The development of sustainable bioplastics for new applications in packaging industry

Marta Musiol[1*], Wanda Sikorska[2], Marek Kowalczuk[3], Grazyna Adamus[4]

Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Sklodowska 34, 41-819 Zabrze, Poland

Abstract— *The advantage of biodegradable plastics is their degradation under the influence of biological systems into substances naturally present in the environment, which are then placed in a natural circulation cycle of matter. Moreover, the biodegradable plastics waste not require additional segregation and separation from households, and are collected together with other organic waste and subjected to recycling under aerobic or anaerobic conditions. Use of bioplastics reduces the harmful effects of waste on the environment, but does not eliminate it completely.*

The article presents the results of (bio) degradation studies under industrial and laboratory (MicroOxymax) composting conditions as well as at atmospheric conditions of commercial disposable dishes from the Nature Works® PLA. Were also carried out investigation of abiotic degradation under laboratory conditions. It was found, from the macro- and microscopic observations, that the tested cups (bio) degraded in the selected environments, wherein in a greater extent under industrial composting conditions than in MicroOxymax. The GPC results, which show significantly reduce in the molar mass of the tested samples after specified incubation times in all environments, indicates that the hydrolytic degradation process occurs predominantly.

Keywords—- (bio)degradation; industrial composting; PLA

I. INTRODUCTION

The constantly increasing demand for new, original products increases amounts of packaging waste. The need for recycling enforces new, environmentally responsible approach to the problem of plastics. The solution may be packaging manufactured from biodegradable polymers, especially those that are susceptible to organic recycling.The common plastic material is composed of synthetic polymers. Most of them aren't found in nature, so are not biodegradable. Progress in the study of the relation between structure and properties of the polymers and their degradation mechanisms led to the development of new polymeric materials that retain the characteristics and usefulness of traditional plastics, but biodegradable. Biodegradable polymers are subject to degradation in the environment such as sea water, compost, as well as under atmospheric conditions [1-16] to the products which are safe for health and the environment. About the real advantages of bioplastics, we can say if, after a period of use such materials are disposed of under conditions that allow their biological decomposition and introduction of degradation products to the natural cycle. Susceptibility of polymers and plastics on biodegradation process depends primarily on their chemical structure. For this reason, the origin of polymers, whether they are derived from renewable resources (biomass) or non-renewable (fossil sources), does not refer to the notion of biodegradability. The chemical structure of the polymers determines their degradation possibility, so the biodegradable polymers can be obtained from both of these sources. There is a common misconception that all biodegradable polymers are derived from renewable resources.

According to the European Bioplastics Association polymer materials can be divided in accordance with the scheme that takes account of their origin and susceptibility to biodegradation, as shown in Figure 1.

The vertical axis of the Scheme indicates the origin of plastic (renewable resources (biomass) or non-renewable (fossil sources)), and the horizontal axis determines their biodegradability:

1) Conventional plastics (non-biodegradable polymeric materials derived from petrochemical sources)
2) Bioplastics
    a. non-biodegradable, derived from renewable resources, bio-PE/PP/PVC, Bio-PET;
    b. biodegradable, derived from non-renewable resources, PBTA, PBS, PCL;
    c. biodegradable, derived from renewable resources, PLA, PHA, starch.

