Utilizing a ≈5.0000 *m* Citric Acid Solution to Formulate a Biodegradable Alternative to Plastic Using Selected New Jersey Leaf Species by Studying Leaf Morphology

Abstract

Increased and continued use of plastic and reliance on materials made of plastic have become a widespread issue for the entire world. Over the past few decades, of the billions of tons of plastic that have been manufactured—91% of this plastic is not recycled (Parker, 2018). With the continued and increased production and use of plastics, this also creates risks to different environments' health and stability. Chemicals added to most plastic products are absorbed by humans' bodies and have been found to alter hormones (Yang, Yaniger, Jordan, Klein, & Bittner, 2011). The goal of this experiment is to find an affordable and reliable leaf type, and method, to produce an environmentally-friendly, biodegradable, leaf-based bioplastic to reduce and possibly reverse damage caused by liquid petroleum gases (LPG) and natural gas liquids (NGL). *Acer saccharum* (Sugar maple), *Ilex opaca* (American holly), *Prunus serotina* (Black cherry), *Robinia pseudoacacia* (Black locust), and *Quercus rubra* (Northern red oak) leaves were used to create five different bioplastic types and were collected along the Point Pleasant Canal. After the leaves were drained of their nutrients in separate ≈5.0000 *m* citric acid and water solutions, various amounts were combined with acetic acid, glycerin, a natural polymer (cornstarch), and distilled water. Once the mixture was heated enough to create a paste-like substance, it was placed on parchment paper to fully solidify into a plastic. The bioplastics were then examined and tested to determine which plastics seem to be the most practical for real-world applications. Two of each plastic type was then submerged in a plastic container with 400 milliliters of ocean water to perform a controlled simulation regarding biodegradability. Statistical analyses were then conducted on the data obtained from the simulation to determine significance and correlation, if any. The plastics' leaf type was then looked at and compared to other leaves' morphology to find leaves with similar characteristics in order to provide various options for ideal biodegradable plastics.

Introduction

The toxic materials injected into plastics can have devastating and deadly effects on animals' health, especially marine creatures. When plastic gets into water environments, not only does it kill sea creatures, but it poses a threat to species invading areas not native to them by using the floating plastic as a transportation device (Fischer, 2009).

Over the years, invisible plastic particles in drinking water have been found in higher and higher concentrations (Ayer & Merino, 2018). A significant component of plastic pollution is microplastics—extremely small pieces of plastic debris in the environment resulting from the disposal and breakdown of consumer products and industrial waste (Lexico, 2019). These microplastics are normally created when large plastic debris is being continuously broken down over time by sunlight and erosion. "Recent studies into water contamination have found microplastics in 83% of tap water samples from major cities around the world and in 93% of samples from the world's top 11 bottled water brands" (Ayer & Merino, 2018). The longer the problem of microplastics resides without being acted upon, the larger the problem will get. Biodegradable plastics are an attainable and achievable solution because they can fully decompose.

Biodegradable plastics show a feasible and viable solution to the ever-growing issue of plastic use. "Biodegradable plastic is plastic that decomposes naturally in the environment. This is achieved when microorganisms in the environment metabolize and break down the structure of biodegradable plastic. The end result is one which is less harmful to the environment than traditional plastics (Connecticut Plastics, 2019)." When comparing biodegradable plastics to a normal plastic product, one can see that the biodegradable plastic has many evident advantages. After regular plastics are formed, they hold carbon within them; this carbon is eventually released into the atmosphere and acts as a greenhouse gas. Although there may be speculation that biodegradable plastics may contain small fragments of metal that are released into the atmosphere when they are decomposed, there is no evidence to support this. The plastics that are going to be created in this experiment contains no chemicals that would pose as a threat to the environment. The issue can also be completely avoided when creating plastics that are 100% decomposable.

Leaves can be found virtually anywhere on the planet, other than Antarctica (British Antarctic Survey, 2015). This makes leaves one of the best materials to be used in the construction of biodegradable plastics. Leaves also pose no negative effects to the environment, unlike petroleum, which is found in many plastics. The petroleum used to make the plastics is released when they are being decomposed or destroyed, which provides a risk to the atmosphere because of the carbon being emitted. However, not only is carbon being emitted into the atmosphere when these plastics are burned, microplastics are contaminating the air as well.

“Scientists recorded a daily rate of 365 microplastic particles per square meter falling from the sky in the Pyrenees Mountains in southern France” (Leahy, 2019). According to National Geographic, “microplastics smaller than 25 microns can enter the human body through the nose or mouth and those less than five microns can end up in lung tissue” (Leahy, 2019). Everywhere one can imagine, microplastics are found in abundance and can not be avoided.

The goal of my research is to find the most effective leaf type to create biodegradable plastics that allows the plastic to biodegrade the quickest and cleanest by looking at the morphology, or physical characteristics of *Acer saccharum*, *Ilex opaca*, *Prunus serotina*, *Robinia pseudoacacia*, and *Quercus rubra* leaves. By using leaves of trees commonly found in North America, and more specifically the North East, I will be able to find an affordable and reliable method, along with leaf type, to use to make biodegradable plastics and reduce and hopefully start to reverse the damage caused to the Earth by these harmful plastic materials. Environmentally-friendly plastics are one of the best, if not the best way to decrease the effects of human affected climate change, microplastics found in bodies of water and drinking water, and plastics taking their toll on marine life.

Methodology

Citric Acid Solution Formation

A ≈5.0000 *m* citric acid solution was created (**Figure 7-8**) to strip the leaves of their nutrients in order to be utilized for the bioplastic creations. Approximately 1758.02 g of solution was created by combining 473.18 g water and 453.59 g citric acid, twice. The resulting solution was divided into five containers, one for each leaf type, and the leaves were each permitted to dissolve for four months. 90.00 g of leaves were put into each container (**Figures 9-10**).

Bioplastic Creation

Five ≈5.0000 *m* citric acid and water solutions, each containing the nutrients of one of the five leaves used, were combined with a constant amount of glycerin, a natural polymer (cornstarch), acetic acid, and distilled water (**Figures 11-12**). 10.00 mL solution, 2.00 g glycerin, 3.00 g cornstarch, 2.02 g acetic acid, and 10.00 mL distilled water were mixed thoroughly

(**Figure 13**) and heated until a paste started to form. It took approximately 2-3 minutes for each of the mixtures to form a plastic (**Figure 14**). When the paste was formed, it was placed into a mold and air-dried for two days or until fully solid (**Figure 15**). Six of each type of bioplastic was created, resulting in thirty bioplastics altogether.

