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Biodegradable packaging based on polyesters

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Abstract. Currently due to the numerous problems caused by synthetic plastics waste and their degradation in the environment, there is a growing interest for the production of biodegradable plastics. A biodegradable material for packaging applications, made from renewable resources such as poly(hydroxybutirate) is being developed. This paper presents some studies that have been conducted on the mechanical properties and the biodegradability of experimental samples from poly(hydroxybutyrate) obtained by bacterial fermentation and mixtures thereof. The effects of biodegradation on certain characteristics of the two biodegradable compounds based on polyhydroxybutirate and hydrophylic polymers have been studied. The biodegradability of polyhydroxybutirate blends were evaluated in natural conditions. These data are useful for the biodegradability prediction of packaging under normal conditions.

Key Words: biodegradable packaging, poly(hydroxybutyrate), plastic wastes, soil.

Introduction. Synthetic polymers are produced from petrochemical resources. Due to their resistance to the action of natural factors of industrial waste and scrap products derived from these polymers, they are a source of environmental pollution and require a rigorous control. Increasingly more it supports the idea that the undegradable thermoplastic polymers are not suitable for short-term applications (i.e. packaging, catering, surgery, hygiene). For these reasons it became necessary to replace conventional plastics with biodegradable polymers, configured especially for packaging (Scott 2002).

Currently due to numerous issues related to synthetic plastics waste and their degradation in the environment is an increasingly intense interest for the production of biodegradable plastics. Polyhydroxyalcanoates represent a family of polyesters that can successfully replace petroleum plastics (Poirier et al 1995). Polyhydroxyalcanoates are completely biodegradable unlike many other plastics materials which are partly biodegradable. Poly(hydroxybutyrate) (PHB) a member of polyhydroxyalcanoates is a material totally biodegradable and is produced by the fermentation of sugars and other chemicals or produced from plants (Lee & Chang 1995).

PHB has attracted commercial interest as a plastic material because its physical properties are remarkably similar to those of polypropylene (PP), even though the two polymers have quite different chemical structures (Payam et al 2012).

Biodegradation of polymers. Degradable polymers are materials which undergo changes as a result of the interactions physical, chemical and biological between microorganisms from the environment and the material. The enzymatic action of the microorganisms lead to significant changes in the structure of material. Resulting products are carbon dioxide, a new biomass and water (in the presence of oxygen: aerobic degradation) or methane (oxygen absent: anaerobic degradation), as defined in European Standard EN 13432:2000. Rate of degradation of a material is important, as the product in question must have a useful life of well known.

The evolution of plastics biodegradability should be taken into account by the following parameters: hydrophobicity, molecular mass, cristalinity, the shape and dimensions of the product (the form of the product may be a thin film or a profile with thick structure).

The changes of physical or chemical properties of polymers are the result of environmental factors, such as light, heat, moisture, chemical conditions or biological activity. The changes of polymer properties consist in bond scission and subsequent chemical transformations. Degradation is reflected in changes of material properties such as mechanical, optical or electrical characteristics.

All plastics are subjected to degradation by microorganisms like bacteria and fungi (Mohan & Srivastava 2010). Biodegradation depends on different factors that include polymer characteristics, type of organism, and nature of pretreatment. The polymer characteristics such as morphology, molecular weight, the type of functional groups and substituents present in its structure, and additives exhibit an important role in its degradation (Shah et al 2008).

They are many standard methods to evaluate biodegradation of polymers. Among them, it can be enumerate: visual observations that present visible modifications of the materials (changes in colour, formation of holes and cracks or biofilms on the surface); weight loss (the method is widely applied); changes in physical and mechanical properties (density, hardness, tensile strength), that are dependent on decrease of molecular mass of polymers.

In this paper we examined the biodegradability of two polymer formulations by evaluating the mass loss and the variation of physical-mechanical properties, due to the action of microorganisms present in the soil.

