Synthesis and Magnetic Properties of Polymer Nanocomposites

by

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Magnetic nanoparticles embedded in polymer matrices have excellent potential for electromagnetic device applications like electromagnetic interference (EMI) suppression. Using chemical precipitation methods and Nanogen™, a microwave plasma method, we have synthesized various nanoparticles including iron, polystyrene-coated iron, iron oxide (both hematite and magnetite), nickel ferrite, and manganese zinc ferrite. We have synthesized polymer nanocomposites of polymethylmethacrylate (PMMA), polystyrene (PS), and polypyrrole (PPy) doped with varying concentrations of these nanoparticles. These nanocomposites were processed using melt blending and sonication techniques. The concentration of nanoparticles was varied in a controlled way. Although polymer processing conditions were optimized to achieve good uniform dispersion of the nanoparticles in the polymer matrix, surface characterization with SEM indicates areas of clustering of the nanoparticles. This agglomeration is attributed to the particle interactions mediated by steric forces in the polymer matrix. Static magnetic properties such as susceptibility and M-H loops were studied using a Physical Property Measurement System (PPMS). The variation of the magnetic responses were consistent with the varying volume concentration of the nanoparticles, the polymers themselves contributing diamagnetic responses. Overall, the reasonable dispersion and control over magnetic properties achieved in our experiments is promising for electromagnetic applications of these materials.
Chapter 1

Introduction, Background and Motivation

Polymer nanocomposites are potentially important due to the fact that they offer a number of significant advantages over traditional polymer composites. Conventional composites usually require a high content of the filler phase to achieve the desired properties of the composite material. Nanocomposites can achieve the same properties with a much smaller amount of the filler, producing materials of lower density and higher processibility. The nanoparticles have advantages over typical micron-sized particles because they can exhibit novel magnetic, optical, thermal, electrical and mechanical properties. Magnetic properties such as coercivity, magnetic saturation, and frequency dependent permeability demonstrated in nanoparticles are very different from those found in bulk materials. The polymers provide a processable matrix in which to disperse the particles. Some properties of nanocomposites such as optical transparency and improved barrier properties cannot be duplicated by conventionally filled resins at any loading. Polymer composites have shown promise in various disciplines, including the automobile industry, the medical field, and as various types of sensors.

In 2002, General Motors began using a polypropylene/clay nanocomposite to fabricate the step-assist for some of its vans. The part was previously made from conventional talc-reinforced material. Replacing it with the nanocomposite material
resulted in increased stiffness, improved ductility at cold temperatures and enhanced appearance. A weight savings of more than 10% was achieved for this particular part, but weight savings can reach 20% depending on the part and material being replaced by the polymer nanocomposite. This was the first commercial automotive exterior application for a polymer nanocomposite based on a plastic such as polypropylene, polyethylene, or polystyrene. Other automotive companies currently use polymer nanocomposites in fuel lines and fuel system components. It is expected that many other parts made up of conventional compounds will eventually be replaced with polymer nanocomposite materials.

Various metals, ceramics, and polymers are considered suitable for use in biomedical applications. However, many drawbacks of these materials make alternatives desirable. Disadvantages of metals include corrosion, high density, much higher stiffness compared to tissues, release of metal ions which may cause allergic reactions, and low biocompatibility. Problems with ceramics include brittleness, low fracture strength, lack of resilience, and low mechanical reliability. Polymers are too flexible and too weak to be used in certain applications, and their properties can be adversely affected by sterilization processes. They also may absorb liquids and swell, or leach undesirable products. Polymer composite materials provide advantages in biomedicine as they overcome many of the shortcomings of these homogeneous materials. While polymer composites are currently used in various medical procedures, many additional applications have been proposed. Some of these applications, both projected and currently in use, include: repair or replacement of bones, bone plates and screws,
cartilage, tendons, ligaments, muscles, finger joints, hips, knees, abdominal walls, vascular grafts, dental composites, and spine cages, plates, rods, screws, and discs.\textsuperscript{25,27, 32, 44}

Polymer nanocomposites have also been developed as candidates for different types of sensing applications. The conductive and absorptive properties of insulating polymers doped with conducting materials, and the absorptive properties of insulating polymers with non-conducting fillers are sensitive to exposure to gas vapors. Therefore, they can be used to monitor the existence and concentration of gases in the environment.\textsuperscript{17, 40} As electrically conductive polymer nanocomposites are subjected to tensile strain and pressure, the electrical resistance changes. This response results in nanocomposites having possible applications as pressure and stretch sensors for detection of deformations and vibrations of mechanical devices such as vehicle parts.\textsuperscript{4, 12}

Electromagnetic interference (EMI) suppression is another area in which polymer nanocomposites could make great advances. One of the NSF supported research projects in our lab is to synthesize polymer composites in which the magnetism and RF properties could be controllably varied. The work reported in this thesis largely contributes towards making and investigating such materials. All electronic devices generate and emit radio-frequency waves that can interfere with the operation of electronic components within the same device as well as other electronic devices. Miniaturization of electronic equipment requires components to be packed very close to each other, which increases the problem of electromagnetic interference. When an electromagnetic wave is incident upon a conductive surface, energy is reflected and absorbed. The ability of a material to shield electromagnetic energy, whether it be unwanted energy entering a system or escaping a
system, is called its shielding effectiveness (SE).\textsuperscript{21, 46} It is comprised of losses due to absorption, reflection, and re-reflection. EMI suppression over a wideband frequency range requires tunability of the impedance (Z), which depends on the tunability of the complex permeability (\(\mu\)) and complex dielectric constant (\(\varepsilon\)). (Note that the electrical conductivity (\(\sigma\)) is contained in the imaginary part of \(\varepsilon\).) The conductivity plays an important role in a material’s ability to shield electromagnetic energy. Conducting materials such as typical metals, along with capacitors and ferrites are commonly used in EMI suppression.\textsuperscript{7, 21, 46} The materials most commonly used in EMI suppression have disadvantages in terms of their weight, corrosion and physical rigidity that could be overcome with the development of new materials. Composite materials such as conducting and insulating polymers doped with magnetic nanoparticles may be lightweight, flexible alternatives to the bulk metal components currently used.

Another motivation for synthesizing polymer nanocomposites is that critical parameters such as loss tangents and impedance matching, which are important in microwave devices, may be controlled in these materials. The loss tangent is a measure of the inefficiency of a magnetic system.\textsuperscript{7} It is the ratio of the imaginary part of complex permeability to the real part of the permeability: \(\tan \delta = \mu''/\mu'\). In composites, one can also similarly define a dielectric loss tangent (\(\tan \delta = \varepsilon''/\varepsilon'\)) representing the dielectric losses. The loss tangents are primarily determined by magnetic and eddy current losses. Eddy currents depend on the resistivity of the material. The addition of nanoparticles in a conducting polymer increases its resistivity, thereby decreasing the eddy current losses. Magnetic losses are controlled by the material grain structure, domain wall resonances
etc. and these can be manipulated effectively in nanocomposite materials by the size
distribution of nanoparticles and their dispersion in the host matrix.\textsuperscript{7}

Impedance mismatch between source and load in circuits is the main source of
signal attenuation during transmission. By manipulating the properties of
nanocomposites to attain desired impedance values at specific frequencies, the
attenuation can be minimized. Since impedance is governed by the ratio of complex
permeability to the dielectric constant, this can be adjusted by the type and amount of
magnetic nanoparticles dispersed in the polymer.\textsuperscript{21, 26}

The integration of multiple device functions into a single multifunctional system
can be achieved by developing multi-layered structures with different magnetic
nanocomposite layers. Layered nanocomposites can be used for EMI suppression and
can also be tuned to exhibit low losses and better impedance matching properties. The
top layers would be designed to have high conductivity and large shielding effectiveness.
The bottom layers close to the device will be tuned towards achieving better impedance
matching.

We synthesized a series of nanocomposite materials comprised of magnetic
nanoparticles embedded in both insulating and conducting polymers, and then studied
their fundamental magnetic properties. The synthesis of nanoparticle systems was carried
out in collaboration with Materials Modification Inc. (MMI), and the synthesis of the
polymer matrices was done in collaboration with MMI and the USF Chemistry
department. Some of the synthesis and all of the magnetic characterization was done in
our lab in the USF Physics department. A Physical Property Measurement System
(PPMS) by Quantum Design was used to study the magnetic properties over varied
temperature (2 K to 350 K) and magnetic field (0 to 7 Tesla). Magnetic measurements such as temperature dependent magnetic susceptibility and hysteresis loops were done on the nanocomposite samples. A brief background on some basics of magnetism is provided below.

There are five classes of magnetic materials: diamagnetic, paramagnetic, ferromagnetic, ferrimagnetic, and antiferromagnetic. All materials are classified according to their electronic structure and how they respond to applied magnetic fields (H). Substances that are purely diamagnetic have no unpaired electrons in their outer shells, and therefore no net magnetic moments. They have a negative magnetic susceptibility ($\chi$), and exhibit a negative magnetization ($M$) in an applied field (see figure 1), where $M$ is the magnetic moment per unit volume and $\chi = M/H$. The Langevin function describes the diamagnetic susceptibility per unit volume: $\chi = -(\mu_0 N Z e^2 <r^2>)/6m$, where $Z$ is the number of electrons, $N$ is the number of atoms per unit volume, and $<r^2>$ is the mean square distance of the electrons from the nucleus. While the susceptibility is temperature dependent in other types of magnetism, it is temperature independent in diamagnetic materials (see figure 1).

