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Poly mtoludine-Cecomposite: Characterization and conductivity study

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Abstract

The present paper includes the characterization of poly m toluidine- Ce composite, synthesized by insitu oxidative polymerization. The structural characterization of PMTD-Ce composite was carried out by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), thermo gravimetric analysis. Conductivity behaviour of PMTD-Ce composite was investigated by Four probe conductivity method. SEM and TEM images of the composite supports successful synthesis of PMTD-Ce composite. Thermal analysis shows enhanced thermal stability of the composite than PMTD. Conductivity study reveals the enhancement in conductivity of PMTD-Ce composite.

Key words: Insitu oxidative polymerization, Four probe conductivity method, SEM, TEM

1. Introduction

Conducting organic polymers like polyaniline, polypyrole, polythiophene and their substituted derivatives have become the polymers of great scientific and industrial importance because of their excellent and remarkable properties[1-3]. Though the unique properties of polyaniline derivatives provide a great scope for applications in various fields, but poor processibility due to insolubility in most of the common solvents and brittleness restrict its use as a commercial polymer[4-6]. To overcome these limitations change in the physical and chemical properties through substitution of specific groups on aromatic rings of polymer chains is one of the well- known routes[7-8]. Poly (m-toluidine) is one of substituted derivative of polyaniline in which –CH_3group is introduced at meta position of benzenoid ring of polyaniline. MacDiarmid and co-workers suggested that substitution of methyl group at meta position, increases steric interactions between benzenoid rings along the polymer chains, resulting decrease in the extent of conjugation[9]. Poly (m-toluidine) shows faster reversibility between oxidized and reduced form therefore chosen as an active conductive polymer along with polyaniline[10-11]

2. Experimental

Synthesis of poly m-toluidine (PMTD) and poly m toluidine- Ce composite was done by insitu oxidative polymerization and Characterization of poly m toluidine-Ce composite was carried out by UV, FTIR, XRD techniques reported earlier.[12] The present paper includes the characterization of poly m-toluidine-Ce composite by thermo gravimetric analysis, Scanning electron microscopy(SEM), Transmission electron microscopy (TEM) and study of conductive properties of the composite. SEM analysis was performed using JEOL, JSM-6400 low voltage (20kV) Scanning electron microscope. TEM analysis was performed using PHILIPS model-CM200, operating voltage range20-2000kV.Thermogravimetric analysis was done by PERKINELMER, USA, specifications- temperature range: ambient to 1500^0c, heating rate:10^0c/min. For conductivity investigations four probe conductivity apparatus was used.

3.Results and Discussion

3.1 Scanning electron microscopy analysis

Fig.3.1 (a) and 3.1(b)indicate the scanning electron micrographs of poly m-toludine and poly m toludine-Ce composite respectively.

SEM micrograph, Fig. 3.1 (a) showed the amorphous nature of undoped Poly m-toludine. These particles are of 8 µm size. SEM micrographs of Poly m-toludine-Cerric nitrate, confirm the impregnation of metal particles in the Poly m-toludine matrix. Some grains are spherical and some are tubular. The particle size in metal doped Poly m-toludine is 60 µm. EDS spectrum also confirm the presence of metal compounds in Poly m-toludine polymer matrix.

