Magnetic Properties of Nanostructured Cobalt and Nickel Oxide Reinforced Polyaniline Composites

B. I. Nandapure[1], S.B.Kondawar[1], A.I .Nandapure[2]

[1]Department of Physics, RTM Nagpur University, Nagpur 440033, India
[2]B. D. College of Engineering, Sevagram, Wardha 442001, India

ABSTRACT

Cobalt oxide (Co_3O_4) and nickel oxide (NiO) nanoparticles were prepared by the simple approach of sol–gel process using starch as a capping agent and cobalt chloride and nickel carbonate as precursor. Conducting polyaniline-cobalt oxide (PANI/Co_3O_4) nanocomposites and polyaniline-nickel oxide (PANI/NiO) nanocomposites were synthesized by in-situ polymerization technique in sulphuric acid medium with ammonium persulphate as oxidizing agent in the presence synthesized nanoparticles of Co_3O_4 and NiO as reinforcing filler in different concentrations so as to study the effect of filler nanoparticles on magnetic behavior of the conducting polyaniline. The synthesized nanocomposites were characterized by XRD, TEM and VSM analysis. The X-ray diffraction (XRD) pattern and transmission electron microscopy (TEM) image shows that nanocrystalline Co_3O_4 and NiO embedded into polycrystalline PANI to form crystalline nanocomposites. VSM study shows that the synthesized NiO and Co_3O_4 are ferromagnetic whereas PANI is paramagnetic. The area of hysteresis loop of the nanocomposites increases with the weight percentage of Co_3O_4/NiO content in polymer matrix.

Keywords*:* conducting polymers; polyaniline; nanostructured cobalt oxide; nickel oxide, nanocomposites; VSM.

1. INTRODUCTION

Polymer nanocomposites (NCs) constitute a class of hybrid materials composed of a polymer matrix and an inorganic component, which has at least one dimension in the nanometer (<100 nm). To improve and extend the functions of these inorganic nanomaterials, one or more components are often incorporated to form multi-functionalized nanocomposites for various applications in the fields of electronics, sensors, catalysis, energy, electromagnetic interference (EMI) shielding, electrorheological (ER) fluids and biomedicine. Conducting polymer composites with nanostructures have attracted significant academic and technological attention because of their unique physical properties and potential applications in nanoelectronics, electromagnetic and biomedical devices [1-13]. Among these conducting polymer composites, materials decorated with inorganic nanoparticles are of particular interest because possible interactions between the inorganic nanoparticles and the polymer matrices may generate some unique physical properties upon the formation of various nanocomposites. Therefore, herein, an attempt has been made to generate novel NC intriguing magnetic properties by encapsulating the inorganic nanoparticles with PANI matrix. Among the extensively studied conducting polymers, polyaniline (PANI) is regarded as the most important and promising one due to the low cost of its monomer, it's easy preparation, its higher conductivity, and other relevant properties in such application fields as chemo-or biosensors, electromagnetic shielding, anticorrosion, electrode materials for secondary batteries, electro chromic devices, and membrane separations [14]. To obtain materials with synergetic advantage between PANI and inorganic nanoparticles, various composites of PANI with inorganic nanoparticles such as CeO_2, TiO_2 [15-18], $BaTiO_3$, MoO_3, SnO_2, Fe_3O_4 [19-20] Co_3O_4, NiO, ZnO [21], PANI-CNT [22-24] are reported. When nanoscopically sized filler particles are magnetic in polymer matrix, then such nanocomposites show enhance magnetic and transport properties due to low dimensional magnetic system and high organic conductor. Magnetic materials based on cobalt oxide and nickel oxide has attracted a great interest in view of their technological and fundamental scientific importance. We present here the preparation of Co_3O_4 and NiO nanoparticles by a simple sol-gel approach of sol-gel method and used it for the preparation of nanocomposites. Cobalt and nickel oxides are important materials that find applications in different fields such as catalysis, gas sensors, NiMH batteries, smart glazing and switch able mirrors as an electrochromic material, as an electrode in molten carbonate fuel cells, mobile phones, cars and toys. In this paper we report the synthesis, characterization and effect of cobalt oxide and nickel oxide as nanosized filler on the magnetic behavior of the conducting polyaniline composites.

