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Research Article

**COMPARATIVE STUDY OF STRUCTURAL AND MORPHOLOGY OF UNDOPED AND TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> AND Mn DOPED POLYTHIOPHENE THIN FILMS.**

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**Abstract:**

*Undoped polythiophene and with dopant TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and Mn thin film synthesized with on glass slide surface using FeCl<sub>3</sub> as an oxidant at room temperature by chemical bath deposition technique. Effect of dopant TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and Mn on properties of polythiophene thin film was then studied. The synthesized polythiophene were characterised by electrochemical techniques. Fourier transform infrared spectroscopy (FTIR), SEM analysis and XRD analysis. Chemical composition of polythiophene film was investigated by FTIR spectroscopy. Surface morphology was influence by dopant, SEM analysis of PTh/TiO<sub>2</sub> image seems to be uniform microporous on the surface and the particles were in nanometer scale. PTh/ V<sub>2</sub>O<sub>5</sub> shows agglomerated nanoparticles of different shape and PTh/Mn shows nanoparticles agglomerated with micropores in between, the size of the agglomeration is found to be increased. In a tube like structure formed by the nanoparticles and seems like random network of interconnected bundles. XRD analysis showed modification from fully amorphous to well developed crystalline structure after doping with TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> and Mn shows little modification.*

**Keywords:** Polythiophene, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Mn chemical bath deposition, Morphology.

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**INTRODUCTION:**

Polymer nanoparticles have received attention due to their diverse nanometer size particles and a series of special performance, polymer nanoparticle composites may possess the unique property superior to that of either the polymer or nanoparticles. In polymer science, owing to interesting chemical and physical properties, conducting polymers have been studied extensively during the last two decades as an important semiconductor material [1-3]. Metal containing polymer composites have attracted the attention of scientific community over a last few decades. Insertion of metal ions into polymer backbone may improve the mechanic, electronic and magnetic properties of polymer [4]. Among the conducting polymers, polythiophene (PTh) and its derivatives have attracted much consideration because of their easy preparation, environmental stability, higher conductivity and photoconduction [5,6]. Stability of polythiophene in air comes from its lower oxidation potential thus polythiophene thin films have been studied by many workers, because of their special electrical properties, considerable thermal stability and oxidation resistance. It has also shown that composite material always has advantages over homogeneous material. Few researchers reported doping of derivatives of polythiophene by  $\text{FeCl}_3$  [7,8] and fabrication of devices using  $\text{FeCl}_3$  doped derivatives of polythiophene [9,10]. An optical and electronics properties of polythiophene are useful for various device applications such as LED, field effect transistors, optical waveguides [11] in optoelectronic devices [12], photovoltaic and photoconductive devices and optical modulator devices [13]. Polythiophenes have also been exploited in sensor applications [14].

**EXPERIMENTAL:****Materials and Methodology**

**Chemicals:** Thiophene (AR grade Merck), Iron chloride (Sd-Fine), Methanol ( $\text{CH}_3\text{OH}$ ),  $\text{TiO}_2$ , Mn,  $\text{V}_2\text{O}_5$  and chloroform are used for the synthesis.

**FTIR:** Bruker Germany spectrometer with a resolution of  $4\text{ cm}^{-1}$  in the range  $450\text{--}4000\text{ cm}^{-1}$  of SAIF IIT Mumbai.

**XRD:** Rikagu Mini Flex 300/600 instrument at Vidyabharti College, Amravati.

**SEM:** JSM-6380 Instrument VNIT College, Nagpur.

**METHODOLOGY:****1-Preparation of undoped polythiophene thin film**

For Synthesis of polythiophene thin film by chemical bath deposition method, primarily substrate were washed with deionized water, boiled in chromic acid and washed with detergent, rinsed in acetone before deposition of thin film. Thiophene is used as monomer for preparation of polythiophene thin films. Monomer solution was prepared by dissolving 0.1 M of thiophene in chloroform, oxidant solution was prepared in a glass beaker with 0.5 M concentration of  $\text{FeCl}_3$  in chloroform the ratio of monomer to oxidant was kept 1:5. Substrates were immersed in bath at room temperature at constant stirring. Monomer solution was added drop wise in an oxidant solution reaction being carried out at room temperature. During precipitation, heterogeneous reaction occurred and deposition of polythiophene took place on substrate. The substrates coated with polythiophene thin films were removed after a time interval of 1 h from the bath, washed with methanol followed by chloroform and acetone repeatedly to remove residual oxidant and unreacted monomers. Dried in air and preserved in an airtight container.