Saltwater Simulation

After each of the bioplastics was created, two of each type were placed in 400 mL of saltwater collected from Mount Street Beach in Bay Head, NJ (**Figure 6**). Approximately 96% of the water on Earth is saltwater, which is why water from the ocean was used to see how effectively the plastics will biodegrade in the real-world. The original mass of the plastics were recorded before they were placed in the water, and were tested at the same time every day for 10 days to determine which plastic will biodegrade at the fastest rate, and which will lose the most mass in total to establish the best plastic for biodegradability (**Table 1**).

Statistics

Statistical analyses were conducted on the data obtained to determine if there was a significant difference between the different leaves. A single factor ANOVA test was run, as opposed to a t-test, because five populations were compared. The p-value calculated from the ANOVA was less than the alpha value of 0.05, which establishes significance between at least one pair of data sets (**Table 2**). Because significance was established, a post-hoc Tukey Test was performed to ascertain where the significance was found in the t-test (**Table 3**). A regression test was also completed for all five sets of data to evaluate correlations.

Determination of Ideal Bioplastic

The ideal bioplastic was determined by looking at the results from the Tukey Test, the total mass lost of each plastic type (**Figures 16-19**), and the correlation from the results of the regression tests run. By examining the results, the bioplastic that significantly lost the most mass compared to the other bioplastics was found. With this newfound ideal bioplastic, online research was conducted to determine leaves that would produce similar products. The leaves found were further examined to prove they exhibited similar qualities to the leaf found by looking at the aforementioned criteria.

Results

The bioplastic masses ranged from 7.72 g to 9.03 g for their original masses and 10.04 g to 16.55 g for their masses after 10 days submerged in saltwater. A single factor ANOVA test calculated a p-value less than 0.05, proving significance between the mass differences in the bioplastics. The p-value calculated from the ANOVA test comparing the mass differences was approximately 0.0490 for a one-tailed display. The Tukey test ascertained the significance between the *P. serotina* and *Q. rubra* bioplastics.

With respect to mass lost per day, trendlines were created for each bioplastic tested in order to analyze slopes and see correlation (**Figures 1-5**). The leaf type that showed the largest positive slope was *Q. rubra* (**Figure 5**), while the leaf type that showed the largest negative slope was *P. serotina* (**Figure 1**). The obtained R^2 values for the *Q. rubra* bioplastics are 0.1079 and 0.1298, showing a weak correlation. The obtained R^2 values for the *P. serotina* bioplastics are 0.0055 and 0.0598, meaning there is less correlation between the *P. serotina* bioplastics than *Q. rubra* bioplastics. Seeing as how the R^2 value is relatively low, the data shows that although the data exhibits a high variability there is still a significant trend between the data points.

Discussion

The *P. serotina* leaves were shown to be the most desirable leaves to create bioplastics because they degraded the most readily between the five types. The Tukey Test, ran after the ANOVA was proven significant, showed that the significant difference was between the *P. serotina* and *Q. rubra* data sets. Because the *P. serotina* leaves showed significant difference and gained the least amount of mass, they are the most ideal leaf to use for creating these bioplastics. The *Q. rubra* leaves are the worst of the leaves to use for bioplastic creation. Although the data was significant, they gained the most mass in total and will take the longest to fully decompose. The p-value obtained for the ANOVA test performed was 0.0490, which proves significance because it is lower than the alpha value of 0.05 used.

For this research, it was hypothesized that sugar maple leaves would be the most effective in creating a biodegradable alternative to plastic. *A. saccharum* leaves were expected to be the best leaf for the bioplastic because not only do they have good shape and are relatively durable, but many animals such as white-tailed deer, moose, and flying squirrels, are known to eat the leaves for the nutrients that they provide (Lake Forest College). The hypothesis was shown to be incorrect because of the results from the ANOVA and Tukey Test performed. It is likely that the *P. serotina* leaves biodegraded the fastest because the leaves contain amygdalin, a bitter crystalline compound that can cause cyanide poisoning if consumed. Because amygdalin is found in the leaves, animals refrain from eating them. This allows the leaves to be weaker and flimsier because they have a natural defense against animals that may try to eat them. *P. serotina* leaves are also commonly used in mulch because they biodegrade quickly, although they are not high in nutrients (Compost Research Centre).

It is highly unlikely that there were any lurking variables not accounted for in this project. All masses, concentrations, and time allotments were kept constant for every part of the project, and the leaves collected were collected at the same day under the same weather conditions. All of the leaves were dissolved for the same amount of time, and all of the ingredients used to create the bioplastics were from the same source for each bioplastic made. The amount of time the combined ingredients were heated for was constant as well, along with the amount of time the plastics were given to dry.

Conclusion

The data collected suggests that *P. serotina* leaves exhibit the best leaf shape to create plastics that will biodegrade readily in the environment. The shape of *P. serotina* is elliptic and ovate, which means that other leaves that have these shapes will likely make similar plastics. Elliptic shaped leaves are about twice as long as they are broad, and include many species of cherry, and beech trees. Ovate shaped leaves are shaped like an egg and have an oval outline and ovoid shape. Many species of plum tree have ovate leaves. Ultimately, leaves that will make bioplastics similar to the one created by the *P. serotina* leaves are ones from beech, plum, and other cherry trees. It is beneficial for bioplastics to be made from more than solely those of *P.*

serotina so they can be readily accessible not only where *P. serotina* is located. It is also important to note that by utilizing morphology when assessing the different bioplastics, this project can be applied anywhere in the world and has more range than solely in New Jersey.

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Table 1: The mass values (g) obtained from the ten bioplastics observed during a ten day testing period. The initial values ranged from 7.72 g to 9.03 g, and the final values ranged from 10.04 g to 16.55 g.

