

The Degradation Kinetics of Commercially Available Polylactic Acid (PLA) Materials Under Differing pH Levels

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Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester — a readily biodegradable systematic polymer — commonly used for biomedical purposes, such as bone fixation screws and devices for drug delivery. This polymer generally degrades into lactic acid or to carbon dioxide and water through a hydrolysis mechanism, where water attacks the ester linkage and cleaves it. However, this process can take several months to years for a partial degradation of PLA, thus, factors that alter the degradation kinetics of PLA should be researched to enhance its applications. This research paper looks at how changes in pH affect PLA degradation, specifically in phosphate buffer solutions with pH 5.1, 5.6, 6.3, 7.0, and 7.7, and one breaker filled with distilled water to act as the control. The change in mass of each PLA strip — initially measured at 0.132g-0.142g using an analytical scale of 3 decimal places — was recorded over a 5-week period. It was observed that PLA submerged in alkaline solutions showed a partial increase in degradation rates. On the other hand, neutral and acidic solutions did not show much degradation. However, the degradation observed was not statistically significant albeit the polylactic acid was marketed at 100%. This may be due to the potential presence of PLA composites, fillers, or coatings that deliberately decrease the degradation rate of PLA in this certain brand. Following this, further degradation research should be conducted on commercially available PLA materials to assess the true extent of their degradability.

Introduction

For decades, conventional plastic polymers derived from petroleum have been the go-to material for industrial production, contributing to rapid technological advancement since the early 20th-century¹. However, their non-biodegradable properties have had profound and long-lasting impacts on the environment, economy, and safety. The increasing awareness of the negative environmental consequences of these plastics has led to an effort to regularize the use of more sustainable options: biodegradable plastics made from biobased sources². One commonly used biodegradable polyester is polylactic acid (PLA). PLA is utilized in various applications, including packaging, textiles, medical implants, and 3D printing. It has especially gained attention in the biomedical field due to its biocompatibility and its ability to tailor mechanical properties³. Such properties can be attributed to the tendency for PLA to metabolize into non-harmful and non-toxic compounds, specifically, carbon dioxide and water. The polyester can also be recycled into its monomer, lactic acid⁴. Common methods are thermal depolymerization and hydrolysis, which produce a monomer solution that can be purified and reprocessed back into PLA without a loss in quality⁵. PLA is synthesized from its naturally occurring monomer, lactic acid, making it an inexpensive and stable material. This monomer is produced during the fermentation of glucose or sucrose and later refined into a higher purity suitable for PLA production⁶.

PLA is principally made via two different processes — polycondensation, and ring-opening polymerization⁷ (Figure 1).

As a hydrolytically degradable aliphatic polyester, PLA is susceptible to hydroxide ions (OH^-) attacking the ester bond linkage. That is, the ether connected to the tetrahedral intermediate group (CH_3CO^-) produces oligomers with alcohol and carboxyl acid end groups, causing polymer degradation⁸ (Figure 2). As a result of this reaction, the polymer chain is degraded into smaller components such as lactic acid or carbon dioxide and water.

PLA is a crucial material in various industries and its degradability plays a big part in its usability. Thus, studying the extent of degradability of commercial PLA is of notable interest. In this experiment, we studied the effect different pH level phosphate buffers have on the degradation rate of commercially sold 1.75mm PLA filaments.

Methodology

Five phosphate buffer solutions of varying pH (6, 6.5, 7, 7.5, and 8) were prepared by measuring out the required mass of NaH_2PO_4 and Na_2HPO_4 and adding them to 50 ml volumetric flasks with distilled water. The solutions were mixed well until all solids dissolved, then transferred into 50 ml beakers. A 50 ml beaker filled with distilled water was used as a control. Strips of PLA were placed in each of the solutions, and the beakers

