

Thermal Studies of Polypyrrole and Cobalt Aluminum Oxide Nano Composites

Sutar Rani Ananda

Centre of excellence in Advanced Materials Research,
Department of Physics,
BMS College of Engineering,
Bengaluru, Karnataka, India
Email: ranidsutar@gmail.com

Murugendrappa M.V

Centre of excellence in Advanced Materials Research,
Department of Physics,
BMS College of Engineering,
Bengaluru, Karnataka, India
Email: murugendrappamv.phy@bmsce.ac.in

Abstract- In the present work Cobalt Aluminum Oxide (CAO) Nano powder was used as loading particles in conducting polymer pyrrole to synthesis Polypyrrole Nano composites (PPy/CAO) by in situ chemical polymerization technique. Thermal studies of different weight percent Nano composites were done by Thermo gravimetric/Differential thermal analysis (TG/DTA). To understand the thermo gravimetric analysis, Nano composites were exposed to different temperatures in muffle furnace for 2 hours and FTIR was recorded immediately for these samples. TGA data reveals that the PPy/CAO has good thermal stability almost same as that of polypyrrole. FTIR data of the Nano composites after exposure to different temperatures supports to the TG/DTA analysis.

Keywords— Polypyrrole; Cobalt Aluminum Oxide; Thermal studies; Nano composites

I. INTRODUCTION

The polymer Nano composite belongs to the class of multi-phase system where very small portion of filler is added in host polymer matrix and these added fillers improves structural, electrical, thermal, chemical and mechanical properties of host polymers. The conducting polymers are excellent hosts for capsuling the nanoparticles of metals, metal-oxides, semiconductors and serves uniform distribution which is important in optoelectronics, electronics and many more applications [1].

Different methods like chemical, electrochemical, emulsion polymerization in different organic and aqueous solvent are used to synthesize the Nano composites. Chemical polymerization is most used method for synthesizing Nano composites due to its benefits as (a) physical properties like particle size and morphology can be controlled by synthesis condition and (b) synthesizing larger amount than laboratory scale which is main drawback in electro polymerization is overcome by this method. Chemical polymerization is categorized in two types (a) blending of nanoparticles in formerly synthesized conducting polymer and (b) in- situ polymerization where nanoparticles were added while polymerization of monomer

and this method gives very good dispersion in polymer matrix [2, 3]. Different application oriented Nano composites of PPy/V₂O₅ [4], PPy/ Fe₃O₄ [5], PPy/SiO₂ [6, 7], PPy/SnO₂ [8] were studied by different group of researchers.

Spinel structures have general chemical formula AB₂O₄ where divalent A and trivalent B are metal cations which normally occupy tetrahedral and octahedral sites respectively. These structures are of great practical interest since their different combinations allows to achieve desired properties such as high mechanical resistance, high thermal stability, low sintering temperature, catalytic properties, low surface acidity and high ability of cations diffusion [9].

In this work spinel structured cobalt aluminum oxide (CoAl₂O₃) in different weight percent is used as filler in polypyrrole to form PPy/CAO Nano composites via in-situ chemical polymerization method using ammonium persulphate as oxidizing agent and thermal analysis of synthesized Nano composites were studied in detail.

II. EXPERIMENTAL SECTION

A. Materials

The chemicals used to synthesize Nano composites are monomer pyrrole (C₄H₅N) (Spectrochem Pvt. Ltd) as a matrix material, oxidizing agent as Ammonium persulphate (APS) (Fisher Scientific) and ternary Cobalt Aluminum Oxide (CoAl₂O₄) (Sigma Aldrich) Nano powder as dispersion.

B. Synthesis of Pure Polypyrrole (PPy) and PPy/CAO Nano composites

In this article, in-situ chemical oxidation polymerization method is used. For the synthesis of pure polypyrrole, 0.6M of APS clear solution is prepared and polymerization of 0.3M pyrrole is initiated by drop wise addition of the APS solution. The constant temperature in the range of 0 °C – 5 °C and constant stirring (500 -600 rpm) of 5 hours using magnetic stirrer is maintained during polymerization. The synthesized polypyrrole is filtered and water content is removed by keeping the powder in muffle furnace for 2 hours at 100 °C. The dried powder is crushed

well, weighed and preserved for further work. This weight of polypyrrole is considered as 100 wt. % [10].