2. EXPERIMENTAL

2.1. *Materials and methods*

Aniline (99%), cobalt chloride (99%) and nickel carbonate (99%) were purchased from Merck. Aniline was distilled before use for polymerization. Ammonium persulphate (APS) (99%) was purchased from Qualigens Fine Chemicals. Other supplement chemicals were of AR grade and used as received.

X-ray diffraction (XRD) analysis was conducted on Philips PW1710 automatic X-ray diffractometer with Cu-K_α radiation (λ=1.5404Å), with a scanning speed of $10°min^{-1}$. TEM analysis of all nanocomposites was carried out on Phillips model-CM200 with resolution 2.4Å. The magnetization measurements of all synthesized samples were carried out using vibrating sample magnetometer (VSM) Lakeshore-3107 model at room temperature in the magnetic field range $\pm$ 8000Oe.

2.2. *Synthesis of Co_3O_4 and NiO nanoparticles*

Cobalt oxide (Co_3O_4) nanoparticles were prepared by the simple approach of sol–gel process [25] in which 0.1M cobalt chloride (precursor) was added to 1gm starch solution and then stirred the solution for 30 minutes. Prepared solution was hydrolyzed by NaOH under constant stirring at room

temperature for 2 hours. The solution was kept overnight and then filtered using membrane filtration assembly, washed using deionized water and ethanol to remove the impurities and then dried at 80°C in hot air oven. Dried sample was treated at different temperatures in order to maintain the stability of compound. The colour of the Co_3O_4 was changed from dark green to black at 100°C to 750°C respectively. This cobalt oxide is used to prepare PANI/Co_3O_4 and PANI/NiO nanocomposites. Similarly nickel oxide nanoparticles were prepared by this process in which 0.1M nickel carbonate used as precursor and colour was changed from faint green to blackish gray at 100°C to 750°C respectively [26].

2.3. *Synthesis of PANI/Co_3O_4 nanocomposites and PANI/NiO nanocomposites*

The PANI/Co_3O_4 and PANI/NiO nanocomposites were prepared by an in-situ chemical oxidation polymerization of aniline using APS as an oxidant in presence of Co_3O_4 and NiO nanoparticles at room temperature in air [27-28]. In a typical procedure, Co_3O_4 nanoparticles was suspended in 1 M H_2SO_4 solution and sonicated for 1 h to reduce aggregation of Co_3O_4 nanoparticles.

The 0.1 M of aniline was dissolved in 100 ml of 1 M H_2SO_4 solution and then mixed with 10 ml of sonicated Co_3O_4 nanoparticles by further sonication for 30 min. The 100 ml of 1 M H_2SO_4 solution containing the APS ($(NH_4)_2S_2O_8$) with an equal molar ratio to aniline was then slowly added drop wise to well dispersed suspension mixture for 2 h with a continuous stirring. After 3 h, a good degree of polymerization was achieved and the blackish green precipitate was recovered. The solution was left in undisturbed position for a night for the completion of chemical reaction. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M H_2SO_4 and dried under vacuum for 24 h. The composite powder thus obtained were conductive emeraldine salt (ES) form of PANI/Co_3O_4. Similarly process has been done for PANI/NiO nanocomposites in which NiO nanoparticles used as reinforcing filler. The different contents PANI/Co_3O_4 and PANI/NiO nanocomposites were synthesized using 5, 10, 15, 20 weight % of Co_3O_4 and NiO with respect to aniline monomer.

3. RESULTS AND DISCUSSION

Figure 1a and 1b shows typical XRD patterns of PANI, Co_3O_4, PANI/Co_3O_4 nanocomposites and NiO, PANI/NiO nanocomposites. XRD pattern of prepared Co_3O_4 and NiO reveals that XRD peaks can be indexed as those of cubic structure with lattice constant 8.06Å and 4.14 Å in accordance with the JCPDS file (80-1537) of Co_3O_4 and JCPDS file (4-835) of NiO respectively. Grain sizes of the Co_3O_4 and NiO crystallites were determined using the Scherer's formula and found to be 14 nm and 23nm [29-30]. The pure PANI powder exhibits two broad peaks at 2θ angles around 20.4° and 26.1°, which indicates the PANI has some degree of crystallinity. These peaks may be assigned to the scattering from PANI chains at interplanar spacing.

