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Long-term influence of soil environment conditions on the structure and selected properties of PLA packaging

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Abstract: Studies on packaging made of polylactide (PLA) subjected to long-term influence of soil environment conditions have been presented in this paper. The scientific objective of this study was to determine changes in selected properties of the PLA packaging after long-term incubation in soil. These changes were investigated by scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis, and gel permeation chromatography. The structure, thermal properties, and disintegration degree of the packaging after their three-year incubation in soil have been discussed. It was found that the PLA packaging did not disintegrate significantly in the soil environment, and slight changes in their structure and lack of significant changes in thermal properties indicate that the efficiency of their degradation in soil conditions after three years is very low. This was mainly due to inadequate temperatures in the soil. It was also found (based on the results of scanning electron microscopy and gel permeation chromatography) that initiation of the biodegradation process took place and that this process is much faster than in the case of conventional non-biodegradable polymers. The results are confirmation that materials obtained of various biodegradable polymers (not only PLA) should be biodegradable only under strictly defined conditions, allocated to a specific type of polymer, i.e. those in which they are easily and quickly biodegradable.

Introduction

Polymeric materials are more and more commonly used in recent years, this is confirmed by the continuous and dynamic production of plastics (PlasticsEurope, 2022). As a consequence of this, an increase in waste in the natural environment originating from used polymeric products is observed. To overcome this, some of these products are processed in mechanical or chemical recycling. Others are disposed of by incineration or storage in landfills. However, it does not completely solve the problem of environmental protection, and some of these materials still cause environmental problems such as air, soil and especially water pollution (Shah et al. 2008).

An opportunity to improve environmental protection is to replace conventional non-biodegradable polymers with environmentally friendly polymers. A group of such polymers are biodegradable ones. These polymers are gaining more popularity in recent years and have attracted great interest. This is due to the fact that they are becoming more available with lower prices and better properties. Moreover, most of them can be processed using well-known machines, equipment, and technology (including extrusion, injection molding, thermoforming, and lamination). However, the significant interest in these polymers stems from their susceptibility to degradation via biological factors (mainly microorganisms)). As a result, they can be relatively easily and quickly biodegraded. The same cannot be said about non-biodegradable polymers, which can decompose over even hundreds of years. The biodegradation process can occur in various conditions like industrial compost, home compost, fresh water, sea water or soil (Bhagwat et al. 2020). However, the effects and duration of the biodegradation process can be very different. This may be due to the process conditions themselves, as well as the type of polymer that undergoes biodegradation. Polylactide (PLA) is an example of such a polymer.

PLA is one of the most important biodegradable polymers (Ahmed and Varshney 2011). It is produced from renewable biomass resources such as cassava, corn, starch and sugarcane (John et al. 2007). PLA has diverse applications in numerous fields such as medical, agriculture, fibres and textile, 3D-print, packaging and compostable waste bags. Great interest in this

polymer results mainly from its relatively easy availability, good processing parameters, numerous applications and low price compared to other biodegradable polymers. Besides, products made of this polymer easily undergo biodegradation in industrial composting conditions. The biodegradation process of this polymer is two-stage. The first stage refers to chemical hydrolysis in the presence of water. In this stage, high molecular weight macromolecules are split into lower molecular weight fragments. In the second stage, microbial biodegradation occurs. This stage is often called the mineralization process. This is the main decomposition process of PLA leading to the formation of water, carbon dioxide and biomass. Some studies also suggest that some microbial enzymes are able to degrade high molecular weight PLA macromolecules (Mehlika et al. 2014). When microbial enzymes of this type are used, the hydrolysis stage does not need to occur.

The two-stage biodegradation process of PLA occurs easily and quickly in industrial compost. This is due to the fact that high temperature (c.a. 60°C) in compost enhances the hydrolysis of PLA, which is the initial mechanism in the reduction of PLA molecular weight before microorganisms mineralize the low molecular weight PLA. In other environmental conditions, the biodegradation process is not as effective, i.e., it may be very slow or hardly occur (Żenkiewicz et al. 2012, Deroiné et al. 2014). For example, in soil or marine conditions, the biodegradation of PLA is much slower compared to industrial compost. In addition to low temperature, other pH values or the type of microorganisms may also be the reason for the lack of visible biodegradation. This statement refers not only to PLA, but also to other biodegradable polymers (Poluszyńska et al. 2021). Therefore, a very important issue is the appropriate selection of biodegradation conditions for each type of biodegradable polymer because not all of them will be easily biodegradable in certain environmental conditions.

