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Study of Undoped and V_2O_5 Doped Polythiophene thin Films by Chemical Bath Deposition Technique

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Abstract: *Polymeric thin films of polythiophene and with different %w/v V_2O_5 were fabricated by Chemical bath deposition method, Using Fecl3 as an oxidant and chloroform as a solvent. The effect of dopant on the properties of polythiophene thin film was studied. The complexation of the polymer was confirmed by Fourier transform infrared (FTIR) .The surface morphology was influenced by dopant.SEM images shows agglomerated nanoparticles of different shapes . XRD analysis of sample were confirmed noncrystalline for undoped PTh and crystal structure has been modified after doping by V_20_5.TGA-DTA result indicates composites of polythiophene V_2O_5 which are found to be more thermally stable than pure polythiophene.*

Keywords: *Polythiophene ,V_2O_5, chemical bath deposition.*

1. INTRODUCTION

The macromolecules that propagate charge along their structural format are conducting polymers. Conductive polymers characterised by controllable conductivity and have special electrical and optical properties comparable to those of metal and inorganic semiconductors**.** These polymers are of substantial interest due to their electronic properties and their potential technological application [1].Among the conducting polymers Polythiophene is one of the promising material Polythiophene, it is a heterocyclic polymer that has particular interest due to its properties that can be used in various applications, such as solar and photovoltaic cells [2, 3] biosensors, tissue engineering scaffolds [4], antistatic coatings. There are several routes for the synthesis of polythiophene like electrochemical and chemical method. Chemical oxidative polymerization gives higher yield and hence is a better route for the polymerization of polythiophene [5]. The synthesis conditions and the nature of the dopant anion play a vital role in the polymerization process as they strongly affect the various properties of the material [6].Polymer thin films are formed by incorporating a metal into highly polar polymer complexes. During the last few decades, the utilization of polymer light emitting diode in various applications has led to intensive interest in these materials [7-9].Among various other methods of film deposition, chemicalbath deposition (CBD) method appears most suitable for integration in large scale fabrication process. The main advantages of the CBD method are its low cost, no requirement of sophisticated instrument, low processing temperature and non-polluting properties [10].Not single reference related to doping of V_2O_5 as dopant for polythiophene thin film synthesis was not reported in literature hence in present research work we used V_2O_5 as a dopant. Present work covers the chemical synthesis of conducting polythiophene and different %w/v of V_2O_5 doped thin film. Structural investigation and characterization with their properties were determined by using FTIR analysis, scanning SEM, XRD, TGA-DTA techniques.

2. EXPERIMENTAL

2.1. Sample Preparation

Thiophene (AR grade Merck),Iron chloride FeCl3 (Sd-Fine),V_2O_5,chloroform (CH3Cl),methanol (CH3OH),acetone were used for the preparation of polythiophene thin films. Micro slides of glass with dimensions 2.5 cm× 7.5 cm were used as substrate. Initially, the substrate were washed with deionized water, boiled in chromic acid and washed with detergent, rinsed in acetone before deposition of thin film. Monomer solution was prepared by dissolving 0.1 M of thiophene in chloroform, the oxidant solution was prepared in a glass beaker with 0.5 M concentration of FeCl3 in

chloroform the ratio of monomer to oxidant was kept 1:5 .In case of PTh +V_20_5 composite material dissolved in chloroform and modified with different %w/v of V_20_5.The substrates were immersed in the bath at room temperature at constant stirring. The monomer solution was added drop wise in the oxidant solution there action being carried out at room temperature. During the precipitation, heterogeneous reaction occurred and the deposition of polythiophene took place on the substrate. The thickness of the polymer layer was controlled with help constant deposition time The substrates coated with polythiophene thin films were removed after a time interval of 1h from the bath, washed with chloroform followed by methanol and acetone repeatedly to remove residual oxidant and unreacted monomers, dried in air and preserved in an airtight container in the same way polythiophene doped with v205 thin film prepared by adding 0.5%w/v and 1% w/v V_2O_5.For structural investigation, samples are characterized using different techniques such as elemental analysis, FTIR analysis, Scanning electron microscopy,. XRD, Thermal analysis using TGA-DTA technique has also been carried out.

2.2. Analytical Techniques

In the present study

FTIR: Bruker germany spectrometer at SAIF IIT Mumbai.

XRD: Rikagu MiniFlex 300/600 instrument at Vidyabharti college, Amravati.