The same process is followed to prepare different weight percent Nano composites. In details, CoAl_2O_4 Nano powder in 10-50 wt. % (in steps of 10 wt. %) is dispersed well in pyrrole solution by using magnetic stirrer and then same process of polymerization, filtration and preservation is followed as polypyrrole.

C. Characterization

The morphology of PPy/CAO Nano composites were studied by SEM using TESCAN VEGA3 scanning electron microscope. Structural studies were confirmed by XPERT-3 X-ray diffraction system with $\text{CuK}\alpha$ radiation of 1.54060 \AA and continuous scan from $10\text{-}80^\circ$ with scan rate of $0.03^\circ/\text{sec}$. [11]. Thermo-gravimetric studies were done at heating rate of $20^\circ\text{C}/\text{min}$ in temperature of 40°C to 730°C . To understand the decomposition and other thermal effect, synthesized Nano composites were exposed to different temperatures (Room Temperature, 100°C , 205°C , 320°C . and 600°C) in muffle furnace for 2 hours and FTIR spectrum was recorded immediately by using PerkinElmer spectrum Two FTIR spectrometer in KBr medium.

III. RESULTS AND DISCUSSION

Fig.1 (a) and (b) are the TG/DTA results of pure polypyrrole and polypyrrole Nano composites. Fig.1 (a) shows percentage weight loss with temperature of polypyrrole Nano composites with different loadings of CAO nanoparticles. It is observed that weight loss occurred in three main stages in all Nano composites. First weight loss is in between $40\text{-}110^\circ\text{C}$ which is due to evaporation of water content from the sample. The second weight loss is due to decomposition of polypyrrole ring which is observed in temperature range of $110\text{-}350^\circ\text{C}$. And the third weight loss observed from $350\text{-}500^\circ\text{C}$ is due to complete melting of polypyrrole but with some leftover residue. It is confirmed from Fig. 1 (a) that all the Nano composites show almost similar thermal stability as that of polypyrrole.

Fig.1 (b) is the variation of derivative weight with temperature for polypyrrole and PPy/CAO Nano composites. It clearly shows that water content gets removed around 70°C , complete decomposition of polypyrrole around 260°C and melting of polypyrrole around 510°C .

To understand the decomposition and melting of PPy/CAO Nano composites, the powder samples were exposed to different temperatures and analyzed by FTIR. Initially pure PPy and 20 wt. % PPy/CAO Nano composite powders were kept in muffle furnace at 100°C in closed crucibles. After 2 hours of continuous exposure to particular temperature, the powder samples were taken out and immediately FTIR spectrum were recorded using KBr medium. Similar process was carried out at different temperatures such as 205°C , 320°C and 600°C .

