



Study of mechanical properties of commercial biopolymers concerning the effect of microbial decomposition in compost I

Kateřina Puková^{1*}, Tomáš Janda², Miroslav Večeřa²,
and Adéla Růckerová²

¹ *Institute of Environmental and Chemical Engineering,
The University of Pardubice, CZ–532 10 Pardubice, Czech Republic*

² *Institute of Chemistry and Technology of Macromolecular Materials,
The University of Pardubice, CZ–532 10 Pardubice, Czech Republic*

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This paper focuses on the verification of properties declared by the manufacturer and, above all, on the confirmation of biodegradability of commercially available polymer blends of the Envira© series produced by TART. This company provided two types of compostable polymer blends based on polylactic acid and starch (further specifications were not available). For this reason, the concerned samples were subjected to infrared spectroscopy and gas chromatography with a mass spectrometer to determine the secondary components contained in the material. The main objective of this work was to map the behaviour and properties of polymer mixtures in an environment rich in microorganisms, i.e. compost. The extent of degradation was evaluated by comparing the results of the mechanical attributes of the samples tested, as well as their structural changes visible in a scanning electron microscope.

Keywords: Biopolymers; Mechanical properties; Degradation; Compost

Introduction

Nowadays, there is hardly any place in the world where the plastic packaging of any kind, or fragments thereof, could not be found. It is thus no surprise that the

* Corresponding author, ✉ Katerina.Pukova@student.upce.cz

world production of packaging materials exceeds hundreds of millions of tons per year. In 2013, the Asia-Pacific region produced more than 7.1 million tons of one of the most commonly used packaging materials: a low-density polyethylene (LDPE) [1]. In the Czech Republic, according to the Czech Statistical Office, over 36 tons of polyethylene was produced in 2015 and subsequently used for bags and sacks [2]. Used material is then an incinerator or landfill, where it remains unchanged for many years. Neither of these variants is optimal and, therefore, there are trends to replace these standard packaging materials with materials biodegradable in a considerably shorter time. The effort to replace conventional plastics with alternative packaging began in the early 1950s. However, natural polymers (starch, cellulose, lactic acid, etc.) could replace the manufactured packaging material based on crude oil [3]. It was not until the turn of the millennium that the interest in bioplastics greatly increased. For example, in 2004, the Japanese company NEC was able to produce thermoplastic polylactic acid (PLA) without use of toxic chemicals, such as halogen or phosphorus, with a sufficiently high molecular weight. Nowadays, this area of packaging materials is so widespread and topical that there are attempts to produce bioplastics from far more substances than just from starch and PLA. These include, for example, chicken feather (in the USA, a problem waste containing large amounts of keratin), milk (protein casein), cellulose (cellulose esters), and polyhydroxyalkanoates produced by bacteria fermenting sugars or lipids [4]. For all materials, either from crude oil or of natural origin, it is important to know the pathway of degradation. The International Union of Pure and Applied Chemistry (IUPAC) defines the process of degradation as follows: "*Chemical changes in a polymeric material that usually result in undesirable changes in the in-use properties of the material*" [5]. Polymer degradation is considered to be any chemical change in properties. The most common changes are the molecular weight decrease due to chain scission and the change in chemical structure. In some cases of degradation, crosslinking may occur in the polymeric chain, mostly useful, but it is considered unsuitable in the degradation process, as it prolongs the decomposition process.

The main objective was to confirm the biodegradability of industrially produced biopolymers. Two commercially available materials declared by the manufacturer as biodegradable and one as a check sample with minimal biodegradability, were selected for this purpose. The samples were placed in a microorganism-rich-environment – an industrially processed compost. The conditions under which testing was carried out were not interfered with in any way, only the humidity of the compost was additionally modified if there was a risk of death of microorganisms. The testing took place for nine months, and a series of samples for testing was always taken after three months. The selected tests were focused on changes in mechanical, thermo-mechanical, and structural properties.

