

Investigation of frequency dependent dielectric properties of polysiloxane – TiO₂ nanocomposites

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Abstract:

The polysiloxane – TiO₂ nanocomposites were prepared by a solvent casting method in triethanolamine and tetrahydrofuran solvents. Fourier transform infrared spectroscopy for structural analysis and surface morphology was carried by scanning electron microscopy. The amorphous nature of polysiloxane observed in the amorphous nature of polysiloxane observed in XRD spectra. The surface morphology was studied by employing scanning electron microscopy and it is found that the nanoparticles are completely embedded in the polysiloxane. Further, the dielectric spectroscopy study reveals that the 0.3 wt % shows low dielectric constant and dielectric loss, as a result, it shows high conductivity of 1.35×10^{-4} S/cm. 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. The quality factor confirms that there is a small damping loss for 0.3 wt % of nanocomposites which is favorable for the high conductivity. Therefore, these nanocomposites can be potential candidates for many high dielectrics engineering applications.

Keywords: Polysiloxane, Titanium dioxide, Nanocomposites, Dielectric

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1. Introduction

The large scientific community have been attracted to the inorganic nanoparticle doped polysiloxane (PS) nanocomposite because of its unique properties such as absorption of heavy metal ions from aqueous and organic solvents [1], corrosion resistance [2], chemical inertness [3], anti-grafting [4] and high permeability of gases [5] made a potential candidate in many different technological applications. It is well known that the polysiloxane has low surface energy, high dielectric [6] and high-temperature resistance [7] up to 760 °C made suitable for insulation, electronic coating, automobile gaskets, sealing and lubricating greases [8]. Besides chemical (in the presence of hydrochloric acid, thionyl chloride, ammonia or organic amines) or thermal (300–400 °C) activation of polysiloxanes, the polymeric modified layer can be obtained by polymerization of precursors with different amount of functional groups, which was realized via utilizing oligomers (tri-, penta- and hexamethylcyclotrisiloxane) with siliconhydride groups [9] or siloxanes [10] as precursors. Such approach allows one to compose polysiloxane layer with well-defined structure having various topologies (linear, comb-branched and dendritic-branched). The multi-step process of modification by oligomers with different amount

of chemically active groups also allows one to build comb-branched and dendritic-branched polymers. However, there is a great challenge in maintaining the transparency which depends on the concentration of filler, a solvent used, preparation methods and curing temperature [9]. The investigation of dielectric properties of the polysiloxane nanocomposites is important to realize the several factors such as surface charge density, polarization effect, charge carrier mobility, damping loss and change in bulk resistance with a small doping of inorganic nanoparticles to determine the suitability of the electronic device packing application. The inorganic oxides dope in the polysiloxane nanocomposite may change the surface energy due to the presence of oxygen vacancies which are predominant at the higher temperature. It is reported that the addition of inorganic oxide nanoparticles may fill the interfacial cracks and improve significantly its electrical properties [10 - 12].

It is often find difficulties to have transparent nanocomposite with homogenous distribution of inorganic nanoparticles in polysiloxane matrix which affects the refractive index (RI) of the nanocomposite. The formation of nods, twists and micro-cracks at the interface of the polymer and

nanostructured inorganic oxide may be causes multiple scattering or diffraction at the interplanar space causes higher damping loss and high impedance value.

In either case, the stability of heterometallic bonds affects the structural features of the resulting materials. As a matter of fact, the multinuclear NMR study of these hybrid materials pointed out the different lability of Si O Me (Me = metal) bonds in solution, depending on the nature of the metal alkoxide [13]. In general, polydimethylsiloxane-oxide gels have been described as nanocomposites based on long and mobile polydimethylsiloxane chains and oxide particles that are nanometric in size [14]. From the literature, it owes that the TiO₂ nanoparticles doped in polysiloxane nanocomposite films may have a smooth surface and low surface scattering which may be reduce the damping loss and impedance value. Therefore, the author made an attempt to investigate the temperature dependent electrical conductivity and dielectric properties of TiO₂ nanoparticles doped polysiloxane nanocomposites.

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 probes method.

2. Materials and Method

2.1 Materials

All chemicals used for the preparation of nanocomposites were analytical grade. The polysiloxane (99.99 % pure), titanium dioxide (TiO₂), triethanolamine (TOEA) and tetrahydrofuran (THF) was purchased from Sigma Aldrich, India.

2.2 Synthesis of polysiloxane – TiO₂ nanocomposites

The nanocomposite films were prepared by a solvent 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 0.6 wt % of TiO₂ 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 into a round Teflon mould and dried in room temperature to remove the solvent and later heated with 50 °C to form a dried thin film of nanocomposites. In a similar procedure, pure polysiloxane thin film was

prepared as following in preparation of nanocomposites [16, 17].