The biodegradation of PLA (polylactic acid) by soil microorganisms has been partially reported (Nakamura et al. 2001, Kim and Rhee 2003, Teeraphatpornchai et al. 2003). The majority of studies on PLA biodegradation in soil have primarily examined bacteria. More than 100 strains of bacteria have already been investigated. In turn, there have been fewer studies that have investigated the potential role of fungi in this process. Interestingly, it was found that some fungi were able to break down only low molecular weight PLA, while others were active on high molecular weight PLA, and especially in PLA copolymer with glycolic acid. A literature analysis also revealed that there are known studies on the degradation ability and mechanism (Kamiya et al. 2007, Kim et al. 2008) as well as bioplastic-degrading enzymes (Lee and Kim 2010). There are also studies on the degradation of PLA in soil modified with various strains of bacteria (Janczak et al. 2020). However, most of the currently conducted studies focus on the analysis of changes in the properties of biodegradable polymers after degradation in soil under laboratory conditions. In addition, specially isolated microorganisms were often used in these studies. Furthermore, the time of biodegradation in soil usually did not exceed 2 years. These conditions were partly due to the newly developed standard (EN17033-2018E:2018). According to this standard the material applied must demonstrate a 90% conversion of the organic carbon to CO_2 by the end of the test, which should not be longer than 24 months.

The studies on biodegradation in soil of PLA packaging presented in this article were not conducted under standardized laboratory conditions. The purpose of the studies was to investigate the influence of soil environment conditions over the period of three years on the structure and thermal properties of PLA packaging, and to demonstrate the factual degree of decomposition of packaging made of polylactide material when exposed to real natural conditions.

Experimental

Materials

In order to accomplish the assumed aims, transparent PLA packaging samples measuring 140×180×80 mm (Fig. 1A) were obtained. The packaging samples were prepared from a film made of PLA type 2003D (NatureWorks LLC, USA). Its melt flow rate was 2.8 g/10 min (2.16 kg, 190°C), density, 1.24 kg/m^3, and melting point, 140–155°C. The polymer contained 3.5% of D monomer units, and was completely transparent.

Sample preparation

The packaging samples intended for the investigation were manufactured in a vacuum thermoforming process using an Illig thermoforming machine *type RV53B*. The heating temperature of the PLA film in this process was set to 250°C. The heating time and vacuum forming time were constant (3 and 2 seconds, respectively). The thickness of the film used in the thermoforming process was 0.4 mm. The obtained packaging samples were then buried in an agricultural field in such a way that they were placed under a layer of soil ca. 10–15 cm thick. The soil environment, at the time of burying the samples (in summer), was characterized by a pH of 7.10 ± 0.09, a redox potential of 321 mV ± 5 mV, humidity of 6.12% ± 0.01%, as well as a total number of bacteria (TNB) of 1.03×10^6 cfu/mL and a total number of fungi (TNF) of 2.77×10^3 cfu/mL. The samples buried in the soil were exposed to soil and atmospheric conditions for three years. After this period, the samples were taken out of the soil and then subjected to further investigation. The primary sample intended for investigation was denoted as PLA “0”, and the sample after the three year incubation in the soil was denoted as PLA “3”.

Methods

After removing the packaging samples from the soil, general observations were performed. Macroscopic photos were taken and a preliminary assessment of the resulting damage was made. Lastly, the shape of the samples after incubation in soil was compared with the original packaging.

After cleaning the samples surface to remove possible organic residue – the geometric surface structure of packaging samples was investigated with the use of a scanning electron microscope (SEM) type Hitachi SU8010 (Hitachi, Japan). The structure was determined using Secondary Electrons (SE) detector and accelerating voltage of 2kV. A 10-nm thick gold layer was sputtered onto the sample to be analyzed by SEM. For that purpose, cathode sputtering apparatus was used, which was equipped with a coating thickness gauge based on a quartz crystal of varying conductivity.