Materials and methods

Characterization of polymers

The tested polymers were polylactic acid and a mixture of polybutylene terephthalate and starch (PBTSt). Low-density polyethylene (LDPE) was chosen as the reference material. The granules underwent basic tests to be characterized. The melt flow index (MFI) was measured according to ISO 1133 using an extrusion plastometer (model "VMP 201", Chemoprojekt, Czech Republic). The temperature and weight values were set according to the technical data sheets supplied with the polymer granules. Before the actual measuring, the samples of granules were always dried for one week at 50 °C.

The determination of water absorption was performed in accordance with ČSN EN ISO 62. To evaluate the water absorption, the samples were pre-dried for 24 hours at 50 °C. Samples measuring 20 × 20 × 0.75 mm were immersed in distilled water at 23 °C 84 days. Absorption of water is given by the relation " $A = 100 (w_t - w_0)/w_0$ ", where w_0 is the initial weight before immersion and w_t is the weight after exposure. After exposure, the surface was dried with a filter paper.

To determine the additives, PLA- and LDPE-based polymer granules were extracted for a week in tetrahydrofuran at 23 °C. Solutions with additives extracted were separated and measured by means of gas chromatography-mass spectrometry (GC-MS). Additives were separated using Agilent Technologies GC 6890N and determined on the MS 5975B Inert XL MSD detector. The capillary column was HP-5MS with a non-polar stationary phase with the length of 30 m and the diameter of 0.25 mm. Helium (purity: 99.999%; Linde Gas, Czech Republic) was used as the carrier gas. The PBTSt sample was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) using the FT-IR Nicolet iS50 device (Thermo Scientific, USA). The measurement was carried out within the wavenumber range 4000–500 cm^{-1} when setting 32 scans in the spectrum and the spectral resolution of 2 cm^{-1} .

Polymer processing

Test specimens were prepared from the polymer granules according to the ČSN EN ISO 527 (Czech standard) for the tensile test and specimens according to the ČSN EN ISO 179 for the impact strength test. The test specimens were manufactured by a company Radka (Czech Republic). The temperatures of individual sections of the injection moulding machine were adjusted according to the accompanying sheets of the individual polymeric materials. An injection pressure of 30.0 bars was applied for all the types of polymers, followed by a hold pressure of 40.0 bars. The cooling time was 30–50 s depending on the type of material. The mould was cooled down to 22 °C.

Polymer degradation environment

The test specimens prepared were exposed to the effects of biological degradation by microorganisms in compost from a municipal composting plant. Table 1 lists the basic characteristics of the compost guaranteed by the manufacturer. The properties of the compost were not modified to ensure maximum consistency with the processes that take place in the real world. Only if there was a risk of its drying out and the subsequent death of microorganisms, the humidity of the compost was adjusted. The testing took place over 12, 24 and 36 weeks. To determine the conditions in which the degradation occurred, the following parameters were measured every week: pH, temperature, and humidity of the compost.

Table 1 Basic characteristics of the compost guaranteed by the manufacturer

Humidity [%]	Flammable substances in a dried sample [%]	pH value	Maximum of non-degradable substances [% wt.]	C : N ratio
35.0–65.0	20.0	6.0–8.5	5.0	30.0 : 1.0

Methods for determination of the extent of degradation

The test samples were subjected to a Brinell hardness test according to ČSN EN ISO 2039-1 and the results recorded in a contractual manner in the form of HK/5/15.6/60, for example. The first number in the code indicates the ball diameter in mm, the second number the load in kg, and the third represents the time of the load effects in s.

Furthermore, the samples were tested by determining the tensile test according to ČSN EN ISO 527, where the parameters of the ultimate tensile strength, modulus of elasticity, and maximum elongation were monitored.

The test was performed on the MTS® 4/M device with a force sensor of 20 kN. The gauge length was 100 mm and the crossbeam speed set to 20 mm min⁻¹. In addition, the impact strength was determined according to the ČSN EN ISO 8256 standard using the Charpy impact test method.

