

P.E.N.G.U.I.N.S

Promoting Emulsion Nullification Greenly Using Innovative Nucleation Surfaces

A Simple Solution to Oil Spill Emulsions

by Zoe Gotthold

ABSTRACT

One of the most dangerous components of an oil spill is the emulsion that forms between the spilled oil and surrounding seawater, as this submerged emulsion can last for many years and is difficult to remediate. This research identified materials that could accelerate the separation of such emulsions, allowing oil to float to the oceanic surface, increasing the efficacy of traditional oil spill removal techniques. This experiment was motivated by an earlier observation that certain plastic containers appeared to destabilize the oil/water emulsions stored within them. Emulsion instability as a result of contact with different plastics was measured using three different tests: 1) visual separation of a column of emulsion over time, 2) growth rate of a drop of emulsion, and 3) microscopic imaging. Open source image analysis software was used to facilitate the large-scale batch processing of data. Twelve plastics were analyzed and compared to glass. Based on regression analysis, plastics that destabilize oil/water emulsions are 1) highly branched, and 2) likely to be at the extreme ends of the polarity scale. These findings were used to develop emulsion destabilizing prototypes; specifically, geometrically complex shapes of alternating polar and non-polar polymers with multiple nucleation sites for emulsion destabilization. The most effective of these prototypes decreased overall emulsion stability by 25%, and decreased the time for the emulsion to begin visually separating by 86%. This research can be used to effectively limit the dangers posed by oil spill emulsion, without the harmful environmental impacts caused by chemical surfactants.

INTRODUCTION

Crude oil spills remain in the environment for many years, harming surrounding wildlife and oceanic chemistry. Crude oil alone is highly corrosive, damaging any organic matter it contacts; however, the more dangerous part of an oil spill is the emulsion that is formed through wave action [1-3]. Spilled oil mixes with the surrounding water to form an emulsion that is more difficult to remove than the original spill and increases the volume of toxic material [4-5]. This emulsion is suspended in the water where sealife swims, and therefore causes even more harm to sealife than the oil itself [6]. Penguins and other seabirds are particularly vulnerable to oil spills, as they feed near the surface of the ocean [7].

Once an emulsion has separated, the oil floats to the surface and can then be removed through traditional methods; however, there is no accepted and environmentally safe method for such separation [8]. Currently, most demulsifiers are environmentally hazardous because they interfere with oceanic chemistry [9]. There is a clear need for a safer alternative to efficiently degrade oil/water emulsions.

This research was based on my earlier observation that contact with poly-methyl-pentene appeared to increase the rate of separation of emulsions. The purpose of this experiment is to determine the overall effects of various plastics on oil spill emulsions, identify the chemical properties that cause these effects, and then exploit these properties to create emulsion destabilizing prototypes. My hypothesized explanation for this observed effect was the difference in polymer side-chain lengths, which could physically disrupt the formation of oil/water micelles and destabilize the overall emulsion [10]. The end goal of this research is to exploit the chemical and physical processes of emulsion separation to develop a system to efficiently and safely remediate oil spill emulsions.

Figure 1 shows the results of a preliminary test demonstrating the differences in behavior between an emulsion stored in a polypropylene (PP) container, a poly-methyl-pentene (PMP) container, and a glass container. All emulsion samples had been stored for the same amount of time. Clearly, the emulsion in the PMP container separates faster. The top images in Figure 1 show what is happening in the center of the cylinders. For PMP, the separation is driven at the interface between the emulsion and the plastic. For glass and PP, the separation is only in the center. This is evidence that interaction with plastic affects emulsion separation.

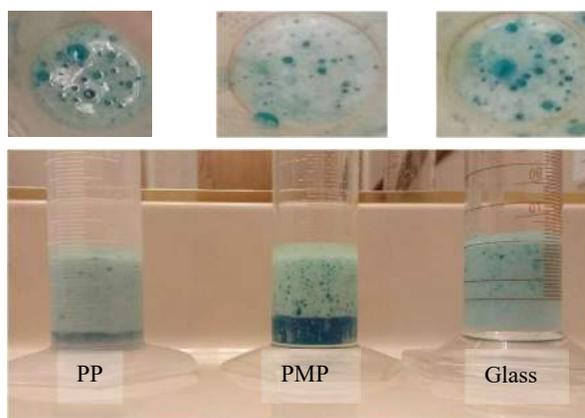


Figure 1: Image illustrating the effect of different materials on emulsion separation. Top pictures show aerial view of the containers below.

MATERIALS, METHODS, AND INTERMEDIATE RESULTS

I began by identifying the effects of various plastics on emulsion stability. To test the efficacy of plastic exposure on decreasing oil spill emulsion stability, I needed a wide variety of plastics and a large amount of emulsion. I created the emulsion using Canola oil as a model for crude oil and distilled water mixed to oceanic salt levels. I created simulated ocean water using *Instant Ocean* aquarium salt and distilled water, with 3.6 grams of salt added per 100 mL of distilled water to match average oceanic salinity. I chose Canola oil as a less caustic and more environmentally friendly substitute for crude oil. For each emulsion, 100 mL of the simulated ocean water and 100 mL of canola oil were mixed using an immersion blender (Hamilton Beach at 16,000 rpm) in 30 second intervals for a total of 2.5 minutes of mixing time. I also added 2 drops of blue food dye to aid in visual determination of oil/water separation [11].

I chose to test 12 readily-available plastics spanning a wide variety of properties: Nylon 6-6, Nylon 6-12, Poly-Methyl-Pentene, ABS, High-Density Polyethylene, Low-Density Polyethylene, Polyethylene, Polystyrene, Polycarbonate, Acetal, PTFE, and Acrylic. I then put the plastics through 3 emulsion-based tests and 1 environmental safety test, narrowing the list after each test to identify a representative sample, as illustrated in the flowchart shown in Figure 2.

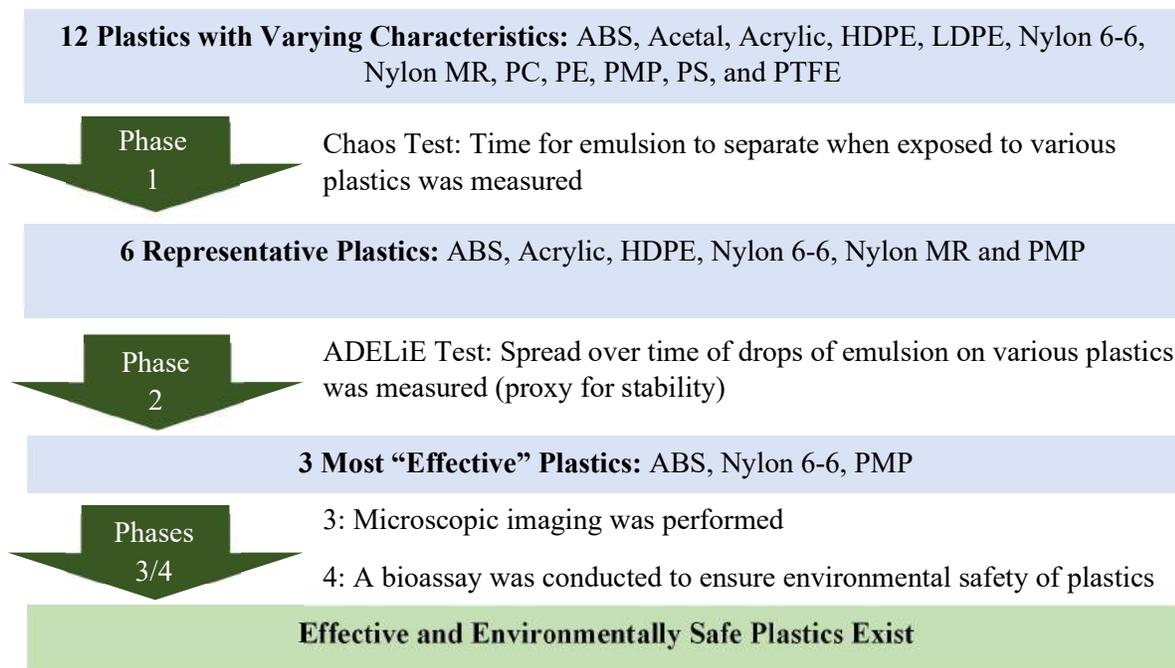


Figure 2: Flow-chart explaining how plastics were narrowed down through each phase to find the most effective plastics for emulsion destabilization.

PHASE 1 TESTING AND RESULTS (CHAOS TEST)

This is a modified version of the traditional “Bottle Test” used for measuring emulsion stability [12]. Essentially, emulsions separate through coalescence and flocculation, the agglomeration and subsequent joining of previously separated oil/water droplets. Visually, this appears as the formation of blue (water) and yellow (oil) areas within the container. I created a stand to hold 8 test tubes of emulsion with different plastic rods centered in each tube (Figure 3). Using a free interval camera app for my cellphone, I then photographed the test tubes every 10 minutes to measure the rate of separation.



Figure 3: Image of Phase 1 test setup (left) and a sample image generated by the interval camera (right)



Figure 4: Sample image from interval camera (left) and the computer-generated black and white representation (right)

To quantify the amount of emulsion over time, I wrote macro scripts in *ImageJ* (an open-source image processing software) to convert each emulsion tube image to a black/white representation of the original emulsion, as shown in Figure 4 [13]. These scripts are shown in Appendix B. I then calculated the percent

white area (emulsion) and graphed it over time. Figure 5 shows an example of one of these emulsion-time graphs; these graphs were used to identify the first time each emulsion reached only 10% of the total volume. I used this time to quantify the effectiveness of each plastic at separating emulsion. Each type of plastic was tested in three separate trials, with the results normalized as a percent change compared to a glass-rod-exposed emulsion, for a total of 48 emulsion-time graphs.

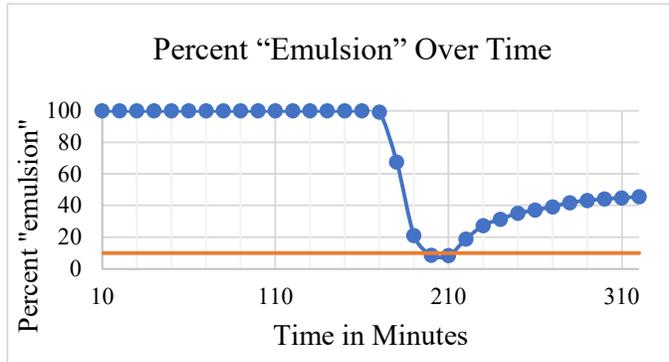


Figure 5: Sample curve showing the amount of pale coloring (representing emulsion) in the tube at a given time. The rise back up is due to the agglomeration of pale yellow oil.

Figure 6 shows the average change in degradation rate compared to glass for the 12 different plastics tested. The error bars represent \pm one standard deviation. The plastics graphed in green caused a significant reduction in separation time, those in yellow were neutral, and those shown in red increased separation time. Based on ANOVA analysis, there is a 99.5% confidence ($\alpha = 0.005$, degrees freedom = 11, F value = 7.81, F critical = 4.51) that these results are statistically significant [14]. Differing plastic exposure affects the rate of degradation in an emulsion.

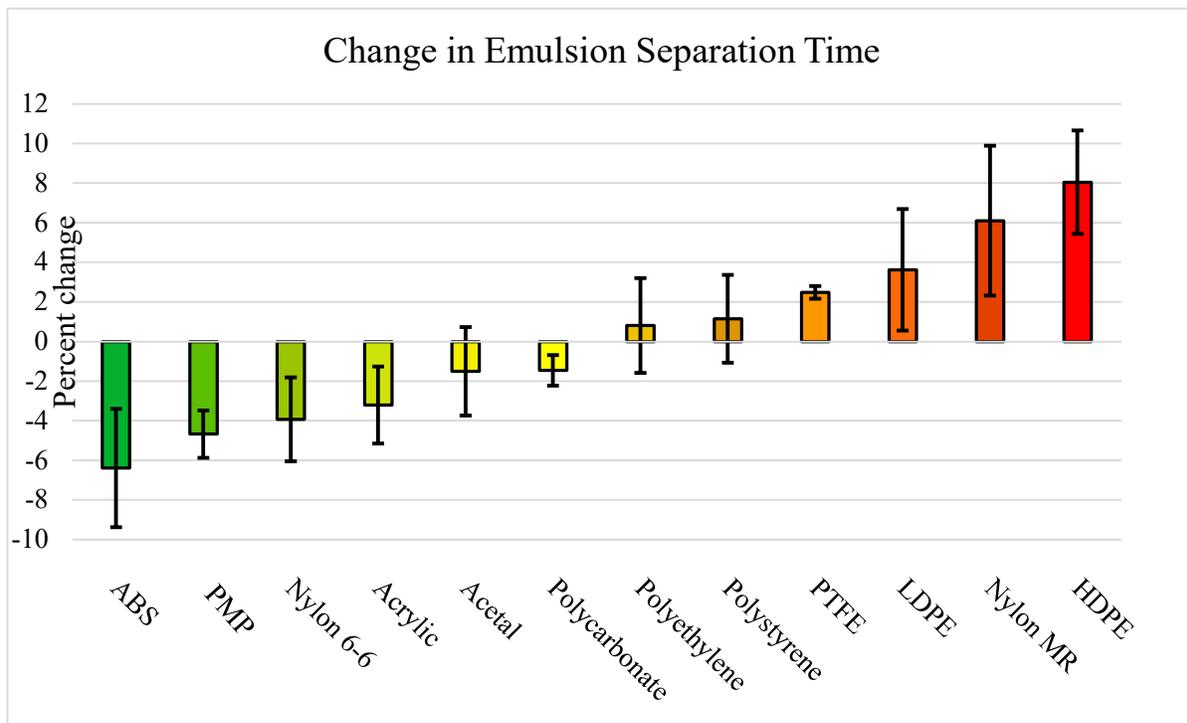


Figure 6: Bar chart showing the change in emulsion separation time for exposure to different plastics compared to glass. Error bars represent \pm one standard deviation.

