



Degradation of bio-based film plastics in soil under natural conditions

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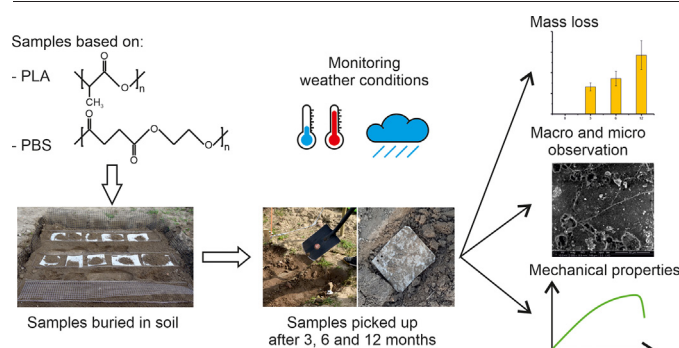
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HIGHLIGHTS

- Biodegradation of bio-based plastics in soil under natural condition was investigated.
- Examined samples in the form of film composed mainly from PLA and PBS.
- After 12 month's loss of mass was observed for sample composed from PBS.
- Erosion of the surface was noticeable after 12 months of degradation.
- Tensile strength at break and thermal stability decreased for samples contained PLA.

GRAPHICAL ABSTRACT



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ABSTRACT

The degradation of bio-based plastic materials in field soil under natural conditions was investigated in this study. Three bio-based plastics materials, which contained polylactide (PLA) with polybutylene adipate terephthalate and additives (PLA_1), PLA-based polyester blend with mineral filler (PLA_2), and polybutylene succinate with mineral filler (PBS_1) in the form of the film, were subjected to soil burial biodegradation processes. The experiments were carried out in a climate with an average annual temperature of 9.4 °C, in winter and summer periods for one year. The degradation of the materials was evaluated by macro- and microscopic observations, weight loss, thermogravimetric analysis, and tensile test. Macroscopic observation indicated that changes in the color of film surface were visible for samples PBS_1 after 12 months of degradation. Using microscopic inspection the erosion of surface samples PLA_1 and PBS_1 after 12 months was observed. Mass loss of samples PLA_1 and PLA_2 after one year of degradation were below 0.6 %. Moreover, for PBS_1 sample, mass loss was equal to 4.3 %. Based on the obtained results of the mass loss, a description of the degradation kinetics was proposed, showing the changes in the thickness of the tested polymer over time. The thermal stability of the samples PLA_1 and PLA_2 decreased during the degradation process by 16.1 and 2.6 °C, respectively, and for PBS_1 increased by 1.7 °C. Tensile strength at break after 12 months of degradation decreased for sample PLA_1 and PLA_2 by 27.3 and 5.8 %, respectively, and increased for sample PBS_1 by 28.2 % compare to unexposed sample.

1. Introduction

Plastic materials are widely used, especially in packaging applications. Most plastics are made from petroleum-based polymers such as polyolefins or polyesters. Conventional plastics are characterized by simply and low cost processing by injection molding or blow molding, and good functional

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properties such as high mechanical durability and excellent chemical stability, what is important from the packaging application point of view (Chanda, 2018). Unfortunately, they have one major disadvantage, which is the long-period of accumulation in the environment. Despite the increase in the efficiency of plastic waste management systems, a large proportion of them end up in the environment. Unmanaged plastics can be found in any environment from high mountains to deep oceans (soil, water). Intermediate products of their disposal in e.g., the combustion process, cause air and soil pollution. The accumulation of plastics and their recycling products in the environment forces the industry to use novel types of materials, which time of accumulation in the environment will be shorter (Kumar et al., 2021).

Bio-based plastics are environmentally friendly due to the fact that they are produced from renewable feedstock. The biggest disadvantage is their high production price. Lowering the costs of using bio-based plastics is mainly focused on reducing the costs of their disposal, e.g. by using them as mulch films (Briassoulis and Mistriotis, 2018). Therefore, one of the very important issues is studying the degradation process of bio-based plastics. Degradation of polymer consists mainly of three steps: biodeterioration, biofragmentation and assimilation (Emadian et al., 2017a). Biodeterioration is a process involving the growth of microorganisms on the surface of a polymer and thus changing its mechanical, chemical and physical properties. Bacteria secrete slime which penetrates the surface of the polymer whereas fungi develop mycelia framework. These microorganisms can penetrate the pores and enlarge their size provoking cracks. Biofragmentation is related to cutting polymer to oligomers and monomers into dissolved form. Microorganisms secrete specific enzymes responsible for polymers scission. They can produce different types of enzymes to specific polymer after period necessary to establish the cell machinery (Lucas et al., 2008). Assimilation is the most important step in biodegradation process in which microorganisms use mainly carbon from monomers to produce CO₂, energy and biomass under the aerobic conditions whereas CO₂ and CH₄ are formed under anaerobic conditions (Briassoulis and Mistriotis, 2018).

The rate of the aforementioned steps is influenced by both the biotic and abiotic conditions but also by the properties of the polymer (Polman et al., 2021). Biotic factors are associated with microorganisms that come into contact with the degraded polymer. The main groups of microorganisms involved in biodegradation process include fungi, bacteria and algae (Briassoulis and Mistriotis, 2018). The exact determination of the biotic factor is difficult due to the abundance of microorganisms in a given environment. Abiotic factors are related to the conditions for which plastic materials are exposed e.g. weather conditions (temperature, precipitation), moisture, oxygen content and soil properties (pH, macro-, meso-, and microelements, and soil texture). The abiotic factors shouldn't be neglected because they have a great influence on biotic factors (Lucas et al., 2008). The properties of polymers influencing the degradation include: chemical structure, polymer chain, crystallinity (Emadian et al., 2017a). The most popular bio-based plastics are polyhydroxyalkanoate (PHA), polylactide (PLA) and polybutylene succinate (PBS). Presently, the PLA and PBS are the most commercially used in many different applications. The progression and application of PLA was made it possible by the commercial marketing of polymers with the trade name INGENIO Nature Works by Cargill Dow LLC (Vink et al., 2003), whereas in the case of PBS it was made possible by Showa Denko K.K. and polymers with the trade name Bionolle (Fujimaki, 1998). These polymers are compostable, but PLA is hardly degradable at ambient temperature because it is resistant to microbial attack (Zaaba and Jaafar, 2020). In order to improve the bio-based polymer properties (e.g., biodegradation) the mineral fillers were added (Misra et al., 2006; Shogren et al., 2003).