The Dynamic Mechanical Analysis (DMA) was also determined for the test samples. The dependence of modulus of elasticity the loss angle on temperature or time, deformation magnitude, and force-frequency information can be obtained from the resulting thermomechanical curves. Using these data, it is possible to characterize the materials in terms of the degree of crystallization, the degree of orientation of the polymer chains and the glass transition temperature (T_g) or the melting point (T_m). The measurement was performed on the DMA DX04T (RMI,

Czech Republic) device according to ISO 6721-5 using the three-point bending flexural test on specimens of $48 \times 4 \times 10$ mm. The bending frequency was 1 Hz and the rate of heating rate was $2 \text{ }^\circ\text{C min}^{-1}$.

The scanning electron microscopy (SEM) was used to visualize the degree of degradation. Under such circumstances, imaging of fractures could be obtained as basic information on the surface topology of the sample while the relevant measurements were performed on the LYRA 3 device (TESCAN, USA).

Results and discussion

Characterization of polymers

The technical sheets of polymer granules list the ITT values. The experimentally measured ITTs of the individual materials did not differ significantly from the values guaranteed by the manufacturer. A comparison of the measured and guaranteed values is given in Table 2.

Table 2 Measurement conditions and resulting melt flow index values

Sample	Measurement conditions		Guaranteed value [g/10 min]	Experimental value [g/10 min]
	Temperature [$^\circ\text{C}$]	Weight [kg]		
PLA	190	2.16	8.00	9.30
PBTSt	160	5.00	4.00	5.35
LDPE	190	2.16	0.75	0.90

The determination of the water absorption of the test polymer samples was continuously evaluated for 84 days. The absorbency of the PBTSt material reached the maximum of water absorbed just before the end of the test, at 75 days. After this time, the material absorbed approximately 11 wt. % of water. LDPE and PLA materials reached the maximum of water absorbed after 384 hours. PLA absorbed approximately 1 wt. % of water. LDPE absorbed only 0.3 wt. %. Continuous results of the measurements of water absorption over time for all materials are shown in Fig. 1. The results illustrate that PBTSt is a type of material capable of absorbing the largest amount of water, which can be attributed to the starch molecules present in the polymer matrix.

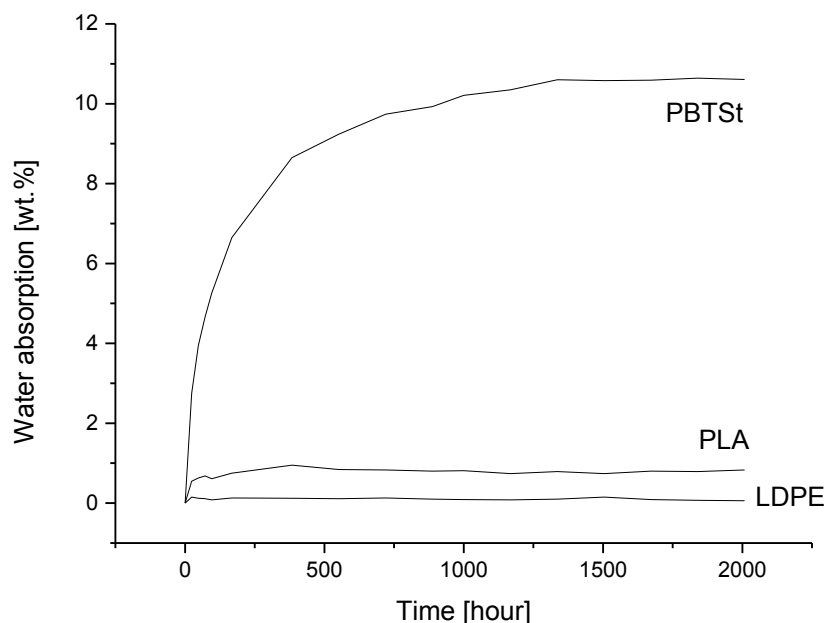


Fig. 1 Absorption of water test materials LDPE, PLA and PBTSt expressed as a percentage by mass relative to time

