Dielectric Properties of Cu based Polymeric Composites in X-band of Microwave Frequency

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Abstract

In this work, the microwave dielectric properties of Cu and PEO based composite sheets are studied in the X-band. The desired composites sheets (thickness ~ 250 μm) are prepared via solution casting method, one of the best methods for sheet preparation. Various characterization techniques including the X-ray diffraction and Scanning Electron Microscopy are used to analyze the presence and uniform dispersion of Cu particles into polyethylene oxide (PEO) matrix. Vector Network Analyzer is employed to obtain the scattering parameters (S_{21}/S_{11}), which are then used to extract the dielectric permittivity of the samples using cavity perturbation technique in the X-band of microwave frequency. The real and imaginary parts (dielectric constant and dielectric loss) of the complex permittivity of synthesized composite sheets are found to be increased with the addition of copper contents (10, 20, and 30 wt %). This enhancement of the dielectric properties in the X-band of microwave frequency may be attributed to the interfacial polarization mechanism. Copyright © VBRI Press.

Keywords: Composite, dielectric permittivity, microwave, X-band.

Introduction

The polymeric composites were given a great interest in many industrial applications due to their desirable characteristics and properties which made them favorable compared to other commercial materials [**1**]. The marvelous combination of characteristics such as the ease of fabrication, low cost, light weight, ease of chemical modification and excellent insulation or good conduction properties have made the polymer one of the most desirable materials for many applications [**2-4**]. However, compared with inorganic materials, organic polymer materials have often low dielectric permittivity, in the range of 2–5 [**5**]. Thus, a key issue is to substantially raise the dielectric permittivity of polymers while retaining their excellent mechanical and physical properties. In order to raise the complex permittivity of the organic polymers, a certain material like metals, ceramics and alloys are added as fillers in the base material of the polymer. Such type of resultant material is popularly known as composite. Various research groups are currently working with polymer-based composites for a diverse application [**6-7**].

In this manuscript, a particulate copper powder is dispersed in the base material of poly ethylene oxide to form Cu/PEO polymeric composites. Poly ethylene oxide or PEO is taken as the base material because of its excellent physical, chemical and thermal properties [**8, 9**]. PEO is a crystalline homopolymer with a chemical formula (-H_2C-O-CH_2-)$_n$. Moreover, PEO is a thermoplastic water-soluble polymer and also soluble in several organic solvents. It exhibits a monoclinic crystal structure with unit cell dimensions, a = 7.96 Å, b = 13.11 Å and c = 19.39 Å and an angle of 124°.48' representing the inclination between a & c axes [**10**]. The copper is taken as filler or dopant because of its wonderful electrical properties. The PEO doped with metallic salts is of practical interest, since it can be used as a flexible solid electrolyte conductor [**11-13**]. For example, the rechargeable electrolyte batteries can be made of Li doped PEO composite [**11**]. However, the pure PEO exhibits some unexpected dielectric properties, which are today of interest for physical research and which may be of practical use in future. It has already been reported that PEO can have variational dielectric permittivity with different types of solvents.

In the present work, the Cu doped PEO composite is prepared via solution casting method and then studied their structural, morphological and microwave dielectric properties in the X-band of microwave frequency. To the best of author's knowledge, such kind of study regarding the preparation and characterization of Cu doped PEO composites in terms of their structural, morphological and microwave dielectric properties in the X-band of microwave frequency has not been done in the past.

Experimental

Sample preparation

The whole experimental procedure for the formation of metal polymer (PEO) composite is mainly consists of four steps as shown in **Fig. 1**. In the first step, a glass beaker is partially filled with acetone (purchased from Fisher Scientific) and placed on magnetic stirrer (manufactured by Remi Equipment's) at a fixed temperature of 80 ºC. The polyethylene oxide powder (Av. *M. W.* ~ 5,000,000, *d* ~ 1.210, Aldrich Chemical Company, Inc.) is mixed slowly in the stirring acetone and continued until the solution becomes transparent. In the second step, the copper powder (*d* ~ 45 µm) is poured into the stirring polymer solution. The third step includes the vaporization process of acetone and hence the magnetic rod bead stops to rotate. As a result, a gel form of Cu doped PEO composite is achieved. In the fourth step, the composite gel is poured out into the petri dish which is then covered and kept in vacuum desiccator to release the air bubbles. Finally, a circular sheet of thickness ~ 250 µm is prepared.

