Screening of different methods to establish the biodegradability of packaging materials - a useful tool in environmental risk assessment approach

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Abstract. The huge development of petroleum-based synthetic polymers which are unable to degrade in landfill or compost-like environment had led to serious environmental issues. In recent years, there has been an increasing interest in the use of biodegradable materials for packaging, agriculture, medicine and other areas. A number of blends made from biopolymers can be the alternative of currently used synthetic polymeric materials. The most common and potential biopolymers are starch, cellulose, gelatin, chitosan, PLA, PHAs, etc. The main advantage of biopolymers is the capability of full biodegradation at accelerated rates, breaking down cleanly into simple molecules found in the environment, such as carbon dioxide, water or methane, under the enzymatic action of microorganisms, in certain period of time. The most used methods for biodegrading biopolymers are: mechanical biodegradation process, use of light and temperature in the biodegradation process and biodegradation in soil or compost, in controlled or environmental conditions. The aim of this study is to describe the mechanism of action over the polymeric materials of each of the processes mentioned above; each of these methods being a useful tool in environmental risk assessment approach.
Key Words: biopolymers, biodegradation, biodegradation methods, organic composite materials.

Introduction. A large variety of synthetic oil based polymers are produced worldwide, at around 300 million tons by year 2015. Many of these polymers are introduced into the ecosystem as industrial waste and as they are not biodegradable they become a major problem for the environment. Oil resources are still used extensively in the production of polymeric materials, leading to concerns regarding environmental sustainability, so the need to use biodegradable polymeric materials plays an important role in the replacement of conventional polymeric materials (Karak 2012). The use of polymers made from renewable and sustainable resources came in the response to this increasing awareness, in order to develop biopolymers constitutes an innovative and promising alternative to reduce greenhouse gas and toxic emissions.

Biopolymers are a wide variety of thermoplastic polymers that are derived from biological resources and fossil resources. Currently, biopolymers market is growing year by year. One major advantage of biopolymers is that they are breaking down cleanly into simple molecules found in the environment, such as CO_2, water or methane, under the enzymatic action of microorganisms, resulting fully biodegradation at accelerated rates (Arrieta et al 2014).

Knowing all of the above, we can see that there is an increased interest in the production and use of biodegradable polymers made from renewable resources, both economically and in terms of waste management and carbon emissions (Pepic et al 2008).

Results and Discussion. In recent years, research conducted in the field of biopolymers has been focused on achieving 100% organic composite materials by replacing non-biodegradable polymeric matrix with biodegradable ones. There are many biodegradable natural polymers such as polysaccharide derivatives, proteins, polyesters, lignin, lipids (fats and oils) and others (Madhavan Nampoothiri et al 2010; La Mantia & Morreale 2011).

The capacity to biodegrade is the property of a material (including polymeric material) to alter its chemical structure under the action of various species of microorganisms. The attack of microorganisms on plastic materials occurs through a complex mechanism that takes place in three phases on the basis of the alteration of the substrate. Primary biodegradation is characterized by the fact that it only produces changes in the functional groups of a polymer without affecting its skeleton. Complete biodegradation involves the complete destruction of the macromolecular support simultaneously with the formation of reaction byproducts (Pelmont 2005).

Many solutions have been proposed for the management of waste plastics, such as recycling, incineration and degradation. The recycling process is not desired because it does not produce quality waste due to the heterogeneous nature of plastics. Incineration of plastics eliminating toxic gases and vapors may be dangerous to health. Due to the coexistence of biotic and abiotic processes, the whole mechanism of degradation of polymers can be considered as the degradation in the environment. A variety of chemical processes, physical and biological degradation, and thus various mechanisms can be involved in the degradation of a polymer (Park & Xanthos 2009).

All polymers go through a few biodegradation stages, as it is mentioned below (Lucas et al 2008; Karak 2012).

- ✓ Biodeteroration stage - The combined action of microorganisms and other organisms in decay of the biodegradable material in small fractions.
- ✓ Depolymerization stage - The microorganisms secrete catalytic agents (enzymes and free radicals) capable of gradually reducing the molecular weight of the polymeric molecules. Some of the polymer molecules are recognized by receptors of microbial cells and can pass through the plasma membrane. Other extracellular molecules remain in the surroundings and may be subject to various changes.
- ✓ Assimilation stage - In the cytoplasm, the molecules transported integrate into microbial metabolism in order to produce energy and new biomass.
- ✓ Mineralization stage - Simple molecules like CO_2, N_2, CH_4, and H_2O various salts of intracellular metabolites that are completely oxidized are released into the environment. This stage is called mineralization.

Polymeric materials that are exposed to environmental conditions (weather, aging and burial) can undergo some transformations (mechanical, light, thermal, chemical) more or less important. These environmental exposures help polymeric materials to biodegrade. In most cases, abiotic parameters contribute to the weakening of the polymer structure and thus promote undesired alterations (Helbling et al 2006; Ipekoglu et al 2007). Sometimes these abiotic parameters are useful as synthetic factors or initiate the process of biodegradation.

