

Assessment of the Impacts of Bioplastics: Energy Usage, Fossil Fuel Usage, Pollution, Health Effects, Effects on the Food Supply, and Economic Effects Compared to Petroleum Based Plastics.

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Abstract

Bioplastics are an increasingly well-known alternative to petroleum-based plastics. They are derived from biological sources instead of oil. An analysis of societal issues involving bioplastics has been carried out. Health, economic, and environmental concerns related to a switch to bioplastics were studied. The possible impacts on energy usage, petroleum usage, and food production including land usage were observed. Bioplastics were found to be superior to petroplastics in terms of energy efficiency, petroleum consumption, and carbon emissions, but inferior to petroplastics in cost and applicability. Negative effects on the food supply were also predicted with a switch to bioplastics. Pollution and safety varied on a plastic-to-plastic basis but in general bioplastics were found to be safer. It has been concluded that bioplastics are not viable for wide scale use in their current form.

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Introduction

Plastics play a pivotal role in modern society. From the vinyl siding on a house to the disposable beverage bottles sold in vending machines, plastics are ubiquitous. Nearly every modern product contains at least a few plastic components, yet synthetic plastics have only existed since the introduction of Bakelite in 1907.¹ Before that point plastic materials had been used, but they were naturally derived. The most widely known of these natural materials is rubber. With the national focus of attention turning to reducing foreign oil imports and environmental impacts of human activities renewed interest has been placed into developing plastics from natural products.² Some background information is required before a discussion of the societal impacts of bioplastics can commence.

I. Basic Introduction to Plastics.

Plastics have proliferated so readily throughout the modern world because of their versatility. Plastics can be flexible or rigid, brittle or resilient, clear or colored, and have many other useful properties. Some plastics are electrically conductive while others are excellent insulators. It is widely divergent properties such as these that allow a plastic to perform almost any role. In general plastics have a high strength to weight ratio that allows products made of plastics to be lighter and less bulky. Plastics are also less costly alternatives to metals and wood for many applications, such as packaging. The ability to add pigments directly to plastics instead of applying paint is also a benefit.³ To summarize, plastics have not become popular because they are a superior material but rather that they are many superior materials.

Plastics are a specific subset of polymers. Therefore to understand plastics one must first understand polymers. A polymer is a molecule made up of a large number of small repeating subunits. A polymer subunit is called a monomer. Polymers come in three major varieties. Inorganic polymers are substances such as concrete or glass. DNA, proteins, and polysaccharides such as cellulose and glycogen are examples of natural organic biopolymers. The monomer units of DNA are nucleic acids. The monomer units of proteins are amino acids. The monomers of polysaccharides are sugars. A single protein often contains hundreds or even thousands of amino acid monomers, which are called residues. The final class of polymers is synthetic organic polymers. Most plastics are synthetic organic polymers. The word organic in this name means carbon based. The reaction by which monomers bond to form a polymer is called polymerization. Polyvinyl chloride or PVC as it is commonly known was the first synthetic organic polymer to be produced. It was polymerized accidentally in 1838 but at the time could not be made into a viable plastic.⁴ Polymers can form in three different ways. A polymer can be linear,

¹ American Chemical Society,

http://acswebcontent.acs.org/landmarks/newproducts_t.html#bakelite

² The Wall Street Journal, *Bioplastics Begin to Get Real*. by Anjali Cordeiro. 10-22-2008.

³ British Plastics Federation, http://www.bpf.co.uk/Plastics_Applications.aspx

⁴ Wade, L.G. Organic Chemistry 6th Edition, (p. 1222) Pearson Prentice Hall, 2006.

branched, or cross-linked. A linear polymer simply has one chain of monomer units per molecule. A branched polymer has one chain that branches out into several side chains. A cross-linked polymer has several chains per molecule bonded together in multiple places.⁵ The main point to take from this is that all plastics are polymers but not all polymers are plastics.



Figure 1: Linear (a), Branched (b), and Cross-Linked (c) Polymers.⁶

Plastics are a moldable type of organic polymer. Most plastics in use today are petroleum based. Plastics can be made into fibers as well as solid continuous objects. Adding gas bubbles to plastics produces foams. Common plastics include nylon, rayon, Kevlar, PVC, lexan, polystyrene, polyethylene, and Plexiglas. Plastics can be broken down into two major classes; thermoplastics and thermo-set plastics. Plastics can also be grouped as commodity, engineering, and specialty plastics. Commodity plastics are low cost, easy to manufacture, and relatively weak. Engineering plastics are about two to three times more expensive than commodity plastics and have superior heat stability and strength. Specialty plastics are very high cost but have unique properties, which make them desirable, such as being able to withstand high temperatures. The raw form of a plastic is called a resin.⁷ To summarize, plastics are differentiated from other polymers by a combination of their organic nature and their ability to be molded or cast into a variety of shapes.

Thermoplastics are the most common type of plastic. Thermoplastics have distinct long, entangled chains. They become a liquid when heated and can be molded and cooled to harden many times with no degradation. This ability to return to a liquid state when heated makes recycling of thermoplastics considerably easier than thermo-set plastics. Thermoplastics tend to be softer than Thermo-set plastics.⁸

Thermo-set plastics were the earliest synthetic plastics. Bakelite is a thermo-set plastic. This type of plastic has bulky short molecules that tend to be composed of between 10 and 20 monomer units. The fact that they can only be molded once sets thermo-set plastics apart. This is due to extensive cross-linking between the bulky molecules. The degree of cross-linking controls the rigidity of the plastic. When a

⁵ Golding, Brage. Polymers and Resins, (p. 4) D. Van Nostrand Company, N.C. 1959.

⁶ Image source: Canadian Building Digest, <http://irc.nrc-cnrc.gc.ca/images/cbd/154f02.gif>.

⁷ Throne, James L. Plastics Process Engineering, (p.1-21) Marcel Dekker, Inc. 1979.

⁸ Ibid.

thermo-set plastic is reheated it decomposes instead of liquefying. This behavior leads to more difficult recycling procedures.⁹

Plastics can also be classified via their monomers. For example polyamides, commonly known as nylon, are formed from diamines and diacids. Polyesters are formed from glycol and diacid. Both polyamides and polyesters are known for their strength when made into a fabric. Polycarbonates are formed from carbonate esters. Lexan is an example of a polycarbonate. Polycarbonates are known for being strong and transparent. These traits lead to their common usage in bullet-resistant glass. Polyurethanes are formed from urethane, which is an ester of carbamic acid.¹⁰ More classifications exist but these can be considered the major ones.

Plastics would not be as useful as they are without plasticizers. A plasticizer is a compound that makes another compound, usually a plastic, more pliable. Plasticizers also increase a plastic's ease of handling and resilience. The majority of plasticizers are esters, specifically, phthalates and adipates. Other types of plasticizers are citrates, epoxies, phosphate esters, polymeric, sebacates, azelates, and trimellitates. Phthalates are the most common plasticizers. More than 300 plasticizers are known and between fifty and one hundred of those are currently used commercially. Some common plasticizing agents are di-2-ethyl hexyl phthalate (DEHP), diisodecyl phthalate (DIDP), and diisononyl phthalate (DINP). PVC is the major product that utilizes plasticizers and it accounts for 95% of plasticizer use. Besides plastics, plasticizers are found in adhesives, cosmetics, and paints.¹¹ Without plasticizers plastics would lose some of the properties that make them so useful.

II. Synthesis of Plastics.

Before detailed syntheses of specific products can be discussed a general knowledge of polymer synthesis is required. In condensation polymers the monomers bond with the loss of a small molecule. If this small molecule is water, as it is in protein polymerization, then the reaction is called a dehydration. Condensation polymers are also known as step-growth polymers. Addition polymers add one monomer at a time at the end of the polymer chain. The end of the chain that is growing will often have a reactive intermediate. There are three types of reactive intermediates that are found at the end of addition polymer chains. The first is a cation, which is a positively charged atom. The second is an anion, which is a negatively charged atom. The third option is a radical, which is an atom with a single non-bonded electron in its valence orbital. Addition polymers are also known as chain-growth polymers. When a polymer is made of 2 or more different monomers it is called a copolymer. Chain branching is caused by hydrogen abstraction where the free radical at the end of the chain in an addition polymer abstracts a hydrogen atom from the middle of the chain causing a branch to form at that

⁹ Ibid.

¹⁰ Wade, L.G. Organic Chemistry 6th Edition, (p. 1233-1236) Pearson Prentice Hall, 2006.

¹¹ Plasticizer Information Center, <http://www.plasticisers.org/index.asp?page=2>

point.¹² This basic introduction to polymer synthesis sets the stage for the product syntheses that follow.

II.a. Nylon.

Nylon, or more specifically nylons, since there are a variety of them, are some of the most common plastics in the world. Nylon is a thermoplastic normally produced as a fiber. It is widely used in the clothing industry as a substitute for silk. Nylon is prevalent to such an extent in the garment industry that a type of women's stockings are called nylons. Nylon is also used in injection molding, metal coating, and tubing. Nylon fabric dries quickly, washes well, and tends to hold its shape. It is also many times cheaper than silk. Nylon was the first synthetic fabric to be sold on the open market when it was released in 1939.¹³ Nylon's instant name recognition makes it a good example of a plastic.

The synthesis of nylon is fairly straightforward. Nylon 6,6 has been discussed here, but other types of nylon follow similar reactions. Adipic acid is mixed with hexamethylene diamine to form a white solid. This white solid is called nylon salt. The nylon salt is heated to 250°C and the water is driven off. Thus, this is a dehydration reaction and an example of condensation polymerization. The product is molten poly(hexamethylene adipamide), which is called nylon 6,6. Molten nylon can be extruded to form a fiber or molded into a solid object.¹⁴

II.b. Rayon.

Rayon is a polymer that is neither fully synthetic nor natural. It is made from the cellulose in wood pulp but chemically treated to alter its properties. It has more in common with cotton than it does with nylon. Polymerization is unnecessary because the reactant, cellulose, is a polymer in itself. Rayon's only uses are as fabrics or absorbent materials. It directly competes against cotton in the fabrics industry and has a fairly low price, although, the cost is not as low as cotton.¹⁵ To sum up, Rayon can qualify as a biopolymer and as such deserves special consideration in this paper.

The production method for rayon is a multi-step process. First the cellulose is purified. Then the cellulose is submerged in a bath of sodium hydroxide solution, which converts some of the cellulose into the sodium salt of cellulose. Next, the cellulose is squeezed, shredded, and allowed to partially oxidize. Then carbon disulfide gas is

¹² Wade, L.G. Organic Chemistry 6th Edition, (p. 1222-1225) Pearson Prentice Hall, 2006.

¹³ Hegde, Raghavendra R., Dahiya, Atul, Kamath, M.G. *Nylon Fibers*, <http://www.engr.utk.edu/mse/pages/Textiles/Nylon%20fibers.htm>

¹⁴ Wade, L.G. Organic Chemistry 6th Edition, (p. 1233) Pearson Prentice Hall, 2006.

¹⁵ Lewin, Menachem. Pearce, Eli M. Handbook of Fiber Chemistry. Marcel Dekker, 1998.

bubbled through the cellulose salt to form xanthate ester groups. The product is called cellulose xanthate. Several non-chemical processing steps later, rayon fibers result.¹⁶

II.c. Kevlar.

Kevlar is a well-known polymer fabric noted for its strength. It is used in body armor and high-end sports equipment. It is also used in tires, brakes, and composite materials. Kevlar's strength to weight ratio is very high. Dupont invented it in 1965. It is formed out of aramid fibers and retains flexibility despite its strength.¹⁷

Kevlar is synthesized in a simple one step reaction. Terephthaloyl chloride is mixed with 1,4-phenylenediamine in a solvent mix of HMPA and DMAC. The reaction is cooled to 3°C and kept under an inert atmosphere of nitrogen. After some waiting period the polymer can be filtered out.¹⁸ Kevlar is wet-spun from a hot solution of sulfuric acid containing high solids.¹⁹

II.d. Polyvinyl Chloride.

Polyvinyl chloride or pvc as it is commonly known is one of the most widely used plastics in existence. Varying the levels of plasticizers and other additives can make pvc soft and flexible, for things like toys and the vinyl seats in cars, or hard and rigid like vinyl siding and pvc water pipes. Pvc is a thermoplastic so it can be melted down and recast once it has served its purpose. Pvc is also commonly used as a rubber substitute. Pvc is found in hundreds of products from inflatable pools and medical storage containers to fabric coatings and shoes, but its number one use is in the construction industry. In fact, greater than seventy percent of all pvc produced annually in the U.S. is consumed by the construction industry. The lightweight and low cost of pvc makes it the favored material for water piping in developing countries.²⁰ To sum up, any discussion of plastics without mention of pvc would be incomplete due to pvc's frequency of use.

The synthesis of pvc is slightly more complicated than the average plastic synthesis. The monomer, vinyl chloride, is usually produced by one of three methods. The first method involves reacting 1,2-dichloroethane with sodium hydroxide in an aqueous solution at high pressure (150 psig) and moderately high temperature (145°C).

