

SYNTHESIS AND MAGNETIC PROPERTIES OF POLYANILINE-BASED MAGNETIC NANOCOMPOSITES FOR EMI APPLICATIONS

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ABSTRACT

Polyaniline (PANI)-based magnetic nano-composites, with Mn-Zn ferrite nanoparticles as disperse phase, can be used for EMI shielding application in electronic devices. In the present work, PANI/Mn_{0.8}Zn_{0.2}Fe₂O₄ composites, having different PANI/Ferrite w/w ratios, were prepared under suitable synthesis conditions to avoid excessive dissolution of the ferrite and favor its dispersion into the polymeric matrix. The Mn_{0.8}Zn_{0.2}Fe₂O₄ stoichiometry was selected because of its highest maximum magnetization value (55emu/g) and a susceptibility of 3.645. The ferrite average crystallite size was calculated as 10.6 nm using Scherrer's formula. XRD, HRTEM and SQUID analyses confirmed the formation of the magnetic nanocomposite. As expected, the saturation magnetization in the nano-composites varied according to the PANI/Ferrite ratio, but without affecting the magnetic susceptibility of the ferrite.

Keywords: electromagnetic interference, nanocomposite, PANI, Mn-Zn ferrite.

1. INTRODUCTION

One of the most critical physical property require of an enclosure for electronic devices is the capability to protect the device against electromagnetic interference (EMI). EMI degrades the performance of an electronic system or subsystem by an unwanted electromagnetic disturbance. Conducting materials can effectively shield electromagnetic waves generated from an electric source [1]; whereas, electromagnetic waves from a magnetic source, especially at low frequencies, can be effectively shielded only by magnetic materials [2-3]. Therefore, a composite material consisting of both conducting and magnetic properties will be suitable for EMI shielding. In this type of material, the main challenge is to select a suitable combination of the structural and functional properties exhibited by the matrix and the disperse phase, which would have the greatest effect on the resulting magnetic and dielectric properties [4]. Since conducting polymers are easy to synthesize and are considered environmentally friendly materials, the composite of conducting polymers bearing magnetic material as the disperse phase, are found to be suitable for EMI shielding applications [5-6]. Soft ferrites are the first-choice materials as efficient absorbers of electromagnetic waves [7-9]. This type of magnetic material offers wide

possibilities for their application in various electronic devices owing to the specific frequency behavior of their complex permeability and sufficiently high resistivity [10–12]. The high initial permeability, low value of effective magnetic-field anisotropy, and low core losses exhibited by nanocrystals of manganese–zinc ferrites (Mn_xZn_{1-x}Fe₂O₄) enable this material to be considered as suitable disperse phase in PANI-based composites for EMI applications. Moreover, the use of ferrite nanocrystals as the disperse phase would improve mechanical strength and machinability of the shield piece when compared with similar composites bearing bulk ferrites. In the present report, the effect of the composition of the disperse phase and the w/w ratio PANI/Ferrite in the nanocomposite on the corresponding structural and magnetic properties will be presented and discussed.

2. EXPERIMENTAL

2.1 Materials

All reagents were of analytical grade and were used without further purification. Required weights of chloride salts of Fe(III), Zn(II) and Mn(II) ions were dissolved in distilled water to achieve a mole ratio Fe/M of two (M = Mn+Zn). The different atomic fractions of Mn ions, 'x' in Mn_xZn_{1-x}Fe₂O₄, were obtained by adding suitable amounts of the Mn salt. NaOH was used as the precipitating agent. Monomer aniline and the ammonium peroxide sulfate salt, (NH₄)₂S₂O₈, (APS), were of analytical grade.

2.2 Synthesis of Polyaniline and Ferrite Nanocrystals

The chemical oxidative polymerization of aniline was carried out at an initial pH 7 without acid to avoid ferrite dissolution under acidic conditions. The required amounts of aniline and water were mixed and sonicated for 10 minutes (solution A). Desired volume of APS oxidant solution was then added to solution A dropwise to achieve a mole ratio of APS/Aniline of two. This ratio provides optimum conductivity properties in the composite as reported by Qiu and coworkers [13]. The mixture was kept inside an ice bath for 3 hours to complete the polymerization process.