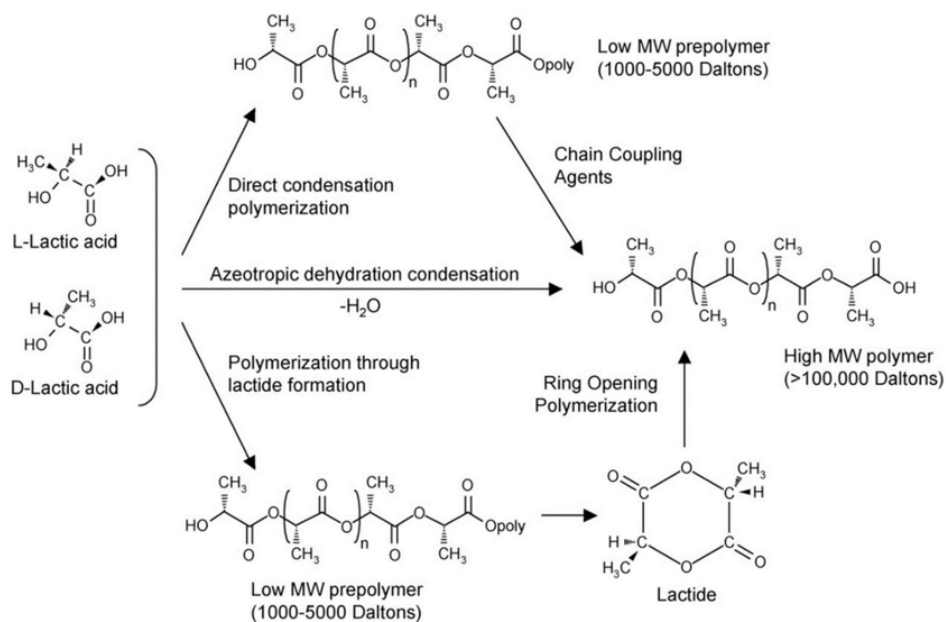


Fig. 1 Synthesis of polylactic acid from L- and D-Lactic Acids⁷

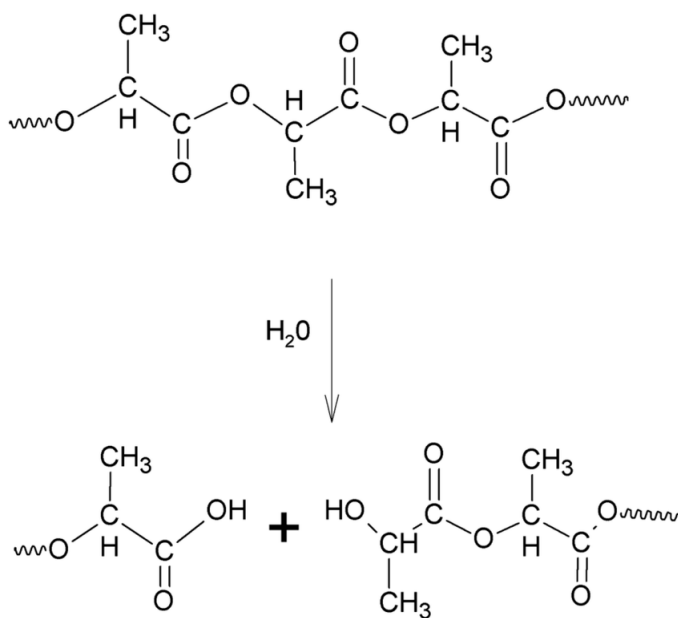


Fig. 2 Simple scheme of PLA degradation via hydrolysis of the ester bond⁸

were covered with parafilm to prevent evaporation. Initially, the PLA was scheduled to remain in the solutions for periods of 2 weeks. However, due to time constraints, the PLA remained in the solutions for a period of 22 days, and then an additional 13 days for a total of 35 days. When the PLA strips were removed from their respective solutions, they were dried for 48 hours in a

fume hood to remove the moisture. The mass of the PLA strips was recorded after drying and added back into their respective solutions.

The first buffer solution was made using Na_2HPO_4 as the acid. However, this substance had solidified due to exposure to humidity, making it difficult to create the other buffer solu-



Fig. 3 Strips of PLA drying inside of the fume hood next to their respective phosphate buffers

tions under the same conditions. To solve this problem, buffer solutions #2 – 5 were made using K_2HPO_4 instead, with the difference in mass accounted for and calculated. Once all the buffers were made, the pH was measured using a pH meter with a 0.1 error. Using a pH probe, the actual pH of each solution was found to be 5.1, 5.6, 6.3, 7.0, and 7.7, respectively, and the independent variables were adjusted accordingly.

Results

The results yielded a general consistency over the 35-day period, with partial degradation seen within the alkaline solutions (Table 3). The observed lack of degradation may be attributed to the fact that the PLA strips were set out to dry in a fume hood rather than dried in a vacuum, which likely trapped moisture in the material and contributed to the overall weight. In addition, the procedure neglected to include a washing step before drying and weighing. As a result, salt from the buffer solutions may have been left on the surface of the PLA filaments and contributed to the weight.

