Dielectric Properties and Fluorescence Applications of Conducting Poly (M-Aminothiophenol) and Its Nanocomposites

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Abstract

Poly(m-aminothiophenol) and its ZnO, CuO nanocomposites are synthesized by chemical oxidative polymerization method using ammonium persulphate as an oxidant in an aqueous HCl. The synthesized poly(m-aminothiophenol) and its nanocomposites are characterized using UV-VIS, FT-IR, XRD, TGA, SEM and TEM. The study of electrical conductivity shows that the synthesized polymer poly(m-aminothiophenol) and its nanocomposites are semiconducting in nature with the order of $\times 10^{-5}$ and $\times 10^{-4}$. The conductivity values are higher for the polymer ZnO and CuO nanocomposites compared to the polymer. The dielectric studies of the polymer and its nanocomposites show that they are lossless materials, and this could be widely applied in the fields of semiconductor, batteries etc. Fluorescence properties of poly(m-aminothiophenol) and its nanocomposites are studied. The results of fluorescence studies of polymer and its ZnO and CuO nanocomposites exhibiting blue light emission and hence they can be used as the light emitting diodes in photonic and electronic applications.

Keywords

Conducting polymers, Poly(aminothiophenol), nanocomposites, dielectric properties, fluorescence.

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INTRODUCTION:

Conducting polymers are the subject of scientific interest due to their unique high electrical conductivity and numerous potential applications. Conducting polymers are typically utilized in electrical, optical and electronic devices. The dielectric properties of heterogeneous polymers [1] play an important role in device applications such as high-performance capacitors, electrical cable insulation, electronic packaging etc. Conducting polymers are usually poly-conjugated structures, which are insulators in their pure state; but when treated with oxidizing or reducing agents they can be converted into polymer salts having reasonable electrical conductivity. Polyaniline (PANI) is one of the most promising conducting polymers because of its unique properties like ease of preparation in aqueous medium, good stability in air, simplicity in doping, improved electronic properties, controllable by oxidation and protonation state, excellent environmental stability, moderately high conductivity in the doped state and its potential applications in electronic devices.[2,3] Incorporation of

a new component into polymer matrix enhances the properties of the polymer. Kondawar et al have reported the enhancement of electrical properties of various conducting polymer composites. [4-7] The incorporation of nano particles into the polymeric network introduces uniform porosity and is expected to be advantageous for many applications.

A derivative of polyaniline, poly(aminothiophenols) (PATP) are interesting electrochemical materials since, unlike aniline and other substituted anilines, they have two groups (–NH_2 and –SH) which can be oxidized. Therefore, they can show electrochemical behavior resembling anilines and thiols. In polymerization of aminothiophenol, the relative position of amino and thiol group is important. 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. [8-10] The possibility of low-cost production methods and the good electrochemical properties make nano CuO to be one of the best materials for electrical, optical, sensing and so forth. [11,12] CuO nanoparticles have a wide range of applications. Moreover, the advance of ZnO and CuO nanoparticles could improve the properties of polymer matrix.

In the present work, poly(meta-aminothiophenol) (PmATP) and its ZnO, CuO nanocomposites are synthesized by chemical oxidative polymerisation method and characterized by different spectroscopic techniques like FT-IR, UV-VIS, XRD, TGA, SEM, and TEM. An attempt has been made to investigate the AC conductivity, dielectric behavior and fluorescence properties of PmATP and its nanocomposites. Interesting results are observed from frequency-dependent AC conductivity, dielectric response and fluorescence emission of the synthesized polymer and its nanocomposites.