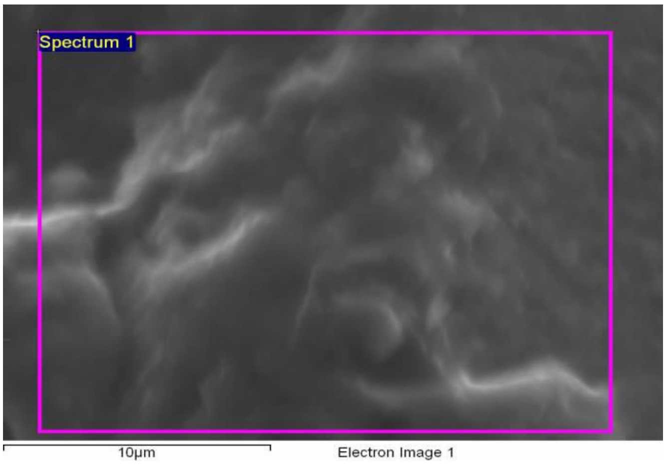


Fig. 3.1 (a) : SEM micrograph of Poly m-toludine

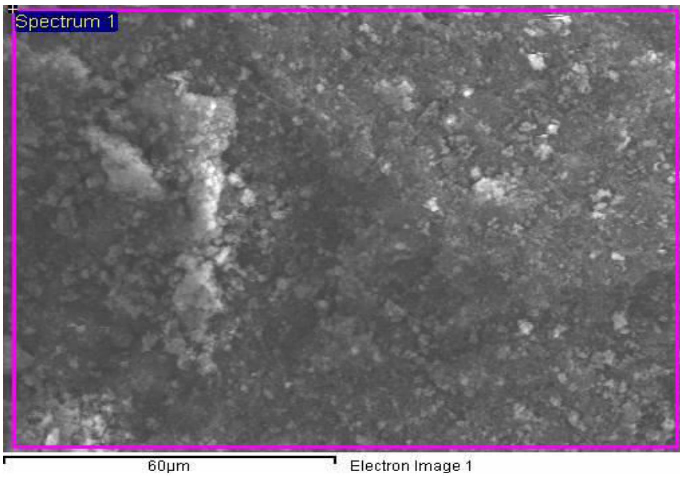


Fig. 3.1 (b): SEM micrograph of Poly m-toludine-Ce composite

3.2 Transmission electron microscopy analysis

Fig. 3.2 (a) and (b) shows TEM images of PMTD and PMTD-Ce composite. TEM images show the transformation of metal particles in the morphology of PMTD polymer particles. Wide range of particle/cluster size was observed starting from 20 nm to 70 nm.

