Abstract. In this paper an overview of novel biodegradable polymers for food packaging is presented. The aim was to present factors influencing polymer degradation and biodegradation in various environments. It was noted that biodegradable polymers are an imperfect alternative for classical polymers and their decomposition strongly depends on degradation environment. It was also shown that there are various approaches in different countries to certification of biodegradable polymer materials, which rather complicates its application than promotes it.

Keywords: polymers, degradation, biodegradation, packaging, poly(lactic) acid, starch, Mater-Bi.

1. Introduction

Due to their durability and resistance to degradation classical polymers (such as those products packaging is made of) tend to stay within the environment long after their final use. As a result, polymers find their way into diverse eco-systems of both terrestrial and marine organisms. There are a lot of studies, which concern the influence of plastics on ecosystems of many organisms.

It is terrifying that many seabirds and mammals die every year from ingestion of traditional plastic. Worldwide statistics show that 43 percent of marine mammal species, 86 percent of sea turtle species, and 44 percent of sea bird species are susceptible to ingesting marine plastic debris [1]. In Newfoundland, 100 hundred marine mammals are killed annually through suffocation from polymer material [2]. Unfortunately, the life of plastic bags does not end with the death of one animal; after a bird or a mammal dies and decomposes the plastic bag will again be released into the environment.

Moreover marine turtles mistake plastic bags for jellyfish, which can look similar while floating on the water. It is common in every region in the world that turtles ingest plastic [3-5]. It can be found in the literature that plastic is the most reported debris found in marine turtles and other marine animals [6].

Due to the numerous problems caused by plastic (traditional) shopping bags, attitude towards them has turned to negative over the world. As a result, governments have taken action to limit their use. A variety of laws to reduce plastic (traditional) dumping into the environment was implemented all over the world. In Europe the Packaging and Packaging Waste Directive (94/62/EC amended by 2004/12/EC) is the tool to reduce packaging and encourage recovery and recycling of materials. The EU countries are obligated to recover and recycle a defined percentage of waste packaging in relation to the aggregate weight of packaging introduced into the market [7].

Based on the review of plastic bag legislation from 2006, different countries found diverse solutions. For instance Bangladesh has introduced bans on bags of polyethylene, whereas France only for all non-biodegradable grocery plastic bags. In European countries like Denmark and Ireland taxes for bags with particular wall thickness [8, 9] were introduced. From 2009, in Poland most of the shops charge a fee from clients for classical plastic bags and some introduced the paper bag.

Generally, marine debris, including plastic bags, drift across political boundaries, thus local or national legislation can solve the problem only partially. The best remedy in this case would be a worldwide agreement, but such agreement does not exist so far. There are several international conventions which deal with marine debris, but they do not have adequate restricting force to ban the flow of plastic from land to sea. Unfortunately, existing treaties have no appropriate tools and mechanisms for solving the problem. The only global treaty that deals with land-based sources of marine debris is the United Nations Convention on the Law of the Sea (UNCLOS). The above-stated means that the problem of plastic bags is still open.
2. Degradation versus Biodegradation of Polymeric Material

The exposure of polymers to environmental conditions like weathering, ageing and burying can cause mechanical, thermal and chemical transformations of a material. Generally, these abiotic parameters make a contribution to the change of polymeric structure and properties [10, 11]. The environmental conditions are usually useful factors to initiate the biodegradation process. Several researches show that abiotic degradation precedes microbial action. That is the reason why the abiotic degradation should not be ignored [12, 13].

Compression, tension, shear, and other forces can contribute to mechanical degradation of a material. These factors do not play a prevailing role in the whole biodegradation process, but can stimulate or sustain it. Moreover the damages can be present at the molecular level, not visible through the microscope. Frequently mechanical degradation can act together with other abiotic parameters like elevated temperature, solar radiation and chemicals [14]. High-energy radiation in the ultraviolet part of the spectrum activates the polymer electrons to higher reactivity and can induce oxidation or cleavage. Such sensitivity to light can be utilized in persistent polymers to enhance their degradability [15]. Tsuji et al. investigated the photodegradation of poly(L-lactide) (PLLA) and poly(ε-caprolactone). They prove that the Norrish II mechanism takes place in the crystalline lattice of PLLA film [16].