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

SEM: JSM-6380 Instrument VNIT College, Nagpur.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

Fourier Transform Infra-Red Spectroscopy of undoped Polythiophene and doped V_2O_5 thin films by using chemical bath deposition method. FTIR spectroscopy is an important investigation of polymer structure that provides information about the complexation and interactions between the various constituents in the polymeric films. Each type of bond has a different natural frequency of vibration, so the identification of an absorption peak in the vibration portion of the infrared region will give a specific type of bonding. The FTIR spectra for pure polythiophene and different %w/v of V_2O_5 doped thin films are shown in Figure 1,1(a)and 1(b).The absorption band in region 2920.03 cm^{-1} is due to aromatic C=C-H stretching frequency of pure polythiophene which is shifted to the ranges 2920.37 cm^{-1} and 2919.58 cm^{-1} in PTh/ V_2O_5composite.The absorption band in the region 1625.13 $cm^{-1}$is due to the aromatic C=C stretching frequency of Pure PTH which is shifted to the ranges 1625.17 cm^{-1}, 1625.96 cm^{-1}.The peak at 1318.17 $cm^{-1}$for Pth is assign for C-C stretching frequency are shifted to 1317.90 cm^{-1}, 1320.84 cm^{-1}.The absorption band in the region 780.91 $cm^{-1}$is due to the C-S stretching frequency of Pure PTH which is shifted to the ranges 780.42 cm^{-1}, 785.58 cm^{-1}.In PTh/ V_2O_5composite the absorption peak at lower frequency 578.19 and 579.58 cm^{-1} observed for V-O-V stretching which is absent in undoped polythiophene.

Table1. *Enclosed the observed vibrational frequencies*

Material	Frequency In cm^{-1}				Stretching
	Ar-C=C-H	Ar C=C	C-C	C-S	V-O-V
UndopedPTh	2920.03	1625.13	1318.17	780.91	
PTh+0.5w% V_2O_5	2920.37	1625.17	1317.90	780.42	578.19
PTh+1w% V_2O_5	2919.58	1625.96	1320.84	785.58	579.58

