

**PREPARATION AND CHARACTERIZATION OF
POLYANILINE-BASED MAGNETIC NANOCOMPOSITES FOR
EMI SHIELDING APPLICATIONS**

By

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ABSTRACT

Among the wide applications of polymers, their use to reduce electronic noise is receiving great attention from the scientific and technological communities. This electronic noise is part of electromagnetic interference (EMI), which is responsible for the degradation of electronic systems or their interference with other electronics devices. The uncontrolled exposure to electromagnetic waves caused by the problems mentioned before can also be conducive to health concerns. Polyaniline (PAni) characteristics of frequency agility, light weight, simple tuning of functional properties and its non-corrosive nature, make this polymer a suitable material for the development of electromagnetic shielding materials where protection against noise without degradation of device performance is the main aim. Tuning of conductive and magnetic properties in PAni-based nanocomposites can be achieved by suitable selection of polymerization conditions and controlled addition of ferrites nanoparticles.

PAni was synthesized by polymerization of aniline in presence of ammonium peroxydisulfate and HCl. The disperse phase consisted of low-coercivity (Zn-Mn ferrites) nanoparticles. Our work was focused on the synthesis of PAni matrix and the ferrite disperse nano-phase as well as the determination of suitable conditions for homogeneous dispersion of the nanoparticles during the polymerization process in order to achieve suitable homogeneity of the magnetic properties in the final composites. The results of magnetic characterization by Vibrating Sample Magnetometer (VSM) magnetometers, and structural and morphological characterization by X-ray Diffraction (XRD), Fourier

Transform Infrared (FT-IR), Scanning Electron Microscope (SEM), High Resolution Transmission Electron Microscopy (HRTEM) techniques respectively, are presented and discussed. The effect of the presence of ferrite nanocrystals on the thermal stability of the nanocomposites has been evaluated by Thermogravimetric analyses (TGA) of the composites produced at different PANi/ferrite molar ratios. The conductivity of synthesized PANi-based nanocomposites has also been calculated from Current Vs Voltage (I Vs V) measurements carried out at room temperature conditions.

RESUMEN

Entre las amplias aplicaciones de polímeros, su uso para reducir el ruido electrónico está recibiendo la gran atención de las comunidades científicas y tecnológicas. Este ruido es parte de interferencia electromagnética (EMI) que es responsable por la degradación de sistemas electrónicos o su interferencia con otros dispositivos electrónicos. Hay también preocupaciones de salud relacionadas a la exposición no controlada a olas electromagnéticas causadas por los problemas mencionados antes. La Polianilina (PAni) por sus características de agilidad de frecuencia, ligero peso, simple reajuste de propiedades y su naturaleza no-corrosiva, le hace un material conveniente para el desarrollo de la aplicación para protección electromagnética, y consiguiendo la inmunización contra el ruido sin la degradación del desempeño. Ajustando las propiedades conductoras y magnéticas en el nanocompuesto basado en PAni pueden lograrse por la selección conveniente de condiciones de la polimerización y la adición controlada de nanoparticles de las ferritas.

PAni se sintetizó por la polimerización de anilina en presencia de peroxidisulfato de amonio y HCl. La fase dispersa consistió en nanopartículas de baja coercividad (ferritas de MnZn). Nuestro trabajo se enfoca en la dispersión de las nanopartículas durante el proceso de polimerización para lograr la conveniente dispersión y homogeneidad de las propiedades magnéticas en el compuesto final. Los resultados de caracterización magnética fueron realizados por un magnetómetro de muestra vibrante (VSM), la caracterización estructural y morfológica fue realizada por difracción de rayos X (XRD), infrarrojo por transformada

de Fourier (FT-IR), el microscopio electrónico de barrido (SEM), microscopio de transmisión electrónica de alta resolución (HRTEM), respectivamente, se presentarán y se discutirán. El efecto de la presencia de nanocristales de ferrita en la estabilidad térmica de los nanocompuestos ha sido evaluada por análisis termogravimétrico (TGA), de los compuestos producidos en diferentes relaciones molares de PANi/ferrita. La conductividad de los nanocompuestos sintetizados basados en PANi también ha sido calculada a partir de mediciones de Corriente Vs Voltaje (I Vs V) llevadas a cabo en condiciones de temperatura ambiente.

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To my wife...

To my Family...

Thanks God...

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1. INTRODUCTION

Conducting polymers have emerged as an important class of electronic materials because of their potential applications in solid state batteries, electrochromic displays, and microelectronic devices, etc. These polymers are a different class of materials than conducting polymers, which are merely a physical mixture of a non-conductive polymer with a conducting material such as metal or carbon powder. Some forms of these intrinsically conducting polymers can be blended into traditional polymers to form electrically conductive blends. The electrical conductivities of the intrinsically conducting polymer systems now range from those typical of insulators ($<10^{-10}$ S/cm) to those typical of semiconductors such as silicon ($\sim 10^{-5}$ S/cm) to greater than 10^4 S/cm (nearly that of a good metal such as copper, 5×10^5 S/cm).

Polymer-based nanocomposites represent a new concept in the development of systems exhibiting functional properties resulting from the synergistic interaction between the disperse phase and the matrix. In our particular case, the many properties of conducting polymers like non-corrosiveness, light weight, mechanical strength, and the possibility to tune electrical conductivity and dielectric behavior, can be utilized along with magnetic properties of ferrite nanoparticles to make multifunctional structures.

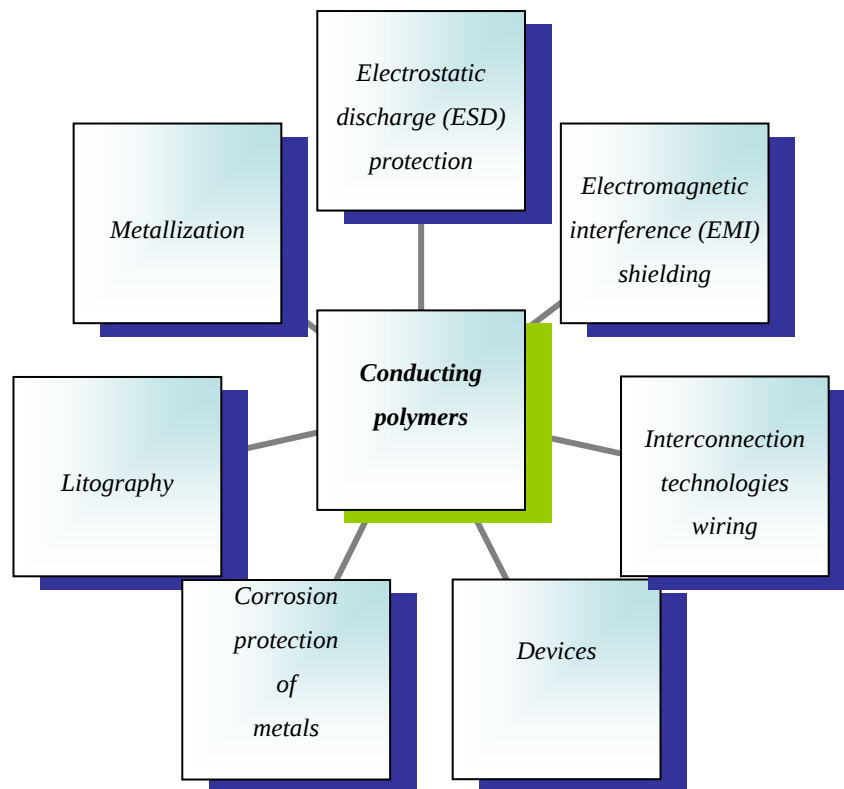


Figure 1. Potential applications of conducting polymers in microelectronics [4]

Conducting polymers have also found potential applications at all levels of microelectronics (Figure 1). This type of materials can effectively shield electromagnetic waves generated from an electric source, whereas electromagnetic waves from a magnetic source, especially at low frequencies, can be effectively shielded only by magnetic materials. Magnetic shields provide a path around sensitive areas to deflect magnetic flux. In addition, shielding may contain magnetic flux around a component that generates flux. The ability to conduct magnetic lines of force is called permeability, and in a magnetic shield, the degree of permeability is expressed numerically. Three types of materials are used for magnetic shielding, namely, high permeability, medium permeability and high

magnetic saturation. Thus, having both conducting and magnetic components in a single system could be used as an EMI shielding material. For such an application typical materials include copper or aluminum, which have high enough conductivity (σ) and dielectric constant (ϵ), which contribute to high EMI shielding effectiveness (SE). Despite EMI shielding systems based on metals having good mechanical and shielding properties; they are heavy, susceptible to corrosion, and possess limited forming capability.

1.1 JUSTIFICATION OF THIS RESEARCH

The particular use of polymer-ferrimagnetic nanoparticles composite for EMI reduction would represent a promising alternative to overcome the above described limitation of metal-based systems. Accordingly, polyaniline (PAni)-ferrimagnetic nanoparticles composite could be considered a potential candidate to replace, or to use together with metallic materials for EMI protection.

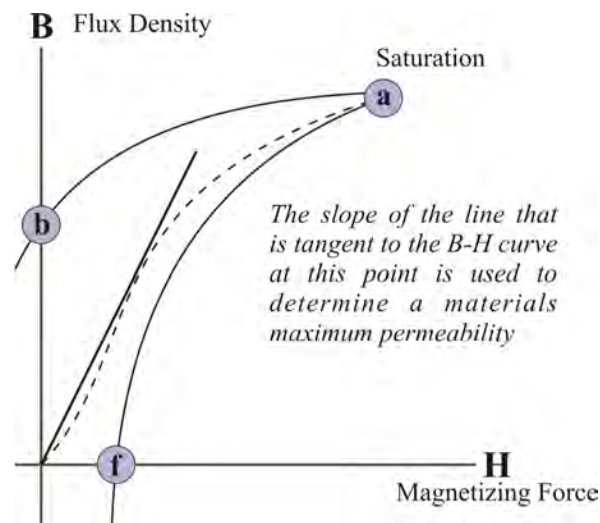


Figure 2. B / H curve

Based on the above considerations, the present research addresses the development of a semiconducting polymer-magnetic nanocomposite. For this purpose, PANi has been selected as a matrix for high-magnetic saturation and permeability ferrite nanoparticles (the disperse phase), as an alternative to conventional metallic shields. Our research work considers the synthesis of PANi, ferrimagnetic ferrite nanoparticles and the preparation of the corresponding PANi/Ferrite nanocomposites $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$, where 'x' is the atomic fraction of Mn.

We have selected manganese-zinc ferrites because of their high initial permeability, low value of effective magnetic field anisotropy, low core losses and response to high-frequency devices such as transformers and magnetic heads [11,36].

Resulting nano-composites will be structurally (XRD, FT-IR), morphologically (SEM, TEM), electrically (room temperature conductivity) and magnetically (room temperature saturation magnetization, coercivity) characterized as a function of the crystal ferrite size, ferrite composition and concentration of ferrite nanocrystals (i.e., PANi/Ferrite molar) percent in the composite.

1.2 OBJECTIVES

1.2.1 Main objective

The main objective is to determine the most suitable conditions for the preparation of PANi-based magnetic nanocomposite exhibiting suitable structural, electrical and magnetic

characteristics for its potential application in the reduction of electromagnetic interference (EMI).

1.2.2 Specific objectives

The following are the specific objectives:

- To determine the suitable conditions to synthesize nanocrystalline $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrites.
- To achieve a homogeneous behavior of the nanocomposite making sure of the suitable dispersion of the ferrite phases within the PANi matrix.
- To determine the structural, electrical and magnetic properties of PANi, ferrite nanoparticles and corresponding nanocomposite as a function of ferrite concentration in the PANi matrix.

1.3 PANI-BASED MAGNETIC NANOCOMPOSITES:

LITERATURE REVIEW

The most suitable route to get an optimum dispersion of the magnetic phase within the PANi matrix is of key importance to judge the effectiveness of this type of nanocomposites as EMI shielding material. Ö. Yavuz *et al* [11] synthesized polyaniline in presence of MnZn ferrite and NiMnZn ferrite, 5.9 micrometers in size. Ferrite particles in suspensions

were contacted with the aniline monomer solution. Yavuz's work used FT-IR analyses to verify the presence of the absorption bands of the monomer from the ferrite surface. In turn, XRD was used to confirm the crystalline structure of bare ferrite powder and that of the ferrite in the nanocomposite. The magnetic characterization of the nanocomposites revealed a room-temperature saturation magnetization as high as 64.2 emu/g when 4 grams of the ferrite powder was mixed with 200 ml of the aniline solution and polymerized.

R. Mathur *et al* [17] worked with the room temperature synthesis of magnetic composites of a copolymer with nanoparticles of MnZn ferrites in different sizes. Mössbauer, X-ray diffraction and infrared studies established the formation of nanoparticles of MnZn ferrite in the size range of 5 - 10 nm depending on the concentration of Zn ions, which also affected the magnetic properties of the nanocomposites.

P. Poddar *et al* [12], used 15 nm manganese zinc ferrites ($\text{Mn}_{0.68}\text{Zn}_{0.25}\text{Fe}_{2.07}\text{O}_3$) synthesized in inverse micelles as the disperse phase for PAni/polypyrrole-based nanocomposites. Poddar's research was focused on the magnetic behavior of those compounds at different temperatures. They also investigated the dispersion of the magnetic phase in a matrix of wax. The measurement of magnetic behavior showed low coercivity for the wax nanocomposite but bigger saturation magnetization for those that are in the polymer matrix. The values of saturation magnetization are not easily comparable because they were presented in emu and the mass of the sample was not provided. Poddar's group has also worked with iron nanoparticles in a poly-methylmethacrylate matrix varying the nanoparticles concentration, which had an approximate size of 20 nm [3]. As expected, the saturation magnetization varied with the nanoparticles concentration in the matrix; for 10%

of Fe the saturation magnetization was 11.5 emu/g. Although they claimed a suitable dispersion of the magnetic phase, no clear experimental evidence on this point was provided.

S. C. Byeon *et al* [18], proposed the importance of the single and polycrystalline nature of manganese-zinc ferrite. The requirements placed on MnZn ferrite for EMI and magnetic head applications become increasingly more stringent. They cannot be fulfilled by simply using a polycrystalline or single crystal material alone; single crystal MnZn ferrite has higher magnetic flux density than polycrystalline MnZn but a lower magnetic permeability and higher magnetic loss than polycrystalline MnZn ferrite. S. Vulpe *et al* [19] reported a novel method to design nanocomposite films based on spin coating under a thermocentrifugal field. The films were made of polyacrylonitrile (PAN) matrix with polyaniline (PAni) nanoparticles aligned in micron wires with a given periodicity dependent on spinning parameters. The results showed high electrical conductivity and variable loss tangents depending on the working conditions. They also designed a diffraction grating for electromagnetic waves with adjustable interfibrils distance and wide percolation phenomena.

K.F. Schoch, Jr. [15] presented in 1994 a review article about the capabilities of polymers in different applications covering power equipment, light emitting diodes and EMI shielding. It was proposed that the present application of conducting polymers is very promising because of the significant advances made in improving the stability and processing (polymers blending) characteristics of these materials.

Polyaniline (PAni) is one of the most common conductive polymers used as a matrix in magnetic composites applied in electronics. R. Sharma *et al* [8] verified that when iron oxides are used as dispersed phase, a critical factor is the dependence of functional properties of the composite with the sizes of the oxide particles and the polyaniline concentration. They used 10-20 nm γ -Fe₂O₃ nanoparticles for their experiments. The maximum saturation magnetization value was 53.37 emu/g for a weight concentration of 1:0.1 (γ -Fe₂O₃: PAni) at ambient temperature. The same report suggested the convenience in adding the disperse phase during the polymerization process in presence de HCl (as required for the protonation of aniline). Despite the improvement on the dispersion of the oxide phase, some agglomeration of the oxides was still observed that was more evident at larger oxide/PAni ratios.

Other investigators such as K. Naishadham [16] also focused on the improvement of the conductivity of the polymer for EMI shielding applications. Two new materials, namely, polyacetylene and PBT doped by ion implantation with iodine, were evaluated as a function of frequency, electrical thickness, doping, polarization, and angle of incidence. The measured conductivity value was used in a multilayer model of the polymer in order to calculate reflection and transmission by the shield for various layer parameters. Obtained results showed that the polymer performed well as EMI shield over a wide frequency band. Multiple layers were found to provide better shielding effectiveness than a single layer with thickness about the same as that of the multilayer.

S. Baek *et al* [22] synthesized aniline with poly-o-aminophenethyl alcohol in aqueous

hydrochloric acid medium. The research addressed the achievement of better conductive properties for EMI applications. XRD, FTIR, UV, conductivity (7.1 to 5.2×10^{-5} S/cm), electrochemical response, and thermo-gravimetric analysis suggested the applicability of this composite as potential conducting material.

The synthesis of PANi is critical in order to obtain the best conductivity values. Previous investigators have used different processes to achieve it. J. L. Wojkiewicz *et al* [13] worked with PANi doped with HCl and polyvinyl chloride (PVC) and PANi doped with camphor sulfonic acid. These materials were used in combination with polyurethane (PU) to enhance the mechanical properties of the final product. DC conductivity values for PANi-PVC were between 1 and 100 Sm^{-1} whereas PANi-PU reported conductivities up to 1000 Sm^{-1} (10 S/cm). The dielectric properties were analyzed in the microwave band ($50 \text{ MHz} - 20 \text{ GHz}$) and the millimeter band ($30 \text{ GHz} - 110 \text{ GHz}$). The shielding effectiveness (SE) measurements showed attenuation up to 30 dB . At very high frequencies, the film thickness became an important parameter.

Z. Zhang *et al* [9] also used PANi-based magnetic nanocomposites where the disperse phases were $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 nanoparticles. They reported sizes of 10 nm for the spherical particles and nano-needles with diameters between $30\text{-}60 \text{ nm}$ and lengths between $500 - 600 \text{ nm}$. This group also remarked the importance of the nanoparticle size and their concentrations in the composite material. Best results were obtained when the $\gamma\text{-Fe}_2\text{O}_3$ /aniline mass ratio was lower than $1\text{:}4$. The dispersion of the magnetic phase was carried out by mixing the aniline solution with nanoparticles treated with H_3PO_4 . The

electric conductivity of the nanocomposite was decreased by increasing the quantity of ferrite nanoparticles in the matrix. Conductivity values of the nanocomposite were around 4.0×10^{-1} S/cm, with a corresponding magnetization of saturation 6 emu/g for 26.8% of Fe_3O_4 . The composite containing $\gamma\text{-Fe}_2\text{O}_3$ nanoneedles reported 16 emu/g for 33.3 wt% of the disperse phase.

The effectiveness of the use of the polyaniline for EMI shielding has been studied and confirmed by several investigators. D. Yuping *et al* [7] investigated the inclusion of silicon rubber in the polyaniline and the interaction of the grain size with the magnetic properties at low frequencies. The aniline solution was polymerized using ammonium peroxydisulfate as the oxidant and HCl to protonate the polymer structure. The silicone rubber (SR) was blended in the aniline solution using a mixing bowl. The cross-linking agent of liquid silicone rubber was ethyl orthosilicate, whereas dibutyl dilaurate was used as the catalyst. It was observed that a decrease in the resistivity of the PANi matrix, occurs at around $1.689 \times 10^6 \Omega\text{cm}$ (Conductivity: 5.92×10^{-7} S/cm), when blended with 20-30 nm SR particles. The conductivity properties, electromagnetic shielding behavior at different frequencies and morphologies of PANi-based nanocomposites were strongly dependent on the different mixture mass ratios. However, no information about magnetic and structural properties of the composite was included in the corresponding publications.

The results of Wojkiewicz [14], indicated that any improvement on the conductivity of the polymer will also enhance the effectiveness of the electromagnetic shielding. The same researcher also reported a novel option for the processing of polyaniline to fabricate

nanocomposites with high conductivities. The performances of the nanocomposite in terms of electromagnetic shielding were evaluated on a wide range of frequencies (50 MHz - 100 GHz). Electromagnetic shielding effectiveness from 30 to 90 dB was found for mono and multi layer samples in the X and Ku bands (is a portion of the electromagnetic spectrum in the microwave range of frequencies 8.2 - 20 GHz). It was also shown that it is possible to achieve PANi-PU blends with high conductivity under electromagnetic radiations ranging between 50 MHz and 110 GHz.

A. K. Giri [20] studied metal - polymer nanocomposites prepared by high energy ball milling for the system iron - polyethylene. An average grain size of 9 nm, coercivity of 230 Oe at room temperature and 510 Oe at 5 K were obtained for the sample containing 0.1 volume fraction of iron in polyethylene after 200h of milling. R. G. Chandran and R. M. Cursetji [21] reported the development of EMI shielding Ni-Zn ferrite for ribbon flat cables used in digital equipments in the operating frequency range of 30 - 200 MHz. They investigated the effect of composition and variation of process parameters on the microstructure and its performance characteristics such as impedance, permeability, loss, etc., among others.

2. THEORETICAL BACKGROUND

2.1 CONDUCTIVE POLYMERS

The common electronic feature of pristine (undoped) conducting polymers is the π -conjugated system which is formed by overlapping of carbon p_z orbitals and alternating carbon-carbon bond length. In some systems, notably polyaniline, nitrogen p_z orbitals and C_6 rings also are part of the conjugation path. Figure 3 shows the monomer units of the pristine forms of several families of conducting and semiconducting polymers, i.e., trans-polyacetylene $[t-(CH)_x]$, the leucoemeraldine base (LEB), emeraldine base (EB) and pernigraniline base (PNB) form of polyaniline [PAN, polypyrrole (PPy), polythiophene (PT), poly(p-phenylene) (PPP), and poly(p-phenylene vinylene) (PPV)].

Each of these polymers is that of an insulator, with an energy gap between filled and empty energy levels. For undoped $t-(CH)_x$ the energy gap arises from the pattern of alternating single (long) and double (short) bonds with an additional contribution due to electron-electron Coulomb repulsion. Interchange of short and long bonds results in an equivalent (degenerate) ground state. The pernigraniline oxidation state of PAN also has a two-fold degenerate ground state. The remaining polymers in Figure 3 are nondegenerate: single and double bond interchange yields electronic structures of different energy.

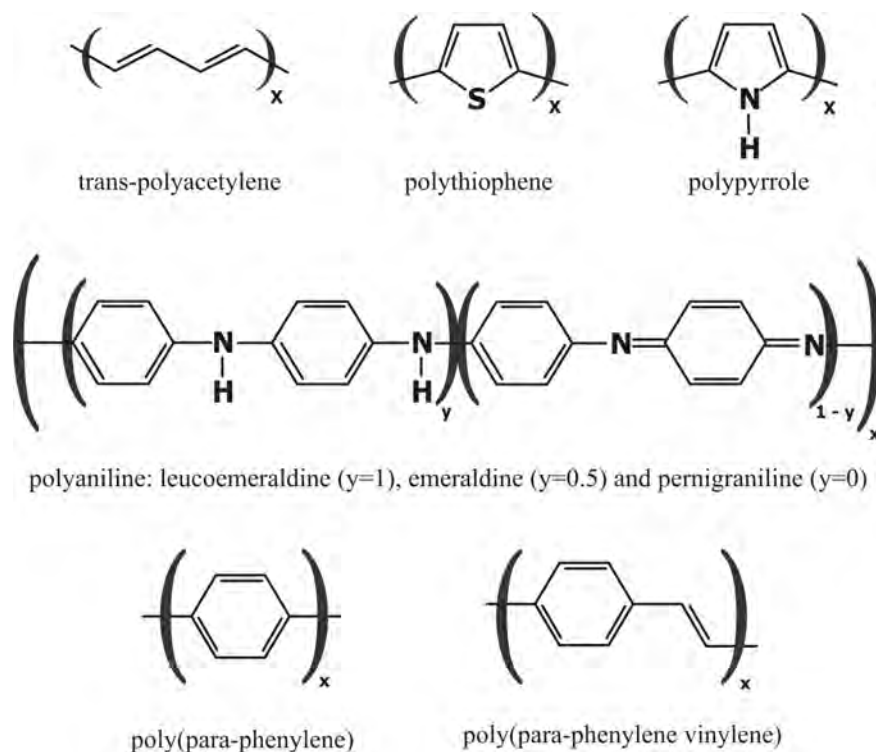


Figure 3. Monomer units of several electronic polymers

2.1.1 Polyaniline as Viewed from a Structural Perspective

Polyaniline and its related derivatives form a diverse family of conducting polymers in terms of both their electronic and structural characteristics. These properties are intimately coupled with the subtle molecular level intrachain and interchain interactions. Amorphous polyaniline (a-PAni) exhibits relatively poor interchain electron transport behavior thus rendering these materials quasi-one-dimensional. Crystalline PAni (c-PAni) salts can, depending on the primary dopant, the presence of water and/or secondary dopants and the sample processing history, display a vastly improved interchain ordering which results in an increase in the overall conductivity. This leads to a three-dimensional band picture and the development of a metallic-like state. Understanding the central structure/property

issues underlying this broad diversity is a formidable goal and requires a detailed knowledge of both the nascent polymer structure and its subsequent evolution.

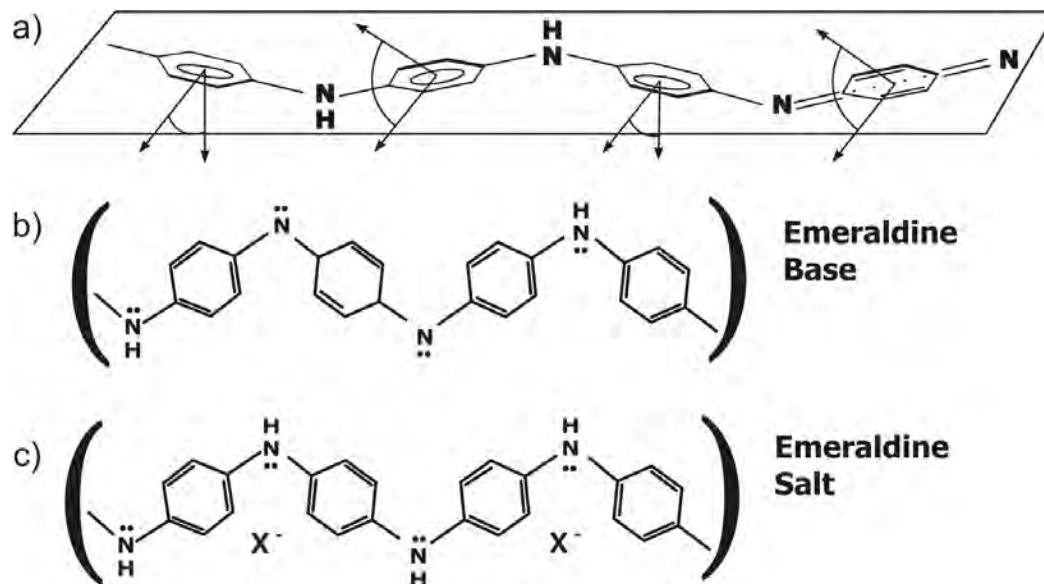


Figure 4. Schematic drawings for PANi showing the ring torsions referenced to the average molecular plane (a) and both, (b) base and (c) salt forms.

The nominal main chain architecture which best describes PANi is given by

$$\left[(C_6H_4 - NH - C_6H_4 - NH -)_{1-x} (C_6H_4 - N = C_6H_4 = N -)_x \right]_n \quad (1)$$

PAni may be prepared in a range of oxidation states varying from the fully oxidized ($x = 1$) pernigraniline form to the fully reduced ($x = 0$) leucoemeraldine form. Emeraldine base, at $x = 0.5$, is essentially an insulator and contains a four monomer chain repeat comprised of three benzenoid rings and one quinoid ring as shown in Figure 4.

These polymers can also be prepared in the conducting salt form, either during synthesis or after reaction with an appropriate acid HX , to yield

$$\left[\left(C_6H_4 - NH - C_6H_4 - NH^+ - \right) (X^-) \right]_n \quad (2)$$

with $y = X^-/N$ where X^- is the counter-ion and $y = 0.5$ is the maximum dopant concentration found in the most heavily doped form. In the best circumstances PANi ES's conductivity can increase (referred to EB) by at least 14 orders of magnitude to well over 1000 S/cm. Either EB or ES can be effectively processed using conventional polymer processing techniques to give useful articles such as fibers, films, and coatings that are also electronically conducting.

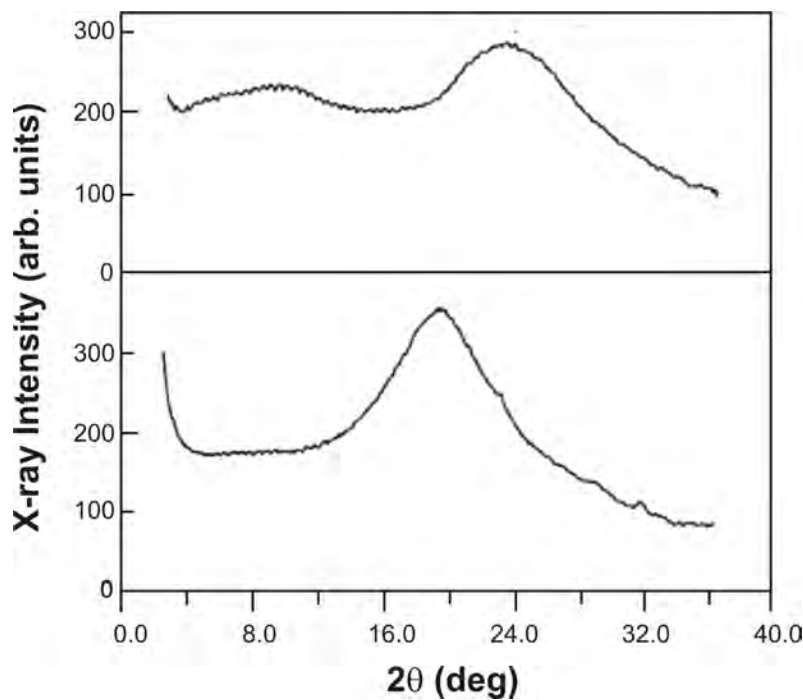


Figure 5. Typical powder diffraction spectra from fully amorphous PANi-EB (bottom) and HCl-doped ES (top) in the class-II form [51].

The presence of modest flexibility about the alternating amine/imine linkages and the disparate torsional response of the two fundamental main chain ring units appear to frustrate the overall interchain packing. These factors, in combination with the possibility

of interchain $N\cdots HN$ hydrogen bonding and the coininsertion of H_2O , yield a parent EB or ES polymer which can be prepared in either a partially ordered state having modest crystallinity or in a fully amorphous form as shown in Figure 5.

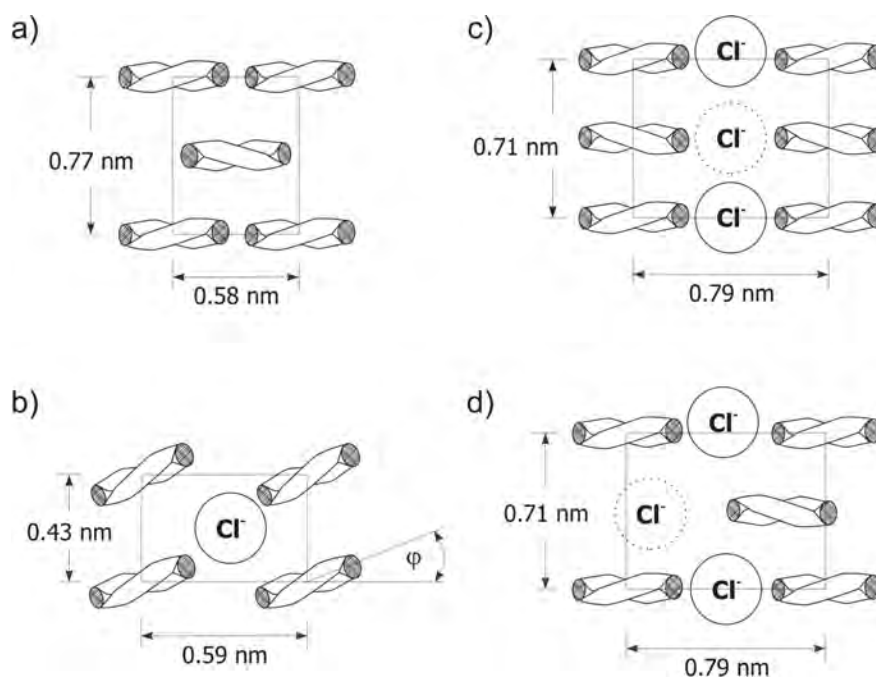


Figure 6. Proposed equatorial packings (perpendicular to the chain axis) for crystalline PANi films and powders in (a) EB-II, (b) ES-I, (c) ES-II, Pc2a and (d) ES-II, P2₁22₁[51].

There is a well-documented polymorphism in which at least two distinctly different structural forms can be recognized. Class I ES-I and EB-I compounds are typically obtained from HCl-doped PANi ES solutions which have been precipitated while class II structures are associated with films formed by casting of EB from organic solvents such as NMP. The proposed crystalline chain packings by Pouget and coworkers [23] for these structures are reviewed in Figure 6. By extending these previous studies to encompass the structural evolution of c-PAni EB-I powders on doping by aqueous HF solutions and c-PAni HCl-doped PANi powder after dehydration and rehydration we are able to further

clarify the nature of structural ordering within the class I family of compounds. The nominal ES-I structure of Figure 6 must be strongly modified in order to incorporate the existence of local chain rotations and lateral displacements which lower the overall symmetry of the unit cell and effectively generate one-dimensional channels, parallel to the polymer chain axis, which enhance the uptake of water into crystalline regions. Moreover these studies indicate a qualitatively different structural evolution during HF-doping to yield a more extensive family of class I structures.

