TECHNICAL BULLETIN: BASICS OF BIODEGRADABLE PLASTICS

1 Introduction

Biodegradable materials are those that can be broken down into natural chemical elements by the exclusive action of biological agents, such as the sun, water, bacteria, plants or animals. In essence, many known substances can be considered biodegradable, the difference lies in the time it takes for biological agents to act to break them down into natural chemicals with little environmental impact.

Biodegradation is the characteristic of some chemical substances that they can be used as a substrate by microorganisms, which then use them to produce energy (by cellular respiration) and create other substances such as amino acids, new tissues and new beneficial organisms for the ecosystem. These microorganisms can be used in the elimination of certain pollutants such as urban organic waste, paper, hydrocarbons, among others. Plastics, on the other hand, are synthetic chemical substances with a macromolecular structure (very long chains formed by repeated simple chemical structures) and from the family of hydrocarbons, and in order to be biodegradable they require the help of special compounds [4]. Polymers derived from gas and oil are commonly added with a package of compounds that give them characteristics required for their use and final disposal, so that plastic products in large proportions, during their degradation processes, generate gases that can affect the energy balance of the biosphere, so the development of new additives that promote its biodegradation is of great importance.

2 Environmental impact of plastics.

In the atmosphere, the balance between the reception of solar radiation and the emission of infrared radiation returns to space the same energy that it receives from the Sun. This balancing action is called the energy balance of the Earth and allows the temperature to be maintained in a narrow margin that makes life possible.

It has been suggested that the action of the human being has altered this delicate balance, through the emissions of the so-called greenhouse gases1, which cause changes in the usual concentrations of certain gases in the atmosphere, such as: Water vapor (H_2O), Carbon dioxide (CO_2), Methane (CH_4), Nitrogen oxides (N_2O), Ozone (O_3) and Chlorofluorocarbons ($CFCl_3$)[5]. Plastic waste contributes to the generation of these gases when they are burned or discarded without control, although it should be noted that their impact is very low compared to the combustion of fluids used in power generation and internal combustion vehicles. To reduce this environmental impact, products have been developed whose addition in a low percentage (between 1 and 5%) in the form of a concentrate (masterbatch) to polyethylene (PE), polypropylene (PP), PVC, PET and other chain polymers carbon, make the polymer carbon chain 100% biodegradable in aerobic (in the presence of oxygen, such as compost, soil) and anaerobic (without oxygen, such as landfill) environments. This would mean that 100% of the polymeric carbon is completely used by microorganisms to transform it into CO_2 or into CO_2+CH_4 (carbon dioxide plus methane). It is presumed that there must be data, provided by these additive producing companies, that support this hypothesis.

There are two classes of additives called "biodegradable" on the market, the "oxo" and the

1 The greenhouse effect originates due to the fact that certain gases, components of a planetary atmosphere, retain part of the energy that the ground emits due to having been heated by solar radiation. It affects all planetary bodies endowed with atmosphere. According to the majority of the scientific community, the greenhouse effect is being accentuated on Earth by the emission of certain gases, such as carbon dioxide and methane, due to human activity.

"organic" (or "hydro"), which are sold as "masterbatches" (concentrates). The "oxo" additive promotes (in theory) the breaking of polymeric chains, thus making the polymer small enough to be used by microorganisms present in the waste disposal environment. The "organic" or "hydro" additive initiates or promotes microbial attack, and this, in some way, triggers the activity of microorganisms to break the carbon-carbon bonds of the polymer chain. Unfortunately, the scientific data and available literature do not fully support the claims being made in the marketplace. Many reports in the indexed literature include "biodegradation" in their titles. However, the meaning and context of the term is applied in a very broad and vague way, and rarely with reference to international regulations on the subject.

In many studies the losses of physical, chemical and mechanical properties are used to affirm that the material is "biodegradable". In some articles it is stated that there is biodegradation because microbial colonization is observed or the formation of biofilms is used to affirm that a material is biodegradable. Weight loss, reductions in molecular weight, carbonyl number, loss in mechanical properties, biofilm formation, microbial colonization do not confirm that microbes are actually using the carbon substrate of the polymer, nor do they provide the amount of carbon used or the time required to complete this microbial utilization [12].

