



RESEARCH ARTICLE

ELECTRICAL CONDUCTIVITIES OF SYNTHESIZED POLY o- PHENYLENEDIAMINE AND ITS NANOCOMPOSITES.

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Abstract

Poly (o-Phenylenediamine) and their metal oxide nanocomposites using different concentrations like 5%, 10% and 15% of SiO₂ nanoparticles were synthesized by chemical oxidative polymerization method using ammonium persulphate as an oxidant in the presence of HCl. The formation of polymers and their nanocomposites were confirmed from the UV-Vis and FT – IR spectroscopy. The formation of Poly (o-Phenylenediamine) nanocomposites were confirmed by the change of polymer colour from red to brown and found to exhibit band at 446nm in UV-visible spectroscopy. The crystalline nature of the synthesized polymers and their nanocomposites were determined from the XRD studies. The SEM images of the polymers recorded at different magnification shows rod like structure and found to change to flake like structures in the polymer nanocomposites synthesized at different concentration of SiO₂ nanoparticles. The TEM recorded at different angle confirms the core shell structures. The stability of the synthesized polymer and its nanocomposites were substantiated from thermal studies carried out using TGA, DTA and DSC. The comparative electrical conductivities of the polymer and its nanocomposites shows that the polymer nanocomposites exhibit higher conductivities compared to the polymer and the electrical conductivity was found to be higher for the polymer nanocomposite synthesized with 15% of SiO₂. The polymer and its nanocomposites show semiconducting nature.

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Introduction:-

Conducting polymers consisting of conjugated electronic structures have received considerable attention in the field of material science due its promising technological applications¹. Among conducting polymers; polyaniline and its derivatives have attracted much attention due to its ease of synthesis^{2,4}. It has been demonstrated that organic compounds, in particular polymers have many interesting properties such as solubility, procesability, environmental stability, and electroactivity⁵. Nanocomposites are generally defined as composites in which the components have at least one dimension (i.e., length, width or thickness) in the size range of 1-100 nm⁶. Nanocomposites differ from traditional composites in a sense that interesting properties can result from the complex interaction of the nanostructured heterogeneous phases. In addition, nanoscopic particles of a material differ greatly in the analogous properties from a macroscopic sample of the same material⁷. Nanocomposites containing organic polymers and

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inorganic particles provide a completely new class of materials with novel properties⁸. SiO₂ is an excellent catalyst support because of its chemical inertia, thermal stability and adsorption of reactants⁹. Silicon oxide is normally generated from sand that is extracted after a fusion of high temperature. Characterisation temperature was determined via the temperature at which the highest Specific Surface Area (SSA) and highest amount of silica were observed which was 700°C¹⁰.

The polymer/silica nanocomposites can improve the physical properties such as the mechanical and thermal properties of the materials and also exhibit some unique properties¹¹. Recently, several groups have combined conductive polymers with metal oxides to generate hybrid composites that possess higher reversible capacity, redox cyclability and structural stability. The properties of composites of such kind are strongly dependent on concentration of polymer¹²⁻¹⁶. An important attractive property of electroactive polymers are in fields of Light Emitting Diodes (LEDs) and solar cells (SC), field effect transistors, photovoltaic cells, and lasers etc¹⁷.

In the present study, Poly (o-Phenylenediamine) (PoPDA) and its nanocomposites were synthesized by chemical oxidative polymerization with different concentrations of SiO₂ nanoparticle. The synthesized polymer and its nanocomposites were characterized and studied for their conducting properties.

Materials and Methods:-

Materials:-

Monomer Poly (o-Phenylenediamine) (PoPDA), Ammonium persulphate (APS, 99.99%), silicon dioxide are product of sigma- Aldrich and Hydrochloric acid were procured from Merck Ltd., India. All chemicals were of analytical reagent grade and were used as received without any further purification in the present study.

Methods:-

Synthesis of Poly o-Phenylenediamine:-

The Poly o-Phenylenediamine and nanocomposites were synthesized by chemical oxidative polymerization technique using a standard procedure with slight modification^{18, 19}. The precipitated polymer was washed with distilled water until the filtrate was colourless then with acetone and methanol to remove excess initiator, monomer and oligomers. Finally the resultant polymer precipitate was dried at room temperature for 24 hours.

