

## **Comparative Study on Thermal Stability and Optical Properties of PANI/CdS and PANI/PbS nanocomposite.**

J. B. Bhaiswar<sup>1</sup>, M. Y. Salunkhe<sup>2</sup>, S. P. Dongre<sup>3</sup>, B.T.Kumbhare<sup>4</sup>

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

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

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

[E-mail-jitendrabbhaiswar@yahoo.co.in](mailto:E-mail-jitendrabbhaiswar@yahoo.co.in).

**ABSTRACT:** PANI/CdS and PANI/PbS nanocomposite has been prepared using chemical oxidation technique. The prepared products were characterized by FT-IR, Transmission electron Microscopy, UV-Spectra and TGA thermogram. FTIR absorption band at  $415\text{ cm}^{-1}$  indicated the presence CdS and PbS nanoparticles in the polymer matrix. TEM showed the CdS and PbS particles are in nanorange with the average diameter of 21 nm. Thermo gravimetric analysis clearly indicated the increased in thermal stability of nanocomposite than the pure PANI. The appearance of characteristic absorption bands around 280, and 450 nm in the UV-Vis spectra confirms the formation of conducting emeraldine salt.

**Keywords:** nanocomposite, TEM, TGA, Polyaniline,

### **I. INTRODUCTION**

Among the conducting polymers, polyaniline (PANI) is under extensive study even today because of its high environmental stability, low cost, and relatively simple polymerization process [1-3]. Polymeric nanocomposites consisting of organic polymers and inorganic nanoparticles in a nanoscale regime represent a novel class of materials that have motivated considerable interest in recent years. This composite material differs from the pure polymer in respect to some of the physical and chemical properties and hence it is useful for many applications in different fields [4]. Among these materials, semiconductor-polymer nanocomposites have recently aroused much attention [5].

II-VI group semiconductor nanomaterials such as CdS, PbS, ZnS and CdSe have been studied extensively due to their strongly size-dependent optical and thermal properties. It is well known that nanocrystalline semiconductor exhibits quantum confinement effect and possesses properties that are different from the bulk molecules [6]. Nanocomposites of conducting polymers and metal nanoparticles have received considerable attention due to the potential possibilities to create suitable materials for electrocatalysis, chemical sensors and microelectronic devices [7]. The incorporation of metallic or semiconducting nanoparticles in conducting polymers such as polyaniline (PANI) is of interest because of the strong electronic interaction between the nanoparticles and the polymer matrix [8, 9]. Metal nanoparticles incorporated into conducting polymers are also known to enhance the conductivity of the polymers. Emeraldine base (EB) of polyaniline has been commonly used, as it is the most stable form of polyaniline. Enzymatic and gas-phase plasma have been utilized in the synthesis of polyaniline [10-13]. We know that CdS nanoparticles are n-type semiconductors while PANI is a p-type semiconductor. It is therefore expected that useful photo conducting nanocomposites can be created by combination of PANI and CdS nanoparticles [14]. In our present investigation we have selected polyaniline among different conducting polymers because of its simple synthesis procedure, good environmental and thermal stability, low cost price, high conductivity and which also exhibits good electrical, optical, magnetic and chemical properties. In the present work we also focus on the comparative study of PANI/CdS and PANI/PbS nanocomposite on thermal and optical properties.

### **II. MATERIALS AND METHODS**

All chemicals used in this investigation were of analytical reagent grade and used as received. Only aniline was distilled prior to use.

#### **2.1. Synthesis of Polyaniline via chemical oxidative polymerization:**

Polymerization was carried out by the chemical oxidation of aniline in the presence of  $\text{H}_2\text{SO}_4$  and APS (Ammonium persulphate) in 100ml distilled water both played the role as dopant and oxidant respectively. (0.4 mol) APS was dissolved in 100ml distilled water in a four-neck round bottom reaction flask and 0.4mol  $\text{H}_2\text{SO}_4$  is also added under mechanical stirring for 2 hours. Aniline (0.4 mol) was stirred with 0.4mol of  $\text{H}_2\text{SO}_4$  in 100ml distilled water. The solution of APS in  $\text{H}_2\text{SO}_4$  was then added drop-wise in the solution of aniline with vigorous stirring on a magnetic stirrer for 3 hours to initiate the aniline polymerization. The reaction was later carried out at room temperature for 6-7 hours with stirring. A dark green

colored PANI suspension was obtained with precipitation. The synthesized PANI was obtained as finely dispersed particles, which were recovered from the polymerization mixture by centrifugation and washed with deionized water repeatedly until the washing liquid was completely colorless. Finally, the mixture was filtered using filtered assembly. After keeping overnight, the dark gray color precipitate was obtained. A precipitate of polyaniline was dried under at 60 – 80°C for more than 8 hours.

