Recycling Polylactic Acid (PLA) - Student Guide

Part I Modified from: *Hydrolysis of Post-Consumer Polylactic Acid Waste* by Rich Gurney at Simmons College and *Recycling Polylactic Acid* by *Beyond Benign: Green Chemistry Education (http://www.beyondbenign.org/k12education/highschool.html)*
Part II Modified from: *Titration of Lactic Acid Solution Produced by PLA Depolymerization* by Carol Higginbotham at Central Oregon Community College

Goal:

In this lab students will learn how to take a renewable product, a polylactic acid (PLA) plastic cup, and extend its usefulness by converting the cup into a cleaning solution. Students will titrate their “homemade” cleaning solution to verify the contents of the solution as lactic acid.

Background:

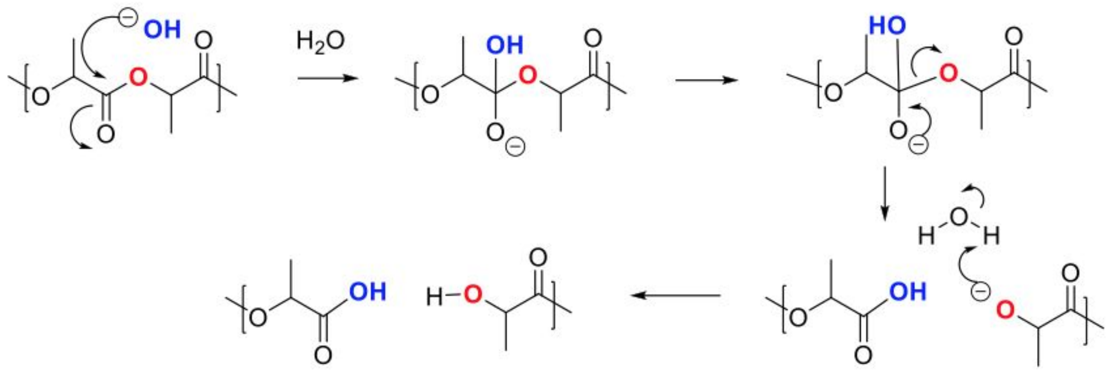
The world produces approximately 200 billion pounds of plastics and nearly half of this plastic winds up in landfills each year. Polyethylene (HDPE/LDPE), polyethylene terephthalate (PET), and polystyrene (PS) are common polymers that constitute plastics, but they have enormous degradation lifetimes. These polymers can persist in the environment for 500 to 1000 years without biodegrading; current composting enzymes and bacteria are unable to break them down any faster.

Because plastics (polymers) have degradation periods significantly longer than their useful lives, they persist in landfills for significant periods of time. Additionally, traditional plastics are produced from petroleum, which is a nonrenewable resource. Taking into account the complete lifecycle of plastics is crucial to why there is a need for alternatives. Plastics are woven into the fabric of US society and examining alternatives to current manufacturing practices is a burgeoning area for chemists.

Polylactic acid (PLA) is a biodegradable polymer derived from natural resources. Lactic acid, which is derived from corn, is the monomer used to create this polymer. PLA degrades under compost conditions into CO_2, H_2O, and humus, all benign components. PLA will generally break down under industrial compostable conditions in approximately 180 days. Because it biodegrades, the volume sent to the landfill can be reduced significantly. Also, the CO_2 released during degradation returns the carbon to the atmosphere with no overall net gain. Since the polymer is made from a corn feedstock, the process uses significantly less petroleum than traditional polymers. It is categorized under plastic resin code #7 or #0 (“other plastics”). While it is recyclable, currently there are no municipal recycling facilities that accept PLA.

Instead of disposing PLA products into landfills or compost facilities, another option of handling them at the end of the product's useful life is to reuse them as other products. One thing to do with PLA materials is to convert them into a lactic acid antimicrobial cleaning solution be depolymerization through hydrolysis (see Figure 1 below).

Figure 1: Hydrolysis of PLA in basic conditions.