Characterization techniques:-

Fourier transform infrared of the synthesized samples were performed using ABB-MB-3000 spectrometer in KBr medium at room temperature. UV-Vis spectra were recorded on a Perkin Elmer Lambda spectrophotometer by dissolving the polymers in DMSO as a solvent. The X-ray powder diffraction patterns were recorded on a panalytical diffractometer (CuK α) radiation source. The XRD measurements were carried out by applying a step scanning method (2 θ ranged from 0-70°) with the scanning speed of 4° min⁻¹. The morphological study of the synthesized polymers was carried out using Scanning Electron Microscopy (SEM model: Jeol 6390 LV) with accelerating voltage of 0.5kV to 30kV. Transmission electron microscopy (TEM model Tecnai T20 G2 S-TWIN) was used to investigate the dispersion of PoPDA/ SiO₂ composites. TGA/DTA was recorded using Perkin Elmer Diamond under a nitrogen atmosphere up to 700°C using a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was measured using Mettler Toledo DSC 822^e from room temperature to 500°C. The electrical conductivity was measured at room temperature by the four-point probe technique using LCR meter HP484A.

Results and Discussion:-

FT-IR spectroscopy:-

FT-IR spectrum of the PoPDA and PoPDA synthesized with 5%, 10% and 15% of SiO₂ are given figure 1. The single peaks at 3227cm⁻¹ is due to the N-H stretching vibrations of the -NH- group²⁰. The two peaks at 3380 and 2953 cm⁻¹ are associated with the asymmetrical and symmetrical N-H stretching vibrations of the NH₂ group respectively. Two strong peaks at 1629 cm⁻¹ and 1531 cm⁻¹ are assigned to the C=C and C=N group in phenazine ring²¹. The peak at 1359 cm⁻¹ and 1286 cm⁻¹ are associated with C-N-C stretching in the benzenoid and quinoid rings²². Furthermore, the bands at 718 cm⁻¹ and 609 cm⁻¹ are the characteristic of C-H out- of- plane bending vibrations of benzene nuclei in the phenazine skeleton²³. However with addition of SiO₂ nanoparticles, the characteristic peaks are slightly shifted to the lower wave numbers with slight increase in their intensities. The shifts in the frequencies are due to the interaction between the SiO₂ nanoparticles and polymer chain which affect the

electron densities and bond energies²⁴. A strong absorption band at 1073 and 804 cm^{-1} are due to the stretching and bending vibration of SiO_2 present in the polymeric backbone²⁵.

UV-Vis spectroscopy:-

The UV-Vis spectra of PoPDA and PoPDA/ SiO_2 nanocomposites with different wt% of SiO_2 nanoparticles (5, 10 and 15%) are given in figure 2. The UV-Vis absorption spectra of PoPDA reveal that the absorption maxima at 452 and 316 nm are originating from the charge transfer-excitation. The PoPDA/ SiO_2 nanocomposites exhibited two major peaks at 280 and 446 nm. The peak at 280 nm is assigned to π - π^* transition of the benzenoid and quinoid ring and the peak at 446 nm is due to π - π^* transition associated with the phenazine ring conjugated to the lone pair of electrons present on the nitrogen of the NH_2 groups. The comparative study of the UV shows that the polymers nanocomposites are slightly shifted to lower wave length compared to the polymer²⁶.

X- Ray Diffraction:-

The X-ray diffraction pattern of PoPDA shows two sharp peaks at $2\theta = 24.95$ and 25.59 . The inter-planar distances are found to be 40.95 nm and 38.74 nm and this is responsible for the crystalline nature of the polymer as shown figure 3. The average crystalline size is calculated using Debye – Scherer equation $D = [0.89] / [\beta \cos\theta]$, Where β is full width of half maxima and the crystalline size of the polymer is found to be 8.340 nm. Generally, polymer is considered to be amorphous but here the synthesized Phenylenediamine polymer is showing crystalline structure due to Phenylenediamine and planar nature of benzenoid and quinoid structure. The XRD studies of the synthesized polymer nanocomposites are found to be amorphous in nature²⁷.