Thermal degradation is also an important parameter in the abiotic degradation and in thermoplastic polymers occurs at the melting temperature. Usually, the ambient temperature is lower than the melting point of such polymers. However, some thermoplastic polymers as PCL with \( T_m \approx 333 \text{ K} \) or composite materials as MaterBi with \( T_m \approx 337 \text{ K} \) demonstrate melting temperatures near to environmental conditions. This is the case for the thermophile stage of composting.

Chemical alteration is another significant parameter for polymers. The most powerful agent provoking the degradation are atmospheric forms of oxygen (\( i.e. \) \( \text{O}_2 \) or \( \text{O}_3 \)), which attack covalent bonds, creating free radicals. The degradation rate depends on the polymer structure and unsaturated links or branched chains, which accelerate this process.

Hydrolysis is a kind of chemical degradation. The polymers have to contain hydrolysable covalent bonds, which are present in ester, ether, anhydride, amide, urea, and urethane groups. It depends on factors like water activity, temperature, pH, and time. The domain morphology is also important. Well-organized crystalline parts of the polymer limit the oxygen and water diffusion, which makes polymer more resistant. Disorganized amorphous regions are more susceptible to oxidative and hydrolytic degradation [14].

Biodegradation is the process in which substances are broken down by the action of microorganisms. The term is often associated with ecology, waste management, and plastic materials (due to their long lifespan) [17]. Nowadays, the complex nature of biodegradation is better understood. It involves several steps like: biodeterioration, biofragmentation, assimilation, and mineralisation [14].

Biodeterioration proceeds on the surface of the polymer where its mechanical, physical and chemical properties are changed. Generally, the term refers to the activity of microorganisms growing on a given material [18, 19]. Bacteria, protozoa, algae, fungi, and lichenaceae are organisms, which are involved in the biodeterioration. They cause the changes on the surface of a material. While microbial species are developing on the polymer, the biodeterioration increases, facilitating the production of simple molecules. Polymers are the carbon and nitrogen sources and growth stimulators for microorganisms [14]. Microbial species can secrete a kind of glue (made of polymers like polysaccharides and proteins) and adhere to polymer surfaces. This substance penetrates into porous structures and alters moisture amount and thermal transfers. The microorganism’s growth in the material increases the size of pores and provokes cracks. As a result, the structure of the material is destabilized [20]. The microbial species that are developing on the polymer surface also contribute to the chemical biodeterioration. Chemolithotrophic bacteria release inorganic compounds like ammonia, nitrates, hydrogen sulphide, thiosulphates, and elementary sulphur, whereas chemoorganotrophic microorganisms liberate organic acids as oxalic, citric, gluconic, glutaric, glyoxalic, oxaloacetic, and fumaric acids. These compounds can alter material surface.

Biofragmentation is an important phenomenon necessary for the following assimilation of the molecules. During this process a high molecular weight polymer is fragmented into a mixture of oligomers and/or monomers. The energy needed for scissions may be of diverse origin as thermal, light, mechanical, chemical, and/or biological. The abiotic involvement was described previously. Microorganisms secrete specific enzymes or generate free radicals to cleave polymers. Oxidoreductases and hydrolases are mainly concerned in the biofragmentation process. Cellulases and amylases belong to hydrolases group and are synthesized by soil microorganisms. They hydrolyse renewable polymers like cellulose and starch. Starch in some commercial composites is co-extruded with polyesters (\( e.g. \) Mater-Bi\textsuperscript{®}) to enhance the biodegradability. If low molecular weight molecules can be identified within degradation media, the polymer is considered as fragmented. A lot of analytical techniques, which are useful
to separate oligomers with different molecular weights, like GPC, HPLC for liquid phase or GC for gaseous phase, are currently available.

The assimilation is the last step of biodegradation process. This phenomenon consists in integration of atoms from fragmented polymers inside microorganisms’ cells. The microbial species assimilate the compounds from fragmentation process, which can stimulate or even inhibit the growth and reproduction of organisms. Monomers are transferred through the cellular membranes with the help of special membrane carriers. Other molecules to which membranes are impermeable can undergo biotransformation reactions to absorbable products.