Thermal properties were determined by differential scanning calorimetry (DSC) with the use of DSC equipment type DSC 1 STARe System (Mettler Toledo, Swiss). DSC measurements were performed under nitrogen with a rate flow of 50 mL/min. About 3 mg of the sample was placed on an aluminum pan for sampling. The samples were successively: heated from 20 to 200°C at 10°C/min, annealed at 200°C for 3 min, cooled to 20°C at 10°C/min, and reheated to 200°C at a rate of 10°C/min. The first and second heating cycles were used in the analysis of thermal properties of the studied samples. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), cold crystallization enthalpy (ΔH_{cc}), and melting enthalpy (H_m) were determined.

Thermal stability was determined by thermogravimetric analysis (TG/TGA) using a Q500 analyzer (TA Instruments, USA). TG measurements were caried out in the temperature range of 20–600°C, under a nitrogen atmosphere and with the heating rate of 10°C/min. Samples of about 10 mg were deposited in an open platinum crucible.

The changes in the number-average molecular weight (M_n) and weight-average molecular weight (M_w) were examined by gel permeation chromatography (GPC). All GPC measurements were conducted in CH_2Cl_2 solvent at room temperature using polystyrene standards and a set of two PLgel 5 µm MIXED-C columns. Eluent flow rate was 0.8 mL/min. About 2 mg of each sample was applied in the preparation of the solutions injected in the GPC columns.

Results and discussion

After being incubated in soil for a period of three years, the PLA packaging was retrieved almost unchanged (Fig. 1B). This demonstrates that it did not disintegrate during the three-year incubation under soil conditions. The shape of both packaging samples (before and after incubation, Figs. 1A and 1B) is similar and the cracks in the sample PLA "3" that can be observed resulted mainly from mechanical damage arising during its removal from the soil. Moreover, it was noticed that the mechanical damage to the incubated sample occurred quite easily. Similar effects were observed by Mehlika et al. (Mehlika et al. 2014). Thus, it can be concluded that PLA packaging after incubation is more susceptible to mechanical damage and is relatively easy to break. On the other hand, the same could not be said of PLA packaging before incubation in the soil, which was more resistant to this type of damage. Greater susceptibility of PLA packaging to mechanical damage after incubation in soil may indicate the beginnings of biodegradation, e.g., hydrolytic biodegradation. However, its progress should not be considered significant because the packaging was preserved almost in its entirety.

The easier susceptibility of PLA packaging to mechanical damage that has been observed is initiated, i.a., by defects occurring in the structure of packaging, as shown in the SEM images (Fig. 2). The nature of the visible changes in the structure of packaging may indicate the next phases of biodegradation, especially mineralization initiated by microorganisms belonging to hydrolases, mainly proteases (serine proteases), lipases (esterase) or cutinases (Satti et al. 2018). This is proven by certain types of pitting with an irregular structure and different depths that can be seen in the images. However, these are not significant changes because they only occur locally. In the SEM images shown, next to the so-called pitting, the packaging has a smooth surface. These types of changes may also indicate that the biodegradation environment did not contain a large enough number of microorganisms or that other factors, such as temperature and humidity, were unsuitable. Similar effects were observed by Adhikari et al. (Adhikari et al. 2016). They indicated, i.a., that some biodegradable materials like PBS and PBS/starch were easily degraded in soil, but PLA needed a longer time for significant degradation.

A significant change that was observed was the change in the transparency of the packaging, i.e., from completely transparent (before incubation) to partially hazy (after incubation) (Figs. 1A and 1B). One of the reasons for the change in this transparency may be the presence of various types of defects in the material structure (e.g. pitting which was observed in SEM examination) causing light scattering. Another reason may be changes in the crystallinity of the material. The change in transparency is not, however, related to the change in the degree of crystallinity of the investigated material, as shown in the DSC examination (Fig. 3, Table 1).