Scanning Electron Microscopy:-

The SEM images of PoPDA and PoPDA/ SiO_2 nanocomposites are given in figures 4a-d. Figure 4a shows the SEM image of PoPDA which is found highly rod like structure. The SEM morphology of polymer nanocomposites with 5%, 10% and 15% of SiO_2 nanoparticles are found to be highly agglomerated and granular in shape (4b), spherical in shape (4c) which decreases the intragranular distance as the concentration of SiO_2 increases in PoPDA and with 15% of SiO_2 (fig.4d), the SEM image with further increases in weight percentage of metal oxide particles a transition from spherical to flake like structure²⁸.

Thermogravimetric Analysis:-

Thermogravimetric analysis (TGA) is used to study the thermal stability of PoPDA and PoPDA/ SiO_2 synthesized at different concentration of SiO_2 nanoparticles like 5, 10 and 15%. The polymer and its nanocomposites are found to have three stages of thermal transition as shown in figure 5 and the thermal degradation of the polymer and its nanocomposites are almost similar. The first thermal transition occurred at 128°C is mainly due to the removal of moisture²⁹. The second thermal transition at 287°C may be attributed to the removal of dopant³⁰ and the final weight loss at 483°C - 700°C correspond to the degradation of the polymer³¹. The total residue was found to be 39.12% (wt %) for PoPDA and for the polymer nanocomposites the total residues are found to increase slightly to 42.05%, 43.85% and 45.78% (wt %) with 5%, 10% and 15% SiO_2 nanoparticles after degradation.

Differential Scanning Calorimetry:-

The DSC of PoPDA and PoPDA/5% SiO_2 , PoPDA/10% SiO_2 and PoPDA /15% SiO_2 are given figure 6 and it shows an endothermic peak at 96.47°C which is due to the glass transition temperature (T_g). The polymer starts to melt are shown by endothermic peak at 370°C which is characteristics of melting temperature³².

Transmission Electron Microscopy:-

Transmission Electron Microscopy images of polymer nanocomposites with 15% of SiO_2 nanoparticle at different angles are given in figure 7 and it found to have aggregated spherical like morphology. The TEM micrograph shows that the particle size of synthesized polymer nanocomposites range from 40-45nm. Moreover the outer shell of the TEM image of the outer core of the particle is more bright compared with the dark inner core and this forms the core-shell feature of the PoPDA/ SiO_2 nanocomposites³³. The formation of PoPDA/ SiO_2 core shell nanocomposites was attributed to the strong electrostatic interaction between PoPDA and SiO_2 .

Electrical conductivity:-

The electrical conductivity of PoPDA and PoPDA/ SiO_2 (5wt%, 10wt% and 15wt %) were determined using four-point-probe technique at room temperature and the results are given in figure 8. The conductivity values of PoPDA and its nanocomposites were evaluated using bulk resistance (R_b) using the formula: $\sigma = (t / A) (1 / R_b)$ 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 electrical conductivity of the PoPDA and PoPDA synthesized with 5, 10, and 15% SiO_2 nanoparticles are found to be 1.79×10^{-8} S/cm, 1.59×10^{-7} , 2.13×10^{-7} and 2.78×10^{-7} S/cm. The results clearly show that the conductivity increases from polymer to the polymer nanocomposites and as the concentration of the SiO_2 increases, the conductivity increases slightly. When added different concentration of metal oxide nanopowder, it was found that the electrical conductivity of polymer SiO_2 nanocomposites was found to improve³⁴. The electrical conductivity of the polymer nanoparticle increase when the polymer was developed with metal oxide used.

Fig 1:- FT-IR spectra of PoPDA and its SiO_2 nanoparticles at different concentrations