Day	*P. serotina* 1 (g)	*P. serotina* 2 (g)	*R. pseudoacacia* 1 (g)	*R. pseudoacacia* 2 (g)	*I. opaca* 1 (g)	*I. opaca* 2 (g)	*A. saccharum* 1 (g)	*A. saccharum* 2 (g)	*Q. rubra* 1 (g)	*Q. rubra* 2 (g)
0	7.83	7.72	8.43	8.53	8.16	8.11	8.3	8.35	8.11	9.03
1	14.28	14.55	16.4	16.3	15.85	14.73	15.84	16.32	15.93	17.97
2	13.34	13.87	15.85	16.77	15.08	14.17	15.14	15.35	15.27	17.96
3	12.99	13.63	15.46	16.17	14.92	13.89	14.78	15.13	14.88	17.21
4	12.68	13.36	15.19	15.69	14.73	13.57	14.26	14.77	14.76	16.78
5	12.54	13.28	14.98	15.59	14.55	13.41	14.4	14.67	14.69	16.63
6	11.97	12.66	14.54	15.54	14.49	13.41	14.42	13.98	14.68	16.7
7	11.39	12.31	14.33	15.49	14.41	12.97	14.27	13.76	14.68	16.61
8	10.85	11.71	13.93	15.32	14.29	12.67	14.15	13.39	14.67	16.59
9	10.72	11.52	13.82	15.24	14.11	12.58	14.07	13.36	14.61	16.59
10	10.04	11.19	13.44	15.09	13.98	12.08	13.48	12.95	14.59	16.55
Mass change (g)	2.21	3.47	5.01	6.56	5.82	3.97	5.18	4.6	6.48	7.52

Table 2: The single factor ANOVA test results. The resulting p-value is highlighted in yellow.

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
1	2	5.68	2.84	0.7938		
2	2	11.57	5.785	1.20125		
3	2	9.79	4.895	1.71125		
4	2	9.78	4.89	0.1682		
5	2	14	7	0.5408		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	18.54266	4	4.635665	5.24954703	0.04897324	5.19216777
Within Groups	4.4153	5	0.88306			
Total	22.95796	9				

Table 3: The post-hoc Tukey Test results. The results of the significant mass changes are highlighted in green. A is the *P. serotina* plastics and E is the *Q. rubra* plastics.

Tukey HSD results			
treatments pair	Tukey HSD Q statistic	Tukey HSD p-value	Tukey HSD inferfence
A vs B	4.4321	0.1182299	insignificant
A vs C	3.0927	0.3149869	insignificant
A vs D	3.0851	0.3166911	insignificant
A vs E	6.2606	0.0342970	* p<0.05
B vs C	1.3394	0.8582027	insignificant
B vs D	1.3469	0.8557170	insignificant
B vs E	1.8285	0.6965222	insignificant
C vs D	0.0075	0.8999947	insignificant
C vs E	3.1679	0.2983483	insignificant
D vs E	3.1754	0.2967221	insignificant

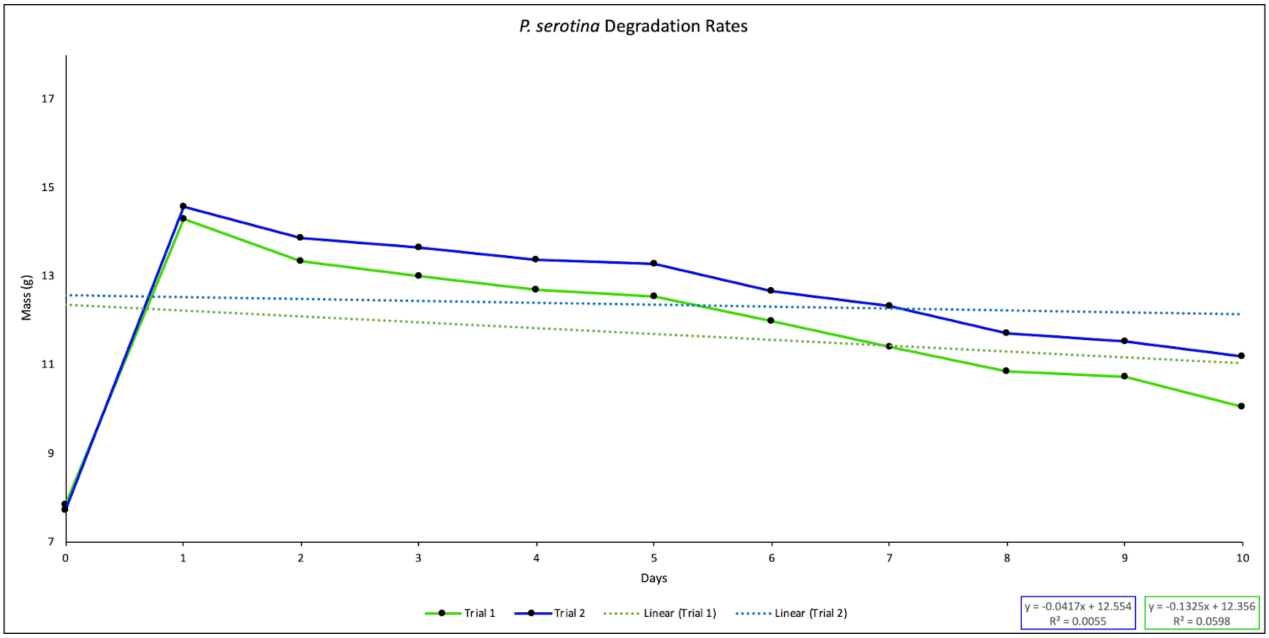


Figure 1: The degradation rates of the *P. serotina* samples. They exhibited the greatest negative slopes of the five leaf types.

