

Article

Anaerobic Degradability of Commercially Available Bio-Based and Oxo-Degradable Packaging Materials in the Context of their End of Life in the Waste Management Strategy

Magdalena Zaborowska ^{1,*} , Katarzyna Bernat ¹ , Bartosz Pszczółkowski ² , Irena Wojnowska-Baryła ¹ and Dorota Kulikowska ¹

¹ Department of Environmental Biotechnology, Faculty of Geoengineering, University of Warmia and Mazury in Olsztyn, ul. Sloneczna 45 G, 10-719 Olsztyn, Poland; bernat@uwm.edu.pl (K.B.); irka@uwm.edu.pl (I.W.-B.); dorotak@uwm.edu.pl (D.K.)

² Department of Materials and Machines Technology, University of Warmia and Mazury in Olsztyn, ul. Oczapowskiego 11, 10-719 Olsztyn, Poland; bartosz.pszczolkowski@uwm.edu.pl

* Correspondence: magdalena.zaborowska@uwm.edu.pl; Tel.: +48-89-523-4118; Fax: +48-89-523-4131

Abstract: There are discrepancies concerning the time frame for biodegradation of different commercially available foils labeled as biodegradable; thus, it is essential to provide information about their biodegradability in the context of their end of life in waste management. Therefore, one-year mesophilic (37 °C) anaerobic degradation tests of two bio-based foils (based on starch (F_S), polylactic acid (F_{PLA})) and oxo-degradable material (F_{OXO}) were conducted in an OxiTop system. Biodegradation was investigated by measuring biogas production (BP) and analyzing structural changes with differential scanning calorimetry, polarizing and digital microscopic analyses, and Fourier transform infrared spectroscopy. After 1 year, F_{OXO} had not degraded; thus, there were no visible changes on its surface and no BP. The bio-based materials produced small amounts of biogas (25.2, F_{PLA} , and 30.4 L/kg VS, F_S), constituting 2.1–2.5% of theoretical methane potential. The foil pieces were still visible and only starting to show damage; some pores had appeared in their structure. The structure of F_{PLA} became more heterogeneous due to water diffusing into the structure. In contrast, the structure of F_S became more homogenous although individual cracks and fissures appeared. The color of F_S had changed, indicating that it was beginning to biodegrade. The fact that F_S and F_{PLA} showed only minor structural damage after a one-year mesophilic degradation indicates that, in these conditions, these materials would persist for an unknown but long amount of time.

Keywords: polymers; starch- and polylactic-acid-based material; biogas production; FTIR and microscopic analyses; DSC



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1. Introduction

The worldwide use of bioplastics (bio-based products) has been increasing, and it is expected that the share of bio-based products on the plastics market will increase by 40% by 2030 [1]. These products are most often used as food packaging, frozen food containers, milk and juice cartons, disposable tableware, or for agriculture purposes [2]. Bio-based products are wholly or partly of biological origin, e.g., based on lignin, cellulose, or starch. These products contain from 20% up to 100% renewable raw materials and can be both biodegradable and non-biodegradable [3]. However, the most desirable are biodegradable or compostable products, which degrade anaerobically or aerobically in the presence of microorganisms. Among biodegradable bio-based products, starch-based materials and polylactic acid (PLA) are the most common, constituting 44% and 24% of the global production capacity for biodegradable polymers, respectively. Other biopolymers produced at an industrial scale are poly(butylene succinate) (PBS) and poly(butyleneadipateterephthalate) (PBAT), which constitute 23% of the global production capacity, and polyhydroxyalkanoates (PHA), which constitute 6% [4]. PLA can be synthesized from renewable biomass

(e.g., molasses, whey, bagasse, potato, tapioca, wheat) via microbial fermentation process by bacteria and fungi [5]. However, the yield of lactic acid produced by fungi is lower than produced by bacteria. The microorganisms used for PLA production are the following: *Lactococcus*, *Enterococcus*, *Streptococcus*, *Leuconostoc*, *Weissella*, some *Lactobacilli*, and *Lactobacillus brevis*. PLA can be produced in batch, fed batch, or continuous fermentation, whereof the first two produce a high concentration of lactic acid and the last one has higher productivity [6–8]. Starch is a natural material, composed of amylose and amylopectin. For bio-based material production, thermoplastic starch (TPS) is the most often used. TPS is formed during, e.g., mechanical shearing under heat or the addition of plasticizers (typically water or glycerol) to starch [9].

Although they should not be confused with bio-based materials, petroleum-based products to which oxidants have been added (i.e., oxo-degradable products) are often classified as biodegradable plastics, and they can degrade via an abiotic–biotic process [10,11]. The additives used in oxo-degradable products facilitate the breakdown of molecular chains, leading to the products' degradation [12]. For example, photodegradation of low-density polyethylene and polypropylene films can be activated using metal oxides (e.g., Fe_2O_3 , Cu_xO , ZnO , and TiO_2) as catalysts [13,14].

