UNIVERSITY OF CALIFORNIA SAN DIEGO

Quantitative Biodegradation of Plastic Foams in Seawater and Compost Environments Using Hydrogen Peroxide Digestion

A Thesis submitted in partial satisfaction of the requirements
for the degree Master of Science

in

Chemistry

by

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2024

The Thesis of Ayden N. Howell is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego

2024

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Acknowledgments

I would like to acknowledge Professor Robert Pomeroy for his assistance as the chair of my committee. His guidance and mentorship cannot be understated.

I would additionally like to thank all the other members of the Pomeroy lab, especially Marissa Tessman, without which the lab surely would have never been operable in the first place.

Abstract of the Thesis

Quantitative Biodegradation of Plastic Foams in Seawater and Compost Environments Using Hydrogen Peroxide Digestion

by

Ayden N. Howell

Master of Science in Chemistry

University of California San Diego, 2024

Professor Robert Pomeroy, Chair

Plastic pollution is overrunning the planet. To combat this, it is important to be able to generate biodegradable alternative plastics and measure their biodegradability. The research aimed to develop a method for quantifying the biodegradation of these plastics using peroxide digestion with Fenton's Reagent. The results show that peroxide digestion can be used in tandem with other analytical methods to quantify biodegradation, namely with mass loss, compression analysis, and supplemental FTIR spectroscopy.

Chapter 1

1.1 What is the Problem?

The development of plastics has had an enormous impact on humanity and the environments we live in. Plastic has become a staple of product design for many decades now, being so malleable and yet structurally sound to be used in containers for the clothes we wear and for the construction of transportation across land, sea, and space. It would be difficult to describe all possible uses of plastics across time and even more difficult to overestimate how valuable plastics have become in our daily lives.

Unfortunately, the usefulness of plastics comes at a cost. The benefits of polymer plastics have now become a greatly unanticipated drawback. As stated, plastics' power relies on their durability and inability to break down. Though this is extremely beneficial for materials that are meant to last and be used for long periods, this creates a buildup of “disposable” plastic trash and waste products that will remain in landfills, oceans, or other environments of choice for far longer than anticipated.

Polymers in all their forms have been building up across Earth, culminating in the present-day situation. The image of sea turtles being suffocated by plastic rings and choking on plastic bags comes to mind immediately. Still, there are numerous other effects plastics have on the environment.

For plastics on a larger scale, the effect of entanglement and choking has been documented as a primary contributing factor towards the deaths of many species across the globe, especially marine life. On a smaller scale, plastics measuring smaller than 5mm, described as microplastics, have been of equal, if not greater concern in recent years. Animals, including humans, can eat Microplastics, which, if sharp enough, can lacerate sections of the digestive

tract. Aside from the physical components, concern is growing over the possibility of microplastics depositing harmful chemicals into the smaller organisms that ingest them, which can then be carried on through the food chain.[i]

Research has been done on the effects of plastics and microplastics on humans. Some chemicals, such as Phthalates and bisphenol A, have been found to have associations with a wide range of detrimental effects, including but not limited to reproductive issues, type two diabetes, and cardiovascular health problems.

1.2 Why is it important?

With these things in mind, the plastic-filled dystopian future becomes slightly easier to imagine. Images of a sea level rising with increasing amounts of plastic particulates floating around large islands made of accumulated waste, further species going extinct due to an unfortunate inability to adapt quickly enough to their rapidly changing environment, the greens of chloroplast being universally replaced by the greens of synthetic paints and dyes, and fearful what-ifs of the effects of microplastics on human body chemistry fill our heads.

As of research done in 2014, somewhere between 5 to 13 million tons of plastic will be disposed of each year.[ii] Estimating 8 million tons, an island of plastic "34 times the size of Manhattan "[iii] will be disposed of yearly. That is about 776 square miles of plastic laid out flat, covering just over 18 percent of San Diego County. You can see if the projections are correct, every 5 years, an island of plastic waste the size of San Diego County is thrown into the ocean, free to choke animals, deposit microplastics into our food chains, and tarnish Earth.

1.3 What is being done?

The world is noticing these issues as they become exceedingly more relevant to the population. With this recognition, work began on ways to decrease plastic pollution on multiple fronts. A few methods include collecting, recycling, and repurposing discarded plastics, creating fewer single-use plastics that are multipurpose and reusable, and reducing the amount of non-biodegradable plastics produced by creating biodegradable alternatives.

Recycling has been a hot topic in the past few decades, with media ingraining the phrase "Reduce, reuse, recycle" into my mind and the psyche of many of the common public. We now have bins dedicated to recycling instead of the all-in-one bins for landfills. Unfortunately, recycling on its own is not enough to bring down plastic pollution to an acceptable level. Plastics especially are difficult to identify and separate from the constant flow of disposed trash. They also come in several forms of polymers that should be recycled in different ways, making even separating plastics from themselves a difficult task.[iv]

Reusable alternatives for single-use plastic are a great way to mitigate plastic waste by simply creating less demand. The example that comes to mind is the more recent use of metal, reusable straws for drinking than plastic straws. They are used for years without issue and are also easily recyclable. Reusable alternatives on their own are, unfortunately, not enough to save us from our current dilemma. Mostly because single-use plastics are still far more common, and even some of these alternatives are made of plastics themselves. So, this issue remains; what happens when we inevitably dispose of reusable plastics?

The final method is to reduce the number of harmful plastics by generating biodegradable plastics. This is being done across the globe by many companies and governments; one, for example, is Algenesis, which develops biodegradable plastics and foams used for shoes, surfboards, and many other products currently dominated by non-biodegradable plastics.

Combining all these efforts is the most effective strategy to solve our current ecological predicament and prevent future crises. But a question remains, how does one determine if a plastic is definitively biodegradable?

1.4 Where did the idea come from?

This question plagues those who wish to create these biodegradable plastics. Fortunately, there is research being done to find a suitable solution. A form of oxidation reaction using a component known as Fenton's Reagent has been used to measure microplastics in large-scale environments.[v]

The basic principle of the experiment relies on the idea that Fenton's reagent chemically filters out any non-synthetic biomaterial within or containing plastics and reacts with them, leaving behind only the plastics to be collected and analyzed.[vi] This is primarily being used to reclaim microplastics from sewage, compost, and seawater.[vii]

In researching these microplastic quantification techniques, it seems possible to expand beyond microplastics into the quantification of regular plastics and plastic foams as well. This could prove to be a valuable way to quantify the degradation of biodegradable plastic foams by comparing pre- and post-degradation variables.

1.5 What is my goal?

The idea quickly became a project that would take over a year to complete. The goal was to develop a method of quantifying the biodegradation of plastic foams in seawater and compost environments using mass loss, FTIR chromatography, and compression analysis.

Chapter 2

2.1 Defining the Environments

The data that was collected came from one of three possible sources: the Scripps Institute of Oceanography Pier, a Seawater Table, and community compost. The Seawater Table and SIO Pier samples were taken with similar variables of time, size, foam type, and environment, whereas the composted samples were slightly larger, degraded over a shorter time scale, and only had a sample variation of two different foam types.

The Seawater table is a mechanism that simulates the ebon flow of the ocean on a large table of seawater, meant to act as a more enclosed and controlled ideal environment to the open waters of the pier. The main difference between the seawater table and the pier is that the table is a closed system, with more of an emphasis on water current and cellular/ algal life than the entire ocean ecosystem. Figure 1 shows how the seawater table creates a more controlled seawater environment than that of the SIO pier, with a constant flow of filtered seawater, and isolation from organisms outside of the collected seawater.

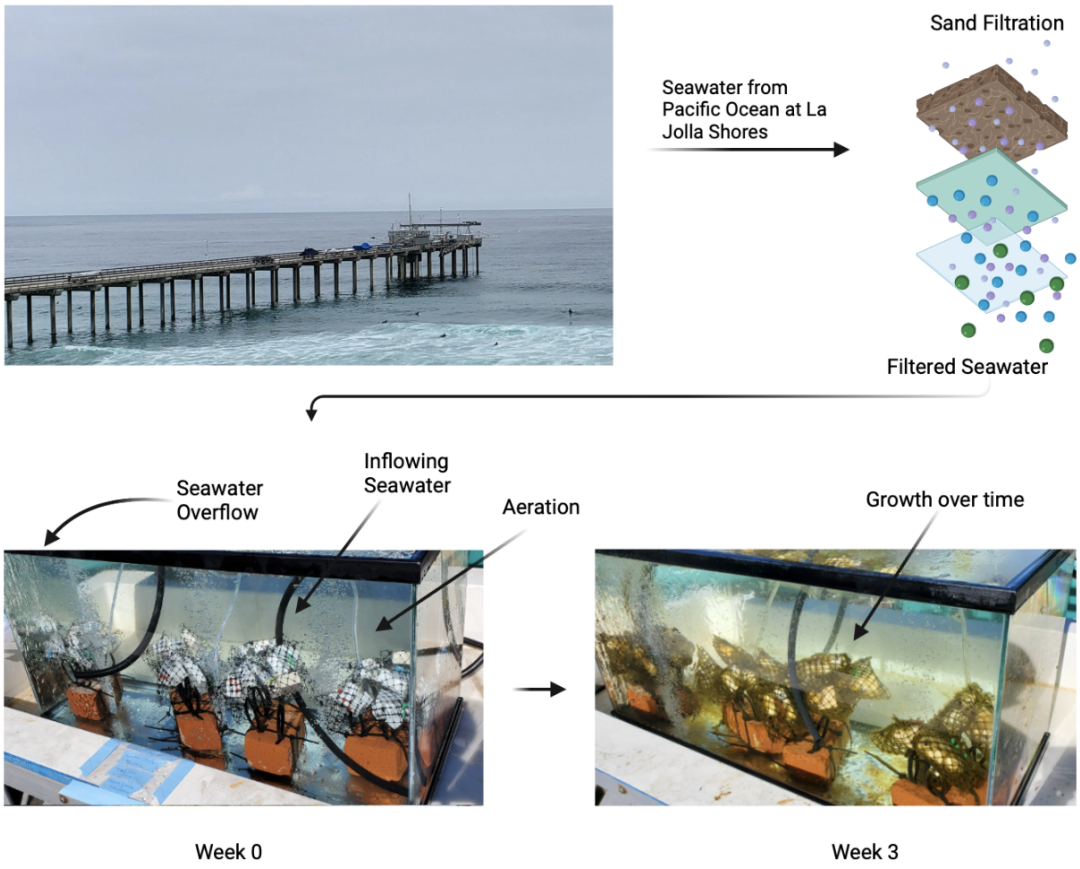

Figure 1: Explanation of Seawater Table workings[viii]

Compared to the seawater table, the SIO Pier samples were placed directly into the ocean and held in a bag to keep them secure. This is a more accurate representation of what would happen to plastics that are disposed of in the ocean, but it is more difficult to control variables for, as the environment itself is not fully controlled, and is dictated by more natural forces.

