

# WHAT MAKES GREEN PLASTICS GREEN?

An understanding of the chemistry of polymers — both petroleum-derived and from natural sources — provides a road map to plastic products being marketed as compostable.

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**G**REEN plastics carry high expectations. They are expected to perform their intended function as bags, packages or film barriers and then, within a reasonable timeframe, essentially disappear in the form of environmentally acceptable degradation products. How they function and disappear is largely a matter of their chemistry. Several products, with varying chemical skeletons, are being promoted as green plastics to the composting and recycling community.

The first part of this article, “How Green Are Green Plastics?” (December 2002), gave an account of terminology and standards related to green plastics, and surveyed the commercial products used in manufacturing collection bags for compostable materials. This second part describes the chemical nature of polymers in the plastic and how the chemistry strongly influences the degradability of the plastic.

## OF MONOMERS AND POLYMERS

In general, the properties of plastics are determined by the constituent *polymers* that are their main ingredient, by additives introduced to improve sometimes otherwise poor physical properties, and by processing. Polymers are long chained molecules composed of multiple and repeated units of one or more monomers (a single identifiable chemical compound). Polymer chemists and engineers can come up with a plastic that meets almost any application requirement by varying the chemical nature of the polymer, the mix of additives, and the method of processing. Tradeoffs sometimes enter the picture, as in the case of plastic collection bags for compostable materials. Those bags must be strong and durable enough for the collection process but then degrade during composting. These “programmed-degradable” plastics have received attention relatively recently; the main efforts of polymer scientists for many years were directed at making plastics maximally stable

under all conditions.

Although the rate of plastics degradation depends on the environment in which it is placed, it also strongly depends on the chemical nature of the polymer. A suitable starting point for understanding the variety of factors perhaps is the extremely environmentally stable polyolefins: polyethylene, polypropylene, poly(vinyl chloride), and polystyrene. (Note: By standard convention, polymer chemists enclose the monomer name in parentheses when it consists of two words.)

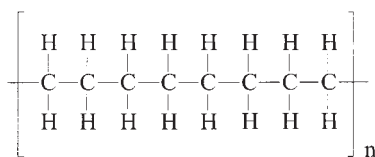
## POLYOLEFINS — THE STANDARD OF STABILITY

Polyolefins are at the top of the list of commodity polymers, accounting for almost 90 percent of all plastics manufactured. They are manufactured from petroleum-based feedstocks. Polyethylene (Figure 1), for example, is polymerized from the monomer compound ethylene,  $\text{CH}_2=\text{CH}_2$  where the = symbol indicates a *double bond*. Double bonds are shorter and stronger in a thermodynamic sense but they are more chemically reactive compared to a single bond. When ethylene is polymerized the double bond is replaced with two single bonds, one

of which attaches to another ethylene monomer in the polymer chain. Single bonds between carbon atoms are especially difficult to break (i.e. they are stable). In part, polyethylene owes its stability to this uninterrupted string of carbon-carbon single bonds. Polyolefins are generally inexpensive and their physical properties, such as melting point, strength, and resistance to water (*hydrophobicity*), are useful for a wide range of applications. It is their favorable cost-performance ratio that makes them the commodity leaders.

Polypropylene (PP) (Figure 2) differs chemically from polyethylene only in having a *side chain* attached to every other carbon atom; in the case of PP, the side chain is a methyl group ( $\text{CH}_3$ ). (The side chain adds specific performance characteristics to the polymer, e.g. makes it more pliable).

Figure 1. Chemical composition and structure of low-density polyethylene (LDPE)



C=carbon atom, H=hydrogen atom, n represents the number of repeated units and can be as large as many thousands

The *backbone* chains of the two polymers are the same.

Polyethylene and polypropylene are *recalcitrant* (resistant) with respect to environmental degradation; even in a compost environment they can last many years. Polyethylene and polypropylene do degrade in the environment by oxidation. Natural daylight can accelerate the oxidation, giving rise to photo-oxidation (photodegradation). The carbon-carbon chains are broken, and in time the plastic will become brittle and eventually fragment. The rate in any case, however, is very slow (nonetheless, anti-oxidation stabilizers still are added to polyethylene and polypropylene to prolong their useful lifetime).

