

Comparative study of Dielectric Relaxation, AC conductivity and Photoluminescence properties of poly (p-aminothiophenol) and its ZnO nanocomposite

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Abstract - Polymer nanocomposites have attracted great attention worldwide academically and industrially due to their interesting electronic, physical properties, chemical stability and their potential technological applications. Poly (p-aminothiophenol) with ZnO nanoparticles are synthesized by *in situ* chemical oxidative polymerization method using ammonium persulphate as an oxidant in an aqueous HCl. The synthesized Poly (p-aminothiophenol) and its ZnO nanocomposite are characterized using UV-VIS, FT-IR, XRD, TGA, SEM and TEM analysis. The study on dielectric properties reveal that the ZnO nanoparticles incorporation has significant influence on the dielectric properties of poly (p-aminothiophenol) and this could be widely applied in the fields of semiconductor, batteries etc. The photoluminescence study show that the polymer and its ZnO nanocomposite exhibit blue light emission and intensity is higher for the polymer nanocomposite compared to the polymer.

Keywords - Conducting polymer, Poly(aminothiophenol), nanocomposites, dielectric, photoluminescence.

I. INTRODUCTION

The growing interest in nano structured conducting polymers is caused by expanding area of their practical application. Conducting polymers can be used in new electronic devices like transistors, displays, sensors, energy-storage and memory cells, materials for shielding electromagnetic irradiation, polymer nanolithography, inhibition of corrosion, membrane constructing, catalysis and medicine [1-3]. Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations [4-5]. The main chains consist of alternative single and double bonds, which leads to broad p-electron conjugation. However, the conductivity of these pure conducting polymers is rather low. In order to achieve highly conductive polymers, doping process is necessary [6-8].

Nanocomposites constitute a new class of material that involves nano-scale dispersion in a matrix. They are generally comprised of multiple nanoscale materials or a nanoscale material incorporated into a bulk material [9]. 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. There are a number of ways to prepare or synthesize nanocomposites. These include electrospinning, *in situ* preparation, film casting, dip coating, physically mixing, layer-by-layer assembly, ionotropic gelation, colloidal assembly, co-precipitation, and covalent coupling. These methods take advantage of hydrogen-bonding, coulombic interactions, hydrophobic effects, electrostatic, and ionic interactions.

Among the conducting polymers, polyaniline attracts greater attention because of its chemical stability under ambient conditions, high electrical conductivity, and simple synthesis [10]. A derivative of polyaniline, aminothiophenols (ATP) are interesting electrochemical materials since thiol and amine have different reactivities [11-13], the effective use of this molecular assembly may give rise to unique morphologies leading to multi-purpose chemical strategies. Moreover, the aromatic ring of ATP intensifies the electrical coupling. Therefore, they can show electrochemical behavior resembling anilines and phenols. In recent years, electrical, optical, and dielectric properties of conducting polymers like polyaniline and substituted polyaniline synthesized by chemical oxidation polymerization have been studied in great detail.

ZnO as one of the multifunctional inorganic nanoparticles has drawn increasing attention in recent years due to its

many significant physical and chemical properties, high catalysis activity, effective antibacterial and bactericide function, intensive ultraviolet and infrared adsorption [14-16]. Moreover, the advance of ZnO nanoparticles could improve the properties of polymer matrix.

In the present work, poly para aminothiophenol (PpATP) and its ZnO nanocomposite are synthesized by chemical oxidative polymerization method and are characterized by different techniques. An attempt has been made to investigate the conductivity, dielectric properties and photoluminescence properties of poly para aminothiophenol and its ZnO nanocomposite.

II. EXPERIMENTAL SECTION

Materials

All chemicals used in the present investigation are of Analytical Reagent (AR) grade and used as received. Monomer p-aminothiophenol (Alfa aesar), Ammonium persulfate (Sigma-Aldrich) and Hydrochloric acid purchased from Merck Ltd., India. The ZnO nanoparticle is purchased from Sigma-Aldrich.