2.1.2 Models for Electrical Conductivity

Much work has focused on the nature of the charge carriers in the highly doped metallic state. They may be spatially localized by structural disorder so that they cannot participate in transport except through hopping. Figure 7 is a schematic view of the inhomogeneous disorder, with individual polymer chains passing through both ordered regions (typically 3 - 10 nm across) and disordered regions. The percent “crystallinity” may vary from near zero to 50 or 60% for polypyrroles and polyanilines, respectively, to greater than 80% for polyacetylenes. The chains in the disordered regions may be either relatively straight, tightly coiled, or intermediate in disorder.

Impurities and lattice defects in disordered systems introduce backward scattering of these electron waves with resulting “Anderson localization”. The ramifications include a finite density of states $N(E_F)$ produced at the Fermi level E_F between mobility edges. When the Fermi level or chemical potential lies in the localized region, $\sigma(T = 0 \text{ K})$ is zero even for a

system with a finite density of states. Mott variable range hopping (VRH) model is applicable to systems with strong disorder such that the disorder energy is much greater than the band width. For Mott's model

$$\sigma = \sigma_0 \cdot \exp \left[- \left(\frac{T_0}{T} \right) \right]^{\frac{1}{(d+1)}} \quad (3)$$

where d is the dimensionality and, for three-dimensional systems,

$$T_0 = c \cdot I \cdot k_B \cdot N \cdot (E_F) \cdot L^3 \quad (4)$$

Where c is the proportionality constant, k_B the Boltzmann constant and L the localization length. If the Fermi level is at an energy such that the electronic states are extended, then finite σ at 0 K is expected. This model assumes that the substantial disorder is homogeneous throughout the isotropic three-dimensional sample.

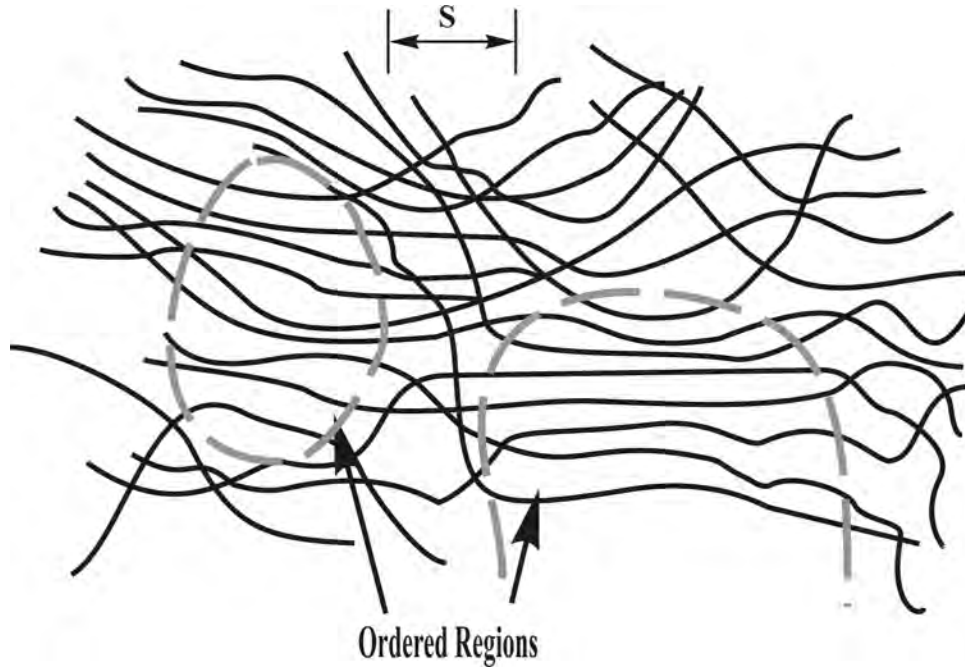


Figure 7. Schematic view of the inhomogeneous disorder in these doped polymers, with individual polymer chains passing through both ordered regions (typically 3 - 10 nm across) and disordered regions (of length “s”).

For isolated one-dimensional metallic chains localization of charge carriers arises for even weak disorder because of quantum interference due to static back-scattering of electrons, contrasting to the strong disorder required for localization in three-dimensional systems. The localization effects in the inhomogeneously disordered (partially crystalline) conducting polymers are proposed to originate from one-dimensional localization in the disordered regions. The inhomogeneous disorder model represents the doped polymer as relatively ordered regions (crystalline islands) interconnected through polymer chains traversing disordered regions, as in Figure 7. Within this model, conduction electrons are three dimensionally delocalized in the “crystalline” ordered regions (paracrystalline disorder may limit delocalization within these regions). To transit between ordered regions, the conduction electrons must diffuse along electronically isolated chains through the disordered regions where the electrons easily become localized. The localization length of these electrons depends on the details of the disorder (e.g., electrons traveling along tightly coiled chains are expected to have much shorter localization lengths than electrons traveling along expanded coil or relatively straight chains).

Photon-induced enlargement of the localization length increases the conductivity with higher temperature. Three-dimensional crystalline order facilitates delocalization. If the localization length for some conduction electrons exceeds the separation between the ordered regions then it will be substantially enhanced.

For conventional metals, many of the electrical transport properties can be described by the Drude model with a single scattering time τ . The model explains high and frequency independent conductivity of metals from dc to the microwave ($\sim 10^{10}$ Hz) frequencies, and a

real part of the dielectric constant (ϵ_r) which is negative below the screened plasma frequency, $\omega_p^2 = 4\pi ne^2/m^*\epsilon_b$; n is the density of carriers, m^* is the carrier effective mass, and ϵ_b is the background dielectric constant. In the low frequency Drude limit ($\omega\tau \ll 1$), the Drude response can be deduced as $\epsilon_r = -\omega_p^2\tau^2/\omega^2$ and $\epsilon_i = \omega_p^2\tau/\omega$, where ϵ_i is the imaginary part of the dielectric constant.

2.1.3 Electrical Conductivity of Conducting Polymers

The $\sigma(T)$ of heavily iodine doped $(CH)_x$ and PF_6 doped PPy down to mK range vary as a function of aging. The highest σ_{dc} at room temperature reported in [37] is $\sim 5 \times 10^4$ S/cm for I_3 doped T- $(CH)_x$ and $\sim 10^3$ S/cm for the highest conducting PPy (PF_6). For both of these materials, σ decreases with decreasing temperature to a minimum at $T_m \sim 10$ K. Below T_m (room temperature), increases by $\sim 20\%$ and then is constant to 1 mK. Some preparations of PAni-CSA show similar behavior. Lower conductivity samples of doped $(CH)_x$, doped polyaniline, and doped polypyrrole become insulating material at low temperatures.

Hydrochloric acid as well as CSA doped polyaniline prepared in chloroform often show quasi-one-dimensional variable range hopping (VRH),

$$\sigma = \sigma_0 \cdot \exp \left[- \left(\frac{T_0}{T} \right) \right]^{\frac{1}{2}} \quad (5)$$

where,

$$T_0 = \frac{16}{[k_B \cdot N \cdot (E_F) \cdot L \cdot Z]} \quad (6)$$

Here L is the one-dimensional localization length and z the number of nearest neighbor chains. Generally, the higher samples have a weaker temperature dependence ($T_0 \sim 700 - 1000$ K, $T < 80$ K), and lower σ samples a stronger temperature dependence ($T_0 \sim 4000$ K). Smaller T_0 is associated with weaker localization and improved intrachain and interchain order.

The microwave frequency dielectric constant provides a measure of the charge delocalization in individual samples. The low temperature dielectric constant, ϵ_{mw} , for a series of emeraldine hydrochloride samples is proportional to the square of the crystalline coherence length, ξ^2 , independent of the direction of orientation of the sample with regard to the microwave frequency electric field, demonstrating that the charge is delocalized three-dimensionally within the crystalline regions of these samples.

The sign, magnitude, and temperature dependence of the 6.5×10^9 Hz dielectric constant for very highly conducting T-[CH(I₃)_y]_x, PPy-PF₆, and m-cresol prepared PAN-CSA are quite striking. Each of these systems has a large ($10^4 - 10^6$) and negative value of ϵ_{mw} . Using the Drude model for low frequencies ($\omega\tau < 1$), plasma frequencies of $\omega_p = 0.01 - 0.02$ eV (~ 200 cm⁻¹) and room temperature scattering times of $\sim 10^{-11}$ sec were calculated. The exact values correlate with the sample preparation conditions. The ω_p are much smaller than one expects from the usual Drude model, suggesting that only a small fraction of the conduction band electrons participate in this low frequency plasma response. Similarly, the value of τ is two orders of magnitude larger than usual for an alkali, noble or transition metal, perhaps associated with the time for electrons to transit the disordered regions.

For the conducting doped conjugated polymers, there are zero, two, three, or one zero crossings of the real part of the dielectric function (ϵ_1) as the frequency is decreased. For the least conducting materials, ϵ_1 remains positive for the entire optical frequency range (50 - 50,000 cm^{-1}), reaching values of several hundred at microwave frequencies. For higher conductivity materials, ϵ_1 crosses zero between 1 and 3 eV (the all-conduction-electron plasma response) and then becomes positive again below 1000 cm^{-1} , reaching values in excess of 10^4 at microwave frequencies. For “metallic” doped PANi and PPy with $\sigma_{\text{dc}} \sim 400 \text{ S/cm}$, ϵ_1 has the previous two zero crossings and a third zero crossing occurs in negative values at a “delocalized conduction electron plasma frequency” of several hundred wavenumbers. For very highly conducting doped polyacetylene, ϵ_1 crosses zero at all conduction electron plasma frequency and remains negative to the lowest measured optical frequencies.

Material	Maximum conductivity, S/m	Structure
Polyacetylene	1.5×10^7	Alternating single and double carbon-carbon bonds
Polypyrrole	2.0×10^5	Five-membered rings containing nitrogen and alternating single and double carbon-carbon bonds
Polyphenylene	1.0×10^5	Directly linked benzene rings
Polyphenylene vinylene	1.0×10^5	A combination of polyacetylene and polyphenylene
Polyphenylene sulfide	1.0×10^4	Benzene rings linked by sulfur atoms
Polythiophene	1.0×10^4	Five-membered rings containing sulfur and alternating single and double carbon-carbon bonds
Polyaniline	1.0×10^3	Benzene rings linked by nitrogen atoms

Table 1. Representative conducting polymers.

Conductivity depends on the number density of charged carriers and how fast they can move in the material; it also depends on the temperature. For semiconductors conductivity generally decreases with lower temperatures. Several conducting polymers are available commercially (Table 1), although materials are presented with values of conductivity higher than those reached by the polyaniline. This allows a synthesis process in aqueous medium, favorable for the dispersion of the ferrite, which comes from a synthesis aqueous medium as well.

All these series claim a high doping level, are not easy processable and blendable with the polymeric matrices. The polyaniline presents a unique conduction mechanism and good stability in the presence of oxygen and water and its electrical properties can be modified by changing oxidation state and protonation state. PANi is a kind of powder with metallic luster, and the conjugations of its molecular chains are strong for a long time [7,52,53].

2.1.4 Increase in Conductivity with Doping

The conductivities of the pristine electronic polymers are transformed from insulating to conducting through doping. Both n-type (electron donating, e.g., Na, K, Li, Ca, tetrabutylammonium) and p-type (electron accepting, e.g., PF₆, BF₄, Cl, AsF₆) dopants have been used. The doping typically is done using vapors or solutions of the dopant, or electrochemically. In some circumstances, the polymer and dopant are dissolved in the same solvent before forming the film or powder. The polymer backbone and dopant ions form a rich variety of new three-dimensional structures.

For the degenerate ground state polymers, the charges added to the backbone at low doping levels are stored in charged soliton and polaron states for degenerate polymers, and as charged polarons or bipolarons for nondegenerate systems. For nondegenerate polymers, high doping results in polarons interacting to form a “polaron lattice” or electrically conducting partially filled energy band. Some models suggest equilibrium between polarons and bipolarons. At high doping levels of $t-(CH)_x$, it is proposed that the soliton energy levels essentially overlap the filled valence and empty conduction bands leading to a conducting polymer.

For the polyaniline emeraldine base (EB) form, the conductivity varies with proton (H^+ ion) doping level (protonic acid doping). In the protonation process, there is no addition or removal of electrons to form the conducting state. Figure 8 schematically demonstrates the equivalence of p-doping of leucoemeraldine base and protonic acid doping of EB to form the conducting emeraldine salt. Both organic acids such as HCSA (camphor sulfonic acid), and inorganic acids, such as HCl, are effective, with the organic sulfonic acids leading to solubility in a wide variety of organic solvents, such as chloroform and m-cresol. The protonic acid may also be covalently bound to the polyaniline backbone, as has been achieved in the water soluble sulfonated polyanilines.

Similar electronic behavior has been observed for protonic acid doped PAN as for the other nondegenerate ground state systems (Figures 9a and 9b). That is, polarons are important at low doping levels, and, for doping to the highly conducting state, a polaron lattice (partially filled energy band) forms. Polaron pairs or bipolarons are formed in less ordered regions of doped polymers.

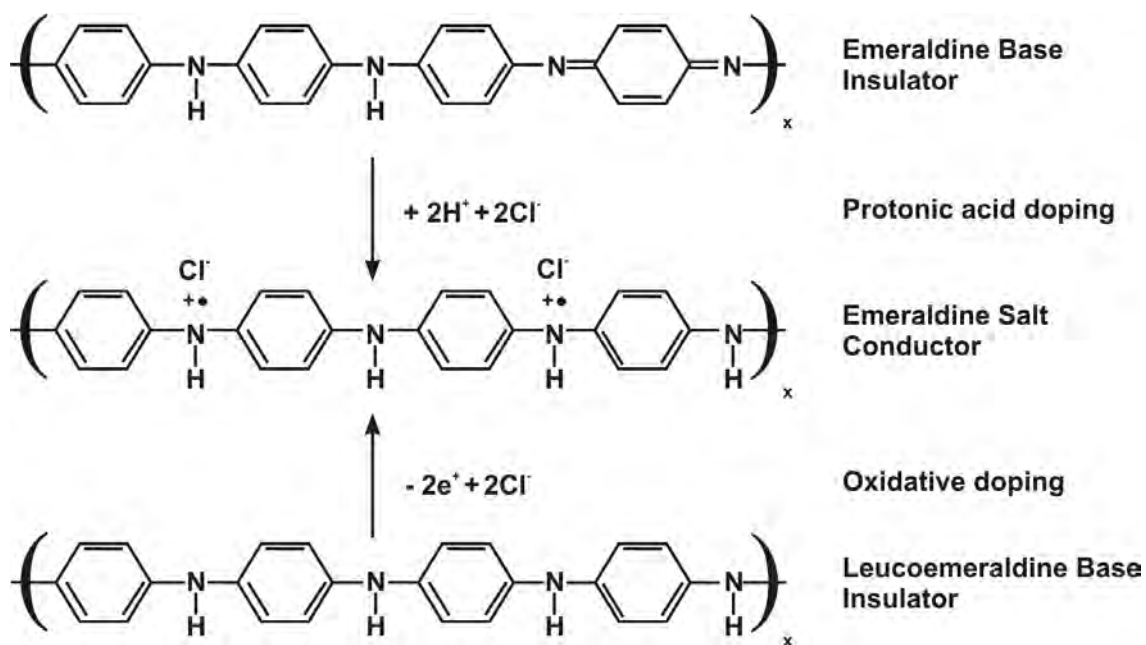


Figure 8. Illustration of the oxidative doping (p-doping) of leucoemeraldine base and protonic acid doping of emeraldine base, leading to the same final product, emeraldine salt.

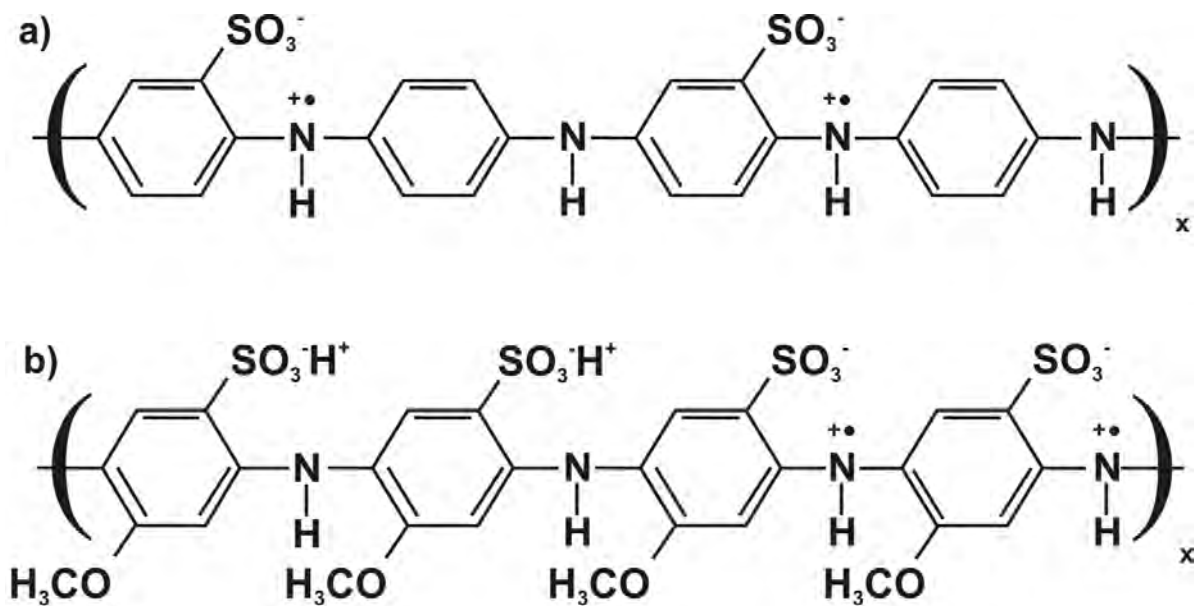


Figure 9. Schematic illustrations of (a) 50% sulfonated and (b) 100% sulfonated polyanilines (self-doped forms).

2.1.5 Others Conducting Polymers Applications

Intrinsically conducting polymers are promising materials for shielding electromagnetic (EM) radiation and reducing or eliminating EMI because of their relatively high σ and ϵ values and their ease of control through chemical processing. Also, they are relatively lightweight compared to standard metals, flexible, and do not corrode. The capabilities are in the range for many commercial (~40 dB) and military (~80 - 100 dB) applications.

The corrosion of steel has long been an important industrial and environmental problem. Polyaniline has been shown to have corrosion protecting capabilities both when doped and neutral. The mechanism for corrosion protection was found to be anodic, i.e., the polyaniline film withdraws charge from the metal, pacifying its surfaces against corrosion. Large values (up to ~1.5 cm) of throwing power were obtained for emeraldine base protected cold rolled steel.

There is a need for low voltage, reliable operation of light emitting polymer devices. One approach is to overcoat the transparent conducting indium tin oxide electrode with a layer of nearly transparent conducting polymer, especially polyaniline, or incorporating networks of conducting polymer fibers in the polymers [27-30].

2.1.6 Related Studies on PANi

All PANi powder samples were prepared by oxidative polymerization of aniline in an

aqueous HCl solution and this synthesis yields class-I ES with a Cl^- concentration, y , approaching 0.5 [31]. Emeraldine base (EB-I) was obtained by immersion of this HCl ES-I in an excess of 0.1M NH_4OH for a minimum of 3 h. Individual portions of this EB-I were thereafter immersed in various aqueous HF solutions with HF concentrations ranging from 25 mM to 995 mM and then dried under dynamic vacuum. These class-I ES powders were then transferred in air to glass or mica walled x-ray capillaries for further diffraction studies. A quantity of the HCl-doped ES-I powder was also transferred into the first chamber of a special dual chambered *in situ* x-ray cell and then dried under dynamic vacuum at ca. 100 °C for 6 h. After drying, a small quantity of degassed water was placed in the second chamber of the evacuated *in situ* cell. The amorphous PANi films (EB-II) were cast from N-Methyl pyrrolidone (NMP), which is an organic solvent. One film was then treated with 1M aqueous HCl solution to yield the respective a-PAni ES-II sample shown in Figure 10. All films and powders were typically handled in air. Therefore all PANi samples discussed hereafter are expected to contain appreciable quantities of absorbed water (especially the ES samples) with the sole exception of the dehydrated sample.

On the above bases, structural modification of PANi by alkaline and acid treatment resulted in viable processes. This feature will be used in our research to explore the different approaches to prepare the PANi/ferrite nanocomposites.

Figure 10 displays a typical powder diffraction spectra from the various indicated class-I PANi samples. The as-prepared HCl-doped ES profile (at the bottom) exhibits the largest proportion of sharp scattering features and is qualitatively similar to other XRD studies [30-32]. This suggests a significant crystalline fraction. Unlike the EB-I results of researchers,

removal of HCl reduces the relative crystalline fraction of material only slightly. There are noticeable shifts in the positions and relative peak intensities indicative of the distinct changes in both the unit cell dimensions and the local structure (determined from the angular peak widths). In addition, a pronounced new peak centered near $2\theta \approx 6.5^\circ$ is clearly resolved.

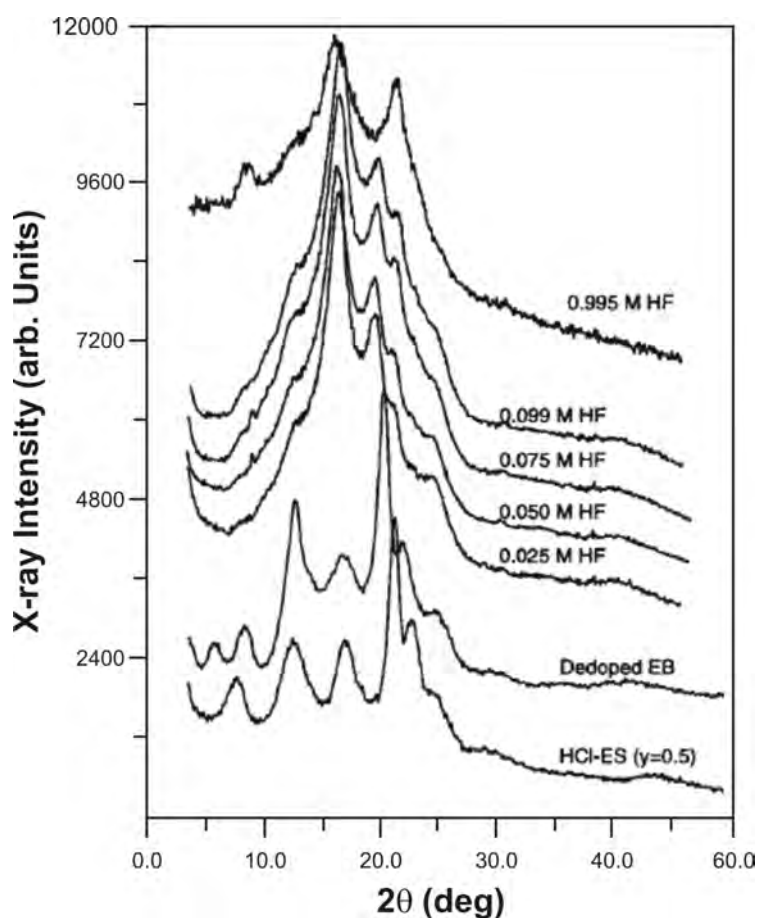


Figure 10. XRD spectra from a series of emeraldine class I powder samples after synthesis (to yield HCl-ES at bottom), treatment with 0.1 M NH_4OH (to give dedoped EB) and then exposure to increasingly stronger aqueous HF solutions. Note that all curves except the bottom one have been vertically offset for clarity [31].

The subsequent XRD spectra of the HF redoped samples display a number of marked changes. While the four profiles spanning the 25 mM to 99 mM HF ES-I samples are

qualitatively similar to one another they are profoundly different from those of either the as-prepared HCl-doped ES sample or the dedoped EB powder. There are, however, at least two subtle systematic variations throughout this intermediate HF-doping sequence. The $2\theta = 30^\circ$ shoulder becomes much less pronounced while the $2\theta = 26^\circ$ shoulder is ultimately identified as a distinguishable peak. The 995 mM sample scan is clearly different from all the preceding curves, and indicates that addition HF uptake (to give $y \approx 0.5$) which is associated with a discrete change to another structural phase. In this case the scattering profile bears a strong resemblance to the H_2SO_4 -doped PANi ES [33]. It should be noted that throughout the entire processing sequence of samples in Figure 10 there appears to be a monotonic decrease in the proportion of scattering which can be attributed to crystalline regions of the films. Moreover these remaining peaks also appear to broaden somewhat. This general trend suggests that c-PAni is “fragile” and that the continued structural variations lower irreversibly the relative crystallinity.

There are other important scattering features that can be resolved. The HCl-ES scan of Figure 10 contains distinctive variations in the widths and shapes of the resolved peaks. Naïvely one expects that simple crystalline polymers tend to produce scattering peaks whose full-width at half-maximum are nearly independent of the crystal orientation and broaden only slightly with increasing 2θ . In this sample the two peaks located near $2\theta = 26^\circ$ and 28° are much narrower than any other resolved peaks including those at lower angles. While an anisotropic crystal habit may play a role in this result, a more likely possibility is that these other peaks are comprised of at least two or more superimposed scattering peaks from a low-symmetry unit cell. Hence a simple d-spacing identification is

somewhat deceptive although we include this in Table 2.

SAMPLE	2 θ , °	d, nm	SAMPLE	2 θ , °	d, nm
HCl-ES	8.9	0.99	Dedoped EB	6.5	1.40
	15.0	0.59		9.8	0.90
	20.4	0.44		15.1	0.59
	25.4	0.35		20.0	0.44
	27.7	0.32		24.3	0.37
	30.5	0.29		26.4	0.34
HF-ES (99 mM)	9.4	0.94	HF-ES (995 mM)	30.0	0.30
	14.7	0.60		36.5	0.25
	19.4	0.46		10.0	0.88
	23.4	0.38		14.6	0.61
	25.5	0.35		19.0	0.47
	29.6	0.30		25.5	0.35

Table 2. Summary of observed d-spacings of PAni samples [34].

Before introducing possible structural models for the aforementioned results it is first necessary to demonstrate the significance of incorporating water uptake into any comprehensive discussion of the unit cell structure. Hence the results of the *in situ* scattering experiment during water uptake in a dehydrated HCl-doped ES-I samples are shown in Figure 11.

The bottom two spectra of the left side panel show in direct relief a comparison of the dehydrated powder and the same powder after exposure to water vapor for just 30 m. While the specific crystalline peak positions remain relatively unchanged, the dehydrated

sample data is significantly different in a variety of important ways. Much of the scattering intensity shifts to lower angle and the relative proportion of scattering by crystalline regions of the power is sharply diminished. Moreover the relative peak intensity ratios are seen to shift strongly. There is an exceptionally large increase in the scattering intensity of the dehydrated sample at the lowest accessible 2θ regions. There are also noticeable changes between the two HCl-ES profiles representing a sample before (Figure 10) and after dehydration. In particular the rehydrated sample exhibits a profile shape closer and it contains a measurable decrease in the relative fraction of crystalline material.

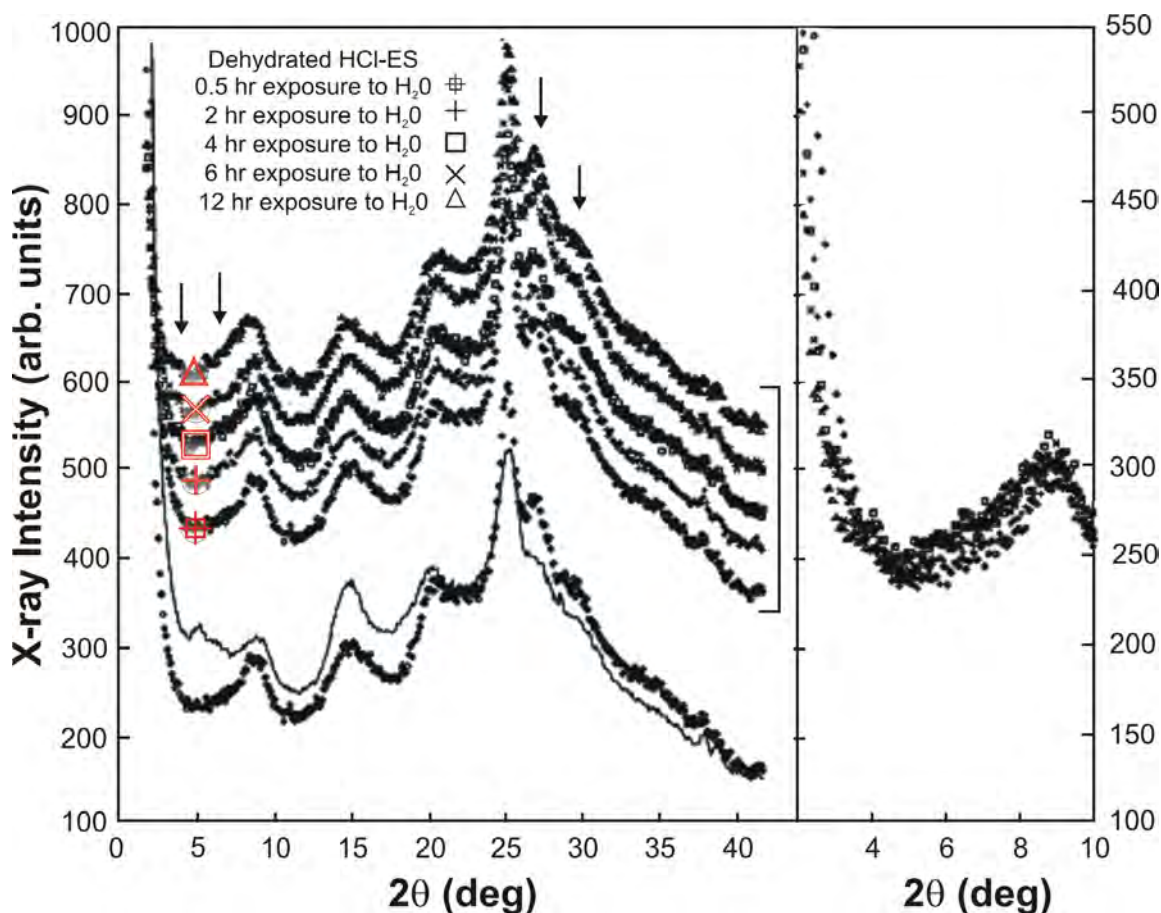


Figure 11. XRD spectra recorded *in situ*, from a dried HCl-ES (class I) sample, during continuous exposure to water vapor. The left panel is arranged so that only the upper five bracketed curves have been vertically offset. The right panel shows the low angle 2θ behavior in greater detail without offsets [35].

These features suggest that water has a profound impact on the crystal structure, the relative crystalline/amorphous proportions and the overall structural homogeneity. Removal of water from HCl-doped ES seems to produce three main effects: the unit cell packing becomes altered without any dramatic changes in the major d-spacings, the level of local disorder within the unit cell is significantly increased and, finally, the degree of structural inhomogeneity at larger scales is also increased. Since the small-angle scattering results of Annis *et al* [24] identify changes primarily along the meridional direction, the increases in intensity of the scattering background seen in their work are also expected to occur likewise (along the meridional direction) and are associated with ordering by both water and halogen counter-ions within any identifiable channels. Closer inspection of the *in situ* profiles, obtained at selected times after constant exposure to water vapor, shows continued evolution of the HCl-doped ES structure. In addition to the rapid recovery of the original ES-I unit cell structure, albeit with a loss in crystallinity, the low-angle scattering in the $2\theta = 2^\circ$ to 4° region smoothly decreases over time. This suggests a gradual return to a more uniform water/halogen- ion ordering along the c-axis. Coupled with this are gradual increases in the scattering intensity in the vicinity of 4° , 7° , 27° at 30° (and denoted by arrows in Figure 11). Hence there are slow changes in the unit cell structure itself.

To recognize the levels of cristallinity of the polymer, in their different forms associated to variations under the effect of different reagents, it allows us to manipulate the polyaniline and to predict the structural results. Again the importance of the concentrations of the acid affects the structure of the polymer, achieving a transformation of PAni EB to PAni ES and to obtain structures specifies inside each product.

2.2 FERRITES

2.2.1 Classification of Magnetic Materials

All materials can be classified in terms of their magnetic behaviour falling into one of five categories depending on their bulk magnetic susceptibility. The two most common types of magnetism are diamagnetism and paramagnetism, which account for the magnetic properties of most of the periodic table of elements at room temperature (Figure 12).

Legend:

- Ferromagnetic
- Antiferromagnetic
- Paramagnetic
- Diamagnetic

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	

Figure 12. A periodic table showing the type of magnetic behaviour of each element at room temperature.

These elements are usually referred to as non-magnetic, whereas those which are referred to as magnetic are actually classified as ferromagnetic. The only other type of magnetism observed in pure elements at room temperature is antiferromagnetism. Finally, magnetic materials can also be classified as ferrimagnetic although this is not observed in any pure element but can only be found in compounds, such as the mixed oxides, known as ferrites,

from which ferrimagnetism derives its name. The value of magnetic susceptible falls into a particular range for each type of material and this is shown in table 3 with some examples.