Mn-Zn ferrite nanocrystals were produced by conventional coprecipitation method. The aqueous solution of 0.11M Fe and 0.055M Mn+Zn was continuously added into the reaction vessel containing 0.725M NaOH under boiling conditions. Ferrites were synthesized at different values of the Mn atomic fraction values 'x'. A reaction time of one hour was long enough to permit the dehydration and atomic rearrangement involved with the conversion of the precursor hydroxide into the ferrite structure. Synthesized nanocrystals were removed out from solution, washed twice with distilled water and dried at 60°C for 24 hours.

2.3 Preparation of PANI/Mn_{0.8}Zn_{0.2}Fe₂O₄ Nano-Composite

Suitable weights of Mn_{0.8}Zn_{0.2}Fe₂O₄ nanoparticles were added to 50 mL of the monomer aniline aqueous solution at 3°C to obtain desired PANI/ferrite %w/w ratio. The mixing was carried out under intense sonication to disperse the nanoparticles. Suitable amount of APS was added drop by drop to the ferrite-aniline suspension to achieve a APS/Aniline mole ratio of 2. All reactants were mixed under the above described conditions for three hours. Final products were washed with distilled water and dried at 65 °C for 12h.

2.4 Characterizations

Structural analysis of the powders were carried out by Siemens D500 x-ray diffractometer (XRD) using the Cu-K α radiation. The particle and nano-composite morphology were examined by high-resolution transmission electron microscope (HRTEM). The room-temperature M-H curves were obtained by using a MPMS SQUID unit at a maximum magnetic field of 7T.

3. RESULTS AND DISCUSSION

3.1 XRD Analyses

Figure 1 shows the XRD patterns of Mn_xZn_{1-x}Fe₂O₄ powders synthesized at different Mn atomic fraction, 'x', and 4 hours of reaction. All peaks correspond to the ferrite structure. The average crystallite size, estimated by using the Debye-Scherrer's equation for the (311) peak, ranged from 6nm to 10 nm with a rising 'x' value. Although a reaction time of 4 hours was found to be suitable for complete formation of the ferrite under mild heating, an additional experiment under more intense heating conditions verified that the ferrite structure could be fully achieved in 5 minutes (Figure 2) at 'x' = 0.8. In these samples the corresponding average crystallite size did not change as compare to mild heating conditions and was found to be about 10.6 nm.

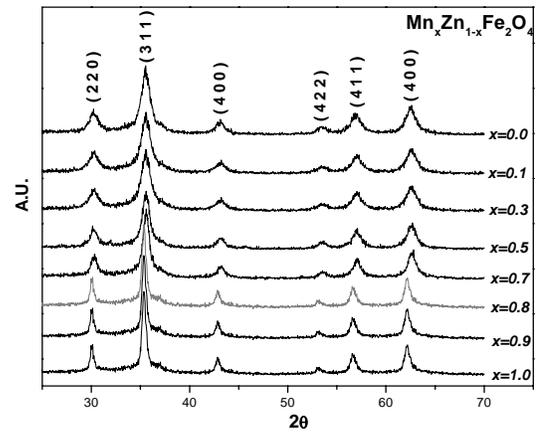


Figure 1: XRD patterns for Mn_xZn_{1-x}Fe₂O₄ powders synthesized at various atomic fractions of Mn ions, 'x'. The reaction time was 4 hours.

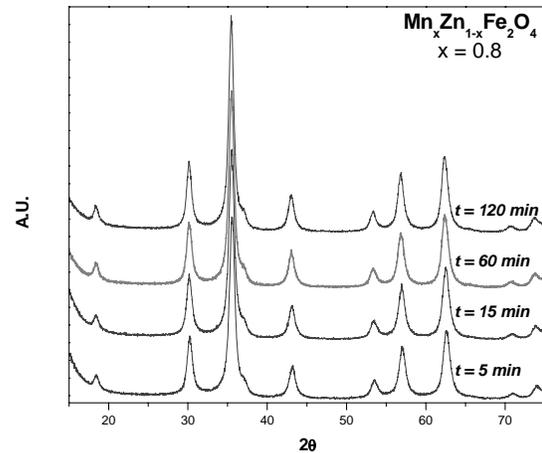


Figure 2: XRD patterns for Mn_{0.8}Zn_{0.2}Fe₂O₄ ferrite powders synthesized at different reaction times.

