Effect of Annealing Temperature on Structure, Electrical and Magnetic Properties of Polyaniline Cobalt Ferrite Composite

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ABSTRACT

PANI/CoFe\textsubscript{2}O\textsubscript{4} nano composites were synthesized by solid state reaction with different amounts of the CoFe\textsubscript{2}O\textsubscript{4} nanoparticles (0.5, 1\& 1.5 gm). The structural, thermal and magnetic properties of the synthesized PANI/CoFe\textsubscript{2}O\textsubscript{4} were studied. The AC conductivity ($\sigma_{ac}$) was studied as a function of frequency up to 10 MHz. The results confirmed the formation of PANI/CoFe\textsubscript{2}O\textsubscript{4} composites. Both of DC and AC conductivities recorded unsaturated behavior with increasing ferrite content. The Magnetic characteristics were carried out at room temperature and were found to be strongly dependent on the nature of magnetic particle size and separation distance between them.

Keywords: Nano composites-microstructure-electrical properties-magnetic properties-Thermo gravimetric analysis (TGA) - Scanning electron microscopy (SEM)

1- INTRODUCTION

Conducting polymers have attracted a considerable attention for their potential applications in various fields such as electromagnetic interference (EMI) shielding, rechargeable batteries, electrodes, sensors, corrosion protection coatings and microwave absorption\textsuperscript{(1, 2)}. The use of conducting polymers gives rise to materials with properties that would be difficult to obtain with the individual components. Since, they have both high magnetic susceptibilities and high conductivity \textsuperscript{(3, 4)}. Conducting polymer inorganic composites possess, not only the nature of the flexibilities and processability of polymers, but also the mechanical strength and hardness of inorganic compounds\textsuperscript{(5)}.

Due to their high conductivity, environmental stability and rather simple synthesis, Polyaniline (PANI) draws a considerable attention in the preparation of new materials for the fabrication of industrial devices\textsuperscript{(6, 7)}. Among the wide variety of nano materials which have been introduced in recent years, magnetic nano particles are highly interesting, due to their potential applications in different fields. Whereas, larger particles are composed of several magnetic domains, below a certain (composition dependent) critical size, magnetic nano particles behave as mono domains, which give rise to interesting properties\textsuperscript{(8, 9)}.

A number of materials have been investigated, mainly iron and iron oxides, ferrites and other metals. Among those, cobalt ferrite (CoFe\textsubscript{2}O\textsubscript{4}) is highly interesting, since, it is a hard material from the magnetic point of view (exhibiting ferromagnetism at room temperature), has a high coercive field and moderate saturation magnetization and in addition to the excellent chemical stability\textsuperscript{(10, 11)}. Coating ferrite nano particles with polymer can enhance the compatibility and probably avoid the aggregation\textsuperscript{(12)}. Polyaniline can be dispersed into metallic fillers like ferrites. The conducting polymer
ferrite composites with an organized structure can be used as electromagnetic (EM) absorption and shielding materials because of their possessed multifunctional electrical and magnetic properties and good shielding effectiveness for various electromagnetic sources. Recently, attentions have focused on the PANI/ferrite composites which have a complementary synergy behavior between PANI and ferrite nano particles \(^{(13, 14)}\). So the current work will be an attempt to prepare Polyaniline cobalt ferrite in nano size at room temperature.

2- SAMPLES PREPARATION

2.1. Synthesis of Cobalt Ferrite Nano Particle

To prepare cobalt ferrite we used alpha chemika (hexahydrate) cobalt (II) nitrate (Co (No\(_3\))\(_2\).6H\(_2\)O) with purity 97% and M.W 291.03, Oxford Ferric Nitrate (Fe (No\(_3\))\(_3\).9H\(_2\)O) with purity 98% and M.W 404.00, citric acid anhydrous, adwic ammonium solution (NH\(_3\)) with purity 33% and M.W 17.03. The synthesis of cobalt ferrite nano particles has been carried out via citrate precursor route. In this method, cobalt nitrate, ferric nitrate and citric acid have been dissolved in distilled water in the molar ratio of 1:1:0.3 respectively. Aqueous ammonium solution has been added to maintain the pH of the solution at 7.0. The resulting solution has been heated at 90ºC with continuous stirring to form a viscous gel followed by hot drying at 100ºC. The gel so formed has been burnt to form dendrite structure which has been crushed in a pastor mortar resulting in brown colored brittle powder. To form cobalt ferrite (CoFe\(_2\)O\(_4\)), the precursor was calcined at 1000 ºC for 2 hr's. To reduce the particle size, cobalt ferrite powder is further grinded for 6 hrs \(^{(10, 11)}\).