The composted samples were placed in an incubator inside a sample of the University of California San Diego's Revelle College compost. The plan is to compare the data from the composted samples to the seawater environments to determine the efficacy of digestion on composted plastic foams. The compost provides a denser population of bacteria and fungi, giving

the microbes more direct access to biodegradation. Compost is considered the most efficient environment and a reference point for comparison.

Compost will be used as the pure baseline for biodegradability, as it is the most reliable and researched of the three environments. The Pier and SWT will be compared to compost to see how the degradation measures up. The SIO samples have the benefit of being exposed to a more accurate representation of the ocean, much like those plastics that get deposited in the ocean would. This gives a much clearer picture of what would happen to the foam samples if they were to be simply thrown into the ocean to degrade. This however does leave SIO samples open to many more variables that could change the course of their degradation. Variables like wave strengths, sea animals, and ocean temperatures can change the course of the experiment drastically without detection. The SWT on the other hand will be in a far more controlled environment, with the main variables affecting the degradation being microbiomes, UV radiation, and seawater itself. The current will be controlled, as will the ecosystem the foams will be subject to. In short, the SIO samples have the benefit of being exposed to an environment more accurate to disposed plastic but will be harder to track sources of degradation. SWT samples will be easier to monitor, and be easier to draw conclusions from, but does not represent the full ocean environment.

2.2 Biodegradable

The term biodegradable will be used frequently throughout the analysis, and though determining the biodegradability of the foams was not the focus of the experiment, it will be important to scientifically define and understand what the term means scientifically.

Biodegradable plastics must be “decomposed rapidly by microorganisms into elements found in nature…”[ix] as defined by the European standard EN 13432:2002. To clarify, this means that plastics that are only broken down by tides, rocks, or other mechanical means cannot be considered biodegradable.

2.3 The Polymers

A variety of polymers were analyzed throughout the experiment, each with a unique chemical makeup that could affect the biodegradability of the foam. Plastic foam samples of Polyurethane (PU), Ethylene Vinyl acetate (EVA), Polyurethane infused with f/2 media (f/2), Polyurethane infused with Iron Stearate (Fe), Thermoplastic Polyurethane (TPU), Polyether Polyurethane (Polyether), Ethylene Propylene Diene Monomer (EPDM), and a final experimental biodegradable foam FDCA.

PU is a polymer chain composed of linkages between Di-isocyanate and polyol segments as shown in Figure 2. This polymer has already been known to biodegrade, but the ability to do so is dependent on several factors. The type of polyol monomers used in the formulation can affect biodegradability, varying chain sizes, allowing for less availability to break the bonds between monomers. Biodegradability is also affected by the structure of the polymer itself, with PU foams having a more accessible surface area with which microbes and fungi can attack, creating more possible sites for biodegradation to occur.[x] This could explain the differences in degradation of the PU foams from the TPU plastic, where the TPU is a thermoplastic, meaning it is less of a foam and more of a conventional plastic that is prone to becoming more fluid and rubbery at higher temperatures. The two form differently, as the foam versions of plastics have gasses introduced during the formation, causing pockets of air to form throughout the polymer.

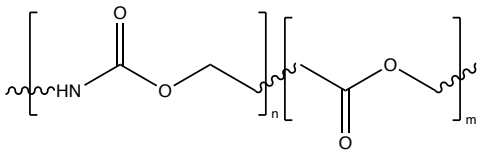

Figure 2: Chemical components and makeup of Polyurethane

The f/2 and Fe samples contain these same components, alongside sodium nitrate, monosodium phosphate, and vitamin B12 from f/2 media and iron stearate embedded into the foam itself. This can be done by incorporating nanoparticles of Fe or f/2 into the polyol or Isocyanate solutions before reacting them to create the foam, or integrating the nanoparticles into the pre-made foam by immersing the foam in a solution of the nanoparticles, or a metal salt solution with components of the desired particle.[xi] In this case, the polyurethane foams were submerged in their respective salt solutions.

Polyether Polyurethane foam was also used as a sample, which is a variation of regular polyurethane, integrating segments of ether bonds into the structure of polyurethane rather than the normal ester bonds. Polyether PU's are meant to be more mold and bacteria-resistant than polyester polyurethanes, so this may lead to them showing less biodegradation.

Ethylene Vinyl Acetate, EVA, is another polymer comprised of two different monomers of ethylene and vinyl acetate, shown in Figure 3. EVA is generally not known to biodegrade, so this was used as a general control across environments.

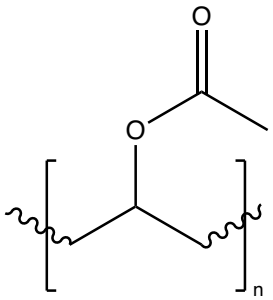

Figure 3: The segments and connection of Ethylene Vinyl Acetate

EPDM rubber is comprised of 3 monomer segments of ethylene, propylene, and diene as the name suggests. These components are all carbon and hydrogen-based, with no ester, ether, or urethane linkages as shown in Figure 4, creating another polymer that would be difficult to biodegrade.

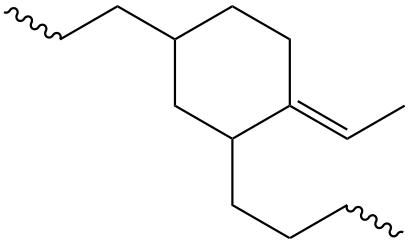

Figure 4: Possible Structure of EPDM Polymer

Finally, the FDCA foam produced by Algenesis is a bio-based, highly degradable foam whose formula cannot currently be disclosed.

Each foam has a noticeable chemical difference in its polymer structure, which provides a range of possible degradation.

2.4 Fenton's Reaction

As noted previously, the process is based on a reaction previously used to purify and collect microplastics from compost and sewage, with the main difference being between the

plastic sizes, and sheer masses of biomaterial to react with. The plastics that were being used in these references are defined as microplastics: plastics that are defined as being smaller than 5 millimeters. Though this is also a field of study that requires more research, the plastics used in this study are around one cubic centimeter in size and are also foam. The other large difference between the studies and this research is the studies were used to separate and filter out microplastics and other artificial debris from either large compost samples or large samples of wastewater, and those that are quantitative are for microplastic collection.

The reaction was performed using thirty percent hydrogen peroxide and an acidic solution of an Iron (II) Sulfate complex. When combined, the resulting solution is known as Fenton's Reagent. Fenton's Reagent contains Iron (III), water, and a hydroxide radical[xii]. Figure 5 shows the total kinetic equation of the formation of radicals in the solution. The key reactant in this equation is the hydroxide radical. The radical form of hydroxide is a chemical that readily oxidizes and breaks down organic materials while leaving the plastic components intact.

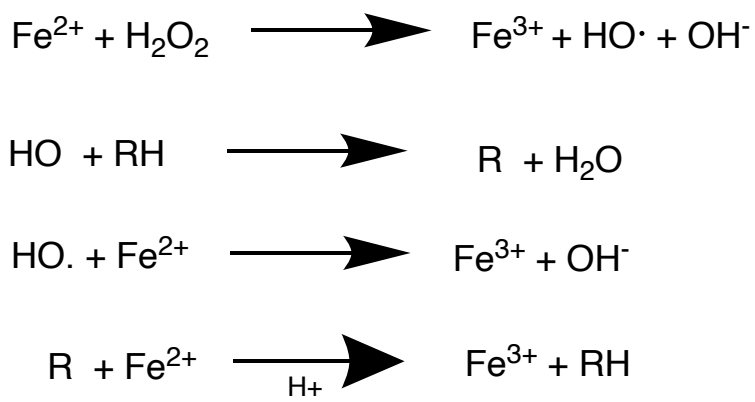

Figure 5: Fenton's Reaction

Over the years, multiple mechanisms have been proposed for how this hydroxide radical interacts with all kinds of organic chemicals to break them down. Some of these mechanisms

show that Fenton's Reagent degrades carbohydrates, as the Hydrogen may be removed from carbons by the hydroxide radical, generating a carbon radical. This reaction has such low kinetic favorability when compared to reactions involving primary alcohols, ethers, and dimethylformamide that it is negligible.[xiiixiv] It is worth noting that these radicals are very short-lived, and only exist for a fraction of a second, making this reaction reliant on readily accessible points for these hydroxide radicals to attack.

Most of these reactions involve the hydroxide radical taking hydrogen from a molecule to form water, leaving behind an electron to form another radical, favoring those involving hydrogen bonding or possible resonance. The resulting radical is due to the dipole or resonance in these structures creating more stable positions for these radicals. The reactivity of alcohols and ethers such as THF and dimethylformamide is explained based on their radical stability, making them more susceptible to breaking down via Fenton's reaction. Conversely, the lack of stable radicals explains why it is poor at breaking down synthetic polymers since EVA and EPDM have structures lacking in more accessible hydrogens. Even the more degradable polyether and polyurethanes only contain small segments of dipole bonding, with fewer points of access for the hydroxide radicals to attack.

Throughout the paper, Fenton's reaction will be referred to as either Fenton's reaction, peroxide digestion, or wet oxidation, as the literature uses each term for the reaction interchangeably.

2.5 Mass Loss

The Fenton reagent removes biomaterial attached to plastics during degradation, leaving the remaining polymer intact. This allows for a comparison of masses before degradation and

after degradation and digestion. With the masses compared, a percent can be yielded of how much less mass the degraded samples have when compared to their previously undegraded masses. This percentage then represents a quantitative measurement of the plastics' biomass accumulation and biodegradation.

2.6 FTIR

Another method of comparing differences in plastics before and after digestion and proving the loss of biomaterial is via Fourier Transform Infrared Spectroscopy (FTIR). Rather than measuring physical characteristics, FTIR can measure chemical differences in materials.

FTIR spectroscopy relies on the idea of light absorption, specifically infrared light: light with a wavelength between 760-100,000 nanometers. An FTIR Spectrometer will fire infrared light at a sample. When this light hits the sample, some wavelengths can be absorbed by specific chemical bonds, causing them to oscillate, vibrate, or rotate. Which wavelengths of light are absorbed is dependent on the energy required to cause the bonds to move. Some bonds move at higher energies, requiring shorter wavelengths to be absorbed, and some move at lower energies, requiring longer wavelengths to be absorbed. The light that makes it through the sample without being absorbed then hits a detector, which measures how much of the infrared light was absorbed throughout the sample and outputs a graph of the data.

This analysis method is very efficient at identifying certain functional groups within a molecule, as different functional groups will vibrate with different frequencies and energies. In the experiment, FTIR spectroscopy was performed mainly to distinguish what chemical differences arose after the foams' peroxide digestion and how they might have changed, as well as to determine the water and biomaterial amount within each sample.

2.7 Compression

The final variable to be measured during the experiment is the compression of the foams. The compression test measures the force required to compress the samples to exactly half their size, measured before and after being placed into their respective degradation environments. This test was more of a quantitative structural stability assessment, with some foams threatening to break during the measuring process, this step requires the most amount of forethought on whether to include in the analysis, as sometimes making this measurement can destroy the sample.