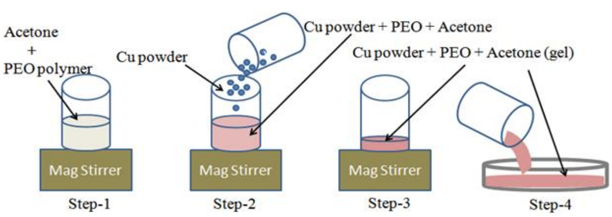

Fig. 1. Solution casting method for the preparation of Cu doped PEO composites.

Characterization techniques

X-ray diffraction (XRD) patterns of the prepared Cu doped PEO composites have been recorded using a diffractometer (Thermo Electron ARL X'TRA) in 2θ range of 15 - 80º with Cu K_α radiation (λ = 1.540562Å), scan rate of 2 deg/min, steps of 0.05 deg and time constant of one second.

The surface morphology of the Cu doped PEO composites has been observed using the field emission scanning electron microscopy (Model: Sigma FESEM, Carl Zeiss). The sample preparation for FESEM is carried out by placing the composite sheet on the aluminium substrate and coated with gold to make the surface electrically conductive.

The microwave dielectric properties of the prepared samples have been measured using vector network analyzer of model Agilent E8364B PNA series. For this measurement, the Cu doped PEO composite sheets are cut precisely into the desired shape of the experiment.

Cavity perturbation theory for permittivity measurement

The cavity perturbation theory is broadly known for the precise and accurate measurement of the complex permittivity of the materials [**14**]. The complex permittivity (relative) is expressed as [**14, 15**]

$$\varepsilon_r = \varepsilon_r' - j\varepsilon_r'' \tag{1}$$

where ε_r' is the real part of the complex permittivity and ε_r'' is the imaginary part of the complex permittivity? The ε_r' and ε_r'' represent the electrical energy storage and electrical energy dissipated (loss) in the system, respectively.

In the cavity perturbation theory, the ε_r' and ε_r'' are evaluated using the resonant frequency (*f*) and the quality factor (*Q*) of the perturbed (*f*, *Q*) and unperturbed (f_0, Q_0) spectra obtained during the VNA measurement. For the measurement of dielectric properties in the X-band of microwave frequency, the X-band rectangular cavity is operated in the TE_{107} mode. In TE_{107} mode, only the *y* component of the electric field exists inside the cavity and has a maximum value at the centre [**16**]. Hence, for the dielectric measurement, the sample is placed at the centre of X-band rectangular cavity whereat the electric filed becomes tangential to the sample. In the cavity perturbation theory, the ε_r' and ε_r'' can be evaluated using the following expressions [**17**]

$$\varepsilon_r' = 1 + \frac{2}{C}\left(\frac{f_0 - f}{f}\right) \tag{2}$$

$$\varepsilon_r'' = \frac{1}{C}\left(\frac{1}{Q} - \frac{1}{Q_0}\right) \tag{3}$$

$$C = \frac{\iiint_{V_s} \boldsymbol{E}_y^* \cdot \boldsymbol{E}_y \, dv}{\iiint_{V_c} |\boldsymbol{E}_y|^2 \, dv} \tag{4}$$

$$\boldsymbol{E}_y = E_{y\,max} \sin\left(\frac{\pi}{a}x\right) sin\left(\frac{p\pi}{L}z\right) \hat{a}_y \tag{5}$$

The notations used here have their usual meanings. The shape factor *C* is ideally equal to $4V_s/V_c$ for the infinitesimally small sample placed parallel to the electric field. The V_s and V_c are the volumes of sample and the resonant cavity, respectively.

