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Synthesis, Characterization and Fluorescence Applications of Conducting Poly O-Phenylenediamine and its ZnO Nanocomposites

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ABSTRACT

Poly (o-Phenylenediamine) and its ZnO nanocomposites were synthesized at different concentrations metal oxide like 5%, 10% and 15% of ZnO by via chemical oxidative polymerization method using ammonium persulphate as an oxidant in the presence of HCl. The prepared polymer and its polymer nanocomposites are found to be soluble in common organic solvents like ethanol, DMSO, toluene etc. The formation of polymers and their nanocomposites were confirmed from the UV-Vis and FT-IR spectroscopy and the morphology was studied using SEM analysis. The formation of nanocomposites has been confirmed from the HRTEM studies. The thermal stabilities of the synthesized polymer and its nanocomposites are determined from TGA/DTA and DSC studies. From the thermal analysis, it was found that the polymer nanocomposites are more stable than the corresponding polymer. The study of electrical conductivity shows that synthesized polymer and its nanocomposites are semiconducting in nature and its fluorescence study shows that the polymer and its nanocomposites can act as green light emitters and this property can be used in various technological applications.

1. INTRODUCTION

Nanocomposites constitute a new class of material that involves nano-scale dispersion in a matrix. Nanocomposites have at least one ultrafine phase dimension, typically in the range of 1-100 nm and exhibit improved properties when compared to micro- and macro-composites[1]. Polymer nanocomposites might be differentiated from the micro-filler filled polymer and nanocomposites contain small amounts are in the range of nanometers in size and have tremendously large specific surface area[2]. The nanocomposites with an organized structure usually provide a new functional hybrid with the synergistic properties of their single components which have attracted considerable attention for their potential application[3]. Among conducting polymers; polyaniline and its derivatives such as polypyrrole, polythiophene etc., have attracted much attention due to its easy synthesis by chemical polymerization method and ammonium persulfate is generally used as an oxidizing agent[4]. Conducting polymer nanocomposite with inorganic nanoparticles and the polymer matrices may generate some unique physical properties upon the formation of various micro/nano composite[5]. Parveen *et al.*[6] says that substituted polyaniline shows higher conductivity than pure polyaniline due to electron delocalization that takes place via substituted group, which increases the conductivity path length and results in high conductivity. These polymer nanocomposites are fussier to change their morphology with small change in concentration of organic or inorganic doping in matrix.

Conducting polymers, a new class of polymeric materials have been used as shell or surface modifiers for semiconductors such as SiO_2, TiO_2, and ZnO nanoparticles[7]. Inorganic nanoparticles, in intrinsically conducting polymer matrix is believed to be an easy route to prepare and design nanocomposites where delocalized π- electrons interact with inorganic particles, resulting in materials of unique or better properties[8].

Zinc oxide nanoparticles can be prepared by different methods and the chemical oxidative polymerization method is more popular due to its cheapness, repeatability, reliability and simplicity[9]. M.J. Zheng *et al.*[10] says that ZnO is one of the most promising semiconductor materials due to its piezoelectric properties, good optical, and high electron transfer capability[11]. It can be used in many applications like battery electrolytes[12], electrochromic display[13], supercapacitor[14], microelectronic device[15], light-emitting-diode[16] and biosensors[17].

Recently oxide based semiconductor nanomaterials are synthesized due to their thermal and photostability[18]. Poi Sim Khiew *et al.*[19] says that Zinc oxide (ZnO) nanostructured materials has unique properties like high isoelectric point, transparent n-type semiconductor with direct wide band gap, biocompatibility, high chemical stability, nontoxicity, high electron transfer capability *etc*[20]. Several ring and N- substituted polymers which are soluble in organic solvents has been prepared directly from polymerization of the corresponding monomer[21]. In the preparation of nanomaterials, the stabilizers are used to modify the surface of nanoparticles to improve the stability of their suspension against flocculation[22]. The dispersion phase used in nanoparticles can increase their strength or reduce their weight and thermal resistance can be increased and their electrical conductivity increases[23].

In this present work, a novel hybrid conducting polymer and its nanocomposites comprising of Poly o-Phenylenediamine (PoPDA) and its ZnO nanoparticles were synthesized and were characterized by different techniques such as FT-IR, TGA/DTA, DSC, SEM, and TEM. The thermal stabilities of the synthesized polymer and its nanocomposites were analyzed and their applications like conductivity study and their fluorescence properties were determined.

