Biodegradable Polymer Characterization Laboratory Unit

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Abstract

A current research area of significant environmental, economic, and scientific importance is biodegradable polymers.[1-4] Biodegradable polymers is also an area that has great promise for being used to integrate life science into the chemical engineering curriculum. To this point, however, high quality laboratory manuals on biodegradable polymers have not been developed. Therefore, a laboratory unit titled "Biodegradable Polymer Characterization" has been developed.

The laboratory unit provides a hands-on educational experience to students by exposing a variety of polymer samples (polyvinyl alcohols, polycaprolactones, polylactic acid) to simulated biomass environments and characterizing the samples against the exposure time. Independent variables that students can explore include biodegradation medium (slurry or soil), microorganism species and concentration, moisture content (for soil), temperature, pH, nutrient species and concentrations, polymer surface roughness, and polymer concentration. Analytical methods available include respirometry, melt index, gel-permeation chromatography, tensile strength, and thermogravimetric analysis. Students are able to study the relationship between polymer structure and biodegradation properties. They are challenged to use statistical methods to determine which polymer physical and chemical property measurements best correlate with biodegradability. Through this process, the students develop a vivid understanding of fundamental principles of polymer science, as well as the importance of societal and environmental issues with polymer materials design, manufacturing, and applications. Pedagogy that has been demonstrated to be effective in improving student learning, e.g., cooperative learning, formative assessment and feedback, and reflective writing, is incorporated into the laboratory materials.

I. Introduction

Synthetic polymers continue to play an important role in the nation's economy as one of the largest sectors of the chemical industry.[5] Application of polymers in biotechnology is experiencing the fastest growth. Large investments by both government and industry in biotechnology are reshaping the career paths for both faculty and graduates of the traditional petrochemical-centered chemical engineering programs. Hiring by traditional petroleum and chemical companies has stagnated for the last two decades, whereas the health care and biotechnology sectors are hiring more chemical engineering graduates. The U. S. Department of Labor projects that the employment of chemical engineers will grow more slowly than the average for all occupations though 2010, and the overall employment in the chemical manufacturing industry is expected to decline. Among manufacturing industries, specialty chemicals, plastics materials, pharmaceuticals, biotechnology, and electronics may provide the best opportunities.[6] Thus, exposure to a laboratory unit on biodegradable polymers is of particular value to chemical engineering students.

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. Of particular concern are polymers used in single-use, disposable applications such as baby diapers. The high molecular weight, covalently bonded polymer molecules are not readily broken down by the waste management infrastructures such as composting. This results in an irreversible buildup of "die-hard" trash that may cause scarring of landscapes, fouling of beaches, and a serious hazard to marine species.

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. These markets include drug delivery systems, biomaterials, flushable diapers, biodegradable agricultural films, controlled release systems for agricultural chemicals, disposable nonwovens, horticultural containers, washable paints, and lubricants.[7-11]

Several structural parameters influence the biodegradability of a polymer. 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. Both molecular weight and crystallinity strongly influence biodegradability and kinetics of biodegradation process.

Proteins are well known example of biodegradable natural polymers. Proteins contain hydrolyzable linkages but do not have regular and equivalent repeating units along their polypeptide chains and are mostly amorphous. All these structural characters of protein make it easier for enzymes to facilitate biodegradation.

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)[12], 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.

The U. S. is faced with global competition in developing and commercializing biodegradable polymers. For example, Japanese companies Mitsui Chemical in Omutu and Shimadzu in Otsu started commercial-scale biodegradable polylactic acid production in 1996 and 1997, respectively. The German company Apack reached a license agreement with Fortum Oyj of Finland on biodegradable polylactide technology in 1999. Recently, Dow Chemical and Cargill created a joint venture in Blair, Nebraska to become the largest biodegradable polylactide producer with annual capacity of 140,000 metric tons. Eastman is marketing a biodegradable polymer under the brand name Eastar Bio®.

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. 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.[13] 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 and 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 a unique 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 can be determined through the use of a respirometer that measures the gas-phase oxygen concentration.

