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AC conductivity and Dielectric behavior of poly (o-phenylenediamine)/ZnO nanocomposites

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Abstract

Poly (o-phenylenediamine) and their nanocomposites with ZnO nanoparticles were synthesized using oxidative polymerization method and the polymer nanocomposites were characterized using FT-IR, UV-VIS spectroscopy and the morphology have been analyzed by XRD, SEM and TEM. The stability of the prepared polymer nanocomposites was studied using TGA, DTA and found to have high thermal stability. The study of ac conductivity, dielectric property revealed that the formed nanocomposites are semiconducting in nature and can be widely used in the field of energy storage and semiconductor devices, in diodes, batteries etc.

Keywords: Polyphenylenediamine, nanocomposites, dielectric property, ac conductivity

1. Introduction

Polymeric composites with high dielectric constant have attracted great attentions in capacitors and charge-storage applications due to their high dielectric strength and good processability^[1]. However, the dielectric constant of general polymer is so low that limits their practical applications. Thus, extensive efforts have been focused on increasing dielectric constant of polymer. Dielectric constant of polymeric materials can be drastically enhanced when volume fraction of conductive filler reaches percolation threshold^[2, 3]. The creation of polymer/inorganic nanoparticle composites having unique physical properties have been attracted much attention in the recent research work. Polymeric materials with high dielectric constants are highly desirable for use in actuators, artificial muscles, and charge-storage devices^[4-11].

The understanding of charge transport mechanism in the composite materials is very important both from fundamental and technological points of view. The impedance measurement is one of the powerful techniques to characterize and realize the charge transport in the complex materials. The studies on dielectric properties of new systems are useful for possible technical applications. Various theoretical models were developed for the description of charge transport in conducting polymers^[12, 13].

It is well known that composites can be produced exhibiting enhanced properties that the constituent materials may not exhibit^[14-17]. For instance, from the combination of different fibers or fillers with polymer matrices one can produce polymer-matrix composites, a material important to the electronic industry for its dielectric properties in the use of capacitors^[18-20]. The polymeric interfaces act as charge-carrier trapping sites^[21]. Therefore, it has become essential to study the effect of interfaces on the charge-carrier generation, transport and storage in polymeric systems. The study of dielectric constant and dielectric loss, as a function of temperature and frequency is one of the most convenient and sensitive methods of studying polymeric structure^[22].

The preparation of nanocomposites of polyphenylenediamine with inorganic nanoparticles is thought to be a potential route to improve the performance of poly phenylenediamine to obtain the materials with synergetic or complementary behavior between polyphenylenediamine and inorganic nanoparticles. Thus, the preparation of a PPDs based nanocomposite is receiving attention since it can exhibit unique properties arising from the electrically conductive PPDs and metal/semiconducting nanoparticles^[23].

In the present study, PoPDA and their nanocomposites with ZnO nanoparticles were synthesized using FeCl₃ as an oxidant and studied applications like dielectric property and ac conductivity.

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2. Materials and Methods

2.1. Materials

The monomer *o*-phenylenediamine, ferric chloride, surfactant Sodium Dodecyl Sulfate was purchased from Merck, all the other chemicals and reagents were of Analytical Grade and used as received without further purification. The nanoparticles of ZnO were purchased from Sigma Aldrich of particle size 50-55nm.

2.2. Methods

2.2.1. Synthesis of poly (*o*-phenylenediamine) with ZnO nanoparticles

The equimolar volume of *o*-phenylenediamine and hydrochloric acid was prepared and ZnO is added in the weight percentages of 10, 20 and 30% to the above solution and kept for vigorous stirring to keep the ZnO suspended in the solution. To this, SDS was added as an emulsifier and ferric chloride was added drop wise as an oxidant. The obtained solutions were kept for stirring at room temperature for 6 hours to polymerize the monomers. The poly (*o*-phenylenediamine)-ZnO nanocomposites (PoPDA/ZnO) precipitate was collected on filtration, washed with deionised water followed by methanol to remove the oligomers and unreacted monomers present in the polymers [24].