Experimental

***Experimental recipes**.* The biodegradability of recipes based on poly(hydroxybutyrate) blends was investigated in order to determine the effects of degradation on characteristics of the materials. Two biodegradable compounds (E1 and E2 – Table 1) containing different amounts of raw materials: poly(hydroxybutyrate), poly(vinyl alcohol) (Yoshie et al 1995), starch and glycerin were melt blended into a laboratory twin screw extruder type Brabender plastograph at 170°C and warm pressed into plates, on laboratory Brabender press at 7.5 barr and 175°C to obtain films with thickness 0,140 mm, 1mm and plates with thickness 4 mm.

Table 1

Experimental recipes

Materials	*E1*	*E2*
Poly(hydroxybutirate), % gr.	48	48
Poly(vinyl alcohol), % gr.	25	12
Starch, % gr.	-	13
Glycerol, % gr.	27	27

***Materials**.* The raw materials used in the experiment were the followings:

- poly(hydroxybutyrate) P226 produced by BIOMER-Germany;
- poly(vinyl alcohol) 71-30, produced by duPont;
- starch produced by S.C. CHIMREACTIV S.A., Bucharest;
- glycerol produced by S.C. CHIMOPAR S.A.

Some properties of the raw materials are presented in the Tables 2-6.

Table 2

Melting temperature and density of raw materials

Materials	*Melting temperature [°C]*	*Density [g/cm³]*
Poly(hydroxybutyrate)	> 175	1.25
Poly(vinyl alcohol)	180-190	1.26
Starch	250	1.5
Glycerol	290 (boiling point)	1.258

Table 3

Characteristics of Poly(hydroxybutyrate)

Properties	*Values*	*Method*
Density, g/cm^3	1.20	DIN 53479
Moisture absorption, %	0,76	23^{o}C, humidity 50%
Hardness Shore, ^oSh_D	54	3 seconds, DIN 53505
Melt index, g/10 min	5-7	163^{o}C, 2.16 kg, 10s - SR EN ISO 1133
Contraction, %	1.66	Calliper
Residues calcined, %	2.0	TGA, 800^{o}C
Melting temperature range, ^{o}C	150-170	DSC
Softening temperature Vicat, ^{o}C	57	Proceding under B50 EN ISO 306
Tensile strength, MPa	13.1	SR EN ISO 527-1
Elongation at break, %	501	SR EN ISO 527-1
Modulus E, MPa	805	SR EN ISO 527-1
Bending stresses at break, MPa	18.8	Do not break DIN 53452
The external fiber tensile, %	3.9	Do not break DIN 53452
Impact resistance Charpy, kJ/m^2	32.7	7,5 J pendulum SR EN ISO 179/1 eU
Notched impact resistance Charpy, kJ/m^2	3.3	7,5 J pendulum SR EN ISO 179/1 eU

Table 4

Characteristics of Poly(vinyl alcohol)

Characteristics	*Values*
Glass transition temperature, ^{o}C	85
Melting temperature, ^{o}C	180-190
Density of amorphous structure at 25 ^{o}C, g/cm^3	1.26
Density of cristalline structure at 25 ^{o}C, g/cm^3	1.35
Solubility	Water
pH of a solution of 5% PVA	5.0...6.5
Molar mass, g/mol	1000 - 100000
Hydrolisys degree, %	86.5 - 99

Table 5

Characteristics of starch

Characteristics	*Values*
Solubility in water (90^{o}C)	50 g/L
pH (2%; water)	6.0–7.5
Reducing material (maltose)	0.7%
Loss on drying	max 10%

Table 6

Characteristics of glycerol

Characteristics	*Values*
Density, g/cm^3	1.26
Molecular mass, g/mol	92

Method. The experimental recipes were formulated with the purpose to observe the effect of composition on microbial degradation phenomena. E1 and E2 contain the same quantities of poly(hydroxybutyrate) and plastifier glycerol, but they differ by presence of two hydrophylic polymers: poly(vinyl alcohol) and starch that are consumed faster by the microorganisms. Starch is the most widely used polymer in the biodegradable applications because of his increased rate of weight loss, by microorganisms consuming.

