# Investigation of frequency dependent dielectric property and thermal study of polysiloxane – ZnO nanocomposites

Md Nasir Ali[1], Dr. Mir Safiulla[2]

1. Research Scholar, Department of Mechanical engineering, Shri Jagdishprasad Jhabarmal Tibrewala University, Jhunjhunu – 333001, Rajasthan, India

2. Professor & Head ( R & D), Department of Mechanical Engineering, Ghousia College of Engineering, Ramanagaram - 562159

**Abstract:**

The polysiloxane – ZnO nanocomposites were prepared by solvent casting method in triethanolamine and tetrahydrofuran solvents. The prepared nanocomposites were characterized by X-ray's diffraction for structural study and surface morphology was carried by scanning electron microscopy. The XRD spectra indicate that the pure polysiloxane is amorphous in nature and ZnO nanoparticles structure remains same even after dispersion in polysiloxane. Further, the DC conductivity shows that the conductivity increases with increase in temperature due to tunnelling phenomena. Among all nanocomposites, 0.3 wt % shows the high DC conductivity of $3 \times 10^{-2}$ S/cm. The dielectric study was carried out by two probe method. It is observed that 0.3 wt % of shows the low imaginary permittivity value of 576 F/m due to the dipole polarization effect. The nanocomposites of 0.3 wt % of shows the lowest tangent loss value of 0.1 due to the non-debye's type of relaxation process where the charge carriers are relaxed at the higher energy state for a longer time.

**Keywords:** Polysiloxane, Titanium dioxide, Nanocomposites, Dielectric

**Author of correspondence:**
Md Nasir Ali
**Email:** mdnasir.mech@gmail.com
Dr. Mir Safiulla
**Email:** safiullamir@gmail.com

## 1. Introduction

Sol–gel chemistry (metallo-organic precursors, organic of phase dispersion of the metal M in siloxane–metal oxide solvents, low processing temperatures, mixing at the molecular based matrices depends strongly on the nature of the metal level) permits the introduction of organic moieties or molecules and on the M/Si ratio. Inorganic and organic compo- oxide–siloxane based hybrids generally exhibit a less efficient can then be mixed at the nanometric scale in virtually degree of dispersion than silica based or zinc oxide based any ratio, leading to hybrid organic–inorganic nanocomposites [1- 4]. Polysiloxane (PS) nanocomposites have unique properties such as corrosion resistance, chemical inertness, heavy metal ion adsorption, anti-grafting and high permeability of gases made a potential candidate for various technological applications. The inorganic nanoparticle gaining a wide attention in scientific communities is due to change in physical and chemical property down to the size [5]. It is well known that the polysiloxane have low surface energy, high dielectric and high temperature resistance up to 760 $^{O}$C made suitable for insulation, electronic coating, automobile gaskets, sealing and lubricating greases. However, there is a great challenge in maintaining the transparency which is depends on the concentration of filler, solvent used, preparation methods and curing temperature [6].

The nanocomposites of polysiloxane have been prepared by high intense ultra sonication in tetrahydrofuran (THF) media. Further, the prepared nanocomposites were characterized by X-ray's diffraction (XRD) method and scanning electron microscopy (SEM) for structural and surface morphology analysis. The temperature dependent DC conductivity was carried out by two probe method.

## 2. Materials and Method
### 2.1 Materials

All chemicals used for the preparation of nanocomposites are analytical grade. The polysiloxane (99.99 % pure), Zinc oxide (ZnO), triethanolamine (TOEA) and tetrahydrofuran (THF) was purchased from Sigma Aldrich, India.

### 2.2 Synthesis of polysiloxane – ZnO nanocomposites

The nanocomposites films were prepared by solution casting method. 5 gm of polysiloxane was dissolved in 150 ml of tetrahydrofuran (THF) and stirred for 72 hrs to obtain a clear solution. Then 0.1, 0.3 and 0.5 wt % of ZnO and 0.25 ml of triethanolamine (TOEA) were mixed with the above solution with high intense ultra sonication until dissolution takes place. The homogeneous mixture then poured in to a round Teflon mould and dried in room temperature to remove the solvent and later heated with 50 ºC to form dried thin film of nanocomposites. In similar procedure, pure polysiloxane thin film was prepared as following in preparation of nanocomposites [7 – 9].

