International Journal of Advanced Technology in Engineering and Science
Vol. No.3, Issue 11, November 2015
www.ijates.com
ijates
ISSN 2348 - 7550

INFLUENCE OF CARBON NANOFILLERS ON DIELECTRIC PROPERTIES OF PMMA NANOCOMPOSITES

Manasi Singhi[1], M. Fahim[2]

[1]Department of Chemistry, Ambedkar Institute of Advanced Communication Technologies and Research, Geeta Colony, New Delhi, (India)

[2]Department of Physics, Zakir Husain Delhi College, University of Delhi, New Delhi, (India)

ABSTRACT

Three different series of polymethylmethacrylate (PMMA) nanocomposites were developed using three different carbon nanofillers namely (i) nanographite powder (ii) COOH functionalized CNT and (iii) graphene. The concentration of nanofillers (<3 wt%) was changed in the step of 0.50 wt.% and nanocomposites were prepared by in-situ polymerization of MMA monomer. Frequency and temperature dependent dielectric behavior of these nanocomposites were studied to investigate the influence of different nanofillers. It was observed that at all temperatures and frequencies dielectric constant of pure PMMA decreased with low wt% of nanofillers and then increased with further increase in filler loading. At room temperature, composite with 1.50 wt% of CNT showed a minimum value of dielectric constant at all frequencies. In the case of graphene-PMMA composites, same dielectric trend was observed. However, at room temperature composite with 0.75wt% of graphene showed a minimum value of dielectric constant at all frequencies. In the case of nanographite- PMMA composites, room temperature dielectric constant decreased with increasing concentration of nanographite and reached a minimum at a filler concentration of 0.75 wt%.

Keywords*: *Nanographite, Graphene, MWCNT, PMMA, In-Situ Polymerization, Dielectric Studies

I. INTRODUCTION

Carbon-based nanofillers, such as carbon black (CB), expanded graphite (EG), graphite nanoplatelet (GNP), carbon nanotube (CNT) and graphene nanosheets (GNS) in non-conducting polymer matrices significantly improve the electrical conductivity of the polymer [1]. CNTs are most effective as conductive fillers, however, their higher production cost is a constraint. Compared to CNTs, the two dimensional GNSs are not as effective in forming conductive networks due to the aggregation of GNSs in the polymer matrix but they are economically viable. Thus, in order to make optimum utilization of the advantages of GNSs as conductive fillers and derive high performances from resultant composites serious efforts have been made in the past [1-3]. A small loading of GNS not only ensures achievement of higher electrical conductivity but also helps in retaining the properties of the base polymer matrix [4]**.** It has been reported that the percolation threshold of PMMA/graphite nanosheets conducting films, at room temperature, was as low as 0.31 vol% which was much lower than that (3.19 vol%) of the composites filled with conventional graphite filler particles. Their results also showed that the high aspect-ratio (width to thickness) structure of graphite nanosheets played an important role in forming conducting network in PMMA matrix [5]. Similarly, for PMMA/graphite nanoplatelet ensembles, the electrical conductivity of the ensemble was found to exhibit an insulator–conductor transition at a very low percolation threshold for GNPs [6]. The percolation threshold of PMMA/GNP at room temperature was only about 1 wt% filler content which is much lower than that of the ensembles filled with conventional graphite particles. GNP/PMMA nanocomposites show vastly improved conductivity as compared to ARG/PMMA and EG/PMMA nanocomposites [7]. In the case of a graphene nanosheet filled ultra-high molecular weight polyethylene (UHMWPE) composite with a segregated structure fabricated by exfoliating graphene oxide nanosheet (GONS) and then water/ethanol mixture solvent-assisted dispersion under ultrasonication, a percolation threshold as low as 0.070 vol.% has been achieved because of the formation of a two dimensional conductive network [8]. Thus, from the literature survey, it was observed that *in-situ* polymerization is the best method to achieve optimum electrical conductivity and other properties in PMMA nanocomposites.

In this paper, three different series of polymethylmethacrylate (PMMA) nanocomposites were developed using three different carbon nanofillers namely nanographite powder, COOH functionalized CNT and graphene. The concentration of nanofillers (<3 wt%) was changed in the step of 0.50 wt.% and nanocomposites were prepared by *in-situ* polymerization of MMA monomer. Frequency and temperature dependent dielectric behavior of these nanocomposites were studied and compared and is being reported in the subsequent sections.