The biodegradation research can be carried out in compost, soil, sea water, municipal solid waste and digestion process (Emadian et al., 2017a). Soil is extremely complex environment which contains a wide range of properties (e.g. mineral particles and organic matter) and microorganisms (Lucas et al., 2008), which enables the plastics degradation to be more feasible with respect to other environments such as water or air

(Emadian et al., 2017b). Depending on the soil environment, the characteristics of bio-plastics biodegradation can be different. This environment is the least researched among those mentioned earlier. Due to the fact that the process of biodegradation in soil under natural conditions is slow, it allows in-depth investigation of the first stage of biodegradation, which is biodeterioration. Studies on biodegradation in soil are especially important for farmers in order to convince them to use bio-based plastics instead of conventional polyethylene (PE) mulch films (Hayes et al., 2017).

The biodegradation of both the pure PLA and the one with additives (other polymers or fillers) in soil was investigated under controlled conditions by Adhikari et al. (2016), Da Silva Gois et al. (2017), Grzabka-Zasadzińska et al. (2018), Harmaen et al. (2015), Karamanlioglu and Robson (2013) Martucci and Ruseckaite (2015), Phetwarotai et al. (2013), Rapisarda et al. (2019), Rudnik and Briassoulis (2011), Wu (2012), and under uncontrolled conditions by Gallet et al. (2001), Hayes et al. (2017), Ho et al. (1999), Hoshino et al. (2001), Janczak et al. (2020), Rudnik and Briassoulis (2011) and Shogren et al. (2003). The number of studies on biodegradation of the PBS in soil is much smaller. So far, the study of biodegradation in controlled conditions has been performed by Adhikari et al. (2016), Puchalski et al. (2018) and under uncontrolled conditions by Hoshino et al. (2001). Most of the studies on the biodegradation of bio-based plastics in soil have been conducted in controlled conditions at temperatures above 25 °C and/or <60 days (Adhikari et al., 2016; Harmaen et al., 2015; Rapisarda et al., 2019; Wu, 2014). Some studies on degradation in soil under natural conditions suffer from no information on weather data and/or soil properties (Gallet et al., 2001; Shogren et al., 2003).

To date, in soil under natural condition the pure PLA bio-based polymer was widely investigated, on the contrary to pure PBS, whereas PLA and PBS with additives received the least attention. In the topical literature there is only one study on comparison of degradation of pure PBS and PLA in soil under natural conditions where the degradation rate was described only through changing the mass loss (Hoshino et al., 2001). Novelty of this study lies in quantification of the degradation degree of both polymers with additives, mainly mineral fillers, in the same natural conditions identified by various indices.

This study aims at bringing new insights about the biodegradation of the novel types of bio-based plastic materials consisting mainly of PLA and PBS in the field soil under natural conditions. The degradation of the studied polymers in the form of film was determined by means of weight loss, macro- and microscopic observations, thermogravimetric analysis as well as mechanical tests revealing the changes in mechanical properties. Based on the obtained results of the mass loss, a mathematical model for the kinetics of degradation was proposed, showing the changes in the thickness of the tested polymer with time.

2. Materials and methods

2.1. Materials

The test materials used in this study mainly consisted of PLA and PBS with various additives. Three different bio-based plastics marked PLA_1, PLA_2 and PBS_1 in the form of a film were taken for experiments. The thickness of the plastic materials was approximately 155 ± 14 , 174 ± 16 and 332 ± 30 μm for PLA_1, PLA_2, and PBS_1, respectively. The first material (PLA_1) contained PLA (70–80 %) blended with polybutylene adipate terephthalate (PBAT) (10–20 %) and plasticizer (10–20 %). The second material (PLA_2) consisted of PLA-based polyester blend (70 %) and mineral filler (30 %) and the third one (PBS_1) being PBS (85–90 %) blended with a mineral filler (<15 %). Abovementioned bio-based plastics have been tested within the Bio-plastics Europe EU Project (Horizon 2020, grant agreement no. 860407). According to the nomenclature adopted in the project the plastic materials marked in this work PLA_1, PLA_2, PBS_1 were as follows: BPE-AMF-PLA, BPE-RP-PLA and BPE-SP-PBS, respectively. Material market by BPE-AMF-PLA (Bio-Plastics Europe - Agriculture Mulch Film - PolyLactic Acid) was provided by NaturePlast SAS (NP, France), BPE-

RP-PLA (Bio-Plastics Europe - Rigid Packaging - PolyLactic Acid) was provided by Arctic Biomaterials OY Ltd. (ABM, Finland) and BPE-SP-PBS (Bio-Plastics Europe - Soft Packaging - PolyButylene Succinate) was provided by NaturePlast SAS (NP, France). Before the use in experiments the film samples were stored in dry, dark and cool desiccator.

2.2. Field experiments

Degradation of test materials in soil under natural conditions has been carried out in an agricultural field in Straszów, Poland (N: 52° 13' 29.8194" E: 18° 57' 9.057") for a period of 12 months (from October 2020 to September 2021). The sites for the placement of tested material samples which were marked out on the cultivated area were weeded first, and then the soil was removed to the depth of 20 cm and sieved through a wire mesh of 1–2 cm to remove gravel and plant materials. Half of the soil was then put back in the dug hole and the soil was mildly leveled. The samples in the form of a film cut into rectangles (110 mm × 100 mm) were weighted before being placed in the wire-type cages to protect them from mechanical damage and animal invasions, and thereafter buried in the field soil dug about 10 cm below the soil surface. Three replicates for each plastic type and timepoint were used. The test specimens were placed at spacing of about 150 mm between the rows and columns. The remaining second part of the soil was gently put on top of the samples and their positions were marked on the soil surface. The growing plants were pruned occasionally. After 3, 6 and 12 months the samples were picked up from the soil, gently cleaned by soft sponge, rinsed with distilled water, then dried at temperature 30 °C to a constant weight, photographed and weighted to determine the mass loss of the tested materials. After drying the samples were stored in a dry, dark and cool desiccator.

2.3. Methods

The weather data (daily air temperature, amount of rainfall and insolation) were collected from the meteorological station (Kolo, Poland N: 52° 11' 58.277" E: 18° 39' 33.547") nearest to the location of the field experiment in Straszów (Poland).