3. Characterization

The X-ray crystallography was carried out by using Philips X-ray diffractometer for the range of 10° to 80° at the rate of 2° per second with CuK α radiation of wavelength $\lambda = 1.5406 \text{ \AA}$. The functional group of the polysiloxane and its nanocomposites were studied by using PerkinElmer1600 spectrophotometer in KBr medium. The nanocomposite was mixed with KBr crystals in the ratio of 1:5 and grounded the mixture to obtained homogeneous compound. The surface morphology of the nanocomposite 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 impedance spectroscopy of the nanocomposite was carried out by Hoki LCR-Q meter from the frequency range of 50 Hz to 5 MHz.

4. Results and discussion

4.1 X-ray crystallography

Figure 1 shows the X-ray diffraction pattern of pure polysiloxane and polysiloxane – TiO₂ nanocomposites for different weight percentages (0.1, 0.3 and 0.6 wt %). The pure polysiloxane (PS) show a broad peak around 14.73° and 23° may be due to the diffraction occurs at the interplanar spacing of the polymer and it indicates the amorphous nature of polysiloxane. The polysiloxane – TiO₂ nanocomposites for different weight percentage show the characteristic peaks of TiO₂ in polysiloxane at 26.30°, 33.22°, 37.62°, 45.02°, 42.12°, 56.34° and 68.21° 42.12° corresponding to the plan of (110), (101), (111), (210), (211), (220) and (301) respectively, which is matched with reported data [14]. The crystallite size of the polysiloxane – TiO₂ nanocomposite is calculated by using the Debye Scherrer equation and it is found to be 13 nm. It is also important to note that the TiO₂ structure is not distracted even after incorporating into the polysiloxane matrix.

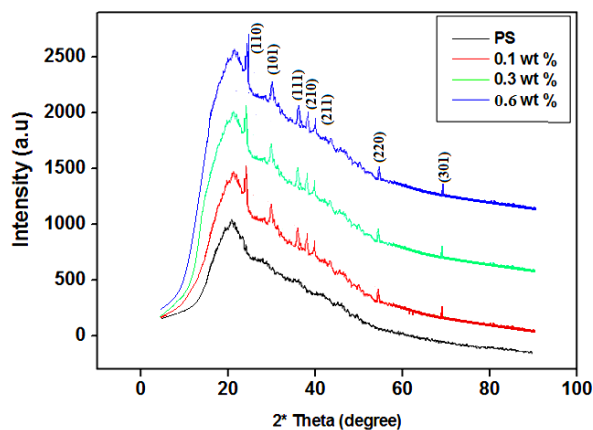


Figure 1 XRD pattern of polysiloxane and polysiloxane – TiO₂ nanocomposites

4.2 Scanning electron microscopy

Figure 2 (a – c) shows the SEM image of pure polysiloxane, TiO₂, and 0.3 wt % of polysiloxane - TiO₂ nanocomposites. From the image of pure polysiloxane (a), it is observed the polysiloxane film have a smooth surface without any crack or agglomeration at the polymer film interface. It is also interesting to note that the solvent aging effect does not appear on its surface and therefore its surface is very smooth. Figure (b) shows that the pure TiO₂ spherical bits are form aliened indusial nanoparticles and which are well connected at the boundary without any agglomeration. When these titanium dioxide nanoparticles doped in polysiloxane matrix in tetrahydrofuran solvent, the nanoparticles embedded into the matrix without any formation of crack as shown in figure (c). The nanocomposite films are dried at 50 °C 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 TiO₂ in nanocomposites.

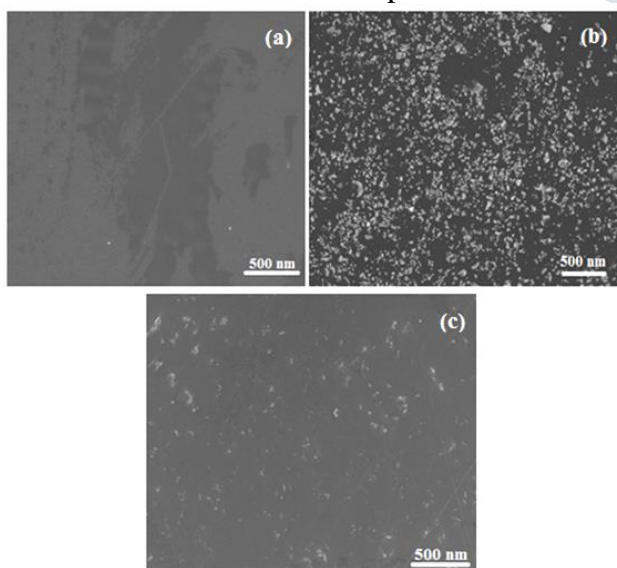


Figure 2 SEM image of polysiloxane, TiO₂ and 0.3 wt % of polysiloxane – TiO₂ nanocomposites

