AC 2010-593: BIODEGRADABILITY OF PLASTICS TESTING IN AN UNDERGRADUATE MATERIALS LABORATORY COURSE

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Biodegradability of Plastics Testing in an Undergraduate Materials Laboratory

Abstract

As a growing concern for the environment has become an important issue nationally and globally, more efforts have been in place to sustain our resources. Sustainable materials are of increasing industrial importance. As such, it is imperative that students are educated about the importance of these materials. One such material is biodegradable polymers. A laboratory procedure for testing biodegradability of polymers was designed for an undergraduate materials laboratory course. Testing biodegradability of plastics allows students to gain a fuller understanding of these materials. Implementing biodegradable testing in a curriculum provides active learning by hands-on testing and encourages students to engage in lifelong learning to continue to build their knowledge of emerging materials. This paper describes an investigation of testing biodegradability of biodegradable plastics by monitoring carbon dioxide evolution and degradation of physical properties. A cost-effective method to test biodegradability is also described.

Biodegradability of Plastics Testing in an Undergraduate Materials Laboratory

Introduction

Sustainable materials are an area of significant interest in today's environmentally conscious society. One sustainable material is biodegradable polymers. Over the last few decades, there has been growth in the use of biodegradable polymers. Plastics have been widely used for their advantageous properties: lightweight, low cost, malleable, and durable. However, traditional petroleum-based plastics break down at a very slow rate in the natural environment and contribute to pollution concerns. Biodegradable plastics are being integrated in new products as a way to reduce pollution. Use of these materials doubled from 2005 to 2009.¹ The global market for biodegradable plastics is approximately \$25 billion a year.² Companies target a wider range of customers by marketing their use of biodegradable plastics and being more "green" than their competitors.

Although there has been a growth in the biodegradable sector, there are also many misconceptions about biodegradability. There is the perception that because a product is made of a biodegradable material it will disappear if discarded in any environment. However, the environment that the plastic is exposed to plays a role in the rate at which it will degrade and if the polymer will degrade at all. There are environmental requirements such as moisture level, sunlight exposure, soil and compost content, oxygen availability, and presence of microorganisms that play an essential part of biodegradation. "Deterioration or loss in physical integrity is also often mistaken for biodegradation."³ Polymer molecules can be broken down or degraded without technically biodegrading. Biodegradation requires microorganisms to convert the material into small molecules such as carbon dioxide and water. It is important for students to understand the distinction between "biodegradation" and degradation."

The most popular industries utilizing biodegradable plastics are the packaging industries, which include grocery bags and food/beverage packaging, and also those industries that manufacture plastic utensils.⁴ These types of products see a quick turnaround time of use from the customer - meaning that those products would reach landfills and dump sites much quicker than other applications. Engineers and scientist need a fundamental understanding of biodegradable plastics to properly use these materials for various applications. The desire to incorporate this topic into an undergraduate Mechanical Engineering Technology curriculum led to the development of biodegradability lab experiment in an undergraduate plastics laboratory. Exposure to such a laboratory unit is of particular value because use of these types of materials is forecasted to grow 13 percent annually from now through 2014.² This growth is due to consumers who demand "green" products and the increased political pressure to reduce packaging waste.⁵ As demand for such materials increases, demand for employees with a knowledge base of these materials will grow. Students not only need to understand these materials but need to understand the proper application of them as well.⁶

Test Description

Since the interest for using biodegradable plastics has grown exponentially, there have been a number of standards developed for testing the material. "Through these standards, industry and governments (and their regulatory agencies) can operate in a clear, safe, and effective manner for the benefit of the general public."⁷ The American Society for Testing and Materials (ASTM) develops standards that have been used worldwide and provide a foundation for comparisons of data for testing performed at various institutions.

The test methods described in ASTM D6400 - Standard Specification for Compostable Plastics and ASTM D 5988-03 Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials After Composting were used as the basis for the test described in this paper.^{8,9} This test method was used because it provides clear guidelines to biodegradability and is designed to evaluate aerobic biological reaction systems under controlled conditions. The ASTM D 5998 method used is equivalent to the International Organization for Standardization (ISO) 17556:2003.

ASTM and ISO terminology as defined on environmentally degraded plastics are as follows:⁷

Degradable plastic - a plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification.

Biodegradable plastic - a degradable plastic in which the degradation results from the action of naturally-occurring microorganisms such as bacteria, fungi, and algae. "Biodegradable plastics must biodegrade in specific environments such as soil, compost, or marine environments. There is no regulation addressing toxic residue, and no specific time requirement for degradation."⁹

Photodegradable plastic - a degradable plastic in which the degradation results from the action of natural daylight.

Oxidative degradable plastic - a degradable plastic in which the degradation results from oxidation.