PHASE 2 TESTING AND RESULTS (ADELiE TESTS)

I developed the ADELiE test as a quick proxy for predicting emulsion stability. ADELiE stands for Area of Drop Extrapolates Lifetime of Emulsion. In Appendix A, I describe how I developed the ADELiE test and verified it is an accurate predictor of emulsion stability¹. As emulsions separate, and the forces separating droplets of the same type weaken, the emulsion flattens out. While a drop of “fresh” emulsion can be nearly spherical, drops of more separated emulsions become disc-like, increasing in area. By measuring the rate of change, or slope, of the area of a given drop of emulsion, one can then extrapolate the rate of separation. The original ADELiE test was conducted in water, but because of testing polymers, this test was performed on plastic.

I set up 7 different squares of materials: 6 representative plastics (ABS, Acrylic, HDPE, Nylon 6-6, Nylon MR and PMP) plus 1 of glass, like the one shown in Figure 7. I took a picture of each plastic every 10 minutes, so I could determine the growth of each emulsion disc over time. I converted each picture to 4 black and white images using *ImageJ*, each depicting the size of one emulsion drop, as shown in Figure 7. I then graphed the size of each drop over time, calibrated against the purple marker shown in the picture. To determine the growth, I calculated the line of best fit, and used the slope as a measure of average growth. This value is indicative of the overall stability—those with larger slopes separated faster and therefore would be less dangerous in an oceanic environment.

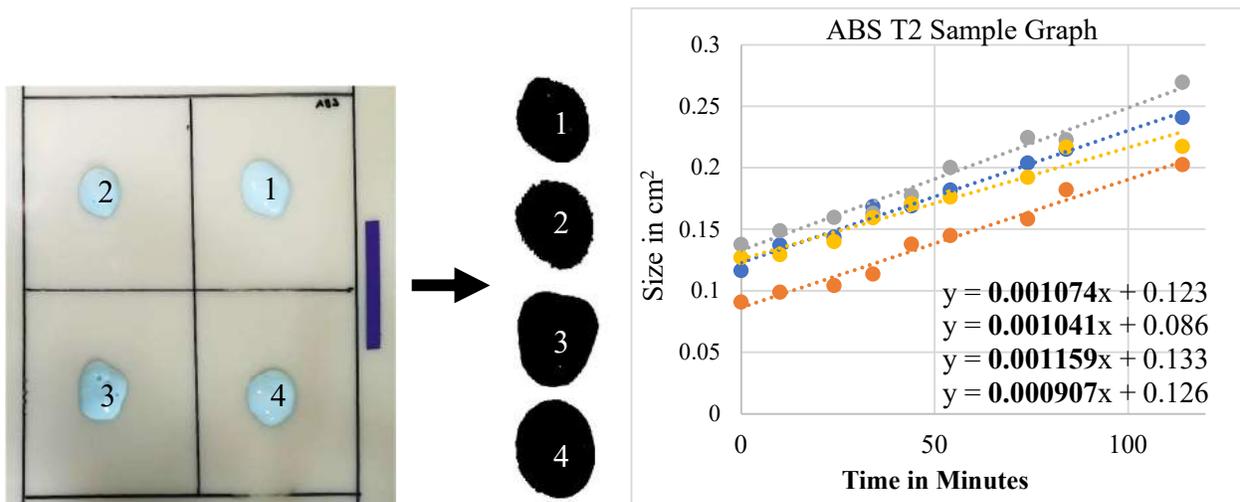


Figure 7: Depiction of how each emulsion drop picture (left) was converted to black/white for measurement (middle). The area of each emulsion drop was graphed over time, with the slope of this graph used to quantify the emulsion separation rate.

¹ The original ADELiE test was conducted in water, but because of testing polymers, this test was performed directly on the plastics. I conducted validity tests to ensure this change would not increase the error of my results.

Figure 8 shows the results of the ADELiE growth test (slope of area versus time averaged from 8 trials) as applied to 6 plastics and glass. Error bars represent \pm one standard deviation. The purple line represents the growth rate of emulsion exposed to glass (used as a reference); those above the line indicate faster degradation than would be expected in standard conditions, while those below the line suggest the material inhibited degradation. Based on ANOVA testing, there is a 99.9% chance these results are not due to chance ($\alpha = 0.001$, Degrees of freedom = 6, F value = 77.6, F critical = 9.16).

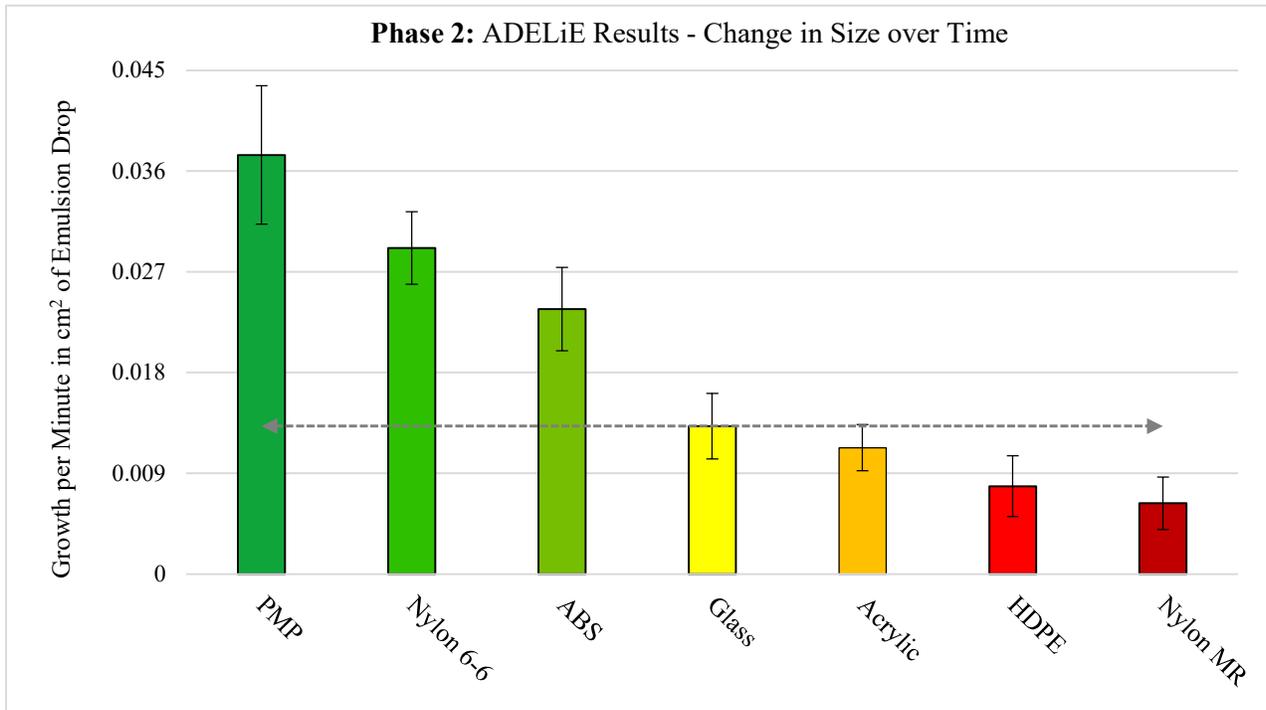


Figure 8: Bar chart representing the growth per minute in cm² of emulsion drops on each of the tested plastics. Error bars represent ± 1 standard deviation.

PHASE 3 TESTING AND RESULTS (MICROSCOPIC IMAGING)

I prepared microscope slides with a one drop of emulsion in the well and a coverslip of the tested plastic. Images of the emulsion at the start and after 30 minutes are shown in Figure 9.

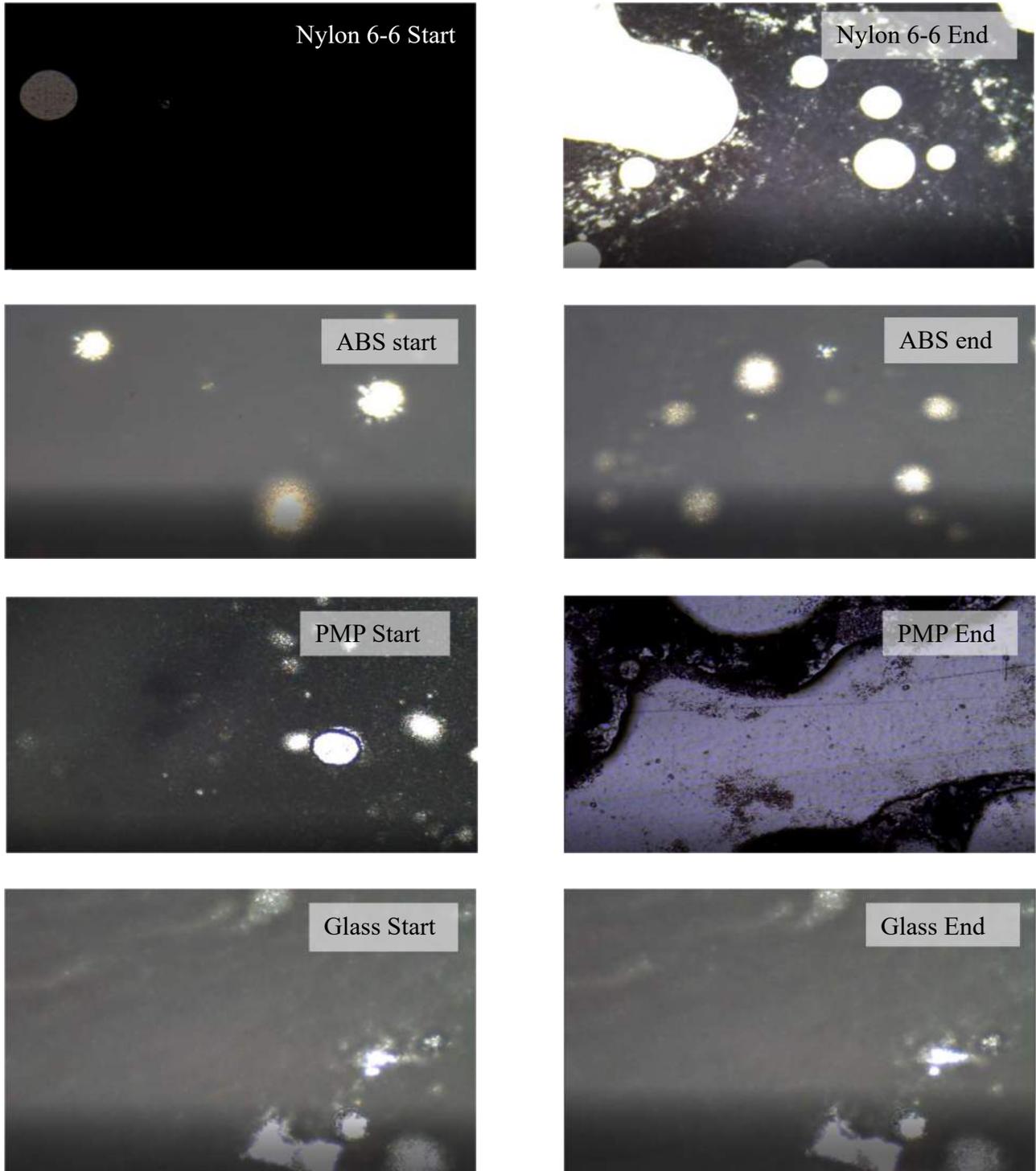


Figure 9: Microscopic images of drops of emulsion on well slides after preparation and after 30 minutes.

