



MOSSBAUER, XRD AND THERMALLY INDUCED STRUCTURAL STUDIES ON POLYANILINE NANOCOMPOSITE MATERIAL CONTAINING DIFFERENT CONCENTRATION OF MAGNETITE NANOPARTICLE

A.K. Barve¹, S.M. Gadegone^{1*}, M. R. Lanjewar² and R.B. Lanjewar^{2*}.

^{1*}Kamla Nehru Mahavidyalaya, Sakardara, Nagpur 440009.

². Department of Chemistry, R.T.M. Nagpur University, Nagpur-440012

^{2*}. Dharampeth M.P. Deo Memorial Science College, Nagpur 440033.

E-mail: rb_lanjewar@rediffmail.com

Abstract

The Mössbauer Spectroscopy of magnetite nanoparticles embedded in a polymeric matrix of PANI was studied because it allows a good dispersion of nanoparticles in the polymeric matrix. All the concentration of iron salts shows quadrupole splitting and hyperfine splitting. From XRD study it is clear that the intensity of the peaks becomes stronger with increasing the nanoparticle loadings, while the two original peaks of PANI show a same intensity at $2\theta = 19.09$ and 25.04° . The properties studied by TGA indicate an improvement in thermal stability of PANI by the addition of different concentration of metal oxide.

Introduction:

IONPs are found naturally in the environment as particulate matter in air pollution and in volcanic eruptions. Either Fe_3O_4 (magnetite) or $\gamma\text{-Fe}_2\text{O}_3$ (maghemite), particles can be generated as emission from traffic, industry and power stations but can also be specifically synthesized chemically for a wide variety of applications. The mechanism for the incorporation of metal oxide into the polymer involves three steps:

- Before the reduction of metal nanoparticles, metal ions coordinate to the functional group of the polymers and form complexes.
- During the formation of zero valence metals (reduction) or metal oxides (oxidation), the particles coordinate weakly to the polymers after

the formation of the respective colloids, polymers act as stabilizers.

- The hydrophilic ends are adsorbed on the surface of the particles while the hydrophobic ends formed a barrier surrounding the metal particles to protect it.

The magnetite nanoparticles possess high surface area to volume ratio, induced dipole interaction and Vander Waal's attractive forces which cause the particles to aggregate¹. To overcome these limitations, it is important to shield the Fe_3O_4 nanoparticles by coating them with macrocyclic surfactant, polymers and inorganic metals².

Mössbauer Spectroscopy is known to be powerful, non-destructive technique for the determination of Fe^{2+} and Fe^{3+} ratios in nanoparticles as well as in polymer matrix. Mössbauer Spectroscopic study has been carried out at room temperature in order to get the information of hyperfine parameters of the magnetite nanoparticles. The peak position in a Mössbauer spectrum is sensitive to extra nuclear environment such that different compounds give different spectra attributable to hyperfine interaction, the interaction between the nuclear charge distribution and extra nuclear electric and magnetic fields. These hyperfine interactions give rise isomer shift (δ), quadrupole splitting (ΔE_Q) and magnetic Zeeman splitting (H_{eff}). From chemist's point of view, these three parameters are the most widely used in the study of structure and bonding characteristics of compounds.

Onset of degradation is increased by the addition of metal oxide. The series of all oxide materials shows first degradation of the compound at a temperature of 250°C-400°C. With increase in concentration of the metal salt, the degradation increases in nanocomposite material. However, the initial concentration of all oxide/PANI molecule also shows breakdown at a temperature above 550°C -650°C which is attributed to a large scale thermal degradation of the polyaniline chain. Such a complete degradation does not observe in higher concentration of oxide material.

In the present work, the iron salt solution has been directly added to the polymeric material via oxidative chemical polymerization. The synthesis by this method involves better interfacial contacts between the organic and inorganic phases and the system does not suffer from intercalation of high molecular polymer chains inside the oxide nanoparticles.

Preparation:

Aniline was purchased from Finar, INDIA. Other reagents as potassium peroxodisulphate, sodium hydroxide and sulphuric acid were of AR grade from Merck. Also ferric chloride hexahydrate and ferrous sulphate heptahydrate purchased from Himedia, INDIA. All these chemicals were used as received without any further purification.

a) For preparation of 0.1M Fe₃O₄-PANI nanocomposite system:

In a conical flask, 5ml aniline and 100ml 0.1M H₂SO₄ was taken. The solution was stirred for half an hour to get a clear and homogenous liquid. The glass beaker was placed in an ice-bath so that the addition of potassium peroxydisulfate takes place in cold condition. The concentration of potassium peroxydisulfate was 0.1M and 100ml of the oxidizing solution gradually added in aniline- H₂SO₄ solution for 30-40 minutes in cold condition. After addition of oxidation agent, the solution turns green in colour resulting in the formation of polyaniline in emeraldine form. In another beaker 10ml of 0.1M ferric chloride and 10ml of 0.05M ferrous sulphate was taken. Both the solution was prepared in HCl (1M) solution. The solution

was stirred for half an hour. After addition of 0.1M NaOH solution to the above reaction mixture, the solution turns black in colour. The oxide solution was then poured to the polyaniline solution. The green colour changes to black indicating the formation of the magnetite-PANI nanocomposites. The solution was stirred vigorously for 5-6 hours to obtain a homogenous mixture of the nanocomposite polymer. The solution was filtered, washed with double distilled water several times and dried in oven at 60°C for 2-3 hours.

