

Synthesis, Spectral and Electrical Study of Conductive Poly (O-Toluidine) / Lanthanide Metal Composites

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Abstract: *Poly o-toluidine- Lanthanide metal composites can be synthesized by insitu polymerization of o-toluidine monomer using ammonium persulphate as chemical oxidant. During the composite formation process o-toluidine get oxidized to poly-o-toluidine and reduction of metal salt takes place. The metal composites were characterized by FTIR, UV-visible spectroscopy, it provide the information about the structure of the metal – polymer composite. The XRD analysis show the size of nano particles where as the morphology of composite were studied by SEM & TEM analysis. Thermal properties of polymer composites were studied using thermo gravimetric analysis. The four probe conductivity measurements revealed the increase in conductivity of doped poly o-toluidine polymers with lanthanide metals.*

1. INTRODUCTION

Since the discovery of intrinsically conducting polymers in 1970's, they have been studied extensively due to their characteristic electronic and redox properties.¹⁻⁵ The metal composites of these conducting polymers are a special class of materials having unique physical properties and numerous potential applications.⁶⁻⁷ The polymer-metal composites represent a new concept in the development of the systems exhibiting functional properties resulting from the synergistic interaction between polymer and metal salt particles.⁸ Now a days conducting polymers have been successfully utilized in preparation of different metal composites.⁹⁻¹¹ These polymer-metal composites have been widely used because of their good environmental, chemical stability and higher electrical conductivity.¹²⁻¹⁴ Our aim in synthesizing poly o-toluidine -metal composites because of their technological applications in electronic sensors, rechargeable batteries, optical devices, protection against corrosion ,conducting paints and others.¹⁵⁻¹⁸

Poly o-toluidine/Cu nano composite were synthesized by M.Vijayakumari et. al by *insitu* polymerization using o-toluidine and cupric sulfate precursors. They observed that during the reaction o-toluidine get oxidized to Poly o-toluidine, cupric sulfate get reduced to copper and metal-polymer composite was formed. FTIR, UV-Visible spectroscopy studies provided the information about the structure of metal-polymer composite. The XRD and SEM analysis showed the size of nanoparticles and morphology of polymer respectively.¹⁹

Kiran Kumari et al.reported use of aqueous binary dopant , ZrOCl₂ in different ratio such as 1:1, 1:2, 2:1 for chemical doping to enhance the conductivity of synthesized poly (o-toluidine). The doping of poly (o-toluidine) was carried out using tetrahydrofuran as solvent. The significant enhancement in DC conductivity has been observed with the introduction of binary dopant. UV-visible studies showed that optical parameters have changed considerably after doping. Both direct and indirect band gaps have been observed in the doped samples. XRD pattern showed the semi crystalline pattern of doped Poly (o-toluidine). FTIR study showed the structural modifications in functional group with doping in POT.²⁰

2. EXPERIMENTAL

2.1. Materials

Acids and bases used in the present work, including hydrochloric acid (HCl, 37%), and ammonium hydroxide (NH₄OH, 24%) were used. In all cases where solution of an acid or base in a specific

concentration was needed, the solution was made using deionized water. Ammonium persulfate (used as oxidant) $[(\text{NH}_4)_2\text{S}_2\text{O}_8, 98\%]$, o-toluidine, acetone, all are AR grade. Freshly distilled Aniline, o-toluidine were used. The metal salts -Lanthanum Oxide $[\text{La}_2\text{O}_3]$, Ammonium Ceric Nitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$, Neodymium (III) chloride hydrate $[\text{NdCl}_2 \cdot x\text{H}_2\text{O}]$ all used are of AR grade.

2.2. Synthesis of Poly o-toluidine and its Composites

Synthesis of poly o-toluidine is reported in our previous paper²¹ For the synthesis of Poly o-Toluidine-Neodymium Composite, 10 ml o-toluidine was mixed in 300 ml 1M HCl with continuous 1 hour stirring. 0.2 g Neodymium chloride hydrate was dissolved in o-toluidine solution. 22 g of APS powder was dissolved in 200 ml 1M HCl. Both solutions were kept for 1 hour. The oxidant APS solution was slowly added from burette in to monomer o-toluidine-Neodymium solution within 40 min. The constant stirring was continued for 24 hour with magnetic stirrer. Initially dark violet color was developed and later on greenish blue color was obtained, finally greenish blue colored product obtained was washed with dilute HCl followed by acetone. The dried product was dipped in large excess of 0.5 M NH_4OH overnight. The filtered product was dried in oven at 50°C . The Poly o-toluidine composites with Cerium Nitrate and Lanthanum oxide were prepared by the similar procedure.

3. CHARACTERIZATION

The structures of as prepared Poly o-toluidine- metal composites were studied by UV-visible spectroscopy using Varian CARY100 scanning spectrophotometer, FTIR spectroscopy using Bruker IFS 66/S FTIR spectrometer, X-ray diffraction using Philips X-ray diffractometer with Cu $K\alpha$ as source of radiation. Morphology of the polymer composites were studied by Scanning electron microscopy SEM on Transmission electron microscopy using JEOL JSM-6400 low voltage (20 kV) scanning electron microscope and PHILIPS, model-CM200, operating voltage range-20-2000kv, Resolution- 2.4\AA respectively. Thermogravimetric analysis of polymer composites was done by PERKIN ELMER, USA. Specifications –temp.range: ambient to 1500°C , heating rate: $10^\circ\text{C}/\text{min}$.

4. RESULTS AND DISCUSSION

4.1. UV-Visible Spectroscopy

Fig 1. (a) Shows the UV-visible spectra of Poly o-toluidine. The prominent peaks at 220nm, 290nm, 540 nm are attributed to the electronic transitions $\pi \rightarrow \pi^*$ transition and polaron on to π^* transition. Fig 1. (b) Shows the UV-visible spectra of Poly o-toluidine- Ce composite. The peaks at 330nm, 490 nm and 650 nm corresponds to $\pi \rightarrow \pi^*$ transition, polaron to π^* and $\pi \rightarrow$ polaron transition. The UV-visible spectra of Poly o-toluidine -Lanthanum composite (Fig-1.(c) shows the peaks at 310 nm, 390 nm, 530nm which can be attributed to $\pi \rightarrow \pi^*$ transition, polaron to π^* and $\pi \rightarrow$ polaron transitions, respectively. (Fig-1. (d)) shows the absorption bands at 350nm, 590 nm corresponds to polaron to π^* transition band. The shift in wavelengths confirms the interaction of Neodymium with polymer backbone of Poly o-toluidine.

Thus UV-visible spectra of Poly o-toluidine metal composites reveal that these composites are in emeraldine state. $\pi \rightarrow \pi^*$ transition peaks indicate presence of π conjugation. The observed peaks thus confirm that the synthesized samples are in conducting form containing metal salt particles. The blue-shift observed in the peaks can be attributed to the lowering of extent of conjugation caused by the repulsion between $-\text{CH}_3$ and the adjacent phenyl ring hydrogen.

