



Scholars Research Library

Der Pharmacia Lettre, 2017, 9 [12]: 64-71  
[<http://scholarsresearchlibrary.com/archive.html>]



## Synthesis, Characterization and Thermal analysis of PbS/MnO<sub>2</sub> doped Polyaniline Nanocomposites

Bhaiswar JB<sup>1</sup>, Meghe DP<sup>1</sup>, Salunkhe MY<sup>2</sup>, Dongre SP<sup>3</sup>

<sup>1</sup>Department of Physics, Nagpur Institute of Technology, Nagpur, India

<sup>2</sup>Department of Physics, Institute of Science, Nagpur, India

<sup>3</sup>Department of Physics, Bhalerao Senior College, Saoner, India

**\*Corresponding author:** Bhaiswar JB, Department of Physics, Nagpur Institute of Technology, Nagpur, India,

E-mail: [jitendrabhaiswar@gmail.com](mailto:jitendrabhaiswar@gmail.com)

---

### ABSTRACT

Synthesized of Polyaniline by polymerization of aniline using chemical oxidation with APS as oxidant. Subsequently, the nanocomposite was synthesized at different weight ratio of PbS and MnO<sub>2</sub>. The characterization of prepared nanocomposite by XRD, TEM and FT-IR. The sharp peaks of XRD indicate the high degree of crystallinity of the nanocomposite. The characteristic FT-IR peaks for PANI-PbS Nanocomposite indicated the PbS and MnO<sub>2</sub> dispersed in the polymer matrix. The Thermal stability of Nanocomposite compared with pure PANI using TGA and DTA. It is observed that thermal stability of PANI/PbS and PANI/MnO<sub>2</sub> are maximum as compared to bulk PANI.

**Keywords:** Polyaniline, Chemical synthesis, Thermal stability, X-ray diffraction, FT-IR, SEM

---

### INTRODUCTION

In Science the term 'nanomaterial' refers to substances consisting of particles with dimensions in the order of 10<sup>-9</sup> m. The nanomaterial exhibit new phenomenon and characteristics most of which we just now begin to explore and understand [1]. The

size scale; aspect ratio and properties of nanomaterials provide advantages in variety of applications, including electrostatically dissipative materials; advanced materials with combined stiffness and strength, as well as automotive components with enhanced mechanical properties [2].

The Thermal properties of Polymer in their pristine and doped states have been the materials of great interest for their applications in modern technologies [3]. Polyaniline has distinct space in science and technology as compares to other conducting polymers, like sensors display devices; separation membranes, and coatings [4,5].

Selection of PbS and MnO<sub>2</sub> nanoparticle as doping material in pure Polyaniline because of its exclusive substantial and chemical properties. [6]. In this study, Nanoparticle of PbS and MnO<sub>2</sub> was utilized to form nanocomposite with PANI. [7].

The main goal in this work is to enlarge the existing knowledge of the preparation of new advanced materials consisting polymer matrix with nanoparticles. Although the large number of studies on composite materials of Polyaniline-PbS/MnO<sub>2</sub> has been reported in literature. In the present work, report the synthesis and details of Thermal properties of Polyaniline and Polyaniline/MnO<sub>2</sub>/PbS nanocomposite at different weight ratio. The nanocomposites were characterized with the help of XRD and FT-IR spectroscopy. Morphological study was done using Transmission electron microscopy.

## MATERIALS AND METHODS

### *Chemical synthesis of polyaniline*

Chemical synthesis of pure aniline using APS as oxidant and H<sub>2</sub>SO<sub>4</sub>. Pure aniline dissolved in 100 ml distilled water with H<sub>2</sub>SO<sub>4</sub> added under magnetic stirring for 2 hours. The solution of ammonium per sulphate in sulphuric acid was then added drop-wise in the solution of aniline. The precipitate of polyaniline obtained with dark green clouded [8]. The precipitate washed with water. A PANI precipitate was dried under at 50–100°C for more than 8 hours.