Biodegradable bio-based products often contain various non-organic additives to increase their thermal stability and mechanical properties. Bio-based materials may contain additives such as stabilizers, plasticizers, fillers, reinforcing agents, colorants, and fire retardants, which influence the biodegradability of these materials [15]. For example, regarding starch-based materials, the most common plasticizers used for the improvement of their thermal stability are polyols (glycerol and sorbitol) [16]. Moreover, to improve their mechanical and thermal properties, sodium silicate [17] or silica [18] can be used. Other common plasticizers used for bio-based material production are glycerol [19], urea [20], or citrate esters [21]. However, these additives decrease both the degree and the rate of degradation of the bio-based products [22]. The complete degradation of bio-based products occurs only under optimized conditions (i.e., optimal temperature, pH), which may be different for different materials. Generally, the large fragments of these products are first fragmented into smaller particles. This fragmentation, as well as incomplete degradation, may cause the biopolymers to be released into the environment as microplastics [23]. Due to the increasing amount of waste from bio-based products, it is necessary to assess the effect of these products on waste management, including organic recycling. Waste from bio-based products can be found in streams of selectively collected plastic waste and biowaste. If bioplastics are handled with conventional plastics, they will likely be recycled or incinerated. However, assuming that they are labeled as bio-based products, they should be collected with biowaste (kitchen waste and green waste). Therefore, it is necessary to carry out the degradation of bio-based products under the process conditions used during the treatment of the biowaste. Mechanical–biological treatment (MBT) plants treat biowaste via anaerobic digestion (AD) and/or aerobic stabilization/composting. In organic recycling of bio-waste, methane fermentation is increasingly used because it improves the economy of MBT plants and provides other benefits like decomposition of organic matter, production of biogas, and reduction of the waste volume. Moreover, the process enables production of naturally used digestate and other substrates for chemical syntheses (e.g., for volatile fatty acids) [24–26]. Therefore, it is important that bio-based products should be completely biodegradable, and after they become a part of compost or digestate in an MBT plant, they should not contaminate these materials.

Due to rapid growth in the amount of bio-based products and their waste, there is a need to determine the optimal conditions for degrading these products, especially under anaerobic conditions. AD can be carried out in MBT plants at mesophilic (35–40 °C) or thermophilic (50–60 °C) temperatures. However, the mesophilic process is more stable and requires a smaller energy input [27]. Generally, anaerobic tests are based on the measurement of biogas or methane production. The principal standard methods for monitoring the anaerobic degradation of bio-based products use mesophilic temperatures. For example,

ISO 14853:2016, used to determine the anaerobic biodegradability of plastic materials in an aqueous medium, calls for exposure of the test polymers to sludge at $35\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ for a period of up to 90 days [28]. This time is longer than the conventional sludge retention time (25 to 30 days) in anaerobic digesters. Massardier-Negotte et al. [29] used ISO 14853 for anaerobic tests and found that, in these conditions, biopolymers (PLA, polycaprolactone, starch/polycaprolactone, and PBAT) degraded slightly or did not degrade.

To determine the degree and rate of anaerobic mesophilic biodegradation of plastic materials, ASTM D5526 may be also used [30]. In this test, the inoculum should be derived from anaerobic digesters operating only with pretreated household waste. Biodegradation should be carried out under dry ($>30\%$ total solids (TS)) and static non-mixed conditions. Another test of polymer biodegradability is provided by EN 13432, which defines the requirements for determining the compostability and anaerobic treatability of plastic packaging materials [31]. Zhang et al. [32] carried out mesophilic anaerobic degradation of nine different bioplastics (based on cellulose, starch, and PLA) according to EN13432. They concluded that only four bioplastics showed substantial biodegradability, but less than 20% of their carbon was converted into methane.

In summary, many products on the market are labeled as biodegradable. However, even though various products can be based on the same main component, e.g., starch or PLA, its content in the products can differ. Moreover, manufacturers use various types of additives in different proportions to improve the functional properties of a material. Unfortunately, however, the manufacturers do not provide detailed information on the composition of their products. Most likely, the types and proportions of the additives are the main factors determining the biodegradability of bioplastics and the time frame for their biodegradation. Thus, reports on the degree of biodegradation of different bioplastics during anaerobic treatment differ substantially [33–36]. Moreover, for waste-management and end-of-life considerations, it is essential to provide information on as many as possible of the commercially available materials that are considered biodegradable. Therefore, the aim of this study was to investigate the degradation of selected bio-based and oxo-degradable products (waste disposal bags) during a long-term (1-year) anaerobic mesophilic biodegradation test. Three different commercially available foil materials were studied by observing changes in their structure with the use of polarizing and digital microscopic analyses, Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC).

2. Materials and Methods

2.1. Bio-Based Materials and Oxo-Degradable Material

In the present study, three different commercially available foils were subjected to anaerobic mesophilic ($37\text{ }^{\circ}\text{C}$) degradation. Two of them were bio-based products: BioBag waste bags made from Mater-Bi[®] material based on starch (F_S) and bags made from polylactic acid (F_{PLA}). The third foil was an oxo-degradable product (F_{OXO}), consisting of conventional polyethylene containing the pro-oxidant additive d2w. Each of the investigated foils was cut to a particle size of $10 \times 10\text{ mm}$. The characteristics of the materials are presented in Table 1. To improve their functional properties, these products, which were purchased on the commercial public market, may have contained other additives. Unfortunately, however, the manufacturer did not provide details of their composition.

Table 1. Characteristics of the materials used in the experiment.

Material	F _{PLA}	F _S	F _{OXO}
Basic characteristics			
VS (% of DM)	99.3	99.9	93.1
COD (g/kg)	71.5	63.9	n.d.
TN (mg/kg)	454.9	408.6	3766.8
Elemental composition			
Carbon, %	57.56	55.36	n.d.
Hydrogen, %	6.88	6.90	n.d.
Oxygen, %	34.86	37.64	n.d.
Nitrogen, %	0	0	n.d.

n.d., not determined; VS, volatile solids; DM, dry mass; COD, chemical oxygen demand; TN, total nitrogen.