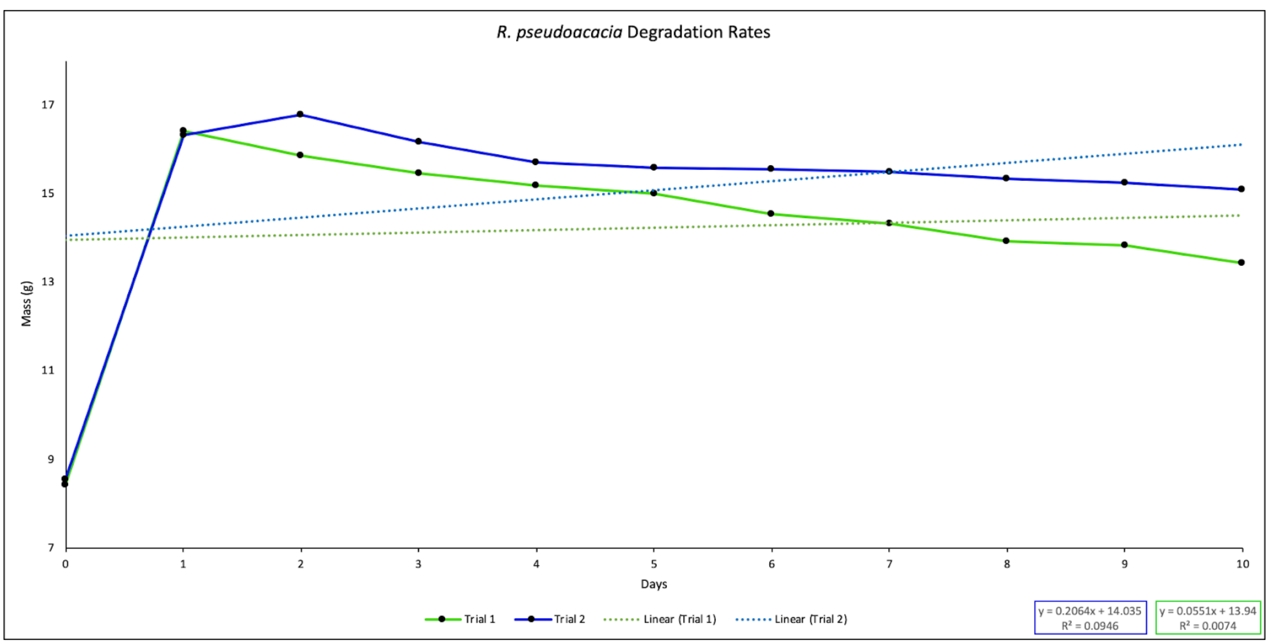


Figure 2: The degradation rates of the *R. pseudoacacia* samples. They exhibited varying slopes.

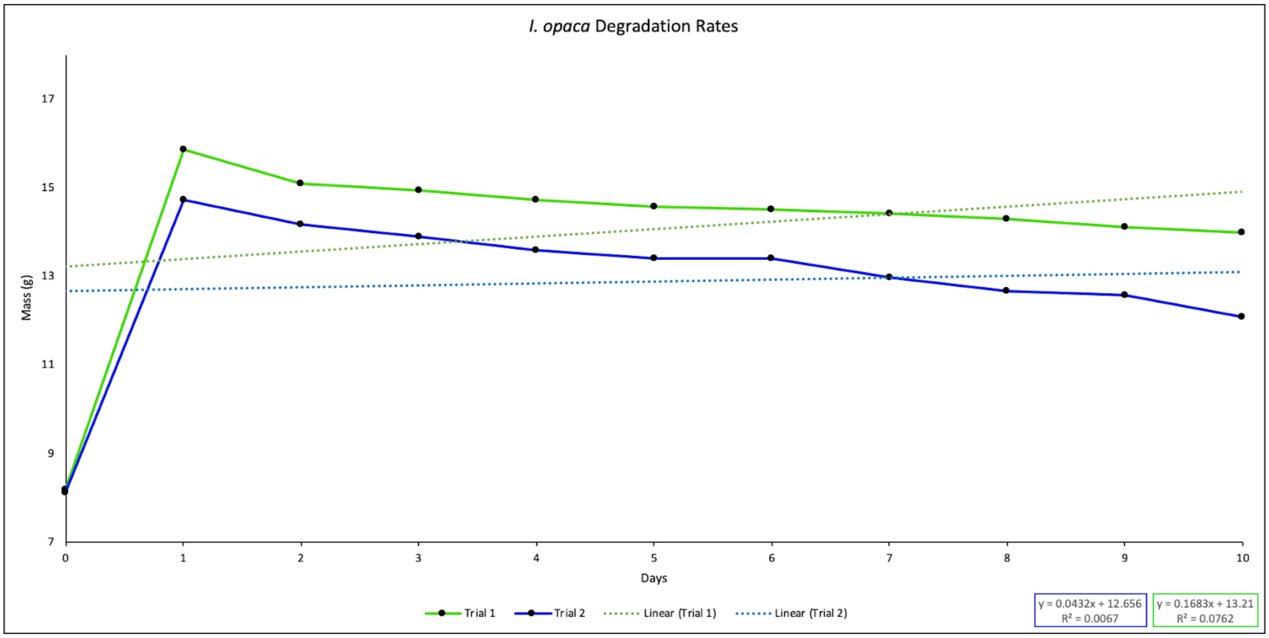


Figure 3: The degradation rates of the *I. opaca* samples. They exhibited varying slopes.

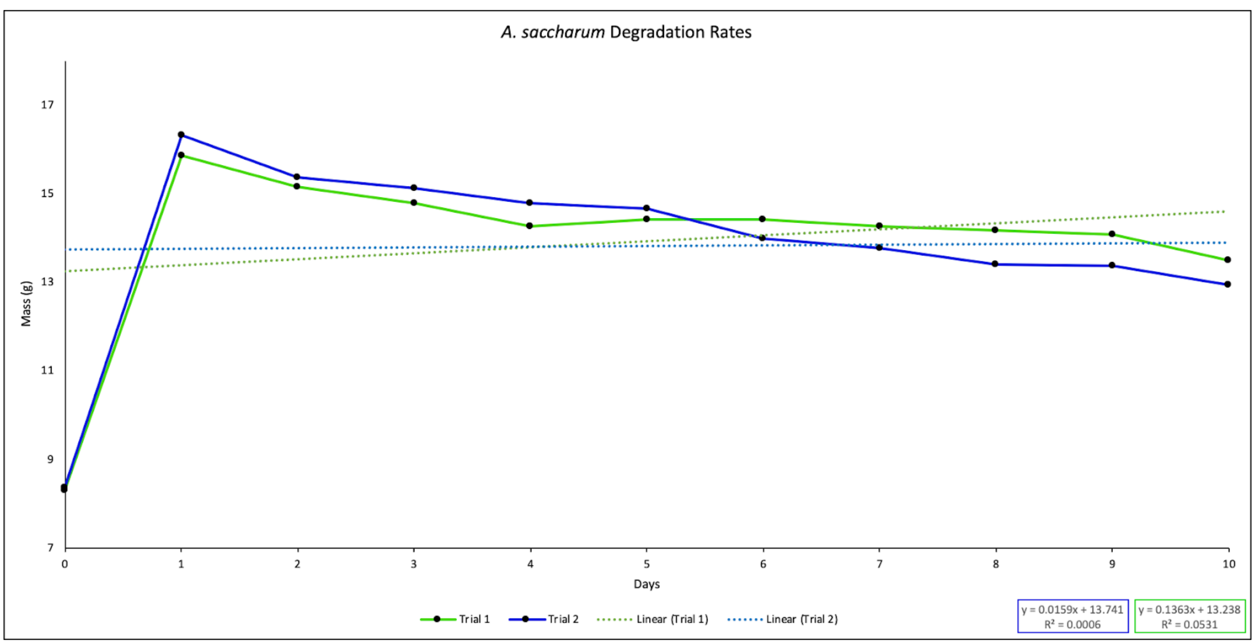


Figure 4: The degradation rates of the *A. saccharum* samples. They exhibited varying slopes.