The experiments assessed biodegradability were based on mass variation and physical-mechanical properties analysis. The studies of weight loss were performed to facilitate the comparative determination of degradation percent in the experimental recipes with and without starch (E1 and E2). The recipes of poly(hydroxybutyrate) blends were cut in order to obtain sample specimens with the following dimensions:

- 10 x 120 x 0.140 mm,
- 150 x 20 x 1 mm,
- 60 x 60 mm.

The samples specimen were weighed and analyzed in terms of physical and mechanical properties, and then they were buried in a garden soil with a pH of 6.5, a temperature of 17–27°C and water content that varied around 30%, for up to 10 months. It were carried out observations at every two weeks. After each period the plates - samples of the biodegradable materials were extracted from the degrading medium and were washed and dried under vacuum at 25°C for 24 h, and then weighed. The degradation was investigated by evaluation of physical and mechanical properties modification and the weight loss. The PHB films were disintegrated and lost 75% and 84% of mass within 10 months. Instead, the plates of 1 mm thickness lost 56% and 60% of mass, and the plates with thickness 4 mm lost 45% and 49% of mass. These values suggest that the thickness of the test specimens influence the rate of degradation of the material, as it varies the amount of material to be consumed by the microorganisms. The films with thickness of 0.140 mm were degraded much faster compared to specimens with a thickness of 1 mm and 4 mm. This is reflected in the percentage of mass loss of the material. Also, from comparison of percentages of mass loss from the two formulations, it is observed that starch and poly(vinyl alcohol) increase the rate of PHB degradation. Visual examination shows significant roughness on the surface of experimental samples of PHB blends films due to microbial attack.

Results. The parameters of the soil garden (temperature, moisture) has an important influence on biodegradability of poly(hydroxybutyrate) blends.

The variation of physical and mechanical properties before buried samples and at the final of the experiments are presented in Table 7.

Table 7

Physical and mechanical properties of the sample E1 and E2 (film semi-transparent, yellow tente) initially and at the end of the degradation experiment

Characteristics	*Method*	*E1 initially*	*E1 final*	*Decrease of the properties %*	*E2 initially*	*E2 final*	*Decrease of the properties %*
Thickness, mm	SR EN ISO 4593/1998	0.140	0.080	43	0.140	0.076	43.57
		1	0.641	36	1	0.625	37.5
		4	2.759	31	4	2.685	33
Tensile strength, daN/cm^2	SR EN ISO 527-3/2000	180	115.39	36	198	126.92	36
Elongation at break, %	SR EN ISO 527-3/2000	560	359	36	530	332	37.4
Density, g/cm^3 $T=23^0C$	SR EN ISO 1183-2005	1.48	0.96	35	1.52	0.95	37.5
Hardness Shore, ^{0}ShA	SR EN ISO 868:2003	64	44.12	31	65	43.6	33

During the experiment by exposing to microbial attack, numerous degradations occurred into the materials which led to the alteration of the physical and mechanical properties. The samples have changed the aspect and they became more opaque.

Since the recipes were formulated on the basis of biodegradable polymeric materials it was expected that under the action of microorganisms from soil to appear scissions of macromolecular chains, leading to the breakdown within samples macromolecular materials. These changes have resulted in the weight loss by appearance of microcavities into materials which led to the decrease of the density. Furthermore the weight loss conducted to decrease of hardness and mechanical properties such as tensile strength and elongation at break. Even if the initial mechanical properties of the E2 recipe were higher than E1, at the final of the experiment, because of the presence of starch in recipe E2, the decrease of the properties was more pregnant, as it can see in table 2. It can be seen that the percentage decrease of properties in E2 was between 33…37.5%, instead the samples from E1 presented decreasing percent between 31…36%. These results show that the material E2 which contain starch exhibit a greater rate of degradation than E1.