2. MATERIALS AND METHODS

2.1 Materials

Monomer o-Phenylenediamine, ammonium persulfate are products of Sigma-Aldrich and Hydrochloric acid was purchased from Merck Ltd., India. All other chemicals and reagents were of Analytical Grade and used as received without any further purification in the present study. The nanoparticle, ZnO was purchased from Sigma-Aldrich with the particle size ranging from 20-30 nm

2.2 Methods

Synthesis of Poly o-Phenylenediamine/ ZnO nanocomposite

Synthesis of PoPDA is carried out via chemical oxidative polymerization and its ZnO nanocomposites were synthesized using different weight percentages like 5%, 10%, and 15% of ZnO. About 0.05 mol of o-Phenylenediamine is dissolved in 1M HCl to form o-Phenylenediamine hydrochloride. Different weight percentage of zinc oxide nanoparticle is added to the above solution with vigorous stirring in order to keep the zinc oxide suspended in the solution. To this above reaction mixture, 0.05 mol of ammonium persulphate $[(NH_4)_2S_2O_8]$ which act as the oxidant was added dropwise slowly with continuous stirring for 6 hrs at 0-5°C to polymerize and the resulting polymer in the form of brown mixture was kept overnight and then filtered. The resultant polymer was washed with distilled water until the filtrate was colorless then with acetone and with methanol to remove excess initiator, monomer and oligomers. Finally, the resultant precipitate was dried at room temperature for 24 hours[23, 24].

2.3 Characterization techniques

The FT-IR spectra of the synthesized polymers and its nanocomposites were performed using ABB-MB-3000 spectrometer in KBr medium at room temperature. UV-Vis spectra were recorded on a Perkin-Elmer Lamba spectrophotometer by dissolving the polymers in DMSO as a solvent. The morphological study of the synthesized polymers was carried out using Scanning Electron Microscopy (SEM model: Jeol 6390 LV) with accelerating voltage of 0.5 kV to 30 kV. Transmission electron microscopy (TEM model Tecnai T20 G2 S-TWIN) was used to investigate the dispersion of PoPDA/ ZnO nanocomposites. TGA/DTA was recorded using Perkin Elmer Diamond under a nitrogen atmosphere up to 700°C using a heating rate of 10ºC/min. The Differential scanning calorimetry (DSC) was measured using Mettler Toledo DSC 822^{e} from room temperature to 500ºC. The electrical conductivity was determined at room temperature by the four-point probe technique using LCR meter HP484A. The Fluorescence study was carried out using the instrument spectrofluorometer with FLUOROLOG-FL3-11 model.

3 RESULTS AND DISCUSSION

3.1 Solubility

The solubility of Poly o-Phenylenediamine (PoPDA) and its nanocomposites synthesized with 5%, 10% and 15% of ZnO nanoparticle in some common organic solvents are given in Table 1. From the table, it is evident that the polymer and its nanocomposites are soluble in DMSO, DMF and THF, partially soluble in toluene and are insoluble in ethanol, methanol, and acetone and n-hexane.

3.2 FT-IR spectroscopy

FTIR spectra of the PoPDA and PoPDA nanocomposites synthesized with 5%, 10% and 15% of ZnO are given figure 1. From the spectra, the peak at 3401 cm^{-1} indicates the presence of –OH residue, probably due to the presence of atmospheric moisture[24]. The single peak at

3302 cm^{-1} is due to the N–H stretching vibrations of the –NH group. The two peaks at 3383, 3199 cm^{-1} are associated with N–H stretching vibrations of NH_2 group in the asymmetrical and symmetrical group's respectively[25]. Two strong peaks at 1639 cm^{-1} and 1531 cm^{-1} are due to the stretching vibrations of C=N and C=H group in phenazine ring[26]. The peaks at 1237 cm^{-1} and 1372 cm^{-1} are associated with C–N–C stretching in the benzenoid and quinoid imine units[27]. Furthermore, the bands at 754cm^{-1} are the characteristic of C–H out of plane bending vibrations of benzene nuclei in the phenazine skeleton are also observed[28]. The shift in the peaks of the polymer nanocomposites is due to the formation of hydrogen bonding between ZnO and –NH group on the surface of PoPDA nanoparticles and this can be explained on the basis of constrained growth and restricted modes of vibration in ZnO grown in the presence of PoPDA[29].

3.3 UV- Vis spectroscopy

The UV- Vis spectra of PoPDA and PoPDA/ZnO nanocomposites synthesized at different percentage of ZnO nanoparticle is shown in figure 2. From the UV spectra, the PoPDA has two major peaks at 257 and 414 nm. The peak at 257 nm is due to π–π* transitions of the benzenoid and quinoid structure of the polymer and the other band 414 nm is assigned to the π–π* transition associated with the phenazine ring which is conjugated to the two lone pair of an electron on nitrogen atom of the NH_2 groups[30]. The PoPDA/ZnO nanocomposites are also had two bands which are slightly higher than the polymer. The peaks at 262 nm and 424 nm are attributed to the π–π* transition of the benzenoid and quinoid structure and π–π* transition associated with the phenazine ring respectively[31].