2.3. Characterization techniques

The FT-IR spectrum of the synthesized samples was recorded on an ABB-MB-3000 FT-IR spectrometer in KBr medium. The UV-Vis spectrum of polymers was taken using Perkin Elmer Lambda UV-Vis- Spectrometer by dissolving the polymers in DMSO as a solvent. The XRD was measured with Bruker AXS D8 Advance using Cu as X-ray source at the Wavelength of 1.5406 Å of angular range from 3° to 135°. Scanning electron microscopy was used to study the morphology of the synthesized polymers using JEOL, JSM-6390LV model. High-resolution transmission electron microscopy was measured using Tecnai T20 G2 S-TWIN of operating voltage 250 kV. TG/DTA was recorded using Perkin Elmer STA 6000 model. Differential Scanning Calorimetry (DSC) was measured using Mettler Toledo DSC 822e from room temperature to 300°C. The Broadband Dielectric Spectrometer (BDS) was measured in pellet form using NOVOCONTROL Technologies, GmbH & Co. Germany, Concept 80 model.

3. Results and discussion

3.1. FT-IR spectra of poly (*o*-phenylenediamine) with different concentrations of ZnO nanoparticles

The FT-IR spectra of synthesized PoPDA nanocomposite with different weight percentages of ZnO nanocompounds like 10, 20 and 30% (PoPDA/10%ZnO, PoPDA/20%ZnO, PoPDA/30% ZnO) are shown in figure 1. The presence of single band at 3348 cm⁻¹ is due to the N-H stretching vibrations of the -NH-group. The two peaks at 3412, 3190 cm⁻¹ are ascribed to the asymmetrical and symmetrical of N-H stretching vibrations of NH₂ group. Two strong peaks at 1681 cm⁻¹ and 1516 cm⁻¹ are associated with the stretching vibrations of C=N and C=C group in phenazine ring. The peaks at 1374 cm⁻¹ and 1252 cm⁻¹ are due to C-N-C stretching in the benzenoid and quinoid imine units. Furthermore, the bands at 723 cm⁻¹ and 579 cm⁻¹ are characteristic of C-H out-of-plane bending vibrations of

benzene nuclei in the phenazine skeleton. The spectra of the nanocomposites have slightly shifted to longer wave number due to formation of hydrogen bonding between oxygen of ZnO and hydrogen of -NH- group present in the polymer. In addition to the above peaks, the M-O peak was observed at 457 cm⁻¹ which is due to M-O bond stretching vibration of ZnO metal oxides which confirms the incorporation of ZnO into the polymeric matrix [25] and S=O peak at 1051cm⁻¹ confirms SDS also incorporated into the polymeric backbone.

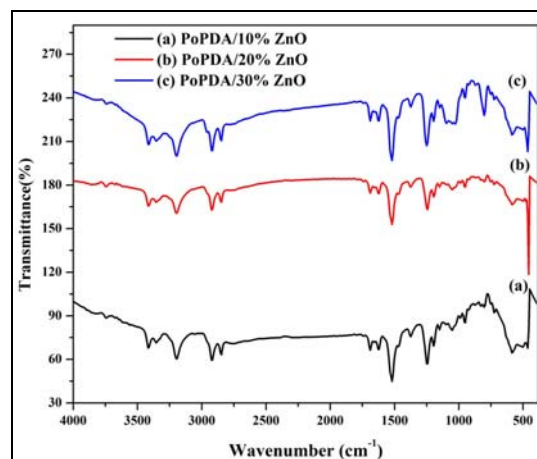


Fig 1: FT-IR spectra of poly (*o*-phenylenediamine) with different concentrations of ZnO nanoparticles

3.2. UV-VIS spectra of poly (*o*-phenylenediamine) with different concentrations of ZnO nanoparticles

The UV-Vis spectra of PoPDA/10%ZnO, PoPDA20%ZnO and PoPDA30%ZnO shows the major peaks at 291 and 438 nm (Figure 2). The band at 438 nm is assigned to π - π^* transition associated with the phenazine ring conjugated to the two lone pairs of electron present on the nitrogen of the NH₂ groups, the peak is broad and it suggests the existence of quinoneimine moieties. The other peak at about 291 nm is mainly assigned to the π - π^* transitions of the benzenoid and quinoid structures.