While, the characteristic peaks of PANI shifted to higher angles in the XRD pattern of PANI/Co_3O_4 and PANI/NiO nanocomposite for the interaction of PANI chains with Co_3O_4 and NiO nanoparticles. XRD study suggests that during in-situ polymerization of aniline, PANI undergoes interfacial interactions with Co_3O_4 and NiO crystallites and loses its own morphology by coating over Co_3O_4 and NiO crystallites [31].

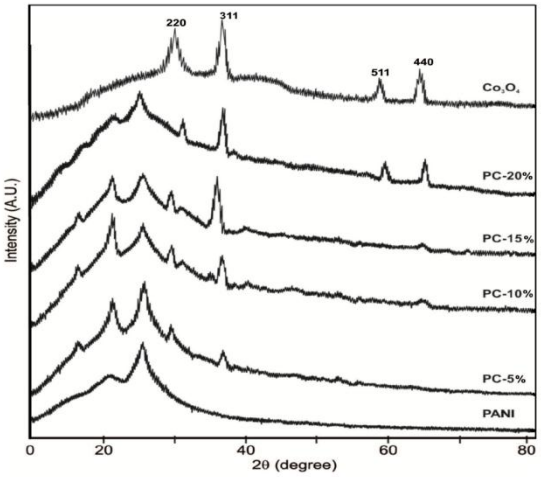

Fig.1a: XRD spectra of Co_3O_4 and PANI/Co_3O_4 nanocomposites

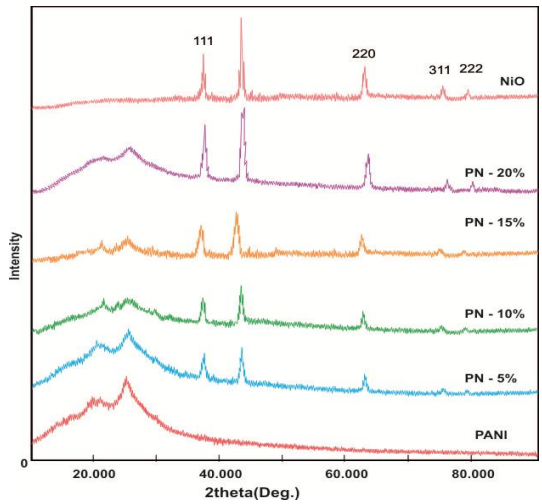

Fig.1b: XRD spectra of NiO and PANI/NiO nanocomposites

Figure 2(a), (b), (c) and (d) shows TEM image of Co_3O_4, PANI/Co_3O_4 (15%) nanocomposites and NiO, PANI/NiO (15%) nanocomposites respectively. From the image of Co_3O_4 and NiO nanoparticles, it is clearly seen that the Co_3O_4 and NiO nanoparticles are mostly irregularly shaped. The size of these particles has a distribution ranging from 10 to 50nm. PANI/Co_3O_4 (15%) and PANI/NiO (15%) nanocomposites exhibit similar shape as that of Co_3O_4/NiO nanoparticles with some aggregation as a result of aniline polymerization and growth encircled the Co_3O_4/NiO nanoparticles which are uniformly dispersed within the polymer matrix [32-34].