II. Experimental Materials and Methods

Industrially important polymer samples are available for students to use. Semicrystalline polyethylene (such as linear low density polyethylene with similar range of melt index) can be used as a non-biodegradable control sample. In the sample results reported herein, Eastar Bio® and polyvinyl alcohol (PVOH) were used. Eastar Bio® is a biodegradable co-polyester developed by Eastman Products. The PVOH utilized was a research grade from Aldrich Chemical Company, Inc. that had an average molecular weight of 9,000-10,000 and a degree of hydrolysis of 80 percent. PVOH was used to provide a polymer that would degrade rapidly.

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 catalyst effect[18] but others believed fillers blocked the diffusion of microorganisms and water and actually reduced biodegradation.[19,21-22]

To be able to measure significant and reproducible degradation within a couple week period, a well-mixed, biodegradable polymer slurry system is preferred over a composting system. However, for class situations in which a longer time frame is available, an automated composting experiment originally developed at Eastman Chemical for testing biodegradable polymers is available for the students (Figure 1).[14-16] The aerobic composting takes place in an environment where temperature, air flow, and humidity are controlled. Compressed air was used for controlled input of air into the composting chamber.

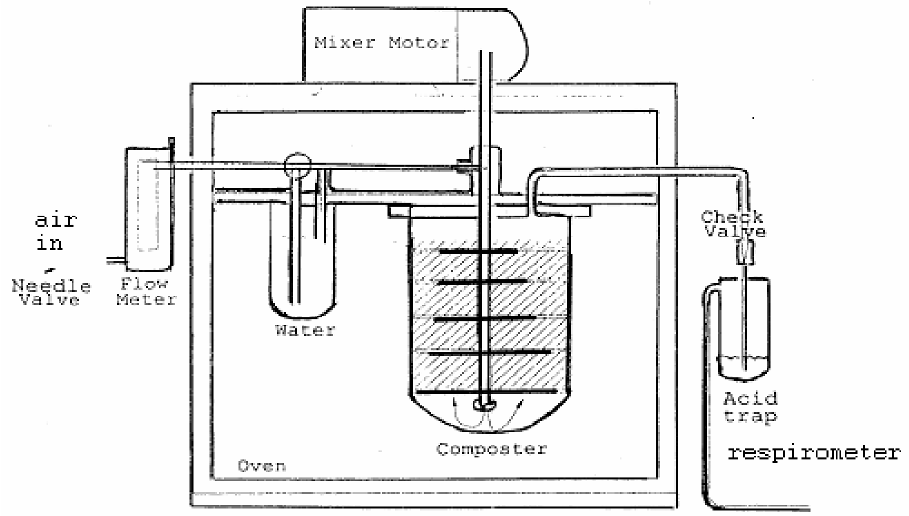

Figure 1. Experimental apparatus for continuously determining biodegradation kinetics using a composter and respirometer.

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.[17] 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. According to the test procedure, activated sludge is collected from a wastewater treatment plant and used at an initial mixed liquid suspended solids (MLSS) concentration of 1000 mg/l. The test medium contained phosphate and bicarbonate buffers to maintain the pH near neutral. In addition, nutrients were added to ensure an adequate supply for microorganism growth. To prevent oxygen consumption due to nitrification processes, allylthiourea (ATU) was added to the medium up to a final concentration of 10mg/L.

The respirometer used was manufactured by Challenge Environmental Systems (AER-200A/ANR-100 advanced aerobic/anaerobic system). The test mixture of polymer, inorganic medium, and inoculum was stirred in a closed flask of the respirometer. The slurry was mixed at rates that provide a maximum oxygen transfer rate that exceeds the maximum oxygen uptake of the microbial reaction in the slurry. Evolved carbon dioxide (CO_2) was absorbed in a 30 percent solution of potassium hydroxide suspended within the headspace of the reaction vessel. The level of biodegradation is determined by comparing the BOD with the theoretical oxygen demand (ThOD).

III. Results

A primary key to a successful biodegradable polymer 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 respirometer rate 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.

Typical results from respirometry are shown in Figures 2-5 for PVOH slurry systems. The control represents 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 (see Figure 2 and 5).[23] The degrees of biodegradation of PVOH were 56% at 25ºC and 64% at 35ºC based on theoretical oxygen demand (see Figure 3). Thus, students are clearly able to see the effect of temperature on the rate of polymer biodegradation. Note that these degrees of biodegradation were achieved in just 7-10 days with most occurring within the first three days (see Figure 4). This allows the slurry experiments to easily fit in with the timeframe of a typical course. Similar results were obtained using Eastar Bio® polymer in slurry bottles at 25ºC and 50ºC (see Figure 6). Student experiments with soil compost systems have been showing significant degrees of biodegradation after 3-4 weeks.