Chapter 3

3.1 Materials

The digestion reaction itself required 500mL of 30% Hydrogen Peroxide and 500g of crystalline Ferrous Sulfate Heptahydrate which were both obtained through Fischer Chemical, and 2.5mL of Concentrated Sulfuric Acid acquired through EMD Millipore Chemicals. Running the reaction required a face shield for any step involving Hydrogen Peroxide, and chemical

In terms of instrumentation, the Mass Balance that was used to determine the weights of foams was a Mettler Toledo New Classic MF model number MS2045 103. The instrument used to test compression force was a Mecmesin Multi-test -dV model 16-1004-12, and the IR was a Nicolet i520 Smart iTX.

3.2 Methods

Samples were placed into their environments and removed at their respective timeframes for analysis. For the Pier and Seawater Table (SWT) Samples, four of each of the seven sample types were removed every month. For compost samples, one sample was removed at a time due to the size of the samples. Pier samples were collected monthly for one year starting in January, SWT samples were collected monthly for six months starting in January, and compost samples were collected every four weeks for 16 weeks starting in May. The total number of samples for the pier, SWT, and compost came out to 308, 120, and 12, respectively.

SIO Pier and SWT samples were organized into colored bags, separated by foam type and time of removal. They were then fully submerged in their respective environments and left to degrade until the designated month of removal. Compost samples were placed into a container with compost from Roger's Garden and then stored in an incubator for degradation until the designated week of removal.

When samples were removed from their respective environments, they were dried and stored in boxes with a 10x10 grid system, with columns labeled with numbers, and rows labeled with letters A through J. This ensured that visually indistinguishable cubes were able to be tracked by their place in the grid system. Moving forward, individual cubes may be referred to by their environment, box number, and then grid assignment. Each cube had a unique assignment within the grid system.

After receiving degraded samples, the foams were weighed, compression tested, and analyzed on the FTIR. Masses were taken by placing a clean weigh boat into the balance and taring before placing each sample into the boat. The masses to the nearest ten-thousandth of a gram were recorded in an Excel sheet.

The compression analysis measured each foam and recorded the force required to compress them to half their height. The foam was placed on the flat table, and the compression arm was lowered until the force reading increased to half of a Newton. The height was then recorded and divided in half to determine the start and end point of the compression process, with the start point being the height of the arm barely touching the cube and the endpoint being exactly half of that. The method took an average force over 5 compressions on each foam, measured in Newtons.

Figure 6 shows the method for the FTIR analysis, which involved nine scans at a resolution of 2 nm. The results were displayed in Absorption for ease of peak comparison. They were then saved as spectrograph (SPA) and Excel files for analysis.

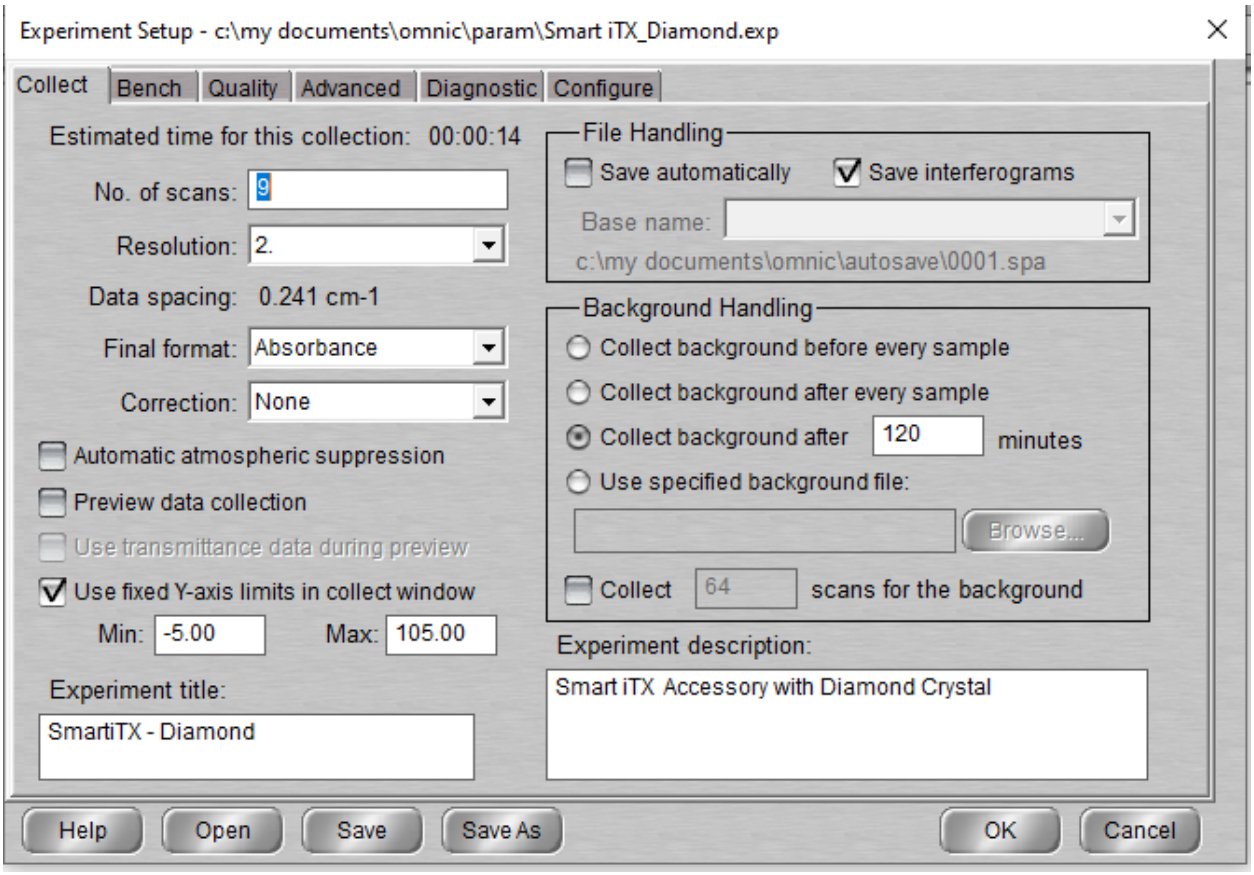

Figure 6: FTIR Method Setup

Next, the samples underwent peroxide digestion. The Iron Sulfate complex was created by Dissolving 7.5g of Iron Sulfate Heptahydrate in 500mL of DI water, forming a blueish solution. Once dissolved, 3mL of concentrated Sulfuric Acid was added. Fenton's Reagent was created by mixing equivolume (30mL each) 30% Hydrogen Peroxide and an Iron Sulfate complex, which formed an amber-orange colored solution of Fenton's Reagent. The samples were then submerged in Fenton's solution to ensure contact with all biomaterials. After 30 minutes the reagent and sample were heated in a water bath to 55 C, the heat was then removed as the exothermic reaction catalyzed itself, reaching upwards of 75-90C during the peak of the reaction before settling back down at 55C. The reaction had a visual indicator of rapid bubbling, volume expansion of the reagent, and a color transition from orange to yellow. The reaction

lasted 5 minutes before cooling down for another 15 minutes. The sample was removed from the solution, rinsed of Fenton's, and left to dry overnight in a vacuum desiccator. IR and mass data were collected again to compare to pre-digested foam data.