Synthesis of Poly (p-aminothiophenol) and its ZnO Nanocomposite

Para aminothiophenol (monomer), ammonium per sulphate (oxidant) and zinc oxide nanoparticle are taken in the ratio of 1:2:1. The monomer is dissolved in 1 M hydrochloric acid and zinc oxide nanoparticle is added to the above solution with vigorous stirring using magnetic stirrer in order to keep the zinc oxide suspended in the solution. The solution is kept stirring for about 5 h at room temperature, after which the brownish black powder obtained as residue. The resultant polymer nanocomposite is 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 is dried at room temperature for 24 hours [17]. Same procedure is adapted to synthesis the polymer.

Characterization Techniques

UV-VIS spectra are recorded from 200-800 nm using SHIMADZU model UV-2450 spectrophotometer by dissolving the polymers in DMSO as a solvent. The FT-IR spectra of the synthesized polymer and its ZnO nanocomposite are studied using Perkin Elmer 1750 FTIR spectrophotometer at room temperature. X-ray diffraction (XRD) is recorded with Bruker AXS D8 Advance diffractometer at room temperature at 2θ angle ranging from 0° to 80° . TGA is recorded using Perkin Elmer Diamond under a nitrogen atmosphere up to 700°C at the heating rate of $20^\circ\text{C}/\text{min}$.

The morphological study of the synthesized polymer and its nanocomposite is carried out using Scanning Electron

Microscopy, model: Jeol 6390 LV with accelerating voltage of 0.5 kV to 30 kV. Transmission electron microscopy, model Tecnai T20 G2 S-TWIN is used to investigate the dispersion of PpATP/ZnO nanocomposites. Photochemical measurements are carried out on a CHI608E electrochemical workstation and a 100 W Xe arc lamp (OSRAM, Germany) was used as the light source. Fluorescence Spectrophotometer of model Varian- Cary Eclipse is used to measure the photoluminescence property of the synthesized polymer and its ZnO nanocomposite using Xenon flash lamp as source and PMT as detector.

III. RESULTS AND DISCUSSIONS

UV-VIS studies

The UV-VIS absorption spectra of the polymer and its ZnO nanocomposite are shown in figure 1a,b. The UV-VIS spectra of the Polymer and its nanocomposite consist of two major absorption peaks around at 262 and 306nm. The first peak at 262 nm is assigned to the $\pi-\pi^*$ transition which is related to the extent of conjugation between the benzenoid rings in the polymer chain. The second absorption peak at 306 nm is assigned to $n-\pi^*$ transition of the Quinonoid rings [18].

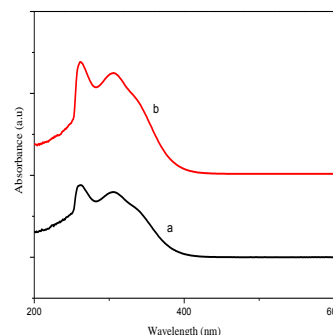


Figure 1. UV-VIS spectra of (a) PpATP and (b) PpATP/ZnO

Introduction of the ZnO nanoparticle in the polymer shows a hypsochromic shift as it is evident from figure 1b. The hypsochromic shift in the polymer nanocomposite is may be due to less conjugation along the polymeric chain due to the incorporated metal oxide into the polymeric matrix.

FTIR analysis

The FTIR spectra of Poly (para aminothiophenol) and Poly (p-aminothiophenol)/ZnO nanocomposite are given in figure 2a,b and from the spectra it is clear that the bands at 1473 and 1695 cm^{-1} are assigned to C=C stretching vibrations of the quinonoid and benzenoid ring present in the polymer. The participation of N-H stretching vibrations of the -NH group is confirmed by the single peak at 3442 cm^{-1} [19]. The peaks at 1298 cm^{-1} are associated with C-N-C stretching in

the benzenoid and quinonoid imine units. The peak at 2550 cm^{-1} corresponds to S-H stretching. Furthermore, the bands at 866 and 783 cm^{-1} are the characteristic of C-H out of plane bending vibrations of benzene nuclei. The strong peak at 1101 cm^{-1} is considered to be stemmed from delocalization of electrons in polymer backbone [20]. The shift in the peaks of the polymer nanocomposite is due to the formation of hydrogen bonding between ZnO and -NH group on the surface of PpATP and this can be explained on the basis of constrained growth and restricted modes of vibration in ZnO on the polymeric backbone [21].