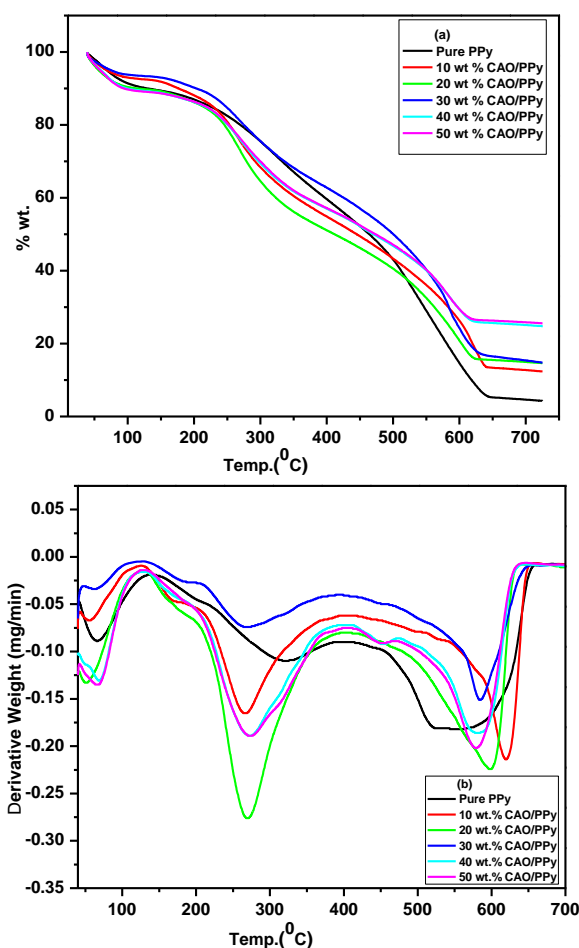


Fig. 1 (a) and (b) TG/DTA Graph of Polypyrrole and PPy/CAO Nano composites

The clear observation shows that there is no much difference in FTIR spectrum at room temperature and at 100°C for both polypyrrole and 20 wt. % PPy/CAO Nano composite. The absorption peak observed at 3441 cm^{-1} , 2930 cm^{-1} in room temperature spectrum is due to O-H and C-H stretches respectively which gets removed at 100°C confirming the evaporation of water and volatile contents from the polypyrrole. The absorption peaks at 1098 cm^{-1} , 916 cm^{-1} and 794 cm^{-1} are due C-H in-plane vibration, C-H out-of-plane (oop) vibration and pyrrole ring vibrations [12] and represents mainly ring type structure of pyrrole which are absent at 205°C which confirms the decomposition of pyrrole ring started at this temperature. At higher temperature of about 320°C all the carbon content gets disappeared from the powder sample of polypyrrole confirming melting of polypyrrole and left with few residues which confirms from presence of N-H stretch at 1628 cm^{-1} . At around 600°C no compound was left in crucible of polypyrrole powder confirming full evaporation of the residues. But for the same temperature, in the crucible of 20 wt. % PPy/CAO sample, blue color powder was left. This powder was cobalt aluminum oxide Nano powder which was used as loading particles in polypyrrole. This is confirmed from the absorption peaks present at 556 cm^{-1}

and 697 cm^{-1} which are due to Co-O stretching and Al-O vibrational frequencies respectively [13].

