Thermal and DC Conductivity Study on Polyaniline/$NiFe_2O_4$ Nano Composites

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Abstract— Polyaniline–$NiFe_2O_4$ nanocomposites (PANI–NiFe2O4) with different contents of $NiFe_2O_4$ were prepared via in situ chemical oxidation polymerization, while the nanoparticles nickel ferrite were synthesized by sol–gel method. The prepared samples were characterized using some techniques such as scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Moreover, the electrical conductivity and sensor properties of the nanocomposites were investigated. The SEM images of the composites showed different aggregations for the different nickel ferrite contents. while the thermal analyses indicated an increase in the composites stability for samples with higher $NiFe_2O_4$ nanoparticles contents. The electrical conductivity of PANI–$NiFe_2O_4$ nanocomposite was found to increase with the rise in $NiFe_2O_4$ nanoparticle content, probably due to the polaron/bipolaron formation.

Keywords: TGA, SEM, Thermal and DC Conductivity

I. Introduction

For many years chemists and physicists have striven to synthesize organic materials with both conducting and ferromagnetic properties due to their potential applications in batteries, electricalmagnetic shields, sensors and microwave absorbents [1–3]. Several approaches such as electrochemical and in-situ chemical polymerizations have been reported to prepare conducting polymer with ferromagnetic property [4–6].

Polyaniline can be easily prepared either chemically or electrochemically from acidic aqueous solutions. The chemical method has a large significance because it is very reasonable method for the mass production of PANI. The most common preparation method is by oxidative polymerization with ammonium peroxodisulfate as an oxidant. Ferrites belong to a special class of magnetic materials, which have a wide range of technological applications. Due to their low cost, ferrite materials are used in various devices like microwave, transformer cores, magnetic memories, isolators, noise filters, etc.[7-10]. The spin-glass state in ferrites exhibits the most interesting magnetic property that causes high field irreversibility, shift of the hysteresis loops, and anomalous relaxation dynamics.
Nickel ferrite ($NiFe_2O_4$) is one of the most important spinel ferrites that have been studied. Stoichiometric $NiFe_2O_4$ considers as n-type semicoductor. It exhibits different kinds of magnetic properties such as paramagnetic, superparamagnetic or ferrimagnetic behavior depending on the particle size and shape. Also, it exhibits unusual physical and chemical properties when its size is reduced to nano size.

II. Experimental procedure

A. *Chemical Synthesis of Polyaniline*

The synthesis was based on mixing aqueous solution of aniline hydrochloride and ammonium persulphate at room temperature, followed by the separation of PANI hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equi molar volume of aniline and hydrochloride acid) was dissolved in distilled water in a volumetric flask to 100 ml of solution. Ammonium persulphate (0.25M) was dissolved in water also to 100ml of solution.Both solutions were kept for 1 hour at room temperature, then mixed in a beaker, stirred with a mechanical stirrer, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter, washed with 0.2 M HCL, and similarly with acetone. Polyaniline hydrochloride powder was dried in air and then in vacuum at 60°C for 24 hours. Polyaniline prepare under these reaction and processing conditions are further referred to as "standard" samples.

B. *Preparation of Polyaniline/ $NiFe_2O_4$composites*

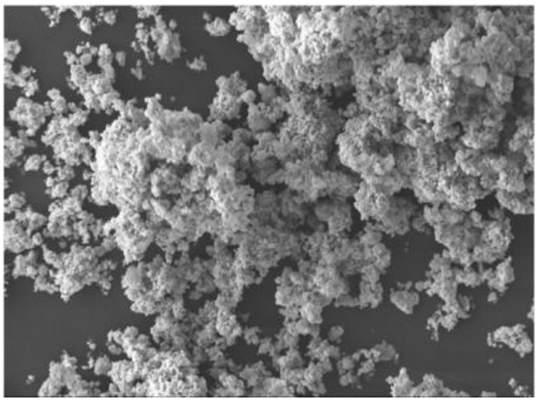
Synthesis of the PANI- $NiFe_2O_4$ composites was carried out by in-situ polymerization method. Aniline (0.1 M) was mixed in 1M HCL and stirred for 15 min to form aniline hydrochloride. $NiFe_2O_4$ particles were added in the mass fraction to the above solution with vigorous stirring in order to keep the $NiFe_2O_4$ homogeneously suspended in the solution. To this solution, 0.1M of ammonium persulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at 5◦C for 4hr to completely polymerize. The precipitate was filtered, washed with deionized water, Acetone, and finally dried in an oven for 24hr to achieve a constant mass. In these way, PANI– $NiFe_2O_4$ composites containing various weight percentage of Wo_3 (10 %, 20 %, 30 %, 40 %, and 50 %) in PANI were synthesized.