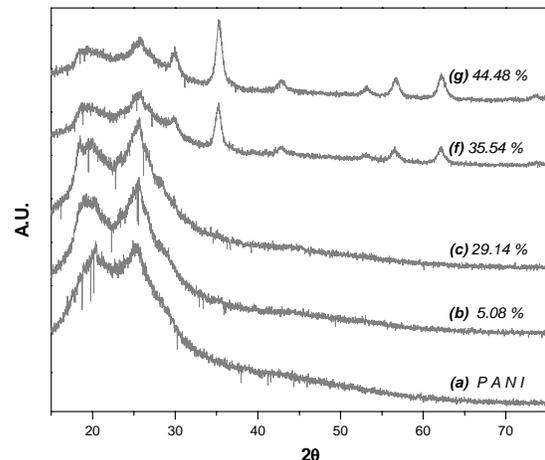


Figure 3: XRD patterns for PANI and PANI-(MnZn) ferrite nanocomposites.

The XRD patterns corresponding to the PANI/Mn_{0.8}Zn_{0.2}Fe₂O₄ composites prepared for different w/w ratios are shown in Figure 3. As seen, as far the

concentration of ferrite nanoparticles in PANI increase, the PANI peak around 20°-25° becomes broader, suggesting a close interaction between the ferrite in PANI matrix. The measurable signal of the ferrite peaks in PANI matrix was observed above 35% w/w of ferrite in PANI.

3.2 HRTEM Observations

HRTEM images of Figure 4 evidence the nanocrystalline nature of the ferrite particles, synthesized for 'x'=0.7. The observed particle size (~10 nm) is in good agreement with the value estimated from XRD analysis.

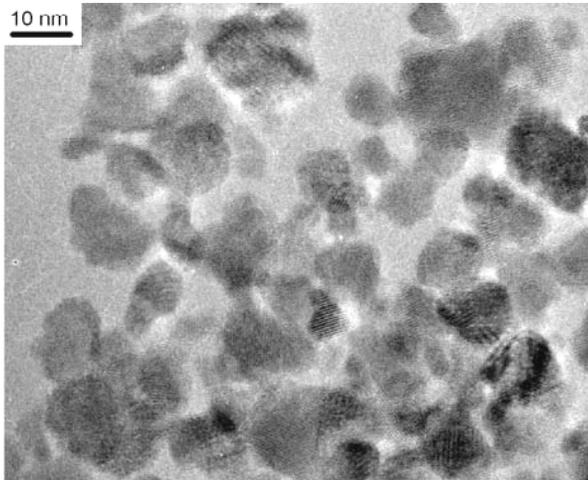


Figure 4: HRTEM image of $Mn_{0.7}Zn_{0.3}Fe_2O_4$ nanocrystals synthesized after 60 minutes of reaction.

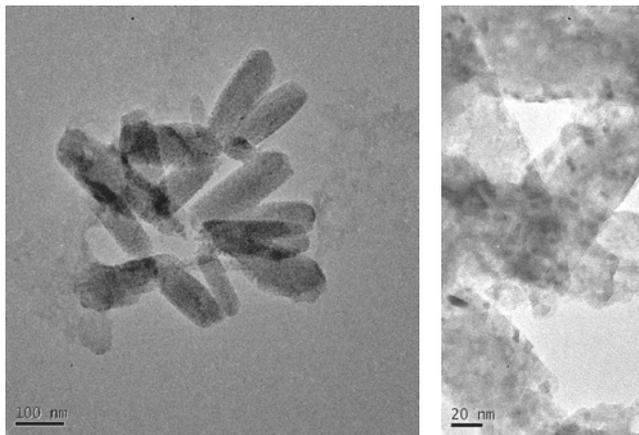


Figure 5: HRTEM images of the PANI/ $Mn_{0.8}Zn_{0.2}Fe_2O_4$ nanocomposite with 24.13 % w/w of ferrite.

Figure 5 shows typical HRTEM images of the Ferrite/PANI nano-composite. Darker spots correspond to the ferrite nanoparticles. It can be seen from that figure that the ferrite nanoparticles are reasonably well dispersed within the polymeric matrix.

