Lab 2: Bioinspired Magnetite Coprecipitation Synthesis with Polyacrylic Acid (PAA)

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MSE 60: Advanced Laboratory in Synthesis and Characterization of Materials

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ABSTRACT *(Kelsey Lawson)*

Magnetite, an oxide phase of iron, is a material known for its strong magnetic properties which are commonly used in medical field applications. In the experiment conducted in this lab, magnetite will be combined with a polyacrylic acid (PAA) polymer to undergo a replication of the crystallization structure of its bioinspired counterparts. This will be compared with a control sample of magnetite analyzed through scanning electron microscope (SEM) images, x-ray powder diffraction (XRD), Raman, and the thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) graphs. Both samples underwent the proper techniques to create an aqueous solution that still held magnetic properties to then be transformed into powders using heat treatments from $25°C$ to $800°C$. Once the powders were formed, they were analyzed under SEM showing remarkable differences in surface texture and spatial distance. The magnetite with PAA revealed to have a smoother more rounded surface that was distanced from neighboring particles whereas the control magnetite was rough and densely packed. Furthermore, the XRD graphs proved that the magnetite with PAA has no crystallinity change when plotted against the control. This idea is also supported from the Raman graphs because the magnetite peaks from the control variable can be identified on the PAA added sample proving that there is no structural change comparing both magnetites in each sample, but the addition of PAA had improved the order. Moreover, only the TGA/DSC graphs showed a difference between the samples in reference to how each sample reacts under a heat treatment. For the control magnetite, it had little to no mass change from an exothermic reaction. This differed dramatically when magnetite contains PAA because the overall mass reduced around 30% in an exothermic decomposition reaction. Finalizing the results, it can be concluded that magnetite with PAA additives was successfully synthesized from a biomimetic method.

INTRODUCTION *(Kelsey Lawson)*

Scientists have been fascinated by magnetic nanoparticles because of their use for biomedical applications (1). Particularly, the magnetite phase of iron, Fe_3O_4, stands out for its use in the medical field due to its superparamagnetic behavior at 20 nanometers or less (1). Magnetite properties are also affected by the shape, purity, and organization of the crystals (2). This plays into "drug delivery, magnetic cell sorting, magnetic resonance imaging (MRI), hyperthermia, and immunoassays" (1). "Currently, these materials generally are only accessible through laborious multi-step functionalization and phase-transfer procedures" (2). When magnetite is in an aqueous solution, the nanoparticles are dispersed in uniform sizes and spacing which achieves long-term colloidal stability for in vivo use (1). In order for these properties to be extracted, the magnetite has to undergo proper synthesis such as "chemical coprecipitation, organic colloids, reverse micelles, [and] hydrothermal" (1). Although, it is noted that chemical coprecipitation is the most prevalent because it directly coats the particles with various water-soluble biocompatible coating agents (1). Yet, within an aqueous dispersion, the particles have poor crystallinity, form individually as aggregates, and are varied in size (1). This can be avoided when conducting reactions at higher temperatures, such as $200\,℃$.

Using strategies from biomineralization within the field of material science would allow for "additive directed synthesis of magnetic-based nanomaterials with control over the dimensions and organizations of the particles and thereby their magnetic properties, using...bioinspired production methods, i.e. using aqueous media and ambient temperatures" (2). Comparing magnetite to other common biominerals, there is far less documentation of bio-mimetic synthesis with controlled morphology (2).

Within this lab, there are two experimental runs using magnetite alone as a control variable and then having magnetite with polyacrylic acid (PAA) added. PAA is a synthetic polymer commonly used for encapsulating cells within the field of tissue engineering (3). However, for this lab, PAA is applied as a weak polyelectrolyte that will be used to stabilize the magnetic nanoparticles of magnetite (4). From this, the interaction of adding a polymer to magnetite versus magnetite alone will be examined throughout the report by analyzing the scanning electron microscopy (SEM) images, characterizing x-ray powder diffraction (XRD), Raman, and the thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) graphs.

OBJECTIVE *(Keven Colchado)*

Using the polyacrylic acid solution, the objective of the lab is to see the effect polymers have on the binding effect of iron ions. This experiment will attempt to replicate the bio-inspired crystallization of magnetite using PAA. The purpose is if we can successfully find a biomimetic method that synthesizes magnetite.