3.4 Scanning Electron Microscopy

The morphology of the PoPDA and PoPDA with 5%, 10% and 15% ZnO was determined using Scanning Electron Microscopy and their images are given in figure 3a-d. The morphology of PoPDA shows ordered rod like structure (3a) and its PoPDA nanocomposites has broken rod like structure (3b-d). When the concentration of the ZnO nanoparticles increases from 5% to 15%, the length of the rod are found to decreases and thus the breaking of the ordered rod like structure has increased and this may be due to the interaction of the ZnO nanoparticles with the polymer. From the image, it is also evident that the PoPDA/ZnO nanocomposites have the properties of both PoPDA and ZnO nanoparticles.

3.5 Thermogravimetric/ Differential Thermal Analysis

The TGA measurement of PoPDA and PoPDA/ZnO nanocomposites synthesized at different concentrations of ZnO nanoparticles like 5, 10 and 15% are shown figure 4. The thermal decompositions of PoPDA exhibit two stages of weight loss behavior. The first weight loss from 54ºC to 98ºC is due to expulsion of water molecules, the evaporation of residual solvents such as acid, methanol and small molecules from polymeric structure. The second weight loss from 354ºC to 700ºC shows thermal degradation of the polymer[32]. The PoPDA/ZnO nanocomposites also show two weight losses and the first weight loss from 51ºC to 118ºC is due to the degradation of water molecule. The second weight loss from 353 ºC to 700ºC is due to the decomposition of polymer. The thermal studies show that the stability of the PoPDA/ZnO nanocomposite is higher than the PoPDA and this may be due to the interaction between ZnO nanoparticles and PoPDA chain[33].

DTA curves of PoPDA and PoPDA/ ZnO nanocomposites at different concentrations of ZnO nanoparticles like 5%, 10% and 15% shows a wide peak with a plateau in temperature range of 427-750°C and this is related to the decomposition of organic moiety as shown in figure 5. The TGA and DTA study confirm that the synthesized polymer and polymer nanocomposites possess good thermal stability.

3.6 Differential Scanning Calorimetry

DSC can be used to obtain the thermal critical points like melting temperature, enthalpy specific heat or glass transition temperature. The DSC of PoPDA and PoPDA nanocomposites synthesized at different concentration of ZnO nanoparticles like 5%, 10% and 15% are given in figure 6. From the figure, it is found that the PoPDA shows an endothermic peak at 86.66°C which is due to the glass transition temperature (Tg) and peak at 369°C is characteristics of melting temperature[34]. The PoPDA/ZnO nanocomposites show two endothermic peaks. The peaks at 89.38°C, 90.50°C and 96.66°C is due to the glass transition temperature (Tg) of the poly nanocomposite synthesized with 5% , 10 and 15 weight percentage of ZnO nanoparticles. The second endothermic peaks at 375.92°C, 377.04°C and 385.72°C is due to the melting temperature of the polymer nanocomposites. From the melting temperature, it is observed that the thermal stability increases with increase in concentration of ZnO nanoparticles. The high thermal stability of the nanocomposites may be due to the incorporation of ZnO nanoparticles in the polymer matrix[35].

3.7 Transmission Electron Microscopy

High-Resolution Transmission Electron Microscopy images of polymer nanocomposites with 15% of ZnO nanoparticle taken at different angles are given in figure 7. The micrographs of polymer nanocomposites exhibit smooth surfaces and are crystalline in nature with the particle size of 20-30 nm. Moreover, the outer core of the TEM image of the nanocomposite is more bright compared with the dark inner core and these forms the core- shell feature of the PoPDA/ZnO nanocomposites and are found to be homogeneous and are uniformly distributed. The size of nanoparticles in the nanocomposites indicates that the surface of nanoparticles has the interaction with PoPDA[36].

3.8 Photoluminescence

Photoluminescence (PL) involves the process of photon excitation followed by photoemission. Most of the molecules occupy the lowest vibrational level of the ground state, and on absorption of light, they are elevated to produce excited state. From this level, the molecule can return to any of the vibrational levels of the ground state, emitting its energy in the form of fluorescence[37]. The Photoluminescence spectra of PoPDA and PoPDA/ZnO nanocomposites synthesized at different concentrations of ZnO nanoparticles are shown in figure 8. The PL pattern has a strong green emission band around 540 nm[38] and this region falls under the green light emission. Y.W. Wang *et al.*[39] says that the singly ionized oxygen vacancy is responsible for the green emission in the ZnO and the emission results from the recombination of a photogenerated hole with an electron occupying the oxygen vacancy.