3. Biodegradable Polymers for Food Packaging

Polyethylene and polypropylene, which are conventional polymers, last in the environment for many hundred years after disposal. Mainly, they are applied for production of plastic bags, which are disposed after one single use. Furthermore, food and other biological substances often stain packaging materials, which makes physical recycling of these materials impractical and generally undesirable. On the contrary, the science offers biodegradable polymers, capable of degrading after disposal in bioactive environments by the enzymatic action of microorganisms such as bacteria, fungi, and algae.

Cellulose is a well-known natural polymer, which after chemical modification is applied in a remarkably diverse set of applications. Until 1993, plastic-grade cellulose acetates were considered as non-biodegradable materials due to their high degree of modification (or substitution) [21]. Nevertheless, studies in simulated compost environments have shown that cellulose acetates with degrees of substitution of up to 2.5 are biodegradable [22]. A decrease in the degree of substitution of cellulose acetate from 2.5 to 1.7 results in a large increase in the rate of its biodegradation. Eastman Chemical Company has developed fully biodegradable cellulose acetates, which are commercially available and find application in osmotic drug delivery and taste-masking, coatings, pressure-sensitive tapes, packaging and wood sealers [23, 24].

Poly(ε-caprolactone) (PCL), polylactidalkanoates (PHAs) and poly(lactic acid) (PLA) are the biodegradable polymers which belong to polyesters. They are water-resistant and may be processed with melt-extrusion method into sheets, bottles, and diverse shaped products, which makes these plastics very promising for use as biopolymers [21].

Polylactidalkanoates are produced from renewable resources by bacterial fermentation of sugar and lipids. They are thermoplastic or elastomeric polymers, depending on the monomer used in the synthesis. These materials, alone or in a blend with synthetic polymer or starch, give packaging films [25]. The polyhydroxybutyrate (PHB) is the most common type of bioplastic polyester, which is obtained in the polymerization of 3-hydroxybutyrate monomer, with properties similar to polypropylene although more stiffer and brittle [26]. Scientists from China produced several PHA polymers from food wastes used as carbon source. The produced materials had various physical and mechanical properties, like flexibility, tensile strength, and melting viscosity. Such production of polylactidalkanoates is rather inexpensive, but until now the project has not found commercial application [27].

Poly(ε-caprolactone) is a thermoplastic biodegradable polyester produced by chemical conversion of crude oil, followed by ring-opening polymerization. It has good water, oil, solvent, and chlorine resistance. Moreover PCL has a low melting point of 331–333 K and low viscosity. PCL is not used for food packaging; it can be mixed with starch to reduce manufacturing costs for refuse bags production [21, 26]. According to the available literature, PCL (and its modifications) undergo biodegradation in the presence of specific microorganisms. Its degradation occurs to different extents, depending on different environments [28-35]. La Carra et al. [30] examined the degradation of pure PCL as a result of the attack by various microorganisms. They observed the growth of microorganism (Pseudomonas, Erwinia and Bacillus) was rising in the presence of the tested polymers. It has also been stated that these microorganisms are capable of biodegrading not only PCL but also other polymers [36].

3.1. Starch Based Polymers

Starch is an abundant, inexpensive, and annually renewable material available from potatoes as well as corn and other crops. It is composed of amylose, a mostly linear alpha-D-(1-4)-glucan and amylopectin, a branched alpha-D-(1-4)-glucan, which has alpha-D-(1-6) linkages at the branch point. Ratios of amylose and amylopectin vary with the starch source [21, 37] (Fig. 1).

Starch can be thermoplastic (TPS), which is obtained by technology similar to extrusion cooking. It has destructurized, noncrystalline form, produced by various heat application. From pure thermoplastic starch, traditional plastic goods can be obtained. However its sensitivity to humidity makes it unsuitable for most applications [21, 37].

