

# **Bioplastic: Engineering the Future**





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# Conventional Plastics

Strong and light weight, replace traditional materials

 PETE	PETE Polyethylene Terephthalate	Soft drink & water bottles	Recyclable
 HDPE	HDPE High Density Polyethylene	Milk jugs	Recyclable
 V	PVC Polyvinyl Chloride	Cosmetics, pacifiers, shower curtains, teething rings, pacifiers, soft toys, portable electronics	Can leach phthalates and lead Not Recyclable Creates dioxin during manufacture & disposal
 LDPE	LDPE Low Density Polyethylene	Food storage, soft and pliable parts	Recyclable
 PP	PP Polypropylene	Reusable microwaveable containers, food storage	Recyclable
 PS	PS Polystyrene	Packing peanuts; disposable cups, plates, plasticware; Styrofoam	Can leach styrene Recyclable, but not usually recycled Most end up in landfills
 OTHER	OTHER PC Polycarbonate PLA Poly Lactic Acid	Reusable water bottles  Disposable cups	Can leach bisphenol-A; Not recyclable  Not Recyclable; Can be composted

# Conventional Plastics

## Thermoplastics

do not undergo a change when heated, so they can be melted & reformed



## Thermosets

melted & formed only once





# Concerns with Conventional Plastics



## Manufacturing

- Most made from petroleum & natural gas
- Some contain hazardous chemicals
- Energy intense
- Air pollution

## Use

- May leach chemicals
- Flammable – metals used for fire resistance
- Controversial health effects

## End of Life

- Some types can be recycled
- 7% of plastics are recycled
- Make up 12% of the US municipal waste stream
- Don't corrode or biodegrade in a landfill

# Health Concerns with Conventional Plastics

- Phthalates in PVC & vinyl products
  - group of chemicals commonly used as plasticizers mainly to soften PVC
  - PVC typically contains 15-20% phthalates
  - Linked to endocrine disruption – may cause reproductive & developmental effects
  - Soluble in oil
- Bisphenol A in polycarbonate
  - Linked to endocrine disruption
  - Toxic to fish
  - Soluble in water
- Metals
  - Bromine flame retardants
  - Lead, cadmium, and tin stabilizers in PVC



up to 25% phthalates



40% lead



1.5% bromine

# Opportunity for Bioplastics

- Reduced reliance on fossil fuels – keep qualities of conventional plastic, and make it out of a natural material?
- Can waste materials – that would otherwise go to a landfill – be used to make bioplastic?
- Toxicity concerns of some existing plastics
- Plastic is not biodegradable and takes up a lot of landfill space – biodegradable versions could reduce amount of waste in landfills

# Bioplastics

- Derived from renewable sources such as vegetable fats and oils and corn starch
- Most are designed
  - To function as well or better than conventional plastics
  - To degrade to non toxic components
- Growing market – makes up 327,000 tons of the 12.3 million tons of flexible packaging material
- 2000-2008 worldwide consumption of biodegradable plastics increased 600%



# Notes for discussion after the Lab

- What are some of the challenges with bioplastics?
  - Same strength, clarity, etc as conventional plastics?
  - Need new equipment to manufacture bioplastics
  - Corn is typically used as a feedstock – concerns with food supply, space to grow corn, is the manufacturing energy really less if you consider the water, food, etc that goes into growing corn
  - How long does it take to breakdown in a landfill?
  - For compostable plastics – is it easy to separate from other plastics so it goes to the composter?





## Green Chemistry Module Level: High School Regents

### Bioplastics



*Image: FreeDigitalPhotos.net*

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## Green Chemistry

Chemical manufacturing is as old as civilization, and the discoveries of bronze and iron came to define the eras that ensued. In modern times, we take for granted a plentiful supply of metals, plastics, dyestuffs and medicines. We have come to depend on the chemical industry to provide us with all the materials we need for our "materialist" society.

But the supply of these materials is not infinite. As the human population grows, and demands an ever higher standard of living, the consumption of the Earth's materials is in danger of getting out of control. It is therefore essential that chemists become responsible stewards of the raw materials that remain. We need to develop methods for chemical processing that are both chemically and environmentally efficient, and which move us towards a sustainable society. We need new materials that can provide what we need without destroying the Earth.

**Green chemistry** is designed to help us meet these needs. It aims not just to treat waste, but to avoid producing waste in the first place. Products and processes should be "benign by design," but they must also be practicable.

In this lab, we will explore how this can be achieved in practice – how we can use chemistry to help solve our environmental problems. We will never be able to build a sustainable society if we don't understand the basic science of where our materials come from, and how they are produced. The goal of this manual is to provide that science, presented within the context of green chemistry.

## The Twelve Principles of Green Chemistry

The basic principles of green chemistry were first laid out by two US chemists, Paul Anastas and John Warner, in their 1998 book, "Green Chemistry: Theory and Practice:"

1. **Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. **Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. **Use catalysts, not stoichiometric reagents:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. **Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. **Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. **Increase energy efficiency:** Run chemical reactions at ambient temperature and pressure whenever possible.