2.2. Measurement of Biogas Production

An anaerobic biodegradation test with measurement of biogas production from bio-based and oxo-degradable foils was performed under mesophilic conditions (37 ± 0.5 °C) with the use of a standard test of gas potential (ISO 14853:2016) with modifications [28]. The measurement lasted 1 year and was carried out in triplicate for each foil with the use of the OxiTop® Control system (WTW Wissenschaftlich-Technische Werkstätten GmbH, Germany), which consists of measuring vessels (bioreactors) with a capacity of 630 mL and measuring heads with built-in pressure sensors. Pressure values obtained from respirometric measurements allowed determination of the volume of biogas produced. To ensure anaerobic conditions, the space above the sample was flushed with nitrogen gas before measurements.

To determine the biogas production from foil, the inoculum (approximately 100 mL) and the foil were introduced into the OxiTop bioreactors. The inoculum was fermented sludge from a closed mesophilic digester chamber from a municipal wastewater treatment plant employing the activated sludge method (north-eastern Poland). The planned initial organic load (OL) was 4 kg VS/m³, indicating that the doses of foils were 0.4 g. Additionally, biogas production by the inoculum alone was determined. The biogas production of the foils themselves was determined by taking the difference between the amount of biogas generated in the bioreactors with inoculum and foil and the amount of biogas generated in the bioreactors with only inoculum.

Additional glass bottles, with volume identical to those of the bioreactors, were prepared to enable sampling of foil pieces from these bottles. These bottles were prepared in the same manner as the OxiTop vessels, which were used only for measuring biogas production. All the bioreactors and bottles were placed in a thermostatic incubator. Every month during anaerobic biodegradation tests, pieces of F_S, F_{PLA}, and F_{OXO} were removed from the inoculum for the microscopic, differential scanning calorimetry (DSC), and FTIR analyses. However, the results of these analyses did not show any changes in comparison with the raw materials during the first year. Changes finally appeared after 1 year, and only these results are shown below.

2.3. Microscopic and FTIR Analysis

The changes on the surface of the bio-based and oxo-degradable materials were analyzed using a Nikon eclipse50i polarizing microscope at a magnification of 100× and digital microscope (Keyence VHX-7000, Osaka, Japan) at a magnification of 1000×. Additionally, the digital microscope allows to determine 3D geometric structure (topography) at the microscale without contact with the investigated foil sample.

The FTIR spectra were collected using a PerkinElmer Spectrum Two (with diamond ATR) brand device within the wavenumber range of 4000–400 cm^{−1} and resolution of 4 cm^{−1} at room temperature and repeated in triplicate for each foil material. Smoothing functions were not employed.

2.4. Differential Scanning Calorimetry Analysis

In the raw foil materials and after 1 year of the degradation, thermal properties of bio-based and oxo-degradable foils were investigated with a differential scanning calorimetry analysis (DSC) on DSC Phoenix 204 F1 differential scanning calorimeter utilizing hit flow method (NETZSCH, Selb, Germany). The measured parameter is free heat flow. Small amounts (ca. 5 mg) of dry samples of each of the foils were placed into aluminum crucibles, sealed, and heated at between 30 °C and 200 °C at a heating rate of 5 °C/min. An empty aluminum crucible was used as reference. The analysis based on the measurement of energy required to establish a zero-temperature difference between the analyzed sample and a reference sample. The thermal characteristics such as the glass transition temperature (T_g), cold crystallization temperature (T_{cc}), cold crystallization enthalpy (ΔH_{cc}), melting temperature (T_m), and melting enthalpy (ΔH_m) were determined from DSC curves.

2.5. Analytical Methods

Volatile solids (VS) as loss on ignition and the contents of COD and TN (as total Kjeldahl nitrogen) in foil materials (if possible) were determined according to APHA [37]. Elemental composition of the materials was determined with the use of Flash 2000 Organic Elemental Analyzer (Thermo Scientific, Milan, Italy).

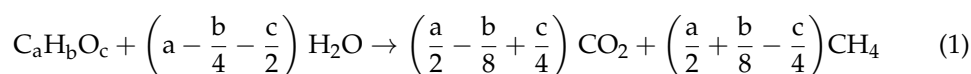
3. Results and Discussion

3.1. Anaerobic Biodegradation Test of Selected Bio-Based and Oxo-Degradable Materials in OxiTop System

Anaerobic biodegradation of pieces of foils of F_S , F_{PLA} , and F_{OXO} were carried out under mesophilic conditions at 35 °C. The OxiTop system allowed measurement of the volume of biogas (in mL) produced during the anaerobic test. During the analyses of biogas volume (BV) from investigated material, two BV profiles were considered. The inoculum alone (I) represents the first profile. The inoculum with the material ($F_S + I$, $F_{PLA} + I$) represents the second profile. The profile of the biogas volume for the material alone is possible to be obtained by subtracting the values of the first profile from the second. As shown in Figure 1, the profiles of biogas volume corresponding to the inoculum alone and to both the inoculum and the foil material were very close to each other. This means that the biogas volume corresponding to the foil material alone would be very low. This was confirmed by the value of BP in liters per kg of organic matter (L/kg VS), that is, the most commonly used units for BP during anaerobic measurements in this kind of system, as the VS content of the foil materials was considered to reflect the organic matter content. The profiles corresponding to the inoculum alone and to both the inoculum and the foil material of F_{OXO} showed no differences indicating lack of degradation; thus, no BV and BP profiles are provided.

The profiles of the biogas volume for the bio-based foil materials of F_{PLA} and F_S showed the initial long lag phases. With F_S , the lag phase was even longer, lasting 70 days, whereas with F_{PLA} , it lasted 60 days. After the lag phase, BP started to increase very slowly until 160–180 day of the measurements, and then, the biogas volumes remained the same until the end of an almost 400-day anaerobic test. The final biogas production for F_{PLA} and F_S was similar: 25.2 and 30.4 L/kg VS, respectively.

