Assessment of the environmental degradation of biodegradable plastic bags

Evaluación de la degradación ambiental de bolsas plásticas biodegradables

Carlos Alfredo Castellón Castro[1]
Luis Neil Tejeda López[2]
Lesly Patricia Tejeda Benítez[3]

[1] Colombian, Chemical Engineer in Project Management, Universidad de Cartagena, Cartagena, Bolívar, Colombia. e-mail: carcasca99@yahoo.com.

[2] Colombian, Chemical Engineer, Universidad de Cartagena, Cartagena, Bolívar, Colombia. e-mail: lntejedal@gmail.com.

[3] Colombian, Ph.D (c) in Environmental Toxicology, Magister in Environmental Engineering, Chemical Engineer, Universidad de Cartagena, Cartagena, Bolívar, Colombia. e-mail: ltejedab@unicartagena.edu.co.

Abstract

Plastic bags are used as disposable materials, and they are released into the environment at an increasing rate. For this reason many manufacturers are producing degradable polymeric material-based bags, like for example the polyhydroxyalkanoates and the polylactates. In this work, the degradability of bags declared as degradable by their manufacturers, was evaluated by exposure to the environment, and compared to those of the conventional bags. Three parameters were studied: weight loss, water absorption and mechanical strength. The results showed that the degradable bags suffered greater weight loss, increased water absorption and lower mechanical strength before and after exposure to the environment than the conventional bags. This show that the chemical modifications made by manufacturers, actually promote their degradation.

Keywords: plastics; disposable materials; tensile stress; photodegradation; weight loss.

Introduction

Since the creation of plastics in the decade of 1940, and due to its great versatility, its production and as well its consume has increased exponentially, contributing to the raise of non-biodegradable solid residues wastes (Al-Salem et al. 2009; Siddique et al. 2008). Between 1960 and 2000 the production of plastic resin increased 25 times (Moore, 2008). In 2013 it was estimated that the 299 million tons of plastic were produced in the world and set free in the environment (Suhrhoff and Scholz-Böttcher, 2016). This has caused big harmful effects upon marine biodiversity. More than 200 species have found to be affected by plastics through lacerations,

intestinal obstructions, nutrient dilution and even death in seabirds, cetaceans, pinnipeds and species of sea turtles. (Cole et al. 2011; Moore, 2008; González et al. 2015). On other side, with the increase of the cost and decrease of the capacity of sanitary landfills, there is a world concern about the disposal of plastics (Bajracharya et al. 2016).

Around a third of the plastics were used in the manufacturing of disposable articles, such as wrappings, bags and other packaging materials, cups and trays for fast foods, increasing the volume of plastics in sanitary landfills and dumps (Yabannavar & Bartha, 1994). The United States Environmental Protection Agency has calculated that in the world are produced between 500,000 million and a billion plastic bags per year. For this reason, as an answer to the attitude of the consumers, the legislative initiatives, and the pressure from environmental groups, some manufacturers have formed various plastic films "environmental friendly" and biodegradable for the manufacturing for shopping