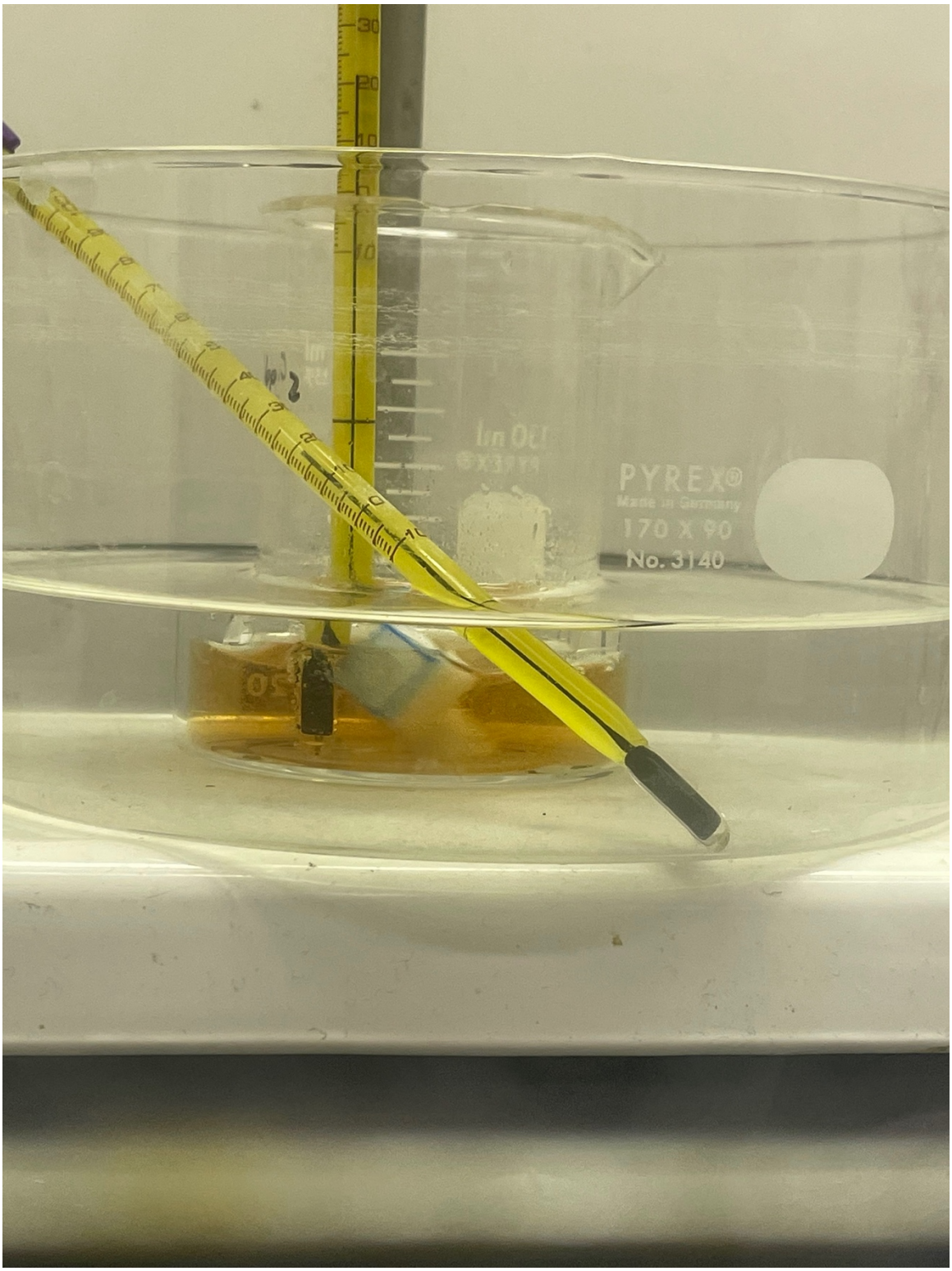

Figure 7: Peroxide Digestion Setup Before Reaction

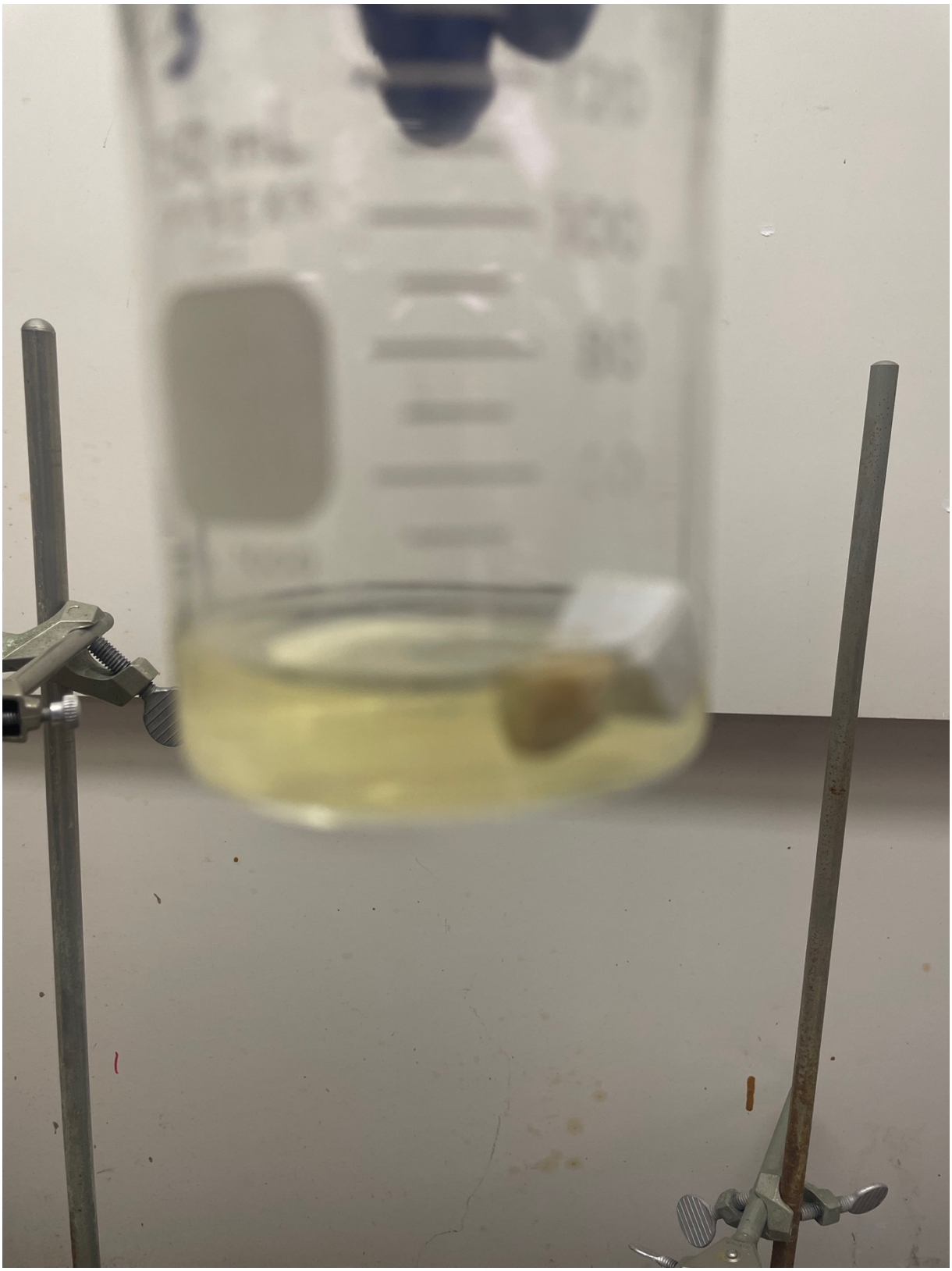

Figure 8: Peroxide Digestion Solution After Reaction

Finally, REEF flip-flop Footbed standards were run to determine the mass loss on unreacted samples. The data for this is shown in Figure 9 where negligible changes in mass occurred because of peroxide digestion alone.

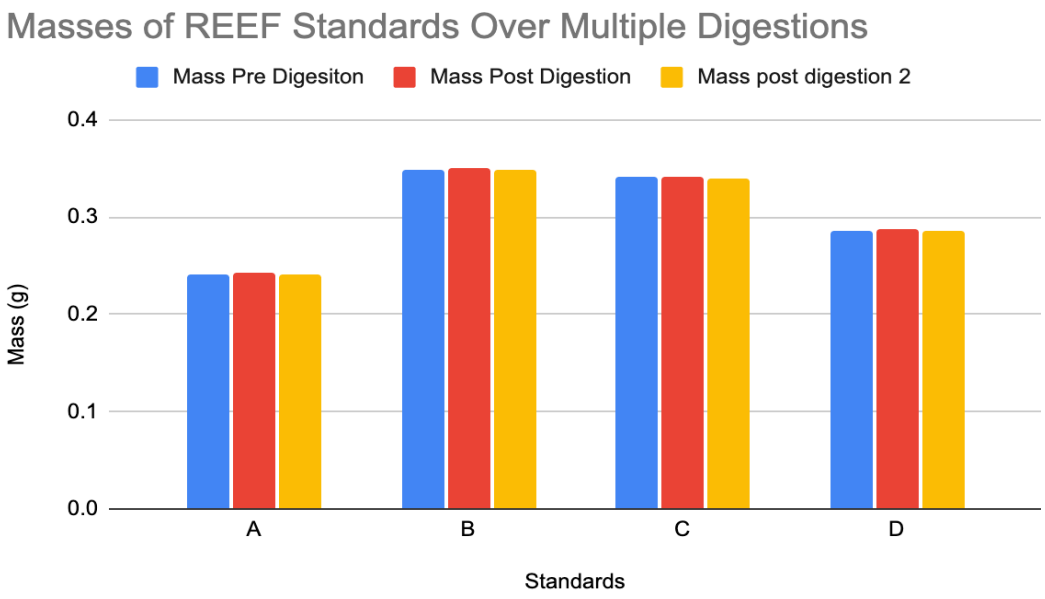

Figure 9: Masses of 4 standard REEF foams before peroxide digestion, after peroxide digestion, and after a second peroxide digestion.

Chapter 4

Table 1: SIO Pier Mass Loss Data

Month of Degradation	REEF (% Mass Loss)	EVA	f/2	Fe	TPU-FC1	Polyether	EPDM
2	5.03	3.29	3.79	2.20	-0.20	8.86	1.33
3	11.61	3.24	11.79	10.66	1.83	19.48	3.22
4	12.39	4.27	10.09	12.10	1.83	17.06	5.49
5	9.23	2.99	8.74	5.34	0.20	11.56	1.28
6	19.45	11.32	24.04	22.34	1.86	19.13	6.26
7	20.23	6.89	17.79	12.08	2.47	15.60	8.07
8	16.48	4.30	13.29	14.83	1.58	15.69	11.19
9	18.08	7.34	21.67	19.35	2.70	22.08	7.81
10	18.55	9.56	9.31	20.51	1.25	19.49	3.98
11	15.11	8.61	15.33	19.42	2.08	12.80	6.36
12	24.74	12.81	22.70	16.52	4.48	17.86	11.27

Table 1 gives numerical data for mass loss between SIO Pier samples before and after peroxide digestion. The values were calculated by subtracting the post-digestion mass from the pre-digestion mass and dividing over the pre-digestion mass to generate a ratio. Then this was multiplied by 100 to determine the percent of mass lost during peroxide digestion. Each data point in Table 4.1 represents an average percent mass loss of the 4 samples of each plastic type, with a total of 336 samples recorded.

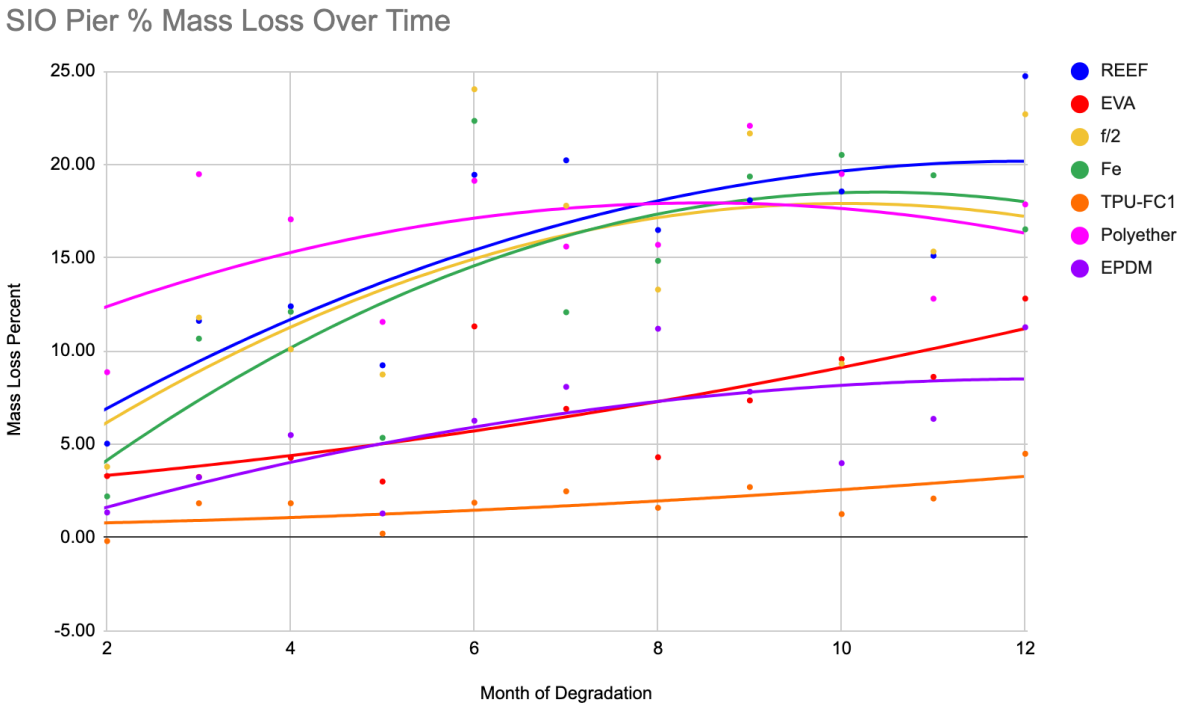

Figure 10: SIO Pier Mass Loss Data

Figure 10 gives a visual representation of the data portrayed in Table 4.1. The data was plotted on a scatterplot, and polynomial lines of best fit were created for each foam.

