In Situ Marine Biodegradation of Poly(lactic) Acid (PLA) and Thermoplastic Starch (TPS) Blends

¹Brittany DeNicholas, ¹Dr. Trevor Harding, ²Daniel Licea, ²Dr. Ruben Gonzalez-Nuñez ¹Materials Engineering - California Polytechnic State University, ²University of Guadalajara

June 6, 2022

Contents

1.0 Abstract
2.0 Motivation
2.1 Recycling Myths
2.2 Degradation of Petroleum Plastics
3.0 Background7
3.1 Biodegradation Process
3.2 What are PLA and TPS?
3.3 Blending PLA and TPS9
3.4 PLA/TPS Biodegradation in the Ocean11
4.0 Gaps in Literature
5.0 Research Question 15
6.0 Method 15
6.1 Design of Experiment
6.2 Materials
6.3 Experiment and Testing 16
6.4 Material Characterization17
6.5 Statistical Analysis
7.0 Results
7.1 Visual
7.2 Tensile
7.3 TGA
7.4 FTIR
8.0 Discussion
9.0 Conclusions
10.0 Future Work
11.0 References

List of Figures

1-2	Mechanical properties of starch/PLA composites over time in a controlled marine environment [23]	12
3	Elongation at break of starch/PLA composites over time [23]	13
4	Pictures of samples at intervals of time spent in marine environment	19
5	Stress vs. Strain curves for all compositions	20
6	Plot of % elongation over time	21
7	Plot of ultimate tensile strength over time	21
8	Plot of Young's modulus over time	22
9	Surface plot of % elongation vs. days vs. % TPS	23
10	Surface plot of ultimate tensile strength vs. days vs. % TPS	23
11	Surface plot of young's modulus vs. days vs. %TPS	24
12	Plot of % weight loss over time	25
13	Plot of degradation temperature over time	26
14	Plot of absorbance at wavenumber 3300 cm ⁻¹ over time	29
15	Plot of absorbance at wavenumber 1750cm ⁻¹ over time	29
16	The percentage of continuity of thermoplastic starch (TPS) phase versus TPS content in samples, which was determined by means of solvent extraction [9]	

List of Tables

Ι	Regression Equations for Mechanical Properties.	24
II	Analysis of Variance for % Weight Loss of All Compositions	27
III	Tukey Method Grouping with 95% Confidence for % Weight Loss of AllCompositions	27
IV	Analysis of Variance for Degradation Temperature for All Compositions	28
V	Tukey Method Grouping with 95% Confidence for Degradation Temperature of All Compositions.	28

1.0 Abstract

Marine life has been suffering from macro- and microplastics since the inception of petroleum-based plastic. Bio-based biodegradable polymers such as PLA and TPS can help mitigate the damage done by petroleum plastics. Blending PLA and TPS can reduce the cost while preventing a significant effect on the material properties. PLA/TPS blend compositions such as 90/10, 80/20, 70/30 could be candidates for a solution. The PLA/TPS blends have been submerged in a marine environment at the Cal Poly Pier in Avila Beach for 8 weeks. Three sample sets containing three of each blend composition were collected every week and tested in order to measure the change in material properties due to biodegradation over time with respect to TPS percentage. Testing via thermogravimetric analysis, tensile testing, and Fourier-Transform Infrared Spectroscopy showed that there were signs of biodegradation, but there is not enough significance to determine if the samples biodegraded in a quantifiable amount over this time-frame.

2.0 Motivation

Since the birth of Bakelite in 1907 there has been a steady and exponential increase in the consumption of plastic products. Plastic has been used for a wide variety of applications such as phone cases, trash bags, shopping bags, keyboards, electronic devices, packaging, textiles, and many more. Plastic's versatility and inexpensiveness has made the material extremely popular for big business. Historically, most plastic materials have been made from crude oil. Unfortunately, mass production and consumption of plastic products made from crude oil has a lot of consequences and negative effects on the environment. Research has proven that plastic made from oil is polluting the ocean and affecting climate change [18].

2.1 Recycling Myths

Plastic has been highly praised for its recyclability, but mostly to sway consumers into believing that the pollutant has little effect on the environment [13]. Efforts have been made to increase and promote the recycling of crude oil plastic, but to no avail. According to the United States Environmental Protection Agency, less than 10% of all recycled plastic waste ended up being recycled in 2018 [8]. This means that of all the plastic products that were put into the recycling bin in 2018, less than 10% of those made it through the recycling process and are able to be reused. Considering that not everyone recycles all their plastic waste, there are millions of tons of plastic being put into landfills every year which doesn't include the amount of waste that makes its way into the ocean to degrade there [8].

2.2 Degradation of Petroleum Plastics

Degradation of a material means that it is losing mass over time. Most oil-based plastics can take several hundred years to degrade [22]. Marine degradation of oil-based plastics involves microscopic pieces of the material, also known as microplastics, releasing from the bulk material and contaminating the ocean. These microplastics, along with the other chemical pollutants released during degradation, are ingested by fish and other marine life that are often included in people's diets [18]. The risk of human exposure to microplastics from seafood is low because the digestive tract is removed before consumption for most fish, but as much as 7 micrograms could be ingested from a single portion of mussels. The long-term effects of microplastics in the human body are still being researched and closely studied [6].

