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Biodegradation in Soil of Commercial Plastic Bags Labelled as "Biodegradable"

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Biodegradability of five commercial plastic bags labelled as "biodegradable" and two referent materials were studied by a soil test for three months. As a control experiment, for studying abiotic degradation under the climatic impact (ultraviolet, temperature, and moisture) a test in a weatherometer was performed. The changes in bag samples after tests were detected by optical microscopy, Fourier-transform infrared spectroscopy, differential scanning calorimetry, and tensile testing. It was found that all the bags may be separated into two groups: based on polyesters and based on polyolefins with oxo-additives. The second group demonstrated an ability to oxidation under UV radiation. The content of chalk filler provided a mass loss of the samples under soil and climatic tests due to its washing out. Three samples on the polyester basis filled with starch (the first group) had different compositions (polymers in the matrix were different). They showed a high biodegradability under soil conditions: mass loss was 14-21%, tensile strength decreased by more than 43%, and the surface was covered by the mycelium net. However, according to FTIR-spectroscopy, at the initial stage only starch filler biodegraded intensively, while polymer matrix was stable.

Keywords: *Commercial plastic bag, polymer composite, biodegradability, soil test, mass loss, climatic oxidation, accelerated weathering test, polylactic acid, polycaprolactone, polybutylene adipate-co-terephthalate, polyethylene, cellophane, microplastic, pro-oxidant, oxo-additive.*

1. Introduction

The global environmental problem of polymer waste stimulates the search for ways to reduce the consumption of non-degradable plastics. First, replacing non-degradable plastics with degradable ones is justified for single-use products, for example, packaging, disposable tableware, and hygiene products. Carrying bags and packing bags based on non-biodegradable poly(ethylene) (PE) are the most popular products in the category of single-use plastics. According to resent market research, 5 trillion plastic bags are used every year[1]. As an alternative to PE, which has exceptional resistance to environmental factors, manufacturers suggest using biodegradable polymers for the production of plastic bags. There are more and more plastic bags on the market that are labelled "eco", "bio" or "biodegradable".

Earlier Feuilloley P., et al.[2] studied the biodegradability of three commercial bags by different biodegradation tests. They selected bags from poly(caprolactone) with starch (60/40 wt.%) by trademark Mater-Bi (Novamont), bags from poly(butylene adipate-co-terephthalate) by trademark Ecoflex (BASF), and conventional PE with oxo-additive by trademark Actimais (SMS Trioplast). The first one biodegraded under the majority of tests, the second one biodegraded a lot less, and the last one did not biodegrade at all. Later Barragán et al.[3] investigated 6 commercial bags (Biofilm, Bio-Flex, Bioplast, Mater-Bi, Mirel, and pure PE) for biodegradability in soil medium for 186 days under laboratory conditions. All the tested bags were completely degraded, except pure polyethylene. Weight loss parameter and chemical composition changes (FTIR-spectroscopy) were employed to estimate the degradation rate. It was found that the most biodegradable sample was poly(hydroxybutyrate) based film. Other authors studied the biodegradation of commercial bags from supermarkets consisting of PE with an oxo-additive[4]. They tested samples in the composting pile for 70 days; the average temperature of the compost was 64°C. However, there were no critical changes in PE structure after the composting: molecular weight decreased just by 32.7% after 42 days of composting. The authors concluded that such bags should not be labelled as biodegradable or biocompostable. PE with oxo-additives sometimes is used as an agricultural film. D. Briassoulis et al.[5] investigated the biodegradation of linear low-density polyethylene (LLDPE) mulching film (20 μm in thickness) with 2.5% of commercial pro-oxidant. It was a longitude study in natural conditions that lasted for 7 years. The authors concluded that physical degradation to small microparticles took place after ultraviolet

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irradiation. However, the mechanism of destruction was abiotic. Biodegradation processes under the influence of microorganisms were not detected. On the other side, materials based on PE may be biodegradable in case of adding high content of biodegradable fillers[6-8]. As biodegradable fillers, it is known about the use of fillers such as coffee films, flax, hay, hemp, sisal, jute, kenaf, coconut coir, beech, wood flour and modified brewers' spent grain[7,9].

Manufacturers change the chemical composition and production technology regularly. For this reason, in different scientific papers the researchers obtain different results for the bags of the same trademarks. For example, Mater-Bi was made of poly(caprolactone), poly(lactic acid), or poly(butylene terephthalate) in the various periods[2,3,10]. It is important to update studies of such materials regularly for providing readers with the latest information. On the other side, some manufacturers label their bags as biodegradable, but in fact, that is not true. It is necessary to identify such cases and publish the results of the studies. The main problem of such studies is the small number of analyzed samples (from one to three), so it is impossible to compare different packaging materials.

Previous studies were carried out according to different methods, which makes it impossible to compare the biodegradability of plastic bags from different manufacturers. The aim of this research was to analyse chemical composition and real biodegradability of a range of commercial plastic bags labelled as "biodegradable" under open-air soil conditions, as well as to compare the obtained results with the referent plastic materials. For the investigation, five different plastic bags and two referent bags (PE and cellophane) were tested. Changes in the mechanical properties, supermolecular structure, chemical composition, microbial staining, and mass loss in complex provides all the necessary information about the real biodegradability of the materials. The comparison of different materials from different manufacturers gives an understanding of the entire market and the place of each of the materials in the general range.

2. Experimental

2.1. Materials description

Several commercially produced plastic bags labelled "biodegradable" used in large Russian retail chains were objects of investigation. The referent materials were plastic bags made of standard PE and cellophane (cellulose film). A description of the objects under investigation according to the labels and average prices based on the data from the open sources are given in Table 1.

2.2. Open-air soil test

For the research, rectangular samples 160×220 mm in size were cut from each bag/film using scissors. A total of 21 samples were tested (three replicates of each product). An open-air soil test was carried out in the Moscow region (Russia). The method was based on the standard ASTM G160-03[11] with necessary adaptations of the standard procedure for the open-air experiment. Each sample was inserted into a paper frame to prevent breakage of the thin polymeric films when immersed in the ground. The paper frame did not distort the test results, as it underwent complete decomposition within 2 weeks in soil. Further, each sample was buried in open-air soil, and a plastic frame made of polyethylene was dug around the sample to avoid damage to the sample by soil fauna (worms, moles, mice). Figure 1a demonstrates the steps of the immersion in soil. The tests were carried out in the open-air natural ground conditions of Moscow region (Russia) (GPS coordinates 55°58'28.2"N 37°57'57.3"E). The sod-podzolic soil with pH between 4,0 to 5,5 is typical for this region. The soil moisture was maintained between 30 and 40% during the experiment. The test lasted 3 months (July, August, and September) with an average daily temperature of 15.7°C.

After exposure to the soil, the samples were carefully removed, cleaned of soil residues, washed with running water, and dried in air to the constant weight. Then the changes in

Figure 1. (a) The procedure of the soil test; (b) The stages of the accelerated weathering test (climatic chamber).

Table 1. The description of the bags under investigation.

Sample notation	Appearance of the bag	Description according to the label	Price (US $/ 1 bag)
TEST 1		Completely degradable and environmentally friendly bag (Russia)	0.12
TEST 2		Biodegradable bags based on polyethylene (LLC "Poliroll", Russia)	0.07
TEST 3		Fully biodegradable bag after 1 year (Flexopack S.r.l., Italy)	0.41
TEST 4		Biodegradable and compostable bag (Mater Bi, Italy)	0.34
TEST 5		Biobased packing bag (Eco Products Group, Kazakhstan)	0.12
REF 1		Conventional polyethylene bag (Russia)	0.13
REF 2		Cellophane (cellulose film) (Russia)	0.19

the appearance, mass, microstructure (optical microscopy), chemical composition (FTIR), thermophysical properties (DSC), and stress-strain properties of the bags' samples were analysed according to the methodology described below.

2.3. Climatic test

To assess the degradation of the samples under the action of abiotic climatic factors, an accelerated weathering test was performed by weatherometer (climatic chamber) (ATLAS UV-Test, USA). During the test, the samples were exposed to three factors: elevated temperature, moisture, and UV radiation. The experiment was conducted according to ASTM D5208[12] (cycle B) with the following test cycle: 1) 4-hour condensation at 50°C and a humidity of 90-100%; 2) irradiation with UV light for 8 hours at 70°C, 340 nm, and 1.35 W/m^2. The exposition of the samples in the climatic chamber was performed for 16 cycles (192 hours). Figure 1b shows the main stages of this test. The test allows for identifying oxo-degradable materials (with prooxidants). After the experiment, the assessment of appearance (including fragmentation) and chemical composition (FTIR) was performed according to the methodology described in Figure 1.