Table1. UV-Visible absorption data of Poly o-toluidine and its composites

Sample	Peak position (nm)
POTD	220, 290, 540
POTD-La	310, 390, 530
POTD-Ce	330, 490, 650
POTD-Nd	350, 590

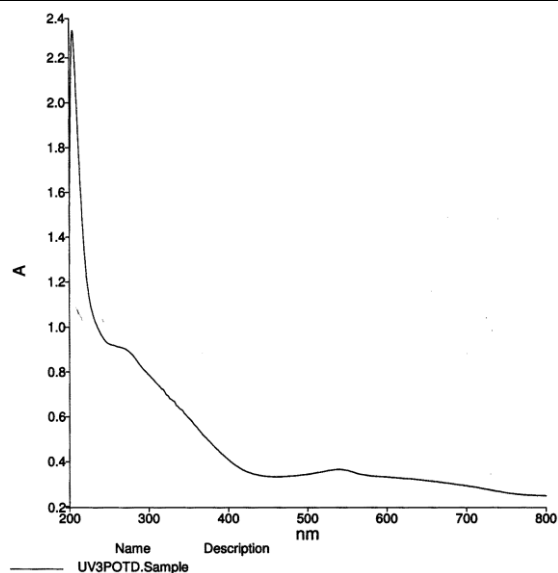


Fig1 (a). UV spectra of Poly o-toludine.

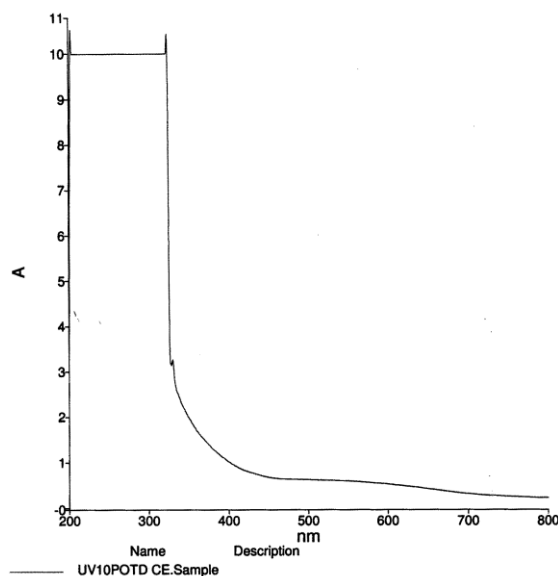


Fig1 (b). UV spectra of Poly o-toludine-Ce composite

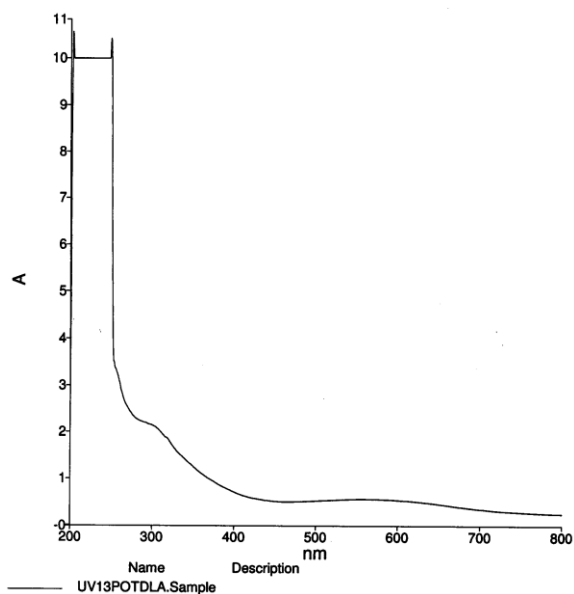


Fig1 (c). UV spectra of Poly o-toludine-La composite

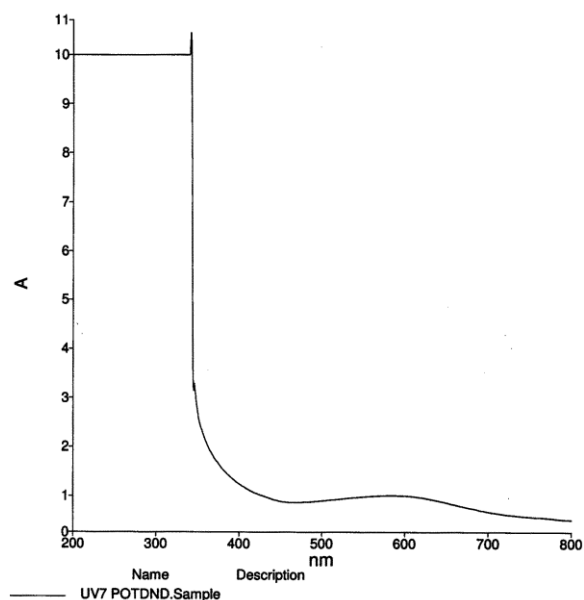


Fig1 (d). UV spectra of Poly o-toludine-Nd composite

4.2. FTIR

(Fig 2-a) shows the FTIR spectra of Poly o-toludine –Neodymium composite. The broad peak at 3369 cm^{-1} is assigned to N-H stretching vibrations. The C-H stretching in CH_3 group corresponds to peak at 2917 cm^{-1} . Quinoid and benzenoid ring vibrations are represented by the absorption bands at 1597 and 1495 cm^{-1} . The absorption peaks at 1303 and 1223 cm^{-1} represent C-N stretching in quinoid, benzenoid structure. 1154 cm^{-1} peak corresponds to interaction of polymer chain with Neodymium metal. 1108 cm^{-1} peak represents the C-H out of plane bending vibrations²².