While all materials are diamagnetic, some exhibit other types of stronger magnetism. Paramagnetism occurs when atoms have unpaired electrons in their outer electron shells, leaving them with net magnetic moments ($\mu$). Atoms with a permanent magnetic moment have a paramagnetic susceptibility $\chi = N\mu^2/3k_B T$, for $\mu B < k_B T$, and the susceptibility is small, positive, and temperature dependent. Above the Curie temperature of a given paramagnetic material, paramagnetism is no longer observed. The magnetic moments are oriented in random directions when there is no applied field, but...
some of them line up in the direction of the field when a magnetic field is introduced.
The magnetic moments don’t interact with each other, and return to random orientations when the field is removed. Figure 2 shows the characteristic magnetic curves of paramagnets.

![Diagram of diamagnetic materials](image1)

**Figure 1.** Plots of magnetization vs. applied field and magnetic susceptibility vs. temperature for diamagnetic materials.

![Diagram of paramagnetic materials](image2)

**Figure 2.** Magnetization and susceptibility plots for paramagnetic materials.
In some ways, ferromagnetism is similar to paramagnetism. The magnetic moments of ferromagnetic materials align parallel to each other in an applied field. Unlike paramagnetic materials, however, nearly all of the electron spins align in the direction of the applied field (see figure 3). This parallel magnetic ordering, due to the very strong electronic interactions between the magnetic moments, is present even when there is no magnetic field. This net magnetization that is present in the absence of a field is referred to as the spontaneous magnetization. There is a maximum magnetization, the saturation magnetization, which can be reached when a ferromagnet is placed in a magnetic field. Increasing the applied field does not increase the magnetization once the saturation point has been reached. The field at which typical ferromagnets saturate is on the order of 1 Tesla, while it is greater than 10 Tesla for paramagnets. Hysteresis is another property of ferromagnets that differentiates them from paramagnets. Hysteresis loops (figure 4), which are plots of magnetization vs. magnetic field, show how a ferromagnetic material “remembers” an applied field after it is removed. This remnant magnetization, along with the saturation magnetization and the coercive field (the field at which the magnetization goes to zero) can be seen in a hysteresis loop. The aligned moments in a ferromagnet become disordered in the paramagnetic phase above the Curie temperature \( T_C \). While both paramagnetic and ferromagnetic materials have positive susceptibilities, those of ferromagnets are orders of magnitude higher than those of paramagnets. The Curie-Weiss law \( \chi = C/ (T-T_C) \) describes the susceptibility of a ferromagnetic material in the paramagnetic region above the Curie point. Figure 5 shows the magnetic susceptibility of ferromagnetic materials.\(^{11}\)
Figure 3. A simplistic view of magnetic domains and magnetization of ferromagnets in an external field.

Figure 4. Hysteresis loop.

Figure 5. Magnetic susceptibility of ferromagnets.
Ferromagnetic materials are composed of regions called magnetic domains.\textsuperscript{11, 23} The sizes of these regions in bulk materials range from approximately 1-100 µm. In zero field, the domains arrange themselves in such a way that the average magnetization cancels out over the bulk of the material. Properties of ferromagnetic materials change as the particle size decreases. Grain size is categorized, from largest to smallest, as either multidomain (MD), pseudo-single domain (PSD), single domain (SD), or superparamagnetic (SPM). Large grains are MD, and have domain walls that separate regions having different magnetization directions. A point is reached as the grain size decreases (typically a few nm) where the grain cannot sustain a domain wall and contains only a single domain whose magnetization is saturated. While MD grains are magnetically soft with low coercivities and remanence, SD grains are magnetically hard and have high coercivities and remanence. The particle size separating the transition from MD behavior to SD behavior in a given material depends on numerous factors, including the saturation magnetization and the shape of the grain. Small MD grains can exhibit a mixture of MD and SD behavior, and are therefore called PSD grains. Superparamagnetism occurs as the particle size is decreased below a critical point within the SD region. SPM grains have no remanence or coercivity. Unlike larger SD and MD particles, there is no net magnetic moment in the absence of a magnetic field. There is a net alignment of magnetic moments when a field is applied, as there is in paramagnetism, but the susceptibility value is much higher for SPM particles. Figure 6 shows the variation in coercivity with particle size.\textsuperscript{23} The maximum coercivity occurs within the SD range. Figure 7 shows the variation in remanence vs. temperature for SD and MD magnetite.\textsuperscript{23}
Figure 6. Plot of variation in coercivity with particle size.\cite{23}

Figure 7. Plot of variation in remanence vs. temperature in SD and MD magnetite.\cite{23}
In antiferromagnetic materials, the spins are coupled with antiparallel orientation.\textsuperscript{11,23} The material’s net magnetic moment is zero, or nearly zero. Above a critical temperature, the Néel temperature ($T_N$), the susceptibility of a ferromagnetic material behaves like a paramagnet $\chi = 2C/(T + \theta)$. There are two situations below $T_N$: with the applied field perpendicular to the axis of the spins $\chi_\perp = 1/\mu$; and with the field parallel to the axis of the spins $\chi_\parallel (0) = 0$. The susceptibility is shown in figure 8. Some antiferromagnetic materials such as hematite ($\alpha$-Fe$_2$O$_3$) have canted spins above a certain temperature, resulting in a weak spontaneous magnetization. Below this temperature, the spins undergo what is called the Morin transition and become parallel (perfectly antiferromagnetic).\textsuperscript{11}

![Figure 8. Plot of magnetic susceptibility vs. T in antiferromagnetic materials.](image)

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Ferrimagnets behave very much like ferromagnets, but their magnetic ordering is like that of antiferromagnets.\textsuperscript{11,23} Like ferromagnets, they exhibit spontaneous magnetization, Curie temperatures, hysteresis, and remanence. Like antiferromagnets, their spins are aligned parallel to each other and in opposite directions, but don’t cancel each other out completely. This leads to a net moment as in the case of ferromagnetic ordering. The resulting magnetization and susceptibility are positive, but much weaker than those of ferromagnetic materials.\textsuperscript{11}
Chapter 2

Synthesis of magnetic nanoparticles

2.1 Introduction

In order to gain experience in the process of particle synthesis, most of the magnetic powders (with average individual particle size ~ 20 to 50 nm) used in the polymer composites were synthesized during an internship at Materials Modification Inc. (a small company located in Fairfax, VA that commercially produces nanopowders). The author benefited from collaborations with researchers at MMI during the nanoparticle synthesis phase of this project. These powders include iron, polystyrene-coated iron, nickel ferrite (NiFe$_2$O$_4$), iron oxide ($\alpha$-Fe$_2$O$_3$ hematite), and iron oxide (Fe$_3$O$_4$ magnetite). The only nanoparticle system used in the composites that was obtained from a different collaborator was manganese zinc ferrite (MZFO), from NRL, which had been synthesized using a standard chemical method based on reverse-micelles. In the following sections, details of different synthetic procedures we followed (physical and chemical) for producing nanoparticles, are provided.

2.2 Synthesis of Iron Nanopowders by Microwave Plasma Method$^{36}$

Iron nanopowders were synthesized by a microwave plasma system, Nanogen.$^\text{TM}$ Its operating parameters are given in Table 1. This method was chosen due to the large quantities of powders that can be produced in comparison to other techniques used for
nanopowder synthesis. Generally, there is a tradeoff between chemical and physical methods. While chemical routes often produce high quality, monodisperse particles, physical methods have the advantage of mass production at the expense of yielding a larger size distribution. Iron pentacarbonyl, (99.5% pure, m.p. -20°C, b.p. 103°C) was the precursor used for iron synthesis. After being injected into the system and heated to approximately 100°C, the vapors from the precursor were carried by argon gas into the plasma region. The plasma was generated by high energy microwaves (see Table 1), which instigated dissociation, ionization, and recombination of the argon gas. A sufficient amount of heat was produced (temperatures reached 1000-2000°C) in this process to decompose the precursor. The following reaction describes the decomposition of the precursor into iron powders:

\[
\text{Fe(CO)}_5 \rightarrow \text{Fe} (s) + 5\text{CO}^\uparrow (g).
\]

The resulting powders were collected in filter bags after passing through a water-cooled reaction column. Figure 9 shows a schematic diagram of this set-up. TEM micrographs of the iron nanopowders in Figure 10 show an average particle size of 10-15 nm, though agglomerations of these particles could have a mean size as large as 100 nm or more. XRD data, shown in figure 11, confirms the iron phase of the powder.
Figure 9. Diagram of Nanogen™ system.

<table>
<thead>
<tr>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetron Power</td>
<td>0-6 KW</td>
</tr>
<tr>
<td>Magnetron Frequency</td>
<td>2450 MHz, CW</td>
</tr>
<tr>
<td>Waveguide</td>
<td>Rectangular</td>
</tr>
<tr>
<td>Plasmatron</td>
<td>‘50mm’ dia. quartz wall, water cooled brass chamber</td>
</tr>
<tr>
<td>Plasma Gas</td>
<td>Argon, Feed rate 2-4 m³/hour</td>
</tr>
<tr>
<td>Carrier Gas</td>
<td>Argon, Feed rate 0.2-0.35 m³/hour</td>
</tr>
</tbody>
</table>

Table 1. Nanogen™ process parameters.\textsuperscript{10}
Figure 10. TEM of iron nanopowders show an average particle size of 10-15 nm.