bags and disposable products to be ecologic alternatives to the traditional oil-based plastic products (Lee et al., 2016). The PAD can be classified according to its origin, natural or synthetic, as shown in Figure 1. The raw materials for the PAD can be from petrochemical, animal, vegetable or of microorganism origin. The synthesis can occur in three main ways: 1. Biosynthesis, such as fermentation, chemosynthesis, or direct application to the natural materials with or without modification, for example, the natural fibers (Krzan et al., 2006). The lactic acid used to produce polylactic acid (PLA) can be obtained through cornstarch fermentation or synthetically derived from oil, and both ways produce biodegradable PLA. The so called bioplastics come from a renewable biomass contribute to decrease the gases from the greenhouse effect, since the atmospheric carbon dioxide is used by plants to produce the carbohydrates. However, the polyethylene derived from the bioethanol is a bioplastic, but it's no biodegradable, what will generate issues in its final disposal (Weiss et al., 2012; Gómez and Michel, 2013).
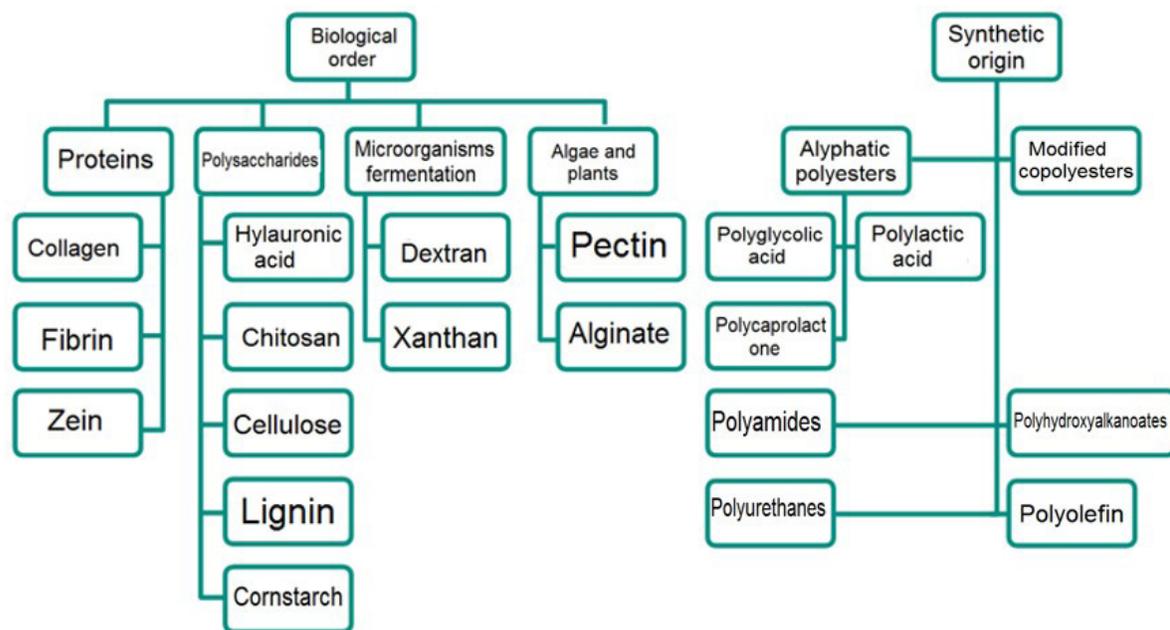

Figure 1. Types of biodegradable plastics
Source: (Krzan *et al.*, 2006)

The biodegradable bioplastics coming from the biomass, were designed to be compostable and/or biodegradable. These types include PLA based resins and polyhydroxyalkanoates (PHA).

The American Society and Materials (ASTM) and the International Standard Organization (ISO) define degradation as "an irreversible process that drives

a meaningful change to the structure of a material, normally characterized by the loss of properties (integrity, molecular mass, structure or mechanical resistance) and fragmentation". The degradation seems affected by the environmental conditions and the product during a period of time that includes one or more stages (Babaee et al., 2015; Krzan et al., 2006).

When the plastics are exposed to an energetic environment characterized by a comparable energy charge to the energy of chemical bonds, that keep them in place of the atoms that constitute the main polymer link, it results in the collapsing of the macromolecular architecture with a notable fragmentation. This corresponds with the beginning of degradation. In the environment, this process is based in a combination of mechanisms and factor: temperature, solar light, oxidation, humidity, mechanical stress and microorganism action (Krzan et al., 2006).

The plastic degradation process includes two stages: disintegration and mineralization. The first stage is linked meaningfully with wear of deterioration of physical properties, such as discoloration, fragility and fragmentation. The second stage is the final conversion from plastic fragments to small CO_2 molecules, water and cellular biomass under anaerobic conditions, as seen on Figure 2 (Krzan et al., 2006).

The polythene environmental degradation, for example, is due to the synergic action of the photo, thermo, exo and biodegradation. Since the biodegradation of commercial high molecular weight polythene advances slowly, the abiotic oxidation is the first step and the speed determining. The environmentally degradable polythene is prepared by mixing biodegradable additives or photoinitiators or through copolymerization. More than 200 different degradation products, including alkanes, alkene, ketones, aldehydes, alcohols, carboxylic acids, ceto-acids, dicarboxylic acids, lactones and esters have been identified in the polythene thermo and photo-oxidation, which can be assimilated by microorganisms (Hakkarainen and Albertsson, 2004).
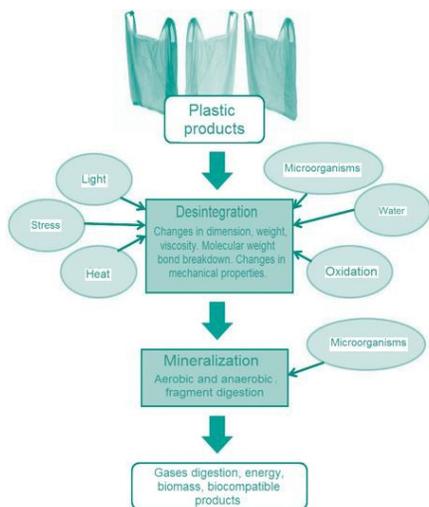