A hydroxide ion from solution bonds to the carbonyl carbon atom. Through electron transfer, the bond between that carbon atom and the red oxygen atom is broken. The red oxygen atom then forms a bond with a hydrogen atom from a water molecule. This continues to occur until the PLA polymer chain is broken down into lactic acid, its monomer form.

Part I: Cups to Cleaners - The Hydrolysis of PLA

Purpose:

In this part of the experiment you will take PLA cups and depolymerize them by hydrolysis to form a antimicrobial cleaning solution of lactic acid.

Materials:

- PLA cups (5.0 g)
- Scissors
- Scale
- Erlenmeyer flask
- 1.4 M NaOH in 1:1 ethanol/water (100 mL per group)
- Graduated cylinder
- Magnetic stir bar
- Watch glass
- Stir/Hot plate
- Ice bath
- 6M hydrochloric acid (approximately 20-25 mL per group)
- pH probe or universal pH paper
- Paper towels
- Plastic spray bottles

Optional Materials:

- Other “green” cleaners for comparison

Procedure:

1. Cut a PLA cup into small pieces using a scissors. The smaller the pieces, the faster the reaction. Do not use any colored parts of the cup or the lip/bottom corners (thicker portions) of the cup.
2. Measure 5.0 grams of the PLA pieces and place them in a clean 250 mL Erlenmeyer flask.
3. Measure 100 mL of the sodium hydroxide/ethanol solution and add it to the flask.
4. Add a magnetic stir bar to the flask.
5. Cover the flask with a watch glass to reduce evaporation.
6. Heat the solution to 90 ^{o}C while stirring. Reduce the heat if the flask begins to vigorously boil.
7. Continue heating until all of the PLA has dissolved and the solution is light yellow in color. (This usually takes 5-15 minutes)
8. Remove from hot plate and let cool on counter, then continue to cool the mixture in an ice bath.
9. Once cool, measure the pH of the solution using pH paper or pH probe. Acidify the mixture by slowly adding 6M hydrochloric acid in 1-2 mL additions until a pH of 4-5 if reached. The solution now contains lactic acid and sodium chloride.
10. Apply the solution onto a section of a dirty surface (dry spaghetti sauce on a plate works well) and wipe clean with a paper towel.
    a. Optional: Apply the other “green” cleaners to a section of the dirty surface for comparison.
11. Save the remaining lactic acid solution for the titration in part two.
12. If other green cleaners are available, clean a different section of the same dirty surface for comparison.

Data Sheet:

Name:	Date:
Plastic Type: Grams of PLA:	Plastic Resin Code Symbol:
Appearance of plastic before it is placed in solution:	

Record observations at 2 minute intervals, until all of the PLA degrades.

Minutes	**Observations** (color, transparency, presence of particulates)
0	
2	
4	
6	
8	
10	
12	
14	
16	

What is the pH of the solution before any acid is added?:	What is the pH of the solution after the acid is added?:
Did the resulting solution effectively clean a dirty surface? How did the solution compare to other green cleaners?	

Part II: The Titration of Lactic Acid

Purpose/Background:

In part I you depolymerized polylactic acid (PLA) to produce a cleaning solution containing lactic acid. In this part of the experiment you will verify the contents of your solution as lactic acid through titration. During the titration you will monitor pH as base is gradually added. The way the pH changes will help you confirm the identity of the acid in your solution. This is possible because lactic acid is a weak acid that will respond to the titration with base in a particular way.

Weak acids do not completely ionize in solution. At any given moment only some of the molecules of these acids have the acidic hydrogens released into solution. How readily a particular weak acid gives up its hydrogen is a way to characterize that substance and can be described using a number called pK_a. Your titration will provide you with the data necessary to compare the accepted pK_a value for lactic acid. If your data matches reasonably well, that supports the assertion that your solution actually contains lactic acid.