II. MATERIALS AND METHODS

Methyl methacrylate (MMA) (Density = 0.936g/cc and Purity = 99%) was obtained from Sigma Aldrich, Germany. COOH functionalized MWCNT (dia 20-30 nm) and length (10-30 micron) purity (95%) was obtained from Nanostructred and Amorphous Materials, Houston, Texas (US). Graphene (Purity = 99.5%, Layer Flake = 4-6 (50-80%), Surface Area ≥ 250m^2/g, Thickness =2-4nm, Lateral Size = 1-10μm, pH = 6-7, Ash ≤ 0.5%, Morphology = Flaky) was obtained from Nanoshel LLC. Nanographite (APS 400 nm) was obtained from Sisco Research laboratories, India. Firstly, *in-situ* polymerization of MMA monomer was carried out in test tubes with the help of ultra-sonication under suitable conditions. Exact amount of nanofiller (nanographite, CNT and graphene) was taken in dry test tubes and then it was sonicated for 5 minutes in dry condition. 10g of MMA monomer and 0.1g of BPO initiator were added to the test tubes. Nitrogen was purged for 1 minute in every test tube to create an inert atmosphere. Test tubes were plugged tightly with cotton and sonicated for 10 minutes at room temperature. Now, these systems were slowly heated to 60°C and sonicated for total 2 hours until the monomer system became viscous and nanofiller got entrapped into the polymer chains. After 2 hours, sonication was stopped and systems were heated for another 2 hours to complete the polymerization under nitrogen atmosphere. After 4 hours polymeric lumps were formed inside the test tube. Test tubes were then broken to take out the polymeric lumps. These polymer lumps were crushed at 20,000 lb pressure in compression moulding machine without heating. Thus, micro cracks developed inside the lumps and then they were granulated. Granules were dried at 60°C under vacuum for 24 hours to remove low molecular weight components. After that, granules were compression moulded to make samples at 165°C and at 15,000 lb pressure. Granules were preheated for 15 minutes and compression moulded for another 15 minutes with a breathing time of 30 seconds. Then, samples were slowly cooled to 65°C by circulating water inside the platen and then they were ejected from the mould. A total of 10 different samples of each series were prepared by varying the weight percentage of nanofillers.

2.1 Dielectric Studies

AC frequency dependent values of parallel capacitance (Cp) and loss tangent or dissipation factor (tanδ or D) of the nanocomposite samples were measured by using Agilent 4263B precision LCR meter. The actual thickness of samples was measured using a micrometre before electroding by application of conductive silver paste using a paint brush. Electroded samples were placed in a sample cell between two electrodes and voltage was applied. The parallel capacitance (Cp) was measured on the LCR meter. Dielectric constant (ε′) was calculated using the formula:

$\varepsilon' = C/C_0$

Where, C_o ($=\epsilon_0 A/d$) is the capacitance with vacuum between parallel plates, and ϵ_0 is the permittivity of free space, A is the area of electrodes, and d is the thickness of the sample. Dissipation factor (D or tan δ) was directly measured on the LCR meter.

III. RESULTS AND DISCUSSION

3.1 CNT-PMMA Nanocomposites

Frequency dependent dielectric behaviour of CNT-PMMA nanocomposites at room temperature is shown in **Fig. 1**. Dielectric constants measured at different frequencies are plotted as a function of increasing CNT weight percentage. It is expected that at lower frequencies the values of dielectric constant will be higher due to contribution of both electronic polarization and orientational or dipole polarization. With increase in frequencies orientational polarization is restricted but electronic polarization are not. Here it is observed that with increasing CNT percentage dielectric constant decreases and then reaches to a minimum and then start to increase but after 1.5 wt. % it falls slightly. This is because at a constant frequency when CNT percentage increases then more and more restrictions are applied to the polymer molecule to polarization and consequently the contribution of orientational polarization decreases monotonically. But at very low percentage of CNT the enhancement in electronic polarization is suppressed by the decrease in dipole polarization and thus the overall polarization decreases resulting the decrease in dielectric constant value. But after a certain percentage the contribution of increase in electronic polarization and decrease in dipole polarization counter balance each other and after that the increase in electronic polarization becomes more significant. As a result of this phenomenon, dielectric constant reaches a minimum and then starts to increase. But after 1.5% CNT loading it is observed that dielectric constant starts to decrease slowly and this can be due to stabilization of electronic polarization after a certain concentration. So again the decrease in orientational polarization determines the nature of the curve.