**2-Preparation of PTh / $\text{TiO}_2$ , PTh/  $\text{V}_2\text{O}_5$ , PTh/Mn thin film.**

The composites thin films were prepared by same procedure only 0.5% w/v  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ , Mn added in oxidant solution. The substrates coated with doped polythiophene thin films were removed after a time interval of 1 h from the bath, washed with methanol followed by chloroform and acetone repeatedly to remove residual oxidant and unreacted monomers. Dried in air and preserved in an airtight container.

**RESULTS AND DISCUSSION:****1. Fourier Transform Infrared (FTIR) investigation**

The IR studies of undoped polythiophene and 0.5% w/v  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ , Mn PTh composites synthesized in present research work are given in Figures- 1, 2, 3, 4.

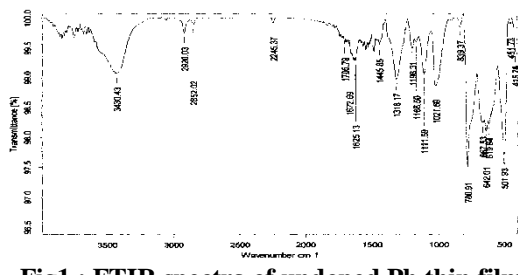


Fig 1 : FTIR spectra of undoped Ph thin film.

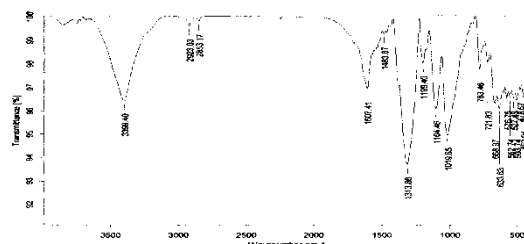
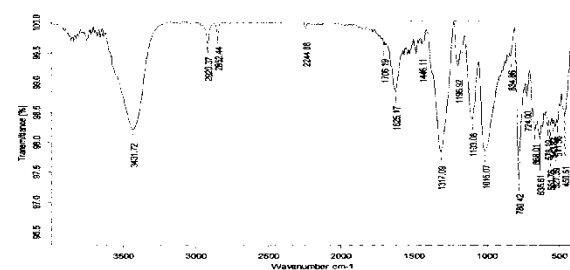
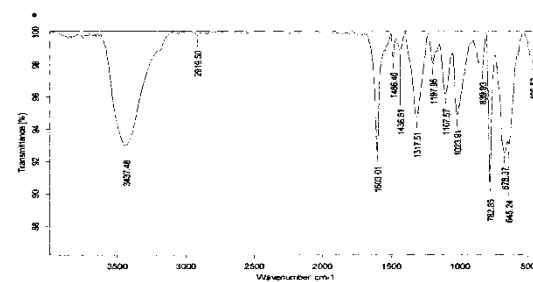
Fig2: FTIR spectra of PTh/0.5% w/v TiO<sub>2</sub> thin film.Fig 3: FTIR spectra of PTh/0.5% w/v V<sub>2</sub>O<sub>5</sub> thin film .

Fig 4: FTIR spectra of PTh /0.5% Mn film.