## 3. Characterization

The X-ray's diffraction study was carried out by using Philips X-ray diffractometer for the range of $10^O$ to $80^O$ at the rate of $2^O$ per second with $CuK_\alpha$ radiation of wave length $\lambda= 1.5406$ Å. The surface morphology of the nanocomposites was characterized by Scanning electron microscopy model of Philips XL 30 ESEM spectroscopy. The nanocomposites films were fixed onto the carbon coated copper grid and introduce into the microscopic sample holder for the image scanning.

Further, the temperature dependent DC conductivity was studied using indigenous two probe Kelvin set up from room temperature to 220 ºC using Keithely source meter by applying silver paste both the side for better connectivity.

## 4. Results and discussion
### 4.1 X-ray's diffraction study

Figure 1 shows the X-ray's diffraction pattern of pure polysiloxane and polysiloxane – ZnO nanocomposites for different weight percentages (0.1, 0.3 and 0.5 wt %). It is observed that the pure polysiloxane (PS) is showing a broad peak around 23º which indicate that the polysiloxane is having amorphous in nature. The broad peaks appeared at 23º is due to the diffraction occurs at the interplanar spacing of the polymer. The polysiloxane – ZnO nanocomposites for different

weight percentages shows the characteristics peaks of ZnO in polysiloxane at 26.30º, 33.22º, 42.12º and 51.23º are corresponding to the plan of (100), (1002), (101), (102), (110), (103), (112) and (201) respectively, which is matched with reported data [10, 11]. The crystallite size of the polysiloxane – ZnO nanocomposite is calculated by using Debye Scherrer equation and it is found that the crystallite size is around 13nm. It is aloes important to note that that the ZnO structure is not distracted even after incorporating in polysiloxane.
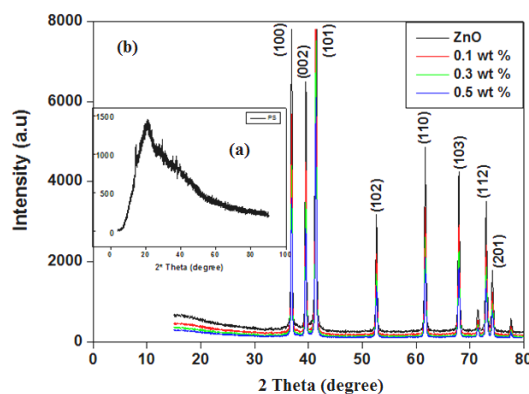


Figure 1 (a, b) shows that the XRD spectra of polysiloxane and polysiloxane – ZnO nanocomposites

### 4.2 Scanning electron microscopy

Figure 3 (a – b) shows the SEM image of pure polysiloxane, ZnO and polysiloxane - ZnO nanocomposites. From the image of pure polysiloxane (a), it is observed the polysiloxane film is having very smooth surface without any crack or agglomeration at the polymer films interface. It is also interesting to note that the solvent aging effect does not appears on its surface and therefore its surface is very smooth. Figure (b) shows the ZnO nanoparticles doped in polysiloxane matrix in tetrahydrofuran solvent, the nanoparticles embedded in to the matrix without any formation of crack. The nanocomposite films are dried at 50 ºC for an hour in presence of helium gas the solvent aging effect almost negligible as a results surface of the nanocomposites appeared very smooth with embedded of ZnO in nanocomposites.
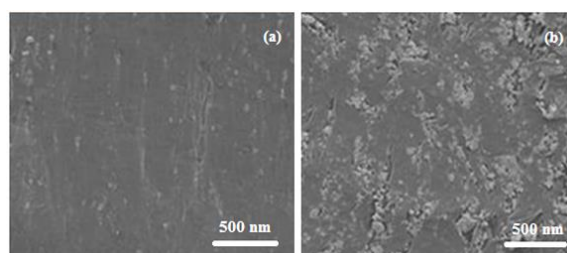


Figure 2 (a, b) shows the SEM image of pure polysiloxane and 0.3 wt % of polysiloxane – ZnO nanocomposites

