Using Biodegradable Polymer Experiments to Examine Structure-Function Relationships

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I. Introduction

Polymers are used widely in modern society because they are light in weight, low in cost, and easy to process materials. However, there is an increasing and global-scale concern over the environmental consequences of products made of polymers when they eventually end up in landfills after their intended uses. Polymers derived from agricultural feedstock can be biodegradable and play a role in helping alleviate the environmental concerns. Biodegradable polymers have a wide range of potential applications in markets currently dominated by petroleum-based materials such as drug delivery systems, flushable diapers, controlled release systems for agricultural chemicals, disposable nonwovens, horticultural containers, washable paints, and lubricants.[1]

Most natural polymers, such as starch, cellulose, and proteins are readily biodegradable through hydrolysis followed by oxidation with the aid of enzymes. Synthetic polymers may attain biodegradability by incorporating hydrolyzable linkages in their backbones. Aliphatic polyesters have been known to be the most easily biodegradable synthetic polymers. Important examples of synthetic biodegradable polymers of industrial scale include polyvinyl alcohols, polycaprolactones (such as Tone polymer by former Union Carbide)[2], and polylactic acid (pioneered by Argonne National Laboratories). Although there are issues related to both cost and monomer supplies, development of lactic acid based biodegradable polymers appears to be most active, and a number of commercial projects are under way.

While there has been a lot of research on biodegradable polymers and increasing commercialization of biodegradable polymers, the availability of educational materials on this important subject are disproportionate to other areas of polymer education.[3] There is an increasing demand for skills in this area from companies involved in the research and product development activities of this class of polymers.[4-6] Therefore, a biodegradable polymer laboratory unit has been developed that has several educational objectives. First, students learn general polymer science principles such as structure-property relationships. Secondly, students learn about various chemical and physical polymer characterization methods. Additionally, students are directly exposed to the environmental issues associated with polymer materials along with the variables controlling the kinetics of polymer biodegradation. Students are challenged to use statistical methods to determine which polymer physical and chemical property measurements best correlate with biodegradability.

The laboratory unit is designed to provide an inquiry-based educational experience to students by exposing a variety of polymer samples to simulated biomass environments and characterizing the samples against the exposure time. It is known that molecular properties of polymers, such as molecular weight distribution, crystallinity, and morphology, will dictate the physical properties of the final products made from these polymers. When a polymer sample undergoes biodegradation, many chemical and physical properties will change. The following chemical and physical properties are measured at various exposure times:

(1) Melt Index (MI), which indirectly measures the average molecular weight of the polymer;
(2) Molecular Weight Distribution (MWD) by gel-permeation chromatography (GPC), which gives detailed molecular information regarding the degree to which the degradation proceeds;
(3) Thermogravimetric analysis (TGA), which indicate the characteristics of the low molecular weight degradation products;
(4) Tensile stress-strain curve, which reflects physical weakening of the polymer due to degradation.

Finally, the degradation kinetics are determined through the use of a respirometer that measures the gas-phase oxygen concentration.

II. Experimental Materials and Methods

Two biodegradable polymers were studied - polyvinyl alcohol (PVOH) and polylactic acid (PLA). PVOH from Aldrich Chemical with an average molecular weight of 9,000-10,000 and a degree of hydrolysis of 80% was used to provide a biodegradable polymer that would be quickly degraded to allow experiments to be performed in as short a timeframe as possible, i.e., ten days. The PVOH was added to slurry reactors at mass loadings of 100mg and 200mg PVOH on a dry weight basis. PLA from Cargill Dow was used to provide a higher molecular weight biodegradable polymer that has recently been successfully commercialized and is used in a variety of products.

The effect of polymer fillers can also be studied by the students. There have been controversial reports that students can try to resolve. Some found filler promotes biodegradation due to a catalyst effect[7] but others believed fillers block the diffusion of microorganisms and water and actually reduce biodegradation.[8-10]

Biodegradation experiments were performed in two environments – slurry and compost. All PVOH tests were performed with a 16-cell respirometer system manufactured by Challenge Environmental Systems (AER–200). This system provided a slurry environment in which the samples could be quickly degraded and monitored in terms of the gas-phase oxygen concentration in each reaction cell. Temperatures studied ranged from 20 C to 45 ºC. PLA tests were performed at room temperature using a compost system modeled after those used by Eastman Chemical in which temperature, air flow, and humidity are controlled (Figure 1).[11] This system provides an environment closer to that experienced by a polymer in a landfill. Degradation could be followed by changes in the particle size distribution of the polymer.