III. Preparation of pellets

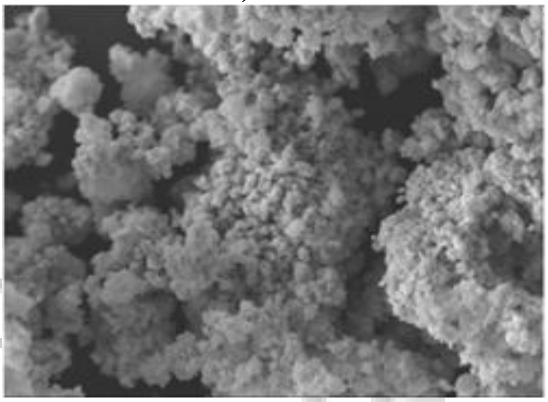
The powders of Polyaniline, Polyaniline/ $NiFe_2O_4$ composites, so obtained from synthesis techniques discussed in early sections were crushed and finely ground in agate mortar in the presence of acetone medium. The powder is then pressed to form pellets of 10mm diameter and thickness varying up to 2mm by applying pressure of 90MPa in a hydraulic pressure. For temperature dependent conductivity studies, a silver paste was coated on both sides of surface of the pellet for providing electrical contacts.

IV. RESULT AND DISCUSSION

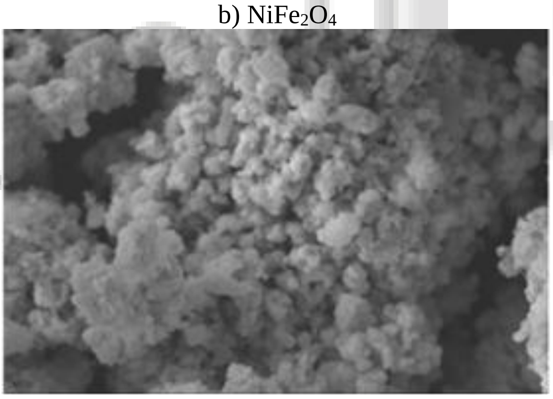
A. *SEM(Scanning Electronic Micrograph)*



a) PANI



b) $NiFe_2O_4$



c) PANI/ $NiFe_2O_4$ 50wt%

Fig. 4.1: shows the SEM image of a) PANI, b) $NiFe_2O_4$ C) PANI/ $NiFe_2O_4$ 50wt%composite

The Scanning Electron Micrograph (SEM) for the prepared polyaniline is shown in fig.4.1 (a). It can be clearly seen that the particles are homogeneous with a smooth surface. The SEM micrograph of PANI/ $NiFe_2O_4$ nano composite for sample is shown in fig.4.1 (b). It is clear that the PANI layers are wrapped on the surface of $NiFe_2O_4$ nano particles appearing as small aggregated globules .The surface of PANI/ $NiFe_2O_4$ particles becomes roughness and pours in addition to brittle nature of the particles. The appearance of brittle fractured surfaces after the annealing could be attributed to the phase separation in the polymer, which in turn, enhance some nano particles to disperse towards the bulk of the polymer matrix leading to improvement in composite morphology.

