The Solution to Pollution is...Plastic? Accelerating Oil Spill Remediation by Using Polymer Exposure to Destabilize Emulsions

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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. A bioassay was conducted to verify that the most destabilizing plastics would have no negative environmental impact if used to aid oil spill remediation. The most destabilizing plastics were poly-methyl-pentene (PMP), acrylonitrile butadiene styrene (ABS), and nylon 6-6. The plastics that stabilized emulsions included nylon 6-12 and high-density polyethylene (HDPE). 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 properties can be exploited in future work to develop an effective polymer-based emulsion removal method, negating the need for toxic chemical dispersants.

INTRODUCTION

Oil spills remain in the environment for many years while harming surrounding wildlife and oceanic chemistry. Crude oil is highly corrosive, damaging organic tissue that it comes in contact with [1-2]. One of the most dangerous parts of an oil spill is the emulsion that is formed through wave action [3]. Spilled oil mixes with the surrounding water to form this emulsion which is even more difficult to remove than the original spill [4-5]. 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 [6-7]. There is a clear need for a safer alternative to efficiently degrade oil/water emulsions. This research was based on an earlier observation that poly-methyl-pentene appeared to increase the rate of separation of emulsion that come in contact with it. The purpose of this experiment is to determine the overall effects of various plastics on oil spill emulsions, and then to determine the chemical processes that cause these effects. One potential explanation for this observed effect is the difference in side chain lengths, which could physically disrupt the formation of oil/water micelles and destabilize the overall emulsion [8]. The end goal is to exploit these chemical and physical properties of emulsion separation to develop a system to remediate oil spill emulsions immediately.

MATERIALS AND METHODS

Simulated emulsion was created using canola oil as a model for crude, distilled water, and salt mixed with an immersion blender [9-10]. 12 plastics were tested 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. Plastics were tested with 3 emulsion-based tests and 1 environmental safety test.

Phase 1 'Chaos' Test: This is based on a traditional bottle test, where emulsion is stored and monitored for separation. [11]. 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. Using an open source interval camera, test tubes filled with emulsion and a plastic rod inserted through the center were photographed every 10 minutes to measure the rate of separation. These photographs were then translated into black/white images to represent the amount of emulsion left over time, using code written in ImageJ, as seen in Figure 1 [12].

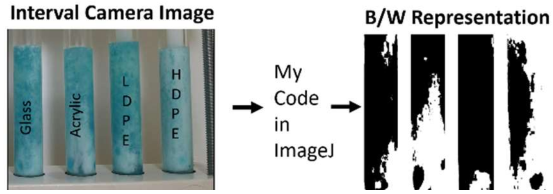

Figure 1 shows how the raw data from the interval camera is translated to B/W representations of emulsion

Phase 2 ADELiE Test: The ADELiE (Area of Drop Extrapolates Lifetime of Emulsion) test was developed in a previous experiment [13]. As emulsions separate, and the forces separating droplets of the same type weaken, the emulsion flattens out. While a "fresh" emulsion can be nearly spherical, emulsions that are nearly separated are more disk-like, with a larger area. By measuring the rate of change of the area of a given drop of emulsion, one can then extrapolate the rate of separation

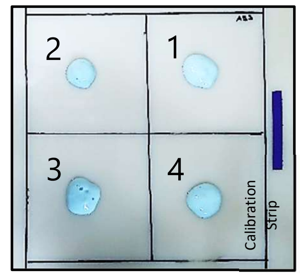

Figure 2 Each picture was converted to 4 black and white images, each depicting the size of one emulsion drop.

7 plastics were tested with 8 trials for each plastic. A drop of emulsion was placed on a section of the plastic and a picture was taken every 10 minutes. The rate of change of the area of the drop over time was calculated as a measure of stability.

Phase 3 Microscopic Imaging: To learn more about the effects of plastic on emulsion separation, 4 microscope slides were prepared; each with a drop of emulsion and a coverslip of the tested plastic. Pictures were taken at the start, and after 30 minutes.

Phase 4 Bioassay: A bioassay using lettuce seeds was conducted to ensure toxic compounds do not leech out of the most promising plastics under the timescales that would be used in emulsion remediation [14].

RESULTS

The results of each phase are shown here. For numerical tests, ANOVA analysis was used to determine the statistical significance of results [15].

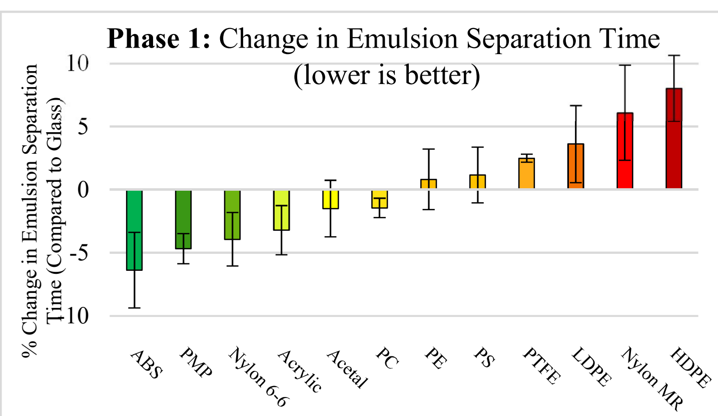

Figure 3 This graph represents the average change in degradation rate compared to glass for the 12 different plastics tested. This change was calculated from averaging the time to reach only 10% emulsion for 3 different trials. The error bars represent ± one standard deviation. Those in the green caused a significant reduction in separation time, those in yellow were neutral, and those in red increase separation time. Based on ANOVA analysis, there is a 99.5% confidence that these results are statistically significant.