To determine the composition of PLA and LDPE polymer samples, the additives were determined by the GC-MS method. Three substances were found in the PLA granules: oleamide, butylhydroxytoluene, and 3,6-dimethyl-2,5-dioxo-1,4-dioxane. Oleamide is added to modify the flow properties and butylhydroxytoluene plays an antioxidant role. The last identified substance, 3,6-dimethyl-2,5-dioxo-1,4-dioxane, is not added to the polymer as an additive, it is a cyclic form of two lactic acid molecules or lactide. A total of five substances were identified in the LDPE granules, i.e. 13-docenosamide added to LDPE to improve the flow, butylhydroxytoluene to control and capture radicals, 6-di-*tert*-butylbenzoquinone and 2-propyltetradecyl sulfuric acid as an antioxidant, and finally, 3-chloro-1-phenylpropene used as a retardant. This analysis could not be performed on the PBTSt sample due to the dissolution of the starch into the solvent and the possibility of congestion of the injection chamber of the chromatograph. In the PBTSt granules, the FTIR method was used to determine stearamide serving as an antistatic, but also as a separator preventing the granules from sticking together.

Polymer degradation environment

For a more comprehensive mapping of conditions under which the degradation of the samples took place in a compost environment, the following parameters were monitored: pH, temperature, and humidity of the compost. Samples were taken at three points at the location of each of the three test series of the specimen, i.e. 9

values from one record. These values were averaged and plotted as shown in Fig. 2 and 3. The temperatures were read *in situ*; the average values in the compost being shown in Fig. 4.

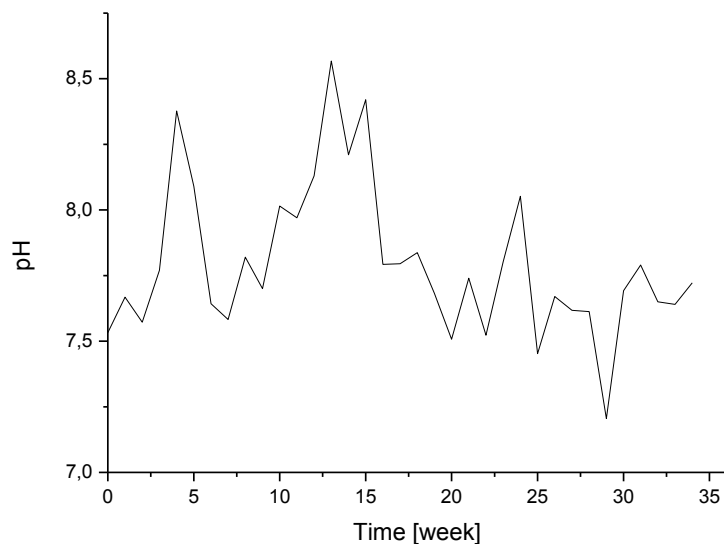


Fig. 2 Development of pH values of compost during the experiment

One of the key factors for the proper composting process is pH value. The main and most noticeable is the overall decrease in pH below 8, which occurred at the 15th week of the degradation test. This trend can be attributed to the progressive formation of acidic composting products; especially, carbon dioxide, released oligomers and monomers released from the source materials.

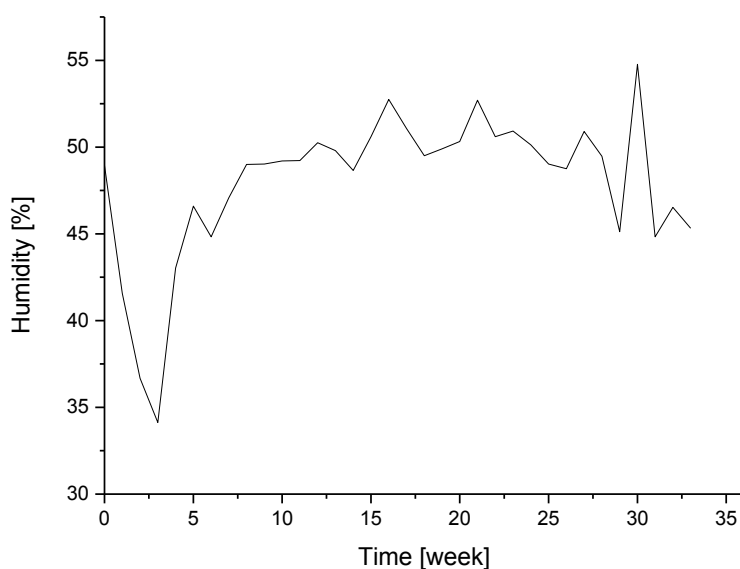


Fig. 3 Variation of the compost moisture during the experiment

The moisture content during the biodegradation of the polymer samples was significantly declining in the course of three weeks from the beginning of the experiment. That is why the compost was continuously irrigated. Fig. 3 shows that another critical drop did not occur and the values were at the optimum level of humidity. From these data, it can be concluded that there was no significant mortality of the microorganisms.