3.2 Graphene-PMMA Nanocomposites

Frequency dependent dielectric behaviour of grapheme-PMMA nanocomposites at room temperature is shown in **Fig. 2**. Dielectric constants at different frequencies are plotted as a function of increasing Graphene weight percentage. It is expected that at lower frequencies the values of dielectric constant will be higher due to contribution of both electronic polarization and orientational or dipole polarization. With increase in frequencies orientational polarization is restricted but electronic polarization are not. Here it is observed that with increasing graphene percentage dielectric constant decreases and then reaches to a minimum and then start to increase but after 1.5 wt. % it falls slightly. This is because at a constant frequency when Graphene percentage increases then more and more restrictions are applied to the polymer molecule to polarization and consequently the contribution of orientational polarization decreases monotonically. But at very low percentage of graphene the enhancement in electronic polarization is suppressed by the decrease in dipole polarization and thus the overall polarization decreases resulting in the decrease in dielectric constant value. But after a certain percentage the contribution of increase in electronic polarization and decrease in dipole polarization counter balance each other and after that the increase in electronic polarization becomes more significant. As a result of this phenomenon, dielectric constant reaches a minimum and the starts it increase. But after 1.5% Graphene loading it is observed that dielectric constant starts to decrease slowly and this can be due to stabilization of electronic polarization after a certain concentration. So again the decrease in orientational polarization determines the nature of the curve**.**

3.3 Nanographite -PMMA Nanocomposites

In the case of PMMA/graphite composites, the dielectric and electrical properties of PMMA are changed drastically by the presence of graphite particles since the dielectric properties of the latter (~12–15) are very different from those of the matrix (~5–8). Electrical conductivities become higher because graphite is conductive and when its volume fraction is higher than a percolation limit (0.50 wt% in the present case). The dielectric permittivities also become high (PG5) indicating nondipolar origin of the polarization such as interfacial polarization. At the interface of two dielectric materials having different permittivities and/or conductivities, charges are accumulated. Thus a layer of dipoles induced by the external electric fields is formed at the interface, resulting in an increase of the total polarization field, i.e., an increase of the dielectric permittivity. Variation of dielectric constant with concentration of graphite at room temperature (31.8 deg C) is shown in **Fig 3**. A minimum dielectric constant was obtained for PG3 (0.75 wt%) composite. A higher or lower concentration than the optimum concentration was found to increase the dielectric constant.

IV. FIGURES

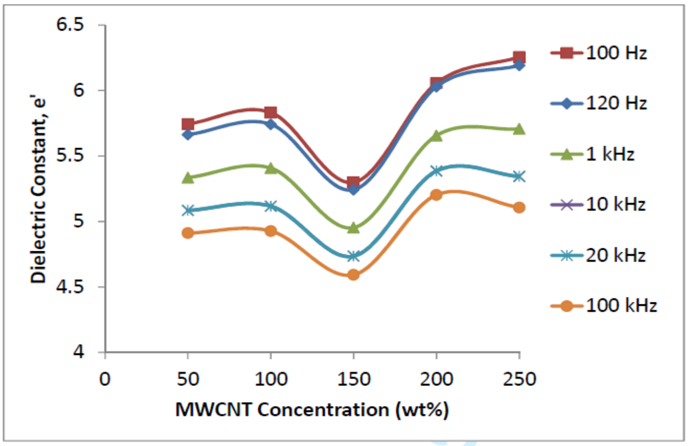


Fig.1: Dielectric constant of CNT-PMMA nanocomposites as a function of CNT wt% obtained at room temperature at different frequencies

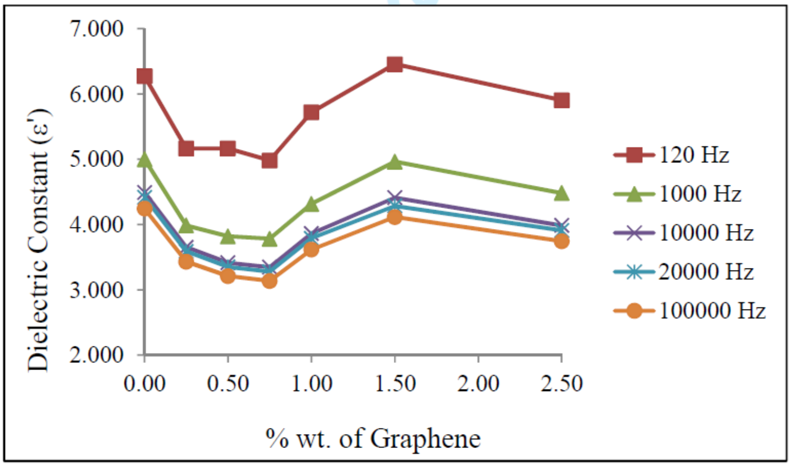
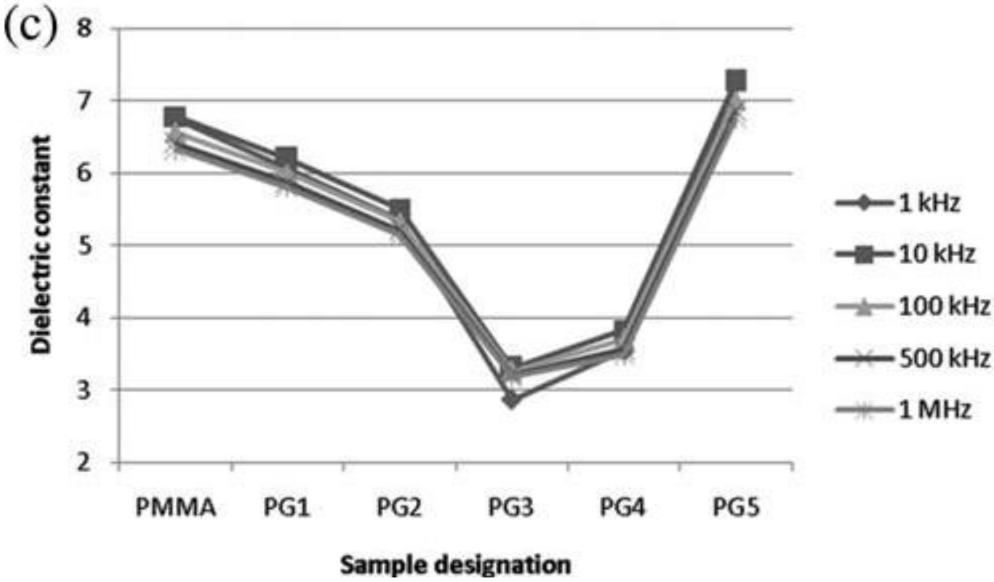