Based on the elementary composition of the foil materials, the theoretical amounts of methane (theoretical methane potential, TMP), assuming complete conversion of organics into biogas, were calculated using the Buswell equation [38]:



The theoretical molar compositions of the methane that could be obtained from one mole of the tested foil materials were as follows:

- F_{PLA} : $C_{4.40}H_{6.31}O_2 + 1.99 H_2O \rightarrow 2.71 CH_4 + 2.08 CO_2$;
- F_S : $C_{9.83}H_{14.70}O_5 + 1.71 H_2O \rightarrow 2.58 CH_4 + 2.03 CO_2$.

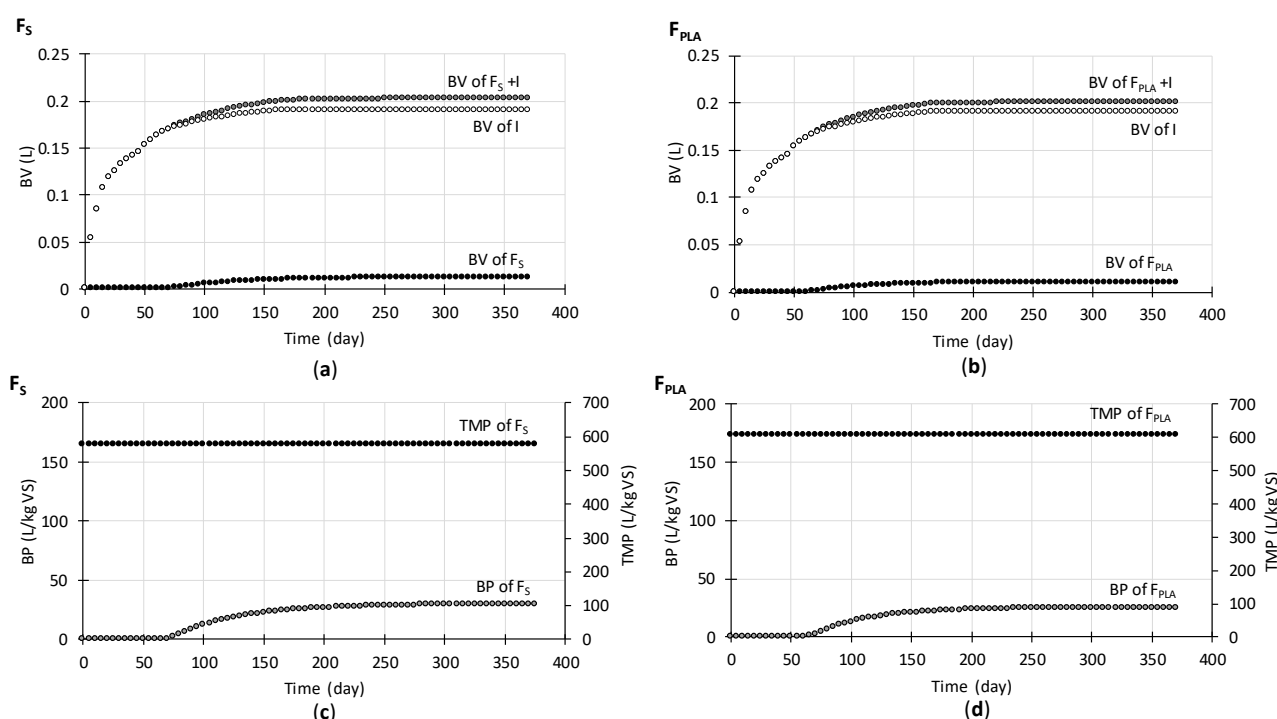


Figure 1. Biogas volume (BV; in L) profiles (a,b) from the inoculum (I) only and bio-based materials with the inoculum ($F_S + I$, $F_{PLA} + I$) and biogas production (BP; in L/kg VS) profiles (c,d) during an anaerobic biodegradation test at 35 °C of bio-based materials of F_{PLA} and F_S ; the values of theoretical methane potential (TMP) of F_S and F_{PLA} (based on the elemental composition) are also shown; the F_{OXO} did not degrade, and thus, no BP was observed and the profiles are not provided.

To calculate the mass of methane and carbon dioxide, molar masses were considered. Then, to determine the theoretical volumes of gases, their densities were considered as 0.717 g/L and 1.978 g/L, respectively (at 0 °C, 101 kPa). The values of TMP of F_S and F_{PLA} (based on the elemental composition) are 577 and 610 L/kg VS, and they are also shown in Figure 1 for comparison with the obtained BP. Assuming that methane content in biogas from F_S and F_{PLA} would be ca. 50% [38], the values of methane production (MP) would be two times lower than biogas production, ca. 12 and ca. 15 L/kg VS, respectively.

Most of the studies assumed that the value of TMP is the maximal value of methane that could be obtained. The ratios of MP/TMP for F_S and F_{PLA} are 0.021 and 0.025. Thus, F_S and F_{PLA} produced methane in amounts constituting only 2.1% and 2.5%, respectively, of the TMP values.