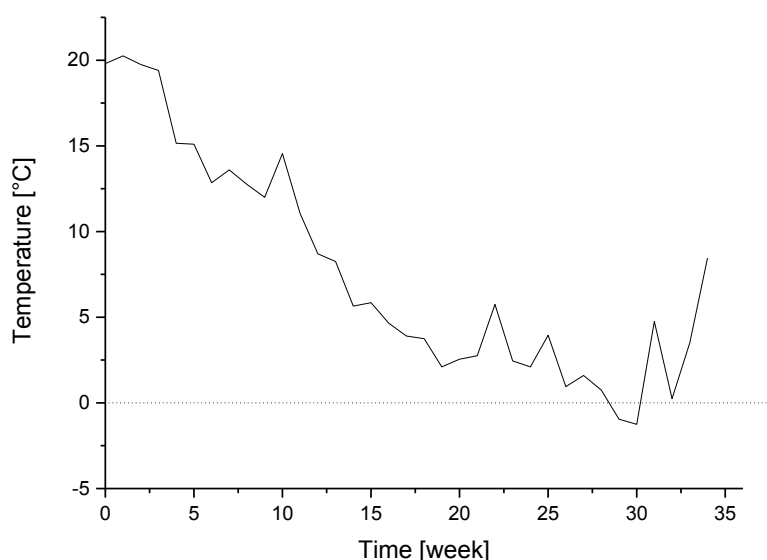


Fig. 4 Development of the compost temperature during the experiment

The composting temperature progress copies ambient temperature. As compost degradation began at the beginning of August, the curve has a declining trend. During the 29th week, the temperature dropped below 0 °C, but the lowest temperatures in the compost were reached during the next 30th week. This critical temperature did not last for a long time and, as can be seen, already in the 31st week, the temperature increased again, rising up above 4 °C. Due to the small volume of compost, it was impossible to prevent this temperature drop, but similar temperature drops did not occur.

Methods for determination of the extent of degradation

The hardness test was performed on specimens of 4-mm thickness. The resulting hardness values of the tested materials are the average of ten measurements; these values are given in Table 3. All the tested materials showed a noticeable hardness reduction trend with longer composting times. The most significant decrease in hardness was recorded in the PLA sample, approximately 16%; however, the PLA samples exhibit the highest measurement deviations. For this reason, a slight increase in hardness after degradation of 36 weeks may be included in the

measurement deviation. The PBTSt material appeared to be the least hard, which could be due to the starch grains that plasticise the matrix polymer. The effect of degradation on the PBTSt material was 15% decrease in hardness, a very similar drop in hardness as that of the PLA sample. As expected, LDPE as a comparative material with a low biodegradation rate, showed the lowest changes in hardness, decreasing by 10% only.

Table 3 Average hardness values depending on the length of degradation

Sample	Degradation time in compost [week]	HK/5/15,6/10	HK/5/15,6/60
PLA	0	322.0 ± 13.2	288.2 ± 15.9
	12	288.7 ± 19.9	260.9 ± 11.8
	24	272.1 ± 9.8	245.7 ± 14.6
	36	292.6 ± 4.1	251.5 ± 7.7
PBTSt	0	39.3 ± 6.7	33.3 ± 5.2
	12	49.0 ± 5.3	42.0 ± 4.5
	24	38.7 ± 3.9	31.9 ± 3.6
	36	33.6 ± 2.5	28.5 ± 2.3
LDPE	0	50.9 ± 4.3	37.7 ± 2.0
	12	49.1 ± 1.9	38.8 ± 1.2
	24	48.7 ± 3.8	37.9 ± 2.7
	36	46.0 ± 3.4	36.0 ± 2.2