### 2.2. Synthesis of PANI-Cds and PANI-PbS Nanocomposites:

The synthesis steps of PANI/Cds and PANI/PbS nanocomposite are similar to the synthesis method of PANI. Different amount of Cds and PbS were dispersed into the APS solution and stirred for 1 hour prior to the addition of aniline. Aniline (0.4 mol) stirred with 0.4mol H<sub>2</sub>SO<sub>4</sub> in 100 ml of distilled water were added drop-wised using burette into the APS-Cds and PbS solution and stirred vigorously to form homogeneous dispersion. Characterizations:

Fourier Transform Infra Red (FTIR) spectroscopy (Model: Perkin Elmer 100) of PANi: Cds and PbS nanocomposite was studied in the frequency range of 400–4000 cm<sup>-1</sup>. TGA thermograms of all samples were recorded on Perkin- Elmer Diamond TGA/DTA in argon atmosphere at a heating rate of 10°C/ min. TEM micrographs of synthesized CdS and PbS were taken on Transmission Electron Microscope PHILIPS model-CM200 with resolution 2.4Å The UV–Vis absorption spectra of the solutions were recorded on a Perkin-Elmer Lambda 35 spectrophotometer in the wavelength range 300–800 nm.

## III. RESULT & DISCUSSION

### 3.1. The FT-IR spectra:

Fig 1. Shows the FT-IR spectra PURE PANI, PANI/CdS & PANI/PbS nanocomposite. PANI samples show specific stretching vibrations for the different structural forms of PANI. The specific groups of PANI and their IR vibration frequencies from the literature are given below:

1. Absorption band near 2900 cm<sup>-1</sup> is assigned to aliphatic C–H stretching of the Polymer
2. Quinonoid ring - 1587 cm<sup>-1</sup>, Benzenoid ring - 1510 cm<sup>-1</sup>
3. C-N stretching - ~1380 cm<sup>-1</sup>
4. Combination modes of benzenoid and quinonoid unit - 1150 cm<sup>-1</sup>
5. SO<sub>3</sub> stretching frequency of the various dopant acids - 1100 cm<sup>-1</sup>
6. Weak absorption band for PbS and CdS -415 cm<sup>-1</sup>