Figure 11. XRD data for iron synthesized in the Nanogen.
2.3 Synthesis of Polymer-coated Iron Nanoparticles

Polymer-coated iron nanoparticles were synthesized by the same microwave plasma method used to produce the iron powders.\textsuperscript{10,36} The only difference in this procedure was that styrene monomer was also injected into the plasma zone from a different port (shown in Fig.9) simultaneously with the pentacarbonyl. The intense heat of the plasma causes the styrene monomer to break down, and the resulting free radicals polymerize on the surface of the iron particles in the reaction column. In addition to minimizing agglomeration and controlling particle size growth, encapsulation of the particles by a polymer also prevents oxidation. In a previous work, Srikanth et al. have also shown that the polymer coating also influences the magnetic interactions between particles and thus the overall magnetization itself.\textsuperscript{36} It can be seen in the TEM micrograph in Figure 12 that the average particle size of the polymer-coated powders is approximately 15-20 nm. Agglomeration of particles in polymer-coated nanoparticles is an issue that is not fully understood yet. As we will show later on, using other synthetic routes for producing polymer nanocomposites, we have observed that particles tend to aggregate in clumps presumably governed by steric forces present in the polymer.
2.4 Synthesis of Nickel Ferrite

Sodium hydroxide was utilized to chemically precipitate nickel ferrite (NiFe$_2$O$_4$) from a mixture of nickel nitrate and iron nitrate. Nickel nitrate hexahydrate and iron (III) nitrate nonahydrate were first calcined separately at 500°C for 5h, which resulted in NiO and α-Fe$_2$O$_3$ hematite. Based on the weight loss, calculations were made to determine how much nickel resulted from each gram of nickel nitrate and how much iron resulted from the iron nitrate, to ensure that the proper ratios necessary for producing nickel ferrite were used. Once the needed amounts were determined, the nickel nitrate and iron nitrate were added to 3L distilled water and stirred constantly with a high-speed emulsifier until dissolved. In a separate beaker, sodium hydroxide was added to distilled water until a pH greater than or equal to 11 or 12 was reached. This mixture was then added drop-wise to the nitrate solution, precipitating solid particles from the liquid.
solution. The solution (precipitate included) was centrifuged and the liquid was discarded. The precipitate was rinsed with distilled water and centrifuged again. The liquid was poured out, and the precipitate was then dried at 125°C while being stirred occasionally. After drying, the resulting powder was ground with a mortar and pestle before calcining at 500°C for 5 hours. XRD results (figure 13) confirmed that the nickel ferrite phase had been successfully synthesized.

Figure 13. XRD data for chemically precipitated nickel ferrite powder.
2.5 Synthesis of Iron Oxide

Iron oxide exists in three different forms, namely hematite, maghemite, and magnetite.\textsuperscript{23} Hematite is the anhydrous iron oxide $\alpha$-Fe$_2$O$_3$ and has a corundum structure. It can exhibit various colors, including black, gray to silver gray, brown to reddish brown, or red. This form of iron oxide has canted antiferromagnetic order. Maghemite $\gamma$-Fe$_2$O$_3$ has the same stoichiometry as hematite, but has very different properties. It is also an anhydrous iron oxide, but it has a distorted spinel structure and is ferromagnetic. Maghemite forms when iron minerals rust. It can also be formed by low-temperature oxidation of magnetite, but inverts to hematite on heating above 250°C. Magnetite is another anhydrous iron oxide Fe$_3$O$_4$ which has an inverse spinel structure. It is black and is also ferrimagnetic. We tried to synthesize each of the three forms of iron oxide, but succeeded only in producing hematite and magnetite with good phase purity.

2.5.1 Synthesis of Iron Oxide ($\alpha$-Fe$_2$O$_3$ Hematite) by Chemical Precipitation Using Ammonium Hydroxide

80g of nanocrystalline iron oxide was prepared by dissolving 400g iron nitrate nonahydrate in 4L of distilled water, and the solution was mixed for an hour using a high-speed emulsifier. Approximately 700mL of ammonium hydroxide was added drop-wise to the solution to raise its pH above 10. At a pH of 8 the iron nitride precipitated. The precipitate was centrifuged and the supernatant discarded. The precipitate was then rinsed several times with distilled water, to eliminate excess NH$_4$OH. It was then dried at 125°C for approximately 8 hours while being stirred occasionally. After the drying, it was ground into a powder with a mortar and pestle before calcining at 500°C for 5 hours.
The XRD information (figure 14) on the powder resulting from chemical precipitation showed that it was single-phase hematite (α-Fe$_2$O$_3$).

![XRD data for chemically precipitated hematite (using ammonium hydroxide)](image)

Figure 14. XRD data for chemically precipitated hematite (using ammonium hydroxide)

### 2.5.2 Synthesis of Iron Oxide (Fe$_2$O$_3$) by Chemical Precipitation Using Sodium Hydroxide

In order to attempt to synthesize another phase of iron oxide, sodium hydroxide was used to chemically precipitate it rather than ammonium hydroxide, which had been used in the previous batch. The chemically precipitated Fe$_2$O$_3$ (NaOH) batch was synthesized, ground, and calcined by following the exact same procedure used to
produce the NH$_4$OH batch. The XRD results (figure 15) showed that the resulting powder was $\alpha$-$\text{Fe}_2\text{O}_3$ (hematite) plus a small amount of an unknown contaminant, so this powder was discarded. Because pure maghemite phase ($\gamma$-$\text{Fe}_2\text{O}_3$) had not been successfully established, further attempts to prepare an uncontaminated batch using this procedure was not pursued.

![XRD data for chemically precipitated hematite (using sodium hydroxide).](image)

**Figure 15.** XRD data for chemically precipitated hematite (using sodium hydroxide).

### 2.5.3 Synthesis of Iron Oxide ($\text{Fe}_2\text{O}_3$) by Nanogen$^\text{TM}$

The Nanogen$^\text{TM}$ was used to produce iron oxide from iron pentacarbonyl in the same way that iron had been produced. Small amounts of compressed oxygen was
added to the plasma in order to form iron oxide nanocrystals. The collected powder had 2-3 phases of iron oxide as seen on the XRD results (figure 16), including Fe₃O₄ (magnetite) and α-Fe₂O₃ (hematite). This powder was then calcined in air at 500°C for 5 hours. The melting point of iron oxide is approximately 1500°C, and since sintering usually takes place at two-thirds of the melting point temperature, this temperature should not have caused any sintering to take place. The XRD (figure 17) showed that the calcined powder had been reduced from 2-3 phases to single-phase hematite.

Figure 16. XRD data for iron oxide produced in the Nanogen.
2.5.4 Synthesis of Iron Oxide (Fe$_3$O$_4$ Magnetite) by Chemical Precipitation Using Ammonium Hydroxide

135.150g of FeCl$_3$ and 49.703g of FeCl$_2$ were added to 3L distilled water in a large beaker and mixed for 30 minutes until all of the particles were dissolved. Ammonium hydroxide was added drop-wise to the solution as it was continuously stirred until the pH was raised above 10. An additional 100mL of ammonium hydroxide was added. The mixture was stirred for another two hours. The solution was centrifuged until all of the liquid had been separated from the precipitate and discarded (approximately 4 times at 4000 rpm for 10 min.), rinsed with distilled water, and centrifuged again. The precipitate was heated in a beaker with a small amount of distilled

Figure 17. XRD for iron oxide produced in the Nanogen, after calcinations.
water at 75°C until dry, stirring occasionally. The dry precipitate was ground into a
powder with a mortar and pestle, and the powder was placed in an evacuated chamber (~
30 torr) for a few hours to remove as much of the hydroxide as possible. XRD results
(figure 18) indicated that magnetite (Fe$_3$O$_4$) had been synthesized.

![Figure 18. XRD for chemically precipitated magnetite powder.](image)

### 2.6 Synthesis of Manganese Zinc Ferrite Nanoparticles

Monodisperse MZFO nanoparticles were synthesized using reverse micelle
technique. Bis-(2-ethylhexl) sodium sulfosuccinate (AOT) was used as the surfactant and
2, 2, 4-trimethylpentane isoocotane was used as oil phase. These particles have an average
size of 15nm, as seen using TEM. ICP analysis determined the stoichiometry of these
particles to be $\text{Mn}_{0.68}\text{Zn}_{0.25}\text{Fe}_{2.07}\text{O}_3$. Because I did not participate in the synthesis of these particles, I will leave the synthesis details to be described elsewhere.\textsuperscript{22} The powder X-ray diffraction confirmed the single phase and crystallinity of the material.

To summarize, in this chapter I have provided details of several synthetic procedures used to produce Fe, iron oxide, and soft ferrite ($\text{NiFe}_2\text{O}_4$ and MZFO) nanoparticles. In the next chapter, I will describe our efforts to make polymers and also different methods that we explored to mix the magnetic nanoparticles into polymers to form composites.
Chapter 3

Synthesis, Structural Characterization, and Processing of Polymer Nanocomposites

3.1 Introduction

Magnetic nanoparticles embedded in polymer matrices have excellent potential for electromagnetic device applications like electromagnetic interference (EMI) noise reduction. While individual nanoparticles are known to possess novel physical properties, devices invariably require many nanoparticles that are held together in a matrix. Polymers offer a number of advantages as host matrix materials. Some desirable aspects are: ease of processing, flexibility, light weight, corrosion-free, etc. Moreover, the dielectric and conducting properties can be used for potential multifunctional applications. The bulk of the research reported in this thesis is concentrated on the synthesis and characterization of various polymer nanocomposites with embedded magnetic nanoparticles.