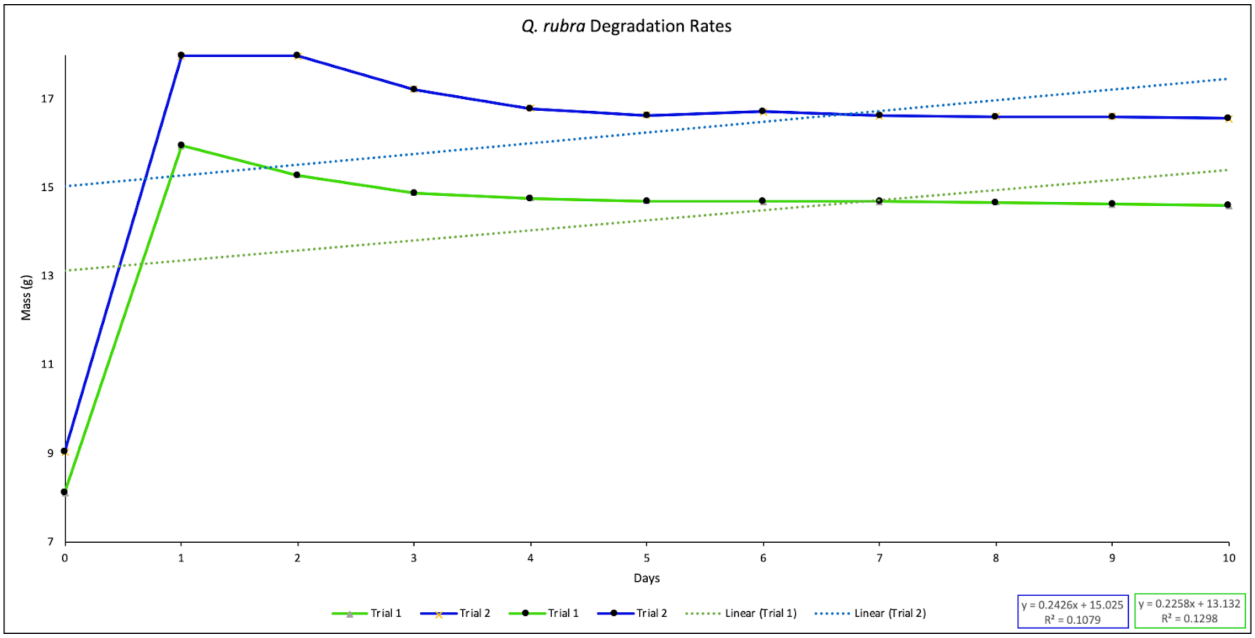


Figure 5: The degradation rates of the *Q. rubra* samples. They exhibited the greatest positive slopes of the five leaf types.

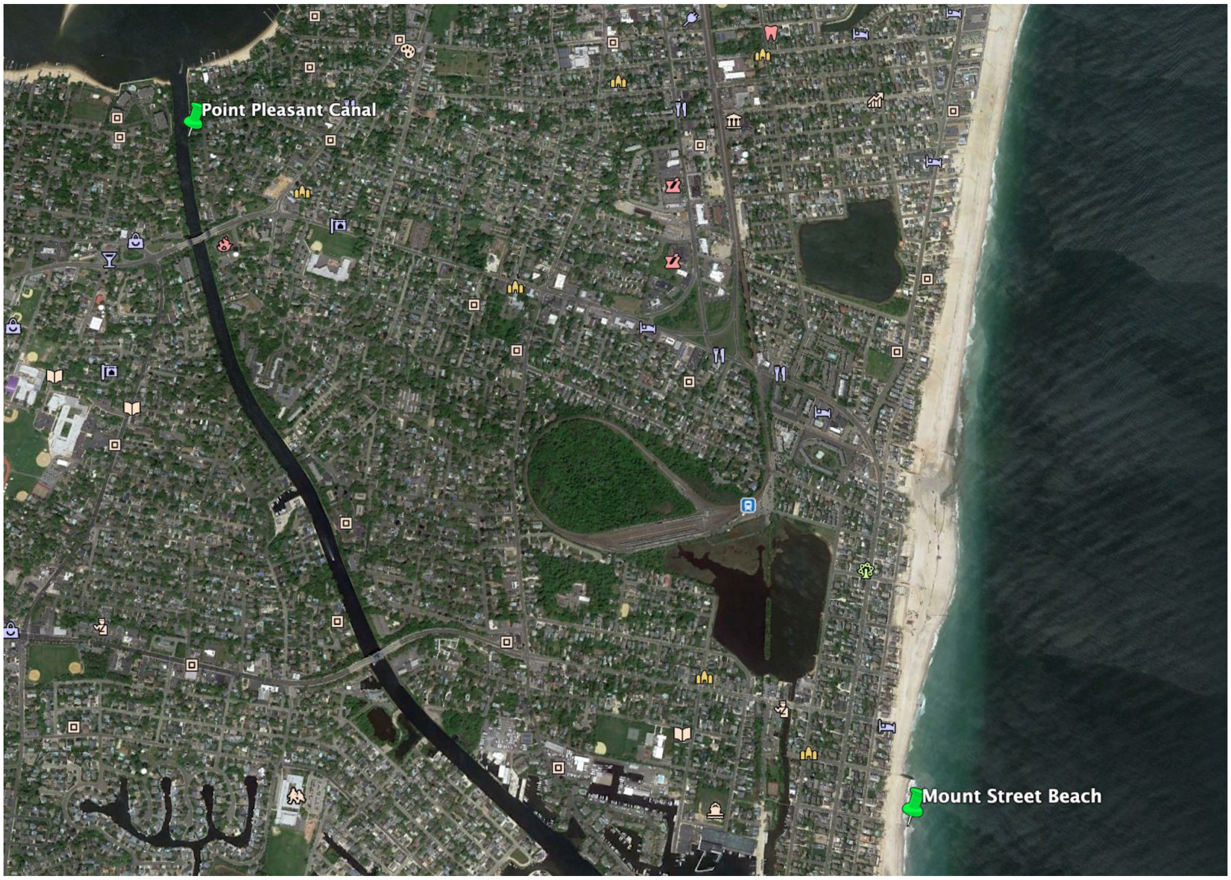


Figure 6: The leaves collected for this study were obtained along the Point Pleasant Canal in Point Pleasant, NJ. The water collected for the simulation was obtained at Mount Street Beach in Bay Head, NJ.