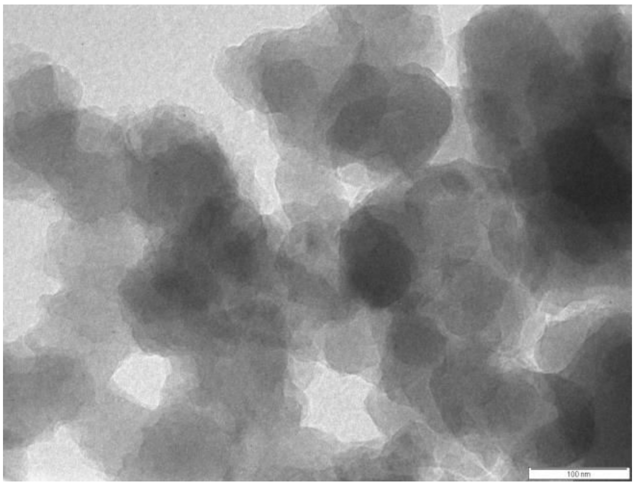


Fig. 3.2 (a) : TEM image : PMTD

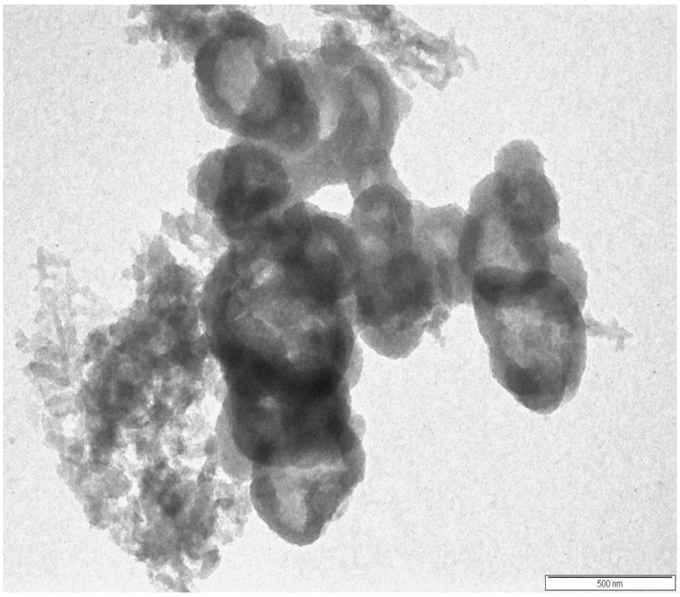


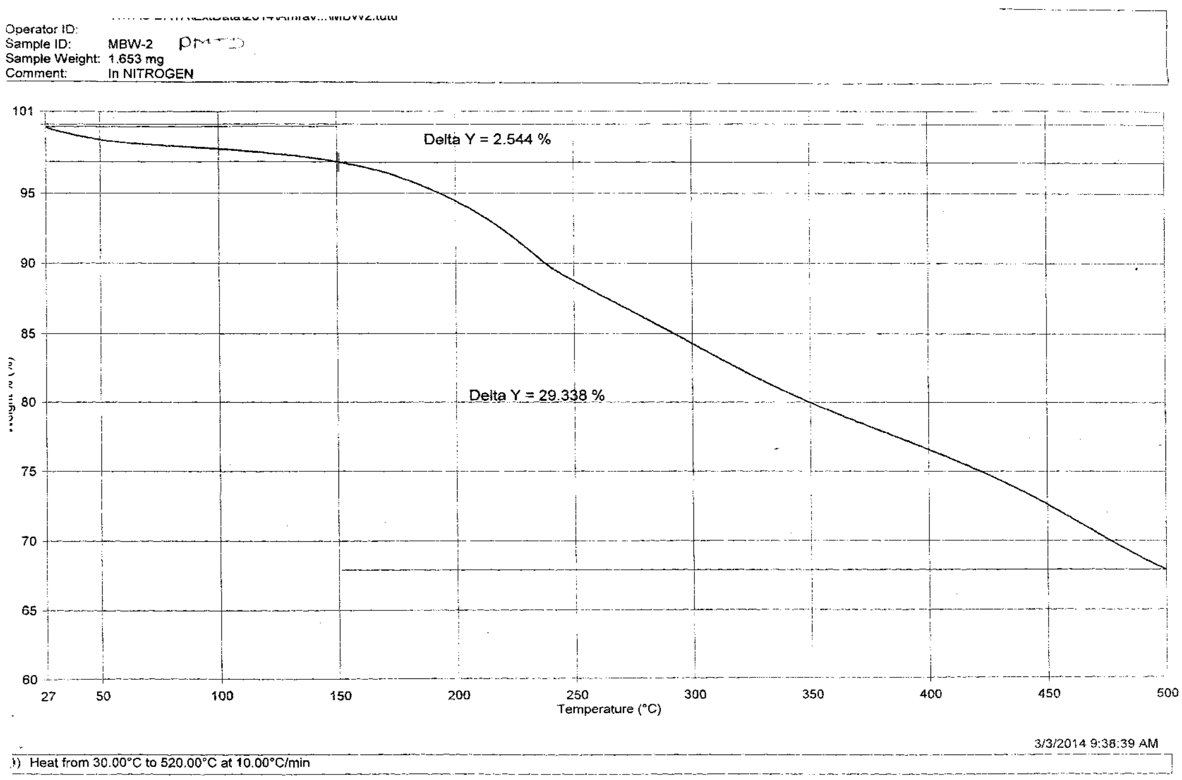
Fig. 3.2 (b): TEM image: PMTD-Ce composite

3.3 Thermogravimetic analysis

TGA curve of Poly m-toludine shows that weight loss occur in two steps. In the first step only 2.544% weight loss is observed upto 150°C. This weight loss is assigned to loss of moisture and low molecular weight oligomers. 29.33% weight loss is observed from 150-500°C, it represent the degradation of PMTD backbone.

TGA result of Poly m-toluidine-ceric nitrate show two step weight loss. In the first step, approximately 2-3% weight loss occurs at temperature about 100°C. This can be attributed to loss of moisture and low molecular weight oligomers from PMTD-Ce composite. 52% weight loss is observed in temperature range 120-500°C; it represents oxidative degradation of PMTD-Ce composite and also indicates the chemical structure decomposition of chemical structure of composite backbone. Thus total 52-53% weight loss occurs in the temperature range 50-500°C.