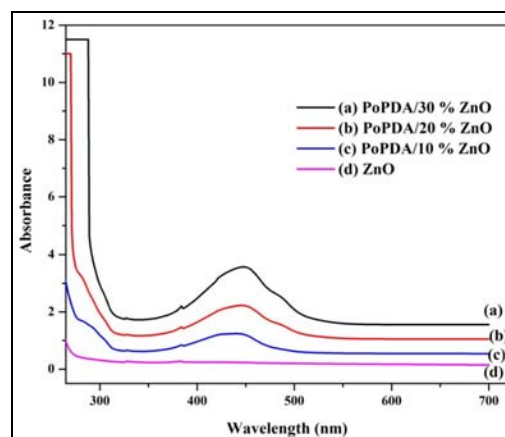


Fig 2: UV-Vis spectra of poly (*o*-phenylenediamine) with different concentrations of ZnO nanoparticles

3.3. XRD of poly (*o*-phenylenediamine) nanocomposites with different concentrations of ZnO nanoparticles

In the XRD pattern of ZnO nanoparticles, the peaks at $2\theta = 31.8^\circ, 34.4^\circ, 36.2^\circ, 47.5^\circ, 56.6^\circ, 62.8^\circ, 67.9^\circ,$ and 69.1° appear, which are ascribed to be (100), (002), (101), (102),

(110), (103), (112), and (201) diffraction peaks of wurtzite ZnO, respectively [26, 27]. The XRD of PoPDA nanocomposites with different concentrations ZnO nanoparticles like 10, 20 and 30% exhibits a series of sharp lines (Figure 3) in the regions of $5^\circ < 2\theta < 30^\circ$ and this may be due to the scattering from PoPDA chains at interplanar spacing [28] and indicate that the PoPDA nanocomposites has good crystallinity at all concentrations of the ZnO

nanoparticles. In the polymer nanocomposites, the diffraction of ZnO nanoparticles was found to decrease and they disperse evenly into the polymeric matrix [29]. The X-ray data of PoPDA nanocomposites with ZnO nanoparticles presents crystalline peaks similar to those obtained from pure PoPDA, revealing that no additional crystalline order has been introduced into the composite [30], and this is confirmed by SEM and TEM analysis.

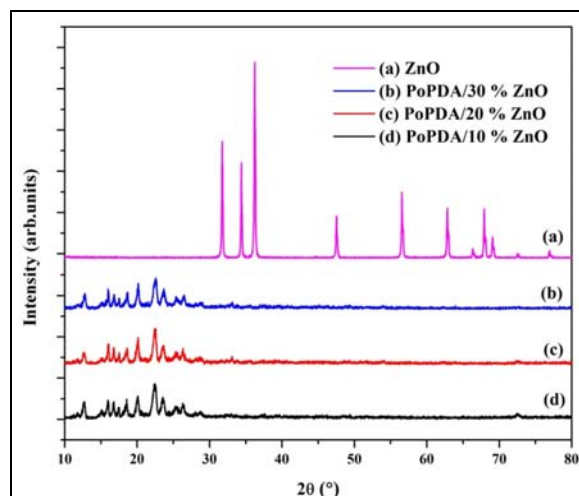


Fig 3: XRD spectra of poly (o-phenylenediamine) with different concentrations of ZnO nanoparticles

3.4. SEM images of poly (o-phenylenediamine) nanocomposites with different concentrations of ZnO nanoparticles

The morphology of the PoPDA nanocomposites with 10%, 20% and 30% ZnO are given in figures 4a-c. The morphology of the polymer nanocomposites synthesized with the different composition of the ZnO nanoparticles are found to have layered like platelets with uniform surface. As

the percentage of ZnO nanoparticles increased the layered platelets is increased. The SEM image of the PoPDA with 30% ZnO is having smooth and even surface with many layers stacked together when compare to 10 and 20% of ZnO nanoparticles. The incorporation of the ZnO nanoparticles in the polymer matrix is not visible in SEM image and this may be due to dispersion of ZnO nanoparticles inside of the polymeric matrix.