To test for the significance of the data, a linear regression t-test was conducted with the values of pH 8 over the 35-day period, as this set of data showed the largest change in mass out of the 6 solutions. The purpose of this test is to establish a quantitative value that determines whether or not the relationship occurred purely by chance⁹. In this linear regression test, β is the slope of the population regression line, df is the degree of freedom, and t is the t-statistic which measures the number of standard errors the estimated coefficient is away from the

hypothesized value. The null and alternative hypotheses for the test are as follows, where H_0 is the null hypothesis and H_a is the alternative hypothesis.

$$H_0 : \beta \neq 0$$

$$H_a : \beta = 0$$

$$df = 1$$

$$t = -0.772$$

$$p - \text{Values} = 0.5816$$

The data was input into a TI-nspire CX II graphing calculator to calculate the t-statistic and p-value through a linear regression t-test function. Assuming the significance level to be 0.05, the results show that there was no significant difference in the degradation rate of PLA strips among the different pH levels tested (6, 6.5, 7, 7.5, and 8) and the control group, because . The mass of PLA strips in each solution remained relatively constant over the course of the experiment, indicating that the degradation rate was slow or negligible under the given conditions. This was an unexpected finding as PLA contains hydrolytically degradable aliphatic ester bonds susceptible to hydroxide ions, which then break into components consisting of lactic acid, carbon dioxide, and water. This suggests that degradation rates should be higher in more alkaline environments. Previous studies have shown that alkaline conditions accelerate the hydrolysis of PLA, leading to faster degradation rates. In Vaid R. and his team's study on the

Buffer #1 (pH 5.1)	Acid NaH ₂ PO ₄ = 5.65g Base Na ₂ HPO ₄ = 1.04g
Buffer #2 (pH 5.6)	Acid NaH ₂ PO ₄ = 5.02g Base K ₂ HPO ₄ = 1.42g
Buffer #3 (pH 6.3)	Acid NaH ₂ PO ₄ = 3.71g Base K ₂ HPO ₄ = 3.32g
Buffer #4 (pH 7.0)	Acid NaH ₂ PO ₄ = 2.03g Base K ₂ HPO ₄ = 5.76g
Buffer #5 (pH 7.7)	Acid NaH ₂ PO ₄ = 0.84g Base K ₂ HPO ₄ = 7.493g
Control (pH 7.0)	50ml distilled water

Table 1 Reagent Mixtures

	Calculations for the mass of NaH ₂ PO ₄ and K ₂ HPO ₄ added to each 1.00M, 50ml phosphate buffer solution. All calculations are assumed to be at the standard temperature and pressure of 1 atm and 25°C.
Step 1	Using the Henderson-Hasselbalch equation, substitute the known values. In this case, the theoretical target pH of the solution and the pK _a of NaH ₂ PO ₄ are given. $pH = pK_a + \log\left(\frac{A}{B}\right)$ $pH = pK_a + \log\left(\frac{HPO_4^{2-}}{H_2PO_4^-}\right)$ $pH - pK_a = \log\left(\frac{HPO_4^{2-}}{H_2PO_4^-}\right)$
Step 2	The base 10 logarithm is rearranged to solve for the ratio of HPO ₄ ²⁻ to H ₂ PO ₄ ⁻ . $10^{(pH-pK_a)} = \left(\frac{HPO_4^{2-}}{H_2PO_4^-}\right)$ $let u = 10^{(pH-pK_a)}$
Step 3	The mols of acid are then calculated by equating the acid/base ratio to $\frac{(0.05-X)}{X}$, where 0.05 - X is the molarity of acid and X is the molarity of the base. 0.05 is the total mols of phosphate in the 1.00M solution. $u = \frac{0.05-x}{x}$ $x = 0.05/(1+u) = \text{molsofNaH}_2\text{PO}_4$
Step 4	The mols of the base are then calculated by subtracting the mols of acid from the total mols of phosphate. $0.05 - 0.05/(1+u) = \text{molsofNaH}_2\text{PO}_4$
Step 5	Finally, multiply the mols of acid and base by their respective molar masses to calculate the theoretical mass. $\text{molsofNaH}_2\text{PO}_4 \cdot \frac{119.98\text{g}}{1\text{mol}} = \text{MassofNaH}_2\text{PO}_4$ $\text{molsofNaH}_2\text{PO}_4 \cdot \frac{141.96\text{g}}{1\text{mol}} = \text{MassofNaH}_2\text{PO}_4$

Table 2 Procedure used to calculate the theoretical masses required for each buffer solution.

