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STUDY ON THE BIOLOGICAL DEGRADATION OF POLYLACTIC ACID IN VARIOUS ENVIRONMENTS

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Abstract: *In the present study, samples of polylactic acid packaging were placed under laboratory conditions closely simulating those of the environment. Sea, ocean and fresh water, soil, sea sand and compost were used as media for studying the degradation behavior of polylactic acid packaging. The factors affecting the biodegradability of the samples, depending on the physicochemical conditions of the environments, were considered: temperature, pH, amount of dissolved oxygen, bulk density and particle size composition. The loss of mass, the thickness of the samples and the influence of the different environments on the tensile characteristics of the polymer material were determined.*
Keywords*: Polylactic acid, Biodegradability, Environmentals, Degradation behavior, Simulated conditions, Tensile characteristics.*

INTRODUCTION

The introduction and substitution of the conventional single-use polymer packagings with these obtained from polylactic acid (PLA) raises a number of questions about their degradation under different atmospheric conditions. This depends on multiple factors which can be classified according to the physicochemical conditions determined by the environment, e.g. temperature, moisture content, pH of the medium, presence of oxygen and nutritious substances, etc., as well as the properties of the polymeric material – molar weight, chemical composition, temperatures of melting and glass transition, crystallinity, porosity, presence of additives and fillers, shape and size of the sample to be degraded and the kind of the various microorganisms existing in the medium (Kale, G., Auras, R., Singh, P., Narayan, R., 2007; Kliem, S., Kreutzbruck, M., Bonten, Ch., 2020; Tokiwa, Y., Calabia, B. 2006; Tsuji, H., Suzuyoshi, K., 2002)

Despite that PLA has been used for decades and there are numerous studies about it, the information about its degradability under various environmental conditions is scarce (Kale, G., Auras, R., Singh, P., Narayan, R., 2007). The literary review indicated that, compared to other biopolymers, PLA degradation is a very slow process because it is durable and can resist degradation for longer periods of time (Hong, L., Yuhana, N., & Zawawi, E., 2021; Ilyas, R., 2021; Kliem, S., Kreutzbruck, M., Bonten, Ch., 2020; Mokhena, T., Sefadi, J., Sadiku, E., John, M., Mochane, M., & A. Mtibe, A., 2018).

The aim of the present study is to follow up the changes of the mass and physicomechanical characteristics of the samples placed for 90 days under laboratory conditions comparable when to the exposure of the single-use packagings to the environment.

EXPERIMENTAL

Materials

Biodegradable PLA packagings containing 70-80% crystalline polylactic acid, 20-30% filler and other biodegradable additives. Sea water from the Black sea with salinity of 17.5‰, dissolved oxygen content 8.08 mg/l, temperature 23.4°C and pH 8.35. Ocean water prepared under laboratory conditions with salinity of 36.8 ‰, temperature 24.9°C, pH 7.38 and oxygen content 8.29 mg/l. fresh water with salinity of 0 ‰, temperature 24.9°C, pH 7.46 and content of dissolved oxygen 8.2 mg/l. The soil from the Burgas region is of the "Smolnitsi" type with a loose density of 1.34 g/cm^3, temperature 22.5 - 25°C, medium pH 6.7–8 and a predominant fraction of particles < 2 μm (42.17%). Black sand from the Black sea coast near Burgas with a loose density of 2.22 g/cm^3, temperature 23-25°C and a predominant fraction of particles ≤250 μm (52.32%). Non-granulated compost of organic manure 65% and ground natural wood with a loose density of 0.60 g/cm^3, fractional composition ≤2 mm (74.69%), medium pH 8.4, moisture content 10% and temperature measured during the experiments 23 – 25°C.

Methods of work

Samples were cut from the biodegradable PLA packaging using a double-sided blade-shaped mock knife. The samples were then subjected to research on their destruction under laboratory conditions simulating different environmental conditions, including: aquatic (seawater, ocean and fresh water) and soils (soil, sea sand and compost).

The PLA samples were placed in seawater, ocean and fresh water for periods of time 30, 60 and 90 days as shown in Fig.1.

Fig. 1. Samples of PLA placed in three types of aqueous media

The preliminarily prepared samples were placed in rows at a certain distance from each other and then covered with 5 cm layer of soil for periods of time 30, 60 and 90 days, as illustrated in Fig.2.

Fig. 2. Samples of PLA placed in the soil media and their covering

Characterization of the aqueous and soil media

A mobile system for electrochemical measurements – two channel gauge Profiline pH/Cond 3320 was used to determine the temperature, salinity, pH and the amount of oxygen dissolved in the aqueous media.