Perhaps the single most important reason for the extreme stability of polyolefins is that they contain only carbon atoms in their backbone (Figs. 1 and 2), and each carbon atom is bonded to four other atoms. The carbon-carbon single bond is very stable. As will be seen, introducing a non-carbon atom (a *heteroatom*) such as oxygen into the polymer backbone significantly reduces environmental stability.

#### HELPING PETROLEUM-BASED POLYMERS DEGRADE

“Activated” polyolefins are polyolefins, usually polyethylene, that have been modified, either during the initial polymerization or afterwards during processing, so as to increase the rate of oxidative degradation. The chains fragment and the plastic becomes a friable powder. Eventually, it is known, the chain fragments become so short that they can be converted by microorganisms in the environment to carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). What is not known, and is the subject of much current research, is the exact time scale for that complete conversion, although it is known that activated polyolefins do not meet the current Biodegradable Polymers Institute-U.S. Composting Council (BPI-USCC) composting label requirements (see Part One of this article). Another unknown is the effect of accumulating residual polyethylene fragments on agricultural productivity should such plastics be used for applications like agricultural plastic mulch, or collection bags that are intended to remain in the compost.

Some people mistakenly think of synthetic polymers polymerized from petroleum feedstocks as necessarily being nondegradable. But there are synthetic petroleum-based

polymers that are biodegradable and compostable. One example is poly( $\epsilon$ -caprolactone) or PCL (Figure 3). PCL is a *polyester* by virtue of containing the ester group of atoms, COO, in its repeating unit. The presence of the oxygen heteroatom in the backbone makes the polymer susceptible to degradation by hydrolysis (i.e. chemical reaction with water). PCL is biodegradable through the action of nonspecific enzymes including the esterases found abundantly in

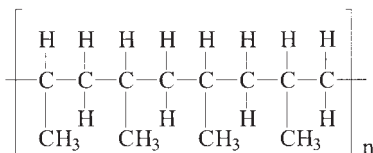
soil. The low melting temperature of PCL (60°C) limits applications but it is often used in combination with other polymers, including starch (see below).

The properties of polymers can be modified by using more than one type of monomer in the polymerization, to produce a *copolymer*. Polymer scientists, aiming to achieve application-specific properties, have studied innumerable combinations of monomers. A variety of biodegradable *copolyesters* have been produced from petroleum-based monomers.

One such copolyester commercially available for collection bags is the Eastar Bio® copolyester, manufactured by Eastman Chemical (Figure 4). The monomers from which it is produced are butanediol, adipic acid, and terephthalic acid. The oxygen-containing linkages are responsible for the polymer’s biodegradability, as with PCL. But the additional chemical compositional elements in the copolyester lead to very satisfactory physical properties during use; for example, the terephthalate component improves chain rigidity. Eastar Bio® biodegrades to the extent of 80 percent in 150 days in a compost environment, according to the manufacturer, and satisfies the BPI-USCC compost label requirements.

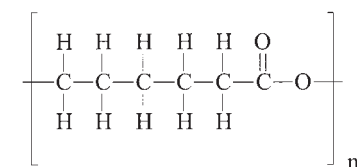
Somewhat similar products, also copolyesters, are Ecoflex® manufactured by BASF and Biomax® manufactured by DuPont. These products may be marketed in the United States for use in film products such as compost feedstock collection bags in the near future.