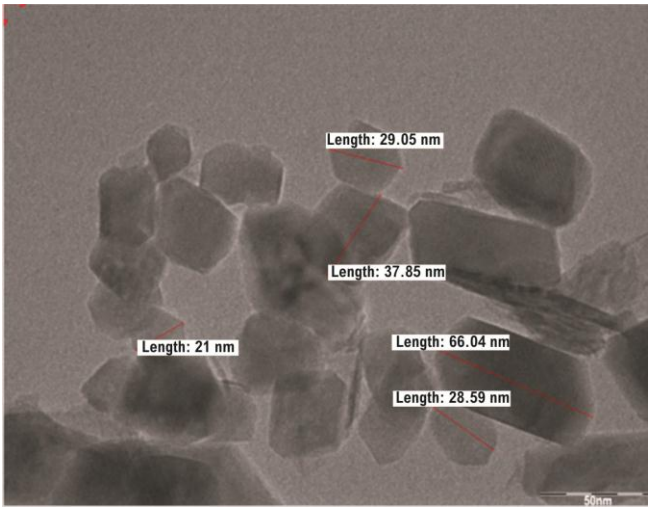

Fig. 2(a): TEM image of Co_3O_4

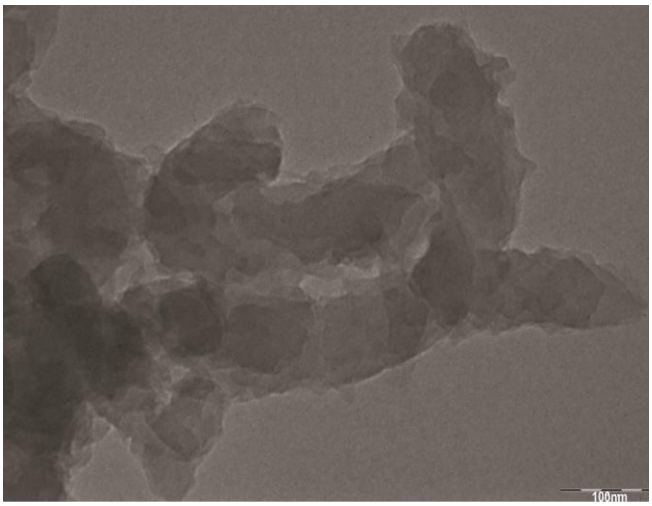

Fig. 2(b): TEM image of PANI/Co_3O_4 (15%) nanocomposites

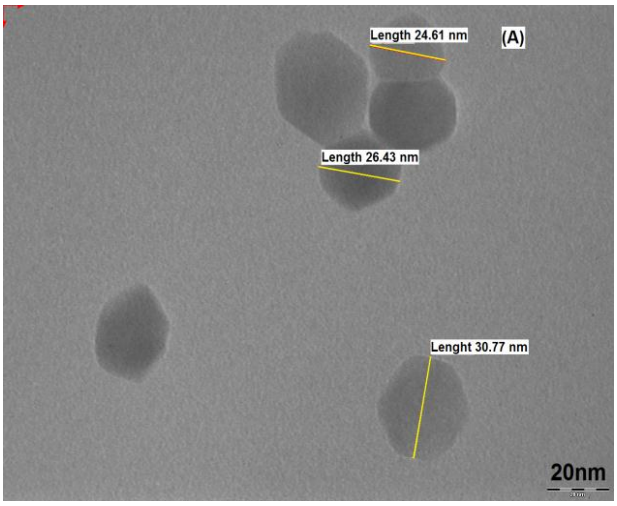

Fig. 2(c): TEM image of NiO

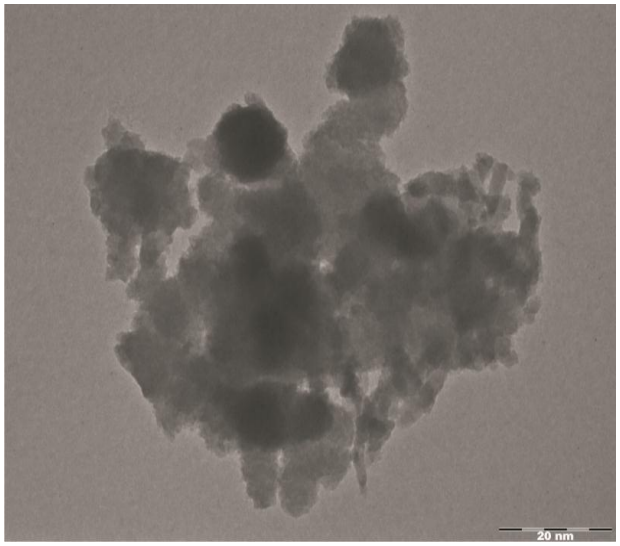

Fig. 2(d): TEM image of PANI/NiO (15%) nanocomposites

Figure 3a, 3b, 3c and 3d shows a typical hysteresis loop obtained at room temperature for PANI, Co_3O_4, PANI/Co_3O_4 nanocomposites and NiO, PANI/NiO nanocomposites. Saturation magnetization (*Ms*) for cobalt oxide and nickel oxide were found to be 0.907 emu/g and 1.19emu/g with coercive field (*Hc*) 401.66 Oe and 452.66Oe and remanent magnetization (*Mr*) at 85.95 $x10^{-3}$ emu/g and 98.4$x10^{-3}$ emu/g indicating that pure Co_3O_4 and NiO are ferromagnetic in nature. *Ms* and *Mr* for PANI were found to be 0.25 emu/g and 5.70 $x10^{-3}$ emu/g without the hysteresis loop indicating paramagnetic as shown in inset [35-36]. Co_3O_4/NiO nanoparticle shows hysteresis loop at room