3.0 Background

Biodegradable plastics would be able to mitigate the damage done by non-biodegradable plastics because biodegradation is not harmful to the environment and doesn't release microplastics or toxic chemicals. Most biodegradable materials consist of oligomers or monomers that can be used as a source of carbon for microorganisms, thus entering back into the carbon cycle [20].

3.1 Biodegradation Process

Biodegradation is the breakdown or degradation into organic matter such as H_2O and biomass by microorganisms such as bacteria, fungi, and algae. This process can happen in a variety of environments such as: soil, compost, landfill and aquatic as long as there are microorganisms present [2]. Biodegradation depends on microorganisms' enzyme apparatus. Without the enzymes being capable of breaking down the material, biodegradation would not occur. There are two different mechanisms that are key to the biodegradation process: hydrolysis and photooxidative-degradation [2].

3.1.1 Hydrolysis

Hydrolysis is a phenomenon when a water molecule breaks a chemical bond. This process mostly happens to naturally occurring polymers such as starches and cellulose because they have polysaccharides in them. The sugars are very easy for microorganisms to consume so they can biodegrade easily in an environment where water is present [15, 17].

3.1.2 Photooxidative-degradation

Photooxidative-degradation often occurs in water-resistant polymers that cannot hydrolyse. This process entails the molar mass reduction through peroxidation at temperatures common for composting (50° C- 70° C) or in light at ambient temperature (~ 25° C) [15].

3.2 What are PLA and TPS?

Biopolymers such as poly(lactic) acid (PLA) and thermoplastic starch (TPS) that are made from organic matter, are also biodegradable via mechanisms such as hydrolysis and photooxidative degradation. PLA is an aliphatic polyester made from lactic acid, the same lactic acid that is found in milk, yogurt, and other fermented products [4]. Currently, the lactic acid is obtained from chemical synthesis or fermentation, usually of corn sugar. TPS is made from starch that can be obtained from a variety of plants and mixed with glycerol, water, or another plasticizer. Due to the simple mixture of two organic materials, TPS is also biodegradable [11].

3.2.1 PLA Synthesis

The manufacturing of PLA can be done in one of several ways: direct polycondensation, azeotropic dehydrative polycondensation, and ring-opening polymerization. The technique used most often, due to its commercial availability, is ring opening polymerization [11]. Ring-opening polymerization (ROP) is a process that opens the cyclic lactide dimer in lactic acid to create long chains that can be connected to form polymers such as poly(lactic) acid [11].

3.2.2 TPS Synthesis

Thermoplastics are defined as "polymers that can flow when heated above melting or vitrification temperature" [19]. To turn starch into processable thermoplastic starch water must be added to the starch and mixed thoroughly. Starch solutions themselves are not stable because hydrogen bonds between starch molecules are more stable than hydrogen bonds between the starch molecules and water [19]. To equilibrate the solution, a plasticizer such as glycerol is added and then the solution can be processed through an extruder. The viscosity increases to create a gelatinous substance. This gelatinous mass is considered TPS because it is able to be processed as long as the water content is maintained. Other hydrophilic polymers are often added to TPS to make it more stable and improve mechanical and processing properties [19].

3.3 Blending PLA and TPS

On its own, PLA is an expensive material. The cost of PLA in 2016, according to a study done by Martien van den Oever et. al., was estimated to be around \$2 per kilogram while the real time cost of other crude-oil based plastics such as PE, PP and PET is between \$0.50 and \$1 per kilogram [12, 21]. It is very common for PLA and TPS, which has an average cost of \$0.45 per

kilogram, to be blended with other polymers or with each other to achieve desired material properties or to reduce cost [7].

3.3.1 Polymer Blending

A polymer blend is a mixture of two or more polymers blended together in a way that creates a new material with unique physical properties [10]. There are several different types of blends that depend on what category of polymers are being mixed together. These blend types include: thermoplastic-thermoplastic, thermoplastic-rubber, thermoplastic-thermoset, rubber-thermoset, and polymer-filler [10]. PLA and TPS are both thermoplastics so mixing them together would result in a thermoplastic-thermoplastic blend. In addition to these blend types there is another qualifying factor when describing polymer blends. A polymer blend can be miscible, immiscible, or partly miscible. For a polymer blend to be miscible, it must be homogeneous on a molecular level and be single-phase. An immiscible polymer blend is heterogeneous, meaning that the interface between the polymer phases carries some interfacial tension that prevents homogeneity on a molecular level [10].

3.3.2 PLA-Starch Blending

Starch and poly(lactic acid) have been blended together in many ways. Blending these two polymers together has become more common practice in recent years because of their potential to reduce environmental pollution. Another reason for blending PLA with starch is to reduce the cost [11, 14]. There are some difficulties to consider when making PLA/TPS blends.

Blending the two materials into one can be difficult and result in an immiscible or heterogeneous mixture due to interfacial tension. This occurs because the materials are not compatible. PLA is a hydrophobic polymer and TPS is a hydrophilic polymer. The two polymer phases do not mix well because PLA will repel the water molecules present in TPS [14]. Miscibility of this blend can be improved by adding a compatibilizer.

3.4 PLA/TPS Biodegradation in the Ocean

PLA blends have been studied in the marine environment, but there is little research on PLA/TPS blends. One study has studied biodegradation of PLA/TPS composites in marine environments while another experiment examined PLA blends with food grade gelatin in seawater [1, 23].