Starch-based biopolymers can be obtained by blending or mixing starch with synthetic polymers. The properties and morphology of these blends can be adjusted easily and efficiently. Full advantage of this phenomenon was taken by Novamont Company to produce Mater-Bi® material. It is mainly formed into films and sheets, which found application in agriculture, waste management, packaging, personal care & hygiene, accessories for animals.
According to the Novamont Company TPS can be blended with synthetic polymers to create three families of materials [37]:

- TPS in composition with synthetic copolymers with hydrophilic and hydrophobic groups (i.e. copolymers of vinylalcohol, polyester-urethanes, ethylene-acrylic acid copolymers, etc.); TPS blended with incompatible synthetic polymers (cellulose derivatives, aliphatic polyesters, etc.);
- TPS blended with incompatible or slightly compatible synthetic polymers, which is partly complexed and/or compatibilised.

Under the Mater-Bi® trademark four classes of biodegradable materials based on thermoplastic starch in composition with synthetic component are produced [37]:

- **Class Z** made of TPS and poly(ε-caprolactone). It is destined for films and sheets. The biodegradation time is 20–45 days in composting conditions. This class includes four grades: ZP03U/A, ZP02U/A, ZI01U/T, which can be processed by film blowing, and ZI01U for extrusion, calendering, and injection moulding.
- **Class Y** composed of TPS in a dispersed form and cellulose derivatives. Biodegradation time of 1 mm thick foil is about 4 months in composting conditions and 30 days in anaerobic conditions. It has one grade YI01U destined for injection moulding.
- **Class V** with the content of TPS more than 85 % and biodegradation time even shorter than Z class. It includes two grades: PE02U for foaming and PE03U for injection moulding. It is suppose to be a replacement for polystyrene.
- **Class A** made of starch and ethylene vinyl-alcohol copolymer. The material is biodegradable during 2 years in an environment simulating a sewage sludge treatment plant, but not compostable. It is used in applications where compostability is not required.

Mater-Bi products are thermoplastic materials based on starch, which after proper disposal are completely biodegraded. The producer believes that living microorganisms transform Mater-Bi products into water, carbon dioxide, and/or methane [39]. The literature offers little information about degradation of Mater-Bi and its composites. There is a small number of studies focusing on the actual biodegradability of these materials.

In 1997 Bastioli [37] described types of Mater-Bi compounds and briefly reported on the effect on biodegradation due to starch presence.

Alvarez et al. [40] also found that Mater-Bi Y/sisal fibres composites are potentially degradable in natural environment or landfills. Starch was more susceptible for degradation than fibres. It was also claimed that the composites demonstrated a reduced water sorption in comparison with the pure polymer.

Alvarez [40] investigated degradation in soil of sisal fibre/Mater Bi-Y biocomposites. The degradation during indoor soil experiments with a mixed microbial population were studied by weight loss, mechanical tests, and microscopic observations. It was found that after 12 months the mechanical properties decreased drastically for the samples filled with fibres and after 15 months of incubation they undergo macroscopic deterioration.

In other research [41] it was found that biodegradation of three commercial polymers: poly(3 hydroxybutyrate) (PHB), a synthetic aliphatic polyester Sky-Green (SG) and a starch-based polymer Mater-Bi (MB) was most advanced in the activated sludge soil among forest soil, sandy soil, and farm soil. *Penicillium simplicissimum* and *Paecilomyces farinosus* degraded PHB moderately well, while the degradation rate by *Aspergillus fumigatus* was lower than expected. *P. simplicissimum* showed the highest degradation rate for Sky-Green and *A. fumigatus* was most effective in degrading Mater-Bi. The
influence on degradation of isolated fungi was collated with incubation temperature. Both SG and MB showed higher degradability at 301 K than at 310 K, and for PHB it was the highest at 310 K.

Degradation of Mater-Bi polymer was also investigated in the compost with sewage sludge by Rutkowska and co-workers [33]. The degradation process of Mater-Bi Y Class samples was verified by weight changes and macroscopic observation. The results of sample disposal in the standard environment under controlled conditions differed from those investigated in natural weather-dependent composting conditions. In the first environment the polymer lost more than 90% of weight, while in the second only 20% after 4 months.