At the beginning of the experiments the soil properties were characterized by pH, C, N, P, K, Mg, Ca, S, B, Mn, Cu, Zn, Fe and soil texture. Sample of soil for analysis were collected according with PN-ISO 10381-2:2007. Soil pH was measured according with the Polish standard PN-ISO 10390:1997. The carbon content in soil was determined using the Turin method, the Ca content by the flame photometry, the S by the nephelometric method, and the content of N was determined by Kjeldahl method. The content of other elements were quantified according of the established standards, namely K - PN-R-04022:1996, Mg - PN-R-04020:1994, P - PN-R-04023:1996, Fe - PN-R-04021:1994, B - PN-93/R-04018:1993, Mn - PN-93/R-04019:1993, Zn - PN-92/R-04016:1992, and Cu - PN-92/R-04017:1992. Texture properties of the soil (sand, silt, and clay) were determined using a laser diffraction method (ISO 13320:2020).

Macroscopic observations of the film surface were carried out using the camera Panasonic DMC-FZ28 whereas microscopic examination of tested films were performed with the scanning electron microscope (SEM) Nova NanoSEM 230 from FEI company (SE Detector, HV: 15 kV, Low Vacuum: 0.3 Torr).

The thermal properties of tested films were carried out using the thermogravimetric analyzer (Netzsch STA 409 PG). The sample was heated from 30 to 600 °C with a heating rate equal to 10 °C/min under air atmosphere. Thermal decomposition of samples was carried out according to PN-EN-ISO-11358-1. Tensile properties of the tested film samples, e.g., stress at break and strain at break, were estimated by using an Instron 5944 (Instron, USA) mechanical testing machine. The size of the tested samples was determined by the size of the samples taken without defects from the field and was equal to 10 × 100 mm². The test was performed with the initial distance of 50 mm between the clamps and a velocity of 50 mm/min. The measurements for the 10 samples were obtained at 23

°C and 50 % relative humidity. The measurements were performed according to standards ISO-527-1:2019 and ISO-527-3:2018.

3. Results and discussions

3.1. Properties of soil and weather conditions

The properties of field soil, in which the biodegradation process was carried out, were determined at the start of the process. The pH of soil was neutral (Table 1) in which nutrients are available for plants. Based on the conducted analysis, the content of macrolelements (N, P and K) in soil was high. The soil richness in mesoelements (Ca, Mg and S) was a low value. On the other hand, the content of microelements in soil (B, Mn, Cu, Zn and Fe) was at the average level. Based on properties of soil texture presented in Table 1, the research was carried out in a sandy loam soil.

Fig. 1a shows the changes of the average air temperature in individual months, while the standard deviations present the minimum and maximum air temperatures in a given month. During the first 7 months of biodegradation tests, the average monthly air temperature was below 11 °C, while the average temperature during the 12 months was 9.4 °C. The range of variation of the instantaneous temperatures ranged from – 20 °C to 35 °C. The total amount of rainfall during the year was 560 mm. The conditions, in which the biodegradation research was conducted, did not differ significantly from the average long-term temperature (7.3 °C) as well as the magnitude of precipitation (607 mm) in Poland. Monthly precipitation above 40 mm occurred mostly when the monthly average air temperature was above 10 °C (Fig. 1b). The number of hours with the sun shining during the day (not overcast sky) was closely correlated with the air temperature.

3.2. Morphological changes

Morphological changes were investigated by macro- and microscopic inspections. Macroscopic observation of tested samples is useful for the initial assessment of the extent of a degradation process. The first stage of degradation, called the biodeterioration, is characterized mainly by a change in the color of the sample's surface. This discoloration can be caused by microorganisms present on the surface of the sample, which can change the pH of materials leading to color changes and promoting damage on material properties by hydrolytic reaction (Mitchell and McNamara, 2010). The next steps of biodegradation (biofragmentation and assimilation) are characterized by the appearance of small/huge holes on the surface of polymer sample, finally leading to its disintegration. Photos of tested samples before and after 3, 6 and 12 months of degradation are shown in Fig. S1. Thorough examination of the surfaces of PLA_1 and PLA_2 films after 3, 6 and 12 months of degradation in soil, no changes due to erosion were noticed neither in the color of the film nor in its original shape. According to

Table 1
Properties of the field soil at the beginning of the process.

Soil properties	Value	Richness of soil
pH	7.30 ± 0.14	Neutral
C org. (%)	0.54 ± 0.01	–
N (%)	0.0112 ± 0.0002	–
P ₂ O ₅ (mg 100 g ⁻¹)	42.5 ± 0.91	Very high
K ₂ O (mg 100 g ⁻¹)	19.1 ± 0.39	Medium
Ca (mg dm ⁻³)	1447 ± 27	–
Mg (mg 100 g ⁻¹)	4.00 ± 0.08	Low
S-SO ₄ (mg 100 g a.d.m. ⁻¹)	0.50 ± 0.01	Very low
B (mg kg ⁻¹)	0.86 ± 0.02	Low
Cu (mg kg ⁻¹)	3.20 ± 0.07	Medium
Fe (mg kg ⁻¹)	896 ± 19	Medium
Mn (mg kg ⁻¹)	104.3 ± 2.2	Medium
Zn (mg kg ⁻¹)	17.8 ± 0.33	Medium
Size of soil particles (mm)	Participation (%)	
Sand (2.0–0.05)	69.74 ± 1.41	
Silt (0.05–0.002)	27.37 ± 0.57	
Clay (<0.002)	2.88 ± 0.07	

a.d.m. stands for air dry matter.

