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Research article

Organic recycling challenges of (bio)degradable packages: Degradation studies of polylactide/cork composites

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Abstract. The drastic increase in the amount of packaging waste from conventional plastics, caused by improper waste management, is a serious challenge for the planet. It is therefore worth considering how we can solve this problem. Thus, it is necessary to develop new polymeric materials that retain the functional properties of traditional plastics but are susceptible to degradation with the participation of microorganisms. The development of new eco-friendly materials requires a holistic approach in terms of their disposal. Organic recycling enables the disposal of biodegradable packaging along with food remains that are difficult to remove. The article presents a study on the degradation of biocomposites of polylactide with cork in various environments (water, buffer, and compost). The obtained results indicate a clear influence of the presence of the filler and its amount on the degradation profile of the composites. In addition, the effect of sample shrinkage was observed, especially during degradation in water, where the pH decreases during the process due to the appearance of degradation products. This effect may be important not only for the degradation profile of the packaging but also during its use. Packaging distorted due to shrinkage may be a sign of improper product storage.

Keywords: *biocomposite, cork, polylactide, hydrolysis, biodegradation, composting*

1. Introduction

The packaging made of conventional polymeric materials, characterized by high mechanical strength, transparency, easy dyeing, lightness, and relative cheapness, has fascinated material engineering since the beginning of the 20th century. But nowadays, one can observe the need for sustainable development and search for wider possibilities of introducing environment-friendly materials that have enormous potential for innovative use [1]. Technological progress and consumer expectations for environmentally friendly products result in the development of strategic actions aimed at the replacement of the petrochemical raw material sources with different ones. Biodegradable polymers produced from renewable raw materials are now an increasingly significant market among all polymers produced in the European Union. The polymer compositions, in addition to the polymer materials, also contain other additives (stabilizers, lubricants, dyes, fillers, *etc*.), which determine their processing opportunities and, thus, the properties of the final products [2]. The use of various types of fillers makes the final material a composite. A traditional polymer composite contains two or more constituent materials: a polymer matrix and a reinforcement filler in the form of fibers, particles, or flakes with significantly different physical or chemical properties that, when combined, give a material with properties different from the individual components such as lower mass, higher strength, and

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most importantly for biodegradable polymers, lower cost. The composite, as a mixture of polymers or plastics and fillers such as natural fibers, also possesses improved mechanical and/or chemical properties, which, by reducing the price of the final products, causes increasing interest in such materials [3]. Conventional polymers as a composite matrix hinder the process of natural biological degradation, which may be desirable, especially in construction materials. However, other industrial areas increasingly require more ecological products. Hence, research is being conducted on various composites called biocomposites containing natural components. In such a case, the matrix should be biodegradable polymers, and the additives should also be of natural origin [4]. The addition of natural fillers such as jute fibers, wood flour or cork can be a way to improve the eco-properties of the biocomposites obtained [2, 4]. Cork as oak bark contains approx. 45% suberin, approx. 27% lignin, approx. 12% cellulose and hemicelluloses and about 6% of waxes and tannins. Its microstructure is different from that of other lignocellulose trees. It is formed as a hexagonal, prismatic honeycomb cell-shaped structure towards the radial and rectangular direction and like a brick wall in the transverse direction. Just because of this structure, cork has a low density of 0.12–0.24 g/cm^3 because 85–90% of its volume is air. This complex and unique structure determines the excellent properties of cork and makes it interesting to use as a natural filler [5, 6]. Cork is characterized by liquid impermeability, renewability, and the possibility of incinerating with energy recovery. Moreover, cork has exceptional elasticity and high vibro-, thermo-, electro-, and acoustic insulation, low friction coefficient, flame retardancy, and chemical and biological resistance [7–9]. Adding cork as a natural filler in various ratios to the polymer matrix gives the possibility of obtaining composites with different programmed properties. Thus, cork can be an ideal "carbon neutral" material in many applications, both common use and industrial application, with advantages mainly in short-life applications [10, 11]. According to our previous work about poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P(3HB-*co*-4HB))/cork compositions, the addition of cork improved their thermal stability. Acidic substances contained in cork can act as a thermal stabilizer. The use of a thermal stabilizer can limit the negative impact of processing temperature on the damage of P(3HB-*co*-4HB) and prevent the use of processing temperatures higher than recommended. The knowledge of their properties shapes the potential use of the tested (bio)composites, and thus, it is possible to obtain new products with programmed properties. In this context, the selected filler will act as a modifier of the functional properties of obtained biocomposites [12]. Due to the growing environmental burden of waste from traditional polymer materials, it seems desirable to introduce to the market biocomposites that, after organic recycling of their waste, will integrate into the natural cycle of matter while limiting the use of fossil sources. The above requirements for a polymer matrix are met by (bio)degradable polyesters such as polyhydroxyalkanoates or polylactide (PLA) [13–15]. In order to determine the degradation profile of polymer materials in the environment, research was conducted in soil [16], water systems [17, 18], as well as compost. However, degradation studies in compost are carried out in piles under laboratory conditions [19] or in home-type composters [20], while the information on the degradation studies in the conditions of industrial composting, especially for the biocomposites with cork, is poor. Therefore, the development of advanced polymeric materials with potential degradability under industrial composting conditions can contribute to improving the environment by reducing the retention of traditional plastic waste at landfills [21–24]. It is worth paying attention to the fact that many parameters have an influence on the degradation profile of biodegradable material [25, 26].

