

The Effects of pH on Biodegradable PLA Plastic

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Abstract

The focus of this study was to observe how polylactic acid (PLA) degradation is affected by varying pH environments. To test this, straw segments were submerged in 3 different pH conditions (pH 4, 7, and 10). The experiment lasted 10 days and mass was measured as a metric of how much the PLA straws degraded into the solution. The initial mass of the straws were measured prior to being submerged in buffer solutions, and recorded again after 1, 7 and 10 days, while photos were taken throughout to record observable reaction rate. Based on previous research, if the straw segments submerged in pH solutions 4-10, the more basic solutions will dissolve more and have a lower mass by day 10. For measuring the mass, the segments were taken out of the tubes and dried in an oven for 24 hours before weighing to get the most accurate readings. As the experiment continued the pH levels were also measured and there was no significant change between each measuring day. The weight of the day 10 segments varied from the initial mass but was not significant enough to accept our hypothesis.

Introduction

Plastic pollution has become a severe environmental issue, impacting wildlife and habitats particularly within the marine ecosystems. Estimates from the World Economic Forum suggest that as of 2022, there are 75–199 million tons of plastic polluting the oceans (Wakefield, 2022). Single-use plastics, such as straws, are a significant contributor to this problem due to their large scale use and low recyclability. To prevent further pollution, biodegradable plastic alternatives such as polylactic acid (PLA) straws have become a popular replacement to minimize the reliance on disposable plastics.

PLA is a biodegradable polymer made from the fermentation and polymerization of natural and renewable resources such as corn, beans, and potatoes. Under chemically favorable conditions, it decomposes into lactic acid which is a non-toxic product found in all ecosystems (Murariu and Dubois, 2016). However, its degradation is influenced by biotic and abiotic factors such as microbial activity, environment pH, and temperature, which determines the rate and extent of its degradation.

Chemically, PLA primarily degrades through a process called acid or base catalyzed hydrolysis (Xu et al., 2011). During this process, water molecules cleave the ester bond within the polymer chain, producing smaller fragments that ultimately degrade into lactic acid as shown by Figure

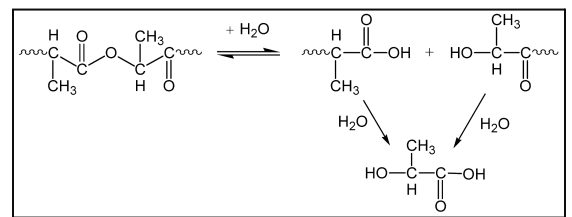


Figure 1: The hydrolysis mechanism of PLA to Lactic Acid (Siddiqui et al., 2021)

1 (Siddiqui et al., 2021). In an aqueous environment, abiotic factors such as temperature and pH are most crucial at determining the kinetics of this reaction. Since lactic acid has a pKa of approximately 4, solutions with a pH greater than 4 will have accelerated hydrolysis since lactic acid is in its dissociated form (Elsawy et al., 2017). Alternatively, when the pH of the solution is less than 4, “auto-acceleration” can occur, which is where the lactic acid aids in the decomposition of PLA.

To test what pH range affects the degradation of PLA the most, small pieces of PLA straws were submerged in buffer solutions with pH levels of 4, 7, and 10. Straw samples were submerged and incubated under a controlled incubator to minimize temperature fluctuations and were weighed

and discarded after 1, 7, and 10 days of experimentation to measure degradation of PLA based on mass loss of the straw.

It was hypothesized that if PLA biodegradable straws are submerged in aqueous solutions of pH between 4-10, the straws in the buffer with a pH of 10 will degrade at a faster rate than the straws placed in more acidic solutions due to having a pH furthest from the pKa of lactic acid, which will accelerate hydrolysis. By experimenting on the effectiveness of varying pH on the decomposition of PLA straws, the study contributes to understanding how PLA plastic alternatives degrade in natural ecosystems and their effectiveness in waste management systems.

Methods

PLA biodegradable straws were cut into uniform 1 cm segments, using a ruler to ensure consistent surface area. The initial mass of each segment was recorded using a calibrated analytical balance, with measurements taken to the nearest 0.002 g to ensure precision throughout the experiment. Buffer solutions at pH 4, pH 7, and pH 10 were provided as part of the laboratory setup. Using a pipette, 10 mL of each buffer solution was dispensed into a total of 27 labeled 10 mL test tubes, organized into three replicates per pH condition for three different time intervals: 1 day, 7 days, and 10 days. Each straw segment was fully submerged in its respective buffer solution and kept at room temperature on the laboratory bench. All samples were exposed to the same ambient conditions to maintain uniformity.