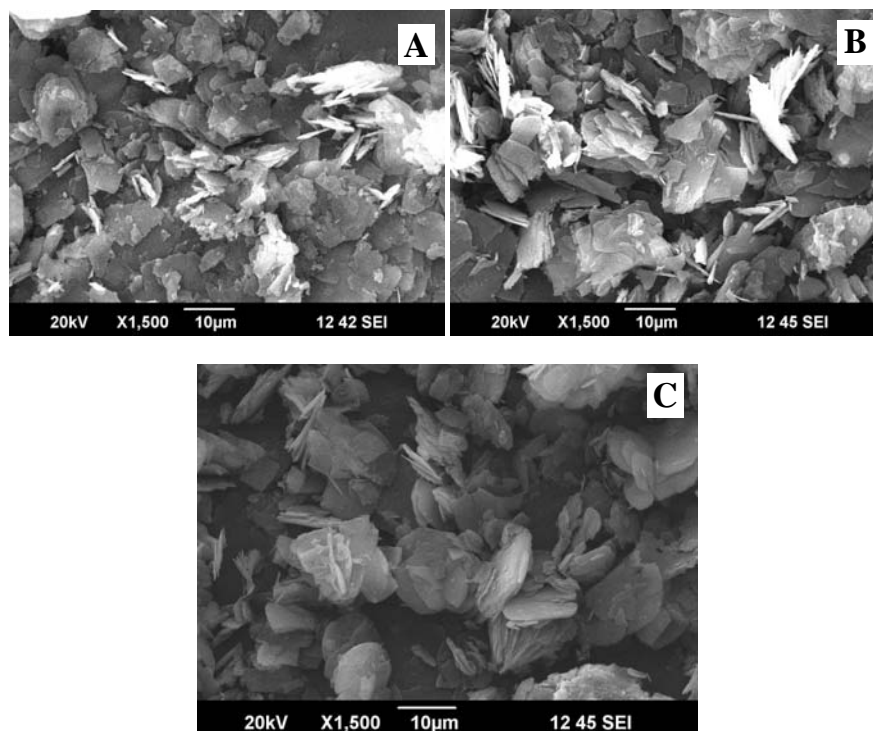


Fig 4a-c: SEM images of PoPDA with 10, 20 and 30% ZnO nanoparticles

3.5. TEM study of poly (o-phenylenediamine) with 30% ZnO nanoparticles

HRTEM was used to image the polymer nanocomposite of PoPDA with 30% ZnO nanoparticles and found to have aggregated spherical like particles with the particle size of 50-55 nm. The TEM image confirms that the ZnO nanoparticles are embedded into the polymeric matrix. The surface of the ZnO nanoparticles was surrounded by a layer

of the polymer and the ZnO nanoparticle was incorporated inside the shell of the polymer. The formation of core-shell morphology of the nanocomposite was evident from the HRTEM [31]. The image also shows the outer lining of a black surface (figures 5a-c) which is due to the ZnO nanoparticles and this confirms the formation of polymer nanocomposites and the ZnO nanoparticles incorporated into the polymer.

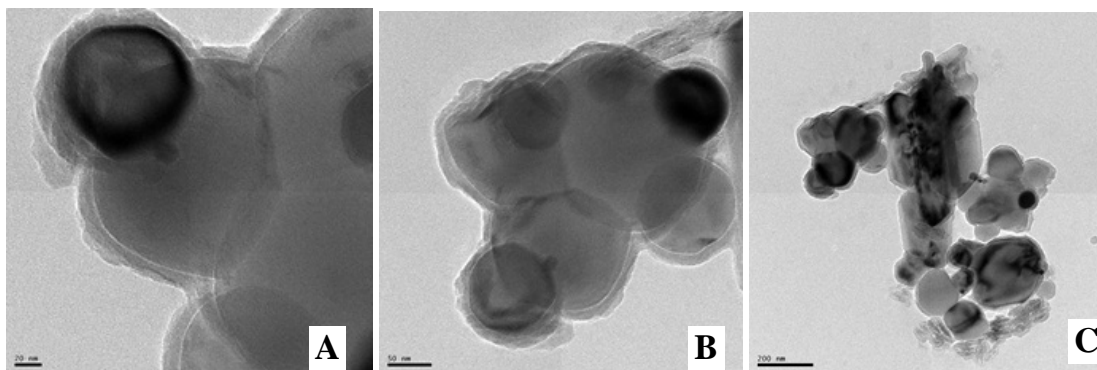


Fig 5a-c: HRTEM images of PoPDA/ 30% ZnO nanocomposites at different magnification