Materials:

- Lactic acid solution prepared in part I
- 6 M HCl (approximately 20 mL per group)
- Graduated pipet
- Deionized water
- Titration apparatus: 50 mL buret, buret clamp, ring stand, stir plate, stir bar, pH probe, 250 mL beaker
    - 0.10 M sodium hydroxide (approximately 50 mL per group)

Procedure:

1. Remove 10 mL of the lactic acid solution from part 1 to use in the titration. Store the remaining lactic acid solution as directed by your instructor for a classroom cleaner.
2. Further acidify the 10 mL of the lactic acid solution using 6M hydrochloric acid until a pH of 2.5 is reached.
3. Using a graduated pipet, add 1 mL of this solution to a clean 250 mL beaker.
4. Add enough water to allow for proper pH measurements.
5. Set up a titration apparatus and titrate the acid solution with the 0.10 M sodium hydroxide.
6. Collect pH data after each small (1 mL or less) addition of base. Collect pH data until the pH is >11 and is constant.

Data Table:

Volume of NaOH (mL)	pH of Solution

Analysis:

1. Generate a graph with pH plotted vs. volume of base added.
2. Write an appropriate conclusion paragraph that addresses the following questions.
    a. What is the volume of base needed to reach the end point for your titration?
    b. What is half of this volume? (At this volume pH = pK_a)
    c. What is the pK_a for the acid titrated in your experiment?
    d. What is the actual pK_a for lactic acid?
    e. Does your experimental result support the idea that you have lactic acid in your solution?
    f. What things could have happened to cause your data to be misleading? Explain each error and the consequence the error would produce.
3. What green chemistry principles does this lab address? Explain.

Instructor Notes:

Part I: Materials for 10 Student Groups:

- 10 PLA cups
- 1-10 scissors
- 1-10 scales
- 10 Erlenmeyer flasks
- 1L of 1.4 M NaOH in 1:1 ethanol/water
- 10 graduated cylinders
- 10 magnetic stir bars
- 10 watch glasses
- 10 stir/hot plates
- 10 ice baths
- 250 mL of 6M hydrochloric acid
- 10 pH probes or 10 strips of universal pH paper
- Paper towels
- Several plastic bottles

Part I: Preparation:

1.4 M NaOH in 1:1 ethanol/water (100 mL per group)

- For 1 liter of solution, dissolve 56 grams of sodium hydroxide in 500 mL of ethanol and 500 mL of water.

6M hydrochloric acid (approximately 20-25 mL per group)

- For 250 mL of solution, dilute 125 mL of 12 M hydrochloric acid with 125 mL of water.

Part I: Procedural Notes:

Amount of Sodium Hydroxide Required for Hydrolysis:

2 moles of sodium hydroxide are required to hydrolyze 1 mole of lactic acid. This means that 0.139 moles of sodium hydroxide is required for 5.00 g of PLA to be completely hydrolyzed. (See calculations below.)

$$5.00\ g\ PLA\ x\ \frac{1\ mole\ PLA}{72.07\ g\ PLA\ x\ n} x \frac{n\ moles\ LA}{1\ mole\ PLA} = 0.0693769946\ moles\ LA\ x\ \frac{2\ moles\ sodium\ hydrxide}{1\ mole\ LA} = 0.139\ moles\ NaOH$$

Acidification:

Acidification is required in order to neutralize hydroxide ions yielding a solution containing lactic acid and sodium chloride.

Part I: Sample Data/Answers:

Name: Answer Key	Date:
Plastic Type: PLA (Polylactic Acid)	Plastic Resin Code Symbol: 7 or “Other”
Appearance of plastic before it is placed in solution: Clear semi-rigid (or semi-flexible) plastic.	

Record observations at 2 minute intervals, until all of the PLA degrades.

Minutes	**Observations** (color, transparency, presence of particulates)
0	Clear solution with the plastic appearing unchanged.
2	Clear solution with the plastic appearing unchanged.
4	Clear solution with the plastic pieces becoming smaller and look like they are becoming hydrated.
6	Solution becoming slightly yellow with the plastic pieces becoming even smaller and looking more hydrated.
8	Slightly yellow solution with plastic pieces no longer present.
10	Slightly yellow solution with plastic pieces no longer present.
12	
14	
16	

What is the pH of the solution before any acid is added?:	What is the pH of the solution after the acid is added?:
pH ~ 11	pH ~ 5

Did the resulting solution effectively clean a dirty surface? How did the solution compare to other green cleaners?