3.4.1 PLA/TPS Composite marine biodegradation

An experiment done by Xiaolei Chen et. al. studied the marine biodegradation of PLA/TPS composites. This experiment used 61.7/38.3 PLA/TPS composite bars submerged in static seawater. The seawater was temperature controlled at 25°C for one year. The study analyzed the weight loss over time of the sample and noticed that most of the loss in weight was coming from the degradation of TPS due to microbes. They also tested the change in crystallinity by looking at the change in glass transition temperature and found that over time, the crystallinity of the material decreased as more weight was lost. The study also examined the change of mechanical properties over time. They found that over time the impact strength, tensile strength, and elongation-at-break decreased significantly as there was less mass in the samples (Figures 1-3). Therefore, they concluded the slight increase in tensile strength and elongation-at-break at

2 months seen in Figures 2 and 3 is due to the plasticizing effect of the water on the starch. This phenomena deteriorated after a couple months because the effects of degradation began to outweigh the plasticizing effects [23].

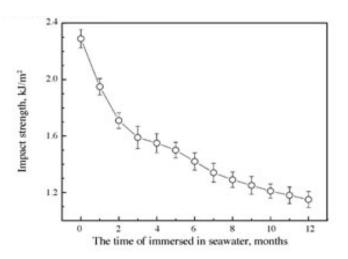


Figure 1: Impact strength of starch/PLA composites over time [23].

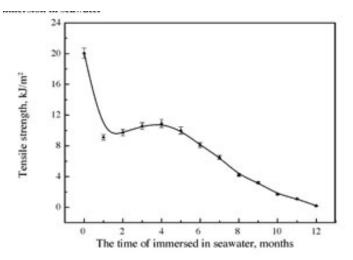


Figure 2: Tensile strength of starch/PLA composites over time [23].

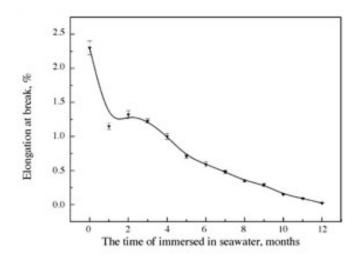


Figure 3: Elongation at break of starch/PLA composites over time [23].

3.4.2 PLA/Starch gelatin marine biodegradation

A study done by Guzman et. al. examined the degradation of PLA/TPS blends using foodgrade gelatin and glycerol in simulated marine conditions. The experiment involved PLA/Starch/Gelatin/Glycerol blend composition ratios of 2/2/2/1, 2/1/2/1, 2/2/1/1, and 3/2/4/1. The strips of material of 0.5 mm in thickness were put into the seawater environment with microorganisms in laboratory conditions for four months and used ASTM WK17751 as a reference for the marine aquarium conditions [1]. This study mainly focused on the visual aspects of biodegradation and the mass lost over time. After 10 days of being submerged in seawater, all samples started to show visual signs of fragmentation; after 4 weeks all samples had been torn to small pieces. The experiment ultimately found that gelatin was the main component that influenced the fragmentation of the materials and that starch blends are much more degradable in a marine environment than other commercially available biodegradable polymers [1].

4.0 Gaps in Literature

There is evidence to suggest that PLA/TPS biopolymers are a potential solution to the plastic pollution in the ocean because of their biodegradability and relatively low cost. While there are some blends being researched in other environments like soil and compost, there is still a wide area left to cover when it comes to understanding how PLA/TPS blends biodegrade in marine conditions. Xiaolei Chen et. al studied PLA/TPS composite materials and found interesting and important data on the behavior of the material as it degrades [23]. However, this was only for a composite and not for a homogeneous blend. This study also used controlled conditions in static seawater and only measured once a month. The study by Guzman et. al. was slightly more relevant in that it used PLA/TPS blends, but it also included gelatin as an additive and used marine aquarium conditions in a laboratory. This study also never specified what types of microorganisms were present in their seawater or what coast the water was from. These factors could have significant effects on the biodegradation of the material because of the high dependence of microorganisms on the rate of biodegradation. Studying how these materials biodegrade in a laboratory can provide useful information, but does not give a comprehensive understanding of what happens when the material reaches the real ocean that is not static, or controlled.

5.0 Research Question

Comparing how well Luminy LX175 and NuPlastiQ GP PLA/TPS blends of 10%, 20% and 30% TPS degrade *in situ* at Cal Poly Pier in Avila Beach, California marine conditions with an average temperature of 55°F and 33.5 psu salinity by testing the change in their mechanical properties, degradation temperature, mass loss, and FTIR spectra by testing samples every 7 days over the course of 56 days [3].

6.0 Method

In order to solve the research question and fill existing gaps in literature the following method was created and executed.

6.1 Design of Experiment

The experiment was designed to submerge samples in situ at Cal Poly Pier in Avila Beach, California for eight weeks. One group of samples were collected every week after the initial start of the experiment. Each group of samples contained three specimens of each PLA-TPS blend. For example, the first collection group contained three specimens with 10% TPS, three specimens of 20% TPS, three specimens of 30% TPS, and three specimens of 0% TPS. Having multiple of each blend in each testing group made it possible to replicate results for each blend every week, therefore increasing the significance and power of the results that were found.