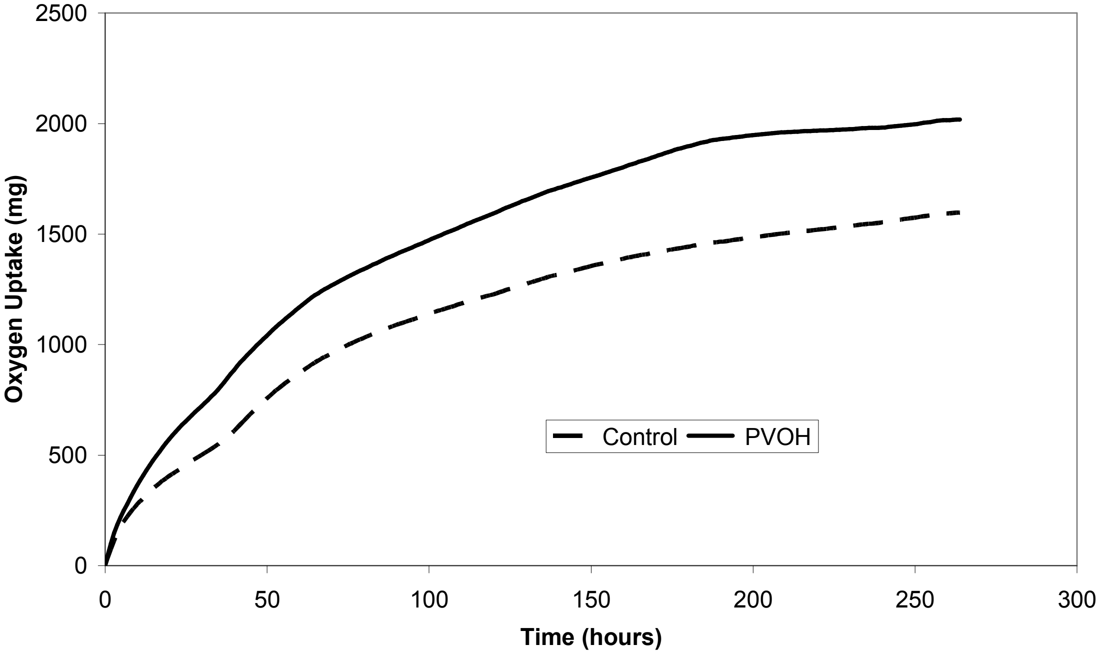

Figure 2. Respirometer cumulative oxygen uptake results for polyvinyl alcohol polymer in slurry bottles at 35ºC.