Answers will vary depending on the other cleaners used. Students may compare ability to remove the stain, residue left behind, streaking, smell, etc.

Part II: Materials for 10 Student Groups:

- Lactic acid solution prepared in part I
- 200 mL of 6 M HCl
- 10 graduated pipets
- Deionized water
- 10 titration apparatuses:
  - 10 - 50 mL buret,
  - 10 buret clamps
  - 10 ring stands
  - 10 stir plates

- ○ 10 stir bars
  - ○ 10 pH probes
  - ○ 10 - 250 mL beaker
- 500 mL of 0.10 M sodium hydroxide

Part II: Preparation:

0.10 M sodium hydroxide (approximately 50 mL per group)

- For 500 mL of solution, dissolve 2 grams of sodium hydroxide in 500 mL of water.

6M hydrochloric acid (approximately 20 mL per group)

- For 250 mL of solution, dilute 125 mL of 12 M hydrochloric acid with 125 mL of water.

Surface for cleaning (optional)

- Smear spaghetti sauce across a plate or piece of glass and allow it to dry overnight.

Part II: Procedural Notes:

Acidification:

Further acidification is necessary in order to lower the lactic acid solution's pH down near the pH of a lactic acid solution without any base present. If 5.00 g of PLA were dissolved in 100 mL of water, the concentration of lactic acid would be 0.694 M and the pH of the solution would be 2.01. (See calculations below.) At the end of part I the pH of the solution is around 5 and needs to be dropped. It is important to know that acidifying to a pH below 2.01 will affect student results as there will be excess acid present and the reaction will require more sodium hydroxide for neutralization.

$$5.00\ g\ PLA\ x\ \frac{1\ mole\ PLA}{72.07\ g\ PLA\ x\ n} x \frac{n\ moles\ LA}{1\ mole\ PLA} = 0.0693769946\ moles\ LA$$

$$Molarity\ of\ the\ LA\ =\ \frac{0.693769946\ moles\ LA}{0.100\ L\ solution} = 0.6937699459\ M\ LA$$

$$pH\ of\ LA\ solution\ =\ -\log(\sqrt{K_a[acid]}) = -\log(\sqrt{1.38\ x\ 10^{-4}(0.6937699459\ M)}) = 2.00945\ =\ 2.01$$

Part II: Sample Data/Answers:

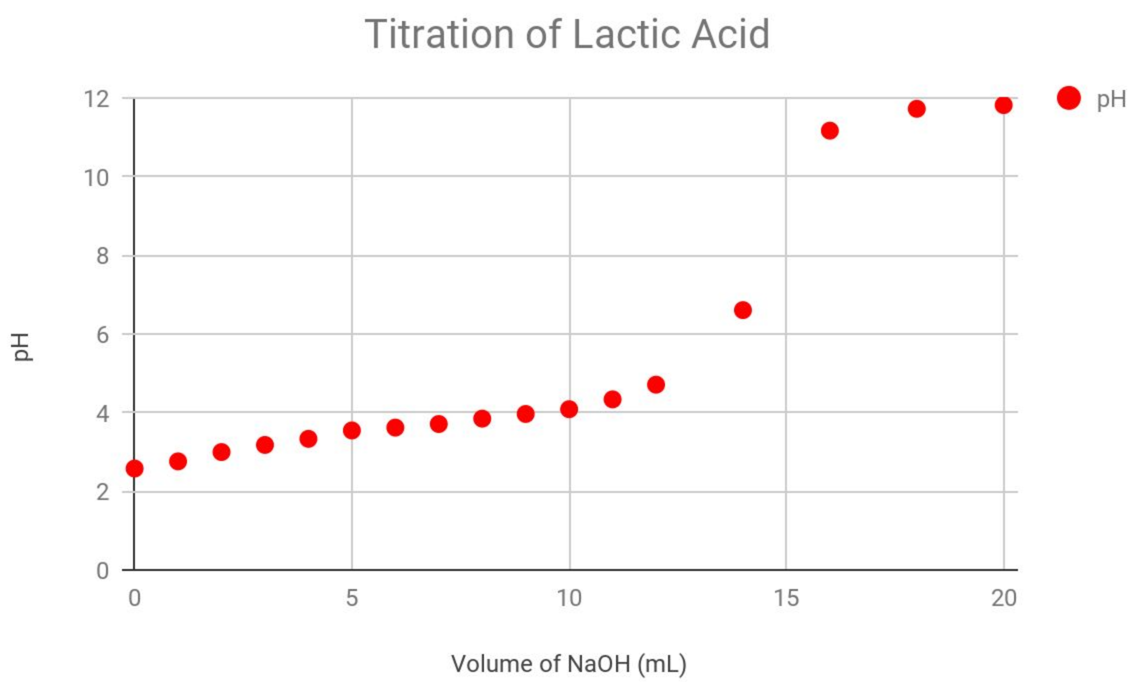
1. Generate a graph with pH plotted vs. volume of base added.