## 5. DC conductivity

Figure 4 shows the DC conductivity of polysiloxane and polysiloxane - ZnO nanocomposites with different weight percentages as a function of temperature from 40 ºC to 220 ºC. It is observed that the conductivity of the polysiloxane and its nanocomposites increases with increase in temperature as well as weight percentages of ZnO in polysiloxane up to 3 wt %. The gradual increase in conductivity is due to the tunnelling of charge carriers from one conducting site to another. Among all the nanocomposites, 0.3 wt % of polysiloxane – ZnO nanocomposite show high conductivity of $3 \times 10^{-2}$ S/cm in compare to other nanocomposites. It is also important to note that the after 0.3 wt % conductivity decrease due to the blocking of charge carriers at the interface of the polymer nanocomposites [10-13].
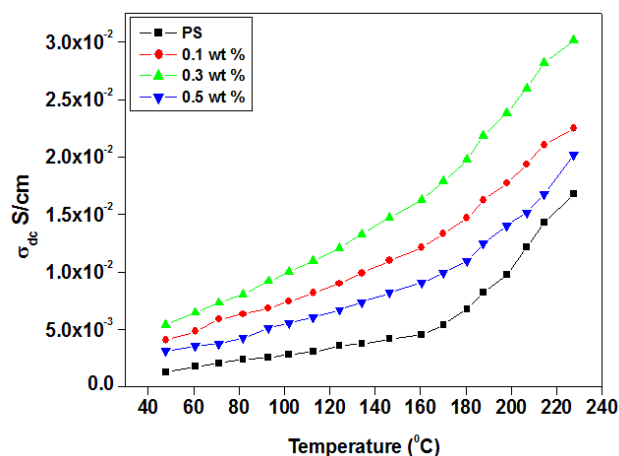


Figure 3 shows the DC conductivity of polysiloxane and polysiloxane – ZnO nanocomposites
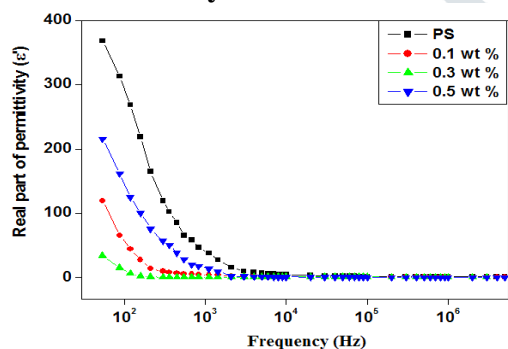
## Dielectric Study



Figure 4 variation of real permittivity against applied frequency

Figure 4 shows the real part of permittivity of polysiloxane and polysiloxane - ZnO nanocomposites as a function of applied frequency from 50 Hz to 5 MHz. It is observed that the real permittivity value decreases with increase in applied frequency up to $10^3$ Hz after that its almost remains constant which is may be due to the dipole polarization where the polarization occurs due to

the Si – O and Zn – O along with symmetry axis. The zinc oxide nanoparticles have many hydroxyl ions due to the hydrophilic nature of nanoparticles and high surface area to the volume ratio causes high surface energy [17]. Among all the nanocomposites, 0.3 wt % of polysiloxane - ZnO nanocomposite shows lowest real permittivity of 400 F/m may be due to the two reason i.e., homogeneous distribution of ZnO nanoparticles in polysiloxane matrix and negligible solvent aging effect causes smooth surface. However, after 0.3 wt % of ZnO in the polysiloxane matrix dramatically increase the real permittivity value due to the blocking of charge carriers at the interface.
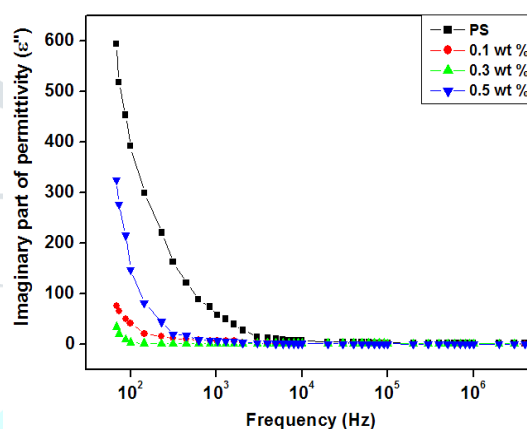


Figure 5 varation of imaginary permittivity

Figure 5 shows the imaginary part of permittivity of polysiloxane and polysiloxane - ZnO nanocomposites with different weight percentages as a function of applied frequency from 50 Hz to 5 MHz. The similar behaviour is observed like a real part of permittivity for polysiloxane and polysiloxane - ZnO nanocomposites except have a smaller in a magnitude of imaginary permittivity. Among all the nanocomposites, 0.3 wt % of shows the low imaginary permittivity value of 576 F/m due to the dipole polarization effect and distribution of ZnO nanoparticles in polysiloxane.