Similarly, Fe₃O₄-PANI nanocomposites were prepared by taking ferric chloride of 0.2M, 0.3M, .04M, 0.5M and 0.6M.

Result and Discussion:

Fig. 1 spectra of Magnetite polyaniline nanocomposite material show doublet peak. These doublet peak are the source of two well-defined quadrupole splitting which corresponds to the Fe²⁺ and Fe³⁺ species of magnetite, respectively.

The spectrum of the Fe₃O₄-PANI nanocomposite is well fitted with two sextets, two of them are identified with the magnetite phase. Additional singlet histogram is observed in the higher concentration of iron salt. This singlet peak arises due to the distribution of the magnetite particles in the polymer molecules producing a slight separation of the nanoparticles, this happens due to the magnetism of the magnetite which makes the nanoparticles are held together³. The singlet that is observed in the sample corresponds to the superparamagnetic behavior (SP) caused by the interaction of the magnetite obtained by chemical oxidation polymerization in the PANI. The values of isomer shift, quadrupole splitting and hyperfine parameters obtained from the fitted data for various concentration of iron salts in PANI matrix are presented in Table 1. These results indicate a relationship with the atomic moment coupling of magnetite nanoparticles as magnetite nanoparticle aggregates are separated from each other by major amounts of PANI matrix which promotes randomness in their atomic/magnetic moments and thereby avoids the exchange forces which result in a superparamagnetic behavior.

Table 1The Mössbauer parameters of Fe₃O₄-PANI nanocomposite material:

| Composite Concentration (M) | Component | Isomer shift (mms ⁻¹) | Quadrupole splitting (mms ⁻¹) | Hyperfine Interaction (kOe) |
|-----------------------------|----------------------|-----------------------------------|---|-----------------------------|
| 0.1 | Fe ³⁺ (A) | 0.32 | 0.02 | 499 |
| | Fe ²⁺ (B) | 0.61 | 0.09 | 469 |
| 0.2 | Fe ³⁺ (A) | 0.27 | 0.05 | 486 |
| | Fe ²⁺ (B) | 0.69 | 0.01 | 455 |
| 0.3 | Fe ³⁺ (A) | 0.34 | 0.00 | 487 |
| | Fe ²⁺ (B) | 0.70 | 0.02 | 453 |
| 0.4 | Fe ³⁺ (A) | 0.30 | 0.04 | 490 |
| | Fe ²⁺ (B) | 0.70 | 0.21 | 455 |
| 0.5 | Fe ³⁺ (A) | 0.28 | 0.03 | 496 |
| | Fe ²⁺ (B) | 0.62 | 0.02 | 490 |
| 0.6 | Fe ³⁺ (A) | 0.26 | 0.03 | 488 |
| | Fe ²⁺ (B) | 0.70 | 0.11 | 467 |

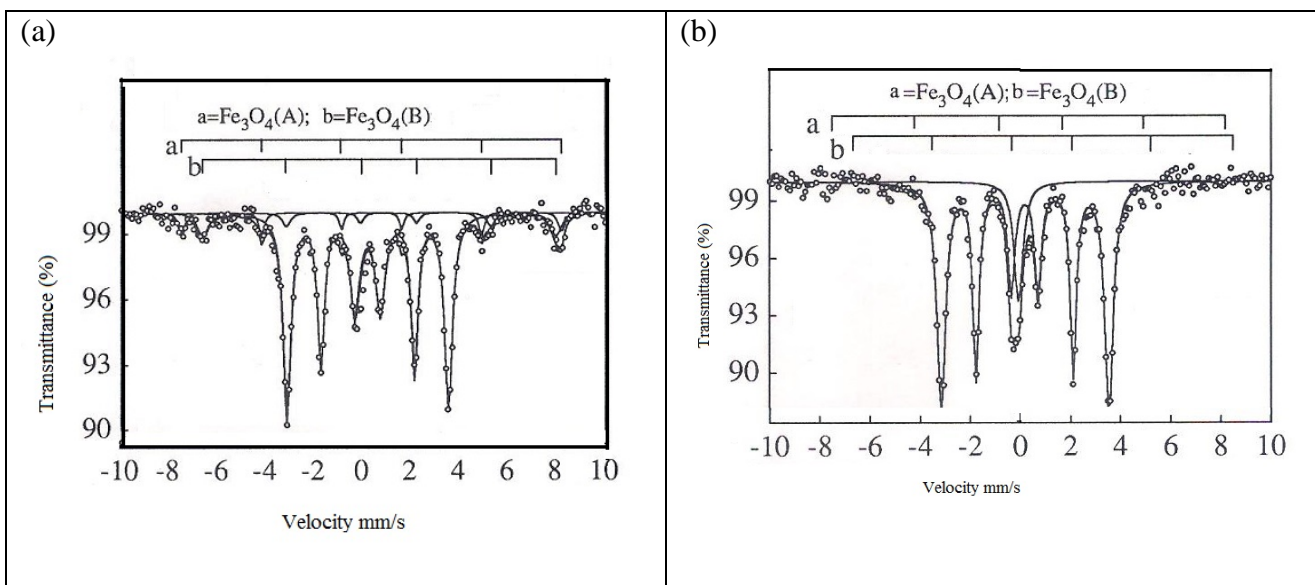
**Fig. 1** Mössbauer spectrum for Magnetite-PANI nanocomposite material**(a) 0.1 M Iron salt concentration****(b) 0.6 M iron salt concentration**