PLA/cork composites have been developed and extensively tested by numerous scientific teams. These composites combine the biodegradability and sustainability of PLA with the unique properties of cork, resulting in materials with potential applications in various industries. The rigorous testing conducted on these composites ensures their reliability and suitability for specific purposes, promoting their adoption in the market [27–29]. However, no research has been found in the available literature on the degradation of this type of material, including the degradation in organic recycling conditions. This work presents the results of degradation studies on PLA-based composites, with 10 and 30 wt% of cork, under industrial composting conditions. In parallel, reference tests of the hydrolytic degradation process were carried out. Hydrolytic degradation studies conducted in laboratory conditions facilitate the understanding of degradation processes that occur under composting conditions.

2. Materials and methods

2.1. Materials

PLA (2002D) received from Natureworks (Minneapolis, USA), $M_n = 200\,000$ g/mol, was used as a matrix in the composites. Cork powder (production residue) provided by Corkpol (Ożarów Mazowiecki, Poland) used as a filler was the same as that used in previous studies [12], eliminating the effect of differences in the filler on the composites with various matrices.

2.2. Cork preparation

The cork received from the manufacturer required preliminary processing before mixing it with the matrix. In this case, a previously developed methodology [12] was used where a cryogenic grinder SPEX SamplePrep 6870 model (Cole-Parmer, Metuchen, USA) was applied. The obtained cork powder with an average particle size of 0.35 mm was mixed with PLA and prepared for further processing.

2.3. Compounding and processing

The composites and neat PLA samples were prepared using the micro-extruder MiniLab (Thermo-Haake, Austin, USA), followed by MiniJet (Thermo-Haake, Austin, USA), a mini injection molding machine. The raw materials before extrusion, both PLA and the cork after grinding, were dried for 4 h at 80 °C in a vacuum oven (Memmert, Büchenbach, Germany). The specimens for the degradation test were prepared according to ISO 527-2 standard [30]. The processing parameters are included in Table 1.

2.4. Degradation environments

2.4.1. Biodegradation test under industrial composting conditions

The biodegradation test utilizing the KNEER system (HORSTMANN, Wągrowiec, Poland) [12] involved incubating the samples in compost for 3 weeks at an average temperature of 63 °C in industrial conditions. Following the process, all the samples were extracted from the compost, cleaned, and analyzed [31].

2.4.2. Abiotic degradation

For the abiotic degradation tests, the samples were placed in screw-capped vials, and then 25 mL of deionized water or phosphate buffer pH = 7.4 (Sigma-Aldrich, Saint Louis, USA) was added. The temperature of the experiment was set at 70 °C (±0.5 °C) according to ISO 15814:1999 as previously used [25]. After a defined period of time, the samples were removed from the medium, cleaned, and dried under a vacuum at room temperature.

2.5. Characterization of the samples

2.5.1. Visual examination

The visual examination of the samples was determined using scanning electron microscopy (SEM). SEM micrographs were done by the Quanta 250 FEG (FEI Company, Fremont, USA) high-resolution environmental scanning electron microscope operated under pressure of 80 Pa. The samples were tested without prior preparation.