Table 2: SIO Pier Compression Data

Month of Degradation	REEF (N)	EVA	f/2	Fe	Polyether	EPDM	TPU-FC1
2	15.13	20.25	3.79	2.20	24.38	25.63	603.88
3	14.00	21.88	15.88	15.25	28.63	21.75	646.38
4	9.63	20.50	14.25	13.63	25.50	25.13	509.25
5	12.88	23.13	14.38	15.63	25.25	29.00	601.38
6	10.75	19.63	12.38	10.88	21.25	28.63	505.63
7	9.50	20.88	11.50	11.63	21.25	27.38	570.75
8	8.13	20.25	10.75	8.88	24.63	33.00	535.75
9	8.63	22.50	6.88	11.38	24.63	38.00	579.75
10	5.63	19.75	11.63	7.38	24.25	33.38	579.75
11	12.63	22.13	9.88	8.25	23.75	34.75	575.00
12	4.63	17.63	4.13	5.38	17.63	14.00	491.25

Table 2 depicts the numerical data for the compression of samples from the SIO Pier. These values are the force exerted to compress each foam to half of its height after being removed from the pier, but before being digested. Each data point in Table 4.2 represents an average compression force of the 4 samples of each plastic type, with a total of 168 samples recorded.

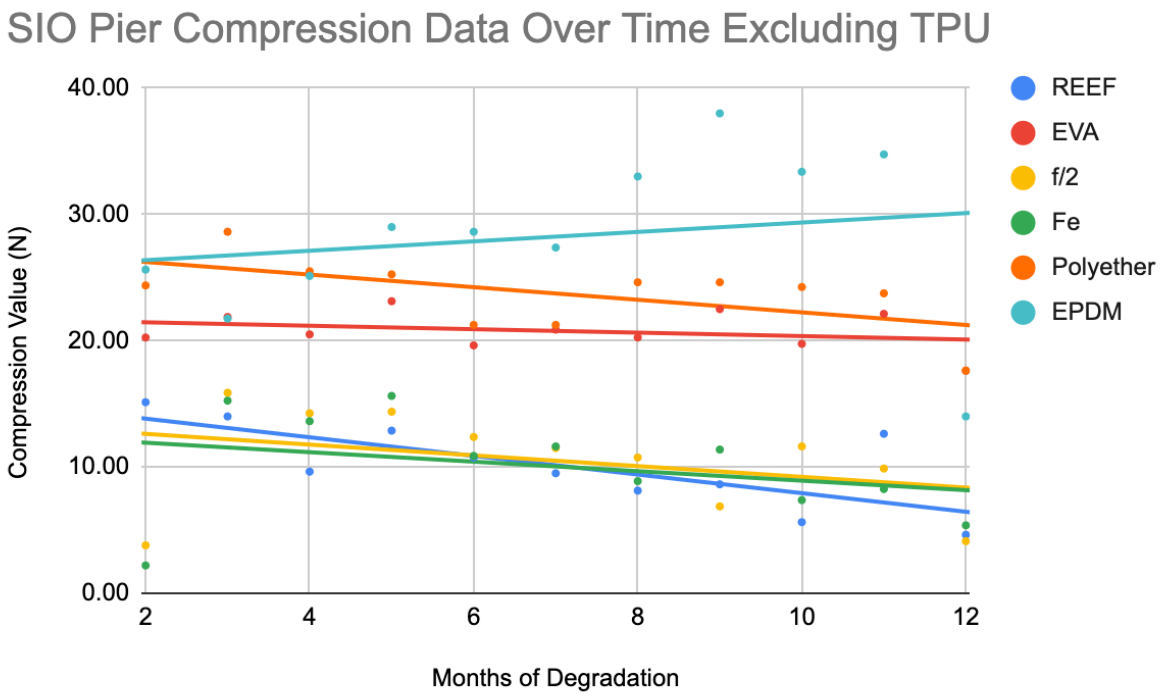

Figure 11: SIO Pier Compression Data

Figure 11 is a visual graph representation of the data in Table 4.2. TPU data was excluded because the data skewed the graph to a degree that made conclusions difficult to draw between the other foams. The TPU data was around 500N compared to the other foams that lay around 10-20N, so the differences are readily apparent without needing to consult a figure. Linear lines of best fit and their relative equations for each foam are given for each foam.

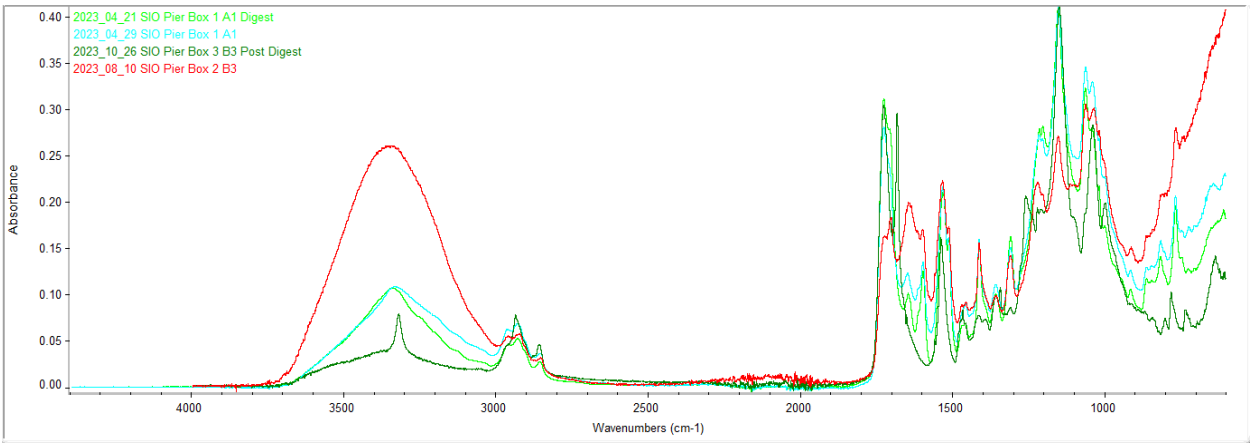

Figure 12: Reef Footbed FTIR Comparison

Figure 12 shows a set of FTIR graphs for the Reef footbed foams. The A1 data comes from Reef foam placed in the SIO Pier environment for 1 month, and the B3 data represents Reef foam from 6 months of degradation. The unlabeled A1 and B3 data represent the foams before digestion but after degradation, and the post-digest data represents the foams after being digested. These points were selected as they were the points with the greatest difference in mass loss percent. They are presented this way to create the clearest comparison of FTIR data among foams of the same type. This was applied to all FTIR graph data.

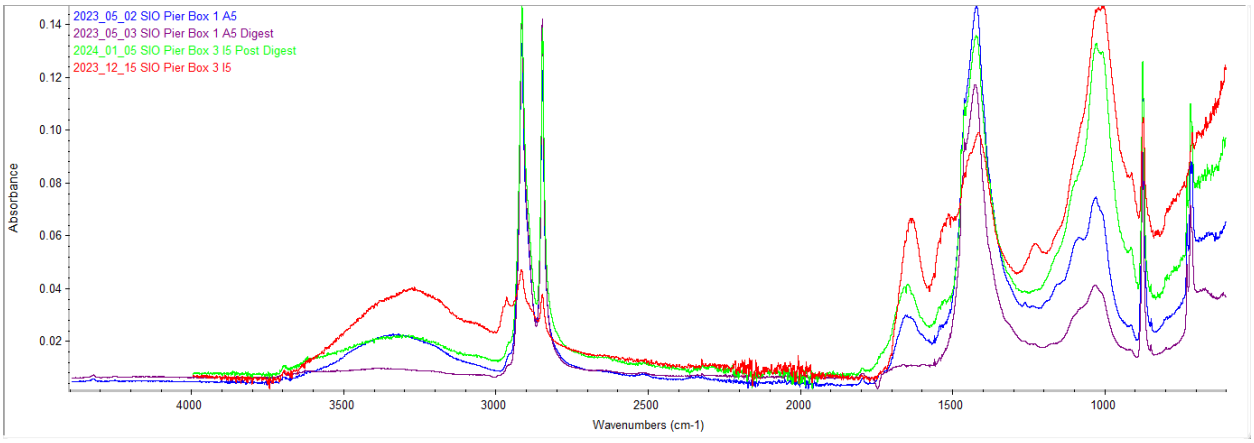

Figure 13: EVA FTIR Comparison

Figure 13 depicts FTIR data for EVA foams from the SIO Pier data. Similar to Figure 4.3, the letter combinations represent foams from different timeframes in the degradation process. Foam A5 is an EVA foam degraded over 1 month, whereas I5 is a foam degraded over 12 months.

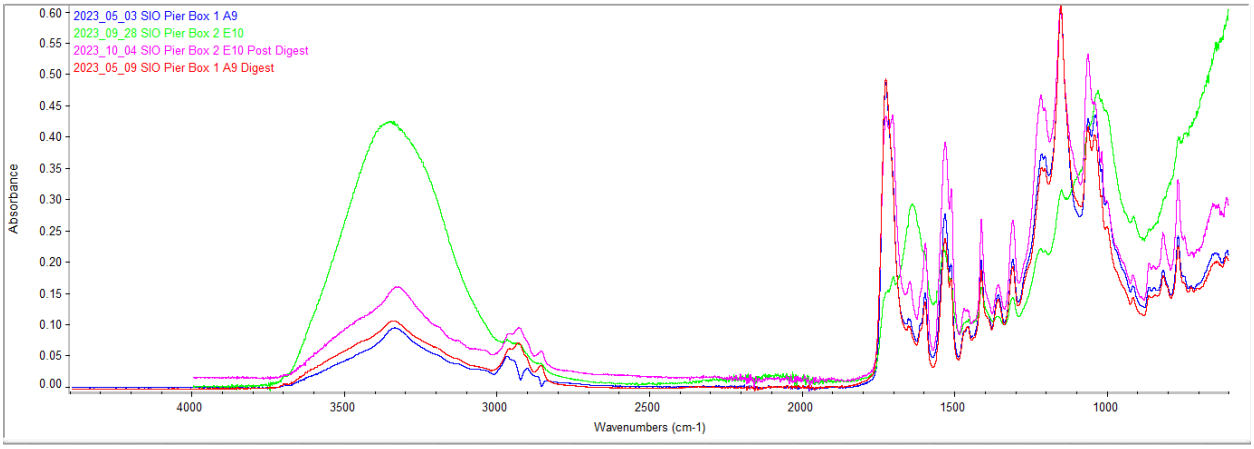

Figure 14: f/2 FTIR Comparison

Figure 14 shows FTIR data for f/2 foams from the SIO Pier, with A9 being a foam that was degraded over 1 month, and I9 being a foam degraded over 12 months.