2.4. Size and mass parameters

The thickness of the samples was determined using a digital micrometer (Megeon 80800, Russia). The mass of the samples before and after experiments was determined using an analytical balance (A&D GR-200, Japan).

2.5. Optical microscopy

To identify signs of deterioration and biological fouling of the bags' samples, the microstructure was analysed using a method of optical microscopy. The study was carried out on an optical microscope Olympus BX3M-PSLED (Japan) with an Olympus LC30 camera. Olympus Steam Basic software was used for image processing. The images were detected in transmitted and reflected light at magnifications of 50×, 100×, and 200×. The initial samples of the bags and the samples after the soil test were subjected to the study.

2.6. FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) was applied to determine the chemical composition of the studied objects, as well as changes in the composition that occur after climatic and soil tests. The investigation was carried out by means of an FTIR spectrometer LUMOS Bruker (Germany) using ATR method (diamond crystal) in a wavelength range of $4000 \leq \nu \leq 600$ cm^{-1}. The carbonyl index was calculated from the ratio of the optical densities (D) of the absorption band of 1715 cm^{-1} (corresponding to vibrations of carbonyl groups) and the absorption band of 1470 cm^{-1} (corresponding to the vibrations of methylene groups in PE)[13].

2.7. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was applied to analyse the composition of polymeric matrix of the bags under investigation. The behaviour of the samples during melting and crystallization allows identifying the type of polymer used. The study was performed by a differential scanning calorimeter DSC 214 Polyma (NETZSCH-Geratebau GmbH, Selb, Germany) according to ISO 11357-3:2018[14] in a temperature range from 20 to 200°C at a scanning rate of 10°C min^{-1}. The sample weight was (10±0.1) mg. The temperature scale and enthalpy of melting were calibrated against an indium standard sample. Temperatures of melting and crystallization were determined by an endothermic maximum of the melting peak and an exothermic maximum of the crystallization peak on the DSC thermograms, respectively.

2.8. Stress-strain properties

The stress-strain properties under tension were studied by a tensile testing machine Devotrans DVT GP UG 5 (Turkey) in an accordance with 527-1:2012 (sample type 3, crosshead velocity of 50 mm/min, gauge length of 50 mm). Test samples were cut from alongside the orientation axis by a stamping press. The tests were carried out for 5 to 7 replicates of each sample. The parameters of tensile strength at break, relative elongation at break, and yield strength were determined by the stress-strain diagrams. The modulus of elasticity under tension was calculated in the region of elastic deformations according to a ratio of stress to elongation values.

To evaluate the effect of open-air testing in soil on mechanical characteristics of the samples, a linear mixed effects simulation was performed. In the model, tensile strength, elongation at break, elastic modulus, and yield strength were fitted as dependent variables, the "before/after open-air soil" test factor was fitted as a fixed effect, and the ID factor of the definite object under investigation (commercially produced plastic bag) was fitted as a random effect. The data were processed in the R version 4.2.1 program[15]. Mixed effects modelling was performed in the lme4 package[16].

3. Results and Discussion

3.1. Characteristics of the bags' samples

To predict the behaviour of the materials under investigation, they were analysed by FTIR (Table 2). Polymer matrix, fillers, and additives were identified according to the Bruker database. Based on the spectroscopic data, it was assumed that samples TEST 1 and TEST 2 were based on poly(ethylene). Besides that, TEST 1 was filled with titanium dioxide (absorption peak at 600-700 cm^{-1}). TEST 2 contained chalk filler and processing additive, presumably siloxane, which was identified only on the surface of this sample. The samples TEST 3, TEST 4, and TEST 5 were made from a polyester matrix filled with polysaccharide component, presumably starch. The referent sample REF 1 is based on poly(ethylene) filled with calcium carbonate.

The DSC method was applied as an additional method for identifying the nature of the polymer matrix. The melting thermograms of REF 1, TEST 1, and TEST 2 had one melting peak with a temperature of ~123-127°C, which also indicated that these bags were made of linear low-density poly(ethylene) (HDPE)[17].

The sample TEST 3 was characterized by one melting peak at 166°C, which could be attributed to poly(lactic acid) (PLA)[18]. In a temperature range of 60-70°C, the glass transition temperature of PLA was observed. The character of the cooling curve of this sample was more typical for poly(butylene adipate-co-terephthalate) (PBAT) with a crystallization temperature of 70-80°C[19]. Apparently, the polymer matrix of the sample was a mixture of PLA and PBAT[20].

The DSC cooling thermograms of TEST 4 and TEST 5 also had exothermic peaks at a range of 80-90°C that allowed assuming PBAT existence in the polymer matrix. According to the label, the sample TEST 4 was made of Mater-Bi material and consisted from PBAT with a high content of corn starch that was proven by the obtained results[21]. In the melting curves of TEST 5, two endothermic peaks were shown – at 60°C and 170°C[22]. Thus, it could be assumed that TEST 5 was a mixture of three polymers – PCL, PBAT, and PLA filled with starch.

The stress-strain behaviour of the initial samples was assessed by parameters of tensile strength at break, relative elongation at break, yield strength, and modulus of elasticity (Table 3). The polyethylene-based samples were characterised by higher fracture strength and elastic modulus than polyester-based ones. The referent sample cellophane (REF 2) had the greatest tensile strength (90.3 MPa) but demonstrated brittle behaviour (relative elongation at break was 11.4%). The polyester-based films (TEST 3, TEST 4, and TEST 5) had moderate values of the analysed parameters.

3.2. Mass and appearance of the samples before and after open-air soil and climatic tests

According to EN 13432[23] and ASTM G 160-03[11], mass loss and destruction of physical integrity (loss of mechanical properties) are the main criteria for assessing the degradability of polymeric materials, in particular biological degradability. Physical, chemical, and biological degradation under the influence of environmental factors' combination was appreciated. Biodegradation was studied via an open-air soil test. The soil experiment lasted 3 months, the climatic test – 192 hours. These time intervals were chosen to assess the beginning of the destruction processes of the studied materials under the influence of various environmental factors.

Table 3 presents mass changes in the materials under investigation after 3 months of the soil test. The samples based on biodegradable polyesters were characterized by a significant value of mass loss – 13.9-15.4% (TEST 3-5). According to the previous works devoted to the biodegradability analysis of easily hydrolysable polyesters, the mass loss for PBAT varied from 5 to 12 wt.% for 2 months in soil[24], for PCL – about 6 wt.% for 3 months in soil[25], for PLA – 1-8 wt.% for 3 months in soil[26]. At the same time, it was proved that the introduction of more than 30 wt.% starch filler into the polyester matrix resulted in an increase in the rate of weight loss in the soil by 5-12 times[27]. It is worth noting that the mass loss indicator may be uninformative due to the course of competing processes of biomass accumulation during biofouling that was proven in the work[28].

At the same time, the samples based on polyethylene with oxo-additives (TEST 1, TEST 2) were characterized by small values of mass loss (0.3-2.5%). The results indicated the resistance of such materials to biological degradation without a preliminary stage of polymer oxidation[29]. The materials used as referent ones showed resistance to degradation (in the case of polyethylene REF 1) and complete degradation (in the case of cellophane REF 2) in the soil which indicated the correctness of the performed experiments. Cellophane is well known as a fully biodegradable material. An early study, it was shown that after 52 days of biodegradation test it lost 85% of mass[30]. Obviously, after 3 months it degrades completely. On the other hand, PE is known as the most resistant to biodegradation polymer[31]. Kalinina et al.[32] have presented the kinetic curves of the adhesion of the aggressive fungi (*Aspergillus niger*) spores to the surface of polymer materials. This method characterizes the ability of a polymer

Table 2. The assumed composition of the bags' samples according to the FTIR and DSC data.

Sample notation	Base polymer	Fillers/additives
TEST 1	Linear low-density poly(ethylene)	Titanium dioxide
TEST 2	Linear low-density poly(ethylene)	Calcium carbonate + mineral colour + siloxane additive
TEST 3	Poly(butylene adipate-co-terephthalate), poly(lactic acid)	Polysaccharide (presumably, starch)
TEST 4	Poly(butylene adipate-co-terephthalate)	Polysaccharide (presumably, starch)
TEST 5	Poly(carpolactone), poly(butylene adipate-co-terephthalate), poly(lactic acid)	Polysaccharide (presumably, starch)
REF 1	Linear low-density poly(ethylene)	Calcium carbonate
REF 2	Cellophane (viscose film)	No

Table 3. The mechanical characteristics under tension for the bags' samples.