Fig. 2 shows the X-ray diffraction (XRD) patterns of PANI/Fe₃O₄ PNCs reinforced with different concentration of nanoparticle. The six different concentration of metal oxide in a polyaniline shows diffraction peaks at $2\theta = 19.09, 25.20, 35.57$ and 53.04° correspond to (100), (110), (311) and (422) crystallographic planes of the spinel phase of Fe₃O₄, respectively. The diffraction peak at 19.09 and 25.20° corresponds to polyaniline chain while the other two peaks corresponds to the magnetite molecule. The shift in the theta (θ) value is due to angle of deflection of molecule.

The average crystallite size can be estimated by XRD pattern, using the Scherrer Equation. The peak at $2\theta = 35.57^\circ$ is chosen to calculate the crystallite size & is found to be 21.77 nm.

Similar results are obtained in the nanocomposites of different oxide concentration, which is about 20.89 nm for 0.1M, 21.08 nm for 0.2M, 21.77 nm for 0.3 M, 21.77nm for 0.4 M, 21.97 for 0.5M and 21.90nm for 0.6M. The two broad peaks at $2\theta = 19.09$ and 26.04° correspond to the (100) and (110) crystallographic planes of the partially

crystalline PANI. This indicates a strong effect of the Fe_3O_4 NPs on the crystallization structures of PANI and the interaction between

PANI backbone and Fe_3O_4 nanoparticle's⁴. The above data matched with the JCPDF no.19-0629.

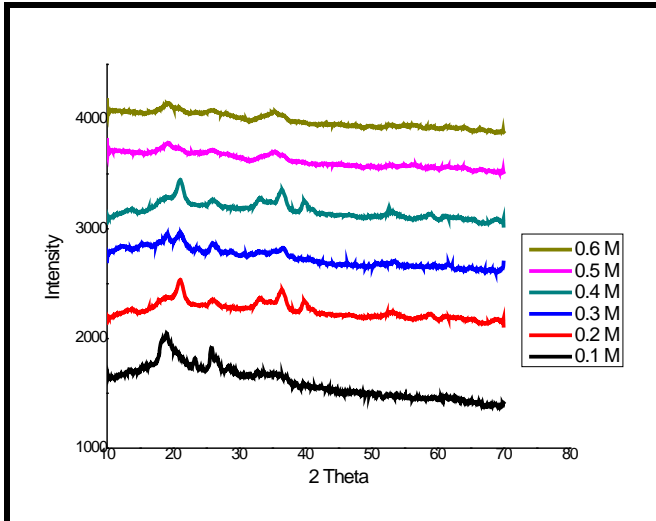


Fig. 2 XRD for Magnetite-PANI nanocomposite material

The thermogram of magnetite-PANI nanocomposites material is as shown in Fig.3a and 3b for 0.1M and 0.6M Fe salt concentration. In case of magnetite PANI, degradation start at 400°C and shows maximum degradation at 425°C incurring about 6.45mg of weight loss (found 6.67mg) which corresponds to the breaking of the organic moiety. Similarly, with increase in concentration the weight loss also increases and for 0.6M the weight loss is calculated to be 11.41mg (found 13.17mg).

Coats-Redfern method was used to study the kinetics of thermal degradation of PANI/MO composites⁵. The mechanisms of solid-state

thermal degradation reaction and corresponding thermal degradation functions $g(\alpha)$. $g(\alpha)=kt$

Activation energy (E) can be calculated from the slope of the curve and pre-exponential factor (A) using the intercept value of the plot of $\ln [g(\alpha)/T^2]$ against the reciprocal of absolute temperature (1/T). From the table given below it is clear that the activation energy of PANI increased with the addition of MO nanoparticles. Activation energy (E) obtained for 0.1M Magnetite/PANI is 64.38KJ/mole while for 0.6M it is 123.10KJ/mole. Significant increase in activation energy indicates high thermal stability.