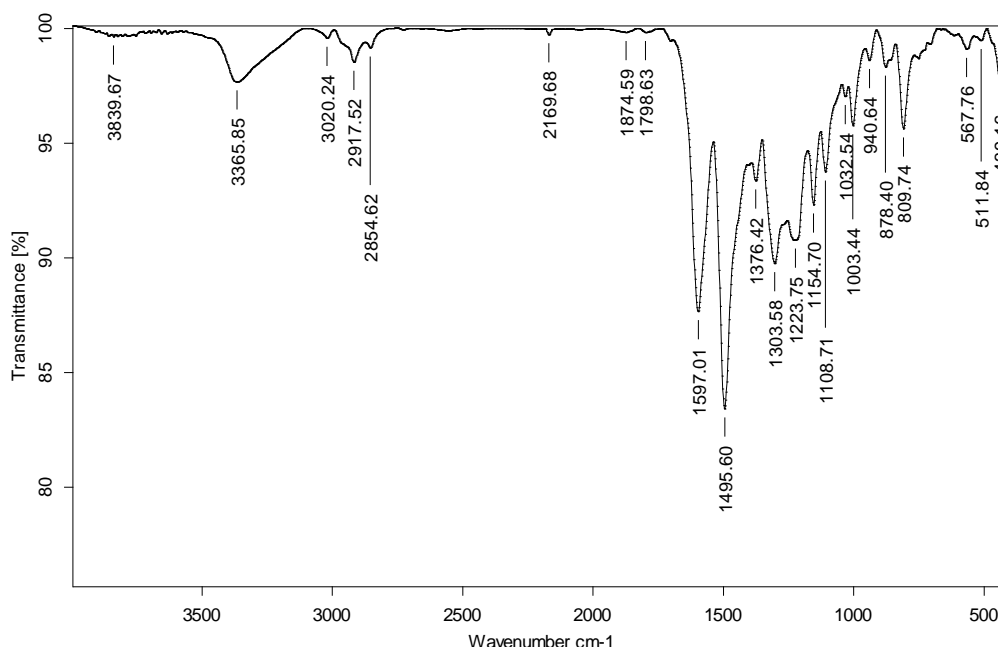


Fig2 (a). FTIR spectrum of Poly o-toludine-Neodymium composite

FTIR Spectra of Poly-o-toludine –Cerium composite, (Fig 2- b) indicate broad peak at 3376 cm^{-1} , it can be assigned to N-H stretching vibrations²³. The absorption band 2914 cm^{-1} corresponds to the C-H stretching in CH_3 group. 1304 and 1218 cm^{-1} corresponds to the C-N stretching oscillations in quinoid and benzenoid ring. The interaction of Cerium metal with poly o-toludine polymer chain.

In FTIR Spectra of Poly-o-toludine –Lanthanum composite, (Fig 2- c), the absorption band due to N-H stretching vibrations is represented by the weak broad peak at 3369 cm^{-1} . The C-H stretching in CH_3 group corresponds to peak at 2917 cm^{-1} . Quinoid and benzenoid ring vibrations are represented by the absorption bands at 1595 and 1497 cm^{-1} . The absorption peaks at 1303 and 1224 cm^{-1} represent C-

N stretching in quinoid, benzenoid structure. 1154 cm^{-1} peak corresponds to interaction of polymer chain with Neodymium metal. 1109 cm^{-1} peak represents the C-H out of plane bending vibrations.

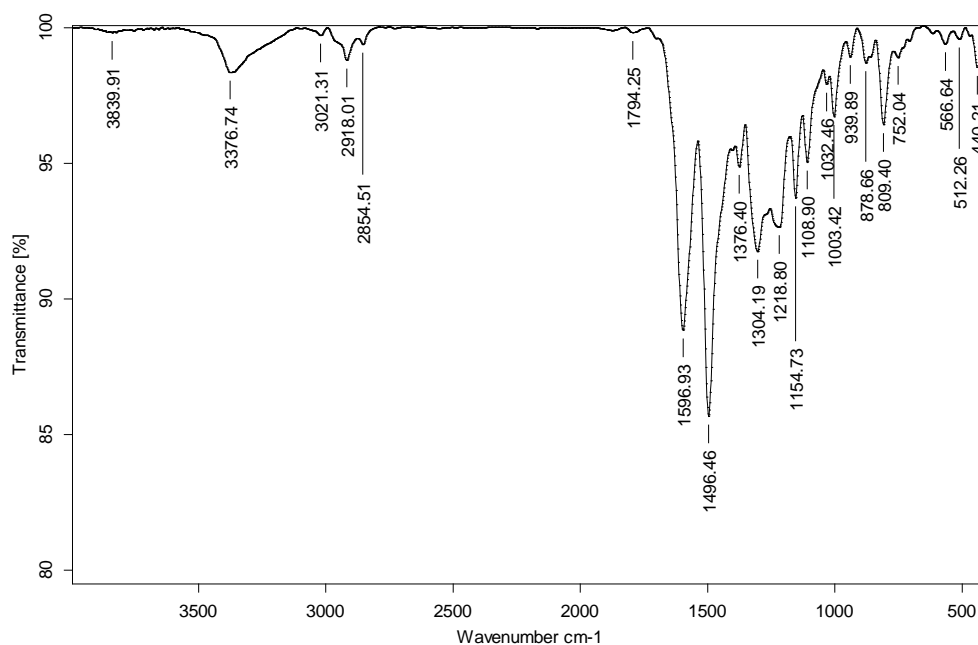


Fig2 (b). FTIR spectrum of Poly *o*-toluidine-Ce composite

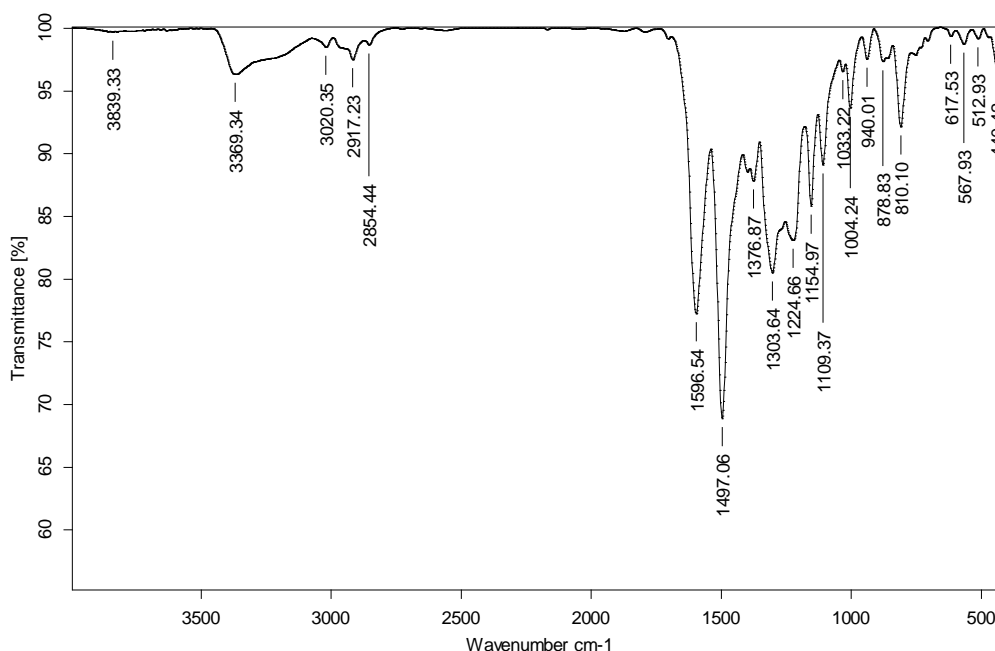


Fig2 (c). FTIR spectrum of Poly *o*-toluidine-Lanthanum composite

4.3. XRD

XRD spectrum of POTD-La composite (Fig. 3 (a)) shows the peaks at $2\theta = 11.27, 22.85, 32.61, 46.80, 58.16^\circ$. The peak at $2\theta = 32.61^\circ$ is sharp and prominent, suggesting formation of POTD-Lanthanum oxide polymer composite, but remaining peaks are broad, this indicates semi crystalline nature of Polyaniline-lanthanum oxide composite and also confirm the interaction of lanthanum oxide with polymer chain of POTD. The average particle size in POTD-La composite was found to be 23.0603 nm. The XRD spectrum of POTD-Ce (Fig. 3 (b)) shows very broad peaks at $2\theta = 9, 19, 24^\circ$, it confirms the amorphous nature of polymer composite POTD-Ce. The average particle size in POTD-Ce composite was found to be 11.3528 nm. The broad peaks at $2\theta = 10, 17, 24^\circ$ are observed in the XRD spectrum of POTD-Nd chloride composite (Fig.3 (c)). These peaks indicate the amorphous nature of this polymer composite. The average particle size in POTD-Nd composite was found to be 20.759 nm.