As shown in Fig. 3, the thermal properties of PLA "0" and PLA "3" samples do not change significantly during

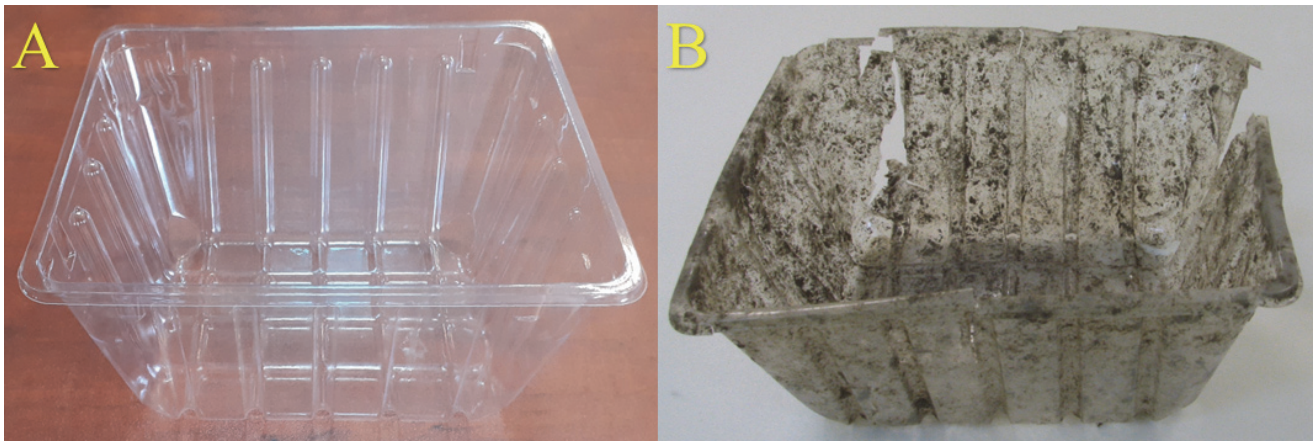

Fig. 1. General images of the investigated samples [A – the packaging used for the tests (before incubation); B – the packaging taken out of the soil after three years incubation]

incubation in soil. Considering the cold crystallization and melting enthalpies of both samples, and the fact that the melting enthalpy of 100% crystalline PLA is 93 J/g (Fischer et al. 1973), the degrees of crystallinity of PLA "0" and PLA "3" samples are 2.8 and 3.4%, respectively. They are very similar, and thus, the haze of the packaging shown in Fig. 1B is not related to a change in the degree of crystallinity of the sample. Comparing the phase transition temperatures in Fig. 3, it can be seen that they are almost the same for both samples, except for the cold crystallization temperature, which in the case of sample PLA "3" is 6.4°C higher than in the case of sample PLA "0". This may be associated with the formation of a smaller amount of crystallites in sample PLA "3", but with larger sizes, due to a lower nucleation rate. Due to the fact that the cold crystallization enthalpy values of both investigated samples are very similar and that the value of the cold crystallization temperature of sample PLA "3" is significantly higher than the cold crystallization temperature of sample PLA "0", coarse-crystalline structures in the incubated sample should be present. The possibility of the formation of such structures is less advantageous due to the reduced light transmission and the increased degree of haze in the material (Sterzyński 2000). Thus, the reason for the haze of the material shown in Fig. 1B is attributed to the presence of defects in the structure of the material as well as the formation of coarse-crystalline structures.

The double melting peak of the PLA crystalline phase seen in Fig. 3 often occurs in polylactide materials. It refers to the stable pseudo-orthorhombic structure (alpha-form) melting at higher temperatures and the orthorhombic structure (beta-form) that melts at lower temperatures (Dintcheva et al. 2017, Donghee et al. 2011). Double melting endothermic peak may also result from the melting re-crystallisation and re-melting process (Tsuji et al. 2005, Sarasua et al. 1998). In