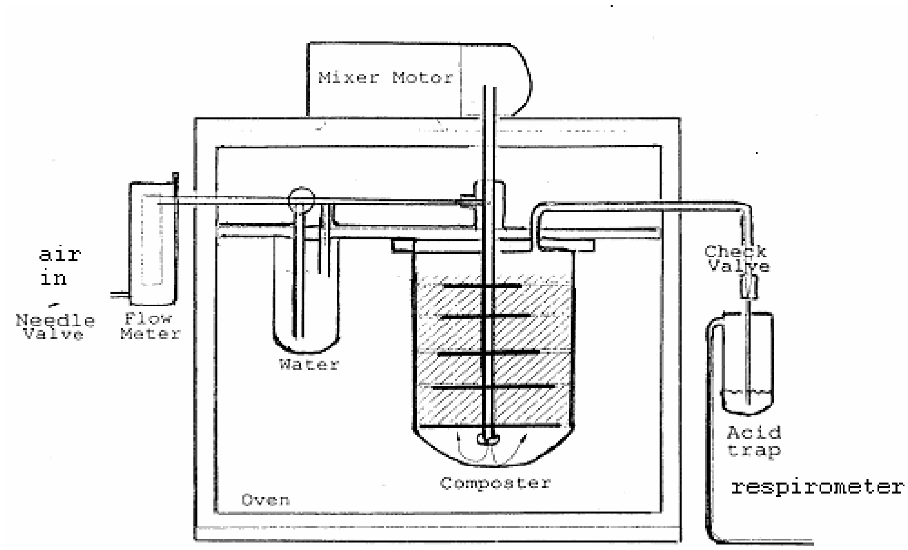

Figure 1. Experimental apparatus for continuously determining biodegradation kinetics using a composter and respirometer.

For the results reported herein, slurry tests were used to measure the total aerobic oxygen uptake associated with biodegradation of a polymer. The slurry tests were conducted in accordance with the ASTM method D5209-92.[12] This method provides the extent and rate of biodegradation of polymeric material by aerobic microorganisms in the presence of municipal sewage sludge and is performed using a respirometer. The inoculums concentration was determined to be 2532 mg/L of mixed liquid suspended solids (MLSS). However, due to the large biomass concentration and high oxygen uptake rate of the sample, the sludge was diluted to the inoculums concentrations given in the different OECD and ISO protocols. The sample was diluted in a two-liter conical flask using the prepared nutrient-mineral-buffer (NMB) solution to give a final test medium inoculums concentration of 500mg/L of mixed liquid suspended solids (MLSS). The test medium contained phosphate and bicarbonate buffers to maintain the pH near neutral. To prevent oxygen consumption due to nitrification processes, allylthiourea (ATU) was added to the medium up to a final concentration of 10mg/L.

III. Results

A primary key to a successful biodegradable polymer lab unit is to be able to perform numerous experiments within the time constraints of a course. Therefore, the sample student data results presented herein are limited to data that demonstrate that this key has been successfully addressed. The biodegradation of the polymers is expected to follow the typical four-stage kinetics of slow enzyme-catalytic oxidation of organic materials. The first stage of attack by the microorganisms is attachment to the polymer sample. Attachment creates a tiny ecosystem for the microbe to act on the material, usually through enzymes, to break the material down into nutritional requirements for the microbes. Since the first step of microbial action is attachment, the control of the surface roughness, such as by embossing and corona treatment, of the polymer samples affects the biodegradation kinetics. The second stage of the biodegradation process is fragmentation of the material. The third stage of the biodegradation process is disintegration. The material is reduced to powders. Finally, the polymer is reduced to carbon dioxide, water, and minerals. The molecular properties of polymers, such as molecular weight, molecular weight distribution, crystalinity, and morphology dictate the way the microorganisms interacted with the polymer samples and have a strong effect on biodegradation kinetics. Crystalline polymers with low free volumes are harder to break down.

A typical result of the respirometric tests is shown in Figure 2 in terms of the cumulative oxygen uptake as a function of time for PVOH at 25°C. The control represents the oxygen consumption due to endogenous respiration of the microbial cells. In biodegradation tests it is important to determine endogenous BOD because the measured BOD data from the test assays with the test substance have to be corrected by these blank values.[13] The effect of substrate concentration on the total oxygen uptake is seen. The result suggests that increasing the concentration of PVOH will provide more carbon for microbial growth consequently increasing the rate of reaction and biological activity of the microorganisms. Hence, the total oxygen uptake increases with increasing substrate concentration.

