

# A Comparative Study on Structural and Thermal Properties of undoped and $\text{TiO}_2$ and $\text{V}_2\text{O}_5$ doped Polythiophene thin film.

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## ABSTRACT

This study reported the doping of polythiophene thin film with dopant  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  with various concentration by in situ polymerisation through chemical bath deposition method. Effect of dopant  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  on properties of polythiophene thin film was then studied the synthesized polythiophene were characterised by electrochemical techniques. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and TGA-DTA analysis. Chemical composition of polythiophene film was investigated by FTIR spectroscopy. XRD analysis showed modification from fully amorphous to well developed crystalline structure after doping with  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$ . TGA-DTA results indicates composites of polythiophene with  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  are found to be most thermally stable than undoped polythiophene. PTh/ $\text{V}_2\text{O}_5$  observe to be more thermal stable than PTh/ $\text{TiO}_2$  composite.

**Keywords:** Polythiophene,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ , chemical bath deposition, thermal stability.

## I. INTRODUCTION

In 2000 The Nobel Prize in Chemistry, was awarded to Alan J Heeger, Alan G MacDiarmid, and Hideki Shirakawa[1-3]. The citation for the award is “for the discovery and development of electrically conductive polymers” Conducting polymers (CPs) are organic conjugated polymers which generally are comprised simply of C, H and simple heteroatoms such as N and S, where electrical properties are created by delocalizing the electrons of p-bond on conjugated chains of polymer [4]. p-conjugated polymers such as polypyrrole (PPy), polyaniline (PANI) and polythiophenes (PTH) have been reported as conducting polymers (CPs)[5]. There have been quite a few experimental and theoretical studies on polythiophenes (PThs), which are one of the most important members of electrically conductive polymers. Dopant plays an important role in conjugated polymers because these polymers become conductive when charge carriers, generated by dopants are present in their structure [6]. There are lots of conjugated polymers and one of the most widely studied conjugated polymers is polythiophene, which becomes highly conductive upon doping[7]. 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 [8].

In polyheterocyclic particular polythiophene is one of the extensively studied electronic materials, because it exhibits relatively high electrical conductivity, good environmental stability, low toxicity and versatility of

synthesis and ease of tailoring to synthesize functionalized polythiophene. The properties of polythiophene are very sensitive to fabrication conditions and to the type of preparation technique used. Therefore, study of the properties of these conducting polymers with respect to different growing as well as ambient conditions is of high importance. 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. Study of polythiophene has intensified over last three decades. Few researchers reported doping of derivatives of polythiophene by  $\text{FeCl}_3$ [9,10]. and fabrication of devices using  $\text{FeCl}_3$  doped derivatives of polythiophene.[11,12] An optical and electronics properties of polythiophene are useful for various device applications such as LED, field effect transistors, optical waveguides<sub>[13]</sub>, in optoelectronic devices [14], photovoltaic and photoconductive devices and optical modulator devices [15]. Polythiophenes have also been exploited in sensor applications[16]. There are several routes for synthesis of polythiophene thin films the chemical bath deposition method for polythiophene thin films is important, chemical bath deposition (CBD) method appears most suitable for integration in large scale fabrication process. In present research work we used  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  as a dopant. Present work covers the chemical synthesis of conducting polythiophene and different %w/v of  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  doped thin film and comparative study of their structural and thermal properties. Structural investigation and characterization with their properties were determined by using FTIR analysis, XRD, TGA-DTA techniques.

## II. EXPERIMENTAL

### Materials and Methodology

**Chemicals:** Thiophene (AR grade Merck), Iron chloride (Sd-Fine), Methanol ( $\text{CH}_3\text{OH}$ ),  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  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:** Rigaku Mini Flex 300/600 instrument at Vidyabharti College, Amravati.

**TGA-DTA:** Rigaku thermos plus EV02 instrument at GVISH College, Amravati

## III. METHODOLOGY

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. 0.5% w/v and 1% w/v  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  added in oxidant solution. 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.

IV.RESULTS AND DISCUSSION

4.1 By Fourier Transform Infrared (FTIR) investigation

The IR studies of undoped polythiophene and polythiophene TiO<sub>2</sub>,V<sub>2</sub>O<sub>5</sub>composites synthesized in present research work are given in Fig-1,2,3,4 and 5 and the related absorbance are given in Table-1 determined by The FTIR spectra for pure polythiophene and TiO<sub>2</sub> complexes are shown below,

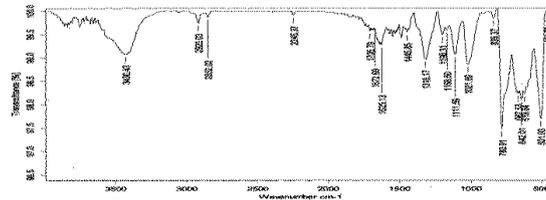


Fig.-1: FTIR of polythiophene without dopant

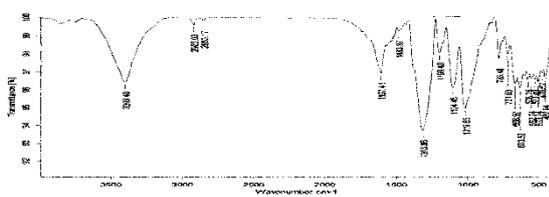


Fig.-2: FTIR of polythiophene with dopant TiO<sub>2</sub> (0.5 % w/v) in PTh thin film.