Various magnetic particles have been dispersed in polymers in bulk form as well as spin-coated thin films. The processing conditions were optimized to achieve good uniform dispersion of the nanoparticles in the polymer matrix. Polystyrene (CH₂CHC₆H₅), poly(methyl methacrylate) (CH₂CCH₃COOCH₃), and polypyrrole (C₄H₃N) were the polymers chosen as the host matrices. Iron-polystyrene (PS) composites were made by two methods, including a melt blending technique and a novel
in-situ ultrasonic polymerization technique. The melt blending technique is widely used in industry for making uniformly mixed composites. However, uniformity is difficult to achieve on the nanoscale. The in-situ method was also done in an attempt to make a more homogeneous dispersion of nanoparticles in the polymeric matrix. Iron-poly(methyl methacrylate) (PMMA) composites were made using the same techniques. PS and PMMA were chosen for their insulating properties and ease of manufacture. Various particles were combined with polypyrrole (PPy), using a common ultrasonic cleaning bath to mix them and a spin-coater (see Figure 19) to form thin film conducting polymer composites. PPy was chosen for it’s electrically conductive properties. The synthesis of nanocomposites involved two main stages: a) polymer synthesis and processing, and b) mixing of nanoparticles with varying concentrations.

![Image](image.jpg)

Figure 19. Spin coater used to coat glass substrates with polypyrrole films.
3.2 Polymerization

The process of polymerization involves small molecules called monomers connecting to other monomers to form large molecules called polymers. There are two common methods of polymerization: condensation polymerization, and chain polymerization. In condensation reactions, two monomers react to form a covalent bond, usually with the elimination of a small molecule such as water, HCl, methanol, or CO₂. The reactions continue until one type of reactant is used up. Chain polymerization consists of three stages: initiation, propagation, and termination. Two reactions occur in the initiation step. A free radical forms in the first step, and reacts with the monomer (such as styrene) molecule in the second. The free radical ruptures the double bond between the two carbons in the monomer, leaving one unpaired electron in each carbon atom. This monomer becomes reactive and propagation occurs when this monomer bonds with other monomers in the same way, always leaving an unpaired electron at the end of the chain. Termination stops the growth of the polymer chain. Recombination is one mode of termination occurring when two polymeric radicals join and form a single polymer. Termination can also occur when a hydrogen atom from one radical transfers to a second molecule, resulting in two polymer chains. This is called disproportionation.

3.2.1 Mechanism of Free Radical Polymerization in Polystyrene

The styrene monomer (99%) was purchased from Sigma-Aldrich (Milwaukee, WI). The styrene contained 10-15 ppm 4 tert-butylcatechol, which prevented it from premature partial polymerization, by reacting with the radicals to yield inactive products that do not participate in further polymerization. This 4 tert-butylcatechol inhibitor was
removed from the styrene monomer using a tert-butylcatechol inhibitor-remover packing column available from Sigma-Aldrich (Milwaukee, WI). Benzoyl peroxide (BPO) (97%) obtained from Sigma-Aldrich was the free radical initiator employed for the polymerization. BPO is thermally unstable and undergoes thermal homolysis to form benzoyloxy radicals. The mechanism for polymerization is shown below.

1) Free Radical Formation From Initiator

![BPO to Benzoyloxy Radical]

2) Addition Of Free Radical To Styrene Monomer

![Benzoyloxy Radical + Styrene Monomer to Polymer]

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3.2.2 Mechanism of Free Radical Polymerization in Poly(methyl Methacrylate)

The methyl methacrylate monomer (99%) was purchased from Sigma-Aldrich (Milwaukee, WI). The monomer was inhibited with 10-100 ppm hydroquinone monomethyl ether (MEHQ). In small concentrations, inhibitors prevent unwanted polymerization. The inhibitor reacts with the radicals to yield inactive products that do not participate in further polymerization. This inhibitor was removed from the methyl methacrylate monomer using a hydroquinone monomethyl ether inhibitor-remover packing column available from Sigma-Aldrich. The free radical initiator employed for the polymerization of the methyl methacrylate was Vazo 52 [2,2′-azobis(2,4-dimethylpentane nitrile)] obtained from Dupont. It is a low temperature polymerization process.
initiator that decomposes to form a cyanoalkyl radical. The mechanism for polymerization is shown below.

1) Free Radical Formation From Initiator

![Free Radical Formation From Initiator]

2) Addition Of Free Radical To Methyl Methacrylate Monomer

![Addition Of Free Radical To Methyl Methacrylate Monomer]

3) Propagation Of Polymer Chain

![Propagation Of Polymer Chain]
4) Termination of Chain via Disproportionation

\[ \begin{align*}
&\text{CH}_2-C-Y + \text{CH}_2-CH-Y \\
&\rightarrow \text{CH}=\text{CH}-Y + \text{CH}_2-CH-Y
\end{align*} \]

3.2.3 Mechanism of Polymerization in Polypyrrole

The pyrrole monomer (98%) was purchased from Sigma-Aldrich (St. Louis, MO). A cationic photoinitiator CYRACURE UVI-6992, a triaryl sulphonium salt, was obtained from the Dow Chemical Company (New Milford, CT). Cationic-initiated photopolymerizations have the advantage of being insensitive to atmospheric oxygen.\(^{24}\) Cationic polymerization occurs by repetition of the mechanism shown below.\(^{30}\) The photoinitiator and the silver nitrate both contribute to the oxidation and proton elimination steps.

1) an oxidation to form a cation radical

![Cation Radical Oxidation](image)

2) the coupling of two cation radicals to form a dication

![Cation Radical Coupling](image)
3) the elimination of two protons to form an aromatic structure

3.3 Methods of Dispersing Particles in Polymeric Matrix

3.3.1 Brabender (Melt Blending) Technique

Melt blending is a technique that disperses an additive into a polymer matrix. In this method the styrene is polymerized before any particles are added. The polymer has to be in the molten state during mixing, and high shear forces are necessary to bring about the mixing.\(^9\) The C.W. Brabender Plasticorder® with a banbury mixer attachment utilized in this melt blending process is a standard industrial piece of equipment used for uniform mixing, shown in figure 20.

Creating a uniformly dispersed composite is dependent upon obtaining the suitable viscosity of the molten polymer. The relationship between shear stress and shear rate in the flow of polymer melts is not one that is constant as in ideal Newtonian liquids, but instead behaves as a pseudoplastic.\(^9,6,18,39\) Consequently, the shear rate results in changes of the apparent viscosity. Figures 21 and 22 show these relationships for pseudoplastic fluids, also called shear-thinning fluids. Newtonian behavior is often exhibited at extreme shear rates, both high and low.\(^6,18,39\) In these regions, the apparent viscosity is nearly constant, as seen in the log-log plot of apparent viscosity vs. shear rate in figure 23.
Fig. 20. Banbury mixer. 9

Figure 21. Shear stress vs. shear rate for pseudoplastic fluids. 39
Figure 22. Apparent viscosity vs. shear rate for pseudoplastic fluids.\textsuperscript{39}

Figure 23. Log-log plot of apparent viscosity vs. shear rate in pseudoplastic fluids.\textsuperscript{39}
Entanglements of the polymer chains result in resistance to flow at low shear rates. At higher shear rates, the molecules are more aligned, there is less chain entanglement, and therefore the viscosity decreases. Agglomerates of particles can be broken down by the fluid mechanical stress in the mixer. Achieving good dispersion requires less energy as the viscosity is increased. Industrial use of the Brabender for purposes of dispersion of additives is widespread, though research has shown that application to the fabrication of nanocomposites does have some problems. Limited shear forces are ineffective in breaking up agglomerations of nano-size particles in polymer melts characterized by a high viscosity during melt mixing. Regions of agglomerations of nanoparticles will maintain their fragile structures in the polymer matrix and may provide little, or no, reinforcing and toughening effects. Another problem occurs with increased concentration of particles. As the concentration of nanoparticles is increased, the tensile yield strength decreases, which may be due to the increased probability of breaking and splitting of the agglomerated regions of nanoparticles in the matrix. These problems, characteristic of particles on the nanoscale, can be reduced with surface treatments, but not completely eliminated.

3.3.2 Novel In-situ Ultrasonic Dispersion Technique

The propagation of ultrasound waves uniformly distributes particles in a solution and induces polymerization through acoustic cavitation: the formation, growth, and implosive collapse of bubbles in the liquid. This process produces intense local heating, high pressures, and very high cooling rates. Although metal-polymer nanocomposites have previously been made using ultrasound radiation, solvents have
been used in the process. An in-situ technique of synthesizing polymer nanocomposites via sonication, without the use of a solvent, has been developed by Prof. Julie Harmon and her group in the USF Chemistry department. Particles are added to liquid monomer in a glass vial, which is attached to a sonicator probe. The solution is subjected to ultrasound waves until it becomes viscous, indicating that polymerization has begun. The viscous matrix prevents the now-dispersed particles from settling to the bottom of the vial. Pictured in figure 24 is the setup of the Branson Sonifier 450, operating at 20 kHz.