10. **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. **Analyze in real time to prevent pollution:** Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. **Minimize the potential for accidents:** Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

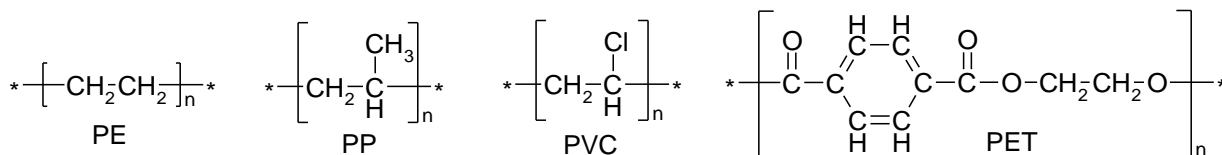
It must be recognized that these represent a target, and we will not be able to satisfy every principle immediately with every process and product. Nevertheless, if we design our chemistry with these principles in mind, we will make great strides towards achieving sustainability.

### Conventional & Bio Plastics

Plastics are everywhere! They are some of the most common and important materials we use every day. Being moldable and easy to work with, they can be made into almost any shape. They are used to make most containers, and in consumer products such as toys and electronics. Modern plastics are strong yet lightweight, which means they reduce transportation costs and they do not use a lot of material for a given purpose.<sup>1</sup> For example, a plastic grocery bag weighs only 6 g, compared to 56 g for a (albeit slightly larger) paper grocery bag. Plastics are long-lasting, and do not corrode, and it is hard to imagine modern life without them. However, these versatile materials have contributed to our "disposable culture," and plastics now make up around 12% of municipal solid waste in the US.<sup>2</sup> Most plastics are based on non-renewable resources such as petroleum. In addition, there have been safety concerns about residual amounts of bisphenol A (BPA) and phthalate plasticizers, though the former is still widely used in plastics in the US and the EU.



Some common plastics include polyethylene (PE), polypropylene (PP), polystyrene, poly(vinyl chloride) (PVC), nylon and poly(ethylene terephthalate) (PET). These are all polymers, which are huge molecules built from many repeating units. As you can see, some such as PE (used for grocery bags and common consumables) have very simple structures, whereas some such as PET (used in clothing and for drinks bottles) are more complex.



Clearly there is a need to develop plastics from renewable resources; these are frequently referred to as bioplastics. Such materials should not only be strong and lightweight, but also biodegradable. Some are manufactured from virgin renewable materials, while others are designed to use biodegradable waste products such as starch or lignin.

<sup>1</sup> For more information, visit Plastics Division of the American Chemistry Council at <http://www.americanchemistry.com/plastics/>.

<sup>2</sup> US EPA, "Plastics", accessed January 20, 2010. <http://www.epa.gov/osw/conserve/materials/plastics.htm>

Some common bioplastics:

Name	Acronym	Made from	Structure
Poly(lactic acid)	PLA	sugar	$\ast \left[ \begin{array}{c} \text{O} \quad \text{CH}_3 \\ \parallel \quad   \\ \text{C} - \text{C} - \text{O} \\   \\ \text{H} \end{array} \right]_n$
Poly(hydroxybutyric acid)	PHB	fermentation of starch	$\ast \left[ \begin{array}{c} \text{O} \quad \quad \text{CH}_3 \\ \parallel \quad \quad   \\ \text{C} - \text{CH}_2 - \text{C} - \text{O} \\   \quad \quad \quad   \\ \text{H} \quad \quad \quad \text{H} \end{array} \right]_n \ast$
Starch-based materials		starch	Carbohydrate-based polymer

PLA is currently being manufactured by BASF and sold as Ecovio®, while PHB is produced by Metabolix as Biopol.

### Procedure

1. Place equal parts corn starch and water in a plastic bag.
2. Add two drops of corn oil to the bag.
3. Using your fingers through the bag, mix the solution well so there aren't any clumps of cornstarch. It is important that the mixture is homogenous – failure to do so will cause uneven cooking and give starchy patches throughout.
4. Once the solution is mixed, place the bag in a microwave oven and heat on high power for about 20-25 seconds. **DO NOT** microwave the bag while it is completely sealed. Leave a small opening for steam to escape.
5. After the sample has cooled, check its physical characteristics such as texture and flexibility.
6. Form the plastic into whatever shape you like. Let the plastic sit out, uncovered, overnight to harden.

### Options:

- Repeat the experiment using more cornstarch than water. How is the product different?
- Repeat the experiment using more water than cornstarch. How is the product different?
- Repeat the experiment using 5 seconds less heating time. How is the product different?

### Recycling and disposal:

The plastic produced in this experiment are non-toxic and biodegradable, so they can be disposed of as regular waste, or composted.