### *Synthesis of PANI-MnO<sub>2</sub>/PbS nano-composites*

The same synthesis process was adapted For preparation of PANI/PbS and PANI/MnO<sub>2</sub> Nanocomposite at different weight ratio of PbS and MnO<sub>2</sub> nanoparticle. The PANI nanocomposite was chemically characterized by infrared spectroscopy, XRD and TGA.

### *Characterizations of nano-composites*

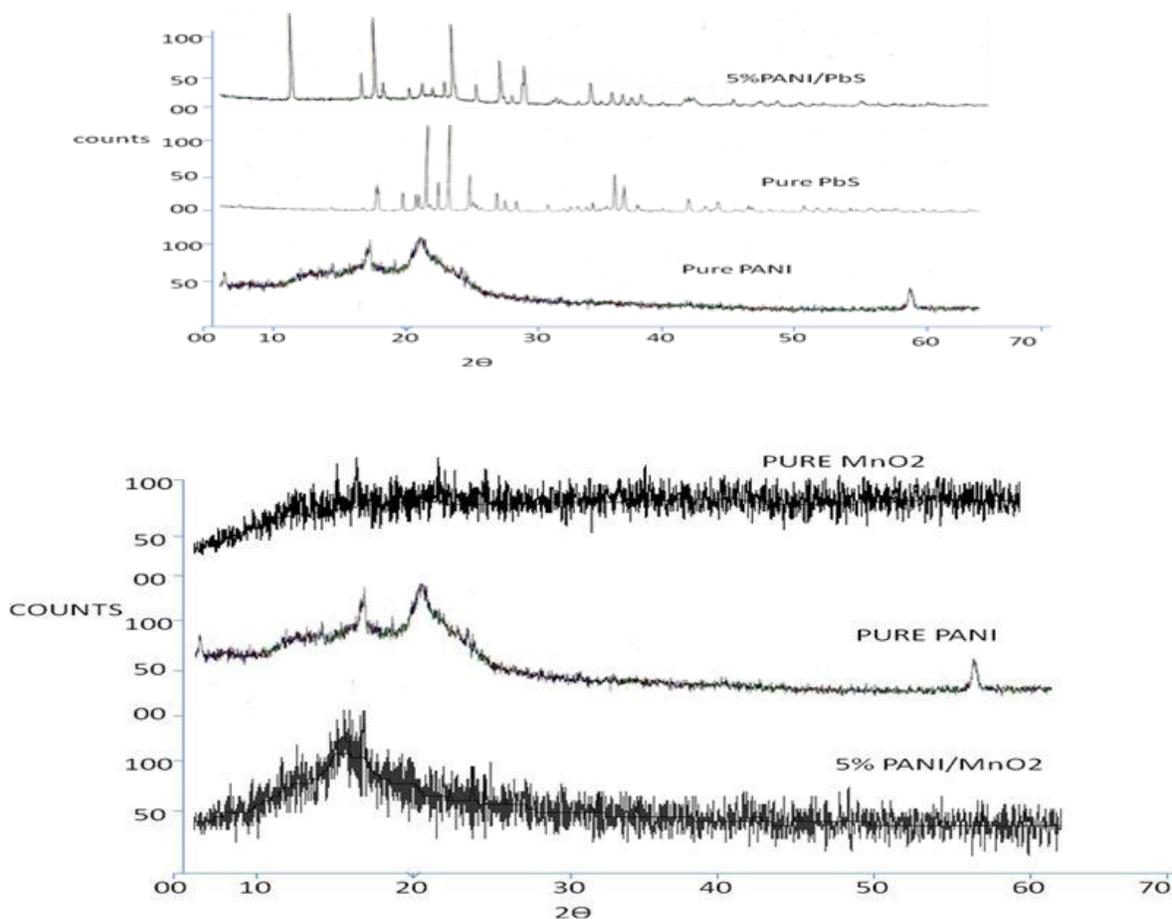
XRD with Philips PW -3071, Using Cu-K $\alpha$  radiation of wavelength 1.544 Å, with scanning rate of 2 ° / min. at 45 KV and 40 mA. Fourier Transform Infra Red (FTIR) spectroscopy (Model: Perkin Elmer 200) with frequency of 400–4000 cm<sup>-1</sup>. Thermal analysis of sample recorded by Perkin- Elmer Diamond TGA/DTA in argon atmosphere at a heating rate of 10°C/ min.