MATERIALS AND METHODS:

Materials

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

Synthesis of Poly(m-aminothiophenol)

The poly(m-aminothiophenol) is synthesized by chemical oxidative polymerisation method in acidic medium. Meta aminothiophenol (monomer), Ammonium per sulphate (oxidant) are taken in the ratio of 1:2. The monomer is dissolved in 1 M hydrochloric acid. The aqueous solution of the oxidizing agent is slowly added into monomer solution. The solution is kept stirring for about 5 h at room temperature, after which the white powder obtained as residue. The resultant polymer PmATP is washed with distilled water until the filtrate is 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. [13]

Synthesis of Poly(m-aminothiophenol)/ZnO Nanocomposite

Meta 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. Then the aqueous solution of the oxidizing agent is slowly added. The resultant solution is kept stirring for about 5 h at room temperature, after which the brownish black powder is obtained as residue. The resultant poly (m-aminothiophenol) / ZnO (PmATP/ZnO) nanocomposite is washed with distilled water until the filtrate is 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. [13]

Synthesis of Poly(m-aminothiophenol)/CuO Nanocomposite

Meta aminothiophenol (monomer), ammonium per sulphate (oxidant) and copper oxide nanoparticle are

taken in the ratio of 1:2:1. The monomer is dissolved in 1 M hydrochloric acid and copper oxide nanoparticle is added to the above solution with vigorous stirring using magnetic stirrer in order to keep the copper oxide suspended in the solution. Then the aqueous solution of the oxidizing agent is slowly added. 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, poly(m-aminothiophenol)/CuO (PmATP/CuO) 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. [13]

Characterization Techniques

The FT-IR spectra of the synthesized polymer and its nanocomposites are studied using Perkin Elmer 1750 FTIR spectrophotometer at room temperature. UV-VIS spectra are recorded from 200-800 nm using SHIMADZU model UV-2450 spectrophotometer by dissolving the polymers in DMSO as a solvent. 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°C/min.

The morphological study of the synthesized polymer PmATP and its nanocomposites are 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 PmATP/ZnO and PmATP/CuO nanocomposites.

Photochemical measurements are carried out on a CHI608E electrochemical workstation and a 100 W Xe arc lamp (OSRAM, Germany) is used as the light source. Fluorescence Spectrophotometer of model Varian-Cary Eclipse is used to measure the fluorescence property of the synthesized polymer and its ZnO, CuO nanocomposites using Xenon flash lamp as source and PMT as detector.

RESULTS AND DISCUSSIONS:

Solubility

The polymer poly(m-aminothiophenol) and its nanocomposites are found to be completely soluble in DMSO, THF, DMF and benzene to give clear solutions and insoluble in water, methanol, n-hexane. They are partially soluble in ethanol and acetic acid.

FT-IR analysis

The FT-IR spectra of PmATP, PmATP/ZnO and PmATP/CuO are given in figure 1 and from the spectra it is clear that the bands at 1471 and 1620 cm^{-1} are assigned to C=C stretching vibrations of the quinonoid and benzenoid ring present in the polymer. The two peaks at 3215 and 3064 cm^{-1} are associated with N–H asymmetrical and symmetrical stretching vibrations respectively.[14] The peaks at 1264 and 1301 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 856 and 752 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. [15]
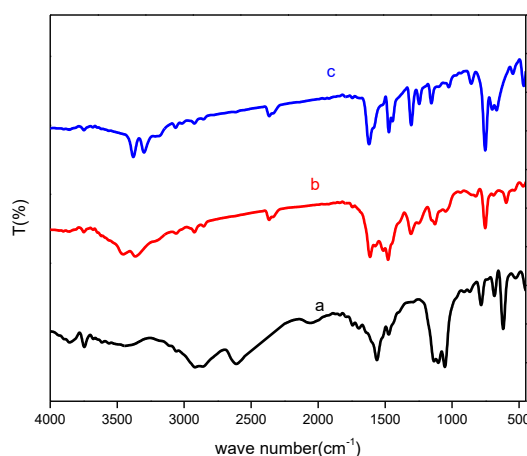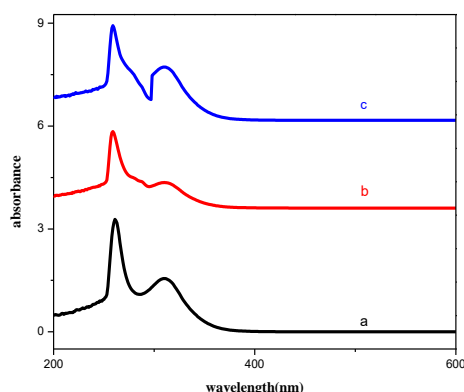

