

## **Biopolymers**

Three ways biopolymer plastics can be produced are through converting plant sugars into plastic, producing plastic inside microorganisms, and growing plastic in corn and other crops. Today more than 99% of plastics are petroleum-based because of availability and cost. However, many companies and organizations are conducting research and developing projects to explore the biopolymer industry. Biopolymers can be extruded, blown, molded, injection-molded, foamed, thermoformed, and coated onto other materials.

### *Polyhydroxyalkanoates (PHA)*

PHAs are polyesters that accumulate in a wide variety of microorganisms. Primary research shows that PHA has a considerably low volume of the biopolymer market, somewhere around 100,000 lbs. per year. PHAs are polyesters, but they can also imitate polypropylene, polystyrene, and polyethylene. PHAs are considered to be the broadest biopolymer because they are their own class and can have many different chemical structures. These polymers have a wide range of properties ranging from stiff and brittle plastics to rubberlike materials. They also can exhibit properties similar to many synthetic polymers. There are currently 100 different monomer types of PHA that have been discovered. PHAs are able to fully degrade into carbon dioxide and water, leaving no environmentally harming waste behind.

In regards to the food packaging industry, PHAs have desirable properties such as good tensile strength, printability, flavor and odor barriers, heat sealability, grease and oil resistance, temperature stability, and are easy to dye.

Fermentation, an alternative method to produce PHAs, will allow you to produce polymers with many different combinations of properties. The price of fermentation is likely to be higher than for PHA production in crops. Possible applications include biodegradable packaging (bottles, containers, sheets, films, laminates, fibers and coatings), disposable razors, golf tees, combs, disposable utensils, dishes, cups, toiletry items, and medical devices.

Over 100 monomers and copolymers can be developed from PHAs. Some of the polymers used are PHB, PHV, PHBV(Metabolix), PHBO, PHBH, PHBD which are for Nodax™ by Protor & Gamble. See below for descriptions of a few of these polymers.

### *Polyhydroxybutyrate (PHB)*

PHB is one of the few monomeric units of PHA that have been introduced into the market in relatively large quantities. It has similar properties to that of polypropylene. PHB tends to be stiff, highly crystalline, brittle, has a high melting point, and low molecular weight. Its high melting point makes processing difficult. PHB is water insoluble and relatively resistant to hydrolytic degradation. This differentiates PHB from most other currently available bioplastics, which are either water soluble or moisture sensitive. PHB shows good oxygen permeability. It has good ultra-violet resistance but has poor resistance to acids and bases. PHB is soluble in chloroform and other chlorinated hydrocarbons. It is biocompatible and hence is suitable for medical

applications. PHB has a melting point of 175°C and glass transition temperature of 15°C. PHB has a tensile strength of 40 Mpa, which is close to that of polypropylene. PHB sinks in water while polypropylene floats. PHB has the lowest molecular weight out of all the PHA monomers. PHB accumulates as energy reserves in many different types of organisms.

#### *Poly (3-Hydroxybutyrate-co-3-Hydroxyvalerate) (PHBV)*

Many advantages are realized when hydroxyvalerate (HV) is added to produce the copolymer PHBV. PHBV copolymer is less stiff, tougher, and easier to process than PHB. It is water resistant and impermeable to oxygen. Depending on the percentage of HV added, the melting point of PHBV is between 100°C-160°C. For example, P(3HB-co-10%3HV) has a tensile strength (Mpa) of 36, 69% crystallinity and a 10% elongation at break. Plant synthesis of different forms of PHB has begun to be researched and would provide an alternative to fermentation.

#### *Poly(lactic acid) (PLA)*

PLA is a thermoplastic and compostable polymer made from lactic acid which can totally degrade in an aerobic or anaerobic environment in six months to five years. PLA has the tensile strength, modulus, flavor and odor barrier of polyethylene and PET or flexible PVC; the temperature stability and processability of polystyrene; and the printability and grease-resistance of polyethylene. The glass transition temperature of PLA ( $T_g$ ) ranges from 50°C to 80°C while the melting temperature ( $T_m$ ) ranges from 130°C to 180°C. PLA can be processed by injection molding, sheet extrusion, blow molding, thermoforming and film forming. PLA can be recycled by chemical conversion back to lactic acid and then repolymerized. Unmodified PLA has limitations such as brittleness, a low heat distortion temperature, and slow crystallization rates.