Fig.2: Dielectric constant of Graphene-PMMA nanocomposites as a function of graphene wt% obtained at room temperature at different frequencies



[PG1 (0.25 wt%), PG2 (0.50 wt%), PG3 (0.75 wt%) PG4 (1.0 wt%) PG5 (1.5wt%)]

Fig.3: Dielectric constant of nanographite -PMMA nanocomposites as a function of nanographite wt% obtained at room temperature at different frequencies

V. CONCLUSIONS

A comparison of the influence of three different carbon nanofillers on dielectric properties of PMMA nanocomposites showed that same dielectric behavior is obtained for all three nanofillers. However, in the case of CNT filled PMMA nanocomposites, dielectric constant first decreased (probably due to decrease in dipole polarization) and then increased after a loading of 1.5 wt%. However, in the case of Graphene filled PMMA nanocomposites dielectric constant decreased with increasing concentration of graphene and reached a minimum at a filler concentration of 0.75 wt%. Similarly, in the case of nanographite filled PMMA nancomposites, a minimum dielectric constant was obtained for 0.75wt%. A higher or lower concentration than the optimum concentration was found to increase the dielectric constant.

REFERENCES

[1] Z. Khattari, M. Maghrabi, T. McNally and S.A. Jawad,Electrical impedance study of elastic alternating propylene-carbon monoxide copolymer(PCO-200), Physica B, 406(13),2011,2565-2569.

[2] E. Kymakis, I. Alexandou and G.A.J. Amaratunga, Single-walled carbon nanotube-polymer composites:electrical,optical and structural investigation, Synthetic Metals,127,2002,59-62.

[3] C.A.Grimes, C. Mungle, D.Kouzoudis, S. Fang, P.C. Eklund,The 500 MHz to 5.50 GHz Complex Permitivity Spectra of Singlewall Carbon Nanotube-Loaded Polymer Composites , Chemical Physics Letters, 319,2000,460-464.

[4] J.M. Yeh, K.C Chang, C.W Peng, M.C Lai, S.S Hwang, H.R Lin and S.J. Liou, Enhancement in insulation and mechanical properties of PMMA nanocomposite foams infused with multi-walled carbon nanotubes , Journal of Nanoscience and Nanotechnology **,** 11(8),2011,6757-64.

[5] S. Kumar, T. Rath, B.B. Khatua, A.K. Dhibar and C.K. Das , Preparation and characterization of Poly (methyl methacrylate)/ Multiwalled carbon nanotube composites, Journal of Nanoscience and Nanotechnolgy, 9(8),2009,4644-4655.

[6] A. Hirsch, Functionalization of single-walled carbon nanotubes, Angewandte Chemie. International Edition in English, 41(11),2002,1853.

[7] CNR Rao, B.C. Satishkumar, A. Govindaraj, M. Nath , Nanotubes, ChemPhysChem, 2(2),2001,78-105.

[8] J.N. Coleman, A.B. Dalton, S. Curran, A. Rubio, A.P. Davey, A. Drury, B. McCarthy, B. Lahr, P.M.Ajayan,S.R. Roth, R.C. Barkle, W.J. Blau, Phase separation of carbon nanotubes and turbostratic graphite using a functional organic polymer, Advanced Materials, 12(3), 2000,213-216.