2.2. Synthesis of Polyaniline (PANI)

To prepare PANI adwic aniline with purity 98.5% and M.W 93.13, adwic hydrochloric acid, oxford ammonium persulphate ((NH\(_4\))\(_2\)S\(_2\)O\(_8\)) with purity 99 % and M.W 228.19, sodium hydroxide, adwic Ethyl Alcohol with purity70 % were used. Polyaniline was chemically synthesized using aniline and ammonium persulfate as oxidant in a 4:1 ratio. 20 mL of the aniline was dissolved in 40 mL of 1 mol L\(^{-1}\) aqueous solution of hydrochloric acid in a 250 mL flask. During the dissolution the flask was kept inside a vessel containing a mixture of ice and salt. Separately, 12g of (NH\(_4\))\(_2\)S\(_2\)O\(_8\) was dissolved in 160 mL of 1 mol L\(^{-1}\) hydrochloric acid aqueous solution. The acid solution of (NH\(_4\))\(_2\)S\(_2\)O\(_8\) was slowly and carefully added into the flask containing the aniline acid solution during a period of 2 hr's and under constant stirring. A green sediment was formed, filtered and dried under dynamic vacuum at room temperature for 72 hr's \(^{(12)}\).

2.3. Incorporation of CoFe\(_2\)O\(_4\) in Polyaniline (PCo)

CoFe\(_2\)O\(_4\) was incorporated in PANI at different concentrations (0.5, 1 & 1.5 gm) by mixing them together using solid state reaction for 1h at 500 rpm. The mixture was then annealed at 400 ºC for two hours followed by murder grinding until a soft powder of annealed PCo was obtained. The present samples were marked according to their ferrite content (0.5 Co, 1 Co, and 1.5 Co respectively), Co for ferrite and P for Polyaniline

3- EXPEREMENTAL RESULTS AND DISCSCUTION

3.1 Crystal Structure

Figure 1 (a, b) shows the XRD pattern for unannealed and annealed samples. From this figure, it can be noticed that all the characteristic peaks were ascribed to CoFe\(_2\)O\(_4\) spinel crystal structure and no other phase impurity was detected \(^{(13)}\), two broad peaks at 2θ = 31.69º and 45º were observed in free PANI, which could be related to an extensive inter chain π–π orbital overlap of densely packed phenyl \(^{(14)}\). Fig.1 (a), shows that the composites of unannealed samples do not contain the diffraction peaks of both ferrite and PANI, each peak separately from the other. Hence, it can be concluded that the
compound was not formed, so we resorted to annealing. From Fig.1 (b), it can be noticed that the composites of annealed samples contain both the diffraction peaks of ferrite and the broad peaks of PANI with somewhat change in the intensity.

Figure 2 (a, b) shows the FTIR patterns for the unannealed and annealed samples respectively. The main characteristic bands of polyaniline are assigned at 3375 cm\(^{-1}\), 1547 and 1471 cm\(^{-1}\), which is attributed to the N-H stretching, C=C stretching vibration of the quinine (Q) ring and benzene (B) ring \(^{15}\). While the bands observed at 1285 and 684 cm\(^{-1}\) may be assigned to the C-N stretching of the secondary aromatic amine and the aromatic C-H vibration respectively. In the region 1032–1273 cm\(^{-1}\), aromatic C-H in plane bending mode was observed. The peak at 1264 cm\(^{-1}\) is ascribed as the electronic like band, which is associated with the vibration mode of N=Q=N (Q refers to the quinonic type rings \(^{16}\). The two strong bands that appear around 747 cm\(^{-1}\) and 400 cm\(^{-1}\) are the characteristic bands of CoFe\(_2\)O\(_4\) spinel ferrite. According to Waldron \(^{14}\) the ferrites can be considered continuously bonded crystals, meaning that the atoms are bounded to all the nearest neighbors by equivalent forces. In spinal ferrites, the metal ions are located into two sub lattices namely tetrahedral (A) site and octahedral [B] site according to the geometrical configuration of the oxygen nearest neighbors. Absorption bands \(\nu_1\) and \(\nu_2\) are assigned to the intrinsic vibration of tetrahedral and octahedral complexes, respectively \(^{14}\). Fig.2 (a) shows that, all the characteristic peaks of cobalt ferrite in free state are observed in the PANI/CoFe\(_2\)O\(_4\) composites. While, the characteristic peaks of PANI aren’t observed in the composites. From fig.2 (b) it is noticed that the annealing of such samples improves the incorporation of the ferrite inside the polymer matrix. The mean bonds which appear in PANI are detected after adding the ferrite to the polymer and then annealed. In comparison between the two figures one can noticed that the peaks at 3375, 1547, 1471, 1285 and 747 cm\(^{-1}\) show a shift to lower wave numbers. Moreover, with an increase in the ferrite content, the intensity of the bands corresponding to PANI characteristics increases distinctively, where the intensity of peaks at 400 and 747 cm\(^{-1}\) corresponding to Co ferrite was greatly diminished. These results reveal that there exists an interaction between ferrite particles and PANI chains. This is produced from the \(\sigma-\pi\) interaction between ferrite and PANI, which includes: (1) the \(\pi\) molecular orbital of PANI overlaps the empty d-orbital of metal ions to form the \(\sigma\)-bond where metallic empty d-orbital is the electron pair acceptor; (2) the \(\pi^*\) molecular orbital of PANI overlaps the d orbital of metal ions to form the p-bond, in which the metal ions is the electron pair donor. In addition, the hydrogen bonding interaction between the polyaniline chains and the oxygen atoms on the ferrite surface occurs in the composites, which make ferrite particles be embedded into polymer chain of PANI \(^{15-17}\).
3.3 Microstructure