Figure 2: Test tubes containing PLA straw segments submerged in buffer solutions of varying pH (pH 4, 7, and 10) on the first day of the experiment. The color differences in the solutions represent distinct pH conditions.

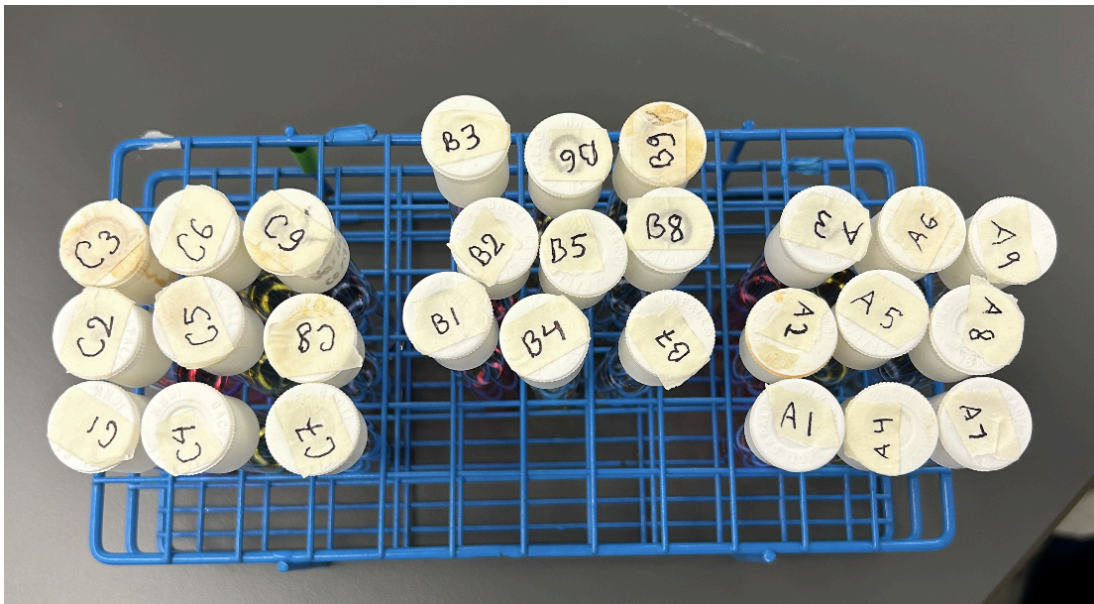


Figure 3: Labeled test tubes organized for the experiment, showing sample IDs for easy identification and tracking throughout the degradation study.

At each specified time interval, straw segments were carefully removed from the buffer solutions using sterile tweezers to prevent contamination. The segments were rinsed thoroughly with distilled water to eliminate any residual buffer solution. Each rinsed straw segment was placed on a weighing boat and dried in a drying oven set at 35°C. The drying process continued until each segment reached a stable mass, ensuring that all moisture had evaporated. The final mass of each dried segment was then recorded using the same analytical balance used for the initial measurements.

The primary data collected were the changes in mass of the PLA straw segments, used to calculate the percentage mass loss with the formula:

$$\text{Percentage mass loss} = \frac{\text{Initial mass} - \text{Final mass}}{\text{Initial mass}} \times 100$$

Photographic documentation was conducted daily to visually capture the degradation of the straw segments over time, providing qualitative data on the physical changes.

We will use the t-score to determine if the initial weight and final weight are significantly different. The formula we will be using is:

$$t' = \frac{|A - B|}{\sqrt{u_A^2 + u_B^2}}$$

A: will be the initial mass of the straw samples.

B: will be the final mass of the straw samples.

$$u_A = u_B = 0.0005$$

Since we measure our mass with three significant figures, we can determine the uncertainty using the rectangular method, which gives: ± 0.0005 .

A small t-score indicates that the two variables are similar to each other, meaning there is no significant or a weak difference between them. However, if $t' > 2$, this suggests a significant difference, and if $t' > 3$, it indicates a strongly significant difference.

Results

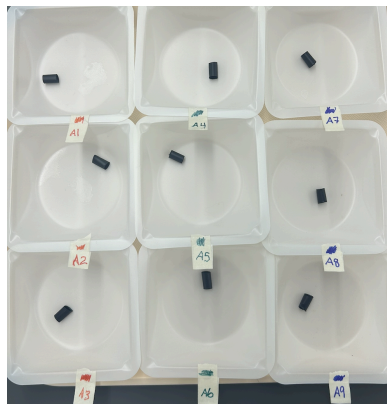


Figure 4: Day 1 samples, dry



Figure 5: Day 10 samples, dry



Figure 6: After day 7, it was noticed that white residue was built up on the bottom of the straw segment (left image). After day 10, (right image) it was noticed that there was shiny residue left on the bottom of the weigh boat. Specifically, for the acidic pH the residue had a pink tinge which was also the colour of the solution.