B. *Thermal Stability*

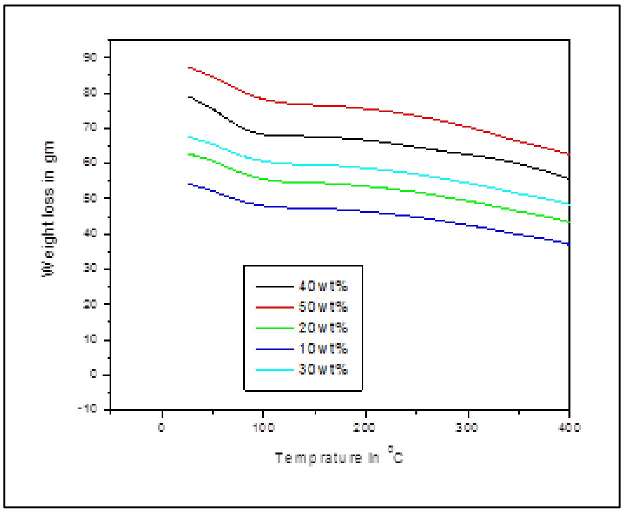
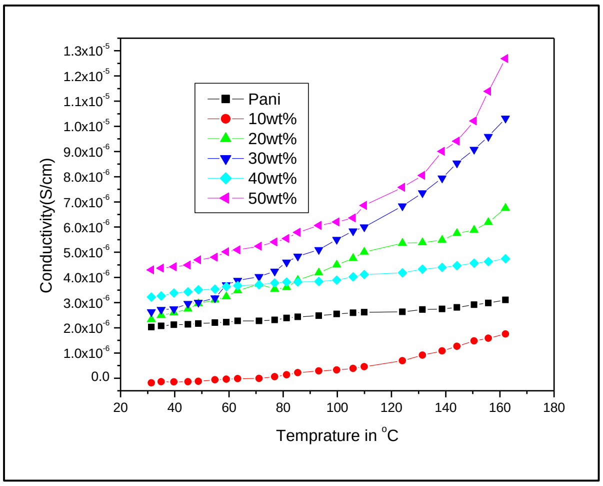


Fig. 4.2: shows the TGA image of a) PANI, b) $NiFe_2O_4$ C) PANI/ $NiFe_2O_4$ different wt% composite

Fig. 4.2 shows the TGA curves of PANI and PANI–$NiFe_2O_4$ nano composites. All curves show a three step weight loss. For all samples, the first step just below 70 °C is accompanied by a weight loss of about 15%. This is probably due to the moisture evaporation, which is trapped inside the polymer or bound to the surface of polymer backbone .The removing of water is easier in the composite with higher surface area or with increasing the interfaces between their particles. The second weight loss lie between 115 and 275 °C with a weight loss ranges from 13% to 17%. This may be attributed to the release of dopant anions compensated the positive charge of PANI chains. The last decomposition stage starts at temperature higher than 275 °C with a weight loss ranges between 56% and 77%. This is due to the complete decomposition of the organic part of the composites.

C. *DC conductivity*



The conductivity of pure PANI and PANI/ $NiFe_2O_4$ nano composites was found to be increased with increase in temperature, exhibiting typical semiconductor behavior. For the PANI/ $NiFe_2O_4$ nanocomposites conductivity values abruptly change the order of magnitude. As the wt% of $NiFe_2O_4$ in PANI increases, the absolute conductivity shifts to lower scales. This tendency of decreasing conductivity after ferrite nanoparticles embedded into PANI matrix was quite typical. This shift is due to the electrical charges being displaced inside the polymer (stronger localization) and/or due to their lower concentration. The decrease in conductivity, by increase in wt% of $NiFe_2O_4$ may be due to particle blockage conduction path by $NiFe_2O_4$ (nano size particle) embedded in PANI matrix. Also, increase in wt% of $NiFe_2O_4$ leads to an increasing inter chain distance, which makes hopping between chains more difficult, resulting in reduction of conductivity.

V. CONCLUSION

PANI/ $NiFe_2O_4$ nano composites have been successfully synthesized by in-situ polymerization method. The SEM results show the formation of the composition at room temperature clarify interaction between nickel ferrite and polyaniline. The composites properties were enhanced by annealing. Unexpected electrical conductivity behavior was noticed recording maxim value at 50wt% ferrite.

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