6.2 Materials

The raw materials used in the blends are extrusion-grade Luminy[®] LX175 (PLA) and NuPlastiQ[®] GP (TPS). The experiment tested samples with a 90%PLA/10%TPS, 80%PLA/20%TPS and 70%PLA/30%TPS compositions that contained 1 per hundred resin of compatibilizer Maleic anhydride, 1 per hundred resin of plasticiser Vinnex[®], and 0.5 per hundred resin of chain extender Joncryl[®].

6.2.1 Sample Preparation

The samples were prepared by Daniel Licea, a PhD student at the University of Guadalajara in Mexico. Each blend and sample of pure PLA and TPS were made in a dogbone shape to be suitable for tensile testing. The dimensions of the gauge length, width, and thickness of these samples were made in accordance with ASTM D638-14.

Once the samples were mailed and received, they were ready to be weighed and labeled before being placed into the seawater tank system. The samples were labeled based on the collection group number and the blend percentage. In order to minimize the risk of confusing the sample types each sample was given a three digit number that corresponds to the TPS percentage and collection group number followed by a number 1-3 to differentiate between the replicates. For example, one sample of the third collection group of 20% TPS was labeled "203-1."

6.3 Experiment and Testing

The polyethylene seawater tank (2'x 2'x 3') was placed on the Cal Poly Pier and the racks for the samples were assembled using 1 inch diameter PVC piping. The samples were placed in polyethylene mesh tubing in order to preserve any large pieces of material that may break away from the bulk during degradation. Each sample collection group had its own mesh tube that contained 1 sample of each blend percentage (0% TPS 10% TPS 20% TPS 30% TPS). The tubes with the samples inside were labeled with markers and color-coded zip ties and attached to the PVC racks. The approximate temperature and salinity of the water at the Cal Poly Pier for the duration of the experiment was 55°F and 33.5 psu respectively [3]. The filtration system at the pier removed most objects above 5 micron in size from the water before reaching the samples.

Samples were collected every 7 days for 56 days. The mesh tube(s) containing the collection group were cut from the PVC rack and preserved in a fridge until testing was able to commence. After at least 24 hours in the fridge, the samples were removed from the mesh, characterized and tested, placed in a ziploc bag, then put back into the fridge until the next testing day.

Tensile testing of the samples was completed before any destructive material characterization techniques as to not introduce mechanical or thermal defects before testing. Each sample was loaded into the Instron 3630, pulled at an extension rate of 5 mm/min according to the ASTM D638-14 for Type IV tensile bars.

6.4 Material Characterization

Characterization techniques such as Fourier-Transform Infrared Spectroscopy and thermogravimetric analysis were used in order to determine changes in bond densities and % weight loss respectively.

6.4.1 Fourier Transform Infrared Spectroscopy

The specimens were characterized in a Jasco 4600 FTIR spectrometer and an absorption spectrum was obtained and the peaks for hydroxyl groups and ester groups were identified. The absorbance at these peaks were recorded for each sample.

6.4.2 Thermogravimetric Analysis

The specimens' % mass loss and degradation temperature were obtained via TA Instrument's Simultaneous DSC-TGA (SDTA). The samples were heated to 400°C at a ramp rate of 20°C per minute.

6.5 Statistical Analysis

Tensile data was statistically analyzed using surface plots, linear regressions, and ANOVA in MiniTab 19 software.

7.0 Results

7.1 Visual

The images of the samples in Figure 4 show how the color of each blend composition changed over time. The samples in the left column show the pure PLA samples which had no significant visual changes for the duration of the experiment with the undegraded samples at the top and the day 56 samples at the bottom. The images in the second column show the 90/10 composition over time. The 90/10 samples started to turn white after 7 days and continued to become whiter as time passed in the marine environment. The third and fourth columns show the 80/20 and 70/39 compositions respectively. These blend compositions turned white after 7 days and did not change for the rest of the experiment.

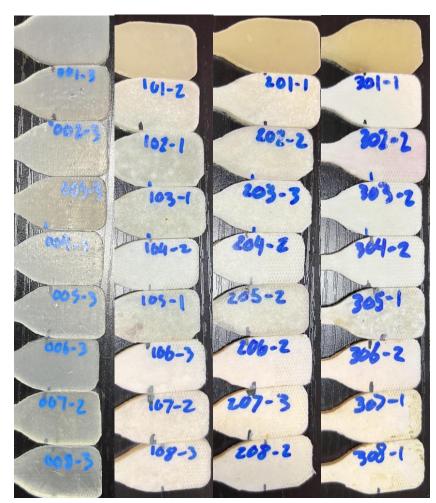


Figure 4: Pictures of samples over time. Increasing in %TPS from left to right (PLA, 10%, 20%, 30%). Increase in days spent in the marine environment from top to bottom (0, 7, 14, 21, 28, 35, 42, 49, 56).

The change in color and texture for the blend samples indicates hydrolysis of the thermoplastic starch. Starch is very hydrophilic so it will absorb water much easier than PLA which is a hydrophobic polymer [14]. The change in color is indicative of hydrolysis of the starch which is an important component of biodegradation [5]. The 70/30 samples have the highest starch content and saw a fast transformation in color while the pure PLA has no starch and saw no change in color.