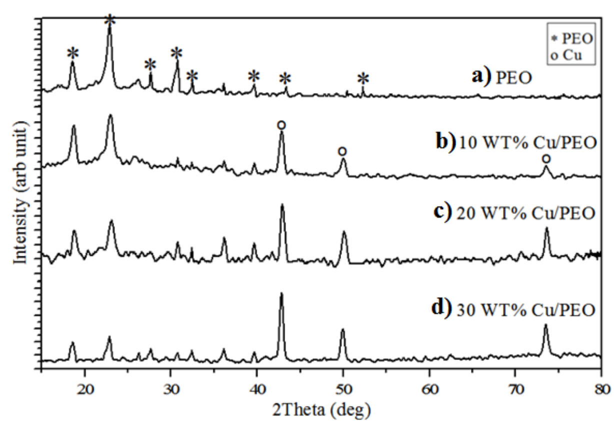

Fig. 2. XRD patterns of Cu doped PEO composites, a) Pure PEO, b) 10 wt%, c) 20 wt%, and d) 30 wt% [17].

Result and discussion

X-ray diffraction analysis

The X-ray diffraction (XRD) patterns of the prepared 0 - 30 wt% Cu doped PEO composites are shown in **Fig. 2** [**17**]. The X-ray diffraction (XRD) patterns of pure PEO, 10 wt%, 20 wt%, and 30 wt% Cu doped PEO are shown in **Figs. 2a, 2b,** and **2c**, respectively. The peaks observed in pure PEO are indicated with stars while the peaks of Cu are indicated by circles. It can be observed in **Fig. 2a** that the highly intense XRD peaks are observed at 2θ = 19.18º and 23.34º, which represent the semi-crystalline nature of PEO [**18**]. In **Figs. 2b, 2c** and **2d,** the XRD peaks of Cu are observed at 2θ = 43.36º, 50.48º, and 74.10º which correspond to (111), (200) and (220) crystal planes, respectively. These XRD peaks are well matched with standard powder diffraction card of JCPDS file No. 04-0836. It is worthy to note here that the XRD peak intensity of Cu increases with increasing the Cu content in the case of composite samples while XRD peaks of PEO are suppressed (as listed in **Table 1** and **Table 2**). This is the indication of the strong bonding between Cu and PEO materials.

Table 1. XRD data analysis for Cu and PEO separately.

PEO (Only two peaks)		Cu (JCPDS: 04-0836)	
2 Theta (degree)	*Peak Intensity (arb. unit)*	*2 Theta (degree)*	*Peak Intensity (arb. unit)*
19.18	48	43.36	100
23.34	100	50.48	40
--	--	74.10	40

Table 2. XRD data analysis for Cu and PEO in Cu/PEO composites where 2θ is in degree and intensity in arb. units.

10 wt% Cu/PEO				20 wt% Cu/PEO				30 wt% Cu/PEO			
PEO		Cu		PEO		Cu		PEO		Cu	
2θ	Int.	2θ	Int.	2θ	Int.	2θ	Int.	2θ	Int.	2θ	Int.
19.26	48	43.36	60	19.26	30	43.36	70	19.18	25	43.36	75
23.38	60	50.48	25	23.38	50	50.48	40	23.35	30	50.48	40
--	--	74.10	25	--	--	74.10	40	--	--	74.10	40

Surface morphological analysis

The surface morphologies of the prepared Cu doped PEO composites captured from field emission scanning electron microscope (FESEM) are demonstrated in **Fig. 3**. The FESEM image of pure PEO is given in **Fig. 3a**) while for 10 wt%, 20 wt%, and 30 wt% Cu doped PEO composites are shown in **Figs. 3b), 3c),** and **3d),** respectively. The effect of Cu filler into the PEO base matrix has been clearly observed in these figures. It is interested to note that in the surface morphologies of the prepared composites, the shrinkages (wrinkles) present at the surface of the composite sheets is getting reduced with higher values of copper contents. Such reduction in the shrinkage may be attributed to the strong adhesion between copper and PEO materials.