2.5.2. Thermal properties

TGA/DSC1 (Mettler-Toledo, Columbus, USA) was used to determine the thermal characteristics of the samples from room temperature to 600 °C at a heating rate of 10 °C/min in nitrogen. The differential scanning calorimetry (DSC) studies were done by means of TA DSC Q2000 apparatus (TA Instruments, New Castle, USA). The heating rate for all runs was 20 °C/min and the experiment was carried out in a nitrogen atmosphere. The analysis was done from –80 to 200 °C. The second heating run was performed after rapid cooling from the melt. The methodology used for the second run made it possible to find the glass transition temperature (T_g).

2.5.3. Gel permeation chromatography (GPC) analysis

The samples were analyzed using the GPC method to determine their molar mass and molar mass

Table 1. Processing parameters for sample preparation.

PLA/cork (mass ratio)	Temperature of plasticizing zone [°C]	Injection temperature [°C]	Injection pressure [bar]	Mold temperature [°C]
100/0	195	195	800	70
90/10	195	195	800	70
70/30	205	210	950	70

dispersity. This was done by dissolving the samples in chloroform (10 µL, 0.3% w/v) and running them through the VISCOTEK VE 1122 solvent delivery system (Malvern Panalytical Ltd, Malvern, UK) at 35 °C and a flow rate of 1 mL/min by the two Mixed C Styragel columns (Agilent, Santa Clara, USA) with a mixed bed, a linear range of M_w = 200–2 00 000. The results help to characterize the size and distribution of the molecules in the sample, which can be important for understanding their properties and potential applications. To generate the calibration curve, narrow molar-mass dispersity polystyrene standards were used, specifically the EasiCal® Pre-prepared Calibration Kits from Polymer Laboratories (Agilent, Santa Clara, USA). These kits serve as a reliable calibration tool for determining the molar mass distribution of polymers.

3. Results and discussion

The changes in the thermal stability of the P(3HB-*co*-4HB) composites with natural fillers, observed with the increase of the filler content and during degradation, create an interesting investigation path [2, 12]. In addition to the observed changes in the thermal properties, cork also has many advantages, making it a quaint filling material [32, 33]. The main aim of the current research was to use PLA as a matrix and to evaluate the influence of the cork presence on thermal stability and the degradation rate of the obtained materials. PLA/cork composites were subjected to hydrolytic degradation in water and in a buffer. During these examinations, the unforeseen shrinkage effect was found in both degradation media. This phenomenon was more visible after degradation in water (Figure 1).

The neat PLA samples after incubation in both media are more disintegrated than the PLA/cork composite samples especially with 30 wt%. It is like in the previous works [34, 35], where the disintegration of the PLA-based material at the early stage of incubation in water at 70 °C was observed. Small fragments of the neat PLA samples after degradation made it challenging to observe changes in the sample size. The presence of cork in composites reduced the sample disintegration, which made it possible to observe the shrinkage effect.

An effect similar to the injection molded PLA and PLA/cork samples was observed for the 3D printed PLA specimens, and it was explained by the changes in the contraction rate caused by processing, the PLA volume changes during crystallization, and the influence of some external factors, as well [36]. The shrinkage effect progressed gradually throughout degradation. Figure 2 shows the changes in the sample size for the PLA/cork (70/30) composite after a specified time (days) of incubation in water at 70 °C. In the case of degradation in compost, no shrinkage effect was observed.

The mass loss of all the samples after 84 days of incubation in water at 70 °C was above 50% (67, 72, and 56% for 100/0, 90/10, and 70/30, respectively). PLA, during degradation above T_g, undergoes the process of bulk erosion with nonlinear mass loss over time [37, 38]. On the other hand, surface erosion