**Figure 2. Chemical composition and structure of polypropylene (PP)**



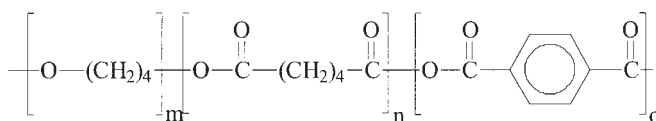
For brevity, the individual C-H bonds in the CH<sub>3</sub> side chain groups are not shown

**Figure 3. Chemical composition and structure of poly( $\epsilon$ -caprolactone)**



C=carbon atom, H=hydrogen atom, O=oxygen atom

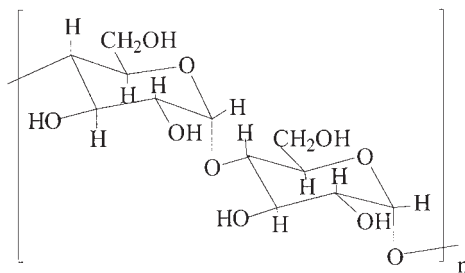
**Figure 4. Schematic representation of a copolyester, poly(butylene adipate-co-terephthalate)**



For brevity, the individual C-H bonds are not shown, and the ring structure is an abbreviation for the phenyl group (C<sub>6</sub>H<sub>6</sub>)

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**Figure 5. Chemical composition and structure of amylose, a major component of starch**



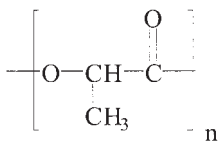
In the figure, the ring structures are simplified; everywhere that there are four bonds coming from a single point, the point is meant to represent a carbon atom.

### NATURAL POLYMERS

Many polymers are also found abundantly in nature. Natural polymers tend to be degradable because organisms have evolved enzymes to attack them. Attention has reasonably turned to such polymers as potential feedstocks for compostable plastics. These manufactured *biopolymers* are inherently biodegradable, and as they are made from renewable resources they have the additional benefit of not depleting fossil resources.

Chief among the biopolymers is starch, a carbohydrate polysaccharide. Starch is produced from corn (maize), potatoes, wheat,

**Figure 6. Chemical composition and structure of the polyester, poly(lactic acid) (PLA)**



tapioca (cassava), rice, and some other plants with annual world production well over 32 million metric tons. Approximately half the total is produced in the United States, mainly from corn, but also from potatoes, wheat and a few other sources. As a raw material, starch is the only biopolymer competitive with polyethylene in terms of price.

The major polymer components of starch are amylose and amylopectin. The chemical structure of amylose is shown in Figure 5. In amylopectin, there are branch points in the chain where segments of chain, identical in chemical structure to the main chain, are attached to the main chain where the  $-CH_2OH$  group is located. The ratio of amylose to amylopectin varies with source plant and affects the physical properties of the starch.

The biodegradability of starch stems mainly from the oxygen atom connecting successive ring structures, and the oxygen atom within each ring. Starch interacts strongly with water (it is *hydrophilic*) and degrades by hydrolysis.

Moreover, starch can be softened by heating and shaped into articles by extrusion or molding; i.e., it is *thermoplastic*. It can therefore be processed using the conventional processing methods of the plastics industry. A significant drawback, however, is that its physical properties are not suitable for many applications, and its hydrophilic nature makes its physical properties (e.g., strength) dependent on relative humidity. There are many strategies for developing practical applications for starch-based plastics, but the strategy that has, to date, been most successful commercially has been to combine it with other compatible, biodegradable (but petroleum-derived) polymers to improve properties.

An example of a successfully commercialized starch-based blend is MaterBi<sup>®</sup>, manufactured by Novamont S.P.A., Italy. The Z-class of MaterBi products contains starch combined with the petroleum-derived polymer, poly( $\epsilon$ -caprolactone) (Fig. 3). Plastic film suitable for, among other things, composting feedstock collection bags is currently being marketed in the United States and abroad. MaterBi satisfies the BPI-USCC compost label requirements.

MaterBi is a hybrid in the sense that it consists of both a renewable component (starch) and a nonrenewable petroleum-based component (PCL). It is also a hybrid in the sense of consisting of a natural polymer (starch) and a synthetic polymer (PCL). These features illustrate that there is no simple correlation among the terms natural-synthetic, renewable-nonrenewable, or compostable-noncompostable.