7.2 Tensile

Each sample was tensile tested to determine how the mechanical properties changed over the course of the experiment. Figure 5 shows a typical stress vs. strain curve for each blend composition and PLA. Mechanical property information such as the % elongation, ultimate tensile strength, and elastic modulus were obtained from the stress vs. strain curves for each composition. Figure 6 shows the change in % elongation over time for each sample type, Figure 7 shows the change in ultimate tensile strength, and Figure 8 shows the change in elastic modulus.

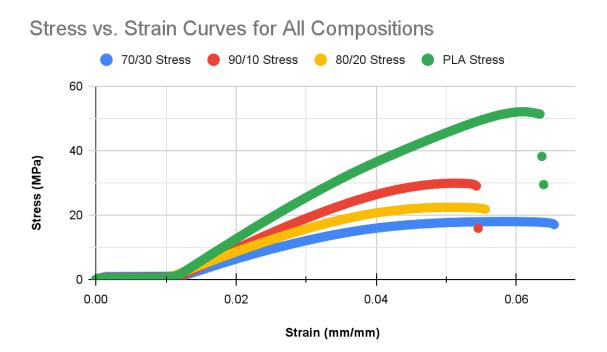


Figure 5: Stress vs. strain curve for all compositions.

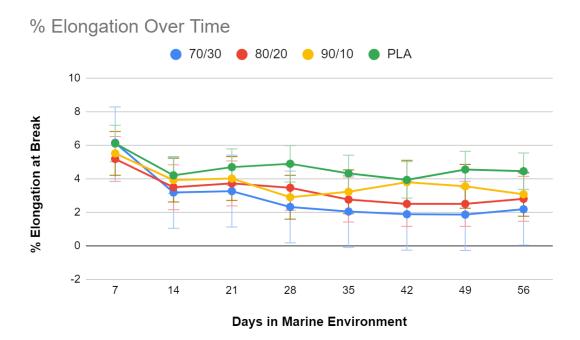


Figure 6: Plot of change in % elongation for all compositions.

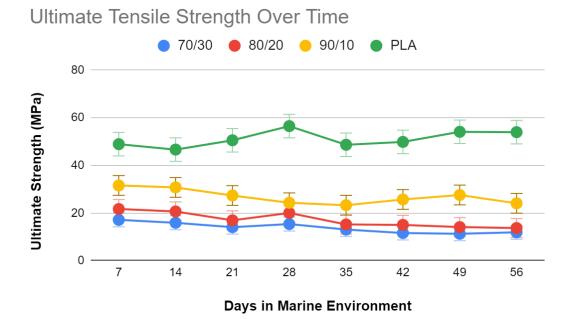


Figure 7: Plot of ultimate tensile strength over time for all compositions.

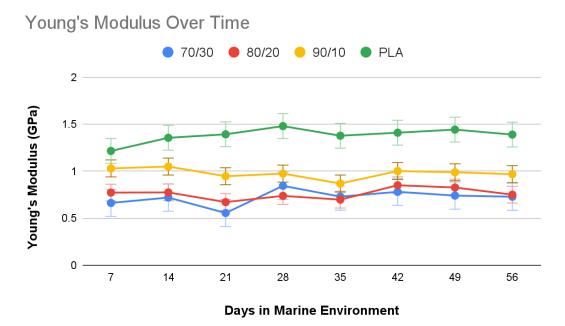


Figure 8: Plot of Young's modulus over time for all compositions.

Using this data, a planar regression was generated for each mechanical property. The % elongation, modulus of elasticity, and ultimate tensile strength were each plotted as a function of %TPS and days in the marine environment as seen in Figures 9-11. MiniTab was used to create regression equations for each mechanical property in order to predict the mechanical properties at a specified %TPS and days in the marine environment.

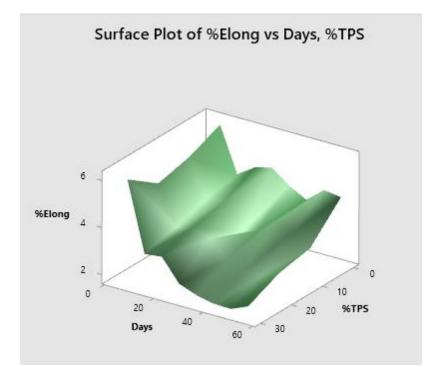


Figure 9: Surface plot of % elongation vs. days in marine environment vs. % TPS.

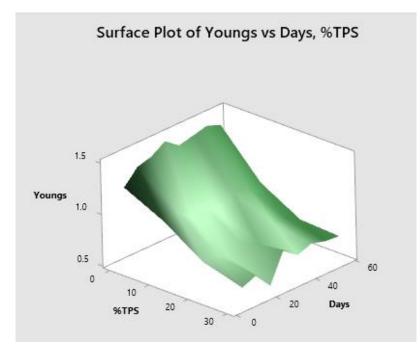


Figure 10: Surface plot of Young's modulus vs. days in marine environment vs. %TPS.

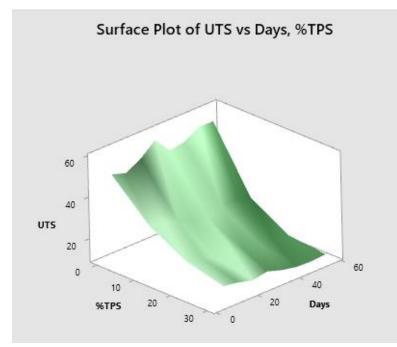


Figure 11: Surface plot of ultimate tensile strength vs. days in marine environment vs. % TPS.

