

Synthesis and investigations of spectral and electrical properties of cobalt nitrate doped poly (m-toluidine)

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Abstract

In the recent years, conducting polymers with pi conjugated electron systems have attracted great interest due to their optical and electrical properties. Among these conducting polymers, Poly (m-toluidine), a derivative of polyaniline, is an interesting and important conducting polymer for the development of conducting composites. In the present work, Poly (m-toluidine) and cobalt nitrate metal salt composites were synthesized by chemical oxidative polymerization technique with potassium dichromate as an oxidant, in hydrochloric acid medium and by chemical doping as suggested by Macdiarmid et al. The prepared doped polymeric composites were characterized by UV-visible spectroscopy and dc conductivity measurement techniques. The UV-visible spectra of composites revealed that the band gap decreases continuously with increases in dopant concentration and the peaks indicating the presence of charged particles/ polarons. The DC conductivity of polymer composites has been measured by two probe method in temperature range of 300-400 K in a specially designed conductivity measurement holder and significant enhancement in dc conductivity has been observed with dopant and also with the increase in temperature, showing the semiconductor nature of synthesized polymer composites.

Keywords— Chemical doping, UV-Visible spectroscopy, DC conductivity

1 Introduction

In the pristine form polymers are generally found to be insulators. When these polymers are chemically treated with oxidizing/reducing agents, some of them behave as conductors with considerable electrical conductivity. Conductive polymers like polyanilines, have attracted scientific and technological importance in recent years due to their scientific importance [1-2]. Polyanilines are very important in scientific world due to

their various properties like good environmental stability, ease processibility and relatively low cost [3-5]. Some of polymeric complexes prepared from conducting polyaniline and its derivative, such as poly (o-toluidine) (POT), Poly (m-

toluidine) (PMT) have generated great interest in recent years, as they are easy to prepare and exhibit excellent electrical, optical, mechanical properties and also due to their solubility in organic solvents [6-7]. Poly (m-toluidine) (PMT), a derivative of polyaniline, has till date not much investigated by researchers as per its scientific potential. This derivative of polyaniline emerged as a promising and important polymer for many technological and commercial applications in different scientific areas because it is easy to be doped by several methods, such as protonation with a protonic acid or by charge transfer with an oxidizing agent, to increase its electrical conductivity and various other physical properties [8].

In the present work PMT was synthesized by chemical oxidation polymerization and PMT-cobalt nitrate polymeric composites were prepared by chemical doping of the host polymer with different concentrations of cobalt nitrate. To find out the influence of the cobalt nitrate on the properties of PMT, the prepared doped polymeric composites were characterized by UV-visible spectroscopy and dc conductivity measurements

2 Experimental methods

The m-toluidine (99.9 %, Merck, India), Potassium dichromate (99 %, S.D. Fine Chemicals, India), hydrochloric acid (99 %, Qualigens Chemicals, India), tetrahydrofuran (99.9 % Merck, India), 28 % ammonia solution in water (S.D. Fine Chemicals, India) and cobalt nitrate (Hi-Media Chemicals, India) all these chemicals were of analytical grade and double purified distilled water were used for polymer preparation. The monomer m-toluidine was used to prepare poly (m-toluidine) taking potassium dichromate as an oxidant in hydrochloric acid medium as suggested by MacDiarmid et al. [9]. The prepared polymeric composites were again cooled down to 280 K for 24 hour to complete the polymerization process.