Poly(lactic acid), or PLA (Figure 6), provides yet another example. It is a synthetic polymer because it is not found in nature — even though the monomer starting material, lactic acid, is found in nature. PLA is produced commercially in large-scale bioreactors through fermentation. Microorgan-



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**Table 1. Origin, degradability, and properties of some plastic film products**

Polymer	Polyethylene	"Activated" Polyethylene	Poly ( $\epsilon$ -caprolactone)	Co- Polyesters	Starch	Starch/Poly ( $\epsilon$ -Caprolactone)	Poly(lactic Acid	Poly (Hydroxybutyrate- co-Hydroxyvalerate)
Synthetic (polymerized from nonrenewable monomer feedstocks)	X	X	X	X		X		
Synthetic (polymerized from renewable monomer feedstocks)							X	
Natural (obtained directly from plants)					X	X		
Natural (obtained by fermentation of renewable monomer feedstocks)								X
Nondegradable	X							
Degradable/not compostable		X						
Degradable/compostable			X	X	X	X	X	X
Favorable film properties (strength, melting temperature, water resistance)	X	X		X		X	X	X

isms are fed sugar feedstocks; the microorganisms convert the sugar feedstocks to lactic acid ( $\text{CH}_3\text{CHOHCOOH}$ ). PLA is synthesized from the isolated lactic acid by conventional means, first to produce a low-molecular weight polymer. That polymer is then depolymerized to produce a cyclic dimer form (lactide) which is repolymerized using metal catalysts to produce a high molecular weight polymer. PLA is also called polylactide.

PLA degrades mainly by hydrolysis even in the absence of microorganisms. It is compostable, but the rate of biodegradability in a composting environment depends on the size and shape of the article (e.g. a bag, cut-

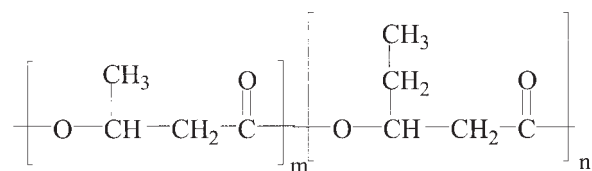
monomers (PHBV) (Figure 7). By varying the ratio of sugar feedstocks, the relative amounts of the two components in the copolymer can be controlled, producing a range of physical properties from brittle to nearly rubber-like. Examples of commercial products are Biopol® and other PHAs manufactured by Metabolix.

Nodax, under development by Proctor & Gamble, consists of a family of copolymers of hydroxybutyrate and one or more hydroxyalkanoates having a longer side chain, where the side chain has anywhere from three to 20 carbon atoms. Nodax can be converted to films, sheets, molded articles, foams, fibers, and nonwoven fabrics, and is both biodegradable and compostable.

Table 1 summarizes some of the features of the plastics described here. It illustrates how both natural and synthetic polymers can be biodegradable and compostable. Whatever the origin of the polymer or how it is made, its degradability in a particular environment, such as a composting facility, is more related to its final chemical makeup than to its origin.

As described in the first part of this article, the various degradable/biodegradable/compostable plastics featured here are important for both the bioplastics industry and the composting industry. Plastics manufacturers continue to improve their products and to produce new products. With respect to compostable plastics, many strategies are being followed, having the aim of combining superior physical properties with low cost. It can be said that development of the nascent bioplastics industry is well under way. ■

**Figure 7. Schematic representation of poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)**



lery). The main applications of PLA to date have been in fiber products and clear packaging containers, but Biocorp North America has announced plans for combining NatureWorks PLA (a product of the Cargill Dow Company) and MaterBi in blends to be used for compost bags.

Fermentation is also involved in the production of polyhydroxyalkanoates (PHAs), a family of polyesters produced naturally by microorganisms. In the case of PHAs, microorganisms produce the polymer directly from supplied sugar feedstocks. Depending on the sugar feedstock provided, and the microorganism used, one or another of the family of polyesters is produced. The polymer is then isolated, purified, and processed. The most significant PHA produced at the present time is a copolyester comprised of hydroxybutyrate and hydroxyvalerate

Whatever the origin of the polymer or how it is made, its degradability in a particular environment is more related to its final chemical makeup than to its origin.

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