Figure 1: FT-IR spectra of (a) PmATP , (b) PmATP/ZnO and ,(c) PmATP/CuO

The PmATP/ZnO and PmATP/CuO nanocomposites have all the peaks of polymer but the values are slightly shifted towards lower wave number. The shift in the peaks of the polymer nanocomposites are due to the formation of hydrogen bonding between ZnO/CuO nanoparticles and –NH group on the surface of the polymer PmATP. [16]

UV-VIS Spectroscopy

The UV-VIS absorption spectra of the polymer poly(m-aminothiophenol) and poly(m-aminothiophenol)/ZnO, poly(m-aminothiophenol)/CuO nanocomposites are dissolved in DMSO are shown in Figure 2. The spectrum of the polymer consists of two major absorption peaks; the first peak at 262 nm is assigned to the π-π* transition of the benzenoid rings which is related to the extent of conjugation between the benzenoid rings in the polymer chain. The intensity of the π-π* absorption maxima is comparable for polymer. The second absorption peak at 315 nm is assigned to $n-\pi$* transition between the HOMO orbital of the benzenoid ring and the LUMO orbital of the quinonoid ring. [17]


Figure 2: UV-VIS spectra of (a) PmATP , (b) PmATP/ZnO and ,(c) PmATP/CuO

When zinc oxide nanoparticle is introduced, hypsochromic shift is observed with peaks at 258 nm, and at 310 nm. In the case of copper oxide nanoparticle incorporation, hypsochromic shift is observed with peaks at 259 nm, and 308 nm. The shift is expected due to less conjugation along the polymeric chain and the incorporated metal oxide nanoparticles into the polymeric matrix.

X-Ray Diffraction Studies

The XRD pattern of poly(meta-aminothiophenol) and its nanocomposites are given in figure 3. The diffraction patterns are typical of crystalline/amorphous nature. The crystalline nature of the polymer and its nanocomposites are shown by the presence of relatively sharp peaks in lower 2θ regions. The amorphous regions are visible by the broad low intense peak at higher 2θ values.
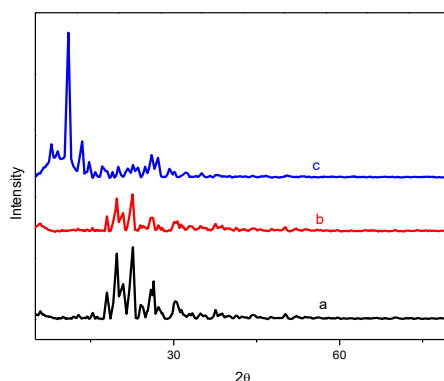
Figure 3: XRD pattern of (a) PmATP, (b) PmATP/ZnO and, (c) PmATP/CuO

The position of the Bragg's peaks (2θ) also gives information on the morphology of the polymers. The polymer exhibits strongest sharp peaks at 2θ values of 17.9̇, 19.7̇, 24.3̇, 25.4̇, 27.9̇ and the broad peaks at 33̇,

37.5˚,40.3, 45.5 are characteristics of the Van der Waals distance between stacks of phenylene rings (poly aminothiophenol rings). [18] The degree of crystalline ordered structural pattern in PmATP, PmATP/ZnO and PmATP/CuO is due to the more intra chain hydrogen bonding or electrostatic interaction through amine and/or thiol groups. The crystallinity and orientation of conducting polymers have been of much interest, because more highly ordered systems can display a metallic conductive state and may influence the anticorrosion performance. [19]