The tensile test values of the initial and exposed samples in the compost are shown in Table 4. The results are given as the average of ten measurements. The highest values of the ultimate tensile strength of the initial unexposed samples were demonstrated by the PLA sample, which can be explained by the high glass transition temperature. Values of the modulus of elasticity were also significantly higher than those for the PBTSt and LDPE samples. The elongation at interruption was at the lowest level with the PLA material. A significant impact of degradation was observed in the PBTSt sample, where the ultimate tensile strength values were reduced by about 50% after 24 weeks. This significant drop was followed by elongation at interruption when the values dropped down to 8 % of the original value. Such a major decrease can be explained by the loss of starch due to the microbial activity in the compost. No significant changes in the tensile test parameters were recorded for the LDPE sample. The effect of microbial degradation is negligible in this case and corresponds to the assumption that LDPE is taken as a control polymer with a minimal biodegradation rate in this experiment.

Table 4 Average tensile test values depending on the degradation progress

Sample	Degradation time in compost [week]	Ultimate tensile strength [MPa]	Modulus of elasticity [MPa]	Elongation [%]
PLA	0	62.4 ± 3.5	3049.3 ± 21.7	6.5 ± 1.9
	12	59.8 ± 3.6	3004.4 ± 70.7	6.5 ± 1.9
	24	56.5 ± 6.3	3023.5 ± 64.4	5.1 ± 0.8
	36	61.3 ± 1.1	2984.5 ± 33.6	4.5 ± 0.8
PBTSt	0	13.8 ± 0.6	19.9 ± 5.8	365.6 ± 60.5
	12	8.1 ± 0.6	165.1 ± 14.4	23.3 ± 5.5
	24	6.4 ± 0.6	163.2 ± 11.2	16.6 ± 2.9
	36	4.6 ± 0.4	53.5 ± 14.5	29.7 ± 8.8
LDPE	0	13.8 ± 0.1	115.7 ± 2.9	69.2 ± 2.5
	12	13.5 ± 0.1	109.5 ± 2.8	70.8 ± 2.2
	24	12.9 ± 0.4	104.7 ± 4.2	69.6 ± 2.5
	36	13.6 ± 0.3	95.1 ± 2.2	70.7 ± 2.4

The results of the impact strength test are given as the average of ten measurements. The resulting values are shown in Table 5.

Table 5 Average impact strength values in relation to the progress of degradation

Sample	Degradation time in compost [week]	Impact strength [kJ m ⁻²]
PLA	0	6.1 ± 0.2
	12	3.4 ± 0.3
	24	3.7 ± 0.4
	36	3.3 ± 0.1
PBTSt	0	87.5 ± 6.7
	12	-----
	24	-----
	36	-----
LDPE	0	86.7 ± 1.4
	12	84.3 ± 2.9
	24	68.4 ± 4.1
	36	63.9 ± 4.8

Degradation processes most affected the PLA material, the impact strength of the specimens dropped almost to half the value of the unexposed material after 12 weeks. The impact strength drop correlates with the tensile test values. Despite the notching modifications to the specimens, the PBTSt material specimen series

did not get damaged in any degree of degradation in the compost. Due to the degradation processes, the PBTSt specimens became much more flexible that, after a hammer strike, only caused the specimens slipped out of the supports without being damaged. Compared to the original values, the LDPE sample showed a 25% decrease in impact strength after 36 weeks of compost exposure.

A DMA analysis was performed to compare the glass transition temperature (T_g) and melting temperature (T_m) of materials without degradation and materials that had undergone 36 week decomposition in the compost. The temperature values measured are shown in Table 6. The melting temperature of the undegraded and degraded PLA samples was not determined because the samples were non-elastic at high temperatures; they remained bent and therefore not deformed by oscillations. However, as with the only type of sample, there is a slight decrease in T_g , which can be attributed to the degradation processes occurring inside the microbial environment. For samples of PBTSt, T_g measured values corresponded to both components contained in the polymeric matrix – PBT and starch. As a result of the 36-week degradation of the two components contained in the PBTSt sample, the melting point decreased. The T_g values for the LDPE sample were within the range of the values generally reported for polyethylene from -125 to -20 °C. The melting point T_m of the LDPE sample did not change even after 36 weeks of compost degradation and corresponded to the tabulated values for LDPE [6].