¹⁶ Ibid.

¹⁷ Dupont, http://www2.dupont.com/Kevlar/en_US/index.html.

¹⁸ Jingsheng, Bao, and coworkers, *Studies on the Semirigid Chain Polyamide- Poly(1,4 Phenylene terephthalamide)*, J. Of Appl. Polym. Sci., 26, 1211 (1981).

¹⁹ Sloan, Ryan and Glenn, Ann, *What is Kevlar?*, http://www.guilford.edu/original/Academic/chemistry/current_courses/Chem110/sloan.html

²⁰ American Chemistry Council, *Polyvinyl Chloride (PVC): It's Hard to Imagine Life Without It*. http://www.americanchemistry.com/s_chlorine/science_sec.asp?CID=1248&DID=4726&CTYPEID=113

However, this method reacts half of the chlorine initially present to salt. The second method for producing vinyl chloride is heating 1,2-dichloroethane to between 250°C and 500°C in the presence of a barium chloride catalyst. The third method is a reaction between ethyne and hydrochloric acid in the presence of a mercuric chloride catalyst. The monomer will not polymerize thermally and is slow to polymerize photochemically. The polymerization is a free radical addition reaction. The polymerization of vinyl chloride can be initiated by a variety of organic compounds that form free radicals. Peroxides are common initiators. The polymer, pvc, is insoluble in the vinyl chloride monomer and so precipitates out as quickly as it is formed. The polymerization must be carried out at low temperature because it is a highly exothermic reaction and high temperatures could cause degradation.²¹

II.e. Lexan.

Lexan is a specialty plastic that is best known for its use in bullet resistant glass. Lexan is clear in its standard form, which makes it a good substitute for glass under harsh conditions. Lexan is impact resistant, abrasion resistant, weather resistant, and is resistant to many chemicals. It also behaves well when exposed to flame. Its impressive properties have led to its use in bomb resistant buildings, high end sports equipment like goggles and ice hockey masks, and airplane windows. Lexan has also seen use in storm-proofing commercial and government buildings.²² The characteristics of Lexan justify its high price in applications where strength and impact resistance are key.

The synthesis of Lexan follows the typical method for polycarbonates. It is produced via a reaction of carbonic acid and a diol. In the case of Lexan the acid chloride of carbonic acid, which is called phosgene, is reacted with bisphenol A, which is a diol, at high temperature. Two molecules of hydrochloric acid are condensed out per monomer added to the chain. The bisphenol A reactant is produced by a condensation of acetone and phenol.²³ Lexan is a thermoplastic, so its resin can be molded into a form, melted, and formed again.

II.f. Polystyrene.

Polystyrene is the thermoplastic that is used to make Styrofoam. Styrofoam is made by a proprietary extrusion method. What is commonly known as Styrofoam is in fact styrene foam produced by expanding polystyrene beads.²⁴ Polystyrene can also be used to make solid products. Computer cases are commonly made out of polystyrene. Toys like model cars and planes are often made of polystyrene. Appliances for the kitchen and hairdryers are also made of polystyrene. Polystyrene is also found in automobiles where it is used to make the knobs for the radio and air conditioning. Clear

²¹ Golding, Brage. Polymers and Resins, (p. 410-414) D. Van Nostrand Company, N.C. 1959.

²² Regal Plastics, <http://www.regal-plastics.com/lexan.html>.

²³ Wade, L.G. Organic Chemistry 6th Edition, (p. 1235) Pearson Prentice Hall, 2006.

²⁴ Dow, *What is Styrofoam?*, <http://building.dow.com/styrofoam/what.htm>.

plastic drinking cups are one of the most common products containing polystyrene. Polystyrene can also be blended with other plastics to form new plastics. Poly(styrene-butadiene-styrene) (SBS) rubber is an example of a polystyrene blend.²⁵ Polystyrene is another example of a relatively cheap consumer plastic.

The synthesis of polystyrene is similar to the synthesis of polyvinyl chloride. Polystyrene is produced by an addition polymerization involving free radicals. Once again, a free radical source like an organic peroxide is required to act as an initiator.²⁶ However polystyrene can also be produced via a cationic addition polymerization. The cationic approach requires an acid catalyst.²⁷ The ability of polystyrene to be synthesized by two different methods yielding the same form is a fascinating characteristic.

II.g. Polyethylene.

Polyethylene is a thermoplastic that comes in many forms, each of which is most useful for certain applications. Ultra low-density polyethylene (ULDPE) has great flexibility at low temperature, which makes it useful in food packaging for refrigerated items. It is also used as stretch wrap and in medical packaging. High Density Polyethylene (HDPE) has good stiffness and crack resistance. It is used in garbage bags, bottle products, and pipes. Low-density polyethylene (LDPE) is a general purpose plastic whose main attribute is low cost. It is used in packaging, plastic grocery bags, toys and coatings. Linear Low Density Polyethylene (LLDPE) is noted for having low odor and high gloss. It is used in automotive parts, trash cans, industrial containers, and packaging. Very low-density polyethylene (VLDPE) is noted for flexibility and strength. It is used in tubing, rubbers, frozen food bags, and blown films. Other forms of polyethylene exist but they are specialty plastics that see limited use.²⁸ The many types of polyethylene allow its use in varying situations.

Polyethylene occurs in different forms because of branching and the method of synthesis determines the level of branching. Low-density polyethylene is highly branched. High-density polyethylene does not have many branches. Linear low-density polyethylene has many short branches. Standard free radical polymerization of ethylene results in LDPE because hydrogen abstraction occurs resulting in branching. If a Ziegler-Natta catalyst is used the product of the polymerization of ethylene is HDPE. A Ziegler-Natta catalyst is a titanium and aluminum containing organometallic complex.²⁹ The characteristics of polyethylene are dependent on the level of branching, which in turn is dependent on the synthesis method used.

²⁵ The University of Southern Mississippi, <http://www.pslc.ws/mactest/styrene.htm>.

²⁶ Ibid.

²⁷ Wade, L.G. Organic Chemistry 6th Edition, (p. 1226-1227) Pearson Prentice Hall, 2006.

²⁸ Dow, <http://plastics.dow.com/plastics/na/prod/polyethylene/>.

²⁹ Wade, L.G. Organic Chemistry 6th Edition, (p. 1225, 1230) Pearson Prentice Hall, 2006.

II.h. Plexiglas.

Plexiglas was one of the first plastics to be mass-produced. Its chemical name is poly (methyl Methacrylate). Plexiglas is a thermoplastic that competes directly against polycarbonates. It has good optical qualities making it a common material for aircraft windows and cockpits. It is lighter and stronger than glass. It is also shatter resistant. The production of Plexiglas totals several billion kilograms annually. Plexiglas is often used to replace glass in light fixtures and other places where its high strength and low cost are beneficial.³⁰

Several methods of synthesis exist for Plexiglas. All the methods employ an addition reaction to polymerize the methyl methacrylate but the synthesis of methyl methacrylate itself is different. One method synthesizes methyl methacrylate by reacting acetone with hydrocyanic acid in the presence of a base producing a cyanohydrin. The cyanohydrin cyano group is hydrolyzed via a manganese dioxide catalyst in a mix of water and acetone solvent. The amide is then reacted with methyl formate transferring the amino and ester groups. Loss of water then produces methyl methacrylate and hydrocyanic acid, which is recycled to the reaction feed.³¹ This method is considered one of the better syntheses because the byproducts of the reaction are water and recyclable hydrocyanic acid.

III. Impacts of Plastics Production.

III.a. Tonnages.

Understanding plastics is vitally important due to the sheer amount produced every year. For 2007 the total amount of plastics resin produced in North America was 115,793 million pounds (dry weight). Of that 92,835 million pounds was thermoplastic resin and 8,951 million pounds was thermoset resin. Breaking the statistics down further, polypropylene was the most produced thermoplastic at 19,445 million pounds, followed by high-density polyethylene at 18,222 million pounds, and pvc at 14,606 million pounds. 1,295 million pounds of nylon were produced in 2007 along with 13,584 million pounds of linear low-density polyethylene and 7,927 million pounds of low-density polyethylene. Polystyrene production totaled 6,015 million pounds. As for Thermoset plastics, the phenolic thermosets were the most produced at 4,838 million pounds while urea and melamine based thermosets totaled 3,471 million pounds. The remaining 642 million pounds of thermoset resin produced was in the form of Epoxy.³² With this much plastic being produced annually just in North America any change in production could have significant environmental and economic consequences.

³⁰ Green, M. M., Wittcoff, H. A. *Organic Chemistry Principles and Industrial Practice*, (p. 137-140) Wiley-VHC, 2003.

³¹ Ibid.

³² American Chemical Council, *PIPS Resin Statistics Summary 2007 vs. 2006*.

Polymer Product	Annual U.S. Production (million pounds)
polypropylene	19,445
High-density polyethylene	18,222
Polyvinyl chloride	14,606
Linear low-density polyethylene	13,584
Low-density polyethylene	7,927
Polystyrene	6,015
Nylon	1,295
Total thermoplastic resin	92,835
Phenolic thermosets	4,838
Urea and melamine based thermosets	3,471
Epoxy	642
Total thermoset resin	8,951
Total plastic resin	115,793

Table 1: U.S. resin production for 2007.³³

III.b. Energy.

Most plastics are made out of petroleum products and so plastics production has an impact on petroleum consumption. The total oil consumption of the world in 2008 was 87.2 million barrels a day. Known oil reserves total 1.24 trillion barrels, which at the current rate of consumption would last 41 years. 99% of plastics feedstock comes from petroleum. Ethylene, propylene, and styrene are extracted directly from crude oil. The amount of oil used to make plastics is 4% of total oil consumption. However, more than 4% of the world's oil production actually is used by plastics since the 4% only accounts for plastic feedstock and not for heat, energy, and transportation used in making and selling plastics.³⁴ Considering the massive amount of oil the world uses in a day even 4% is a very large quantity of oil.

The energy required to manufacture plastics is considerable. The plastics industry in the United States consumes about 6% of all the energy used by American industries. In 1998 the plastic resin and plastic materials companies in the U.S. used 1,070 trillion Btu of energy. That much energy was worth about \$6 billion. The rubber and plastics product manufacturers used 320 trillion Btu in 1998. 320 trillion Btu was worth approximately \$3.5 billion.³⁵ With the large amounts of energy involved even small increases in efficiency would lead to significant energy savings.

³³ Ibid.

³⁴ British Plastics Federation, *Oil Consumption*.

http://www.bpf.co.uk/Oil_Consumption.aspx.

³⁵ U.S. Department of Energy and The society of the Plastics Industry, Inc. *Improving Energy Efficiency at U.S. Plastics Manufacturing Plants*.2003

III.c. CO₂ Emissions.

With the mounting concern over global warming due to greenhouse gas emissions the carbon dioxide emissions of the plastics industry require discussion. The plastics industry generated greater than 2% of the total carbon emissions from U.S. manufacturers. In 1994 the U.S. plastics industry was responsible for 4.7 million metric tons of carbon dioxide emissions. The plastics industry had the third highest carbon emissions in the chemical sector behind industrial organic chemicals and industrial inorganic chemicals. The total carbon emissions resulting from energy consumption for the chemical industry were 78.3 million metric tons of carbon dioxide.³⁶ In the intervening years plastics production has increased and one can assume that carbon emissions have increased as well.

III.d. Economy.

The plastics industry plays a significant role in the U.S. economy. In 2006 the U.S. plastics industry employed 1,130,300 workers. It had shipments, or total sales, valued at \$378.83 billion. The plastics industry had a total of 18,585 facilities in the U.S. The plastics industry is the third largest industry in the United States. Plastic exports totaled \$43.04 billion, while plastic imports totaled \$37.58 billion. 85.4% of the plastics apparently consumed are produced domestically, while 14.6% of apparent consumption was of imports. The top five export markets for the American plastics industry were Canada, Mexico, China, Belgium, and Japan. The top five import sources for plastics were Canada, China, Germany, Mexico, and Japan. The total worker wages for the U.S. plastics industry was \$28.3561 billion.³⁷ The plastics industry is clearly one of the cornerstones of the American economy.

Number of plastics facilities in the U.S.	18,585
Number of employees of the plastics industry	1,130,300
Total worker wages of the plastics industry	\$28,356,100,000
Value of U.S. plastic sales	\$378,830,000,000
Plastics exports from the U.S.	\$43,040,000,000
Plastics imports to the U.S.	\$37,580,000,000

Table 2: Plastic Economic Statistics.³⁸

III.e. Health.

The health risks associated with plastics have recently gained media attention. The main health risks of pure plastics involve their monomers. Sometimes monomers become trapped in a polymer matrix during manufacturing and then leach out later.

³⁶ U.S. Department of Energy, *Carbon Emissions in the Chemical Industry*, 1998.
http://www.eia.doe.gov/emeu/efficiency/carbon_emissions/chemicals.html.