Figure 6 shows the variation of tangent loss as a function of applied frequency for different weight percentages of ZnO in polysiloxane. It is observed that the tangent loss value decreases with increase in frequency up to $10^3$ Hz after that it's almost constant for all compositions. Among all the nanocomposites, 0.3 wt % of shows the lowest tangent loss value of 0.1 due to the non-debye's type of relaxation process where the charge carriers are relaxed at the higher energy state for a longer time. Hence, 0.3 wt % of polysiloxane – ZnO nanocomposite can be used as low $k$ – dielectric materials electrochromic and electrochemical device, capacitor, varistor etc
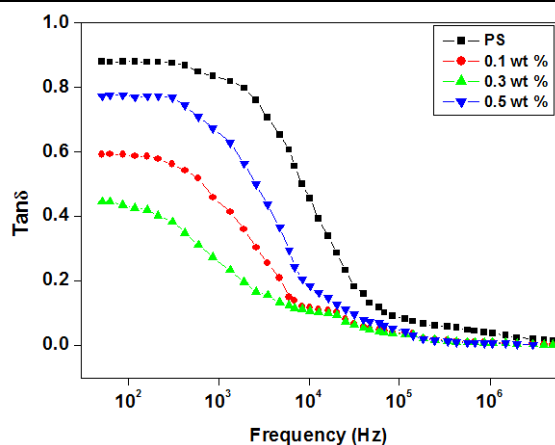
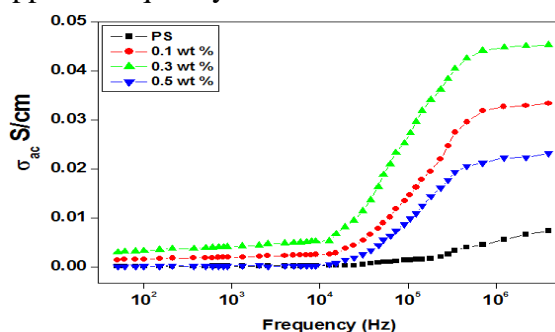Figure 6 shows the tangent loss as a function of applied frequency



Figure 7 the ac conductivity of polysiloxane - ZnO nanocomposites

Figure 7 shows the variation of $\sigma_{ac}$ conductivity for different weight percentages of ZnO in polysiloxane as a function of frequency. It is observed that the conductivity of pure polysiloxane and its nanocomposites increase with an increase in frequency. The conductivity of the nanocomposites depends on the several factors such as size and shape of the nanoparticles, distribution factor, the orientation of nanoparticles in a polymer matrix, surface morphology, grain boundary which define the bulk resistance of the samples. Therefore, it is very carefully illustrated the solvent casting process without any aging effects results in smooth surface morphology that influences the conductivity [18]. Among all the nanocomposites, 0.3 wt % shows the high conductivity of 0.05 S/cm due to the low dielectric constant and tangent loss due to the favorable surface morphology without any agglomeration or cracking on the surface and also null solvent aging effect [19]. Therefore, these nanocomposites can be potential candidates for the self-cleaning coating materials in superhydrophobic glass, capacitors, varistor etc.

## 6. Conclusion

The polysiloxane – ZnO nanocomposites have been prepared by solvent casting method in triethanolamine and tetrahydrofuran solvents. The structural study was carried out by X-ray's diffraction. The XRD pattern shows that the structure of ZnO in polysiloxane and it is found that the crystallite size is around 13nm. The SEM image of $TiO_2$ shows rod like structure embedded in polysiloxane with smooth surface morphology without any crack or agglomeration. The temperature dependent conductivity shows that the conductivity increases with increase in temperature as well as ZnO weight percentage up 0.3 % in polysiloxane. Among all nanocomposites, 0.3 wt % shows the high DC conductivity of 3 x $10^{-2}$ S/cm due to the tunnelling phenomena.. Therefore, these nanocomposites can be potential candidates for many high dielectrics engineering applications.

## 7. References

[1] Klonos P, Sulym IY, Borysenko MV, Gun'ko VM, Kripotou S, Kyritsis A, Pissis P. Interfacial interactions and complex segmental dynamics in systems based on silica-polydimethylsiloxane core–shell nanoparticles: dielectric and thermal study. Polymer. 2015;58:9–21.