3.9 Electrical Conductivity

The Electrical conductivity at room temperature of PoPDA and PoPDA at different concentration of ZnO nanoparticles like 5, 10, and 15% are shown in figure 9. The conductivities of polymer and its nanocomposites were evaluated using bulk resistance (Rb) using the formula

$$\sigma = (t/A)\ (1/Rb)\ S/cm \quad \text{----------------------} \ (1)$$

Where, t is the thickness of the pellet, A is the area of pellet, Rb is the bulk resistance of the pellet. The conductivity of the polymer increases with the addition of ZnO nanoparticles from 10^{-8} into 10^{-6}. The electrical conductivity of the PoPDA was found to be 1.4271×10^{-8} S/cm and the electrical conductivities of PoPDA/ZnO nanocomposites synthesized with 5%, 10%

and 15% ZnO nanoparticles are found to be, 1.6321×10^{-6}, 1.8491×10^{-6} and 2.347×10^{-6} S/cm respectively. The conductivity result shows that the conductivity increases from polymer to the polymer nanocomposites and as the concentration of the ZnO nanoparticle increases, the conductivity increases slightly. When added different concentration of metal oxide nanopowders, it was found that the electrical conductivity of polymer and metal oxide nanocomposites was found to improve[40].

4. CONCLUSION

The PoPDA and PoPDA/ZnO nanocomposites have been successively prepared via chemical oxidative polymerization method. The synthesized polymer and nanocomposites were characterized using FT-IR, UV-Vis spectroscopy is confirmed the formation of the polymers. The morphologies of the polymer and its nanocomposites studied by SEM analysis shows the rod like structures. The formation of polymer nanocomposite was confirmed by HRTEM analysis. The thermal stabilities of the polymers and its nanocomposites were confirmed from TGA/DTA and DSC studies and found that the polymer nanocomposites are more stable than the polymer. The electrical conductivities of the polymer and its nanocomposites shows semiconducting in nature and the conductivity is higher in polymer nanocomposites than the polymer. The PL study shows that the polymer and its nanocomposites have the capacity to emit green light this shows that the synthesized polymer and its nanocomposites can be used in different applications.

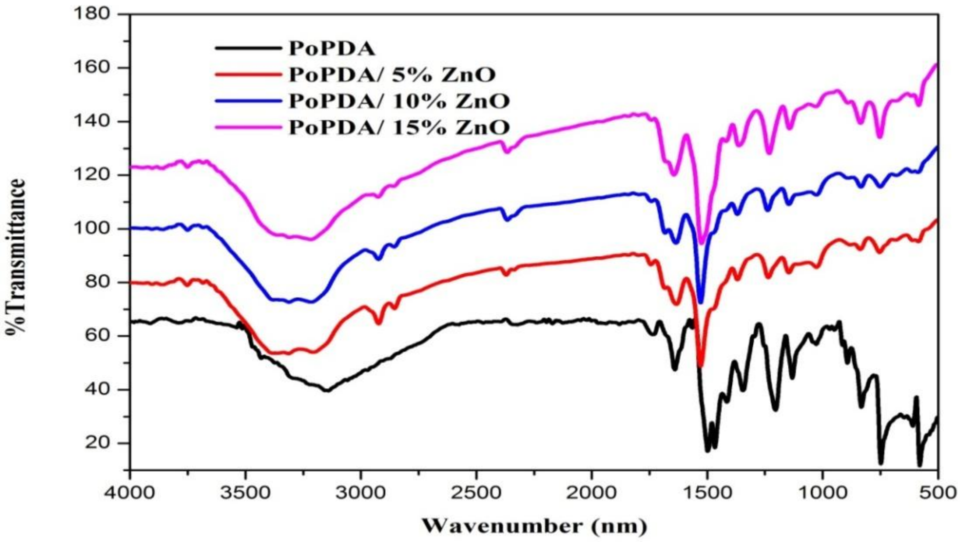


Fig 1: FT-IR spectra of PoPDA and its ZnO nanoparticles at different concentrations