PHASE 4 TESTING AND RESULTS (BIOASSAY)

Based on the earlier experiments, exposure to plastic does affect the stability of oil spill emulsions. However, plastic is typically seen as a threat to the health of our oceanic ecosystem. Would adding plastic-based systems to oil spills simply trade one threat for another? Two of the major concerns with plastics in the ocean are animals ingesting the plastic and harmful chemicals leeching out. Ingestion would not be a concern, as oil spills are often miles across and the subsequent polymer-based remediation solutions would likely be physically large, yet chemicals could still leech out. To determine if this is a concern, I conducted a bioassay using lettuce seeds [15]. I created treated water by storing water in 4 graduated cylinders, one made of poly-methyl-pentene, one glass with a lining of ABS, another glass with a lining of Nylon 6-6, and a control where the water was stored in just glass. After one week, I added 2 mL of this treated water to each of 4 petri dishes with 15 *Lactuca Savita* (Bibb lettuce) seeds. After 6 days of growth, I measured and calculated the average length of the embryonic roots.

Figure 10 shows the growth of the lettuce plants exposed to ABS after 6 days in the bioassay. As one can see, most plants grew quite prolifically, and expanded beyond the plastic cover. Overall, these plants had the longest average embryonic roots; however, that difference is not statistically significant.

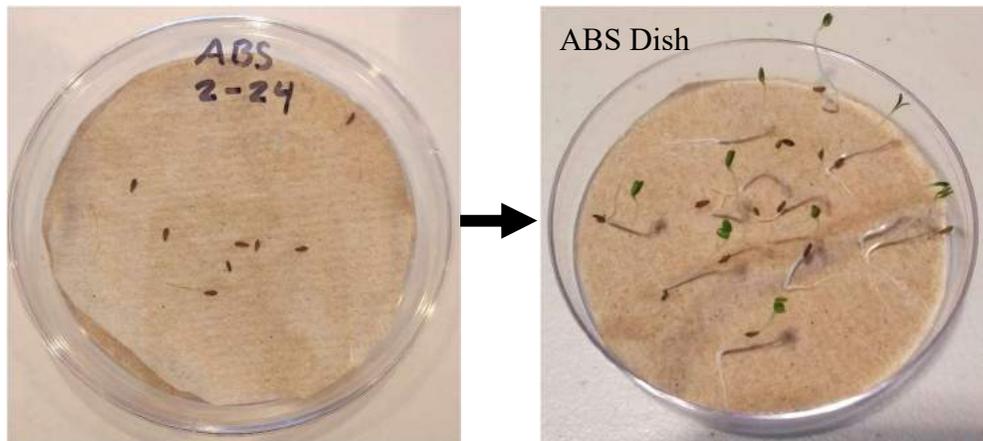


Figure 10: Growth of lettuce plants after 6 days into the bioassay.

Once all of the roots were measured, I computed the average size and standard deviation of the sample. Figure 11 shows all 4 water conditions. Based on ANOVA analysis, these results are not statistically significant ($\alpha = 0.05$, degrees of freedom = 3, F value = 0.59, F Critical = 2.77). This means that exposure to plastic does not pollute water to a degree that would affect the health of organisms living in that water.

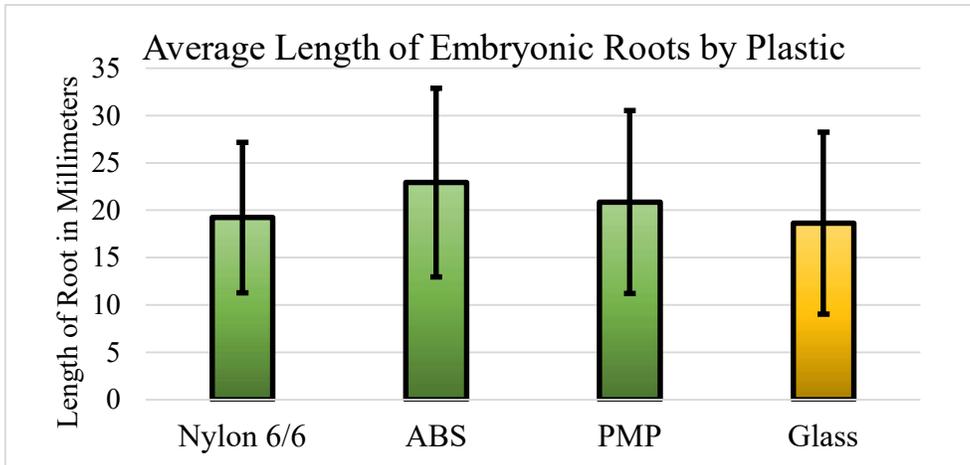


Figure 11: Bar graph representing the average length of embryonic roots. Error bars show \pm one standard deviation

RESULTS

Exposure to different plastics has a statistically significant effect on the stability of an oil/water emulsion. Figure 12 lists the tested plastics in order of their effect, combining results from the different phases of testing. Plastics that decreased the stability the most are listed at the top, while the ones that stabilized the emulsions are listed at the bottom.

Plastics that help destabilize emulsions are considered desirable for the purpose of this experiment because they could increase the rate of cleanup of oil spills. Conversely, plastics that increase emulsion stability should be avoided in an oil spill situation.

All three emulsion-based tests produced the same general results: PMP, Nylon 6-6, and ABS all increase the rate of destabilization of the emulsions they come in contact with. Moisture-Resistant Nylon and high-density Polyethylene both consistently decrease the rate of destabilization in emulsions they come in contact with.

The plastics that decreased emulsion stability were also tested for environmental impact. There was no statistically significant difference between plants grown in plastic-exposed water and those grown in pure water, so this would be an environmentally safe solution if used in oil spill remediation.

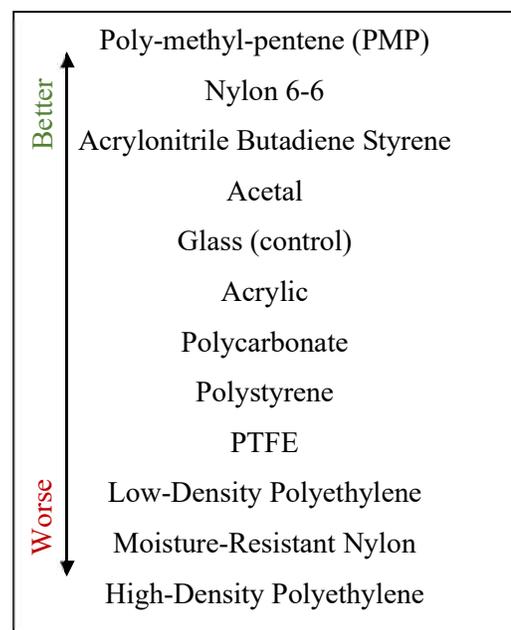


Figure 12: List of plastics ordered by their ability to destabilize emulsions through contact.

DISCUSSION

There is no single factor that ties together all the different plastics that had a positive effect on decreasing emulsion stability. However, by comparing plastics with drastically different effects yet similar chemical structures, some patterns emerge. My original hypothesis included an explanation for this difference in plastic separation behavior based on side-chain length. However, graphing side chains against stability rankings (Figure 13) showed there was no correlation ($R^2 = 0.0464$). I reject my hypothetical explanation. I then analyzed other factors to understand the differences in effects on emulsion stability.

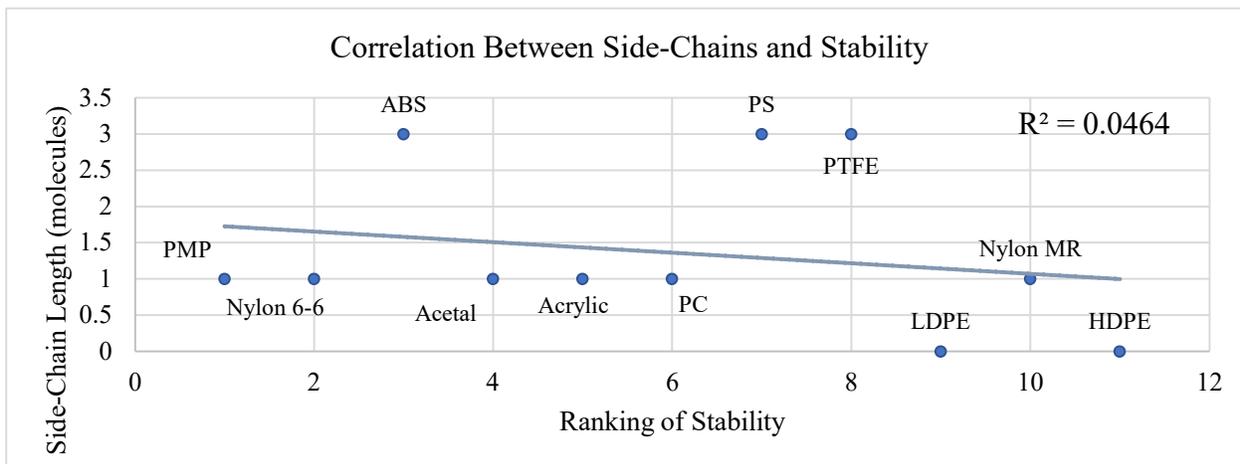
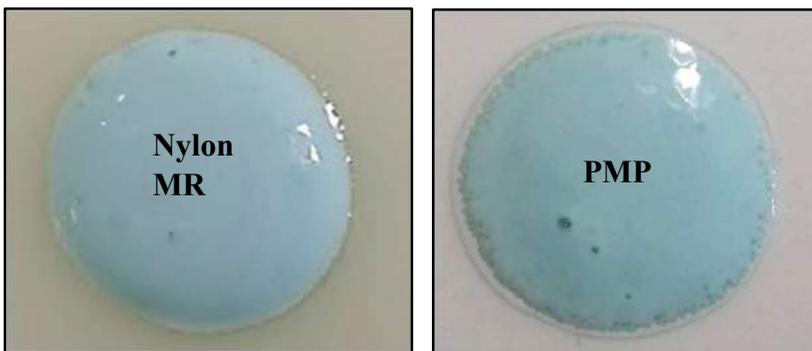


Figure 13: Linear regression analysis of the correlation between the side-chain length of different polymers and stability.

For example, the oil ring surrounding the PMP-exposed emulsion drop in Figure 14 is unique to non-polar plastics. It suggests polarity could be a potential factor, “drawing” the oil out of the overall emulsion.



One clear difference between the plastics is polarity. As a pure hydrocarbon, PMP is highly non-

polar, while Nylon MR is of a medium polarity, and Nylon 6-6 is quite polar [16]. This leads to a potential parabolic trend in polarity; both highly polar and non-polar polymers lead to destabilization, as shown in Figure 15. Logically, this makes sense. Water is highly polar and would be attracted to similarly polar

Figure 14: Close-up of emulsion drop on moderately-polar polymer (Nylon MR) and non-polar polymer (PMP). Note the oil ring around the drop placed on PMP.

substances. Oil is non-polar and would be attracted to non-polar substances. If either component were “pulled out” of the emulsion, the emulsion would quickly destabilize.

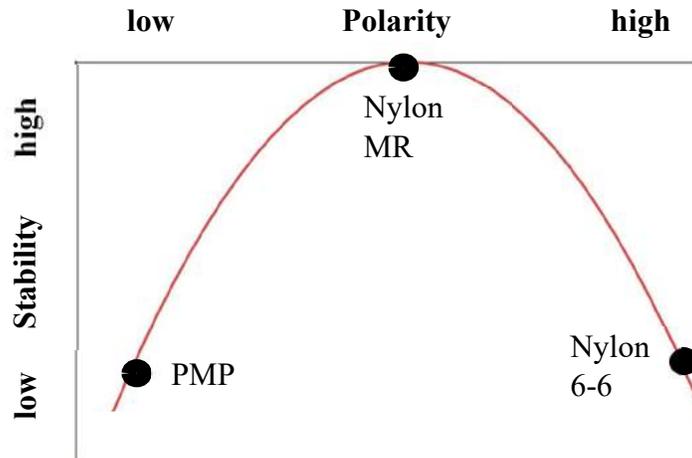


Figure 15: Representation of the parabolic trend of the effect of polarity on stability.