3.2. Poly(Lactic Acid)

Poly(lactic acid) can be synthesized by biological and chemical methods. The first one is more environmentally friendly, due to its renewable character. It is based on starch and other polysaccharides fermentation. It can be produced from corn, sugar beet, sugar cane, potatoes, and other biomasses [42]. The second one was developed by industrial sector.

Carothers developed the first polymer made from lactic acid with low molecular weight and poor mechanical properties in 1932. In 1954 DuPont patented the polymer with high molecular weight and better properties [43].

Cargill Dow LLC and Mitsui Toatsu developed two different chemical methods to produce PLA. Cargill’s solutions apply solvent-free continuous process and a novel distillation method. On the contrary, the other company converts monomer directly to high molecular weight PLA by a solvent-based process with the azeotropic elimination of water by distillation [14]. Nowadays, the Cargill Company uses specially engineered yeast, which converts sugar to lactic acid. It is an innovative solution, which reduces costs and environmental footprint.

Lactic acid (2-hydroxy propanoic acid) contains an asymmetric carbon in its structure, which gives two optically active configurations. D- and L-enantiomers (Fig. 2) can be produced by bacteria and the amount of both is adjustable, but some bacteria can produce only one isomer, whereas the chemical process gives the racemic mixture of both D- and L-enantiomers.

These two forms vary in chemical and physical properties because of the presence of a pendant methyl group on the alpha carbon atom. PLLA has a crystalline structure, while PDLLA (composed of DL-lactic acid monomers) is anamorphous biodegradable polymer. Poly(L-lactic acid) has better mechanical properties and is less susceptible to degradation due to more ordered and compact structure. These enantiomers have also different glass-transition temperature: $T_g$ for PLLA is 328–338 K whereas for PDLLA – 332 K [42].

Nowadays, there are several methods used for the synthesis of PLA. Big companies like Cargill (the owner of NatureWorks), PURAC Biomaterials (from the Netherlands) and other are improving production methods of poly(lactic acid). Four basic methods of PLA synthesis can be found in the literature (see Fig. 3).

The nomenclature of poly(lactic acid) is connected with different routes of preparation. Polymers derived from lactic acid by polycondensation are related to poly(lactic acid) whereas the ones obtained from lactide by ring opening polymerisation are named polylactide. Generally both types are referred to PLA [44].

PLA is presently used in packaging (films, thermoformed containers, and short shelf life bottles). Cargill Dow LLC obtains fibers by conventional melt-spinning processes for clothing and other uses. PLA products have a silky feel, durability, and good moisture-management properties (moisture is quickly wicked away from the body, keeping the wearer dry and comfortable) [14].

High molecular weight poly(lactic acid) is water insoluble. If water penetrates into the bulk of the polymer matrix, PLA is subjected to degradation as a result of hydrolysis on the ester group. The chemical bonds in the amorphous phase are attacked and long polymer chains are fragmented into shorter ones. Water soluble oligomers, which are close to the surface, are able to liberate from the matrix. Therefore, microorganisms can assimilate these degradation compounds. During the degradation process the amount of carboxylic chain ends increases, which autocatalyses the esterhydrolysis. Whereas water soluble oligomers (entrapped inside the matrix) contribute to the autocatalytic effect [42, 45].

Poly(lactic acid) is totally biodegradable when composted at 333 K and above. The first step of the degradation is proceeding by hydrolysis to water-soluble compounds and lactic acid. Then microorganisms are able to metabolize these products into carbon dioxide, water and biomass (Fig. 4) [17].