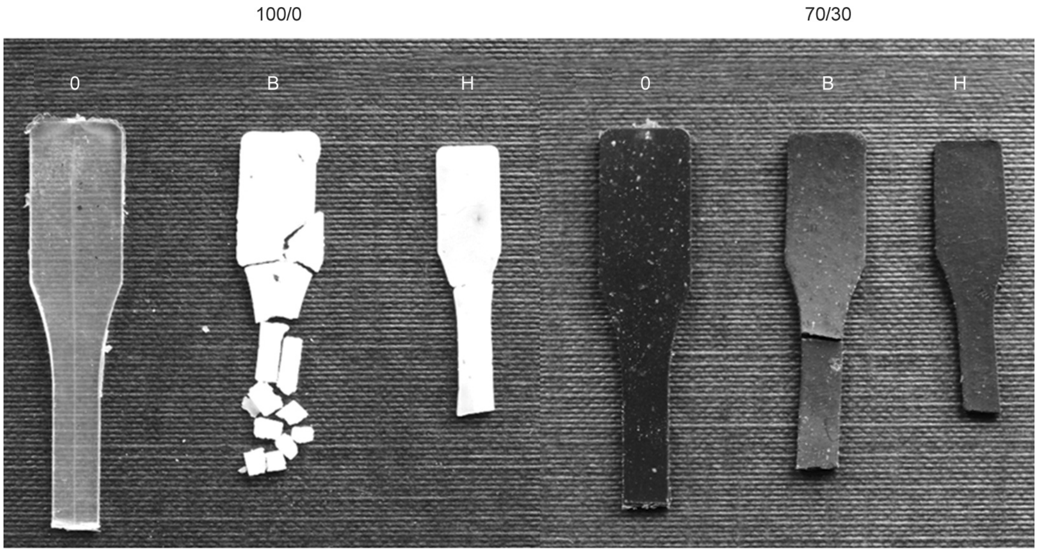

Figure 1. Macroscopic images of the neat PLA and PLA/cork composites with the mass ratio of 70/30 before (0) and after 84 days of incubation in buffer (B) and in water (H) at 70 °C.

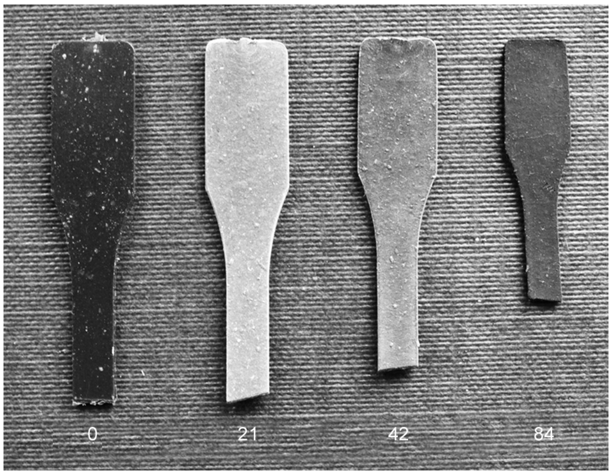

Figure 2. Macroscopic images of the PLA/cork (70/30) sample after incubation in water at 70 °C.

causes the volume to decrease, but the shape of the sample remains the same with time [39]. T_g of PLA in investigated samples is around 63 °C, so the degradation experiments were conducted above T_g of PLA. However, the shrinkage of the samples, which starts after 21 days of incubation, can also suggest the presence of a surface erosion mechanism.

The surface changes of the PLA and PLA/cork films were examined by means of SEM (Figure 3).

For the 70/30 sample, whose disintegration was less visible (see Figure 1), SEM analysis (Figure 3) also shows the smallest cracks in comparison to the neat PLA and 90/10 sample. Only after 84 days of incubation in the buffer a significant amount of small pinholes were observed. The difference in the erosion process of the samples follows from the variance in the pH of the degradation media. The PLA hydrolysis is an autocatalyzed process because the breakage of ester linkages of the PLA main chain can be catalyzed by the carboxylic acid end groups of PLA oligomers. The acid remaining inside the sample or released to the medium causes the acceleration of the hydrolysis rate [40]. Thus the creation of acid products during hydrolysis leads to pH reduction [41]. After 14 days of incubation of all samples in water, the pH of the medium drops from 6.3 to below 3.0. The relatively quick release of the acid degradation products into the water during the experiment could cause the erosion mechanism to be more of a surface process. During the degradation of PLA in water, various phenomena may occur like diffusion of water into the polymer matrix, the release of PLA degradation products and ions into the environment, or their remaining in the polymer matrix, which can cause deviations from the degradation reaction mechanisms [39]. In the buffer experiment, the mass loss is below 50% for all the samples after 84 days, and shrinkage is not so visible.