Sample notation	Thickness (mkm)	Tensile strength at break (MPa)	Relative elongation at break (%)	Modulus of elasticity (MPa)	Yield strength (MPa)
TEST 1	19±1.7	26.3±5.3	760±122	316±20	17.1±1.3
TEST 2	20±1.3	17.7±3.2	459±98	184±21	9.6±1.2
TEST 3	25±1.6	21.2±1.0	262±46	148±23	9.5±0.4
TEST 4	26±1.6	18.8±2.3	298±36	134±27	10.4±0.6
TEST 5	16±1.9	20.0±2.9	150±17	139±14	7.7±1.2
REF 1	24±2.7	28.2±4.0	602±50	227±23	16.2±1.9
REF 2	34±1.1	90.3±3.8	11±1	2792±157	53.0±4.9

to biodegrade under the influence of microorganisms. Thus, among several polymers (cellophane, acetyl cellulose, polymethylmethacrylate, epoxy resin, polyethylene), cellophane was shown as the most prone to biodegradation, while PE was identified as the most bioresistant. The same results were obtained in the current study.

Considering the value of mass loss for three months in soil, the theoretical period of complete degradation of the materials under environmental conditions at a constant rate of degradation was determined. According to the calculations, the samples based on biodegradable polyesters should decompose in 1.2-1.8 years. In an article[33] for The Australasian Bioplastics Association, manufacturers of Mater-Bi-based bags claim that their bags decomposing within 1 (one) year, and manufacturers of the Kazakh TEST 5 bag for the portal https://weproject.media/ say that their bag is capable of decompose within 100 days in compost[34]. The samples REF 1, TEST 1, and TEST 2 based on PE were characterized by estimated periods of complete degradation in soil from 10 to 87 years. However, these calculated periods are not truly reliable, as they were calculated assuming a constant mass loss rate.

The results of the three-factor climatic test (temperature, moisture, UV-radiation) were consistent with the soil test in terms of mass loss (Table 4). For some samples (TEST 1, REF 1), an increase in mass was observed that could be explained by an accumulation of oxygen-containing groups[35]. A decrease in weight for the samples based on starch-filled biodegradable polyesters (TEST 3-5) could be explained by their high ability to hydrolyze in a humid environment[36].

After the open-air soil test, the appearance of the tested samples was analysed (Figure 2). Additionally, scoring of the intensity of microbial growth on the samples was carried out according to ASTM G 160-03[11] (Table 4). The samples TEST 1, TEST 2, and REF 1 had no colour change or defect formation. While the samples based on polyesters underwent darkening, the formation of cracks and roughness, as well as biofouling by fungi mycelium. The samples TEST 3 and TEST 4 were characterised by moderate microbial staining (growth) (30 to 60% coverage). The sample TEST 5, which had the smallest thickness, changed colour and shape, it physically degraded after soil. The microbial staining rating for this sample after 3 months of the soil test was 4 (60% to complete coverage).

3.3. Microstructure of the samples before and after open-air soil test

Figure 3 shows the results of the microstructure analysis of the bags' samples before and after the soil test. According to transmitted light microscopy micrographs, fine filler particles were detected in the matrix of sample REF 1 (filled polyethylene). After the soil test, the structure of this sample did not change, however, the separate areas of micro fungi mycelium growth were found on the surface of the material. Surface degradation is typical for hydrophobic polymers such as polyethylene[37]. However, the process of layer-by-layer biological destruction is so slow that polyethylene is considered a non-degradable plastic. The samples TEST 1 and TEST 2 (PE with oxo-additives) were characterized by a uniform initial structure with the presence of different fillers. During exposure to soil, no changes in the structure of these samples were revealed. Only a few scratches were present on the surface of these materials. No signs of biofouling were found. Thus, it was shown that oxo-additive PE had a lower biofouling capacity than the referent polyethylene (REF 1). Apparently, oxo-additive containing toxic metal compounds is able to inhibit adhesion and colonization of microorganisms on the samples[38]. In the studies of other authors[29,39], the acceleration of biological fouling of the surface of PE with oxo-additives was shown only in the case of its preliminary oxidation with an increase in the hydrophilicity of this polymer.

The samples TEST 3, TEST 4, and TEST 5 having a common chemical composition showed a significant degree of degradation under soil conditions. According to the obtained microphotographs, heavy growth of microorganisms covering the entire surface of these test samples was observed. For these materials, not only a formation of a mycelial network on the film surface was observed, but also an intensive growth of microorganisms inside the samples (bulk erosion) was identified. TEST 5 was characterized by an uneven initial structure with numerous defects, which allowed microorganisms easily colonize its surface and penetrate into the sample. Biodegradable polyesters, such as poly(caprolactone), poly(butylene adipate-co-terephthalate), and poly(lactic acid), are known to have a high rate of biodegradation under the action of microorganisms[40]. The revealed patterns of biological fouling of these materials once again prove the polyester nature of the polymer matrix of the bags' samples (TEST 3-5).

Table 4. The results of visual assessment of microbial staining (growth) according to ASTM G160-03[11] and the relative mass loss after 3 months of the open-air soil test, and the relative mass loss after 192 hours of the climatic test.

Sample	Soil test				Climatic test	
	Microbial staining (rating)	Mass loss (wt.%)		Estimated period of degradation (years)***	Mass loss (wt.%)	
		AM*	SD**		AM	SD
TEST 1	0 (none)	0.3	0.1	87.1	+1.7	0.2
TEST 2	0 (none)	2.5	1.3	10.0	2.3	1.1
TEST 3	3 (moderate)	14.4	1.7	1.7	11.7	1.5
TEST 4	3 (moderate)	13.9	1.7	1.8	12.6	1.8
TEST 5	4 (heavy)	20.8	1.4	1.2	19.2	1.6
REF 1	1 (trace)	0.4	0.2	58.0	+0.8	0.1
REF 2	non-determined	100.0	-	0.3	100.0	-

* arithmetic mean value; ** standard deviation; *** at a constant rate of degradation in soil

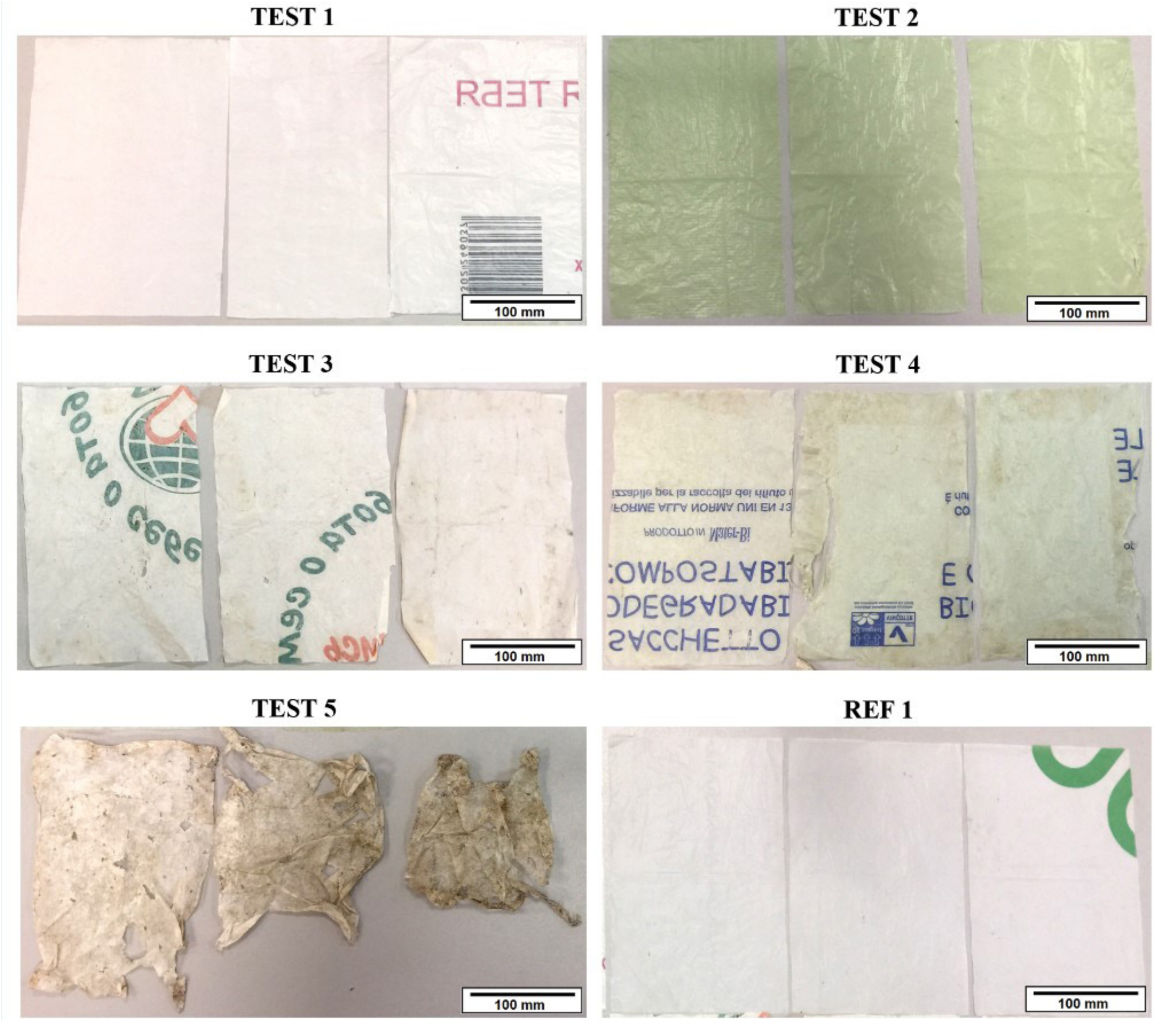

Figure 2. The samples after 3 months of the open-air soil test (photographs).