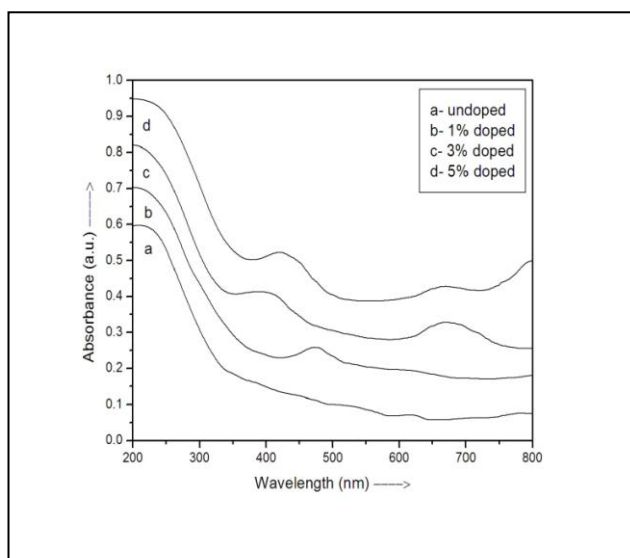
Now the dark colored PMT powder was dried in a vacuum at a temperature 350 K for 24 hour to obtain a moisture free polymer composites. Now 2 gram of ground powder of PMT and cobalt nitrate with different concentrations 1, 3, and 5 % (w/w) were added by the method prescribed by MacDiarmid et al. [9]. At last, these doped composites were placed in vacuum oven at 380 K for 6 hour to obtain doped polymer composites for characterization. Samples for UV-visible spectra were prepared by dissolving a small amount of doped polymer in tetrahydrofuran in quartz cuvetts. A (Hitachi 330, Japan) UV-visible spectrometer was used to investigate the absorption spectra in the wavelength range of 200-800 nm. The dc conductivity of both PMT powder and doped polymer composites were measured by using a two probe method in the temperature range 300-400 K using Pico-ammeter (Keithley 617, U.S.A).

2.1 UV-Visible spectra

The UV-Visible spectra of pure and cobalt nitrate doped PMT polymer composites with dopant concentrations of 1, 3 and 5 % (w/w) are shown in Fig. below

The electronic spectra showed absorption bands at ~ 330, 435, 680 and 790 nm. The band at about 330 nm appeared due to the $\pi - \pi^*$ exciton transition [10]. The polaron absorption band at ~ 435 nm depicts the $\pi - \pi^*$ electronic transitions of benzene rings [11]. The absorption band at ~ 680 nm is attributed to excitonic transitions and it is very sensitive to the overall oxidation of the polymerization [12]. The polaron absorption bands, visible at 435 [13] and 790 nm, are due to the π -polaron and polaron- π^* band transitions respectively and are conformation of the conductive form of the PMT [14].

The optical band gap (E_g) of the polymer composites was



determined using the Tauc's relation [15];

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the energy of the incident photon and A is a proportionality constant. The value of energy band gap and position of absorption band for different dopant concentration is given in the Table 1. The band gaps for the 1, 3 and 5 % (w/w) cobalt nitrate-PMT polymeric complexes are found to be 5.19, 4.96 and 4.63 eV respectively, and for the undoped PMT, 5.36 eV. The band gap decreased continuously with increase in dopant concentration. It is fact that the values of energy band gap is also influenced by various factors like experimental conditions during the synthesis, degree of polymerization, monomer-oxidant ratio, temperature, etc. [16-17].

Table 1. The value of energy band gap and absorption band for various dopant concentrations.

S.No	Dopant Concentration (w/w)	Band gap (eV)	Absorption band (nm)
1	undoped	5.36	330
2	1%	5.19	435
3	3%	4.96	680
4	5%	4.63	790

2.2 DC Conductivity

The dc conductivity of PMT-cobalt nitrate polymeric composites was measured by a two probe method using a specially designed sample holder in the temperature range 300-400K. The observed value of dc conductivity for different dopant concentrations at the temperature is tabulated in the Table 2 below. The electrical conductivity, σ , of an ohmic material can be determined by the relation given below;

$$\sigma = l/RA(S/cm) \quad (2)$$

Where l is the thickness of pellet, A is the cross-sectional area of pellet, and R is the resistance of the pallet. For the pure PMT sample, the conductivity was 5.23×10^{-7} S/cm, while in the case of the 1, 3 and 5% (w/w) doped polymer composites, the values of conductivity at room temperature (300 K) were 5.78×10^{-6} , 1.89×10^{-5} and 5.44×10^{-4} S/cm, respectively. It means dc conductivity increased with the increase in doping concentration. At 400 K, the

S.No	Dopant concentration (w/w)	Conductivity at 300 K (S/cm)	Conductivity at 400 K (S/cm)
1	undoped	5.23×10^{-7}	8.51×10^{-6}
2	1%	5.78×10^{-6}	9.99×10^{-5}
3	3%	1.89×10^{-5}	4.74×10^{-5}
4	5%	5.44×10^{-4}	9.67×10^{-4}

corresponding dc conductivity values were 8.51×10^{-6} , 9.99×10^{-6} , 4.74×10^{-5} and 9.67×10^{-4} S/cm, respectively. Thus, the conductivity increased significantly with temperature, showing the semiconductor nature of doped polymer samples.