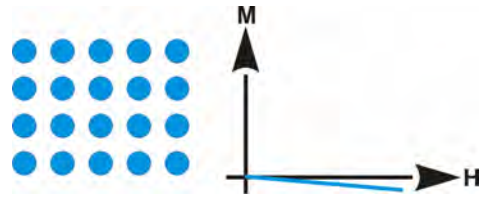
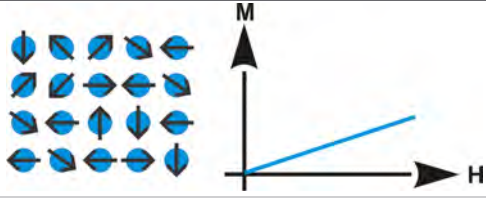
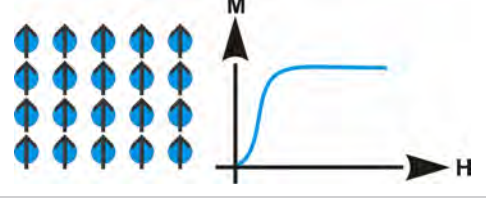
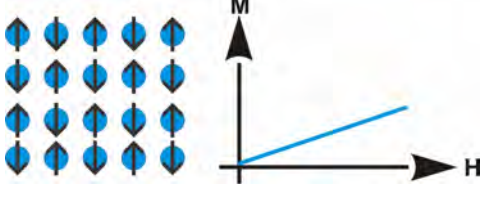
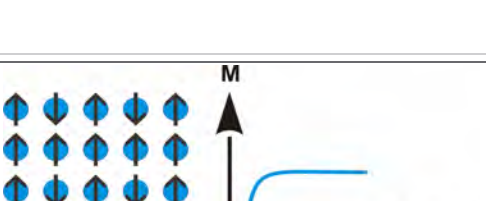
Type of Magnetism	Susceptibility	Atomic / Magnetic Behaviour	
Diamagnetism	Small and negative	Atoms have no magnetic moment	
Paramagnetism	Small and positive.	Atoms have randomly oriented magnetic moments	
Ferromagnetism	Large and positive function of applied field, microstructure dependent	Atoms have parallel aligned magnetic moments	
Anti ferromagnetism	Small and positive.	Atoms have mixed parallel and anti-parallel aligned magnetic moments	
Ferrimagnetism	Large and positive, function of applied field, microstructure dependent	Atoms have anti-parallel aligned magnetic moments	

Table 3. Summary of different types of magnetic behaviour.

2.2.1.1 Diamagnetism

In a diamagnetic material the atoms have no net magnetic moment when there is no applied field. Under the influence of an applied field (H) the spinning electrons precess and this

motion, which is a type of electric current, produces a magnetization (M) in the opposite direction to that of the applied field. All materials have a diamagnetic effect; however, it is often the case that the diamagnetic effect is masked by the larger paramagnetic or ferromagnetic term.

2.2.1.2 *Paramagnetism*

There are several theories of paramagnetism, which are valid for specific types of material. The Langevin model, which is true for materials with non-interacting localised electrons, states that each atom has a magnetic moment which is randomly oriented as a result of thermal agitation. The application of a magnetic field creates a slight alignment of these moments and hence a low magnetization in the same direction as the applied field. As the temperature increases, then the thermal agitation will increase and it will become harder to align the atomic magnetic moments and hence the susceptibility will decrease.

2.2.1.3 *Ferromagnetism*

Ferromagnetism is only possible when atoms are arranged in a lattice and the atomic magnetic moments can interact to align parallel to each other. This effect is explained in classical theory by the presence of a molecular field within the ferromagnetic material, which was first postulated by Weiss in 1907. This field is sufficient to magnetise the material to saturation. In quantum mechanics, the Heisenberg model of ferromagnetism describes the parallel alignment of magnetic moments in terms of an exchange interaction between neighboring moments.

Weiss postulated the presence of magnetic domains within the material, which are regions

where the atomic magnetic moments are aligned. The movement of these domains determines how the material responds to a magnetic field and as a consequence the susceptibility is a function of applied magnetic field. Therefore, ferromagnetic materials are usually compared in terms of saturation magnetization (magnetization when all domains are aligned) rather than susceptibility.

2.2.1.4 *Antiferromagnetism*

In the periodic table the only element exhibiting antiferromagnetism at room temperature is chromium. Antiferromagnetic materials are very similar to ferromagnetic materials but the exchange interaction between neighboring atoms leads to the anti-parallel alignment of the atomic magnetic moments. Therefore, the magnetic field cancels out and the material appears to behave in the same way as a paramagnetic material. Like ferromagnetic materials these materials become paramagnetic above a transition temperature, known as the Néel temperature, T_N . (Cr: $T_N = 37^\circ\text{C}$).

2.2.1.5 *Ferrimagnetism*

Ferrimagnetism is only observed in compounds, which have more complex crystal structures than pure elements. Within these materials the exchange interactions lead to parallel alignment of atoms in some of the crystal sites and anti-parallel alignment of others. The material breaks down into magnetic domains, just like a ferromagnetic material and the magnetic behaviour is also very similar, although ferrimagnetic materials usually have lower saturation magnetizations. For example in Barium ferrite ($\text{Ba}_{0.6}\text{Fe}_2\text{O}_3$) the unit cell contains 64 ions of which the barium and oxygen ions have no magnetic moment, 16 Fe^{3+} ions have moments aligned parallel and 8 Fe^{3+} aligned anti-parallel giving a net

magnetization parallel to the applied field, but with a relatively low magnitude as only $\frac{1}{8}$ of the ions contribute to the magnetization of the material. Ferrimagnetic materials are, in general, oxides of iron combined with one or more of the transition metals such as manganese, nickel or zinc, e.g. MnFe_2O_4 .

Almost every item of electronic equipment produced today contains some ferrimagnetic material: loudspeakers, motors, deflection yokes, interference suppressors, antenna rods, proximity sensors, recording heads, transformers and inductors are frequently based on ferrites. The ferrimagnets possess permeability to rival most ferromagnets but their eddy current losses are far lower because of the material's greater electrical resistivity. Also it is practicable (if not straightforward) to fabricate different shapes by pressing or extruding - both low cost techniques.

2.2.2 Magnetic Hysteresis

Ferromagnetic and ferrimagnetic materials have non-linear initial magnetization curves, as the changing magnetization with applied field is due to a change in the magnetic domain structure. These materials also show hysteresis and the magnetization does not return to zero after the application of a magnetic field. Figure 13 shows a typical hysteresis loop; the two loops represent the same data, however, the red loop is the polarisation ($J = m_0 M = B - m_0 H$) and the blue loop the induction, both plotted against the applied field.

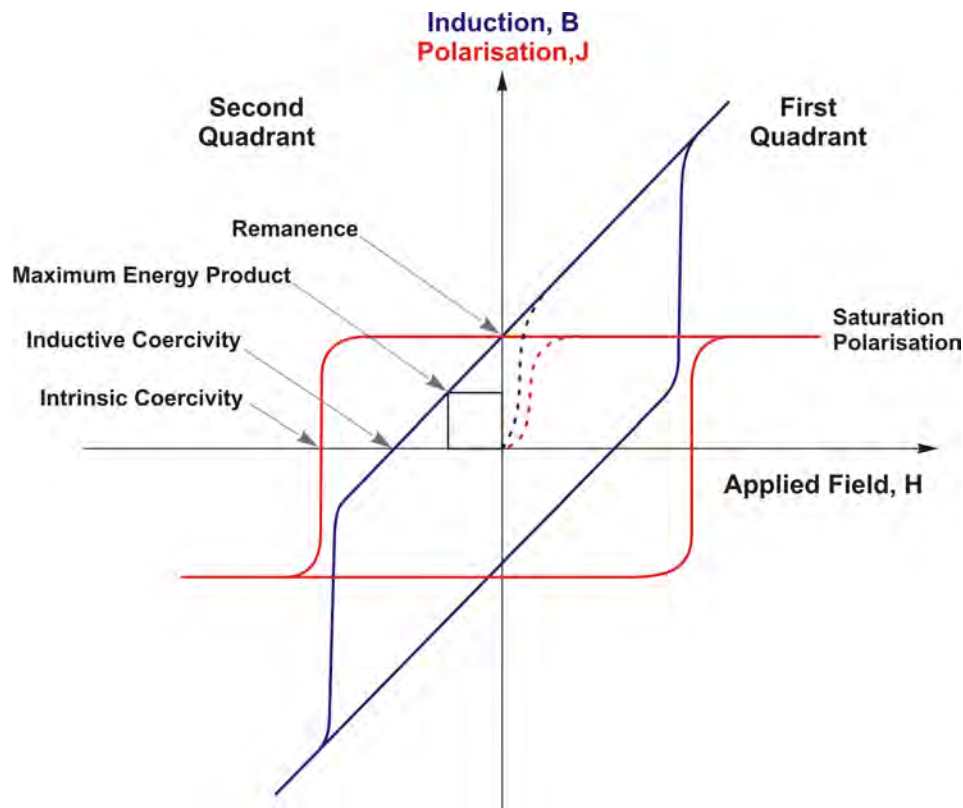


Figure 13. A typical hysteresis loop for a ferro- or ferri- magnetic material.

Illustrated in the first quadrant of the loop is the initial magnetization curve (dotted line), which shows the increase in polarisation (and induction) on the application of a field to an unmagnetised sample. In the first quadrant the polarisation and applied field are both positive, i.e. they are in the same direction. The polarisation increases initially by the growth of favourably oriented domains, which will be magnetised in the easy direction of the crystal. When the polarisation can increase no further by the growth of domains, the direction of magnetization of the domains then rotates away from the easy axis to align with the field. When all of the domains have fully aligned with the applied field saturation is reached and the polarisation can increase no further.

If the field is removed the polarisation returns along the solid red line to the y-axis (i.e. $H = 0$), and the domains will return to their easy direction of magnetization, resulting in a decrease in polarisation. In Figure 13, the line from the saturation point to the y-axis is horizontal, which is representative of a well aligned material, where the domains are magnetised in the easy direction of the crystal at the saturation point.

If the direction of applied field is reversed (i.e. to the negative direction) then the polarisation will follow the red line into the second quadrant. The hysteresis means that the polarisation lags behind the applied field and will not immediately switch direction into the third quadrant (i.e. negative polarisation). The polarisation will only decrease after a sufficiently high field is applied to:

- nucleate and grow domains favourably oriented with respect to the applied field
- or
- rotate the direction of magnetization of the domains towards the applied field

After applying a high enough field saturation polarisation will be achieved in the negative direction. If the applied field is then decreased and again applied in the positive direction then the full hysteresis loop is plotted.

If the field is repeatedly switched from positive to negative directions and is of sufficient magnitude then the polarisation and induction will cycle around the hysteresis loop in an anti-clockwise direction. The area contained within the loop indicates the amount of energy absorbed by the material during each cycle of the hysteresis loop.

2.2.2.1 *Magnetic parameters*

The hysteresis loop is a means of characterising magnetic materials, and various parameters can be determined from it. From the first quadrant the saturation polarisation, J_s and hence the saturation magnetization, M_s can be measured. Most of the useful information, however, can be derived from the second quadrant of the loop, and indeed it is conventional only to show this quadrant. The field that is produced by the magnet after the magnetising field has been removed is called the remanence, B_r or J_r . The reverse field required to bring the induction to zero is called the inductive coercivity, ${}_bH_c$, whereas the reverse field required to bring the magnetization to zero is called the intrinsic coercivity, ${}_jH_c$. The maximum value of the product of B and H is called the maximum energy product, $(BH)_{MAX}$ and is a measure of the maximum amount of useful work that can be performed by the magnet. $(BH)_{MAX}$ is used as a figure of merit for permanent magnet materials.

2.2.2.2 *Permeability*

Permeability is a material property that describes the ease with which a magnetic flux is established in a component. It is the ratio of the flux density to the magnetizing force and is represented by the following equation:

$$\mu = \frac{B}{H} \quad (7)$$

It is clear that this equation describes the slope of the curve at any point on the hysteresis loop. The permeability value given in papers and reference materials is usually the maximum permeability or the maximum relative permeability. The maximum permeability is the point where the slope of the B/H curve for the unmagnetized material is the greatest. This point is often taken as the point where a straight line from the origin is tangent to the

B/H curve.

The relative permeability is arrived at by taking the ratio of the material's permeability to the permeability in free space (air).

$$\mu_r = \frac{\mu_{material}}{\mu_{air}} \quad (8)$$

where: $\mu_{air} = 1.256 \times 10^{-6}$ H/m. The shape of the hysteresis loop tells a great deal about the material being magnetized. Relative to other materials, a material with a wider hysteresis loop has: lower permeability, higher remanence and higher coercivity. A material with the narrower hysteresis loop has: higher permeability, lower remanence and lower coercivity (Figure 14).

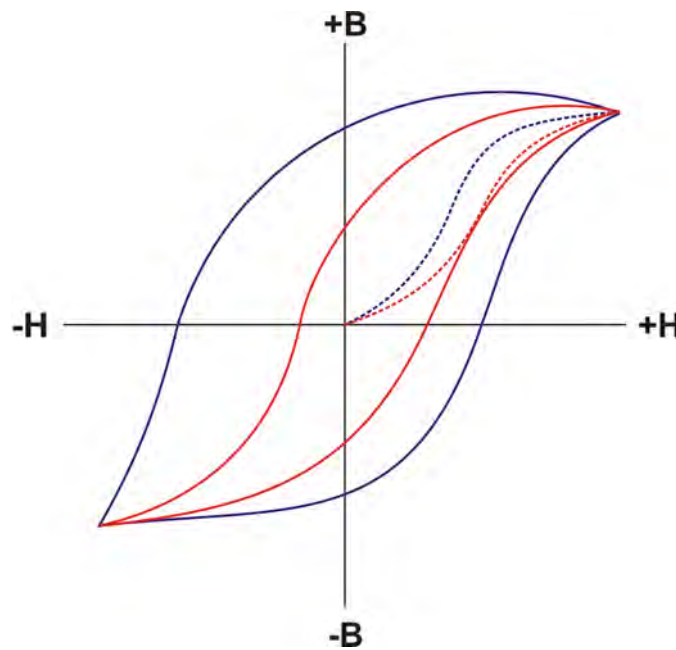


Figure 14. The hysteresis curves of two different materials.

2.2.3 Soft Magnetic Materials

Soft magnetic materials are those materials that are easily magnetised and demagnetised. They typically have intrinsic coercivity less than 1000 Am^{-1} . They are used primarily to enhance and/or channel the flux produced by an electric current. The main parameter, often used as a figure of merit for soft magnetic materials, is the relative permeability (μ_r , where $\mu_r = B/\mu_0 H$), which is a measure of how readily the material responds to the applied magnetic field. The other main parameters of interest are the coercivity, the saturation magnetization and the electrical conductivity.

The types of applications for soft magnetic materials fall into two main categories: AC and DC. In DC applications the material is magnetised in order to perform an operation and then demagnetised at the conclusion of the operation, e.g. an electromagnet on a crane at a scrap yard will be switched on to attract the scrap steel and then switched off to drop the steel. In AC applications the material will be continuously cycled from being magnetised in one direction to the other, throughout the period of operation, e.g. a power supply transformer. A high permeability will be desirable for each type of application but the significance of the other properties varies.

For DC applications the main consideration for material selection is most likely to be the permeability. This would be the case, for example, in shielding applications where the flux must be channelled through the material. Where the material is used to generate a magnetic field or to create a force then the saturation magnetization may also be significant.

For AC applications the important consideration is how much energy is lost in the system as the material is cycled around its hysteresis loop. The energy loss can originate from

three different sources: 1). hysteresis loss, which is related to the area contained within the hysteresis loop; 2). eddy current loss, which is related to the generation of electric currents in the magnetic material and the associated resistive losses and 3). anomalous loss, which is related to the movement of domain walls within the material. Hysteresis losses can be reduced by the reduction of the intrinsic coercivity, with a consequent reduction in the area contained within the hysteresis loop. Eddy current losses can be reduced by decreasing the electrical conductivity of the material and by laminating the material, which has an influence on overall conductivity and is important because of skin effects at higher frequency. Finally, the anomalous losses can be reduced by having a completely homogeneous material, within which there will be no hindrance to the motion of domain walls.

2.2.3.1 *Soft Ferrites*

At high frequency metallic soft magnetic materials simply cannot be used due to the eddy current losses. Therefore, soft ferrites, which are ceramic insulators, become the most desirable material. These materials are ferrimagnetic with a cubic crystal structure and the general composition $MO.Fe_2O_3$, where M is a transition metal such as nickel, manganese or zinc.

MnZn ferrite, sold commercially as ferroxcube, can be used at frequencies up to 10 MHz, for example in telephone signal transmitters and receivers and in switch mode power supplies (also referred to as DC-DC converters). For this type of application the driving force to increase frequency is to allow miniaturisation.

Additionally, part of the family of soft ferrites, are the microwave ferrites, e.g. yttrium iron garnet. These ferrites are used in the frequency range from 100 MHz to 500 GHz, for waveguides for electromagnetic radiation and in microwave devices such as phase shifters.

2.2.3.2 DC Applications

One of the main DC applications is in the field of magnetic shielding. A high permeability magnetic material is used to encapsulate the device that requires shielding. Figure 15 illustrates a simple example of magnetic shield where a tube/sphere of high permeability material channels the magnetic field away from the inside of the tube/sphere. The effectiveness of the shield can be expressed in terms of the shielding factor, S , where S relates to the field outside (B_o) and inside (B_i) the shield by equation 9

$$S = \frac{B_o}{B_i} \quad (9)$$

For a sphere, S can be calculated by equation 10, where μ_r = relative permeability, d = thickness of wall and D = diameter.

$$S = \frac{4}{3} \cdot \frac{\mu_r d}{D} \quad (10)$$

It is clear from equation 10 that the higher the permeability then the better the material will be at shielding. It is also apparent that as the shield gets larger then either the permeability of the material or the wall thickness must increase to compensate.

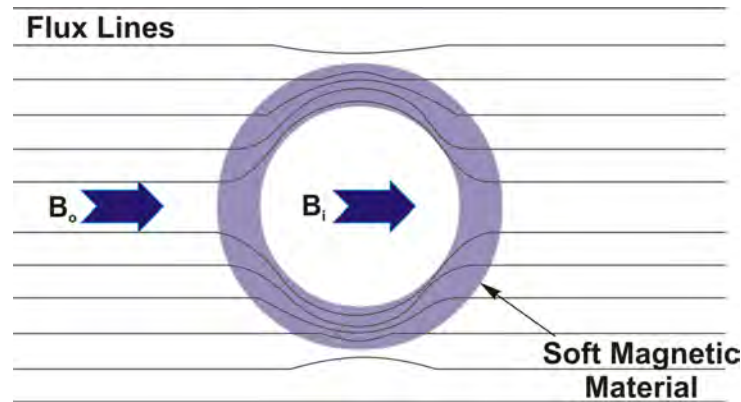


Figure 15. Magnetic shielding by a tube/sphere of soft magnetic material.

2.2.4 Structural Characteristics

The most frequently used soft ferrites are the spinels. Spinel can be used in the 3-30 GHz band. The crystal structure of spinels is isomorphous with that of the mineral $\text{Mg}^{2+}\text{Al}_2^{3+}\text{O}_4^{2-}$. When trivalent Al is substituted by Fe^{3+} , magnesium ferrite $\text{Mg}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$ is formed. Mg ferrite is well suited for microwave applications, because it has a very high specific resistance ($10^8 - 10^{10} \Omega\text{cm}$). When the divalent Mg is substituted by Fe^{2+} , magnetite, Fe_3O_4 , is formed. Practically, any divalent metal ion (Ni, Co, Mn, Cu, etc.) can be substituted to form a spinel ferrite. The cubic unit cell contains eight formula units, with 16M_1^{3+} and eight M_2^{2+} cations. In a normal spinel the 8M_2^{2+} ions occupy the eight tetrahedral A sites, and the 16M_1^{3+} ions occupy the 16 B octahedral sites. In the inverted spinel, eight of the 16M_1^{3+} occupy all the tetrahedral sites (Figure 16).

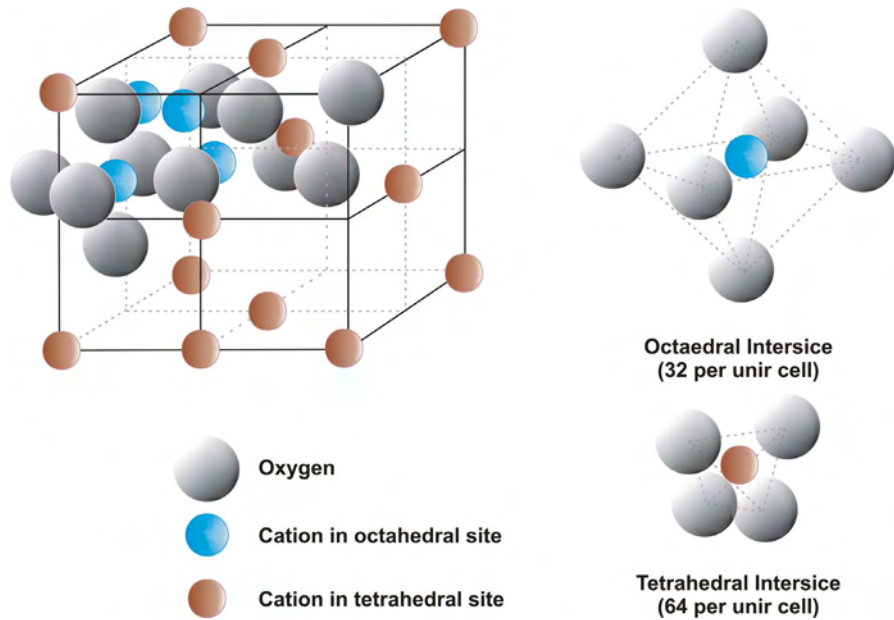


Figure 16. Spinel structure.

To understand the magnetic properties of the ferrites one has to consider the Néel model of ferrimagnetism. There are three A-A, B-B and A-B superexchange interactions. All these interactions are negative, i.e. antiferromagnetic, the strongest being the A-B interaction, rendering the two sublattices to be aligned antiparallel to each other, i.e. antiferromagnetically. In the inverted spinel structure, the eight M_2^{3+} magnetic ions in the A sublattice cancel the magnetism of the eight M_2^{3+} ions in the B sublattice. The observed ferrimagnetic moment is due to the uncompensated spins of the remaining eight M_2^{2+} cations. In the inverted spinels the distribution of the ions is: $\left\{ \text{Fe}^{3+} \downarrow \left[M^{2+} \uparrow \text{Fe}^{3+} \uparrow \right] \text{O}_4 \right\}$. In normal spinels, the net magnetic moment is composed as $\left\{ \text{Mn}^{2+} \downarrow \left[\text{Fe}^{3+} \uparrow \right] \text{O}_4 \right\}$. The magnetization of $\text{Mn}^{2+}\text{Fe}_4^{3+}\text{O}_4^{2-}$ corresponds to $5 \mu_B$, Fe_3O_4 has $4 \mu_B$ due to $(+5-5+4) \mu_B$,

$\text{Ni}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$ has $2 \mu_B$, $\text{Li}_{0.5}^{2+}\text{Fe}_{1.5}^{3+}\text{O}_4^{2-}$ has $2.5 \mu_B$ magnetic moment. Spinel ferrites with room temperature magnetization up to 5 kG can be synthesized, with T_N up to 600 K. Figure 17 illustrates the thermomagnetic properties of the most important spinel ferrites.

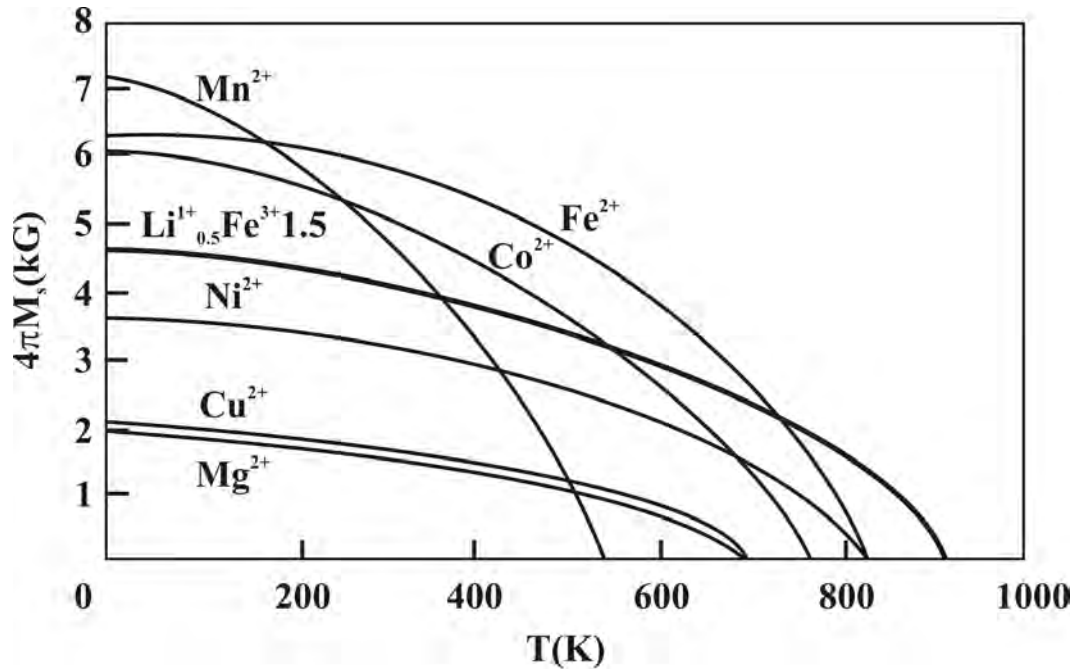


Figure 17. Thermomagnetic properties of spinel ferrites [25].

One of the very attractive properties of the ferrites is the possibility of mixing different compositions. Not only the magnetic moments, the strength of the superexchange, and the Néel temperature of the ferrites, but also the degree of the inversion can be changed. For example, $\text{Zn}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$ is a normal spinel, where Zn occupies all of the octahedral sites. Zn is nonmagnetic; so there is no magnetic moment, and no A-B interaction. The antiferromagnetically coupled Fe moments produce zero net magnetization for $\text{Zn}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$. However, if Zn is added to the inverted ferrite, the Zn occupies the A sites replacing the Fe^{3+} ions. The replaced Fe^{3+} ions move to the B sites and replace Fe^{2+} there.

As a result, the net moment is now the sum of two Fe^{3+} ions at the B sites. Magnetic ions are removed by substituting Zn, and the magnetization is increasing with increasing amount of nonmagnetic substitution; this effect is the basis to create mixed ferrites, most widely used materials in microwave technology.

There are typical substitutions to modify the magnetic properties of ferrites: addition of Al reduces the magnetization; Co^{2+} reduces the anisotropy, because the sign of the anisotropy of Co compensates for the anisotropy of Fe; addition of Mn reduces the loss tangent, i.e. the dielectric losses; addition of Zn increases the magnetization; unfortunately, T_N is reduced. One of the most popular spinel is the mixed $\text{Mn}_x\text{Mg}_y\text{Fe}_z\text{O}_4$ ferrite. The magnetic state of Mn^{2+} is the same as of Fe^{3+} . The saturation magnetization ($4\pi M_s$) of MgMn ferrite can be varied from 1200 to 2800 G, depending on the degree of inversion upon the sintering temperature and rate of cooling the linewidth is several G. The temperature sensitivity $dM/dT = 2.6 \times 10^{-3}$, is relatively high. MnMg ferrites are used at low power for the 7 - 15 GHz spectrum. Addition of Al increases the power handling capacity of the MgMn ferrite, at a price of reducing T_N . For high power applications NiFe_2O_4 ferrites are preferred. These materials are lossy due to the orbital state of Ni, a relaxing ion. The magnetization of pure Ni ferrite is 3200 G, $T_N = 570^\circ\text{C}$.

2.2.5 Static Magnetic Properties

As we stated before, low-coercivity, high-remanence, soft magnetic material, having a square hysteresis loop, is required for microwave operation and electromagnetic radiation.

For a magnetic material to be applied in microwave devices and EMI shielding, the most important static magnetic properties, to be controlled, are: the saturation magnetization ($4\pi M_s$, G), anisotropy constants (K_1 , K_u , erg/cm³), Néel temperature (T_N , K), magnetostriction constants (λ_c), remanent magnetization (M_r , G), permeability (μ), coercivity (H_c , G) and the temperature derivative of these quantities. In general, high T_N , low coercivity, high M_r , high μ , and low λ_c are required for EMI shielding applications. Low anisotropy is one of the conditions for low coercivity and low losses. The magnetization specifications depend on the operating conditions and on the actual device design. The dependence of these parameters on frequency and temperature limits the stability of ferrite devices. The problem is enhanced at high power levels, due to the dissipation into lattice heating [25].

By proper substitution in both magnetic sublattices, the temperature dependence of the magnetization can be controlled to have a plateau, i.e. $dM/dT \approx 0$ near room temperature. Another possible way to reduce temperature sensitivity is to use permanent magnets, having temperature coefficients opposite to the ferrites.

On the above basis ferrites are the choice materials for microwave applications. Ferrites are ferrimagnetic oxides, characterized by the arrangement of oxygen anions around metal cations in various geometric groups, forming tetrahedral, octahedral, dodecahedral oxygen coordination polyhedral around the cations. The magnetic interaction between cations is the superexchange, mediated by the intermediate oxygen ion. In ferrites, the magnetic cations are forming magnetic sublattices. The magnetic structure inside of a sublattice is

usually collinear ferromagnetic, but the different sublattices are coupled antiferromagnetically. Due to the different number of magnetic ions in different sublattices, there is a resulting magnetic moment, giving rise to ferrimagnetism. The nature of the superexchange interaction depends not only on the type of the magnetic ion, but strongly depends on the bond length and bonding angle [25,26].

2.3 BRIEF INTRODUCTION TO SHIELDING THEORY

Electromagnetic energy consists of a magnetic (H-field) and an electric (E-field) component perpendicular to each other and propagates at right angles to the plane containing the two components. The ratio of E to H is defined as the wave impedance (Z_w , in ohms) and depends on the type of source and the distance from the source. Large impedances characterize electric fields and small ones characterize magnetic fields. Far from the source, the ratio of E to H remains constant and equal to 377Ω , the intrinsic impedance of free space. In EMI shielding, there are two regions, the near field shielding region and far field shielding region, need to be considered. When the distance between the radiation source and the shield is larger than $\lambda/2\pi$ (where λ is the wavelength of the source), it is in the far field shielding region. The electromagnetic plane wave theory is generally applied for EMI shielding in this region. When the distance is less than $\lambda/2\pi$, it is in the near field shielding and the theory based on the contribution of electric and magnetic dipoles is used for EMI shielding. SE in decibel (dB) is a measure of the reduction of EMI at a specific frequency achieved by a shield, such as a coating, and is defined as:

$$SE = 10 \log \frac{P_o}{P_t} = 20 \log \frac{E_o}{E_t} = 20 \log \frac{H_o}{H_t} \quad (11)$$

where P_o , E_o and H_o are the power, the electric and magnetic field intensities incident on the shield and P_t , E_t and H_t are the counterparts transmitted through the shield.[1]

2.3.1 Mechanisms of Shielding

The primary mechanism of EMI shielding is usually reflection. For reflection of the radiation by the shield, the shield must have mobile charge carriers (electrons or holes) which interact with the electromagnetic fields in the radiation. As a result, the shield tends to be electrically conducting, although a high conductivity is not required. For example, a volume resistivity in the order of $1 \Omega\text{cm}$ is typically sufficient. However, electrical conductivity is not the scientific criterion for shielding, as conduction requires connectivity in the conduction path (percolation in case of a composite material containing a conductive filler), whereas shielding does not. Although shielding does require connectivity, it is enhanced by connectivity. Metals are by far the most common materials for EMI shielding. They function mainly by reflection due to the free electrons in them. Metal sheets are bulky, so metal coatings made by electroplating, electroless plating or vacuum deposition are commonly used for shielding. The coating may be on bulk materials, fibers or particles. Coatings tend to suffer from their poor wear or scratch resistance [2].

A secondary mechanism of EMI shielding is usually absorption. For significant absorption of the radiation by the shield, the shield should have electric and/or magnetic dipoles which interact with the electromagnetic fields in the radiation. The electric dipoles may be provided by BaTiO_3 or other materials having a high value of the dielectric constant. The

magnetic dipoles may be provided by Fe_3O_4 or other materials having a high value of the magnetic permeability, which may be enhanced by reducing the number of magnetic domain walls through the use of a multilayer of magnetic films.

The absorption loss is a function of the product $\sigma_r\mu_r$ whereas the reflection loss is a function of the ratio σ_r/μ_r where σ is the electrical conductivity relative to copper r and μ is the relative magnetic permeability. Silver, copper, gold and aluminum are excellent for reflection, due to their high conductivity. Superpermalloy and mumetal are excellent for absorption, due to their high magnetic permeability. The reflection loss decreases with increasing frequency, whereas the absorption loss increases with increasing frequency.

Other than reflection and absorption, a mechanism of shielding is multiple reflections, which refer to the reflections at various surfaces or interfaces in the shield. This mechanism requires the presence of a large surface area or interface area in the shield. An example of a shield with a large surface area is a porous or foam material. An example of a shield with a large interface area is a composite material containing a filler which has a large surface area. The loss due to multiple reflections can be neglected when the distance between the reflecting surfaces or interfaces is large compared to the skin depth.

The losses, whether due to reflection, absorption or multiple reflections, are commonly expressed in dB. The sum of all the losses is the shielding effectiveness (in dB). The absorption loss is proportional to the thickness of the shield.