3 Biodegradation mechanisms in polymers [2]

In the biodegradation of polymers, two key steps must occur. First, depolymerization, or chain breaking, to convert the polymer backbone into small oligomeric fragments. The process responsible for this step may be a non-biological degradation process, such as hydrolysis or oxidation, catalyzed by the aforementioned additives.

However, chain breaking can also be caused by a biological degradation process that can take place by the action of enzymes or products (such as acids or peroxides) secreted by microorganisms (bacteria, fungi, etc.), known as extracellular enzymes. , which can fulfill their function as "endo" (with a random break or internally linked in the polymer) or as "exo" (with a sequential break of the terminal unit of the monomer). The first step is important because the long structure of the material, similar to macromolecules, cannot pass through the outer membranes of living cells.

The second step, known as mineralization, occurs inside the cell where small oligomeric fragments are converted into biomass, minerals and salts, water, and gases such as CO_2 and CH_4.

Most of the methods that measure the limit of the biodegradation are respirometric, which are mainly related to the measurement of the evolution of carbon dioxide. Other methods include determination of weight average molecular weight (Mw) loss; measurement of loss of physical properties of the polymer (for example, tensile strength according to ASTM D3826); measuring the increase in the size of the microbial colony in the culture in contact with the material; and using known methods employing classical oxygen, (for example, the determination of biochemical (or biological) oxygen demand (BOD)) and radioactive tracking techniques using the radiocarbon isotope (carbon-14,14C).

Biodegradation involves the use of the plastic substrate as a carbon source for the metabolism of microorganisms. Biodegradation results from the production of CO2 in aerobic environments or CH4 in anaerobic environments, characteristic of a humic material. A humic material is an important component of the biodegradation process because it can improve the productivity of agricultural land. Therefore, compostable polymeric materials are a biological recycling of polymeric carbon. Composting is an accelerated degradation of heterogeneous organic matter by a mixed microbial population in a moist, hot, aerobic environment under controlled conditions. A typical compost system is comprised of a diverse microbial population in a moist, aerobic environment over a temperature range of 40 to 70°C.

The simple exposure of a polymeric material, natural or synthetic, to a biologically active environment does not guarantee its biodegradation. Some factors are important in biodegradation, including macromolecule size, structure, and chemistry; the microbial population and enzyme activity; and several specific environmental conditions are required such as darkness, high humidity, and suitable mineral and other organic variables, such as temperature, pH, and appropriate amounts of oxygen.

Conventional plastics resist biodegradation primarily because of their molecular size, structure, and chemical composition. Some research has conducted studies on the biodegradation of synthetic polymers and, in general, molecular weight has been found to be the critical factor in the process. For high molecular weight synthetic polymers, only aliphatic polyesters and some aliphatic-aromatic copolymers were established as biodegradable. It has been established that PE (polyethylene) oligomers become biodegradable at a Mw (weight average molecular weight) of less than 500, although more rigorous tests are necessary to confirm this assertion. Polyvinyl alcohol (PVOH) is probably the only carbon-chain synthetic polymer that is completely biodegradable, although recent studies indicate that PE can gradually convert to biodegradable with pre-treatment with surfactants or an oxidation process.

4 Biodegradation in commercial plastics (such as Polyethylene)[13].

Plastic is very strong, waterproof and still very cheap. Without plastic, it would be impossible to transport food without health risks to millions of households around the world and sell it at affordable prices. It is even difficult to imagine a packaging material with a lower environmental impact if the entire life cycle of the material is taken into account, from its synthesis as a raw material to its final disposal. The problem is that ordinary or recycled plastic that is discarded in the environment stays there for decades. Current technologies have made it possible to produce plastic items such as shopping bags, garbage bags, packaging, etc. suitable for your application, but will degrade harmlessly at the end of their useful life.

