Bioplastics Made from Industrial Food Wastes

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Abstract – It is common knowledge that plastics create problems. Manufacturing of plastics requires multiple amounts of petroleum and emits vast amounts of CO_2 thus influencing our environment and resources. Of the millions of tons of plastic generated only a few percents are recovered for recycling. The rest fills our landfills, waters and lands and will stay there forever. Many efforts have been made to limit fossil fuel use and reduce the environmental impact and new plastics derived from organic matter, called bioplastics, emerged. Various monomers suitable for polymer production can be derived from biological sources including starch, cellulose, fatty acids, sugars and proteins and these can come from industrial food wastes. This article provides an overview of currently produced bioplastics, the chemistry and microbiology behind polymer synthesis and fermentation, possible use of organic wastes, and discusses various projects that could be easily integrated into an engineering curriculum.

Keywords: bioplastics, fermentation, polymerization, environmental sustainability, industrial waste

Industrial Food Waste as an Engineering Topic of Interest

Dealing with industrial wastes could and should be introduced to university students not only because it provides many engineering topics for research and investigation but also is often regarded as a hot and interesting topic amongst students. The brewing industry's needs and problems related to the processes, resources used, and wastes created [1] can be solved at universities often at little cost while providing an excellent hands-on learning experience to the students. Engineering projects in the real world require the combination of innovation and diverse disciplines as brewing related developments provide an opportunity to seek assistance from non-engineering students and faculty.

A previously presented paper about introducing the process of brewing to the engineering program [2] outlined the steps used in beer brewing process and discusses various topics that could be easily integrated into a university curriculum. The authors implied that the use of beer brewing as means of piquing student interest and motivation could be beneficial and help spark student interest and possibly assist in retaining engineering students.

Beer is defined as a fermented alcoholic beverage made of malted cereals, water, hops, and yeast. The cereals used in beer production do not contain sufficient quantities of fermentable sugars in the harvested state and must first undergo modification during the malting and mashing steps to yield carbohydrates that yeast can convert during the fermentation step into ethyl alcohol and carbon dioxide. Many countries allow additional substances to be used. For instance, expensive barley malt is often supplemented with less expensive unmalted cereals such as corn, rice, or wheat.

Brewing industry tries to focus on recycling all materials and by-products that are generated throughout the brewing processes. Where possible, breweries can also resell these materials and by-products, which eliminates the need for disposal, as well as provides a source of revenue. Waste and by-product management can also be driven by the secondary market value of by-products. The biggest brewing waste is spent grain. It is generally used for the

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production of low value composts, livestock feed or disposed of in landfill as waste. Brewer's grains provide protein, fiber, and energy which make them desirable in a variety of diets. In the U.S., brewer's grains and other brewer's by-products are fed to pigs, sheep, horses, dairy and beef cattle, and poultry. The chief concern about the use of wet brewer's grains relates to spoilage. An uncovered pile of wet brewer's grains usually have a storage life of less than 5 to 7 days [3]. The grains can be burned as an alternative fuel to fire a steam boiler that provides heat in the brewing or grain drying processes or powers a turbine for electricity generation. Another strategy is to use an agricultural anaerobic digester to break down the leftover grain into methane. This methane can be used to power brewery systems that run on natural gas including the boiler. This has the potential to create a perpetual material to energy loop that conserves energy, saves money, and reduces waste production. Breweries can also look outside their own operations for opportunities to reduce the impact of their waste production. Coors Brewing has been producing ethanol, a petroleum alternative, with their spent grain. In Japan, the Akita Research Institute of Food and Brewing has developed a new technology that drastically reduces the cost of producing polylactic acid, the spent grain-derived foundation for the production of biodegradable plastics [4].

POLYLACTIC ACID

Plastics use in commercial products over the last couple decades has grown exponentially. While plastics are cheap to produce, they are also most commonly derived through the polymerization of oil-based products, which are not typically biodegradable. Due to an effort to limit oil use and reduce the environmental impact, the new field of bioplastics, plastics made from organic polymers, has emerged [5]. Polymers found in nature, or biopolymers, can be derived from a plethora of plants, vegetables, and even industrial waste products.

Based on the abundance of brewer's spent grain in the Mercer University area (the new "Macon Beer Company" brewery just recently opened in downtown Macon and the popularity of home brewing among Macon residents), the authors decided to investigate the possibility of making bioplastics from this brewing waste. Using the available published process [6] it has been decided to investigate the production of polylactic acid (PLA).