Electromagnetic radiation at high frequencies penetrates only the near surface region of an electrical conductor. This is known as the *skin effect*. The electric field of a plane wave penetrating a conductor drops exponentially with increasing depth into the conductor. The depth at which the field drops to 1/e of the incident value is called the skin depth (δ), which is given by:

$$\delta = \frac{1}{\sqrt{\pi \cdot f \cdot \mu \cdot \sigma}} \quad (12)$$

where f = frequency, μ = magnetic permeability = $\mu_0\mu_r$, μ_r = relative magnetic permeability, $\mu_0 = 4\pi \times 10^{-7} \text{ Hm}^{-1}$, and σ = electrical conductivity in $\Omega^{-1} \text{ m}^{-1}$. Hence, the skin depth decreases with increasing frequency and with increasing conductivity or permeability. For copper, $\mu_r = 1$, $\sigma = 5.8 \times 10^7 \Omega^{-1} \text{ m}^{-1}$, so δ is 2.09 μm at a frequency of 1 GHz. For nickel of $\mu_r = 100$, $\sigma = 1.15 \times 10^7 \Omega^{-1} \text{ m}^{-1}$, so δ is 0.47 μm at 1 GHz. The small value of δ for nickel compared to copper is mainly due to the ferromagnetic nature of nickel.

2.3.2 Composite Materials for Shielding

The *skin effect* is the tendency of an alternating electric current (AC) to distribute itself within a conductor so that the current density near the surface of the conductor is greater than that at its core. That is, the electric current tends to flow in the “skin” of the conductor.

Due to the skin effect, a composite material having a conductive filler with a small unit size of the filler is more effective than one having a conductive filler with a large unit size of the

filler. For effective use of the entire cross-section of a filler unit for shielding, the unit size of the filler should be comparable to or less than the skin depth. Therefore, a filler of unit size 1 μm or less is typically preferred, though such a small unit size is not commonly available for most fillers, and the dispersion of the filler is more difficult when the filler unit size decreases.

Polymer-matrix composites containing conductive fillers are attractive for shielding due to their processability (e.g. moldability), which helps to reduce or eliminate the seams in the housing that is the shield. The seams are commonly encountered in the case of metal sheets as the shield, and they tend to cause leakage of the radiation and diminish the effectiveness of the shield. In addition, polymer-matrix composites are attractive for their low density. The polymer matrix is commonly electrically insulating, and does not contribute to shielding, although the polymer matrix can affect the connectivity of the conductive filler, and connectivity enhances the shielding effectiveness. In addition, the polymer matrix affects the processability.

Electrically conducting polymers are becoming increasingly available, but they are not common, and tend to be poor in the processability and mechanical properties. Nevertheless, electrically conducting polymers do not require a conductive filler in order to provide shielding, so that they may be used with or without a filler. In the presence of a conductive filler, an electrically conducting polymer matrix has the added advantage of being able to electrically connect the filler units that do not touch one another, thereby enhancing the connectivity.

2.3.3 EMI Shielding with PANi

Although many speculations and suggestions of PANi for EMI shielding application are present, the first systematic study of PANi for EMI shielding was reported by Shacklette and coworkers in 1992 [38,39], in which PANi was melt blended with polyvinyl chloride (PVC) to form a composite with conductivity of 20 S/cm. Electromagnetic interference shielding effectiveness (EMI SE) of the PANi composites, as well as other composites of metal fillers, were measured over a frequency range from 1 MHz to 3 GHz and theoretically calculated for both near and far field. The measured SE agreed well with the theoretical calculations in both near and far field as per the expressions derived by the authors. It was found that the higher the conductivity, the higher the SE of the composites. It was also concluded that as long as the distribution of the conductive fillers is uniform, which was difficult for metal fillers to achieve, and the size of the filler is smaller than the wavelength of the radiation, the frequency dependence of the SE was independent of the nature of the fillers. Far field SE as high as 70 dB was obtained for the PANi composite.

Trivedi and Dhawan [40] grafted PANi on surfaces of fabrics and measured their EMI SE using the coaxial transmission line method in the frequency range of 1000 kHz to 1 GHz. The results showed that at higher frequencies (0.1 MHz to 1 GHz), the SE is at 16 - 18 dB; while at lower frequencies; it is more than 40 dB. It was pointed out, as per the paper, that the level of doping and type of dopant, as well as the thickness of the PANi layer, had strong effect on the SE of the PANi grafted fabrics. Conductivity is the only important parameter in calculating the SE of metals due to their higher microwave frequency loss

tangent ($\tan \delta$), far more above 1. However, in the case of ICPs, the permittivity and $\tan \delta$ are both important for calculation of their SE due to the lower $\tan \delta$ of ICPs, which are between 0.5 and 7.0. The direct current (DC) and microwave conductivities of doped PANi vary from ca. 10^{-2} S/cm to ca. 600 S/cm at room temperature [1,24,38].

EMI shielding performance of a given material is different in near field and far field. SE of camphor sulfonic acid (CSA) doped PANi film, single or double layered, spin coated from m-cresol solution on an insulating substrate was measured both in the near field with a dual-chamber box and in the far field with a transmission line method at a frequency range 0.1 - 1000 MHz. In the near field measurement, the SE decreased with the increase of the frequencies, indicating the electromagnetic wave reflection from the polymer film. In addition, the double-layer films (20 mm) had deeper slopes and higher SE values. In the far field measurement, the SE of either the single-layered (10 mm) or double-layered film was independent on frequency, and both increased with the decreasing of surface resistance of the film, which agreed with theoretical values obtained from a good-conductor approximation. For example, the highest SE of 39 dB was achieved for the three-layered (30 mm) film at 1 GHz with surface resistance of 3 Ω/sq . The increase of the SE was due to absorption and possibly the conductivity increase as per the authors [45].

To increase the SE or conductivity of PANi, mixtures of PANi with conducting powders including silver, graphite and carbon-black were prepared in the following procedure [42-44]. Emeraldine base (EB) form of PANi was firstly mixed separately with these powders and then dissolved in N-methyl-2-pyrrolidone (NMP). The solutions were cast to form the

corresponding films, which were doped with hydrochloric acid (HCl) subsequently. The final films were denoted as ES/Ag, ES/graphite and ES/carbon-black, respectively. EMI shielding measurements, which were carried out according to ASTM D4935-89 (Figure 18) at room temperature in the frequency range of 10 MHz to 1 GHz, showed that the SE of all films were independent of the testing frequency, and were approximately in agreement with theoretical SE by using plane wave theory.

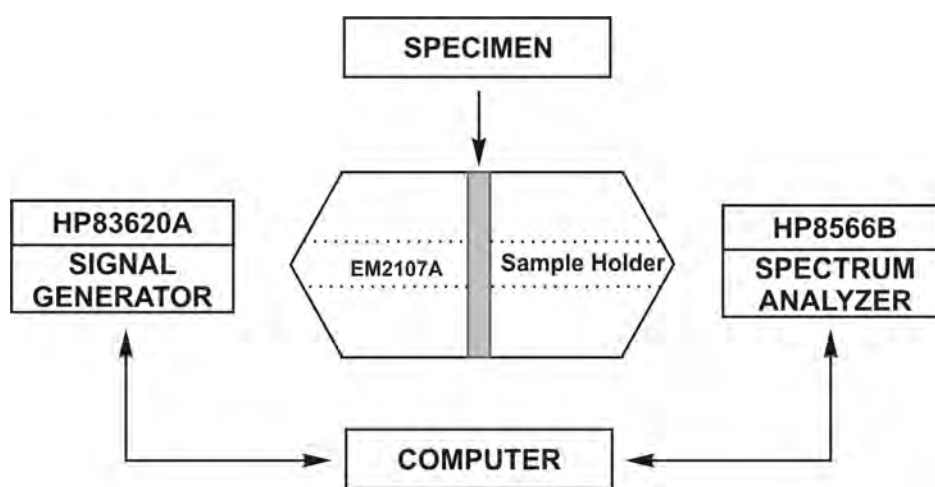


Figure 18. Experimental setup for measuring EMI shielding efficiency based on ASTM D4935-89 method [44].

EMI SE measurements, which were carried out on a standard microwave test bench over the X band (8.2 - 12 GHz), showed that the SE increased with the increase of conductivity as well as thickness of the testing sample. For the lower conducting composites, increase of ca. 2 - 3 dB was observed on changing the PANi loading from 14.4% to ca. 16% with the same thickness, while an increase of 9 - 10 dB was achieved by increasing the thickness from 2 to 3.5 mm. For the higher conducting composite, a sharp increase of ca. 10 dB was observed with PANi loading increased to ca. 19.35%, whereas increasing of thickness affected little the SE of the sample. The SE of the samples preserved their effectiveness

over a year as revealed by repeating the experiment 1 year later. According to Wessling [50], highly conductive blends of PANi with PVC, polymethylmethacrylate (PMMA) or polyester developed by Ormecon Chemie [50], with conductivities of ca. 20 S/cm and in some cases up to 100 S/cm, exhibited EMI SE at the range of 40 to 75 dB for both near and far field. But a considerable improvement in mechanical properties was still needed, in addition to the higher necessary thickness of 2 - 3 mm of the blends than the technically acceptable thickness of 0.5 - 0.8 mm for practical uses.

3. METHODOLOGY

3.1 MATERIAL SELECTION

3.1.1 The Polymer: Polyaniline (PAni)

Polyaniline was selected as the matrix due to its common use in microelectronics and micromachining, well-known processing conditions, relatively high conductivity and low cost, and desirable mechanical and thermal properties. PAni is one of the so-called doped polymers, in which conductivity results from a process of partial oxidation or reduction. Functional properties of this polymer can be easily tunable by controlling the processing conditions (concentration of reactants, temperature of polymerization, among others). In addition, the synthesis is very simple and does not demand any type of sophisticated equipment. Moreover, products consisting of polyaniline compounds can be considered environmental-friendly since they can be disposed without environmental risks.

A series of successful results have been reported with intrinsic conductive polymers (ICPs), in EMI shielding, such as Polyacetylene (PA), poly-p-phenylene-benzobisthiazole (PBT), polythiophene (PTh), poly(p-phenylene-vinylene) (PPV), polypyrrole (PPy) [7-11] to name a few. Unfortunately, all these series claim a high doping level, and are not easy processable and blendable with the polymeric matrices. Polyanilines, a particular class of conductive polymers, proved to have a metallic behavior when doped with different

counterions [12]. In consequence, the metallic properties have been intensively studied related to EMI [28].

3.1.2 The Magnetic Disperse Phase: Ferrite Nanoparticles (MnZn Ferrites)

Ferrite nanoparticles exhibiting high permeability and saturation magnetization values will be considered as the disperse phase. Candidate materials include: magnetite (Fe_3O_4), $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ and $\text{Mg}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$. Among these ferrites, MnZn has been chosen due to its well established high magnetic permeability, low core losses [11,17] and response to high frequency devices [25,36].

3.2 MATERIALS SYNTHESSES

The preparation of the magnetic nanocomposite involved the following steps: synthesis of the polymer, synthesis of ferrite nanoparticles and dispersion of the nanoparticles within the polymeric matrix. As a first attempt, the synthesis of PANi considered the PANi ES (acid – doped) and PANi EB (undoped) types. The corresponding syntheses protocols are detailed as follows.

3.2.1 Synthesis of Polyaniline (PANi)

3.2.1.1 The PANi-Ferrite nanocomposite: Preparation Method “A”

PANi ES was prepared by the synthesis method described in literature [6]. The reagents

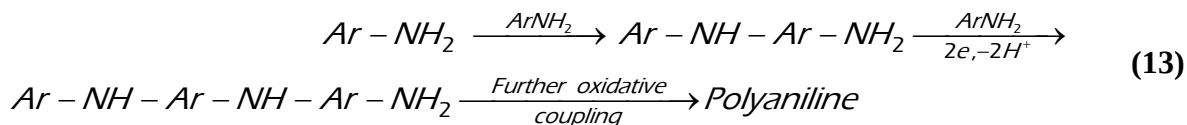
include: Hydrochloric acid (HCl), Ammonium peroxydisulfate (APS), ACS, 98.0% min $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and Aniline, ACS, 99 %.

For the preparation of 50 ml of monomer solution, aniline (1.139 ml) was first dissolved in 48.862 ml of HCl (1N) solution. A calculated amount of ammonium peroxydisulfate is dissolved in 25 ml of distilled water, and added to the above solution with constant stirring for about 30 - 40 min. The beaker containing the resulting solution is placed inside an ice-bath for 3 hours, maintaining stirring. The synthesis of PANi at low temperature (avoid 0 °C) favors the formation of longer chains length (and hence, high molecular weight), under this conditions a less amount of structural defect in the polymer can be expected. The dark green precipitate resulting from the polymerization reaction is washed repeatedly with HCl solution and water until the filtrate becomes transparent. This precipitate is then dried in an oven at 40 °C. Solid PANi is powdered in a mortar and finally compressed to form pellets.

3.2.1.2 *The PANi-Ferrite nanocomposite: Preparation Method “B”*

As a second preparation method, PANi Emeraldine Base (PANi EB) is synthesized. In this case aniline (1.139 ml) is dissolved in 48.862 ml of distilled water. A calculated amount of ammonium peroxydisulfate in water, was added dropwise to the above solution under constant stirring for about 30 - 40 min. The beaker containing the resulting solution is placed inside an ice-bath for 3 hours. The dark blue precipitate resulting from the polymerization reaction is washed repeatedly with distilled water until the filtrate becomes transparent. This precipitate is then dried in an oven at 60 °C. Solid PANi EB is powdered in a mortar and finally compressed to form pellets. For subsequent characterization.

In both of the above syntheses, the role of the oxidant is to remove a proton from the aniline monomer. The polymerization reaction represented as a Reduction of Nitro Compounds, method for the synthesis of anilines (Ar-NH₂) and is summarized as follows:



where Ar: Androgen receptor.

The factors affecting the polymerization process are the pH of the solution, type and concentration of the acids, dissolution and electronegativity of the conjugate base associated with a given acid [27].

3.2.2 Synthesis of Ferrite Nanoparticles by Co-Precipitation

In the conventional co-precipitation method, a solution containing Fe(III) and M(II), (where ‘M’ is divalent metal cation) at suitable Fe/M mole ratios is contacted with a hot alkaline solution (60 – 90 °C). The hydrolysis reaction leads to the formation of a mixed paramagnetic Fe-M hydroxide, which undergoes dehydration and atomic rearrangement conducive to stoichiometric ferrite structure with no need of further annealing, according to the following reaction:



The nucleation rate is quite high at the beginning of the precipitation process whereas the excess of OH⁻ ions provides a net negative surface charge to the nuclei limiting their further growth and aggregation. Under these conditions polydisperse particles of less than

30 nm in diameter are typically produced.

3.2.3 Preparation of PAni EB/Mn_{0.8}Zn_{0.2}Fe₂O₄ Nano-Composites

Suitable mol 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 nanocomposites at various ferrite molar percent represented by content of ferrite in the final composite (ferrite/composite). The mixing was carried out under intense sonication to help suitable dispersion of nanoparticles in the monomer solution. 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 12 h.

The ferrite was added during the mixing of the reagents to promote greater interaction between nanoparticles and the chains that were developed through the polymerization of aniline.

3.3 MATERIALS CHARACTERIZATION

The techniques used to characterize our products are described below:

3.3.1 X-Ray Diffraction (XRD)

The crystalline structures of various polymeric composites were investigated by Wide-

Angle X-Ray Diffraction (WAXD), using a powder X-Ray diffractometer (Siemens D 500 model) with $\text{CuK}\alpha$ source and βNi filter (Figure 19). All the scans were recorded in the 2θ regions of $15 - 75^\circ$ at a scan rate of 0.02° per second.



Figure 19. XRD Siemens D5000 – Material Science and Engineering Department UPRM.

X-ray Diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties (strain state, grain size, epitaxy, phase composition, preferred orientation, and defect structure) of these phases. XRD is also used to determine the thickness of thin films and multilayers, and atomic arrangements in amorphous materials (including polymers) and at interfaces. Figure 20 shows the basic features of an XRD experiment set up, the diffraction angle 2θ is the angle between the incident and diffracted X rays [51]. From 2θ values for reflection, 'd' values were calculated using Bragg equation and average crystallite size calculated of ferrite

nanoparticles by Scherrer's equation.

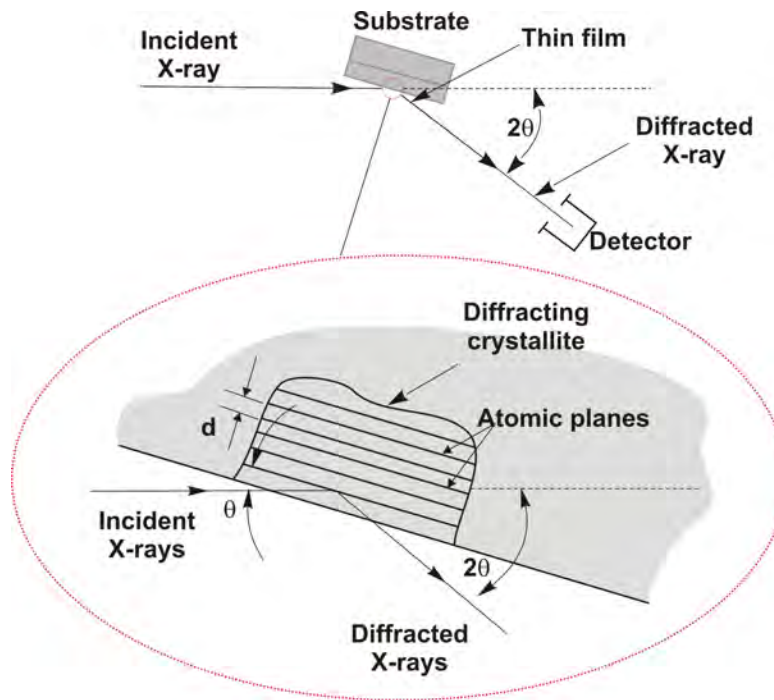


Figure 20. Basic features of a typical XRD experiment.

Considering the some important properties of crystalline materials, crystals consist of planes of atoms that are spaced a distance d apart (Figures 21 and 22), but can be resolved into many atomic planes, each with a different d -spacing. To distinguish between these, we introduce a coordinate system for the crystal whose unit vectors a , b , and c are the edges of the unit cell (Figure 22). For the familiar cubic crystal, these form an orthogonal system. Any atomic plane can now be uniquely distinguished by its Miller indices. These are the three reciprocal intercepts of the plane with the a -, b -, and c -axes and are reduced to the smallest integers having the same ratio. Thus, an (hkl) plane intercepts the crystallographic axes at a/h , b/k , and c/l ; examples are shown in Figure 22. The d -spacing between (hkl) planes is denoted d_{hkl} , and for cubic crystals, it is where a_0 is the lattice constant of the

crystal (see Figure 20)

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad (15)$$

when there is constructive interference from X rays scattered by the atomic planes in a crystal, a diffraction peak is observed. The condition for constructive interference from planes with spacing d_{hkl} is given by Bragg's law:

$$\lambda = 2 \cdot d_{hkl} \cdot \sin \theta_{hkl} \quad (16)$$

where θ_{hkl} is the angle between the atomic planes and the incident (and diffracted) X-ray beam (Figure 20). For diffraction to be observed, the detector must be positioned so that the diffraction angle is $2\theta_{hkl}$, and the crystal must be oriented so that the normal to the diffracting plane is coplanar with the incident and diffracted.

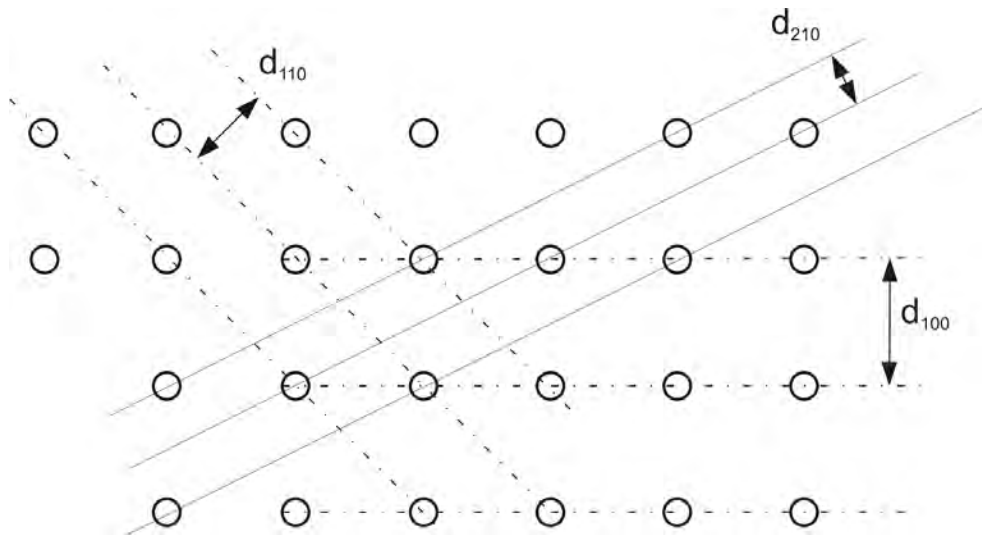


Figure 21. Several atomic planes and their d-spacings in a simple cubic (sc) crystal

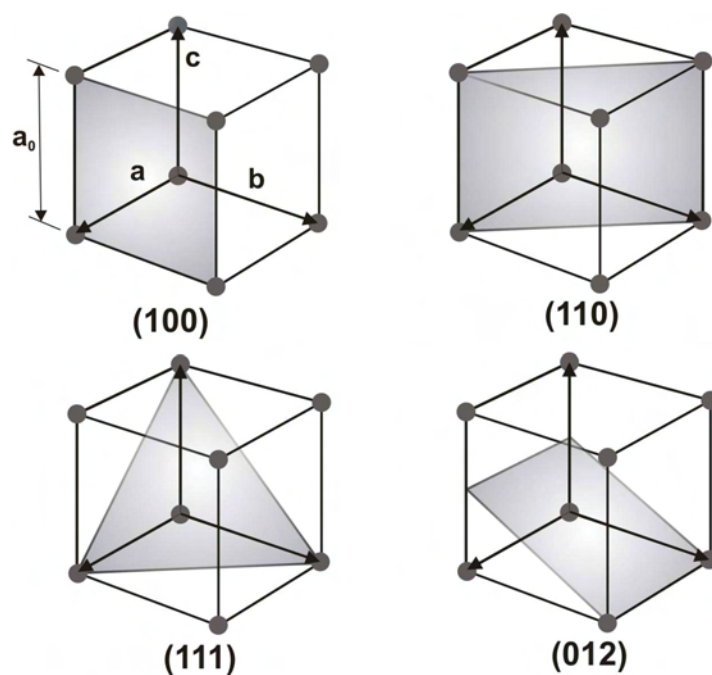


Figure 22. Miller indices of atomic planes in an sc crystal. As an example consider the (012) plane. This intercepts the a-, b-, and c-axes at ∞ , 1, and $1/2$ respectively, and thus, $h = 1/\infty = 0$, $k = 1/1 = 1$, and $l = 1/(1/2) = 2$.

X rays and so that the angle between the diffracting plane and the incident X rays is equal to the Bragg angle for a single crystal or epitaxial thin film, there is only one specimen orientation for each (hkl) plane where these diffraction conditions are satisfied [51].

3.3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopic studies were carried out. PANi samples with different dopant ions were analyzed by using “Shimadzu FTIR 8201” spectrometer (Figure 23).

As one of the few techniques that can provide information about the chemical bonding in a material, it is particularly used for the nondestructive analysis of solids and thin films, for

which there are few alternative methods. Chemical bonds vary widely in their sensitivity to probing by infrared techniques. For example, carbon-sulfur bonds often give no infrared signal, and so cannot be detected at any concentration, while silicon-oxygen bonds can produce signals intense enough to be detected when probing submonolayer quantities, or in the order of 10^{13} bond/cc. Thus, the potential utility of infrared spectrophotometry (IR) is a function of the chemical bond of interest, rather than being applicable as a generic probe.



Figure 23. Shimadzu FTIR 8201 – Physic Department UPRM.

The goal of the basic infrared experiment is to determine changes in the intensity of a beam of infrared radiation as a function of wavelength or frequency (2.5 - 50 μm or 4000 - 200 cm^{-1} respectively) after it interacts with the sample. The centerpiece of most equipment configurations is the infrared spectrophotometer. Its function is to disperse the light from a broadband infrared source and to measure its intensity at each frequency. The ratio of the

intensity before and after the interaction of light with the sample is determined. The plot of this ratio versus frequency is the infrared spectrum (Figure 24).

Let us define I_0 to be the intensity of the light incident upon the sample and I as the intensity of the beam after it has interacted with the sample. The goal of the basic infrared experiment is to determine the intensity ratio I/I_0 as a function of the frequency of light (w). A plot of this ratio versus the frequency is the infrared spectrum. The infrared spectrum is commonly plotted in one of three formats: as transmittance, reflectance, or absorbance. If one is measuring the fraction of light transmitted through the sample, this ratio is defined as

$$T_w = \left(\frac{I_t}{I_0} \right)_w \quad (17)$$

where T_w , is the transmittance of the sample at frequency w , and I_t is the intensity of the transmitted light. Similarly, if one is measuring the light reflected from the surface of the sample, then the ratio is equated to R_w , or the reflectance of the spectrum, with I_t being replaced with the intensity of the reflected light I_r . The third format, absorbance, is related to transmittance by the Beer-Lambert Law:

$$A_w = -\log T_w = (\varepsilon_w)(b \cdot c) \quad (18)$$

where c is the concentration of chemical bonds responsible for the absorption of infrared radiation, b is the sample thickness, and ε_w , is the frequency-dependent absorptivity, a proportionality constant that must be experimentally determined at each w by measuring the absorbance of samples with known values of bc . As a first order approximation the Beer-Lambert Law provides a simple foundation for quantifying FTIR spectra. For this reason, it is easier to obtain quantitative results if one collects an absorbance spectrum, as

opposed to a reflectance spectrum. Prior to the introduction of FTIR spectrophotometer, infrared spectra were usually presented in the transmittance format, because the goal of the experiment was to obtain qualitative information. With the growing use of FTIR technology, a quantitative result is more often the goal. Today the absorbance format dominates, because to first order it is a linear function of concentration [51].

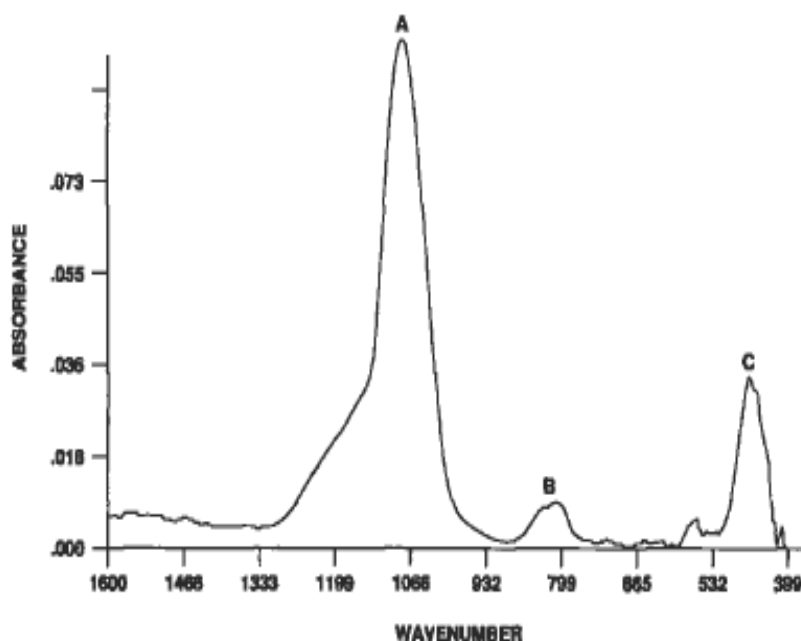


Figure 24. The FTIR spectrum of the oxide of silicon (thin film deposited by CVD). Primary features: (a), asymmetric stretching mode of vibration; (b), bending mode of vibration; (c), rocking mode of vibration.

3.3.3 Scanning Electron Microscope (SEM)

To observe the morphology of nanocomposites, is used a Scanning Electron Microscope model JSM-6390LV (Figure 25) which is a high-performance, low cost, scanning electron microscope with a high resolution of 3.0 nm. The customizable GUI interface allows the instrument to be intuitively operated, and Smile Shot™ software ensures optimum

operation settings. This equipment belongs to Biology Department, Microscopy center in University of Puerto Rico at Mayagüez.

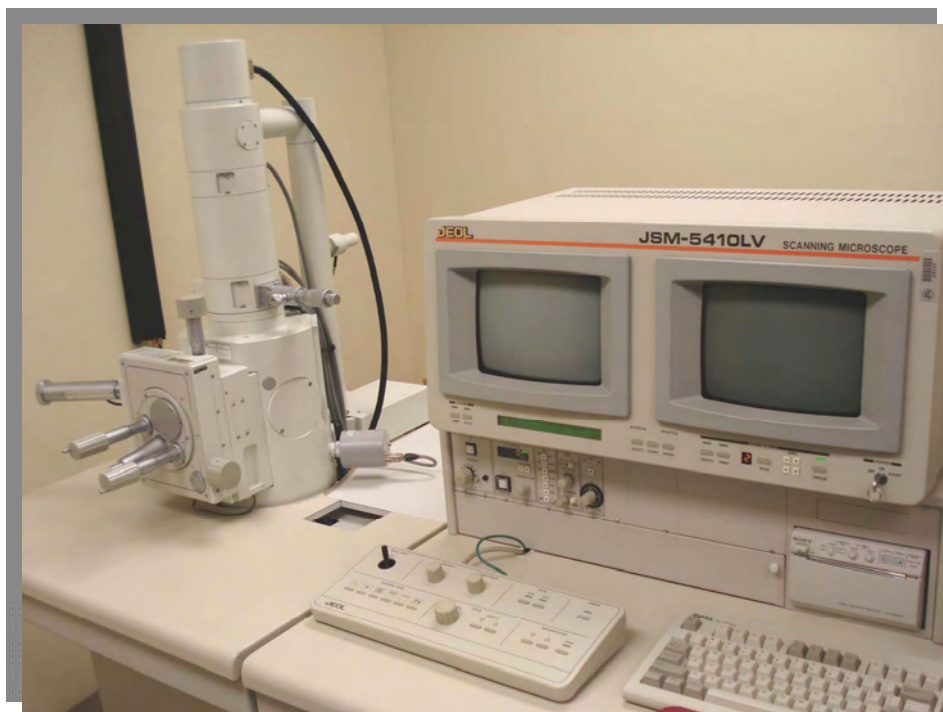


Figure 25. Scanning Electron Microscope - Biology Department UPRM

For the purpose of a detailed materials characterization, the optical microscope is supplanted by two more potent instruments: the Transmission Electron Microscope (TEM) and the Scanning Electron Microscope (SEM). Because of its reasonable cost and the wide range of information that it provides in a timely manner, the SEM often replaces the optical microscope as the preferred starting tool for materials studies.

The SEM provides a highly magnified image of the surface of a material that is very similar to what one would expect if one could actually “see” the surface visually. The resolution of the SEM can approach a few nm and it can operate at magnifications that are easily

adjusted from about 10X – 300,000X.

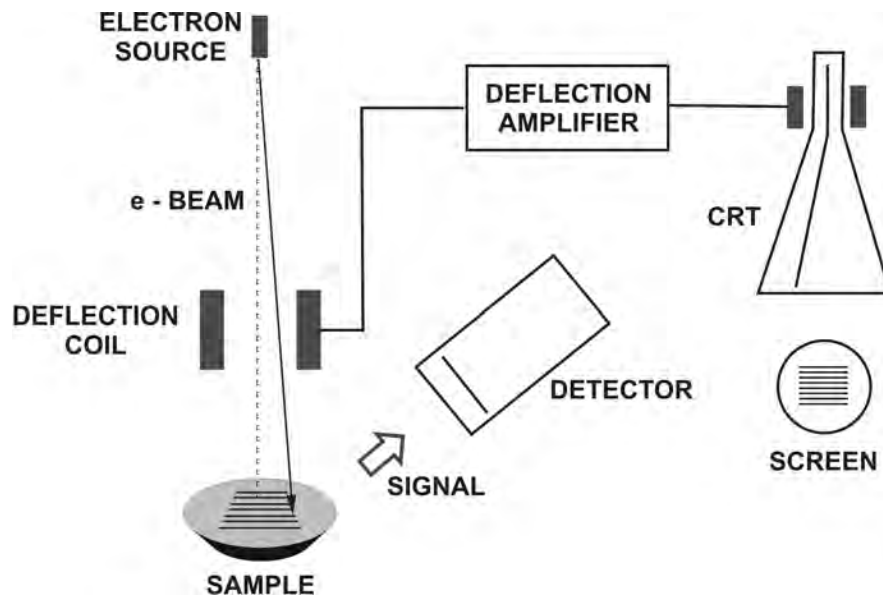


Figure 26. Schematic diagram of the operation of an SEM.

In the SEM, a source of electrons is focused (in vacuum) into a fine probe that is rastered over the surface of the specimen, Figure 26. As the electrons penetrate the surface, a number of interactions occur that can result in the emission of electrons or photons from (or through) the surface. A reasonable fraction of the electrons emitted can be collected by appropriate detectors, and the output can be used to modulate the brightness of a cathode ray tube (CRT) whose x- and y-inputs are driven in synchronism with the x-y voltages rastering the electron beam. In this way an image is produced on the CRT; every point that the beam strikes on the sample is mapped directly onto a corresponding point on the screen. If the amplitude of the saw-tooth voltage applied to the x- and y-deflection amplifiers in the SEM is reduced by some factor while the CRT saw-tooth voltage is kept fixed at the level necessary to produce a full screen display, the magnification, as viewed on the screen, will be increased by the same factor [51].