Hydrolytically degradable plastic - a degradable plastic in which the degradation results from hydrolysis.

Compostable plastic - a plastic that undergoes degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known, compostable materials and leaves no visually distinguishable or toxic residue.

Biobased - an organic material in which carbon is derived from a renewable resource via biological processes. Biobased materials include all plant and animal mass derived from CO₂ recently fixed via photosynthesis, per definition of a renewable resource.

Two distinct but complementary lab experiments were developed and executed as a derivative of the ASTM D5988-03 and ASTM D6400. The first is biodegradability in soil / compost, by monitoring carbon dioxide evolution in a biometer flask and in glass jars, as a low cost alternative. The second is biodegradability in soil / compost by monitoring loss of mass and reduction in physical properties via tensile testing. For both experiments the same testing conditions and test specimens were used. The second test is a complimentary test that technically measures degradation and not biodegradation. This component was added because this laboratory course is based out of a Mechanical Engineering Technology program and the course outcomes involve understanding mechanical and physical testing of polymers.

This laboratory experiment is part of a 10-week, quarter-long plastics testing laboratory. The experiment involves one two-hour laboratory session dedicated to setting up the test, weekly monitoring (15-20 minutes per two-hour session), and a final two-hour session dedicated to completion of the lab and breakdown of the test set up. When weekly monitoring is performed, the remaining lab time is used for other laboratory experiments. Weekly monitoring should be completed for at least nine weeks. This biodegradability experiment is completed as a group lab with groups sharing data. Each lab section consists of three groups of four or five students. Each group is responsible for setting up three flasks: one for the positive control, one for the negative control, and one for the actual test samples (biodegradable polymer). Each group also sets up one bin for measuring degradation in soil by loss of mass and reduction of tensile properties.

Biodegradation by Monitoring Carbon Dioxide Evolution Test

Plastic biodegradability in soil/compost by monitoring carbon dioxide evolution was tested in both biometer flasks and glass jars. Biometer flasks are designed for use in studying and determining carbon dioxide evolution for aerobic biodegradation of an organic chemical in natural soils and can be quite costly. The glass jars were used as a low-cost alternative to the biometer flasks. These specialized flasks cost approximately \$120 per flask. The test was conducted using soil, compost, and the test sample in a closed incubator glass vessel (biometer flask or glass jar) at room temperature. The carbon dioxide that evolved was trapped by means of 0.5 KOH solution contained within each vessel. The KOH solution was then titrated with 0.5 HCl at a frequency of three to four days for the first two to three weeks and every one to three weeks thereafter. From the titration, the amount of CO₂ evolved can be determined as described in the “Calculations” section.

When testing biodegradability in soil, a polymer that technically biodegrades in soil needs to be used. Poly-(3-hydroxyalkanoates), PHAs are ideal for this test. One such PHA is PHBV, a copolymer of hydroxybutyrate and hydroxyvalerate, such as Telles' Mirel™. This same polymer will more readily degrade in compost. If a more accelerated version of this test is desired, compost can be used instead of soil.

Biodegradability Testing Using Biometer Flasks

Equipment / Reagents required to set up test:

One (1) Biometer Flask assembly 250 mL

10 mL Syringe
15-gauge syringe needle
Scale to weigh samples
Moisture meter
pH meter
0.5N Potassium Hydroxide (KOH)
Ascarite-20 mesh; 20-35 grams per biometer flask
Soil
Compost
Test Sample
Glycerol

Procedure to set up the test:

1. Obtain approximately 100 grams of soil that must be sieved to a particle size of at least 2mm.
2. Add 1 gram of compost to each 25 grams of soil.
3. Test soil's pH (pH must be between 6 and 8).
4. Test moisture content of soil (50-70%).
5. Obtain sample material (approximately 500 mg). There should be approximately 200-1000 mg of sample for every 500 grams of soil.
6. Record all data in a log sheet.

For the following steps, please refer to Figure 1 for part identification:

7. Add test sample and soil/compost to the biometer flask (Part I).
8. Coat rubber stopper with a layer of Glycerol and place on flask (Part H).
9. Completely fill Part F with Ascarite and close air tight.
10. Coat rubber stopper with a layer of Glycerol and place on side tube (Part C).
11. With syringe and needle add 10 mL of 0.5 KOH into side tube (Part D).
12. Remove syringe after KOH is deposited and cork or seal the needle (Part A and B).
13. Ensure that filter stopper (Part G) is closed (horizontal position).
14. Place biometer flask in a dark cabinet.