**XRD analysis**

The X-ray diffraction pattern of PANI/PbS nanocomposite at weight ratio (Figure 1) shows sharp and well defined peaks, indicating the crystallinity of the synthesized materials. The observed  $2\theta$  values strongly in resemblance with the standard JCPDS (JCPDS No.78-1285 & 86) which enumerate maximum degree of crystallinity. The broad peak of synthesized PANI/MnO<sub>2</sub> nanocomposite itself is situated at approximately  $2\theta = 25.60^\circ$  and d-spacing  $3.4759\text{\AA}$  indicated the low degree of crystallinity of the polymers. The crystalline size determined using Scherer formula from the full width at half maximum.

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

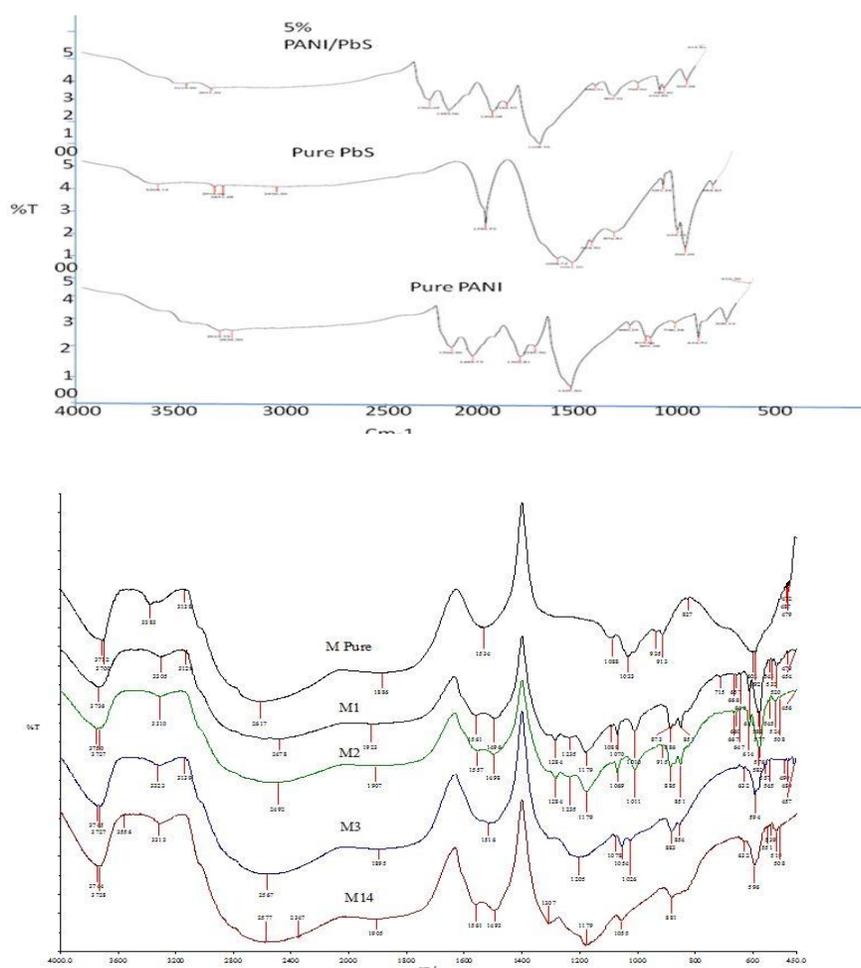
Where D is the average crystallite size (in nm), k is the shape factor having Value of 0.94,  $\lambda$ - X-ray wavelength ( $1.5418\text{\AA}$ ),  $\beta$  - width at half maximum.