Weight losses were assessed by samples weighting on laboratory balance type Precisa, at every two weeks. The variation of experimental recipes weight loss is presented in the Figures 1-6.

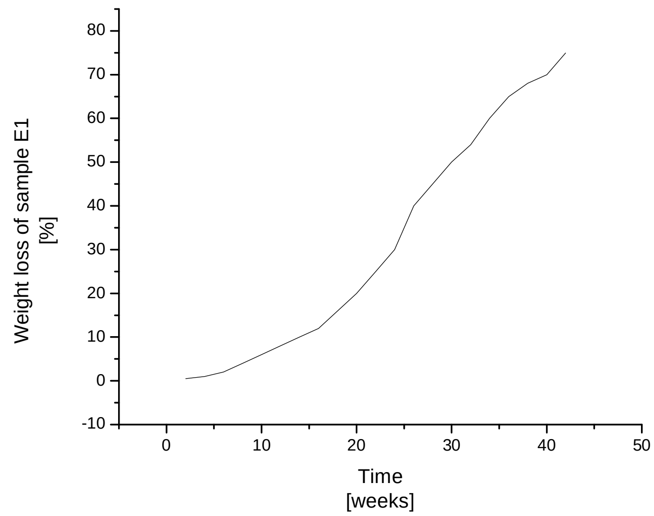

Figure 1. The weight loss variation of sample E1, sample with thickness 0.140 mm.

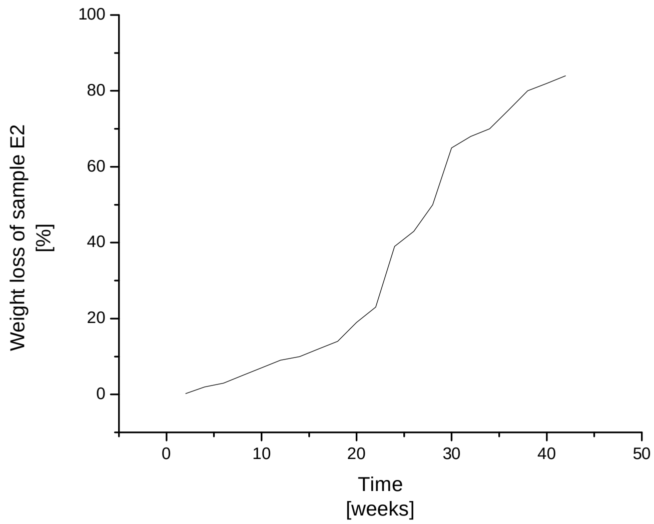

Figure 2. The weight loss variation of sample E2, sample with thickness 0.140 mm.

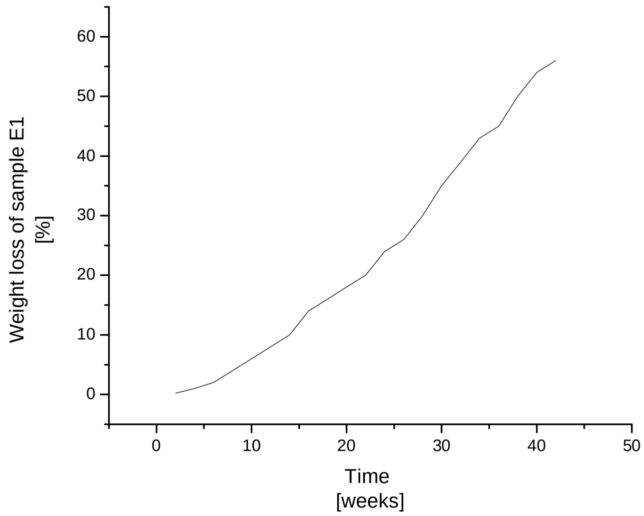

Figure 3. The weight loss variation of sample E1, sample with thickness 1 mm.