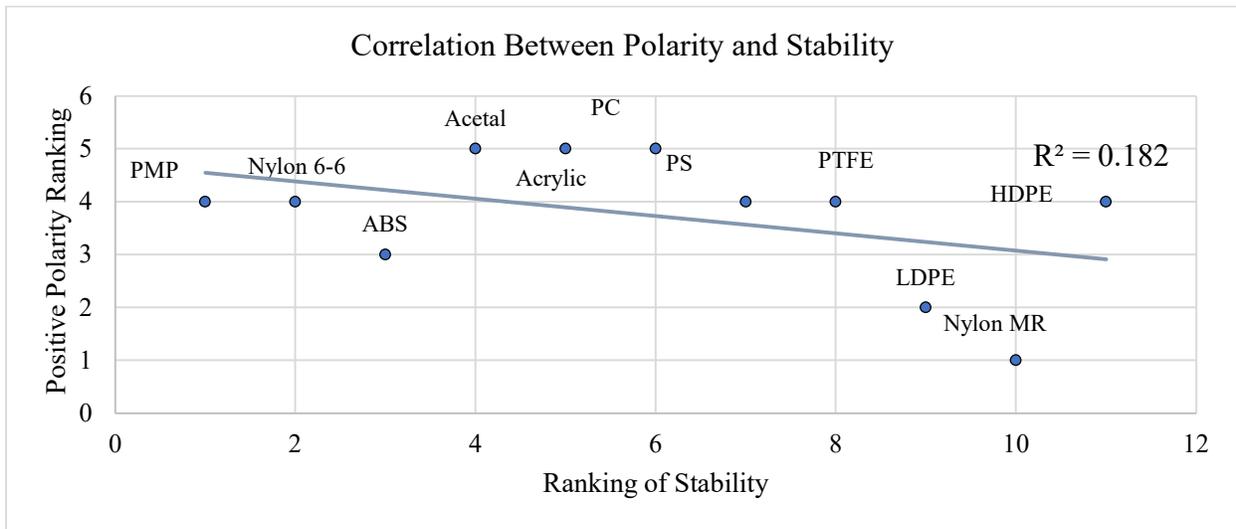


Figure 16: Linear regression analysis of the correlation between polarity of the polymers and their effect on stability.

I approximated polarity by comparing the polar and non-polar bonds within each polymer’s molecular structure. Graphing the absolute value of this polarity measure against the tested plastics (Figure 16) shows a slightly stronger correlation than the correlation between side-chain lengths of the polymer and stability ($R^2=0.182$).

However, polarity does not account for the entire difference in effects. For example, low-density polyethylene and high-density polyethylene have the same elemental structure, but differ in the amount of branching [17]. LDPE is highly branched, whereas HDPE is a single carbon backbone with minimal

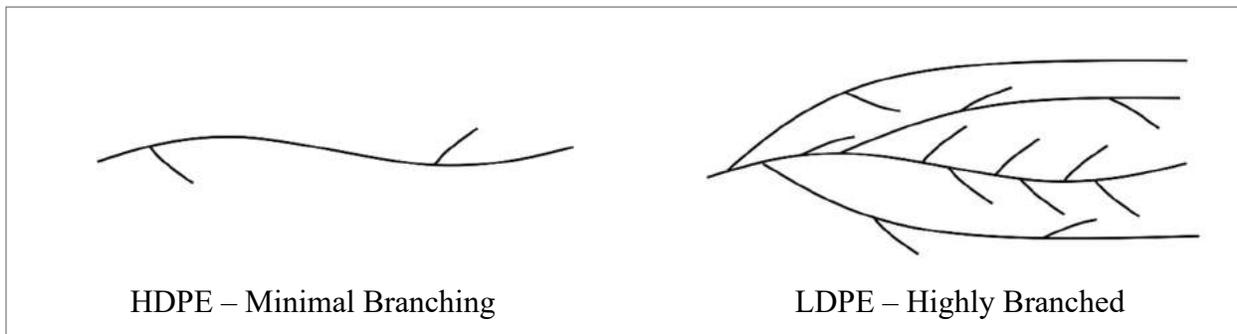


Figure 17: Representation of the differences in branching between HDPE and LDPE.

branching, illustrated in Figure 17. This is what causes the difference in density. LDPE also has a weaker effect on stabilizing emulsions, indicating branching may affect the emulsion, perhaps through “poking” the emulsion and destabilizing the individual micelles.

I gave “branching” a value between 0 and 4 based off the bonding angles of a single monomer. This correlation, as shown in Figure 18, is stronger than both the correlation between the polarity value and stability, and the correlation between the side-chain length of the polymer and stability.

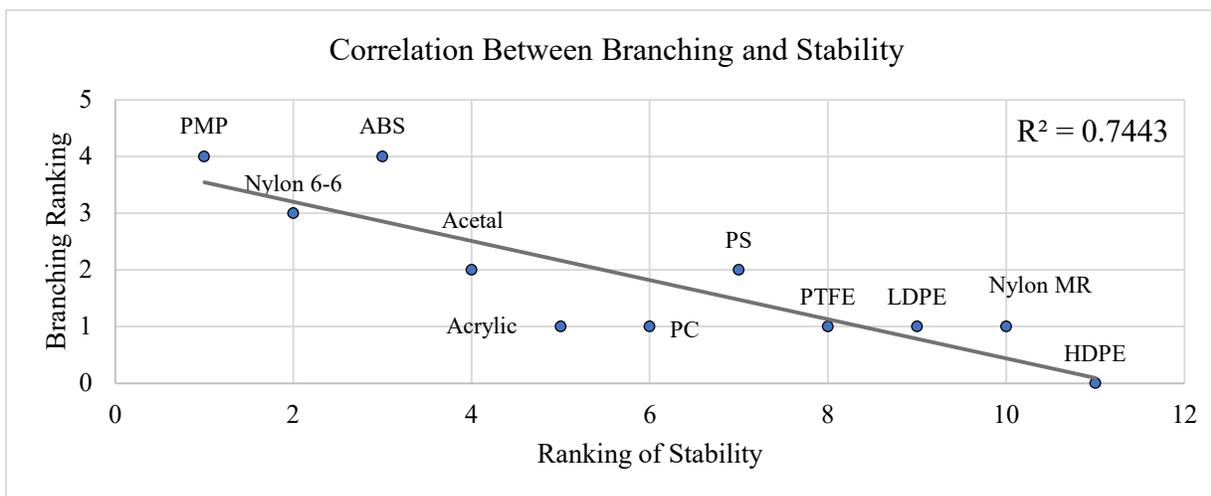


Figure 18: Linear regression analysis of the branching of each polymer and stability.

Both polarity and branching were correlated with stability; however, neither alone was completely predicative. I calculated the “Polarity x Branching Factor” by multiplying the branching and polarity values,

and graphed that against the ranking of stability for each polymer (Figure 19). The linear fit to this data has an R^2 value of 0.9025, which indicates that this factor is an accurate measure of the effect of plastics on destabilizing emulsions

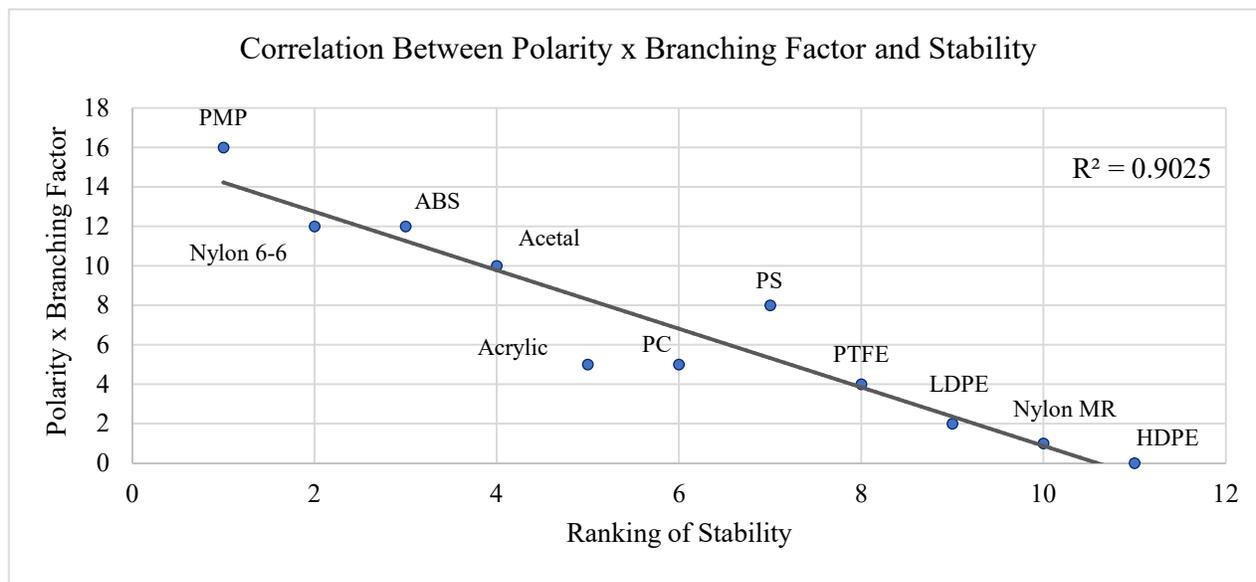


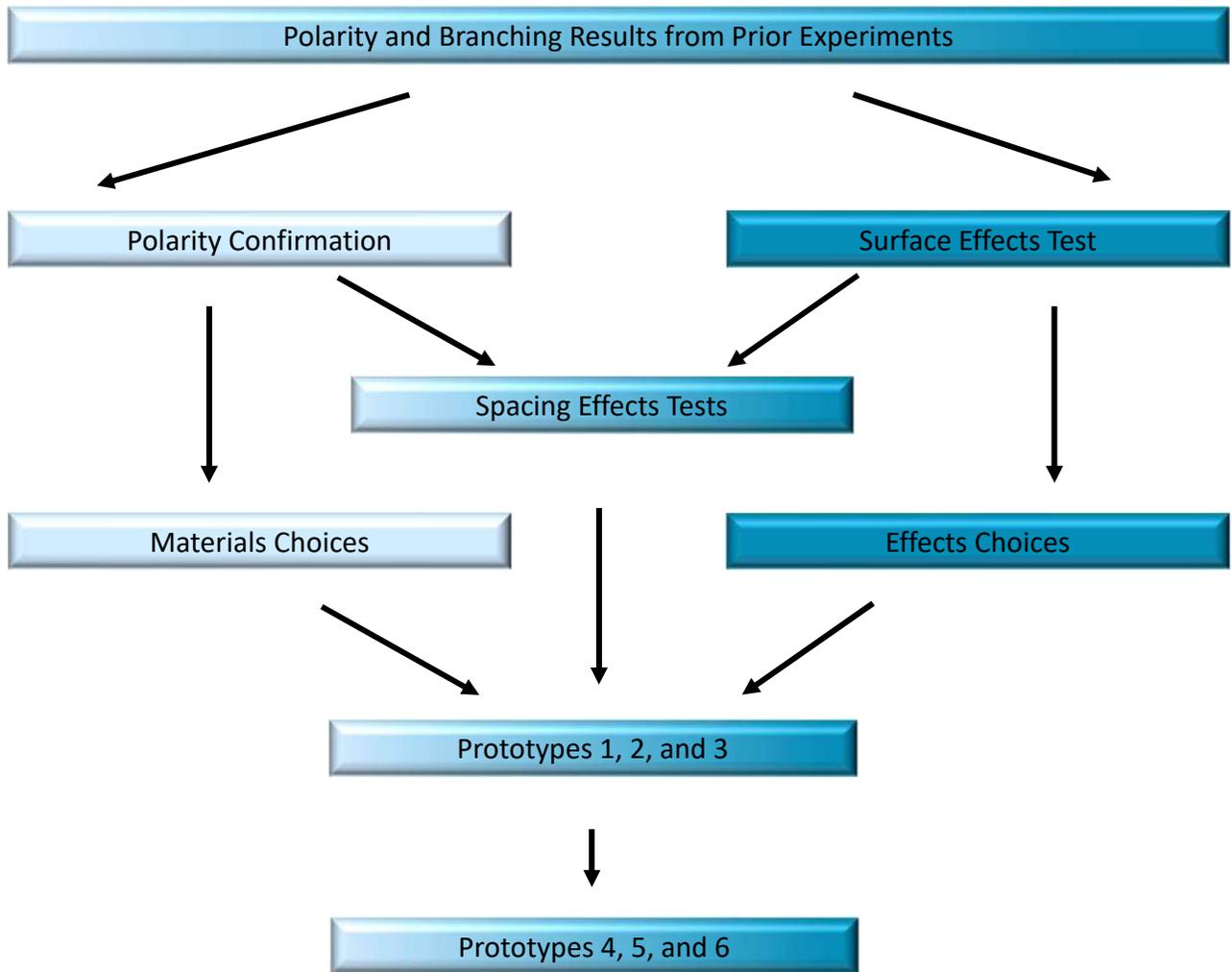
Figure 19: Linear regression analysis of the product of the polarity and branching factors of each polymer against the ranking of stability

PHASES 1-4 CONCLUSION

Exposure to plastics has a clear effect on the stability of oil/water emulsions. In all three emulsion-based experiments, the same, statistically-significant, results emerged. Out of the plastics tested, the most effective emulsion de-stabilizer is Poly-Methyl-Pentene, while High-Density Polyethylene had the greatest stabilizing effect. There appears to be two main factors affecting plastic effects on emulsion behavior: polarity and branching. Both highly polar and highly non-polar plastics decreased the stability of emulsions. This is likely due to the hydrophilic or hydrophobic properties of such plastics attracting either the water or the oil and destabilizing the emulsion. The more “branched” a plastic is, the more of a destabilizing effect occurs. This is likely due to a physical effect such as disrupting the individual micelles.