MATERIALS AND EXPERIMENTAL METHODS *(Keven Colchado)*

Materials

250 mL Beaker	Wax Paper	Thermo Variomag Poly Stir Plate	Magnetic Stirring Rod	Scale	Magnet	100 mL DI Water
Ar Gas	Glass tube	Weighted paper	Iron(iii) Chloride	Iron(ii) Chloride	Tube Tray	Spatula
Capsule Tubes	PAA	pH Meter	Razor Blade	Pipette	Centrifuge	1 mol NaOH
	Ultra Sonicator	Oven	Silicon Wafer	XRD Machine		

Bioinspired Materials Lab

First, prepare 100 ml of DI water. In a 250 mL, beaker put about 100 mL of DI water. Seal the beaker with wax paper and then a hole will be punctured on top with the glass tube connected to the Ar gas. Allow the gas to flow for 30 minutes. This process is necessary so that the oxygen in the water would not react with the iron ions of the solvent. Zero the scale to a weighted paper and then measure about 162 mg ferric chloride. Once measured, the ferric chloride concentration will be inserted into a capsule with a lid which will be closed tightly. Then the steps for measuring the concentration will be repeated iron(ii) chloride. There will need to be about 89 mg of iron(ii) chloride. The next step is to prepare the Poly(acrylic acid) solution or PAA. A portion of PAA will be poured into a jar which would then be diluted with water. The mixture will be 10 percent water. This step is necessary to make the PAA solution less viscous. The next 40 mL of gassed water will be poured into a 250 mL beaker. A stirring rod will be placed inside and the beaker will be sealed with wax paper. The beaker will be placed on the stirring plate and connected with a pH meter. The stir plate will run at 250 rpm. A tube will be punctured through the wax paper to allow Ar gas to enter the beaker and remove the air inside. Holes will be made on the wax paper using a razor blade. Next 400 microliters of PAA will be added to the solution while keeping the beaker sealed as much as possible. Then the ferrous and ferric chloride will be shaken then added to the beaker at the same time. Using a pipette, NaOH will be added to the solution until the pH stays between 8.9-9. The First 2 mL of NaOH is added then 100-micron liters are added to keep the solution to desired pH range. Once the solution stays to the desired range, the solution will continue to stir for an hour. Then the solution will be collected by being transferred to separated tubes. The whole process involving stirring,

maintaining pH range constant will be repeated but without the PAA. In the end, to see if the particles are magnetic, a magnet is used to move the particles inside the tubes.

Characterization Lab

First, with a small pipette, the 2:2:1 solutions will be poured into six smaller tubes and the controlled solution on a separate six smaller tubes. The tubes will be sealed shut. Then the centrifuge will be set up to 13k rpm and time to 15 minutes. Then the 12 tubes will be placed in the centrifuge, equally distanced from each other. This is to balance the centrifuge. Once closed then the centrifuge will run. Afterward, the tubes will be placed in the tube tray. With a separate capsule, liquid from each tube will be poured into a new capsule. The 2:2:1 liquid and controlled solution liquid will be in separate tubes. Repeat with the second set with a different capsule. Once the liquid has been removed, DI water will be added to the small tubes with the solids. This is so that we could remove the residue material away from the material. The solutions will then be mixed using an Ultra Sonicator. The machine will need to be washed before attaching each sample to the needle. Then the tube will be placed back into the centrifuge equally balanced with the DI water and at 13k rpm for two minutes. This process will be repeated two more times. The samples will be stored inside an oven to dry overnight. The material will again be mixed with water. The particles will then be placed on a silicon wafer capsule and closed. It will be used for the SEM process. Next, the XRD machine will be used. The first package called general bd scattering will be selected and the prompts on the screen will be followed. The machine will need to be aligned with the particle inside its chamber. To do so, the wafer with the sample will be placed in the center of the chamber and the yellow prompt on the screen will be selected once the chamber door is closed. After alignment, 2 theta scans will be selected and the x-ray will turn on. Lastly, the measurements will be collected.