**Figure 1:** XRD pattern of PANI/PbS and PANI/MnO<sub>2</sub> nanocomposites.

**FT-IR spectroscopy**

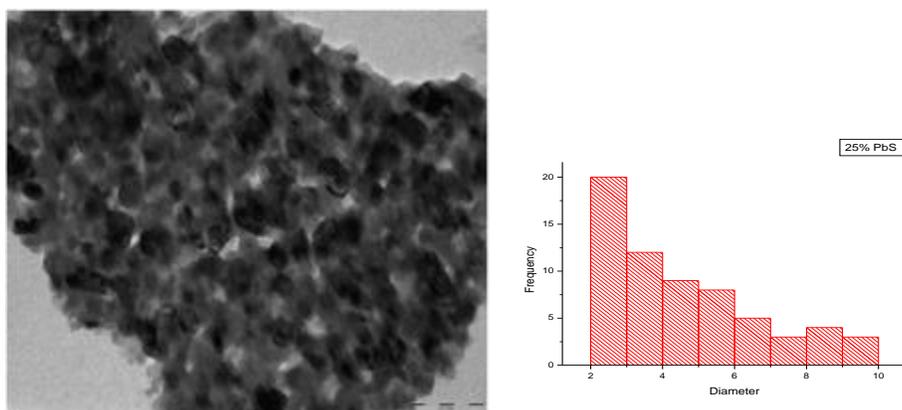
Figure 2, Shows Fourier transfer infra red spectra of bulk Polyaniline, PANI/PbS and PANI/MnO<sub>2</sub> nanocomposites with at different weight ratio. The vibration frequency observed at 509 cm<sup>-1</sup>, 888 cm<sup>-1</sup>, 1146 cm<sup>-1</sup>, 1245 cm<sup>-1</sup>, 1485 cm<sup>-1</sup> and 1566cm<sup>-1</sup>. The bands at 509 cm<sup>-1</sup> and 888 cm<sup>-1</sup> due to para distributed rings, respectively. A band appearing near 1245 cm<sup>-1</sup> represents the C–N stretching vibration [9]. The appearance of frequency bands in range 1450–1600 cm<sup>-1</sup> is non-symmetric stretching modes. The band at 1566 cm<sup>-1</sup> is for quinoid rings, while the lower bands 1485 cm<sup>-1</sup> is for benzenoid rings. The broad band observed at 3280–3500 cm<sup>-1</sup> is due to the N–H stretching. Thus the FTIR spectra peak clears the presence of PbS and MnO<sub>2</sub> nanoparticle in polymer matrix.



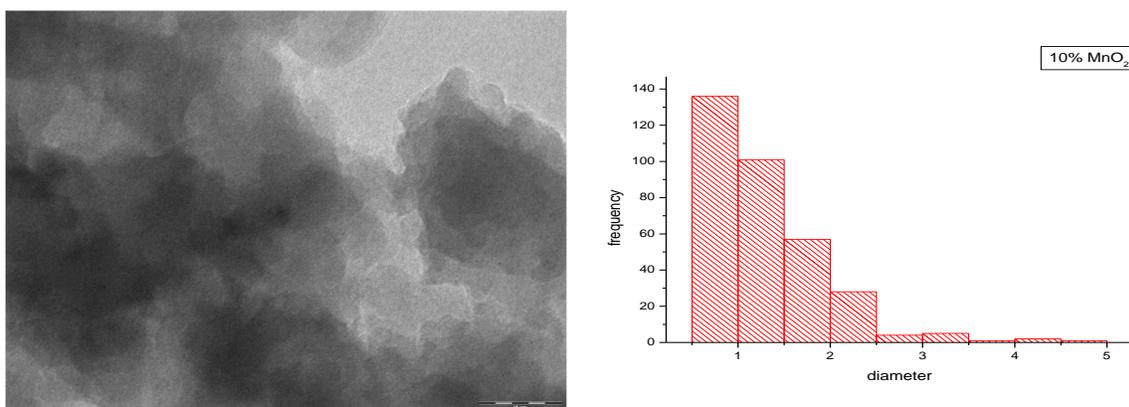
**Figure 2:** FT-IR Spectra of PANI/PbS and PANI/MnO<sub>2</sub> nanocomposite.