Materials derived from biological sources including starch, cellulose, fatty acids, sugars, proteins, and other sources can all be consumed by microorganisms, especially by bacteria which can convert these raw materials into various monomers that are suitable for polymer production [7]. These monomers have been used to produce various bio-based plastics including PLA. These polymers often are biodegradable and thus considered sustainable, environmentally friendly, and less petroleum dependent.

Polylactic acid is a thermoplastic and was discovered in 1932 by Carothers from DuPont, who produced a low molecular weight product by heating lactic acid under vacuum [8]. Lactic acid (LA) can be produced via chemical synthesis or microbial fermentation, however the bio-product is healthier and more desirable for food, drink, and pharmaceutical industries because it is easier to metabolize by a living organism. Since fermentation processes require only bacteria, simple sugars, and a warm controlled climate; numerous commercial waste products can be recycled for the production of lactic acid. Once LA has been harvested, it can be polymerized into PLA using various methods, each of which requires varying concentrations of lactic acid and additives. Condensation polymerization showed in Figure 1 is the most common method used today [9]. PLA tends to have a low to moderate degree of polymerization without additives.

PLA can be manufactured with a wide range of properties because lactic acid exists in four different molecular forms [8]. It can be made into a polymer with molecular weight ranging from a few thousands to over a million. Low cost PLA is colorless, glossy, brittle, with tensile strength of 50-62 MPa, Young's modulus of 384-481 MPa, glass transition temperature of 55-60ºC and melting temperature of 175ºC [7,10].

Polylactic acid can be easily shaped into film and fiber; spun bond and melt blown on existing processing equipment. PLA has practical medical applications as dissolvable sutures, as matrices for drug delivery, and bone fracture internal fixation devices. Other applications include its role as agricultural plant growth promoter, in textiles, and non-woven applications such as fiberfill, crop covers, geotextiles, wipes, diapers, and binder fibers. PLA can easily replace PET, HIPS, PVC and cellulosics in high-clarity packaging and also as candy wraps, optically enhanced films, and shrink labels. In order for PLA to be processed on large-scale production lines for injection molding, blow molding, thermoforming, and extrusion, the polymer must possess adequate thermal stability and maintain molecular weight and properties. These properties are related to catalysts, solvents and other additives added during the polymerization. Also different oligomers can be mixed in to produce PLA copolymers [10].

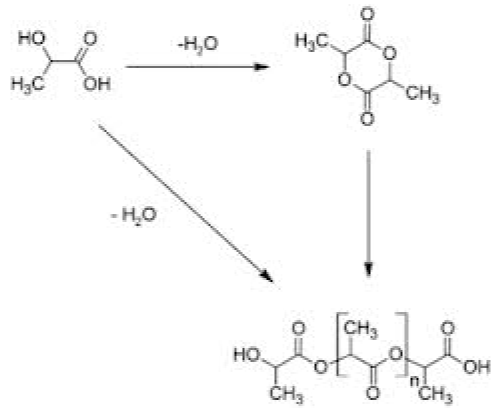

Figure 1. Polymerization of lactic acid through condensation [9].

Since all elements present in biopolymers are organic, bioplastics are desirable for breaking down into non-toxic substances. The biodegradability of the plastic largely depends on the strength of the bonds. Since bioplastics contain more oxygen, due to being organic molecules, they degrade faster in a moist environment. If cost effective methods for the production of bioplastics are discovered, toxicity levels in dump sites would decrease. PLA decomposes by depolymerization to lactic acid in presence of water and does not require any biological agents, enzymes or microbes, to degrade like other biodegradable polymers. It fully decomposes under composting conditions at temperatures of 60ºC and above in six months to two years.

In an effort to keep the biodegradability of bioplastics while manipulating the mechanical properties for specific purposes, several different additives and plasticizers are used in the polymerization processes of bioplastics. Glycerol, $C_3H_8O_3$, improves ductility but also decreases the tensile strength in the final product. Various citrate esters are used to lower the glass transition temperature. Different acids and bases with carboxyl and hydroxyl groups create cross-linked bonds. In order to increase the degree of polymerization and prevent the monomers from reacting back on the forming polymer chain (or the creation of a ring dimer) metal catalysts are often used, for example tin octoate. The primary issue with using metal catalysts for polymerization is that they are most often toxic. In an effort to create a biodegradable plastic, polymerization methods in which high degrees can be obtained without the use of toxic catalysts are ideal.