Using sieve analysis system AS200 control B, Retsch GmbH, Germany, the granulometric composition (*G*) of the soil samples was determined as the ratio between the fraction mass (m_i, g) and the mass of the total amount of the material (*m*, g) taken for analysis, expressed in %.

The loose density ($\rho_н$) in g/cm^3 of the sea sand, the compost and the soil was determined as the ratio of the mass (*m*, *g*) in unit volume (*V*, cm^3) of the sample.

Characterization of the PLA samples

The mass loss (*W*) in % of the PLA samples was determined as follows: the initial mass of the sample W_0 (g) was weighted on an analytic balance. After the expiration of the experimental periods of 30, 60 and 90 days during which the samples were kept in the different simulated media, the samples were dried and cleaned from traces of water and sand and weighted again to determine their current weight W_i (g). The mass loss was calculated as the difference between the initial and current weights relative to the initial weight.

The physicochemical characteristics – Young modulus (*E*, MPa), tensile strength (σ, MPa) and elongation at break (ε, %) of the pure PLA and the one after being kept in the different by type media – aqueous and soil, were measured on Instron 4203 apparatus at speed of 5 mm/min and room temperature according to EN ISO 50527-1.

RESULTS AND DISCUSSION

One of the factors affecting the degradation of the biopolymers is their degree of water absorption (Rudeekit, Y., Numnoi, J., Tajan, M., Chaiwutthinan, P., Leejarkpai, T., 2008). The latter depends on the morphology, molecular weight, purity and the shape of the sample, as well as the technique of processing the polymer. The process of hydrolysis induced by the water uptake ensures the functionality of the biopolymers and their degradation by microorganisms in biological systems.

Behaviour of the PLA samples in aqueous media

After keeping the samples immersed in seawater for 12 weeks (90 days) at temperature of 25°C, the total mass of the samples studied did not show significant change. Similar tendency was observed for the samples immersed in ocean and fresh water. The mass loss of the PLA samples under the simulated conditions of 25°C temperature of water and samples thickness of 0.22 mm was insignificant – from 0.014 to 0.55%. The results obtained are in accordance with these reported by (Tsuji, H., Suzuyoshi, K., 2002) and indicate that degradation of samples of 0.32 mm PLA films in aqueous media under simulated conditions does not result in loss of mass even for period of one year (Bagheri, A.R., Laforsch, C., Greiner, A., Agarwal, S., 2017).

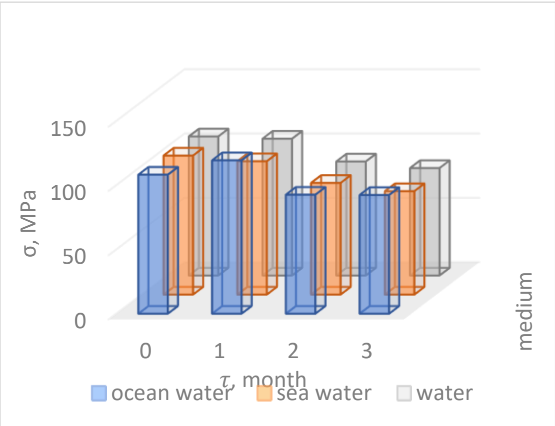

Fig. 3. Tensile strength of PLA samples in aqueous media

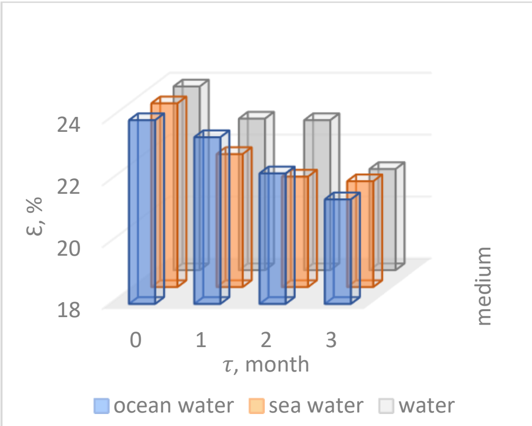

Fig. 4. Elongation at break of PLA samples in aqueous media

It was found by the study of the tensile strength (σ, MPa) of the PLA samples immersed in aqueous medium for the experimental period of 90 days that the values decreased for all the media studied (Fig.3). The decrease of the tensile strength for the three aqueous media varied within narrow range as for seawater it was 19.67% while for the ocean water it was 14.42%. The elongation at break ($\mathcal{E}$, %) slightly increased during the period of 90 days by about 6% for all the samples studied regardless of the aqueous medium type – Fig.4.