*TEM analysis of nanocomposites*

Figure 3 shows. The morphology of PANI/PbS and PANI/MnO<sub>2</sub> nanocomposites is found out based on the TEM images. The TEM image of PANI/PbS and PANI/MnO<sub>2</sub> nanocomposite observed in the Figure 3 synthesized in the aniline monomer to PbS and MnO<sub>2</sub> feed ratios. TEM images of the Nanocomposite shows that dark spot, with particular edge axis suggesting that the fillings of synthesized nanocomposite are not distributed uniformly. The morphology of all synthesized nanocomposites with different weight ratio shows dark spot at fixed edge which indicated the formation of PANI/PbS and PANI/MnO<sub>2</sub> nanocomposite with particle size are 100 nm in range [10]. The maximum information is not collected from the TEM micrograph of PANI/MnO<sub>2</sub> nanocomposite.



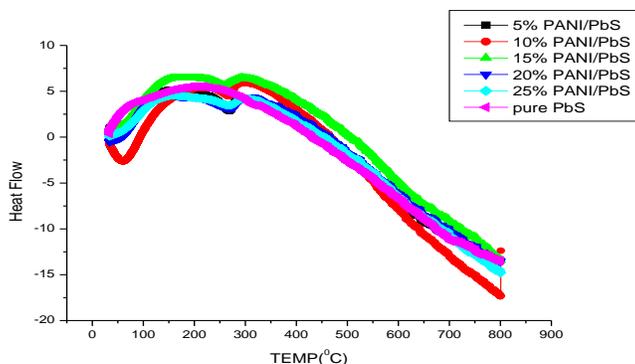
**Figure 3:** TEM images of PANI/PbS nanocomposites.



**Figure 4:** TEM images of PANI/MnO<sub>2</sub> nanocomposites.

## RESULT AND DISCUSSION

### DTA analysis of pure PANI and PANI/PbS nanocomposite.

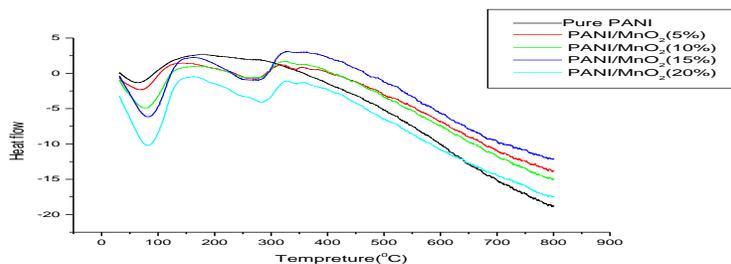


**Figure 5:** DTA analysis of Pure PANI and PANI/PbS Nanocomposite.

Figures 5 and 6 show differential thermal analysis of PANI/PbS (5-25%) nanocomposite. It indicated only endothermic peaks at about 230°C to 245°C due to the evaporation of water molecules. The curve change above 350°C due to the degradation of composite. The decreased onset value of temperatures from 284°C (pure PANI) to 242.59, 244.15, 233.06, 227.55 and 237.25°C for different wt ratio of PANI/PbS nanocomposite indicated good thermal stability of nanocomposite which attributed retardation effect of nanostructures PbS. The exothermic peak at 99-160°C is due to the series of chemical reactions [11]. Table 1 given below gives the information of thermal parameter of pure Polyaniline and nanocomposite. Some change in the melting temperature and enthalpy in PANI/PbS (5-25%) nanocomposite indicated miscibility with PANI matrix.

**Table 1:** Thermal parameter of pure PANI and nanocomposites

S. No	Materials	Melting Temp (°C)	Onset Temp (°C)	Enthalpy change (J/g)	Specific Heat ( $\Delta C_p$ (J/g*) (°C)	Peak area
1	Pure PANI	-	284	-	12.27	-
2	5% PANI/PbS	268.31	242.59	47.37	9.98	264.377
3	10% PANI/Pbs	267.88	244.15	34.46	6.52	167.613
4	15% PANI/PbS	256.81	233.06	30.4788	6.479	123.622
5	20% PANI/PbS	267.13	227.55	60.699	16.192	308.70
6	25% PANI/PbS	266.42	237.25	36.8611	9.405	152.234