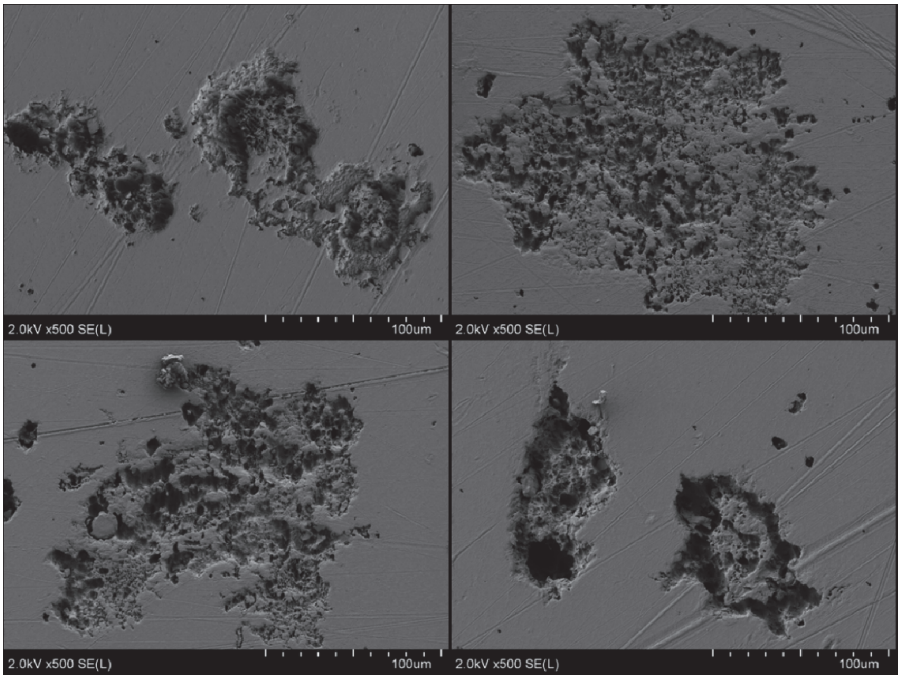

Fig. 2. SEM images of the surface geometrical structure of PLA packaging after three years incubation in a soil environment

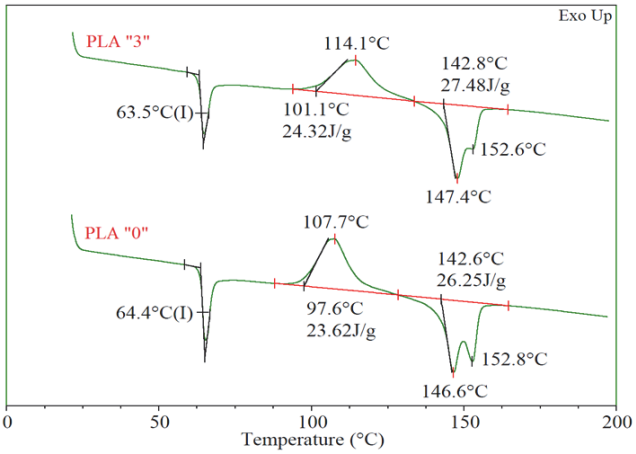

Fig. 3. DSC data of samples PLA "0" and PLA "3" (first heating)

this case, based on the information presented in Fig. 3, it can be observed that recrystallization into more stable crystalline structures is more difficult in samples after incubation in soil. This is indicated by the increasing ratio of the melting enthalpy corresponding to the lower temperature peak to that relating to the higher temperature peak.

The obtained results presented in Fig. 4 (after removing the thermal history) indicate that the thermal properties of polylactide itself do not change significantly after incubation in soil. The temperatures of the phase transitions [glass transition temperature (T_g) and melting temperature (T_m)] as well as the melting enthalpies of the crystalline phases (ΔH_m) are similar (the differences are below 1°C) (Table 1). This proves that there were no significant changes in the structure of the macromolecules in the investigated material, especially their degradation. This may have been due to temperature in the soil being below the glass transition temperature of PLA, which is a key parameter for degradation of the studied material (Weir et al. 2004, Kale et al. 2007, Saadi et al. 2012). Degradation of PLA should be much greater near its glass transition temperature (T_g, 55–65°C). At this temperature PLA begins to change from a glass-like state to a rubber-like state, while increasing water absorption. As a consequence of this, it accelerates hydrolysis of the ester linkages and microbial activity (e.g. thermophilic bacteria) (Itavaara et al. 2002, Kale et al. 2007). This activity is further enhanced by increasing the polymer hydrophilicity due to water absorption into the polymer matrix (Södergard et al. 1996, Siparsky et al. 1997). Therefore, for effective PLA degradation, microbial attack at a high temperature must be guaranteed (Adhikari et al. 2016).