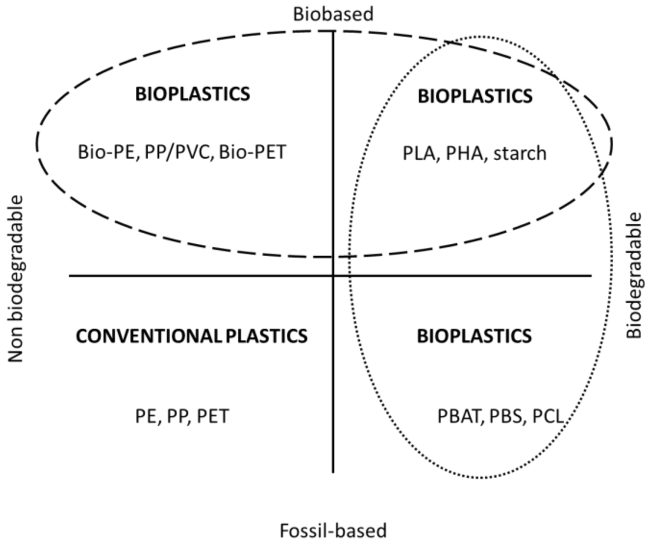


FIGURE 1. SCHEME OF POLYMERIC PLASTICS [FOLDER PLASTICE: BIOPLASTICS – OPPORTUNITY FOR THE FUTURE, WWW.PLASTICE.ORG]

Now the market offers a biodegradable plastic more and more manufacturers. The most common commercially produced materials can be classified into the following groups:

- The starch-based materials
- PLA-based materials
- PHA-based materials (PHB, PHBV, etc.)
- Materials based on aliphatic-aromatic polyesters
- Cellulose-based materials (e.g., cellophane, etc.)
- Materials based on lignin.

The plastics, in addition to the polymer materials also contain other materials and/or additives, what determines their processing opportunities, and thus the properties of the final product. Plastics may include: stabilizers, lubricants, dyes, fillers, etc. In the case of bioplastics is important that these additives were also biodegradable. There are also various composites containing natural components (biocomposites). The composite is a mixture of polymers or plastics and fillers are added in order to improve their mechanical or chemical properties or to reduce the price of the material. Biocomposites very often contain natural fibers (eg hemp) or sawdust. [17-21]

There are two main aspects, under which, the consumer decides on the choice of plastic: economic/commercial and environmental aspect. Although aspects of the environmental and economic/commercial should not be treated separately, but in practice the predominant aspect is the final price of the product.

Within the framework of research the susceptibility on the composting process of commercial PLA rigid package, in the form of disposable cups, as well as the correlation between structure and functional properties of packaging material was determined.

II. MATERIALS

Degradation study of commercial disposable PLA (NatureWorks®) rigid packaging, labeled as cup250, was conducted.

The packaging was produced by I.L.P.A. Srl (ILIP) whose representative on the Polish market is the *EcoMaster®* company.

III. METHODS

3.1 (Bio)degradation under industrial composting conditions

(Bio)degradation processes under industrial composting conditions (organic recycling) were performed at the Station of Mechanical-Biological Waste Treatment in Zabrze, Poland. Samples were incubated in a KNEER container system that we described before [13]. In the container system the samples were incubated for 21 days at average temperature of 59 ºC, from April to May 2011.

3.2 Biodegradation under laboratory composting conditions

Biodegradation study under laboratory composting conditions was performed using COLUMBUS INSTRUMENTS S/N 110315 respirometer Micro-Oxymax equipped with a computer as a controller and a device for recording, archiving and presenting data. Micro-Oxymax performs periodic measurements in a closed system, which means that the air in the measuring chamber is pumped by a gas sensor and returns to the chamber. The system, work in standard conditions, automatically compensates for changes in pressure and temperature. In the respirometric test the samples were incubated in compost for 42 days at average temperature of 58 ºC, with moisture content 53% and pH 7.8.

3.3 Abiotic degradation under laboratory conditions

For abiotic degradation experiments samples (5 cm x 1 cm strips) with average mass of 0.1 g were first dried under vacuum at room temperature to a constant mass to eliminate ultimate water content and were then incubated in screw-capped vials with air-tight PTFE/Silicone septa, containing 25 ml of distilled water. The degradation experiment was being conducted for over 70 days at 70 °C (± 0.5 °C) as was described before [14].

3.4 Degradation under natural weathering

The samples were placed on the testing site at the latitude 50° 18' 52,68" N and longitude 18° 46' 16,20 " E. Experiments were conducted between March and April , 2011 with daily rainfall below 1.0 mm (http://www.wunderground.com/) The average open air temperature was 1.6 ºC.