temperature due to small particle size and increasing tendency of uncompensated moments at the disordered particle surface resulting from the reduced coordination of the surface spins. That means, favorable conditions for ferromagnetic ordering (or spin uncompensation) develop gradually with decrease in particle size.

PANI/Co_3O_4 and PANI/NiO nanocomposites shows a small hysteresis loop leads to ferromagnetism and area of hysteresis loop depending on concentration of Co_3O_4/NiO in PANI matrix. The SQR for nanocomposites are reported in table 1(a) and 1(b), which shows that composites do not have the properties of a recording medium as like pure Co_3O_4/NiO but are good conductors as compared to Co_3O_4/NiO. Such materials are finding applications as soft magnetic materials.

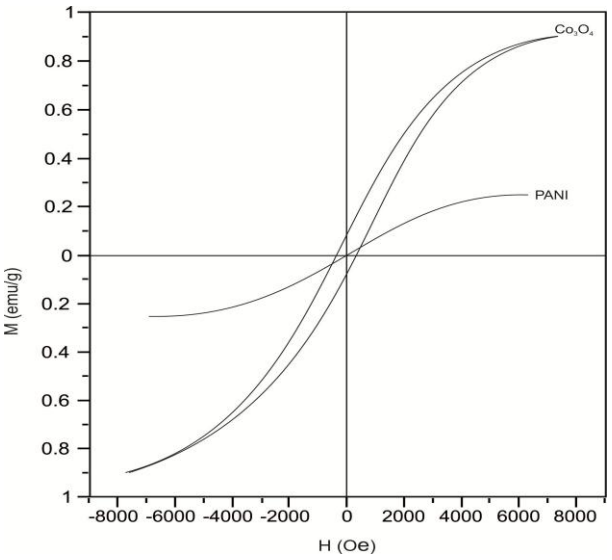

Fig.3a: Variation of magnetization with applied field of PANI and Co_3O_4

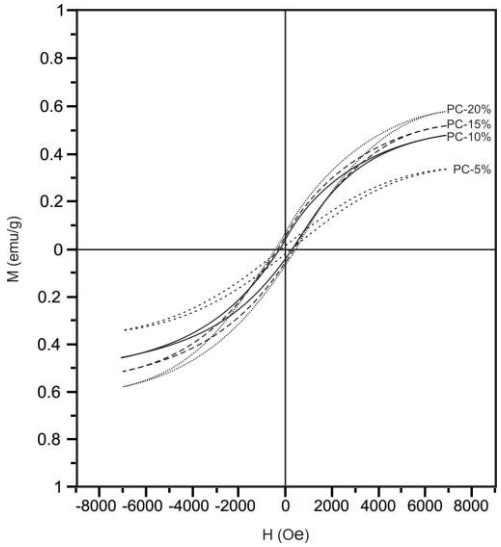

Fig.3b: Variation of magnetization with applied field of PANI/Co_3O_4 nanocomposites