Thermogravimetric Analysis

The thermal stability of the polymers and its nanocomposites are evaluated using thermogravimetric analysis and shown in Figure 4. The thermal behavior of the polymer and its ZnO, CuO nanocomposites are similar and exhibits a three-stage decomposition pattern. The first weight loss step starts from 220 to 270ºC which corresponds to the loss of free acids, and volatile molecules in polymer matrix. The second step is in the TGA curves between 270 and 400ºC because of loss of dopant, sublimation, and removal of low molecular weight polymer/oligomer from the polymer matrix. While the third weight loss step occurs between 400 and 730ºC which is due to the complete degradation and decomposition of the polymer backbone.
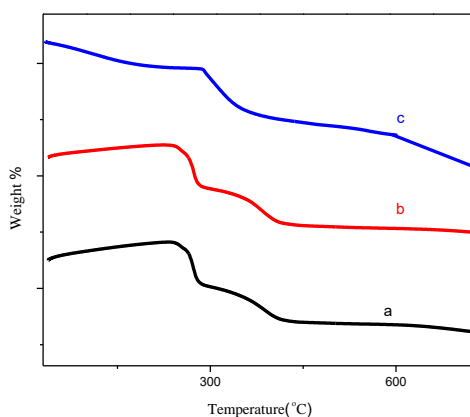

Figure 4: TGA of (a) PmATP, (b) PmATP/ZnO and, (c) PmATP/CuO

Scanning Electron Microscopy

The Scanning Electron Microscopy (SEM) micrographs are used to investigate the morphology of the polymer and polymer metal oxide nanocomposites. Poly(meta-aminothiophenol) displays agglomerated structure. The polymer metal nanocomposites PmATP/ZnO exhibit flake like structure and PmATP/CuO exhibit pollen grain morphology which may result from intramolecularly hydrogen bonded between amino and thiol units. [20] Figures 5-7 show the SEM Images of (a) PmATP, (b) PmATP /ZnO, and (c) PmATP /CuO.
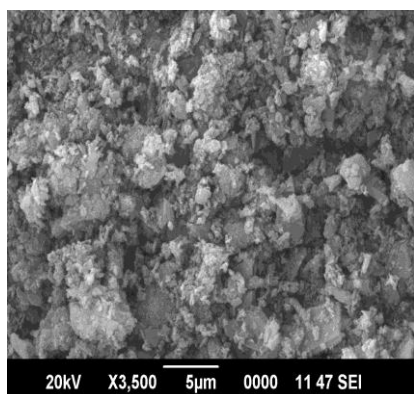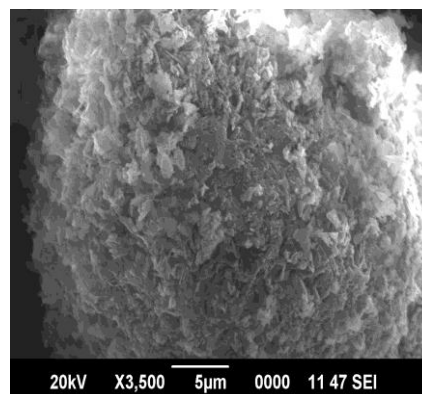

Figure 5: SEM image of PmATP
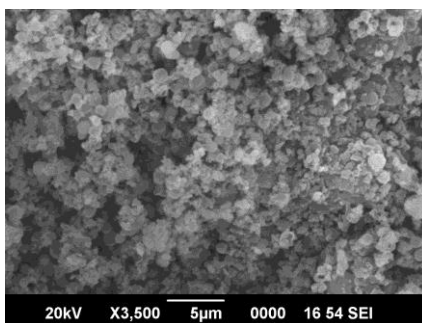

Figure 6: SEM image of PmATP/ZnO

Figure 7: SEM image of PmATP/CuO

Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) images of polymer nanocomposites are given in figure 8 and 9. The micrographs of polymer nanocomposites exhibit smooth surfaces the spongy sheet like features which confirm the formation of the nanocomposites. The sheet like structures exhibit both dark (metal oxide nanoparticle) and light coloured region (polymer) which are indicating that more of nano ZnO and CuO are incorporated. The nanocomposites are found to be homogeneous and are uniformly distributed. The nanoparticles in the nanocomposites indicate that the surface of nanoparticles have the interaction with the polymer PmATP.
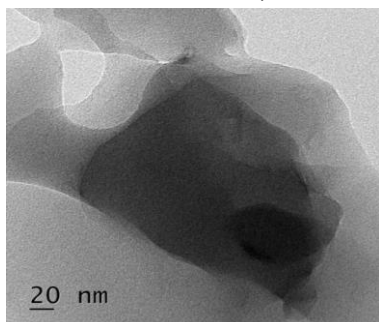