RESULTS

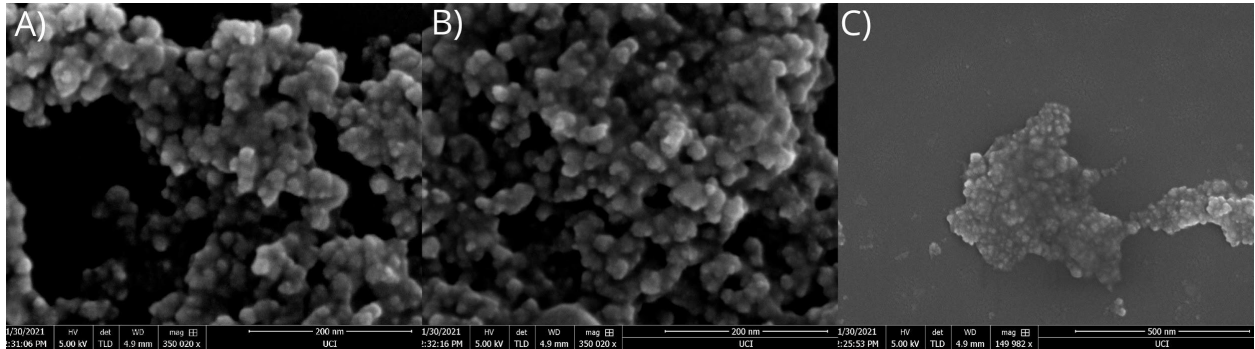**SEM** *(Thaily Serrano-Alamo)*

Figure 1. (Magnetite Control no PAA) This structure is more rigid. There is no uniformity in the structure.
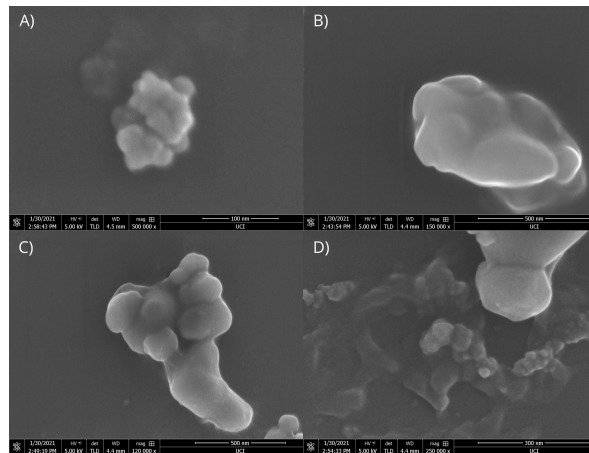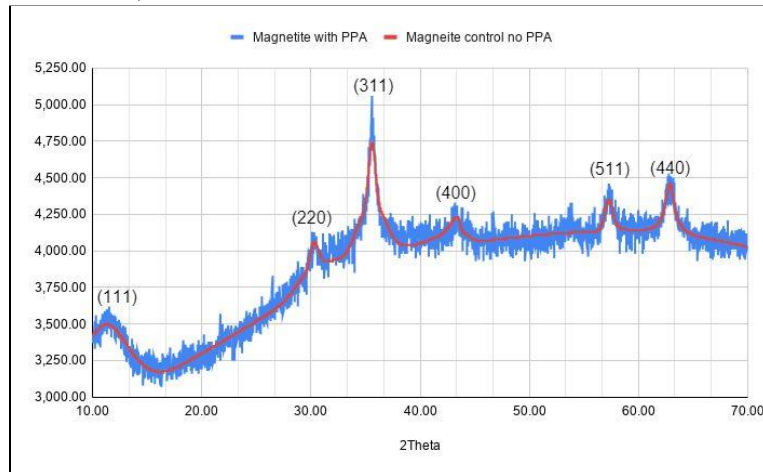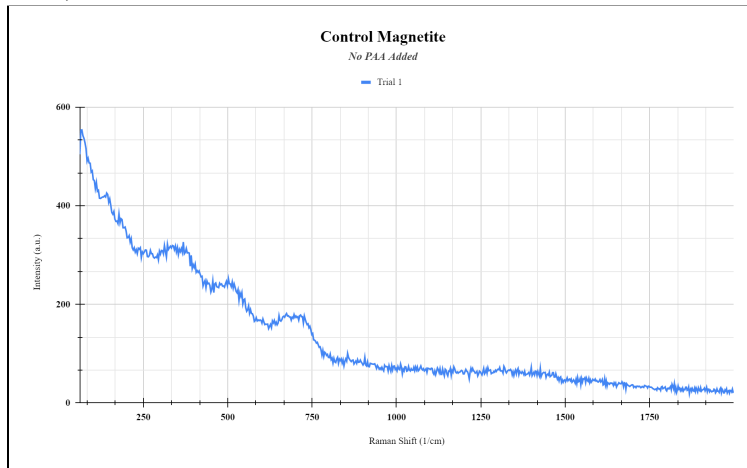