3.3.4 Thermogravimetric Analysis (TGA)

TGA of PAni ES/EB with MnZn were recorded over a temperature range of 25 °C to 900 °C in nitrogen atmosphere using a METTLER thermal analyzer TGA/SDTA 851 (Figure 27), in order to analyze the thermal behavior pattern of these blends.



Figure 27. METTLER thermal analyzer – Material Science and Engineering Department UPRM.

The basic principle in TGA is to measure the mass of a sample as a function of temperature. This, in principle, is a simple measurement but offers an important and powerful tool in solid state chemistry and materials science. The method, for example, can be used to determine water of crystallisation, follow degradation of materials, determine reaction

kinetics, study oxidation and reduction, or to teach the principles of stoichiometry, formulae and analysis.

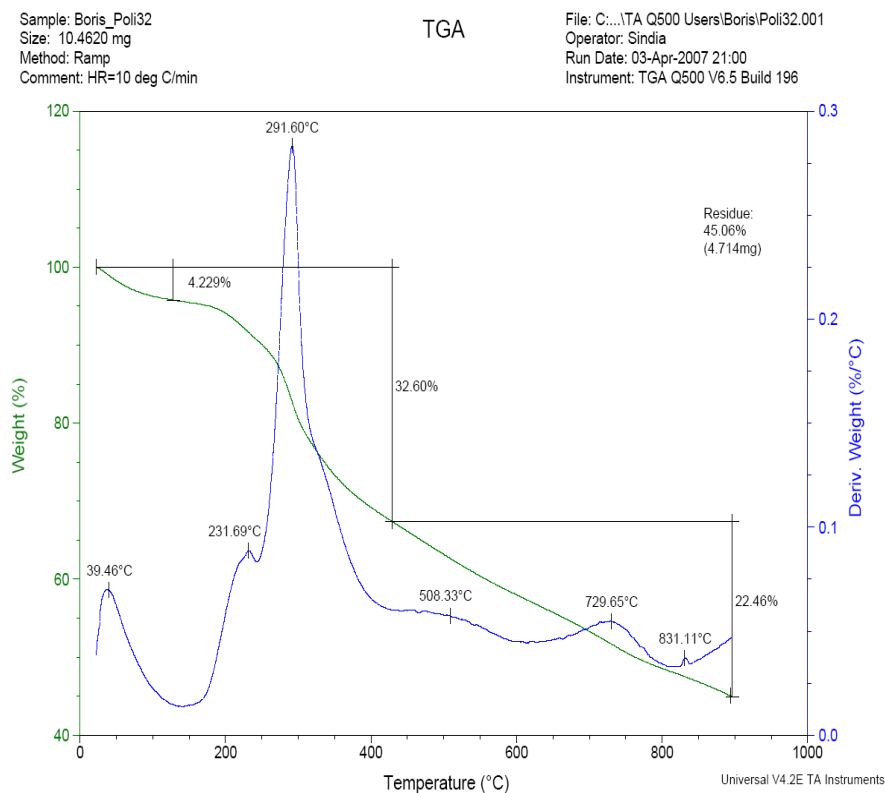


Figure 28. The TGA and DTA curves of a PANi-MnZn composite

Many thermal changes in materials (e.g. phase transitions) do not involve a change of mass. In DTA one instead measures the temperature difference between an inert reference and the sample as a function of temperature. When the sample undergoes a physical or chemical change the temperature increase differs between the inert reference and the sample, and a peak or a dip is detected in the DTA signal. The technique is routinely applied in a wide range of studies such as identification, quantitative composition analysis, phase diagrams, hydration-dehydration, thermal stability, polymerisation, purity, and reactivity.

3.3.5 Transmission Electron Microscopy (TEM)

With the objective of evaluation of the ferrite dispersion conditions, a 200 kV high-resolution Philips CM200 ULTRA TWIN TEM (Figure 29) with 0.19 point resolution, Ge light element energy-dispersive x-ray spectroscopy (EDS), and full image processing and analysis capabilities were used. This equipment belongs to Materials Science Center in University of Wisconsin.



Figure 29. TEM Philips CM200 UT - Materials Science and Engineering Department - University of Wisconsin.

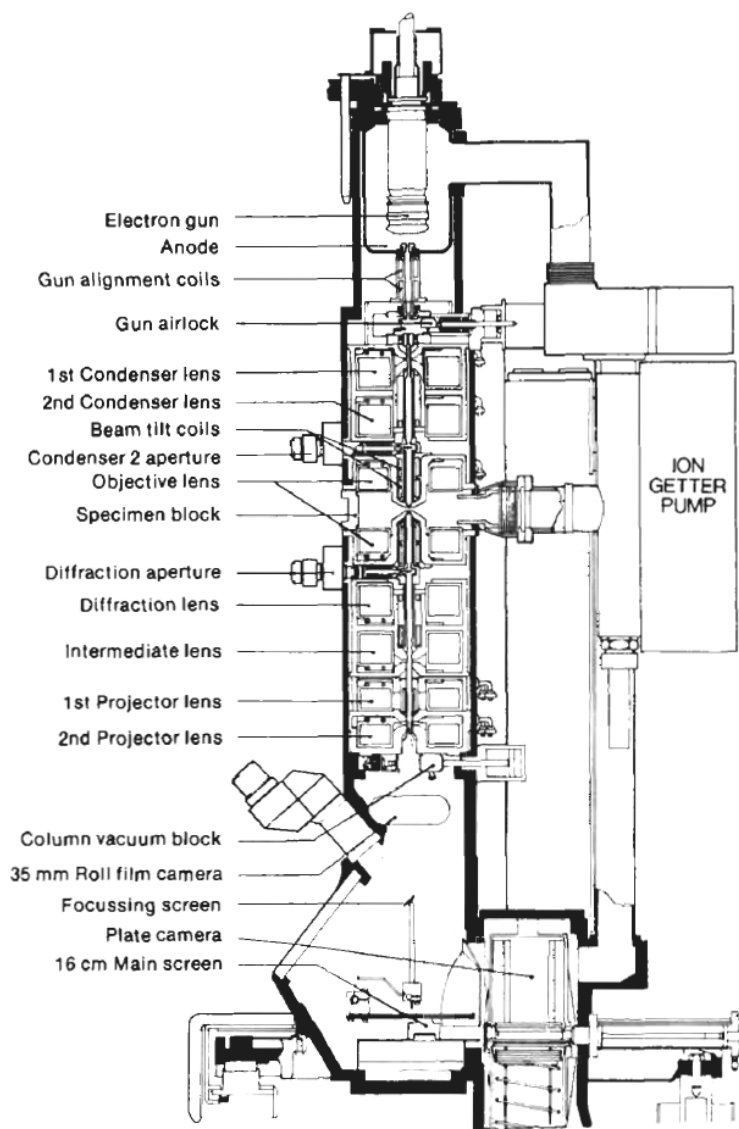


Figure 30. Schematic diagram of a TEM instrument, showing the location of a thin sample and the principal lenses within a TEM column.

TEM's strong cards are its high lateral spatial resolution (better than 0.2 nm "point-to-point" on some instruments) and its capability to provide both image and diffraction information from a single sample. In addition, the highly energetic beam of electrons used in TEM interacts with sample matter to produce characteristic radiation and particles; these signals are often measured to provide materials characterization using EDS, EELS,

EXELFS, backscattered and secondary electron imaging, to name a few possible techniques.

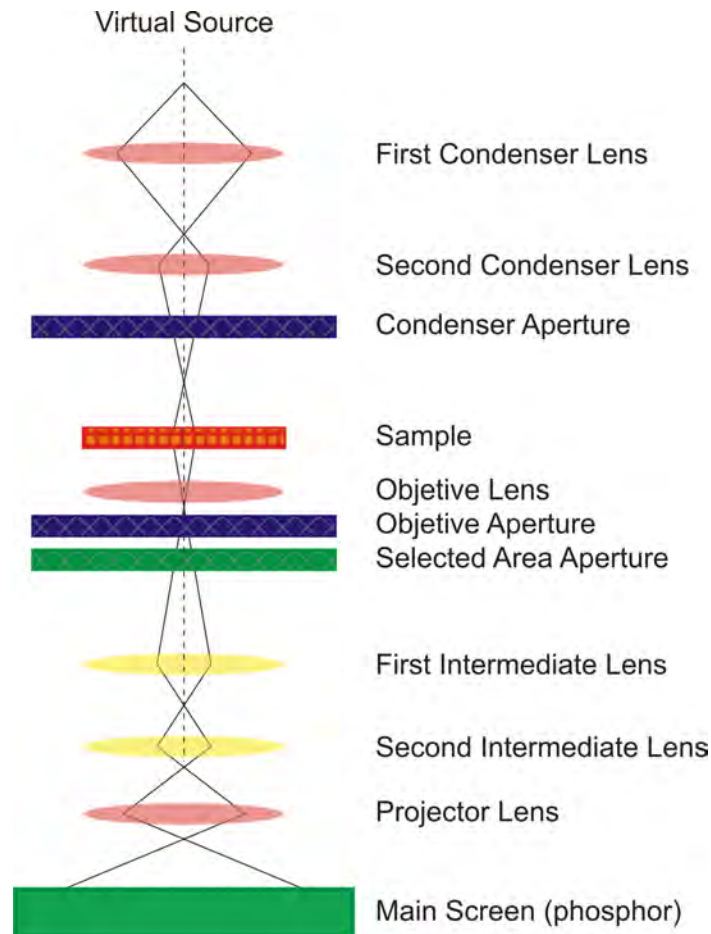


Figure 31. Schematic representation for the ray paths of both unscattered and scattered electrons beneath the sample.

A technical explanation of a typical TEMs working is as follows:

1. The “Virtual Source” at the top represents the electron gun, producing a stream of monochromatic electrons.
2. This stream is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first lens (usually controlled by the “spot size knob”) largely determines the “spot size”; the general size range of the final spot that strikes the sample. The second

lens (usually controlled by the “intensity or brightness knob” actually changes the size of the spot on the sample; changing it from a wide dispersed spot to a pinpoint beam.

3. The beam is restricted by the condenser aperture (usually user selectable), knocking out high angle electrons (those far from the optic axis, the dotted line down the center).
4. The beam strikes the specimen and parts of it are transmitted.
5. This transmitted portion is focused by the objective lens into an image.
6. Optional Objective and Selected Area metal apertures can restrict the beam; the Objective aperture enhancing contrast by blocking out high-angle diffracted electrons, and the Selected Area aperture enabling the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample.
7. The image is passed down the column through the intermediate and projector lenses, being enlarged all the way.
8. The image strikes the phosphor image screen and light is generated, allowing the user to see the image. The darker areas of the image represent those areas of the sample that fewer electrons were transmitted through (they are thicker or denser). The lighter areas of the image represent those areas of the sample that more electrons were transmitted through (they are thinner or less dense).

A schematic of a TEM instrument, showing the location of a thin sample and the principal lenses within a TEM column, is illustrated in Figure 30 and Figure 31 shows a schematic for the ray paths of both unscattered and scattered electrons beneath the sample.

3.3.6 Vibrating Sample Magnetometer (VSM)

The magnetic characterization of various polymeric composites was investigated by VSM technique (Figure 32).



Figure 32. 7400 Series VSM - Material Science and Engineering Department UPRM.

In order to obtain a measurement of the magnetic induction it is also possible to use various moving-coil instrument. The simplest of these is the rotating coil which rotates at a fixed angular velocity. Therefore the amplitude of the generated voltage by rotating coil is proportional to the magnetic induction and therefore the amplitude can be used to measure magnetic induction (B) or magnetic field (H) in free space. The signal can be read directly as an AC voltage or converted to a DC voltage which is proportional to the amplitude.

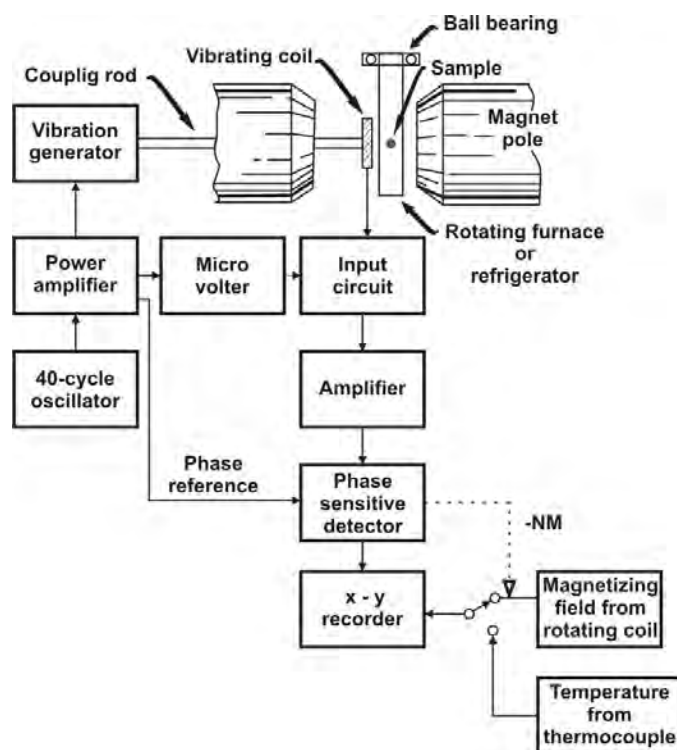


Figure 33. Schematic diagram of a vibrating coil magnetometer.

The vibrating-coil magnetometer is based on the same principles as the previous technique, but is used primarily as a method of determining the magnetization (M). The arrangement is shown in Figure 33. The coil vibrates between the sample and a region of free space and thereby acts as a gradiometer by measuring the difference in induction in the two positions. The output of vibrating coil magnetometer is independent of H , but is dependent on M [55].

The vibrating-sample magnetometer (VSM) is identical in principle to the vibrating-coil magnetometer except that the sample is moved instead of the coil. The VSM was first described by Foner and has now almost completely superseded the vibrating-coil device.

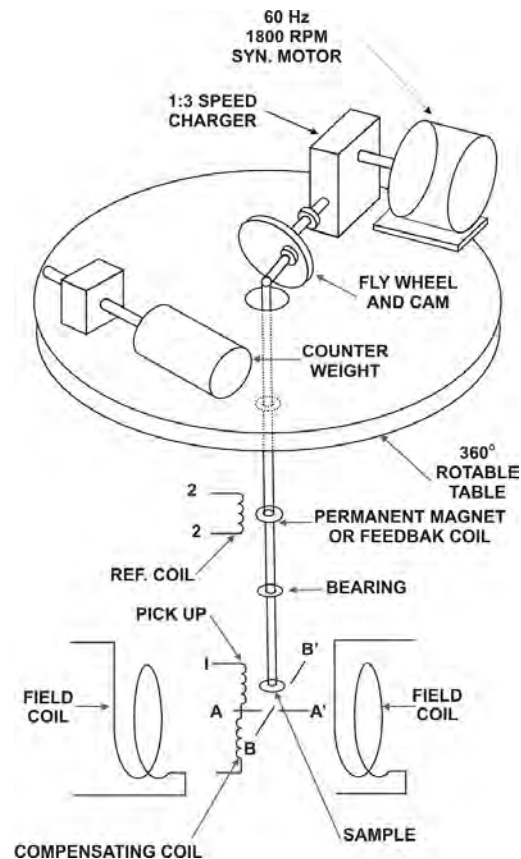


Figure 34. Schematic diagram of a vibrating sample magnetometer.

A VSM is really a gradiometer measuring the difference in magnetic induction between a region of space with and without the specimen. It therefore gives a direct measure of the magnetization. A schematic of a typical VSM is shown in Figure 34. The specimen in general has to be rather short to fit between poles of the electromagnet. The method is therefore in most cases not well suited to the determination of the magnetization curve or hysteresis loop because of the demagnetizing effects associated with the short specimen. However it is well suited for the determination of the saturation magnetization (M_s).

The detected signal, being an AC signal of fixed frequency, is measured using a lock-in

amplifier. A reference signal is provided for the lock-in amplifier as shown in Figure 34 by using a permanent magnet and a reference pick-up coil. Magnetic moments as small as $5 \times 10^{-4} \text{ A m}^2$ ($5 \times 10^{-5} \text{ emu}$) are measurable with a VSM. Its accuracy is better than 2% [55].

3.3.7 Conductive Measurement Techniques

The conductivity measurements were done on pressed pellets. The pellets were prepared in a 4350 series press Carver for preparing pellets (Figure 35), applying a pressure of 5000 pounds under vacuum conditions during one minute. The pellets had a diameter of 12.8 mm and the thickness varying with the content of material to fabricate each sample from 1.12 mm to 1.79 mm.



Figure 35. 4350 serie press Carver - Material Science and Engineering Department UPRM.

DC conductivities were determined from current-voltage measurements. A digital 6517A electrometer and K20 programmable temperature controller (Figure 36) was used to measure the voltage and to provide the current. The volume resistivity of sample was calculated by the following equation

$$\rho = R \cdot \frac{A}{L} (\Omega \cdot \text{cm}) \quad (19)$$

Where R is the volume resistance of the measured sample (Ω), A the width of the sample (cm^2); and L the effective length of the sample (cm).



Figure 36. 6517A electrometer and K20 programmable temperature controller – Physics Department University of Puerto Rico at Rio Piedras.

Conductivity is the ability of a material to conduct electric current. The principle by which instruments measure conductivity is simple: two plates are placed in the sample, a potential is applied across the plates (normally a sine wave voltage), and the current that passes

through the solution is measured. Conductivity (σ), the inverse of resistivity (R), is determined from the voltage and current values according to Ohm's law

$$\sigma = \frac{1}{R} = \frac{I \text{ (amps)}}{V \text{ (volts)}} \quad (20)$$

Since the charge on ions in solution facilitates the conductance of electrical current, the conductivity of a solution is proportional to its ion concentration.

4. RESULTS AND DISCUSSION

4.1 MATERIAL SYNTHESIS AND CHARACTERIZATION

(PANI, FERRITE, COMPOSITE)

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.

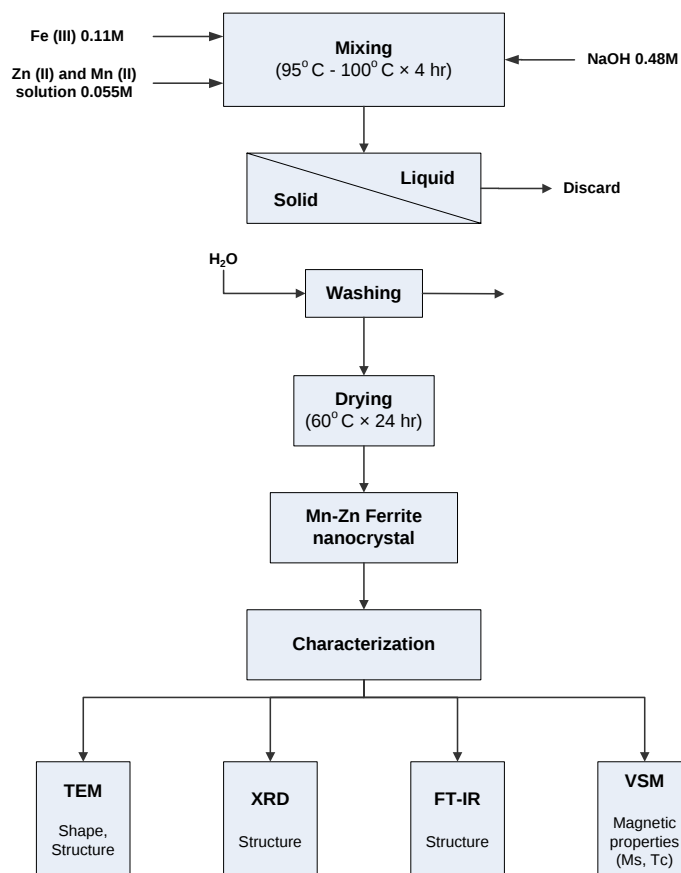


Figure 37. Synthesis procedure for MnZn ferrite nanoparticles.

Ferrites were synthesized at different values of the Mn atomic fraction 'x'. A reaction time of one hour was long enough to permit the dehydration and atomic rearrangement involved in the conversion of the precursor hydroxide into the ferrite structure. Synthesized nanocrystals were removed from the solution; then washed twice with distilled water and dried at 60 °C for 24 hours.

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 drop by drop 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 in order to complete the polymerization process.

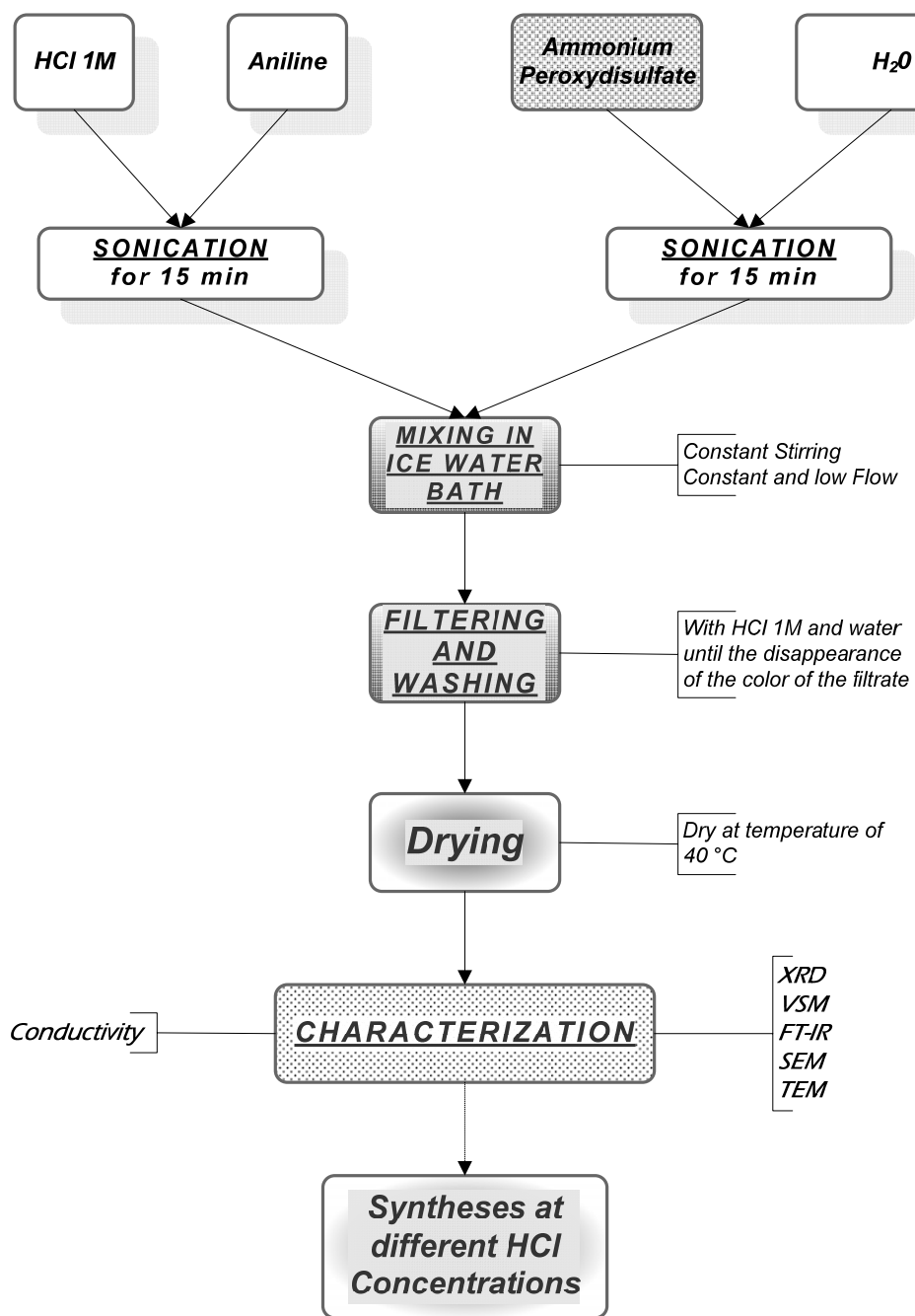


Figure 38. Preparation procedure of PANi ES-MnZn ferrite nanocomposite. The Mn atomic fraction 'x' was 0.8 in all tests: Method A.

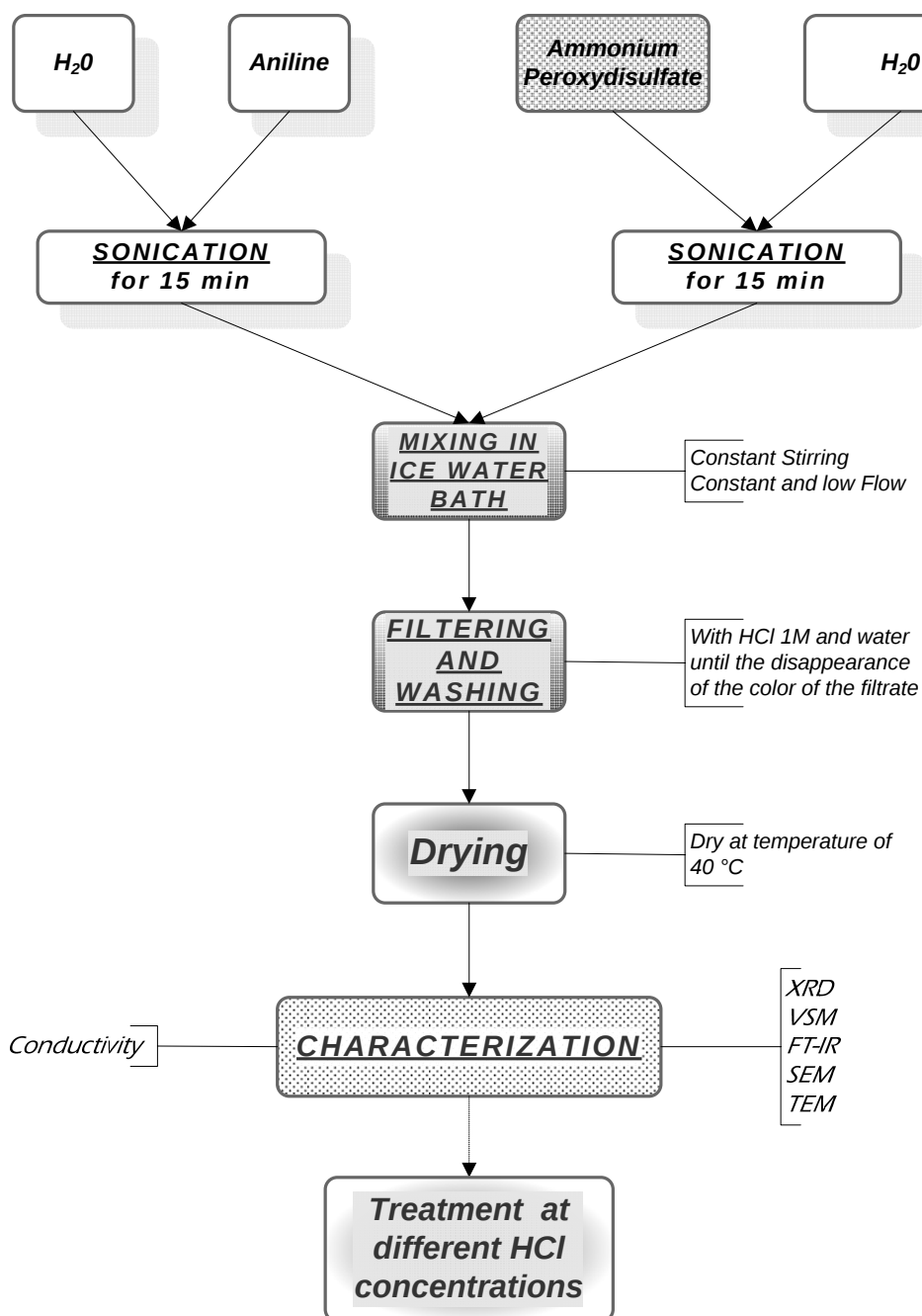


Figure 39. Preparation procedure of PAni EB-MnZn ferrite nanocomposite. The Mn atomic fraction 'x' was 0.8 in all tests: Method B

Series of composites made under the conditions of PANi EB are related in the table 4. The content of nanoparticles in the composite (% mol) is related to the aniline at initial conditions of synthesis:

No.	Sample	Ferrite (g)	% Ferrite (molar percent)
1	Poli 33	0.00	0.00
2	Poli 34	0.10	3.33
3	Poli 35	0.20	6.49
4	Poli 36	0.30	9.37
5	Poli 37	0.40	12.11
6	Poli 46	0.50	14.67
7	Poli 38	0.60	17.25
8	Poli 44	0.70	19.50
9	Poli 39	0.80	21.69
10	Poli 40	1.00	25.62
11	Poli 41	1.20	29.23
12	Poli 42	1.40	35.26
13	Poli 43	1.80	38.24

Table 4. Magnetic nanocomposites PANi EB-MnZn prepared at different ferrite molar percent, synthesized with 2:1 APS: PANi ratio. Molar fraction of ferrite, 'x' = 0.8.

4.2 STRUCTURAL CHARACTERIZATION OF PANI/MNZN COMPOSITE

4.2.1 XRD Analyses

4.2.1.1 The MnZn ferrite

Figure 40 show the XRD patterns of the solid produced at different atomic fractions of Mn ions 'x'. A reaction time of 4 hours was found to be suitable for complete formation of the ferrite under mild heating. As seen, all peaks correspond to ferrite structure. According to Scherrer's equation:

$$t = \frac{k\lambda}{\beta \cdot \cos\theta} \quad (21)$$

where λ is the X-ray wavelength, k is the shape factor, t is the average diameter of the crystals (in angstroms), θ is the Bragg angle (in degrees) and β is the line broadening measured at half-height and expressed in units of 2θ . The value of k depends on several factors, including the Miller index of the reflecting plane and the shape of the crystals. If the shape is unknown, k is often assigned a value of 0.89.

For the diffraction pattern of PAni-MnZn, ('x' = 0.8) composites prepared under basic conditions, it chooses the reflection peak at $2\theta = 43.18^\circ$ ($d = 2.11 \text{ \AA}$) was chosen to calculate the average crystallite size of the ferrite powders in the composite. Thereby, the average crystallite size of the magnetic particles as MnZn in the composites was estimated to be about 9.71 nm. Was selected the 'x' = 0.8 value for the $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrite, due to higher magnetization values, which will be presented in the following section. By XRD was verified the formation of ferrite structure for all 'x' values analyzed. Additional experiments under more intense heating conditions verified that the ferrite structure could be fully achieved in 5 minutes (Figure 41) at 'x' = 0.8. In these samples the corresponding average crystallite size did not change as compared to mild heating conditions, and was

found to be about 10.2 nm. The lattice constant was calculated to be $a=8.3002 \text{ \AA}$, which compares well with the value of $8.34 \text{ \AA}$ as found in literature [28].

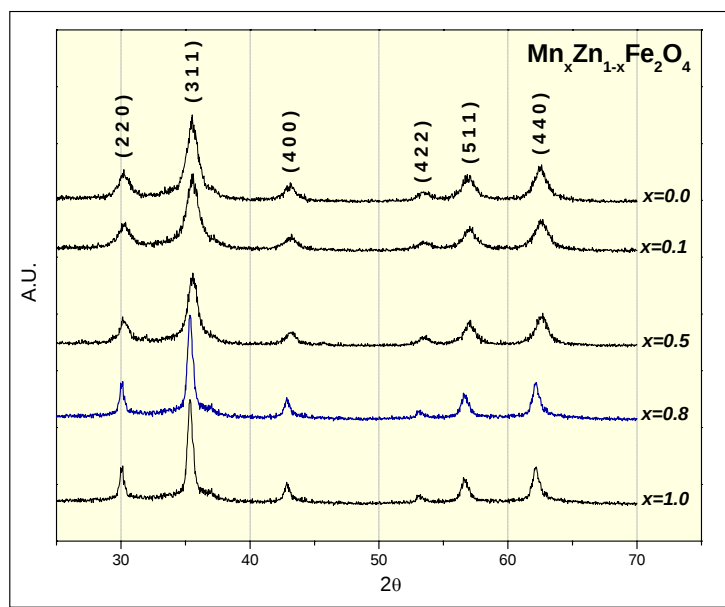


Figure 40. XRD patterns for $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ powders synthesized at various atomic fractions of Mn ions, 'x'. The reaction time was 4 hours under mild heating.

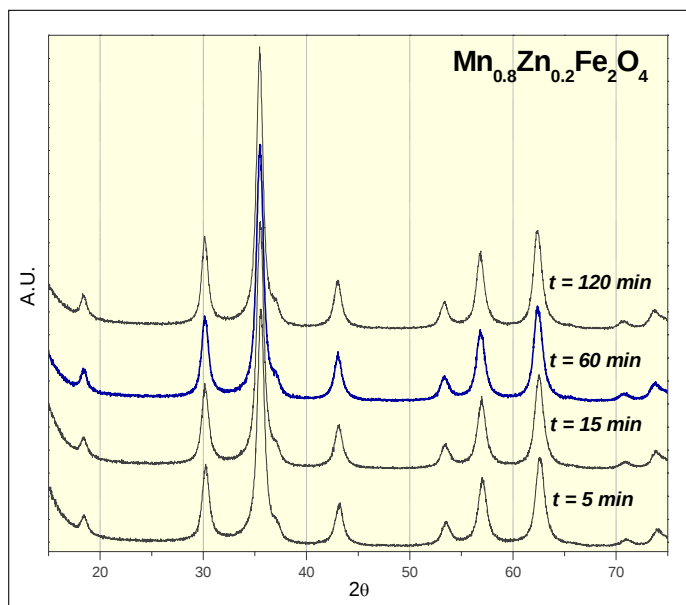


Figure 41. XRD patterns for $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ ferrite powders synthesized at different reaction times, with heating on burner.