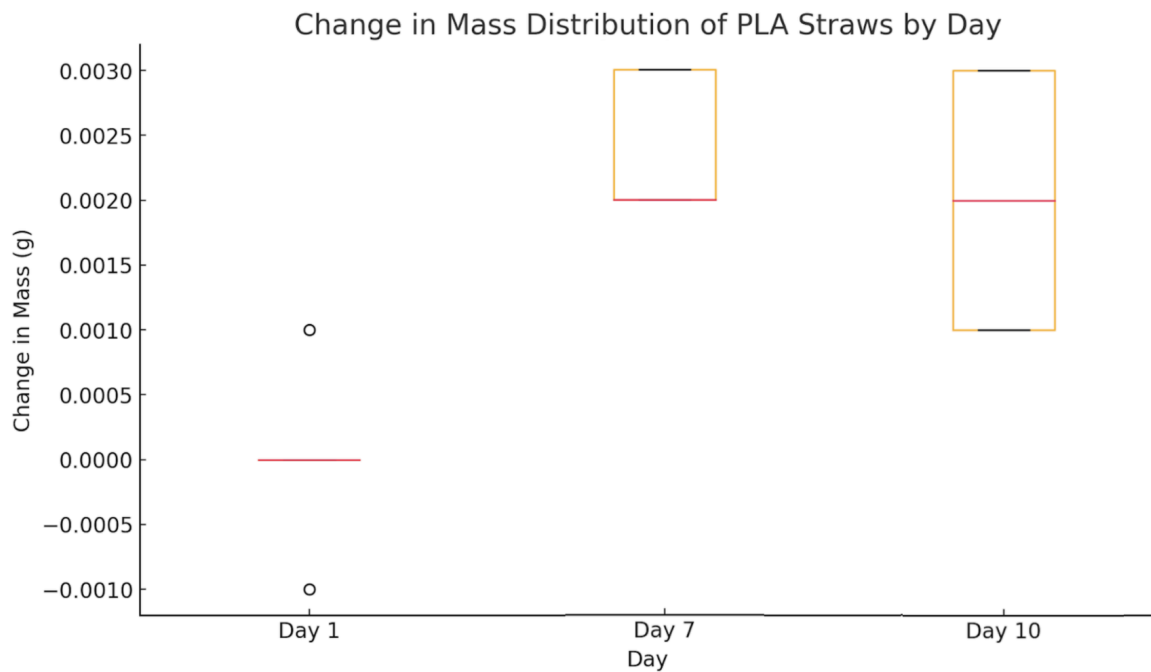


Figure 7: Change in mass across all PLA straw samples by day.

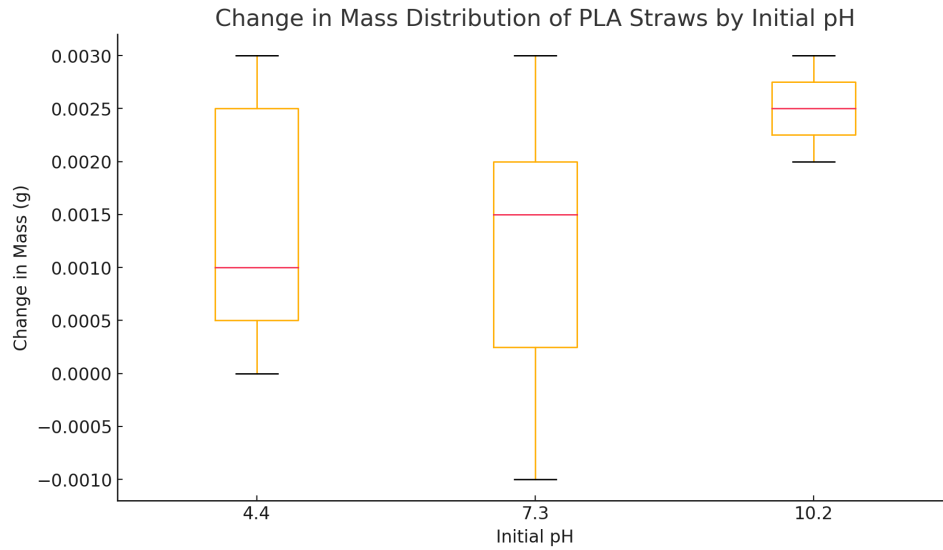


Figure 8: change in mass of straw segments by the initial pH.