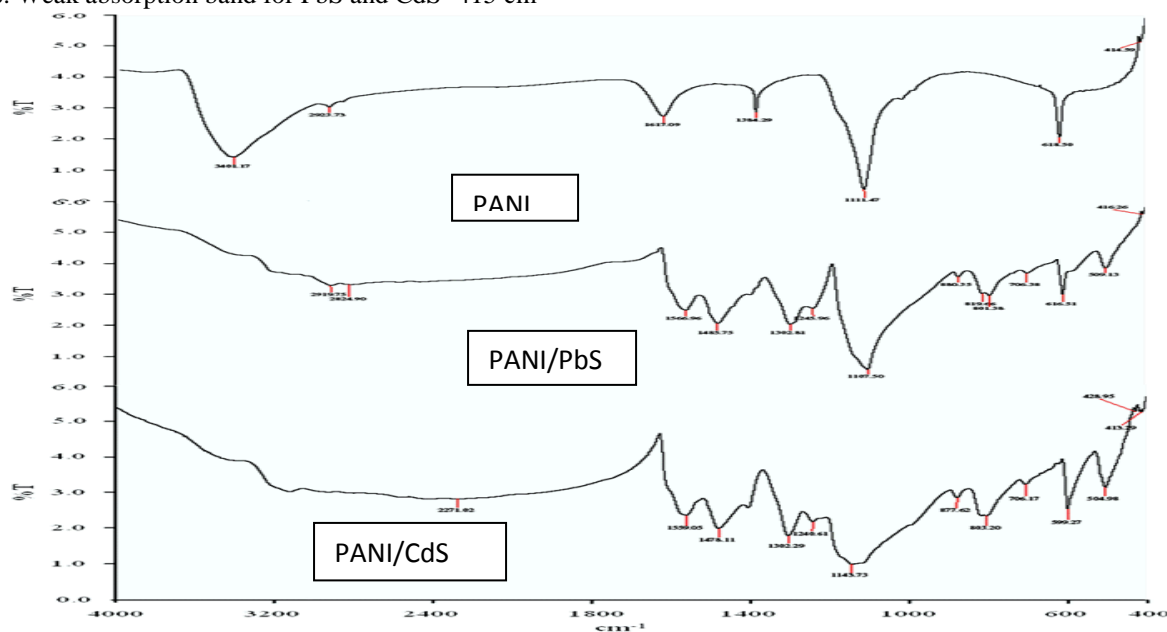


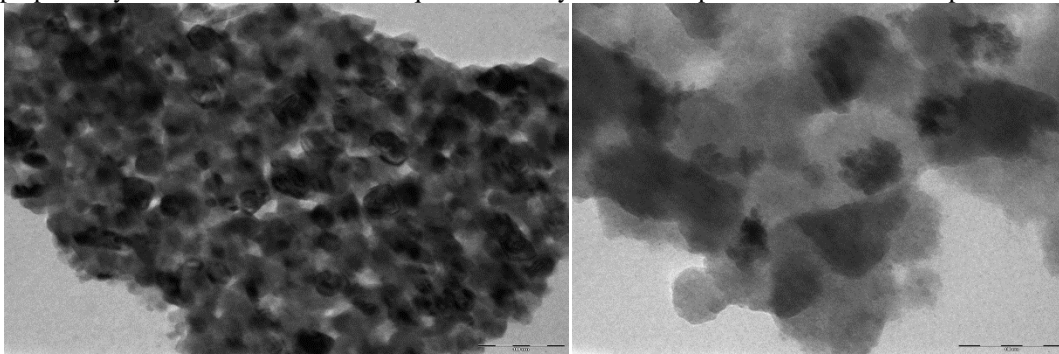
Fig.1.FT-IR spectra of PANI/CdS, PANI/PbS and Pure PANI.

All the spectra show the characteristics band of PANI. Thus, the IR study clearly indicates that PbS and CdS are definitely incorporated into the polymer matrix.

### 3.2. TEM ANALYSIS:

Figure 2(a) and 2(b) represent the TEM micrographs of synthesized PbS and CdS respectively, which clearly indicate the formation of particles of size less than 21 nm. Fine nanoparticles of PbS are clearly seen in

the images as compared to that of CdS. These images reveal the formation of nanocomposite of PbS and CdS as prepared by chemical oxidation technique and clearly shows fine particles of PbS as compared to that of CdS.



2(a) TEM of PANI/PbS

2. (b)TEM of PANI/CdS

**3.3. UV-SPECTRA:**

The UV-Vis absorption spectra of the pure PANI and PANI/CdS and PANI/PbS nanocomposites prepared by the microemulsion technique are shown in Fig. 3(a) &3(b). The existence of two characteristic absorption bands around 280, & 450 nm confirms the formation of doped PANI and comparable to the known spectral features of precisely characterized redox species of PANI [15]. The absorption maximal at 280 nm is due to the  $\pi * -\pi *$  transition within the benzenoid segment. The second shoulder-like absorption band at 450nm is attributed to the doping level of PANI.

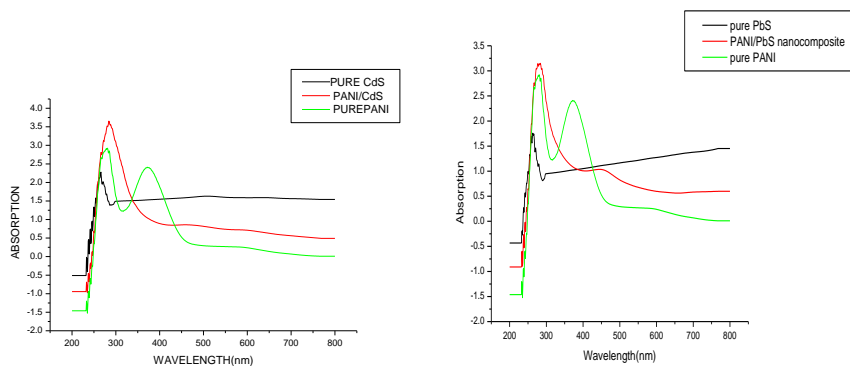


Fig.3(a) UV of PANI/PbS

3(b).UV of PANI/CdS

As CdS and PbS were incorporated with PANI [Figs. 3(a) and (b)], the characteristic peak assigned to the doping level of the PANI chain shifted to longer wavelengths, indicating the interaction between quinoid rings and PbS and CdS. The  $\pi-\pi^*$  transition of PANI in the nanocomposites was also shifted to longer wavelengths.

**3.4. TGA ANALYSIS:**

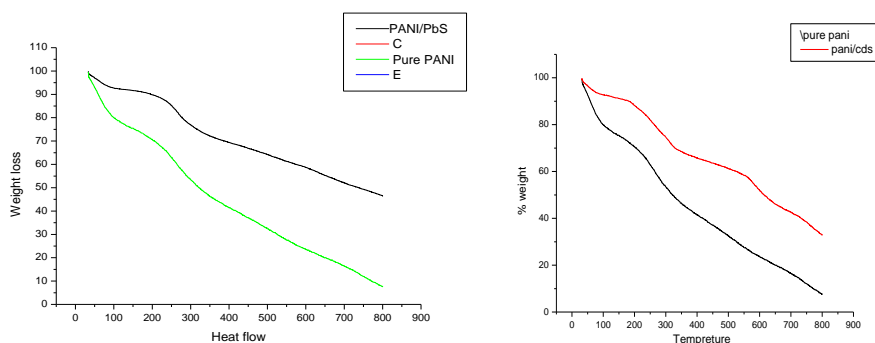


Fig.4(a) TGA of PANI/PbS

4(b). TGA of PANI/CdS

The TGA thermograms of PANI-CdS and PANI-PbS nanocomposites are shown in fig.4 (a) and fig.4 (b) respectively. It was observed that a PANI/CdS and PANI/PbS nanocomposite shows weight loss of 12 to 7% at