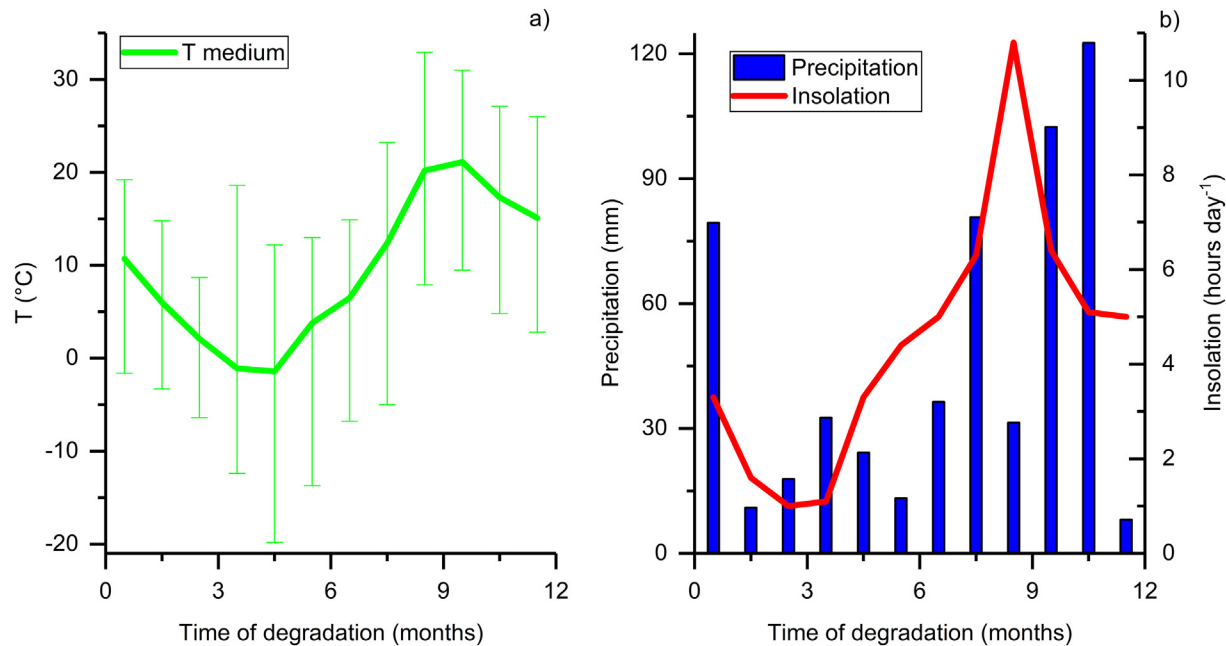


Fig. 1. Changes of air temperature (a), precipitation and insolation (b) during the degradation process.

explanations by Rudnik and Briassoulis (2011), microorganisms that degrade PLA are not easily found in natural environments. For PBS_1, the color change of the sample was observed only after 12 months of degradation. Additionally, small holes appeared on the surface of the film. The

results obtained for the PBS_1 test after 12 months prove the presence of all steps of degradation. The lack of the surface changes in all tested polymers after 3 and 6 months of degradation was mainly due to environmental conditions. During the first 6 months of degradation, the average air

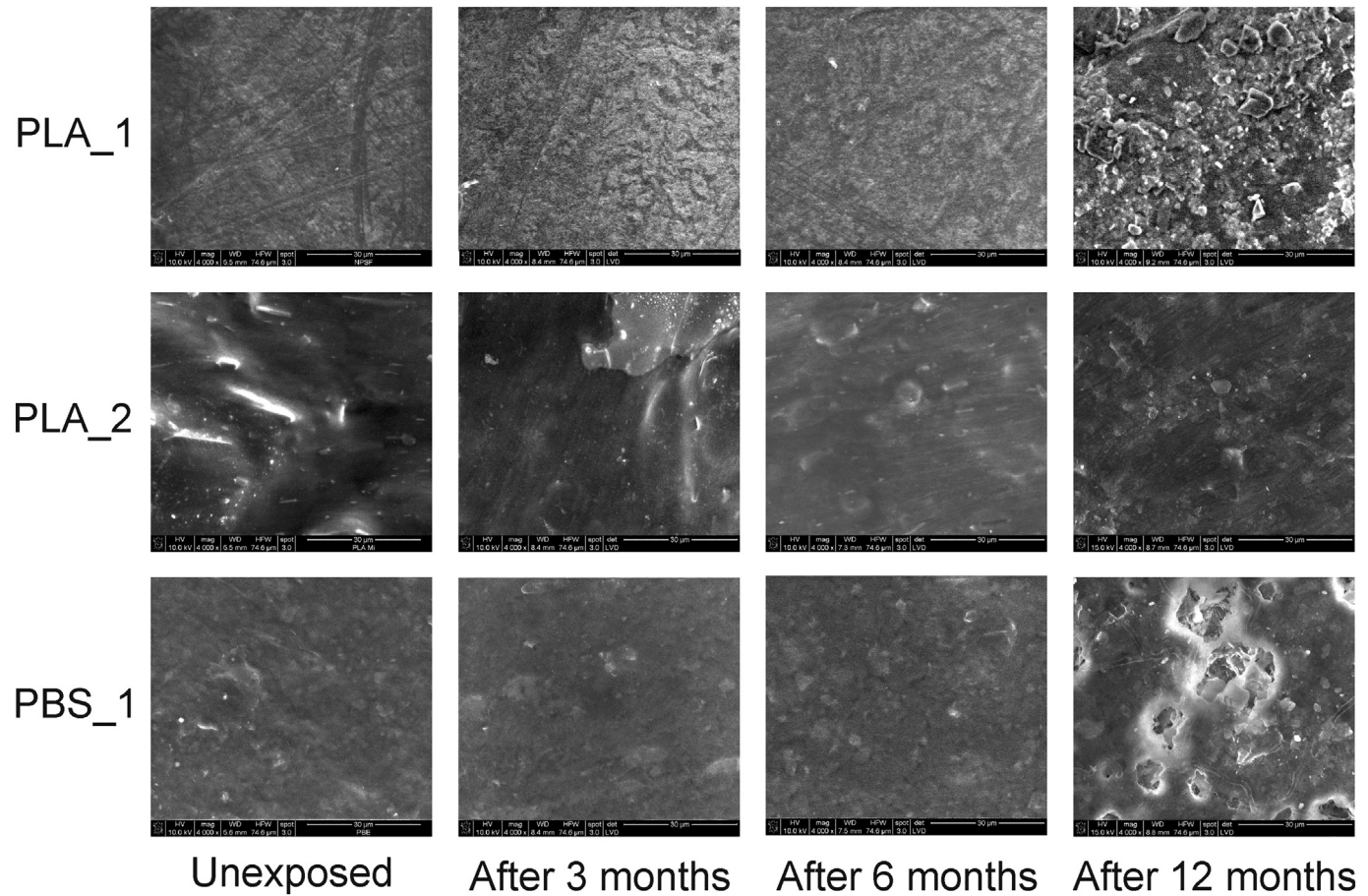


Fig. 2. Microscopic observation by using SEM of polymer surface at magnification × 4000.

temperature was only 3.4 °C, with the total rainfall of only 180 mm. Very low rate of degradation of PLA in soil under natural conditions was noticed by Hoshino et al. (2001). Also, on a laboratory scale the indiscernible degradation rate of PLA was observed when temperature was equal to 25 °C (Karamanlioglu and Robson, 2013). A more in-depth study of morphologic changes was performed by scanning electron microscopy. The samples before degradation were characterized by a relatively smooth texture. However, the shapes typical for technological processes of film production were visible as well as, especially for PLA_2, where mineral fillers have been embedded in the polymer matrix.