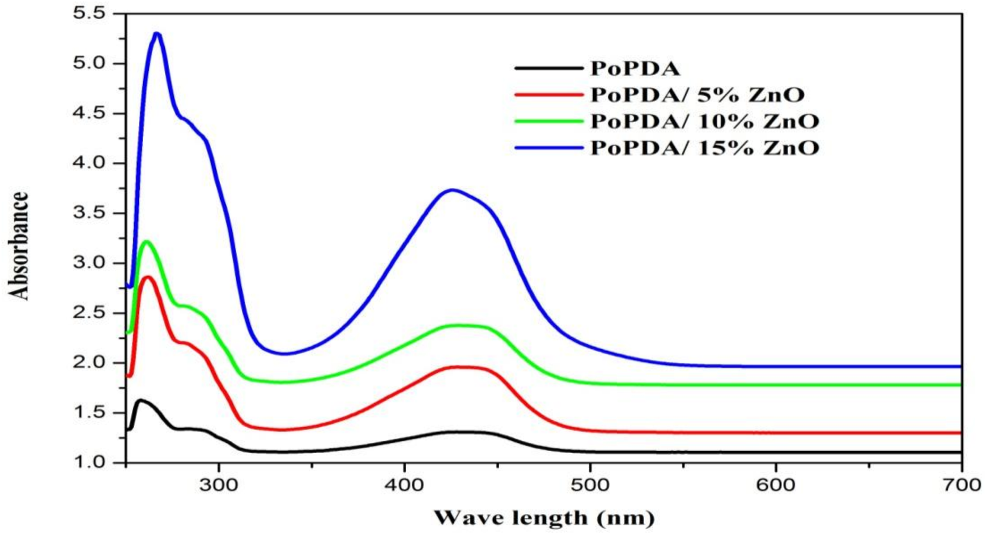
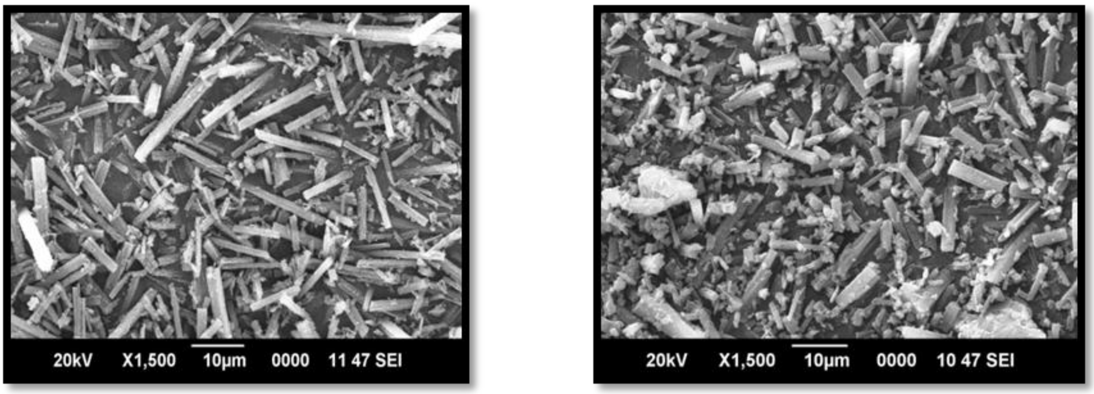


Fig 2: UV-Vis spectra of PoPDA and its ZnO nanocomposites at different concentrations

(a)PoPDA **(b) PoPDA/ 5% ZnO**



(c) PoPDA/ 10% ZnO **(d) PoPDA/1 5% ZnO**

Fig 3: SEM images of PoPDA and its ZnO nanocomposites at different concentrations