The absorption band in region  $2920.03 \text{ cm}^{-1}$  is due to aromatic C=C-H stretching frequency of undoped polythiophene which is shifted to the ranges  $2923.03 \text{ cm}^{-1}$ ,  $2920.37 \text{ cm}^{-1}$  and  $2919.50 \text{ cm}^{-1}$  in PTh/TiO<sub>2</sub> composite, PTh/ V<sub>2</sub>O<sub>5</sub> composite and PTh/Mn. The absorption band in region  $1625.13 \text{ cm}^{-1}$  is due to aromatic C=C stretching frequency of undoped polythiophene which is shifted to ranges  $1607.41 \text{ cm}^{-1}$ , for TiO<sub>2</sub> doped and  $1625.17 \text{ cm}^{-1}$  for V<sub>2</sub>O<sub>5</sub>,  $1603.01 \text{ cm}^{-1}$  for Mn doped PTh and Peak at  $1313.17 \text{ cm}^{-1}$  for Polythiophene is assign for C-C stretching frequency are shifted to  $1313.86 \text{ cm}^{-1}$  in TiO<sub>2</sub> and  $1317.90 \text{ cm}^{-1}$  for V<sub>2</sub>O<sub>5</sub> doped thin film and  $1317.51 \text{ cm}^{-1}$  for Mn doped film. The absorption band in the region  $780.91 \text{ cm}^{-1}$  is due to the C-S stretching frequency of undoped polythiophene which is shifted to the ranges  $783.46 \text{ cm}^{-1}$  in PTh/TiO<sub>2</sub> composites. The absorption peak at lower frequency  $721.83 \text{ cm}^{-1}$  assigned for Ti-O stretching and  $552.74 \text{ cm}^{-1}$  for Ti-O bending of PTh thin film. TiO<sub>2</sub> composite. In case of V<sub>2</sub>O<sub>5</sub> doped polythiophene V-

O-V stretching vibration observe at  $578.19 \text{ cm}^{-1}$ ,  $579.58 \text{ cm}^{-1}$ . In PTh/Mn composite the absorption peak at lower frequency  $466.53$  observed for coordination of Mn with Sulphur which is absent in undoped polythiophene. film.

## 2. XRD analysis

A typical XRD pattern obtained for undoped polythiophene and TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Mn doped Polythiophene composite are shown in Figure 5, 6, 7, 8. In case of undoped polythiophene no sharp peak observed, this indicates the polymer under investigation is nanocrystalline in nature. XRD analysis 0.5% w TiO<sub>2</sub> doped polythiophene shows 5 peaks at  $2\theta$   $25.507, 38.00, 48.199, 55.36, 69.01$ . In XRD analysis of 0.5% w V<sub>2</sub>O<sub>5</sub> doped polythiophene shows one peak at  $2\theta = 26.27$ . In Mn composite only one intense peak observed at  $2\theta = 35.07$  showing little change in crystallinity of the polythiophene after addition of Mn.

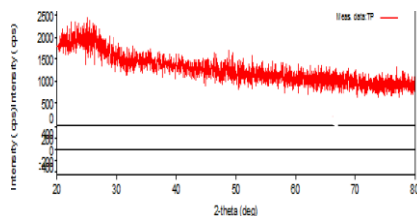
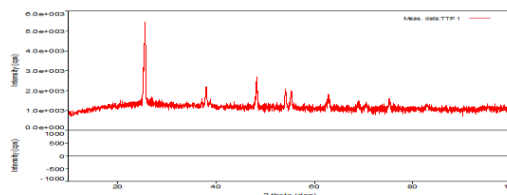


Fig-5: XRD of undoped polythiophene.

Fig-6: XRD of 0.5% w/v TiO<sub>2</sub> doped polythiophene

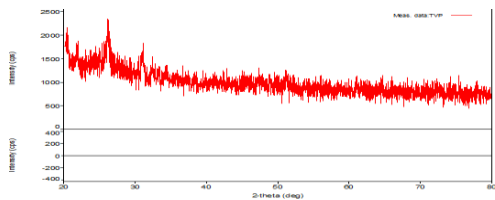
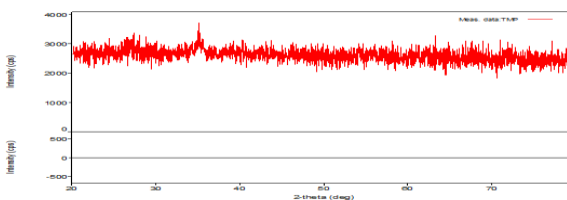
Fig-7: XRD patterns of 0.5% V<sub>2</sub>O<sub>5</sub>.