5. Dielectric study

Figure 3 shows the real part of permittivity of polysiloxane and polysiloxane - TiO₂ 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 10³ 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 Ti – O – Ti along with symmetry axis. The titanium dioxide 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 - TiO₂ nanocomposite shows lowest real permittivity of 1200 F/m may be due to the two reason i.e., homogeneous distribution of TiO₂ nanoparticles in polysiloxane matrix and negligible solvent aging effect causes smooth surface. However, after 0.3 wt % of TiO₂ in the polysiloxane matrix dramatically increase the real permittivity value due to the blocking of charge carriers at the interface. Figure 6 shows the imaginary part of permittivity of polysiloxane and polysiloxane - TiO₂ 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 - TiO₂ 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 584 F/m due to the dipole polarization effect and distribution of TiO₂ nanoparticles in polysiloxane.

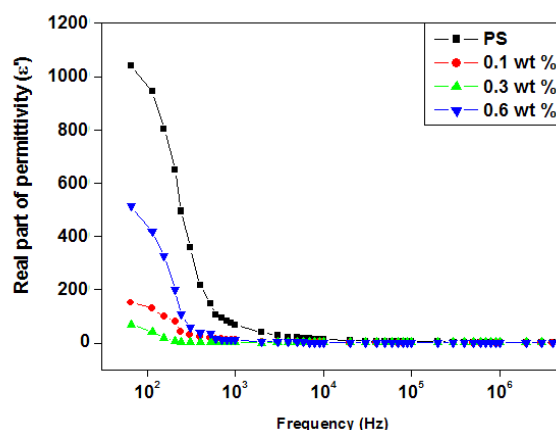


Figure 3 shows the real part of permittivity as a function of applied frequency for polysiloxane and polysiloxane – TiO₂ nanocomposites

Figure 4 shows the variation of quality factor (Q) as a function of applied frequency for different weight percentages of polysiloxane and its nanocomposites. The damping loss of nanocomposite at the mid frequency range is may be due to the different types of energy loss such as

vibrational energy, translation energy and kinetic energy at the higher frequency range. It is observed that the damping loss of polysiloxane and polysiloxane – TiO₂ nanocomposites of all compositions have the value less than 0.5 indicates that the vibrational energy and translation energy loss is almost zero is due to the embedded TiO₂ in polysiloxane [18]. For all the nanocomposites, the hump are formed at the mid-frequency range between 10⁴ to 10⁵ Hz is due to the steady state of electron flow at the equilibrium. Among all the nanocomposites, 0.3 wt % of polysiloxane – TiO₂ nanocomposites show the lowest value of 2 because of the fact that there is no free space in between the nanoparticles and polymer matrix results in no oscillation at all.

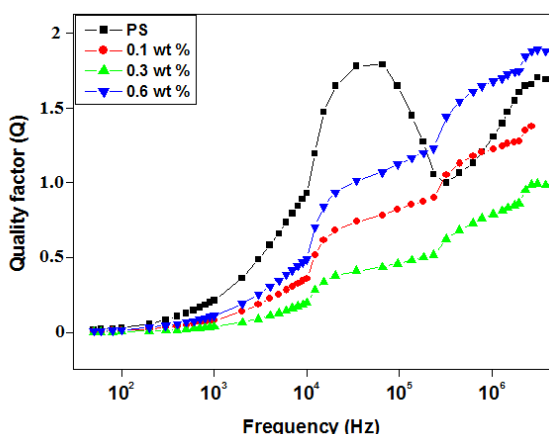


Figure 4 shows the quality factor as a function of applied frequency for polysiloxane and polysiloxane – TiO₂ nanocomposites.

Figure 5 shows the real part of electric modulus of polysiloxane and polysiloxane - TiO₂ nanocomposites with different weight percentages. It is observed that the real electric modulus value initially at the lower frequency almost constant for all the compositions and after 10⁴ Hz the electric modulus increase due to independent dipole formation. It also indicates that the lower frequency associated with magnetic field perpendicular to the electrical field. However, it is found that with a magnetic field decreases with increase in the frequency range may result gradually increase in electric modulus. Among all the nanocomposites, 0.3 wt % shows higher electric modulus of 0.0392 which is followed by other compositions and pure polysiloxane. Another reason could be for higher electric modulus is due to the formation of permanent dipole of Si – OH and Ti – O – Ti along with symmetry axis due to the hydrophilic nature of TiO₂ and high surface energy [19].