4.2.1.2 The polyaniline (PAni)

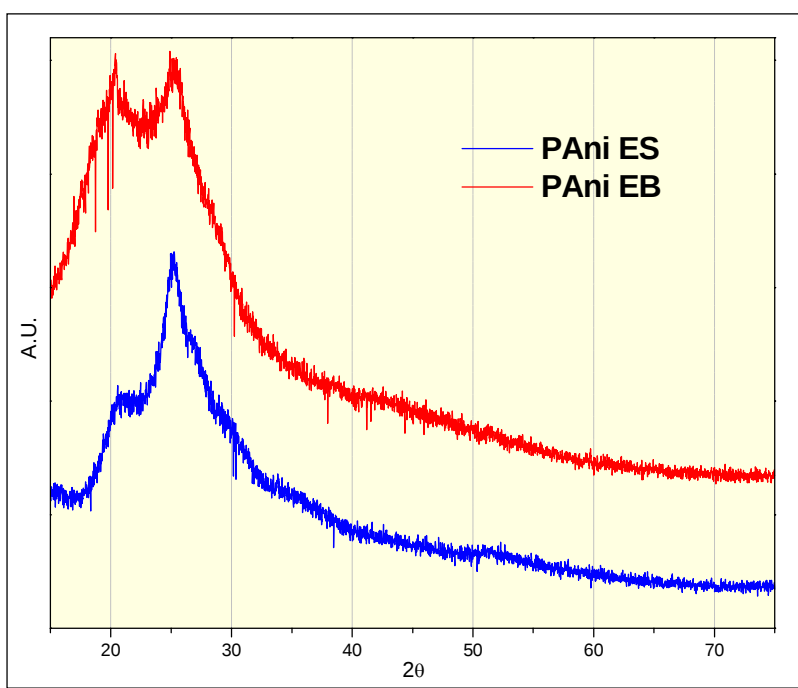


Figure 42. XRD pattern of PAni EB and PAni ES samples.

The Figure 42 shows two samples of PAni ES (synthesized in HCl 1N) and PAni EB (Synthesized at alkaline conditions) structures. The broad peaks are centered, more or less, at the same diffraction angles; however, the PAni EB structure showed broader XRD peaks that suggests poor crystallinity. Evidently, the variation in the polymerization conditions should have promoted some re-arrangement of the polymer chains.

We know that the acid concentration affect the polymer crystallinity, this fact was verified in the results shows in Figure 43. This is experimental evidence that polymer can change structure from PAni EB. Low concentration of acid (0.1N) presents a crystalline distortion, which is characteristic of the PAni EB, but the increment of acid concentration arise a transformation to PAni ES.

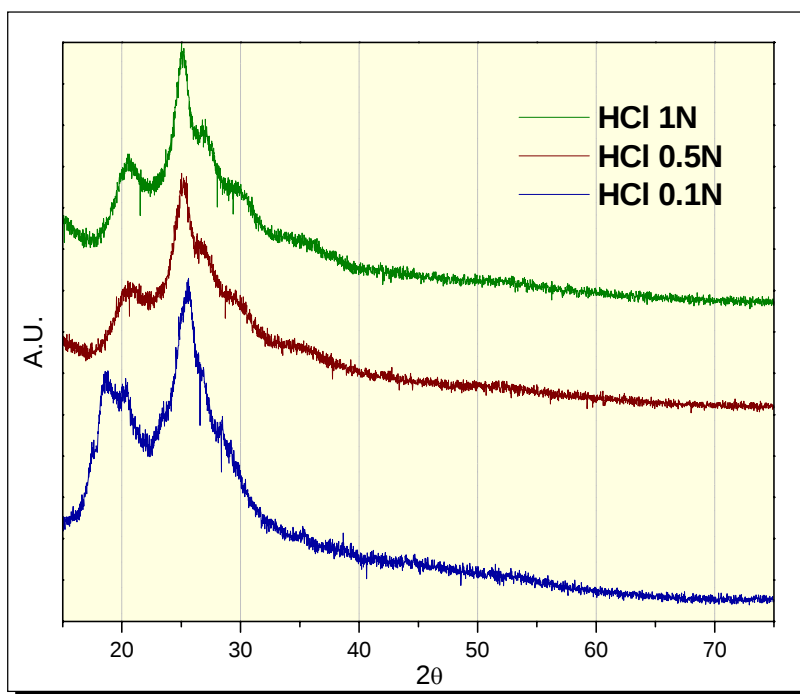


Figure 43. PANi ES (Polymers synthesized without ferrite) prepared at three different HCl concentrations.

The fact of carrying out the synthesis in a basic form showed favorable results in the structure of the compound. However, in order to verify whether the conductive PANi ES phase can be developed post-synthesis, initially synthesized PANi EB was contacted with HCl solution at different concentrations, this results are include in the section related to the experiments of acid treatment to PANi EB-MnZn composites.

Based on the above considerations, the following section will detail the XRD results for the composites prepared in abscense of acid and under a suitable Aniline/APS mole ratio of 2 (Figure 44).

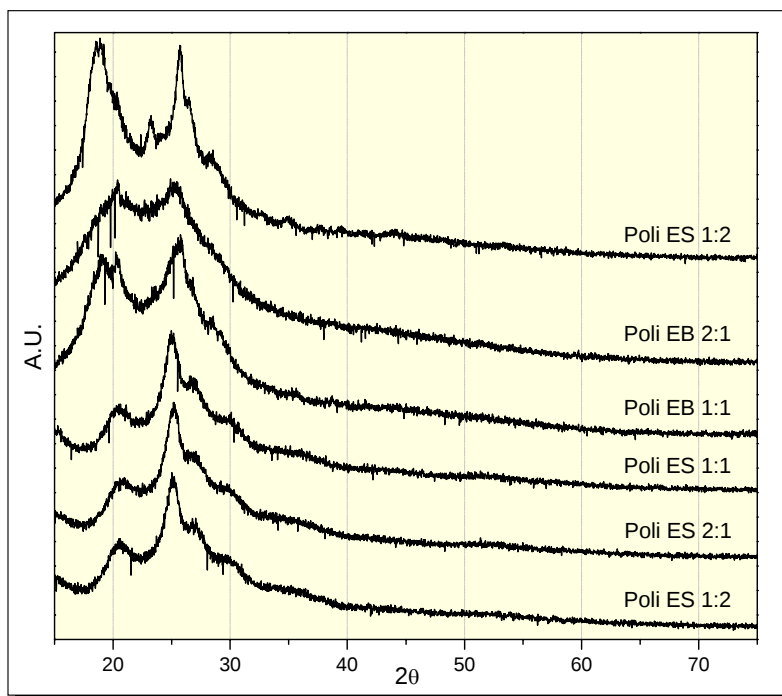


Figure 44. Analysis of PANi synthesized with and without acid to different molar ratios of APS and Aniline.

4.2.1.3 The PANi-Ferrite nanocomposite: Preparation Method “A”

XRD patterns of nanocomposite prepared with PANi ES at different ferrite molar percent are shown in Figure 45. The XRD of the ferrite is presented only for comparison purpose.

The absence of the ferrite peaks even in those composites prepared with higher amounts of ferrites (i.e., higher Ferrite/Composite molar ratios) is attributed to the extremely low quantities of ferrite in comparison with the polymer (Figure 45a); the increment in the amounts of ferrite in the nanocomposite did not improve the identification of the corresponding XRD peaks (Figures 45b and 45c).

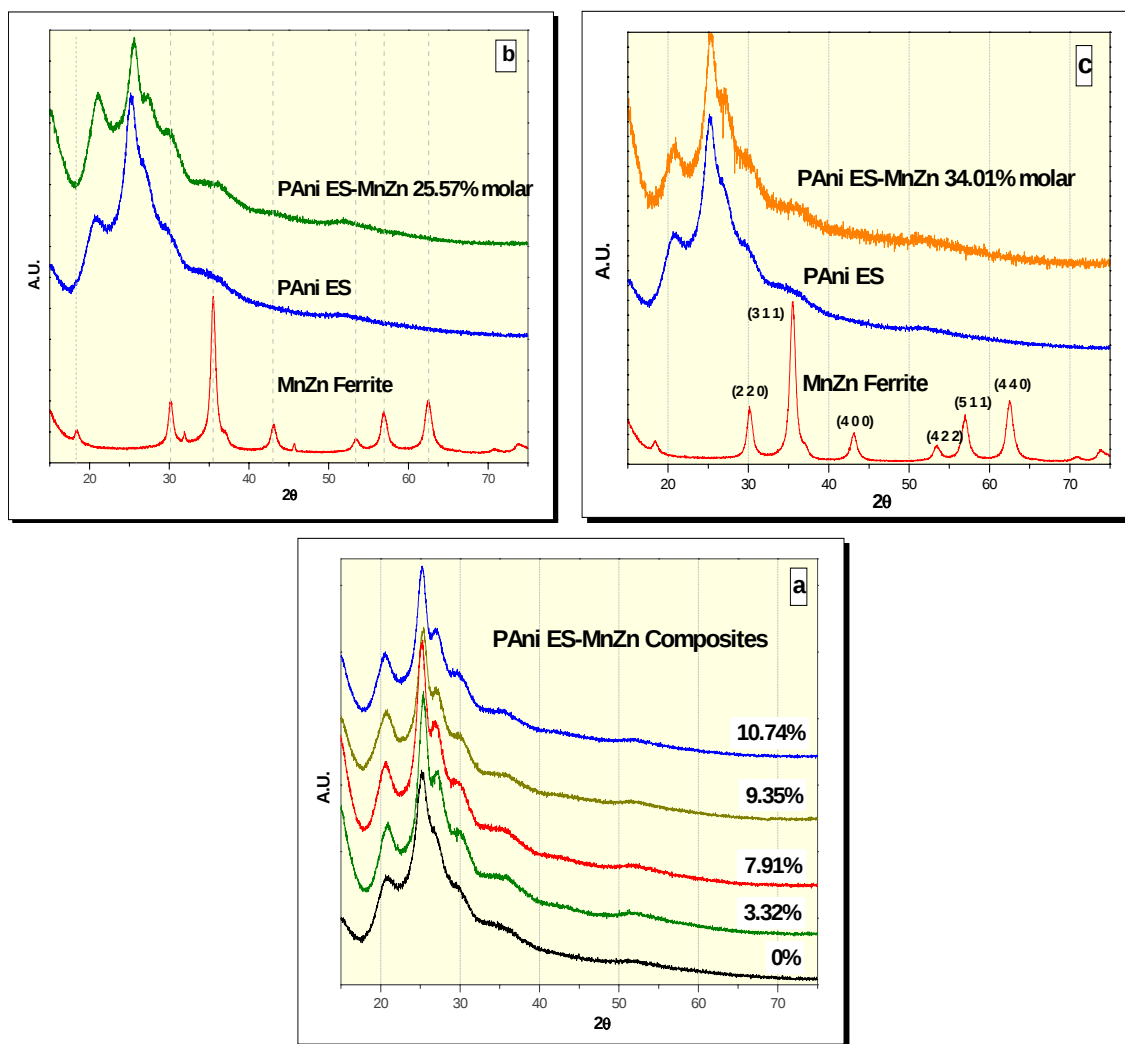


Figure 45. XRD Analysis for PANi ES, MnZn and PANi ES-MnZn. a) composite at different molar ratios; b) shows a comparison between the ferrite and the composite at 25.57% molar and c) analysis of composite at maximum ratio of the ferrite in the composite.

The absence of the ferrite XRD peaks is attributed to the chemical dissolution of ferrite nanocrystals by concentrated HCl solutions. This effect was also suggested by Meixiang Wan *et al* [28]. Then, to avoid the chemical dissolution of the ferrites by the strong acid, it was decided the preparation of the magnetic nanocomposites under neutral or alkaline conditions. Although this alternative will make the electrical conductivity go down, a subsequent acid treatment of the composite, to promote the PANi EB to PANi ES

conversion, could favor the reinstatement of the conductivity. Another attempt was based on the evaluation of an optimum ratio of Aniline to APS in order to enhance the conductivity in the polymer prepared under non-acidic conditions

4.2.1.4 *The PAni-Ferrite nanocomposite: Preparation Method “B”*

As it was stated before, the nanocomposite was prepared following the same synthesis procedure as described before, but using distilled water instead of the HCl 1N solution during the aniline polymerization stage. The XRD patterns corresponding to the PAni EB-Mn_{0.8}Zn_{0.2}Fe₂O₄ composites prepared for different Ferrite/Composite mole ratios are shown in Figure 46. As the proportion of the ferrite nanoparticles in the polymer increases, the characteristic PAni EB peak, around 20° - 25°, becomes broader. This broadening in the characteristics PAni peak can be related to some structural change in the polymer caused by the close interaction with the disperse ferrite phase [11]. The measurable signal of the ferrite peaks in PAni EB matrix was observed above a Ferrite/Composite mole ratio of 21.69%. The presence of the XRD peaks for the polymer and the disperse phase suggests the formation of the Ferrite/PAni nanocomposite under these conditions.

As expected, the increase in the proportion of the polymer caused the masking of the ferrite peaks. This can be explained by the thicker coating of PAni on MnZn ferrite. For pure PAni EB, the expected poorly crystalline structure is observed [8].

Based on these results, the possibility to retake the PAni ES structure was explored by contacting the PAni EB based nanocomposites with a HCl solution.

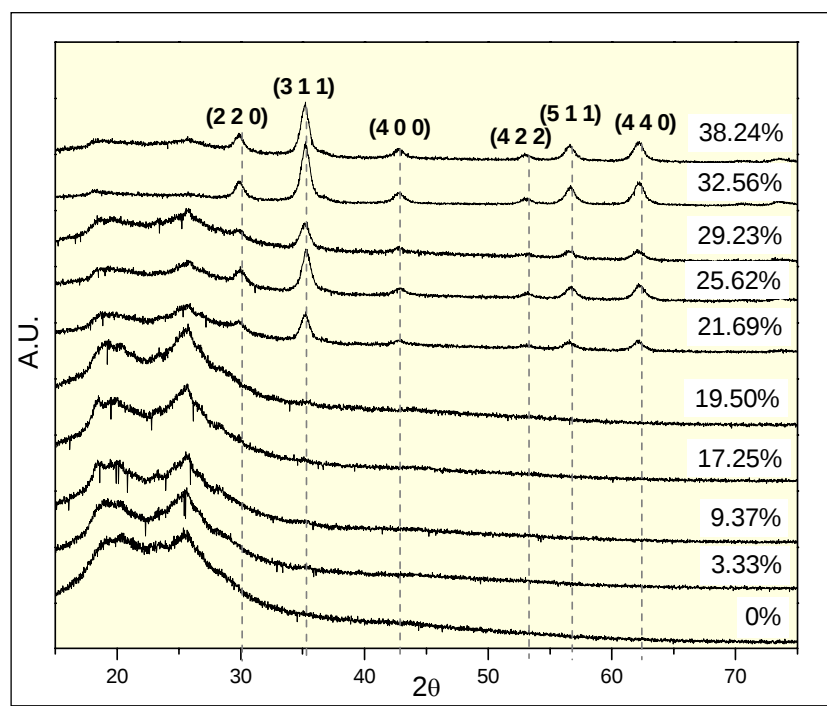


Figure 46. XRD patterns for PANi EB and PANi-MnZn ferrite nanocomposites at different Ferrite/Composite molar percent. Zero percent means bare polyaniline.

4.2.1.5 The PANi-Ferrite nanocomposite in acid bath

As Figures 47, 48 and 49 evidences, ferrite peaks were not detected in the XRD patterns of the nanocomposites after their treatment with HCl 1N, even for a Ferrite/Composite mole ratio as high as 25.62%.

The absence of XRD peaks corresponding to ferrite in the nanocomposite treated with HCl suggests the dissolution of nanoparticles after treatment with such a concentrated acid. However, the polymer suffered the expected phase transformation from PANi EB to conductive PANi ES.

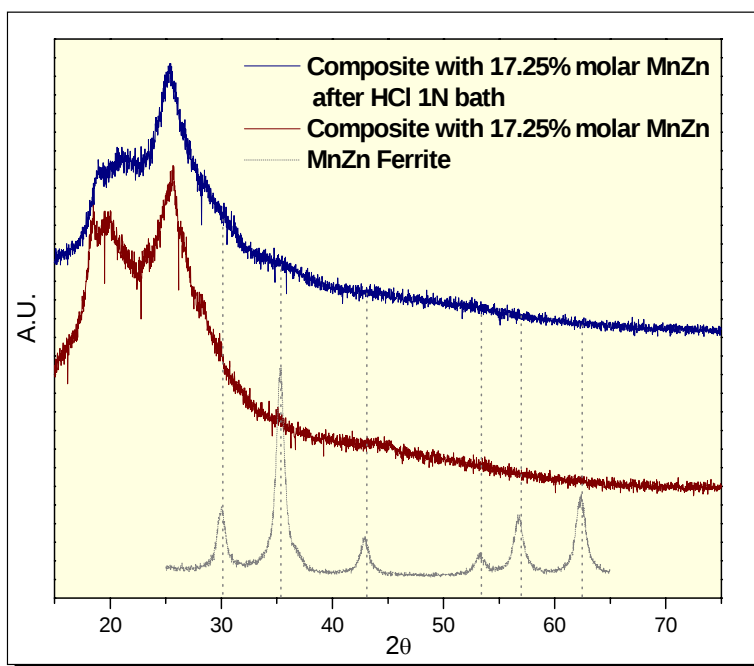


Figure 47. XRD patterns of PANi EB-MnZn ferrite composite, prepared at 17.25% Ferrite/Composite molar percent, before and after acid treatment with HCl 1N. The pattern for the ferrite is included only as reference.

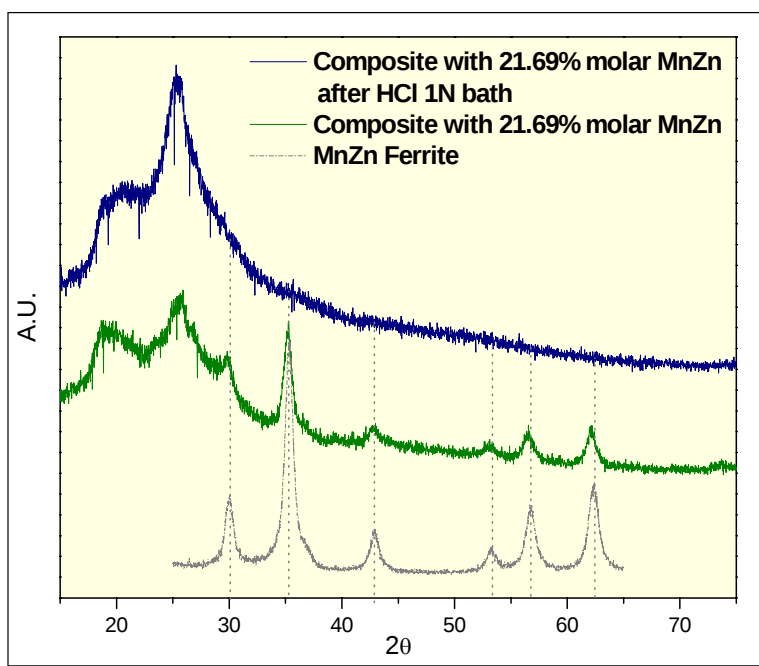


Figure 48. XRD patterns of PANi EB-MnZn ferrite composite, prepared at 21.69% Ferrite/Composite molar percent, before and after acid treatment with HCl 1N. The pattern for the ferrite is included only as reference.

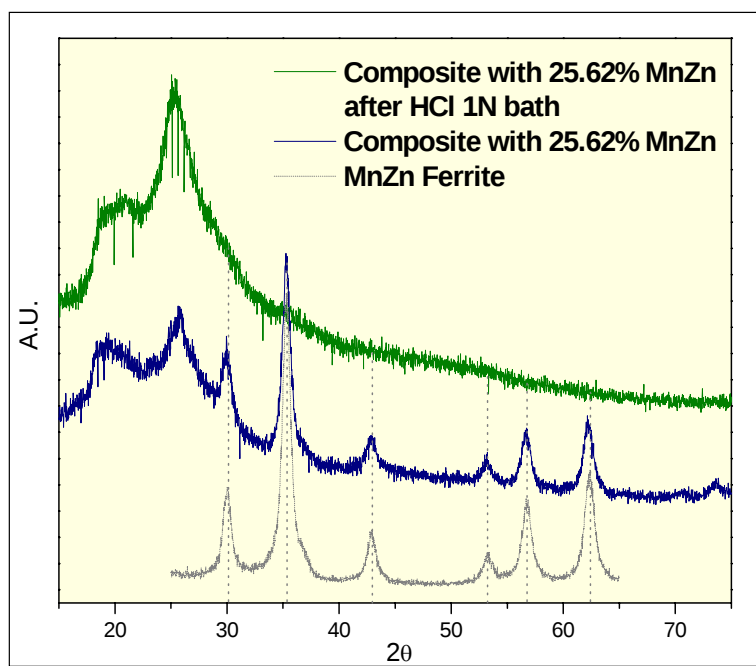


Figure 49. XRD patterns of PANi EB-MnZn ferrite composite, prepared at 25.62% Ferrite/Composite molar percent, before and after acid treatment with HCl 1N. The pattern for the ferrite is included only as reference.

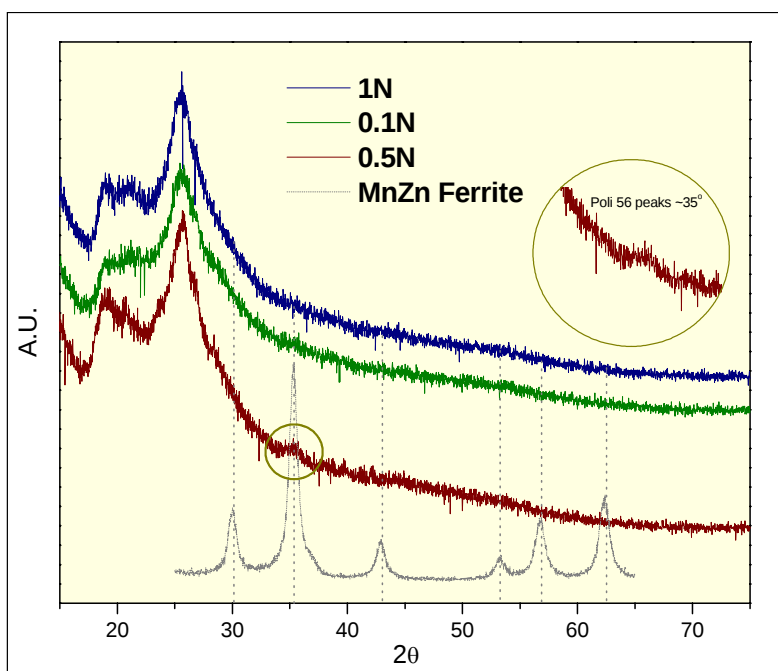


Figure 50. XRD patterns of composite samples of PANi EB-MnZn, 19.50% ferrite molar percent, after HCl bath with different acid concentrations.

In order to evaluate the possibility to inhibit the excessive dissolution of the ferrite nanoparticles in the polymeric matrix, the nanocomposite prepared in absence of acid was treated with HCl solutions at concentrations below 0.1N. For this purpose, the composite of PANi EB with 19.50% molar percent of ferrite as selected. The results, showed in Figure 50, did not show appreciable differences with respect to the previous ones: the ferrite peaks were not detected in any case. Only a minor presence of the ferrite was detectable for the powder produced at 0.5N HCl.

Evidently, the formation of the nanocomposite can be achieved under non-acidic conditions; however, any attempt to get the PANi ES structure would be conducive to the loss of the disperse phase.

4.2.1.6 *The PANi-Ferrite nanocomposite synthesized in different acid concentrations*

It was verified that any attempt to get the PANi ES from starting PANi EB would be conducive to the loss of the disperse phase, and hence of the magnetic properties of the composite. On this basis, the direct formation of the PANi ES based nanocomposite was attempted but now using more dilute HCl concentrations (0.1N and 0.5N) during the polymerization process. As the XRD patterns of Figure 51 shows, the ferrite peaks were not detected in the products: the acid concentration could have been high enough to dissolve the ferrite nanoparticles. A different behavior of the composite was observed when the polymerization process tookplace in presence of HCl 0.1N and the ferrite particles.

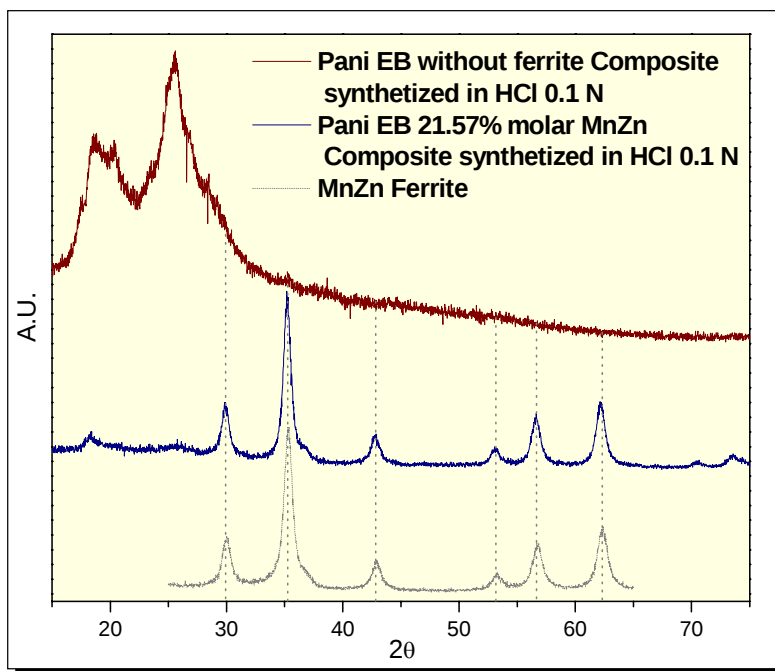


Figure 51. XRD patterns of composite PANi EB-MnZn at 21.57% ferrite molar percent synthesized with 0.1N acid concentration and PANi ES synthesized at 0.1N acid concentration.

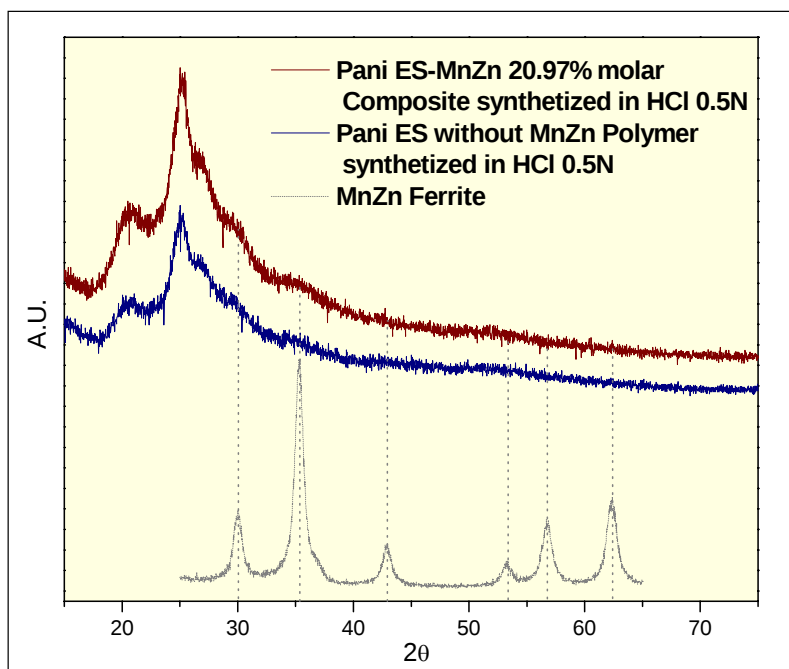


Figure 52. XRD patterns of composite PANi EB-MnZn ferrite at 20.97% ferrite molar percent synthesized with 0.5N acid concentration and PANi ES synthesized at 0.5N acid concentration.

The XRD patterns of Figure 52 evidence a reorganization in the structure of the polymer and the co-existence of the ferrite reflections suggesting its effective and stable incorporation in the nanocomposite structure. For this acid concentration, the coating of the ferrite nanoparticles by the polymer would have been more efficient to protect them from chemical dissolution.

4.2.2 SEM and HRTEM Observations

SEM observations were done on the polymer and the composite powders coated previously with gold to improve the image quality.

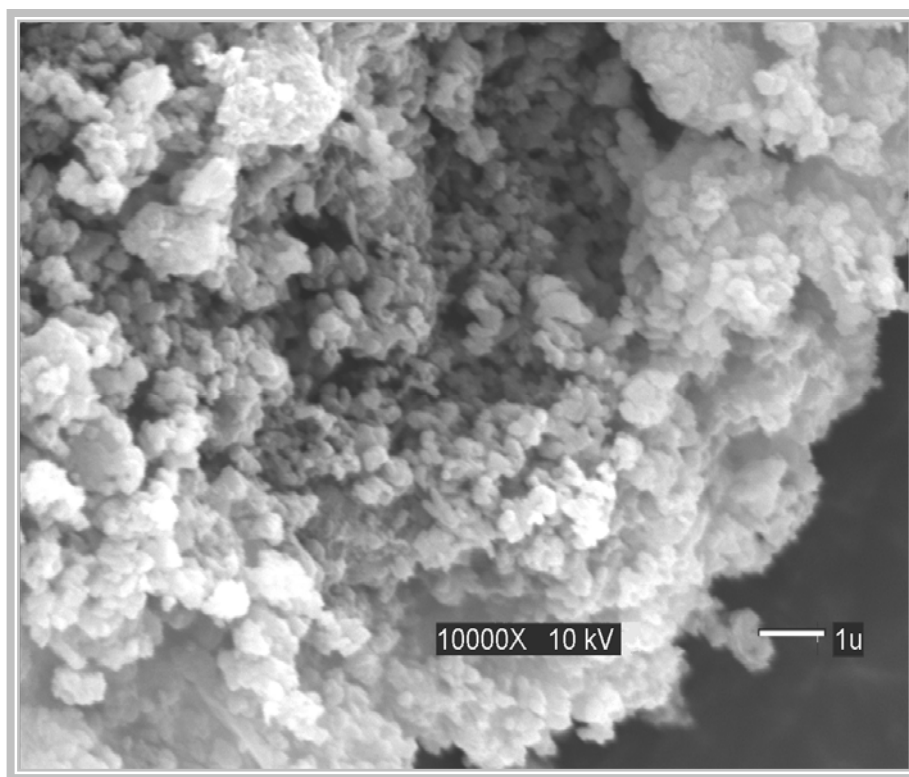


Figure 53. SEM image of powdered polymer PANi EB.

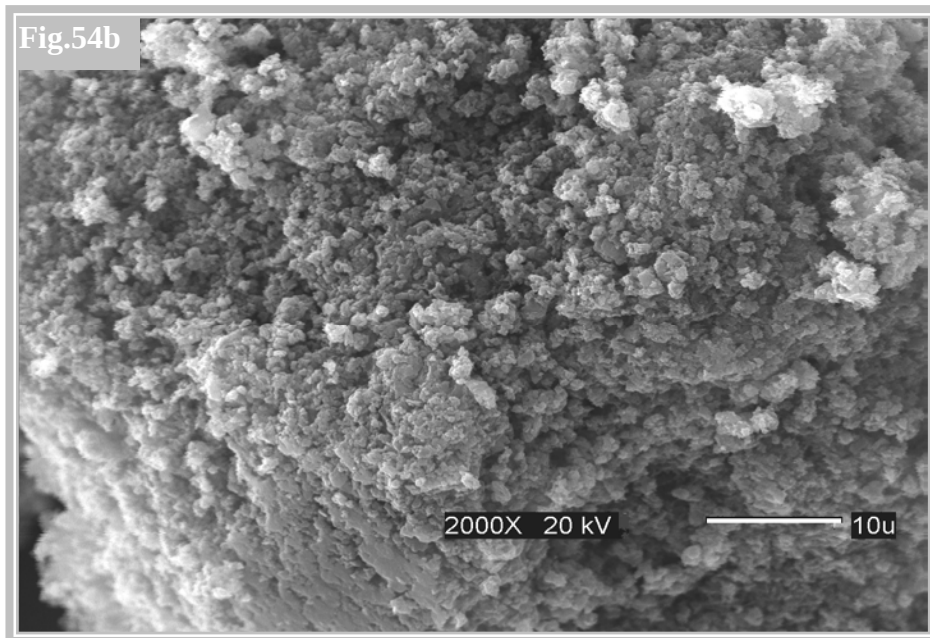
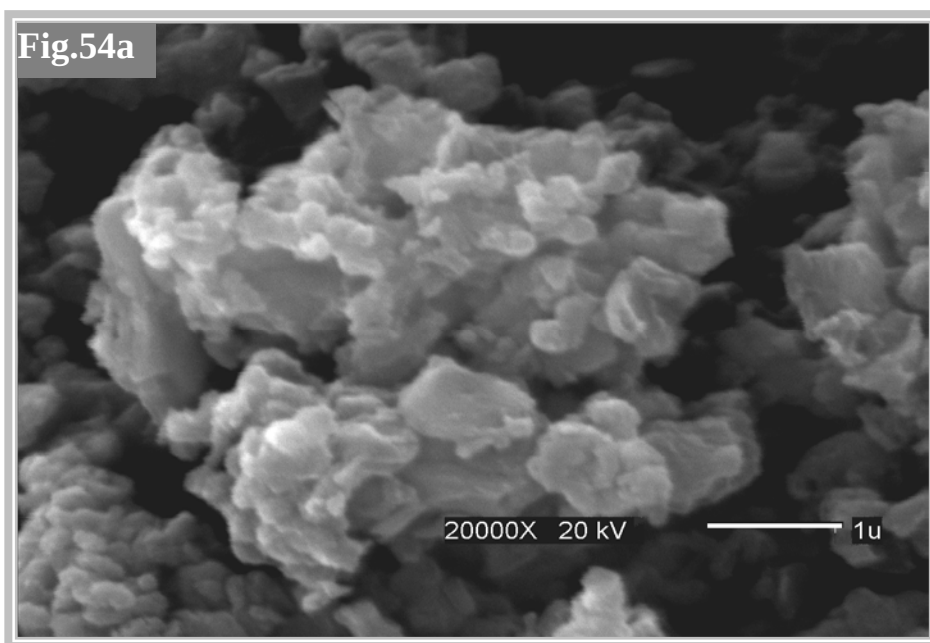


Figure 54. SEM images of PANi EB particles with 19.50% MnZn molar percent at two scales a) 20000X and b) 2000X.