PRODUCTION OF PLA AS A RESEARCH PROJECT

Spent grain can constitute as much as 85 percent of a brewery's total by-product [11]. In Japan, the Akita Research Institute of Food and Brewing has developed a new technology that drastically reduces the cost of producing polylactic acid, the spent grain-derived foundation for the production of biodegradable plastics [4]. Based on this process the authors have decided to investigate the procedures required for lactic acid production and further polymerization and how to accommodate them in the existing engineering laboratories.

The lactic acid production requires the understanding of chemistry of beer, carbohydrates in plant matter (grain) and the chemical reactions that transition the organic molecules into different organic compounds. Malting (germination) of grain breaks the husk and creates enzymes that help with degradation of starchy endosperm during mashing (heating below boiling temperature) of the wort. Starch (complex sugar) turns into simple sugars (mono-, di-, and tri-saccharides [12]) and amino acids. Those fermentable sugars are fermented into alcohol and carbon dioxide or other organic compounds. In beer fermentation brewer's yeast is used to create ethyl alcohol and byproducts that influence the beer character and flavor [13]. The carbohydrates present in the wort are: maltose (45%), maltotriose (15%), glucose (10%), sucrose (5%), fructose (2%) and dextrin (23%). The dextrins (maltotetraose and larger) are unfermentable for the yeast [14]. Both yeast and bacteria, as living organisms, require, beside sugars, nutrients to thrive thus wort with all the grain components including proteins, lipids, nucleic acids and minerals seem to be the perfect medium for their growth.

In case of lactic acid fermentation lactic acid bacteria (LAB) metabolizes the sugars. There are sixteen genera of LAB, some twelve of which are active in a food context. They are Gram-positive organisms, mesophilic, and can grow in a range of temperatures (4 to 45ºC). Generally they prefer a pH in the range 4 to 4.5, but certain strains can tolerate and grow at pHs above 9 or as low as 3.2 [14]. Ethanol and carbon dioxide are produced alongside LA but in rather small quantities (5% of total end product).

Based on the complexity of chemistry and biology of fermentation the authors decided to seek assistance from experts in the fields of organic chemistry and microbiology. The appropriate faculty at Mercer University have been contacted and consulted during the project. Chemistry professionals helped us understand the chemistry behind lactic acid production and polymerization while the biology specialists provided the background about microorganisms, fermentation, bacteria selection, and supplies. The following steps have been undertaken.

PLA from Synthetic Lactic Acid

In order to determine the quality of polylactic acid produced from industrial waste, chemical grade lactic acid was turned into PLA through direct polymerization condensation [15]. Lactic acid and hydrochloric acid, acting as a catalyst for the process, were heated above 121˚C. The PLA obtained from chemical grade lactic acid was highly viscous and resembled that of a resin rather than that of a plastic.

Preparation of Parent Bacteria Culture

Due to the unpredictability associated with biological microorganisms, it is important to maintain as much experimental control as possible. Thus for harvesting lactic acid through the fermentation by lactobacillus, first, a parent culture of bacteria was prepared. To best facilitate and promote the growth of the lactobacilli, a broth specifically designed for this strain of bacteria was prepared [16]. As lactobacillus grows, lactic acid is produced and the overall pH of the solution decreases. However, there is a threshold in the acidic environment created at which the bacteria stop to grow.

Culturelle Probiotic [17] containing Lactobacillus Rhamnosus GG (LGG) has been selected for the fermentation of industrial food wastes in this project. LGG primarily exists in the human digestive system but it is also used in various food products, usually dairy products such as yogurt, fermented milk, pasteurized milk, and semi-hard cheese. LGG is generally known to help maintain a "good balance" of bacteria in the stomach and intestines by preventing the growth of harmful bacteria [18]. Each Culturelle capsules provides a minimum of 10 billion live cells of the lactobacillus strain strong and fertile enough to survive the stomach acids and colonize successfully in highly acidic environments. One capsule of Culturelle Probiotic was added to the broth and fermented for 36 hours at 37 ˚C with the pH level being monitored to ensure the culture was growing. The parent culture was frozen, only to be unthawed to add to samples before fermentation.