The pH was also measured through day 1, 7 and 10 to view if the degrading of the straw segments changed the pH. There was not a large change in the pH between each weigh session.

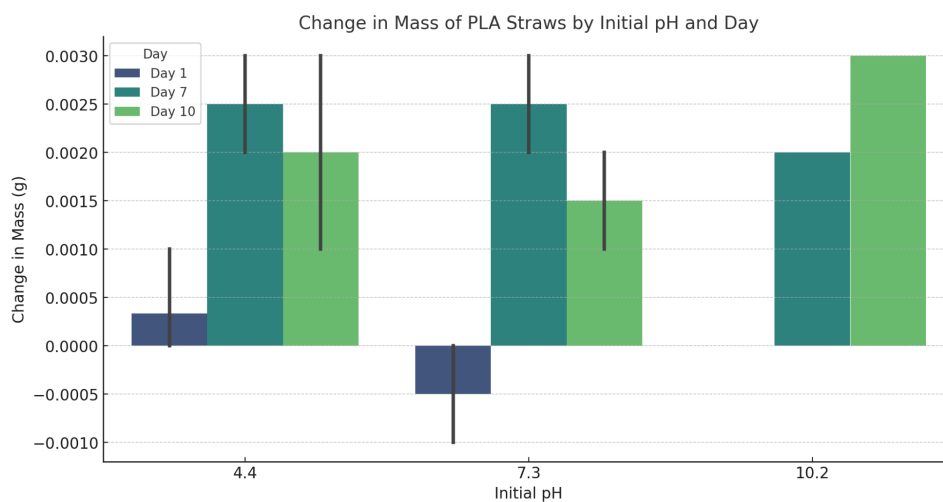


Figure 9: Change in mass of straw segments by initial pH and by day (1,7,10). This graph shows the change in mass of our samples separated by day and by pH. The values are scaled in terms of mass loss as the positive values.

	Sample	pH	t-score	p-value
After 1 Day (Group A)	A-1	4.4	0	0.423
	A-2	4.4	1.414213562	
	A-3	4.4	0	
	A-4	7.3	1.414213562	0.423
	A-5	7.3	0	
	A-6	7.3	0	
	A-7	10.2	0	0.423
	A-8	10.2	1.414213562	
	A-9	10.2	0	
After 7 Days (Group B)	B-1	4.4	2.828427125	0.372
	B-2	4.4	1.414213562	
	B-3	4.4	5.656854249	
	B-4	7.3	4.242640687	0.074
	B-5	7.3	1.414213562	
	B-6	7.3	2.828427125	
	B-7	10.2	2.828427125	0.812
	B-8	10.2	2.828427125	
	B-9	10.2	1.414213562	
After 10 Days (Group C)	C-1	4.4	2.828427125	0.064
	C-2	4.4	4.242640687	
	C-3	4.4	7.071067812	
	C-4	7.3	7.071067812	0.023
	C-5	7.3	7.071067812	
	C-6	7.3	4.242640687	
	C-7	10.2	7.071067812	0.031
	C-8	10.2	4.242640687	
	C-9	10.2	4.242640687	

Table 1: T-score and p-values of straw samples across treatments and days

To verify these findings according to statistics, the t-test was conducted across treatment groups to determine if mass changes were significant, and not due to random chance. Using a two-tail 95% confidence interval (CI), the significance level of 0.10 for the p-score was established to evaluate the data. The criteria for statistically significant mass changes involve a high t-score (2 or higher) and p-value below the significance level. According to Table 1, the treatment groups of all pHs failed to meet the p-value and t-score criteria until days 7 and 10. Samples B4-B7 on day 7 showed high t-scores and possessed a p-score below the significance level, showing that the neutral pH may have begun the degradation of the straws at a faster rate compared to the other treatment groups. By day 10, all treatments showed very high t-scores, with the exception of sample C-1, which possessed a high enough t-score, but significantly lower than the other samples. This suggests that acidic conditions may not favour the hydrolysis of PLA straws over longer periods of time, aligning with findings from a study conducted by Xu et al.

Discussion

Following analysis of triplicate samples of straws submerged in varying pH conditions, subtle differences in degradation were noted. A combination of visual and statistical analysis was used to determine the effect of pH on PLA straw degradation.