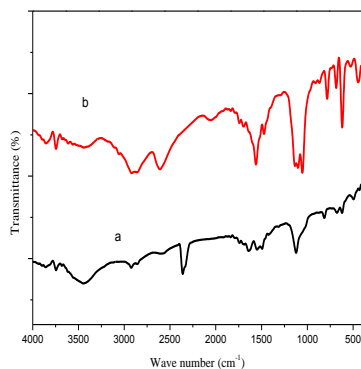


Figure 2. FTIR spectra of (a) PpATP and (b) PpATP/ZnO

XRD Studies

X-ray diffraction (XRD) technique is used for characterization of materials as it provides the important information about the internal structure of matter such as nature of the solid sample (amorphous or crystalline), atomic spacing and crystal structure. Figure 3a,b shows the XRD pattern of PpATP and PpATP/ZnO. From the figure it is evident that the polymer and its ZnO nanocomposite are crystalline/amorphous nature. The crystalline nature of synthesized PpATP and its ZnO nanocomposite are observed by the various sharp crystalline peaks in the XRD pattern [22]. The peak widths in XRD pattern of Poly para aminothiophenol are broadened by incremental addition of ZnO nanoparticles as shown in figure 3b which implies an increase in the amorphous character of PpATP/ZnO. The amorphous nature of the nanocomposite results in higher ionic diffusivity and conductivity [23].

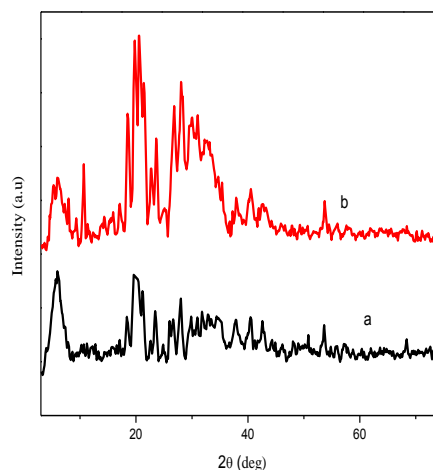


Figure 3. XRD pattern of (a) PpATP and (b) PpATP/ZnO

Thermogravimetric Analysis

The thermal stability of the PpATP and PpATP/ZnO nanocomposite are evaluated using thermogravimetric analysis and it's shown in Figure 4 a,b. The thermal behavior of the polymer and its ZnO nanocomposite is similar and exhibits three stages of decomposition.

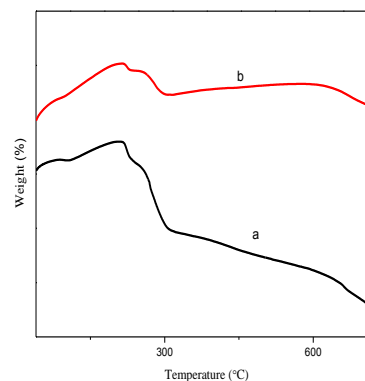


Figure 4. TGA curves of (a) PpATP and (b) PpATP/ZnO

The first weight loss starts from 200 to 300°C which corresponds to the loss of free acids, and volatile molecules in polymer matrix. The second step is in the TGA curves between 300 and 650°C is due to loss of dopant, sublimation, and removal of low molecular weight polymer/oligomer from the polymer matrix, while the third weight loss between 650 and 732°C is due to the complete degradation and decomposition of the polymer backbone.

Surface morphology

The surface morphology of the polymer and its nanocomposite have been characterized by Scanning Electron Microscopy (SEM). The SEM images of Poly (p-aminothiophenol) and ZnO embedded in polymer PpATP

are shown in Figures 5 and 6. From the SEM images it is observed that the synthesized polymer and nanocomposite are in crystal form [24]. The morphology of the PpATP exhibits smooth nanofiber form and the polymer nanocomposite exhibits nanorod structure. The morphology differs from polymer to polymer ZnO nanocomposites.