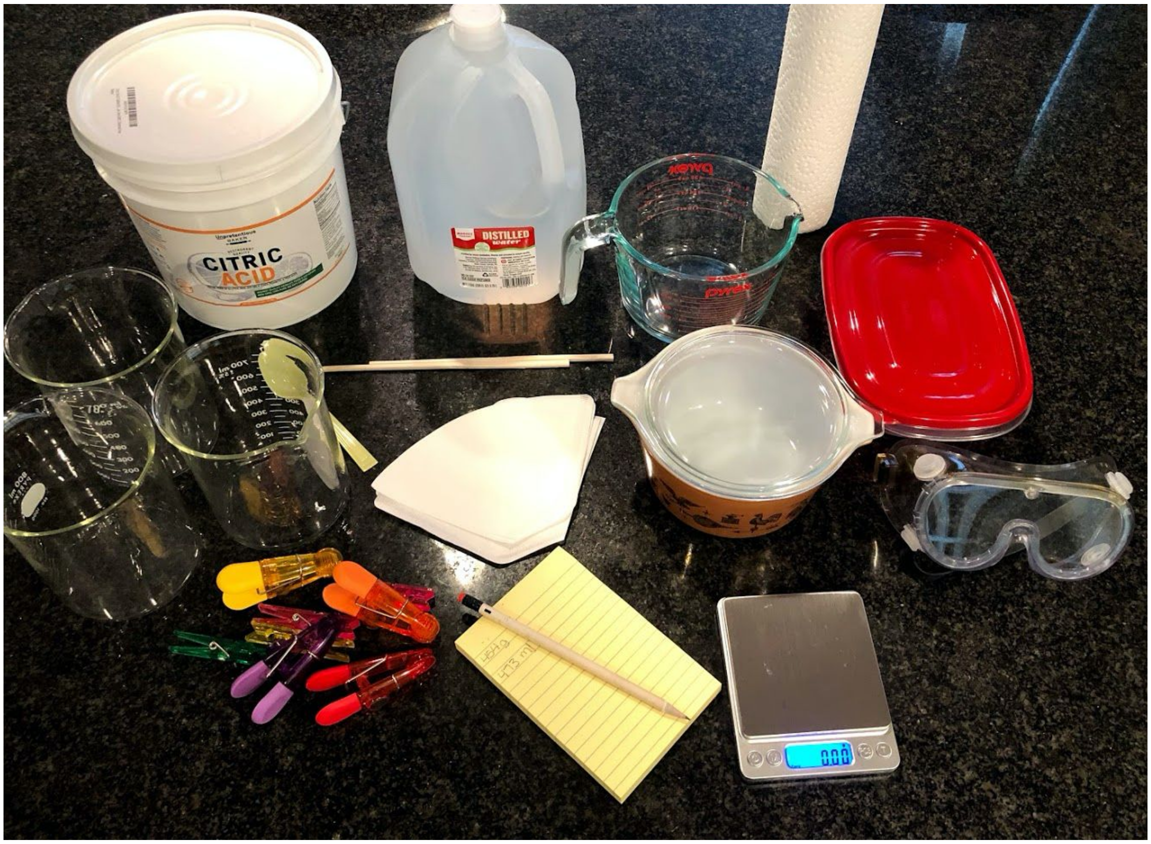


Figure 7: The materials used for the creation and filtration of the ≈5.0000 citric acid solution.

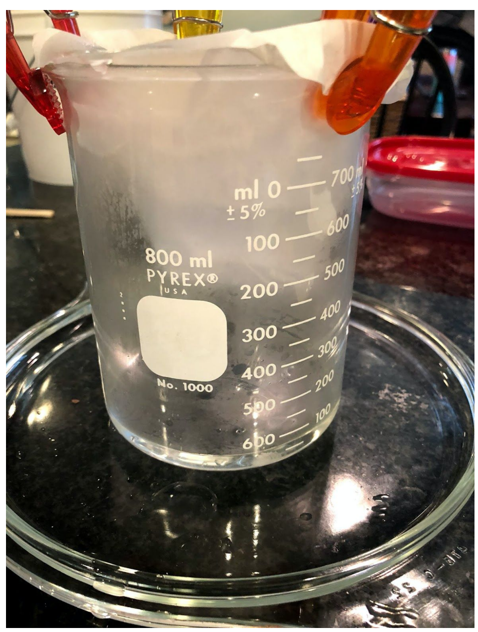


Figure 8: The citric acid solution being filtered to remove impurities.

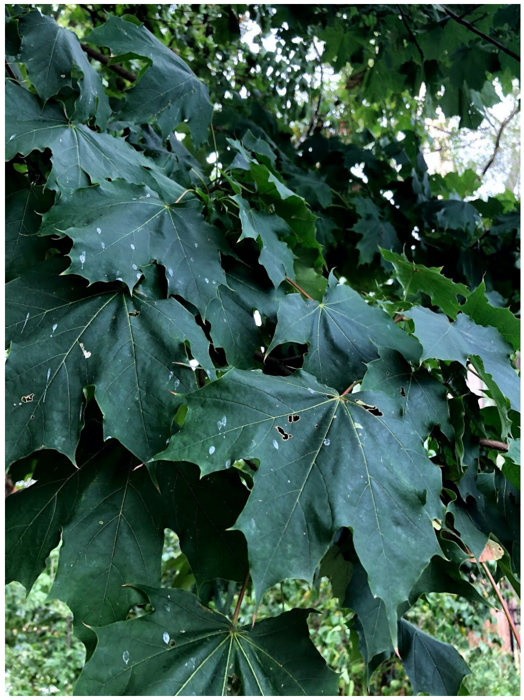


Figure 9: The *A. saccharum* leaves gathered were collected from this tree branch along the Point Pleasant Canal.

Figure 10: *I. opaca* leaves being measured on a balance to ensure exactly 90.00 grams are put in solution.