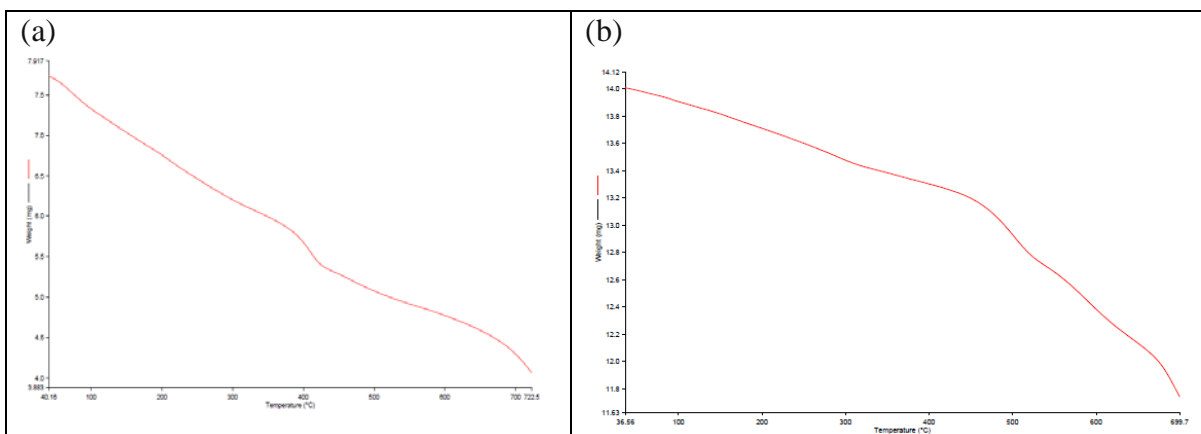
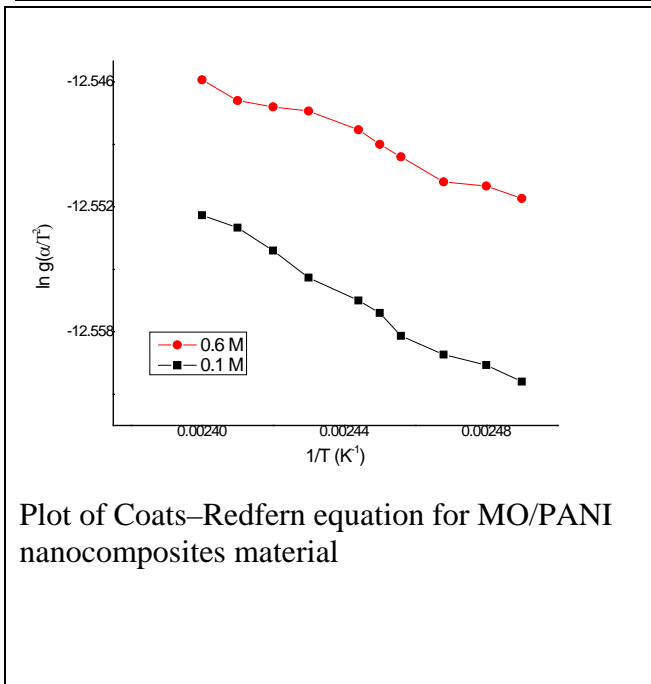


Fig. 3 Thermogravimetric analysis for Magnetite-PANI nanocomposite material

(a) 0.1 M Iron salt concentration

(b) 0.6 M iron salt concentration



Conclusion:

All the spectra show a well-developed magnetic hyperfine splitting nanocomposite materials, and no trace of superparamagnetic behavior was observed. XRD result indicates that Fe_3O_4 nanoparticles have been successfully incorporated on the surface of PANI matrix chain through the oxidative polymerization method. Thermal stability of PANI/metal oxide composites slightly increases with increase in the concentration of metal oxide. This shows that metal oxide has an interaction with the polymer molecule.

Reference:

1. Gupta, A. K., and Gupta, M., 2005, *Biomaterials*, 26, 3995–4021
2. Jeong, U., Teng, X. W., Wang, Y., Yang, H., and Xia, Y. N., 2007, *Adv Mater.*, 19, 33–60.
3. Cohen, R. L., 1976, Academic Press New York., 1, 226.
4. Qiu, G., Wang, Q., and Nie, M. 2006, *J. Appl Polym Sci.*, 102, 2107–2111.
5. Coats, A. W., and Redfern, J. P., 1964, *Nature*, 68, 201.