3.5 Visual examination of the surface

Microscopic observation of the materials' surface was done by means of a Zeiss optical microscope (Opton-Axioplan) equipped with a Nikon Coolpix 4500 colour digital camera.

3.6 Gel Permeation Chromatography (GPC) analysis

The weight average molar mass (M_w) of the PLA samples was determined by GPC experiments conducted in chloroform solution at 35 ºC and a flow rate of 1 ml/min using a Spectra-Physics 8800 solvent delivery system with two Mixed C Styragel columns in series and a Shodex SE 61 refractive index detector. Sample solutions in $CHCl_3$ (10 µl, 0.5% w/v) were injected into the system. Polystyrene standards with low dispersity were used to generate the calibration curve.

3.7 Weight measurements

The weight of degraded samples was determined using an electronic balance RADWAG WAS 160/X with a precision of 0.1 mg.

3.8 Thermal properties

Thermogravimetric analysis (TGA) was performed with a TGA/DSC1 Mettler-Toledo thermal analyser at a heating rate of 10 °/min in a stream of nitrogen (60 mL/min). The obtained TGA data was analysed using the Mettler-Toledo Star System SW 9.30.

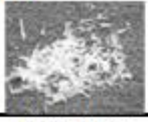
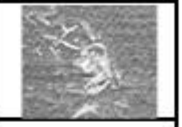
3.9 pH analysis

The pH measurements of the solutions were carried out at T = 23.0 ± 2.0 °C using a Mettler Toledo SevenMulti S40 pH-meter (resolution: ± 0.1 mV, ± 0.001 pH units) equipped with a InLab Science Pro 3-in-1 electrode featuring an ARGENTHAL™ reference system with a Ag^+ trap and reference inner electrolyte composed of 3 mol/l KCl (Metrohm, Switzerland). The electrode was calibrated using buffers (Mettler Toledo, Switzerland) of pH = 4.01 ± 0.02, pH = 7.00± 0.02 and pH = 9.21 ± 0.02 at T = 23.0 ± 2.0 °C.

IV. RESULTS AND DISCUSSION

Macroscopic visual evaluations of the PLA rigid packaging after specified degradation time in the selected environments are presented in Tab. 1. The disintegration of the cup250 samples was observed after abiotic degradation under laboratory conditions starting from the 7th day of incubation and also after 42 days incubation under laboratory composting conditions (in Microoxymax).

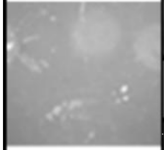
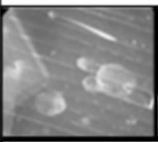
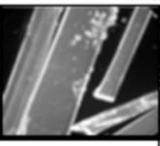
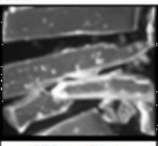
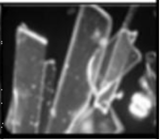
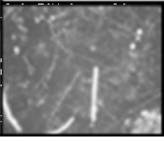
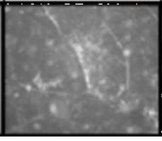
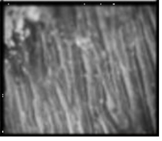
TABLE. 1
THE MACROSCOPIC CHANGES OF THE CUP250 SAMPLES DURING INCUBATION IN THE SELECTED ENVIRONMENTS

Degradation time [days]				
0	7	14	28	42
	Water			
				
	Compost		Weather conditions	Microoxymax
				

The loss of sample transparency was observed after incubation in water at 70°C, and after 14 days degradation under industrial composting conditions. These results correlate with our previous study in which the sample turbidity was resulted from the crystallization process [14]. The observed loss of sample transparency and hence increase in crystallinity of investigate samples could be associated with the hydrolytic degradation process that occurs in a privileged way in the amorphous regions of the material [10].

Photomicrographs of the cup250 samples surface before and after a specific degradation time in selected environments are presented in Tab. 2. After 7 days of sample incubation in water at 70°C surface cracking were observed. This results may be connected with the orientation of the lamellar associated to the type of processing. For the sample after incubation under industrial composting conditions longitudinal cracking and flaking were observed.