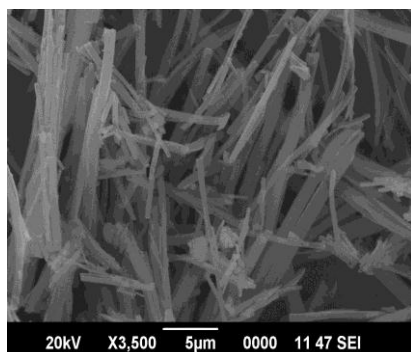


Figure 5. SEM images of PpATP

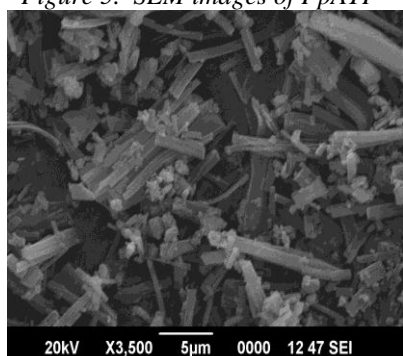


Figure 6. SEM images of PpATP/ZnO

TEM analysis

TEM image of polymer nanocomposite is given in figure 7 and it shows a light coloured crystalline sheet like structure for Polymer ZnO nanocomposite. When ZnO is introduced in the polymer matrix, it shows both dark (metal) and light coloured region (polymer) and confirms the formation of nanocomposite. In PpATP/ZnO, ZnO nanoparticle is tightly bounded with PpATP and exhibiting sponge like sheet structure.

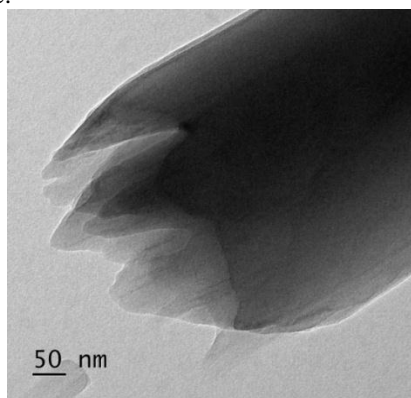


Figure 7. TEM images of PpATP/ZnO

IV. APPLICATIONS

4.1. AC Conductivity

Impedance measurements are a flexible tool for electrical characterization of materials. The ionic conductivity (σ) is calculated using the standard equation $\sigma = t / (R_b A)$. Where σ is the ionic conductivity, t is the thickness of the sample, R_b is the bulk resistance obtained from the intercept on the real axis at the high frequency end of the Nyquist plot and A is the most common area covered by the electrodes in contact with the sample [25]. The variation of AC conductivity with frequency for pure poly para aminothiophenol and its ZnO nanocomposite are shown in figure 8a, b.

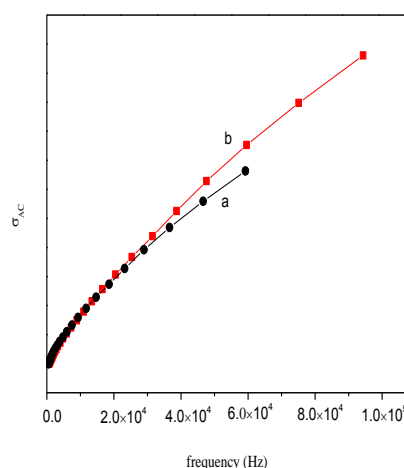


Figure 8. Variation of conductivity with frequency for (a) PpATP and (b) PpATP/ZnO

From the figure it is observed that there is a small increase in the electrical conductivity in the polymer nanocomposite compared to the polymer at the low frequency region. But, especially at higher frequencies, there is an abrupt increase in the conductivity in the PpATP/ZnO. The high AC conductivity in nanocomposite may be due to small polaron hopping in the polymer backbone [26].

3.8. Study of Dielectric Property

The variation of dielectric constant (ϵ') and dielectric loss (ϵ'') as a function of frequency of pure poly para aminothiophenol and its ZnO nanocomposite are shown in Figure 9 and 10. It is observed from the figures that the dielectric constant and dielectric loss decrease rapidly at lower frequencies and showed almost frequency independent behavior at higher frequency region.

