



## Synthesis, Characterization and Thermal Properties of Polythiophene Composites†

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Polythiophene (PTh) and its composites are currently subject of intense investigation due to their wide application in electronic, gas sensing and optoelectronic devices. The stability of polythiophene in the oxidized form, its high conductivity and an interesting electrochemical behaviour allow this material to use it for contemporary application. Therefore, its thermal analysis becomes crucial. The oxidant concentration dependant thermal analysis of PTh/PVAc studied in the present article. The PTh/PVAc composite films were synthesized by chemical polymerization method by using  $\text{FeCl}_3$  as an oxidant in organic medium. The two samples (S1 and S2) of composite were synthesized using 140 and 150 monomer to oxidant ratio respectively. The samples were characterized by FTIR, XRD and TG-DTA. The thermal properties of composites were studied from TG-DTA. It was found that the thermal properties are monomer to oxidant ratio dependent.

**Key Words:** Thermal properties, Polythiophene, Composites, Oxidant.

### INTRODUCTION

Conducting polymers like polyaniline, polypyrrole and polythiophene (PTh), are well studied polymers. Among these conducting polymers, polythiophene has been much interested due to its environmental stability, high electrical conductivity and its applications<sup>1,2</sup>. The stability of polythiophene in the oxidized form, its high conductivity and an interesting electrochemical behaviour allow this material to use as electrode materials for electrochemical supercapacitors. Polythiophene compounds have very high application prospects due to their high ionization potential and storage stability. Recent developments in chemical gas sensor have provided simple, yet efficient strategic suited to environmental applications. Indeed, chemical sensors are often cheap, reliable, real time and field portable alternatives that do not compromise detection sensitivity<sup>3</sup>. The most notable property of these materials, electrical conductivity, results from the delocalization of electrons along the polymer backbone-hence the term synthetic metals. However, conductivity is not the only interesting property resulting from electron delocalization. The optical properties of these materials respond to environmental stimuli, with dramatic shifts in response to changes in solvent, temperature, applied potential and binding to other molecules. Both changes and conductivity changes are induced by the same mechanism-twisting of the polymer backbone, disrupting conjugation

making conjugated polymers attractive as sensors that can provide a range of optical and electronic responses. Gnanakan *et al.*<sup>4</sup> reported an organic acid doped electronically conducting polymer nanomaterial, polythiophene-tartaric acid (PTh-TA) nanoparticles, prepared by cationic surfactant-assisted dilute polymerization method. FT-IR, UV-visible spectroscopy, X-ray diffraction, SEM and electrical conductivity studies characterized the physical properties of the synthesized polymer.

In the present work, the thermal properties of polythiophene (PTh)/polyvinyl acetate (PVAc) composites are studied with the different concentration of oxidant.

### EXPERIMENTAL

Thiophene monomer, anhydrous iron(III) chloride ( $\text{FeCl}_3$ ), polyvinyl acetate (PVAc) and methanol from SD Fine Chemicals (AR grade) were used in the present study. The thiophene monomer was used as received. Composite PTh-PVAc prepared according to<sup>3</sup> by chemical oxidative polymerization method with oxidant to monomer ratio 140 (S1) and 150 (S2). The samples of polythiophene powder were characterized by using infrared (FT-IR), X-ray, TG-DTA techniques. The FTIR spectra of powders were recorded on Shimadzu (Model-8201) FTIR in the KBr medium at room temperature in the region  $1600\text{-}600\text{ cm}^{-1}$  at a  $0.97\text{ cm}^{-1}$  resolution averaging 16 scans. The X-ray diffraction pattern of powders was recorded on a Phillips-1730 (PAN alytical) X-ray diffractometer using

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$\text{CuK}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The diffractogram was in terms of  $2\theta$  in the range  $5^\circ$ - $99^\circ$ . The thermal property of powders was investigated by using TG-DTA.

## RESULTS AND DISCUSSION

**FTIR analysis:** FTIR spectra of film S1 and S2 displayed in Fig. 1(a) and (b) respectively. The spectra recorded in the range of  $4000$ - $650 \text{ cm}^{-1}$  to confirm polymerization. Broadening of peaks obtained at and around  $668$ ,  $874$ ,  $1013$  and  $1394 \text{ cm}^{-1}$  for both films indicates formation of polythiophene in counter polymer (polyvinyl acetate) matrix. The slight shifting of peaks may be due to different concentration of  $\text{FeCl}_3$ . The peak around  $3344 \text{ cm}^{-1}$  is assigned for CH stretching. The conjugation band around  $1583 \text{ cm}^{-1}$  may imply polymerization and conductivity<sup>5</sup>.