³⁷ SPI, *Plastics Industry Data*,
<http://www.myplasticsindustry.com/showspecificfiles/myplasticsindustry/data.html>.

³⁸ Ibid.

Under certain conditions a polymer can monomerize. Polystyrene has been found to leach styrene into water and food. Styrene is a possible carcinogen and endocrine disruptor³⁹. Some polycarbonates like Lexan have been found to leach bisphenol-A when heated or exposed to acid. Bisphenol-A is a hormone disruptor that can mimic estrogen.⁴⁰ Vinyl Chloride, the monomer of pvc, is a known carcinogen.⁴¹ Some plastics are more likely to leach monomers than others.

The main health risks associated with plastics do not come from plastics themselves but from additives like plasticizers. Di-Isonoyl Phthalate (DINP), a plasticizer used in pvc was found to be a likely carcinogen.⁴² Di-Isodecyl Phthalate (DIDP) is a plasticizer and also was found to be a likely carcinogen.⁴³ Di(2-ethylhexyl)phthalate (DEHP), a plasticizer used in pvc was deemed to be so dangerous that its use was banned in Europe. It was found to be carcinogenic and it caused reproductive harm in that it showed high toxicity in fetuses.⁴⁴ The problems with DEHP were especially concerning because of its use in medical equipment.⁴⁵ Safer plasticizers can often be substituted lessening the risk.

IV. Disposal of Plastics.

A significant portion of the waste generated in the U.S. comes from plastics. In 2006 the total municipal solid waste produced in the U.S. was 251 million tons. Plastics accounted for 11.7% of that total. While the amount of waste continues to accumulate, the number of landfills is shrinking. In 2006 only 1,754 landfills were operating in the United States while there had been 7,924 landfills in 1988.⁴⁶ The lack of space to put more garbage increases the importance of recycling.

³⁹ An endocrine disruptor is a chemical that affects the body's hormone levels. They can mimic hormones, inhibit hormones, or effect the production of hormones. EPA, *What are Endocrine Disruptors?* <http://www.epa.gov/endo/pubs/edspoverview/whatare.htm>.

⁴⁰ National Geographic, *Plastic Water Bottles*, by Paul McRandle. Issue # 101 March/April 2004.

⁴¹ ATSDR, Department of Health and Human Services, *Tox FAQs for Vinyl Chloride*, July 2006. <http://www.atsdr.cdc.gov/tfacts20.html>.

⁴² European Commission, Joint Research Centre, *Di-Isonoyl Phthalate (DINP) Summary Risk Assessment Report*, 2003.

⁴³ European Commission, Joint Research Centre, *Di-Isodecyl Phthalate (DIDP) Summary Risk Assessment Report*, 2003.

⁴⁴ European Commission, Scientific Committee on Emerging and Newly Identified Health Risks. *The Safety of Medical Devices Containing DEHP- Plasticized PVC or Other Plasticizers on Neonates and Other Groups Possibly at Risk*. 2-6-2008.

⁴⁵ FDA, *FDA Public Health Notification: PVC Devices Containing the Plasticizer DEHP*. <http://www.fda.gov/cdrh/safety/dehp.html>. 2002.

⁴⁶ EPA, *Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2006*.

Plastics, especially thermoplastics, are readily recycled. In 2006 31% of HDPE bottles and 30.9% of plastic soft drink bottles were recycled in the United States. Overall, however only 6.9% of plastics were recycled.⁴⁷ The reason that a relatively small amount of plastic was recycled is that it is cheaper to make new plastic than to recycle old plastic in most cases. Sorting the plastics before melting them is key because mixing plastics could potentially ruin the whole batch.⁴⁸ Plastics can be recycled either chemically or mechanically. The mechanical method implies shredding the plastic and then melting it so that it can be remolded. The chemical method involves treating the plastic by a chemical process to break it back down to its monomers from which it can be used as plastic feedstock.⁴⁹ Plastics are excellent candidates for recycling because it is generally a straightforward process that is more energy efficient.

Plastics can be disposed of by composting if they have the appropriate level of biodegradability. The ability of a plastic to biodegrade is independent of its source. Some petro-plastics are biodegradable and some bioplastics are not biodegradable. The degree and speed with which a plastic breaks down is dependent on the conditions. Certain microbes can degrade plastics. Other composting procedures use high heat and excess oxygen to slowly oxidize a plastic. Ultraviolet radiation can also degrade some plastics. The description of a plastic as compostable can sometimes be misleading. Some supposedly compostable plastics do not degrade in a standard composter. Composting plastics leads to a release of the carbon sequestered in them.⁵⁰

Another option for disposing of plastics is incineration. Commercial incineration units can destroy plastics while leaving very few particulate emissions. Some plastics can be burned to completion resulting in only water and carbon dioxide as waste products. Plastics are very energy dense and so their combustion can be used to generate power. For example, burning HDPE results in 18,700 Btu per pound. Fuel oil combustion by comparison results in 20,900 Btu per pound. The capacity of incinerators in the United States is 97,000 tons per day.⁵¹ Burning chlorinated polymers like pvc creates chlorine compounds like hydrochloric acid and various dioxins, which are highly toxic.⁵²

V. Basic Introduction to Bioplastics.

⁴⁷ Ibid.

⁴⁸ Duchin, Faye and Lange, Glenn-Marie, *Prospects for the recycling of plastics in the United States*. Structural Change and Economic Dynamics 9, 1998.

⁴⁹ Waste Online, *Plastic Recycling Information Sheet*.

http://www.wasteonline.org.uk/resources/InformationSheets/Plastics.htm#_How.

⁵⁰ Mohee, R. and Unmar, G., Determining biodegradability of plastic materials under controlled natural composting environments. *Waste Management* 27. 2007.

⁵¹ SPI, *Incineration*.

<http://www.plasticsindustry.org/AboutPlastics/content.cfm?ItemNumber=793&navItemNumber=1124>

⁵² DOE, *Burning Plastic*.

<http://www.newton.dep.anl.gov/askasci/chem00/chem00031.htm>.

Biopolymers are a subset of polymers. The difference between biopolymers and petro-polymers is that the monomers of a biopolymer are derived from a living source. Two main types of biopolymers exist. The first type is synthesized directly by an organism. The second type is produced in a synthetic chemical reaction from biological reactants. Examples of the first type include DNA, RNA, proteins, and polysaccharides. The second type includes most of the biopolymers used to make bioplastics. Japan and Europe have led the way in biopolymer development. Some biopolymers can serve as direct substitutes for other polymers but others cannot.⁵³ In summary, biopolymers are simply polymers that come from a biological source.

Bioplastics are plastics made out of biopolymers. Some, like biopolyethylene, are identical to their oil derived form except that the source of the monomers is different. Others are unique and have no petro-polymer equivalent. Bioplastics can be made using plant, animal, or bacterial sources. Some bioplastics are biodegradable while others are not. This is advantageous, as many products need to be resilient and not degrade in the environment.⁵⁴ The field of bioplastics is still in its infancy but is developing rapidly.

The feedstocks for bioplastics come from a variety of biological sources. Starch based bioplastics are usually made from wheat, corn, rice, potatoes, barley, and sorghum. Cellulose based bioplastics are commonly made from wood. Natural oils from soy, palm, and other plants have also been used to make bioplastics. Other bioplastics rely on bacteria to supply raw materials. An example of an animal derived monomer is hyaluronic acid (HA). It can also be extracted from bacteria. Genetically engineered organisms have been made to increase the yield of certain bioplastic components and in some cases to actually produce specific biopolymers.⁵⁵ To summarize, bioplastics come from a wide range of sources, but many of the plant-based bioplastics are derived from food crops.

A wide variety of bioplastics exist, but only a few have been put into major commercial production. Starch based bioplastics make up the majority of the bioplastics market. Cellulose based plastic is another example of a bioplastic made out of a naturally occurring polymer. Cellulose and Starch do not need to be polymerized since they are already polymers. Other common bioplastics include polylactid acid, polyamide 11, biopolyethylene, and poly-3-hydroxybutyrate.⁵⁶ Efforts to put other bioplastics into large-scale production are ongoing.

VI. Synthesis of Bioplastics.

⁵³ U.S. Congress, Office of Technological Assessment, Biopolymers: Making Materials Nature's Way, (p. 2-7,51-52, 59), Diane Publishing Co. 1993.

⁵⁴ Phillips, A. L., *Bioplastics Boom*, (p. 109) American Scientist, Volume 96, number 2, March-April 2008

⁵⁵ U.S. Congress, Office of Technological Assessment, Biopolymers: Making Materials Nature's Way, (p. 35-46), Diane Publishing Co. 1993.

⁵⁶ Department of Energy, *Making Bioplastics*, <http://www.newton.dep.anl.gov/askasci/mats05/mats05122.htm>

VI.a. Starch.

Starch based plastics account for 80% of the bioplastics market. They are thermoplastics that are blended with plasticizers and additives like sorbitol and glycerin. Pure starch can absorb water from the air and degrade. Organisms can also metabolize pure starch, as it is a carbohydrate. The fact that starch disintegrates in liquids makes it ideal for drug capsules. Blends of starch and other plastics are used to make plant pots, drinking cups, disposable shopping bags, cutlery, coated cardboard, and diaper foil. Esters and Ethers of starch also behave as thermoplastics but have been too expensive to put into production.⁵⁷

Starch based plastics can be prepared in a wide variety of ways. The source of the raw starch is usually corn but could be any plant high in starch like potatoes. Starch can be imbedded in other polymers like polyethylene, polystyrene, and pvc. Imbedding starch does not bind it to the synthetic polymer. Instead, the starch is suspended in a polymer matrix. Imbedding starch in another plastic enables more plastic to be produced while utilizing less of the petro-plastic. Starch can be chemically blended with hydrophilic polymers by substitution, followed by copolymerization, oxidation, and hydrolysis. This is often done with pvc. The blending process produces a copolymer that has monomers of both the synthetic plastic and starch. Starch can be foamed by an extruder making a product that can replace Styrofoam in some applications. Thermoplastic starch is commonly prepared by melting starch at high heat and pressure. The low cost of starch makes it especially attractive to use in blended forms with synthetic polymers.⁵⁸

In order to improve its mechanical properties starch can also be chemically modified. Numerous methods of modification exist. Acetylation is carried out by dissolving the starch in water, adjusting the pH to 8.0 through the addition of 1M sodium hydroxide, stirring the mixture while adding acetic anhydride, lowering the pH to 4.5 with 0.5M hydrochloric acid, filtering the slurry, washing the slurry with water, then drying the slurry with air. Oxidation is carried out by dissolving the starch in water, raising the pH to 9.5 via the addition of 2M sodium hydroxide, slowly adding NaOCl to the slurry at 30°C, then adjusting the pH to 7 with the addition of 1M sulfuric acid, filtering, washing with water, and finally air-drying. Acid thinning is carried out by creating a slurry of starch in 0.15M hydrochloric acid, stirring the slurry for eight hours at 50°C, filtering, washing with water, then air-drying.⁵⁹

⁵⁷CTC Clean Tech Consulting GmbH, *Starch & Starch Blends*, <http://www.bioplastics24.com/content/view/69/34/lang,en/>.

⁵⁸ Kim, Dae-Hyun, Na, Seong-Ki, and Park, Jong-Shin. *Preparation and Characterization of Modified Starch-Based Plastic Film Reinforced with Short Pulp. I. Structural Properties*, Journal of Applied Polymer Science, Vol.88, 2003.

⁵⁹ Lawal, O.S., *Composition, physicochemical properties and retrogradation characteristics of native, oxidized, acetylated, and acid-thinned new cocoyam (Xanthosoma sagittifolium) starch*, Food Chemistry 87 (p. 205-218) 2004.

VI.b. Polylactic Acid.

Polylactic Acid is a thermoplastic made from lactic acid. Lactic acid is a common organic acid. PLA, as it is known, is transparent and is similar to polyethylene and polypropylene in behavior. The main use of PLA has been packaging. Meat, fruit, vegetable, and yogurt containers have all been made of PLA. It can be processed on standard plastics machines. This means switching a processing plant from petro-plastics to PLA is very simple. PLA and PLA blends have also seen use in the medical industry where they are used to make implants, plates, nails, and screws for surgery. They are stable and do not biodegrade under standard conditions. The major limiting factor in the use of PLA is the fact that in its unblended form it softens at 60°C.⁶⁰

Polylactic acid can be synthesized a number of different ways. One method is direct condensation of the acid free in solution. Another method is a ring opening polymerization of the ester derivatives of the acid. This second method requires a zinc or tin catalyst. To achieve high purity in the polymers using the second method high temperature and a vacuum are required. A recently developed method of synthesizing polylactic acid is via lipase catalysis. The lipase CAL-B at 60°C was found to effectively polymerize lactic acid. The first two methods currently dominate production but the enzymatic approach shows promise.⁶¹

VI.c. Polyhydroxybutyrates.