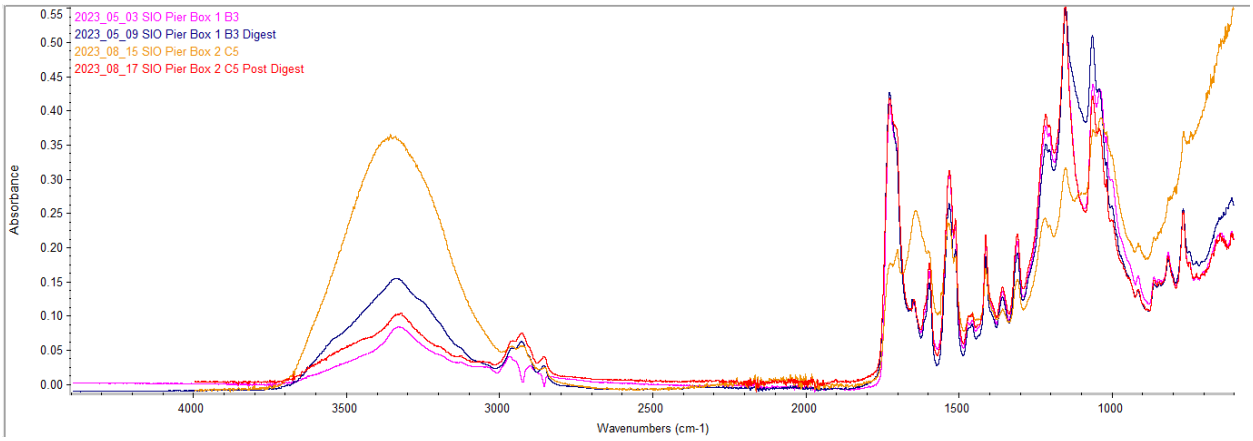

Figure 15: Fe Stearate FTIR Comparison

Figure 15 represents FTIR data for Fe Stearate foams from the SIO Pier, with B3 being a foam that was degraded for 1 month, and C5 being a foam that was degraded for 6 months.

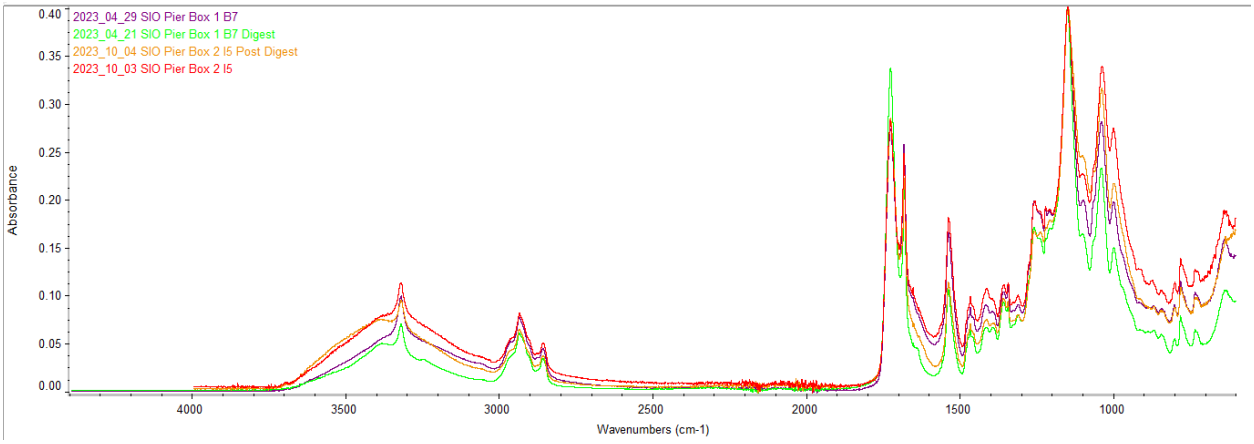

Figure 16: TPU FTIR Comparison

Figure 16 represents FTIR data for TPU plastics from the SIO Pier, with B7 being a plastic degraded for 1 month, and I5 being a plastic degraded for 8 months.

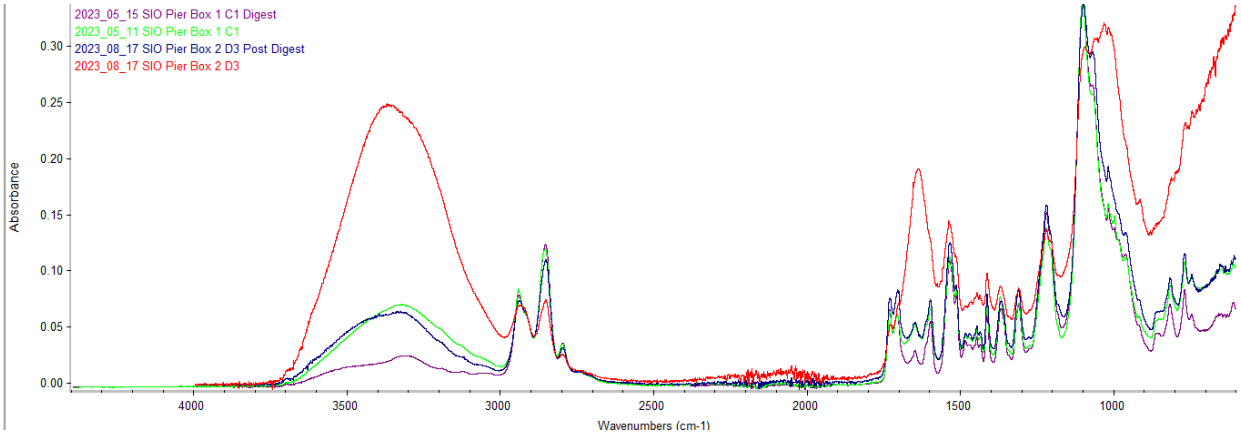

Figure 17: Polyether FTIR Comparison

Figure 17 portrays FTIR data for Polyether foams from the SIO Pier environment, with C1 being a polyether foam degraded for one month, and D3 being a foam degraded for 6 months.

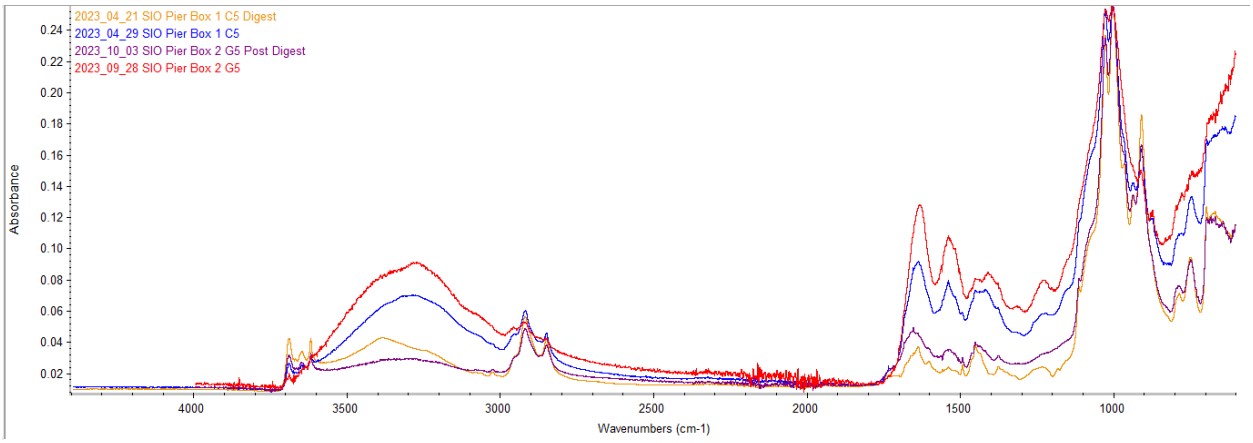

Figure 18: EPDM FTIR Comparison

Figure 18 represents FTIR data from EPDM foams from the SIO Pier data, with C5 being an EPDM foam degraded over 1 month, and G5 being a foam degraded over 7 months.

Table 3: SWT Mass Loss Data

Month of Degradation	Reef (% Mass Loss)	EVA	f/2	Fe	TPU	EPDM
3	7.02	0.14	6.39	6.78	0.70	1.96
4	21.27	0.30	26.69	21.57	1.14	5.01
5	20.15	6.60	25.80	25.28	1.63	4.01
6	27.67	12.10	29.90	26.14	1.88	5.54
7	29.84	5.42	10.94	8.63	0.45	4.13

Table 3 gives numerical data for the percent mass loss on SWT samples throughout their degradation. This was calculated in an identical way to that of Table 4.1.

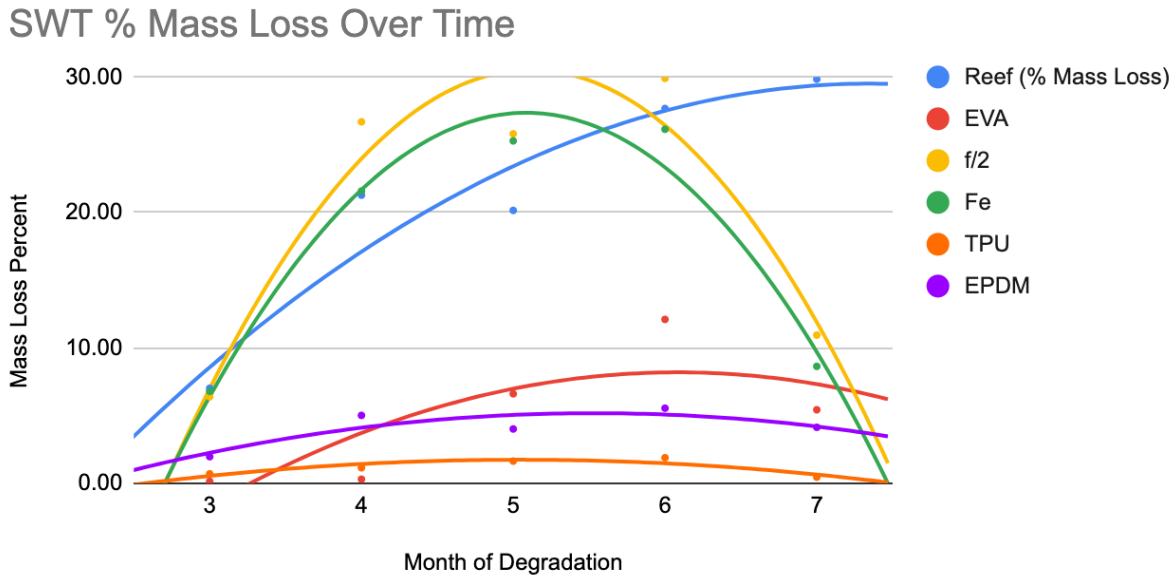

Figure 19: SWT Mass Loss Data

Figure 19 gives a graphical representation of the data from Table 4.3. The equations associated with the figure are a polynomial line of best fit for each set of foams.

Table 4: SWT Compression Data

Month of Degradation	Reef (N)	EVA	f/2	Fe	EPDM	TPU
3	14.17	20.50	14.88	16.00	16.50	435.38
4	13.88	17.88	13.88	16.75	16.50	484.13
5	14.63	20.00	15.25	16.75	15.38	548.75
6	14.00	23.00	15.25	17.50	16.63	526.00
7	12.00	19.25	15.88	13.63	16.38	521.00

Table 4 Gives the compression data for samples from the SWT environment. The data was acquired identically to Table 4.2. Once again, TPU is significantly separated from the rest of the data, and because of this, was excluded from Figure 4.11.