The Scanning Electron Micrograph (SEM) for the prepared polyaniline is shown in fig. 3 (a). It can be clearly seen that the particles are homogeneous with a smooth surface. The SEM micrograph of unannealed PANI/CoFe\textsubscript{2}O\textsubscript{4} nano composite for sample (0.5Co) is shown in fig. 3 (b). It is clear that the PANI layers are wrapped on the surface of CoFe\textsubscript{2}O\textsubscript{4} nano particles appearing as small aggregated globules\textsuperscript{(10)}. Fig. 3 (c) shows the SEM micrograph for 0.5Co sample after heat treatment. The surface of PCo 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\textsuperscript{(18)}, which in turn, enhance some nano particles to disperse towards the bulk of the polymer matrix leading to improvement in composite morphology.

![Fig. (3): SEM microscope for (a) polyaniline (b) unannealed 0.5Co (c) annealed 0.5Co](image)

3.4 Thermal Analysis

Figure 4 (a, b) shows typical TGA thermo grams of the weight loss as a function of temperature for unannealed and annealed PCo nano composite. For rough samples fig. 4 (a), the nano composite undergoes only two weight loss steps. The initial weight loss ranging from (41-468) °C and (34-333) °C indicating a weight loss of 12.5% and 3.4% for 0.5 Co and 1.5 Co respectively, is due to the
expulsion of water molecules, the dopant (HCL) from PANI chains and due to the volatilization of lower weight PANI. The second weight loss ranging from (468- 499.9) °C and (333-499) °C indicating weight loss of 4.4% and 8.8% for 0.5 Co and 1.5 Co respectively, is attributed to the thermal degradation of the PANI chains (10). It is observed that the second a weight loss stage of 1.5Co, shifted to a lower temperature level. Which could be attributed to the strong interaction between the PANI and CoFe₂O₄ nano composite which will restrict the thermal motion of the PANI in the PCo composite and enhances a thermal stability. The decomposition temperature of the PCo nano composite also depends on the amount of CoFe₂O₄ nano composite present in PANI.

The obtained PANI/CoFe₂O₄ nano composite shows enhanced thermal stability making it useful as conducting polymer in high temperature applications (13). Figure 4b shows that the thermal behavior of annealed PANI/CoFe₂O₄ nano composite, which is confirmed by some structural changes that occurred after annealing. The nano composite shows a different weight loss stage for 0.5Co undergoes 4 steps, the weight losses in the range (30-88) °C, (88-122) °C, (123-157) °C and (157-500) °C indicating weight loss of 5.8%, 1.4%, 1.1% and 11.3% respectively. The 1.5Co undergoes 3 steps of weight losses ranging from (34-67) °C, (67-149) °C and (149-500) °C indicate weight loss of 3.3%, 2.7% and 7.5%, respectively. It noticed that the annealed samples shows more thermal stability because the remaining weight is 19.7% and 13.5% for annealed 0.5 Co and 1.5 Co respectively, but this weight loss was 17% and 12% for the unannealed 0.5 Co and 1.5 Co, respectively (15).