There are discrepancies concerning the time frame for the biodegradation of different biopolymers, and most researchers have not provided information on biogas yield. Bátori et al. [36] found that some biopolymers, such as starch, cellulose, pectin, and poly(hydroxyalkanoate), can be degraded at hydraulic retention times commonly used in biogas plants. Shin et al. [39] reported that 89% of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB/HV; 92/8, w/w) could be degraded within 20 days under anaerobic mesophilic conditions. Similarly, Noda et al. [33] found that 80% of 14-C-labeled poly(3-hydroxybutyrate-co-3-hydroxyoctanate) biodegraded after 25 days under anaerobic conditions at 37 °C. Yagi et al. [35] found that during mesophilic (37 °C) anaerobic degradation, PHB was over 90% biodegraded in 10 days, whereas PLA was only 7% biodegraded in 90 days, and PBS did not degrade. Kolstad et al. [34] tested the degradability of a commercially available PLA product at two temperatures: 21 °C (under simulated landfill conditions) and 35 °C. The duration of the tests was 13 months (390 days) and 170 days, respectively. The authors found that, in a year-long psychrophilic test, the amorphous and semicrystalline PLA did not produce a significant volume of biogas. At 37 °C, it was predicted that amorphous PLA would yield approximately 189 L/kg (40% of the theoretical potential), whereas

it was observed that the semicrystalline samples did not generate a significant volume of methane.

3.2. Microscopic Analyses and Topography of the Investigated Materials

The small amount of biogas produced by the bio-based materials is connected with the fact that, until 365 days of anaerobic degradation had passed, pieces of the foils were still visible in the inoculum, and these fragments only started to show damage. Polymer degradation can be determined based on the changes in the surface, e.g., formation of holes and/or cracks, and changes in color or roughness parameters. Moreover, thermal properties (DSC) or the results of FTIR analyses can provide information about the structural changes in the material [40].

The foils used in the present study came from commonly available bags for waste collection. Initially, each of the foils had a green color and was smooth. Microscopic analyses at 100-fold magnification showed no changes after 1 year of degradation of the F_{PLA} material, but analyses at 1000-fold revealed some pores in the material structure (Figure 2). Analyses of surface topography indicated that, after long-term anaerobic degradation, the structure of F_{PLA} had become more heterogeneous than that of the raw material (Figure 3). The distance between the valleys and peaks decreased after degradation, which may have been caused by diffusion of water into the material structure and may indicate that the foil's thickness was gradually decreasing and it was being degraded [41].

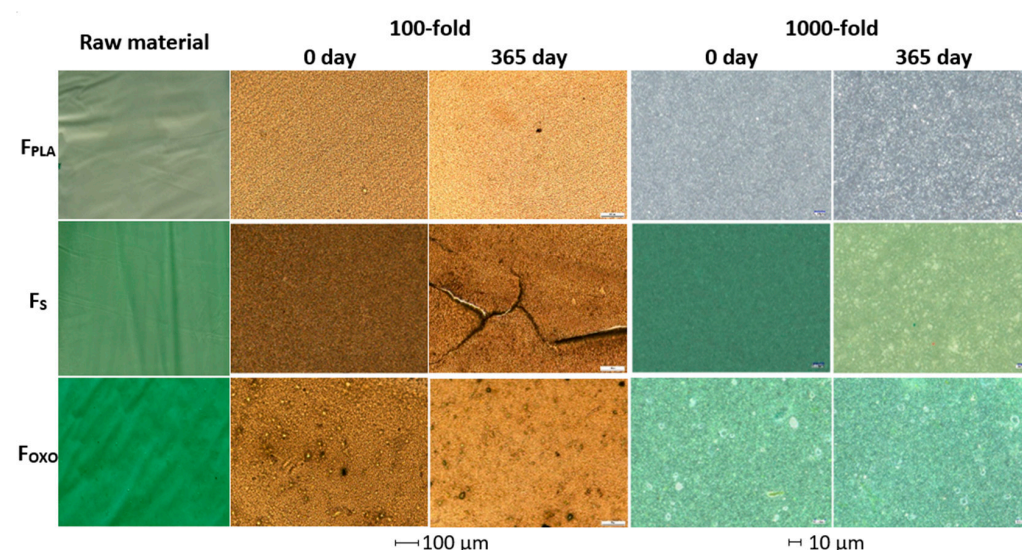


Figure 2. Polarizing and digital microscopic images of raw foil materials and of foil materials after a 365-day anaerobic mesophilic degradation test.

In contrast to F_{PLA} , the F_S material changed visibly after 1 year of degradation, and individual cracks and fissures were visible in its structure (Figure 2). These changes corresponded to slightly higher biogas production from F_S than from F_{PLA} . A change in the color of the material was also observed. Such changes in the color of a polymer may be considered an important indicator of the biodegradation process [42]. Lee et al. [43] observed that, during anaerobic degradation of a foil consisting of a mixture of PLA and pure lactic acid, its color changed from transparent to white after 10 days of the process, whereas a foil consisting of pure PLA did not change color during this time. In the study present here, the analyses of F_S surface topography indicated that, after degradation, the structure of the material became more homogeneous (Figure 3). The change in the color of the bio-based product may be one of the indicators of the biodegradation of the polymer. Fortunati et al. [44] observed changes of color of the PLA material during composting due to hydrolytic degradation of the polymer, which led to a change in the refraction index. This was caused by water absorption and/or the presence of hydrolysis product. The same results were obtained by Arrieta et al. [45] during composting of PLA and plasticized

PLA/PHB films. Moreover, the authors suggested that an increase in lightness of plasticized films may be caused by loss of the plasticizer and the compression of macromolecular chains of polymer. The color change of bio-based products may also correspond to the embrittlement of materials, which is associated with increase in crystallinity [46].