Polyhydroxybutyrates (PHB) are a bioplastic form of polyester. They behave similarly to polypropylene. The raw material used is sugar. It is commonly blended with other plastics. In blended form it is used in many applications like glue and hard rubber. Cellulose Acetate is the most common additive to PHB. Cork, Starch, and various organic compounds can also be added to PHB to change its characteristics.⁶²

PHB is produced by bacteria, algae, and genetically modified plants. The polymer itself is synthesized directly by the organism requiring no extra polymerization step. The actual production of the polymer within the cell is a complex enzymatic process. The raw material for the biological synthesis is Acetyl-CoA, which is part of the TCA cycle in metabolism. First, a β -Ketothiolase catalyzes the production of acetoacetyl-CoA by condensing two molecules of acetyl-CoA together. Next, acetoacetyl-CoA reductase reduces the acetoacetyl-CoA producing β -hydroxybutyryl-CoA. The final step is carried out by PHB synthase, which catalyzes the polymerization of β -hydroxybutyryl-CoA to PHB. The PHB is present as cysts within the cytoplasm of the cell. Therefore, the cell

⁶⁰ CTC Clean Tech Consulting GmbH, *Polylactic Acid (PLA)*, <http://www.bioplastics24.com/content/view/70/35/lang,en/>.

⁶¹ Lassalle, V.L. and Ferreira, M. L., Lipase-catalyzed synthesis of polylactic acid: an overview of experimental aspects. *Journal of Chemical Technology and Biotechnology* vol. 83, 2008.

⁶² CTC Clean Tech Consulting GmbH, *Polyhydroxybutyrates (PHB)*, <http://www.bioplastics24.com/content/view/71/36/lang,en/>.

must be destroyed to harvest the PHB⁶³ The production of this plastic requires bioreactors since microorganisms produce the polymer. Metabolix has developed an alternative method of making PHB using genetically engineered switchgrass. The PHB is formed as granules within the grass negating the need for bioreactors.⁶⁴

VII. Production of Bioplastics.

The production of bioplastics is small but growing. The total bioplastics consumption in Europe is estimated to be 50,000 tons while the total plastics consumption in Europe is 40 million tons. The annual worldwide production capacity of bioplastics is 300,000 tons. The current bioplastics could only cover 5-10% of the plastic market. Bioplastics have yet to reach the performance and level of diversity of petro-plastics. 100 billion tons of biomass are produced by plants per year. To put that in perspective the global consumption of plastics is 200 million tons.⁶⁵

VIII. Thesis.

There are a series of important societal questions that must be considered with regard to bioplastics. How will bioplastics production influence our dependence on fossil fuels? Do bioplastics emit more or less carbon during production than petroleum-based plastics? How does the production of bioplastics compare in terms of costs? How does bioplastics production influence the food supply? How biodegradable are bioplastics? How much energy is consumed by the production of bioplastics? What are the health concerns of utilizing bioplastics? The purpose of this project was to evaluate the impact that a switch from petro-polymers to biopolymers might have on fossil fuel consumption, carbon emissions, economics, food production, pollution, energy consumption, and the health of humans and the environment.

Analysis

I. Fossil Fuel Consumption.

Bioplastics have the potential to reduce fossil fuel consumption. The feedstock of a bioplastic is not derived from petroleum while the feedstocks of petro-plastics are. Bioplastics production consumes fossil fuels however, because the farming and processing operations commonly use fossil fuel as energy sources. Thus the production method an individual company uses dictates the amount of fossil fuels that can be saved by a switch to bioplastics. NatureWorks, a manufacturer of polylactic acid (PLA), claims

⁶³ Galindo, Enrique, Peña, Carlos, Núñez, Cinthia, Segura, Daniel, and Espín, Guadalupe *Molecular and bioengineering strategies to improve alginate and polyhydroxyalkanoate production by Azotobacter vinelandii*, *Microbial Cell Factories*, 6:7, 2007.

⁶⁴ Metabolix, *Metabolix Announces that Mirel™ Bioplastic Resins are Certified to European Vinçotte Biodegradability for Soil and Fresh Water Standards*. <http://ir.metabolix.com/releasedetail.cfm?ReleaseID=344306>

⁶⁵ European Bioplastics, *Bioplastics at a Glance*, <http://www.european-bioplastics.org/index.php?id=182>.

a 68% reduction of fossil fuel use over traditional plastics.⁶⁶ Metabolix claims a 95% reduction in fossil fuel use over petroleum plastics for its Mirel brand of PHB.⁶⁷ The energy for the farm equipment, fertilizer production, and the bioplastics factories does not necessarily have to come from fossil fuels. Alternative energy like solar, nuclear, hydroelectric, biomass, geothermal, and wind could supply all the necessary energy if the required investment was made. Since total energy consumption for plastics and bioplastics has been discussed in another section an analysis of fossil fuel savings would best be conducted by only considering the plastic feedstocks.

By definition bioplastics have no fossil fuel feedstocks. The feedstocks of petroplastics on the other hand are almost entirely fossil fuel based. HDPE requires 49 GJ/metric ton of feedstock in a cradle-to-factory analysis. Here the fossil fuel feedstock is treated as its energy equivalent. PET requires 39 GJ/metric ton in feedstocks and Polystyrene requires 48 GJ/metric ton.⁶⁸ These are all substantial amounts of petroleum and a switch to bioplastics would eliminate these feedstock demands.

If all plastics in the world were replaced by bioplastics and the energy used in the process came from renewable sources the fossil fuel savings would be approximately 3.49 million barrels a day. That is 4% of the world's fossil fuel usage.⁶⁹ To put that in perspective, Saudi Arabia, the world's top oil producer, produces 10.67 million barrels a day. The amount of oil saved would exceed the daily consumption for every country except the United States, China, and Japan. The savings in fossil fuel would also be equivalent to a little less than a third of daily United States oil imports.⁷⁰ This is of course a simplified case. Current bioplastics do not have the properties to replace all the world's plastics and not all the energy used in production is likely to be renewable. The oil savings would vary from process to process and also from location to location. The oil savings would vary with location because of transport costs.

II. Carbon Emissions

Polyhydroxybutarates (PHB) have some benefits in terms of carbon emissions compared to petroleum-based plastics. The fact that petroleum is not used as a feedstock is a distinct advantage. Carbon dioxide is given off by the agricultural equipment and processing equipment though. It was found via a life cycle assessment that 2.6 Kg of carbon dioxide was emitted per kilogram of PHB produced. This figure varies widely from study to study however. Polypropylene production generates 3.4 Kg of carbon dioxide per kilogram of plastic. The manufacture of high and low-density polyethylene

⁶⁶ NatureWorks LLC, *NatureWorks LLC Announces World's First Greenhouse-Gas-Neutral Polymer*. 2005.

⁶⁷ Metabolix, *Metabolix Announces Results of Life Cycle Assessment for Mirel Bioplastics*. 2007.

⁶⁸ Narayan, Ramani and Patel, Martin, *Review and Analysis of Bio-based Product LCA's*.

⁶⁹ British Plastics Federation, *Oil Consumption*.

http://www.bpf.co.uk/Oil_Consumption.aspx

⁷⁰ DOE, *Country Energy Profiles*. <http://tonto.eia.doe.gov/country/index.cfm>

emits 2.5 and 3.0 kilograms of carbon dioxide per kilogram of plastic respectively. This is summarized in Table 3. The carbon emissions of PHB were lower than that of PP and LDPE while being slightly higher than those for HDPE.⁷¹ To sum up, PHB has lower total carbon emissions than some of the petro-plastics it could replace.

Type of Polymer	Petropolymer			Biopolymer		
	LDPE	PP	HDPE	PHB	PLA	TPS
CO ₂ emissions (Kg CO ₂ / Kg polymer)	3.0 Kg	3.4 Kg	2.5 Kg	2.6 Kg	1.8 Kg	1.14 Kg

Table 3: Carbon dioxide emissions for polymer production.⁷²⁷³⁷⁴

Polylactic acid (PLA) has even lower life-cycle carbon emissions. First-generation PLA production resulted in 1.8 Kg of carbon dioxide emissions per Kg of plastic made. Improvements to the process are expected to reduce this further. PLA production emits less carbon dioxide than most other polymers. Manufacture of polypropylene, LDPE, and nylon all result in more carbon emissions. Since PLA does not require petroleum feedstocks the carbon emissions result from the equipment used to harvest the plant crop and from the energy required to run the manufacturing process.⁷⁵

Thermoplastic Starch (TPS) requires little processing and thus has the lowest Carbon emissions of the three bioplastics given here as examples. The life-cycle carbon emissions for TPS are 1.14 Kg carbon dioxide produced per Kg of plastic manufactured. This is considerably lower than all common petroleum based plastics. Starch foams vary between 0.89 and 1.43 Kg carbon dioxide produced per Kg of plastic. The blends of starch and other plastics have emissions as high as 3.60 Kg carbon dioxide per Kg plastic.⁷⁶ To summarize, starch based plastics are the most favorable in terms of carbon emissions.

To put these carbon emissions reductions into perspective various comparisons have been made. If all of the U.S. production of polypropylene were replaced with PHB, the reduction in annual carbon emissions would be 7.06 million metric tons. Similarly, replacing all HDPE production in the United States with PLA or TPS would lead to a

⁷¹ Harding, K. G., Dennis, J. S., von Blottnitz, H., Harrison, S. T. L., *Environmental analysis of plastic production processes: Comparing petroleum-based polypropylene and polyethylene with biologically-based poly-β-hydroxybutyric acid using life cycle analysis*. Journal of Biotechnology, 130, (p. 57-66), 2007.

⁷² Ibid.

⁷³ Vink, Erwin T. H., Rabago, Karl R., Glassner, David A., Gruber, Patrick R., *Applications of life cycle assessment to NatureWorks polylactide (PLA) production*. Polymer Degradation and Stability 80, (403-419), 2003.

⁷⁴ Narayan, Ramani and Patel, Martin, *Review and Analysis of Bio-based Product LCA's*.

⁷⁵ Vink, Erwin T. H., Rabago, Karl R., Glassner, David A., Gruber, Patrick R., *Applications of life cycle assessment to NatureWorks polylactide (PLA) production*. Polymer Degradation and Stability 80, (403-419), 2003.

⁷⁶ Narayan, Ramani and Patel, Martin, *Review and Analysis of Bio-based Product LCA's*.

reduction of carbon emissions of 5.78 and 11.2 million metric tons respectively. Replacing HDPE with PHB would actually emit more carbon dioxide. Furthermore, replacing all LDPE production in the U.S. with PHB, PLA, or TPS would lead to large reductions in carbon emissions. This is summarized in Table 4. This level of carbon emissions reduction is very significant.

	PHB	PLA	TPS
PP	7.06	14.1	19.9
HDPE	More carbon emissions	5.78	11.2
LDPE	1.44	4.31	6.69

Table 4: Total CO2 emissions savings of replacing plastic in row with bioplastic in column; savings in (million metric tons).

Bioplastics serve as a means to sequester carbon dioxide as long as the plastic does not degrade. The plants, from which bioplastics are made, absorb carbon dioxide as they grow. The carbon is stored as polysaccharides as a result of photosynthesis. When the plant material is used as a feedstock to make a bioplastic the carbon becomes part of the biopolymer that makes up the plastic. If the plastic is composted or incinerated the carbon will be released as carbon dioxide, but if the plastic is not biodegradable and not disposed of by incineration then atmospheric carbon would have been successfully sequestered. This is not a feasible way to halt global warming however, because the amount of carbon dioxide is too great to be effected by carbon sequestration in plastics.⁷⁷ Also, in order to successfully sequester carbon the plastic must not be biodegradable and would therefore pollute.

III. Economics of Bioplastics.

The other advantages of bioplastics would be meaningless if they were too expensive to produce. The Mirel bioplastic made by Metabolix is about double the price of an equivalent petroplastic. Ingeo, a bioplastic made by NatureWorks LLC is only slightly more expensive than equivalent petroleum based plastics. In general bioplastics are always more expensive than the petroleum based plastics they are intended to replace but prices have fallen as development continues and oil prices have become unstable.⁷⁸ Added price stability is a potential benefit of bioplastics. Prices of bioplastics should continue to fall as the industry grows and more efficient production methods are developed.

A switch to bioplastics would affect raw material prices. The cost of whatever crop or combination of crops used to make the bioplastics would certainly increase. The

⁷⁷ EPA, *Carbon Sequestration in Landfills*, 1995.

http://64.233.169.132/search?q=cache:8ZELMiAFJ7gJ:www.epa.gov/climatechange/wycd/waste/downloads/ICF_Memo_Carbon_Sequestration_in_Landfills.pdf+plastics+carbon+sequestration&hl=en&ct=clnk&cd=2&gl=us&client=firefox-a.