Fig. 4 also shows that no cold crystallization occurred in both samples. This indicates that both samples formed the maximum number of crystallites during cooling in the DSC analysis. Moreover, the number of these crystallites in both samples must have been similar because the melting enthalpies of these samples are not significantly different from each other.

The PLA packaging after incubation in soil also shows similar heat stability to packaging before incubation (Figs. 5A and 5B). In the case of the incubated sample (PLA "3"), only slightly lower values of the temperatures $T_{5\%}$, T_{max} and $T_{95\%}$ are observed (Table 1). The slight decrease in these values (from 1.7°C in the case of $T_{95\%}$ to 8°C in the case of $T_{5\%}$) may indicate only a slight degradation of PLA macromolecules and that the thermal stability of the PLA packaging after 3 years incubation in the soil hardly changed. This is also confirmed by the results of GPC measurements (Table 2), where the reduction in average molecular weights did not exceed 8%, and the degree of polydispersity (PD) did not change.

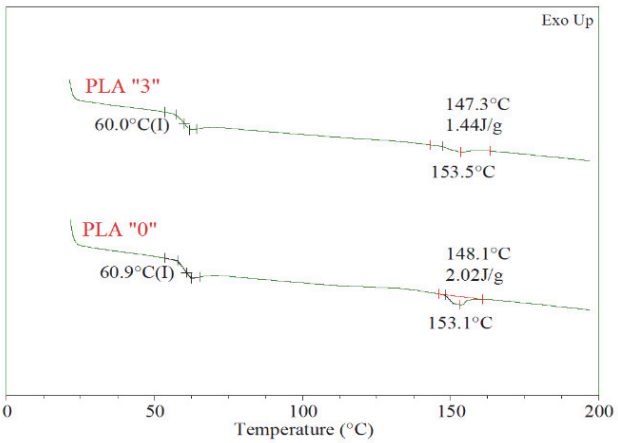

Fig. 4. DSC data of samples PLA "0" and PLA "3" (second heating)

Table 1. DSC and TG data of the studied samples

	Sample	PLA „0"	PLA „3"
DSC analysis	T_{g1} [°C]	64.4	63.5
	T_{g2} [°C]	60.9	60.0
	T_{cc1} [°C]	107.7	117.1
	T_{m1} [°C]	166.6 152.8	147.4 152.6
	T_{m2} [°C]	153.1	153.5
	ΔH_{cc1} [°C]	23.62	24.32
	ΔH_{m1} [°C]	26.25	27.48
	ΔH_{m2} [°C]	2.02	1.44
TG analysis	$T_{5\%}$ [°C]	336.6	328.6
	$T_{max.}$ [°C]	369.9	366.2
	$T_{95\%}$ [°C]	387.3	385.6

Table 2. Changes in average molecular weights (number – M_n and weight – M_w) and the degree of polydispersity (PD) of samples PLA "0" and PLA "3"

Sample	M_n [Da]	M_w [Da]	PD
PLA „0"	100 500	186 400	1.85
PLA „3"	92 500	171 800	1.86