PHASE 5 PROTOTYPE DEVELOPMENT

This last phase of my experiment is really an engineering challenge. The overall goal was to develop a prototype that would decrease the stability of oil spill emulsions by at least 20%. The flowchart below represents the tests (mini-phases which I will refer to as Phase 5.1, 5.2, and 5.3) I used in selecting both the materials and the physical manipulations I used in my prototype creations.



PHASE 5.1 POLARITY CONFIRMATION

To further confirm the results of my earlier polarity testing, I ran a visual test where I placed a drop of emulsion onto two plates, one polar and one non-polar. As you can see, the different behavior on each plate (which did not occur in the control) indicates a polarity effect on emulsion stability. On the left side, oil bubbles (in a paler color) are forming, while on the right, a water sheen is beginning to emerge. This indicates an attraction between the non-polar left side and the oil, and the polar right and water.



Figure 20: Example from visual polarity test

PHASE 5.2 SURFACE EFFECTS TEST

This test was based on the idea that if monomer branching can affect emulsion stability, so should surface texture. I modified 6 ABS rods using sanding and ABS paint. I created ABS paint from a mixture of ABS printing filament and acetone. I created 6 samples: sanded w/60 grit paper, rod partially dissolved in acetone and etched, painted w/smooth brush, painted w/rough brush, wrapped in ABS filament, sanded w/200 grit paper, and unmodified control.

Using a stand I built and a cellphone interval camera, I conducted an industry “bottle test,” taking pictures every 10 minutes of the separation over time to quantify the effects of each of these modifications. I took each of those interval camera images, and using code I wrote in ImageJ, converted each into a b/w image indicating “water” and “emulsion + oil” regions. I then graphed the amount of “emulsion + oil” over time (found using ImageJ batch processing), which follows a logistic regression, and found the time to reach only 65% emulsion + oil and found the % decrease in separation time as compared to the control.

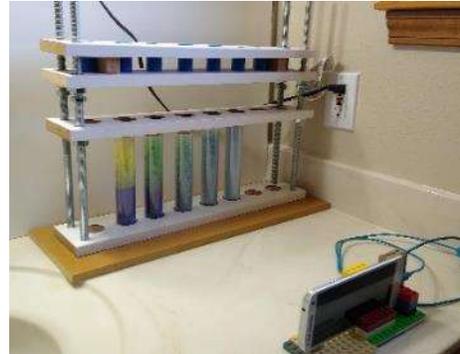


Figure 21: Photo of stand set-up used for holding modified rods. Emulsion shown in various stages of separation

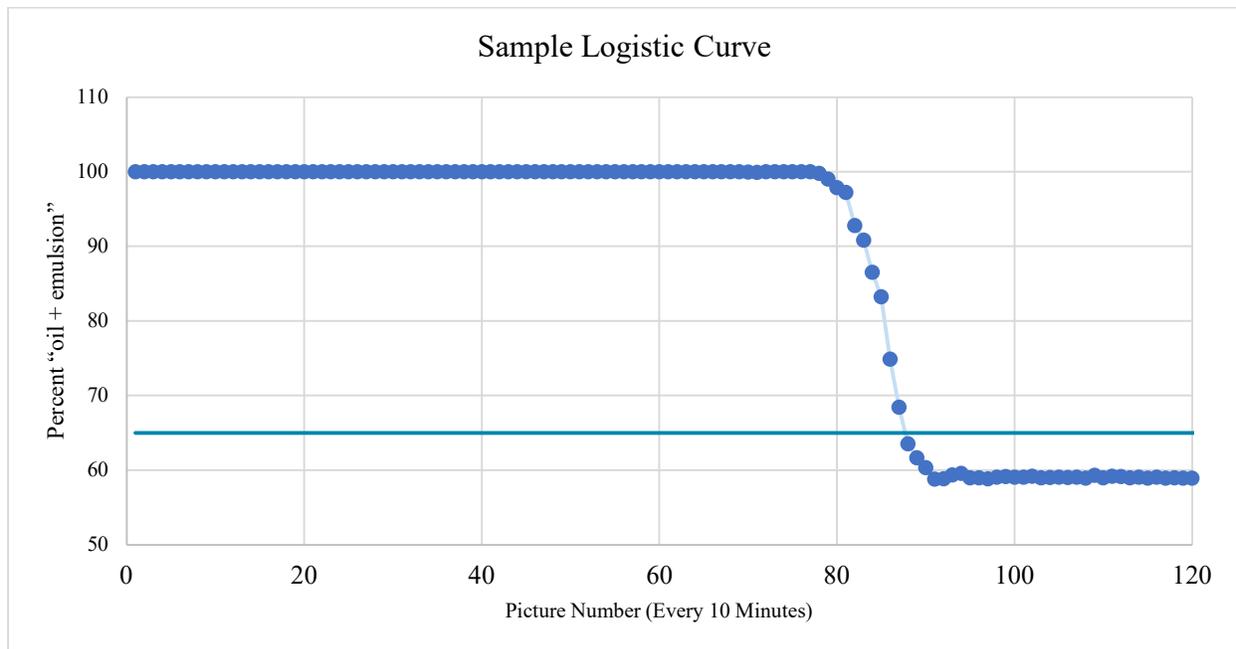


Figure 22: Sample logistic curve showing the separation of emulsion over time. The same code was used to produce this graph as was used in phases 1 and 2.

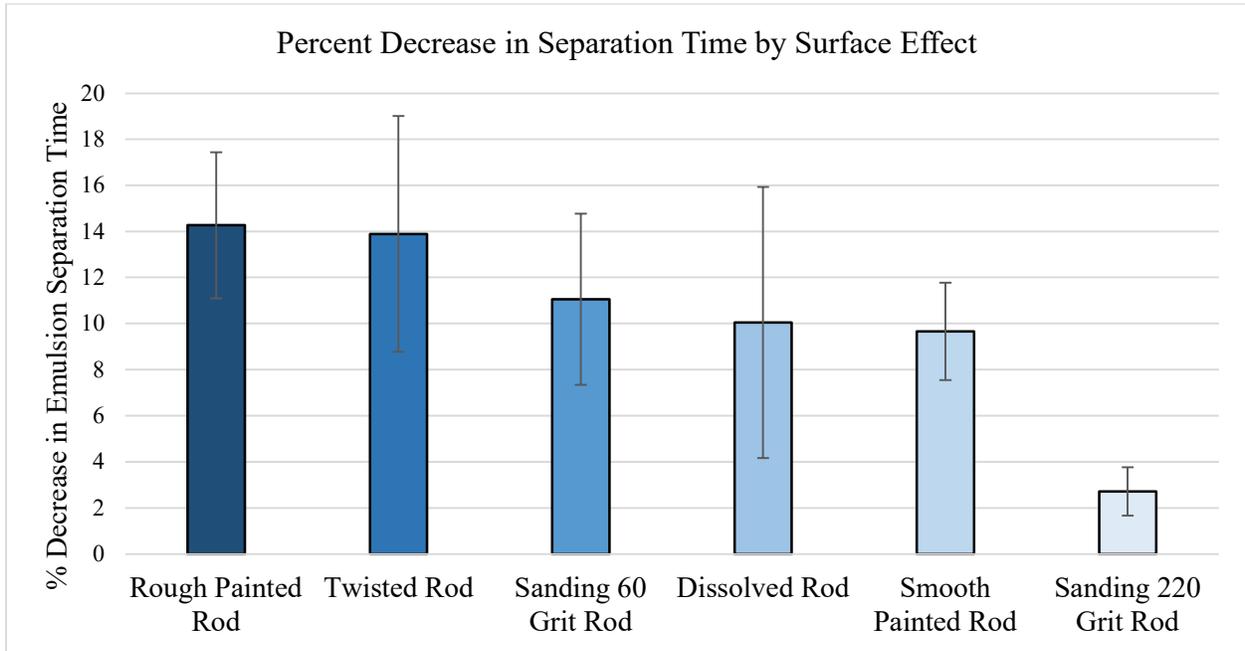


Figure 23: Bar chart showing the efficacy of various surface effects on emulsion destabilization.

This graph suggests the most effective surface effects are roughly painting the surface, adding extra filament, and sanding the surface with 60 grit sandpaper. Based on ANOVA analysis, these results are statistically significant.

PHASE 5.3 SPACING EFFECTS TEST

Using a 3-D pen, I created “jail cells” of varying widths to test the effect of spacing on emulsion stability. I created both a “control” set (ABS pen on ABS plastic), and a “polarity” set (PLA pen on PMP plastic), as the polarities of PLA and PMP differ greatly. I used my previously developed ADELiE test to measure emulsion separation over time. In ADELiE, the rate of spread of a drop of emulsion is correlated with its rate of destabilization. I took pictures of the setup shown to the right every 10-20 minutes, and then graphed the width at three different points over time. Using ImageJ, I calculated the widths across the “blob.” Using ImageJ, I was able to exactly portion the measurements to measure the same point on the emulsion each time. I then graphed each measurement over time to find the slope, which I used as the ADELiE measurement.

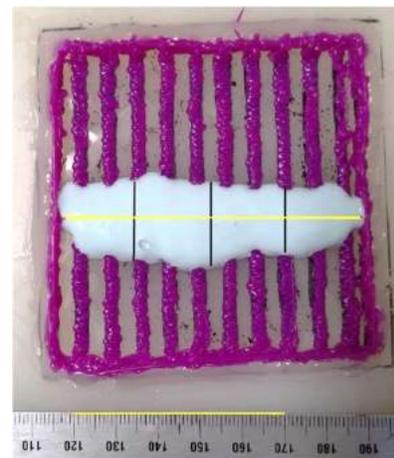


Figure 24: Sample jail cell. The black lines through the emulsion mark the left, mid, and right measurements

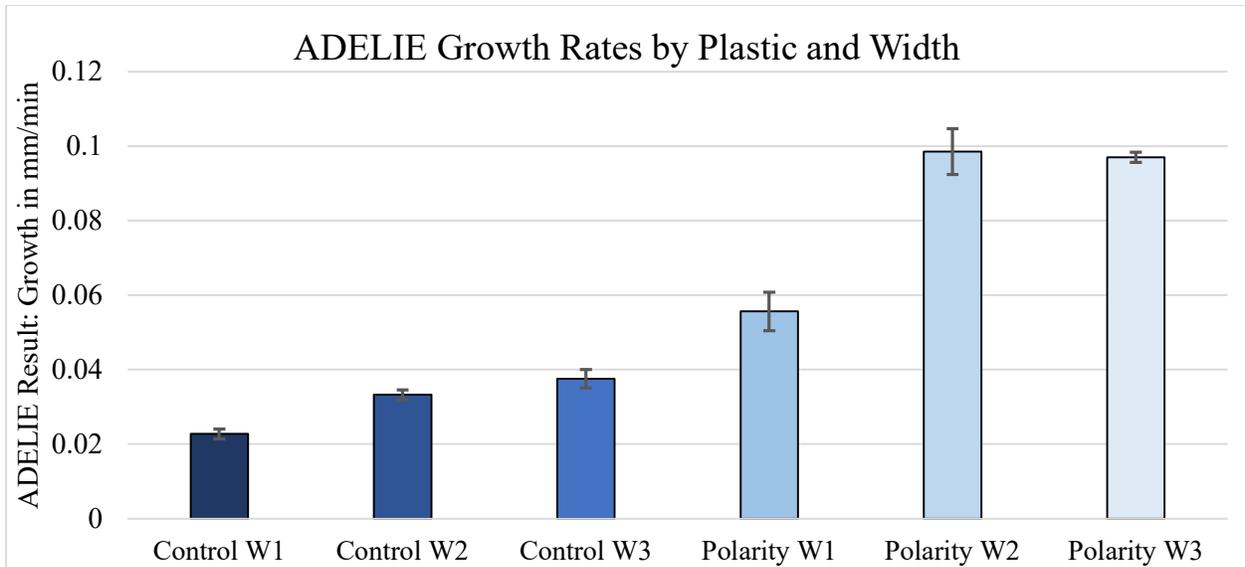


Figure 25: Bar chart showing the efficacy of the spacing tests, both the polar/non-polar (designated as “Polarity”) and the tests on equal polarity (“control”). The W refers to the width of each “jail bar” W3 is the widest.

As you can see, the “polarity” tests outperformed the “control” tests at all three values. The optimal spacing appears to be between 2 and 3 filament widths. Based on ANOVA analysis, these results are statistically significant.

PROTOTYPE DEVELOPMENT

PROTOTYPE 1

I made 6 main prototypes for testing. The first prototype was called the “Spikey Ball.” The design was inspired by the roughly-painted ABS rod, which I believe was effective due to its many points. Its shape is based off the Stellated Dodecahedron. The entire ball was printed out of ABS plastic, which is moderately polar. This prototype was printed on the Richland Public Library’s STEAMspace 3-D printer. I expected this to be one of the lowest performing prototypes because I did not add surfaces of differing polarities, and its existence serves as a control for the “Mod Spikey Ball.”