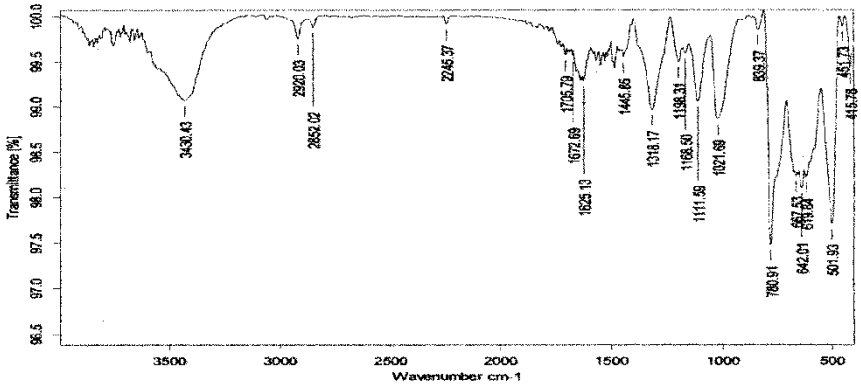

Figure1. *FTIR spectra of undoped polythiophene thin films*

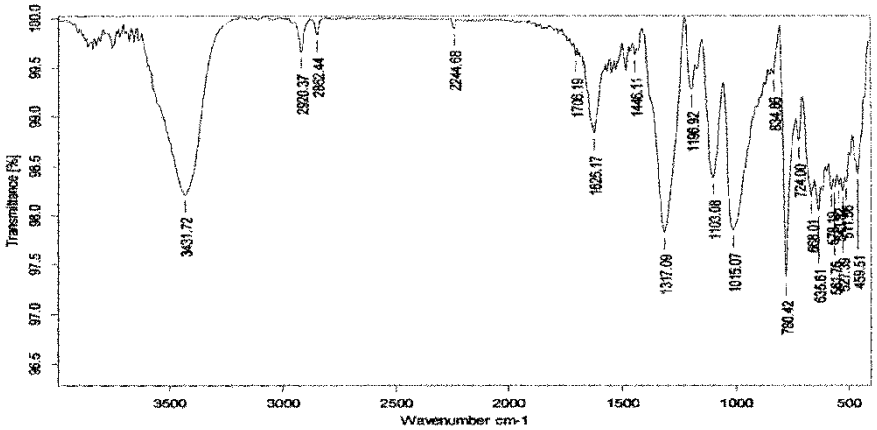

Figure1(a). *FTIR spectra of PTh /0.5%w/vV_2O_5 composite thin films.*

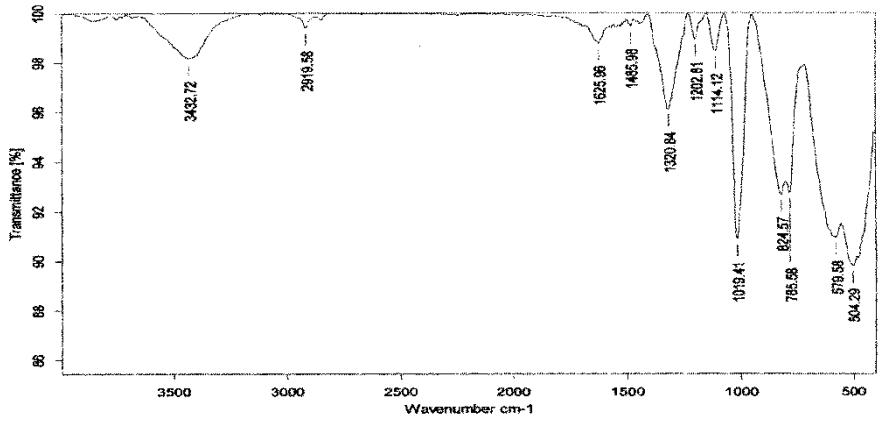

Figure1(b). *FTIR spectra of PTh /1 %w/v V_2O_5 composite thin films*

3.2. XRD Analysis

The XRD profiles of pure polythiophene and doped V_2O_5 with deferent %w/v are shown in Figure2,2(a) and 2(b).In case of polythiophene no sharp peak observed indicating the polymer under investigation is nanocrystalline in nature In XRD analysis of0.5 %wV_2O_5 doped polythiophene shows one peak at 2 theta =26.27 and 1% w/v V_2O_5 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.

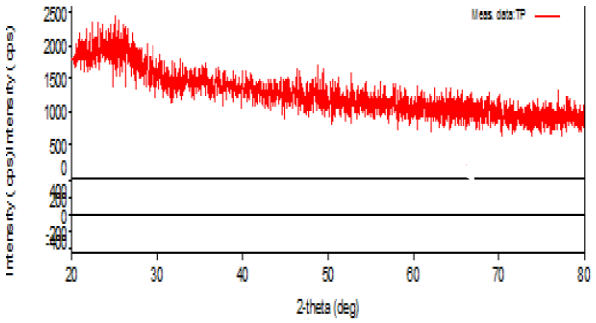

Figure2. *XRD patterns of pure Pth and0.5% w/v V_20_5 doped composite*

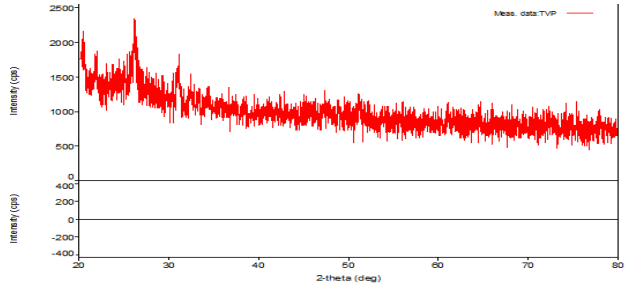

Figure2(a). *XRD patterns of polythiophene 0.5% w/v V_20_5 doped composite*

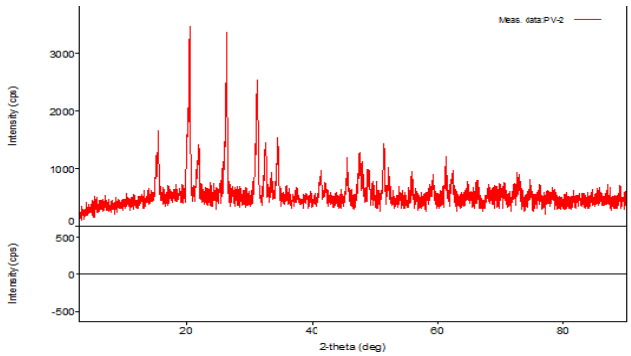

Figure2(b). *XRD patterns of Polythiophene 1% w/v V_20_5 doped composite.*

3.3. SEM Studies

The SEM images of the pure polythiophene and pth/V_2O_5 composites thin film are observed the film shows different surface morphology due to different weight % of v_20_5 doping. Figure 3,3(a),3(b) shows is observed in pure polythiophene thin film. The grains are highly agglomerated highly irregular shape some grains are irregular in structure some of them are elongated and some are spherical in shape .