Table 6 *The resulting T_g and T_m temperatures (points) of undegraded samples and those degraded for 36 weeks in compost*

Sample	Degradation time in compost [week]	T_g [°C]	T_m [°C]
PLA	0	65.0	-----
	36	63.0	-----
PBTSt	0	52.0	132.0
	36	52.0	120.0
LDPE	0	-23.0	117.0
	36	-22.0	117.0

The SEM method was used to determine with a higher accuracy the impact of composting on the materials used. Before the actual measurement, the samples were covered with a carbon layer to ensure their conductivity. Fig. 5 captures the fracture edges of undegraded PLA sample specimens and those after the 12-week degradation in the compost. It is clear from the figure that the degradation in the PLA sample has not significantly advanced, and the surface of the material decomposes very slowly. The impact of degradation, however, was reflected in the results of mechanical tests.

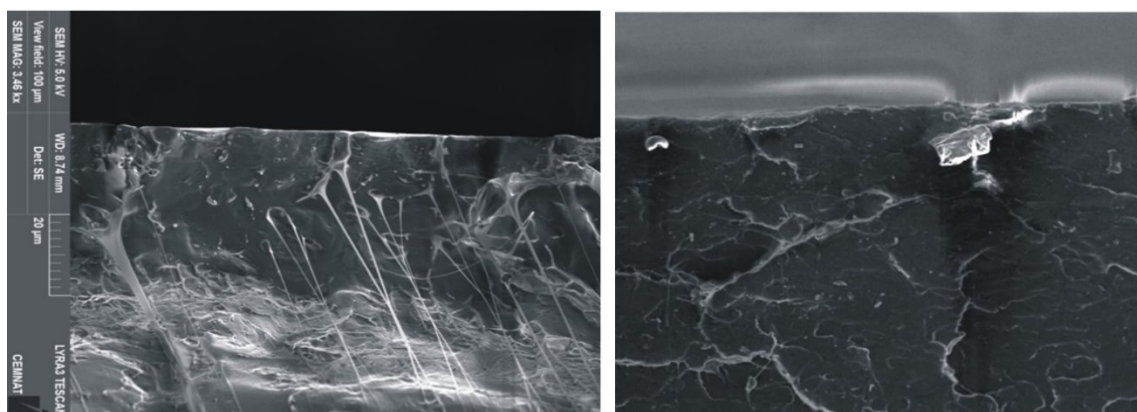


Fig. 5 A SEM image of the fracture edge of the PLA sample without degradation (left) and that of the fracture edge of the PLA sample after 12-week degradation in compost (right), at 100 µm magnification

Fig. 6 shows the fracture edge of the PBTSt sample without degradation and that after 24 weeks of degradation in the compost. It is clear from the comparison of the PBTSt images that the material undergoes degradation in a relatively large extent already after 24 weeks in the compost. The images clearly show that the amount of starch grains is reduced to a depth of several tens of microns. These images support the results of the PBTSt tensile test.