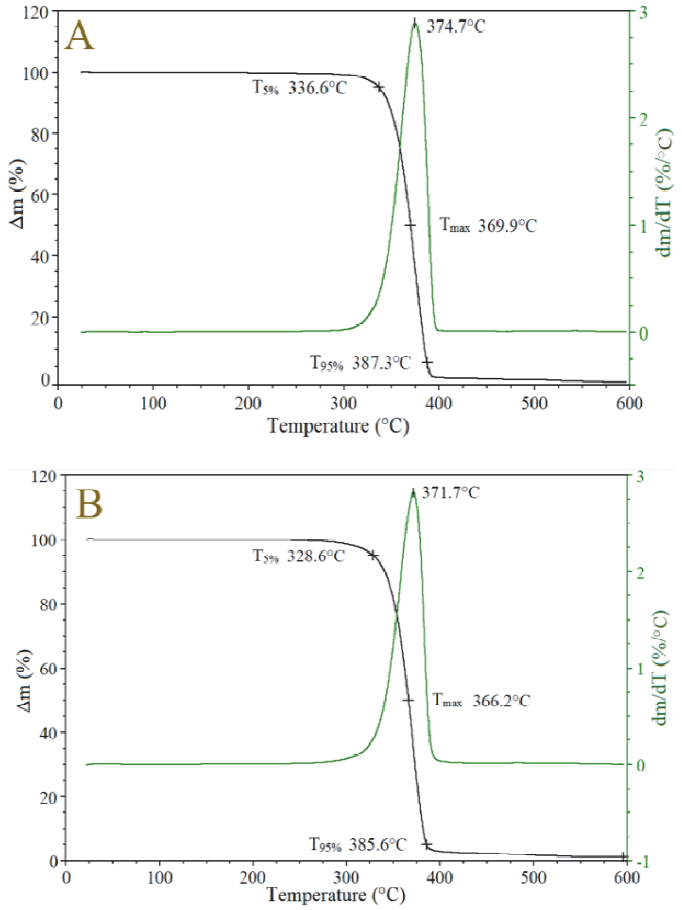

Fig. 5. Results of thermal investigations (A – TG/TGA analysis of sample PLA "0"; B – TG/TGA analysis of sample PLA "3")

Conclusions

- The studies of the long-term influence of soil conditions on packaging obtained from PLA showed that this type of packaging does not undergo significant biological decomposition in soil environment conditions. Changes in its structure and thermal properties after a long-term exposure to these conditions are too small to clearly state that this type of packaging undergoes significant decomposition after 3 years in soil environment. Apart from the subtle changes described above, the incubated packaging samples did not disintegrate in any way or even lose their original shape.
- Nevertheless, based on some research results (i.a. SEM, GPC), it can be concluded that the initiation of the biodegradation process took place and that this process is much faster than in the case of conventional non-biodegradable polymers.
- Generally, the degradation rate of PLA packaging in soil is very low. Therefore, new biodegradable polymers with properties similar to PLA that have a higher degradation rate in soil and are safe for the environmental microorganisms should be developed in the future.
- The results of our study are strong confirmation that materials obtained of various biodegradable polymers (not only PLA) should be biodegradable only under strictly defined conditions, allocated to specific type of polymer, i.e., those in which they are easily and quickly biodegradable. Therefore, in the case of waste bioplastics degradation in soil, the biodegradability of each individual polymer should be considered.

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Długoterminowy wpływ warunków środowiska glebowego na strukturę i wybrane właściwości opakowań z PLA

Streszczenie: W pracy przedstawiono wyniki badań opakowań otrzymanych z polilaktydu (PLA), które poddane zostały długotrwałemu oddziaływaniu warunków środowiska glebowego. Celem naukowym badań było określenie zmian wybranych właściwości opakowań z PLA po długotrwałej inkubacji w glebie. Zmiany te badano za pomocą skaningowej mikroskopii elektronowej, różnicowej kalorymetrii skaningowej, analizy termograwimetrycznej, a także chromatografii żelowej. Dokonano analizy struktury, właściwości cieplnych oraz stopnia dezintegracji opakowań po trzyletniej inkubacji w glebie. Stwierdzono, że opakowania wytworzone z PLA nie ulegały znacznemu rozpadowi w środowisku glebowym, a niewielkie zmiany obserwowane w ich strukturze i brak istotnych zmian właściwości cieplnych wskazują, że efektywność ich degradacji w warunkach glebowych po trzech latach jest bardzo niska. Było to spowodowane głównie niedostateczną temperaturą w glebie. Stwierdzono również (na podstawie wyników skaningowej mikroskopii elektronowej i chromatografii żelowej), że miała miejsce inicjacja procesu biodegradacji, a także, że proces ten jest znacznie szybszy niż w przypadku klasycznych polimerów niebiodegradowalnych. Otrzymane rezultaty badań wskazują na to, że materiały wytwarzane różnych rodzajów polimerów biodegradowalnych (nie tylko PLA) powinny być poddawane procesowi biodegradacji wyłącznie w ściśle określonych warunkach, dedykowanych dla danego rodzaju polimeru, tzn. takich w których łatwo i szybko ulegną one rozkładowi biologicznemu.