120°C which is less than PANI. Similarly it shows second stage of degradation between 150-300°C. Above 300°C, polymer degradation takes place slowly up to 800°C unlike pure PANI which almost degrades at 800°C. A remarkable feature of PANI shows that almost 91% weight loss at 800°C. Also it was observed that as the weight % of CdS/PbS nanoparticles increases in PANI matrix, this residue goes on increasing. As the weight % of CdS and PbS increases in the PANI matrix, the % residue goes on increasing which is 36% for PANI-CdS (5%) and 42% for PANI-PbS (5%) nanocomposites. The TGA studies point out the inference that, PANI-CdS and PANI-PbS nanocomposites are thermally more stable than PANI salt. Again if we compare the results of both the composite, it was found that PANI-PbS nanocomposites are thermally more stable than PANI-CdS nanocomposites.

#### IV. CONCLUSIONS

Polyaniline-coated cadmium sulphide and Lead sulphide nanocomposites have been synthesized by chemical oxidation technique. The appearance of characteristic absorption bands around 280, and 450 nm in the UV-Vis spectra confirms the formation of conducting emeraldine salt. The concentration of the CdS and in nanocomposites was low as a very weak vibration absorption peak at  $415\text{ cm}^{-1}$  was observed in the FTIR spectrum. The average size of the nanocomposites is estimated to be 21 nm with Observed in the TEM micrograph. The thermal stability for the nanocomposites has been improved as major mass losses occurred at higher decomposition temperature as compared to the pure polymer in the TGA profile.

#### REFERENCES

- [1]. S. H. Lee, J. W. Yoon, and M. H. Suh, *Macromol. Res.*, 10, (2002), 282.
- [2]. W. Yin and E. Ruckenstein, *Synthetic Metals*, 108, (2000), 39.
- [3]. Y. Roichman, G. I. Titelman, M. S. Silverstein, A. Siegmann, and M. Nakris, *Synthetic Metals*, 98, (1999), 201.
- [4] Pfaendner R, 2010. Nanocomposites: Industrial opportunity of challenge *Polymer Degradation and Stability*, 95 (3): 369-373.
- [5] R. Vijaya Kumar, O. Palchik, Y. Koltypin, Y. Diamant, A. Gedanke, *Ultrason. Sonochem.* 9 (2002) 65.
- [6]. K.K. Nanda, S.N. Sarangi, S. Mohanthy, S.N. Sahu, *Thin Solid Films* 322 (1998) 21.
- [7]. Huang K, Zhang Y, Han D, et al., 2006. One-step synthesis of 3D dendritic gold/polypyrrole nanocomposites via a self-assembly method. *Nanotechnology*, 17 (1): 283-288.
- [8]. Smith JA, Josowicz M, Engelhard M, et al., 2005. Gold-polyaniline composites: Part II. Effect of nanometer sized particles. *Physical Chemistry Chemical Physics*, 7: 3619-3625.
- [9]. Smith JA, Josowicz M, Janta J, 2005. Gold-polyaniline composites: Part I. Moving electrochemical interface. *Physical Chemistry Chemical Physics*, 7: 3614-3618.
- [10]. S Bhadra, D Khastgir, N K Singha and J H Lee, "Progress in preparation, processing and applications of polyaniline" *Progress in Polymer Science*, vol. 34, no. 8, pp. 783-810, 2009.
- [11]. E. M. Genies, A. Boyle, M. Lapkowski and C. Tsintavis, "Polyaniline : A historical survey" *Synthetic Metals* vol.36, no.2, pp. 139-182, 1990.
- [12]. S. Kobayashi and A. Makino, "Enzymatic Polymer Synthesis: An Opportunity for Green Polymer Chemistry" *Chemical Reviews*, vol. 109, no. 11, pp. 5288-5353, 2009.
- [13]. D. Debamot, T. Merian and F. Poncin-Epaillard, "Film Chemistry Control and Growth Kinetics of Pulsed Plasma-Polymerized Aniline" *Plasma Chemistry and Plasma Processing* vol.31, no.1, pp. 217-231, 2011.
- [14]. Godowsky, D. Y. *Advances in Polymer Science* 153, 163-205, 2000.
- [15]. B. Wessling, *Synth. Met.* 85 (1997) 1313.