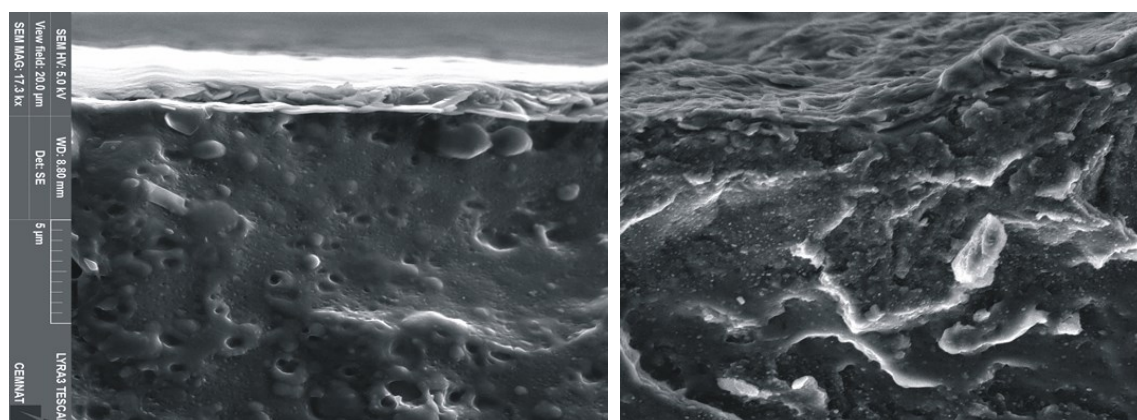


Fig. 6 A SEM image of the fracture edge of the PBTSt sample without degradation (left) and an image of the fracture edge of the PBTSt sample after a 24-week degradation in the compost (right), at 20 µm magnification

Images of the fracture edge of the LDPE sample without degradation and after 12 weeks of degradation in the compost are shown in Fig. 7. It is apparent that the sample surface has been slightly disturbed. However, this finding cannot be considered as a direct degradation of the material, but only a mechanical weakening of the thin layer of the material by possible oxidation.

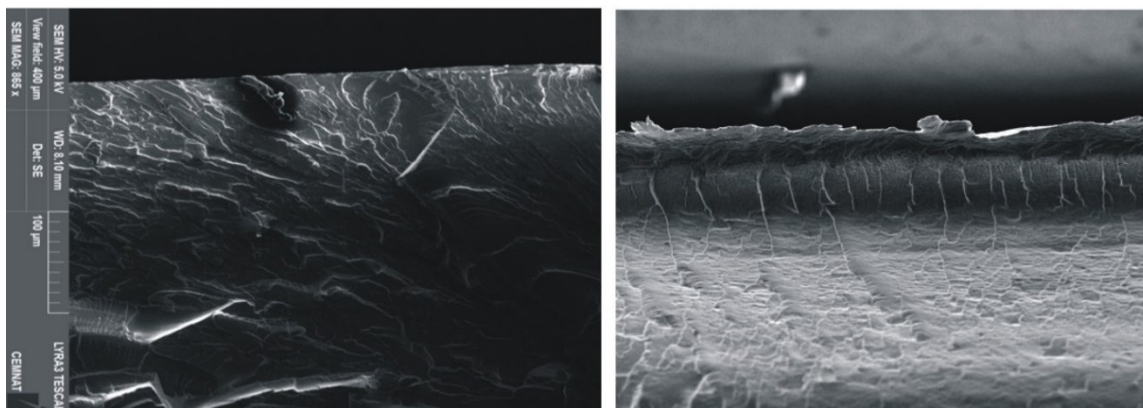


Fig. 7 A SEM image of the fracture edge of the LDPE sample without degradation (left) and an image of the fracture edge of the LDPE sample after 12-week degradation in the compost (right), at 400 μm magnification

Conclusions

This paper deals with characterization of commercially available biopolymers when studying their degradation in an environment rich in microorganisms. Environmental substrate selected for monitoring the process of biodegradation was compost which was monitored for the duration of the experiment in terms of humidity, pH, and temperature. The test materials were a mixture of polybutylene terephthalate and starch, polylactic acid, and a low-density polyethylene as a low degradation control polymer. The specimens were placed in the compost and the degradation rate was monitored in 12-, 24- and 36-week intervals. The degree of degradation of polymer samples was evaluated in terms of changes in mechanical, thermo-mechanical, and optical properties. Mechanical tests showed that all the tested materials degrade in the compost environment. Specimens made of PLA showed certain decrease in the values of all the mechanical properties monitored. The highest degree of degradation was observed in the PBTSt sample. The decrease was apparent in the tensile test in particular. Changes were also manifested in the impact strength of the material where degradation caused that the specimens were more resilient than the original non-degraded material. The PBTSt material was the only one after degradation in the compost to show a decrease in the melting point. All the visible changes can be seen on the SEM images. Finally, the LDPE material was only disturbed on the surface layer.

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