3.3 Magnetic Measurements

Figure 6 shows the room-temperature M-H loops for $Mn_xZn_{1-x}Fe_2O_4$ nanocrystals synthesized at different Mn atomic fraction values, 'x'. These loops are typical of ferromagnetic compounds, although the lack of saturation can also suggest the presence of superparamagnetic particles. As seen, the degree of magnetic saturation and the corresponding magnetization values were strongly dependent on the composition of the ferrites in the range evaluated. In Mn-Zn ferrites divalent and Fe^{3+} ions occupy both A- and B- sites in the ferrite structure, with Zn^{2+} preferring A-sites. The incorporation of magnetic Mn^{2+} for non-magnetic Zn^{2+} ions explains the observed enhancement in the maximum magnetization with a rising 'x' value. For minor proportions of Mn^{2+} ions, i.e. low 'x' values, the ferrite becomes a normal spinel, i. e., no more Mn^{2+} in B-sites and no more Fe^{3+} in A sites. This ionic redistribution can explain the observed drop in magnetization. In absence of Mn substitution ('x'=0) a compensated anti-ferromagnetic behavior should be established in $ZnFe_2O_4$. This figure also evidences that even for x = 0 and 0.1, produced ferrites exhibited a small magnetization. It could be due to some inversion degree in the $ZnFe_2O_4$ structure where a small part of Zn^{2+} may still remain in B-sites and a part of Fe^{3+} in A-sites. The drop in magnetization observed for 'x' values above 0.8, can be attributed to the decrease in A-B type interactions in the $MnFe_2O_4$ structure ('x'= 1.0) in comparison with those interactions in the $Mn_xZn_{1-x}Fe_2O_4$ one.

The M-H loop for the $Mn_{0.8}Zn_{0.2}Fe_2O_4$ ferrite precipitated under more intensive heating conditions and after one hour of reaction is shown in Figure 7. The maximum magnetization and magnetic susceptibility was found to be about 55 emu/g and 3.645, respectively. The inset shows a well-saturated M-H branch correspond to ferrite/PANI (15% w/w ferrite) nanocomposite. It can be seen that the magnetic susceptibility of the ferrite particles did not change when embedded in the polymeric matrix.

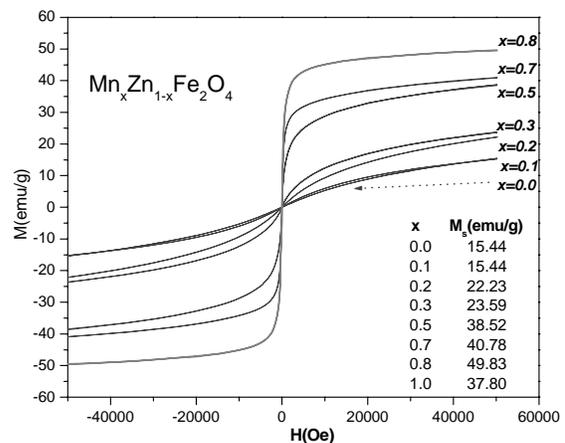


Figure 6: Room temperature M-H loops for $Mn_xZn_{1-x}Fe_2O_4$ ferrites at different Mn atomic fractions, 'x'.

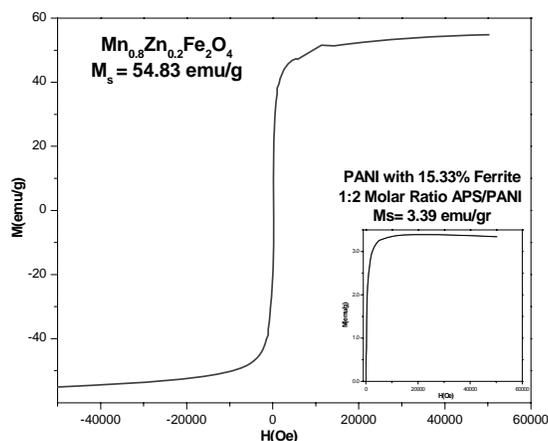


Figure 7: Room temperature M-H loop for $Mn_{0.8}Zn_{0.2}Fe_2O_4$ powder synthesized after one hour of reaction. The inset shows the M-H curve for the corresponding PANI/Ferrite nanocomposite.

4. CONCLUDING REMARKS

We have successfully synthesized $Mn_xZn_{1-x}Fe_2O_4$ nanoparticles and PANI/Mn-Zn nanocomposite. Obtained results suggest the viability in preparing composites consisting of PANI and Mn-Zn ferrite nanocrystals exhibiting good crystallinity and suitable magnetic properties for potential EMI applications. Ongoing work is focused on the optimization of the mechanical (hardness), magnetic and electrical conductivity properties of the nanocomposites.

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