Figure 2. Environmental plastic degradation process
Source: (Krzan *et al.*, 2006)

The PAD degradability assessment has been a difficult scientific and technical challenge, since the variety of the applied degradable materials. With the goal to standardize the technique and assessment criteria, a series of parameters were established by the different normalization organisms that also are used as a base for the certification systems (Krzan et al., 2006). To evaluate the PAD degradability several techniques have been proposed. The mass loss is a quantitative that co-relates well with the gas detachment quantity that, at same time, is a biodegradation measure based in the microbial respiration. Some authors have assessed the plastic degradation environmentally degradable using a mass loss parameter. For example, Qian et al., (2016) determined the mass loss of the normal polyhydroxybutyrate – cohydroxyvalerate samples (PHBV), the ones modified with calcium nano-phosphate and magnesium and with the zein corn protein, exposing them to samples a of a Tris-HCl solution. In other study, Torres-Huerta et al., (2014), determined that the mass loss of the Polyethylene terephthalate (PET) with polylactic acid (APL) and chitosan in an accelerated environment, using UV lamps. On other hand, Wu et al., (2015) used this method in 2.5-furandicarboxylic acid polyesters after the soil degradation. Another used method to evaluate the degradability of a plastic material is the water absorption. Some authors have used this method in their studies. For example, Babaee et al., (2015) determined the humidity absorption in thermoplastic nanocomposites reinforced with cornstarch modified with cellulose nanofibers. These composites are capable of absorbing the environmental humidity, which conducts it to hydrolytic excision of the polymer chain, leading its enzymatic and chemical degradation (Krzan et al., 2006). Finally, the measurable changes in the mechanical properties can be attributed to the microbial biodegradation and oxidation (DEFRA, 2015). This essay was done by Kijeńska et al., (2010) in polythene and polypropylene co-polymers of low density filled with haystack after a 12 month exposition to compost and the soil

In our country, for many years, plastic bag reduction campaigns have been implemented, in a way that the stores have printed mottos such as "If taking care of your planet is what you want, less bags you should use". Additionally, the supermarkets and big surfaces have been using for a long time plastic bags made with degradable plastics, either oxo, photo or biodegradables. Recently, the Environment Ministry launched the campaign "ReemBÓLSAle al Planeta" (Refund to the Planet) with the goal to motivate people to not use plastic bags, but to use reusable bags for

shopping. And with the approval of the resolution that regulates the rational use of one-use-only, useless and non-reusable bags in an 80% by 2020 and by the year 2025 its complete deletion in the whole country. The law indicates that bags lesser to 30×30 can't be used, all the bags should be more resistant with the goal to avoid the use of double bags for heavy objects, and they must have an educational messaged printed that invites to a responsible consume.

In this study, all the declarations done by the biodegradability manufacturers of their bags were studied, using mass loss, humidity absorption and tension resistance loss techniques.

Materials and methods

Materials. 10 types of selected bags were identified as degradable (BDPB), acquired from the main chain stores from the city of Cartagena, which have claimed to be biodegradable to the public opinion, and printed with the color of their respective logos. Additionally, ten types of conventional polythene (CPB), bought in a plastic supplies stores.

Bag exposition. The samples of each bag, in their corresponding dimensions, were tied with staples to a plastic sheet, which at the same time was placed on a table in a semi-exterior space of the lab, that is to say, with a transparent plastic roof, to allow the light go through, and without air conditioning. During the exposition, the registered temperatures in the city of Cartagena, ranged between 28 and 33°C with a relative humidity ranging between 75 and 88% and no precipitation was present.