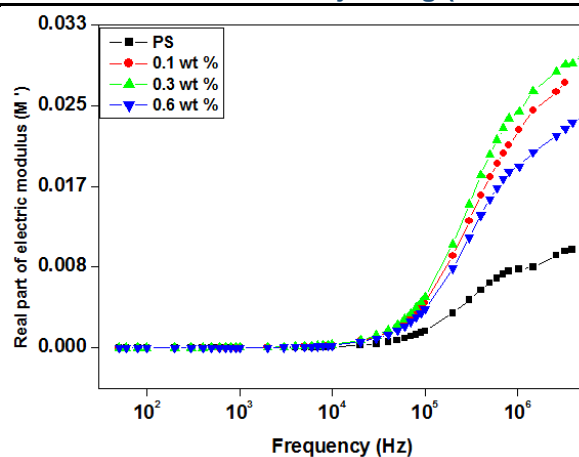


Figure 5 shows the real part of electric modulus as a function of applied frequency for polysiloxane and polysiloxane – TiO₂ nanocomposites

Figure 6 shows the imaginary part of electric modulus of polysiloxane and polysiloxane - TiO₂ nanocomposites with different weight percentages as a function of applied frequency from 50 Hz to 5 MHz. The similar behaviour is observed like the real part of electric modulus for polysiloxane and polysiloxane - TiO₂ nanocomposites except higher in a magnitude of the imaginary electric modulus. Among all the nanocomposites, 0.3 wt % of shows the highest value of imaginary electric modulus of 0.0492 due to the formation of permanent dipole polarization and distribution of TiO₂ nanoparticles in the polysiloxane [20].

Figure 10 shows the variation of tangent loss as a function of applied frequency for different weight percentages of TiO₂ in polysiloxane. It is observed that the tangent loss value decreases with increase in frequency up to 10⁴ 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 – TiO₂ nanocomposite can be used as low k – dielectric materials electrochromic and electrochemical device, capacitor, varistor etc [21].

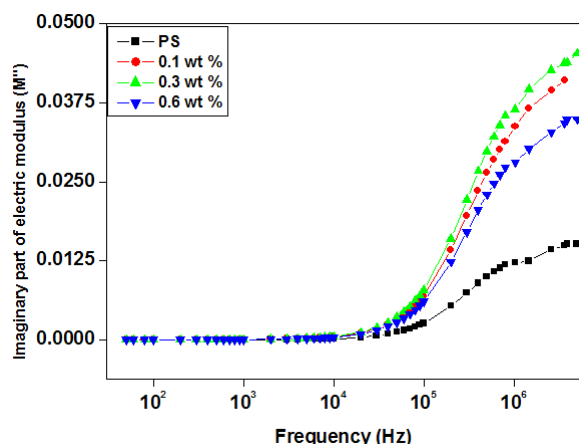


Figure 6 shows the imaginary part of electric modulus as a function of applied frequency for polysiloxane and polysiloxane – TiO₂ nanocomposites

Figure 7 shows the variation of σ_{ac} conductivity for different weight percentages of TiO₂ 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 [22]. Among all the nanocomposites, 0.3 wt % shows the high conductivity of 1.35×10^{-4} 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 [23]. Therefore, these nanocomposites can be potential candidates for the self-cleaning coating materials in superhydrophobic glass, capacitors, varistor etc.

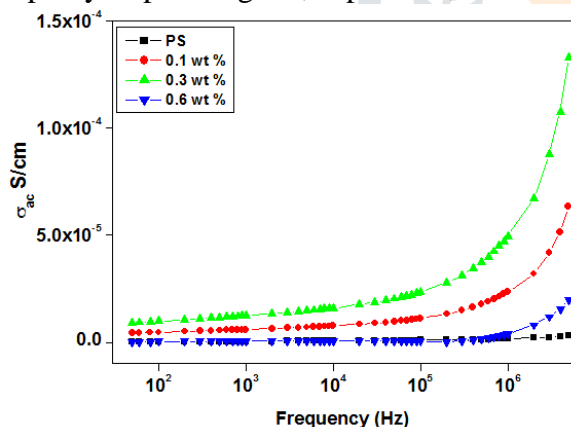


Figure 7 shows the variation in AC conductivity as a function of applied frequency for polysiloxane and polysiloxane – TiO₂ nanocomposites

7. Conclusion

The polysiloxane – TiO₂ nanocomposites have been prepared by a solvent casting method in triethanolamine and tetrahydrofuran solvents. The structural study was carried out by X-ray diffraction and Fourier transmission infrared spectroscopy. The dielectric spectroscopy study reveals that the 0.3 wt % shows low dielectric constant and dielectric loss, as a result, it shows high conductivity of 1.35×10^{-4} S/cm. 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. The quality factor confirms that there is a small damping loss for 0.3 wt % of nanocomposites which is favorable for the high conductivity. Therefore, these nanocomposites can be potential candidates for many high dielectrics engineering applications.