Possible – and current – applications include food packaging, disposable bottles, floral wraps, disposable utensils, dishes, cups, fast food service ware, paints, medical devices, and compost and grocery bags.

### **Petroleum-based Polymers**

These polymers are made from petroleum-based products. Nearly all of these types of polymers include atoms of carbon and hydrogen in the basic monomeric unit. Petroleum contains the carbon and hydrogen atoms necessary to form the monomers desired, and thereby form the polymers.

There are many possible forms of polymers based on petroleum products and because polymers can be combined to form polymers with new properties and characteristics, there are literally a limitless number of polymers that can be created from petroleum. Although there is the possibility of an enormous number of polymers, there are only five different polymers that make up the bulk of the plastic industry's production:

The polymers are listed below along with their abbreviation.

- Polyethylene terephthalate – PET

- Polyethylene - HDPE or LDPE
- Polyvinyl chloride – PVC
- Polypropylene – PP
- Polystyrene – PS

It is estimated that these five polymers make up well over 90% of thermoplastic production and almost 90% of total plastic production. The common reason these plastics are produced in such abundance is price. These plastics can be used in many applications, often with superior properties, for a lower cost than other materials or plastics that could be used in the same application. Below is a break down of the approximate percentages that each of these plastics account for in the global plastic industry.

#### **Approximate Breakdown of the Global Plastic Production**

Polyethylene terephthalate 6%  
Polyethylene 40%  
Polyvinyl chloride 20%  
Polypropylene 19%  
Polystyrene 9%  
- Approximate Total 94%

The properties and applications of these five main polymers are discussed and compared below:

#### *Polyethylene*

Polyethylene is produced in greater amounts than any other type of plastic. This is because it can be produced with an incredible range of properties at a low cost. It is possible to have a wide range of properties because polyethylene is produced in several forms having different densities. The density of a polymer is directly linked to the crystallinity, an important factor that affects many material properties of that polymer, such as stiffness, impact strength, and permeation.

In general, polyethylene has a good toughness, excellent chemical resistance, near zero moisture absorption, and good ease of processing. The low glass transition temperature of  $-110^{\circ}\text{C}$  will allow good retention of mechanical properties, even at low temperatures. The service temperatures of polyethylene range from  $-40^{\circ}\text{C}$  to  $93^{\circ}\text{C}$ . The two most commonly produced types of polyethylene are High-density Polyethylene (HDPE) and Low-density Polyethylene (LDPE).

#### *High-density Polyethylene*

High-density Polyethylene is the harder of the two forms. It is commonly used in milk containers, lids, laundry detergent containers, and other durable containers. HDPE is also used to make sporting goods, electrical insulation, and toys.

HDPE is made up of monomer chains that are nearly linear, allowing the monomer chains to bond very closely to each other, causing the higher density. HDPE has

relatively high tensile strength and rigidity because the high-density implies high crystallinity.

#### *Low-density Polyethylene*

Low-density Polyethylene is a relatively soft form of PE. It is commonly used in trash bags, food packaging, grocery bags, dry-cleaning bags, and squeeze bottles. LDPE is also used to make diaper liners and agricultural covers.

LDPE is made up of monomer chains which are branched chains, meaning the chain of monomers has “branches” of monomer material out from the main chain. The branched form of the polymer does not allow the monomer chains to form as close as the linear form of the HDPE. The density is decreased in this way. LDPE is relatively soft, flexible, and possesses a higher impact strength than HDPE because the low-density causes weaker bonds to be formed between the monomers within the polymer.

#### *Polyvinyl Chloride*

Polyvinyl chlorides are the second highest produced plastic based on worldwide consumption. These plastics are prevalent because they can literally be processed by more techniques than any other plastic. This is because the chemical structure of the polymer allows a large range of formations. The low cost of production along with the moderate heat resistance, good toughness, and good chemical properties it possesses make polyvinyl chloride a very popular polymer.