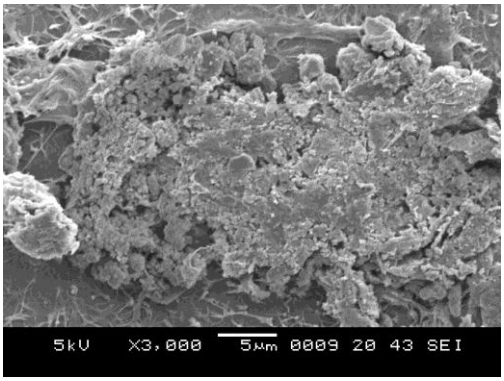

Figure3. *SEM image of undoped polythiophene thin film*

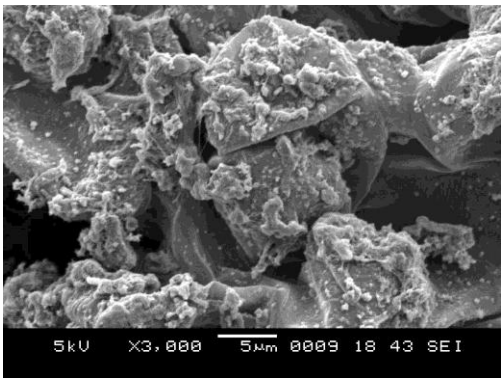

Fig3(a). *SEM image of 0.5%w/vV_2O_5 doped polythiophene thin film.*

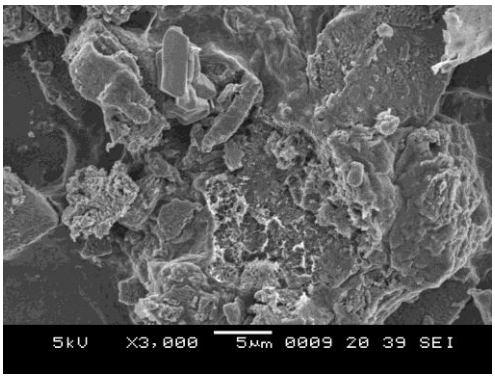

Fig3(b). *SEM image of 1%w/v V_2O_5 doped polythiophene thin film*

3.4. TGA-DTA Analysis

Thermogravimetric and Differential thermal analysis of Polythiophene and different %w/v of V_20_5 composite was carried out in air atmosphere .TGA was performed on Rigaku TG8121 thermal analyser with platinum pan in the temperature range room tempreture to 550^{o}C.Tthe thermogram of polythiophene and composite as shown in figure-4,4(a),4(b). Three major weight losses are observed one around 50-80^0 weight loss about 1-3% due to elimination of moisture, evopouration of solvent as well as unreacted monomer. Second weight loss around 280-300 ^{0} is due to loss of dopant component of polythiophene. Third major drop in weight observed at 350-400^0 and beyond the range is due to degradation of polythiophene itself. DTA shows two exothermic maxima at near about 400^0 and 450 ^{o}