Mechanical degradation. Mechanical biodegradation can occur due to mechanical compression, tension and/or shear forces. The causes that make these forces occur are numerous, for example constraints during the installation process, aging due to charging, water and air turbulence, snow pressure and damage done by birds. Frequently, at microscopic level the damage is not immediately visible, but the molecular degradation can begin.

Mechanical factors do not predominate during the biodegradation process, but mechanical damage can activate or accelerate the biodegradation process (Briassoulis 2005). In environmental conditions, mechanical stress is acting in synergy with other abiotic parameters like temperature, solar radiation and chemicals to speed up the degradation process.

Hydrolytic degradation of polymers. Synthetic polymers that have hetero links in their structure are often susceptible to hydrolytic degradation, followed by microbial bio-assimilation, while polymers with carbon bonds are subjected to the process of degradation of lipid peroxidation, and the carboxylic acids of low molecular weight formed from this process are further used as carbon source by bacteria and fungi (Ojeda et al 2009).

This process can be controlled by the peroxidation process. It is possible to control photolysis, photo-biodegradation, hydro-thermal biological degradation and biodegradation using chemical structures and additives (Eubeler et al 2009)

The polymeric materials can be used as a potential source of carbon and energy for heterotrophic microorganisms, including bacteria and fungi, and additives added to the polymer matrix can serve as nutrients for the microorganism's degradation process. The uptake of polymer by microorganisms is limited by the structure of their cell membrane. Degrading enzymes can help decrease the size and molecular weight of dimers, monomers and oligomers, prior to the takeover by a wider range of microorganisms (Eubeler et al 2009).

Photo-induced degradation of polymers. Most polymers can be degraded by photolysis by lowering the molecular weight of molecules. Accelerating degradation is usually possible using varying light intensity, but the photo-degraded polymers are only small particles which are still intact and able to act as stressors in the environment (Eubeler et al 2009). There are several photosensitive materials in the market. The energy carried by photons can create unstable states for different molecules. The energy transfer can be achieved by photo-ionization, luminescence, fluorescence and thermal radiation. This strategy is used by manufacturers of polyolefins to enhance the biodegradability of plastic bags, packaging, agricultural films, etc.

Some materials are photosensitive. The energy carried by photons can create unstable states in different molecules. The energy transfer can be achieved by photoionization, luminescence, fluorescence and thermal radiation. Sometimes, the strength of the material can be affected by contaminants that will occur in the manufacture process. In other cases, the photosensitive molecular structure is added on purpose into the polymer matrix to induce the process of biodegradation using light (agencies prooxidant that can be activated depending on light intensity and exposure time). This strategy is used by the manufacturers of polyolefins to enhance the biodegradability of plastic bags, packaging, agricultural films, etc.

In abiotic degradation, the action of sunlight is one of the most important parameters that need to be taken into consideration. Norrish reactions can induce photo degradation reactions that transform polymers expressed by photoionization (Norrish I) and chain scission (Norrish II). Norrish photolysis may cause reactions, and/or crosslinking reactions or oxidation processes (Nakamura et al 2006).

Biodeterioration processes of polymers. Biodeterioration is superficial degradation that modifies the mechanical, physical and chemical properties of a given polymer. It is done mainly by microorganisms that grow on the surface or inside the material. Microbial growth depends on the formation and properties of polymeric materials. Specific environmental conditions are also important parameters. Microorganisms involved in biodeterioration are diversified and belong to bacteria, fungi and lichens species. They may form consortia with a structured organization called biofilms. This microbial carpet is working in synergy and causes serious damage to certain plastic materials. The development of various microbial species in a specific order, increase the biodeterioration process, thereby facilitating the production of simple molecules. All these substances act as sources of carbon and nitrogen, as well as growth factors for the microorganisms. Recent studies show that air pollutants are potential sources of nutrients for certain microorganisms (Lucas et al 2008). The most important factor in terms of biodegradation is aerobic biodegradation using bacteria or fungi (Eubeler et al 2009).

Composting is one of the oldest methods used to process organic waste. The biological properties of the compost are equally important for the conservation and application, as well as its chemical properties. Respiratory activity composting is one of the main indicators of maturity and usefulness in various applications (Ozimek & Kopec 2012). The compost is defined as an organic matter that has been decomposed and recycled for fertilizing and soil amending purposes. Modern, methodical composting is a multi-step, closely monitored process with clearly defined inputs of water, air, and a precise carbon-nitrogen rate.

Physical method. Microbial species can adhere to the surface of the material due to secretion of a kind of glue. This substance is a complex matrix made of polymers (ex. polysaccharides and proteins). This slime infiltrates the porous structure and changes the pore size and distribution and the degree of humidity. This microbial matrix function is to protect the microorganisms against adverse environmental conditions (eg. exposure to UV light).

Chemical method. Extracellular polymers produced by microorganisms can act as surfactants that facilitate the exchange of the hydrophilic and hydrophobic phases. These interactions are favoring the penetration rate of microbial species. Biodeterioration may also be the result of chemical oxidation processes. Some bacteria and some fungi can assimilate chemoliotrofe iron cations and/or magnesium matrix by oxidative reactions.