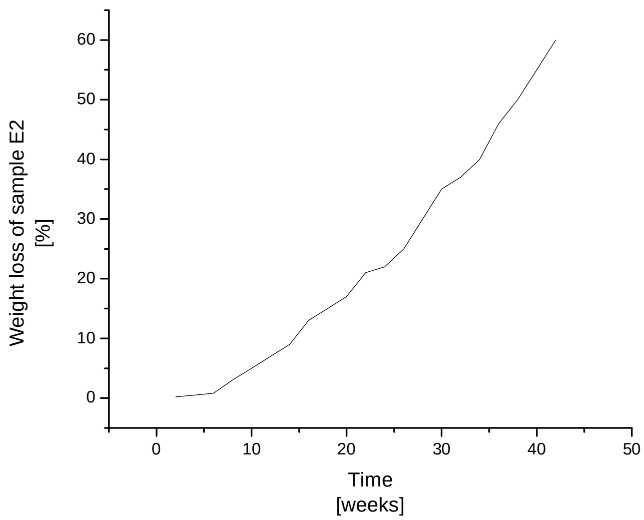

Figure 4. The weight loss variation of sample E2, sample with thickness 1 mm.

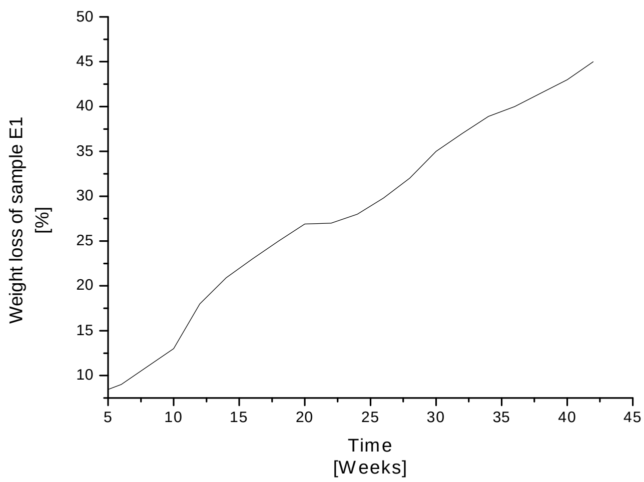

Figure 5. The weight loss variation of sample E1, sample with thickness 4 mm.

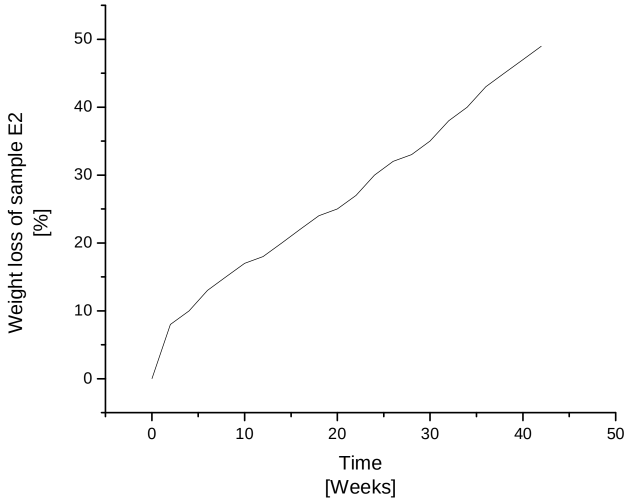

Figure 6. The weight loss variation of sample E2, sample with thickness 4 mm.

Conclusions. It were obtained, two types of recipes based on poly(hydroxybutyrate) and hydrophilic polymers such as poly(vinyl alcohol) and starches, and glycerol plasticizer. By warm pressing it were obtained films and plates of different thicknesses. They were sampled standard specimens which were buried in garden soil.

The biodegradation was assessed by weight loss and performing samples analyses on physical and mechanical properties initially and at final experiment after 10 monts.

It was found that the degradation rate of the biodegradable compounds is dependent on the raw materials and their content and also upon the initial parameters of degrading medium. The experimental data demonstrated the effects of biodegradation on certain characteristics of the plastics and the results offer informations about applications area.

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