Fig. 3.3 (a) : TGA curve of poly m-toludine



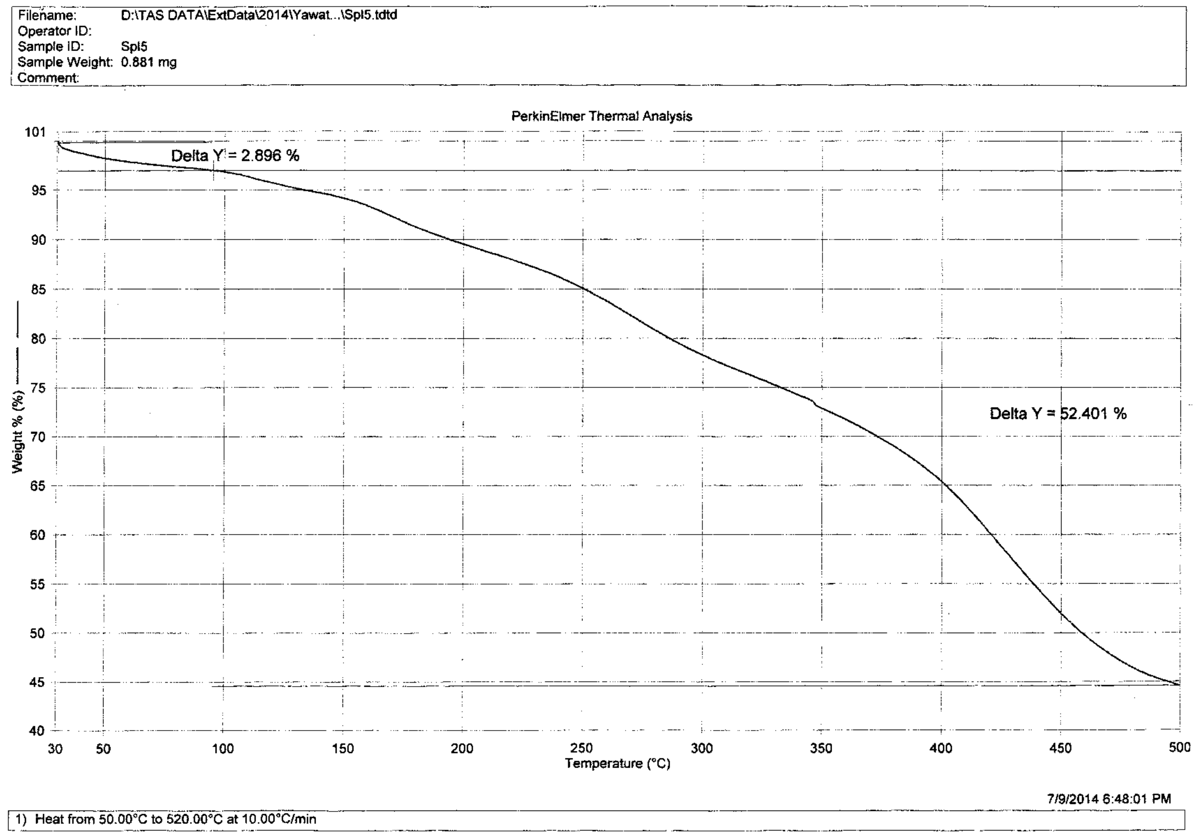


Fig.3.3 (b) : TGA curve of PMTD-Ce composite

3.4 Conductivity Measurements

The conductivity measurements were carried out by Four-probe method to determine the influence of dopant metals on polymer electronic properties. The synthesized polymer, poly m-toludine and poly m toludine-Ce composite were pressed under pressure into pellets with 0.3 cm radii and approximately 0.05 cm thickness.