⁷⁸ The Wall Street Journal, *Bioplastics Begin to Get Real*. By Anjali Cordeiro. 10-22-2008.

increase in corn prices as a result of ethanol production is a good example of this effect. Corn prices have risen dramatically over the past several years as more and more ethanol is produced as an alternative fuel. From 2007 to 2008 the price of a bushel of corn increased by \$0.80. It was estimated that \$0.41 of that increase was directly linked to ethanol production.⁷⁹ A \$0.41 increase is significant for a crop that normally costs around \$3 a bushel. As the demand and thus the price of the plant feedstocks rise, the demand and therefore the price of fossil fuels would fall. The decline in oil usage would not be great enough to have a major impact on global prices. Oil producing countries regulate production in an attempt to keep prices stable. This analysis neglects the economic complexities involved but the principle is clear.

Regional economic effects are also likely in a switch to bioplastics. In order to cut transportation costs it is probable that bioplastics production plants would be built closer to the major agricultural areas of the country. This would cause a shift in industry from the costal areas of the United States, near the oil refineries, to the Midwest. The impact on jobs would be negligible as it is likely that as many jobs would be created as would be lost. The existing plastics processing plants could be retrofitted to work with bioplastics. An example of such a geographic shift effect can be found in oil production. As crude oil production shifted to the Middle East in the 1950's American refining operations moved from the gulf coast to the ports of the northeast of the Atlantic coast as a means to reduce costs. Both being near major seaports and the major fuel consumption centers of the U.S. led to transport costs being reduced. Not all refineries moved and jobs were not lost in total.⁸⁰

IV. Food supply.

The switch to bioplastics has the potential to affect the world's food supply in a number of ways. Bioplastics derived from food crops like corn, soy, sugar cane, and others would directly decrease the amount of those crops that would be available for food. Bioplastics derived from non-food crops like switch-grass would indirectly affect food production by competing for land with food crops. Bioplastics derived from agricultural waste or algae would have little to no impact on the food supply. Given the fact that food shortages exist in many regions of the world interfering with the world's food supply is a major concern.

Polylactic acid (PLA) is derived from sugars. Sugar can be made from a variety of plants. The total annual yield of sugar if all corn were used for making sugar would be 318 million metric tons. For sugarcane it would be 156 million metric tons, for rice it would be 318 million metric tons, and for potatoes it would be 14 million metric tons. The annual production of plastics in the U.S. totals 52.5 million metric tons. The

⁷⁹ Fortenbery, Randall T. and Park, Hwanil, *The Effect of Ethanol Production on the U.S. National Corn Price*. Staff Paper Series, University of Wisconsin-Madison. 2008.

⁸⁰ Abrahamson, Sherman R., *The Shifting Geographic Center of Petroleum Production and Its Effect on Pricing Systems, Economic Geography*, Vol. 28, No. 4, (pp. 295-301) Oct., 1952.

production of PLA requires 147% the mass of the plastic to be imputed as sugar. Therefore the sugar requirement if all U.S. plastic production were switched to PLA would be 77.2 million metric tons. This would require about 24.3% of the world's supply of rice or corn. Alternatively, PLA production would consume 49.5% of the world's sugar cane or 551% of the world's potato production. The total production of sugar, derived from all crops, in the world is 1.3 billion metric tons. American (PLA) production would consume 5.94% of the entire world's sugar production if all plastics made in the U.S. were replaced by PLA.⁸¹ Results are summarized in Table 5. This is clearly not feasible but PLA could not replace all plastics to begin with.

	Corn	Rice	Potato	Sugar cane	Total sugar
Percentage of crop	24.3%	24.3%	551%	49.5%	5.94%

Table 5: Percentage of various crops worldwide required to switch all U.S. plastics to PLA.

Thermoplastic starch (TPS) is primarily made from corn. Each kilogram of TPS produced requires 0.971 Kg of corn as feedstock. Therefore in order to meet the U.S. production of 77.2 million metric tons of plastic, 75.0 million metric tons of corn would be required. This would be about 14.2% of the world's annual corn production.⁸² TPS is less able to substitute for other plastics than PLA and the percentage of the world's corn production consumed make a complete switch to TPS impractical.

In order to maintain stability in the global food market the U.S. government could convert Conservation Reserve Program (CRP) land into bioplastics cropland. The CRP encourages farmers to set land aside in order to preserve the soil and natural environment. As of 2006, 36 million acres of farmland were being left unused as part of the CRP.⁸³ Each acre of land could produce 7280 pounds of corn on average, which is about 3.64 tons.⁸⁴ Therefore the total amount of corn that could be produced if all the CRP land were put into use would be 131 million tons annually. This would be enough to convert all plastics production to either TPS or PLA, but just barely enough in the case of PLA.

V. Pollution.

⁸¹ Kawamoto, Hiroshi, *Trends in Research and Development of Plastics of Plant Origin- From the Perspective of Nanocomposite Polylactic Acid for Automobile Use-*, Science & Technology trends. (p. 62-75) 2006.

⁸² Dornburg, Veronika, Lewandowski, Iris, and Patel, Martin, *Comparing the Land Requirements, Energy Savings, and Greenhouse Gas Emissions Reduction of Biobased Polymers and Bioenergy*, Journal of Industrial Ecology, Volume 7, number 3-4, (p.93-116), 2004.

⁸³ USDA, Conservation Reserve Program Summary and Enrollment Statistics FY 2006.

⁸⁴ Oklahoma Department of Agriculture, Food and Forestry, Oklahoma State Department of Education, *Corn Field Math*, 2008.

Consuming less energy in manufacturing and emitting less carbon dioxide during production are both beneficial but greater savings can be achieved by recycling. Recycling is almost always more energy efficient and releases less carbon dioxide than making a new product. Currently bioplastics are produced in such small quantities compared to the production of petroplastics that the infrastructure for recycling has not yet developed. In principle most bioplastics should be easily recyclable because they are predominantly thermoplastics. One major problem with efforts to recycle bioplastics is that if they become mixed with petroplastics they can contaminate the whole batch. For example, if an amount as small as 0.1% by mass of a bioplastic were recycled with polyethylene terephthalate resin (PET) the entire batch of plastic would be rendered useless. As the production and use of bioplastics increases it is expected that dedicated recycling processes will be developed rendering bioplastics as easy to recycle as petroplastics.⁸⁵

Petroleum based commodity plastics are resistant to most microbes, water, and mechanical stress. All three of these properties render them resilient in the environment. When biodegradability is required some petroplastics are blended with additives susceptible to oxidation or hydrolysis. Photo-degradation and enzymatic degradation are two other options.⁸⁶ Certain bacteria can break down plastics via enzymes. Even plastics that do not generally degrade can be converted. Some bacteria have been found that convert Styrofoam into polyhydroxyalkanoates (PHA), a biodegradable plastic.⁸⁷ In general bioplastics biodegrade more easily and at a greater rate than average petroplastics. This is good for some applications and bad for others. Even for bioplastics, composting often has to be done at very specific conditions like high heat and oxygen levels or in the presence of certain microorganisms, for the desired degradation to take place.⁸⁸

VI. Energy Consumption.

Polyhydroxybutarates (PHB) require less energy, when the energy of production and feedstocks are combined, than petroleum based plastics with similar characteristics. The total life cycle energy requirements for PHB are 44.7 MJ per Kg plastic produced. Polypropylene requires 85.9 MJ per Kg, HDPE uses 73.7 MJ per Kg, and LDPE uses

⁸⁵ American Recycler, *Growth of bioplastics concerns recyclers*, By Brian R. Hook, 2008. <http://www.americanrecycler.com/0108/growth.shtml>.

⁸⁶ Stevens, E.S., *Green Plastics: An Introduction to the New Science of Biodegradable Plastics*. Princeton University Press, 2002.

⁸⁷ ACS, *Microbes convert 'Styrofoam™' into biodegradable plastic*, 2006. http://portal.acs.org/portal/acs/corg/content?_nfpb=true&_pageLabel=PP_ARTICLEMAIN&node_id=222&content_id=CTP_003309&use_sec=true&sec_url_var=region1&__uuiid=b02cf60b-2415-43bb-954d-e6fafd06cd26.

⁸⁸ Gross, Richard A. and Kalra, Bhanu, *Biodegradable Polymers for the Environment*, Science, Vol 297, (p 803-807), 2002.

81.8 MJ per Kg produced.⁸⁹ This is summarized in Table 6. The energy requirements for PHB are about half that of the petro-polymers. That is a significant energy savings.

Type of Polymer	Petropolymer			Biopolymer		
	LDPE	PP	HDPE	PHB	PLA	TPS
Energy requirements (MJ/Kg-polymer)	81.8	85.9	73.7	44.7	54.1	25.4

Table 6: Energy requirements for polymer production.^{90,91,92}

Polylactic acid (PLA) currently consumes more energy in production than PHB. A kilogram of first generation PLA requires 54.1 MJ of energy input during its life cycle. Improvements to the process are expected with predicted values going as low as 7.4 MJ per Kg of PLA produced. 54.1 MJ is still significantly less than the energy consumption figures for most petro-plastics. The calculations include the oil feedstock in the energy requirement for the plastics.⁹³

Thermoplastic starch has the lowest energy requirements of the bioplastic examples given. The life cycle requirement for TPS is 25.4 MJ per Kg plastic produced. This is less than a third of the energy required to produce most petro-plastics. Starch based foams vary in energy requirements from 32.4 to 36.5 MJ per Kg produced. Starch blends go up to 52.3 MJ per Kg produced.⁹⁴ The starch blends are mostly petro-plastic. To summarize, the energy savings of starch-based plastic over petro-plastics are considerable.

To put the total energy savings, combining energy contained in the feedstocks with energy used in the production process, of bioplastics into perspective several comparisons have been made. If all U.S. PP production was switched to PHB, PLA, or TPS the annual energy savings would be 363, 280, and 529 PJ respectively. Similar energy savings are obtained by switching HDPE or LDPE production to the bioplastics PHB, PLA, and TPS. TPS has the potential for the most energy savings but also has the most limited potential use. These results are summarized in Table 7. The potential energy

⁸⁹ Harding, K. G., Dennis, J. S., von Blottnitz, H., Harrison, S. T. L., *Environmental analysis of plastic production processes: Comparing petroleum-based polypropylene and polyethylene with biologically-based poly-β-hydroxybutyric acid using life cycle analysis*. Journal of Biotechnology, 130, (p. 57-66), 2007.

⁹⁰ Ibid.

⁹¹ Vink, Erwin T. H., Rabago, Karl R., Glassner, David A., Gruber, Patrick R., *Applications of life cycle assessment to NatureWorks polylactide (PLA) production*. Polymer Degradation and Stability 80, (403-419), 2003.

⁹² Narayan, Ramani and Patel, Martin, *Review and Analysis of Bio-based Product LCA's*.

⁹³ Vink, Erwin T. H., Rabago, Karl R., Glassner, David A., Gruber, Patrick R., *Applications of life cycle assessment to NatureWorks polylactide (PLA) production*. Polymer Degradation and Stability 80, (403-419), 2003.

⁹⁴ Narayan, Ramani and Patel, Martin, *Review and Analysis of Bio-based Product LCA's*.

savings are enormous considering one petajoule of energy is equivalent to 31,250 metric tons of coal.⁹⁵

	PHB	PLA	TPS
PP	363PJ	280PJ	529PJ
HDPE	240PJ	162PJ	399PJ
LDPE	133PJ	99PJ	202PJ

Table 7: Total energy savings of replacing plastic in row with bioplastic in column. Note: PJ=Peta Joule= 10^{15} Joule.

VII. Health.

Unlike petroleum-based plastics, bioplastics have not been implicated in any health problems.⁹⁶ The monomers either do not leach into products or are relatively harmless when they do. Pure starch can be metabolized as previously discussed. Caution on bioplastics is still warranted, as they are a developing industry whose health implications may only become apparent with further study.

Although, the bioplastics themselves have so far been deemed safe some steps in their production can have adverse health effects. When growing crops for bioplastics it is common to use pesticides and artificial fertilizers.⁹⁷ Pesticides can leach into drinking water. Known health risks of certain pesticides include birth defects, cancer, and nerve damage.⁹⁸ Inorganic fertilizers often contain toxic heavy metals like cadmium.⁹⁹ Fertilizers have also been linked to harmful algae blooms including red tide.¹⁰⁰ These problems can be avoided if organic farming techniques are used but that slightly limits production.¹⁰¹

The safety of the plasticizers in bioplastics is more understood than the safety of the bioplastics themselves. The plasticizer used is not governed by whether the plastic is

⁹⁵ Syracuse University, *Energy Content of fuels (in Joules)*, http://physics.syr.edu/courses/modules/ENERGY/ENERGY_POLICY/tables.html.

⁹⁶ BusinessWeek, *The Bioplastics Bandwagon*, By Mara Der Hovanesian.

http://images.businessweek.com/ss/08/06/0619_bioplastics/index_01.htm

⁹⁷ Washington Post, *One Word: Bioplastics. But Are They Better?* By Eviana Hartman.