	pH6	pH 6.5	pH 7	pH 7.5	pH 8	Control
Feb 20	0.137g	0.137g	0.142g	0.132g	0.138g	0.142g
Mar 14	0.136g	0.139g	0.141g	0.131g	0.139g	0.144g
Mar 27	0.137g	0.136g	0.141g	0.129g	0.135g	0.144g

Table 3 Mass of PLA strips in each phosphate buffer over a 35-day period.

hydrolytic degradation of PLA, a 0.6% mass loss occurred after 25 days for PLA fibers in pH 10, while no significant change was observed for lower and neutral pH conditions during the same time frame. Additionally, PLA fibers in pH 10 experienced a 40% loss in tensile strength compared to 10% for lower and neutral pH conditions over the 25-day period¹⁰.

$$WL\% = (W_0 - W_f) / W_0 \times 100$$

The commercially bought orange PLA 1.75mm filament used in this experiment is marketed as 100% PLA, but the actual composition of the filament may not be known. Although the specification sheet detailing the exact material composition cannot be found, the lack of appreciable degradation observed in (Table 4) suggests the commercial PLA filament may have contained composites or additives that inhibited the hydrolysis mechanism. For example, some manufacturers add stabilizers or antioxidants to enhance the shelf life of PLA, which could inhibit the degradation process. In Plota and Masek's study that evaluated the antioxidant capacity and stabilization efficiency of cannabidiol (CBD) extract in PLA, the addition of CBD significantly increased the oxidation resistance of PLA polymers. This was concluded because the difference in polar components of the SFE before and after 400 hours of weathering was much lower for PLA with CBD content compared to pure PLA, indicating that the cannabidiol extract was effective in preserving its structural integrity¹¹.

The presence of additives or composites with properties similar to Plota's study may have provided molecular networking that reduced the susceptibility of the PLA to hydrolysis, thus contributing to the slow or negligible degradation rate observed in the experiment. The fillers in these types of composites can create an entangling effect, strengthening the network or inhibiting the diffusion of water into the material altogether¹² (Figure 5). In conclusion, consumers should be aware and warned of the reality that not all materials marketed as degradable products are really as such.

The negligible degradation observed in this experiment, despite testing in alkaline conditions expected to catalyze PLA hydrolysis, suggests that commercial PLA filament may contain additives or composites that impede the hydrolysis mechanism. Though marketed as 100% PLA, the pure material that previ-

ous studies have used in the past has readily degraded in alkaline conditions, so the composition of commercially available PLA is often unknown. Hence, consumers should be aware of claims that products are fully biodegradable or environmentally friendly, as marketing does not always match reality. The negligible degradation of the marketed 100% PLA filament underscores the importance of verifying manufacturers' claims through independent testing.

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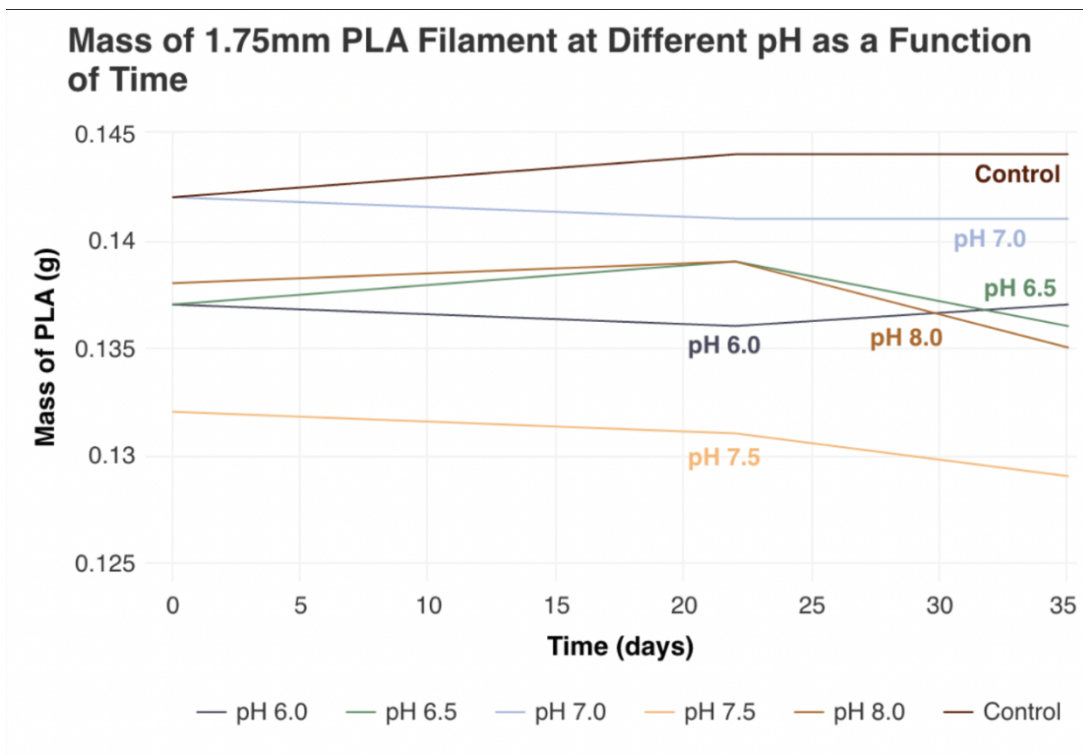