The SEM studies confirm macroscopic observations and lack of changes in morphological structure of the surface of samples after 3 and 6 months of degradation in soil (Fig. 2). Natural conditions of the process did not favor quick degradation of the films made of biodegradable materials. Changes were observed only after one year. In this case, the effects of surface erosion and disintegration of the materials can clearly be seen especially in PBS_1 material. After 12 months the changes were also noticeable for PLA_1 using SEM technique what confirms mainly surface erosion of the polymer. Surface degradation of polymer was mainly caused by microcracks which indicate the biofragmentation stage of a degradation process. For sample PLA_2 degradation of surface was not visible.

3.3. Degradation kinetics

In order to determine the degradation kinetics, the mass loss (ML) was calculated based on the Eq. (1) (Martucci and Ruseckaite, 2015).

$$ML = \frac{m_0 - m_t}{m_0} \cdot 100 \quad (1)$$

where: m_0 is the sample mass before burying (g), and m_t denotes the sample mass after degradation time t (g). Before the mass of each the sample was determined, the samples were thoroughly washed, dried and stored in a desiccator. The ML analysis is burdened with an error that may be due to an incomplete removal of soil from the film surface. However, the use of more harsh methods of removing soil from the polymer could cause its damage.

Throughout the 6 months of degradation, the ML for all samples was below 0.5 % (Fig. S2). The very low level of degradation of the tested polymers was mainly due to the prevailing environmental conditions. During this experimental period, the average monthly air temperature was below 11 °C, and the sum of monthly precipitation, except for the first month, was below 33 mm. In the period between the 6th and 12th month of degradation, which is the summer time in Poland, the average monthly air temperature was above 11 °C. The increase in air temperature caused a significant raise of ML (4.3 %) for PBS_1. For the PLA_1 and PLA_2 tests, between the 6th and 12th month of the degradation process, the increase in weight loss was not as visible as for the PBS_1 test. After 12 months of degradation in soil, the ML for the PLA_1 and PLA_2 samples was 0.23 and 0.57 %, respectively.

In the studies by Hoshino et al. (2001), on biodegradation of the PLA without additives in soil under natural conditions for 12 months, the ML was below 2 %. In contrast, the mean ML of PBS without additives after 12 months of degradation was 26.5 %. Smaller mass losses in our research were caused by the lower average air temperature and lower precipitation than those in the studies conducted by Hoshino et al. (2001). It should also be emphasized that despite the higher temperature in the studies of Hoshino et al. (2001), the degradation of PLA was very small. The loss of PLA mass in soil after 2 months being >1 % is visible when the temperature is above 37 °C (Karamanlioglu and Robson, 2013; Tokiwa and Calabia, 2006). An accurate comparison of the obtained results is difficult due to diminishing sample dimension and different process conditions (temperature, soil properties, etc.) changing in time. The dimensions of samples used by Hoshino et al. (2001) and Karamanlioglu and Robson (2013), were in the range 20–115 × 20–25 mm and the thickness in the range 10–200 µm being different from the ones used in this study. According to

Chamas et al. (2020) the degradation rate of flat plastics (in the form of a film) is proportional to the surface area S (m²) and the rate constant k (kg s⁻¹ m⁻²) (Eq. 2).

$$-\frac{dm}{dt} = k \cdot S \quad (2)$$

Assuming that degradation takes place only at a flat polymer surface, the degradation rate is linearly proportional to the surface area (S). Dividing the rate constant (k) by density of plastic (ρ) we received the specific surface degradation rate (k_d) with dimension m s⁻¹. Mass loss of plastic is connected with decrease of its thickness by the following equation:

$$-\frac{dm}{dt} = k_d \cdot \rho \cdot S \quad (3)$$

After mathematical transformation the integration of Eq. (3) lead to the subsequent equation:

$$\frac{m_t}{\rho \cdot S} = \frac{m_0}{\rho \cdot S} - k_d \cdot t \quad (4)$$

The expression $m/(\rho \cdot S)$ in Eq. 4 enables calculation of medium thickness of the film based on mass loss. The k_d index was calculated based on the difference in film thickness at the beginning and after 1 year of degradation.

For samples PLA_1 and PLA_2, the k_d was respectively equal to 0.4, 0.6 µm·year⁻¹, whereas for PBS_1 it was equal to 14.4 µm year⁻¹ (Table 2). The comparison of k_d with the literature data is difficult due to the fact that not all authors in their research papers concerning degradation provided the surface, thickness, density of the film and weight loss during the process. In addition, the tests were carried out in various process conditions (e.g., temperature, humidity, compost, type of soil). In research carried out by Hoshino et al. (2001) during 12 months degradation of PBS and PLA films in soil at natural condition the lower k_d values were observed, being equal to 0.37 and 0.02 µm year⁻¹, respectively. The significant impact of temperature on the k_d values was noticed by Karamanlioglu and Robson (2013). Namely, increased temperature from 37 to 45 °C during degradation of PLA in soil caused growth in the k_d value from 2.0 to 580 µm year⁻¹, respectively. An environment rich in microorganisms (compost) can degrade the PLA at a temperature of 37 °C at the rate 40 µm year⁻¹ (Karamanlioglu and Robson, 2013).

3.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) provides information about thermal decomposition. The tested bio-based polymers decomposed in the temperature range from 300 to 410 °C (Fig. 3a). The residual mass of the samples at 600 °C was related to the ash content in the sample, as the thermal analysis was carried out in an oxygen atmosphere. The ash content in the individual samples PLA_1, PLA_2, and PBS_1 was 3.06, 32.6, and 11.0 wt%, respectively. The presence of ash in the tested samples was caused by mineral compounds added to polymers in order to improve their properties. When analyzing the course of the DTG curves, it was observed that both the PLA_1 and PBS_1 samples had one peak at 357.8 and 391.3 °C, respectively, at which the decomposition rate was at its maximum (Fig. 3b). For the PLA_2 sample, two peaks were observed at the temperatures of 339.0

Table 2
Changes in thickness of the samples during degradation process.