Behaviour of the PLA samples in different types of soil

Under identical laboratory conditions, the film samples shaped as 0.22 mm thick two-sided blades and buried in soil, sea sand and compost biodegradation was not observed. This is confirmed by other authors too (Karamanlioglu, M., Robson, G., 2013; Kliem, S., Kreutzbruck, M., Bonten, Ch., 2020) which found that even after keeping them for one year in soil at temperatures from 25 to 37°C no weight loss was observed for the PLA samples. For the period of 90 days at temperature 23-25°C, the change of the samples mass was negligible although the stay has certain effect on the processes of ageing since the samples became brittle.

The tensile strength of the samples kept in soil for 90 days at temperature of 23-25°C decreased by about 26% for all types of soils used – Fig.5. Similar tendency for period of 11 months was observed by other authors (Massardier-Nageotte, V., Pestre, C., Cruard-Pradet, T., Bayard, R., 2006; Rudnik, E., Briassoulis, D., 2011) according to which the decrease of the tensile strength was accompanied by brittle fracture is due to processes of ageing occurring by the degradation of the PLA films.

The following changes were observed for the elongation at break (Fig.6) of the films kept in different media: in sea sand, it remained unchanged; in soil, it decreased by about 6.35% and the greatest change was found for the samples buried in compost – about 20%. The results obtained were probably due to the lower loose density and particles size of the compost. These factors are determining the gas diffusion into the medium, which, in turn, creates conditions for enhanced activity of the microorganisms, and bacteria present in the medium.

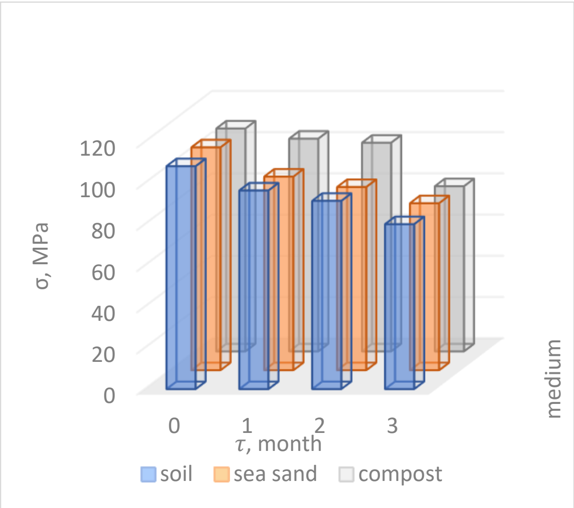

Fig. 5. Tensile strength of PLA samples in soil medium

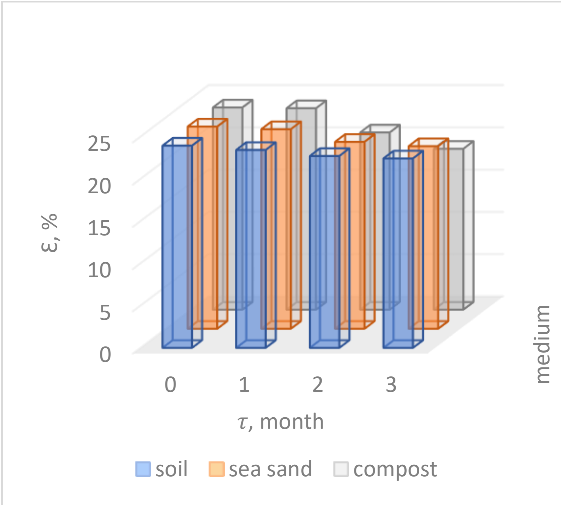

Fig. 6. Elongaton at break for PLA samples in soil medium

Thus, it has certain positive effect on the biological degradation of PLA.

CONCLUSIONS

Despite the existence of numerous publications on the subject, the results from the experimental work carried out under laboratory conditions simulating various types of media, presented in this study, indicate for some difficulties in monitoring and comparing the stages of PLA biodegradation. Due to the complexity and the regional differences, it is almost impossible to carry out reproducible research work under the different environmental conditions. In most cases, the results obtained will differ or even contradict each other, which make it impossible to establish particular period of biodegradation and draw reliable and valid conclusions. It is of substantial importance to define clearly the specifications of the physicochemical conditions, period of degradation, temperature, exposure to UV light, geometry of the tested sample, etc.

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