Fig 8 : XRD diffractogram of PTh/0.5%w Mn composites.

### 3.Scanning Electron Microscopy

The SEM images of undoped and TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Mn doped polythiophene composites thin film are shown in figures-9,10,11,12. TiO<sub>2</sub> doped image seems to be uniform microporous on the surface and the particles were in nanometer scale. Nanoparticles agglomerated grain structure observed. The grains are highly agglomerated shape but they are well interconnected each other. PTh/ V<sub>2</sub>O<sub>5</sub> The grains are highly

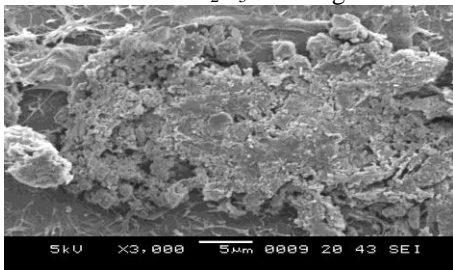


Fig 9 : SEM image of undoped PTh thin film.

agglomerated highly irregular shape some grains are irregular in structure some of them are elongated and some are spherical in shape. SEM photographs of Mn doped polythiophene thin films shows nanoparticles agglomerated with micropores in between .the size of the agglomeration is found to be increased. A tube like structure formed by the nanoparticles and seems like random network of interconnected bundles.

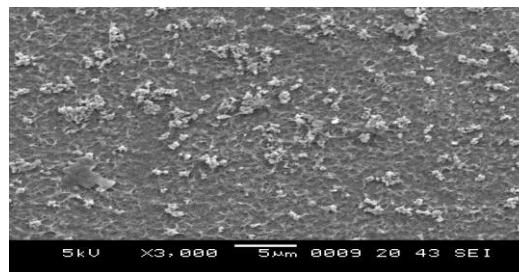
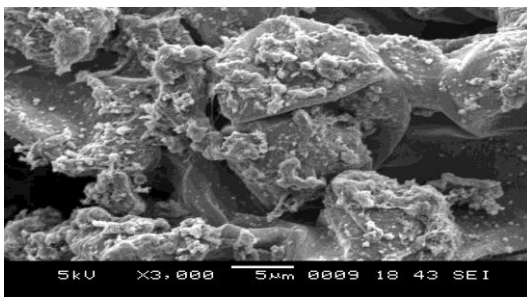
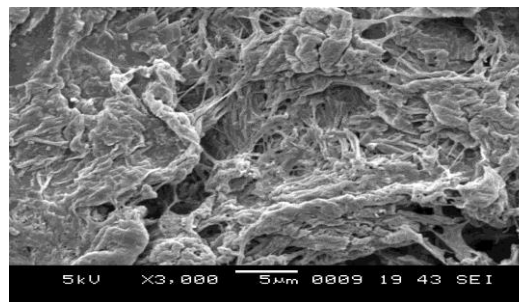
Fig 10 : SEM image of 0.5 % w/v TiO<sub>2</sub> thin film.Fig. 11: SEM image of 0.5%w/v V<sub>2</sub>O<sub>5</sub>

Fig- 12 : SEM of PTh with 0.5% Mn thin film.

### CONCLUSION:

Polythiophene thin films has been synthesised at room temperature by chemical bath deposition method. polythiophene can be doped by TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Mn in chloroform with formation of complex Polythiophene TiO<sub>2</sub> and Polythiophene V<sub>2</sub>O<sub>5</sub> and Polythiophene Mn composites thin films were prepared by in situ doping .The result of FTIR proved the formation of polythiophene and PTh/ TiO<sub>2</sub> and PTh/ V<sub>2</sub>O<sub>5</sub> Polythiophene Mn complex. The amorphous nature of PTh has been confirmed by XRD. XRD patterns of the composites exhibited peaks corresponding to TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> and shows

modification from amorphous to the well-developed crystalline structure after doping and Mn composite shows little change in structure . Morphology of thin film were analysed by SEM it shows change in morphology after doping.

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