Time of degradation (months)	Thickness of the film (µm)		
	PLA_1	PLA_2	PBS_1
0	155.5	173.5	331.8
3	155.3	173.1	330.7
6	155.3	172.9	330.8
12	155.1	172.9	317.4
Absolute loss in thickness, k_d (µm year ⁻¹)	0.4	0.6	14.4

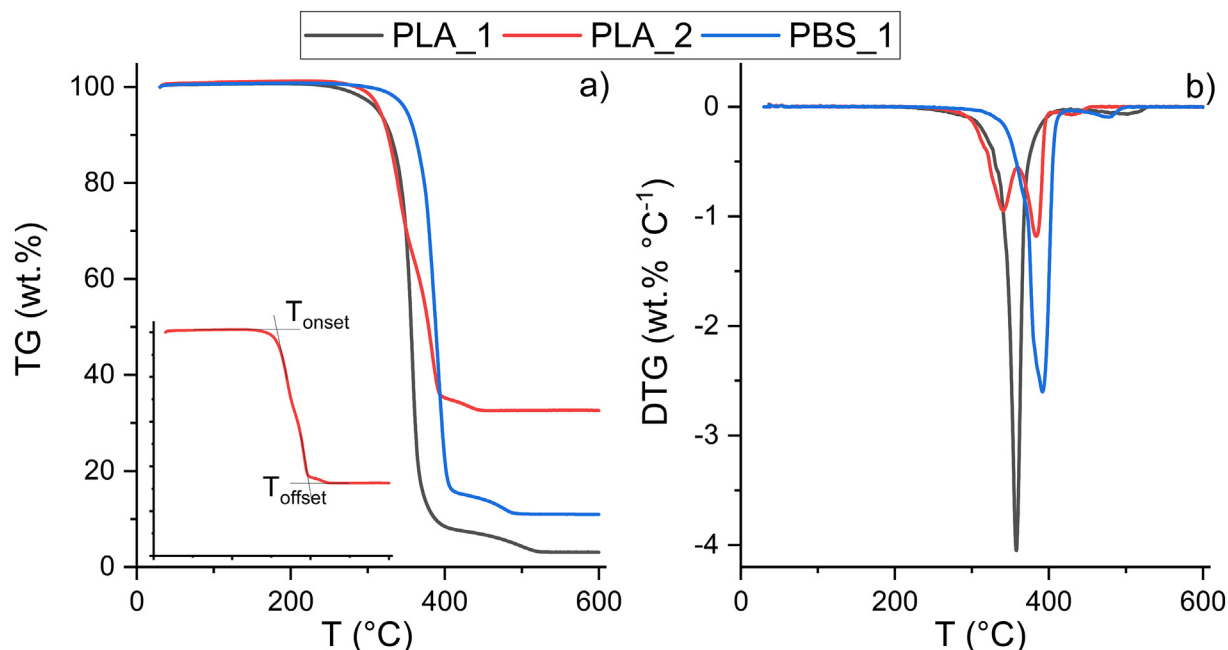


Fig. 3. Changes of mass during thermal decomposition for unexposed samples: a) TG curves, b) DTG curves.

and 383.3 °C. The occurrence of two peaks can be caused by the fact that mineral filler can create with some part of polymer a thermally stable and the heat resistant composite (Saravana and Kandaswamy, 2019). The improvement of such composite properties can be attributed to effect of heterogeneous nucleation of the mineral filler in the matrix of a polymer (Liang et al., 2015). For individual trials, the shape of the TG and DTG curves did not change significantly after 3, 6 and 12 months of degradation.

The changes in thermal properties of the polymer during degradation were determined from the TG curves at the T_{onset} and T_{offset} temperatures (Fig. 3a). T_{onset} defines the initial temperature of the polymer thermal decomposition, also called thermal stability of the sample (Radu et al., 2021). In contrast, T_{offset} is the final temperature of thermal decomposition. For PLA_1 and PLA_2 trials, thermal stability of samples decreased with the elapsed time of degradation. After 12 months of degradation, T_{onset} decreased by 16.1 and 2.6 °C for PLA_1 and PLA_2 samples, respectively (Fig. 4). However, the elapsed time of degradation had no effect on the final temperature of polymer decomposition (T_{offset}). During the degradation of PLA with additives in soil, after 5 months, a decrease in the thermal stability of the samples was observed in the studies conducted by Grzabka-Zasadzińska et al. (2018), Radu et al. (2021) and Da Silva Gois et al. (2017).

The reduction in thermal stability may be attributed to breakage of the bonds in the entire volume of the tested sample. A different nature of the T_{onset} and T_{offset} changes was observed for the PBS_1 trial. With the passing degradation time, T_{onset} and T_{offset} grew by 1.7 and 4.3 °C after 12 months, respectively. Similar properties of the polymer were obtained by Radu et al. (2021) when composting the PLA/PHB sandwich-structured composite trial for 8 months. This behavior of the polymer was explained by the fact that only the polymer surface was degraded. The thermal analysis shows that the thermal stability of the samples is influenced by the type of polymer used, rather than the type of additives.

3.5. Mechanical properties

To illustrate the changes in stress-strain characteristics of investigated material as the result of degradation, the representative engineering stress-strain curves were derived, as shown in Fig. 5. The measurements were carried out in machine direction (MD) and transverse direction (TD).

The PLA_1 film being a blend of PLA and PBAT was the flexible plastic where the yield point is clearly visible not only before but also after degradation. Moreover, the PLA_1 was non-isotropic material from the