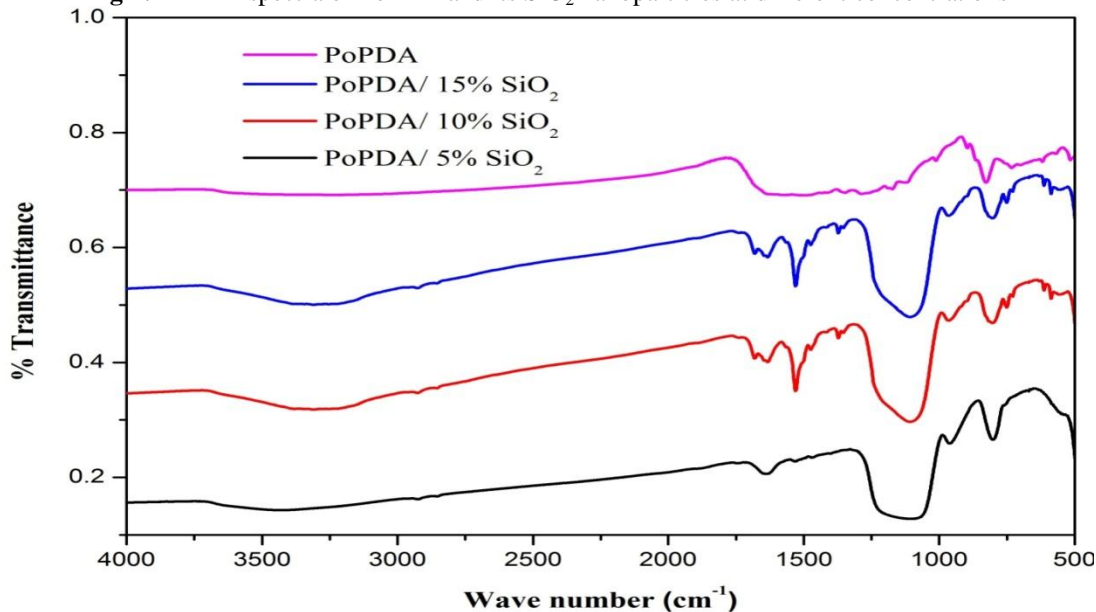


Fig 2:- UV-Vis spectra of PoPDA and its SiO_2 nanoparticles at different concentrations.