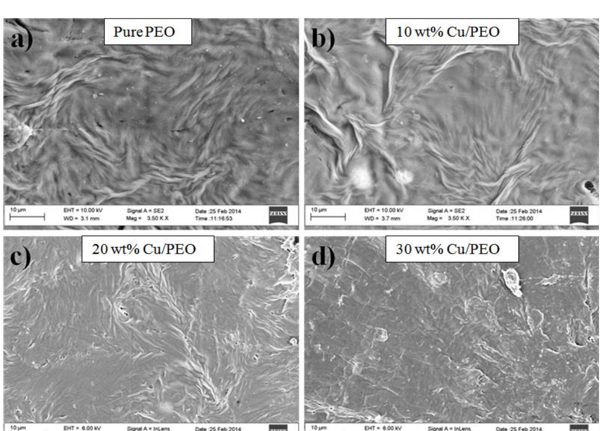

Fig. 3. FESEM images of Cu/PEO nanocomposite thin films, a) Pure PEO, b) 10 wt%, c) 20 wt%, and d) 30 wt%.

Microwave dielectric properties

The real and imaginary parts of the complex permittivity are calculated using equations (2) and (3) at two different X-band microwave frequencies of 9.35 GHz and 10.87GHz. **Figs. 4a** and **4b** show the plots of real part vs. Cu content and imaginary part vs. Cu content at both the microwave frequencies 9.35 GHz and 10.87 GHz, respectively [**19**]. It is obvious from **Fig. 4** that the dielectric constant and the loss factor are found to increase with increasing copper content for both the frequency values in X-band of microwave frequency. An enhancement in the real part of the complex permittivity may be attributed to the interfacial polarization between PEO polymer and Cu filler particles [**20**]. Additionally, the dielectric constant of the composites depends on the capacitance value, which is directly proportional to the quantity of charge stored on either surface of the sample [**20**]. Because of the copper filler (conducting filler) into the PEO base matrix, the number of accumulated charges will be increased due to the polarization produced at polymer – filler interface. This gives an additional contribution to the charge quantity because of the polarization. From this point of view, the dielectric constant of the composites should be higher than that of pure polymer. This supports the above experimental results of enhanced dielectric constant as given in **Fig. 4**. Similar results were reported by Azizurrahaman *et al.* for powdered Cu/PEO composites [**20**].

The enhancement in the imaginary part of the complex permittivity with the increased value of Cu filler concentration may be attributed to the interfacial polarization mechanism of the heterogeneous system. The imaginary part (loss factor) in both cases (**Fig. 4a** and **Fig. 4b**) shows the increasing trend with addition of Cu into the PEO matrix. These are the results of Cu/PEO composite sheets which just match with the results of Cu/PEO powdered composites [**20**]. This increasing dielectric loss factor may assist to design the electromagnetic wave absorber for the X-band of microwave frequency.

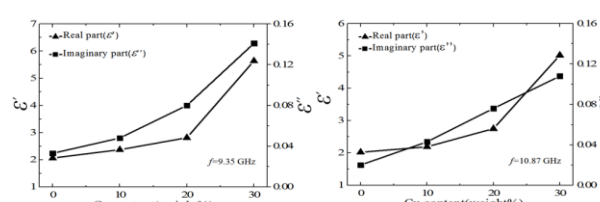

Fig. 4. The plots of real and imaginary part of complex permittivity of Cu/PEO thin film composites with Cu filler concentrations, at (a) 9.35 GHz, and (b) 10.87GHz [19].