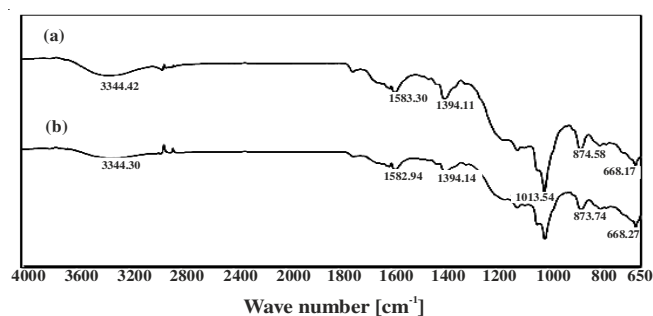


Fig. 1. FTIR spectra of polythiophene samples (a) S1 and (b) S2

**XRD analysis:** The X-ray diffraction pattern of S1 and S2 shows amorphous nature. A broad peak was observed at about  $2\theta = 26.83^\circ$  (S1) and  $27.31^\circ$  (S2). These peaks are due to the scattering from polythiophene chains at the interplanar spacing. However, the position of maximum intensity of the amorphous halos was different from each other for the both samples. The average chain separation can be calculated from the maxima using relation reported in reference<sup>6</sup>. The average chain separation was found to be  $4.15$  and  $4.07 \text{ \AA}$  for S1 and S2 respectively.

**TG-DTA analysis:** The TG and DTA of PTh-PVAc composite films S1 and S2 are plotted as a function of temperature in Fig. 2(a) and (b). Continuous weight loss is observed for both samples. The weight loss at  $50^\circ\text{C}$  is  $4\%$  for S1 and  $5\%$  for S2. The S1 shows minimum weight loss and hence it is stable as compared to S2. The  $\Delta C_p$  for S1 and S2 is found to be  $0.229$  and  $0.216 \text{ J/g } ^\circ\text{C}$  respectively. The maximum value of  $\Delta C_p$  is observed for sample S1. An endothermic peak appears for S1 and S2 at  $75$  and  $78^\circ\text{C}$  respectively on the DTA curve. The change in enthalpy ( $\Delta H$ ) for S1 is  $-15.859 \text{ J/g}$ . The total weight loss is also observed minimum that is  $56\%$  for S1.

## Conclusion

The polymerization of polythiophene-polyvinyl acetate composites was confirmed from FTIR spectra. The broadening of peaks obtained at and around  $668$ ,  $874$ ,  $1013$  and  $1394 \text{ cm}^{-1}$  for both films indicates formation of polythiophene in counter polymer (PVAc) matrix. The XRD study revealed that the

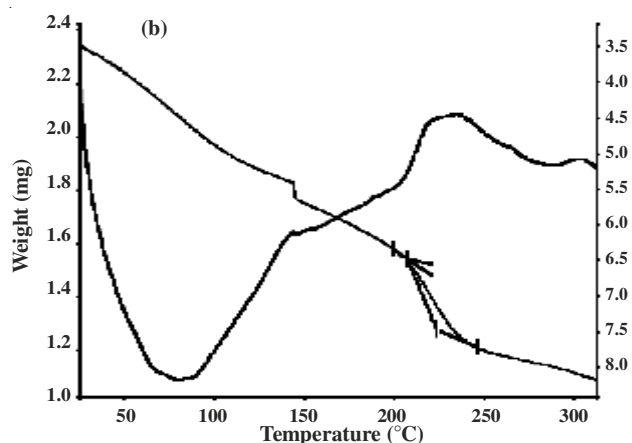
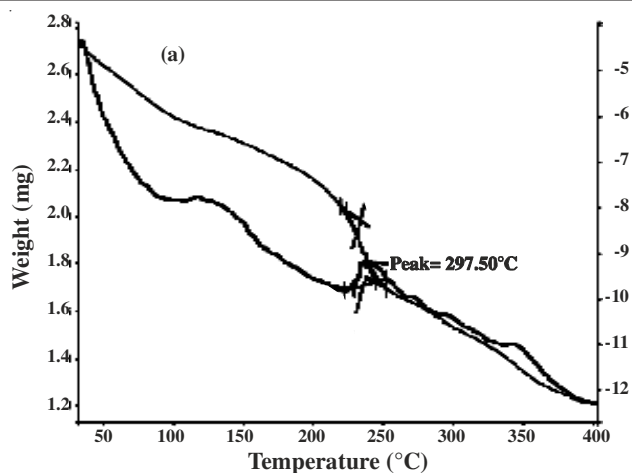


Fig. 2. TG-DTA of polythiophene samples (a) S1 and (b) S2

average chain separation was found to be increase with oxidant concentration. From TG-DTA study, it is found that the sample S1 showed minimum weight loss and hence it is stable as compared to S2.

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