Polyvinyl chlorides, similar to polyethylene, can be produced in a variety of grades, flexible to rigid. They are also often used to alloy with other specially designed polymers in order to improve properties and reduce cost. There are many good qualities; however polyvinyl chloride requires some extra attention during the methods of melting and processing into plastic forms.

Polyvinyl chlorides are used as packaging materials for food and drugs because they are nontoxic, odorless, and tasteless. They are also used for decorative packaging for products requiring only an ordinary amount of protection, as well as for common items such as credit cards. These plastics can also be used in printing inks and can be effectively used in coating paper and sometimes other plastics.

Another application for polyvinyl chlorides is in construction, where the rigid form is used for pipes and rain gutters. In general, polyvinyl chlorides can be produced with a wide range of hardness ranging from thin, flexible films to rigid molded pieces by adding different plasticizers in the production process. They have excellent water and chemical resistance and good strength.

#### *Polypropylene*

Polypropylene is extremely versatile and, as such, is available in many grades and is found combined with many other polymers to form copolymers. A much stronger, heat resistant, and rigid form of polypropylene can be produced with glass fiber reinforcements. Polypropylene has superior resistance to flexural fatigue stress cracking

and excellent chemical properties. However, alone it has somewhat poor properties at extreme temperature ranges. Although polypropylene retains its strength and stiffness at elevated temperatures, it has a slightly limited heat resistance and the useful life of the product is lessened at higher temperatures. Also, it has a problem with poor low temperature performance. This problem can be overcome with the use of fillers and copolymers.

Polypropylene is used in the packaging industry for packaging, food containers, and bottles. Outside of packaging, polypropylene is used for luggage, molded parts for automobiles, and household appliances.

### *Polystyrene*

Polystyrene is very easy to process and has a relatively low cost. It can be found in many grades for all types of processes and often competes successfully with more expensive plastics. The basic form of polystyrene is brittle with poor chemical and heat resistance, but can be combined with other polymers to remedy these mechanical shortcomings while still maintaining a low cost. Industry practice for polystyrene has long been that any waste that occurs in the production process can be fed back into the production cycle with no loss.

Polystyrene is commonly used in food packaging, lids, meat trays, as well as cookie and candy packages. An expanded version of polystyrene, named Styrofoam, is used for many things including take-out containers, fast food tubs, egg containers, and is used as a filler for the shipping industry to pad items in transport. It is also used outside of the packaging industry for shower doors, toys, and disposable kitchenware.

A great deal of the polystyrene that is produced is in the form of High Impact Polystyrene because of the brittleness of the basic form of the polymer. Adding rubbers to polystyrene produces these high impact polymers. The more rubber that is added, the greater the impact strength becomes, but as a result the stiffness decreases as well. Polystyrene has good chemical stability and most household fluids have no effect on its stability.

Polystyrene has long been blended with Polyethylene in an effort to combine the lower water vapor permeability and good stress cracking of polyethylene with the ease of processing and high rigidity of polystyrene. This process can only be achieved through the use of mixing agents because of the incompatibility of polystyrene and polyethylene. The blend of these two polymers is often used to form a multilayer film for packaging of foods that contain fat.

### *Polyethylene Terephthalate (PET)*

Polyethylene terephthalate is a form of polyester with a broad range of mechanical properties that make them a replacement in some applications for metals like die-cast aluminum and zinc. It possesses an excellent balance of mechanical properties because the degree of crystallinity and the level of orientation in the finished product can be controlled. However, to control these properties it is necessary to pay particular attention

to the temperature range that the plastic is molded to achieve the desired crystallization levels.

Different grades of polyethylene terephthalate are used in many different processes, such as appliances and electronics, but particularly in stretched injection blow molded beverage bottles and film production. Polyethylene terephthalate is used in the plastic bottling industry because it combines optimal processing, mechanical and barrier properties. One of the biggest advantages this polymer has is that the recycling of all types of polyethylene terephthalate is easily accomplished.

Polyethylene terephthalate is characterized by its toughness and ability to provide a good barrier to gases. To produce a product with high heat resistance and stiffness, glass fibers can be used to reinforce the polymer. Very few other plastics can be produced with such a wide range of properties.