   Sample Data Table:

Volume of NaOH (mL)	pH of Solution
0	2.578
1	2.760
2	2.997
3	3.178
4	3.333
5	3.546
6	3.619
7	3.710
8	3.847
9	3.965
10	4.087
11	4.337

12	4.710
14	6.605
16	11.167
18	11.723
20	11.817

Sample Graph:



2. Write an appropriate conclusion paragraph that addresses the following questions.
   a. What is the volume of base needed to reach the end point for your titration?
   Typically students will find the volume required for titration to be about 15-17 mL.
   b. What is half of this volume? (At this volume pH = pK_a)
   This will be half of the volume listed in 2a.
   c. What is the pK_a for the acid titrated in your experiment?
   The pK_a is the pH at the halfway point. Typically students will find the pK_a to be between 3.7 and 4.0.
   d. What is the actual pK_a for lactic acid?
   The pK_a for lactic acid is 3.86.
   e. Does your experimental result support the idea that you have lactic acid in your solution?
   Students will typically find that their experimental pK_a is sufficiently close to the actual pK_a of lactic acid and thus supports that the solution contains lactic acid.
   f. What things could have happened to cause your data to be misleading? Explain each error and the consequence the error would produce.
   Error may include inaccurately adding 1 mL additions. Depending on the tools used, error may include accurate determination of the pH. Depending on the tool used, error may include ability to read plotted data accurately.

3. What green chemistry principles does this lab address? Explain.
   Principle #1: reduce waste, principle #7: use of renewable feedstocks, and principle #10: designing for degradation are addressed.

   Principle #1: Rather than throwing away the PLA cups used in this experiment they were repurposed into a classroom cleaner reducing waste.
   Principle #7: The PLA cups used in this experiment come from corn which is a renewable feedstock.
   Principle #10: The PLA cups used in this experiment were designed for degradation.

Suggested Student Readings to Relating to the Lab:

1. Smithsonian Magazine. Elizabeth Royte. August 2006. Accessed November 2017. Corn Plastic to the Rescue: Wal-Mart and others are going green with "biodegradable" packaging made from corn. But is this really the answer to America's throwaway culture?
2. Medical Plastics News. Pyam Ramnes. October 24, 2017. Accessed November 2017. Friend of the earth: How bioplastics can be used in the medical field
3. Chemical and Engineering News. Alexander H. Tullo. Volume 95, Issue 41, p. 30-34. October 16, 2017. Accessed November 2017. 3-D printing: A tool for production Interest from manufacturers and big chemical companies shows that 3-D printing isn't just for hobbyists
4. Live Science. Mindy Weisberger. April 17, 2018. Accessed April 2018. Lab 'Accident' Becomes Mutant Enzyme That Devours Plastic
5. Chris Jordan's Gallery. Accessed November 2017. Running the Numbers: Portraits of Global Mass Culture