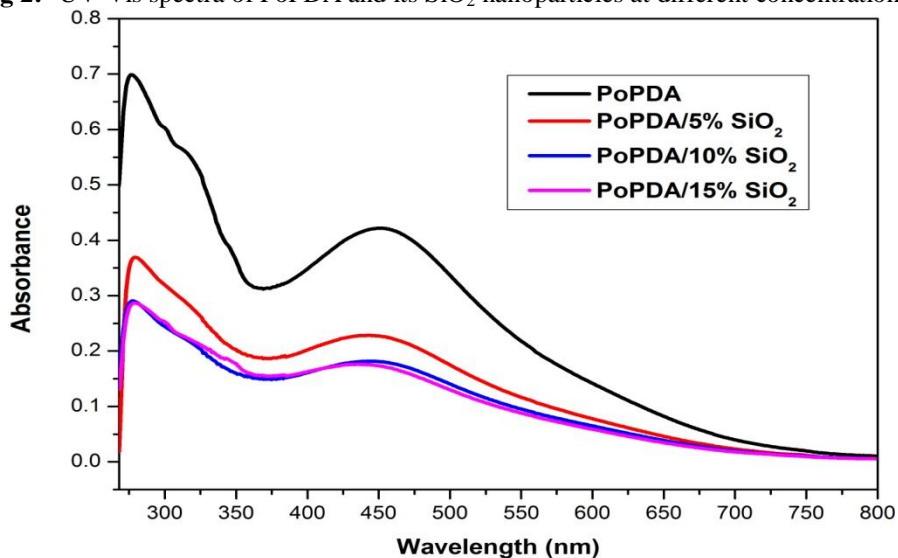


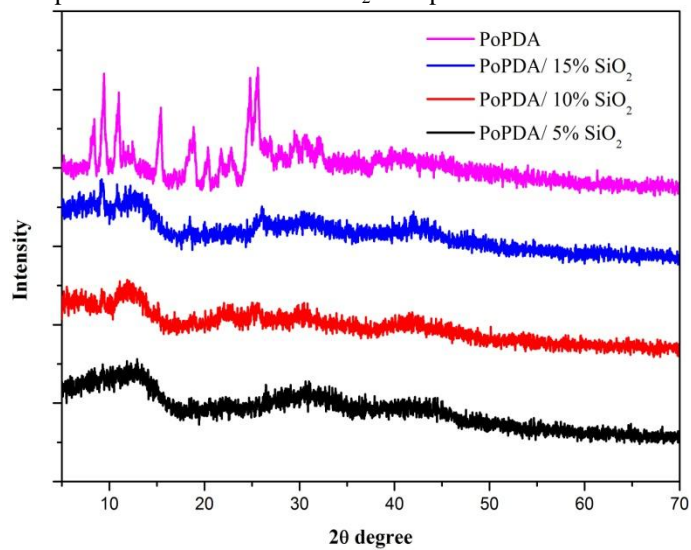
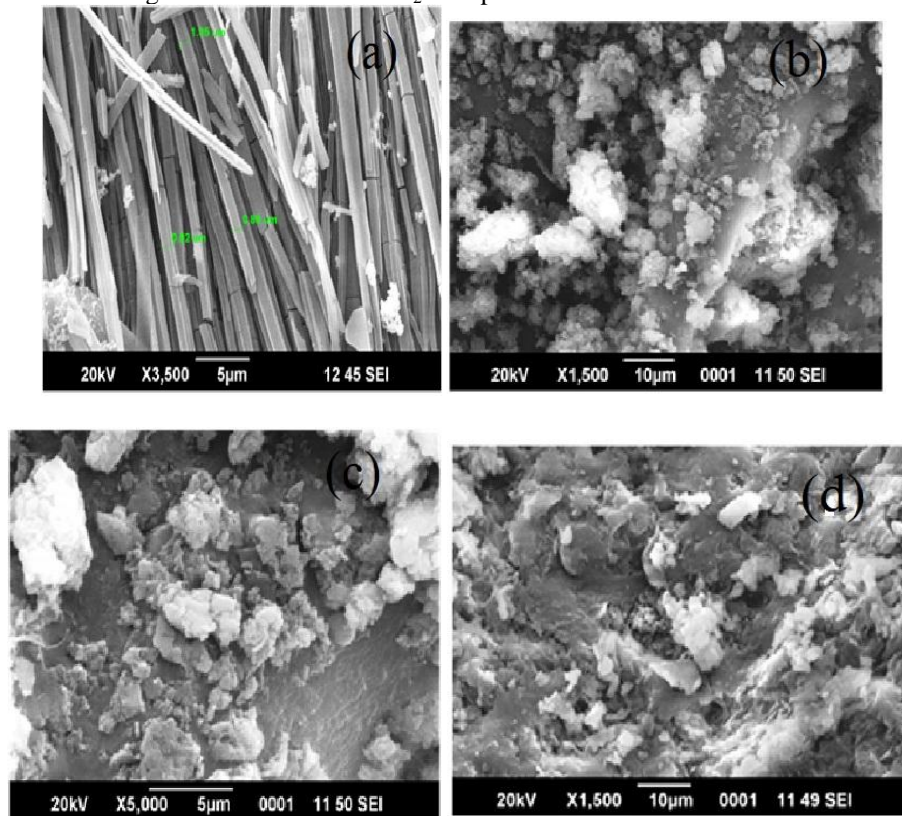
Fig 3:- XRD spectra of PoPDA and its SiO₂ nanoparticles at different concentrations**Fig 4:-** SEM image of PoPDA and its SiO₂ nanoparticles at different concentrations.