Figure 2. (Magnetite with PAA) The structure is more smooth. Does not have a uniformity structure either.

XRD *(Thaily Serrano-Alamo)*
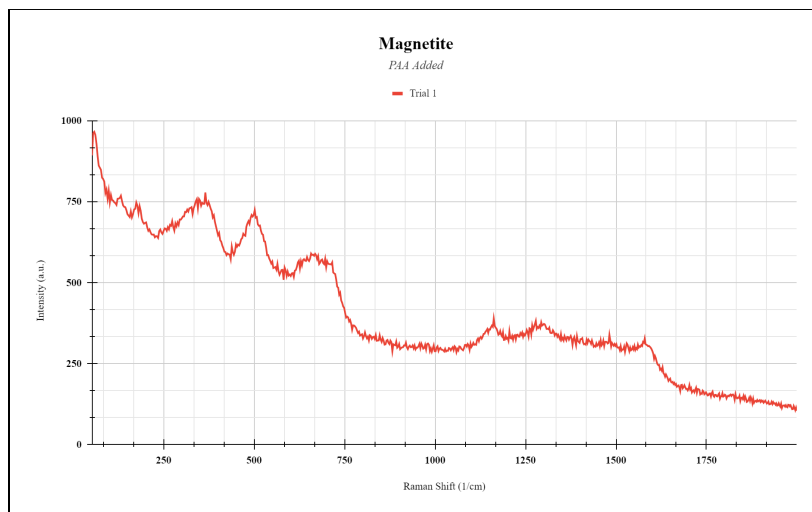

Graph 1. Magnetite with PPA is more rigid compared to Magnetite with no PPA. Both have a basic shape.
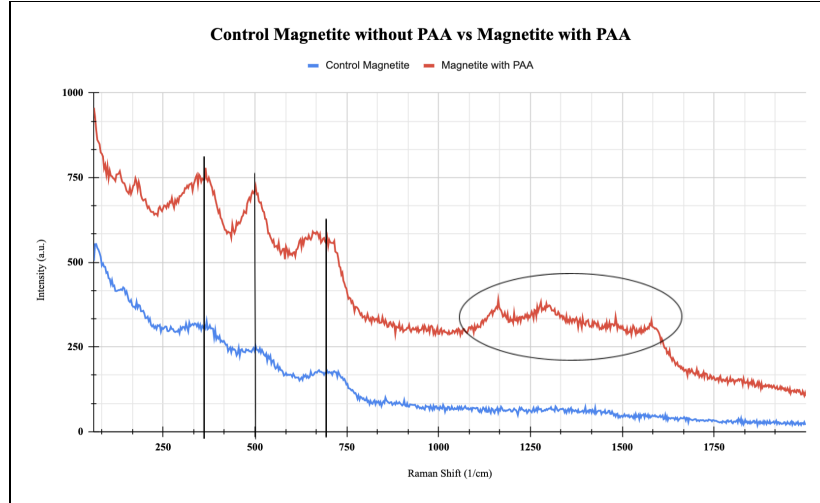
Raman *(Kelsey Lawson)*

Graph 2. The magnetite sample without added PAA is shown above and has a downward trend of intensity. The data shown is from a data set provided shown in the appendix.


Graph 3. The magnetite sample with PAA added is represented above showing a negative trend just like the control magnetite. The data shown is from a data set provided shown in the appendix.

Graph 4. Both the Raman graphs of the control magnetite and the magnetite with PAA are shown above. As indicated by the lines, there are three similar points of contact between the two, but then the magnetite sample with PAA has some peaks at the end towards the higher temperatures. The data shown is from a data set provided shown in the appendix.