3.4. Chemical composition of the samples before and after open-air soil and climatic tests

FTIR-spectroscopy (ATR-method) allowed analysing the changes in the chemical composition and microstructure of the samples. Figures 4 and 5 show FTIR-spectra of the initial samples, as well as the samples after biodegradation and climatic tests.

Since standard polyethylene-based carrier bags typically contain additional processing fillers and additives, the chemical composition of the referent bag (REF 1) was analysed. According to the FTIR data, REF 1 is a PE filled with chalk. After the soil and climatic tests, a decrease in the absorption band intensity at 1410 cm^{-1} (vibrations of Ca-O bonds in calcium carbonate) was shown[41]. This fact indicated washing out of a water-soluble fraction of the chalk filler and was consistent with a slight mass loss (0.3-0.4%) in the soil test.

After 192 hours of the climatic experiment, the polyethylene-based samples TEST 1 and TEST 2 were fragmented, so they may be identified as oxo-degradable ones. Such materials contain prooxidants accelerating the oxidation of PE under UV-radiation in the presence of oxygen[42]. The carbonyl index of these samples calculated from the ratio of D_{1715}/D_{1470} was (0.12±0.01). The role of photocatalysts for TEST 1 can play the titanium dioxide filler (absorption peak at 600-700 cm^{-1})[43]. In comparison, REF 1 based on PE without oxo-additives subjected to the same test showed no evidence of oxidation.

Besides that, the change in the ratio of the intensities of absorption bands corresponding to the vibrations of C-H bonds in methylene CH_2 groups was found in case of the climatic test. Thus, an increase in the ratios of the bands 2915/2847, 1472/1462, and 730/719 cm^{-1} was shown that indicating an increase in the degree of polyethylene crystallinity as a result of the destruction of amorphous regions[44]. However, the formation of terminal methyl groups was not observed, indicating that the molecular weight of the polymer did not change. FTIR data did not show noticeable changes in the TEST 1 sample after biodegradation test. However, the mechanical properties of this sample changed significantly after that test: elongation at break decreased by 97% and modulus of elasticity decreased by 144%, apparently, it indicated the physical degradation.

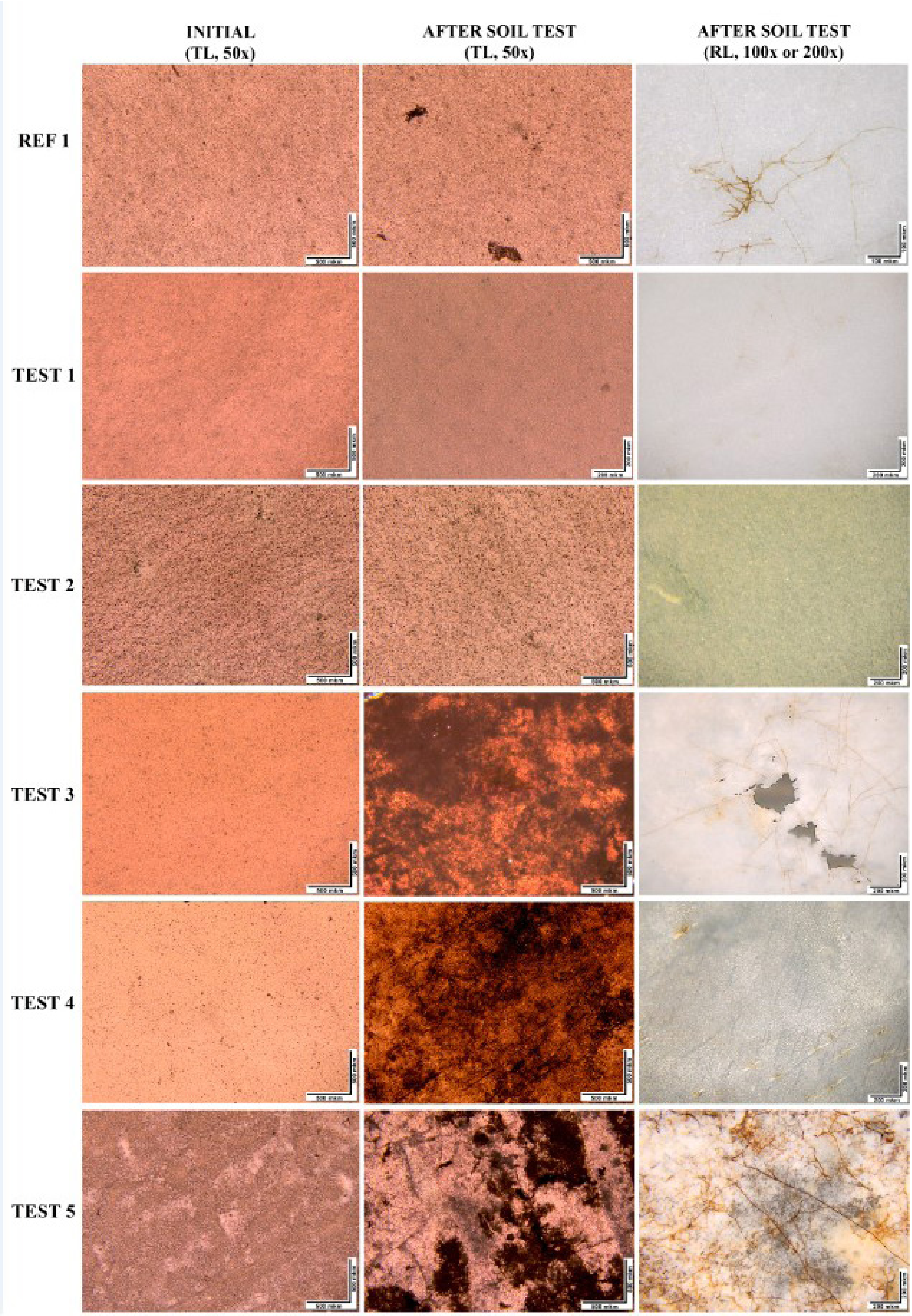

Figure 3. Microphotographs of the initial samples and the samples after the soil test (optical microscopy, transmitted (TL) and reflected (RL) light, magnification of 50×, 100×, and 200×).

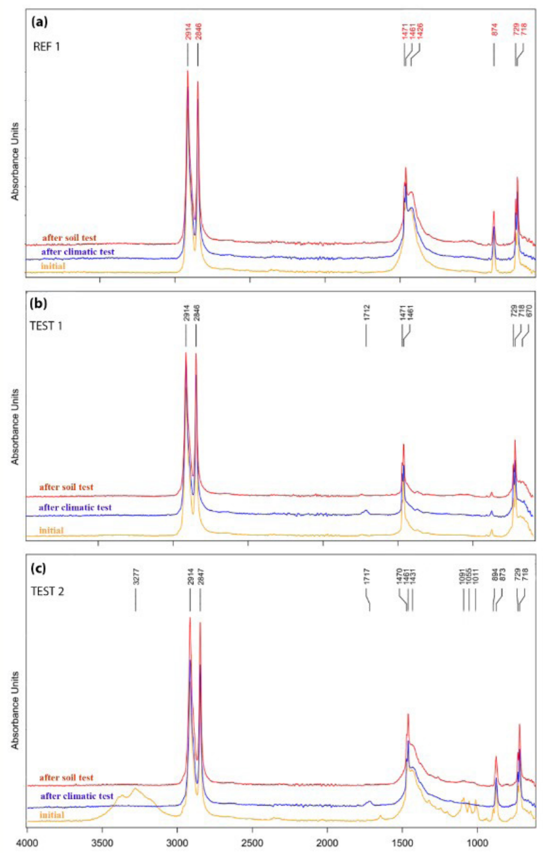

Figure 4. FTIR spectra of REF 1 (a), TEST 1 (b), and TEST 2 (c) samples after the biodegradation test in soil and after the climatic test compared to the initial samples.