National and international studies are focused on finding a "green" formulation that complies with the intrinsic biodegradability cycle of biopolymers (Figure 1) and that allows obtaining a commercial polymeric material (such as Polyethylene), 100% biodegradable (Figure 2).

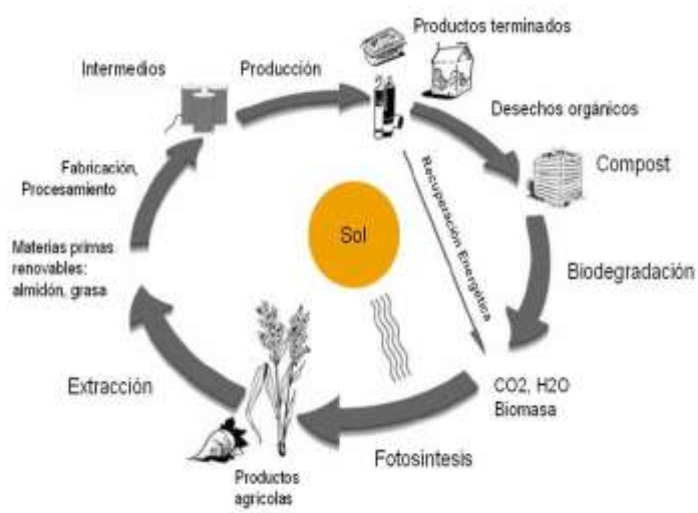

Figure 1 Cycle of Biopolymers [6].

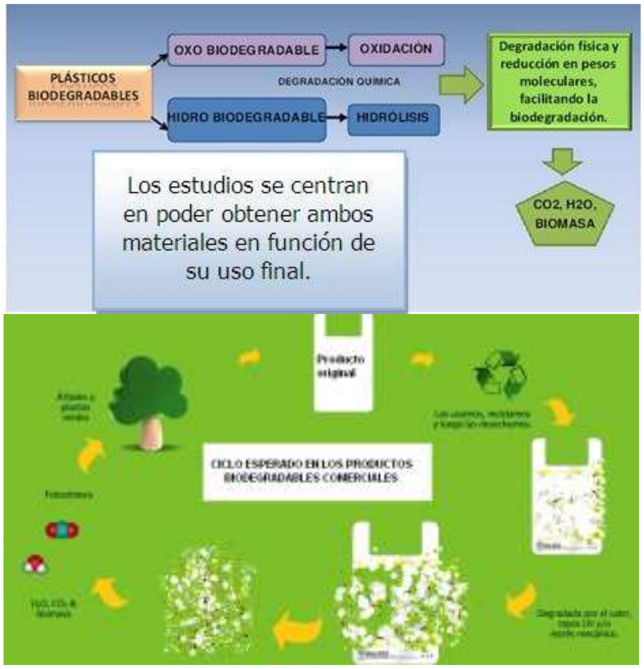

Figure 2 Biodegradation Cycle

These "green" plastics fall into two broad categories, namely:

1. Oxo-biodegradable plastics, manufactured as a by-product of petroleum refineries, degraded in the environment by an additive-initiated oxidation process and then biodegraded, after its molecular weight has been reduced to the point where natural microorganisms can gain access to the material.
2. Hydro-biodegradable plastics, wholly or partially made from crops, that biodegrade in a highly microbial environment, such as composting.

4.1 Oxo-biodegradable plastics

Producers of additives affirm that once an adequate proportion of their product is included in the resin, this additive, through an oxidation process2, will promote the breaking of the polymeric chains in order to obtain the carbon substrate that will serve as food for the microorganisms in the ecosystem.

Under aerobic conditions (in the presence of oxygen), the carbon is biologically oxidized into CO_2 within the matrix, releasing energy that is used by the microorganisms for their vital processes. Under anaerobic conditions (without oxygen), CO_2 and CH_4 are produced.

In short, Oxo-biodegradation would occur in two phases

1. Occurrence of oxidation / fragmentation under the combined action of:
   - Light
   - Heat
   - Mechanical stress and oxygen
2. Biodegradation
   - Characterized by the measurement of the CO2 emitted.