24 hours after the start of the experiments, the test tubes were taken out of the incubators for analysis, and no visible changes were apparent. After taking the weight, it was found that most of the segments had not changed weight, and the few that did only had a +/- 0.002 change which could be due to a source of error, as described in Figure 4. After day 7, there were noticeable differences in mass values, as well as visual indications of degradations in specific straw samples, notably samples B1 and B9. Both samples possessed visual white streaks across the surface, indicating some form of straw degradation, particularly on the outer coating. After day 10, all of the segments had a loss in weight. Some had up to 0.005 loss of weight compared to day 1. Some segments decreased and some increased in mass over the course of 10 days. The increase could be due to a source of error in weighing or in drying out the segments. When comparing the photos of day 1 to day 10 dry samples, there was no immediate visible damage. However, when inspecting day 10 samples closer the edges of the straws had frayed and showed visible dullness on the surface. On the weighing boats, a shiny film outlining the shape of the straw was present, suggesting that the coating melted off the straws.

Once the physical testing was completed, the data was compiled into data tables and analyzed through the t-test to determine statistical significance on the change in mass. Figure 6 depicts the change in mass across pH treatment groups, separated by the weighing checkpoints of days 1, 7

and 10. Across all treatments, the straws lost weight over the course of the experiment, ranging from 0.0020g at pH 4.4 to 0.0030g at the highest pH condition of 10.2. These findings are supported by literature, as the pKa value of polylactic acid is 3.84 (Elsawy et al., 2017). Optimal hydrolysis reactions on PLA plastic occur at pHs above or below 3.84, which is represented by the data. In accordance with the t-test data calculated in Table 1, it can be concluded that the null and alternative hypotheses have been rejected, therefore accepting the main hypothesis. The accepted hypothesis states that biodegradable straws will degrade the fastest in basic conditions, and in this case the treatment group of pH 10. Across treatment groups over the course of 10 days, the straws in the basic solution met the testing criteria in terms of p-values and t-score in addition to the greatest decrease in mass.

Although the results were conclusive, error is still a factor to consider when analyzing results. In the box-and-whisker plot depicted by Figure 8, the interquartile range (IQR) and outliers raise questions on the range of data presented. Both treatment groups of pHs 4.4 and 7.3 possessed a greater variability in mass change compared to the pH 10.2 group. Based on the means, a general conclusion can be made that the basic treatment group displayed the greatest change in mass, while the difference between neutral and acidic conditions will need further discussion. Due to the scale and size of the experiment, only three straws in each pH condition were used. This may be the cause for the high variability, as greater sample numbers will provide a curve closer to a Normal distribution. The instruments used in the experiment may also be a cause for scrutinization. To measure the mass, a portable scale was used. This scale measured up to ten thousandth decimal place, but did not go to more precise measurements. Due to the small size of the straw segments, the use of a higher precision analytical balance will help to both quantify the

mass with more precision and minimize errors. To address these issues, it would be optimal to increase the overall scale and duration of the experiment to open the possibility to map a rate graph in addition to reducing error across the board.

One unexplored aspect of the experiment was to quantify the mass rate between straws in similar conditions to find the most optimal pH. With a greater number of treatments, it is possible to identify the most effective pH for degradation of biodegradable plastic, and therefore apply the results to assist in reducing plastic waste in a global context. By finding the optimal pH values for PLA plastic degradation, the term biodegradable can be quantified and enforced to ensure that straws properly degrade in natural environments. If straws are not manufactured in such a way, alterations to the PLA structure or waste management can be addressed to result in proper degradation of these plastics. Through continuous contribution to the knowledge of biodegradable plastics, the path towards a greener future gets closer by the day.

Conclusion

The study reveals that PLA across different pH levels (4, 7, 10) shows similar trends based on the t-scores, which are relatively consistent. For example, t-scores mostly range from 1.41 to 7.07 across all environments throughout the days, indicating the levels of degradation are relatively similar despite pH differences. This suggests that while pH plays a role, it may not significantly influence PLA degradation within the given timeframes (1, 7, and 10 days). The results imply that time has a more pronounced impact on PLA degradation, with similar dissolution behavior observed in acidic, neutral, and alkaline conditions over the studied periods.

Acknowledgments

This study was conducted on the land of the Musqueam people located at UBC, where the unceded land provides opportunities for learning and discovery. The development of the manuscript and experimental measures were supported by Professor Celeste Leander and Teacher Assistant Miriam Fenniri. The lab equipment and experimental reagents were provided by the Lab Technician Mindy Chow.

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