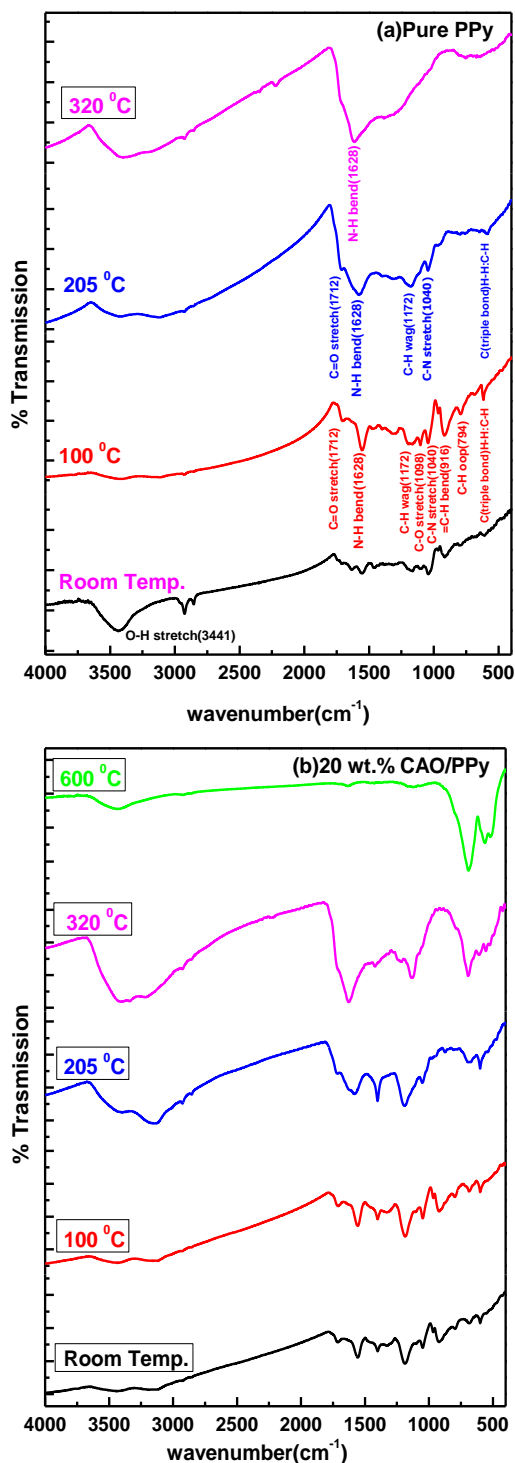


Fig.2 (a) and (b) FTIR spectrums recorded for pure polypyrrole and 20 wt. % PPy/CAO Nano composite after exposing to different temperatures.

IV. CONCLUSION

Successful synthesis of PPy/CAO Nano composites was achieved by in-situ chemical polymerization method. Thermo gravimetric and differential thermal analysis shows almost similar thermal stability as that of polypyrrole by the addition of cobalt aluminum oxide Nano powder as filler material. The recorded FTIR spectrums of Nano composites after exposing to different temperatures shows evaporation of water and volatile compounds at $100\text{ }^{\circ}\text{C}$, onset of decomposition and melting of polypyrrole starts around $205\text{ }^{\circ}\text{C}$ and $320\text{ }^{\circ}\text{C}$ respectively. The FTIR spectrum recorded at different temperatures are in good agreement with the TG/DTA data.

Acknowledgments

The authors would like to acknowledge the World Bank funded project Centre of Excellence on Advanced Materials Research under TEQIP-1.2.1.

References:

- [1] R.P. Singh, B.K. Oh, J.W. Choi, Sens. Transduc. J. ,(2009),105, 104,
- [2] Zare EN, Lakouraj MM, Mohseni M. Biodegradable polypyrrole/dextrin conductive nanocomposites: synthesis, characterization, antioxidant and antibacterial activity. Synth. Met. (2014);187:9–16
- [3] Wallace GG, Spinks GM, Kane-Maguire LAP, et al. Conductive electroactive polymers. Boca Raton (FL): CRC Press; (2008).
- [4] L iu Z, Liu Y, Zhang L, et al. Controlled synthesis of transition metal/conducting polymer nanocomposites. Nanotechnology. (2012);23:335603–335613
- [5] Jianfeng Zhao, Shichao Zhang, , Wenbo Liu, , Zhijia Du, Hua Fang, Volume 121, 1 March (2014), pp 428–433
- [6] Tuyen LTT, Kamloth K, Liess HD. Electrical properties of doped polypyrrole/silicon heterojunction diodes and their response to NOx gas. Thin Solid Films. (1997);292:293–8.
- [7] Liu XH, Wu HY, Ren FL. Controllable fabrication of SiO(2)/polypyrrole core-shell particles and polypyrrole hollow spheres. Mater Chem Phys. (2008);109(1):5–9.
- [8] Zhang J, Wang S, Xu M, et al. Polypyrrole-coated SnO2 hollow spheres and their application for ammonia sensor. The Journal of Physical Chemistry C. (2009);113:1662–1665.
- [9] L. Gamaa, M.A. Ribeiroa, B.S. Barros b, R.H.A. Kiminamic, I.T. Weberd, A.C.F.M. Costa, Journal of Alloys and Compounds 483 (2009) 453–455
- [10] M.V. Murugendrappaa, Ameena Parveenb, M.V.N. Ambika Prasad, Materials Science and Engineering: A, 1–2 (2007), pp371–374
- [11] Sutar Rani Ananda and Murugendrappa M.V, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering Vol:10, No:10, 2016, pp1264 – 1269.
- [12] Erlon R. Cordeiro, Antonio W. C. Fernandes, Alessandra F. C. Pereira, Mateus M., da Costa, Marcio L. F. Nascimento, Helinando P. de Oliveira, Quím. Nova vol.38 no.8 São Paulo Sept. (2015)
- [13] Natalia Betancur Granados, Eongyu Yi, Richard Laine, Oscar Jaime Restrepo Baen, Matéria (Rio J.) vol.20 no.3 Rio de Janeiro (2015)