A measurement of the amount of CO_2, or CO_2 and CH_4, as a function of the amount of carbon introduced into the process, is a direct measure of the total amount of carbon substrate used by the microorganisms (percent biodegradation). It is on this basis that several standards (ASTM, ISO, EN, OECD) are based to measure the biodegradability of these new plastics, with the use that microbes give to chemical substances and biodegradable plastics [12]

Oxo-biodegradable Plastics (produced with polyolefin resins) which, as indicated above, are characterized by containing additives (formed by metal salts such as iron, magnesium, nickel, cobalt) that would cause the polymer to fragment. Ionic metals catalyze the natural degradation process, which in plastic materials is normally very slow, accelerating it from many years to a few months. In theory, these additives can be incorporated in a range of 1 to 4% in conventional plastic formulations, facilitating the polymer oxidation process and breaking the chains into small molecules, which would culminate in their degradation by biological action (Figure 3).

2 Oxidation is the chemical reaction from which an atom, ion or molecule gives up electrons, acquiring oxygen atoms present in the atmosphere.

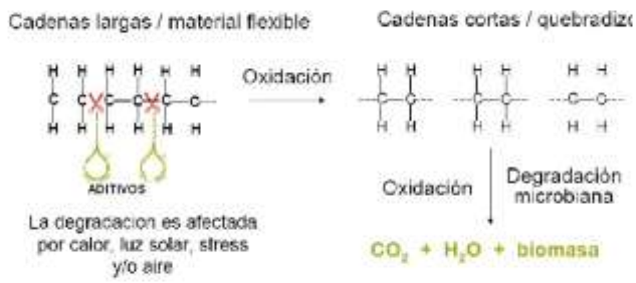

Figure 3 Action scheme of oxo-biodegradable additives.

However, oxo-biodegradable plastics have found strong opposition in the European Bioplastics (EB) association, which maintains that they do not comply with the EN 13432 standard, which establishes four basic principles that compostable materials must comply with:

- Composition (percentage of heavy metals and volatile solids)
- Biodegradation (measurement of the CO_2 emitted in a given time)
- Disintegration (capacity of disappearance of the compound)
- Quality of the final compound (agronomic and ecotoxicity tests)

In June 2005, EB published an article where it established its position in relation to oxo-biodegradable plastic bags in general. At that time they stated that these plastics do not comply with the European Directive 94/62/EC on Packaging and its Waste, with reference to its biodegradability (biodegradable under composting conditions), since polymer particles cannot be considered degradable (albeit very small) and some metallic compounds present in these products (catalysts), which is why they were classified and labeled under the EU Directive 67/548/EEC on Hazardous Substances, causing adverse effects in humans and the environment. In July 2009, it also maintained its position on so-called oxo-biodegradable plastics.
Some studies indicate that some heavy metals such as cobalt Co (II) have been found in higher concentration of 4,000 mg/kg in "oxo-biodegradable" additives. Other reports point out, for example, that so-called 'oxo-biodegradable' PE products cannot be fragmented into small enough particles after exposure to UV light or dry heating, since after fragmentation, PE still resistant to biodegradation, and therefore the potential for persistence in the environment and bioaccumulation of released metals and PE fragments in various organisms, such as occur in the oceans and landfills. Although, on the other hand, evaluations carried out by the companies that manufacture the additives, with high concentrations of metals coming from oxo-biodegradable (OBD) type bags, both in plants and animals, reveal that the presence of these metals does not exceed the limits permissible for the health of living beings [4]. All of the above indicates that it is necessary to delve into this topic in order to obtain additives that allow the proper use of the polymer in the form of a finished product, but also allow it to decompose in periods of time in accordance with environmental regulations.