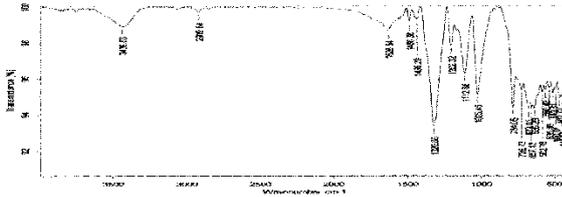


Fig.-3 : FTIR of polythiophene with dopant TiO<sub>2</sub> (1 % w/v) in PTh thin film.

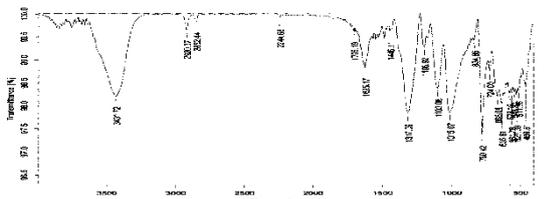


Fig.-4: FTIR of polythiophene with dopant V<sub>2</sub>O<sub>5</sub> (0.5 % w/v) in PTh thin film.

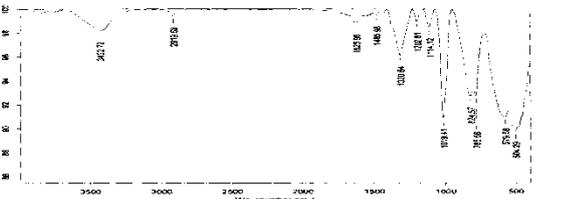


Fig.-5 : FTIR of polythiophene with dopant V<sub>2</sub>O<sub>5</sub> (1 % w/v) in PTh thin film.

Table -1

Material	Frequency In cm <sup>-1</sup>				Stretching	Bending
	ArC=C-H	Ar C=C	C-C	C-S		
Pure PTh	2920.03	1625.13	1318.17	780.91	-	-
PTh+0.5w% TiO <sub>2</sub>	2923.03	1607.41	1313.86	783.46	721.83	552.74
PTh+1w% TiO <sub>2</sub>	2919.64	1626.54	1320.60	784.05	726.73	560.42
					<b>V-O-V</b>	
PTh+0.5w% V <sub>2</sub> O <sub>5</sub>	2920.37	1625.17	1317.90	780.42	578.19	
PTh+1w% V <sub>2</sub> O <sub>5</sub>	2919.58	1625.96	1320.84	785.58	579.58	

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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  $2923.03 \text{ cm}^{-1}$  and  $2919.64 \text{ cm}^{-1}$  in Polythiophene/TiO<sub>2</sub> composite and  $2920.37 \text{ cm}^{-1}$ ,  $2919.58 \text{ cm}^{-1}$  for Polythiophene/ V<sub>2</sub>O<sub>5</sub> composite. 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  $1607.41 \text{ cm}^{-1}$ ,  $1626.24 \text{ cm}^{-1}$  for TiO<sub>2</sub> doped and  $1625.17 \text{ cm}^{-1}$  and  $1625.96 \text{ cm}^{-1}$  for V<sub>2</sub>O<sub>5</sub>. Peak at  $1313.17 \text{ cm}^{-1}$  for Polythiophene is assigned for C-C stretching frequency are shifted to  $1313.86 \text{ cm}^{-1}$ ,  $1320.60 \text{ cm}^{-1}$  in TiO<sub>2</sub> and  $1317.90 \text{ cm}^{-1}$ ,  $1320.84 \text{ cm}^{-1}$  for V<sub>2</sub>O<sub>5</sub> doped polythiophene thin 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  $783.46 \text{ cm}^{-1}$ ,  $784.04 \text{ cm}^{-1}$  in polythiophene/TiO<sub>2</sub> composites. The absorption peak at lower frequency  $721.83 \text{ cm}^{-1}$ ,  $784.05 \text{ cm}^{-1}$  assigned for Ti-O stretching and  $552.74 \text{ cm}^{-1}$  and  $580.42 \text{ cm}^{-1}$  for Ti-O bending of Polythiophene+0.5% w/v and Polythiophene+1% w/v TiO<sub>2</sub> composite. In case of V<sub>2</sub>O<sub>5</sub> doped polythiophene V-O-V stretching vibration observed at  $578.19 \text{ cm}^{-1}$ ,  $579.58 \text{ cm}^{-1}$ .