Table2

Polymer-composite	2θ degree	θ	radian	COSθ	β(FWHM)	β(FWHM) radian	D=Kλ/βCOSθ
POTD-La	11.7796	5.8898	0.1031	1.0000	0.2342	0.0041	33.9051
	22.8531	11.4266	0.2000	1.0000	0.4015	0.0070	19.7774
	32.6157	16.3079	0.2854	1.0000	0.2007	0.0035	39.5649
	46.8078	23.4039	0.4096	1.0000	0.8029	0.0141	9.8901
	58.1690	29.0845	0.5090	1.0000	0.6528	0.0114	12.1643
POTD-Ce	10.0432	5.0216	0.0879	0.9961	0.3642	0.0064	21.8305
	15.1306	7.5653	0.1324	0.9912	0.5015	0.0088	15.9320
	24.6094	12.3047	0.2153	0.9769	0.3307	0.0058	24.5154
POTD-Nd	10.0432	5.0216	0.0879	0.3043	0.3642	0.0064	71.4617
	15.1306	7.5653	0.1324	0.2847	0.5015	0.0088	55.4733
	24.6094	12.3047	0.2153	0.9660	0.3307	0.0058	24.7932

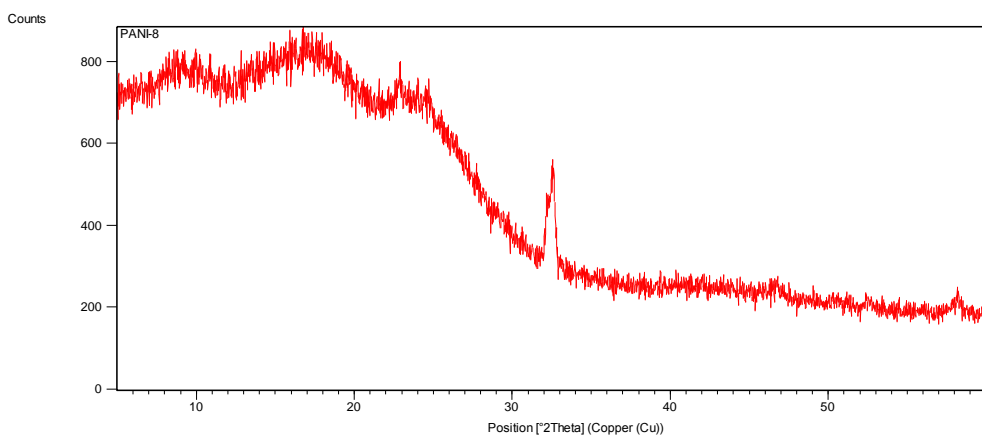


Fig3 (a). XRD spectrum of Poly *o*-toludine-Lanthanum composite.

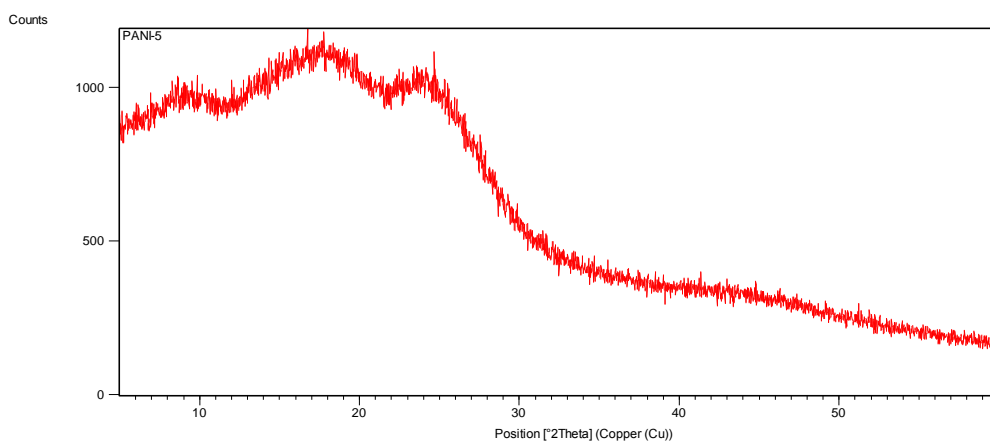


Fig3 (b). XRD spectrum of Poly *o*-toludine-Cerium composite.

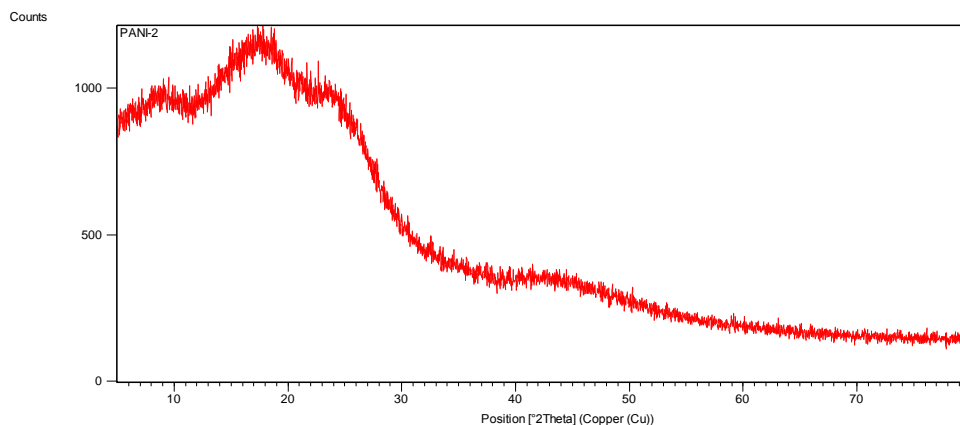


Fig3 (c). XRD spectrum of poly *o*-toludine-neodymium composite.

4.4. Scanning Electron Microscopy

Fig. 4 (a) to (d) showed the scanning electron micrographs of Poly o-toludine, Poly o-toludine-Cerric nitrate, Poly o-toludine-Lanthanum oxide and Poly o-toludine-Neodymium chloride. SEM images indicate the presence of metal particles in the Poly o-toludine matrix. These figures indicate that, the surface of these polymer composites was rough and exhibit more or less spherical morphology. SEM images showed that the distribution of metal particles is not uniform.