Table I shows the regression equations and R-squared value for the equations. The R^2 values for % elongation, ultimate tensile strength and Young's modulus are below that of an ideal fit, but when considering the nature and uncontrollability of the ocean's environment, high R^2 values would be difficult to obtain. That being said, the error in the data itself is very high. While these regressions have relatively good fits, the error indicates that there may not be a significant trend.

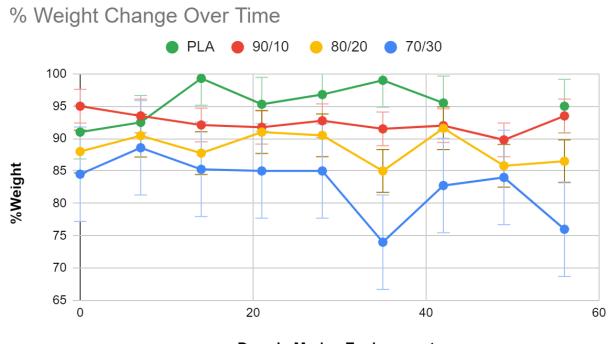
Property		Equation	R-Squared
% Elongation	=	5.8 - 0.04109*Days - 0.0579*%TPS	65.59%
Ultimate Tensile Strength	=	47.88 - 0.0765*Days - 1.2167*%TPS	84.37%
Young's Modulus	=	1.2562 + 0.00113*Days - 0.02206*%TPS	83.23%

 Table I: Regression Equations for Mechanical Properties

Results

7.3 TGA

One sample of each composition was tested for every week of collection to determine the % weight loss over time as seen in Figure 12. The degradation temperature was also measured and the changes in T_d for each composition is shown in Figure 13.



Days in Marine Environment

Figure 12: Plot of % weight loss over time for all compositions.

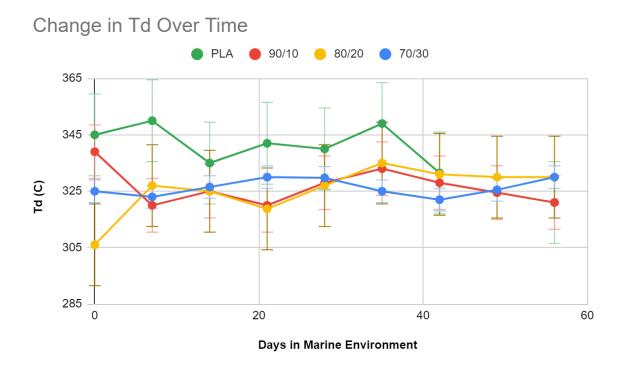


Figure 13: Plot of degradation temperature over time.

The % weight loss over time does not seem to have a significant trend as indicated by the length of the error bars. The error in this data shows that, while there could be a potential decreasing trend in % weight loss over time, it is not significant enough to confidently make that conclusion. The degradation temperature does not have any significant changes over time. This is to be expected because the materials, though possibly biodegrading, are not undergoing a dramatic change in chemical structure. Biodegradation would break the bonds holding the chains together but would not change the overall chemical structure and therefore, the degradation temperature should not change.

ANOVA with Tukey comparison was used to determine if the % weight loss and degradation temperature of the compositions were significantly different from each other throughout the experiment. Table II and Table III shows that % weight loss for the PLA, 80/20 blend and 70/30 blend were significantly different from each other, but the 90/10 blend did not differ significantly from the 80/20 blend and PLA. Table IV and Table V show that the PLA had a different average degradation temperature compared to the blends, but the blends did not have significantly different degradation temperatures.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	783.8	261.270	26.95	0.000000009
Error	31	300.6	9.696		
Total	34	1084.4		-	

Table II: Analysis of Variance for % Weight Loss of All Compositions

Table III: Tukey Method Grouping with 95% Confidence for % Weight Loss of All	
Compositions	

Factor	Ν	Mean	Grouping
PLA	8	95.55	А
90/10	9	92.433	AB
80/20	9	88.511	В
70/30	9	82.79	С

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	1060	353.34	6.63	0.001
Error	31	1651	53.27		
Total	34	2711		-	

Table IV: Analysis of Variance for Degradation Temperature for All Compositions

Table V: Tukey Method Grouping with 95% Confidence for Degradation Temperature of All Compositions

Factor	Ν	Mean	Grouping
PLA	8	339.19	А
90/10	9	326.50	В
80/20	9	326.31	В
70/30	9	325.53	В

7.4 FTIR

FTIR spectra were obtained for each composition every 7 days. The characteristic peaks of interest were determined to be at wavenumbers 3300 and 1750. The peak at the 3300 wavenumber indicates the presence of hydroxyls or O-H bonds which are found in both water and starch. The peak at 1750 indicates the presence of esters or C=O bonds which are found in PLA [9]. The absorbance at these wavenumbers was recorded over the duration of the experiment to determine if those bonds were breaking or forming (Figure 14-15).