Mass loss test. A 2 x 2 cm^2 material simple was placed in a desiccator with CaSO (0% humidity) for three days and later, the initial mass of the samples was registered (W_1) using an analytic balance. The pieces were exposed to the weathering for six weeks, and then again placed in the desiccator and weighted (W_2). The mass loss was calculated for each piece according to the equation proposed by Qian et al., (2016):

$$PP = \frac{W_1 - W_2}{W_1} \times 100\% \qquad (1)$$

The average of three replicas for each simple was reported.

Humidity absorption test. This test was done according to the ASTM E104 parameter. All the specimens for the water absorption were cut in 2x2 cm dimensions

and dried at 60°C for 24 h. The dry samples were put in a desiccator with $CaSO_4$ (0% humidity) for three days, and later its initial mass was registered (W_1). The samples were then transferred to a desiccator with $CaSO_4$ (98% humidity) and its mass was registered every 20 minutes, until reaching a constant mass (W_2). The water absorption (WA) was calculated as it follows:

$$AA = \frac{W_2 - W_1}{W_1} \times 100\% \qquad (2)$$

The average of three replicas for each simple was reported.

Mechanical resistance test. The mechanical tests were done according to the ASTM D638 parameter. The samples were cut in 7x1 cm. Before the test, all the test samples were conditioned for three days in a desiccator with 55% of relative humidity at room temperature. The traction tests were held using an Instron (M350-10- CT) test machine with a 500N load and a test speed of 4mm/min. This test was made before the exposition to the environment and six weeks later after it. At least five replicas were tested for each simple.

Statistical Analysis. All the experiments were done in a triplicate for each group, with the exception of the mechanical resistance test that was done five times. The results were expressed as the mean ±standard deviation. The statistical analysis was held by a T-test. A P<0.05 was considered statistically meaningful. The values for each test for the two bag groups were analyzed to establish if correlations between the different variables existed. Due to the fact that the data was normal for the Kolmonorov-Smirnov, the Pearson parametric data was used.

Results and discussion

General observations. The BDPB (Biodegradable Plastic Bags), as well as the CPB (Conventional Plastic Bags), suffered changes, like color loss and deformation. The denominated BDPB, also lost its printed ink and showed cracks in its surface.

Mass loss. The mass loss results for the two types of bags tested are shown in Figure 3. During the six weeks of testing, the BDPB, suffered a a 74% mass loss with an standard deviation of 6%, while at the same time, the CPB only lost a 22% of its initial mass with a 9% standard deviation. Using the Test-T, meaningful

differences were found between the two groups with a P < 0.01 value, which indicates that its weight loss is meaningfully different to those of the BDPB and CPB. Thus, we can confirm that the input additives in the resins which are used to manufacture the BDPB allow mass decrease of these bags in a 74% in average, in a period of six weeks. Other authors have evaluated the degradation using the mass loss of polymer bags with other additives in accelerated environments as a parameter. For example, Torres- Huerta et al., (2014), exposed polyethylene terephthalate (PET) with polylactic acid (PLA) and chitosan in an accelerated environment using UV lamps. The input of these additives allowed the increase of mass loss in the materials after the exposition, showing that the resin modification of the polymers with chemical additives make environmental degradation easier, in this case, seen in a material mass loss.
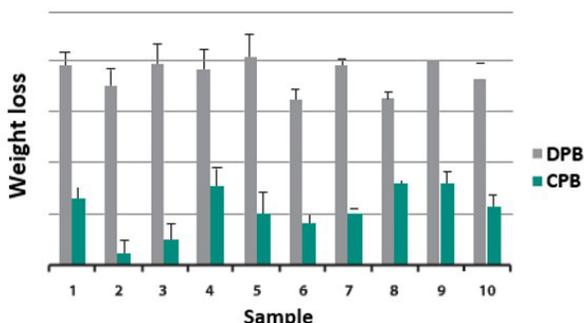

Figure 3. Mass loss. BDPB: Biodegradable plastic bags.
CPB: Conventional Plastic Bags.
Source. The authors.

Humidity absorption. The average water absorption is presented in Figure 4. After 60 min, the BDPB absorbed in average 73.9% of the humidity with an standard deviation of 1.6%, while the CPB only absorbed 56.1% of the water with a 1.79% deviation. The statistical meaning of the difference between these two is high, taking in account that using the paired Test-T, the P value is < 0.0001. We can deduce that the BDPB have additives that favor the humidity absorption, with the goal to improve the degradation conditions. Kakroodi et al., (2014) found that the water absorption of the polythene reinforced with hemp fibers increased with the percentage increase of the hemp in the mixture, proving that the chemical modification of the resins affects its behavior in the environment.