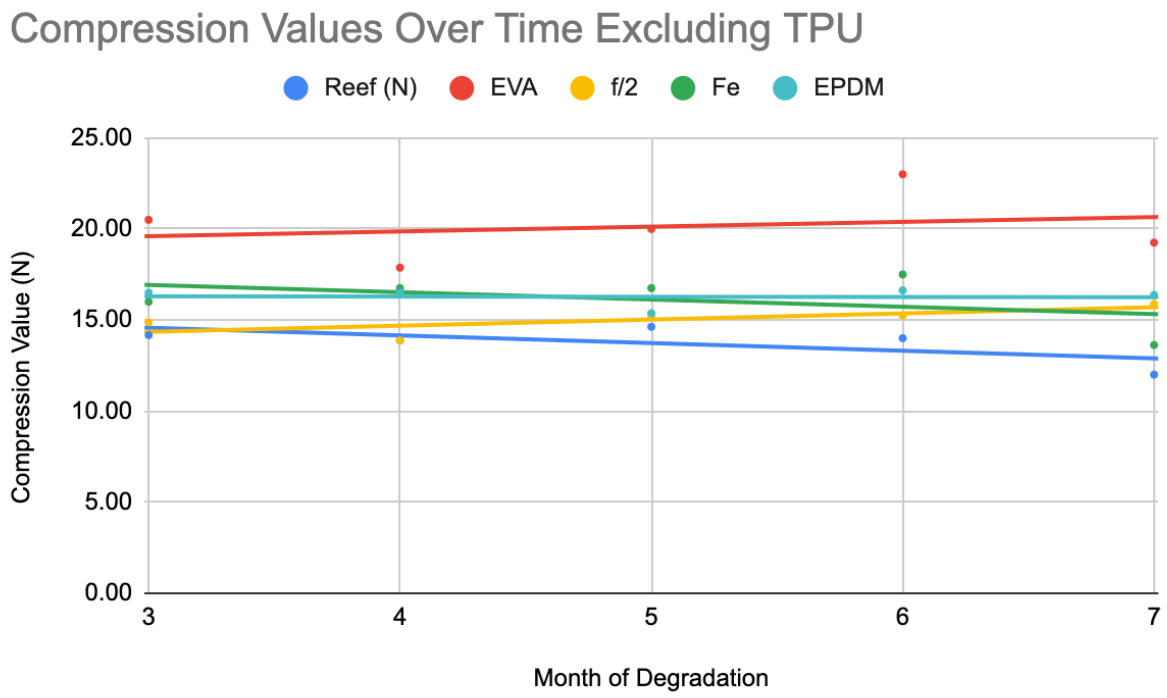

Figure 20: SWT Compression Data

Figure 20 is a graph of the data from Table 4.4, with the exclusion of TPU data. Linear trendlines were estimated for each foam, with their equations displayed on the right of the graph.

Table 5: Compost Mass Loss Data

Weeks of Degradation	FDCA (% Mass Loss)	EVA
0	5.04	0.42
4	41.34	-6.49
10	82.88	-1.14

Table 4.5 contains data from the foams in the compost environment. The data was obtained in the same way as in Tables 4.1 and 4.3. Each data point represents one foam that was recorded. Initially, there were 6 of each type of sample that were intended to be recorded, but after the third data point, the FDCA cubes were no longer measurable as they had degraded almost entirely.

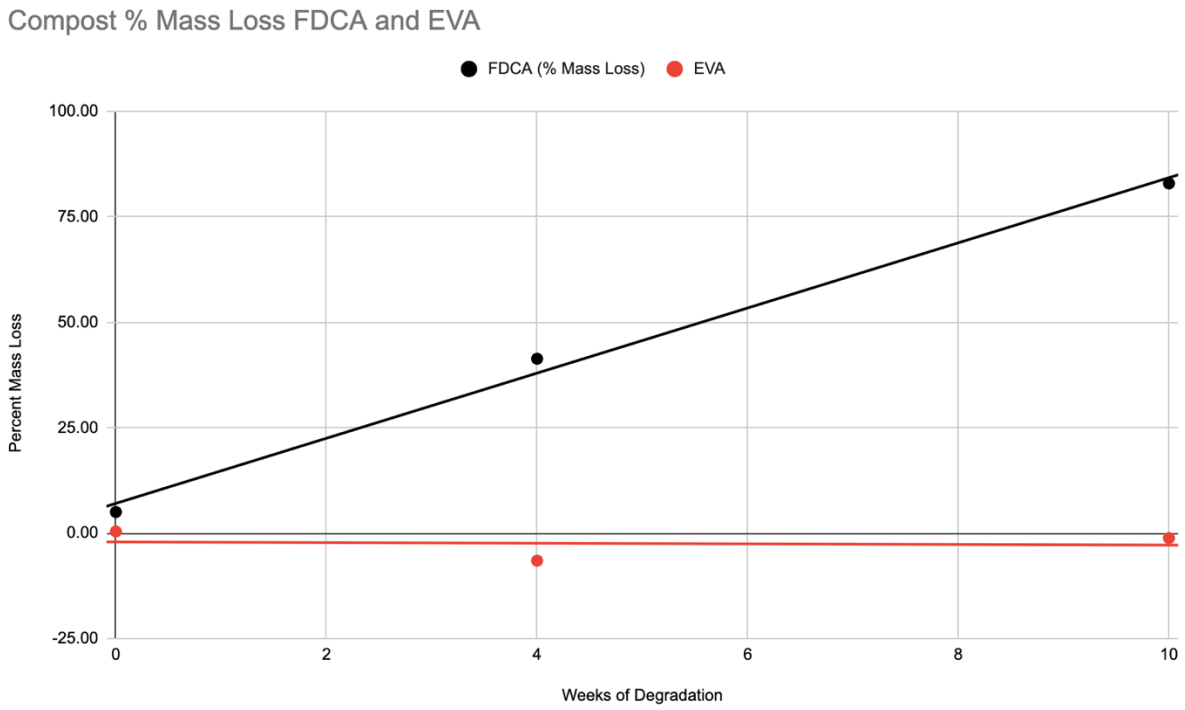

Figure 21: Compost Mass Loss Data

Figure 21 graphs the data from Table 4.5, with linear trendlines estimated and shown at the top of the graph.

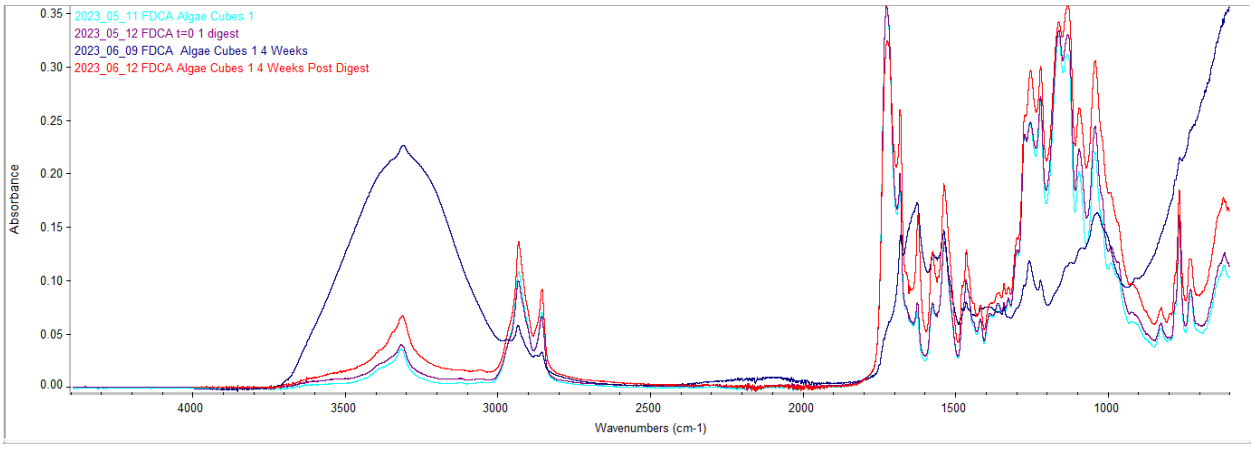

Figure 22: FDCA Compost FTIR Comparison

Figure 22 represents FTIR data for FDCA foams from the SWT, with t=0/ cube 1 being the non-composted standard.

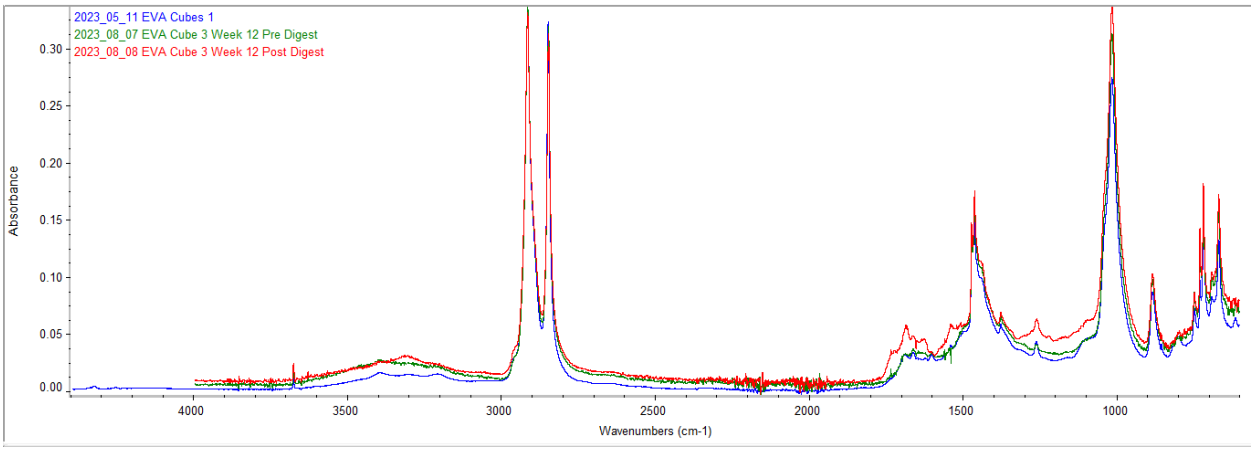

Figure 23: EVA Compost FTIR Comparison

Figure 23 represents FTIR data for EVA foams from the SWT, with cube 1 being a non-composted standard.

Chapter 5

5.1 Analysis

The mass loss data is the clearest to assess. Figures 4.1, 4.10, and 4.12 all tell a similar story. The Biodegradable foams (Polyurethane, f/2, Fe, Polyether, and FDCA) all have significantly higher percentages of mass loss during peroxide digestion. This is due to the biomass of organic material growing more favorably on these biodegradable foams. With more organic growth, more material was broken down during Fenton's reaction, creating a larger difference in mass.

The curves shown on each of the mass loss figures may be explained by algal growth cycles, with certain months providing more growth than others. This is shown in the graph, with the greater mass loss being between months 4-7. Months 4-7 were between May and August.

Each graph also shows that the more biodegradable polyurethane foams not only degrade similarly but degrade at a nearly identical rate, with a mass % loss rate following a negative parabolic trend over the year that could become a sin curve given more years of data, given from the line of best fit from Figure 9. This shows that the mass loss percent aspect can be used as a quantifiable aspect of biodegradation, where biodegradable foams can be categorized by their rate of percent mass loss over time, and non-biodegradable foams can be categorized as a different rate. These trendlines can be attributed to natural growth and decay cycles of biomaterial in the area, becoming most abundant during the summer, and decaying during the colder months.

