

ANALYSIS OF DIELECTRIC PROPERTIES OF POLYSILOXANE-TiO₂ COMPOSITES AND ITS FREQUENCY

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Abstract:

Flexible polydimethylsiloxane-titania (PDMS-TiO₂) nanocomposites of different composition are prepared using two mixing methods/techniques. In the present study, PDMS elastomer is used as base matrix and titania (TiO₂) as ceramic filler. The effect of titania on thermal, electrical, and mechanical properties is investigated for different composites at various concentration of titania. A variety of electrical and mechanical tests are performed on the resultant composites and found that dielectric constant of composites increased significantly with the increase in titania concentration whereas volume resistivity of composites decreased. The effect of titania concentration is also studied with respect to tensile strength, % elongation at break (% E. B.), and tensile modulus. The effect of pressure on dielectric constant and resistivity of composites has also been studied in order to determine the piezoelectric behavior of the composites.

Keywords: poly(dimethylsiloxane), dielectric properties, Nanocomposites,

1. Introduction

Over the past decade, there has been growing interest in nanocomposites, a new class of reinforced polymers produced by the introduction of nanoparticles into a polymeric matrix. The large specific surface area of nanoparticles makes them very reactive, thereby giving

nanocomposite coatings unique and remarkable properties. Multiple characteristics, including hydrophobicity, flame resistance, and the UV resistance of coatings, can be improved by adding small quantities of nanoparticles. Furthermore, these coatings can be applied to all surfaces. The difficulties encountered during the elaboration of nanocomposites generally involve the choice of base polymer as well as the nature of the nanoparticles (both in terms of size and quantity), the optimization of the production process, and, in particular, the verification of the homogeneous dispersal of nanoparticles within the polymeric matrix. 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.

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 degree of nanoparticle agglomeration in a sample reflects the quality of the dispersal. One of the limitations to the development of nanocomposites is the ability to develop manufacturing processes that favour the homogeneous and reproducible dispersal of nanoparticles within nanocomposites. Poor dispersal increases the number and size of the aggregates, leading to the deterioration of the properties of the materials.

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. 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. 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

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.

Synthesis of polysiloxane – TiO₂ nanocomposites

The nanocomposite films were ready by a dissolvable projecting strategy. 5 gm of

polysiloxane was broken down in 150 ml of tetrahydrofuran (THF) and blended for 72 hrs to get a reasonable arrangement. Then 0.1, 0.3 and 0.6 wt % of TiO₂ and 0.25 ml of triethanolamine (TOEA) were blended in with the above arrangement with high extreme ultra-sonication until disintegration happens. The homogeneous blend then filled a round Teflon shape and dried in room temperature to eliminate the dissolvable and later warmed with 50 °C to frame a dried meager film of nanocomposites. In a comparable strategy, unadulterated polysiloxane flimsy film was ready as continuing in readiness of nanocomposites.

3. Characterization

The X-ray crystallography was completed by utilizing Philips X-beam diffractometer for the scope of 10° to 80° at the pace of 2° each second with CuK α radiation of frequency $\lambda = 1.5406 \text{ \AA}$. The utilitarian gathering of the polysiloxane and its nanocomposites were concentrated by involving PerkinElmer1600 spectrophotometer in KBr medium. The nanocomposite was blended in with KBr precious stones in the proportion of 1:5 and grounded the combination to got homogeneous compound. The surface morphology of the nanocomposite was portrayed by Scanning electron microscopy model of Philips XL 30 ESEM spectroscopy. The nanocomposites films were fixed onto the carbon-covered copper matrix and bring into the infinitesimal example holder for the picture filtering. Further, the impedance spectroscopy of the nanocomposite was done by Hoki LCR-Q meter from the recurrence scope of 50 Hz to 5 MHz.

4. Results and discussion

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. 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.

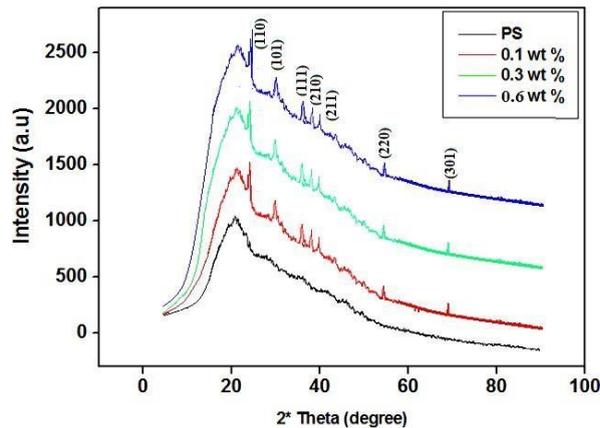


Figure 1 XRD pattern of polysiloxane and polysiloxane – TiO₂ nanocomposites

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 wellconnected 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.

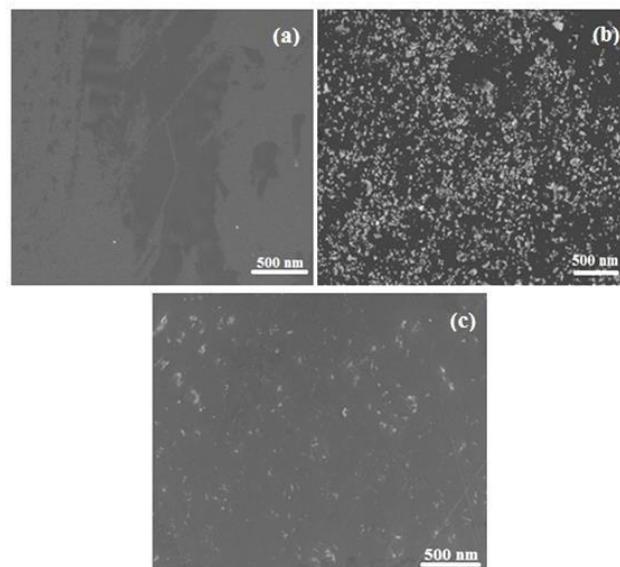


Figure 2 SEM image of polysiloxane, TiO₂ and 0.3 wt % of polysiloxane – TiO₂ nanocomposites

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 10^3 Hz after that it almost remains constant which 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. 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 reasons 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 magnitude of imaginary permittivity. Among all the nanocomposites, 0.3 wt % shows the low imaginary permittivity value of 584 F/m due to the dipole polarization effect and distribution of TiO₂ nanoparticles in polysiloxane.