<http://www.washingtonpost.com/wp-dyn/content/article/2008/07/17/AR2008071702295.html>

⁹⁸ EPA, *Pesticides and Food:*

Health Problems Pesticides May Pose. <http://www.epa.gov/opp00001/food/risks.htm>.

⁹⁹ Minnesota Department of Health, *Heavy Metals in Fertilizers.*

<http://www.health.state.mn.us/divs/eh/risk/studies/metals.html>.

¹⁰⁰ University of Maryland Center for Environmental Science, *Increasing Use of Urea as a Fertilizer May Be Causing More Toxic Algae Blooms in Coastal Waters.*

<http://www.umces.edu/HABs.htm>.

¹⁰¹ Stanhill, G., *The comparative productivity of organic agriculture*, Agriculture, Ecosystems & Environment, Volume 30, Issues 1-2, (p 1-26) January 1990.

a bioplastic or a petroplastic. The hazardous plasticizers found in standard petroleum based plastics could be used in bioplastics. However, most bioplastics also use bioplasticizers. Examples of these plasticizers include sorbitol, glycerin, and Triethyl Citrate (TEC), which is derived from citric acid. All three of these bioplasticizers have low toxicities. Any leaching that occurred would result in such low plasticizer concentrations that no health effects would be observed.¹⁰² Just as normal plasticizers can be used in bioplastics so can bioplasticizers be used in petroplastics.

Conclusions

The mainstream media has been devoting more and more attention to bioplastics as demonstrated by the newspaper and magazine articles cited in this paper. These articles generally paint an overoptimistic picture of the use of biomaterials in plastics. Bioplastics have many advantages over petroplastics but they have yet to live up to the hype. When all factors are taken into account replacing a significant portion of plastics with bioplastics is not a viable option at this time.

Several attributes make a switch to bioplastics attractive. Bioplastics production consumes fewer fossil fuel resources than petroleum based plastics because no fossil fuel feedstocks are used. They emit less carbon dioxide than petro-plastics over their life cycle. Bioplastics consume less energy to produce than petroleum based plastics. They have fewer health concerns associated with them. Also, bioplastics are generally compostable. All these traits would encourage the transition to bioplastics but this is not the whole story.

Bioplastics also have several serious shortfalls. For example, bioplastics production is often more energy intensive than petroplastic production due in large part to the need for agricultural inputs in addition to the actual plastic processing. It only comes out ahead in the life cycle analysis because the petroleum feedstocks of petroplastics are included in the energy calculations. Another example is that bioplastics cost more than petroleum-based plastics, although, the price difference between petroplastics and bioplastics can largely be attributed to the immaturity of the bioplastics industry. Lower prices for bioplastics are expected in the near future. It is debatable whether consumers would be willing to shoulder the extra cost. The most serious problem of bioplastics production is the impact on the food supply. Since bioplastics are commonly derived from food crops shortages and price increases could result from scaled up production. Finally, recycling poses another problem for a switch to bioplastics. Widespread recycling operations do not exist yet for bioplastics. Mixing bioplastics into other plastics when recycling can lead to unusable products. This is a concern because recycling is the most energetically and environmentally favorable option for making plastic based products. To sum up, the disadvantages of bioplastics take away much of their appeal.

One thing above all others inhibits a switch to bioplastics. Despite all the advantages and disadvantages the limiting factor that makes a major shift to bioplastics

¹⁰² MSDS for TEC, sorbitol, and Glycerin.

production impractical is the fact that bioplastics have the mechanical characteristics to replace so few plastics. Even if all bioplastics comparisons to plastics were favorable their lack of necessary physical properties would severely limit their use. This is the key point that most of the media overlooks. All the benefits in the world are irrelevant if the product cannot be used.

Based on the findings of this paper several recommendations can be made. First, research into bioplastics development should continue to be funded so that bioplastics with more diverse applications can be created. In regard to current bioplastics, one should not be favored over the others since they each have limited uses and similar benefits as well as problems. Second, the infrastructure for bioplastics recycling should be developed so that if and when a shift to bioplastics takes place the inability to recycle will not be a limiting factor. This would include assigning each bioplastic its own recycling code to aid identification and sorting during the recycling process. Third, methods of bioplastics production must receive further study in order to raise overall efficiency and reduce energy consumption. Fourth, Bioplastics should not be made out of food crops or crops that compete for the same land as food crops when possible. This would mean not subsidizing or mandating the production of TPS or PLA from corn or any other food crop. Fifth, more effort needs to be placed into increasing the recycling rates of current petroplastics. Sixth, public funds should not be used to subsidize the production of any bioplastic. Any public funding should be used exclusively for research. The benefits of bioplastics are not great enough to warrant spending public money to prop them up if they are not economically viable. To conclude, bioplastics are a technology in their infancy, even though they may not currently be feasible, they could hold much promise for the future.

Appendix

A five-day WISE (Web-based Inquiry Science Environment¹⁰³) instructional module was created based on the research done for this project (presented in the main body of the document) focusing on the effects a switch to bioplastics would have on the economy, environment and human health. WISE is a web application that allows educators to post lessons on various topics to be used in the classroom. A WISE module can consist of pages that present information, ask students questions, allow students to model processes, encourage students to discuss information amongst themselves, as well as give instructions for laboratory work. WISE is meant to work by having students build up scientific knowledge from basic principles, adding new and more complex ideas as time goes on, as in a spiral curriculum, making science problems personally relevant to students, and training students to use scientific inquiry throughout their lives.¹⁰⁴

An instructional module was designed for high school students; the goals of the unit are outlined below. If accepted by the WISE project design team, the unit will be made available for use worldwide. More information about the WISE program can be found at: <http://wise.berkeley.edu/>

Goals

Goal #1: To educate public school students on the basics of plastics and bioplastics.

Goal #2: To get students to understand effects of a switch to bioplastics from petroplastics in terms of pollution, energy consumption, fossil fuel consumption, and health effects.

Goal #3: To allow students to link modern science to issues they deal with every day, i.e., to show them why science should matter to them. To show them that the issue of bioplastics affects the quality of the air they breathe, global warming, and the safety of their food.

Goal #4: To get students thinking critically about the benefits and costs associated with a switch from plastics to bioplastics in order to make recommendations on what they think should be done.

Driving Question.

Would it be better to replace all plastics with bioplastics? What would be the effects on the economy, environment, and human health?

Day 1: Begins with a short quiz to gauge students' pre-existing knowledge of plastics and bioplastics. Next comes an introduction to polymers and plastics. What is a polymer?

¹⁰³ Hsi, Sherry and Linn, Marcia C., Computers, Teachers, Peers. Lawrence Erlbaum Associates, Inc. 2000.

¹⁰⁴ Ibid.

What is a plastic? Basic definitions and statistics are presented. Common plastics and the synthesis of these plastics discussed.

Day 2: Bio-thermoplastic Lab. Simple starch based plastic with glycerin as plasticizer is made by the students. The students are asked to explore “How does the addition of a plasticizer change the characteristics of the starch?”

Day 2: Bio-thermoset plastic lab. Albumin (egg white) is poured into a mould and solidified with near boiling water by the students. The students are asked, “What is the temperature at which the protein polymer sets?”

Day 3: An introduction to bioplastics. What is a bioplastic? Basic definitions and statistics are presented. Common bioplastics and the synthesis of these bioplastics are discussed.

Day 4: The impact of bioplastics are presented. How would the switch to bioplastics affect numerous aspects of society? Is a switch to bioplastics feasible and worthwhile?

Day 5: A continuation of discussion from day 4. A short quiz and survey are given to the students at the end of class.

Screenshots from the module are presented in order here:

Index of Activities **Cancel**

Select an activity to jump directly to it.

1. [Introduction](#)
2. [Biothermoplastics lab: Thermoplastic starch](#)
3. [Biothermoset plastic lab: Egg whites](#)
4. [Introduction to Bioplastics](#)
5. [Effects of switching from Petroplastics to Bioplastics](#)
6. [Conclusion](#)

Plastics play a vital role in modern society. From the vinyl siding on a house to the disposable beverage bottles sold in vending machines, plastics are everywhere. However, the plastics we use everyday do have their downsides. Plastics production uses large quantities of oil and energy while contributing to pollution. Some plastics also have associated health concerns. Bioplastics have been proposed as a solution to the problems with plastics. In this project you will be introduced to bioplastics and analyze the effects of switching from petroleum based plastics to bioplastics. You will then formulate your own view on whether bioplastics are feasible or not.



Image courtesy of [Sulfo](#)



Assessment

In order to gauge your pre-existing knowledge of plastics and bioplastics we begin with a short quiz/ survey.

1. In a few sentences describe what you think the definition of a plastic is.

2. Most of the plastics currently used are derived from what?

- Plants
 - Petroleum
 - Minerals
-

[Next Page>>>](#)

Page:
1 of 2

1. A bioplastic differs from a petroplastic in what way?

- It is derived from biological sources instead of oil
- It is organic
- They are the same

[<<< Previous Page](#)

Page:
2 of 2

I am done with ALL questions and ready to submit my FINAL answers



Introduction to Plastics

Before we can begin our discussion of bioplastics we must first review what a plastic is. Plastics are a moldable type of organic polymer. Organic means carbon based and polymer means a molecule composed of a large number of small repeated subunits. These subunits are called monomers. Most plastics presently in use are petroleum based. Plastics can be made into solid continuous objects or fibers. Gas bubbles can also be added to plastics to produce foams. Common plastics include nylon (used mainly in clothing), PVC (commonly made into plastic water pipes), polystyrene (most often found as Styrofoam containers), and polyethylene (found in plastic food containers). Plastics can be broken down into two major classes; thermoplastics and thermo-set plastics.

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Monomers

Monomers are the building blocks of polymers. Polymers come in three major varieties. Inorganic polymers are substances such as concrete and glass. The monomer of glass is silicon dioxide, although other substances are added to prevent crystallization. Natural organic polymers include DNA, proteins, and polysaccharides. The monomer units of DNA are nucleic acids as shown in the image below. The monomer units of proteins are amino acids. The monomers of polysaccharides are sugars. The third class of polymers is synthetic organic polymers. Most plastics are synthetic organic polymers.

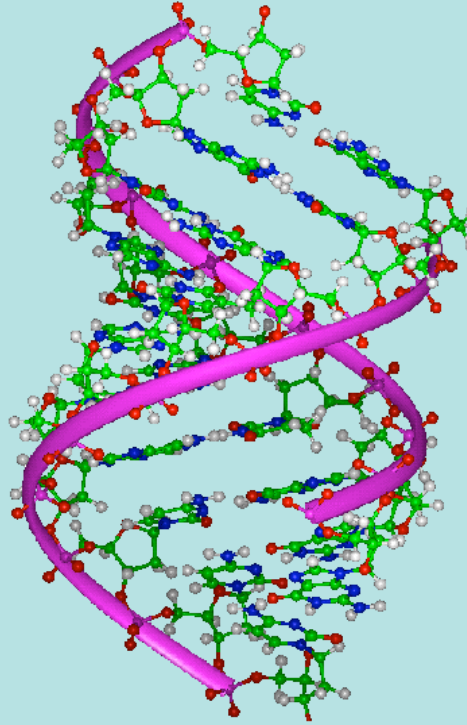


Image courtesy of [Berkeley University](#)



Polymerization

The reaction by which monomers bond to form a polymer is called polymerization. There are two major ways polymerization can take place. In condensation polymers the monomers bond with the loss of a small molecule. When the small molecule is water, as it is in protein synthesis, the reaction is called a dehydration. Addition polymers add one monomer at a time at the ends of the polymer chain. A reactive intermediate is usually present at the reactive end of addition polymer chains. There are three possible types of reactive intermediates: cations, anions, and radicals. Cations are positively charged atoms. Anions are negatively charged atoms. Radicals are atoms with a single non-bonded electron in its valence orbital. Several molecular structures can be achieved through polymerization. A linear polymer has a single chain of monomer units per molecule. A branched polymer has one chain that has several side chains attached. A cross-linked polymer has several polymer chains bonded to each other in multiple places.

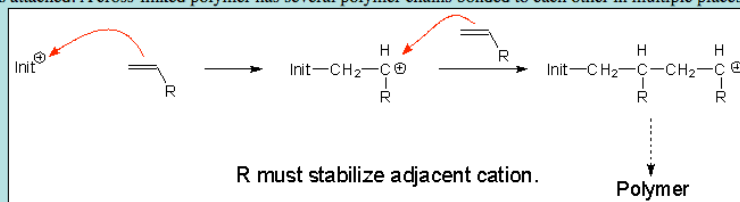


Image courtesy of [Rochester University](#)

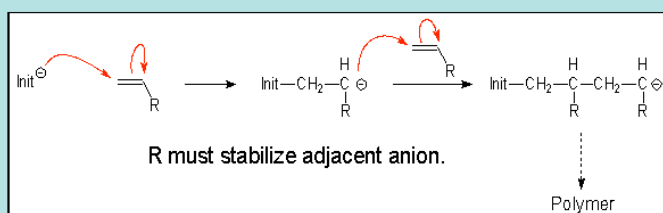


Image courtesy of [Rochester University](#)

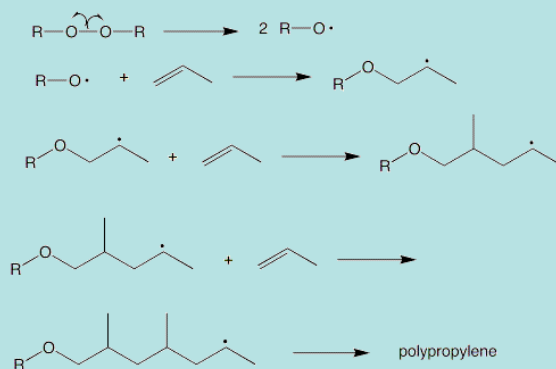





Image courtesy of [Portland State University](#)

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 **Notes**  

SAVE NOTE

How many items made of plastic do you use in an average day?