Fig. 4 Mass of each 1.75mm PLA filament at different pH as a function of time.

	pH 6	pH 6.5	pH 7	pH 7.5	pH 8	Control
%ML Feb 20 - Mar 14	-0.73%	1.46%	-0.70%	-0.76%	0.72%	1.41%
%ML Mar 14 - Mar 27	2.21%	-2.16%	0.00%	-1.53%	-2.88%	0.00%

Table 4 The percent mass loss (%ML) is calculated using the following equation

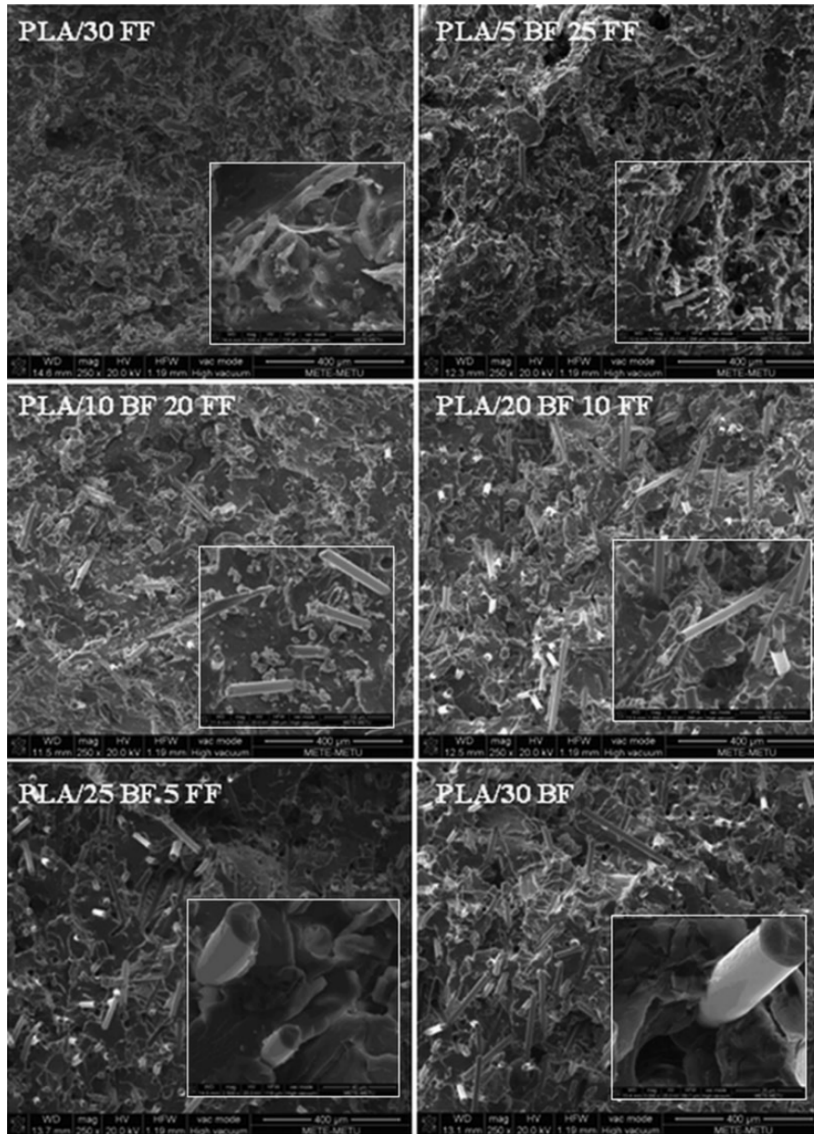


Fig. 5 Electron microscopy of several variants of composite in polylactic acid, showcasing a crosslinked polymer network. The fillers may entangle the strands such that the network remains intact even after degradation.¹²