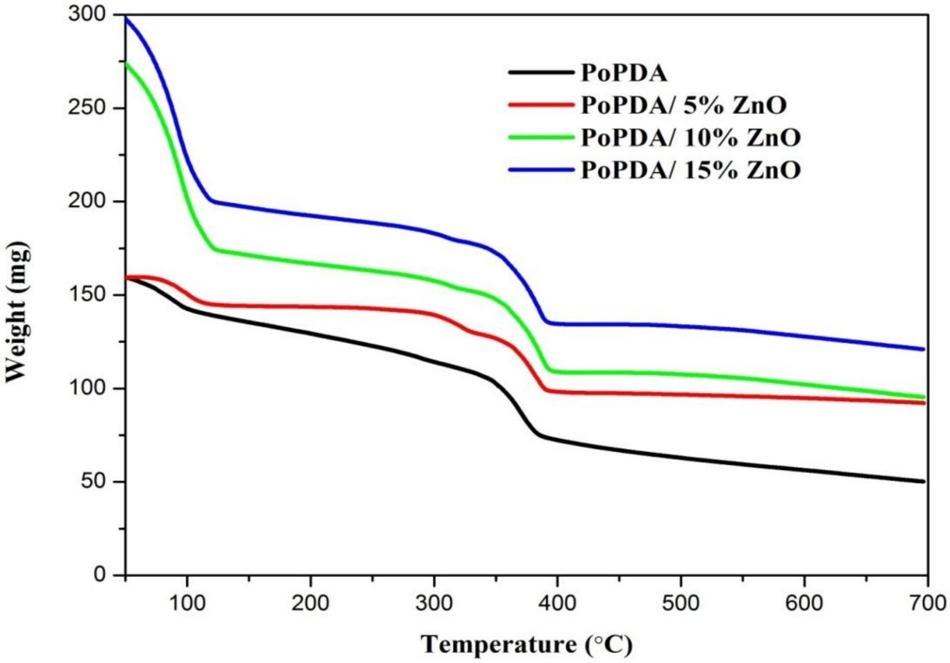


Fig 4: TGA of PoPDA and its ZnO nanocomposites at different concentrations

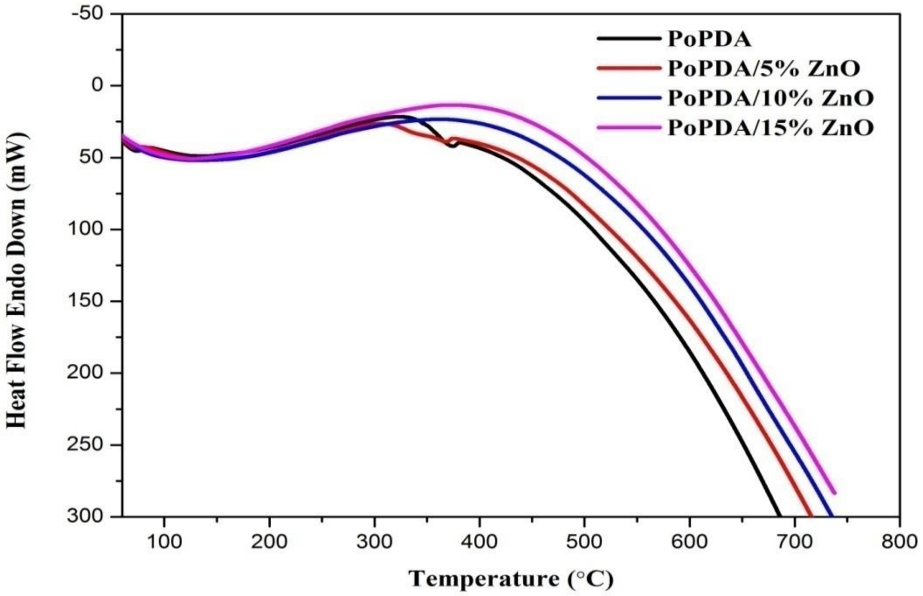


Fig 5: DTA of PoPDA and its ZnO nanocomposites at different concentrations

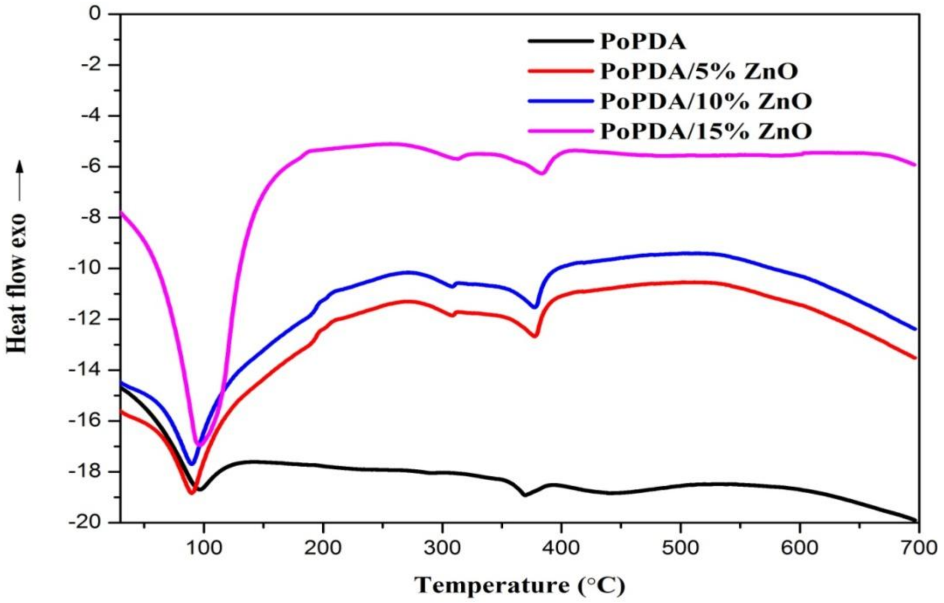


Fig 6: DSC of PoPDA and its ZnO nanocomposites at different concentrations