TABLE. 2
PHOTOMICROGRAPHS (120X) OF THE CUP250 SAMPLES SURFACE BEFORE AND AFTER A SPECIFIC DEGRADATION TIME IN SELECTED ENVIRONMENTS

Degradation time [days]				
0	7	14	28	42
	Water			
				
	Compost		Weather conditions	Microoxymax
				

The changes in weight average molar mass (M_w) for the PLA samples during incubation in the selected environments were determined by GPC technique. Systematic decrease of molar mass of the investigated sample was observed (Fig. 1)

Moreover, a greater reduction of M_w values of samples incubated in water was observed. The changes of molar mass suggest that under the investigated composting conditions a hydrolytic degradation mechanism has occurred.

Fig. 1 show also difference between the rate of molar mass decrease during incubation under laboratory and industrial composting conditions. This may be caused by the difference in moisture content of the compost. Minor changes of M_w were observed for the sample after natural weather testing.

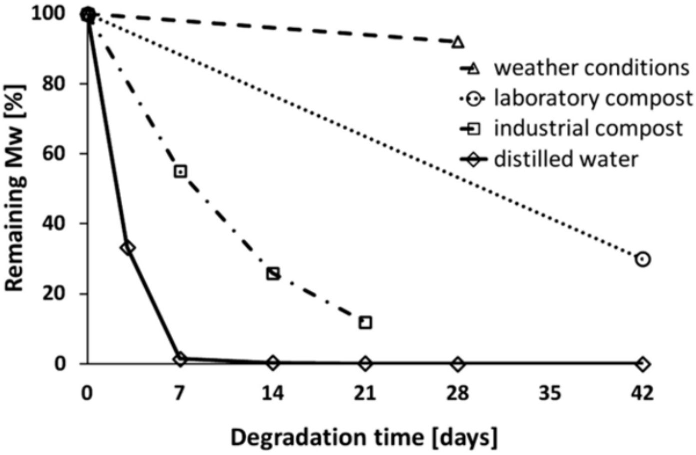


FIG. 2. REMAINING MW OF A CUP250 SAMPLE AS A FUNCTION OF INCUBATION TIME DURING DEGRADATION PROCESS IN SELECTED ENVIRONMENTS

The course of degradation in water at 70ºC was also monitored by determining the weight loss of the samples after a specific incubation time and obtained results are presented in Fig. 3. The weights loss of cup250 sample increases continuously since the beginning of the degradation process.

