

STRUCTURAL PROPERTIES OF POLYPYRROLE - LEAD OXIDE COMPOSITES

*Rohinikumar Hilli¹, Sangshetty Kalyane², Arunkumar Lagashetty³, Aparna Shetty⁴

¹Sri Prabhu Arts, Science College, Shorapur, Dist: Yadgiri, Karnataka, India

²Bheemanna Khandre Institute of Technology, Bhalki, Bidar, Karnataka, India

³Reshmi UG & PG College, Kalaburagi, Karnataka, India

⁴Govt Autonomous First Grade College, Kalaburagi, Karnataka, India.

ABSTRACT

Conductive polymers based nanocomposites are a promising class of polymer nanomaterials which have unusual combination properties of conductive metals and insulated plastics. These materials are expected to be widely applied in the new growing technology specially in display and storage devices. PPy-PbO composites both overcome the inadequate mechanical property of polypyrrole and give a conductive property to the world's most abundant material PbO. PPy and its composites PbO have been synthesized chemically using potassium permanganate and potassium per sulfate as oxidants. The prepared PPy composites have been characterized. Fourier transform infrared (FTIR) tool for varied bonding nature. The X-ray diffraction (XRD) study has also carried out to know the presence of PbO in the polymer. The elemental analysis and the thermo gravimetric analysis measurements is undertaken to know the presence of lead oxide in the said polymer. Scanning electron microscopy (SEM) was used to study the morphological behaviour of composite samples. Four probe technique was used to study the electrical behaviour of the PPy/PbO nanocomposite.

Key Words: Characterization, Composition, Lead Oxide, Nanomaterial, Polypyrrole,

Introduction:

Oxidation of pyrrole in organic solvents resulted in the formation of polypyrrole by chemical and electrochemical oxidation in aqueous medium having positive charge on its backbone [1]. Among the transition metal oxides, leadoxide (PbO) has gained considerable interest in the fabrication of PPY hybrid materials by its special characteristics like high refractive index, thermal stability, UV protection, High electron mobility and wide band gap along with variety of applications [2]. The main aim of the present work is to explore the potential application of inorganic nano composites as high performance materials [3]. Firstly inorganic PPY/PbO composites are synthesized secondly FeO₃ is used as oxidizer to enhance the processibility and mechanical properties of PPY in the present study [4]. Finally these materials can be prepared in different composition of percentage for studying the structural properties, morphology and high conducting studies [5]. Unique electrical properties of composite materials has gained attention towards the

synthesis of composite materials in the recent years [6], inorganic nanocomposites with a reduced structure provides new functional hybrid of inorganic materials [7]. Lead oxide (PbO) is one of the n-type semiconductor and nontoxic material with a good photo catalytic activity [8]. The structure and morphology of PbO have an important effect on its properties and applications its electrical and optical properties are better due to the reduced carrier scattering in one dimensional structure [9]. The combining capacity of this inorganic composite materials has lead to the extensive studies towards the incorporation of nanosized particle [10] Features such as high thermal stability of these nano composites has facilitated its synthesis [11]. Electrochemical properties like biocompatibility have gained commercial value by its significant role of electrical conduction by conductivity oxidized and insulating reduced state which is the basis of tremendous technological bio sensing [12]. Inorganic composite materials such as prepared lead and polypyrrole including various transition /nontransition metal oxide were used for the present study. In the present investigation made to report on our observations of structural morphology and electrochemical properties of PPY and its nano composites with PbO fabricated by chemical polymerization pyrrole with FeCl_3 . The final product were characterized by scanning electron microscope(SEM),X-Ray diffraction studies(XRD), energy dispersive analysis by EDS, thermo gravimetric and differential thermal analysis (TGA & DTA), FTIR spectra (FTIR).the interaction between PPY and PbO nano composites were changed to different concentration like 10%, 20%, 30%, 40%, 50% PPY-PURE.