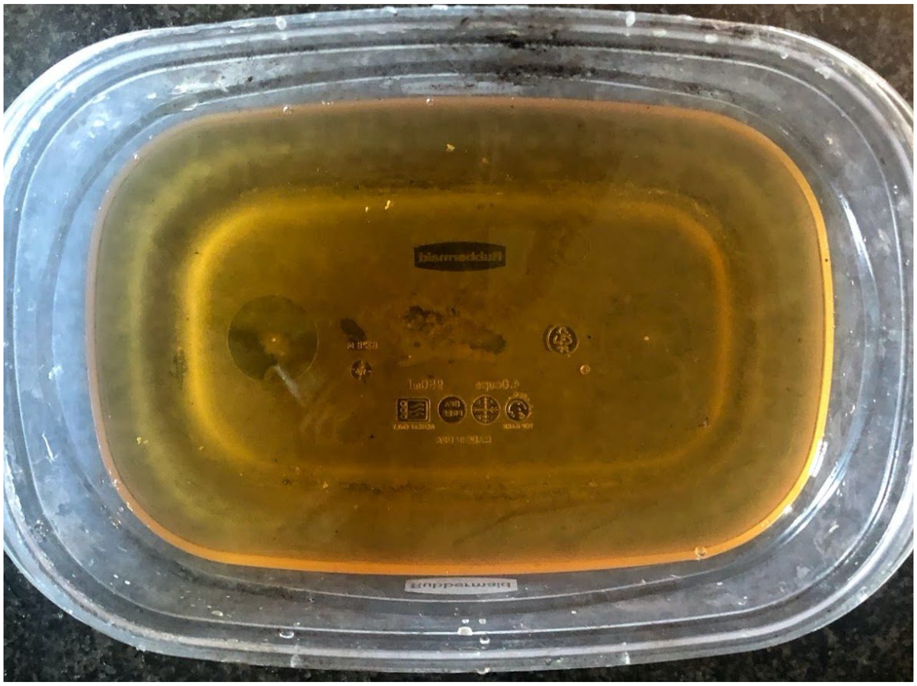


Figure 11: The resulting citric acid solution after the *I.* opaca leaves were stripped of their nutrients.

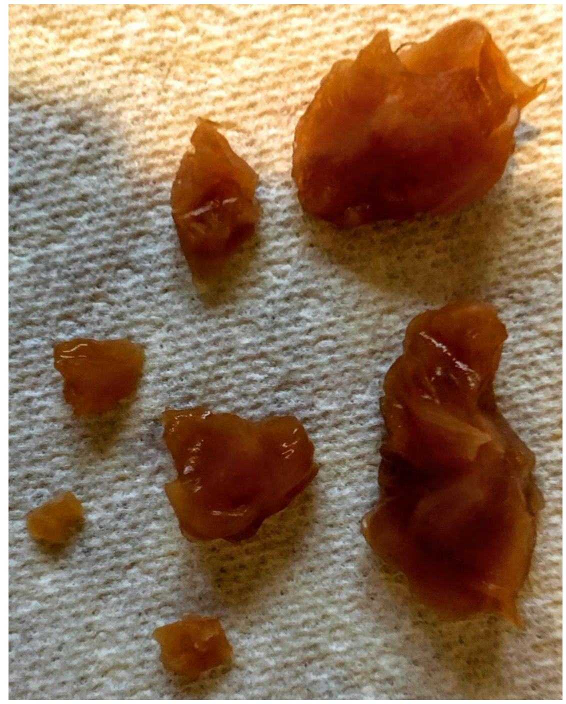
Figure 12: The materials used for the formation of the plastics using the citric acid solution containing the extracted leaf nutrients.

Figure 13: The resulting mixture when the glycerine, acetic acid, distilled water, nutrient-filled *I. opaca* citric acid solution, and natural polymer were combined.

Figure 14: The paste formed when the mixture in Figure 13 was heated at medium heat for two minutes.

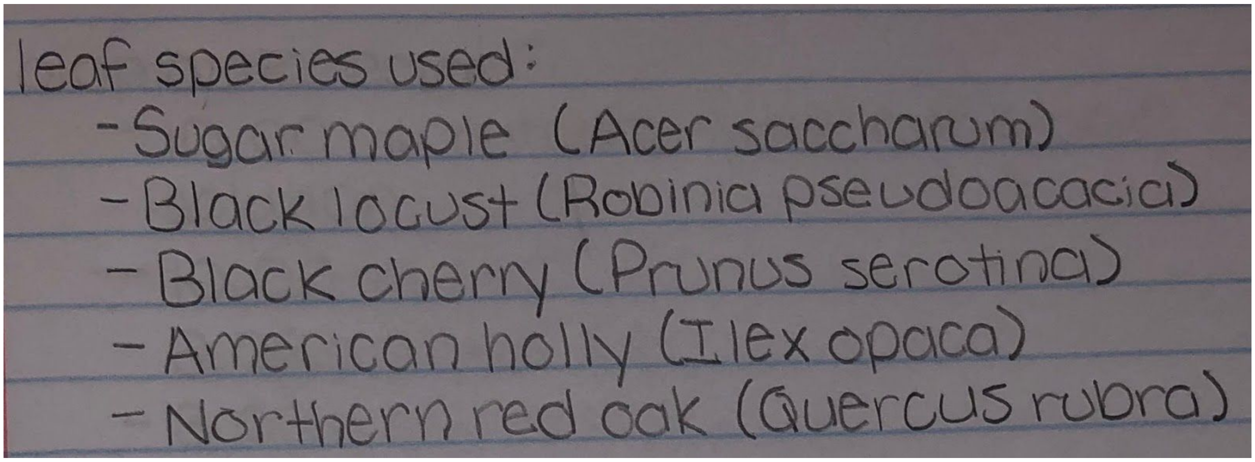
Figure 15: One of the six final *I. opaca* bioplastics created from the solution. Each of the plastics was allowed to air-dry for two days.

Figures 16-17: One of the *P. serotina* bioplastics after one day in saltwater and ten days in saltwater. The bioplastic lost 4.28 grams between the first and tenth day.