Enzimatic method. Some material considered recalcitrant polymers (e. g., polyurethane, polyvinyl chloride and polyamide) are subject to microbial deteroration. The vulnerability of these polymers is attributed to microbial biosynthesis of lipases, esterases, and proteases. The enzymes involved in the biodeterioration require the presence of some cofactors (cations present in the matrix material and coenzymes synthesis by microorganisms) to break up the specific (Pelmont 2005).

Biodeterioration of thermoplastic polymers can be achieved through two different mechanisms: erosion of the entire material or erosion of the surface of the material. In the case of mass erosion, lost fragments of the whole mass of the polymer and molecular weight change due to breaking ties. This is caused by chemical lysis (e. g. H_2O, acids, bases, and transition metals radicals) or by radiation but not by enzymes.

Thermal degradation. Thermal degradation of the thermoplastic polymer occurs at the melting temperature when the polymer is transformed from solid to liquid. In general, the ambient temperature is lower than the melting point of the thermoplastic polymer. However, several thermoplastic polymers, such as PCL, or other composite materials exhibit a melting temperature close to ambient temperature. This is called the stage of thermophilic composting. Otherwise, the temperature may influence the organization of macromolecular framework.

Industrial thermoplastic has different properties depending on the nature and proportion of monomers which produce the final copolymer material. Inside the crystalline regions, there is a crystal polymorphism which may influence biodegradation.

Chemical degradation. Chemical transformation is still a very important parameter in abiotic degradation. Air pollutants can interact with polymers and alter their macromolecular properties (Briassoulis 2005). Among the chemicals that cause degradation, oxygen is the most powerful. The atmospheric form of oxygen (O_2 or O_3) attacks the covalent bonds producing free radicals. Oxidative degradation depends on the polymers structure. The oxidation may be concurrent or synergistic to degradation by light to produce free radicals.

Well organized molecular framework (crystalline domains) prevents diffusion of oxygen and water, this way limiting chemical degradation. Oxidative and hydrolytic degradation of the material is carried out easier in certain regions molecular disorganized (amorphous domains).

Hydrolysis and pyrolysis of polymers. Hydrolysis is another way by which polymers can undergo chemical degradation. Water degradation is possible only if the polymer contains hydrolysable covalent bond groups as esters, ethers, anhydrides, amides, carbamide (urea), ester amide (polyurethane), and so on. The hydrolysis is dependent on parameters such as water activity, temperature, pH and time. The design of materials with controlled life-span requires choosing specific monomers to obtain a copolymer with the desired hydrophilic characteristics.

Pyrolysis is the chemical decomposition of a substance by subjecting it to extreme heat and it is a method of treatment for polylactic acid. Co-pyrolysis techniques have received attention in recent years because it represents an alternative method for converting waste into fuel; specific benefits of this method include: reduction in waste, chemicals recovery and replacement of traditional fuels (Wang & Aimin 2008; Xiaoqing et al 2010; Raquez et al 2013).

Biofragmentation. Fragmentation is a necessary phenomenon necessary for later stage called assimilation. A polymer is a molecule with a high molecular weight that can not pass the cell wall and/or the cytoplasmic membrane. It is essential for splitting several links to provide a mixture of oligomers and/or monomers. The energy needed to fulfill the split may have different origins: heat, light, mechanical, chemical and/or biological. Abiotic involvement has been described previously. This section focuses on the biological aspect of fragmentation. Microorganisms use different ways to rip polymers. They secrete enzymes or generate free radicals.

Enzymes are proteins that lower the catalytic activation energy of molecules promoting chemical reactions. These proteins have a remarkable diversity and specificity, but are slightly distorted by heat, radiation, surfactants, and so forth (Lucas et al 2008).

Conclusions. Biopolymers are a wide variety of thermoplastic polymers that are derived from biological resources and fossil resources and one major advantage of biopolymers is that they are fully capable of biodegradation at accelerated rates, under the enzymatic action of microorganisms, or under some abiotic factors.

The biodegradation of different packing materials is a very important process for our environment health. This review presents screening of different methods to establish the biodegradability of packaging materials.

The four stages of a biodegradation process are: biodeterioration stage, depolymerization stage, assimilation stage and the mineralization stage in which the simple molecules like CO_2, N_2, CH_4, and H_2O various salts of intracellular metabolites that are completely oxidized are released into the environment.

Biodeterioration is superficial degradation that modifies the mechanical, physical and chemical properties of a given polymer. It is done mainly by microorganisms that grow on the surface or inside the material. Microbial growth depends on the formation and properties of polymeric materials. Specific environmental conditions are also important parameters. The biodeterioration can be done either by chemical method or by enzymatic or physical methods.

Knowing all of the above, we can see that there is an increased interest in finding and studying more methods from which the biodegradation process will become more efficient and the ability to produce biodegradable polymers made from renewable resources will be a goal for the next research studies.

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