![Fig. (4): TGA thermo grams of for PANI/CoFe₂O₄ nano composite at 0.5Co and 1.5Co (a) unannealed (b) annealed](image)

### 3.5 Electrical Properties

#### 3.5.1 DC- Conductivity

Figure (5) shows the room temperature conductivity of PANI/CoFe₂O₄ as a function of the CoFe₂O₄ concentration. The dc conductivity was found to be increase with increasing cobalt ferrite concentration up to 1Co, and then decreased after that for both of annealed and unannealed PCo composites at 1.5 Co. The dc conductivity curves of PCo composite increase if the composite contains more than 20% weight of PANI (21, 22, 23). This increase in conductivity with increasing cobalt ferrite content could be attributed to the extended chain length of polyaniline which facilitates the polarization of charge carriers and variation in distribution of CoFe₂O₄ particles which may support for more number of charge carriers to polarize between favorable localized sites causing increase in conductivity (19). On the other hand, the decrease in conductivity at high cobalt ferrite content could be
attributed to particle blockage of the conduction path by Co embedded in PANI matrix. Also, the increase in the concentration of Co leads to a larger number of polarons where the inter polarons coupling gets progressively stronger even though disorder is present. This leads to severe pinning of polarons, thus restricting their contribution at higher frequencies, leading to the reduction of conductivity \(^{(21, 22)}\). From this, it could be concluded that the annealing improved the sample behavior.

3.5.2 Frequency Dependence of ac Conductivity

Figure 6 (a, b) shows the frequency dependence of ac conductivity of unannealed and annealed samples at room temperature up to 10 MHz. The frequency dependence shows two regions, nearly frequency independent at relatively low frequency followed by frequency dependent region at high frequencies. On the other hand, the frequency independent region for the unannealed composites is narrow comparing by the annealed one. This could be attributed to the effect of annealing in increasing the the concentration of polarons which are moving along small distances in the polymer chain. The increasing in \((\sigma_{ac})\) at high frequency range, was explicated in the fact that the pumping force of the applied frequency that helps in transferring the charge carriers between the different localized states as well as liberating the trapped charges from the different trapping centers \(^{(13, 14)}\).

Fig. (5): Concentration dependence of the dc electrical conductivity for unannealed and annealed composite

Fig. (6): The frequency dependence of the ac conductivity for (a) unannealed (b) annealed PCo composite.
3.6 Magnetic Properties (VSM)

Magnetization measurements for cobalt ferrite and annealed PCo composites were carried out at room temperature up to 20 kOe and depicted in fig.7 (a) for CoFe$_2$O$_4$ ferrite, which recorded about 50 emu/g saturation magnetization and 550 coercivity. The values of saturation magnetization (Ms), coercivity (Hc) and remanence magnetization (Mr) for PCo were extracted from fig. 7 (b) and shown in fig. (8) against cobalt ferrite content. It is observed from this figure that saturation and remnant magnetization of PCo increased with increasing of CoFe$_2$O$_4$ ratio, which is normally expected due to the increase of ferrite volume fraction. The coercive force Hc is firstly increased more than the free cobalt ferrite recorded 657.6 Oe, then decreased once more with increasing ferrite content reaching the Hc values near to the free ferrite one at high concentration. This behavior could be attributed to the nature of magnetic particle size and separation distance between them (20). The present magnetic particles as a filler are relatively large in size (higher domain size), randomly oriented, uniformly dispersed and isolated from each other; in addition to their porous nature as seen in fig. 3 (c). These factors will enhance the coercivity of the PCo composites than cobalt ferrite. By increasing the ferrite content in the polymer matrix, the separation distance between magnetic particles will decreased leading to increasing in the magnetic particles interaction which weakness the coercivity. For the other point of view, the mixing process, PANI is deposited on the ferrite surface and crystallite boundaries, and covers the ferrite surface defects, such as pores and cracks. Consequently, the PCo composites show lower values of coercivity compared to that of Co ferrite (9). It could be concluded that the PCo composites are ferromagnetic in nature and will work as a good absorber of the microwave in the GHz range (11).

Fig. (7): M–H hysteresis loop of (a) CoFe$_2$O$_4$ (b) PCo composites at different ratio
PANI/CoFe$_2$O$_4$ nano composites have been successfully synthesized by solid state reaction. The XRD, SEM and FTIR results show the formation of the composition at room temperature clarify interaction between cobalt ferrite and polyaniline. The composites properties were enhanced by annealing. Unexpected electrical conductivity behavior was noticed recording maxim value at 1wt% ferrite. The magnetic parameters of cobalt ferrite were improved after being incorporated in PANI matrix recording about 20% increasing in Hc.

**REFERENCES**


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