Figure 24. Branson Sonifier 450, glass vial, and oil bath.
3.3.3 Ultrasonic Cleaning Bath

A common ultrasonic cleaning bath (Branson B200 with an output frequency of 40 kHz) was also used to disperse particles in liquid solutions. Particles were added to the monomer in a glass vial which was then sealed. The vials were placed in the cleaning bath, and ultrasound waves dispersed the particles by the same mechanism of cavitation as discussed in the previous section. The lesser exposure time in this method prevented undesired polymerization.

3.4 Polystyrene Composites

3.4.1 Properties of Polystyrene

Polystyrene is a thermoplastic polymer. It is one of the few polymers that can be prepared by radical, ionic, and stereospecific polymerization.\textsuperscript{43} In industry, free radical polymerization is the most widely used method. The chemical arrangement of polystyrene prepared by free radical polymerization is atactic, meaning that the side groups are arranged randomly along the backbone of the polymer. This results in an amorphous structure. The $T_g$, or glass transition temperature, for polystyrene is 100°C.\textsuperscript{3} The glass transition temperature is the temperature above which individual segments of the macromolecular chain can regroup.\textsuperscript{43} Below $T_g$, amorphous polystyrene is brittle, rigid, and hard. Above $T_g$, polystyrene behaves like rubber or viscous liquid. It is a very electrically insulating material, having a volume resistivity greater than $10^{14}$ Ω.
3.4.2 Fabrication of Fe-PS Nanocomposites Via the Brabender (Melt Blending) Technique

Bulk polystyrene was synthesized in the following manner: 200g of styrene monomer was de-inhibited using the inhibitor remover column available from Sigma-Aldrich. The initiator, 0.2% BPO (by weight), was added to the monomer and degassed with nitrogen. The styrene/initiator solution was poured into multiple glass vials, with each vial containing no more than 10ml of the mixture. Nitrogen gas was bubbled through the solution for a period of one minute, and then the vials were capped immediately following the degassing. The vials were placed in a conventional oven and heated at a temperature of 125°C for four days. The polystyrene was removed from the glass vials and dissolved in toluene in a 10% solution under constant stirring. Methanol was added drop-wise to the dissolved solution to precipitate the polystyrene. The precipitate was removed from solution and oven dried under vacuum for three days at 130°C. Dissolving the polystyrene in a solvent and precipitating it is a standard practice that removes any unpolymerized monomer and small-chain polymers. The accepted glass transition temperature of polystyrene is 100°C, though it is cited by different references as ranging from 80°C-100°C. This range in values can be attributed to the fact that the T_g is dependent upon the rate at which the temperature is changed during the measurement. Lower cooling rates result in lower values of the T_g. A differential scanning calorimeter (TA Instruments DSC2920) and its corresponding software (TA Instruments Advantage version 2.5.0, 2002) were used to evaluate the glass transition temperatures of our samples. The synthesized PS was found to have a T_g of 98°C, as seen in the DSC results in figure 25. By testing the T_g of the polystyrene and
comparing it to the standard values, it was further ensured that all of the monomer had been either polymerized or removed during the process of dissolving and precipitation. The presence of any unpolymerized monomer would have decreased the $T_g$.

Figure 25. DSC results for the glass transition temperature for neat PS prepared by Brabender.

The melt blended iron/ polystyrene nanocomposites were fabricated using the C.W. Brabender Plasticorder® with a banbury mixer attachment. The Brabender was set to equilibrate at a temperature of 140°C. Once equilibrated, 18g of the neat polystyrene was [added], together with 10% (by weight) Fe nanoparticles. The mixture was melt blended for 5 minutes; this produced the master batch. Figure 26 shows the DSC results for the $T_g$ of the 10% Fe/PS composite.
The presence of the Fe did not seem to affect the glass transition temperature. 0.5% and 1.0% nanocomposites were made by melt blending a portion of the master batch with neat polystyrene under the same temperature conditions. The neat polystyrene control was also melt blended under the same conditions. After cooling, each composite was broken into smaller pieces and passed through the Brabender once more for five minutes.

3.4.3 Fabrication of Fe-PS Nanocomposites Via In-situ Ultrasonic Polymerization Technique

Neat polystyrene was synthesized before composites containing various iron concentrations were made. 7g of de-inhibited styrene monomer was placed in a glass test tube and degassed by bubbling nitrogen gas through it. This vial was then attached to the sonicator probe (a Branson Sonifier 450). A seal was formed between the tube and the
sonicator with an O-ring. The vial was then lowered into a container filled with icy water and blocked off from light with a black screen. The black screen helped prevent photoinitiation, and also drew the heat generated by the process away from the monomer to prevent polymerization. The sonifier was then turned on and the monomer was sonicated for one hour. The vial was removed from the ice bath, and an initiator (0.2% by weight of BPO) was then added to the monomer. After being flushed with nitrogen gas a second time, the vial was reattached to the sonifier probe and then lowered into a heated oil bath at a constant temperature of 45°C. The solution was sonicated under heat until the monomer became visibly viscous. This change in viscosity indicated that polymerization was taking place. The probe was removed; the test tube was flushed with nitrogen gas and then placed in a conventional oven at a temperature of 125°C. The styrene was allowed to polymerize at this temperature for four days.

Iron nanoparticle/polystyrene composites were made in concentrations of 0.5%, 1%, and 10% by the same method as the neat polystyrene. A schematic of the process is seen in figure 27. Nanoparticles were added to the styrene monomer before sonication, which dispersed them in the solution. Fe nanoparticles can be seen in the SEM image of the polymer matrix in figure 28. While we associate the few bright spots in the SEM image with the Fe nanoparticles, it was initially puzzling to find so few of them. However, this can be reconciled with the fact that steric forces at the polymer surface prevent particles from remaining at the surface, and we believe that the majority of the particles migrate below the surface.
An initial batch of PS had been prepared and discarded due to it’s $T_g$ of approximately 80°C, a number significantly lower than the accepted value, which indicated the presence of unpolymerized monomer. A second batch was synthesized, and Figures 29 and 30 show the DSC results of the neat sonicated polystyrene and the 10% Fe/PS sonicated composite. The $T_g$ of the sample containing Fe seems to be slightly lower than the neat PS, dropping from approximately 97°C to approximately 91°C.

Figure 27. Schematic of fabrication of Fe-PS nanocomposites via a novel in-situ ultrasonic polymerization technique.
Figure 28. SEM image of the Fe nanoparticles inside the PS (sonicated) matrix. The bright dots are iron nanoparticles and the ridges are associated with the polymer surface.

Figure 29. DSC results for the glass transition temperature for neat PS prepared by ultrasonic polymerization.
3.5 PMMA composites

3.5.1 Properties of PMMA

PMMA is another amorphous thermoplastic that is polymerized via free radical polymerization. Its $T_g$ is approximately 105°C, similar to that of PS. It is hard, rigid, transparent, has good outdoor weatherability, and is more impact-resistant than glass. It is an electrically insulating polymer whose resistivity is greater than $10^{15}$ Ω.
3.5.2 Method for Fabricating the Fe-PMMA Nanocomposites Via the Brabender (Melt Blending) Technique

PMMA was first synthesized in the following manner: 200g of methyl methacrylate monomer was de-inhibited using the inhibitor remover column available from Sigma-Aldrich. The initiator, 0.2% Vazo 52 (by weight), was added to the monomer and degassed with nitrogen. The methyl methacrylate/initiator solution was poured into multiple glass vials, with each vial containing no more than 10ml of the mixture. Nitrogen gas was bubbled through the solution for a period of one minute, and then the vials were capped immediately following the degassing. The vials were placed in a conventional oven and heated at a temperature of 60°C for four days. The PMMA was removed from the glass vials and dissolved in methylene chloride in a 10% solution under constant stirring. Methanol was added drop-wise to the dissolved solution to precipitate the PMMA. The precipitate was removed from solution and oven dried under vacuum for three days at 130°C. Dissolving the PMMA in a solvent and precipitating it ensured that any unpolymerized monomer and small-chain polymers were removed. The accepted glass transition temperature of PMMA is cited by references as approximately 105°C. The neat PMMA was found to have a $T_g$ of approximately 123°C, as seen in figure 31. Figure 32 shows a slightly lower $T_g$ of 119°C for the 10% Fe/PMMA composite. It is believed that these values may be higher than the accepted value due to a high molecular weight, which can cause variations in the $T_g$. By testing the $T_g$ of the PMMA and comparing it to the standard values, it was further ensured that all of the monomer had been either polymerized or removed during the process of dissolving and
precipitating it. The presence of any unpolymerized monomer would have decreased the 
$T_g$. 

![Figure 31. DSC results for the glass transition temperature for neat PMMA prepared by Brabender.](image)

![Figure 32. DSC results for the glass transition temperature for 10% Fe/PMMA composite prepared by Brabender.](image)
Melt blended Fe-PMMA composites were made using the C.W. Brabender Plasticorder®. The Brabender was set to equilibrate at a temperature of 210°C, slightly above PMMA’s melting temperature of 200°C. Once equilibrated, 18g of the neat PMMA was added, together with 10% (by weight) Fe nanoparticles. The mixture was melt blended for 5 minutes; this produced the master batch. 0.5% and 1.0% nanocomposites were made by melt blending a portion of the master batch with neat PMMA. The neat PMMA control was also melt blended under the same conditions. After cooling, each composite was broken into smaller pieces and passed through the brabender once more for five minutes. Figure 33 shows an SEM image of an iron-PMMA nanocomposite sample.