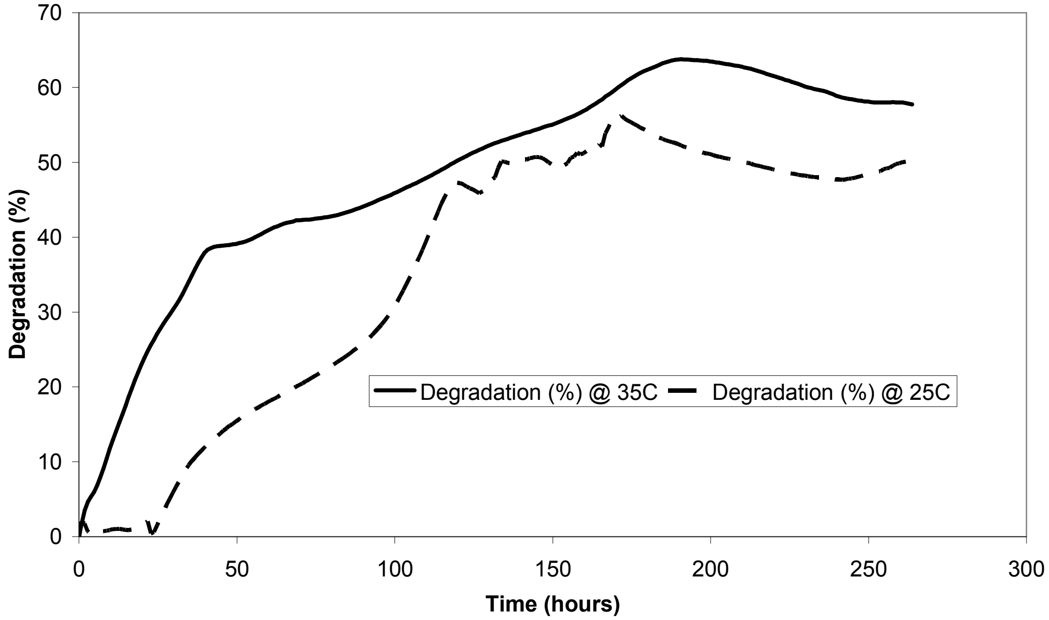

Figure 3. Effect of temperature on the degradation % for polyvinyl alcohol polymer in slurry bottles at 25ºC and 35ºC.

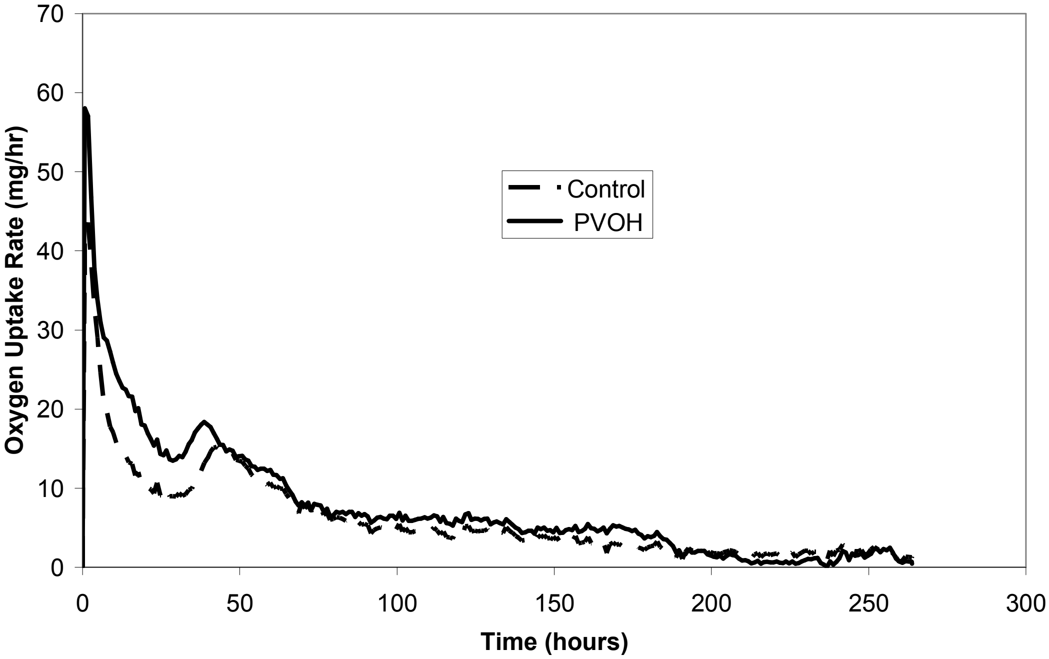

Figure 4. Respirometer oxygen uptake rate results for polyvinyl alcohol polymer in slurry bottles 35ºC.