DTA analysis of PANI/MnO<sub>2</sub> nanocomposite

**Figure 6:** DTA analysis of PANI/MnO<sub>2</sub> nanocomposite

Differential thermal analysis curve for PANI/MnO<sub>2</sub> shows an endothermic peak at 35°C to 120°C and an exothermic peak at 180-316°C. The endothermic for removal of water and exothermic for cross-linking reaction. From the Table 2 PANI/MnO<sub>2</sub> Nanocomposite show decreased in onset value of temperature indicated good interfacial interactions between the metal oxides with the bulk PANI matrix. This clearly indicated that the metal oxides nanomaterial absorbed maximum heat. Melting temperature in nanocomposite indicated the crystalline nature. Pure Polyaniline is amorphous in phase indicated by XRD. Some change in the melting temperature and enthalpy in PANI/MnO<sub>2</sub> (5-20%) nanocomposite indicated miscibility with PANI matrix [12].

**Table 2:** Thermal parameter of pure PANI and PANI/MnO<sub>2</sub> nanocomposites.

S. No	Material	Melting Temp (°C)	Onset Temp (°C)	Enthalpy Change (J/g)	Specific Heat (J/g*°C)	Peak Area (mJ)
1	5% PANI/MnO <sub>2</sub>	269.84	162.57	156.07	25.81	859.18
2	10% PANI/MnO <sub>2</sub>	281.83	203.77	152.63	27.472	918.17
3	15% PANI/mnO <sub>2</sub>	275.01	196.38	169.72	25.668	1753.54
4	20% PANI/MnO <sub>2</sub>	283.41	200.85	145.73	28.03	1396.72

## CONCLUSION

The synthesized of pure Polyaniline and nanocomposite using chemical synthesis with APS as oxidant. The XRD pattern of nanocomposite revealed the grain size of composite in the nanorange and it is in polycrystalline in nature. The FT-IR spectra of nanocomposite suggested that the metal oxides were well dispersed in the polymer matrix. The TEM study revealed the formation of agglomeration and little uniform distribution of Nano particles on the surface of PANI Matrix. The DTA analysis of nanocomposites clearly indicated the maximum thermal stability of PANI/PbS nanocomposite as compared to PANI/MnO<sub>2</sub> Nanocomposites.

## REFERENCES

1. Mickova, I., Ab-Durauf, P., Grcev T, Arsov L, Bulletin of the chemist and technologists of Macedonia, **2006**. 25 (1): 45-50.
2. RezaNabid M, et al., *Int. J. Electrochem. Sci.* **2008**. 3: 1117-1126.
3. Pawar, S.G., et al. Polyaniline: TiO<sub>2</sub> nanocomposites: Synthesis and characterization, *Arch. Appl. Sci. Res* **2010**. 2 (2):194-201.
4. Jianqiang, et al. Gold nanoparticles with special shapes: Controlled synthesis, surface-enhanced Raman scattering, and The Application in Biodetection, *Sensors* **2007**. 7: 3299-3311.
5. Olad, A., and Rashidzadesh, A., *Iranian Journal of Chemical Engineering*, **2008**. 5 (2).
6. Hafizuddin, M., et al. *Solid state science and Technology*, **2009**. 17 (1):126-131.
7. Zifeng, Y.L., *Journal of natural gas chemistry*, **2005**. 14: 35-39.
8. Moghaddam, AB., Synthesis of ZnO Nanoparticles and Electrodeposition of Polypyrrole/ZnO Nanocomposite Film, *Int. J. Electrochem. Sci.* **2009**. 4: 247-257.
9. Gangopadhyay, R., and De, A., Polypyrrole–ferric oxide conducting nanocomposites. I. Synthesis and Characterization. *Eur. Polym. J.* **1999**. 35.
10. Rodrigues, P.C., et al. Thermal treatment and dynamic mechanical thermal properties of polyaniline. *Polym.* **2002**. 43: 5493–5499.
11. Gospodinova, N., Terlemezyan, L., Microstructure and thermal behavior of poly (o-anisidine)/poly (ethylene terephthalate) composite, *Prog. Polym. Sci.* **1998**. 23: 1443.
12. Bhaiswar, JB., Dongre, SP., and Salunkhe, SP., *International Journal of Scientific And Research Publication*, January **2013**. 1: 2:2250-3153.