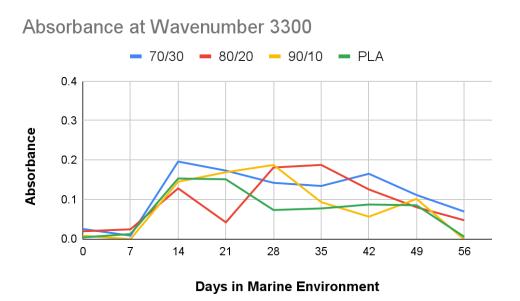


Figure 14: Plot of absorbance of hydroxyls over time for each composition.

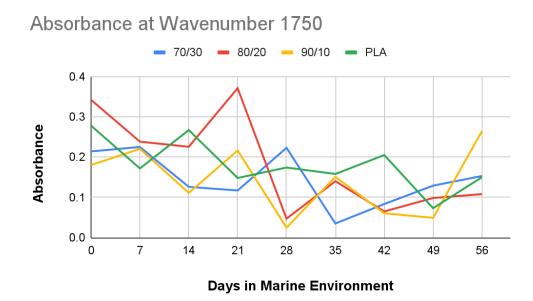


Figure 15: Plot of absorbance of esters over time for each composition.

The absorbance of hydroxyls increased for all compositions after 7 days. This increase in absorbance indicates that the samples absorbed water. The 70/30 blend had the highest maximum absorbance and reached the maximum faster than the other blends. PLA had the lowest maximum absorbance which is explained by its hydrophobic nature. The 90/10 and 80/20 blends reached a similar maximum at 28 and 35 days respectively. The plot of the absorbance of ester bonds suggests that there could be a decreasing trend over time, but it is too inconsistent to conclude that this is due to biodegradation of PLA.

8.0 Discussion

The absorbance of water in the blends being overall higher than the PLA could suggest that the blends are undergoing hydrolysis which is also seen in the change of color of the blend samples over time (Figure 14, Figure 4). While the blends may be hydrolyzing, it is too early to determine if this hydrolysis is being catalyzed by enzymes to cause biodegradation. The filtration system at the Cal Poly Pier filtered out most things above 5 micron in size. The filtered water could have prevented samples from exposure to microorganisms and there is currently no data on what microorganisms are present in the marine water in Avila Beach after filtration. If the filtration system completely prevented the samples from being exposed to microorganisms, then biodegradation would not be possible and thus, this experiment would be a study of abiotic degradation; that is, degradation that occurs only by means of water, temperature, salinity, and pH.

The tensile, TGA, and FTIR data suggests that the PLA is significantly different from the blends and that the 70/30 blend is significantly different from the other compositions. The PLA is expected to be significantly different because it contains no TPS, but the 70/30 blend standing out from the other blends so significantly in a short amount of time was not expected. After further research, literature suggests that PLA/TPS blends with TPS content above 20% and below 80% exist in a co-continuous phase [9]. In blend compositions with 20% or less, the TPS is encapsulated by the PLA so it is more protected from the water as seen in Figure 16. The data is consistent with this idea and that is shown through the groupings determined in the Tukey comparisons that show the % weight loss for the 70/30 blend is significantly different from the other blends (Table III). It is also shown in the FTIR data that the 70/30 blend had the highest maximum absorbance of hydroxyls and reached its maximum faster than the other blends (Figure 14). The higher

absorbance of water and significantly lower % weight loss could be due to the existence of a cocontinuous phase (Figure 16) in the 70/30 blend because the co-continuous phase exposes the TPS to the water and it is not being protected as much by the PLA compared to the other blends.

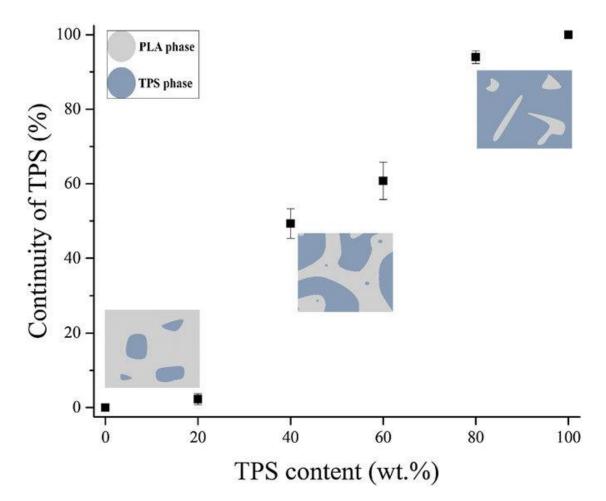


Figure 16: The percentage of continuity of thermoplastic starch (TPS) phase versus TPS content in samples, which was determined by means of solvent extraction [9].

9.0 Conclusions

- The data makes some weak suggestions that the blends could be biodegrading, but there is not enough statistical significance to confidently determine how fast or how much the blends are biodegrading for the length of this experiment.
- The 70/30 blend's results are consistent with literature that claims PLA/TPS blends with TPS composition above 20% are a co-continuous phase and this phenomenon explains why the 70/30 had more dramatic changes compared to the other blend compositions.
- 3. The filtered marine water may have prevented the samples from exposure to microorganisms that would be crucial to biodegradation.
- 4. Results show that PLA is resistant to deterioration, fragmentation, and degradation in the tested abiotic conditions.