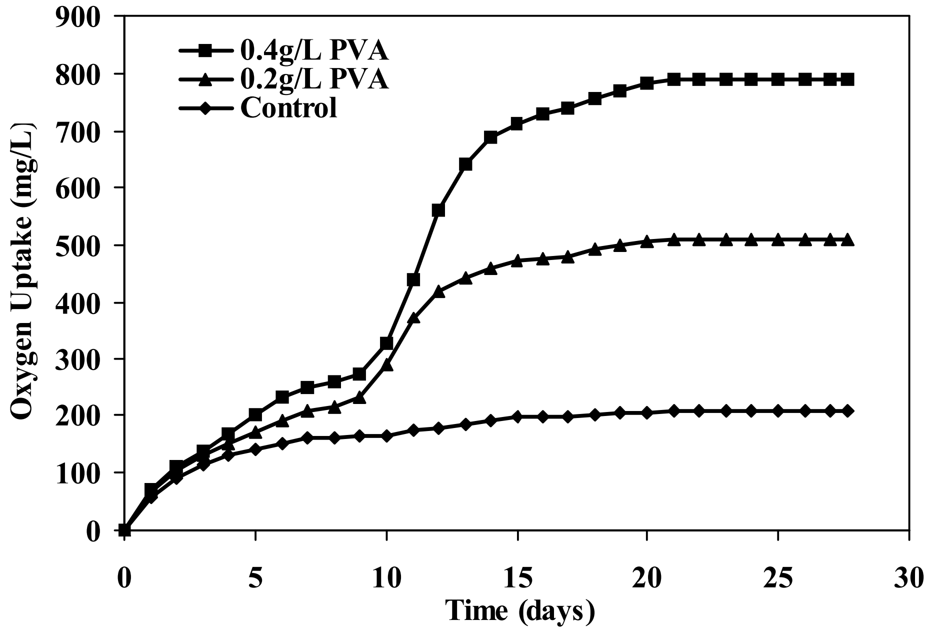

Figure 2. Respirometer cumulative oxygen uptake results for polyvinyl alcohol in slurry bottles at 25ºC.

The degrees of biodegradation of PVOH were 44.2-44.6% based on ThOD at 35ºC. The reason for the low degradation was probably that the microorganisms and enzymes responsible for the degradation of PVOH are ineffective at high temperatures. On the other hand, the degrees of biodegradation of PVOH were 79.9-83.1% based on ThOD at 25ºC. The test at 25 ºC exceeds the limit value of 60% thus proving the ready biodegradability of PVOH in an aqueous environment at an optimum temperature of 25ºC. Additional experimental results are available elsewhere.[14]

IV. Website

As a resource for students performing the experiments, as well as students with a general interest in biodegradable polymers, a biopolymer website has been generated (www.ncat.edu/biopolymer/). This site is structured to provide quick tutorials on biopolymer related topics, a glossary of relevant terms, and opportunity to explore data from typical lab experiments.

V. Laboratory Module Assessment

This biodegradable polymer lab experience is now used in CHEN 410 (Chemical Engineering Lab II) and CHEN 665 (Polymer Engineering) courses. CHEN 410 is a required lab course for chemical engineering students. During fall 2004, a class of twelve undergraduate students used the lab materials that have been developed. The students were surveyed and the results are summarized in Table 1.

Table 1. CHEN 410 Survey Data

Rate how this experiment has contributed to preparing you with each of these outcomes:	**Average Rating***
Ability to apply knowledge of mathematics, science and engineering	4.17
Ability to design and conduct experiments	4.33
Ability to analyze and interpret data	4.33
Ability to function on a multidisciplinary team	4.00
Ability to identify, formulate and solve engineering problems	3.50
Ability to communicate effectively	4.17
Knowledge of polymer structure/function relationships	3.83
Knowledge of environmental considerations associated with the use of plastics	3.50
Knowledge of microbiology involved in biodegradation processes	3.50

* Scale ranges from 1 for Strongly Disagree to 5 for Strongly Agree

VI. Conclusions

Instructive polymer biodegradation data can be collected in the 1-2 week timeframe that is conducive to use within a course. A manual and website for the biodegradable polymer laboratory unit has been produced that contains introductory material, learning objectives, detailed experimental procedures, cooperative learning exercises, formative assessment exercises, reflective writing exercises, and supporting reference materials. The unit has shown promise as an effective tool for teaching basic polymer concepts in the context of life science and environmental issues.

VII. Acknowledgement

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