PROTOTYPE 2



The second prototype is known as the Modified Spikey Ball. The design was inspired by the roughly-painted ABS rod, and the filament-wrapped rod. While the base is still ABS, the added material is PLA, which is significantly more polar. I used a spacing of 2.5 filament widths because of the results of the Spacing Test. The base was printed at the Richland Public Library, and I added the PLA filament using a 3-D pen. I expected this prototype to perform significantly better than the original “Spikey Ball” due to the added polar material.

PROTOTYPE 3

The third prototype was my jellyfish. This is made using alternating polar and nonpolar plastics. The other main design category was the “jellyfish,” which was primarily inspired by the prospect of mixing polar and non-polar materials. The “tentacles” of the jellyfish alternate between non-polar PMP and polar ABS, chosen for their branching and differences in polarity. This is a standard jellyfish, with no modifications to the tentacles. To build the jellyfish, I used 25 μ m-thick ABS and PMP sheets, and strung them together on a wire with glass beads. I expected this to be the lowest performing of the jellyfish.



PROTOTYPES 4-6 (BASED ON ORIGINAL 3)

PROTOTYPE 4



Another design was one that I called the Flat Jellyfish. This jellyfish was inspired by the original jellyfish, which was effective, but the tentacle layout appeared to be inhibiting the agglomeration of separated oil/water. The same overall area of ABS and PMP was used to create this. As you can see in the image, all the oil and water can move freely, uninhibited by different “sections.” To build the jellyfish, I again used 25 μ m-thick ABS and PMP sheets, glass beads, and wire. I expected this to jellyfish prototype to slightly outperform the original because it allows for better agglomeration.

PROTOTYPE 5

Another design was the braided jellyfish. This jellyfish is the same as the original jellyfish, with an added twist braid of 5 μ m-thick ABS and PMP. This was primarily inspired by the high-performer “Filament-Wrapped ABS” from the Surface Effects Test. This “braid” has many sharp points which can serve as nucleation points—regions where oil or water can begin to agglomerate. All the prototypes from the second round are jellyfish because of their greater effectiveness over the Spikey Balls. I thought this prototype would significantly outperform the original jellyfish, because of the added nucleation sites.



PROTOTYPE 6



My last design was the sanded jellyfish. This improvement on Prototype 3 was primarily inspired by the 3rd-place finisher in the Surface Effects Test, rod sanded with 60 grit paper. This was chosen over the 1st-place winner because of the difficulty of creating ABS paint, and a need for a PMP surface texture. Other than sanding, no changes to the original model were made. Because of the efficacy of the sanding in the Surface Effects Test, I thought this sanded model would be the most effective of all the models overall.

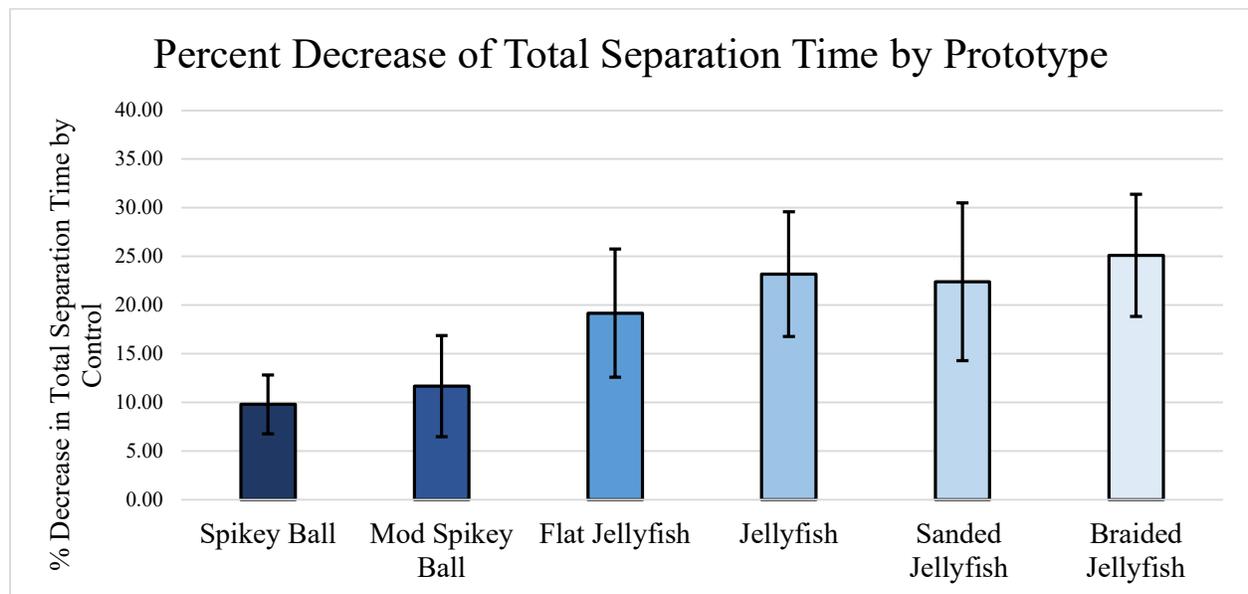


Figure 26: Bar chart showing the comparative efficacies of my various prototypes\

I met my design goal! The most effective model was actually the Braided Jellyfish, which decreased the total separation time by 25%, well over my goal of 20%. Based on ANOVA analysis, these results are statistically significant.

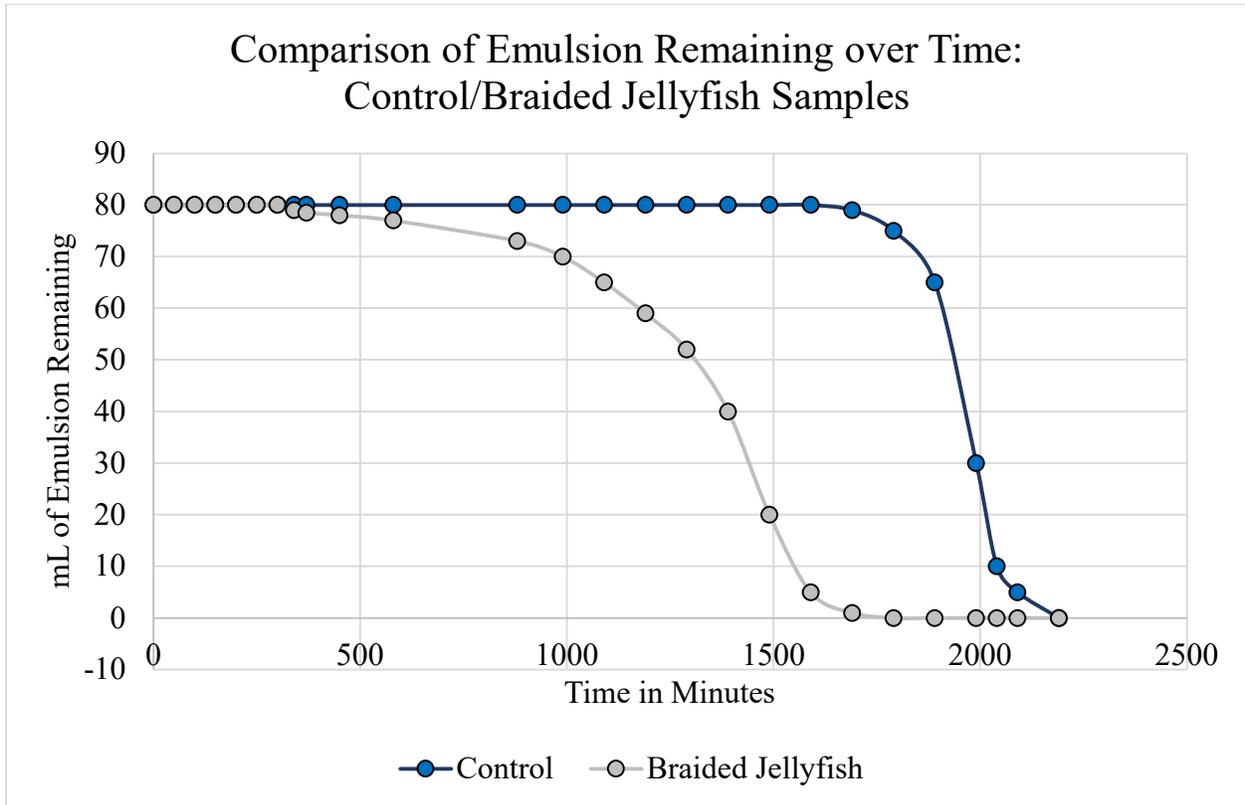


Figure 27: Graph comparing the separation over time of both the control and affected emulsion

When graphing the separation over time for both the control and the affected emulsions, I noticed a stark difference in separation times. This graph demonstrates that difference. While the control emulsion takes longer to begin to separate visibly, once it begins to separate, it finishes quite quickly. Overall, the affected emulsions still separate far faster on average.

This prompted me to graph the decrease in the time for the emulsion to begin separating for each prototype. They were roughly proportional to the overall separation time decreases for each prototype. The most drastic effect was from the Braided Jellyfish, with a Start Time Decrease of 86.4%. The relationship between the overall and start effects appeared to be related.

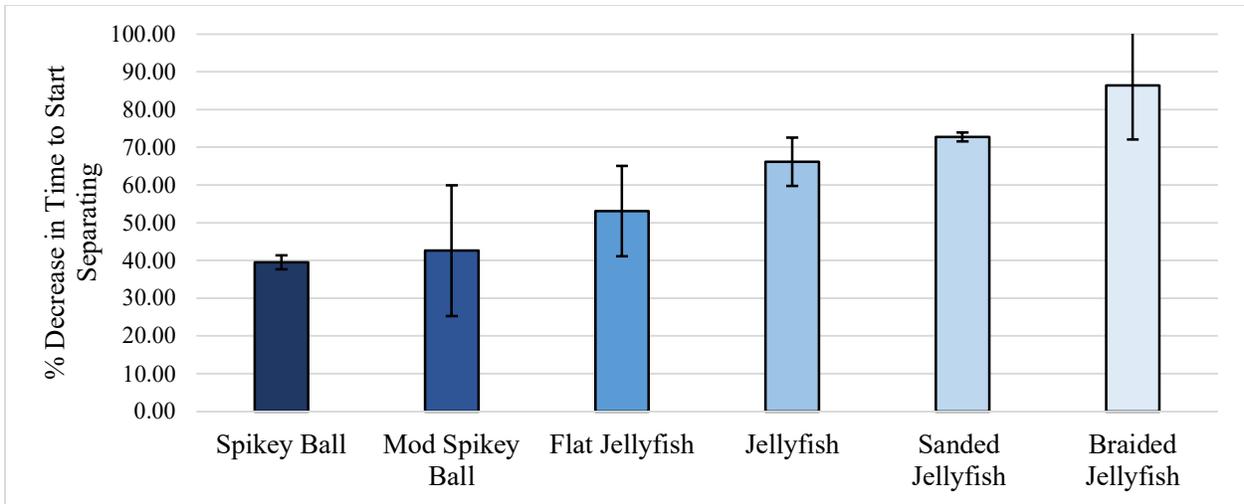


Figure 28: % Decrease in time to begin separating by prototype

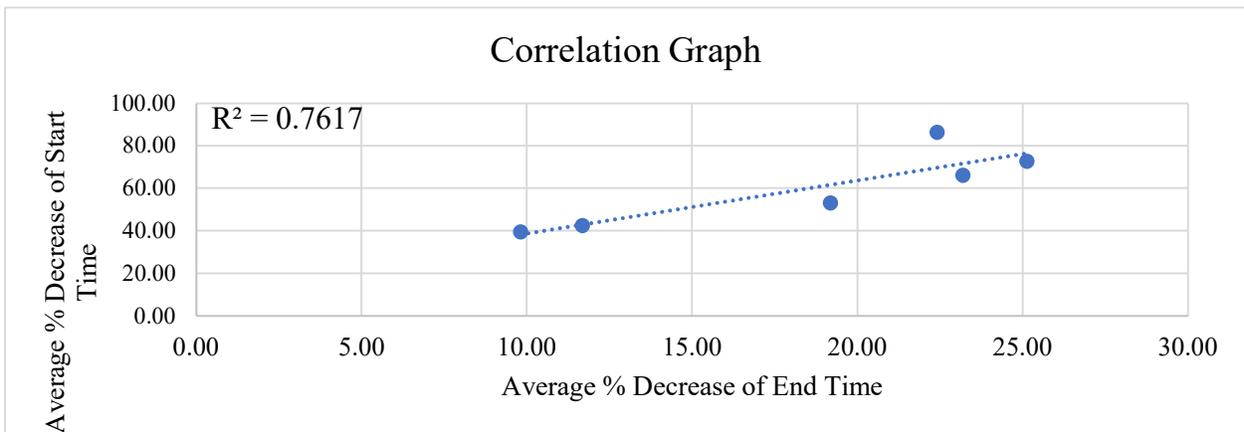


Figure 29: Correlation graph between average % decrease of end time and average % decrease of start time by prototype

This proportionality that I noted inspired me to conduct a correlation analysis. I found a strong correlation between the start time and overall time decreases. When graphing the ratios of start and end time decreases, there was no statistically significant difference between the prototypes (f value = 0.334, f crit. = 5.99).