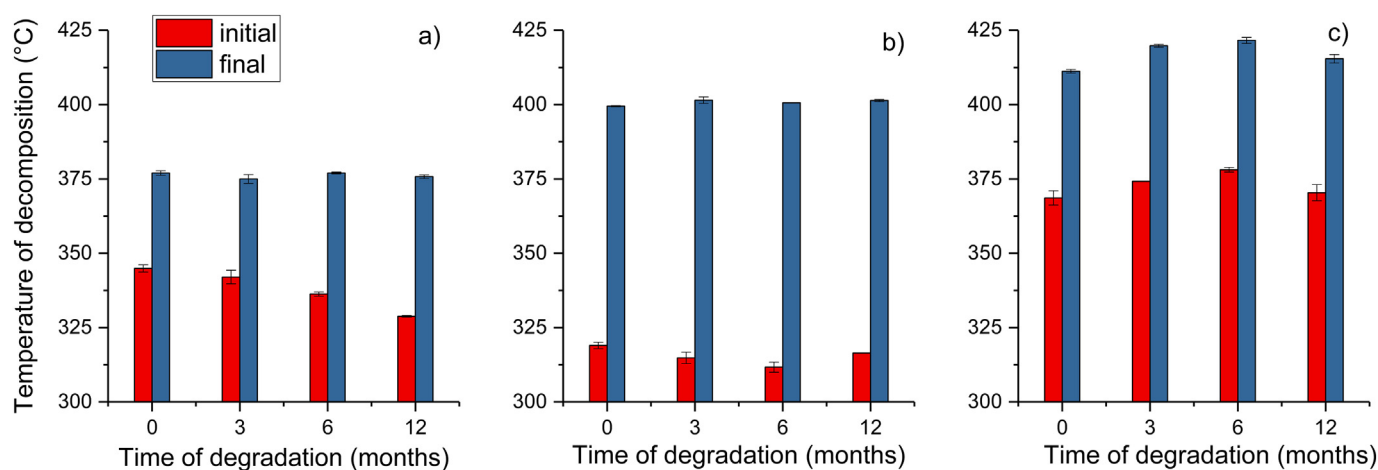


Fig. 4. Changes of initial and final temperature of decomposition: a) PLA_1, b) PLA_2, c) PBS_1.

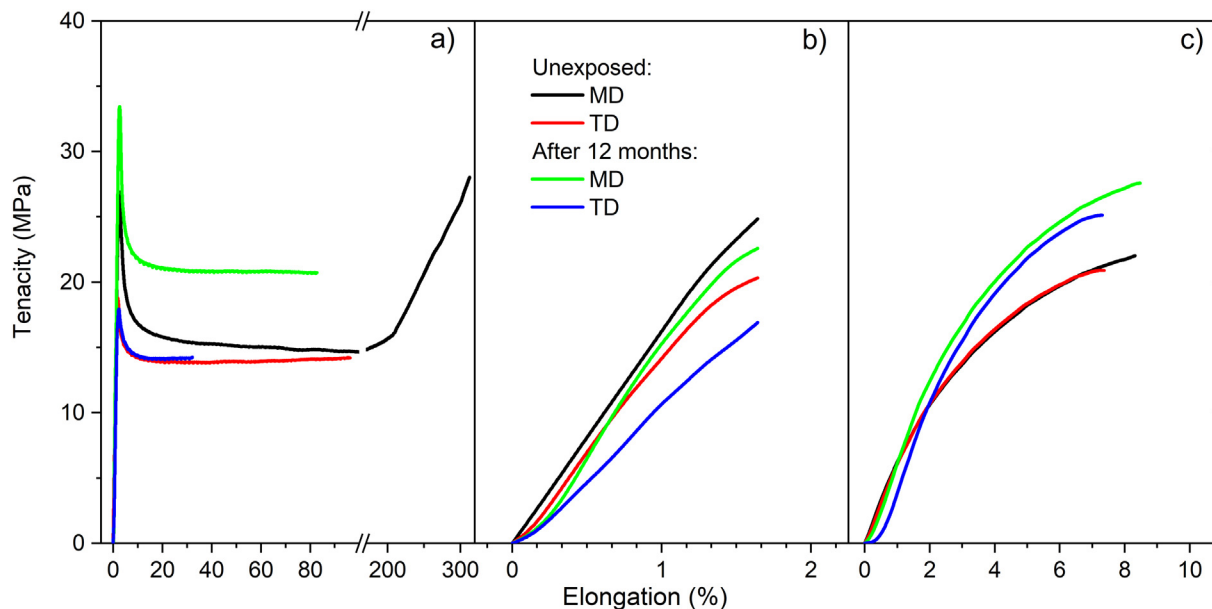


Fig. 5. The representative stress-strain curve of investigated material before and after 1 year of degradation in the field condition for: a) PLA_1, b) PLA_2, c) PBS_1.

mechanical point of view. The initial deformation in machine direction was linearly elastic and afterwards, it was a nonlinear transition with characteristic the yield stress point. Then, a large strain was processed under plateau stress until densification accompanied with notable rise of the stress. In contrast, the mechanical test realized in the transverse direction was stopped on the plateau stress, and the densification phenomenon was not visible. The degradation in soil of PLA_1 film has resulted in change of mechanical properties. The densification phenomenon was not visible in MD and the non-isotropic character of material was accentuated, but the yield stress point was still clearly visible. As a conclusion from the study on the changes in the mechanical properties of PLA_1, it should be noted that the material becomes less ductile, but the yield point is still visible after one year. Considering that PLA is not an elastic material it is reasonable to assume that after one year of degradation PBAT is present in film and performs, albeit in a less significant role, as a plasticizer.

The second investigated material was the PLA_2 film which is a PLA-based polyester blend with mineral filler. The material before and after degradation was brittle, as it was expected based on the properties of polylactide. Additionally, the mechanical properties of investigated materials were non-isotropic in view of stress factor and the tenacity measured in the MD being higher than in the TD. The yearly degradation of the material resulted in slight decrease in mechanical properties; both strength and strain rate reduces, which indicates the beginning of PLA degradation. The material probably exhibited minor structural changes which affect its ability to fragmentation. This result is in accordance with other works realized in the field conditions performed by Puchalski et al. (2017).

The last of investigated material was the PBS_1 film, and in Fig. 5c the evolution stress-strain curve in the degradation process for PBS film is presented. Notably, the material was highly isotropic in terms of mechanical properties. The stress-strain curves are similar for both the MD and TD directions with slightly lower strainability in the TD direction. This property was retained even after one-year degradation. The changes after the one-year degradation are very interesting, as the strength of the material increased in both MD and TD directions at the same time. Moreover, the strain is still similar to the one before the degradation. The increase in tensile strength of PBS film in the first stage of degradation is visible, which shows how differently the degradation process affects the mechanical properties of the investigated materials. In the case of biodegradable aliphatic polyesters the degradation is not always accompanied by decrease in mechanical properties. Sometimes the deterioration of these properties

appears after a longer time, so this aspect of degradation will be studied in the forthcoming years.

