Nguyen ST, Aksay IA, Prud'Homme RK, Brinson LC (2008) Functionalized graphene sheets for polymer nanocomposites. *Nat Nanotechnol* 3:327–331
 7. Hummers WS, Offeman RE (1958) Preparation of graphitic oxide. *J Am Chem Soc* 80:1339–1339
 8. Singh RK, Kumar R, Singh DP (2016) Graphene oxide: strategies for synthesis, reduction and frontier applications. *RSC Adv* 6:64993–65011
 9. Moon Y-E, Yun J (2011) H-Il Kim, Y-S Lee, Effect of graphite oxide on photodegradation behavior of poly (vinyl alcohol)/graphite oxide composite hydrogels. *Carbon Lett* 12(3):138–142
 10. Madhu BJ, Bindu K, Hamsa S, Sowmya CP, Shruthi B, Manjunath A, Virupakshappa GH (2011) Dielectric behavior and AC conductivity studies on Co 0.4 Ni 0.6 Fe₂O₄ nanoparticles synthesized via combustion method. In: IEEE conference publications, international conference on nano science, engineering and technology (ICONSET), 2011, 373. <https://doi.org/10.1109/ICONSET.2011.6167984>
 11. Madhu BJ, Banu SR, Kavya M, Shruthi B, Vasanthkumar MS, Sanamma TV, Surendra M (2011) Dielectric behavior and AC conductivity studies on cobalt nanoferrites synthesized using combustion method. In: IEEE conference publications, international conference on nano science, technology and societal implications (NSTSI11), 2011. <https://doi.org/10.1109/NSTSI.2011.6111787>
 12. Madhu BJ, Kavya M, Banu SR, Shruthi B, Sowmya CP, Jayanna HS (2012) Dependence of dielectric parameters and AC conductivity of Mg-Co-Zn nanoferrites synthesized via combustion method. *Adv Mater Res* 584:295–298
 13. Madhu BJ, Angadi VJ, Mallikarjuna H, Manjunatha SO, Shruthi B, Kumar RM (2012) Dielectric behavior and AC conductivity studies on nickel nanoferrites synthesized by solution combustion method. *Adv Mater Res* 584:299–302
 14. Madhu BJ, Rashmi BN, Banu A, Seema GA, Shruthi B, Jayanna HS (2013) Anomalous dielectric and AC conductivity behavior of the nanocrystalline Ni-Cu ferrite synthesized via combustion method. *AIP Conf Proc* 1512:1008–1009. <https://doi.org/10.1063/1.479138411>
 15. Madhu BJ, Kiran T, Gurusiddesh M, Shruthi B (2016) Synthesis, characterization and dielectric behavior of polyaniline/Ni_{0.5}Zn_{0.5}Fe₂O₄ nanocomposites. *Macromol Symp* 361(1):24–29
 16. Shaikh PA, Kambale RC, Rao AV, Kolekar YD (2009) Studies on structural and electrical properties of Co_{1-x}Ni_xFe_{1.9}Mn_{0.1}O₄ ferrite. *J Alloys Compd* 482:276
 17. Hong X, Yu W, Wang A, Chung DDL (2016) Graphite oxide paper as a polarizable electrical conductor in the through-thickness direction. *Carbon* 109:874–882
 18. Jung I, Dikin DA, Piner RD, Ruoff RS (2008) Tunable electrical conductivity of individual graphene oxide sheets reduced at “low” temperatures. *Nano Lett* 8:4283–4287
 19. Guan H, Liu S, Duan Y, Cheng J (2006) Cement based electromagnetic shielding and absorbing building materials. *Cem Concr Compos* 28:468–474
 20. Li N, Huang Y, Du F, He XB, Lin X, GaO HJ, Ma YF, Li FF, Chen YS, Eklund PC (2006) Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites. *Nano Lett* 6:1141–1145

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.