Look at the contents of your backpack and your clothes. How much is made of plastic? It should be fairly simple to tell if rigid objects are made of plastic but for fabrics you must check the tags.

SAVE NOTE



Thermoplastics

Thermoplastics are the most common type of plastic. They become a liquid when heated and can be melted, molded, and cooled to harden many times without degrading. This property makes recycling thermoplastics fairly easy.

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Thermo-set plastics

Thermo-set plastics differ from thermoplastics in that they decompose when heated instead of melting. This is due to the fact that they are composed of short bulky polymer molecules with extensive cross linking (bridging between polymer chains). More cross-linking enhances rigidity so thermo-set plastics tend to be stiff and brittle. The decomposition upon heating makes thermo-set plastics more difficult to recycle than thermoplastics.

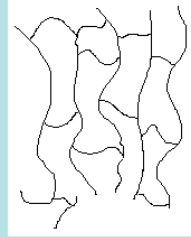
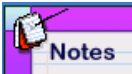


Image courtesy of [Lasalle University](#)

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SAVE NOTE

Have you ever reheated food in a plastic container with a microwave? Did the plastic get softer and start to melt?

If you noticed significant softening or melting, what does this imply about the plastic?

Is the plastic a thermo-set plastic or a thermoplastic?

SAVE NOTE



Plasticizers

Without plasticizers, plastics would not find nearly so many uses. A plasticizer is a compound that makes another compound, usually a plastic, more pliable and resilient. It also eases the handling of the plastic. The most common plasticizers are a class of chemicals called Phthalates. Polyvinyl chloride (PVC) accounts for 90% of plasticizer use. Plasticizers are also found in cosmetics, paints, and adhesives.

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Nylon Synthesis

Nylon, or more specifically nylons, since there are a variety of them, are some of the most common plastics in the world. Nylon is a thermoplastic normally produced as a fiber. It is widely used in the clothing industry as a substitute for silk. Nylon is prevalent to such an extent in the garment industry that a type of women's stockings are called nylons. Nylon is also used in injection molding, metal coating, and tubing. Nylon fabric dries quickly, washes well, and tends to hold its shape. It is also many times cheaper than silk. Nylon was the first synthetic fabric to be sold on the open market when it was released in 1939. Nylon's instant name recognition makes it a good example of a plastic and will be the only synthesis example given. The synthesis of nylon is fairly straightforward. Nylon 6,6 has been discussed here, but other types of nylon follow similar reactions. Adipic acid is mixed with hexamethylene diamine to form a white solid. This white solid is called nylon salt. The nylon salt is heated to 250°C and the water is driven off. Thus, this is a dehydration reaction and an example of condensation polymerization. The product is molten poly(hexamethylene adipamide), which is called nylon 6,6. Molten nylon can be extruded to form a fiber or molded into a solid object.

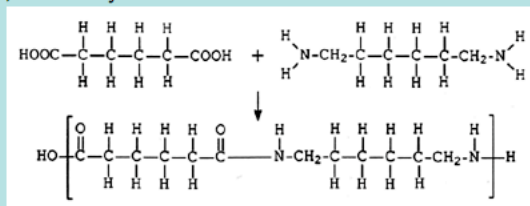


Image courtesy of [Purdue University](#)

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Plastics production

Understanding plastics is vitally important due to the sheer amount produced every year. For 2007 the total amount of plastics resin produced in North America was 115,793 million pounds (dry weight). Of that 92,835 million pounds was thermoplastic resin and 8,951 million pounds was thermoset resin. Breaking the statistics down further, polypropylene was the most produced thermoplastic at 19,445 million pounds, followed by high-density polyethylene at 18,222 million pounds, and pvc at 14,606 million pounds. 1,295 million pounds of nylon were produced in 2007 along with 13,584 million pounds of linear low-density polyethylene and 7,927 million pounds of low-density polyethylene. Polystyrene production totaled 6,015 million pounds. As for Thermoset plastics, the phenolic thermosets were the most produced at 4,838 million pounds while urea and melamine based thermosets totaled 3,471 million pounds. The remaining 642 million pounds of thermoset resin produced was in the form of Epoxy.

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 **Notes**  

SAVE NOTE

Does the amount of plastic produced annually in the U.S. surprise you?

How much do you think you use per year?

SAVE NOTE



Energy Usage and oil consumption

Most plastics are made out of petroleum products and so plastics production has an impact on petroleum consumption. The total oil consumption of the world in 2008 was 87.2 million barrels a day. Known oil reserves total 1.24 trillion barrels, which at the current rate of consumption would last 41 years. 99% of plastics feedstock comes from petroleum. Ethylene, propylene, and styrene are extracted directly from crude oil. The amount of oil used to make plastics is 4% of total oil consumption. However, more than 4% of the world's oil production actually is used by plastics since the 4% only accounts for plastic feedstock and not for heat, energy, and transportation used in making and selling plastics. The energy required to manufacture plastics is considerable. The plastics industry in the United States consumes about 6% of all the energy used by American industries. The carbon emissions from energy and oil usage for plastics are thus significant, contributing to global warming.

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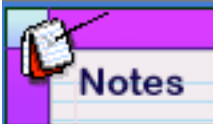


Economy

The plastics industry plays a significant role in the U.S. economy. In 2006 the U.S. plastics industry employed 1,130,300 workers. It had shipments, or total sales, valued at \$378.83 billion. The plastics industry had a total of 18,585 facilities in the U.S. The plastics industry is the third largest industry in the United States.

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SAVE NOTE

Did you expect the plastics industry to account for so much of the U.S. economy? Why or why not?

SAVE NOTE

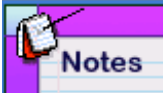


Health Risks of Plastics

The health risks associated with plastics have recently gained media attention. The main health risks of pure plastics involve their monomers. Sometimes monomers become trapped in a polymer matrix during manufacturing and then leach out later. Under certain conditions a polymer can monomerize. Polystyrene has been found to leach styrene into water and food. Styrene is a possible carcinogen and hormone disruptor. Some polycarbonates like Lexan have been found to leach bisphenol-A when heated or exposed to acid. Bisphenol-A is a hormone disruptor that can mimic estrogen. Vinyl Chloride, the monomer of pvc, is a known carcinogen (cancer causing agent). Some plastics are more likely to leach monomers than others. The main health risks associated with plastics do not come from plastics themselves but from additives like plasticizers. Di(2-ethylhexyl)phthalate (DEHP), a plasticizer used in pvc was deemed to be so dangerous that its use was banned in Europe. It was found to be carcinogenic (cancer causing) and it caused reproductive harm in that it showed high toxicity in fetuses. The problems with DEHP were especially concerning because of its use in medical equipment.

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SAVE NOTE

Have you ever noticed that if a water bottle is left in a hot car the water will taste odd?

Is this due to the plastic leaching into the water?

Knowing what you now know about the health effects of plastics does the use of plastics in food products concern you?

SAVE NOTE

Discussion

Will you reconsider microwaving food in plastics or carrying around a plastic water bottle. Why or why not? Based on what you know about biochemistry from any biology or physiology classes you have taken; what symptoms could be induced by a hormone disruptor?

Order: [New->Old](#) [Old->New](#) [Collapse All](#) [Expand All](#) Display: [Summary](#) [Normal](#)

Displaying comments for period: none [[Change](#)]
[Create a new comment](#)



Recycling

Plastics, especially thermoplastics, are readily recycled. In 2006 31% of HDPE bottles and 30.9% of plastic soft drink bottles were recycled in the United States. Overall, however only 6.9% of plastics were recycled. The reason that a relatively small amount of plastic was recycled is that it is cheaper to make new plastic than to recycle old plastic in most cases. Sorting the plastics before melting them is key because mixing plastics could potentially ruin the whole batch. Plastics are excellent candidates for recycling because it is generally a straightforward process that is more energy efficient.

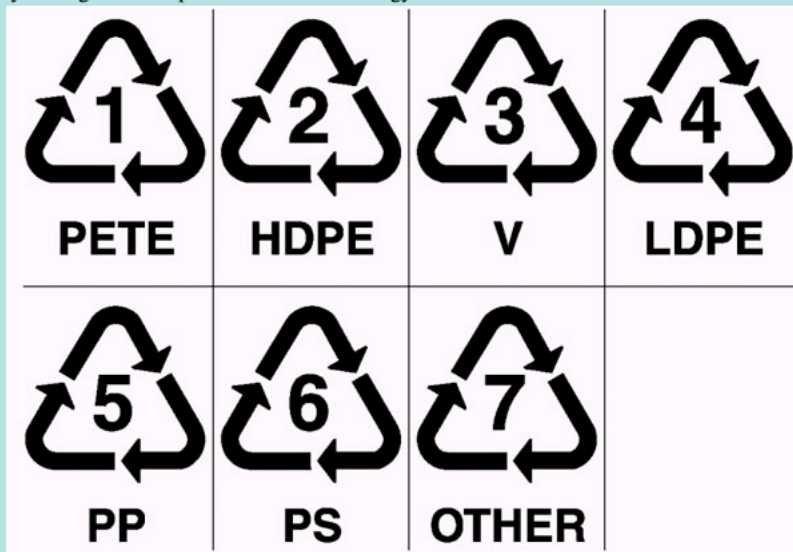
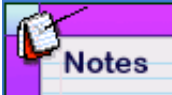


Image courtesy of [Crossplastics](#)

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SAVE NOTE

You can identify what kind of plastic a product is made of by looking at the triangular recycling symbol. #5 (PP) is polypropylene while #4 (LDPE) is low-density polyethylene. Find a plastic product around you. What is it and what kind of plastic is it made of?

Why is it important to sort plastics during recycling?

Do you think all plastics could be recycled simply by grinding them up and melting them? Why or why not?

SAVE NOTE



Thermoplastic Starch

Thermoplastic Starch is one of the simplest bioplastics to produce. The monomer is glucose. It is composed of two different polymers of glucose; amylose and amylopectin. The ratio between these two polymers influences the physical properties and has a relationship to the pH. One important piece of information to note is that you are not synthesizing the amylose and amylopectin polymers during this lab. They were polymerized by the enzymes in the plant the starch was made from.

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In this lab you will be making thermoplastic starch.

Materials:

- 1.) Hot plate or other heating element.
- 2.) Glass stirring rod or spatula.
- 3.) 500ml Pyrex beaker or a non-stick pot.
- 4.) Aluminum foil.
- 5.) Watch glass.
- 6.) 20 grams of starch from any source.
- 7.) 120mL of water.
- 8.) 15mL glycerin.
- 9.) 1mL 1M HCl. Any widely available acid will work, even a weak acid like vinegar (acetic acid). Although a larger volume must be added.

- 1.) Add the water to the beaker or pot.
- 2.) Stir in 20g of starch.
- 3.) Add 1mL 1M HCl and mix thoroughly.
- 4.) Add between 0 and 15mL of glycerin. Each group should add a different amount in order for the class to have a variety of samples.

Notes  

SAVE NOTE

What effect will varying the amount of glycerin have on the final product?

What is the glycerin doing in this experiment?

SAVE NOTE

- 1.) Slowly heat the solution with constant stirring.
- 2.) When the solution begins to thicken raise the heat and take it to a boil.
- 3.) Continue stirring until the solution is a clear highly viscous fluid.
- 4.) Pour the fluid into moulds made of aluminum foil. Flat sheets can be made as well as more complex shapes.
- 5.) Let the plastic cool.
- 6.) Leave the plastic in a place that will dry it out. Near a heater or sunny window would be best. If the humidity is very high the plastic can be dried in an oven at between 60-70°C.
- 7.) Place a small sample, about 2g, of your finished plastic on a watch glass and slowly heat it.

SAVE NOTE

What does the finished plastic feel like?

Is it hard and brittle or soft and flexible?

What happens when the finished product is reheated?

SAVE NOTE



Assessment

Answer these questions based on the starch lab.