MATERIALS AND METHOD

Analytical reagent grade pyrrole & PbO were used in the present study was purified by distillation and stored in dark at 4°C . Insitu polymerization method is used for polymerization of pyrrole using potassium permanganate as oxidant.

EXPERIMENTAL:

Synthesis of PPY/PbO nanocomposite

Ethanol solution of pyrrole is prepared by addition of known quantity (3 or 4 ml) distilled pyrrole in 25ml of ethanol & stirred well for 10 min. To this solution add 25 ml $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ drop wise with continuous stirring. The suspension was allowed to stay for complete polymerization. Finally the suspension was filtered, washed thoroughly with distilled water and dried under acetone in order to remove the unreacted pyrrole and excess ferric chloride. A black precipitated of polypyrrole was obtained which was dried for 1 hr at $60-70^\circ\text{C}$. Fine grinded powder was taken in different wt % of PbO (10%, 20%, 30%, 40%, and 50%) and added to the polypyrrole solution. This reaction mixture was stirred for 3 hrs at $0-5^\circ\text{C}$ with magnetic stirrer in order to disperse PbO in the polymer solution.

Characterization Methods:

The fine powder of Polypyrrole-PbO was made by placed in a plate and carried ot for X-Ray diffraction studies, The fine powder Polypyrrole-PbO calculated by using Rigaku Corporation 's advanced Smart Lab 3kW with power of 200 VAC±10% 50/60 Hz 3Ø 30A diffractometre operated in the 2θ range 20- 70° at a scan speed of 5 ° per minute.

The scanning electron micrographs of pyrrole and PbO composite were analyzed using a SEM model S-3400N of Hitachi, made in Japan and EDS on Norman System7 of Thermo Fisher Scientific Company of USA with a Tungsten filament and secondary electrons and back scattered electrons detectors respectively. Thermo gravimetric analysis (TGA&DTA) was carried out using an STA 2500 Instrument at a heating rate of 10° min⁻¹ in inner N₂ atmosphere.

Fourier transform infrared (FT-IR) spectra were recorded with a spectrum Two spectrometer over the wave number range of 4000- 450 cm⁻¹.The spectra of PANI-PbO composites were taken using KBr disks.

Results and Discussion

Morphological characterization-SEM Analysis:

SEM micrographs of PPy-PbO different composite with varied resolution are shown in Figure 1. All micrographs reveals the complete encapsulation of PbO particle in PPy matrix and agglomeration of grains having spherical morphology with average particle size around 10 μm. These images shows the incorporation of PbO into PPy in strong effect on morphology of PPy. An irregular shaped particle with agglomeration as well as same close compactness is observed on composite images. Same part shows varied development of crystalline nature is also observed. The average grain size of PPY-PbO composite was calculated using the equation $D = 1.56 C/MN$ where C is the length of the line, M is the magnification and N is the no. of intercept, and it increases with the increase in PPY-PbO wt % nanocomposite