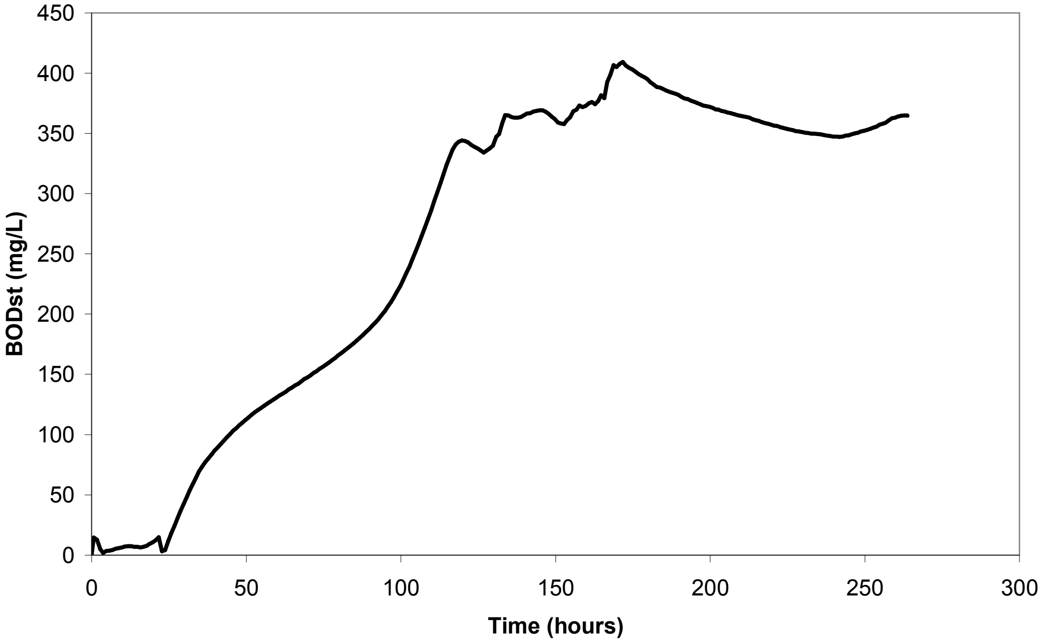

Figure 5. Short-term BOD results for polyvinyl alcohol polymer in slurry bottles 35ºC.

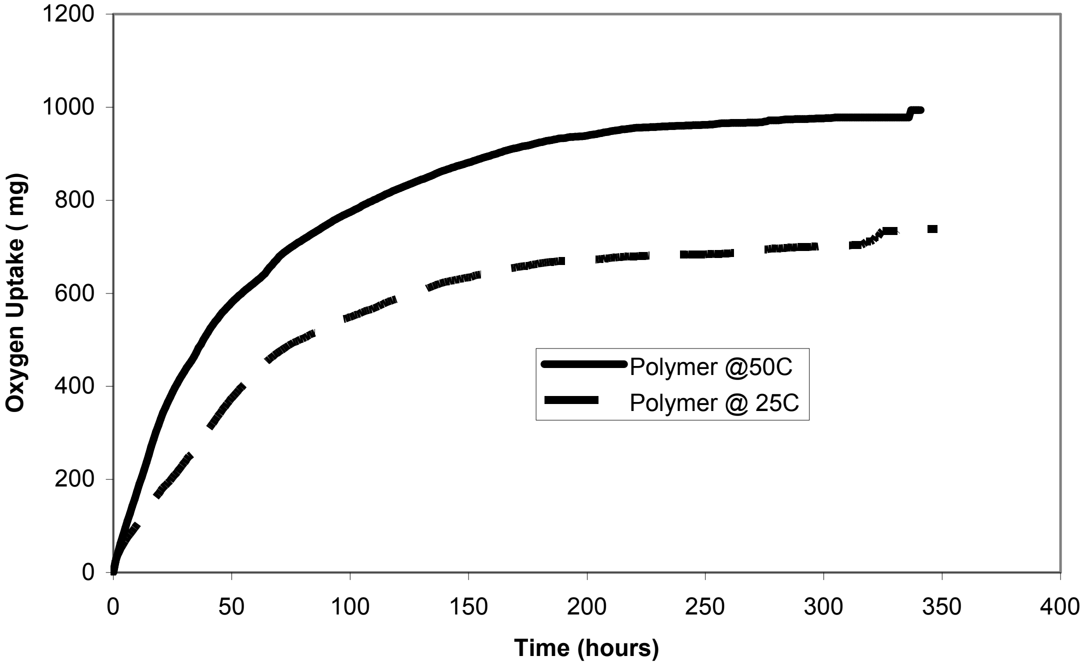

Figure 6. Respirometer cumulative oxygen uptake results for Eastar Bio® polymer in slurry bottles at 25ºC and 50ºC.

IV. Conclusions

Instructive polymer biodegradation data can be collected in the 1-2 week timeframe that is conducive to use within a course. A manual 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, however, the effectiveness of the unit still needs to be addressed through standard university-wide course evaluations and pre- and post-use student surveying.

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