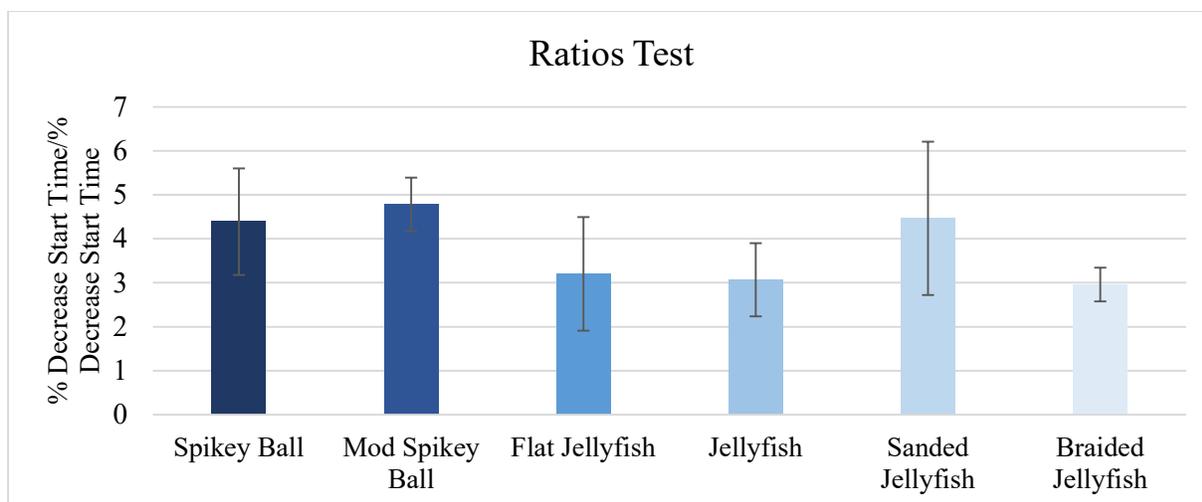


Figure 30: Ratios Test showing a lack of statistically significant differences between each prototype in their ratios between % start time decrease and % end time decrease.

CONCLUSION

I exceeded my design goal! Three Jellyfish designs (original, sanded, and braided) all decreased total emulsion separation time by over 20%. Primarily, these effects were the result of a decrease in the time the emulsion took to start visually separating. I believe this works because my prototypes create multiple nucleation sites for emulsion separation throughout the sample. By contrast, in my controls, only the few nucleation sites that naturally occurred allowed for destabilization. The most effective prototypes were mixtures of oleophilic and hydrophilic polymers, with rough surfaces and points to allow for multiple oil and water nucleation sites. In the future, I plan to improve on these prototypes: because of the success of the braided and sanded jellyfish, I plan to combine them into one braided/sanded jellyfish. I plan to explore bioplastics because of their higher polarity. Additionally, I plan to test a new design composed primarily of intertwined braids, as each turning point in the plastic braid provides a new nucleation site. Now, I need to get my research out into the world, where my prototypes can be tested in real-world oil spills to reduce the danger posed by oil spill emulsions.

APPENDIX A: DEVELOPMENT OF ADELiE TEST

I developed the ADELiE measurement as a simple test to quickly predict the long-term stability of oil/water emulsions. I conducted preliminary experiments that indicated the spread of an emulsion drop suspended in water was indicative of its overall stability. This experiment refined and quantified that relationship.

EMULSION CREATION

I created emulsions of different stabilities and named them as shown in the Factorial Grid in Table A1. I created 6 emulsion types, two each using freshwater, normal ocean, and estuary salinity levels. Each type was mixed at low Intensity (14,500 RPM) and high Intensity (16,000 RPM) using a standard kitchen Immersion Blender. I measured the rpm's using a tachometer. For each code I conducted 3 trials, making a total of 18 separate emulsions. I split each of my 18 emulsions into 3 cylinders, and then measured the emulsion remaining over time, giving a total of 54 separate stability trials.

For every emulsion, I used 100 mL of distilled water and 100 mL of Canola oil. I also added 4 drops of green stain to identify the emulsion discs in my photographs. I added no salt to the freshwater emulsions, 3.4 grams of salt to the normal ocean emulsions, and 2.0 grams of salt to the estuary emulsions. I mixed every emulsion for 2.5 minutes over a span of 5 minutes. For the different intensities, I used a two-speed immersion blender. [18-19]. In total I created 200 mL of emulsion, 150 of which I used in my stability testing, and 6 in my ADELiE test.

Factorial Grid	Freshwater (0 ppt)	Normal Ocean (3.4 ppt)	Estuary (2.0 ppt)
Low Intensity (14,500)	FW1	NO1	ES1
High Intensity (16,000)	FW2	NO2	ES2

Table A1: Color-code chart for each of the emulsion conditions.

ADELiE TEST EXPLANATION

The ADELiE test stands for **A**rea of **D**rop **E**xtrapolates **L**ifetime of **E**mulsion. The ADELiE test was my measure for the spread of a drop of emulsion. I would suspend 1.5 mL of emulsion into a Pyrex container with 20 mL of distilled water. I then placed the bowl into a stand where I held my phone camera at a constant distance from the water. I took a photo of the set-up, including a ruler for calibration.

The basic ADELiE test was performed immediately after mixing the emulsion. However, the results of that test proved to be somewhat erratic, and the emulsion did not conform to the expected circular behavior to minimize surface area. Based on my results from the first experiment, I decided to also measure the area of

the emulsion disc after 15 minutes had elapsed. This technique minimized much of the error. Given that I had two sizes for a single emulsion disc, I also calculated the percent growth of these discs. This gave me a sense of how quickly the bonds were being destroyed in my emulsion.

I used *Image-J* to analyze the area of the discs. By using the Adjust Image feature, I was able to calculate the area of “green” in my image.

STABILITY

One of the major limiting factors to studying emulsion stability is the sheer amount of time it takes for emulsions to degrade. One technique used in the crude oil industry to reduce this time cost is known as the bottle test. A small amount of demulsifier is added to the emulsion to speed up separation, and the emulsions is then shaken to mix the emulsion and demulsifier. I used a modified version of the bottle test where I stirred in 3 mL of a 0.66 molar xylitol solution to speed up my own tests.

For each of the 18 trials, I separated the emulsion into 3, 50mL test tubes. Using an interval camera (Auto Cam) I took pictures every 5, 10, or 20 minutes depending on the emulsion stability. I graphed the amount of emulsion remaining over time, and fit the data to a 4-parameter logistic curve. I chose this fit because the emulsion separation generally follows a symmetric logistic curve, as shown in Figure A1.

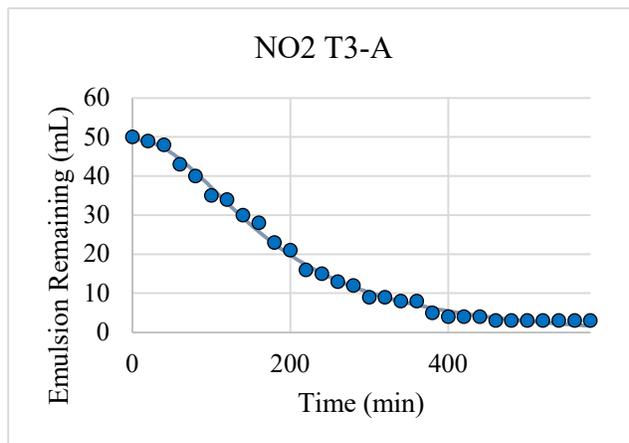


Figure A1 is the stability graph for NO2 Trial 3. The addition of xylitol appeared to have made the demulsifying behavior more linear.

Figure A1: Representative graph of emulsion remaining over time.

THE SLOPE VALUE

To mathematically analyze the correlation between stability and my test’s variables, I needed to have a way to describe the stability with a single number. I found that the amount of emulsion left over time follows a logistic curve. The equation for the amount of emulsion (y) at a given time (x) is described by this equation:

$$y = d + \frac{a - d}{1 + \left(\frac{x}{c}\right)^b}$$

where a is the starting amount of emulsion, b is a coefficient describing the curve, c is the time value when half of the emulsion remains, and d is the amount of emulsion remaining after the separation has finished (illustrated in Figure A2):

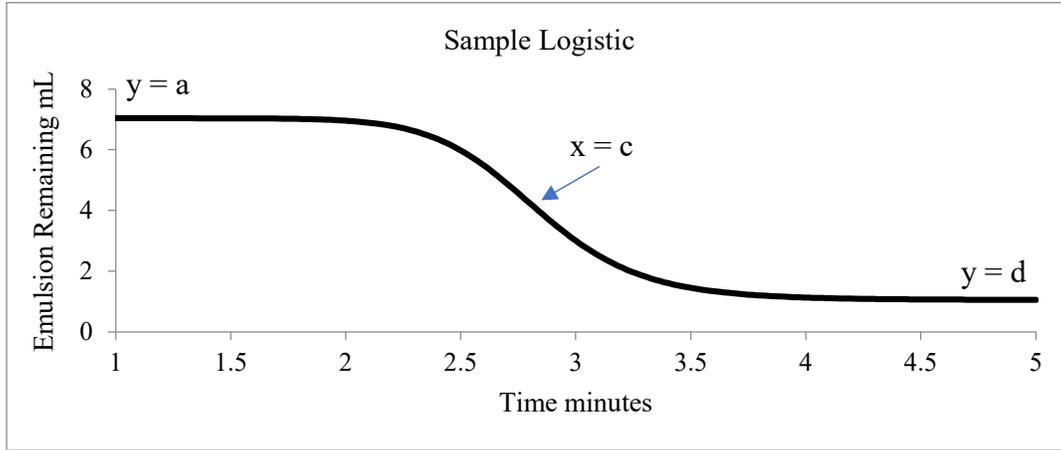


Figure A2: Image illustrating the definitions of the coefficients on a 4-parameter logistic curve

To describe the stability with a single value, one can just take the value of “ c ”, the amount of time it takes half of the emulsion to degrade. One could also use some value for the slope of the graph to discern the stability as a rate of degradation between a set of points.

I decided to quantify stability as the slope at $x=c$. This provided a measure of how quickly the emulsion was separating at its most volatile point. I found the slope as an expression of constants as shown in the calculations below. By using the power rule, I was able to find the slope at $x=c$ for any of my 54 emulsions.

Taking the derivative of that equation, we know that:

$$\frac{dy}{dx} = \frac{-a + d}{\left(1 + \frac{x}{c}\right)^2} \times \frac{bx^{b-1}}{c^b}$$

However, I am using the slope when $x=c$. When x is set to c , the equation simplifies to:

$$\frac{dy}{dx} = \frac{(d - a)b}{4c}$$

By using the expression $\frac{(d-a)b}{4c}$ I can find the slope at c using only the parameters given by the logistic fit.

This allows me to describe the stability of each emulsion with a single number.

ADELiE TESTS

I took multiple measurements of the ADELiE test in order to determine the most accurate results. I measured the emulsion after 0 minutes had elapsed, as well as after 15. I then compared the two results and found the percent growth of the emulsion size. Figure A3 is the Percent Growth data set. The linear regression correlation of 0.87 shows that this test is a viable measure for the ADELiE test.