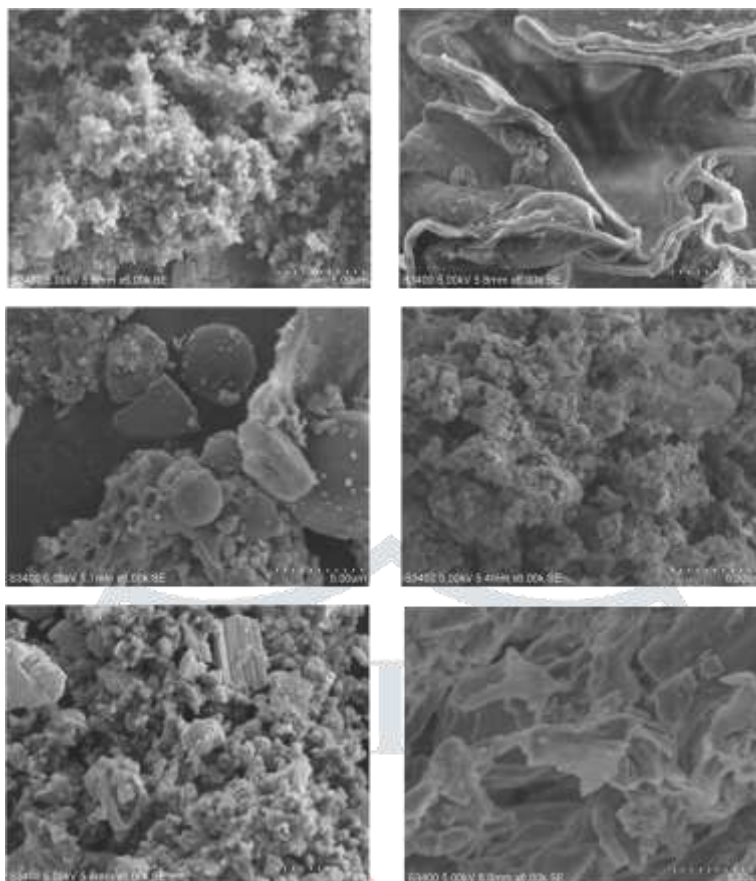


Figure-1: SEM image of PANI and Composite

FTIR Analysis:

Figure-2 shows the FTIR spectra of prepared PPy-PbO composites with varied wt% of PbO respectively. The characteristics absorption band of said composites are 1041.65 cm^{-1} S-O bonding interaction between PPy-PbO. The bonds at 896.8 cm^{-1} , 771.82 cm^{-1} , 772.28 cm^{-1} , 785.89 cm^{-1} , 774.11 cm^{-1} are due to C-C bonds made for aromatic ring. Peaks at 2661.97 cm^{-1} , 2675.38 cm^{-1} , 2734.36 cm^{-1} , 2685.73 cm^{-1} one due to the interaction between PPy-PbO by formation of H-bonding. The interaction of H-N band and Oxygen of PbO.

The PPy-PbO composites shows different concentration in the displacement of peak when PbO are added in PPy. These shifts include 1041.64 cm^{-1} - 1550.77 cm^{-1} , 2675.38 cm^{-1} - 2734.36 cm^{-1} , 1545.14 cm^{-1} - 1549.19 cm^{-1} , 774.11 cm^{-1} - 785.89 cm^{-1} , 1041.65 cm^{-1} - 1042.29 cm^{-1} . The PPy-PbO composite bonding S-O and oxygen of PbO, the peak displacement which was observed in FTIR spectra. The FTIR graph shows the interaction of N-H group PPy on the surface of PbO for instance of C-N, C-C bonds are shifted towards higher frequency.