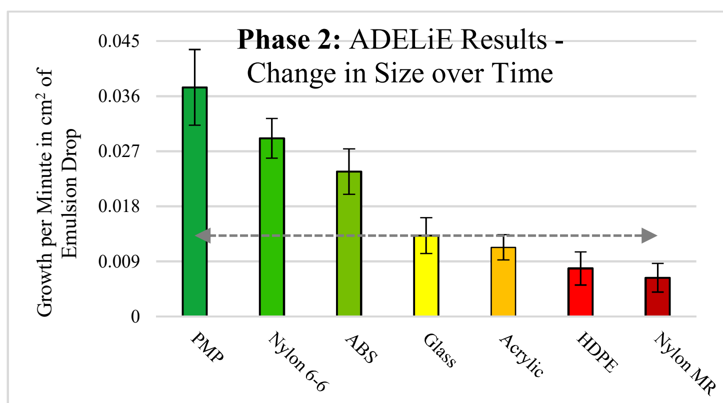

Figure 4 This graph shows the results of the ADELIE growth test (slope of area versus time averaged from 8 trials) as applied to 6 plastics and glass. Error bars represent ± one standard deviation. The purple line represents the growth rate of emulsion exposed to glass; those above the line indicate 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.

Phase 3: Within that time-frame, the emulsion exposed to PMP fully separated. The emulsion exposed to Nylon 6-6 almost fully separated, and that exposed to ABS saw the introduction of several new oil nodules. The emulsion exposed to glass had almost no change.

Phase 4: There was no statistically significant difference between the health of lettuce plants germinated in water exposed to plastic and those germinated in water exposed to glass.

DISCUSSION

More than identifying the most effective plastics for emulsion destabilization, the purpose of this experiment was to determine the properties behind those effects. Using linear regression analysis, various properties were compared to the stability ranking from the first tests, with results in Table 1. The original hypothesis was found to be incorrect as side-chain length is uncorrelated to stability.

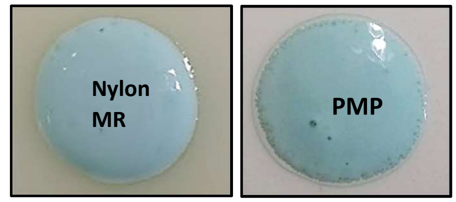

Figure 5 Comparison of Nylon MR (polar) plastic without an oil ring and PMP (non-polar) plastic with an oil ring

Polarity was tested for correlation because an oil ring was noted surrounding emulsion droplets on non-polar surfaces (figure 5). Extremity of polarity was graphed against stability and found to be somewhat correlated to stability. Additionally, branching within the polymer was compared to the effects on stability and found to be more correlated. When combined, those factors account for most of the difference in stability, as seen in figure 6.

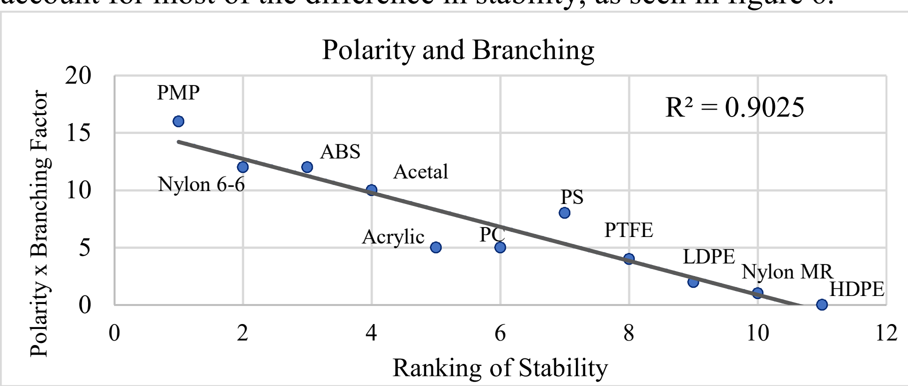

Figure 6 Linear regression of polarity x branching values with the overall ranking of stability

Polymer Property	R^2 Value
Side-chain length	0.046
Polarity	0.182
Branching	0.744
Polarity x Branching	0.903

Table 1 displays the R^2 values of the linear fits from graphing the polymer properties against the stability ranking of that polymer, as a measure of correlation

CONCLUSION AND FUTURE WORK

- **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 **PMP**, while **HDPE** had the greatest stabilizing effect. The list of plastics is shown in figure 7.
- There appear 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 the **increased porosity** allowing for the absorption of emulsion components

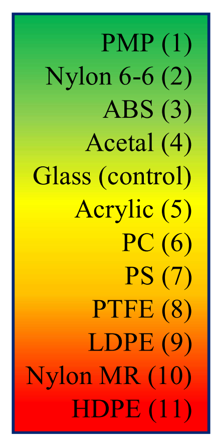

Figure 7 listing the polymers tests in order from most destabilizing to least

For future research, a 'super-polymer' will be developed, potentially using organic materials, with highly polar regions and high levels of branching for use in separating emulsions in oil spill remediation.

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