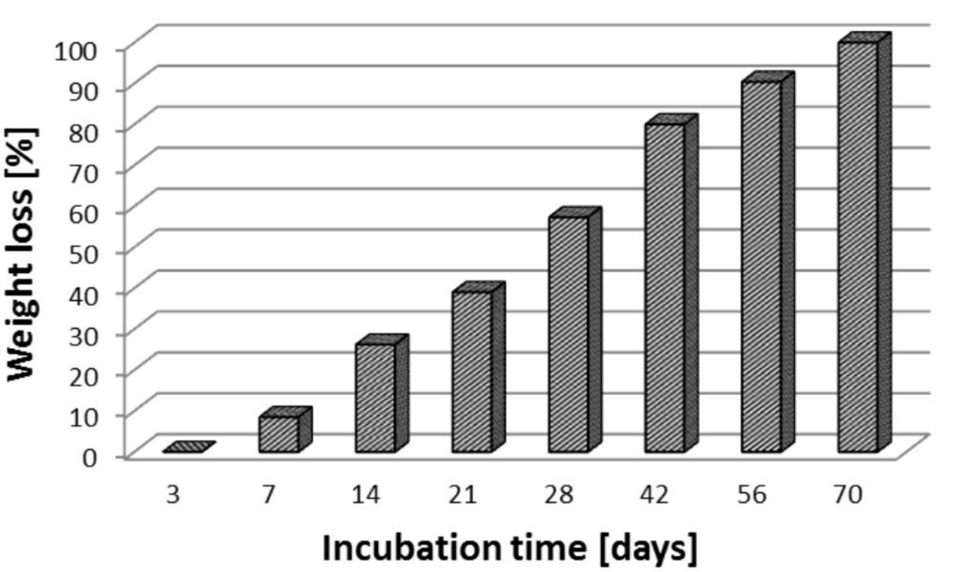


FIG. 3. WEIGHT LOSS OF A CUP250 SAMPLE AFTER DEGRADATION IN WATER AT 70ºC

In our previous study electrospray ionization multistage mass spectrometry (ESI-MS^n) was used to determine the structure of water soluble products formed during the hydrolytic degradation of the PLLA samples [14]. This leads to the conclusion that the decrease of pH in water solutions after cup250 sample incubation, which accompanied the process, resulted from the appearance of low molecular acidic degradation products (Fig. 4).

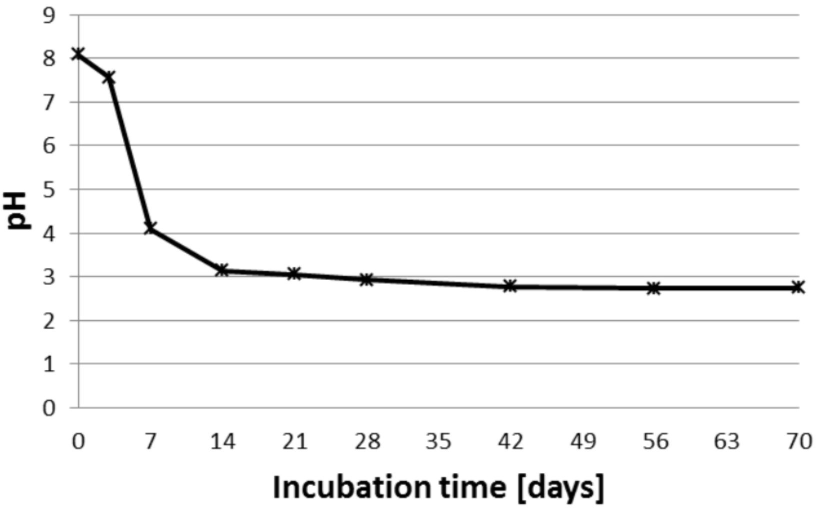


FIG. 4. PH OF THE WATER SOLUTIONS AFTER INCUBATION OF THE CUP250 SAMPLE AT THE TEMPERATURE 70 °C UNDER LABORATORY CONDITIONS

The influence of different environment on the cup250 sample degradation has been characterized by thermogravimetric analysis (TGA) and obtained results are presented in Fig. 5 and 6. Weight reduction of 100% occurred prior to 400°C for all the samples. The degradation of investigated material undergoes one stage of mass loss in all the environments. After 21 days of sample incubation in water and under industrial composting conditions decrease of thermal stability was observed. This change could be originated from the molecular weight reduction during degradation of the polymer. [22] Thermal stability of the sample was lower after incubation in water which correlates with molecular weight changes (see fig..)