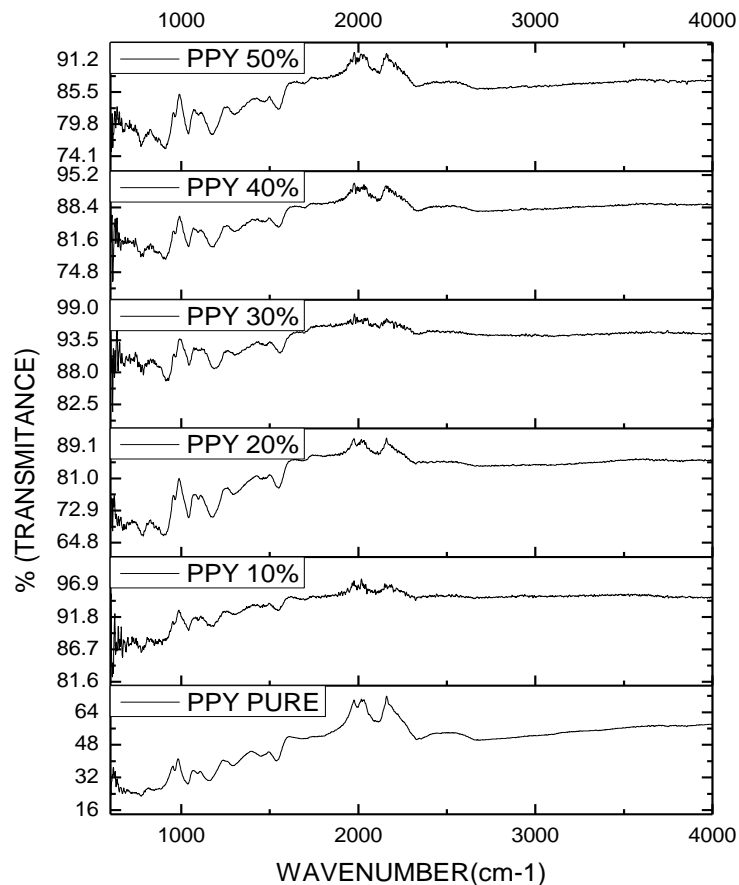


Figure-2: FTIR spectra of prepared PPY-PbO composites with varied wt% of PbO

XRD Analysis:

Figure-3 shows XRD pattern of PPY-PbO as prepared PbO-PPY composite with different wt% of PbO. This analysis is used to explain the structure of PPY-PbO composites and investigate the effect of various amounts of PbO composites on the PPY structure. The broad diffraction peak at 20° to 45° is due to the periodicity of the PPY chain, indicating good crystallinity. The average crystallite size is equal to 3 nm, which is calculated using the Scherrer formula $D = 0.9\lambda / \beta \cos\theta$. The XRD pattern of PPY does not show any Bragg's reflection due to its amorphous nature, but the composite shows Bragg's reflection due to the development of crystallinity with PbO. The comparative observation of these patterns confirms the increase in crystallinity with an increase in the wt% of PbO in the polymer. It is also observed that the shifting of peaks is due to the encapsulation of PbO particles in the PPY matrix.

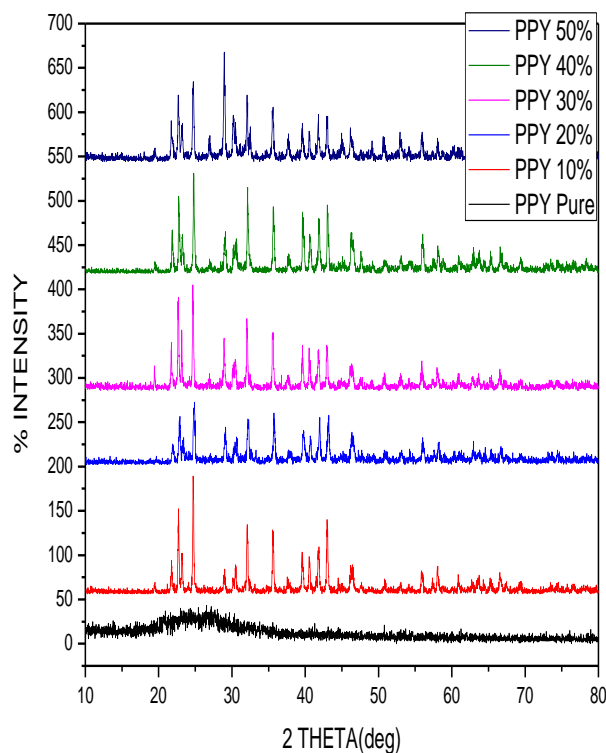


Figure-3 XRD pattern of PANI & Composite

TGA and DTA analysis:

Thermal gravimetric analysis of PPy and PbO nanocomposite material under nitrogen and oxygen atmosphere at 60% RH as observed from the figure 4, it shows the thermal stability of PbO is much higher than the PPy in the temperature range of 30-600°C. As PPy is hydroscopic nearly 7.9 wt% weight loss at 200°C due to evaporation of water residual only 2 wt% loss for PPy-PbO nanocomposite, as the temperature increase the weight loss again occur in 450°C, in case of PPy the weight reduces largely with only endothermic peak 288°C observed in fig-4. finally weight loss occur at 534°C PPy is almost 100% much more than that of the PPy-PbO nanocomposite. The DTA curve of PPy at N₂ atmosphere in fig-4b and the curve PPy under O₂ atmosphere shows the end of a sharp exothermic peak at 460.5°C because additional oxygen involved the reaction, all the result shows the binding of PPy into the PbO nano composite exothermic peak are not regular and move to the high temperature they increase the thermal stability and orderliness of PPy chains.