#### 4.2 XRD Studies

A typical XRD pattern obtained for undoped polythiophene and TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> doped Polythiophene composite are shown in Figure 6, 7, 8, 9 and 10. In case of undoped polythiophene no sharp peak observed, this indicates the polymer under investigation is nanocrystalline in nature. XRD analysis of 0.5% w/v TiO<sub>2</sub> doped polythiophene shows 5 peaks at  $2\theta$   $25.507, 38.00, 48.199, 55.36, 69.01$  while that of 1% w/v of TiO<sub>2</sub> shows 12 intense peaks which were absent in pure polythiophene. This shows modification of fully amorphous polythiophene to well developed crystalline structure.

In XRD analysis of 0.5% w/v V<sub>2</sub>O<sub>5</sub> doped polythiophene shows one peak at  $2\theta = 26.27$  and 1% w/v V<sub>2</sub>O<sub>5</sub> doped polythiophene shows peaks at  $2\theta = 20.523, 22.01, 26.404, 31.272, 32.63, 33.56, 34.608, 45.64$ , which does not found in pure polythiophene suggesting the increase in degree of crystallinity of the complex.

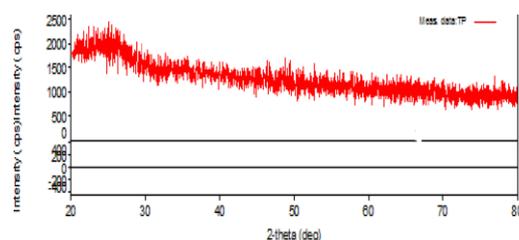
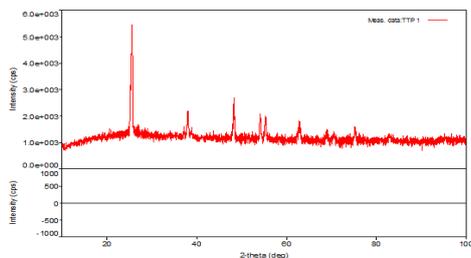


Fig.-6: XRD of undoped polythiophene.



0.5% w/v TiO<sub>2</sub> doped polythiophene.

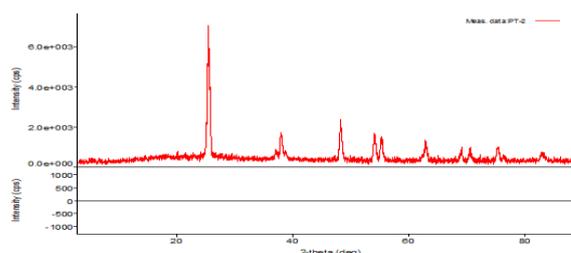
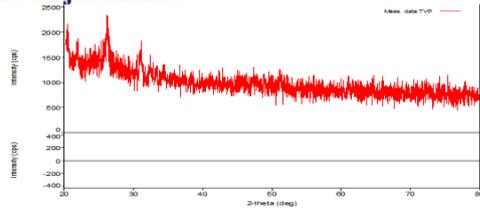
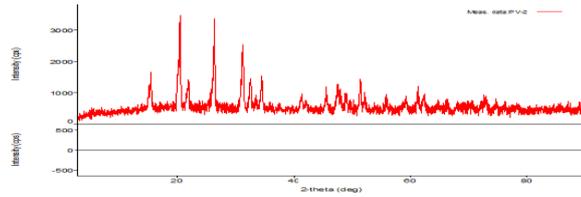


Fig-8: XRD of 1% w/v TiO<sub>2</sub> doped polythiophene.

Fig-7: XRD of



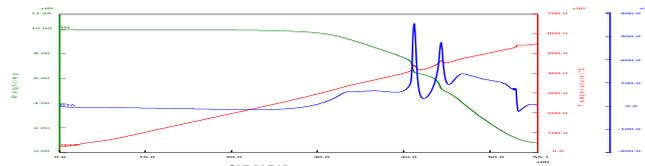
**Fig-9: XRD patterns of polythiophene 0.5% w/v V<sub>2</sub>O<sub>5</sub> doped composite.**



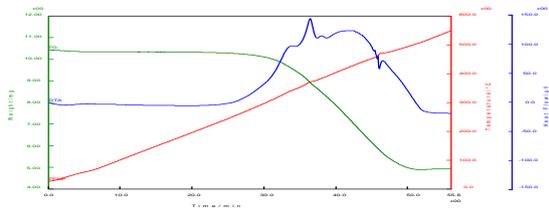
**Fig-10 : XRD patterns of Polythiophene 1% w/v V<sub>2</sub>O<sub>5</sub> doped composite.**