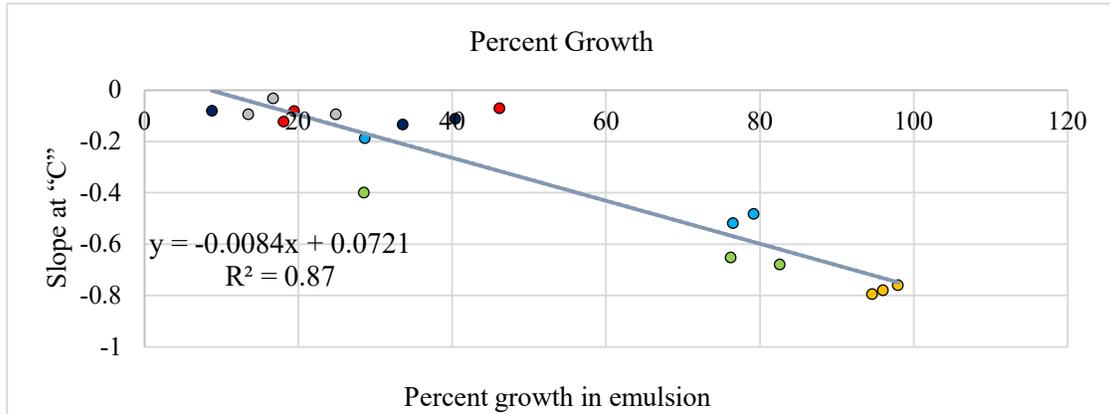


Figure A3: Linear regression correlation between the growth in emulsion size over time and the stability of the emulsion

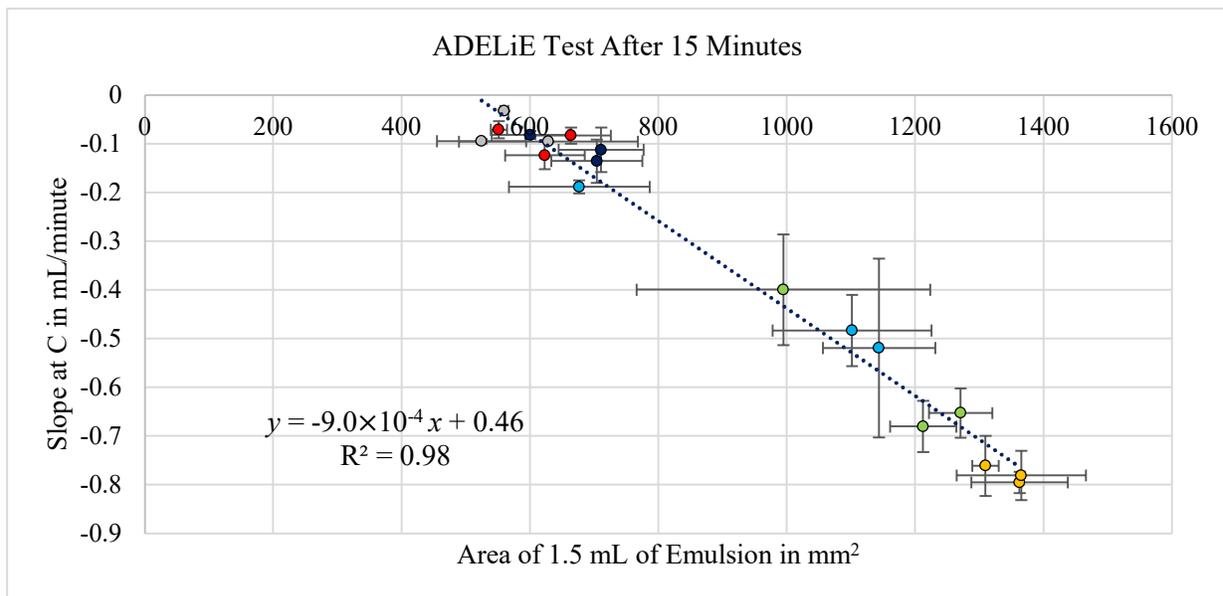


Figure A4: Linear regression correlation between the size of a drop of emulsion after 15 minutes and the stability of that emulsion.

Figure A4 shows the correlation between the ADELiE measurement after 15 minutes and my measure of emulsion stability. A linear trend appears to fit the data quite well. The line of best fit has an R^2 value of 0.98. The error bars represent the standard deviation in both the emulsion disc size and the slope for each trial.

DISCUSSION

With R^2 values close to 1, both versions of the ADELiE test are correlated with stability². I believe this correlation is the result of the tightness of the bonds between the molecules in the emulsion. The tighter those bonds, the harder it is for the oil/water particle to flocculate, and the more spherical the emulsion samples will be. I believe I had to wait 15 minutes to allow the emulsion to “equalize”. When I first added the emulsion to the water, it was irregularly shaped which likely meant my model of using the area to approximate how the emulsion as a sphere, was inaccurate.

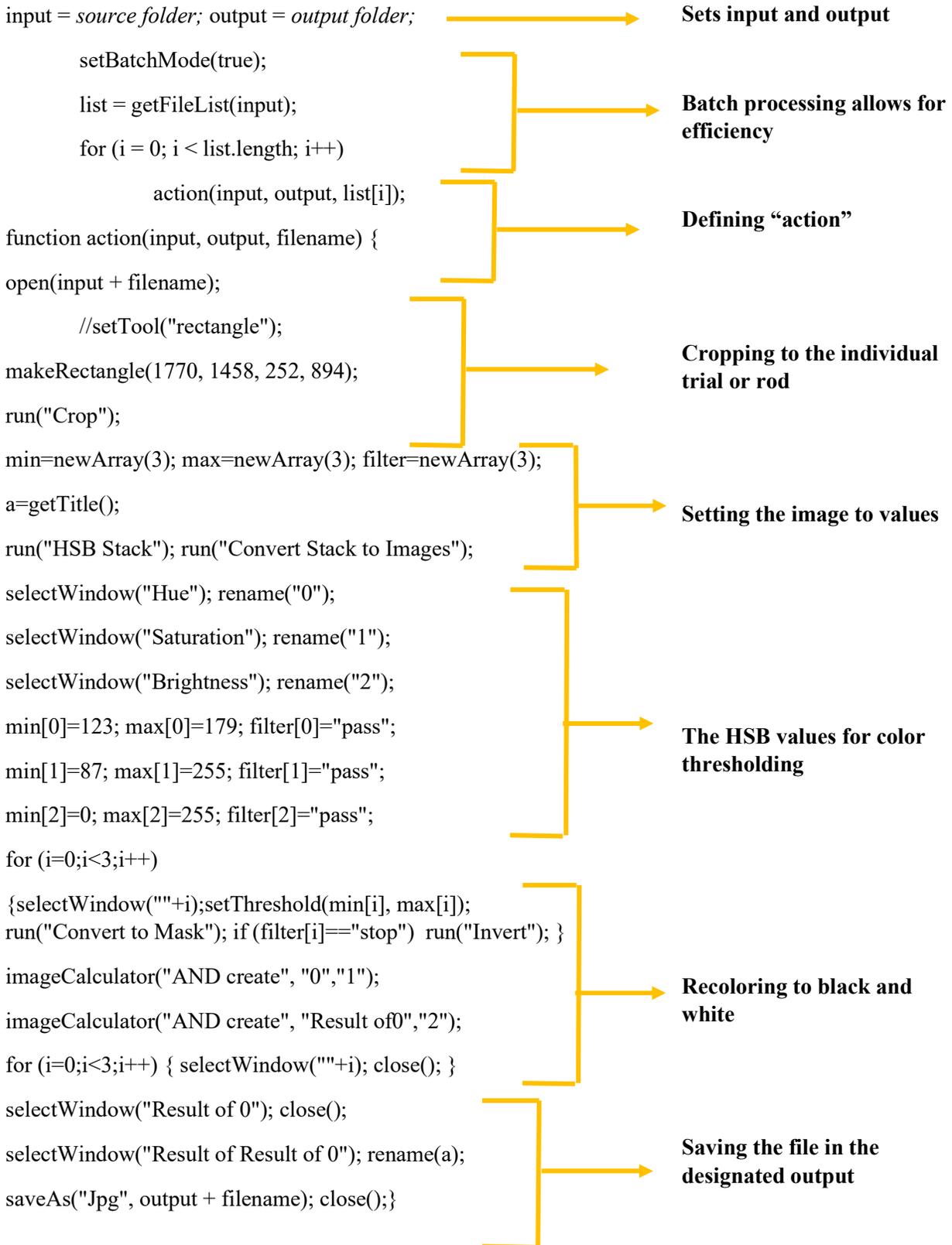
CONCLUSION

I developed the ADELiE test to determine the best method for predicting the stability of water/oil emulsions. I compared the stability described by the slope of the graph at the inflection point with the ADELiE test in three different styles. The ADELiE test after 15 minutes was the most highly correlated to the stability of my emulsions. The R^2 value of a linear fit to that data was 0.98, meaning that it was highly likely the linear trend I noted is due to an underlying behavior of emulsions as opposed to chance.

This finding is highly important. For one, this means that the behavior of oil/water emulsions can be predicted. This is important in its own right for chemists who want to study emulsions more in depth. These findings are also important to aid workers who are helping focus on the most dangerous emulsions formed in an oil spill. Personally, this finding helps me as I can now streamline further experimentation into cleaning up oil spills and separating the emulsion.

² While the size of the emulsion disc after 15 minutes proved the most effective test of emulsion stability when the emulsion was suspended in water, I found that the percent growth was a more accurate test when the emulsion was placed onto plastic. The most important results of this experiment are the connections between the spread of an emulsion and its stability.

APPENDIX B: IMAGE ANALYSIS CODE SAMPLE (ImageJ macro language)



REFERENCES

1. How Oil Harms Animals and Plants in Marine Environments. (n.d.). Retrieved from <https://response.restoration.noaa.gov/oil-and-chemical-spills/oil-spills/how-oil-harms-animals-and-plants-marine-environments.html>.
2. DeNapoli, D. (2011). *The great penguin rescue: 40,000 penguins, a devastating oil spill, and the inspiring story of the worlds largest animal rescue*. New York: Free Press.
3. Henríquez, C. (2009). W/O Emulsions : formulation, characterization and ... Retrieved from https://www.researchgate.net/publication/283378697_WO_Emulsions_formulation_characterization_and_destabilization.
4. Understanding Oil Spills And Oil Spill Response. (2018, January). Retrieved from <https://www.epa.gov/sites/production/files/2018-01/documents/ospguide99.pdf>.
5. Cassiday, L. (2014, April). Emulsions: Making Oil and Water Mix. Retrieved from <https://www.aocs.org/stay-informed/inform-magazine/featured-articles/emulsions-making-oil-and-water-mix-april-2014>.
6. Chang, Stephanie, Stone, Jeremy, Kyle, Piscitelli, & Marina. (2014, May 9). Consequences of oil spills: a review and framework for informing planning. Retrieved from <https://www.ecologyandsociety.org/vol19/iss2/art26/>.
7. International Bird Rescue. (n.d.). Retrieved December 2018, from <https://www.bird-rescue.org/our-work/research-and-education/how-oil-affects-birds.aspx>.
8. Yu, L., Han, M., & He, F. (2017). A review of treating oily wastewater. *Arabian Journal of Chemistry*, 10. doi: 10.1016/j.arabjc.2013.07.020
9. Alvarado, V., Wang, X., & Moradi, M. (2011). Stability Proxies for Water-in-Oil Emulsions and Implications in Aqueous-based Enhanced Oil Recovery. *Energies*, 4(7), 1058–1086. doi: 10.3390/en4071058
10. Wang, G., Yu, B., Chen, S., & Uyama, H. (2017). Template-free synthesis of polystyrene monoliths for the removal of oil-in-water emulsion. *Scientific Reports*, 7(1). doi: 10.1038/s41598-017-06572-7
11. The Chemistry of Food Colorings. (n.d.). Retrieved from <https://www.acs.org/content/acs/en/education/resources/highschool/chemmatters/past-issues/2015-2016/october-2015/food-colorings.html>.
12. Stability of oil emulsions. (n.d.). Retrieved September 2018, from https://petrowiki.org/Stability_of_oil_emulsions.
13. How to Compute the Area of Irregular Shapes using ImageJ ? (2016, September 24). Retrieved from <https://helloacm.com/how-to-compute-the-area-of-irregular-shapes-using-imagej/>.

14. Singh, G., Hadoop, & Budding Data Scientist. (2019, March 11). A Simple Introduction to ANOVA (with applications in Excel). Retrieved from <https://www.analyticsvidhya.com/blog/2018/01/anova-analysis-of-variance/>.
15. Lettuce Seed Bioassay. (n.d.). Retrieved from <https://www.wwoa.org/resources/public-education/lettuce-seed-bioassay/>.
16. Libretexts. (2019, June 5). 6.1: Electronegativity and Polarity. Retrieved from https://chem.libretexts.org/Courses/Oregon_Institute_of_Technology/OIT:_CHE_202_-_General_Chemistry_II/Unit_6:_Molecular_Polarity/6.1:_Electronegativity_and_Polarity.
17. What is the Difference Between LDPE, LLDPE, ect. (n.d.). Retrieved from <https://www.usplastic.com/knowledgebase/article.aspx?contentkey=508>.
18. Ross, S., Chen, E. S., Becher, P., & Ranaut, H. J. (1959). Spreading Coefficients and Hydrophile-Lipophile Balance of Aqueous Solutions of Emulsifying Agents. *The Journal of Physical Chemistry*, 63(10), 1681–1683. doi: 10.1021/j150580a028
19. Roodbari, N. H., Badiei, A., Soleimani, E., & Khaniani, Y. (2016). Tweens demulsification effects on heavy crude oil/water emulsion. *Arabian Journal of Chemistry*, 9. doi: 10.1016/j.arabjc.2011.08.009