1. Was your prediction about the effects of varying the glycerin amount correct?

2. What makes thermoplastic starch a thermoplastic?

3. What are the two polymers that make up starch?

4. What class of biological molecules do the components of starch belong to?

5. What is the monomer of starch?

6. Why do you think the acid was added?

I am done with ALL questions and ready to submit my FINAL answers

7. Based on your observations of the characteristics of TPS, what applications would it be useful for?

8. What plastics do you think TPS could possibly replace based on your observations from this lab?

9. Based on the ease of manufacture and the availability of the raw materials do you think TPS is cheaper or more expensive than the average plastic?

10. Based on the number of starch based crops, could TPS be manufactured in suitable quantities?



Biothermoset plastic lab

You will make a plastic out of egg whites. They are primarily composed of the protein albumin. Once again the polymerization was carried out by a biological system via enzymes. Proteins denature when heat is applied. the polymers can then tangle, solidifying the fluid.

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Materials:

- 1.) Hot plate or other heating element.
- 2.) 500mL Pyrex beaker.
- 3.) Aluminum foil.
- 4.) Thermometer.
- 5.) Watch glass.
- 6.) Pliers, tongs, or some other tool for holding the mold.
- 7.) 100mL water.
- 8.) 15mL egg whites.

- 1.) Add the water to the beaker.
- 2.) Form a mould for the egg whites from aluminum foil.
- 3.) Place the mould on the surface of the water.
- 4.) Place the thermometer in the beaker.
- 5.) Slowly heat the water.
- 6.) Note the temperature at which the egg white turns white and solidifies.
- 7.) Allow the plastic to cool.
- 8.) Place a small sample, 2g, of your finished plastic on a watch glass and heat it.

SAVE NOTE

At what temperature did the egg whites solidify? Is this the temperature at which the egg whites become a plastic?

What does the plastic feel like?

How much does it deform before it rips?

What happened when you reheated your plastic?



Assessment

Answer the following questions based on the egg whites lab.

1. What makes egg whites a thermo-set plastic?

2. What is the major polymer in this plastic?

3. What class of biological molecules does the polymer belong to?

4. What does the temperature at which solidification occurred (when the egg whites become a plastic) correspond to chemically?

I am done with ALL questions and ready to submit my FINAL answers

5. Based on the characteristics of this plastic do you think it could directly replace any current petroleum based plastic?

6. What products (if any) could you make out of egg white based plastic?

7. Based on the relatively high cost of egg whites, do you think this bioplastic would be more or less expensive than a petroplastic?

Biopolymers are a subset of polymers. The difference between biopolymers and petro-polymers is that the monomers of a biopolymer are derived from a living source. Two main types of biopolymers exist. The first type is synthesized directly by an organism. The second type is produced in a synthetic chemical reaction from biological reactants. Examples of the first type include DNA, RNA, proteins, and polysaccharides. The second type includes most of the biopolymers used to make bioplastics. Some biopolymers can serve as direct substitutes for other polymers but others cannot. In summary, biopolymers are simply polymers that come from a biological source.

Bioplastics are plastics made out of biopolymers. Some, like biopolyethylene, are identical to their oil derived form except that the source of the monomers is different. Others are unique and have no petro-polymer equivalent. Bioplastics can be made using plant, animal, or bacterial sources.



Starch

Starch based plastics account for 80% of the bioplastics market. They are thermoplastics that are blended with plasticizers and additives like sorbitol and glycerin. The lab you did used glycerin as the plasticizer. Pure starch can absorb water from the air and degrade. Organisms can also metabolize pure starch, as it is a carbohydrate. The fact that starch disintegrates in liquids makes it ideal for drug capsules. Blends of starch and other plastics are used to make plant pots, drinking cups, disposable shopping bags, cutlery, coated cardboard, and diaper foil.

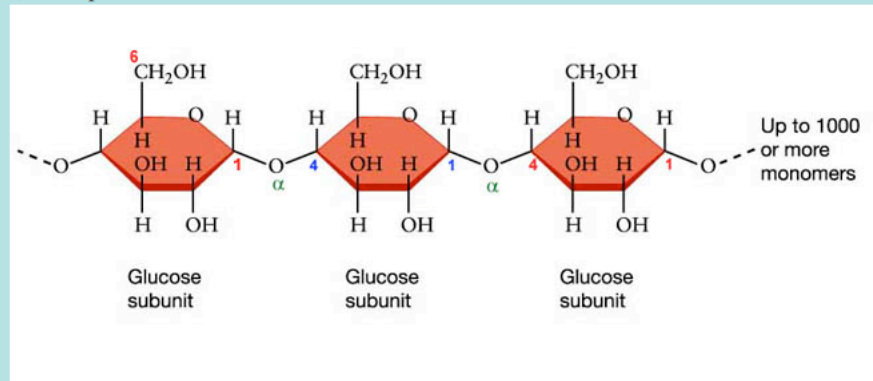


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Other Bioplastics

Poly(lactic acid) (PLA) and poly(hydroxybutyrate) (PHB) are two other important bioplastics. PHB is produced by enzymes in bacteria and genetically modified plants. The raw material for PHB is sugar. It behaves similarly to polypropylene. Poly(lactic acid) is a polymer of the common organic compound lactic acid. This is the same substance that forms in your muscles when you exercise. PLA is transparent and similar in properties to polyethylene.

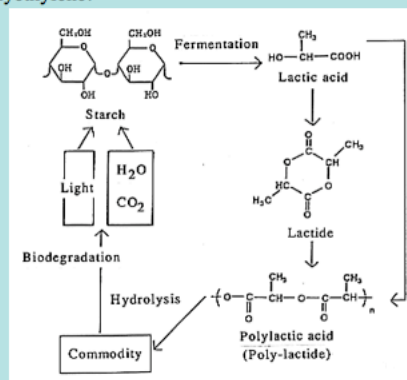


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Effects of switch to bioplastics on energy usage

Bioplastics have the potential to reduce fossil fuel consumption. The feedstock of a bioplastic is not derived from petroleum while the feedstocks of petro-plastics are. Bioplastics production consumes fossil fuels however, because the farming and processing operations commonly use fossil fuel as energy sources. Thus the production method an individual company uses dictates the amount of fossil fuels that can be saved by a switch to bioplastics. NatureWorks, a manufacturer of polylactic acid (PLA), claims a 68% reduction of fossil fuel use over traditional plastics. Metabolix claims a 95% reduction in fossil fuel use over petroleum plastics for its Mirel brand of PHB. The energy for the farm equipment, fertilizer production, and the bioplastics factories does not necessarily have to come from fossil fuels. Alternative energy like solar, nuclear, hydroelectric, biomass, geothermal, and wind could supply all the necessary energy if the required investment was made. If all plastics in the world were replaced by bioplastics and the energy used in the process came from renewable sources the fossil fuel savings would be approximately 3.49 million barrels a day. That is 4% of the world's fossil fuel usage. To put that in perspective, Saudi Arabia, the world's top oil producer, produces 10.67 million barrels a day. The amount of oil saved would exceed the daily consumption for every country except the United States, China, and Japan. If all the United States plastics production were switched to bioplastics the energy savings would be in the range of hundreds of Petajoules. Note: 1 Peta Joule= 10^{15} Joules. The energy requirements in MJ/Kg-polymer of the petropolymers LDPE, PP, and HDPE are 81.8, 85.9, and 73.7 respectively while for the Biopolymers PHB, PLA, and TPS they are 44.7, 54.1, and 25.4 respectively.

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Effects on carbon emissions of a switch to bioplastics

Switching to bioplastics has the potential to reduce carbon emissions. The CO₂ emissions in Kg CO₂/ Kg polymer are 3.0, 3.4, and 2.5 for the petropolymers LDPE, PP, and HDPE respectively. For the biopolymers PHB, PLA, and TPS they are 2.6, 1.8, and 1.14. To put these carbon emissions reductions into perspective various comparisons have been made. If all of the U.S. production of polypropylene were replaced with PHB, the reduction in annual carbon emissions would be 7.06 million metric tons. Similarly, replacing all HDPE production in the United States with PLA or TPS would lead to a reduction of carbon emissions of 5.78 and 11.2 million metric tons respectively. Replacing HDPE with PHB would actually emit more carbon dioxide. Furthermore, replacing all LDPE production in the U.S. with PHB, PLA, or TPS would lead to large reductions in carbon emissions.

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Effects on the economy of switching to bioplastics

The other advantages of bioplastics would be meaningless if they were too expensive to produce. The Mirel bioplastic made by Metabolix is about double the price of an equivalent petroplastic. Ingeo, a bioplastic made by NatureWorks LLC is only slightly more expensive than equivalent petroleum based plastics. In general bioplastics are always more expensive than the petroleum based plastics they are intended to replace but prices have fallen as development continues and oil prices have become unstable. One exception is TPS which is cheaper to make than many plastics. Added price stability is a potential benefit of bioplastics. Prices of bioplastics should continue to fall as the industry grows and more efficient production methods are developed. A switch to bioplastics would affect raw material prices. The cost of whatever crop or combination of crops used to make the bioplastics would certainly increase. The increase in corn prices as a result of ethanol production is a good example of this effect. Corn prices have risen dramatically over the past several years as more and more ethanol is produced as an alternative fuel. From 2007 to 2008 the price of a bushel of corn increased by \$0.80. It was estimated that \$0.41 of that increase was directly linked to ethanol production. A \$0.41 increase is significant for a crop that normally costs around \$3 a bushel. As the demand and thus the price of the plant feedstocks rise, the demand and therefore the price of fossil fuels would fall. The decline in oil usage would not be great enough to have a major impact on global prices. Oil producing countries regulate production in an attempt to keep prices stable. This analysis neglects the economic complexities involved but the principle is clear.

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Effects on the food supply of switching to bioplastics

Bioplastics derived from food crops like corn, soy, sugar cane, and others would directly decrease the amount of those crops that would be available for food. Bioplastics derived from non-food crops like switch-grass would indirectly affect food production by competing for land with food crops. Bioplastics derived from agricultural waste or algae would have little to no impact on the food supply. Given the fact that food shortages exist in many regions of the world interfering with the world's food supply is a major concern. Hypothetically if all the plastics production in the United States were switched to PLA it would consume 5.94% of the world's sugar supply.

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Effects on pollution of switching to bioplastics

Consuming less energy in manufacturing and emitting less carbon dioxide during production are both beneficial but greater savings can be achieved by recycling. Recycling is almost always more energy efficient and releases less carbon dioxide than making a new product. Currently bioplastics are produced in such small quantities compared to the production of petroplastics that the infrastructure for recycling has not yet developed. In principle most bioplastics should be easily recyclable because they are predominantly thermoplastics. One major problem with efforts to recycle bioplastics is that if they become mixed with petroplastics they can contaminate the whole batch. For example, if an amount as small as 0.1% by mass of a bioplastic were recycled with polyethylene terephthalate resin (PET) the entire batch of plastic would be rendered useless. As the production and use of bioplastics increases it is expected that dedicated recycling processes will be developed rendering bioplastics as easy to recycle as petroplastics.

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Effects on health of switching to bioplastics

Unlike petroleum-based plastics, bioplastics have not been implicated in any health problems. The monomers either do not leach into products or are relatively harmless when they do. Pure starch can be metabolized. Caution on bioplastics is still warranted, as they are a developing industry whose health implications may only become apparent with further study. The plasticizer used is not governed by whether the plastic is a bioplastic or a petroplastic. The hazardous plasticizers found in standard petroleum based plastics could be used in bioplastics. However, most bioplastics also use bioplasticizers. Examples of these plasticizers include sorbitol, glycerin, and Triethyl Citrate (TEC), which is derived from citric acid. All three of these bioplasticizers have low toxicities. Any leaching that occurred would result in such low plasticizer concentrations that no health effects would be observed. Just as normal plasticizers can be used in bioplastics so can bioplasticizers be used in petroplastics.

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Discussion

Now that you have read the evidence, do you think bioplastics are currently a viable option? Why do you think so? Do you think more research into bioplastics still needs to be done before a major switch can take place?

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Assessment

This quiz is meant to gauge what you have learned from this module.

1. What is a plastic?

2. What differentiates a bioplastic from a petroplastic?

3. Polymerizations fall into which two general categories?

- elimination and subtraction
 - addition and elimination
 - addition and condensation
-

4. The reactive ends often found in polymers are what type?

- radical
- cation
- anion
- all of the above

5. Which uses less fossil fuel inputs polypropylene or thermoplastic starch?

6. Does the production of PHB generate more or less carbon emissions than HDPE?

7. What is a plasticizer and what does it do?

8. Do you think switching plastics production to bioplastics is feasible at this time? Why? Give two reasons.

9. Would the two bioplastics you made in the labs be useful for making products like plastic bags or bottles?

10. Would switching to bioplastics lower manufacturing costs or raise them? Does this vary depending on the plastic?



Assessment

This survey is intended to provide feedback of what you thought about this module.

1. How much do you think you have learned from this module?

2. Do you have any suggestions for improving this module?

3. Do you think it is useful to study modern research outside the main curriculum in a high school chemistry class.

I am done with ALL questions and ready to submit my FINAL answers