The temperature dependent DC conductivity is measured at 68 to 122 K. The electrical conductivity of conducting polymers results from mobile charge carriers introduced into carriers - π electronic system through doping. The electrical conductivity of PMTD-Ce composite was found to be greater than pure metal. The variation in the conductivity of polymer-metal composite depends on the polymer content and sample morphology. The age factor directly affects the conjugation and chain length of PMTD.

It is observed from the Fig. 3.4 (a) and 3.4 (b), plots of 1000/T vs log ρ in both polymer and its composite observed nearly straight lines, indicating the conduction in these samples through an activated process having single activation energy in the temperature range 68-122 K. DC conductivity of these polymers increases exponentially with temperature, exhibiting semiconductor characteristics. Thus it was observed that the incorporation of Cerium metal particles into polymer PMTD matrix significantly affect the conductivity of PMTD.

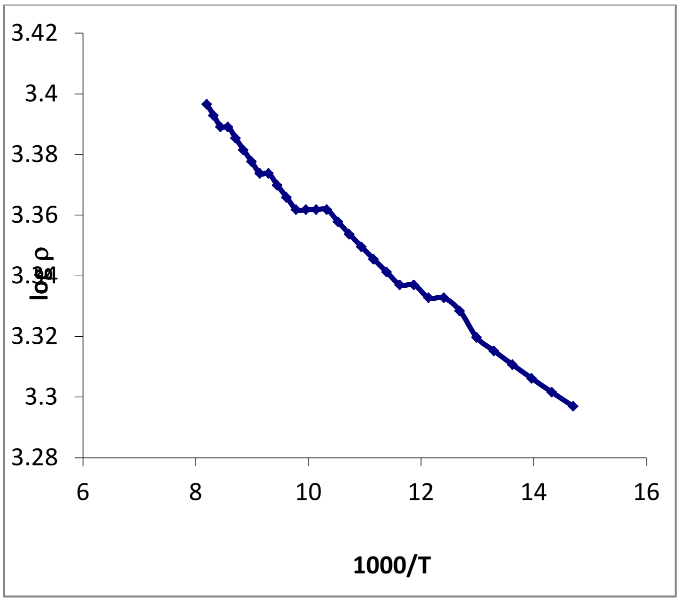


Fig. 3.4 (a): Plot of resistivity log ρ vs. 1000/T for Poly m-toludine

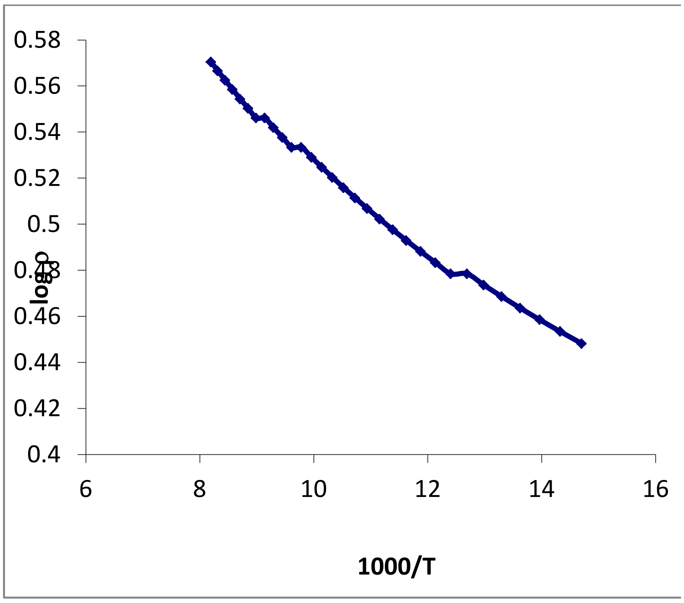


Fig. 3.4 (b): Plot of resistivity log ρ vs. 1000/T for Poly m-toluidine-Ce composite

4. Conclusion

SEM and analysis supports successful synthesis of synthesized PMTD and PMTD-Ce composite. Thermal analysis indicates enhanced thermal stability of PMTD-CE composite. The doping of Ce metal show the better conductivity.

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