Fermentation

Once the parent culture was prepared, several different sugar solutions were prepared to ferment along with the lactobacilli: refined cane sugar; brewer's dry barley malt, wort, and spent grain. Before fermenting spent grain, sugar and malt solutions were fermented to gain an understanding of the lactic acid fermentation. The sugar and malt solutions were prepared with varying amounts of malt sugar with deionized water. The wort and spent grain were provided by The Macon Beer Company and the sugar concentration was unknown. In order to create ideal conditions the lactobacilli culture was grown in an oven at 37 ˚C for 40-72 hours. The culture has completed the fermentation process once there was no significant change in pH levels over an interval of time, meaning no more lactic acid was being produced.

Filtration

Filtration of the samples occurred multiple times during the process of obtaining lactic acid: after extracting remaining sugars from spent grain, and during and after fermentation. The spent grain extract contained large pieces of grain that were unwanted during fermentation. Furthermore, once the lactobacilli have finished fermenting, the samples had to be filtered to remove bacteria and any waste created in order to purify the lactic acid. Additional filtration can be performed as an intermediate step during dehydration of the lactic acid but also it can reduce the overall yield of lactic acid due to its loss in the filter paper. Two filtration methods were implemented in the overall filtration process, a two-stage strainer and a vacuum filter with 0.45 μm filter papers. The lactobacillus and other small contaminants were removed from the samples after using the vacuum filter, ending the production of lactic acid in the sample.

Concentration

Since the solutions used to feed the lactobacilli were primarily composed of water, the lactic acid after fermentation and filtration was still relatively dilute. In order to remove the excess water from the samples and increase the concentration of lactic acid, the water was removed from the samples through evaporation.

The polymerization temperature of lactic acid is approximately 120 ˚C and above this temperature individual lactic acid molecules start to polymerize and form polylactic acid. However, without the aid of a metal catalyst the lactic acid wants to form lactide, or a lactic acid ring, see Figure 1. When lactide is formed, the chain of polylactic acid is broken, reducing the degree of polymerization. In order to evaporate water from the sample while minimizing the amount of lactide produced, the sample was heated to 105 ˚C.

Polymerization

Numerous catalysts and solvents can be used to obtain a wide range of degree of polymerization when synthesizing polylactic acid. In order to compare results to synthetic lactic acid crude LA samples will be polymerized through direct condensation, similar to that of the experiment performed with chemical grade lactic acid.

Samples were heated to 150˚C and monitored over a two hour period. This method yielded an amorphous polylactic acid with a low degree of polymerization in which mechanical properties could not be tested. Further polymerization methods will be pursued in future research.

Spent Grain Samples

Unlike the malt and wort samples, the sugars had to be drawn out of the spent grain through a process similar to industrial liquefaction in a steam explosion reactor. The grain was simmered in deionized water for 2 hours, strained and cooled.

Comparison of Samples

The acidity threshold in which lactobacilli can grow in each sample was determined through monitoring the pH levels through the fermentation process. For all sample types of varying sugar concentration, the resulting pH of samples was found to be approximately 3.3. The main differences amongst samples were not the final pH but the rate at which the pH changed. Due to providing other nutrients other than sugars to feed the bacteria, it was found that wort and spent grain samples had pH levels approximately 0.15 and 0.50 lower than the malt samples after the first 24 hours. Figure 2 shows the PLA produced from each type of sample after polymerization. The visible differences in the samples are the color and transparency. This is due to the difference in sugar concentration as well as other impurities present in the samples.

Future Research

Further research is being performed to determine a feasible method in which the harvested lactic acid can be polymerized to a higher degree. With a higher degree of polymerization the samples will be solid rather than viscous, allowing for mechanical properties to be tested.

Providing the polymerization of LA is successful the authors will propose the process of turning brewer’s spent grain into PLA to the breweries and consider using other food industries wastes, for example potato skins from the local potato chip manufacturer.

Figure 2. PLA samples polymerized from: synthetic lactic acid, malt, wort, and spent grain (from left to right).

CONCLUSIONS

Brewing can and should be introduced to university students not only because it provides many engineering topics for research and investigation but also for the reason that it is often regarded as a hot and interesting topic among the students. The brewing industry's needs and problems related to the processes, resources used, and wastes created can be solved at universities often at little cost while providing an excellent hands-on learning experience to the students. Engineering projects in the real world require the combination of innovation and diverse disciplines. Also, brewing studies provide an opportunity to seek assistance from non-engineering students and faculty.

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