3.6. TGA and DTA of poly (o-phenylenediamine) nanocomposites with different concentrations of ZnO nanoparticles

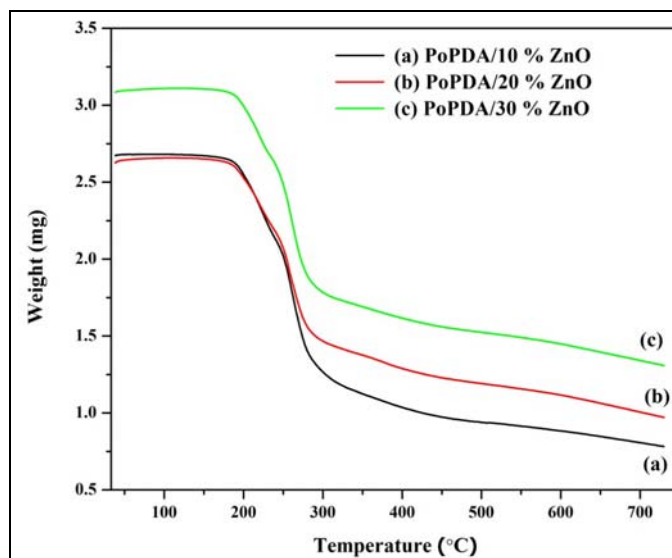


Fig 6: TGA spectra of poly (o-phenylenediamine) nanocomposites with different concentrations of ZnO nanoparticles

PoPDA synthesized with the different concentrations of ZnO nanoparticles like 10%, 20%, 30% are found to have three stages of thermal transition that lead to weight loss (Figure 6). The first thermal transition from 200 to 220°C is ascribed to the removal of dopants molecules. The second thermal transition from 230 to 290°C corresponds to the loss of low molecular weight oligomers or side products present in the polymer compound. The third transition is observed between 300 °C to 734 °C with a weight loss of ~30%, which can be attributed to the degradation of benzenoid and quinonoid repeating units of the polymeric backbone. The residue left at the end of the heating process is found to be 0.7995 mg for PoPDA with 10%ZnO, 1.0206mg for PoPDA with 20%ZnO and 1.3855mg for PoPDA with 30%ZnO

nanoparticles. When the percentage of ZnO nanoparticles increased, the amount of residue present was found to be more which confirms the incorporation of metal oxide into the polymer. The DTA curves of PoPDA with 10%, 20% and 30% ZnO nanoparticles shows an exothermic plateau in temperature range 400-705°C which is mainly related to the decomposition of organic moiety (Figure 7) and these peaks are related to the main stage of decomposition of the polymeric backbone.

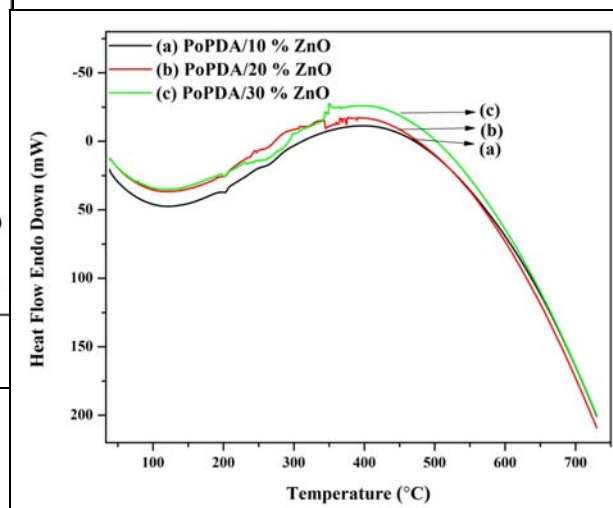


Fig 7: DTA spectra of poly (o-phenylenediamine) nanocomposites with different concentrations of ZnO nanoparticles

3.7. DSC spectrum of poly (o-phenylenediamine) nanocomposites with ZnO nanoparticles

The DSC spectrum of poly (o-phenylenediamine) with 30 weight percentage of ZnO nanoparticles shows an endothermic peak at 213°C is due to the glass transition temperature (Figure 8). The polymer starts to melt above 260°C which is shown by endothermic peak at 271.22°C which is characteristics of melting temperature polymer nanocomposites.