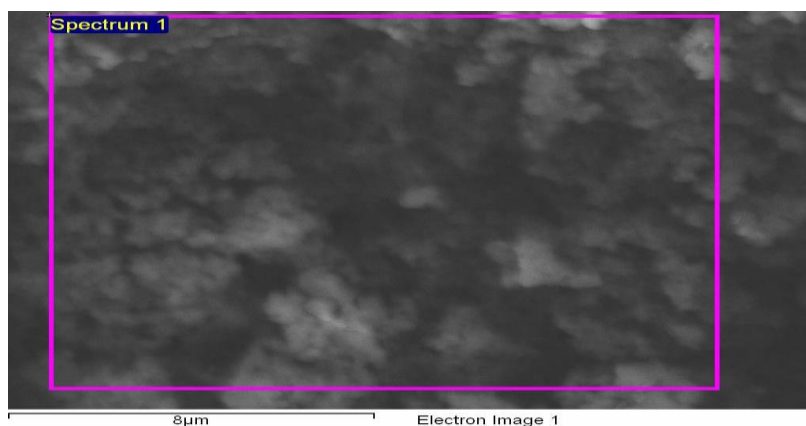


Fig4 (a). SEM micrograph of poly o-toludine

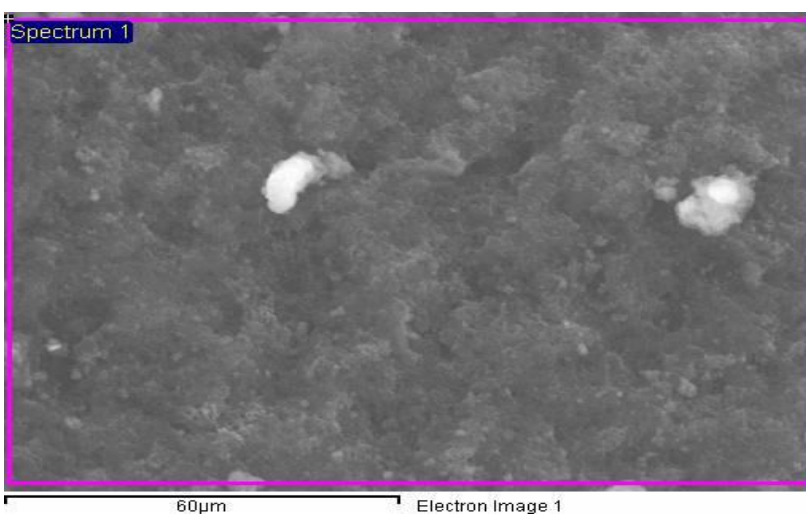


Fig4 (b). SEM micrograph of Poly o-toludine-Ce composite

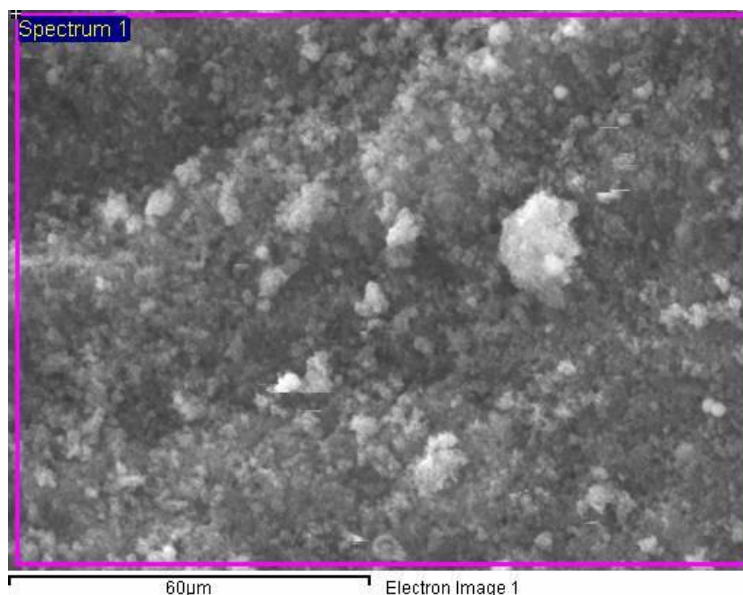
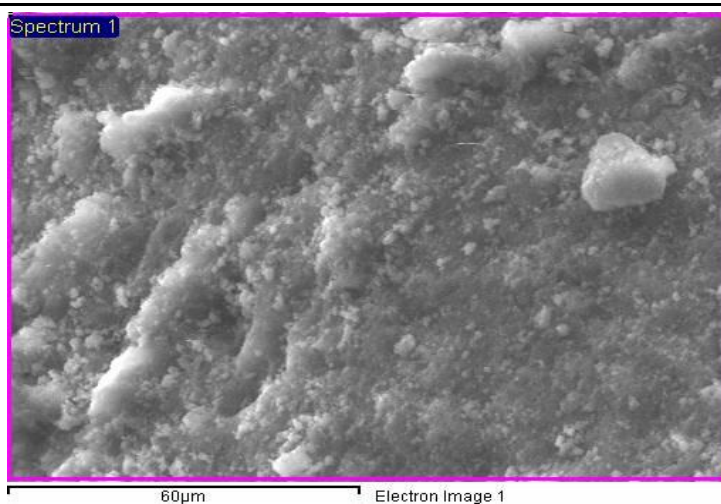


Fig (c). SEM micrograph of poly o-toludine-La composite



Fig(d). SEM micrograph of poly o-toludine-Nd composite

4.5. Transmission Electron Microscopy

Fig. 5 (a) to (d) shows TEM images of poly o-toludine, POTD-La, POTD-Ce, POTD-Nd. TEM images indicate the amorphous nature of polymers and metal particles are deposited on the surface of POTD polymer. Dark spots indicate the metal particles and gray portion indicate the POTD polymer. Hence it is clear that metal-salt particles are attached to polymer chain but the distribution of metal particles is not uniform. The particles are nearly spherical and the particle size is about 11-25 nm. Hence the molecules of metal-salt form the weak bonds with polymer chain in POTD composites.