Mechanical resistance. The obtained results for the tension resistance before and after the six weeks are presented in Chart 1. The initial value was lesser for the BDPB (23.4 MPa) compared to the value of the CPB (31.7 MPa), is one of the main disadvantages of the biodegradable materials, since they lose versatility in their applications. The tension resistance after a six week exposition to the environment was of 8.1 MPa for the BDPB, decreasing in a 65%, and of 13.7 MPa for the CPB, decreasing a 57% in comparison to the initial value. Abdullah et al., (2013) evaluated the mechanical properties of the polythene terephthalate reinforced with polyoxymethylene after 672 hours of exposition of accelerated ware chambers. They found out that the changes in the mechanical properties of the co-polymers decreased in a 50% when they were reinforced, and only a 2% when they weren't. This shows that the chemical modifications done to the o improve their biodegradability also decrease their mechanical resistance.
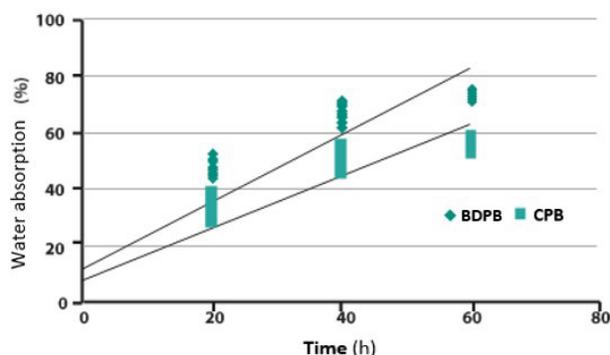

Figure 4. Water absorption BDPB: Biodegradable plastic bags.
CPB: Conventional plastic bags.
Source: The authors

Chart 1. Tension resistance

Bag type	Tension Resistance (MPa)		Decrease (%)
	Initial	6 weeks	
BPD	23.4* (2**)	8.1 (1)	65 %
BCP	31.7 (3)	13.7 (2)	57 %

Water absorption BDPB: Biodegradable plastic bags. CPB: Conventional plastic bags. * Average of five samples. ** Standard deviation. **Source:** The authors.

Correlation analysis. The correlation coefficients between the variables, as same as its P values are show on Chart 2. The results show that the three variables strongly correlate. The resistance negatively with the mass loss (R =-0,96) and the water absorption (R = -0,97); and these last two correlate positively(R = 0,94). This shows the difference between these two parameters, showing a bigger mass loss, more water absorption and less tension resistance in the BDPB than in the CPB.

Chart 2. Pearson correlation analysis

	Mass loss	Water absorption	Tension resistance
Pérdida de masa		0.94 (< 0.001)	-0.96 (< 0.001)
Water absorption	0.94* (< 0.001)**		-0.97 (< 0.001)
Tension Resistance	-0.96 (< 0.001)	-0.97 (< 0.001)	

* Correlation Coefficient R. ** P value.
Source: los The authors.

Conclusions

The experimental study and the statistical analysis done allow to conclude that the BDPB show a higher deterioration than the CPB, thus, having a lesser permanence in the environment after its use. However, it is necessary to continue developing campaigns that allow the rational use of these products, focusing on the environmental reservation.

References

Abdullah, M., Dan-mallam, Y., Megat Yusoff, P. (2013). Effect of Environmental Degradation on Mechanical Properties of Kenaf/Polyethylene Terephthalate Fiber Reinforced Polyoxymethylene Hybrid Composite. *Advances in Materials Science and Engineering*. 8.

Al-Salem, S., Lettieri, P., Baeyens, J. (2009). Recycling and recovery routes of plastic solid waste (PSW), a review. *Waste Management*, 29, 2625–2643.

ASTM D638 - 14. (2002). *Standard Test Method for Tensile Properties of Plastics.*

.ASTM E104-02. (2012). *Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions.*

ASTM D 883. (1991). *Standard terminology relating to plastics.*

Babaee, M., Jonoobi, M., Hamzeh, Y., Ashori, A. (2015). Biodegradability and mechanical properties of reinforced starch nanocomposites using cellulose nanofibers, *Carbohydrate Polymers*, 132, 1-8.