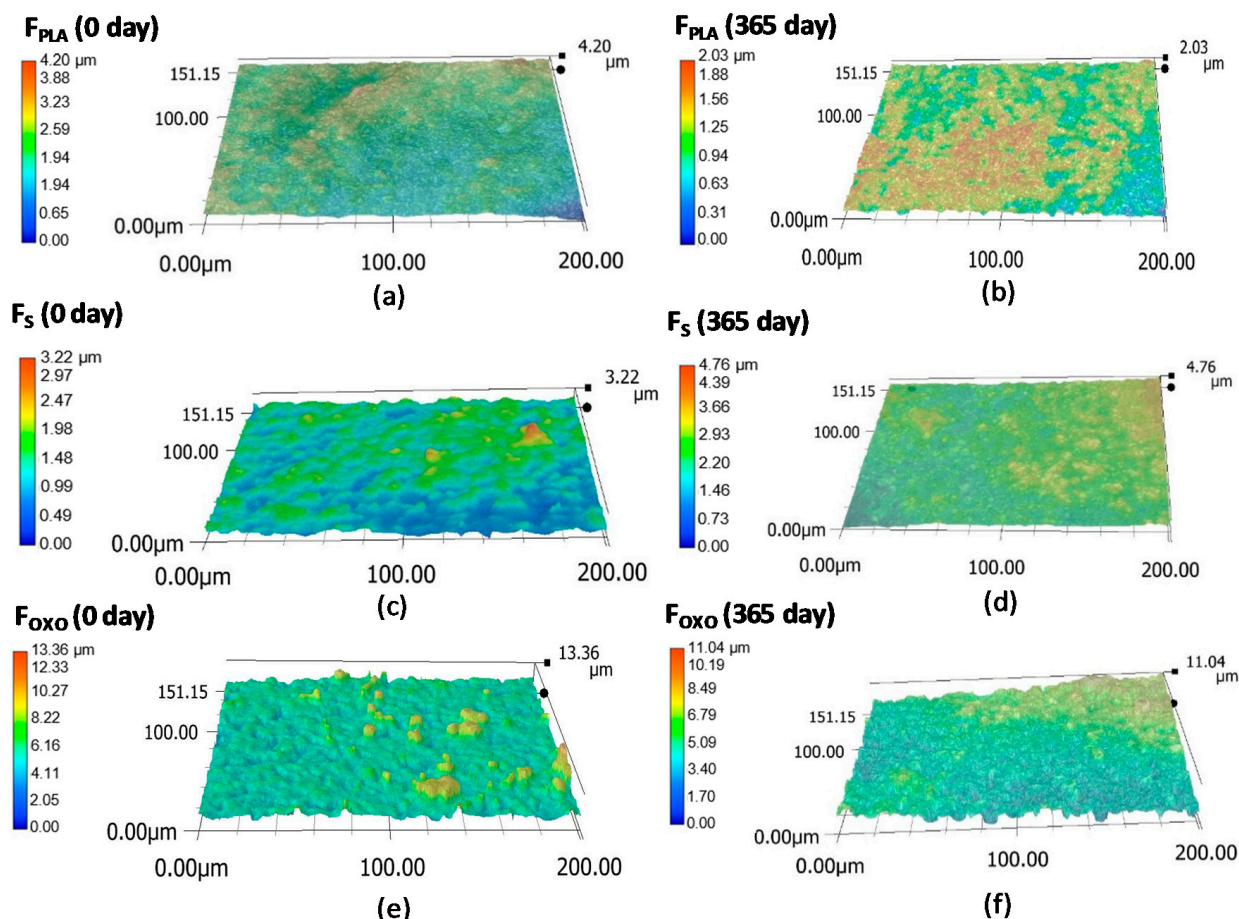


Figure 3. Topography of raw foil materials (a,c,e) and of foil materials after a 365-day (b,d,f) anaerobic mesophilic degradation test.

Microscopic analyses of F_{OXO} did not show any changes in the foil's structure (Figure 2), whereas an analysis of surface topography showed a decrease in the height of the peaks and the depth of the valleys on the material surface (Figure 3). This may have been caused by washing away the pro-oxidant additive.

3.3. Differential Scanning Calorimetry (DSC) Measurements

Regarding the DSC curve of raw foil of F_{PLA} before degradation, the cold crystallization peak was observed at 75 °C. After one-year degradation, this peak was not noted, which may indicate the hydrolysis of F_{PLA} and the rapid increase in polymer matrix crystallinity [47]. A shift in the melting point from 166 °C (F_{PLA} before degradation) to 164 °C (F_{PLA} after degradation) was observed. Moreover, the enthalpy of the melting process decreased by about 2 J/g. The decrease of F_{PLA} melting point during degradation may be connected with molecular mass reduction [48]. The glass transition temperature increased after degradation from 55 °C to 66 °C, and no enthalpy changes were observed (Figure 4).

Regarding raw foil of F_S before degradation, the three melting points at 64 °C, 118 °C, and at 152.8 °C were observed (Figure 4). Aldas et al. [49] reported that the melting point in starch-based material Mater-Bi at 56.3 °C and 107.3 °C corresponded to poly(ϵ -caprolactone) (PCL) and poly(butylene adipate-co-terephthalate) (PBAT) addition, respectively. Whereas a melting point at ca. 150.3 °C refers to the melting of the plasticized starch fraction [49,50].

Abdullah et al. [51] found that glass transition temperature and melting temperature of starch-based bioplastics decrease with the decrease of starch to glycerol ratio (glycerol is a common plasticizer for producing starch-based bio-based products). In the presented study, after one-year degradation of F_S , a shift of all peaks of the DSC curve was observed. However, the area under both curves was similar, which indicated no enthalpy changes for F_S before degradation and after the process.