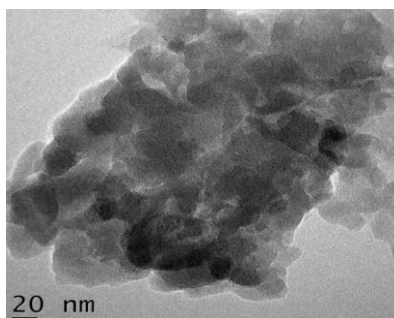**Figure 8:   TEM image of PmATP/ZnO**

Figure 9: TEM image of PmATP/CuO

APPLICATIONS:

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. [21] The Nyquist plot obtained for the polymer and its nanocomposites at room temperature are shown in Figure 10. The ionic conductivities of the PmATP, PmATP/ZnO and, PmATP/CuO nanocomposite are calculated and the values are found to be in the order of $x10^{-5}$ and $x10^{-4}$ S/cm respectively. The conductivity results show that the conductivity of the polymer and its nanocomposites are semiconducting in nature. The polymer ZnO, CuO nanocomposites have higher conductivity values than the corresponding polymer PmATP.
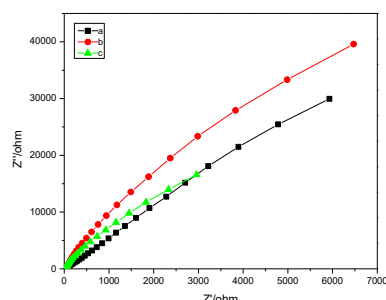

Figure 10: Nyquist impedance spectra of (a) PmATP, (b) PmATP/ZnO, and (c) PmATP/CuO

Dielectric Studies

The dielectric constant is a crucial parameter required to design of electronic and electrical devices and furthermore, as a function of frequency, they reveal much information on the chemical or physical state of the polymer. Figure 11 and 12 show the variation of dielectric constant (ε') and dielectric loss of (ε'') as a function of frequency of poly(m-aminothiophenol) , poly(m-aminothiophenol)/ZnO and poly(m-aminothiophenol)/CuO nanocomposites. It is observed that dielectric constant and dielectric loss are found to decrease with increase in the frequency. The decrease in dielectric constant with frequency can be attributed to the decrease in polarization with frequency. At very low frequencies dipoles follow the field. As the frequency increases dipoles begin to lag behind the field and ε' slightly decreases. When the frequency reaches the characteristic frequency dielectric constant drops. [22]
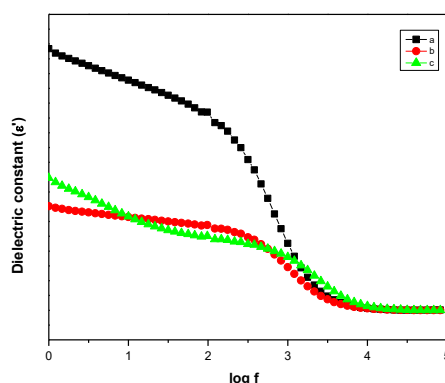

Figure 11: Plot of dielectric constant V/s frequency of (a) PmATP, (b) PmATP/ZnO, and (c) PmATP/CuO
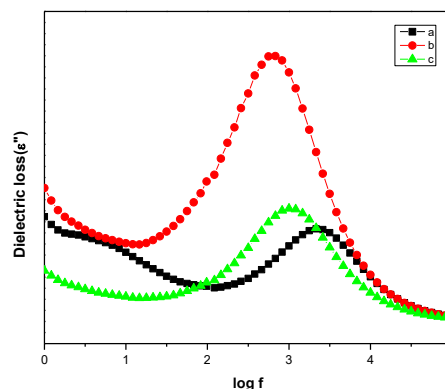