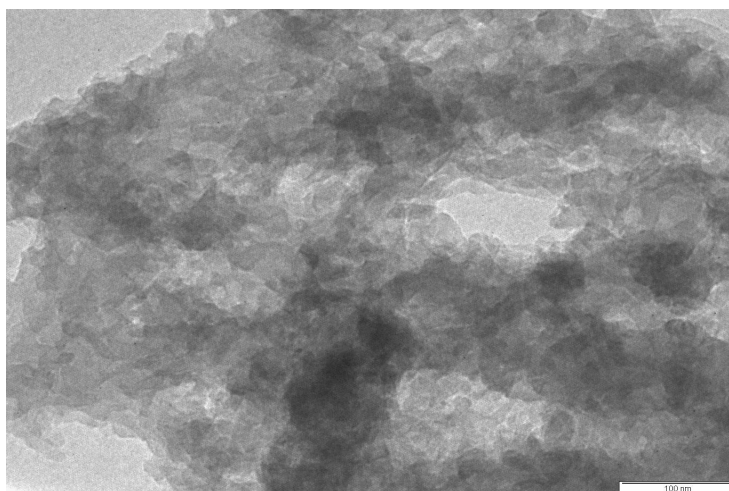


Fig5 (a). TEM image: POTD

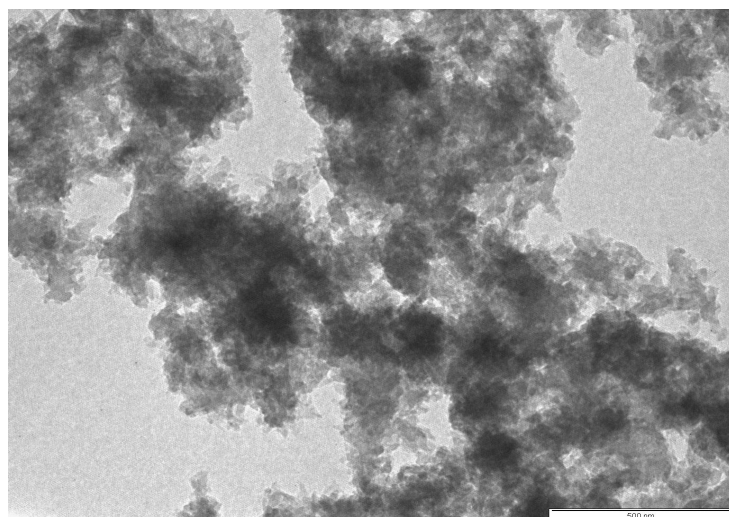


Fig5 (b). TEM image: POTD-La composite

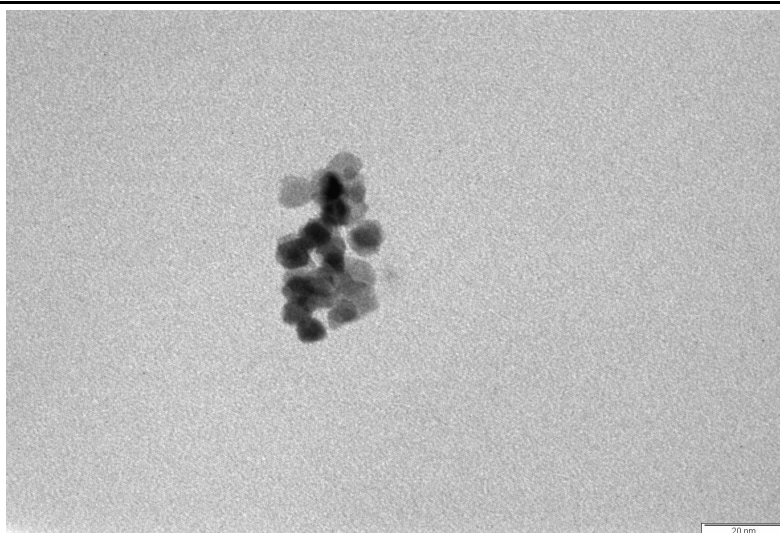


Fig5 (c). TEM image: POTD-Ce composite

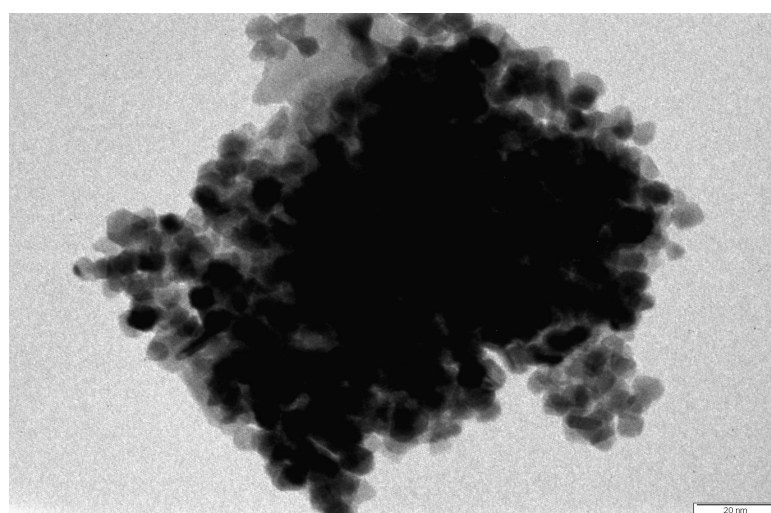


Fig5 (d). TEM image: POTD-Nd composite

4.6. TGA

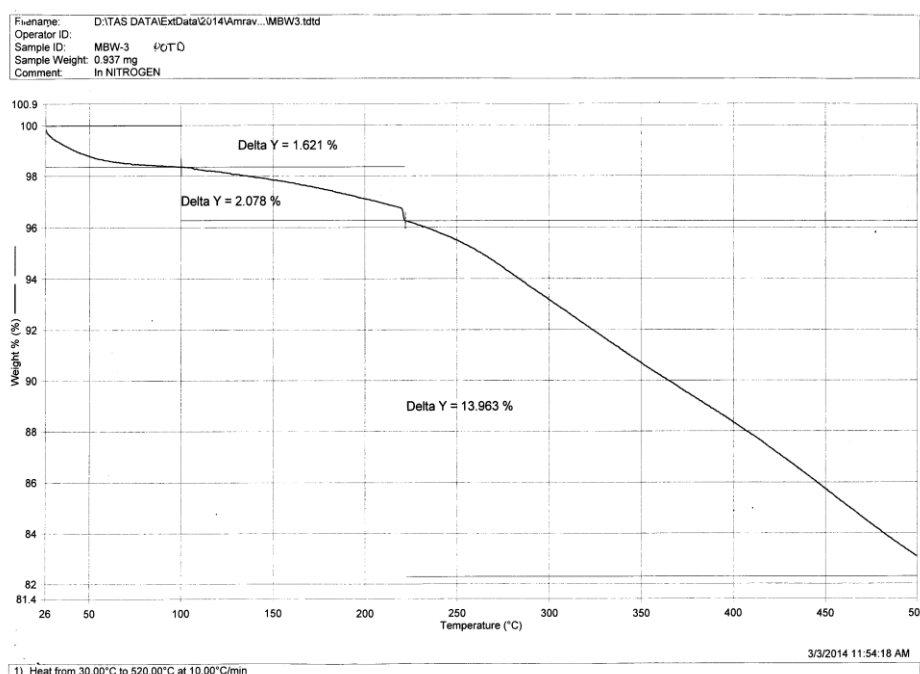


Fig6 (a). TGA curve of POTD

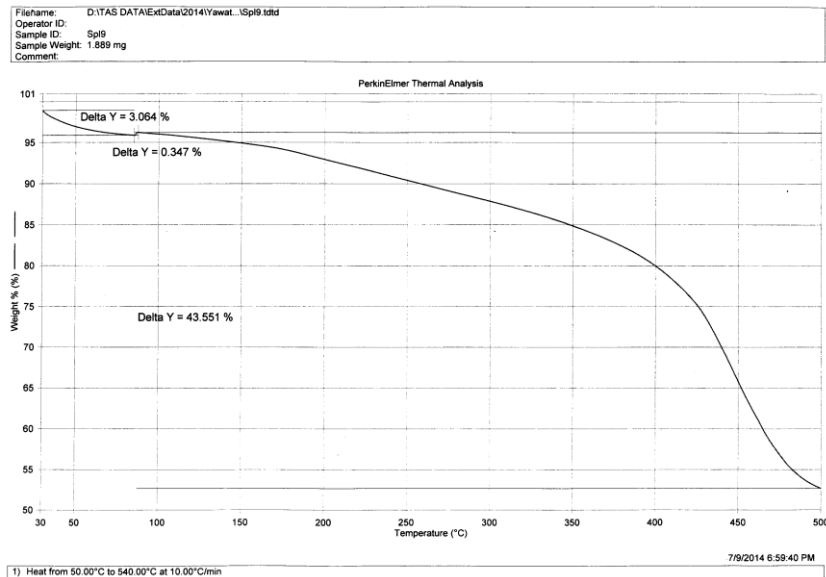


Fig6 (b). TGA curve of POTD-La composite

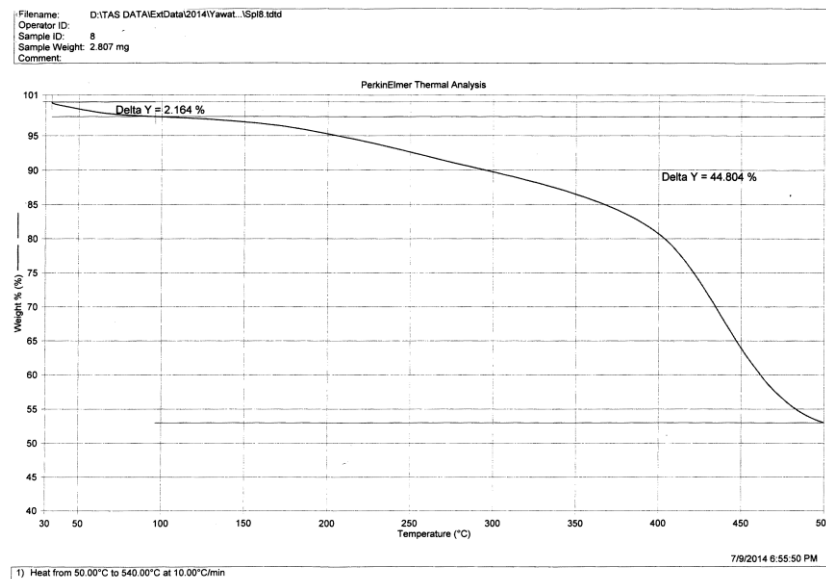


Fig6 (c). TGA curve of POTD-Ce composite

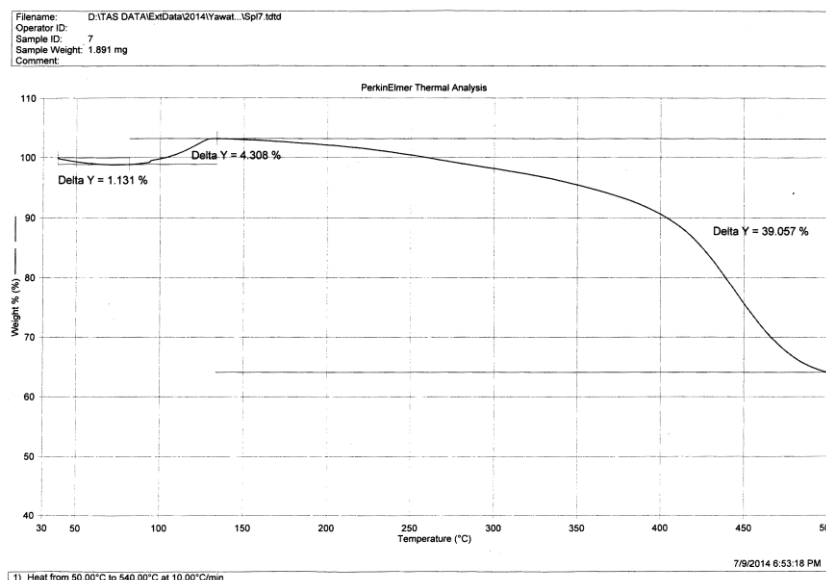


Fig6 (d). TGA curve of POTD-Nd composite

Fig. 6 (a) to (d) shows the TGA curve of Poly o-toludine, Poly o-toludine-Neodymium chloride composite, Poly o-toludine-Cerium nitrate composite and Poly o-toludine-Lanthanum oxide composite.

TGA curve of Poly o-toludine-Neodymium composite shows weight loss in three steps. From 50-140°C only 2.03% weight loss is observed, it may be due to loss of water molecules and oligomers having small molecular weight. In the second step 10% weight loss is observed in temperature range 200-400°C which can be assigned to co-evolution of water molecules. 30% weight is lost in temperature range 400-500°C, it can be assigned to POTD-Nd composite backbone degradation.

4.7. Conductivity

The conductivity measurements were carried out by Four-probe method to determine the influence of dopant metals on polymer electronic properties. The synthesized POTD composites with lanthanide metals - La, Ce, Nd 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 POTD-metal composite is found to be greater than pure metal. The variation in the conductivity of polymer-metal composite depends on the polymer content and sample morphology.²³ The age factor directly affects the conjugation and chain length of PANI.²⁴

It is observed from the Fig. 7 (a) to (d), plots of $1000/T$ vs $\log \rho$ in all polymers and their composites are 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 metal particles into polymer matrix significantly affect the conductivity of polymer.

Table3. Conductivity values of POTD-metal composites

Polymer	Conductivity (S/cm)
Poly o-toludine	0.004538
Poly o-toludine-La	0.0870
Poly o-toludine-Ce	0.3724
Poly o-toludine-Nd	0.06871