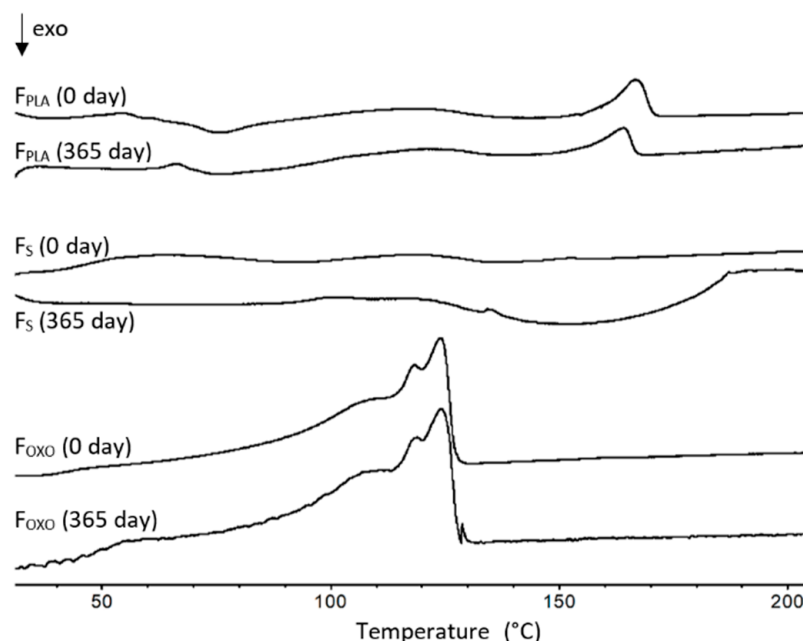


Figure 4. The DSC curves of raw foil materials and of foil materials after a 365-day anaerobic mesophilic degradation test.

DSC analyses for F_{OXO} material (in raw material and after one-year degradation) showed typical DSC curves of polyethylene, without substantial changes due to pro-oxidant additive. Contant-Rodrigo [52], during thermal characterization of polypropylene with the addition of pro-oxidant, also showed that the additive did not modify the DSC curve. In the presented study, the DSC curve of the material after the long-term degradation did not change. Melting process was in the range from 114 °C to ca. 128 °C. The melting point was observed at 124 ± 0.1 °C. A slightly lower melting point value (117–119 °C) was obtained by Benitez et al. [53] for linear low-density polyethylene.

3.4. FTIR Spectra

The FTIR spectra of investigated foils allowed to detect their chemical composition before and after long-term degradation (Figure 5). The spectrum of raw material of F_{PLA} showed typical bands for pure PLA. The peak between 3612 and 3000 cm^{-1} indicated hydrogen-bonded (intra- and intermolecular) –OH groups. The bands located at 2964–2880 cm^{-1} corresponded to asymmetric and symmetric vibrations of the –CH₃ groups. The peak at 1710 cm^{-1} represented asymmetric stretching of carbonyl C=O groups by lactide [45,54], which may indicate the amorphous phase of PLA. The peaks at 1263, 1133, and 1098 cm^{-1} corresponded to stretching vibrations of the C–O–C and –CH–O– groups. The band at 931 cm^{-1} combined contributions of both –CH₃ rocking and deformation of the carboxylic –OH···H groups [55]. At 874 and 727 cm^{-1} , the O–CH–CH₃, esters and/or C–C, and rocking vibrations of –CH₃ groups were noted. After one-year anaerobic degradation, no shifts or new peaks appeared in FTIR spectra of F_{PLA} . However, the intensity of all bands increased, indicating minor degradation. The increase in peak corresponding to carbonyl C=O groups is associated with the increase in the number of carboxylic end groups in the polymer chain due to hydrolytic degradation [45].