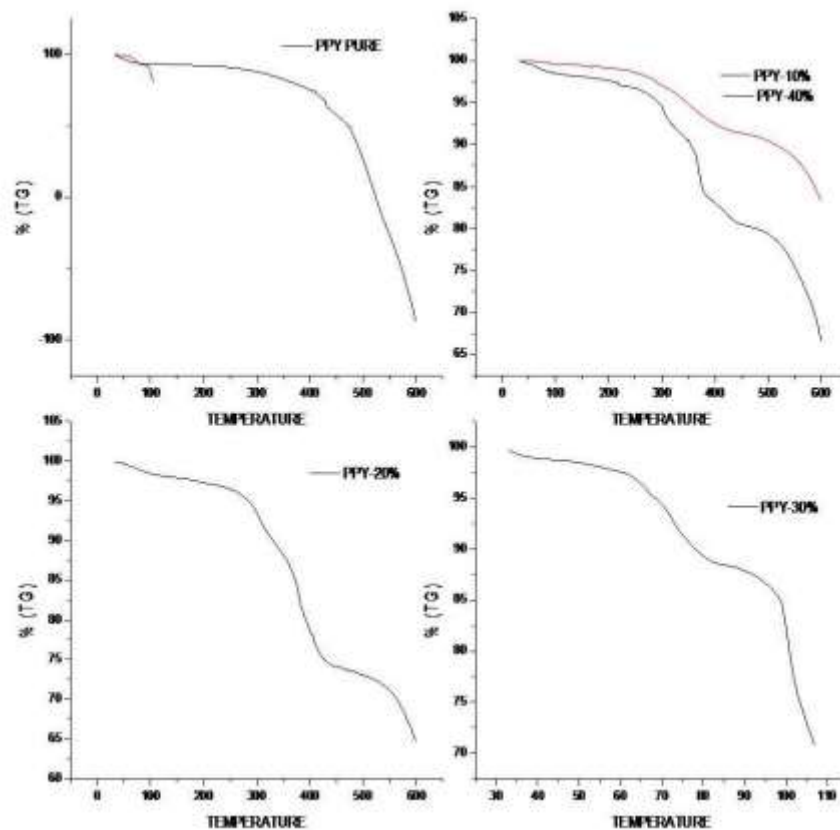


Figure-4: Thermal gravimetric analysis of PPY and PbO

Conclusion:

We have successfully synthesized PPY and CdO doped PPY. All SEM micrographs reveals the complete encapsulation of PbO particle in PPY matrix and agglomeration of grains having spherical morphology with average particle size around 10 μm . These images shows the incorporation of PbO into PPY in strong effect on morphology of PPY. An irregular shaped particle with agglomeration as well as same close compactness is observed on composite images. Same part shows varied development of crystalline nature is also observed. The characteristics absorption band of said composites are 1041.65 cm^{-1} S-O bonding interaction between PPY-PbO. The bonds at 896.8 cm^{-1} , 771.82 cm^{-1} , 772.28 cm^{-1} , 785.89 cm^{-1} , 774.11 cm^{-1} are due to C-C bonds made for aromatic ring. Peaks at 2661.97 cm^{-1} , 2675.38 cm^{-1} , 2734.36 cm^{-1} , 2685.73 cm^{-1} one due to the interaction between PPY-PbO by formation of H-bonding. The interaction of H-N band and Oxygen of PbO. The broad diffraction peak at 20° to 45° is due to periodicity of the PPY chain indicates the good crystallinity. The average crystallite size is equal to 3nm, which is calculated using the Scherer formula $D = 0.9\lambda / \beta \cos\theta$. The XRD pattern of PPY is not showing any Bragg's reflection due to amorphous nature but the composite shows the Bragg's reflection due to development of crystallinity with PbO. Thermal gravimetric analysis of PPY and PbO nanocomposite material shows the thermal stability of PbO is much higher than the PPY in the temperature range of 30-600 $^{\circ}\text{C}$. As PPY is hydroscopic nearly 7.9 wt% weight loss at 200 $^{\circ}\text{C}$ duet evaporation of water residual only 2 wt% loss for PPY-PbO nanocomposite, as the temperature increase the weight loss again occur in 450 $^{\circ}\text{C}$, in case of PPY the weight reduces largely with