Figure 33. SEM image of one representative PMMA nanocomposite sample. The ridges are associated with the standard polymer surface and the bright regions are Fe nanoparticles on the surface.
3.5.3 Fabrication of Fe-PMMA Nanocomposites Via the In-situ Ultrasonic Polymerization Technique

Fabrication of Fe-PMMA nanocomposites via the in-situ ultrasonic polymerization technique was also attempted, unsuccessfully. The exact procedure described previously for making the Fe-PS composites was followed, but the methyl methacrylate/iron composites would not completely polymerize after oven treatment. We therefore utilized the melt blending technique for all of the PMMA composites.

3.6 Polypyrrole Composites

3.6.1 Properties of Polypyrrole

Polypyrrole is a polymer that is relatively inexpensive and easy to fabricate. It exhibits high electrical conduction and good environmental stability.\(^{16}\) It is transparent green in its nonconducting form and black in its oxidized conducting form.\(^{41}\) Unfortunately, it has poor mechanical properties such as brittleness, and cannot be fabricated or molded in a desirable form.\(^1\) Both chemical and electrochemical methods can be used to make it.

3.6.2 Fabrication of Polypyrrole Composites Via Sonication Followed by UV Polymerization

Although electrochemical methods seem to produce superior thin film samples, the inability to obtain the required equipment for this forced us to choose chemical methods of polymerization, along with photopolymerization using a UV (365nm) lamp. The synthesis of polypyrrole thin films was carried out by referring to a commercial
procedure.$^{24}$ Pyrrole ($\text{C}_4\text{H}_5\text{N}$) was the monomer used, and silver nitrate ($\text{AgNO}_3$) was the electron acceptor used for polymerization. CYRACURE UVI6992 from Dow, a cationic photoinitiator, was chosen due to the fact that cationic photoinitiators exhibit faster curing rates than radical photoinitiators. Time was spent experimenting with different ratios of pyrrole, silver nitrate, and the photoinitiator. Before attempting to make any films, small amounts of the solutions were left in the beakers to polymerize.

Polymerization via UV light was compared to thermal polymerization. Except for a thin film that would appear on the surface, the solutions in the beakers exposed to UV light changed from yellow in color to black, but never seemed to polymerize. On the other hand, those in the oven did harden. It was possible that the intensity of the UV lamp being used was not high enough to polymerize the amount of solution in the beakers, so thin films were tested next before discarding the method completely. Fortunately, this worked, and the films exposed to UV only were much smoother than those cured under UV and then in the oven. A crude check of the resistances of some of the samples was done using a FLUKE85 multimeter (see Table 2). The films polymerized by UV light and then the oven had the highest resistance, followed by the films polymerized by UV only. These results are not precise due to the fact that the films varied in thickness and the method of measurement was not precisely uniform, but they at least show that the polymer is in fact conductive, and the resistance values are typical for these materials.
<table>
<thead>
<tr>
<th></th>
<th>UV only</th>
<th>UV + oven</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PPy 1-layer</td>
<td>7.98 kΩ</td>
<td>48.5 kΩ</td>
</tr>
<tr>
<td></td>
<td>6.82 kΩ</td>
<td>51.3 kΩ</td>
</tr>
<tr>
<td>Neat PPy 2-layer</td>
<td>10.16 kΩ</td>
<td>120.2 kΩ</td>
</tr>
<tr>
<td></td>
<td>13.75 kΩ</td>
<td>129.6 kΩ</td>
</tr>
<tr>
<td>PPy-nickel ferrite 10%</td>
<td>16.10 kΩ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.30 kΩ</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Approximate resistances taken across ½-inch length of polypyrrole films

The AgNO₃ added to photopolymerizable formulations in amts. 10-15mol% provide the necessary e- acceptor properties for photopolymerization to take place and gives the amount of NO₃ sup.-anions required for charge balance inside the polymer. This is equivalent to a pyrrole/salt molar ratio 8:1. Increasing the amount of photoinitiator decreases curing time, but also causes a slight decrease in conductivity, so a balance is necessary for optimum results. 0.3 wt% of CYRACURE UVI6992 was used in all of the mixtures. The solutions were made by combining the PPy and AgNO₃, then stirring and sonicating in the ultrasonic cleaning bath until completely mixed. The particles and photoinitiator were then added and the solution was sonicated for an additional 10 minutes.

Numerous films were made by varying the starting amounts of solution and spin coater settings. The films were then polymerized and compared. Of the spin coater settings tested, none of them produced films that were noticeably different from the others, so one of them was randomly chosen to use for all samples. The starting amount of solution was also chosen, and the ratios of solution ingredients had already been decided on. For every type of powder, three sets of films were made that varied in concentrations: 0.5%, 1%, and 10%, plus one set of neat polypyrrole films. Two subsets
of each of these sets were made: one set polymerized under UV light only, and the other polymerized under UV followed by oven treatment. For each of these subsets, films of one layer, two layers, and three layers were made. In addition, extra single layer films were made, but were scraped and treated as a powder. The resulting films can be compared to each other as well as to other systems such as non-conducting polymer/particle composites. Figure 34 is a schematic of the UV polymerization process.
The set of neat polypyrrole samples was completed first, and the PPy/chemically precipitated Fe₂O₃ (hematite) set was started. After combining all ingredients, the 0.5% solution was stirred and then further mixed by ultrasound before spin-coating it onto glass substrates. A complete set was made, but there was a problem with the iron oxide particles agglomerating. The 1% solution was prepared in the same way, but the solution sat for five minutes before spinning in order to allow the heavier agglomerated particles to settle at the bottom of the beaker. Solution was then siphoned from the top and spun onto a substrate. Though a few particles were visible, these films were much smoother and appeared to be more uniform than the previous set. The problem with this method is that there is no way of knowing the exact concentration of particles; but since the exact same conditions were used for every set of concentrations, it can be assumed that the relative concentrations were equal.

In addition to the chemically precipitated iron oxide (Fe₂O₃ hematite), composites were also made of PPy with Nanogen-produced iron oxide (Fe₂O₃ hematite), iron oxide (Fe₃O₄ magnetite), polystyrene-coated iron (Figure 35), manganese zinc ferrite (MZFO) (Figure 36), and nickel ferrite (NiFe₂O₄).
The SEM images PS coated Fe-nanoparticles dispersed in polypyrrole matrix synthesized using photo-polymerization technique. Clustering of the particles at various scales can be seen.

Figure 35. The SEM images PS coated Fe-nanoparticles dispersed in polypyrrole matrix synthesized using photo-polymerization technique. Clustering of the particles at various scales can be seen.

Figure 36. The SEM images MZFO nanoparticles dispersed in polypyrrole matrix synthesized using photopolymerization technique.
Chapter 4
Magnetic Properties

4.1 Introduction

The basic materials synthesis characterization and magnetic measurements were done on a large number of samples. Since all the details would make it too voluminous, we restrict our discussion in this chapter to some representative samples. Static magnetic properties of the prepared samples, such as temperature dependent magnetization $M(T)$ and $M$-$H$ loops, were studied using a commercial Physical Property Measurement System (PPMS) from Quantum Design. Hysteresis loop measurements were done at two fixed temperatures (10 K and 300 K) while varying the applied field from +30 kOe to -30 kOe. Field-cooled (FC) and zero-field cooled (ZFC) magnetization measurements were done from 10-300 K in an applied field of 100 Oe. The standard procedure for conducting ZFC and FC measurements is as follows: for FC magnetization data, samples were first cooled in the presence of a magnetic field of 100 Oe from 300 K to 10 K, and data collected while warming up. In the case of ZFC, samples were cooled in the absence of a field, the field of 100 Oe was switched on at 10 K and again the data collected while warming up the sample to 300 K.
4.2 Fe Powder Measurements

Figure 37 shows the M-H curves for the iron powder alone. As is expected in ferromagnetic materials, the saturation magnetization $M_s$ of the iron at room temperature is slightly lower than at 10K (0.940 emu vs. 0.986 emu). As the system was cooled from room temperature down to 10K, there seems to be a slight increase in remnant magnetization $M_R$. The coercivity $H_C$ also increases from 182 Oe at 300K to 205 Oe at 10K. Bulk Fe is a soft ferromagnet and coercivity is expected to be less than 100 Oe depending on the purity of the material. However, the coercivities can go up in fine-grain iron powders. The large coercivities we see are consistent with this trend. At the same time, we cannot rule out the possibility of a thin surface oxide layer on the Fe particles which would also result in increased coercivity.

Figure 38 shows the ZFC and FC magnetization measurements. It is difficult to interpret the effective variation of the data for powders as several mechanisms could contribute to the downturn in magnetization as temperature is decreased. Freezing of moments in small particles at low temperatures is well known. Also in soft magnetic powder samples, mechanical alignment of individual particles in the field direction can also contribute to complex behavior.
Figure 37. Room temperature and 10K M-H curves for iron powder. The inset shows a closer view of the hysteresis.