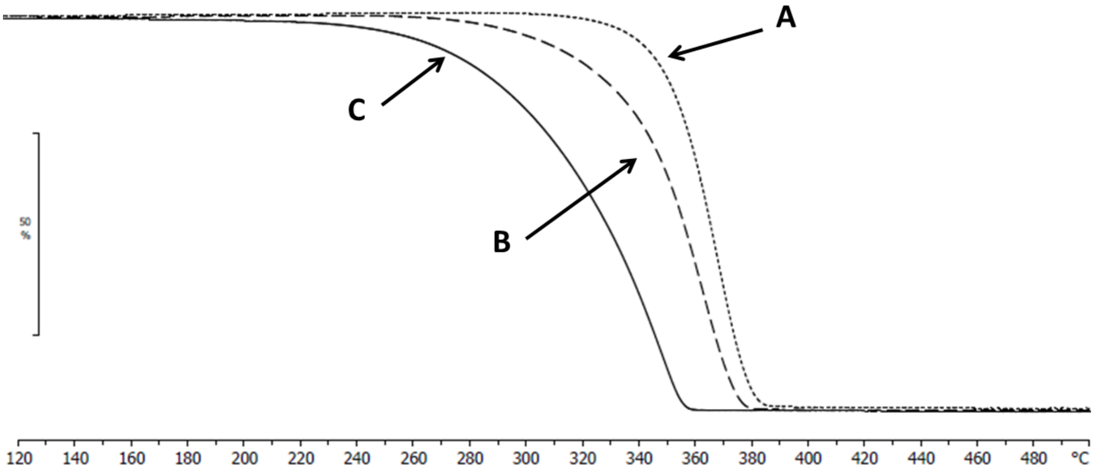


FIG. 5. TG THERMOGRAMS OF A CUP250 SAMPLE BEFORE (A) AND AFTER 21 DAYS INCUBATION UNDER INDUSTRIAL COMPOSTING CONDITIONS (B) AND IN WATER AT 70 °C (C).

The increase in the number of chain ends per mass caused by the presence of shorter polymer chains occurred during the degradation of the polymer promote the depolymerization by back-bitting (intramolecular trans-esterification) which is a dominant degradation pathway at the temperature range of 270°C to 360°C [22]

The first derivative (DTG) of the TG curve is useful method to easier notice slight changes in the curves. The DTG curves are a good indicator of the temperatures at which the various stages of thermal decompositions occurred. The decomposition temperature became lower after 21 days incubation in both environments.

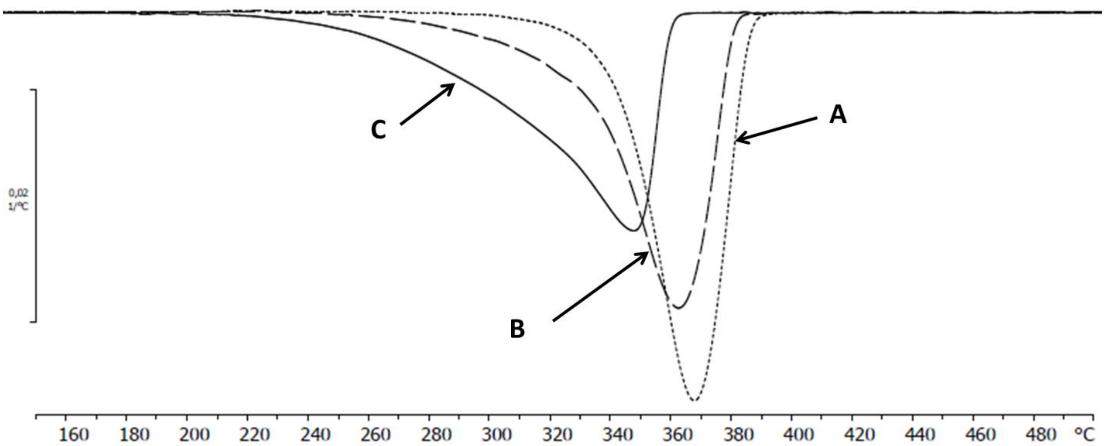


FIG. 6. SELECTED THE FIRST DERIVATIVE TG THERMOGRAMS BEFORE DEGRADATION A, AND AFTER 21 DAYS OF INCUBATION B UNDER COMPOSTING CONDITIONS, C IN WATER AT 70 °C.

V. CONCLUSION

The combination of biodegradability with production of bioplastics from renewable resources, give a unique opportunity to adapt the whole life cycle of materials to the natural cycle of matter circulation: plastics are produced from renewable raw material and then return to nature. Such a life cycle cannot be achieved for conventional plastics, and thus bioplastics are currently the best reflection of natural materials. Plastics still require human intervention, but the difference between bioplastics and natural material decreases more and more.

The visual examination of the surface and the significantly reduce in the molar mass of commercial disposable dishes from the Nature Works® PLA indicates that during incubation in all environments the hydrolytic degradation process occurs predominantly.

ACKNOWLEDGEMENTS

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