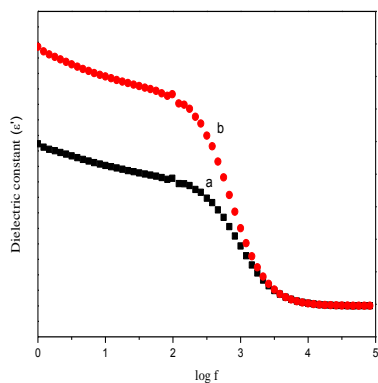


Figure 9. Plot of dielectric constant V/s frequency of (a) PpATP and (b) PpATP/ZnO

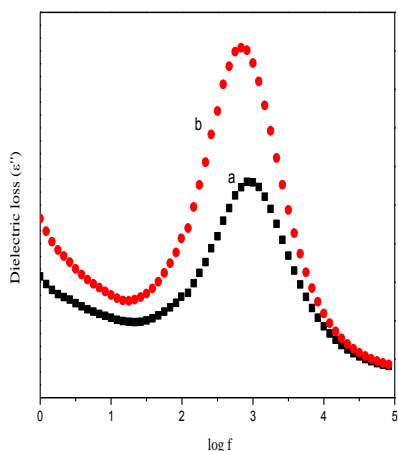


Figure 10. Plot of dielectric loss V/s frequency of (a) PpATP and (b) PpATP/ZnO

Generally, the relaxation phenomena in dielectric materials are associated with frequency dependent orientation polarization. At lower frequency, the permanent dipoles align themselves along the field and contribute fully to the total polarization of the dielectric materials. At higher frequency, the variation in the field is very rapid for the dipoles to align themselves to contribute to the polarization and hence, the dielectric permittivity becomes negligible. Therefore, the dielectric constant and also dielectric loss decrease with increase in frequency [27,28].

3.9. Photoluminescence property

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 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. The Photoluminescence properties

of PpATP and PpATP/ZnO at different concentrations are studied and the results are given in figure 11 and 12.

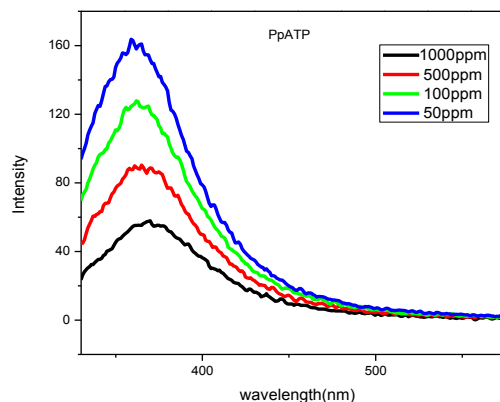


Figure 11. PL spectra of PpATP at different concentrations

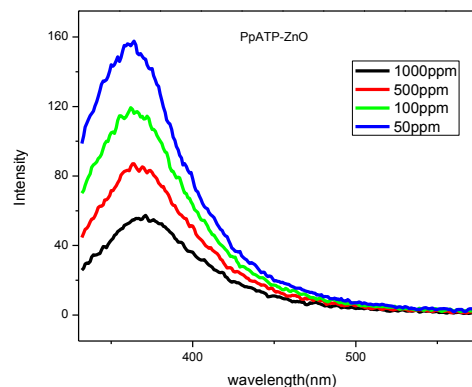


Figure 12. PL spectra of PpATP/ZnO at different concentrations

The study clearly reveals that the photoluminescence pattern has a strong emission bands around 340-430 nm and this region falls under the blue light emission [29]. The Photoluminescence results show that the emission intensity of poly(p-aminothiophenol) and poly(p-aminothiophenol)/ZnO nanocomposite are lower at their highest concentration of 1000ppm and attain the highest emission intensity at their lowest concentration of 50ppm. The comparison of the PL property show that the emission intensity of polymer nanocomposite is slightly higher compared to the polymer.

V. CONCLUSION

The poly(para aminothiophenol) and poly(p-aminothiophenol)/ZnO have been successfully synthesized by chemical oxidative polymerization method and characterized by different techniques like FT-IR, UV-VIS,

XRD, SEM and TEM. The characterization by UV-VIS, FT-IR suggest the formation of quinonoid and benzenoid structure which confirm the formation of polymer and its ZnO nanocomposite. The thermal properties are studied using thermal analysis and confirm that the polymer nanocomposite is more stable compared to polymer. The morphology of PpATP and PpATP/ZnO are evaluated from the SEM and X-ray diffraction studies. The formation of polymer nanocomposite is confirmed by TEM. The conductivity and dielectric studies of the polymer and its ZnO nanocomposite show that they are lossless materials and this could be widely applied in the fields of semiconductor, batteries etc. The poly(p-aminothiophenol) and poly(p-aminothiophenol)/ZnO are found to be blue light emitters and they exhibit very good photoluminescence property which can be applied in photonic and electronic device applications.

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