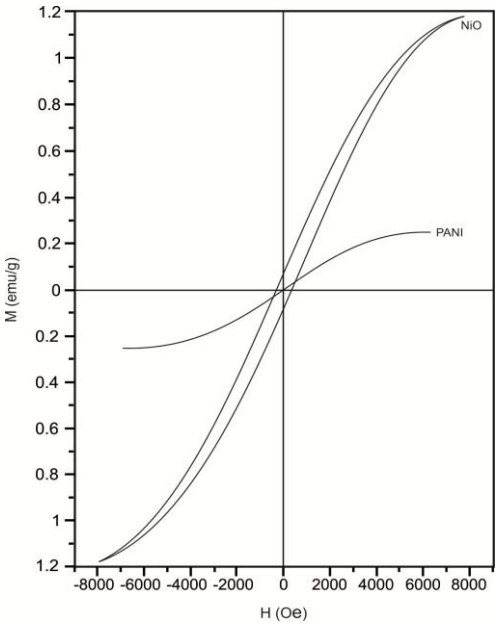

Fig.3c: Variation of magnetization with applied field of PANI and NiO

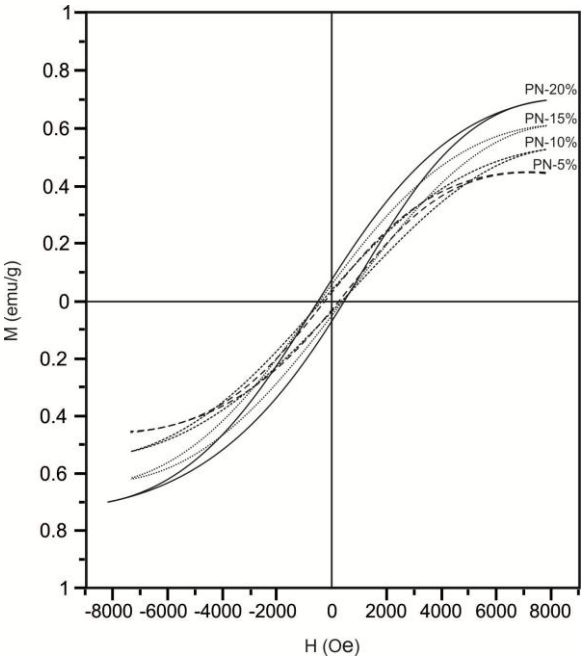

Fig.3d: Variation of magnetization with applied field of PANI/NiO nanocomposites

Table1a. Magnetic parameters of Co_3O_4 and PANI/Co_3O_4 nanocomposites

Materials	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	SQR
PANI	0.25	5.7×10^{-3}	-----	22.8×10^{-3}
Co_3O_4	0.90	85.9×10^{-3}	401.66	95.5×10^{-3}
PC-5%	0.34	30.5×10^{-3}	225.85	89.7×10^{-3}
PC-10%	0.47	42.7×10^{-3}	274.93	90.8×10^{-3}
PC-15%	0.52	51.9×10^{-3}	309.19	99.8×10^{-3}
PC-20%	0.58	57.2×10^{-3}	340.96	98.6×10^{-3}

Table.1b. Magnetic parameters of PANI, NiO and PANI/NiO nanocomposites

Materials	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	SQR
NiO	1.19	98.4×10^{-3}	452.66	82.68×10^{-3}
PN-5%	0.45	39.5×10^{-3}	238.48	87.7×10^{-3}
PN-10%	0.53	45.4×10^{-3}	296.46	85.6×10^{-3}
PN-15%	0.61	56.3×10^{-3}	312.12	92.2×10^{-3}
PN-20%	0.7	68.2×10^{-3}	352.16	97.4×10^{-3}

4. CONCLUSION

PANI/Co_3O_4 and PANI/NiO nanocomposites were successfully prepared by in-situ polymerization. XRD pattern of pure Co_3O_4 and NiO nanomaterials reveals cubic phase and PANI reveals polycrystalline nature. The average particle size of Co_3O_4 and NiO determined from XRD spectra using Debye-Scherer formula were found to be 14nm and 23nm respectively. From XRD study of nanocomposites, PANI undergoes interfacial interaction with Co_3O_4/NiO crystallites and shows the peaks of pure oxides as well as PANI. TEM image of PANI/Co_3O_4 and PANI/NiO nanocomposite shows that the nanoparticles are uniformly dispersed within the polymer matrix. VSM study shows that the synthesized Co_3O_4 and NiO are ferromagnetic whereas PANI is paramagnetic. The area of hysteresis loop of the nanocomposites increases with the weight percentage of Co_3O_4/NiO content in polymer matrix.

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