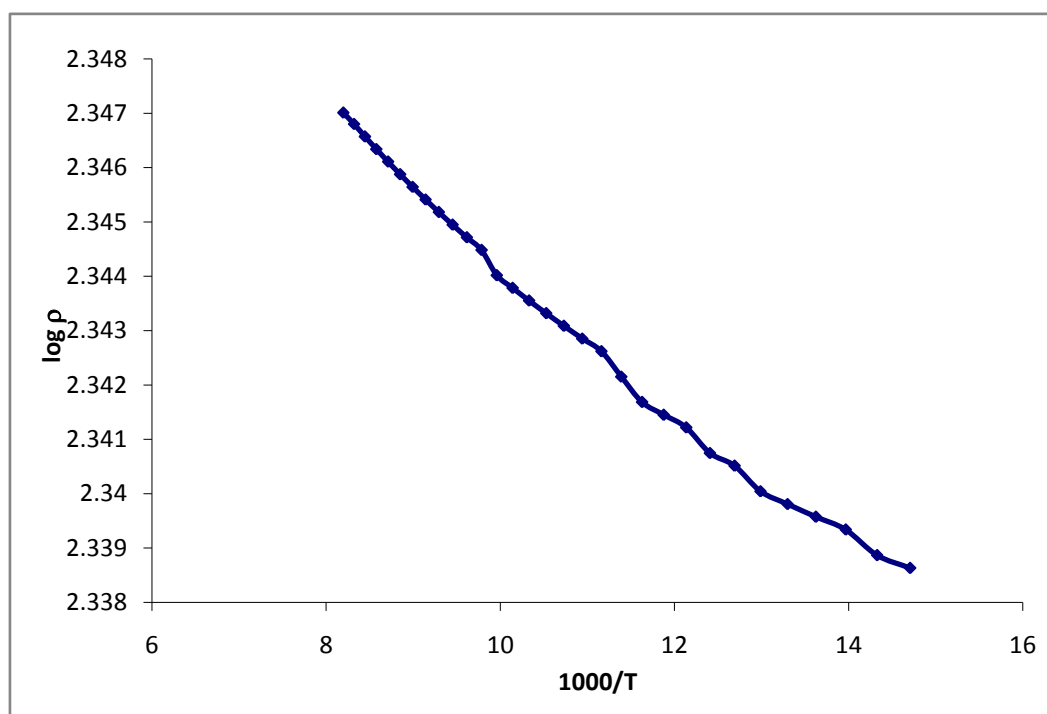


Fig7 (a). Plot of resistivity $\log \rho$ vs. $1000/T$ for poly o-toludine

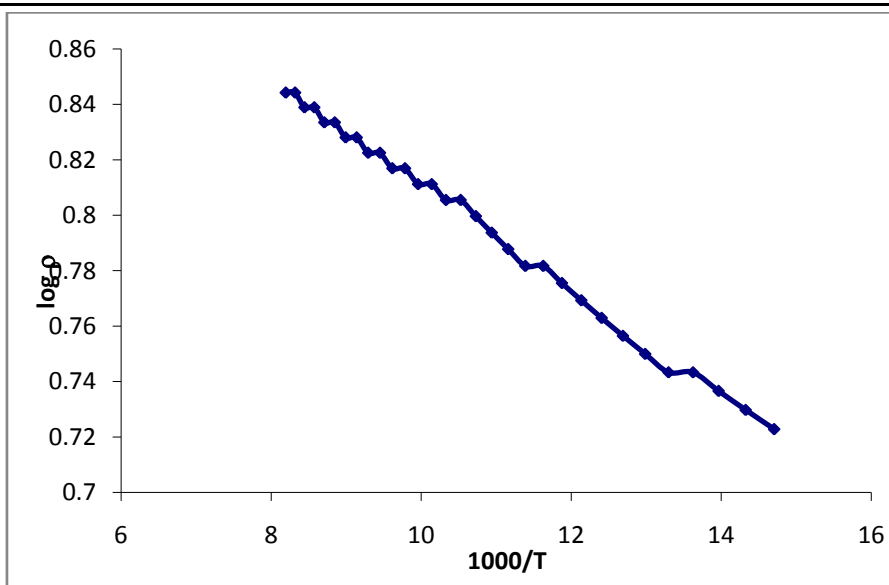


Fig7 (b). Plot of resistivity $\log \rho$ vs. $1000/T$ for poly o-toludine-La composite

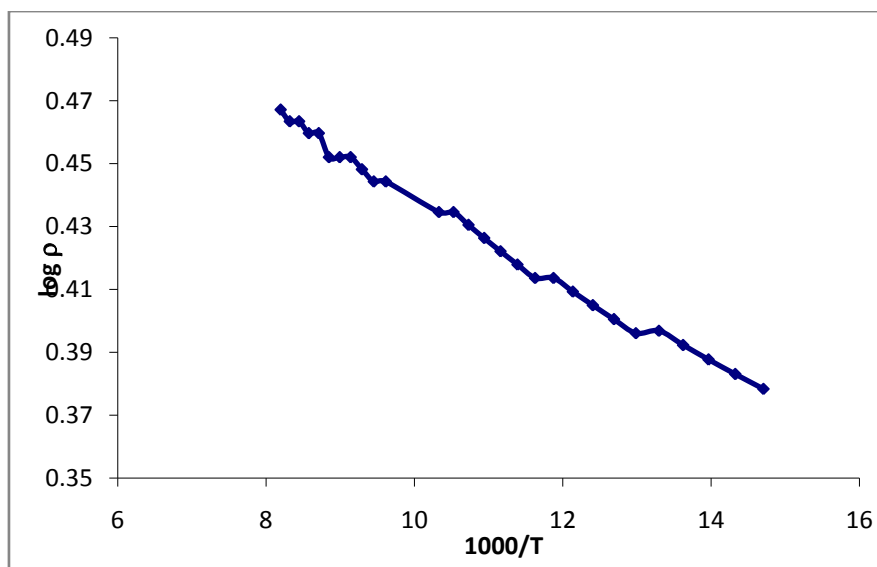


Fig7 (c). Plot of resistivity $\log \rho$ vs. $1000/T$ for poly o-toludine-Ce composite

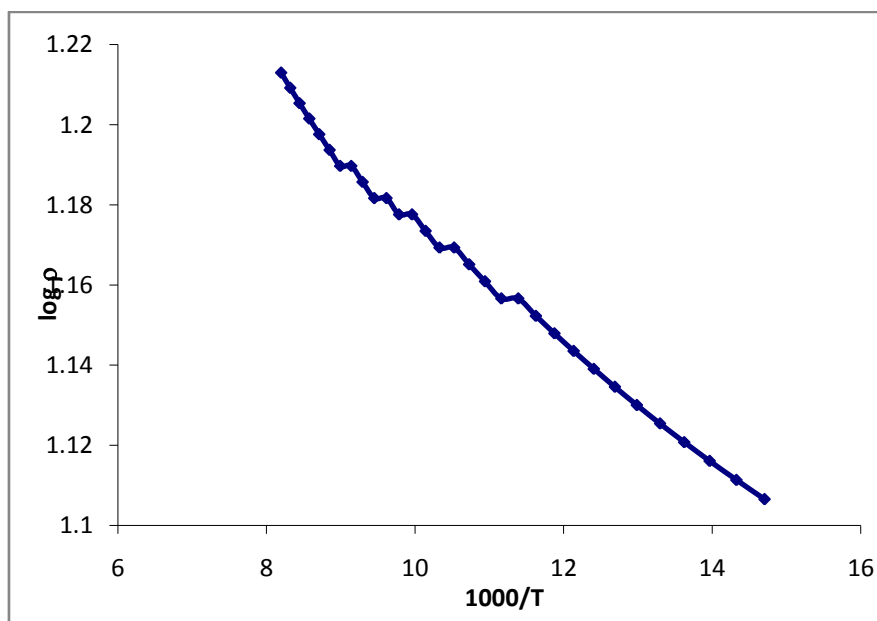


Fig7 (d). Plot of resistivity $\log \rho$ vs. $1000/T$ for Poly o-toludine-Nd composite

5. CONCLUSION

Poly o-toludene- lanthanide metal composites- POTD-La, POTD-Ce, POTD were synthesized successfully by chemical oxidation polymerization method. The interaction between lanthanide metals and POTD polymer backbone was confirmed by FTIR. The blue shift observed in the UV spectra of POTD-metal composites as compared to parent polymer confirmed the interaction of dopant metals on the poly o- toludine chain. The TGA results indicated the higher stability of POTD-metal composites than the parent polymer. Scanning electron micrographs showed that there were significant microstructural differences between poly o-toludine and POTD-La, POTD-Ce, POTD-Nd composites. TEM images assigned the amorphous nature of polymer composites. The XRD patterns of POTD- metal composites showed that the metal composites have highly ordered structure and more crystallinity. The Four probe conductivity measurements indicated that the poly o-toludine metal composites possess higher conductivity than POTD.

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