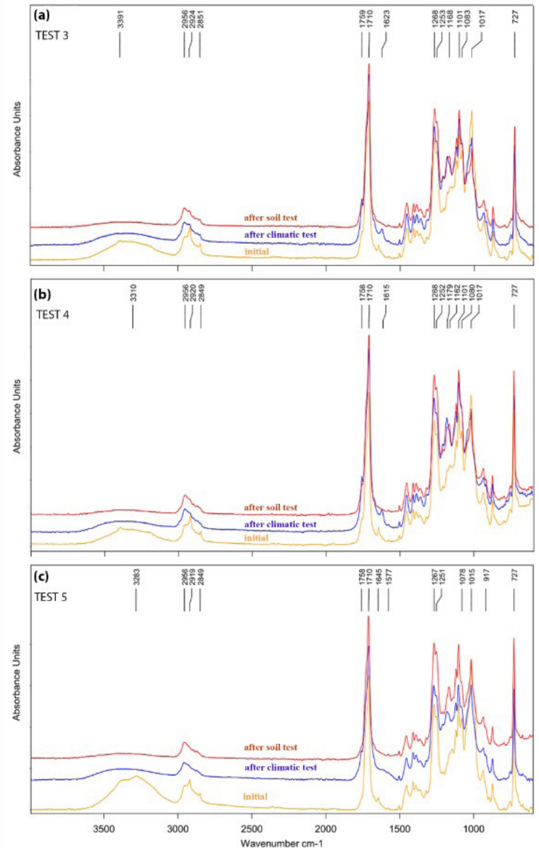

Figure 5. FTIR spectra of TEST 3 (a), TEST 4 (b), and TEST 5 (c) samples after the biodegradation test in soil and after the climatic test compared to the initial samples.

The sample TEST 2 was also based on PE with oxo-additives. This fact was evidenced by more intensive oxidation during the climatic test compared to the referent PE (REF 1). It is important to note that the mass of the sample decreased somewhat both after the soil test (-2.6 wt.%) and after the climatic test (-3.3 wt.%). In the previous work, it was shown that after an environmental test in a climatic chamber calcium carbonate may be partly washed out from the surface of such composite, based on polyethylene filled by $CaCO_3$[45]. It was also shown that particles of $CaCO_3$ may act as photodegradable additives to polyethylene. In addition, calcium carbonate was introduced to reinforce the polyethylene matrix and reduce the cost of the material[46]. It may be concluded that mass loss of the TEST 2 sample occurred because of two processes: washing out of the material components, and photodegradation of PE matrix. FTIR-spectra of this sample after both soil and climatic test showed the disappearance of several absorption bands, apparently associated with the washing out of the processing additives (presumably, silicone nature) that sweated onto the film surface. The decrease in the intensity of the absorption band at 1410 cm^{-1} was a result of soil and climatic tests and also indicated a partial washing of the water-soluble fraction of calcium carbonate. This also affects the mass loss as a result of being in the humid media.

The molecular weight of the polyethylene-based samples (TEST 1, TEST 2, and REF 1) remained unchanged after soil and climatic tests. Theoretically, they can be used as a carbon source for microorganisms. However, low-density polyethylene usually used for such types of bags is characterised by hydrophobicity and a high molecular weight that impedes colonisation and assimilation by microbiota[47]. According to different studies, the biodegradation of PE is possible only in the case of its preliminary oxidation. Oxygen-containing functional groups form in the chain at the initial stage[48]. Oxo-additives (photosensitizers) work on this principle. Based on the obtained results, the rate of oxidation (accumulation of carbonyl groups) for the samples containing oxo-additives (TEST 1, TEST 2) was 2 times higher than that of the ordinary PE. However, it is worth noting that PE was generally oxidized by UV light, so the carbonyl index did not increase after the soil test.

After the soil and climatic tests, the mass index decreased significantly for the polyester-based materials: TEST 3, TEST 4, and TEST 5. According to the calculations, these samples would be completely decomposed for about 1-2 years in soil; therefore, they can be classified as biodegradable in accordance with EN 13432[23] and ASTM G 160-03[11] because the significant mass of the samples was lost and physical integrity was destructed.

According to FTIR, the samples TEST 3, TEST 4, and TEST 5 were made from a polyester matrix filled with polysaccharide particles, presumably starch. These polyester-based samples had a significant mass loss after the soil test (13.9-20.8 wt.%) which indicated their high biodegradability. It is interesting to track changes in their chemical composition using FTIR, especially the fact of depolymerisation. As a result of degradation, main chains scission could occur followed by the reduction of polymers' molecular weight. It can be monitored by FTIR of redistribution of the ratio of methyl (CH_3) and methylene (CH_2) groups[48]. The process of depolymerisation occurred for all the polyester-based samples expressed in the growth of optical density of the bands 2845 and 2920 cm^{-1} with the simultaneous reduction of optical density of the bands 2875 and 2955 cm^{-1} attributed to stretching vibrations of C-H bonds in CH_2 and CH_3 groups, respectively.

For these samples, a significant decrease in tensile strength was observed (by 43-69%), which is one of the main criteria for the degradation of materials. It should be noted that the thickness of the bags is an important factor stimulating the degradation of materials as a result of the accelerated diffusion of destructors into the bulk of the sample. Thus, sample TEST 5, which had the smallest thickness of all polyester materials, had the highest rate of mass loss up to a complete change in colour and loss of integrity under biodegradation in soil conditions.

After both soil and climatic tests, the relative content of carboxylic groups in the samples TEST 3-5 increased (FTIR range from 1680 to 1800 cm^{-1}). Moreover, after the climatic test, a noticeable increase in the optical density of the band 1758 cm^{-1} occurred, which indicated the formation of terminal carboxyl groups as a result of the hydrolytic cleavage of the macromolecules[49]. The found patterns are consistent with the results of the work of other authors[50,51].

There was a noticeable decrease in the optical densities of the absorption bands in the region of 950-1300 cm^{-1}, which corresponded to the vibrations of C-O-C bonds both in the polyester and in the polysaccharide[52]. However, the most characteristic for polysaccharides, in particular starch, is a wide band at 1010 cm^{-1}, corresponding to the vibrations of glycosidic bonds. This band is superimposed on the characteristic bands of polyester – at 1020, 1100, 1175, and 1260 cm^{-1}. In addition, the polysaccharide filler corresponds to an absorption band in the region of 3000-3500 cm^{-1}, related to vibrations of OH-bonds. After the soil and climatic tests, a decrease in the optical density of the absorption bands characteristic of the polysaccharide filler was found, which indicated precisely its degradation at the initial stage. Moreover, the most noticeable decrease in the content of polysaccharide filler was observed after the soil test. The obtained results complied with the study of F. Ruggero et al.[21].

Table 5 demonstrates qualitative characterization of the changes in the absorption FTIR peaks intensity for all the materials after the soil and climatic tests. Below is a description of which functional groups correspond to the indicated FTIR peaks. There were no noticeable changes in chemical composition of the referent polyethylene (REF 1). New peaks at 1712 cm^{-1} appeared on the FTIR spectra of TEST 1 and TEST 2 after the climatic test. For sample TEST 1, the ratio of absorption bands 2915/2847, 1472/1462 and 730/719 cm^{-1} changed. The polyester samples (TEST 3, TEST 4, and TEST 5) were characterized by similar FTIR spectra. After the soil test of these samples, the absorption bands in the ranges of 900-1200 cm^{-1} and 3000-3500 cm^{-1} decreased. In addition, there was a mutual change in the intensities of the absorption bands at 2845, 2920, 2875, and 2955 cm^{-1}.

3.5. Thermophysical properties of the samples before and after open-air soil test

The dynamics of change in thermophysical properties of the samples after the soil was analyzed by DSC method. According to the temperatures and enthalpies of melting and crystallization of the polymers in the composition of the bags' samples, an assessment of the intensity of degradation of the polymers' ordered phases was performed[53]. Figures 6 and 7 present DSC heating and cooling curves for the bags' samples before and after the soil test, correspondently.

It can be seen from the figures that the crystalline formations in the polyethylene-based samples (TEST 1, TEST 2, REF 1) remained practically unchanged after degradation in soil. A slight decrease in PE melting and crystallization temperatures were observed for REF 1 (PE without oxo-additives).