TGA/DSC *(Kelsey Lawson)*
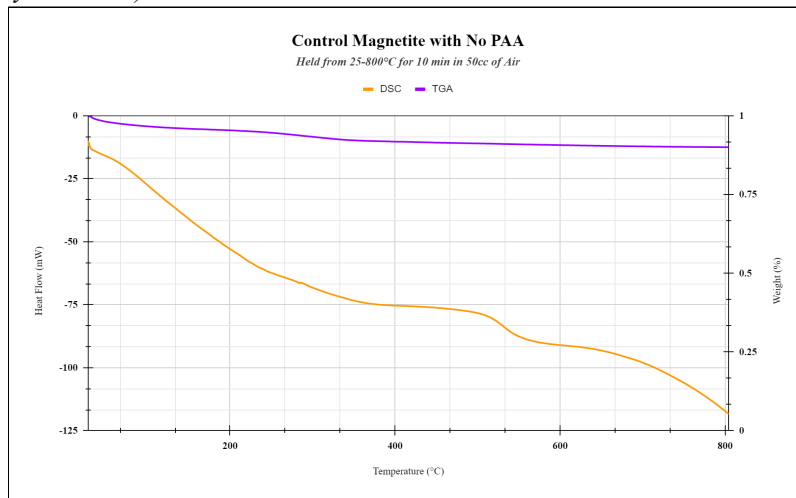
Graph 5. Both the DSC and TGA data for the control magnetite have been plotted above. There are no distinguishing characteristics of either curve. The data shown is from a data set provided shown in the appendix.
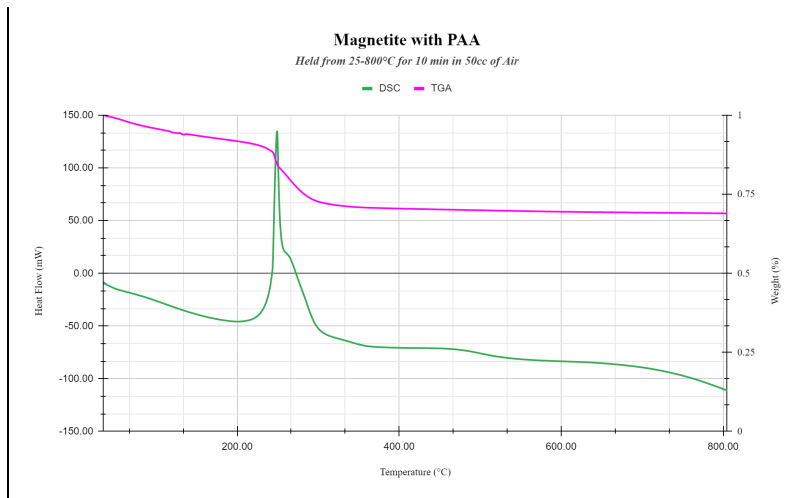
Graph 6. Both the DSC and TGA data for the magnetite with PAA have been plotted above. Both curves show a drastic change at ~275℃. The data shown is from a data set provided shown in the appendix.

DISCUSSION

SEM *(Thaily Serrano-Alamo)*

The SEM images show the different structures of both of our samples. The control sample, with no PPA, has no uniformity and the structure looks further apart. The image with the PPA is smoother and the structure looks closer together. It seems like the empty spaces from magnetite got filled with PPA. Making the structure look more full and smooth. Even though the SEM images are showing differences in shape, the crystal structure does not change as evidenced in the x-ray diffraction. So PAA filled in the empty spots of magnetite, without changing its atomic crystal structure.

XRD *(Thaily Serrano-Alamo)*

Graph 1 shows both the intensity peaks of magnetite with PAA and magnetite with no PPA. For magnetite with no PPA, the graph looks smoother. This indicates that it is crystalline. This means that at certain angles the x-ray was able to atoms in the crystal structure. When magnetite gets mixed with PPA, the graph is in a similar shape as the control but it is extremely more rigid. This is because the polymer PPA is in an amorphous state. Amorphous has random

molecular structures which cause the x-ray to scatter at different angles. This makes very thin, closely packed peaks that make the graph overall rigid. If there was an x-ray scatter of just PPA, most likely it would not have any defined peaks since the graph of magnetite with PPA does not have any new peaks. What makes it have the unique graph that has peaks but at the same being rigid is mixing both a crystalline structure and an amorphous structure. Overall the structure did not change.