The biodegradation mechanisms of PLA are influenced by numerous factors, including the structure and hydrolysis media. The diffusion coefficients of the soluble oligomers depend mainly on molar mass, degree of swelling of the matrix, macromolecular conformation, rigidity, chemical structure, molecular weight distribution, impurity/monomer residue, stereochemistry, chain mobility, and crystallinity. The amorphous domain is more susceptible to biodegradation process [44].
Kale with co-workers [46] tested polylactide bottles in real and simulated composting conditions. The authors analyzed molecular weight, the percentage of carbon dioxide released from organic carbon content of the sample. After 15 days in real composting conditions, the macroscopic observations showed that the bottle was already in pieces, mostly from parts with higher thickness. Agarwal and team [47] wanted to determine if microbes significantly enhance the degradation of PLA. They prepared two reactors: biotic (typical solid composting) and abiotic with sterile water. The biodegradation indicators were oxygen and carbon dioxide concentrations, weight loss, average molecular weight measured with Gel Permeation Chromatography, structural order, and crystallinity of polymer determined by X-ray Diffraction. As a result they found that there was only slight difference in PLA properties between the biotic and abiotic systems. Thus, it can be stated that no important microbial enhancement of degradation occurred. It is interesting that this method showed a 35 % weight loss at 333 K in sterile water. The weight change proceeded, because the temperature of the sample was maintained above its $T_g$. Therefore, low molecular weight oligomers created by the hydrolysis reaction diffused away, resulting in a decrease of the weight of the sample.
Biodegradable Polymers for Food Packaging – Factors Influencing their Degradation and...

Table 1
Certification schemes and labels for environmentally degradable polymers [52]

<table>
<thead>
<tr>
<th>Country</th>
<th>Organization</th>
<th>Standards compliance</th>
<th>Symbol</th>
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</thead>
<tbody>
<tr>
<td>Germany</td>
<td>International Biodegradable Polymers Association and Working Groups</td>
<td>DIN V 54900 or EN 13432 or ASTM D6400</td>
<td><img src="image" alt="Symbol" /></td>
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<tr>
<td>USA</td>
<td>Biodegradable Products Institute</td>
<td>ASTM D6400</td>
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<tr>
<td>Japan</td>
<td>Biodegradable Plastics Society</td>
<td>ISO 14851 ff. and OECD 301C and JIS K 6950 ff.</td>
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<td>Belgium</td>
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Regarding available scientific literature, there were a lot of studies about degradation behaviours of biodegradable polymers by microorganisms. Sixty percent of the PLA film was degraded after two weeks in the liquid culture containing Amycolatopsis species isolated from the soil [48]. Moreover, the degradation of PLA was studied in microbial culture of Fusarium moniliforme and Pseudomonas putida by Torres and his team [49]. The process was monitored by weight loss, size exclusion chromatography and visual examination. Microbial activity was monitored by means of changing pH and lactic acid formation. After 32 weeks of incubation, the samples appeared completely disintegrated in the microbial medium.

Tsuji and Suzuyoshi undertook the study of the biodegradation of aliphatic polyesters, poly(ε-caprolactone) (PCL), poly[(R)-3-hydroxybutyrate] (R-PHB), and poly(L-lactide) (PLLA) films in static [50] and natural dynamic seawater [51]. Morphological changes using polarizing optical microscopy, molecular weight changes with GePermeation Chromatography (GPC), and mechanical properties by tensile testing were investigated. They concluded that the natural dynamic seawater conditions accelerate the biodegradation of the samples in comparison with the controlled static seawater. The mechanical degradation of the R-PHB and PLLA films was larger in the natural dynamic seawater than that of the PCL films.

4. Standard Testing Methods for Polymer Packaging

A standard testing practice for biodegradable and compostable materials is relatively new. The first standard referring to polymer bio-/degradation was established by the American Society for Testing and Materials (ASTM) in 1999, although in the past (1992–1997) several standard practices for testing biodegradation of organic compounds in aqueous media had already been issued by the International Organization for Standardization (ISO). In Europe there are more and more technical Committees which are involved in these standards like: Deutsches Institut für Normung (DIN), Austrian Standard Institute (ÖNORM), British Standards Institute (BSI), Association Française de Normalisation (AFNOR), Ente Nazionale Italiano di Unificazione (UNI).

Standards for environmental degradable polymers (EDPs) testing is a tool for verification and confirmation of materials properties on the same scientific basis, which
gives reliable and accountable results. They contain the ground for testing including basic requirements, specifications and labels. Labelling is a significant tool for communication and promotion. Table 1 presents some of the presently available labels, their certifying bodies, and the required standards. It is important to note that if the product is “compostable” it must be biodegradable although the inverse situation is not so obvious. On the other hand, if a product is biodegradable in composting conditions (i.e. municipal composting facilities or household compost piles) then it can be declared as compostable [52].

References