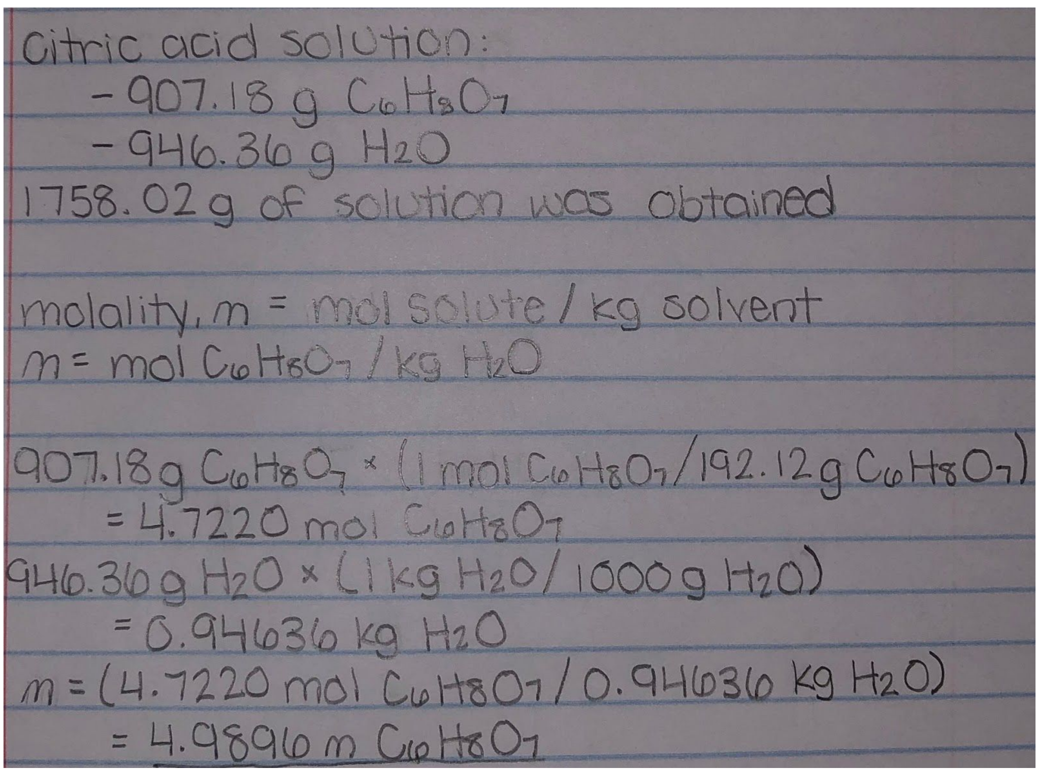
Figures 18-19: One of the *Q. rubra* bioplastics after one day in saltwater and ten days in saltwater. The bioplastic lost only 1.42 grams between the first and tenth day.

Appendix



leaf species used:
- Sugar maple (Acer saccharum)
- Black locust (Robinia pseudoacacia)
- Black cherry (Prunus serotina)
- American holly (Ilex opaca)
- Northern red oak (Quercus rubra)

Figure 20: A record of the leaf species collected and used for this research.



citric acid solution:
- 907.18 g $C_6H_8O_7$
- 946.36 g H_2O

1758.02 g of solution was obtained

molality, m = mol solute / kg solvent

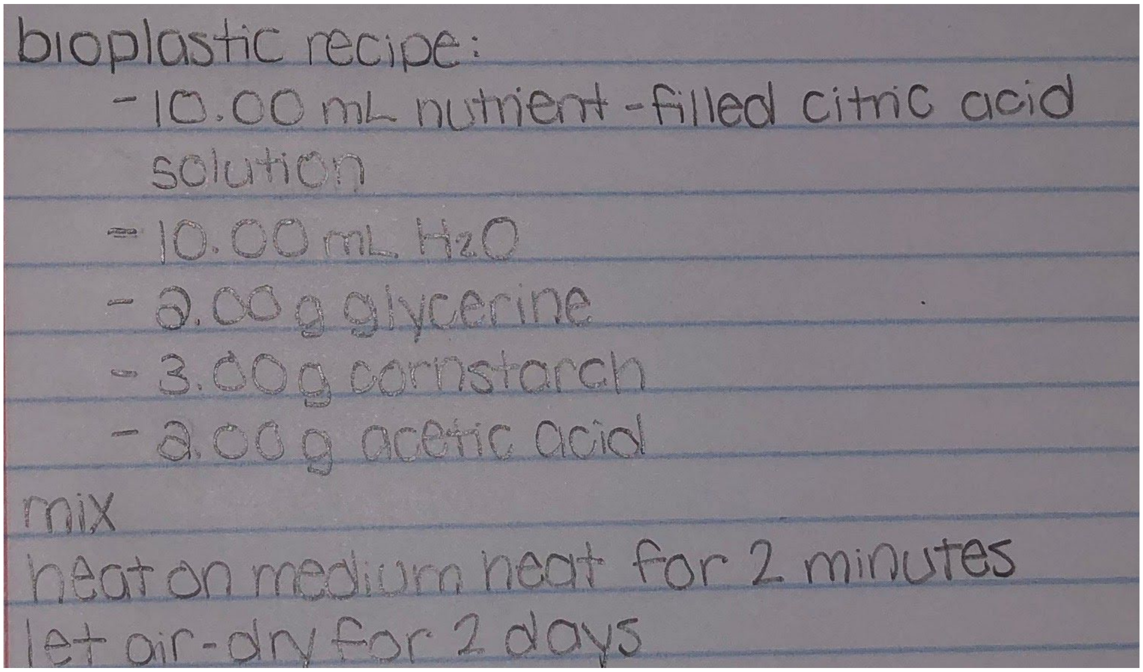
m = mol $C_6H_8O_7$ / kg H_2O

907.18 g $C_6H_8O_7$ × (1 mol $C_6H_8O_7$ / 192.12 g $C_6H_8O_7$)
= 4.7220 mol $C_6H_8O_7$

946.36 g H_2O × (1 kg H_2O / 1000 g H_2O)
= 0.94636 kg H_2O

m = (4.7220 mol $C_6H_8O_7$ / 0.94636 kg H_2O)
= 4.9896 m $C_6H_8O_7$

Figure 21: The amounts of citric acid and water used to create the solution, along with the calculations to determine the molality of the solution.


bioplastic recipe:
- 10.00 mL nutrient-filled citric acid solution
- 10.00 mL H_2O
- 2.00 g glycerine
- 3.00 g cornstarch
- 2.00 g acetic acid

mix
heat on medium heat for 2 minutes
let air-dry for 2 days

Figure 22: The recipe used to create the bioplastics from the different solutions made.