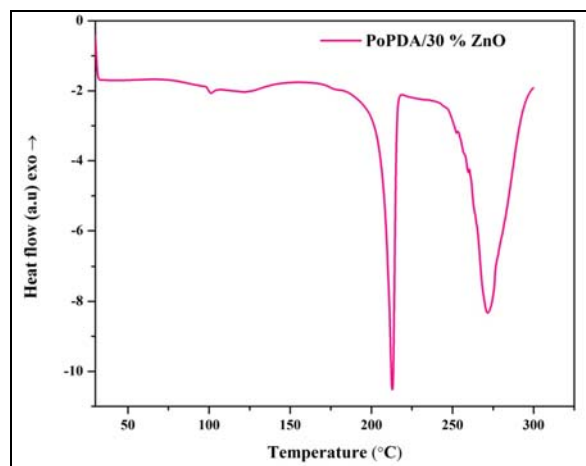


Fig 8: DSC spectrum of poly (o-phenylenediamine) nanocomposites with ZnO nanoparticles

3.8. Study of AC conductivity

The complex impedance spectra of synthesized polymers and the polymer nanocomposites with different weight percentages of ZnO nanoparticles were evaluated by plotting real (Z') and imaginary part (Z'') of complex impedance. From the plot the bulk resistance (R_b) for the prepared samples was evaluated by analyzing the impedance data using ZSimpdemo software. The conductivity values of polymers and their nanocomposites with 10, 20 and 30% of ZnO nanoparticles were evaluated using bulk resistance (R_b) using the formula,

$$\sigma = (t / A) (1 / R_b) \text{ S/cm}$$

Where, t is the thickness of the pellet, A is the area of pellet and R_b is the bulk resistance of the pellet.

The conductivity of PoPDA nanocomposites prepared with 10, 20 and 30% ZnO nanoparticles are given in figure 9. The conductivity of the polymer nanocomposites increased upon the addition of ZnO nanoparticles. The conductivity of PoPDA with 10, 20 and 30 % ZnO nanoparticles are found to be 1.1839×10^{-5} S/cm, 1.3204×10^{-5} S/cm and 1.5409×10^{-5} S/cm respectively. The increase in conductivity upon addition of ZnO is due to the incorporation of nano metaloxide [32], which significantly increases the conductivity to the order of 10^{-5} S/cm.

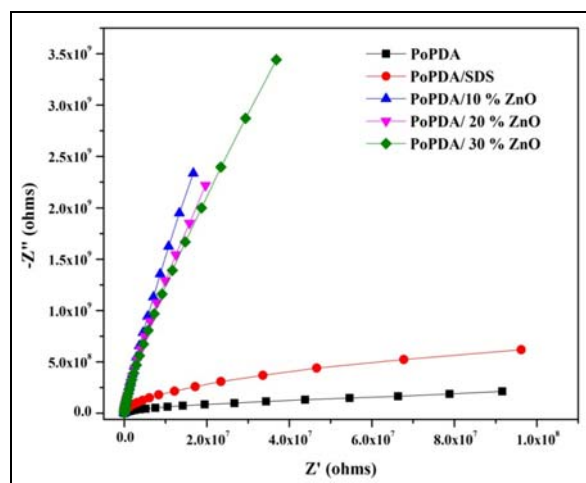


Fig 9: Complex Impedance Spectra of Poly (o-Phenylenediamine) and their Nanocomposites with Different Concentrations of ZnO Nanoparticles

3.9. Variation of ac conductivity with frequency

The σ_{ac} conductivity of pure PoPDA, PoPDA prepared with SDS and PoPDA nanocomposites synthesized with 10%, 20% and 30% ZnO nanoparticles at room temperature from the frequencies 10Hz to 1MHz are presented in figure 10. The conductivity of pure PoPDA and its polymer nanocomposites increases with increase in frequencies and obeys universal power law [33]. The conductivity is almost constant up to 300 kHz and increases suddenly with increase in frequencies from 400 kHz to 1 MHz which are the characteristic property of the disordered materials [34]. Among all PoPDA nanocomposites synthesized 30 wt% ZnO shows higher conductivity than the rest of the nanocomposites.