Conclusion

The Cu doped PEO composite sheets (thickness ~ 250 μm) have been prepared successfully via solution casting method. The XRD patterns of the prepared samples indicated the strong adhesion between the Cu and PEO particles. The FESEM images demonstrated the surface morphology of the Cu doped PEO composites. The shrinkage minimization at the surface of the prepared samples has been observed with the higher Cu content. The complex permittivity of the Cu doped PEO composites has been measured in the X-band of microwave frequency using VNA system. The real and imaginary parts of the complex permittivity are increasing with the increase of Cu contents. This enhancement of real and imaginary parts of the complex permittivity may be attributed to the interfacial polarization effect between PEO and Cu particles (heterogeneous system). Hence the conducting filler material plays an important role to enhance the microwave dielectric properties.

References

1. Mort, J.; "Electrical properties of polymer", John Wiley & Sons. New York, **1982**.
2. Epstein, A.; Joo, J.; Kohlman, R.; Macdiarmid, A.; Weisinger, J.; Min, Y.; Tsukamoto, J.; *MRS Proceedings*, **1993**, *328*, 145.
3. Tummala, R.R.; "Electronic packaging for high reliability, low cost electronics" Kluwer Academic Publishers, **1999**.
4. Lau, J.; "Chip on board technologies for multichip modules" Kluwer Academic Publishers; **1994**.
5. Immergut, E. H.; Brandrup, J.; McDowell, W.; "Polymer handbook" Wiley, New York, **2008**.
6. Ansari, A.; Akhtar, M. J.; *RSC Adv.*, **2016**, *6*, 13846.
7. Ansari, A.; Akhtar, M. J.; *Mater. Res. Express*, **2017**, *4*, 016304.
8. Bailey, F. E. Jr.; Poly (Ethylene Oxide), 1st Edition, Academic Press, Elsevier Inc., **1976**.
9. Varshney, S. K.; Zhang, J. X.; "Hetero-functional polyethylene glycol and polyethylene oxide, process for their manufacture", US Patent 7009033, assigned to Polymer Source Inc. (Dorval, CA), March 7, **2006**.
10. Salih, A. A.; Ramadin, Y.; Zihlif, A.; *Ibn Al-Haitham J. For Pure & Appl. Sci*., **2010**, *23*.
11. Young, W. S.; Epps III, T. H.; *Macromolecules*, **2009**, *42*, 2672.
12. Koduru, H. K.; Iliev, M. T.; Kondamareddy, K. K.; Karashanova, D.; Vlakhov, T.; Zhao, X. Z.; Scaramuzza, N.; *J. Phys.: Conf. Ser.*, **2016**, *764*, 012006.
13. Qi, Y.; Chen, W.; Mai, L.; Zhu, Q.; Jin, A.; *Int. J. Electrochem. Sci.*, **2006**, 1, 317.
14. Chen, L. F.; Ong, C. K.; Neo, C. P.; Varadan, V. V.; Varadan, V. K.; Microwave electronics measurement and materials characterization, John Wiley & Sons Ltd, **2004**, pp. 250-261.
15. Jha, A. K.; Akhtar, M. J.; *IEEE Transactions on Instrumentation and Measurement*, **2014**, *63*, 2632.
16. Roger, H. F.; Time-harmonic electromagnetic fields, **1961**.
17. Jha, A. K.; Azizurrahaman; Akhtar, M. J.; "Microwave characterization of nanocomposite powders using cavity-based optimization approach" 2014 IEEE Conference on Antenna Measurements & Applications (CAMA), Antibes Juan-les-Pins, **2014**, pp. 1-4.
18. Sangawar, V. S.; Bhagat, R. N.; *Int. J. Innovative Res. Sci., Eng. Tech.*, **2013**, *2*, 6539.
19. Ansari, A.; Akhtar, M. J.; Microwave characterization of polymeric nanocomposites containing copper nanoparticles as conducting filler, Proc. of the Intl. Conf. on Nanotechnology for Better Living, **2016**, Vol. 3, No. 1, p. 329.
20. Azizurrahaman, A. K. Jha, Akhtar, M. J.; *Adv. Powder Tech.*, **2015**, *26*, 1281.