The temperature and enthalpy of PLA peak of TEST 3 both for heating and cooling curves decreased after exposure to soil, which indicated the sample degradation[54]. The thermograms referred to TEST 4 did not show any melting peaks, and the crystallization peak of PBAT was unchanged, therefore, no

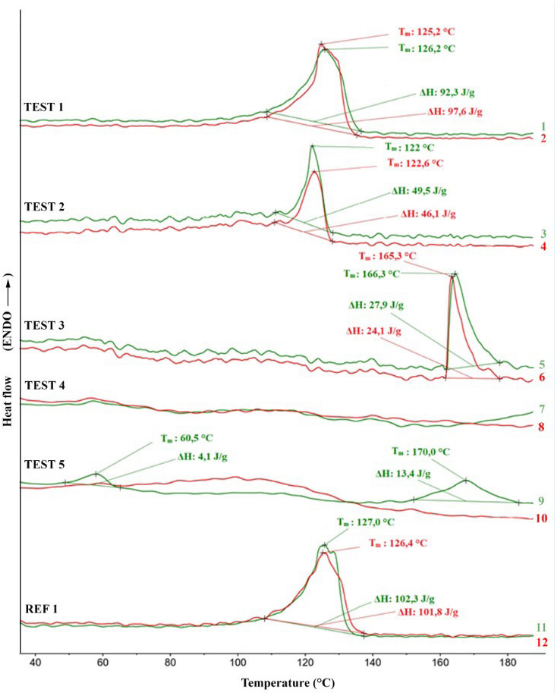

Figure 6. DSC first heating thermograms of TEST 1 (curves 1 and 2), TEST 2 (curves 3 and 4), TEST 3 (curves 5 and 6), TEST 4 (curves 7 and 8), TEST 5 (curves 9 and 10) and REF 1 (curves 11 and 12) samples after the biodegradation soil test (red curves) compared to the initial samples (green curves).

Table 5. The change in the absorption FTIR peaks intensity (functional groups) of the materials after the soil and climatic tests compared to the initial ones (by FTIR ATR).

Wavenumber (cm^{-1})	Bond	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5	REF 1
AFTER SOIL TEST							
3000-3600	-OH	0	--	--	--	--	0
2955-2956	-CH$_3$	N/A	N/A	-	-	-	N/A
2914-2925	-CH$_2$- (crys)	0	0	+	+	+	0
2875-2877	-CH$_3$	N/A	N/A	-	-	-	N/A
2846-2851	-CH$_2$- (amor)	--	-	+	+	+	0
1758-1760	-COOH	N/A	N/A	0	0	0	N/A
1710-1720	-C=O	+	0	+	+	+	0
1470-1472	-CH$_2$- (crys)	0	0	N/A	N/A	N/A	0
1460-1462	CH$_2$ (amor)	--	-	N/A	N/A	N/A	0
1410-1430	-Ca-O	N/A	--	N/A	N/A	N/A	-
1000-1030	-C-O-C-	N/A	N/A	--	--	--	N/A
AFTER CLIMATIC TEST							
3000-3600	-OH	0	--	-	--	--	0
2955-2956	-CH$_3$	N/A	N/A	-	-	-	N/A
2914-2925	-CH$_2$- (crys)	0	0	+	+	+	0
2875-2877	-CH$_3$	N/A	N/A	-	-	-	N/A
2846-2851	-CH$_2$- (amor)	-	-	+	+	+	0
1758-1760	-COOH	N/A	N/A	+	+	+	N/A
1710-1720	-C=O	+	+	++	++	++	0
1470-1472	-CH$_2$- (crys)	0	0	N/A	N/A	N/A	0
1460-1462	CH$_2$ (amor)	--	-	N/A	N/A	N/A	0
1410-1430	-Ca-O	N/A	--	N/A	N/A	N/A	-
1000-1030	-C-O-C-	N/A	N/A	--	-	--	N/A

N/A – not applicable, 0 – unchanged, (+) – increase, (-) – decrease, (++) – strong increase, (--) – **strong decrease.**

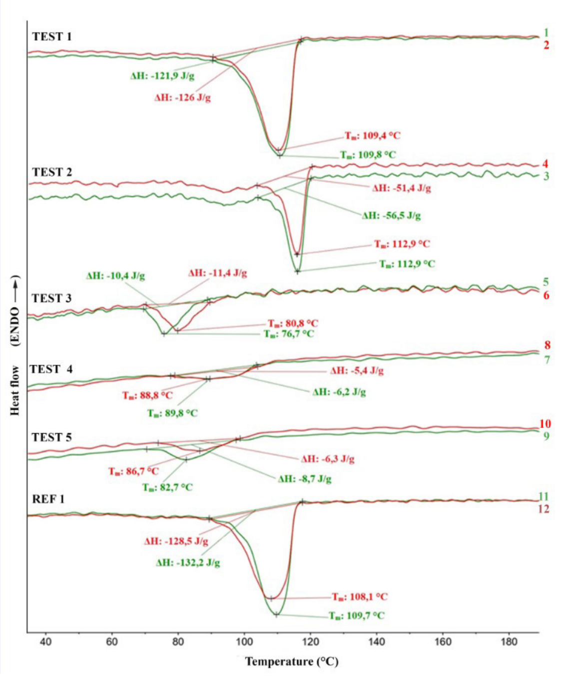

Figure 7. DSC cooling thermograms of TEST 1 (curves 1 and 2), TEST 2 (curves 3 and 4), TEST 3 (curves 5 and 6), TEST 4 (curves 7 and 8), TEST 5 (curves 9 and 10) and REF 1 (curves 11 and 12) samples after the biodegradation soil test (red curves) compared to the initial samples (green curves).

conclusions about the degradation of crystalline structures were made. After the soil test, TEST 5 was characterized by amorphization of the structure, which indicated its intensive destruction.

3.6. Stress-strain properties of the samples before and after open-air soil test

As a rule, during the degradation of materials, the formation of numerous defects occurs, which causes an increase in rigidity and brittleness (the growth of modulus of elasticity)[55]. Figure 8 demonstrates the relative change in mechanical properties of the samples before and after the open-air soil test. During the open-air soil test, the samples REF 2 (cellophane) and TEST 5 lost their integrity, so their properties were not analysed. The value of elastic modulus for all the samples increased. However, after the biodegradation test in soil the mechanical properties of the referent polyethylene (REF 1) were improved: tensile strength increased by 41%; elongation at break – by 18%; modulus of elasticity – by 82%. This could be explained by an increase in macro chains flexibility in the moist environment with the subsequent recrystallization of the feed-through chains[6]. For the rest of the samples, the tensile strength dropped by 10-69%. The elongation at break decreased: for TEST 1, TEST 3, and TEST 4 – by 96-97%, and for TEST 2 - by 27%. These data were comparable to those obtained in the previous studies that examined the embrittlement of bio bags after outdoor tests[19,56,57].

Table 6. The results of linear modelling stress-strain properties of the samples before and after soil test.

Dependent variable	Intercept		Stage		Plot ID (random effect)	Residual SD
	β ± SE	p-Value	β ± SE	p-Value	SD	
Tensile strength (MPa)	18.5 ± 3.6	0.003	-4.3 ± 1.6	0.011	8.3	5.2
Elongation at break (%)	185.5 ± 96.1	0.105	-222.9 ± 44.7	<0.001	220.2	149.6
Modulus of elasticity (MPa)	332.4 ± 58.7	0.002	149.2 ± 23.3	<0.001	136.9	81.1
Yield strength (MPa)	10.4 ± 1.6	0.001	-1.4 ± 0.4	<0.001	3.8	1.3

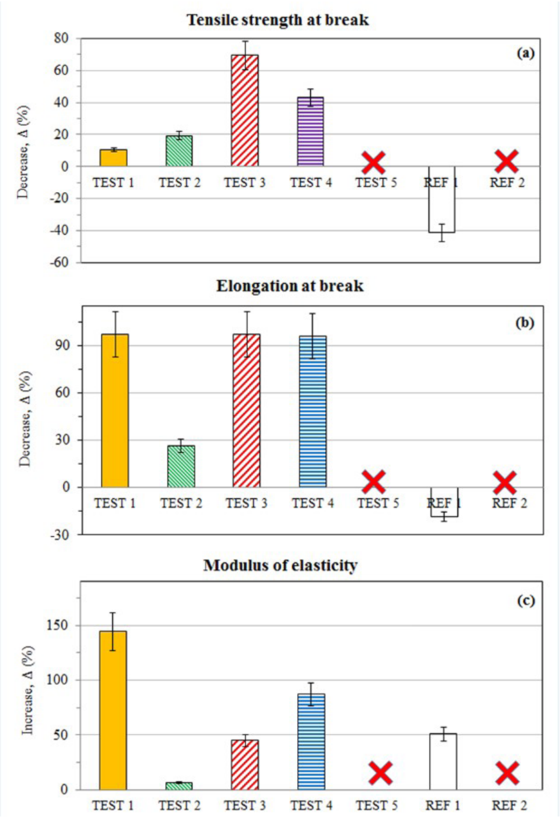

Figure 8. The relative change of the mechanical properties after the biodegradation test compared to the initial samples: (a) tensile strength at break, (b) relative elongation at break, (c) modulus of elasticity.