When comparing the two graphs, there is no clear difference between the width of the peaks. This means that the grain size in the crystalline structure did not change with the mixture of PPA. By using the Scherrer equation on the highest peak, the crystal size can be determined.

$$B(2\theta) \ = \ \frac{K\lambda}{Lcos\theta} \text{ (Scherrer equation)}$$

$$K = .9, \ \lambda \ = \ 1.5418, \ L \ = \ 0.017 \ radian, \ \theta \ = \ 17.73$$

$$B(2\theta) \ = \ 85 \ A$$

Raman *(Kelsey Lawson)*

As shown in the results section, both of the Raman graphs for the control magnetite and the magnetite with PAA have a downward trend in their intensity. However, the PAA additive in magnetite had caused the trail of the curve to peak subtly from ~1160℃ to ~1600℃ as seen in Graph 4. This is the biggest difference between the two curves. Moreso, ignoring the peak intensity variance, both magnetite with and without the PAA has three peaks at ~370℃, ~500℃, and ~570℃ respectively. This implies that the magnetite with PAA exhibits the same structural properties as the control magnetite and the PAA can be related to the end peaks and the shift up in intensity. Also, the addition of PAA is shown to increase the structural order of magnetite due to the peaks becoming more defined. When comparing the three similar peaks, the magnetite

with PAA reveals higher sloped peaks that reach a defined tip and are very distinct from each rise and fall. For the control magnetite, the peaks are subtle and blend in with the neighboring slopes.

TGA/DSC *(Kelsey Lawson)*

Unlike the Raman graphs, neither of the TGA/DSC graphs for either magnetite sample show similarities. For the control magnetite in Graph 5, the TSC curve subdued over the entire temperature range assuming that there was no mass change. Looking at Graph 6, magnetite with PAA has caused a drastic reaction to the temperature change around 250℃ that can be characterized as a single-stage decomposition. This means the magnetite with PAA had lost around 30% of the initial mass when the temperature increased whereas the magnetite alone resulted in less than 10% mass loss. Likewise, the control magnetite curve for the DSC data also follows a simple curve with a partial flatline around 400℃ to 500℃. This does not show too much change in the sample's reaction temperature but because the overall trend is decreasing, it can be classified as an exothermic reaction. Furthermore, because the curves for TGA and DSC are negatively sloped, this relates the best to a decomposition physicochemical process. Contrasting the control sample, magnetite with PAA has a sharp peak seen in Graph 6 right where the TGA curve decreases at ~400℃. This extreme contour of the peak for magnetite is characterized as endothermic reactions but combined with the decreasing mass from TGA, the physicochemical process for adding PAA to magnetite is evaporation.

CONCLUSION *(Thaily Serrano-Alamo)*

In this lab magnetite was combined with PAA. Then the powder sample was analyzed using three different techniques: SEM, XRD, Raman and TGA/DSC. From the different techniques, it showed how PAA affected the properties of magnetite. The SEM images show that by adding PAA it makes the structure smoother and rounder. XRD showed that the overall

crystal structure was not changed by PAA. The Raman shift graph also supports that there is no crystal structure change. TGA/DSC actually showed a change in how the sample reacts to temperature when adding PAA. By mixing PAA the sample reduces in mass in an exothermic decomposition.

References

(1)   Ravikumar, C., and Bandyopadhyaya, R. (2011). *Mechanistic Study on Magnetite*

        Nanoparticle Formation by Thermal Decomposition and Coprecipitation Routes. (115),

        1380-1387. American Chemical Society.

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        Copolypeptides. (25), 711-719. Advanced Functional Materials.

(3)   Sundararaghavan, H. G., and Burdick, J. A. (2017). *Cell Encapsulation.* **5**, 115-130.

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Appendix

Hyperlink to Google Sheets Data used for Raman and TGA/DSC graphs: *Raw Data for Raman & TGA/DSC Graphs* *(Kelsey Lawson)*