In Table 3 the comparison the mechanical properties of unexposed film samples and after 12 months of degradation are presented. The main parameters such as tensile modulus, tensile strength at yield, elongation at yield, tensile strength at break, elongation at break in the MD and TD have been calculated from the strain-stress curves. Additionally, the statistical analyses were performed using OriginPro 2015. The data recordings before and after degradation were subjected to one-way analyses of variance (ANOVA), and the means were compared by

Table 3

Comparison of the tensile properties of unexposed film samples and after 12 months of degradation (E – tensile modulus, σ_y – tensile strength at yield, ϵ_y – elongation at yield, σ_b – tensile strength at break, ϵ_b – elongation at break, MD – machine direction, TD – transverse BPE-AMF-PLA direction, MEAN – mean values, CV – coefficient of variation in percentage.

Tensile parameters	Unexposed				After 12 months of biodegradation			
	MD		TD		MD		TD	
	MEAN	CV	MEAN	CV	MEAN	CV	MEAN	CV
PLA_1								
E (MPa)	1569.1 ^b	4.9	1394.7 ^a	5.2	1900.3 ^c	6.5	1388.1 ^a	5.9
σ_y (MPa)	27.1 ^b	6.3	17.6 ^a	7.0	34.0 ^c	2.3	18.2 ^a	8.8
ϵ_y (%)	2.50 ^b	8.2	1.97 ^a	9.1	2.56 ^b	4.6	2.01 ^a	13.4
σ_b (MPa)	28.9 ^c	2.7	13.4 ^a	9.1	21.0 ^b	4.4	14.2 ^a	7.7
ϵ_b (%)	315.4 ^c	3.3	98.0 ^b	12.4	85.4 ^b	14.2	33.2 ^a	15.0
PLA_2								
E (MPa)	2910.8 ^c	10.4	1674.0 ^a	5.4	1982.5 ^b	11.8	1547.3 ^a	8.3
σ_y (MPa)*	–	–	–	–	–	–	–	–
ϵ_y (%)	–	–	–	–	–	–	–	–
σ_b (MPa)	24.3 ^{bd}	4.7	20.4 ^{bc}	2.0	22.9 ^b	6.0	16.9 ^a	10.5
ϵ_b (%)	1.42 ^a	9.0	1.72 ^a	4.8	1.55 ^a	13.9	1.60 ^a	13.6
PBS_1								
E (MPa)	687.6 ^a	6.7	664.1 ^a	7.7	815.9 ^b	9.5	786.5 ^b	7.6
σ_y (MPa)*	–	–	–	–	–	–	–	–
ϵ_y (%)	–	–	–	–	–	–	–	–
σ_b (MPa)	21.3 ^a	8.8	20.0 ^a	11.7	27.3 ^b	11.0	25.6 ^b	7.0
ϵ_b (%)	8.37 ^b	3.3	7.32 ^a	4.2	8.36 ^b	10.2	7.04 ^a	4.3

a, b, c and d – mean comparison by Tukey's test at $p = 0.05$. Means followed by the same letters a, b, c and d are not significantly different.

* Yielding phenomenon was not visible.

Tukey's tests at $p = 0.05$. The means values followed by the same letters a, b, c and d are not statistically different. Statistical analysis allowed quantitative evaluation of changes occurring in the materials after degradation process under field conditions.

The first analyzed material was PLA_1 which is a blend of PLA and PBAT with addition of the mineral filler. The main significant changes in mechanical parameters were observed for the elongation at break where the value strongly decreased from the 315 % to 85 %, and from 98 % to 33 % in MD and TD directions, respectively. Other changes were observed mainly in the MD where the increase of tensile modulus and tensile strength at yield was significant according to statistical analysis, while the tensile at break shown a significant decrease.

The next investigated sample was a PLA_2, which is PLA-based polyester blend with addition of the mineral filler. The statistical analysis showed that the only significant changes result from a degradation process. The beginning of the second step of degradation that is ability to the biofragmentation of the examined materials has been confirmed by a decrease of tensile strength at the break and tensile modulus values measured in both the MD and TD directions. Tested materials exhibit the ability to fragmenting and lose their primary mechanical properties. In contrast, changes of a different nature were observed in the PBS_1 sample. In this case, all the values of the measured parameters increased except for the elongation. Moreover, the sample is isotropic in terms of mechanical properties not only before but also after degradation.

4. Conclusions

Research carried out in this study indicate that the biodegradation process of bio-based plastic materials in field soil under natural conditions was slow because average temperature of the ambient air was low. During the first six months of soil burial tests the average air temperature was equal to 3.4 °C, than between 7 and 12 months, average air temperature increased to 15.4 °C.

Macroscopic examination of the samples after 12 months showed that color changes on the film surface appeared only for the sample PBS_1. Using microscopic observation no erosion of the surface samples after 6 months was visible for all samples. However, after 12 months of degradation erosion of surface samples was visible for all samples. The greatest surface erosion was observed for the sample PBS_1. The less visible degradation of the film surface was observed for the sample PLA_1.

Low air temperature in the first 6 months of degradation caused that mass loss for all samples was low and below 0.35 %. In the next 6 months of degradation, when temperature was higher, mass loss was observed mainly for the sample PBS_1 and after 12 months of degradation was equal to 4.3 %. However, for samples PLA_1 and PLA_2 mass loss was insignificant and equal to 0.23 and 0.57 %, respectively. The changes in the thickness of the tested polymer over time were described by a kinetic model. Calculated specific surface degradation rate from this kinetic model was highest for the sample PBS_1 being equal to 11.6 µm per year.

After one year of degradation of investigated bio-based plastic materials their thermal stability and tensile strength at break for samples PLA_1 and PLA_2 decreased whereas these indices increased for the sample PBS_1. The increase of thermal and mechanical properties for the sample PBS_1, for which the highest mass loss was observed, could be attributed to the breakage of side chains in polymer and structural evolution on supramolecular level. Deterioration of properties for samples PLA_1 and PLA_2 was probably caused by breakage of the backbone chain of polymer during small mass loss and structural changes on the supramolecular level. The results of this research clearly show the slow degradation of studied materials and irreversible effects on the physical properties of these materials. The hypothesis about supramolecular structural evolution will be the subject of future investigations.

CRedit authorship contribution statement

Radosław Slezak: Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Validation, Writing – original draft. **Liliana**

Krzystek: Writing – review & editing. **Michał Puchalski:** Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft. **Izabella Krucińska:** Writing – review & editing. **Adam Sitarski:** Resources.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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