10.0 Future Work

Due to the data being mostly inconclusive, some future work may include:

- 1. Further analysis of all the blend compositions such that each data point is made of at least three replicates.
- 2. Repeating the experiment for a longer duration.
- 3. Expanding the breadth of the blend compositions being tested.
- 4. Repeat the testing with samples dried in an oven to obtain more accurate TGA results and to measure the change in weight due to the water.
- 5. Study of microorganisms present in filtered marine water.

11.0 References

[1] A. Guzman-Sielicka, H. Janik, and P. Sielicki, "Proposal of new starch-blends composition quickly degradable in marine environment," *Journal of Polymers and the Environment*, vol. 21, no. 3, pp. 802–806, 2012.

[2] A. Hodzic, "Re-use, recycling and degradation of Composites," *Green Composites*, pp. 252–271, 2004.

[3] A. McGaraghan, "Cal Poly Pier," *California HABMAP*, 30-Jul-2019. [Online]. Available: https://calhabmap.org/cal-poly-pier. [Accessed: 04-Dec-2021].

[4] Abedi, Elahe, and Seyed Mohammad Bagher Hashemi. "Lactic acid production producing microorganisms and substrates sources-state of art." Heliyon vol. 6,10 e04974.
12 Oct. 2020, doi:10.1016/j.heliyon.2020.e04974.

[5] C. A. Rodrigues, A. Tofanello, I. L. Nantes, and D. S. Rosa, "Biological oxidative mechanisms for degradation of poly(lactic acid) blended with thermoplastic starch," *ACS Sustainable Chemistry & Engineering*, vol. 3, no. 11, pp. 2756–2766, 2015.

[6] C. Giacomo Avio, G. Duflos, M. Fossi, and L. Gilliam, Food and Agriculture Organization, Rome, Italy, tech., 2017.

[7] Corn, Part of A Global Economy, Corn Refiners Annual Report 2007, Corn Refiners Association, Washington D.C., USA, 2007.

[8] Environmental Protection Agency, "Plastics: Material-Specific Data," *EPA*, 2019. [Online]. Available: https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data. [Accessed: 29-Nov-2021].

[9] Esmaeili, Mohsen & Pircheraghi, Gholamreza & Bagheri, Reza & Altstädt, Volker.
(2018). The impact of morphology on thermal properties and aerobic biodegradation of physically compatibilized poly (lactic acid)/co-plasticized thermoplastic starch blends.
Polymers for Advanced Technologies. 29. 10.1002/pat.4407.

[10] J. Parameswaranpillai, S. Thomas, and Y. Grohens, "Polymer blends: State of the art, new challenges, and opportunities," *Characterization of Polymer Blends*, vol. 1, pp. 1–6, 2014.

[11] J. Ren, *Biodegradable poly*(*lactic acid*): *Synthesis, modification, processing and applications*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2011.

[12] K. New Media Publisher GmbH, "Real Time Price List," *Raw Materials & Prices*,2021. [Online]. Available:

https://plasticker.de/preise/pms_en.php?kat=Mahlgut&aog=A&show=ok&make=ok. [Accessed: 04-Dec-2021]. [13] L. Sullivan, "How big oil misled the public into believing plastic would be recycled," *NPR*, 11-Sep-2020. [Online]. Available: https://www.npr.org/2020/09/11/897692090/how-big-oil-misled-the-public-into-believing-plastic-would-be-recycled. [Accessed: 29-Nov-2021].

[14] M. Akrami, I. Ghasemi, H. Azizi, M. Karrabi, and M. Seyedabadi, "A new approach in compatibilization of the poly(lactic acid)/thermoplastic starch (PLA/TPS) blends," *Carbohydrate Polymers*, vol. 144, pp. 254–262, Jun. 2016.

[15] M. M. Reddy, "Oxo-degradation of Polyethylene," dissertation, RMIT University, Melbourne, Australia, 2008.

[16] Merlic, C. A., & amp; Strousse, J. (2000, June 22). IR Absorption Table. WebSpectra.Retrieved June 2, 2022, from https://webspectra.chem.ucla.edu/irtable.html

[17] N. Karak, "Biodegradable polymers," *Vegetable Oil-Based Polymers*, pp. 31–53, 2012.

[18] R. Labbe-Bellas, "Plastic in the Environment," in *Plastic & climate: The hidden costs* of a plastic planet, Washington, DC: Center for International Environmental Law (CIEL), 2019, pp. 69–77.

[19] R. Shanks and I. Kong, "Thermoplastic starch," Thermoplastic Elastomers, 2012.

[20] Siracusa, Valentina. "Microbial Degradation of Synthetic BiopolymersWaste." *Polymers* vol. 11,6 1066. 20 Jun. 2019, doi:10.3390/polym11061066.

[21] Van den Oever, Martien & Molenveld, Karin & van der Zee, Maarten & Bos,Harriëtte. (2017). Bio-based and biodegradable plastics – Facts and Figures. Focus on food packaging in the Netherlands. 10.18174/408350.

[22] WWF-Australia, "The lifecycle of plastics," *WWF*, 02-Jul-2021. [Online]. Available: https://www.wwf.org.au/news/blogs/the-lifecycle-of-plastics#gs.gychs3. [Accessed: 29-Nov-2021].

[23] X. Chen, L. Wang, J. Shi, H. Shi, and Y. Liu, "Environmental degradation of starch/poly(lactic acid) composite in seawater," *Polymers and Polymer Composites*, vol. 19, no. 7, pp. 559–566, 2011.