Figure 38. ZFC and FC magnetizations for iron powder.
4.3 PMMA Measurements

4.3.1 Neat PMMA

Figure 39 shows the room temperature and 10K M-H curves for neat polymethylmethacrylate (PMMA). It has a weak diamagnetic response to the applied field, but appears to have a small amount of unknown impurity contributing a very weak non-linear deviation near zero field that could be a paramagnetic effect. Small traces of paramagnetic impurities are found in nearly all materials, and so it is not surprising in these polymers. However, as we will see, these trace impurities do not affect the quality of our ferromagnetic composites.

Figure 39. Room temperature and 10K M-H curves for neat PMMA.
4.3.2 Fe-PMMA Nanocomposites

The magnetic measurements of PMMA nanocomposites having Fe concentrations of 0.5%, 1%, and 10% are shown in figures 40 through 44, and the important magnetic parameters extracted from these curves is summarized in Table 3. All three concentrations have approximately the same coercive field $H_C$ of 260 Oe at 300K. This large coercivity suggests that a natural oxide layer is present on the iron particles. At 10K the coercivity increases to approximately 530 Oe in the 0.5% sample, and roughly 550 Oe in both the 1% and 10% samples. Lower thermal activation energy of spins at lower temperatures explains the increase in coercivity and is consistent with the trend expected in nanoparticulate systems.47

It can be seen that the remnant magnetization $M_R$ increases by 36% in the 0.5% and 1% samples as the temperature is cooled from 300K to 10K, and by 50% in the 10% sample. This increase in remnant magnetization is expected below the superparamagnetic-ferromagnetic transition temperature, which is above 300K for iron nanoparticles of average size 20nm, due to reduced thermal activation energy. Interparticle interactions, which depend on the iron concentration in the PMMA matrix, strongly influence the remnant magnetization. Since agglomeration of nanoparticles into larger clusters is observed in all our polymer composite samples, interactions are expected to play a significant role in the magnetic response. These interactions lead to a non-linear increase in $M_R$ as the concentration of iron is increased. The magnetic interactions are generally expected to be dipolar in nature, although in strongly coupled clusters, exchange interactions are also possible.47
As the temperature is lowered from room temperature to 10K, the saturation magnetization $M_S$ in the three samples increases by 6-11%. Like the remnant magnetization, the saturation magnetization also increases non-linearly with iron content. The $M_S$ in a nanoparticle system is generally lower than that of the bulk materials and is strongly influenced by the supporting matrix.\textsuperscript{47,8,13} This lowering can be ascribed to surface spin disorder and canting.\textsuperscript{47,14} Because of spin disorder within a thin shell of 1 to 2 nm in say 20 nm particles, nanoparticles are often modeled as “core-shell” structures. These large variations in the saturation magnetization with temperature as well as nanoparticle concentration cannot be accounted for by standard mean-field dependence of the magnetization of the iron or iron-oxide phase.\textsuperscript{47} Due to the fact that some of the samples did not completely saturate at the highest applied field, it is possible that the projected saturation magnetizations were underestimated.

Figures 43 and 44 compare the FC and ZFC curves for the three concentrations. None of these curves show any characteristic sharp change in magnetization associated with the well established ferromagnetic to superparamagnetic transition in single-domain nanoparticles. This indicates that the particles (mostly in clusters) in the polymer matrix are predominantly ferromagnetically coupled at room temperature. These results are consistent with the M-H results, as all samples show sizeable coercivity. If the particles had retained their single domain character and were superparamagnetic, there should be no coercivity seen in the M-H curves.\textsuperscript{47}
Figure 40. Room temperature and 10K M-H curves for 0.5% iron. In the inset, we have shown a closer view of the hysteresis.

Figure 41. Room temperature and 10K M-H curves for 1% iron. In the inset, we have shown a closer view of the hysteresis.
Figure 42. Room temperature and 10K M-H curves for 10% iron. In the inset, we have shown a closer view of the hysteresis.

Figure 43. FC-ZFC magnetization for Fe-PMMA 0.5% and 1%.
Figure 44. FC-ZFC magnetization for Fe-PMMA 10%.

<table>
<thead>
<tr>
<th>Composite</th>
<th>$H_C$ (Oe)</th>
<th>$M_R$ (emu/gm)</th>
<th>$M_S$ (emu/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300K</td>
<td>10K</td>
<td>300K</td>
</tr>
<tr>
<td>PMMA+0.5% Fe nanoparticles</td>
<td>260</td>
<td>528</td>
<td>.0037</td>
</tr>
<tr>
<td>PMMA+1% Fe nanoparticles</td>
<td>260</td>
<td>554</td>
<td>.0059</td>
</tr>
<tr>
<td>PMMA+10% Fe nanoparticles</td>
<td>260</td>
<td>554</td>
<td>.05</td>
</tr>
</tbody>
</table>

Table 3. The measured magnetic parameters for the Fe-PMMA nanocomposite samples.

4.4 Polystyrene Measurements

The magnetic data taken on polystyrene and iron-polystyrene composites is shown in figures 45-48. Like the neat PMMA, the neat polystyrene exhibits weak diamagnetism with a weak paramagnetic effect at low fields due to a small amount of
unknown impurities. The remnant magnetization at room temperature increases from \(~.002\) emu in the sample containing 1\% iron to \(~.004\) emu in the 6\% composite. As the temperature in the 6\% iron sample is cooled from 300 K to 10 K, the \(M_R\) increases from \(.0039\) emu to \(.0048\) emu. The coercive field is approximately 340 Oe at 300 K for the two iron concentrations of 1\% and 6\%, and in the 6\% sample increases as the temperature is lowered to 10 K to a field of \(~ 470\) Oe. This increase is expected in nanoparticle systems due to lower thermal activation energy of spins at lower temperatures. The ZFC-FC temperature dependence of magnetization is shown in figure 48. The ZFC curve shows a broad peak around 100 K which we identify as the blocking temperature. The occurrence of the peak at lower temperatures than for PMMA composites (where such a peak is not seen up to 300 K), indicates that the average cluster sizes are much smaller in polystyrene composites.

Figure 45. M-H curves for sonicated neat polystyrene.

Figure 46. Room temperature M-H curve for sonicated Fe-PS 1\%.
4.5 Polypyrrole Measurements

4.5.1 Neat PPy

Figure 49 shows the diamagnetic response of the neat polypyrrole films to an applied field at room temperature and 10K.
4.5.2 MZFO-PPy Nanocomposites

Manganese zinc ferrite (MZFO) particles are soft magnetic in nature with small coercivities and large saturation magnetizations. For this composite, we have used Mn-Zn ferrite nanoparticles as there is considerable interest in conducting polymers with soft ferrimagnetic inclusions for RF device applications such as electromagnetic interference (EMI) suppression. Unlike the other powders used, the MZFO particles were suspended in solution, making the process of dispersing them in the pyrrole monomer easier than dispersing the powder alone would have been. Unfortunately, the concentration of MZFO particles in solution was unknown, so we had to compare relative amounts of solution rather than exact concentrations of particles as was done in the composites discussed previously. 10 µL and 100 µL of solution were each combined with 9.88g of the mixture of monomer, silver nitrate, and photoinitiator for comparison. The signal of the small concentration in the 10 µL sample is overshadowed at both 300 K and 10 K by the diamagnetic polypyrrole matrix, as can be seen in Figure 50. A dramatic difference is seen in Figure 51 in the 100 µL sample. The higher concentration of MZFO in the PPy matrix results in a strong ferromagnetic response of the composite at 10 K as well as at room temperature. The saturation magnetization is approximately 0.229 emu at room temperature and has a slightly higher value of 0.242 emu at 10 K. The M-H curve at 300 K shows a coercivity of 265 Oe. An increased coercive field of approximately 510 Oe is seen at 10 K. The remnant magnetization is .033 emu and .047 emu at 300 K and 10 K, respectively. The ZFC-FC curves in Figure 52 show that the blocking temperature is above 300 K. This increase in blocking temperature is again due to agglomeration of particles into clusters in these composites. In another study, a controlled experiment was
done where the MZFO nanoparticles were embedded in paraffin wax and no such clustering is possible. Figure 53 shows the M-T and M-H data for these MZFO particles for comparison with the composites consisting of MZFO nanoparticles embedded in polypyrrole. In the case of the MZFO particles embedded in paraffin wax, ZFC and FC magnetization measurements show a blocking temperature of 48 K, consistent with the single domain nature of the ~ 15 nm MZFO particles. The M-H curve supports this, showing hysteresis in the blocked state at 10 K, but none in the superparamagnetic state at 300 K. This blocking temperature indicates the ferromagnetic to superparamagnetic transition characteristic of highly monodisperse nanoparticles. The increased blocking temperature above 300 K for manganese zinc ferrite particles embedded in polypyrrole suggests that clustering and partial agglomeration of the nanoparticles occurred during the in-situ polymerization process. This is confirmed in the SEM images shown in a previous chapter.
Figure 51. 10K and room temperature M-H curves for MZFO 351-PPy 100µL.