Figure 12: Plot of dielectric loss V/s frequency of (a) PmATP, (b) PmATP/ZnO, and (c) PmATP/CuO

Similar trend of variation of dielectric constant with frequency are observed for CuO and ZnO doped PmATP nanocomposites. The decrease of the dielectric constant ε' can also explain from interfacial polarization. The interfacial polarization arises as a result of difference in conducting phase. Generally, the dielectric losses at high frequencies are much lower than those occurring at lower frequencies. This kind of dependence of dielectric loss ε'' on frequency is typically associated with losses by conduction. [23]

Fluorescence studies

The fluorescence studies show that the synthesized polymer PmATP and the nanocomposites PmATP/ZnO, PmATP/CuO are having emission spectra. The fluorescence spectra of polymer at 1000 ppm exhibited the highest emission intensity of 100 and found to increase to 180 with the decrease of concentration to 50 ppm and the results are shown in figure 13.
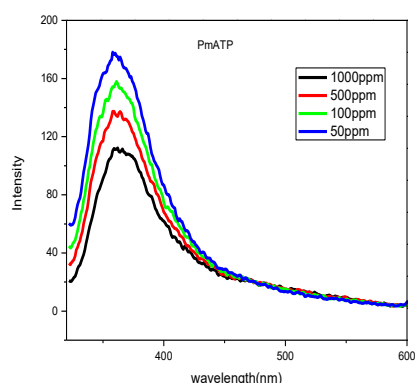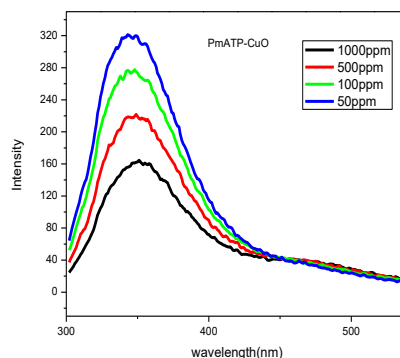
Figure 13: Emission spectra of PmATP at different concentrations

The same trend is followed in the fluorescence spectra of PmATP/ZnO and PmATP/CuO and the results are shown in figure 14 and 15. The fluorescence spectra of PmATP/ZnO at 1000 ppm exhibited the highest emission intensity of 110 and found to increase to 180 with the decrease of concentration to 50 ppm. In the case of PmATP/CuO, the fluorescence spectra exhibiting the emission intensity of 150 and found to increase to 320 with the decrease of concentration from 1000 ppm to 50 ppm. The fluorescence studies clearly reveal that the pattern have a strong emission bands around the blue light region. [24] The comparison of the fluorescence property show that the emission intensity of polymer nanocomposites are higher compared to the polymer.
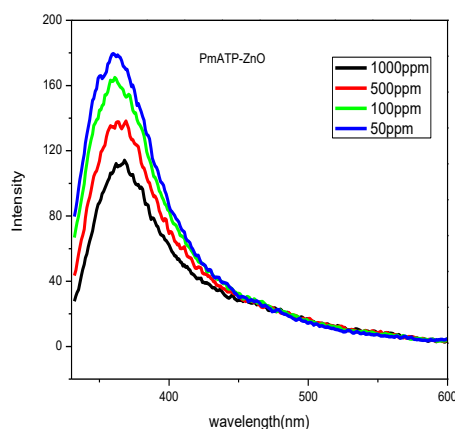
Figure 14: Emission spectra of PmATP/ZnO at different concentrations

Figure 15: Emission spectra of PmATP/CuO at different concentrations

CONCLUSION:

The poly (m-aminothiophenol), poly(m-aminothiophenol)/ZnO and poly(m-aminothiophenol)/CuO 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 nanocomposites. The thermal properties are studied using thermo gravimetric analysis and confirm that the polymer nanocomposites are more stable compared to the corresponding polymer. The morphology of PmATP and its ZnO,CuO nanocomposites are evaluated from the SEM and X-ray diffraction studies. The formation of polymer nanocomposites are confirmed by TEM analysis. The conductivity and dielectric studies of the polymer and its nanocomposites show that they are semiconducting in nature and lossless materials which could be widely applied in the fields of semiconductor, batteries etc. The fluorescence studies show that poly(m-aminothiophenol), poly(m-aminothiophenol)/ZnO and poly(m-aminothiophenol)/CuO are found to be blue light emitters. They exhibit very good fluorescence property which can be applied in photonic and electronic devices.