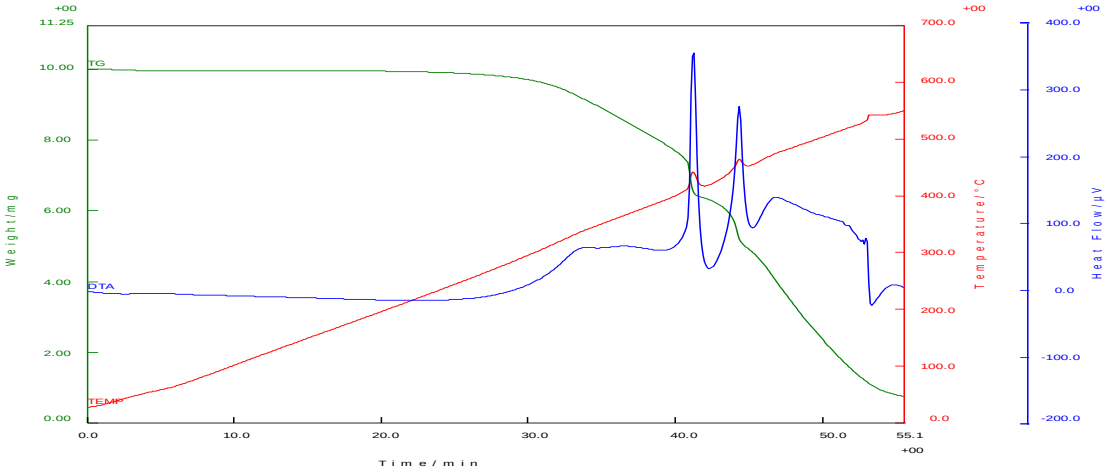

Figure4. *TGA-DTA of undoped polythiophene*

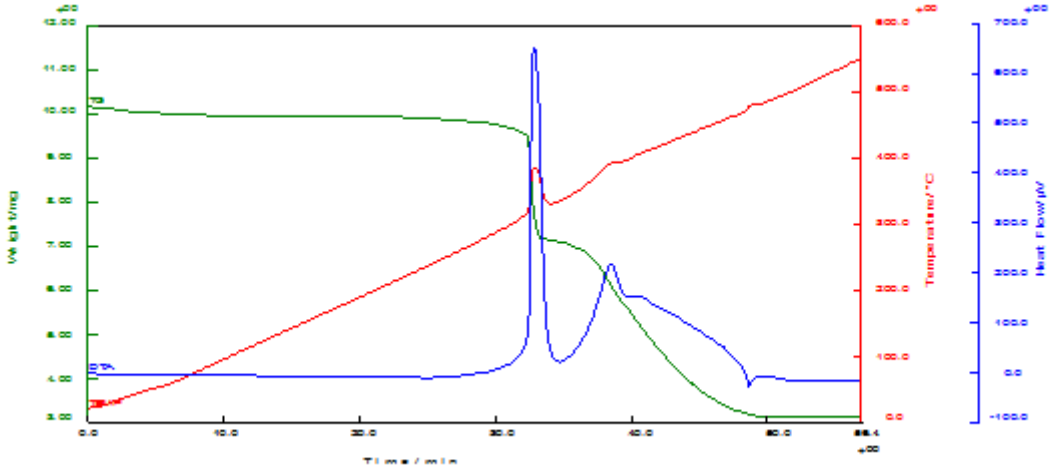

Figure4(a). *TG-DTA of polythiophene 0.5%w/v V_2O_5 doped*

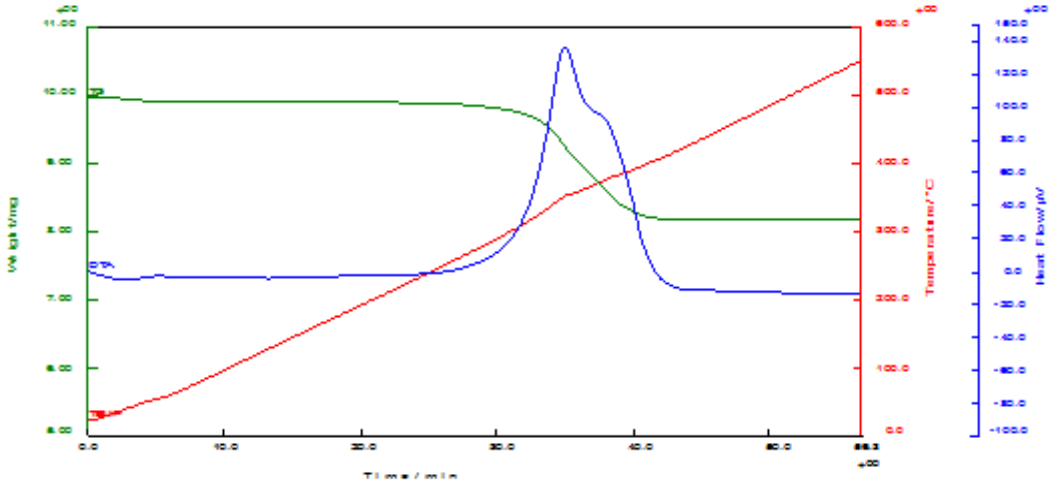

Figure4(b). *TGA-DTA of polythiophene 1%w/v V_2O_5 doped*

4. CONCLUSIONS

We have demonstrated the successful synthesis of nanostructure polythiophene thin film by chemical bath deposition Technique. Polythiophene can be doped by V_20_5 in chloroform with the formation of complex .The result of FTIR proved the formation of polythiophene. Morphology of thin film were analysed by SEM shows change in morphology after doping. XRD shows modification from

amorphous to the well developed crystalline structure. Thermal properties of nanocomposites were investigated by TG-DTA analysis shows composites of polythiophene with V_2O_5 are found to be more thermally stable than undoped polythiophene.

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AUTHORS' CONTRIBUTIONS

Authors may use the following wordings for this section:"„AuthorR.S.Futane "designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript.'Author"V.M. Raut" and Author"S.D.Dhande" managed the analyses of the study. All authors read and approved the final manuscript."

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