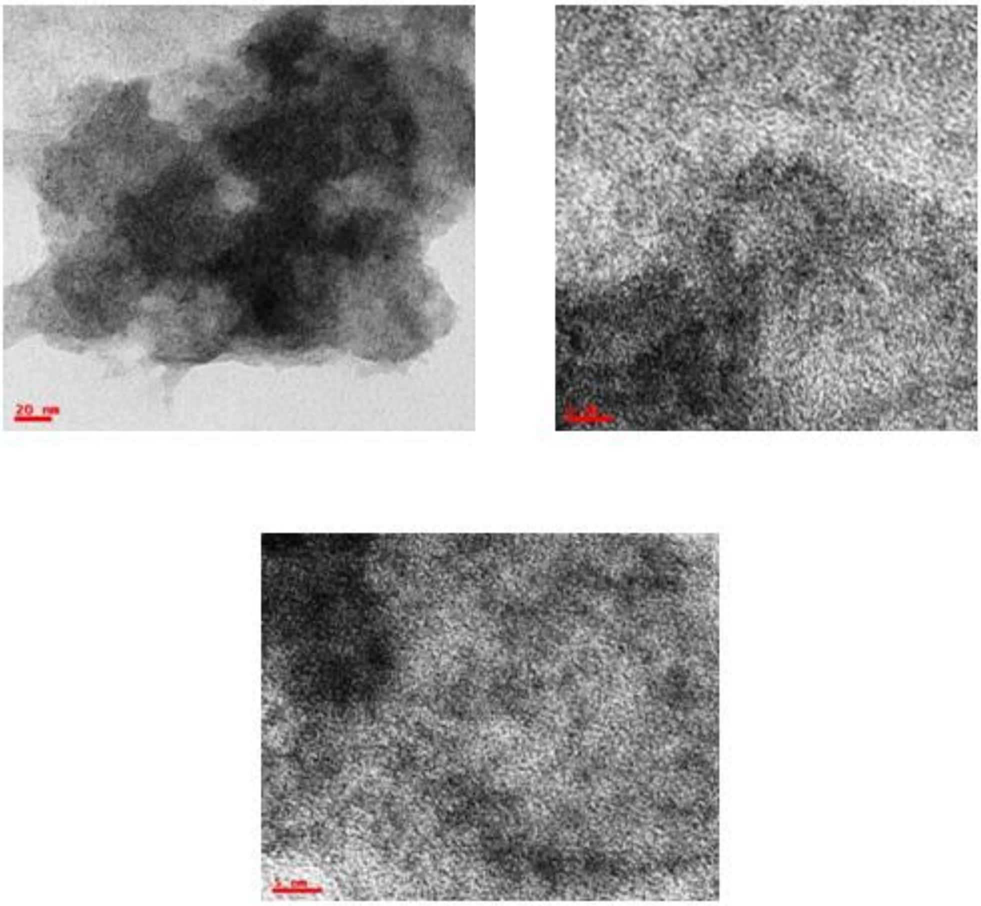


Fig 7: TEM images of PoPDA/ 15% ZnO nanocomposites at different angles

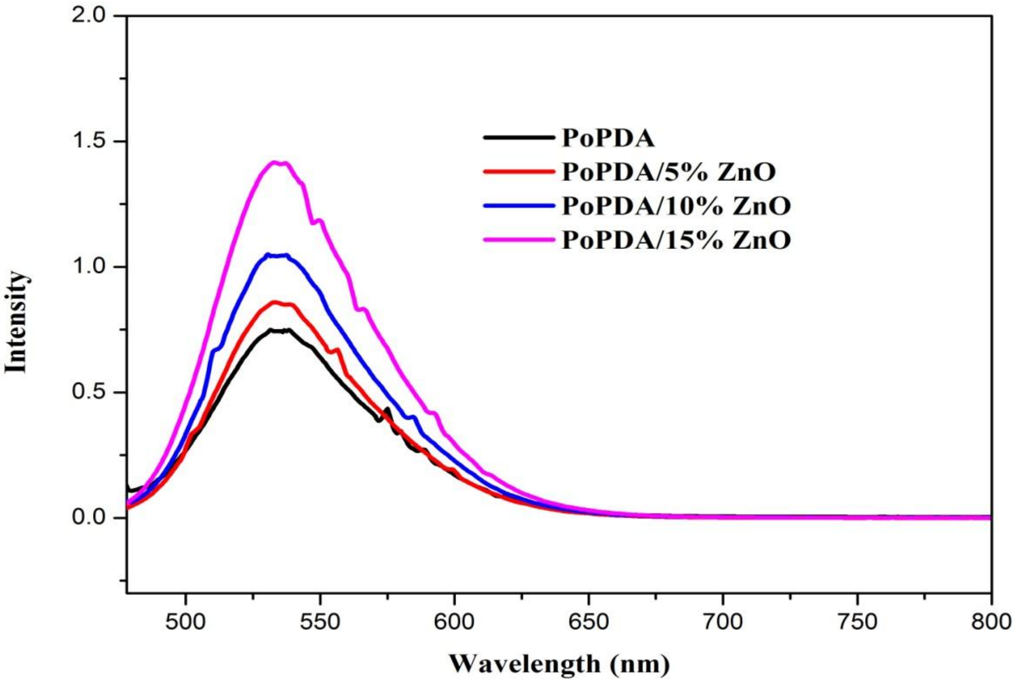


Fig 8: Photoluminescence of PoPDA and its ZnO nanocomposites at different concentrations

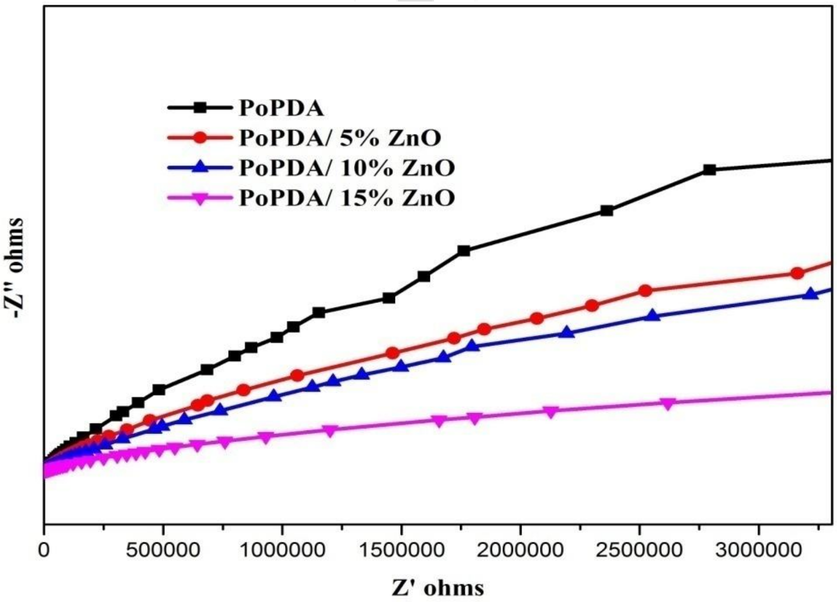
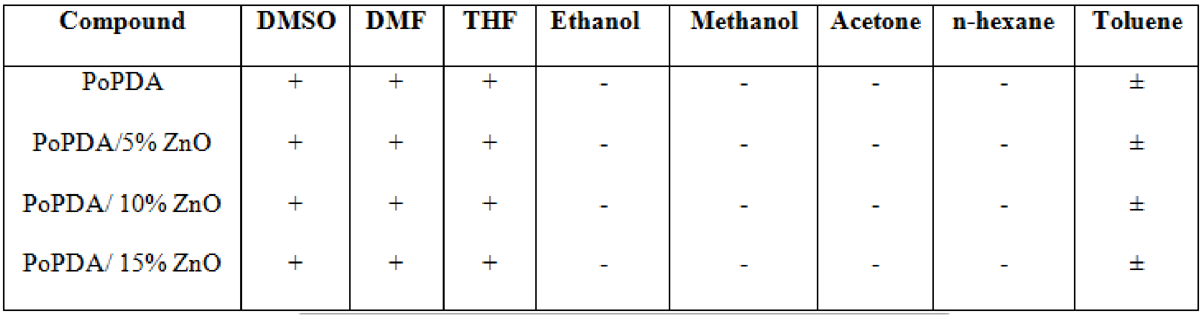


Fig 9: Electrical conductivities of PoPDA and its ZnO nanocomposites at different concentrations

Table 1: Solubility of polymer and nanocomposites in some common organic solvents



Compound	DMSO	DMF	THF	Ethanol	Methanol	Acetone	n-hexane	Toluene
PoPDA	+	+	+	-	-	-	-	±
PoPDA/5% ZnO	+	+	+	-	-	-	-	±
PoPDA/ 10% ZnO	+	+	+	-	-	-	-	±
PoPDA/ 15% ZnO	+	+	+	-	-	-	-	±

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