Figure 1 - Biometer Flask
(EPA, 1998)

Equipment / Reagents required for testing titration for CO₂ Evolution:

0.5N Potassium Hydroxide (KOH)
0.5N Hydrochloric Acid (HCl)
Phenolphthalein
Pipettes
Stand with burette holder
10 mL syringe
100 mL beaker

Procedure for Titration:

1. Set up burette stand and burette.
2. Fill burette with HCl (ensure burette nozzle is closed before adding HCl).
3. Open the filter stopper (Part G) (vertical position).
4. Remove cork or seal from needle and attach syringe to remove KOH.
5. Put the KOH into the beaker and add 10 micro-liters (μL) of Phenolphthalein to the KOH.
6. Slowly open valve of burette and allow HCl to drip into beaker of KOH.
7. Gently swirl beaker while HCl is added. When color turns clear, close valve and record how much HCl was used.
8. Dispose of contents in the beaker.
9. With syringe and needle refill biometer flask with 10 mL of 0.5 KOH back into side tube (Part D).
10. Remove syringe after KOH is deposited and cork or seal the needle (Part A and B).
11. Close filter stopper (Part G) (horizontal position).
12. Place biometer flask in a dark cabinet.
13. Repeat steps 1-13 for each flask.

Biodegradability Testing Using Glass Jars (Low-cost Method)

Equipment / Reagents Required for Test Set Up:

One (1) wide-mouth one quart (or 1 liter) glass jar with lid	Soil
Scale to determine mass of samples	Compost
Moisture meter	Test Sample
pH meter	Distilled water
0.5N Potassium Hydroxide (KOH)	One (1) 100 mL beaker and One (1) 50 mL beaker

Procedure to set up the CO₂ evolution with glass jars:

1. Obtain approximately 200 grams of soil that must be sieved to a particle size of at least 2mm.
2. Add 1 g of compost to each 25 grams of soil.
3. Test soil's pH (pH must be between 6 and 8).
4. Test moisture content of soil (50-70%). Adjust moisture as necessary by adding distilled water.
5. Obtain sample material (approximately 1000 mg). There should be approximately 200-1000 mg of sample for every 500 grams of soil.
6. Record all data in a log sheet.
7. Add test sample and soil/compost to the glass jar.
8. Place 50 mL of distilled water in the 100 mL beaker inside the jar.
9. Place 20 mL of 0.5 KOH in the 50 mL beaker inside the jar.
10. Place lid on the glass jar and ensure air tight seal.

11. Place glass jar in a dark cabinet.

For Testing:

Follow steps for titration from the biometer flask test except at Step 10, refill the beaker with 20 mL of KOH.

Sample log sheet:

Date:		Days of Testing:	
Flask or Jar	Material	HCl (mL)	g CO ₂

Calculations:

After the titration results are gathered, the following calculations are required to obtain the carbon dioxide evolved and the percent of mineralization from the specimens. Percent mineralization is the percent of carbon in the polymer that has been converted to CO₂.

To calculate the carbon dioxide evolved, use the following equations:

According to Section 12 of ASTM D5988-03:

- Since $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
12 grams of carbon in the polymer and / or soil yields 44 grams of CO₂

$$Z_n = Z_b - Z_t$$

Z_n= mL of HCl needed to titrate the CO₂ from only the sample

Z_b= mL needed to titrate blank (KOH used for titration)

Z_t = mL of HCl to titrate test substance

Correcting for Normality of HCl (if 0.25 N is used, change equation)

m moles of CO₂ = (0.5 N x mL HCl)

mg of CO₂ = (0.5 N) x mL HCl x 44)

Carbon dioxide evolved is determined by multiplying the HCl titration by 22.

To calculate percent mineralization, first calculate the Molar Mass (MM) of carbon dioxide, CO₂.

- The formula for carbon dioxide is composed of one atom of carbon and two atoms of oxygen.
- Atomic mass carbon = 12.01 (from the Periodic Table).
Atomic mass of oxygen = 16.00 (from the Periodic Table).
- Molar Mass (MM) for carbon dioxide
= atomic mass carbon + (2 x atomic mass oxygen).

$$\begin{aligned}\text{Molar Mass (MM)} &= 12.01 + (2 \times 16.00) \\ &= 12.01 + 32.00 \\ &= 44.01\text{g/mole}\end{aligned}$$

Therefore, CO₂ is $12.01/44.01 \times 100 \% = 27.3 \%$ carbon by mass.

For example, if you have 100 grams of CO₂ that have been evolved from the sample, there is 27.3 grams of carbon. Therefore, if you had a 100 gram biodegradable sample which has 60 grams of carbon, then you have 27.3 mass of carbon evolved / 60 grams of carbon in the sample = $27.3/60 \times 100 = 45.5 \%$ mineralization. Carbon content of the sample is determined by knowing the molar mass of the repeat unit for the polymer and calculating the carbon fraction of that mass.