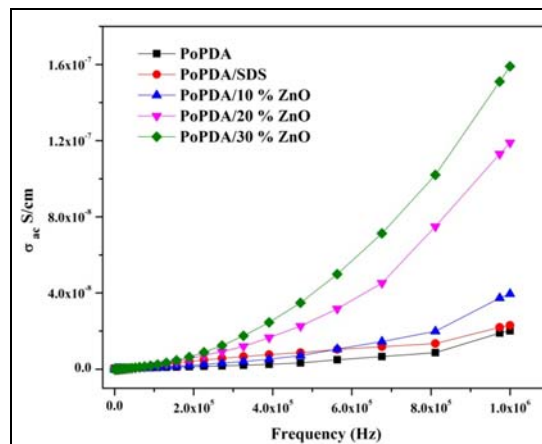


Fig 10: Plot of σ_{ac} Vs Frequency of Poly (o-Phenylenediamine) and their Nanocomposites with Different Concentrations of ZnO Nanoparticles

3.10. Dielectric analysis

3.10.1. Dielectric analysis of poly (o-phenylenediamine) nanocomposites with different concentrations of ZnO nanoparticles

The dielectric analysis of the synthesized PoPDA and with SDS and the polymer nanocomposites synthesized with the different concentrations ZnO nanoparticles like 10, 20 and 30% were carried out and the plot of ϵ' and ϵ'' against frequency for the PoPDA with ZnO nanocomposites with different weight percentages are given in the figure 11, 12 respectively. From the figure it was found that both ϵ' and ϵ'' were found to increase with the decrease in frequency behind 2 Hz for all the synthesized polymer nanocomposites. The increment in ϵ' with decrease of frequency reveals that the systems exhibit strong interfacial polarization at low frequency.

As the percentage of ZnO nanoparticles increased the dielectric permittivity is found to increase. Among the polymers and polymer nanocomposites, the polymer nanocomposites prepared with 30% of ZnO nanoparticles are found to have high permittivity values with the dielectric constant of 1.05 when compared to the PoPDA and PoPDA prepared using SDS and polymer nanocomposites synthesized with 10 and 20% ZnO nanoparticles. The increment in dielectric constant at 30% of ZnO nanoparticles is due to the dielectric relaxation i.e., because of the movement of dipole and charge carriers (dopant) in the presence of to the applied alternating field. [35]

The dielectric loss i.e., ϵ'' decreases with increase in frequency for the entire polymer and its nanocomposites.

The polymer nanocomposites are having low dielectric loss when compare to polymers. Among them PoPDA with 30% ZnO has low dielectric loss when compared to the other synthesized polymeric materials. The low frequency dispersion for ϵ' and no loss peak for ϵ'' are characteristics of charged carrier systems [36].

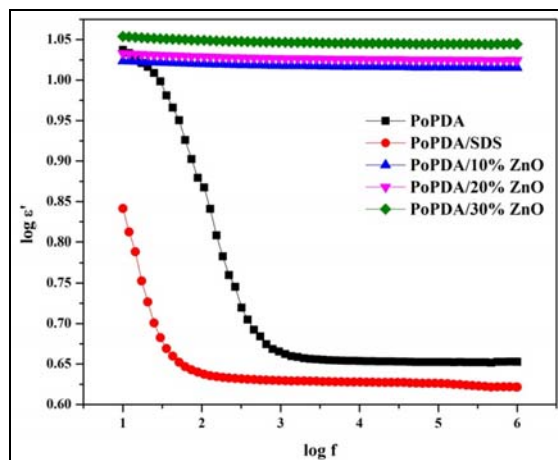


Fig 11: Plot of $\log \epsilon'$ Vs \log Frequency of Poly (o-Phenylenediamine) and their Nanocomposites with Different Concentrations of ZnO Nanoparticles