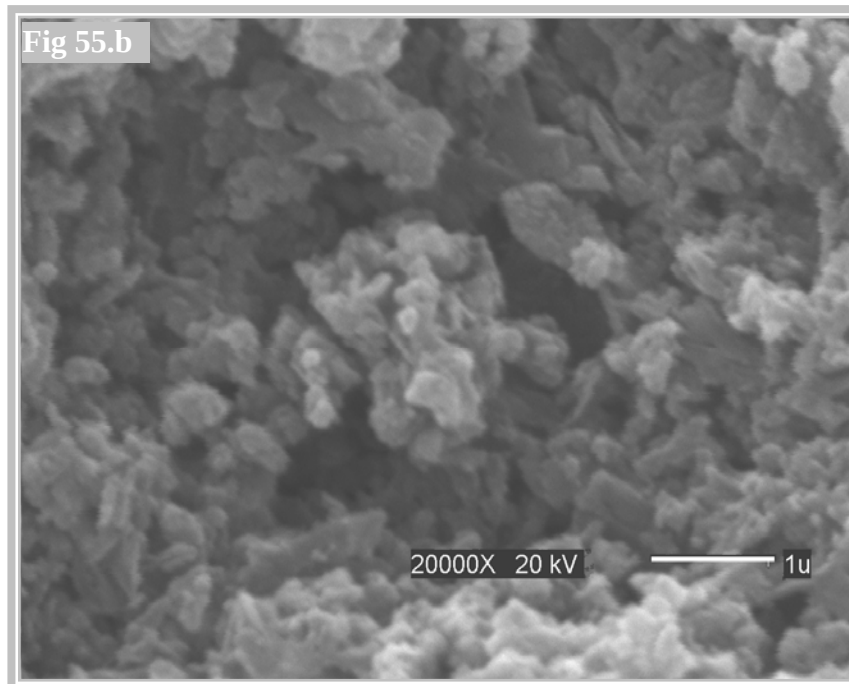
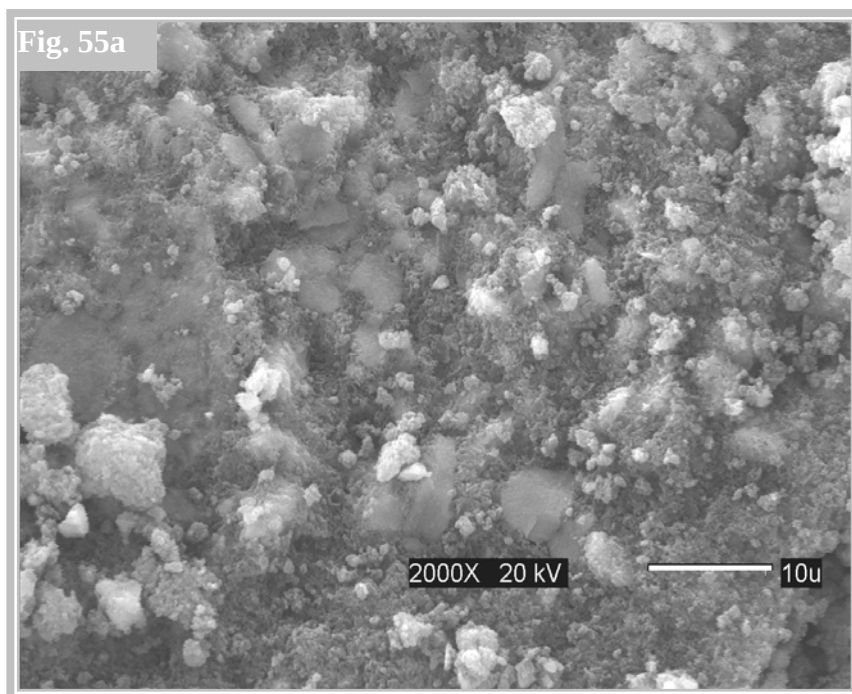


Figure 55. SEM images of PANi EB particles with 40.83% MnZn molar percent at two scales a) 2000X and b) 20000X.

Figure 53 represents the SEM image of powdered polyaniline EB. This sample was produced in absence of acid. It exhibits a porous and irregular structure. There are a large number of clews whose diameter is about one micrometer.

Figures 54 and 55 correspond to the SEM images of the magnetic nanocomposite prepared at different Ferrite/PAni EB molar percent. The irregular shapes and the porous nature of the compacted powders are evidenced by the images taken at high magnifications.

HRTEM image of Figure 56 evidences the nanocrystalline nature of the $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrite particles, synthesized for 'x' = 0.8. The observed particle size (~10 nm) is in good agreement with the value estimated from XRD analysis, suggesting the formation of single crystal.

Figure 57 shows typical HRTEM image of the Ferrite/PAni nano-composite. . This image was obtained after treating the composite with NMP in order to get a thin and transparent film as required for TEM observations. It can be seen from this figure that the ferrite nanoparticles are reasonably well dispersed within the polymeric matrix. The nanosize of ferrite particles is clearly evidenced.

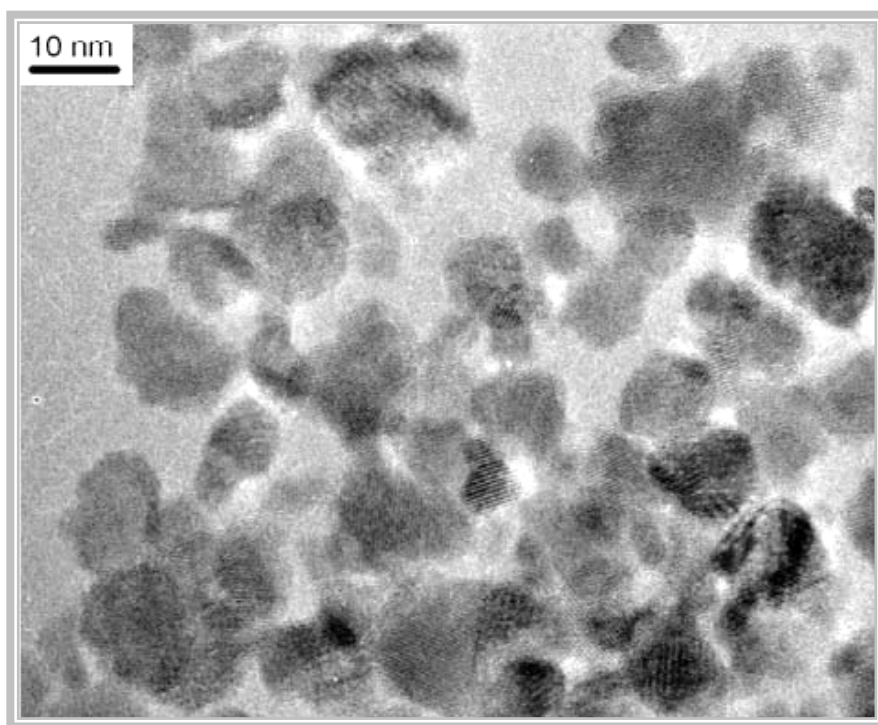


Figure 56. HRTEM image of $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nanocrystals synthesized after 60 minutes of reaction.

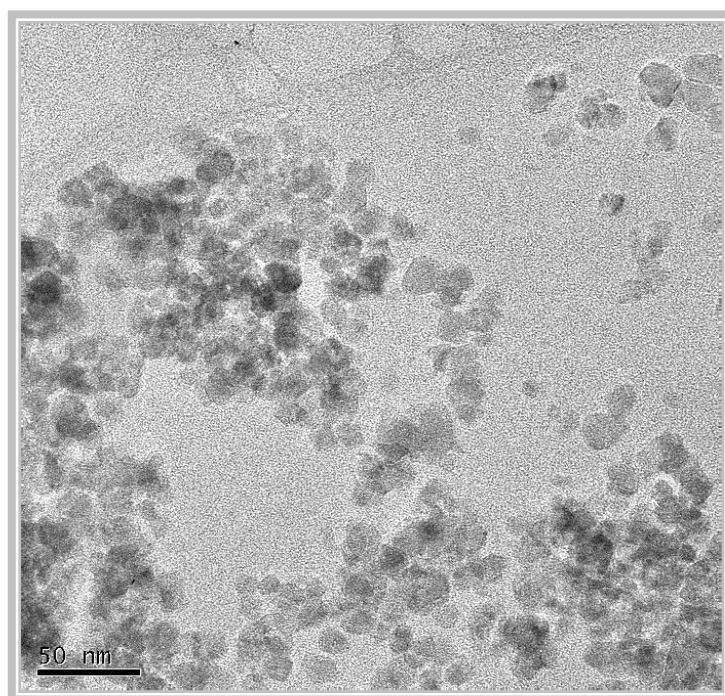


Figure 57. HRTEM image of PANi ES-MnZn 3.98% ferrite molar percent in NMP.

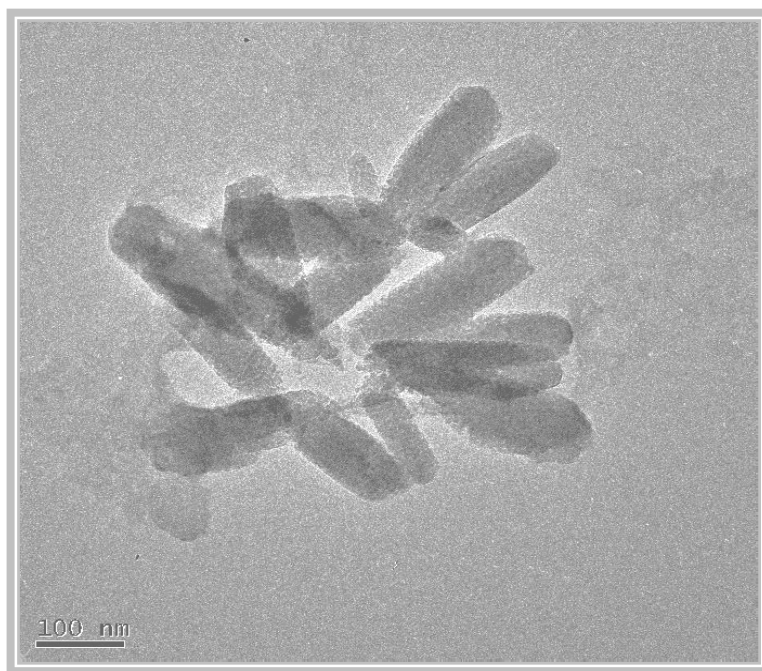


Figure 58. HRTEM images of the PANi ES-Mn_{0.8}Zn_{0.2}Fe₂O₄ nanocomposite with 34.03% ferrite molar percent. Scale 100 nm.

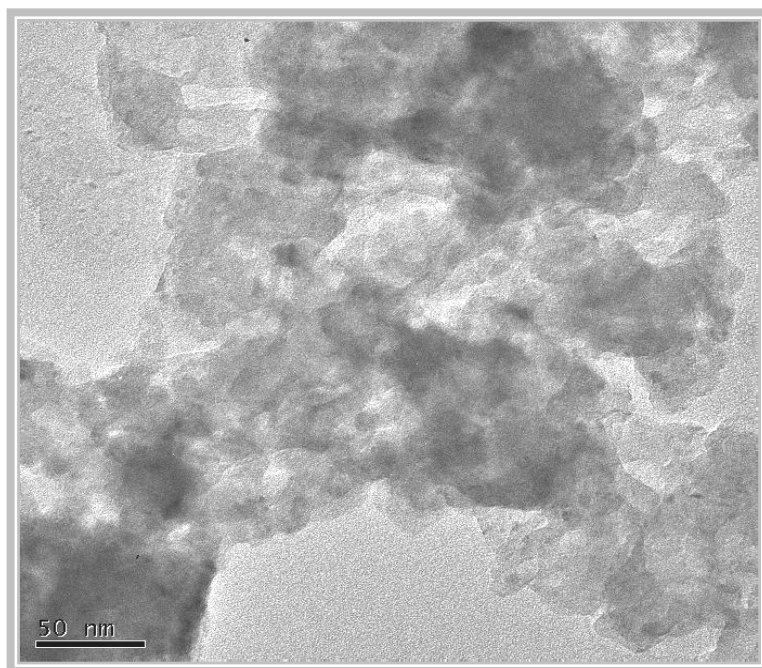


Figure 59. HRTEM images of the PANi ES-Mn_{0.8}Zn_{0.2}Fe₂O₄ nanocomposite with 34.03% ferrite molar percent. Scale 50 nm.

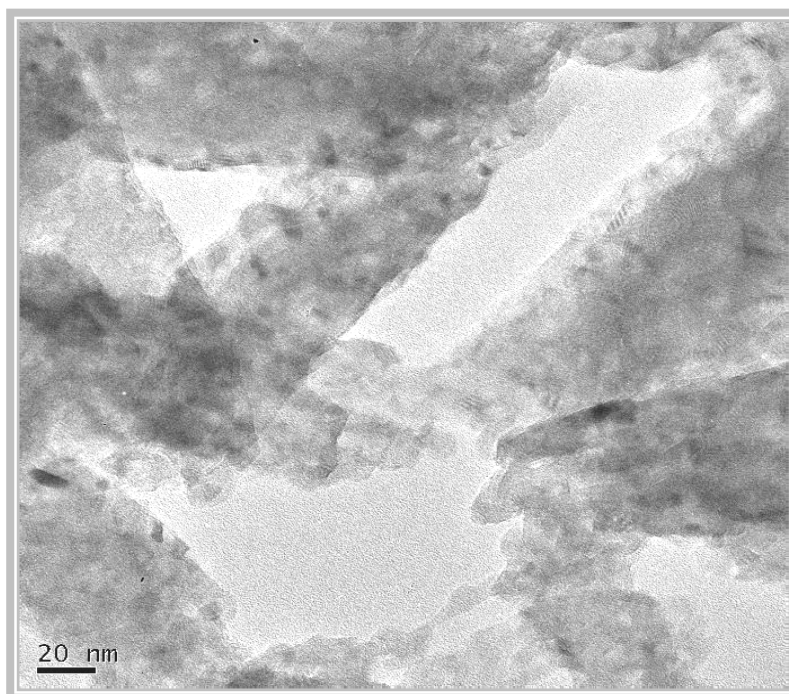


Figure 60. HRTEM images of the PANi ES-Mn_{0.8}Zn_{0.2}Fe₂O₄ nanocomposite with 34.03% ferrite molar percent. Scale 20 nm.

Figures 58, 59 and 60, shows typical HRTEM images of the PANi ES Ferrite nanocomposite produced .in acid conditions of HCl 1N concentrations and 34.03% ferrite molar percent. Darker spots correspond to the ferrite nanoparticles. It can be seen from the figure that the ferrite nanoparticles are reasonably well dispersed within the polymeric matrix, as represented by the shaded area.

4.3 MAGNETIC CHARACTERIZATION

4.3.1 VSM Analyses

4.3.1.1 *The MnZn ferrite*

Figure 61 shows the room temperature M-H loops for Mn_xZn_{1-x}Fe₂O₄ nanocrystals

synthesized at different Mn atomic fraction values, 'x'. These loops are typical of ferri-magnetic 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.

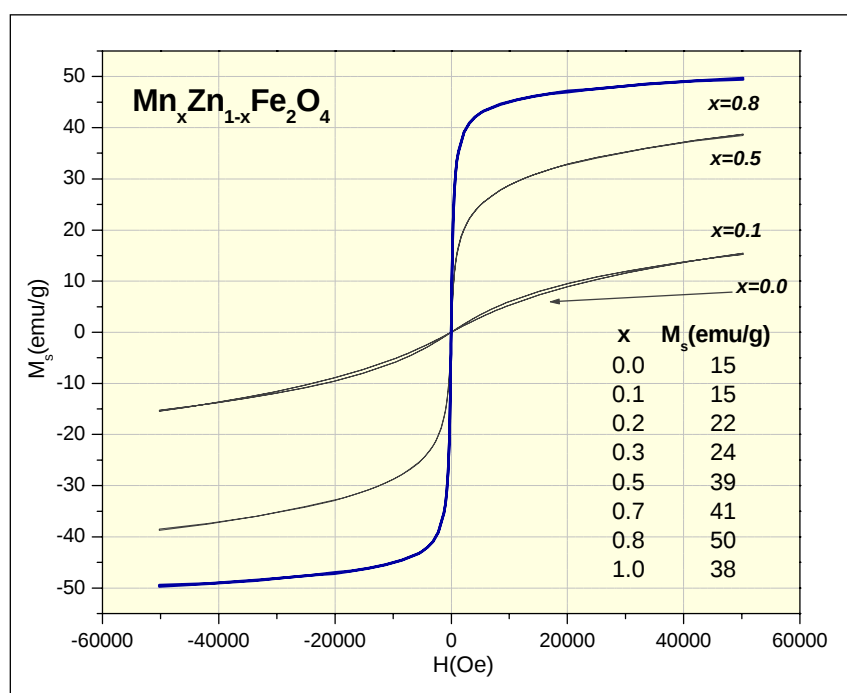


Figure 61. Room temperature M-H loops for $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrites at different Mn atomic fractions, 'x'.

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 shows that even for $x = 0$ and 0.1, ferrites produced exhibited a small magnetization. .

The M-H loop for the $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ ferrite precipitated under more intensive heating conditions and after one hour of reaction is shown in Figure 62. The maximum magnetization was found to be about 55 emu/g. The maximum magnetization was slightly above that 50 emu/g that was obtained with the ferrite was synthesized under moderate heating conditions provided by a hot plate.

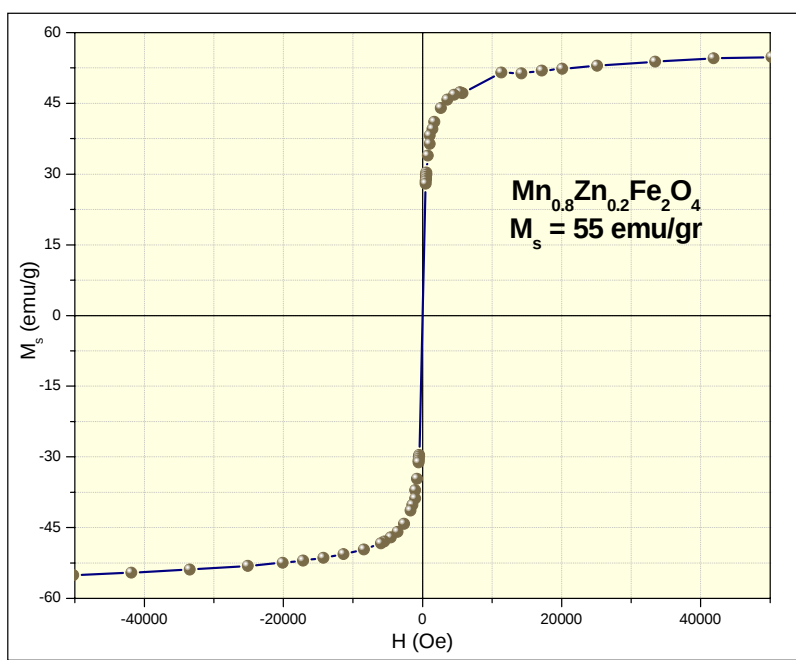


Figure 62. Room temperature M-H loop for $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ powder synthesized under kore intensive heating conditions and after one hour of reaction.

4.3.1.2 The PAni-Ferrite nanocomposite: Preparation Method “A”

The analyses of the system PAni ES-MnZn ferrite was carried out. The magnetization of the compound correspond to the prospective behavior an evident increment in

magnetization corresponding to the increment of ferrite nanoparticles in the composite.

The Figure 63 show the room-temperature M-H loops for the PAni ES-MnZn ferrite composite prepared with different ferrite mole percents in initial mixtures. The observed values of magnetization are 3×10^{-3} emu/g for the sample with 2.51% ferrite molar percent and 1.4×10^{-3} emu/g for the sample with initial 1.69% ferrite molar percent. The low magnetization values can be due to the loss of ferrites by chemical dissolution as discussed in the above sections. Despite the low magnetization values, it was observed the rise in magnetization with the increase of ferrite contents in the composite.

Figure 64 shows the room temperature M-H loops for the PAni ES-MnZn ferrite nanocomposite with 25.57% ferrite molar percent. The saturation magnetization of the composite was still low (6.8×10^{-3} emu/g) but larger than the composites prepared with lesser amounts of ferrite. Also in this case, the low magnetization exhibited by this composite can be attributed to the dissolution of ferrite by the concentrated HCl used during the polymerization of the aniline. These results are in agreement with XRD results that showed the absence of the ferrite reflections in the corresponding patterns.

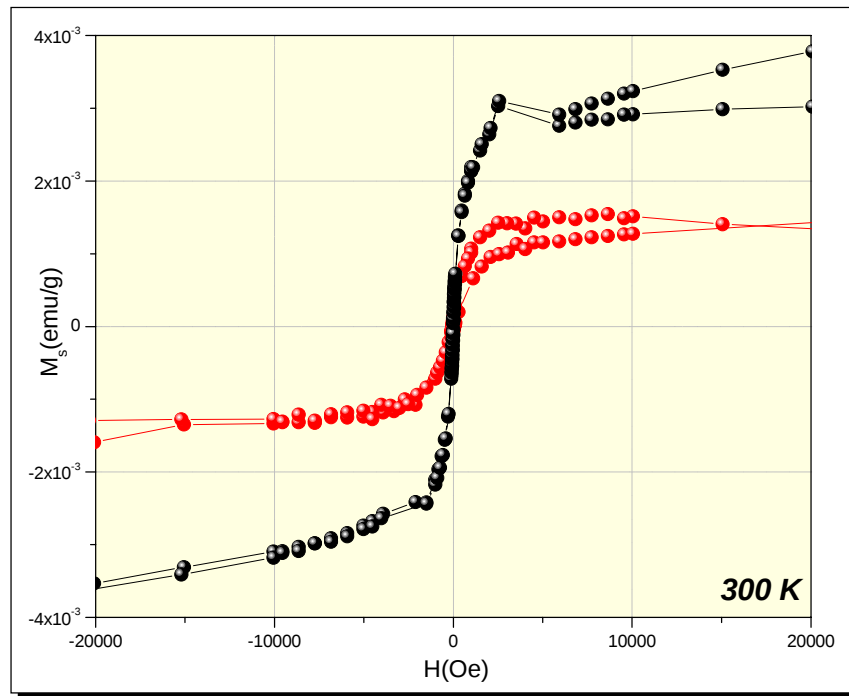


Figure 63. Room temperature M-H loop for PANi ES with-MnZn at two different ferrite mole percents. Red circles correspond to the composite with 1.69% ferrite whereas black circles correspond to the composite bearing initial 2.51% ferrite.

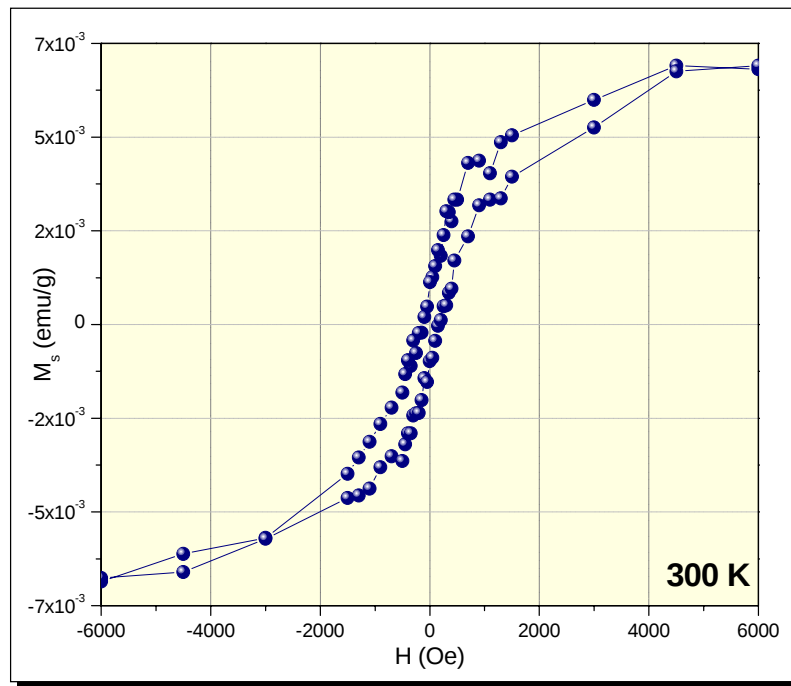


Figure 64. Room temperature M-H loop of PANi ES-MnZn 25.57% ferrite molar percent at 300K.

4.3.1.3 The PAni-Ferrite nanocomposite: Preparation Method “B”

Figure 65 shows the well-saturated M-H loops for the composites produced in absence of HCl. In this case, the presence of the ferrite was evidenced by the large magnetization values when compared with the previous results. As expected, the magnetization was strongly dependent on the amount of ferrite: the larger the mole percent of ferrites in the composite, the higher the saturation magnetization. The magnetization values varied from 4.6×10^{-3} emu/g up to 18.7 emu/g, for ferrite mole percents of 3.3% and 32.3%, respectively. It can be seen that the magnetic susceptibility of the ferrite particles, given by the slope at the origin of the M-H curve, did not change when embedded in the polymeric matrix.

Concentration, (Molar ratio percent)	M_s (emu/g)
3.33%	4.5824×10^{-3}
9.37%	10.137×10^{-3}
17.25%	10.268×10^{-3}
21.69%	3.0357
25.62%	4.8921
32.56%	18.678

Table 5. Variation of the saturation magnetization in the PAni EB based composites with the ferrite mole percent

As expected, the higher ferrite molar percent the higher magnetization in the composite. On the above basis, the tuning on magnetic properties of the nanocomposite just by controlling the ferrite mole percent, has been demonstrated.

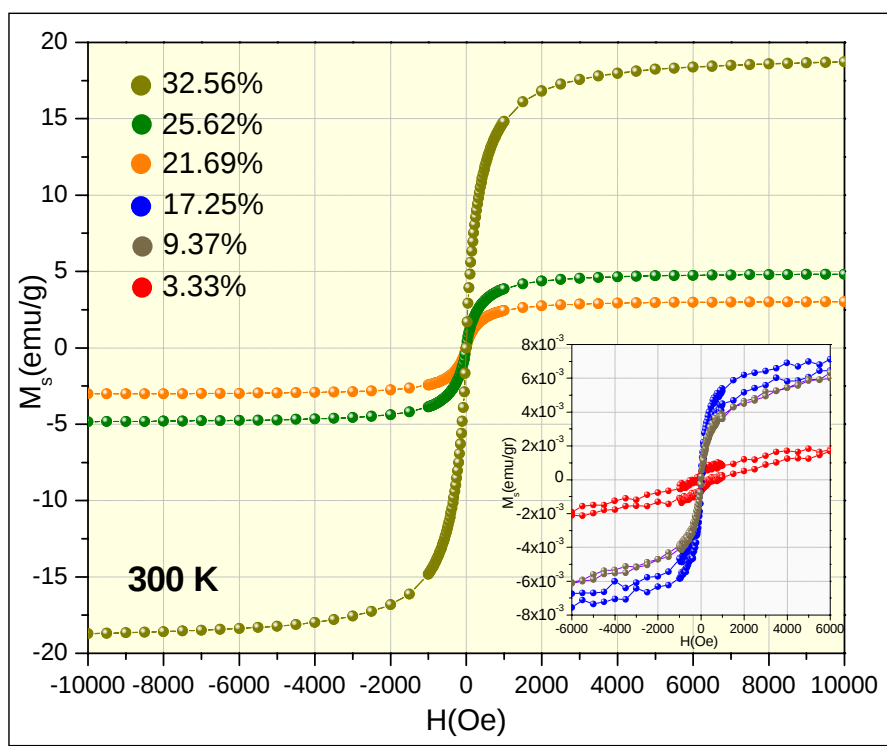


Figure 65. Room temperature M-H curves for PAni EB/Ferrite nanocomposites at different molar percent. The inset shows the M-H profiles for composites prepared at very low ferrite mole percents (3.33%, 9.37% and 17.25%).

4.3.1.4 The PAni-Ferrite nanocomposite in acid bath

The powdered PAni EB based composites were subsequently treated with HCl 1N as an attempt to develop the PAni ES structure but keeping the magnetic properties in the composite.

Concentration, (Molar ratio percent)	Before acid treatment, M_s (emu/g)	After acid treatment, M_s (emu/g)
25.62%	4.8921	3.06×10^{-4}
19.23%	3.0357	4.51×10^{-4}

Table 6. Magnetization change of PAni EB based composite after treatment with HCl 1N.

Table 6 summarizes the obtained results. Again, the acid treatment made the magnetization to drop drastically. Also in this case, a chemical dissolution of the ferrites can be suggested. Accordingly, any attempt to develop the PANi ES phase from the PANi-EB one should consider the use of another acid or HCl solutions more dilute than 1N.

In order to evaluate the effect of the HCl concentration on the magnetic properties of the PANi EB based composite, the powdered products were treated with 0.5N and 0.1N HCl aqueous solutions. The selected composites were prepared at ferrite mole percents of 25.6% and 19.23%. The corresponding M-H data are shown in Figures 66 and 67.

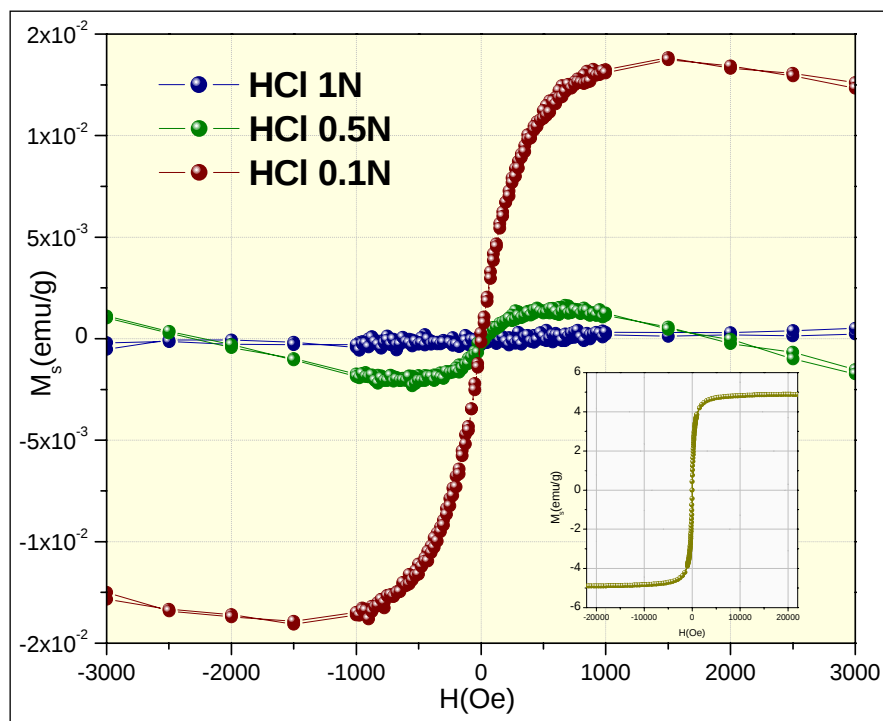


Figure 66. Room temperature M-H loop of PANi EB-MnZn ferrite nanocomposite (25.62% ferrite) after treatment by HCl at different concentrations. The inset show the same composite (25.62% ferrite) before treatment by HCl.