Table 6 demonstrates the results of a linear mixed effects simulation of the obtained data on stress-strain properties. The models obtained for all four conditionally dependent variables (strength at break, elongation at break, modulus of elasticity, yield strength) had a satisfactory random effect and residual SD values, which indicated their informational comparability. However, in the second model, for the parameter of elongation at break, the intercept value was determined unreliably, which showed the insufficiency of this parameter alone to characterize the degree of degradation of materials. Apparently, the variability of the elongation parameter of the samples depends on some additional factors not considered in the analysed model. The other three parameters (tensile strength, modulus of elasticity, and yield strength) had p-Values for intercept less than 0.01, which indicated their reliability. Full data on mechanical characteristics is given in supplementary material (Table S1).

4. Conclusions

The study of the biodegradability of commercial plastic bags by means of soil tests for 3 months was conducted. As a control experiment, the model climatic test in a weatherometer was performed. A number of commercially produced plastic bags labelled “biodegradable” sold in large retail chains were tested. According to the results, two bags’ samples were made from polyethylene with oxo-additive, which accelerated the oxidation of polymer under UV radiation. It could be assumed that with a decrease in molecular weight these materials could be biodegradable; however, over the studied period of three months, they did not show the ability to biodegrade. A high content of chalk filler and low molecular weight processing additives in the composition led to a slight mass loss (up to 3 wt.%) after the soil test due to the washing out of these components.

Three of the analysed samples contained aliphatic polyesters and polysaccharide fillers. It was found that they had different polymer matrices: PBAT+PLA, PBAT, PBAT+PCL+PLA. These samples showed an appreciable degree of biodegradation in soil conditions: mass loss was 14-21 wt.%; reduction in tensile strength was more than 43% from the initial one. The main components of these materials had the ability to degrade hydrolytically which classified them as biodegradable materials. At a constant rate of biodegradation, the estimated period of complete decomposition of these materials would be less than 2 years. According to the FTIR data, after the first 3 months in soil, only degradation of the filler (presumably starch) occurred in these materials. Any degradation signs of the polymer matrix were not detected.

The criteria for the reduction of mechanical properties, in particular, tensile strength and elongation at break, are often used to characterize the degree of polymeric materials degradation. It is important to note that all the materials labelled as “biodegradable” and the referent cellophane were characterized by a decrease in these indicators. Whereas the referent polyethylene bag, on the other hand, tended to strengthen after being exposed to the soil. This was explained by the ability of polyethylene to rearrange its structure over time with an increase in the degree of crystallinity.

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6. References

1. Romano A, Sotis C. Odi et Amo: a nudge to reduce the consumption of single-use carrier bags. Waste Manag. 2021;120:382-91. http://dx.doi.org/10.1016/j.wasman.2020.09.021.
2. Feuilloley P, César G, Benguigui L, Grohens Y, Pillin I, Bewa H, et al. Degradation of polyethylene designed for agricultural purposes. J Polym Environ. 2005;13(4):349-55.
3. Barragán DH, Pelacho AM, Martin-Closas L. Degradation of agricultural biodegradable plastics in the soil under laboratory conditions. Soil Res. 2016;54(2):216-24.
4. Musioł M, Rydz J, Janeczek H, Radecka I, Jiang G, Kowalczuk M. Forensic engineering of advanced polymeric materials Part IV: case study of oxo-biodegradable polyethylene commercial bag – Aging in biotic and abiotic environment. Waste Manag. 2017;64:20-7.
5. Briassoulis D, Babou E, Hiskakis M, Kyrikou I. Degradation in soil behavior of artificially aged polyethylene films with pro-oxidants. J Appl Polym Sci. 2015;132(30):1-19.
6. Zykova AK, Pantyukhov PV, Mastalygina EE, Chaverri-Ramos C, Nikolaeva SG, Saavedra-Arias JJ, et al. Biocomposites of low-density polyethylene plus wood flour or flax straw: biodegradation kinetics across three environments. Polymers (Basel). 2021;13(13):1-15.
7. Zykova AK, Pantyukhov PV, Popov AA. Degradation of highly filled biocomposites based on synthetic polymers and natural polysaccharides under the action of climatic weathering and biodegradation. IOP Conf Ser Earth Environ Sci. 2021;720(1)
8. Rogovina S, Aleksanyan K, Vladimirov L, Prut E, Ivanushkina N, Berlin A. Development of novel biodegradable polysaccharide-based composites and investigation of their structure and properties. J Polym Environ. 2018;26(4):1727-36.
9. Hejna A, Korol J, Kosmela P, Kuzmin A, Piasecki A, Kulawik A, et al. By-products from food industry as a promising alternative for the conventional fillers for wood–polymer composites. Polymers (Basel). 2021;13(6)
10. Aldas M, Pavon C, Ferri JM, Arrieta MP, López-Martínez J. Films based on mater-bi® compatibilized with pine resin derivatives: Optical, barrier, and disintegration properties. Polymers (Basel). 2021;13(9)
11. ASTM: American Society for Testing and Materials. ASTM. G160-03: Standard practice for evaluating microbial susceptibility of nonmetallic materials by laboratory soil burial. West Conshohocken: ASTM; 2003.
12. ASTM: American Society for Testing and Materials. D5208-14: Standard practice for Fluorescent Ultraviolet (UV) exposure of photodegradable plastics. West Conshohocken: ASTM; 2022.
13. Rajandas H, Parimannan S, Sathasivam K, Ravichandran M, Su Yin L. A novel FTIR-ATR spectroscopy based technique for the estimation of low-density polyethylene biodegradation. Polym Test. 2012;31(8):1094-9. http://dx.doi.org/10.1016/j.polymertesting.2012.07.015.
14. ISO: International Organization for Standardization. ISO 11357-1:2018: Plastics — differential scanning calorimetry (DSC) — part 3: determination of temperature and enthalpy of melting and crystallization. Geneva: ISO; 2018.
15. Ulrike A, Groemping MU. Package ' SOAs .' Vienna, Áustria: Cran; 2022;
16. Bates D, Mächler M, Bolker BM, Walker SC. Fitting linear mixed-effects models using lme4. J Stat Softw. 2015;67(1)
17. Adeniyi AG, Abdulkareem SA, Iwuozor KO, Abdulkareem MT, Adeyanju CA, Emenike EC, et al. Mechanical and microstructural properties of expanded polyethylene powder/mica filled hybrid polystyrene composites. Mech Adv Mater Structures. 2022:1-10. http://dx.doi.org/10.1080/15376494.2022.2059822.
18. Kawai T, Rahman N, Matsuba G, Nishida K, Kanaya T, Nakano M, et al. Crystallization and melting behavior of poly (L-lactic acid). Macromolecules. 2007;40(26):9463-9.
19. Sousa JC, Arruda SA, Lima JC, Wellen RMR, Canedo EL, De Almeida YMB. Crystallization kinetics of poly (butylene adipate terephthalate) in biocomposite with coconut fiber. Rev Mater. 2019;24(3):e12419.
20. Teamsinsungvon A, Ruksakulpiwat Y, Jarukumjorn K. Preparation and Characterization of Poly(lactic acid)/Poly(butylene adipate-co-terepthalate) Blends and Their Composite. Polym Plast Technol Eng. 2013;52(13):1362-7.
21. Ruggero F, Carretti E, Gori R, Lotti T, Lubello C. Monitoring of degradation of starch-based biopolymer film under different composting conditions, using TGA, FTIR and SEM analysis. Chemosphere. 2020;246:125770. http://dx.doi.org/10.1016/j.chemosphere.2019.125770.
22. McKeen LW. Introduction to use of plastics in food packaging. In: Ebnesajjad S, editor. Plastic films in food packaging. USA: Elsevier; 2016.
23. CEN: European Committee for Standardization. EN 13432 - Packaging: requirements for packaging recoverable through composting and biodegradation. Brussels: CEN; 2015.
24. Qi R, Jones DL, Liu Q, Liu Q, Li Z, Yan C. Field test on the biodegradation of poly(butylene adipate-co-terephthalate) based mulch films in soil. Polym Test. 2021;93:107009. http://dx.doi.org/10.1016/j.polymertesting.2020.107009.
25. Lyu JS, Lee JS, Han J. Development of a biodegradable polycaprolactone film incorporated with an antimicrobial agent via an extrusion process. Sci Rep. 2019;9(1):1-11. http://dx.doi.org/10.1038/s41598-019-56757-5.
26. Satti SM, Shah AA, Marsh TL, Auras R. Biodegradation of Poly(lactic acid) in Soil Microcosms at Ambient Temperature: Evaluation of Natural Attenuation, Bio-augmentation and Bio-stimulation. J Polym Environ. 2018;26(9):3848-57. http://dx.doi.org/10.1007/s10924-018-1264-x.
27. Wilfred O, Fan Z, Wang W, Tai H, Marriott R, Liu Q, et al. Journal of Nano Research Biodegradation of Polylactic Acid and Starch Composites in Compost and Soil. Int J Nano Res. 2018;1:1-11.
28. Weinstein JE, Dekle JL, Leads RR, Hunter RA. Degradation of bio-based and biodegradable plastics in a salt marsh habitat: another potential source of microplastics in coastal waters. Mar Pollut Bull. 2020;160:111518. http://dx.doi.org/10.1016/j.marpolbul.2020.111518.
29. Gomes LB, Klein JM, Brandalise RN, Zeni M, Zoppas BC, Grisa AMC. Study of oxo-biodegradable polyethylene degradation in simulated soil. Mater Res. 2014;17:121-6.
30. Lamot E, Voets JP. Microbial biodegradation of cellophane. Z Allg Mikrobiol. 1978;18(3):183-8.
31. Kumar Sen S, Raut S. Microbial degradation of low density polyethylene (LDPE): a review. J Environ Chem Eng. 2015;3(1):462-73. http://dx.doi.org/10.1016/j.jece.2015.01.003.
32. Kalinina IG, Gumargalieva KZ, Semenov SA, Kazarin VV. Resistance of polymer materials to microfungi during their adhesive interaction. Russ J Phys Chem B. 2018;12(1):155-7.
33. Marine Litter. High rates of marine biodegradation for all MATER-BI bioplastics [Internet]. 2017 [cited 2022 Mar 27]. Available from: https://bioplastics.org.au/marine-litter-high-rates-marine-biodegradation-mater-bi-bioplastics/
34. Weproject.media. About the production of biopackages, and where in Astana you can buy them [Internet]. 2018 [cited 2022 Mar 27]. Available from: https://weproject.media/articles/detail/o-proizvodstve-biopaketov-i-gde-v-astane-mozhno-ikh-kupit-
35. Dintcheva NT, Gennaro D, Teresi R, Baiamonte M. Pro-degradant activity of naturally occurring compounds on polyethylene in accelerate weathering conditions. Materials (Basel). 2019;12(1)