4.2 Plásticos Hidro-biodegradables.

The main difference between Oxo-biodegradable and Hydro-biodegradable additives lies in the post-degradation residues. The process by which this type of biodegradation occurs is through **Hydrolysis[3]**. Originally, this type of degradation was only found in the so-called biopolymers such as polysaccharides and aliphatic polyesters, which are high-cost products that are not used in commercial packaging such as bags and covers; however, studies on the additivation that allows synthetic polymers to become compostable are being carried out at the international level worldwide, with results

3 Hydrolysis is a chemical reaction between water and another substance which, when dissolved in water, its constituent ions combine with hydronium, oxonium or hydroxyl ions.

interesting. Post-degradation residues are intended in this case to become "compost4" (Figure 4), to form part of the food chain of microorganisms.

Figure 4. Representation of compost.

One drawback that needs to be addressed is that compostable plastics are only economically and environmentally viable if there are industrial composting facilities available to process them in large quantities. There are not enough facilities in most cities or towns, and many composters do not use plastics of any kind in their feedstock, because it is expensive to separate compostable plastic from other plastics [13]. Another problem with compostable plastics is that it would harm the recycling process by entering a normal plastic waste recycling stream.

Compostable plastics are not really "renewable" when you consider the hydrocarbons burned by the machines that work the land, plow the land, make the fertilizers and pesticides and then transport them to the farm, sow the seeds, spray the crops, etc. Generally, these types of plastics are thicker and heavier; therefore, more trucks are needed to transport them, using more fuel and taking up more space on the road [13].

Analyzed from this global perspective, PE continues to be an excellent packaging material, with one of life cycles with less environmental impact, a high yield rate (based on the ratio kg of packaging / kg of packaged material) and that can be recycled. Despite this, the companies that produce and transform PE are working on mechanisms to reduce their environmental impact at the time of their final disposal.

On the other hand, alternatives that allow the reuse, recycling and recovery of plastic products should be encouraged, ensuring that, once their function has been fulfilled, they can be recovered and reprocessed to become new products, thereby reducing consumption. of scarce and non-renewable raw materials, reduce the energy cost associated with the conversion of those raw materials into semi-finished products and, above all, reduce the amount of waste that is dumped in landfills.

5 Feasibility, viability and challenge[1, 3]

The different known waste treatment systems are: recycling, composting, incineration and landfills, of which composting is the most suitable treatment for biodegradable plastics.

Composting is the decomposition process to which biodegradable waste materials are subjected, in order to obtain a product, compost, useful as a fertilizer. It is used in horticulture, agriculture and forestry as it improves the soil by increasing the drainage of clay soils, improves water infiltration and aeration of the same. For the composting process to take place, several conditions are needed that must all occur simultaneously: humidity, temperature, acidity, presence of oxygen and bacterial inocula.

Its economic viability, however, depends on the good separation of waste by consumers in different containers (the mixture of plastics would affect quality), and on the existence of a market for

4 Compost, compost or compound (sometimes it is also called organic fertilizer) is the product obtained from composting, and constitutes a "medium degree" of decomposition of organic matter, becoming a good fertilizer for plants.

the final product that can bear the costs of the process. Thus, one of the necessary requirements is a clear labeling that distinguishes them from conventional plastics and a good public awareness and education campaign.

Furthermore, the technical challenges of biodegradable plastics necessitate an integrated life cycle approach that requires an integration of policies, regulations and standards. It is essential to overcome the obstacles of fragmented regulations and standards that exist in many countries and especially in developing countries. Likewise, it must be taken into account that in many parts of the world the main problem related to plastic waste is sanitation in the collection areas, rather than its accumulation in landfills. Without an education process, there is a risk that biodegradable plastics will be thrown anywhere, with the false perception that they will be assimilated by the environment.

The use of biodegradable plastics will definitely help our communities in diverting organic waste from landfills to recycling. Why? For example, collecting organic waste in biodegradable and compostable bags will also provide an option for communities considering recycling their organic waste without having to make the heavy capital investments required to collect and separate organic waste. organic solid waste from those that are not.

Being aware of the global cost savings inherent in the use of biodegradable products is a matter of education. Over time, people and governments will come to realize the long-term economic advantages of biodegradable products, relative to solid waste disposal. Although there is currently no study carried out in this regard, it is expected that with the cost savings resulting from the elimination of the "remove the bag" operation, during the garbage burning processes, for example, the difference disappears in the overall cost between conventional and biodegradable polyethylene bags.