REFERENCES:

[1]. Kumari, K.; Ali, V.; Rani, G.; Kumar, S., Lakshmi, G., Zulfequar, M. Materials Science and Application, 2, 1047-1057, (2011).

[2]. Shukla,S.K.; Bharadvaja, A.; Tiwari, A.; Parashar, G.K.; Dubey, G.C. Adv. Mat. Lett., 1(2), 129, (2010).

[3]. Gupta, M. C.; Borkar, A. D.; Umare, S. S.; Polym. Plast. Technol. Eng., 40, 225, (2001).

[4]. Kondawar, S.B., Agrawal, S.P., Nimkar, S.H., Sharma, H.J., Patil, P.T., Adv. Mat. Lett. 3(5), 393-398, (2012).

[5]. Kondawar, S.B.; Deshpande, M.D.; Agrawal, S.P.; International Journal of Composite Materials, 2(3), 32-36, (2012).

[6].Nandapure, B.I., Kondawar, S.B., Salunkhe, M.Y., Nandapure, A.I., Adv. Mat. Lett., 4(2), 134-140, (2013).

[7]. Nandapure, B.I., Kondawar, S.B., Salunkhe, M.Y., Nandapure, A.I., J. Compo. Mater., 47(5), 559–567, (2012).

[8] R. Wu, C. S. Xie, Mater. Res. Ball., (2004).

[9] M. Kitano, M. Shiojiri, Powder Technol., (1997).

[10] Yang Y, Chen HL, Zhao B, Bao XM. J Cryst Growth., (2004).

[11] Anderson, P.W. Absence of Diffusion in Certain Random Lattices. Physical Review, 109, 1492-1505, (1958).

[12] Anderson, P.W., Halperin, B.I. and Varma, C.M. Philosophical Magazine., 25, 1-9, (1972).

[13] Irudaya Antonat Sophia, G. Gopu, C. Vedhi., Open Journal of Synthesis Theory and Applications., 1, 1-8, (2012).

[14] He D. Wu Y. Xu BQ. Eur Polym J., 43, 3703–3709, (2007).

[15] M.R. Nabid, R. Sedghi, A. Bagheri, M. Behbahani, M. Taghizadeh, H. Abdi Oskooie, M.M. Heravi, J. Hazard. Mater., 203, 93, (2012).

[16] Mathavan,T. Archana J. Hayakawa Y. Anitha K. Jothirajan M.A. Divya1 A. Milton Franklin Benial A. International Journal of ChemTech Research., 7, 1253-1258, (2015).

[17] A. Elmansouri, A. Outzourhit, A. Lachkar et al., SyntheticMetals, vol. 159, no. 3-4, pp.292–297, (2009).

[18] C. Saravanan, S. Palaniappan, and F. Chandezon, Materials Letters, vol. 62, no. 6-7, pp. 882–885, (2008).

[19] H. Xia and Q. Wang, Chemistry of Materials, vol. 14, no. 5, pp.2158–2165, (2002).

[20] S. Murlidharan, K. L. N. Phani, S. Pitchumani, S. Ravichandran and S. V. K. Iyer, Journal of the Electrochemical Society, Vol. 142, No. 5, pp. 1478-1483, (1995).

[21] Porselvi Linganathan, Jhancy Mary Samuel, American Journal of polymer Science., 4,107-116, (2014).

[22] Abd El-Kader, F.H., Osman, W.H., Mahmoud, K.H. and Basha, M.A.F. Physica B: Condensed Matter, 403, 3473-3484, (2008).

[23] Cao, Y., Li, S.Z., Xuea, Z. J., Guo, D., Synthetic Metals, 16(3), 305-315, (1986).

[24] Bylander EG. J. Appl. Phys.: 49: 1188, (1978).