Measuring Degradation in Soil by Loss of Mass and Reduction of Tensile Properties

Polymer degradation can also be tracked by monitoring the loss of mass and loss of mechanical properties over time. This method, however, is not a true indicator of biodegradability. Biodegradability, by definition, requires that the polymer be broken down into simple molecular units such as carbon dioxide and water. The findings of these tests can be related to biodegradability but cannot be used to conclude that biodegradation is, in fact, occurring. This aspect of the experiment compliments the biodegradability testing, especially for laboratories in mechanical engineering technology or mechanical engineering where the main focus of the curriculum is mechanical and physical properties of polymers. The test described below should be run for a minimum of nine weeks.

Equipment / Reagents required for testing:

2 quart plastic bins

500 grams of soil per bin, prepared as described in the “Glass Jar Test”

Test Samples: 1 inch x 6 inch strips of plastic sheet (3 mil) or film and paper

- Fifteen (15) samples of the test substance
- Fifteen (15) samples of a negative control (known non-degradable plastic such as polyethylene)
- Fifteen (15) positive control samples (kraft paper or cellulose filter paper)
- Spray bottle

- Distilled water

Scale to record mass of samples and soil

Equipment capable of tensile testing

Procedure for testing:

1. Prepare soil and place half of soil in bin.
2. There should be approximately 200-1000 mg of sample for every 500 grams of soil.
3. Week 1:
 - a. Record mass of three of each type of sample (test, negative and positive controls).
 - b. Add to bin and cover entirely with remaining soil. May need to have several layers of soil and samples or place samples in horizontally.
 - c. Record mass of entire bin.
4. Monitor mass of entire bin each week. If mass of bin has decreased, add distilled water equal to the mass loss. Use a spray bottle to evenly disperse water.
5. Weeks 3, 5 and 7:
 - a. Repeat Steps a-c from Week 1.
6. Week 9
 - a. Remove all samples from soil.
 - b. Clean samples carefully. Rinse with water and pat dry.
 - c. When samples are completely dry, record mass.
 - d. Test samples for tensile strength and percent elongation following ASTM D638 Standard Test Method for Tensile Properties of Plastics or ASTM D882 - 09 Standard Test Method for Tensile Properties of Thin Plastic Sheeting depending on thickness of samples.
 - e. Record tensile properties (such as stress at maximum load, strain at break %).

Sample data log sheet:

SAMPLE MASS	Test Sample			Positive Control			Negative Control		
	1	2	3	1	2	3	1	2	3
Control (no soil exposure)									
2 week Exposure									
4 week Exposure									
6 week Exposure									

Graphs can be made of the data to show loss of mass and loss of properties versus time. Student testing has shown that after six weeks of soil exposure, thin films can be so degraded that they cannot be tested for tensile properties; it is also difficult to get accurate mass readings with fragmented samples that are too weak to thoroughly clean. Use of sheet stock (3 mil thickness) of the PHA plastic allowed for students to see degradation in properties and mass. If a high level of degradation is desired with sheet stock, it is recommended that compost be used as the biodegradation media versus soil, as compost has a higher level of microbial activity that is conducive to faster degradation.

At the request of the polymer supplier, actual data cannot be included in this paper. Data from similar testing to determine percent mineralization of biodegradable polymers and reference materials is available for instructor's reference for comparable data in journal articles.^{12,13,14,15}

Related Instructional Information

The following is supplemental information that can be used as suggested readings for the students regarding the biodegradability of plastics:

- Green Plastics Knowledge center
http://www.greenplastics.com/reference/index.php?title=Main_Page
- Biodegradable Plastics
<http://www.biodegradableplastics.org/>
- Bio-Tec Environment
<http://www.bio-tec.biz/>
- American Society for Testing and Materials
<http://www.astm.org/index.shtml>
- International Organization for Standardization
<http://www.iso.org/iso/home.htm>
- Biodegradable Plastic Resin Information
<http://www.bioplastic.org/>
- Biodegradability of Polymers: Regulations and Methods of Testing
http://www.wiley-vch.de/books/biopoly/pdf_v10/vol10_19.pdf

Other articles and books can be found in the bibliography of this paper.

Conclusion

Students who have participated in the Biodegradability Lab have expressed that doing so has increased their interest in Sustainable Materials. One student commented that the lab:

“...greatly increased my interest in polymers, especially new polymers made from sustainable processes.”

Testing biodegradability of plastics in an undergraduate materials course will expand a student's knowledge for the selection of innovative materials for various applications. By including these materials in the curriculum, there is an opportunity to convey the importance of having a full understanding of the benefits and limitations of new materials. As use of these types of materials increase, there will be a demand for employees with this knowledge base.

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