The other cause inhibiting market growth for biodegradable products may be more difficult to overcome. There is still a great mistrust of so-called "biodegradable" products among many people involved in solid waste management. This mistrust dates back to the late 1980s and early 1990s, when several major US companies introduced "biodegradable" products to the market, including garbage and waste bags.

When these products proved not to be as biodegradable as they claimed, attorneys general in ten US states filed lawsuits against the manufacturers for false or unsubstantiated environmental claims. It is at this point, therefore, where new technologies are being focused to meet the standards endorsed by the "American Society for Testing and Materials" (ASTM).

Currently you can already find supermarket bags, garbage bags, aprons, gloves, covers for agricultural and fruit and vegetable use made of biodegradable plastic. More products, such as wrappers for cigarette and chewing gum boxes, rigid products such as plastic bottles and cups will be available soon. In Europe, especially in Germany, Northern Italy, Holland and Scandinavia, the biodegradable bag is widely used in the collection of organic waste.

In short, biodegradable plastics can be recycled or incinerated, their nature does not affect any composting process or activity in which they are introduced. They are capable of carrying out physical, chemical, thermal or biological decomposition in such a way that the final products of composting will be carbon dioxide, biomass and water.

The first step is already given. The second consists of a global education on the subject, in general awareness of the benefits that biodegradable plastics will bring to our environment. It is not only about the creation of marking systems in which, preferably with colors or an international logo, the nature of said plastics is specified, but also about the will of all to allow them to carry out their work.

6 Bibliographic references.

1. Narayan, Ramani. [On line] Materials, "Biodegradability: Myths and realities", August 2010. [Quoted on: September 01, 2010.] www.plastico.com/.
2. Bastioli, Catia. "Handbook of Biodegradable", Rapra Technology, UK, 2005.
3. Stephen, Michael. "WHY DEGRADABLE?", la Global Plastics Environmental Conference (GPEC®), 2009.
4. Castellón, Hello. "Oxo-Biodegradable Plastics vs. Biodegradable Plastics: what is the way? Technical Services American Resin Corporation, CORAMER, C. A.
5. Application Department. "Introduction to polymers", Research and Development C. A. (Revised in 2009).
6. European Plastics (EB). Paper Position: "Recommendation on the implementation of compostable packaging", 2005.
7. European Plastics (EB). "Position on "Degradable" PE Shopping Bags", 2005.
8. Boletín Técnico Informativo N° 21 – Degradación de los Materiales Plásticos, Plastivida Argentina, 2006, www.plastivida.com.ar.
9. Barriga Salamanca, Ángela, "Plastics with eco-label, In the age of biodegradables", Revista del Plástico, 2004, http://www.plastico.com/tp/secciones/TP/ES/MA IN/IN/ARCHIVO/ARTICULOS/doc_35446_HTML.html?idDocumento=35446
10. Harrington, R. "UK Government questions oxo-bio"s eco-claims". Food Production Daily, 2010.
11. European Plastics (EB). Paper Position: "Oxo-Biodegradable" Plastics, 2009.
12. European Plastics (EB). Paper Position: "Life Cycle Assessment of Bioplastics", 2008.
13. IPCC (Inter-Governmental Panel on Climate Change o Panel Intergubernamental del Cambio Climático), 2007: Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team: Pachauri, R.K. and Reisinger, A. (publishing editors)]. IPCC, Geneva, Switzerland, 104 pp.

This Bulletin was prepared by the Marketing Management of Poliolefinas Internacionales, C.A. (POLINTER), with the support of Research and Development, C.A. (INDESCA), in Caracas- Venezuela, in 2011 and revised in July 2017.

If you wish to make any comments or suggestions, please write to us at the email address: info@polinter.com.ve, which can be accessed through our website www.polinter.com.ve or through our commercial agent: Corporación Americana of Resins, CORAMER, CA (http://www.coramer.com).