Figure 52. ZFC-FC magnetizations for MZFO 351-PPy 10µL and 100µL composites.
Hematite exhibits canted antiferromagnetism above -10°C (263 K), and perfect antiferromagnetism below -10°C. The magnetic moments of the Fe$^{3+}$ ions are ferromagnetically coupled within a specific plane, but antiferromagnetically coupled between the planes. The observed magnetic response is close to zero in

**4.5.3 α-Fe$_2$O$_3$-PPy Composites**

Hematite exhibits canted antiferromagnetism above -10°C (263 K), and perfect antiferromagnetism below -10°C. The magnetic moments of the Fe$^{3+}$ ions are ferromagnetically coupled within a specific plane, but antiferromagnetically coupled between the planes. The observed magnetic response is close to zero in

![Figure 53. ZFC-FC (top panel) and M-H (bottom panel) curve for manganese zinc ferrite nanoparticles suspended in paraffin wax. In the inset, we have shown the zoom view of the loops.](image-url)
antiferromagnetic materials. Figure 54 shows the M-H curves of the chemically precipitated $\alpha$-Fe$_2$O$_3$-PPy 0.5% composites. The magnetic response is primarily diamagnetic due to the polypyrrole matrix. At low fields there is a very weak paramagnetic signal that was not present in the neat PPy. The ZFC-FC curves in figure 55 are too noisy because of low signal, so we do not attempt any interpretation but just show the raw data.

The magnetic response to an applied field of $\alpha$-Fe$_2$O$_3$-PPy 0.5% composites containing Nanogen-produced hematite is shown in Figure 56. At 300 K the response is diamagnetic. At 10 K a very slight ferromagnetic response is coupled with the diamagnetic response of the PPy. The neat PPy showed no ferromagnetism at either temperature. The XRD showed that the Nanogen-produced hematite was single-phase $\alpha$-Fe$_2$O$_3$ after calcination, so the ferromagnetic response is most likely due to the very slight magnetic response that can be exhibited in antiferromagnetic materials. Though the sample tested by XRD was single-phase $\alpha$-Fe$_2$O$_3$, it could also be a possibility that the entire batch was not completely reduced to a single phase during calcination. Traces of other phases present in the pre-calcined iron oxide, including the ferrimagnetic $\gamma$-Fe$_2$O$_3$, could cause the same ferromagnetic response.
Figure 54. M-H curves for chemically precipitated $\alpha$-Fe$_2$O$_3$–PPy 0.5% composites.

Figure 55. FC-ZFC magnetizations for chemically precipitated $\alpha$-Fe$_2$O$_3$–PPy 0.5% composites.

Figure 56. M-H curves for Nanogen-produced $\alpha$-Fe$_2$O$_3$–PPy 0.5% composites.
4.5.4 Fe$_3$O$_4$-PPy Composites

Fe$_3$O$_4$, or magnetite, is a ferrimagnetic phase of iron oxide. Figures 57 and 58 show the magnetic response of the Fe$_3$O$_4$-PPY 0.5% and 10% samples, respectively. The response of the 0.5% composite is diamagnetic at both room temperature and 10 K. The diamagnetic background of the PPy gives a much stronger signal than the ferromagnetic response of the doped magnetite particles. The diamagnetic response in the 10% sample still overpowers the ferromagnetic response at 300 K, but a ferromagnetic response is clearly seen. The ferrimagnetism of the magnetite at this concentration at 10 K is much more pronounced. The coercivity should be significantly greater at 10 K for a monodisperse nanoparticle system, but the coercive field is surprisingly nearly the same at both temperatures, with a value of approximately 55 Oe. This suggests that there is agglomeration of the nanoparticles, or a presence of larger multi-domain particles. The remnant magnetization is only slightly higher at 10 K than at 300 K (~6E-5 emu vs. ~5E-5 emu). The saturation magnetization at 10 K cannot be determined from this M-H curve. Figure 59 shows the ZFC-FC curves.
Figure 57. M-H curves for Fe₂O₄-PPy 0.5% composites.

Figure 58. M-H curves for Fe₂O₄-PPy 10% composites.

Figure 59. ZFC-FC curves for Fe₂O₄-PPy 10% composites.
4.5.5 NiFe$_2$O$_4$-PPy Composites

Figures 60 and 61 display the M-H curves for the nickel ferrite-polypyrrole composites in concentrations of 0.5%, and 10%. There is no coercivity at room temperature for either sample, and the coercive fields at 10 K are ~315 Oe and ~380 Oe for the 0.5% and 10% samples, respectively. The remnant magnetizations at 10 K are ~1.2E-4 emu in the 0.5% sample, and 0.0027 emu in the 10% sample. Except for the 10% sample at room temperature, whose $M_S$ is 0.0055 emu, the saturation magnetizations of the two samples cannot be determined from the graphs without subtracting a paramagnetic or diamagnetic background that would lead to possible error in estimation of $M_S$. Figures 62 and 63 show the ZFC-FC magnetizations for the samples. The ZFC curve indicates a clear tendency to peak at around 250 K. The transition is very broad, again indicative of large cluster size distribution.

![Figure 60. M-H curves for NiFe$_2$O$_4$-PPy 0.5% composites.](image1)

![Figure 61. M-H curves for NiFe$_2$O$_4$-PPy 10% composites.](image2)
4.5.6 Polystyrene-coated Fe-PPy Composites

In figure 64 we have shown the M-H curves at 10 K and 300 K for polypyrrole composites doped with 1% PS-coated Fe nanoparticles. The diamagnetic response of the polymer matrix overshadows the ferromagnetic response of the nanoparticles at this concentration. The M-H curves of the 10% composite are shown in figure 65. The ferromagnetic response of the PS-coated Fe is clearly seen at this higher concentration. A coercivity of $H_C=114$ Oe is observed at 300 K. Clustering or partial oxidation of the particles, or a combination of the two may be the source of the coercivity. The diamagnetic contribution from the polymer matrix results in the negative slope in magnetization that is observed at high magnetic fields. At 10 K the coercivity goes up to 433 Oe. Lower thermal activation energy of spins at lower temperatures causes an increase in the coercive field with decreasing temperature for superparamagnetic systems.
Our observations are likely due to the magnetic behavior of blocked single domain particles combined with the response of regions of multi-domain agglomerates.

Figure 64. M-H curves for polystyrene-coated Fe-PPy 1% composite.

Figure 65. M-H curves for polystyrene-coated Fe-PPy 10% composite
In this chapter we have reported the results of standard magnetic characterizations of representative samples of polymer nanocomposites. Further measurements such as transport properties, shielding effectiveness, etc. will be done on these materials as research on this project continues.
Chapter 5

Summary and Future Work

We have successfully synthesized a series of nanocomposite materials comprised of magnetic nanoparticles embedded in both dielectric and conducting polymers. The various types of dopant particles that were made include: iron, polystyrene-coated iron, nickel ferrite, hematite, magnetite, and manganese zinc ferrite, synthesized by either chemical precipitation methods or the Nanogen™, which uses microwave plasma to produce the nanoparticles. The dielectric polymers PMMA and polystyrene were polymerized in bulk form via free radical polymerization involving thermal energy. The conducting polymer polypyrrole was polymerized in the form of thin films via UV radiation. The nanoparticles were dispersed in the polymeric matrices by two methods: melt-blending was used for both PMMA and PS composites, and ultrasonic techniques were used for PS and PPy composites. We then studied the fundamental magnetic properties of the composites, which show systematic changes with varying particle concentration.

Future work on this project will begin with optimizing the neat polymer films. Though bulk samples of the dielectric polymer composites have been made and studied, spin coating methods need to be integrated into the synthesis process in order to make thin films suitable for multi-layered structures. We have begun this process, and it has
proven to be a very simple and unproblematic transition. Thin films of conducting polymer composites were successfully made, but improvements to the process could possibly result in consistently smoother, more uniform films. While we used chemical methods to polymerize the pyrrole, others have shown that electrochemical polymerization produces polypyrrole films of much superior quality. This will be explored in order to remedy the current issues of brittleness and non-uniformity of the conductive films.

Future efforts will also include working toward improving the dispersion of the particles in the polymeric matrices. Agglomeration due to the size of the particles and steric forces inhibited our success in achieving uniform dispersion in all of the composites. Perhaps using surfactants on the nanoparticles would reduce the amount of clustering. Utilizing dispersion methods other than melt-blending and sonication could possibly minimize this problem further.

Following the optimization of the quality of the single-layer films, additional studies of their properties need to be done. Measurements of the complex impedance and shielding effectiveness of each composite need to be completed. In addition, transport measurements like resistivity, magnetoresistance should be taken.

After the ideal single layers have been synthesized and manipulation of their properties is mastered, they should be combined into multilayer devices. The multilayer composites will consist of top layers having high conductivity and large shielding effectiveness, and bottom layers intended for accomplishing better impedance matching. We will then investigate the RF response in these layered nanocomposite materials. The
final step in the project will be to monitor the device performance and EMI-suppression of an electronic device coated with the nanocomposite materials.
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31) Poddar, P., J. L. Wilson, H. Srikanth, S. A. Morrison, and E. E. Carpenter. Magnetic properties of conducting polymer doped with manganese zinc ferrite nanoparticles. (accepted to be published in *Nanotechnology*)


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Appendices
Appendix A: Journal Publications

Poddar, P., J. L. Wilson, H. Srikanth, S. A. Morrison, and E. E. Carpenter. Magnetic properties of conducting polymer doped with manganese zinc ferrite nanoparticles. (Accepted, Nanotechnology)


Appendix B: Conference Presentations


Wilson, J.L. *Static and dynamic magnetic studies of magnetic nanoparticle composites.* USF graduate student research symposium (2003), Tampa, FL.
Appendix C: Internships