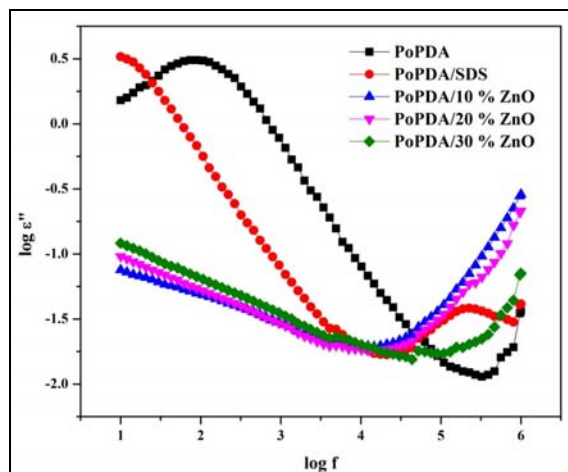


Fig 12: Plot of $\log \epsilon''$ Vs \log Frequency of Poly (o-Phenylenediamine) and their Nanocomposites with Different Concentrations of ZnO Nanoparticles

3.10.2. Variation of tangent loss with frequency

The plot of tangent loss ($\tan \delta$) against frequency for PoPDA, PoPDA synthesized with SDS, PoPDA nanocomposites with different concentrations of ZnO nanoparticles are given in figure 13. The $\tan \delta$ show high dissipation loss at low frequency in the PoPDA and PoPDA with SDS and this high dissipation may be due to DC conduction losses. At low frequencies dielectric loss is found to increase and then decreases. Peak appearing at a characteristic frequency suggests the presence of relaxing dipoles in the samples. At higher frequencies these exhibit almost zero dielectric loss which suggests that these polymers are lossless materials at frequencies above 10^3 Hz frequency [37]. The PoPDA nanocomposites with ZnO nanoparticles did not show any characteristic loss peak in the analyzed frequency range and this show that the polymer

nanocomposite can withstand high amount of energy without any loss.

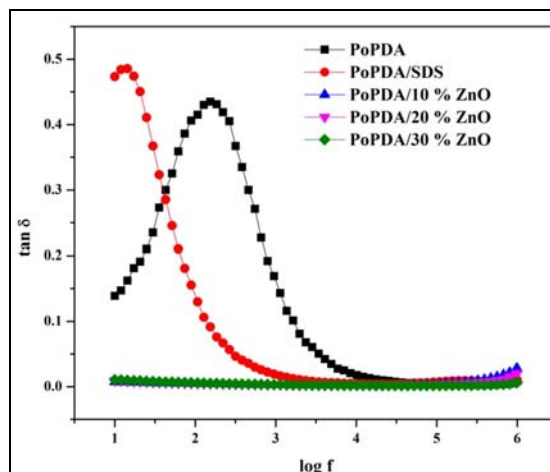


Fig 13: Plot of $\tan \delta$ Vs \log Frequency of Poly (o-Phenylenediamine) and their Nanocomposites with Different Concentrations of ZnO Nanoparticles

4. Conclusion

The ZnO nanocomposites of PoPDA have been successively prepared via chemical oxidative polymerization method. The synthesized polymer nanocomposites were characterized using FT-IR, UV-Vis spectroscopy and from the result it is confirmed the formation of the polymers. The morphology was studied by XRD, SEM, TEM and confirmed that the synthesized nanocomposites were of highly crystalline in nature and the formation of core shell type morphology of ZnO nanoparticles incorporated into the polymer shell were confirmed. From the thermal analysis like TG/DTA, DSC, the polymer stability were analyzed and found to be thermally more stable. The PoPDA/ZnO nanocomposites have increased in electrical conductivity when compare to the PoPDA. Dielectric analysis of the polymer and their nanocomposites shows that these materials can be used as energy storage devices, semiconductor devices, piezoelectric transducers, dielectric amplifiers etc.

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