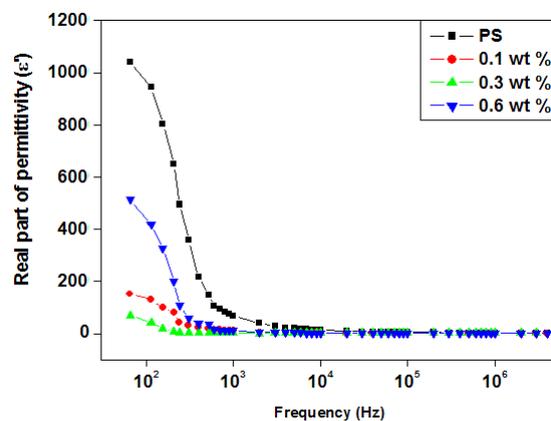


Figure 3 shows the real part of permittivity as a function of applied frequency for polysiloxane and polysiloxane – TiO₂ nanocomposites

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 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. For all the nanocomposites, the hump are formed at the mid-frequency range between 10^4 to 10^5 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.

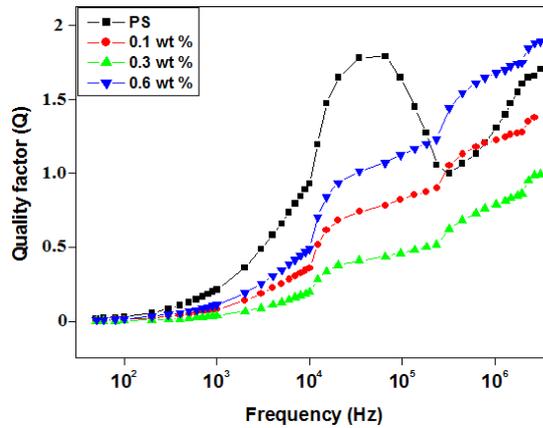


Figure 4 shows the quality factor as a function of applied frequency for polysiloxane and polysiloxane – TiO₂ nanocomposites.

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.

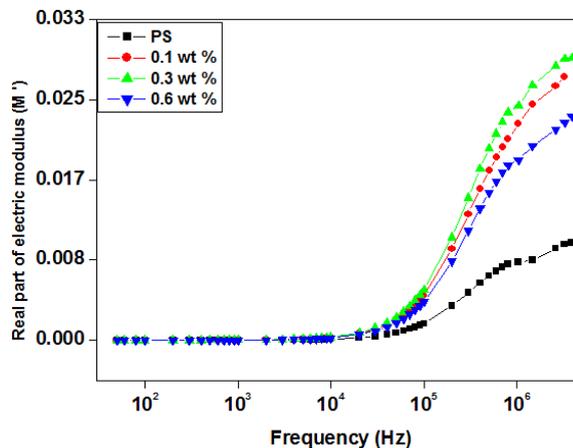


Figure 5 shows the real part of electric modulus as a function of applied frequency for polysiloxane and polysiloxane – TiO₂ nanocomposites

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.

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.

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

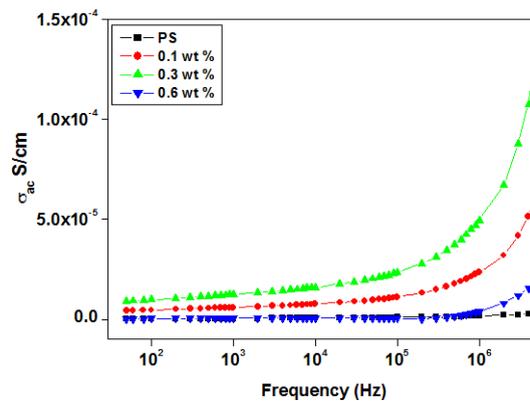


Figure 7 shows the variation of σ_{ac} conductivity for different weight percentages of TiO₂ in polysiloxane as a function of frequency. It is observed that the conductivity of pure polysiloxane and its nanocomposites increase with an increase in frequency. The conductivity of the nanocomposites depends 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. 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. Therefore, these nanocomposites can be potential candidates for the self-cleaning coating materials insuper hydrophobic 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 arranged by a dissolvable projecting

strategy in triethanolamine and tetrahydrofuran solvents. The underlying review was done by X-beam diffraction and Fourier transmission infrared spectroscopy. The dielectric spectroscopy study uncovers that the 0.3 wt % shows low dielectric consistent and dielectric misfortune, accordingly, it shows high conductivity of $1.35 \times$ affirmative S/cm. Among all the nanocomposites, 0.3 wt % of shows the most reduced digression misfortune worth of 0.1 due to the non-debye's sort of unwinding process where the charge transporters are loose at the higher energy state for a more drawn out time frame. The quality variable affirms that there is a little damping misfortune for 0.3 wt % of nanocomposites which is ideal for the high conductivity. Therefore, these nanocomposites can be potential candidates for many high dielectrics engineering applications.

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