Table 2. The value of d.c. conductivity at temperature 300 K and 400 K.

3. Conclusion

PMT-cobalt nitrate polymeric samples were prepared by a chemical oxidation polymerization method. The doping process induced structural and chemical changes in the prepared polymer complex, which led to changes in the optical and electrical properties. The band gap of the doped polymer composites decreased with an increase in dopant concentration. The polymer composites prepared were semiconducting in nature as their conductivity increased with increase in temperature. The DC conductivity of the prepared polymers increased with increase in dopant concentration which was suggested to be due to extensive delocalization of π -electrons in the synthesized polymer.

References

- [1] W. Westerweele, P Smith, A.J Heeger,. "Inverted" polymer light-emitting diodes on cylindrical metal substrates. *J. Adv. Mater.* **1995**, 7, 788.
- [2] A.G MacDiarmid. Polyaniline and polypyrrole: where are we headed?. *Synth. Met.* **1997**, 84, 27.
- [3] A Kumar, V Ali and S. Kumar, Effect of protonation and chemical doping of poly (o-toluidine) with copper sulphate on spectral and electrical properties of the host polymer. *J. Macromolecular Phy. Part B.* **2012**, 52, 1.
- [4] A. Kumar, V. Ali and S. Kumar. Synthesis and Spectroscopic Investigations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Doped Poly (m-Toluidine). **2013**, 62, 8.
- [5] A.A. Syed and M.K. Dinesan, . Anion-exchange studies on electrically conducting polymers: Polyanilines. *React. Polym.* **1992**, 17, 145.
- [6] C.Y. Yang, Y Cao, P Smith, A.J. Heeger, Morphology of conductive, solution-processed blends of polyaniline and poly(methyl methacrylate). *Synth. Met.* **1993**, 53, 293.
- [7] M. Angelopoulos, A. Ray, A.G. MacDiarmid and A.J. Epstein, Polyaniline: processability from aqueous solutions and effect of water vapor on conductivity. *Synth. Met.* **1987**, 21, 21.
- [8] W. S. Huang, B. D. Humphrey, and A.G MacDiarmid, Polyaniline a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. *J. Chem. Soc. Faraday Trans.1.* **1986**, 82, 2385.
- [9] A. G. MacDiarmid, R. L. Mammone, J. R. Krawczyk, S. J. Porter, Reduction potentials: Key to doping phenomena in polyacetylene (CH_x). *Mol. Cryst. Liq. Cryst.* **1984**, 105, 89.
- [10] A. Kumar, V. Ali, and S. Kumar, Studies on conductivity and optical properties of poly (o-toluidine)-ferrous sulphate composites. *Int. J. Polym. Anal. Ch.* **2011**, 16, 298.
- [11] K. Tzou, and R. V. Gregory, A method to prepare soluble polyaniline salt solutions — *in situ* doping of PANI base with organic dopants in polar solvents. *Synth. Met.* **1993**, 53, 365.
- [12] P. Savitha, and D Sathyanarayana, Donor-acceptor-based poly(toluidine-co-chloroaniline)s: Synthesis and characterization. *Polym. Sci. Part A: Polym. Chem.* **2005**, 43, 1579.
- [13] K.G. Neoh, E. T. Kang and K. L. Tan, Spectroscopic studies of protonation, oxidation and light irradiation of polyaniline solutions. *Polym.* **1992**, 33(11), 2292.
- [14] D.Mahanta, G Madras, S Radhakrishnan and S. Patil, Adsorption of sulfonated dyes by polyaniline emeraldine salt and its kinetics. *J. Phys. Chem.B.* **2008**, 112,10153.
- [15] Tauc, J. (1974). Chapter 4, Amorphous and Liquid semiconductors, 159, Plenum Press, New York.
- [16] A. Elmansouri, et al.. Spectroscopic Characterization of Electrodeposited Poly(o-toluidine) Thin Films and Electrical Properties of ITO/Poly(o-toluidine)/Aluminum Schottky Diodes. *Hindawi Pub. Corp. Active and Passive Electronic Components.* **2007**, Doi:10.1155/2007/17846.
- [17] A. A.Syed, and S. R. Taqui., Polyanilines: Materials and Applications in Specialty Polymers: Materials and Applicatons; Mohammad, F. Eds.; I.K. Publishing House: NewDelhi, **2007**, 21-69.