only endothermic peak 288°C observed in fig-4. finally weight loss occur at 534°C PPy is almost 100% much more than that of the PPY-PbO nanocomposite.

References:

1. X. Liang, Y. Liu, Z. Wen, L. Huang, X. Wang, H. Zhang, *Journal of Power Sources*, 2011, 196, 6951–6955.
2. M. Falla, A.A. Diagne a, M. Guène a, C. Della Volpe b, P.L. Bonora b, F. Deflorian b, S. Rossi b, *Bull. Chem. Soc. Ethiop.*, 2006,20(2), 279-293
3. Althues H, Henle J, Kaskel S. Functional inorganic nanofillers for transparent polymers. *Chem Soc Rev* 2007; 36: 145465.
4. Njugun J, Peilichowski K. Polymer nanocomposites for aerospace applications: fabrication. *Adv Eng Mater* 2004; 6: 193210
5. Phang, W. J.; Lee, W. R.; Yoo, K.; Ryu, D. W.; Kim, B.; Hong, C. S. pH-Dependent Proton Conducting Behavior in a Metal-Organic Framework Material. *Angew. Chem., Int. Ed.* 2014, 53 (32), 8383– 8387
6. Kobayashi, Y.; Jacobs, B.; Allendorf, M. D.; Long, J. R. Conductivity, Doping, and Redox Chemistry of a Microporous Dithiolene-Based Metal–Organic Framework. *Chem. Mater.* 2010, 22 (14), 4120–4122
7. Cook, J.; Oreskes, N.; Doran, P. T.; Anderegg, W. R. L.; Verheggen, B.; Maibach, E. W.; Carlton, J. S.; Lewandowsky, S.; Skuce, A. G.; Green, S. A.; Nuccitelli, D.; Jacobs, P.; Mark Richardson; Winkler, B.; Painting, R.; Rice, K. *Environ. Res. Lett.* 2016, 11 (4), 048002.
8. Malik, R. S.; Tripathi, S. N.; Gupta, D.; Choudhary, V. *Int. J. Hydrog. Energy* 2014, 39 (24), 12826–12834. Natile MM, Glisenti A. New NiO/Co₃O₄ and Fe₂O₃ / Co₃O₄ nanocomposite catalysts: synthesis and characterization. *Chemistry of Materials.* 2003; 15(13):2502-2510
9. ontreras A, Lopez, Bedolla E. Mg/TiC composites manufactured by pressureless melt infiltration. *Scripta Materialia.* 2004; 51(3):249-253.
10. Goeders, K. M.; Colton, J. S.; Bottomley, L. A. (2008). Microcantilevers: Sensing Chemical
11. Interactions via Mechanical Motion. *Chem. Rev.*, 108, 522-542
12. Joseph MC, Tsotsos C, Baker MA, Kench PJ, Rebholz C, Matthews 126. A, Leyl A. Characterisation and tribological evaluation of nitrogen-containing molybdenum-copper pvd metallic nanocomposite films. *Surface and Coating Technology.* 2005; 190(2-3):345-356.