### 4.3 TG-DTA analysis

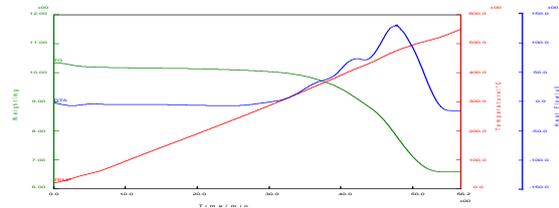
Thermogravimetric and differential thermal analysis of Polythiophene and different %w/v of TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> composite was carried out in air atmosphere .TGA was performed on Rigaku TG8121 thermal analyser with pt. pan in the temperature range from room tempreture to 550°C.The thermogram of polythiophene and composite as shown in fig-11,12,13,14,and 15. Three major weight losses are observed one around 70-80<sup>0</sup>weight loss is about 1-3% due to elimination of moisture,evopouration of solvent as well as unreacted monomer .second weight loss around 280-300<sup>0</sup> is due to loss of dopant component of polythiophene. Third major drop in weight observed at 350-400<sup>0</sup> and beyond the range is due to degradation of polythiophene itself. In case of DTA shows two exothermic maxima at near about 400<sup>0</sup>and 450°C.weight loss in each step is enclosed in Table 2,Table -3.



**Fig.-11: TG-DTA thermogram of undoped polythiophene**

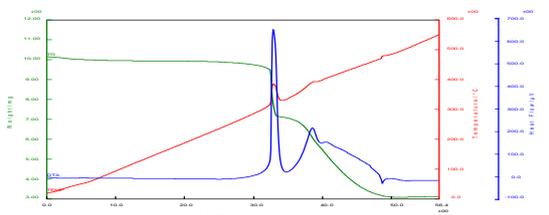


**ig-12: TG-DTA thermogram of 0.5% w/v TiO<sub>2</sub> doped polythiophene.**

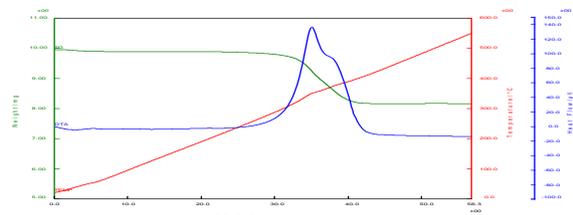


**Fig-13: TG-DTA thermogram of 1% w/v TiO<sub>2</sub> doped polythiophene.**

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**Fig-14 : TG-DTA of polythiophene 0.5%w/v V<sub>2</sub>O<sub>5</sub> doped.**



**Fig-15 : TG-DTA of polythiophene 1%w/v V<sub>2</sub>O<sub>5</sub> doped.**

**Table 2 : Weight Loss in each step for undoped and TiO<sub>2</sub> doped composite.**

S.N.	Polymer Composite	Weight Loss (%)				
		Step I 50-100 <sup>0</sup> C	Step II 300-350 <sup>0</sup> C	Step III 400-500 <sup>0</sup> C	Total wt loss (%)	Residue
1.	UndopedPTh	0.44	4.86	75.91	81.21	18.79
2.	PTh+0.5% w/v TiO <sub>2</sub>	0.51	3.34	66.26	70.71	29.89
3.	PTh+1% w/v TiO <sub>2</sub>	1.20	3.59	58.26	63.05	36.95

**Table 3 : Weight Loss in each step for undoped and V<sub>2</sub>O<sub>5</sub> doped composite.**

S.N.	Polymer Composite	Weight Loss (%)				
		Step I 50-100 <sup>0</sup> C	Step II 300-350 <sup>0</sup> C	Step III 400-500 <sup>0</sup> C	Total wt loss (%)	Residue
1.	UndopedPTh	0.44	4.86	75.91	81.21	18.79
2.	PTh + 0.5% w/v V <sub>2</sub> O <sub>5</sub>	0.83	6.67	39.76	47.26	52.74
3.	PTh + 1% w/v V <sub>2</sub> O <sub>5</sub>	0.52	3.18	31.99	35.69	64.31

## V. CONCLUSION

Polythiophene thin films has been synthesised at room temperture by chemical bath deposition method.polythiophene can be doped by TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> in chloroform with formation of complexPolythiopheneTiO<sub>2</sub> and PolythiopheneV2O5 composites thin films were prepared by in situ doping in different weight to volume percentages.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>complex. The amorphous nature of PTh has been confirmed by XRD. XRD patterns of the composites exhibited peaks corresponding toTiO<sub>2</sub> and V2O5and shows modification from amorphous to the well-developed crystalline structure after doping thermal properties of nanocomposites were investigated by .TG-DTA analysis shows composites of polythiophene are found to be more thermally stable than pure polythiophene.

## VI. ACKNOWLEDGEMENT

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