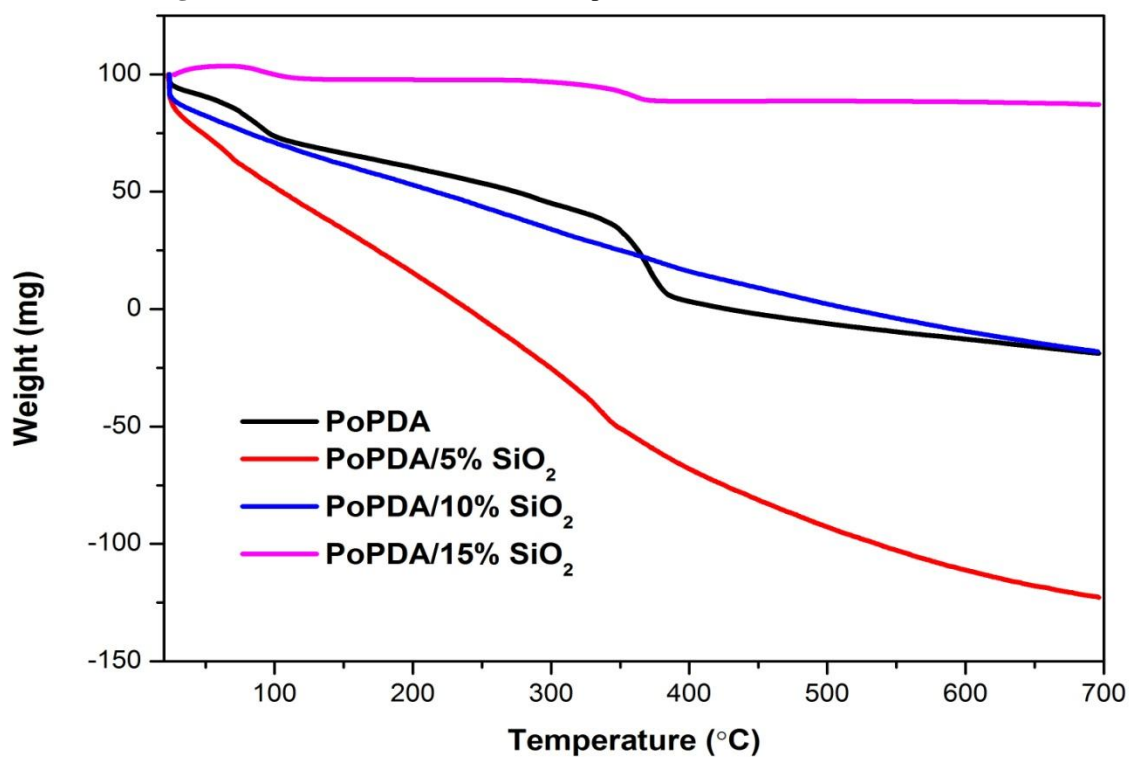
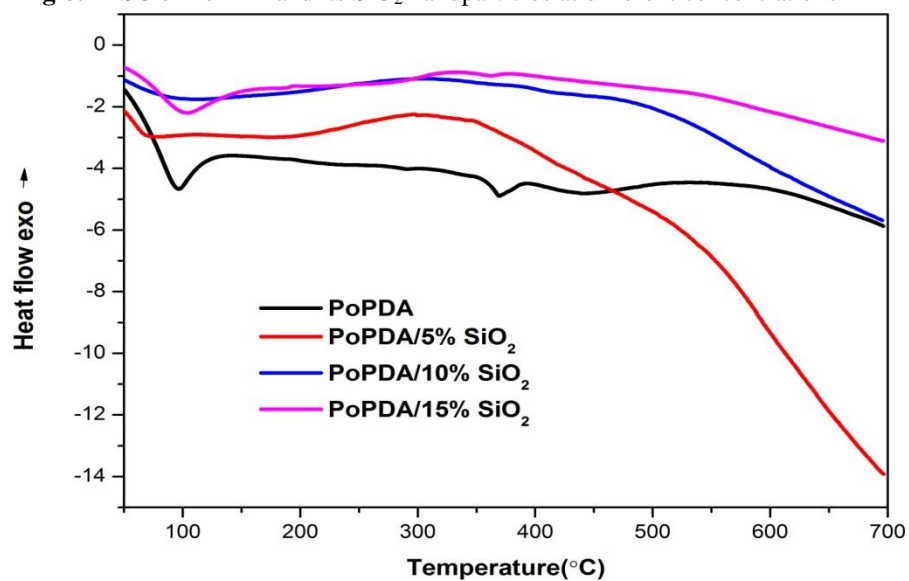
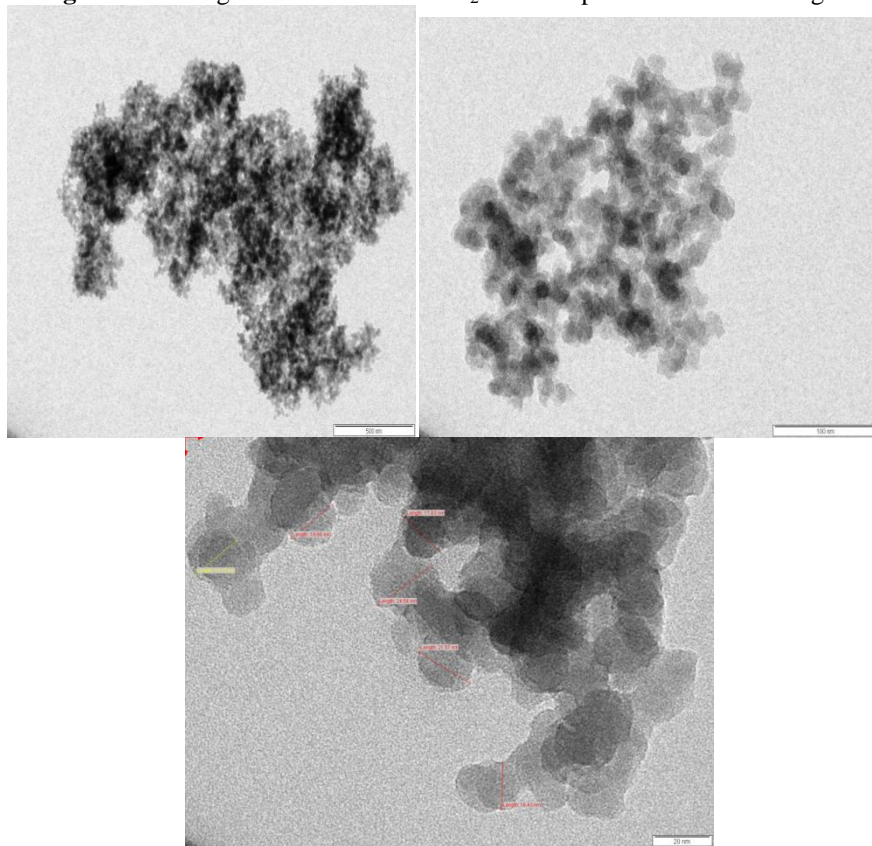
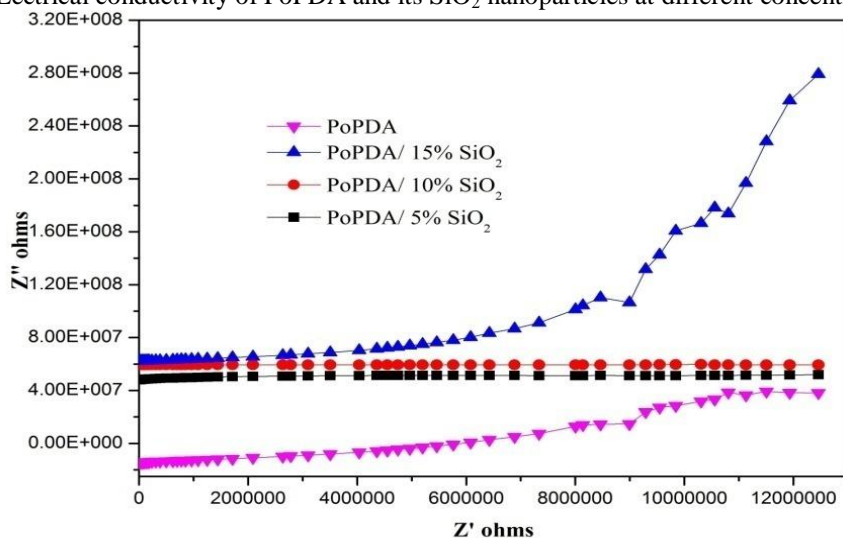
Fig 5:- TGA of PoPDA and its SiO₂ nanoparticles at different concentrations.**Fig 6:-** DSC of PoPDA and its SiO₂ nanoparticles at different concentrations

Fig 7:-TEM image of PoPDA/ 15% SiO₂ nanocomposites at different angles**Fig 8:-**Electrical conductivity of PoPDA and its SiO₂ nanoparticles at different concentrations

Conclusion:-

The PoPDA and PoPDA /SiO₂ nanocomposites have been successively prepared via chemical oxidative polymerization method. The synthesized polymer and nanocomposites were characterized using FT-IR, UV-Vis spectroscopy and it is confirmed the formation of the polymers. The morphology of the polymer and its nanocomposites studied by SEM shows different morphology depending on the polymer and its nanocomposites. The XRD studies confirmed that the synthesized nanocomposites were amorphous in nature unlike the polymer. The formation of core shell type morphology of SiO₂ nanoparticles was confirmed from TEM analysis. The thermal stabilities of the polymers and its composites were confirmed from the TGA/DAT and DSC studies. The

conductivity studies of the polymer and its nanocomposites of PoPDA shows semiconducting in nature and the conductivity is higher in polymer nanocomposites than the polymer.

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