[2] Okamoto M, Suzuki S, Suzuki E. Polysiloxane depolymerisation with dimethyl carbonate using alkali metal halide catalysts. Appl Catal. 2004; 261:239–45.

[3] Protsak IS, Kuzema PO, Tertykh VA, Bolbukh YM, Kozakevych RB. Thermogravimetric analysis of silicas chemically modified with products of deoligomerization of polydimethylsiloxane. J Term Anal Calorim. 2015; 121:547–57.

[4] Mironuk IF, Kurta SA, Gergel TV, Voronin EP, Cheladin VL, Kyrta OC. The chemosorbtion of oligomeric polymethylsiloxane on the surface of fumed silica. Phys Chem Solid State (in Ukr). 2009;10:157–65.

[5] Guo J, Saha P, Liang J, Saha M, Grady BP. Multi-walled carbon nanotubes coated by multi-layer silica for improving thermal conductivity of polymer composites. J Term Anal Calorim. 2013;113(2):467–74.

[6] Roy A.S, Gupta S, Seethamraju S, Madras G, Ramamurthy P.C, Impedance spectroscopy of novel hybrid composite films of polyvinylbutyral(PVB)/functionalized mesoporous silica, Composites Part B 2014; 58:134-139.

[7] Roy A.S, Gupta S, Sindhu S, Parveen A, Ramamurthy P.C, Dielectric properties of novel PVA/ZnO hybrid nanocomposite films, Compos. Part B Eng. 2013; 47: 314-319.

[8] Fragiadakis D, Pissis P. Glass transition and segmental dynamics in

poly(dimethylsiloxane)/silica nanocomposites studied by various techniques. J Non-Cryst Solids. 2007; 353:4344–52.

[9] Klonos P, Kyritsis A, Pissis P. Interfacial dynamics of polydimethylsiloxane adsorbed on fumed metal oxide particles of a wide range of specific surface area. Polymer. 2015;77:10–3.

[10] Lewicki J. P, Liggat J J, Richard A. P. Mogon P, Rhoney I. Investigating the ageing behavior of polysiloxane nanocomposites by degradative thermal analysis. Polymer Degradation and Stability. 2008; 93: 158-168

[11] Chengjie L, Meng X, Xiaowen Z, Lin Y, In Situ Synthesis of Monomer Casting Nylon-6/Graphene-Polysiloxane Nanocomposites: Intercalation Structure, Synergistic Reinforcing, and Friction-Reducing Effect. ACS Appl. Mater. Interfaces, 2017; 9: 33176–33190

[12] Paquien, J.-N., J. Galy, and J.-F. Gérard. Rheological studies of fumed silica–polydimethylsiloxane suspensions. Colloids Surf. A, 2005; 260: 165–172

[13] Davis A, Yeong Y. H, A. Steele, Bayer I. S, Loth E, "Superhydrophobic nanocomposite surface topography and ice adhesion," ACS Applied Materials & Interfaces, 2014; 6: 9272–9279.

[14] Tabakci M, Ersoz M, Yilmaz M, A Calix[4]arene-Containing Polysiloxane Resin for Removal of Heavy Metals and Dichromate Anion. J. Macromol Sci A: Pure & App Chem. 2006; 43: 57

[15] Hammer P, Schiavetto M.G, Dos Santos F.C, Benedetti A.V, Pulcinelli S.H, Santilli C.V, Improvement of the corrosion resistance of polysiloxane hybrid coatings by cerium doping. J. Non-Cryst. Solids. 2010; 356: 2606

[16] Barletta M, Rubino S V G, Puopolo M, Venettacci S, Functionalized polysiloxane coatings on hot-rolled and high-strength Fe 430 B steel: Analysis of mechanical response and resistance to chemicals. Appl. Polym. Sci. 2014; 131: 40624

[17] Dewasthale S, Andrews C, Graiver D, Narayan R, Water Soluble Polysiloxanes. Silicon. 2017; 9: 619

[18] Jodeh S, Khalaf B, Radi S, Tighadouini S, Salghi R, Samhan S, Warad I, Jodeh D, New Polysiloxane Surfaces Modified with Ortho-, Meta-, or Para-Nitrophenyl Moieties for Cadmium Removal from Water. J Surf Eng Mat & Adv Tech. 2016; 6: 18