Compression testing also revealed similarities among biodegradable foams compared to their non-biodegradable counterparts. Including TPU skewed the data and made it difficult to

visualize, so it was excluded from both compression graphs. However, their respective tables show the compression of TPU to be over one order of magnitude greater than the foams (500 compared to 25). With TPU excluded, however, we can see again that the polyurethane foams stand distinct from the non-biodegradable foams, except for EPDM interspersed among the SWT data. We expect that biodegradable foams would have to decrease compression forces over time, while the non-biodegradable foams would stay roughly flatlined, supported by all data trends except for f/2 data from the SWT. This could be due to the shorter timeframe of the experiment not allowing for enough data points to show as clear of similarity and trend as that of the SIO samples. Otherwise, it holds that only the biodegradable samples had downward trends in their compression forces. It is also noted that the non-biodegradable foams have a positive trendline, which could be due to the foams not degrading but getting denser with time, causing the compression force to rise, creating yet another point of quantifiable difference between biodegradable and nonbiodegradable foams.

FTIR data shows how well different biomaterials grew on each of the foams. With the Reef Footbed, Fe Stearate, Polyether, and FDCA foams, a large difference in the peaks around 3300 nm from degraded but not yet digested samples shows a significant increase in alcohol groups. This coincides with known FTIR data of common lipopolysaccharides, a molecule found in living bacteria[xv]. These spectra showed up only in biodegradable foams after they had been exposed to their environments for significant periods. This indicates bacterial and algal growth on these foams, as opposed to the spectra of EVA or TPU, which look nearly identical across all time frames.

Each method has proven a useful way to discern biodegradable foams from non-biodegradable foams. With the variables combined, the data reads clearly that the polyurethane

foams and the polyether foams biodegraded when compared to the EVA, TPU, and EPDM foams, which coincides with our original understanding of the foam compositions. The best method for quantitatively determining biodegradation is mass loss, showing a clear separation of biodegradable and non-biodegradable foams, with equations derived from their percent mass losses that can be used to predict further degradation of similar foams. Compression also gives a clear indicator of which foams are biodegradable and which are not by the separation of foam types by compression factor and the positive or negative slopes of their respective trendlines, with biodegradable foams showing a negative trend in compressive force and nonbiodegradable foams showing a positive trend. FTIR helps determine algal and bacterial growth but requires the quantitative evaluation of the other two methods.

5.2 Error

A few questions arose throughout the experiment that needed to be tested. One such question was if we could shorten the digestion time from 4 hours, seeing as the process was lengthy, with many samples to get through. A separate experiment was done with semi-degraded foams that were not being used for mass loss to test the digestion timeframe. This data is shown in Table 5.1. It was proven that the process could be shortened. The initial process took 2 hours of letting the foams soak in Fenton’s reagent before heating for another 2 hours. This is because the process was developed from a method used for large-scale industrial compost and sewage environments searching for microplastics among several pounds of material. After doing a time variable experiment, it was determined that the process could be shortened to half an hour of soaking followed by a half hour of heating for our foams. The foams only take around 20 to 30 minutes to allow the Fenton's reagent to integrate itself throughout the foam, and another 30

minutes for the full reaction to heat up to the required 60 degrees Celsius and react. This cut the reaction time down to 25% of what it initially was, saving hours per day.

Table 6: Percent Mass Loss Per Digestion Timeframe

Sample	2 hours	4 hours	1 hour
1	3.8476	6.7084	4.1570
2	4.6539	3.0505	5.2886
3	4.8570	2.7778	4.6262
Average	4.4528	4.1789	4.6906

Another question was whether the hydrolysis of the ocean water influenced the foams themselves as opposed to them only being degraded by biomaterial, and if this hydrolysis would influence the digestion process. To address this concern, the foam was also tested by hydrolyzing undegraded foams to various degrees and digesting them to determine mass loss. The results of this experiment are given in Figure 24. The hydrolysis seemed to make the foams themselves more brittle, and subject to crumbling. During digestion, the foams would begin to fade and shed small particles. These small particles were collected via filtration after digestion and weighed alongside the foams to determine if mass loss was significant in this way.

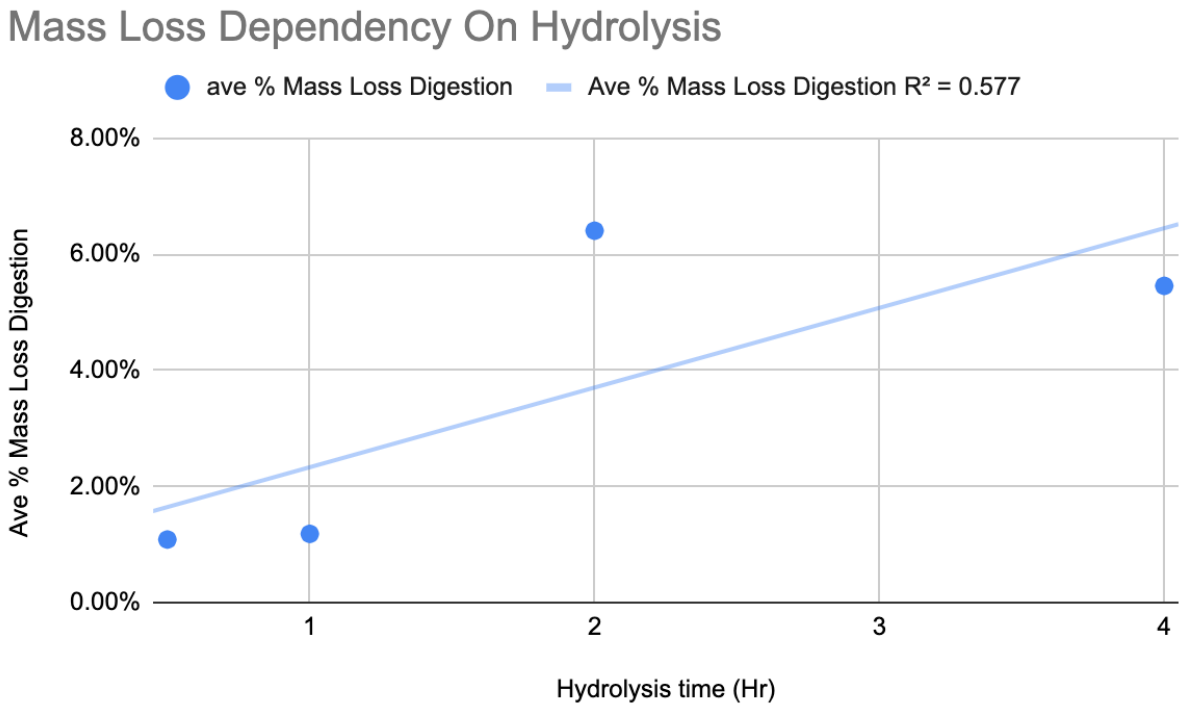

Figure 24: Hydrolized Mass Loss Over Time

5.3 Moving Forward

All experiments, no matter how well thought out and performed they are, can be improved. More data points or a longer timeframe would be the simplest changes to make, allowing for a more precise and accurate prediction to be made. Additionally, if any of the processes could be automated, it would make the experiment less liable to human errors, and more controlled in terms of the variables at play. Biology plays a huge role in the precision. Biological systems vary quite a bit from sample to sample and will never display the precision chemists are accustomed to.

The three analytical methods used worked well when used simultaneously, as they can support each other's findings. When comparing them against each other, however, they show different strengths and weaknesses. Mass loss was the simplest analysis, requiring only an

analytical balance, and not being difficult to understand or calculate. The data from mass loss shows a definitive difference between Polyurethane foams and non-polyurethane foams, but other variables can lead to mass loss that were not under investigation. Some of these variables include non-organic material attaching itself to the foams, and the foams themselves degrading or being physically broken apart by the degradation process. Another drawback to measuring mass loss is that it does not measure degradation as much as it measures biomaterial growth, which is correlated to degradation but is not synonymous with it. Mass loss would be best used as supplemental data to another analytical method, or done in a far more contained environment.

Compression testing proved to be a good tangential method for determining the density of foams. This method did require a rather unique instrument, which is more expensive and has more complicated techniques than simple mass measuring. However, it comes with a more direct method of identifying changes in polymer composition. Compression testing could more viably be used to determine biodegradation compared to mass loss alone.

Finally, FTIR is the method that most definitively shows how the foams change in their environments with time. The instrument itself is the most complex and most expensive of the methods, but with that instrument comes proof of chemical change in the materials. The possibilities of FTIR can grow greatly beyond the use in this paper. If the foams and possible biomaterial growth are added to a library or database that can identify individual foam types and what biomaterial has grown on them. FTIR would be the best method for determining the biodegradability of foams, but requires the most money and effort to be put in. On top of these things, the FTIR also proves that the samples were completely dried when left to dry in the desiccators overnight, as there is no difference between the spectrographs of the 1 month-

degraded standards for each of the foams. The spectra indicate that no water or Fenton's reagent was residually left within the foams after drying.

This experiment was well thought out and performed to the best of my ability, but improvements must always be made. More data points or a longer timeframe would be the simplest changes to make, allowing for a more precise and accurate prediction. Additionally, if any of the processes could be automated, it would make the experiment less liable to human errors, and more controlled in terms of the variables at play.

Some samples would be analyzed later than others, possibly drying them out more, or allowing for more algal growth, or decay. Ideally, a stricter timeframe of the full analysis process from removal from the environment to peroxide digestion to mass loss, compression, and FTIR would assist in making the data more structured.

Another common issue for the project that could persist into the future is the ability to distinguish and identify samples during digestion. During the experiment, only a few samples could be digested in one beaker, as they needed to be visually distinguishable enough to record the data before and after digestion accurately. Fortunately, many of the samples were of different colors, allowing EVA, EPDM, TPU, and Reef Footbed samples to be digested together. The difficulty came from attempting to distinguish Reef Footbed, f/2, Fe, and Polyether samples from one another. This issue also made it such that if samples were dropped or mixed up in any way, as they were at one point before the implementation of the grid system, there was no way to determine which samples belonged in which part of the grid before weighing them.

Fortunately, the experiment was intended to test efficacy and proof of concept. Can peroxide digestion be used as a method for quantitative biodegradation when combined with

mass loss, compression testing, and FTIR analysis? Yes, it can. These combined methods provide multiple possible avenues to prove biodegradation.

Moving forward, in addition to automating and streamlining the processes described here, other methods, such as fluoroscopy or thorough electron microscopy, could be tested. Other environments could also be tested, as the only environments tested in this experiment relied on the proximity of the Pacific Coast of southern California. Other environments with varying temperatures, airiness, and ecosystems could greatly affect the biodegradation of foams.

Other foams could additionally be assessed. This experiment included a small variety of possible foams, preferring to test biodegradable foams easily available, and easily acquired nonbiodegradable foams. Plastics come in many more forms that require their analysis.

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