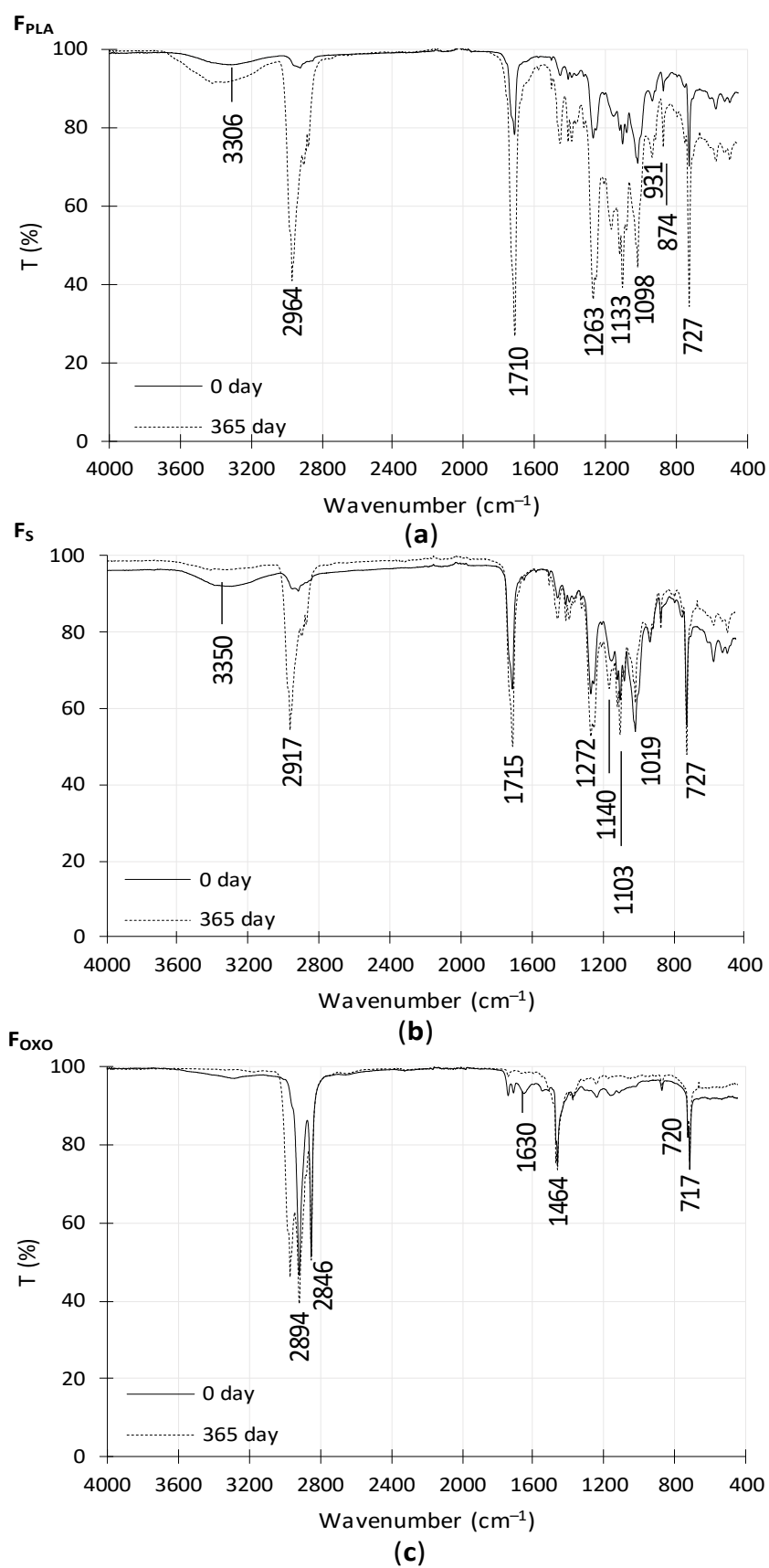


Figure 5. FTIR spectra of raw foil materials and of foil materials after a 365-day anaerobic mesophilic degradation test; (a) F_{PLA} , (b) F_S , (c) F_{Oxo} .

Infrared spectra for the raw material of F_S exhibited bands characteristic of plasticized starch. Over the one-year anaerobic degradation, no new peaks appeared in the IR spectra, and transmittance across all peaks slightly changed, indicating minor degradation. The peaks between 3600 and 3100 cm^{−1} and between 1270 and 900 cm^{−1} related to O–H stretching groups and to C–O stretching and hydrogen bonding peaks, respectively. Peaks at 1140 and 1103 cm^{−1}, indicated the C–O stretching of the C–O–H group, which is a typical starch group in hydrogen bonding. The peak at 1016 cm^{−1} corresponded to the C–O stretching of the C–O–C group of the starch glycosidic bonds [56]. The peak located at 727 cm^{−1} represented four or more adjacent methylene (–CH₂–) groups. The bands at 2917 cm^{−1} corresponded to C–H stretching in aliphatic and aromatic groups. The bands at 1715, 1272 cm^{−1}, and 1019 cm^{−1} corresponded to the carbonyl groups C=O, the C–O link, and the stretching of phenylene groups, respectively.

Regarding F_{OXO}, the FTIR spectrum was typical for polyethylene. The difference was a small band at 1630 cm^{−1} corresponding to a double bond (or aromatic rings), which was indicated probably as a result of surface antioxidant addition. This band was not noted after 365 days of anaerobic degradation, and the F_{OXO} spectrum was as for pure PE. This means that antioxidant additive was washed away or assimilated by bacteria [57]. The peaks located at 2894 and 2846 cm^{−1} belong to C–H stretching asymmetric and symmetric vibrations. The band at 1464 cm^{−1} related to CH₂ scissoring groups, whereas the bands at 720 cm^{−1} and 717 cm^{−1} indicated CH₂ rocking vibration.

In summary, due to the development of the market of bio-based products, their waste may appear in the waste management system. As was mentioned, such kind of waste can be found in different streams, i.e., mixed municipal waste and selectively collected plastic waste or biowaste. Given the priorities in the waste management hierarchy, bio-based products should be collected with biowaste and biologically treated. Thus, researchers and future studies should focus on searching for the most optimal conditions for biodegradation of bio-based products and potential microorganisms that have the capability to degrade these polymers. The knowledge about the microbiological community structure involved in the biodegradation and the pathways of biodegradation of bio-based materials during composting or anaerobic digestion would provide valuable information. For waste management and end-of-life scenarios, it is essential to provide as much information as possible to create a database on the biodegradability of commercially available bio-based materials. This information may also be useful for assessing regulations for the management of bio-based materials.

4. Conclusions

During one year under mesophilic anaerobic conditions, F_{OXO} did not degrade (no biogas was produced). Moreover, no microscopic changes were found in the foil structure. The bio-based materials (F_S and F_{PLA}) produced small amounts of biogas, 25.2 and 30.4 L/kg VS for F_{PLA} and F_S, respectively, whereas TMP indicated that even 610 and 577 L/kg VS could be obtained. The structure of bio-based foils started to show damage. However, the individual cracks and fissures were visible in the structure of F_S. This indicates that they were in the initial phase of degradation. Although the manufacturers labeled these commercially available bio-based products as biodegradable, this study found that they did not disintegrate even after 1 year of mesophilic anaerobic degradation, indicating that the foils would persist for an unknown but lengthy amount of time. Thus, providing guidelines for bio-based foil treatment remains a challenge in waste management.

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