References

- [1] 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
- [2] 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
- [3] 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
- [4] Dewasthale S, Andrews C, Graiver D, Narayan R, Water Soluble Polysiloxanes. *Silicon.* 2017; 9: 619
- [5] 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
- [6] Dünki S. J, Reyes E. C, Opris D. M, A facile synthetic strategy to polysiloxanes containing sulfonyl side groups with high dielectric permittivity. *Polym. Chem.* 2017; 8: 715
- [7] Racles C, Cozan V, Bele A, Dascalu M, Polar silicones: structure-dielectric properties relationship. *Designed Monomers and Polymers,* 2016; 19: 496
- [8] Giaveri S, Gronchi P, Barzoni A, IPN Polysiloxane-Epoxy Resin for High-Temperature Coatings: Structure Effects on Layer Performance after 450 °C Treatment. *Coatings.* 2017; 7: 213
- [9] Riehle N, Thude S, Götz T, Kandelbauer A, Thanos S, Tovar G.E.M, Lorenz G, Influence of PDMS molecular weight on transparency and mechanical properties of soft polysiloxane-urea-elastomers for intraocular lens application, *Eur. Polym. J.* 101 (2018) 190
- [10] Lu K, Erb D, Liu M, Phase transformation, oxidation stability, and electrical conductivity

- of TiO₂-polysiloxane derived ceramics. *J Mater Sci.* 2016; 51: 10166
- [11] Huang P, Shi H.Q, Xiao H.M, Li Y. Q, Hu N, Fu S.Y, High performance surface-modified TiO₂/silicone nanocomposite. *Scientific Reports.* 2017; 7: 5951
- [12] 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
- [13] 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
- [14] Li W, Liang R, Hu A, Huang Z, Zhou Y N, Generation of oxygen vacancies in visible light-activated one-dimensional iodine TiO₂ photocatalysts, *RSC Adv.*, 2014; 4: 36959
- [15] Shen Y, Wang L, Zhang H, Wu T, Pan H Y, Preparation and characterization of titania/silicone nanocomposite material. *Mat. Sci. Engg.* 2015; 87: 012021
- [16] Roy. AS. Antistatic and dielectric properties of one-dimensional Al²⁺:Nd₂O₃ nanowire doped polyaniline nanocomposites for electronic application. *Sensors and Actuators A* 2018; 280: 1
- [17] Lee J W, Cho H. B, Nakayama T, Suzuki T, Suematsu H, Niihara K, Internal structure control of the TiO₂ nanotubes and polysiloxane nanocomposites by nanosecond pulsed electric field. *Journal of Asian Ceramic Societies.* 2014; 2: 97
- [18] Chiu Y C, Huang C C, Tsai H C. Synthesis, characterization, and thermomechanical properties of siloxane-modified epoxy-based nanocomposite. *J. Appl. Polym. Sci.* 2014; 131: 40984
- [19] Ma T, Yang R, Zheng Z, Song Y. Rheology of fumed silica/polydimethylsiloxane suspensions. *Journal of Rheology* 2017; 61: 205
- [20] Cassagnau, P. Melt rheology of organoclay and fumed silica nanocomposites, *Polymer* 2008; 49: 2183
- [21] Kirst, K. U., F. Kremer, and V. M. Litvinov, Broad-band dielectric spectroscopy on the molecular dynamics of bulk and adsorbed poly(dimethylsiloxane). *Macromolecules* 1993; 26: 975
- [22] Roy AS, Gupta S, Seethamraju S, Ramamurthy PC, Madras G. Fabrication of Poly(Vinylidene Chloride-Co-Vinyl Chloride)/TiO₂ Nanocomposite Films and Their Dielectric Properties. *Science of Advanced Materials.* 2014; 6: 946
- [23] Ansari JN, Khasim S, Parveen A, Hartomy O AA, Khattari Z, Badi N, Roy AS. Synthesis, characterization, dielectric and rectification properties of PANI/Nd₂O₃:Al₂O₃ nanocomposites. *Polymers for Advanced Technologies.* 2016; 27: 1064