Bajracharya, R., Manaloa, A., Karunasenaa, W., Laua, K. (2016). Characterisation of recycled mixed plastic solid wastes, Coupon and full-scale investigation, *Waste Management*, 48, 72–80.

Cole, M., Lindeque, P., Halsband, C., Galloway, T. (2011). Microplastics as contaminants in the marine environment, a review. *Marine Pollution Bulletin*, 62, 2588–2597.

Department for Environment, Food and Rural Affairs. DEFRA. (2015). *Review of standards for biodegradable plastic carrier bags*, Reino Unido.

Gómez, E., Michel, F. (2013). Biodegradability of conventional and bio-based plastics and natural fiber composites during composting, anaerobic digestion and long-term soil incubation. *Polymer Degradation and Stability*, *98*(12), 2583-2591.

González, C., Machain, N., Campagna, C. (2015). Legal and institutional tools to mitigate plastic pollution affecting marine species, Argentina as a case study, *Marine Pollution Bulletin*, *92*(1-2), 125-33.

Hakkarainen, M., Albertsson, A. (2004). Environmental Degradation of Polyethylene Long Term Properties of Polyolefins. *Advances in Polymer Science*, 169:177-200.

ISO 472 Plastics – vocabulary, amendement 3 (1993). *General terms and terms relating to degradable plastics.*

Kakroodi, A., Kazemi, Y., Rodrigue, D. (2013) Mechanical, rheological, morphological and water absorption properties of maleated polyethylene/hemp composites: Effect of ground tire rubber addition. *Composites Part B: Engineering*, 51: 337-344.

Kijeńska, M., Kowalska, E., Pałys, B., Ryczkowski, J. (2010). Degradability of composites of low density polyethylene/polypropylene blends filled with rape straw, *Polymer Degradation and Stability*, *95*(4), 536-542.

Krzan, J., Hemjinda, S., Miertus, S., Corti, A., Chiellini, E. (2006). Standardization and certification in the area of environmentally degradable plastics, Polymer *Degradation, and Stability*, *91*(12), 2819–2833.

Lee, S., Choe, H., Kim, S., Park, D., Nasir, A., Kim, B., Kim, K. (2016). Complete genome of biodegradable plastics-decomposing *Roseateles depolymerans* KCTC 42856(T) (=61A(T)), *Journal of Biotechnology*, 220, 47-8.

Moore, C. (2008). Synthetic polymers in the marine environment, a rapidly increasing, long-term threat, *Environmental Research*, 108, 131–139.

Qian, J., Ma, J., Su, J., Yan, Y., Li, H., Shin, J., Wei, J., Zhao, L. (2016). PHBV-based ternary composite by intermixing of magnesium calcium phosphate nanoparticles and zein, In vitro bioactivity, degradability and cytocompatibility. *European Polymer Journal*. 75, 291–302.

Siddique, R., Khatib, J., Kaur, I. (2008). Use of recycled plastic in concrete, a review, *Waste Management*, 28, 1835–1852.

Suhrhoff, T., Scholz-Böttcher, B. (2016). Qualitative impact of salinity, UV radiation and turbulence on leaching of organic plastic additives from four common plastics - A lab experiment, *Marine Pollution Bulletin*. 102(1), 84-94.

Torres-Huerta, A., Palma-Ramírez, D., Domínguez-Crespo, M., Del Ángel-López, D., De La Fuente, D. (2014). Comparative assessment of miscibility and degradability on PET/PLA and PET/chitosan blends, *European Polymer Journal*, 61, 285-299.

Weiss, M., Haufe, J., Carus, M., Brandão, M., Bringezu, S., Hermann, B. (2012). A review of the environmental impacts of biobased materials, *Journal of Industrial Ecology,* 16, S169–S181.

Wu, H., Wen, B., Zhou, H, Zhou, J., Yu, Z., Cui, L., Huang, T., Cao, F. (2015). Synthesis and degradability of copolyesters of 2, 5-furandicarboxylic acid, lactic acid, and ethylene glycol, *Polymer Degradation and Stability*, 121, 100-104.

Yabannavar, A., Bartha, R. (1994). Methods for Assessment of Biodegradability of Plastic Films in Soil, *Applied Environmental Microbiology*, 60(10),3608–3614.