36. Muthuraj R, Misra M, Mohanty AK. Hydrolytic degradation of biodegradable polyesters under simulated environmental conditions. J Appl Polym Sci. 2015;132(27):1-13.
37. Ghatge S, Yang Y, Ahn JH, Hur HG. Biodegradation of polyethylene: a brief review. Appl Biol Chem. 2020;63(1). http://dx.doi.org/10.1186/s13765-020-00511-3.
38. Abdelmoez W, Dahab I, Ragab EM, Abdelsalam OA, Mustafa A. Bio- and oxo-degradable plastics: insights on facts and challenges. Polym Adv Technol. 2021;32(5):1981-96.
39. Ammala A, Bateman S, Dean K, Petinakis E, Sangwan P, Wong S, et al. An overview of degradable and biodegradable polyolefins. Prog Polym Sci. 2011;36(8):1015-49. http://dx.doi.org/10.1016/j.progpolymsci.2010.12.002.
40. Ienczak JL, de Aragão GMF. Biotechnologically produced biodegradable polyesters. In: Lendlein A, Sisson A, editors. Handbook of biodegradable polymers: isolation, synthesis, characterization and applications. Hoboken: John Wiley & Sons, Inc.; 2011. p. 23-44.
41. Reig FB, Adelantado JVG, Moya Moreno MCM. FTIR quantitative analysis of calcium carbonate (calcite) and silica (quartz) mixtures using the constant ratio method. Application to geological samples. Talanta. 2002;58(4):811-21.
42. Chiellini E, Corti A, D'Antone S, Baciu R. Oxo-biodegradable carbon backbone polymers - Oxidative degradation of polyethylene under accelerated test conditions. Polym Degrad Stabil. 2006;91(11):2739-47.
43. Asghar W, Qazi IA, Ilyas H, Khan AA, Awan MA, Rizwan Aslam M. Comparative solid phase photocatalytic degradation of polythene films with doped and undoped TiO2 nanoparticles. J Nanomater. 2011;2011:461930.
44. Pagès P. Characterization of polymer materials using FT-IR and DSC techniques. In: Artiaga Díaz R, editor Thermal analysis. Fundamentals and applications to material characterization [Internet]. Coruña: Universidade da Coruña; 2005 [cited 2022 Mar 27]. p. 121-40. Available from: http://ruc.udc.es/dspace/handle/2183/11499
45. Akhmetshina Z, Mastalygina E, Pantyukhov P. Oxidative degradation of polyethylene filled with nanosized crushed shells of sea oysters. Key Eng Mater. 2021;887:123-8.
46. Dweiri R. Processing and characterization of surface treated chicken eggshell and calcium carbonate particles filled high-density polyethylene composites. Mater Res. 2021;24(3)
47. Gilan I, Hadar Y, Sivan A. Colonization, biofilm formation and biodegradation of polyethylene by a strain of Rhodococcus ruber. Appl Microbiol Biotechnol. 2004;65(1):97-104.
48. Al-Salem SM, Behbehani MH, Al-Hazza'a A, Arnold JC, Alston SM, Al-Rowaih AA, et al. Study of the degradation profile for virgin linear low-density polyethylene (LLDPE) and polyolefin (PO) plastic waste blends. J Mater Cycles Waste Manag. 2019;21(5):1106-22. http://dx.doi.org/10.1007/s10163-019-00868-8.
49. Fu Y, Wu G, Bian X, Zeng J, Weng Y. Biodegradation Behavior of Poly(Butylene Adipate-Co-Terephthalate) (PBAT), Poly(Lactic Acid) (PLA), and Their Blend in Freshwater with Sediment. Molecules. 2020;25(17)
50. Boonmee C, Kositanont C, Leejarkpai T. Degradation of Poly (Lactic Acid) under Simulated Landfill Conditions. Environ Nat Resour J. 2016;14(2):1-9.
51. Arrieta MP, López J, Rayón E, Jiménez A. Disintegrability under composting conditions of plasticized PLA–PHB blends. Polym Degrad Stabil. 2014;108:307-18. http://dx.doi.org/10.1016/j.polymdegradstab.2014.01.034.
52. Hong T, Yin J-Y, Nie S-P, Xie M-Y. Applications of infrared spectroscopy in polysaccharide structural analysis: Progress, challenge and perspective. Food Chem X. 2021;12:100168. http://dx.doi.org/10.1016/j.fochx.2021.100168.
53. Fosse C, Bourdet A, Ernault E, Esposito A, Delpouve N, Delbreilh L, et al. Determination of the equilibrium enthalpy of melting of two-phase semi-crystalline polymers by fast scanning calorimetry. Thermochim Acta. 2019;677:67-78. http://dx.doi.org/10.1016/j.tca.2019.03.035.
54. Righetti MC, Gazzano M, Di Lorenzo ML, Androsch R. Enthalpy of melting of α′- and α-crystals of poly(L-lactic acid). Eur Polym J. 2015;70:215-20. http://dx.doi.org/10.1016/j.eurpolymj.2015.07.024.
55. Varlamov AA, Rimshin VI, Tverskoi SY. The modulus of elasticity in the theory of degradation. IOP Conf Ser Mater Sci Eng. 2018;463(2):022029.
56. Yu F, Wu Z, Wang J, Li Y, Chu R, Pei Y, et al. Effect of landfill age on the physical and chemical characteristics of waste plastics/microplastics in a waste landfill sites. Environ Pollut. 2022;306:119366. http://dx.doi.org/10.1016/j.envpol.2022.119366.
57. Kijchavengkul T, Auras R, Rubino M, Ngouajio M, Fernandez RT. Assessment of aliphatic-aromatic copolyester biodegradable mulch films. Part I: field study. Chemosphere. 2008;71(5):942-53.

Supplementary material

The following online material is available for this article:

Table S1 - The mechanical characteristics under tension for the bags samples before and after open-air soil test.