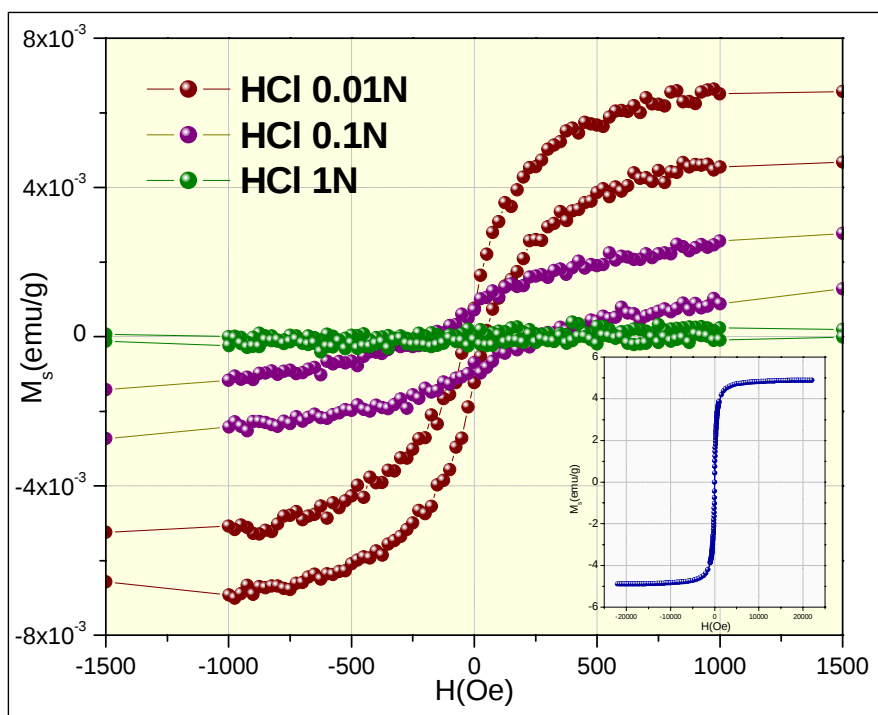


Figure 67. Room temperature M-H loop of PANi EB-MnZn ferrite nanocomposite (19.23% ferrite molar percent) after treatment by HCl at different concentrations. The inset shows the same composite (19.23% ferrite molar percent) before treatment by HCl.

As evidenced by the data shown in Table 7, the acid treatment of the PANi EB based nanocomposite causes a drastic drop in the magnetization values even for acid concentrations as low as 0.01N. One possible reason could be the porosity of the polymer coating of the nanoparticles, which favors the diffusion of the acid solutions and subsequent dissolution of the ferrite nanocrystals. The evaluation of the re-establishment of the PANi ES structure by acid treatment of the PANi EB one should be re-attempted by after producing a more homogeneous and less porous film of the nanocomposites.

Concentration, (Molar ratio percent)	Before acid treatment, M_s (emu/g)	HCl Concentrations	After acid treatment, M_s (emu/g)
25.62%	4.8921	1	3.06×10^{-4}
		0.5	1.54×10^{-3}
		0.1	1.35×10^{-2}
19.23%	3.0357	1	4.51×10^{-4}
		0.1	2.76×10^{-3}
		0.01	6.57×10^{-3}

Table 7. Variation in magnetization of the nanocomposite PAni-MnZn with 19.23% and 25.62% ferrite molar percent, after contact with HCl at different concentrations.

4.3.1.5 *The PAni-Ferrite nanocomposite synthesized in different acid concentrations*

So far we have determined that the optimum conditions for the formation of the magnetic nanocomposite involve the polymerization of aniline under acid-free conditions. However, if the purpose is to develop the PAni-ES phase by acid treatment, the ferrite disperse phase would be lost by chemical dissolution from the powdered products. Therefore, we also explored another option: the formation of the nanocomposite under less acidic conditions. For this purpose, the formation of the composite by using HCl 0.5N and 0.1N during the polymerization stage was evaluated.

Figure 68 shows the M-H loops for the composite (21% ferrite mole percent) prepared in presence of HCl 0.5N. The M-H loop for the pure polymer is presented just for comparison. As expected the polymer behavior is typical of a diamagnetic material. The

magnetization of the composite was 16.469×10^{-3} emu/g, which is low for a nominal mole percent of ferrite as high as 21%. Figure 69 shows the well-saturated M-H loop for the sample synthesized in presence of HCl 0.1N. This composite exhibits a quite high magnetic response (24.8 emu/g). Evidently, this low concentration of acid did not affect the chemical stability of the ferrite nanocrystals inside the polymeric matrix. Since the polymerization took place in an acidic environment, some rise in the conductivity of the composite should also be expected.

The analysis of the electrical conductivity for these composite are discussed in the following sections.

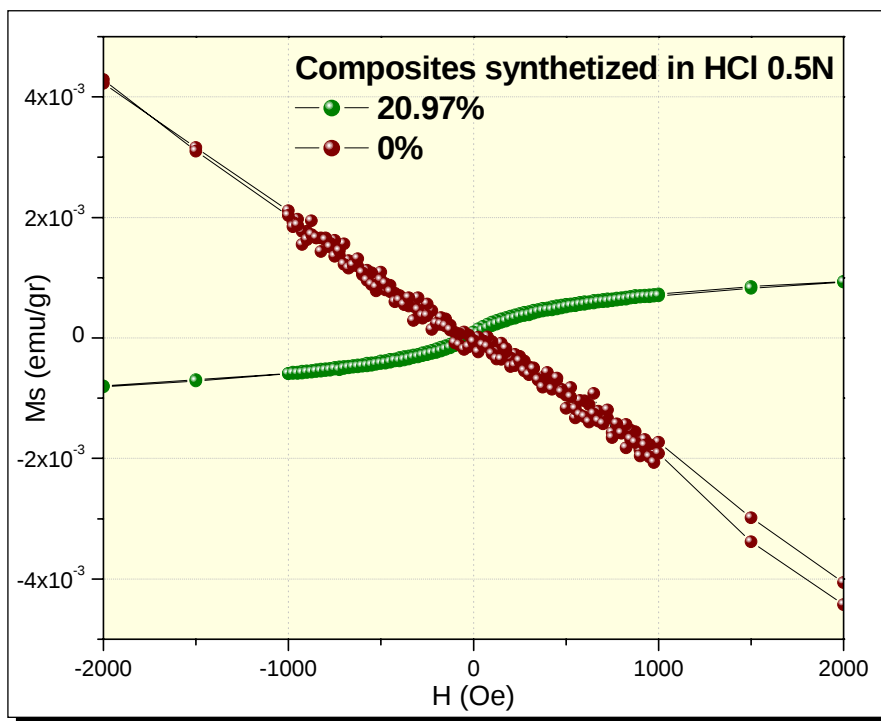


Figure 68. Room temperature M-H loop of pure PANi-ES (0%) and PANi EB based composite (21% ferrite mole percent), synthesized in presence of HCl 0.5N

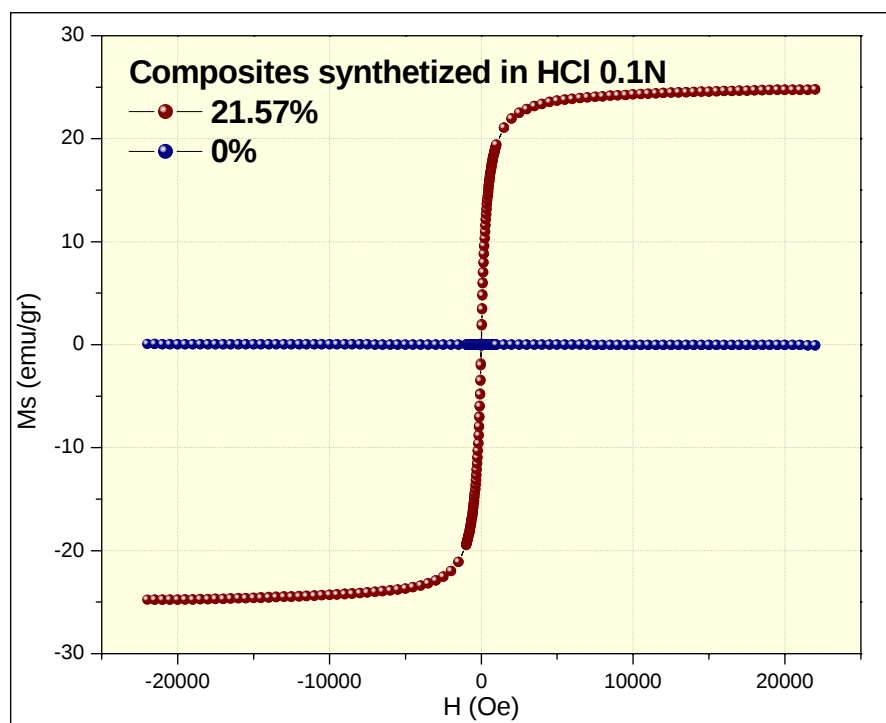


Figure 69. Room temperature M-H loop of pure (0%) and PANi-ES-based composite (21.6% ferrite mole percent), synthesized in presence of HCl 0.1N.

4.4 FTIR SPECTROSCOPY OF PANI/MNZN COMPOSITES

4.4.1 FTIR Analyses

4.4.1.1 The MnZn ferrite

Figure 70 shows the spectrum FT-IR for the MnZn ferrite powder ($x = 0.5$) produced after 2 and 4 hours of reaction time. The heating was carried out using a hot-plate. The bands in the spectrum for 2 hours (2978 cm^{-1} , 2900 cm^{-1}) can be assigned to a OH^- based precursor co-existing with the metal-oxygen vibration centered at 540 cm^{-1} in the ferrite structure. The absence of those precursor bands after 4 hours of reaction suggested the complete conversion of the intermediate into the ferrite phase. It must be recalled that only five minutes were required to form the ferrite phase when a gas burner was used instead of the

hot plate o heat the reacting solution.

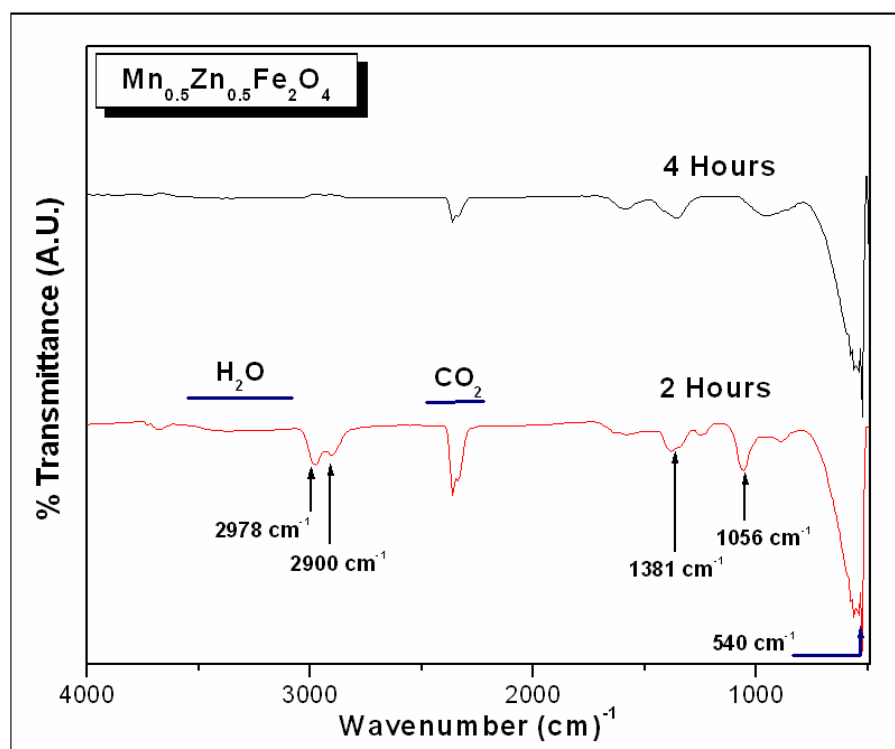


Figure 70. FT-IR spectra of the MnZn ferrite ($x'=0.5$)

4.4.1.2 The polyaniline (PAni)

Figure 71 shows the FTIR spectra of bare PAni EB, which was synthesized from aniline in absence of HCl. The band at 1573 cm^{-1} and 1504 cm^{-1} are attributed to the C=N and C=C stretching modes of vibration for the quinonoid and benzenoid units of the polymer, while the bands at 1296 cm^{-1} and 1172 cm^{-1} are assigned to the C–N stretching mode of benzenoid units. The peak at 817 cm^{-1} is attributed to C–C and C–H for the benzenoid unit. As an example, in Table 8, are summarized the main wavelengths and assignments of the detected active IR-bands.

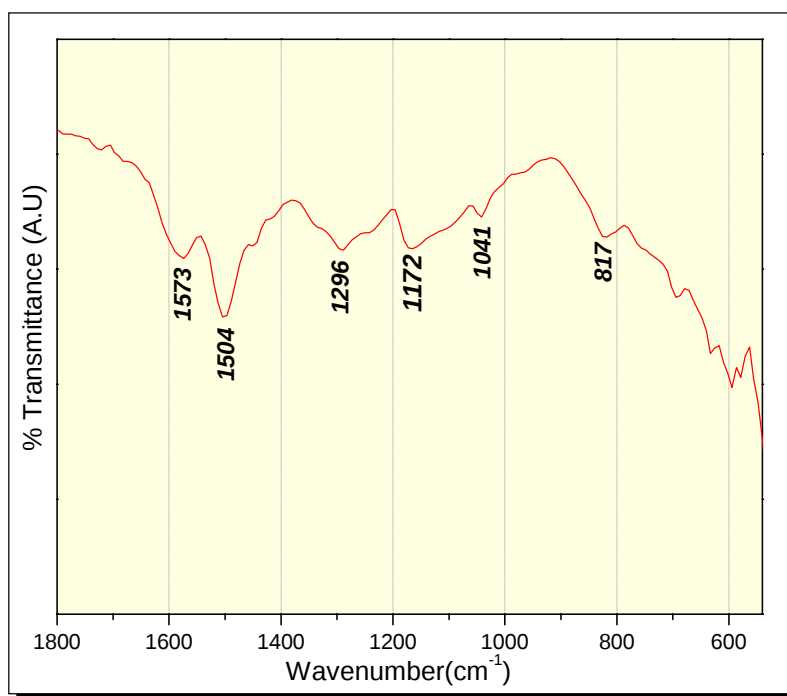


Figure 71. FT-IR spectrum of polymer PANi EB

Reference absorption bands (cm ⁻¹)	Vibrational assignments	Experimental absorption bands (cm ⁻¹)
1590	Benzenic-quinonic nitrogen	1573
1490	C-C aromatic	1504
1330	Aromatic amine	1296
1250	C-O aromatic	
1118	C-O-C ether	
1190	C-N-C	1172
1030	C-H in-plane	1041
920	Poly-conjugated system	
830	C-H out-of-plane	817

Table 8. FT-IR modes for Pani-type polymers [54]

4.4.1.3 The PANi-Ferrite nanocomposite: Preparation Method “B”

The FT-IR spectrum for the composite PANi EB-MnZn ferrite (32.6% ferrite), showed in Figure 72, show bands around 600 and 400 cm^{-1} that are attributed to the stretching vibration of tetrahedral and octahedral group complexes of ferrites, respectively. The IR absorption bands of solids in the 100 – 1000 cm^{-1} range are usually assigned to vibrations of ions in the crystal lattice. In ferrites the metal ions are situated in two different sub-lattices, designated tetrahedral and octahedral according to the geometrical configuration of the oxygen nearest neighbors [11]. All other bands correspond to vibration modes in the polymeric matrix. Observed results suggests the effective formation of the ferrite/polymer composite.

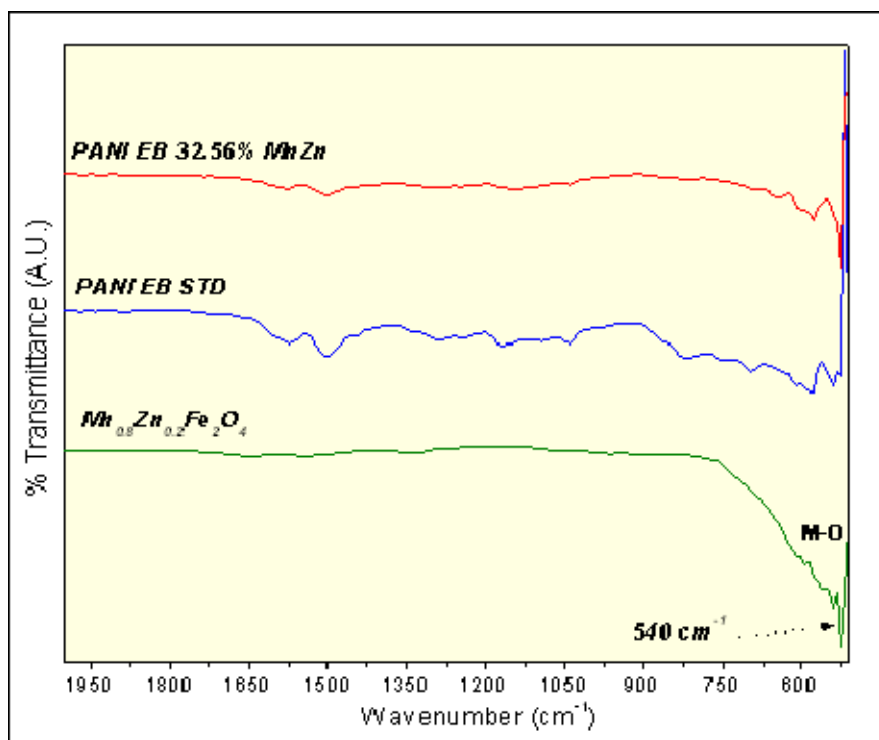


Figure 72. FT-IR spectra of MnZn ferrite, pure PANi EB and composite with a Ferrite/Pani mole percent of 32.56%.

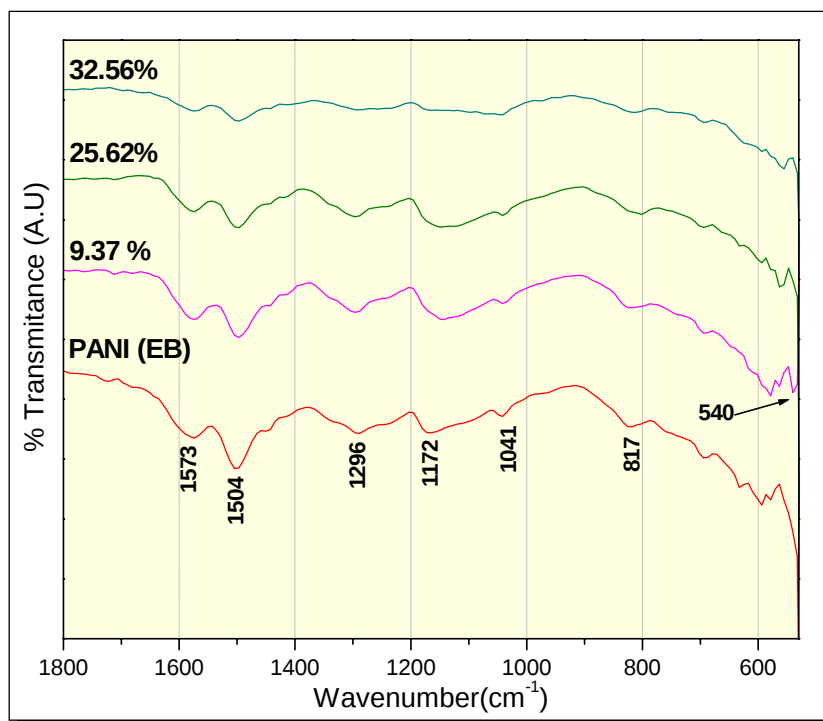


Figure 73. FT-IR spectrum of PANi EB-MnZn ferrite nanocomposites at different molar percent.

Figure 73 shows the FTIR spectra of bare PANi EB and PANi EB-MnZn ferrite nanocomposites at different molar Ferrite/ PANi EB mole percent. The incorporation of ferrites in the nanocomposites leads to a shift of some FTIR bands of the polymer in the composite when compared to bare PANi EB; a small band appears at 550 cm^{-1} , due to the vibrations of $\text{Mn}^{2+}\text{-O}_2^{2-}$ bond, evidences to the incorporation of Mn.

However, this band is very weak, a fact that was not expected for such a large amount of ferrite nanoparticles (well detected in the corresponding XRD patterns in the previous sections). It can be due to the coating of ferrite nanoparticles by the polymer, which avoid a suitable interaction of the ferrite particles with the incident radiation during IR measurements.

4.5 THERMO GRAVIMETRIC (TG) ANALYSES PANI-MNZN COMPOSITES

4.5.1 TGA Analyses

4.5.1.1 The MnZn ferrite

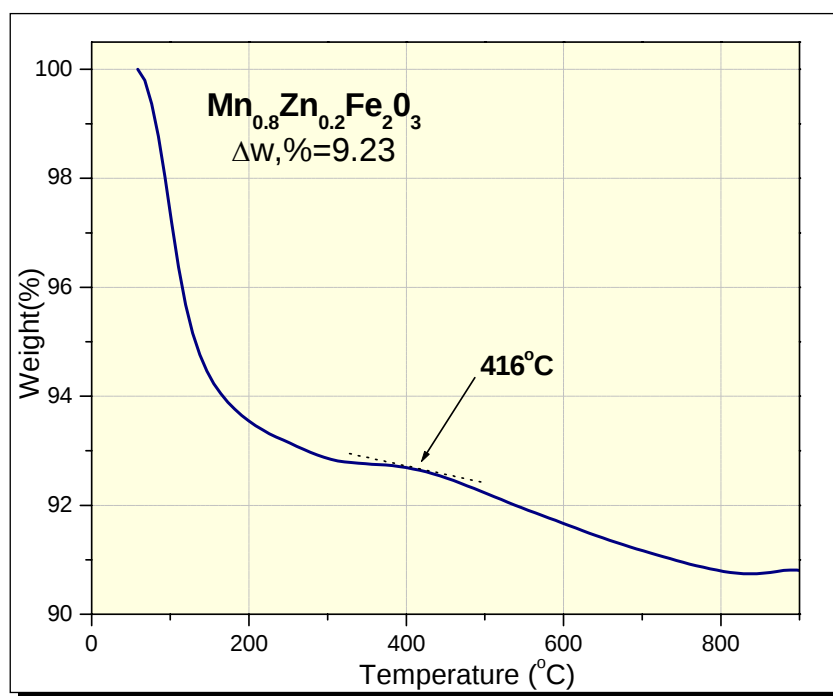


Figure 74. TG of MnZn ferrite nanoparticles ('x' = 0.8)

The thermo-gravimetric profile suggests a high thermal stability of the ferrite prepared at 'x' = 0.8. Only a weight loss ($\Delta W, \%$) of 9% was obtained (Figure 74). The first step could be due to the release of moisture and molecular water from the ferrite. The second decomposition step started at 416 °C and can be attributed to the decomposition of iron manganese ions in the ferrite.

4.5.1.2 The polyaniline (PAni)

Evidently, the PAni EB is quite unstable under high temperature conditions. Around 59% in weight was lost when the sample was heated from room-temperature up to 900 °C. The drastic weight loss is consequence of the thermal decomposition by pyrolysis of the polymer (Figure 75).

The decomposition temperatures obtained from thermograms of pure polyaniline exhibits two-stage weight-loss behavior. The first loss of weight appears at around 80 °C, mainly resulting from the evaporation of residual solvents, small molecules and water molecules. The second weight loss occurs at over 475 °C and is attributed primarily to the degradation of the polymer backbone [32].

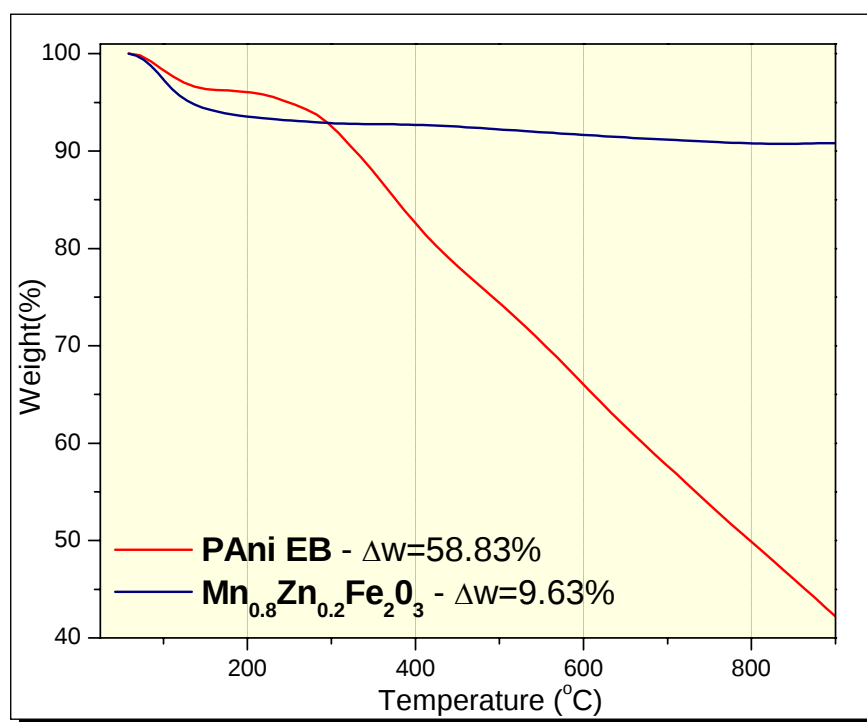


Figure 75. TGA profile of pure PAni EB. The TGA profile for the MnZn ferrite nanoparticles was included only for comparison.

4.5.1.3 The PAni-Ferrite nanocomposite: Preparation Method “B”

The thermogravimetric analysis was performed under a nitrogen atmosphere to minimize undesired oxidation reactions in the ferrite, and let PAni EB be thermally decomposed almost completely. TG analyses of pure PAni EB and PAni EB-MnZn nanocomposites prepared at different ferrite molar ratios are shown in Figure 76. As seen, the presence of ferrite nanoparticles increase the thermal stability of the nanocomposite. For instance, the weight loss in the pure PAni EB was 20% at 300 °C. This value was only 7% for the PAni EB bearing ferrite nanoparticles (32.6% mole percent). All weight loss results at 300 °C are presents in Table 9.

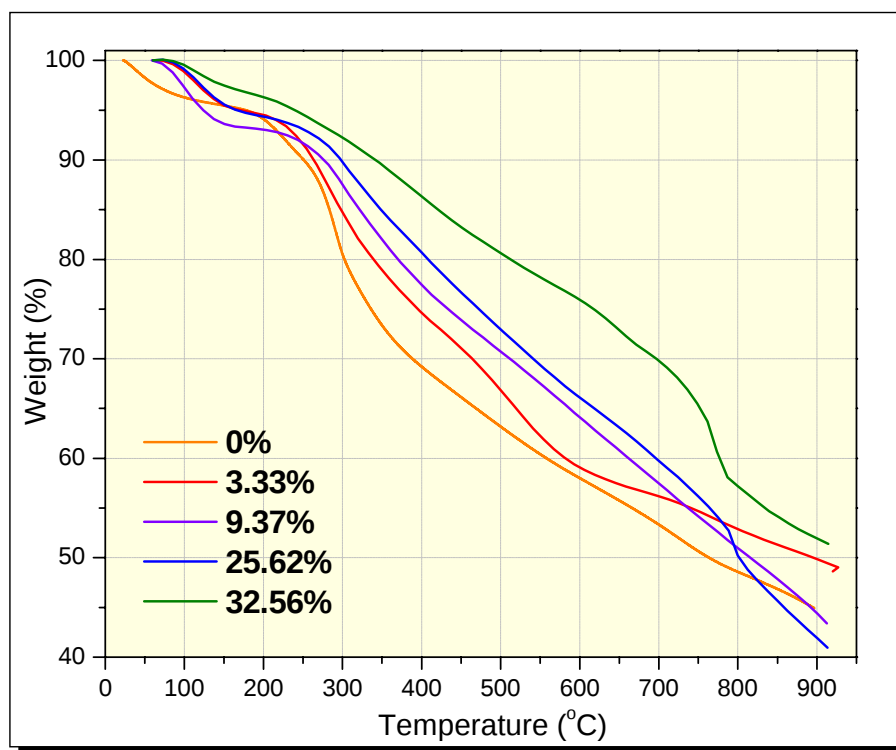


Figure 76. TG of PAni EB-MnZn nanocomposites at different ferrite molar percents.

The TGA profile of the PAni-MnZn ferrite composite (32.6% ferrite mole percent) showed decomposition with three step weight loss. The first step (50 - 100 °C) indicates the loss of

water from the polymer matrix and the ferrite; the second weight loss took place between 200 and 250 °C and may be attributed to loss of volatile elements bound to the PAni EB chain. In the third step (700 °C), the thermal breakdown of the ferrite structure (and some oxidation of Mn ions) should have taken place.

Composition (% ferrite molar percent)	ΔW (%)
0	14.30
3.33	11.90
9.37	9.78
25.62	7.50

Table 9. Weight loss (ΔW) of PAni EB-MnZn nanocomposites at different ferrite molar percent. Analysis at arbitrary temperature (T_x) = 300 °C.

These results indicated that there are possibly some interaction between MnZn particles and PAni EB backbone [31].

4.6 MEASUREMENTS OF ELECTRICAL PROPERTIES

The calculated conductivity values are shown in table10.

Molar %	Conductivity (S/cm)
0	1.92×10^{-3}
3.33	1.57×10^{-3}
12.11	1.67×10^{-3}
19.23	9.79×10^{-4}
19.5	9.79×10^{-4}

Table 10. Electrical conductivity of the nanocomposites as a function of the ferrite mole percent in PAni EB matrix.

The maximum conductivity of the PAni EB was 1.92×10^{-3} S/cm. As Figure 77 shows, the conductivity of nanocomposite decreases with the increase of the content of magnetic nanoparticles. It can be due to partial blockage of the conductive path by magnetic particles embedded in the composite [9] and decrease of doping degree in this nanocomposite prepared under non-acidic conditions [33]. The obtained conductivity values can still be considered typical of semiconductive material.

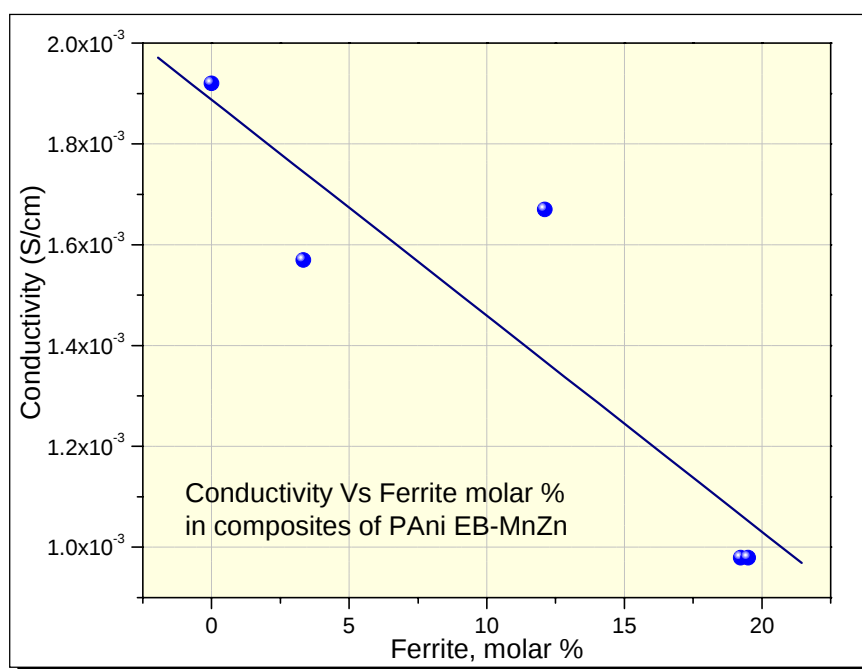


Figure 77. Effect of the content of the magnetic nanoparticles on room temperature conductivity of the PAni EB-ferrite nanoparticles composite. The line is presented as eyes guide only.

Electrical and magnetic properties of PAni-MnZn strongly depends on the HCl concentrations values. Magnetic response in the composites was observed when the HCl concentration was below 0.01N, in the case of synthesis of the composite in water and subsequent acid treatment. On the other hand, the PAni-ferrite composite prepared in presence of 0.01N HCl exhibited a conductivity at room temperature of about 6.85×10^{-4}

S/cm, which is much lower than the composite prepared using HCl 1N (7.78×10^{-3} S/cm). For this latter sample, no magnetic behavior was observed; as we proposed before, the extremely acid preparation condition should have chemically dissolved the ferrite nanoparticles. The conductivity for the pure PANi EB, synthesized by using HCl 0.1N from the very beginning of the polymerization process was increased up to 2.4×10^{-3} S/cm. The conductivity went down to 1.8×10^{-4} S/cm in presence of 21.6% mole of ferrite; however, in this case, the composite kept its magnetic response (Table 11). This value was comparable to the one obtained for the pure PANi-EB without ferrite.

Composition, (% ferrite molar percent)	Conductivity (S/cm)
0	2.4×10^{-3}
21.57	1.8×10^{-4}

Table 11. Conductivity comparison of pure PANi EB and composite sample of PANi EB-MnZn ferrite synthesized in HCl acid 0.1N.

5. CONCLUDING REMARKS

We have successfully synthesized $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles and prepared PANi/Mn-Zn nanocomposite. The magnetic phase was formed by single crystal nanocrystals, as suggested by XRD and HRTEM analyses.

The results obtained 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.

The synthesis of both the conductive (Emeraldine Salt, ES) and non-conductive (Emeraldine Base, EB) phase were achieved. Moreover, the reversibility of the $\text{EB} \rightleftharpoons \text{ES}$ transition was also verified.

A suitable dispersion of the magnetic phase within the polymer was attained by adjusting the parameters of synthesis. The functional properties of the PANi/Ferrite magnetic nanocomposite were tuned by suitable control of the proportion of ferrite nanocrystals in the polymer matrix. Varying the acid concentration in the solution made possible to control the loss ferrite in the nanocomposite and hence, optimize the conducting properties. As expected, the magnetization and electrical conductivity of the nanocomposite was dependent on the relative amount of the ferrite nanocrystals in the PANi matrix.

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