The melt processing conditions during the sample formation have an influence on the molar mass decrease and crystallization of PLA. The amount of the molar mass reduction depends on the temperature during the processing and mixing time [42]. Also, the addition of the filler can cause the molar mass to decrease (Table 2). The molar mass decreased with the increase of the cork content by 8 and 20% for

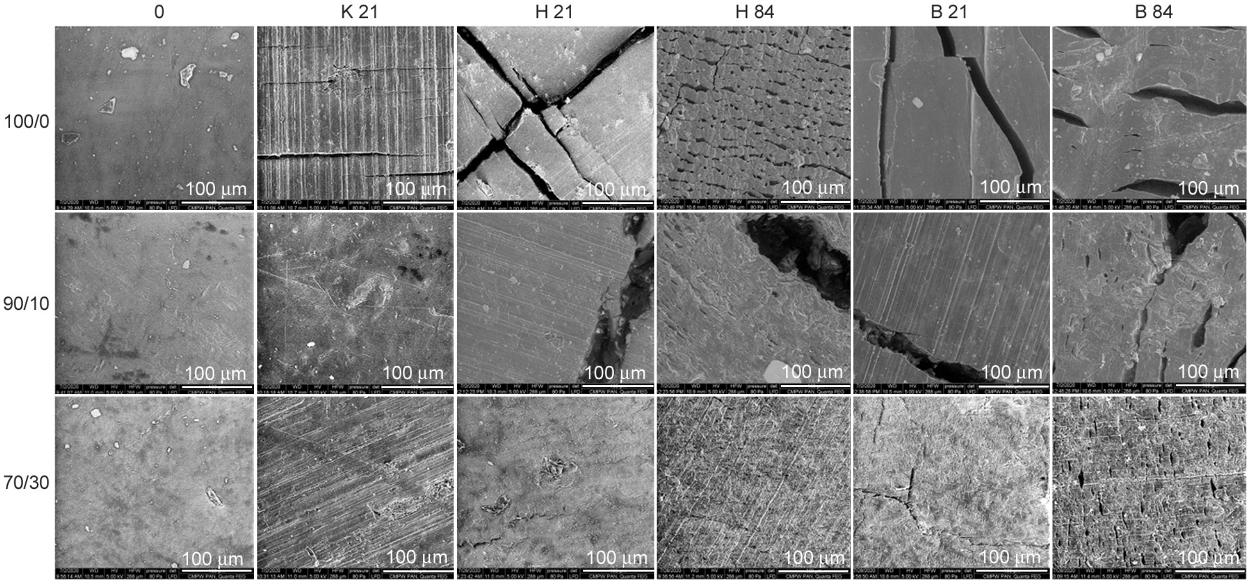

Figure 3. SEM micrographs of the neat PLA (100/0) and the PLA/cork composite samples with the mass ratio of 90/10 and 70/30 before (0), after 21 days of degradation in KNEER system (K 21) as well as after 21 (H 21) and 84 (H 84) days of degradation in water and buffer respectively (B 21 and B 84).

90/10 and 70/30, respectively, in relation to the neat matrix. This phenomenon was observed in earlier studies for different fillers. Even a small amount of moisture in the fibers accelerates the degradation of PLA. Drying the fibers before blending reduces this effect [43, 44]. Figure 4 and Table 2 present the molar mass (M_w) and dispersity (M_w/M_n) of the investigated samples before and after incubation in different environments.

During degradation in the composting conditions where the humidity level is 50%, a higher amount of hydrophobic cork in the composite caused the lower molar mass reduction, by 19, 39 and 69% for 70/30, 90/10, and 100/0, respectively, in relation to the output samples of respective composite (70/30 and 90/10) and neat matrix (100/0) (Figure 4). This tendency is similar after 7 days of degradation in water (55, 65 and 87% molar mass reduction for the composite (70/30 and 90/10) and neat matrix (100/0)), respectively but after 14 days the mass reduction for 90/10 is lower than for 70/30 (80 and 89% respectively) (Table 2). This phenomenon can be caused by easier penetration of water inside the samples facilitated by the presence of the filler, since after degradation of the outer layer of the sample cork, a hydrophobic filler [12] repels water, increasing its availability for PLA. After this time period, the value of dispersity (M_w/M_n) for 90/10 and 70/30 equals 3.8 and 2.5, respectively, which also confirms the faster elution of degradation products from the 70/30 sample. Lack of the shrinkage effect until 14 days of incubation indicates the bulk erosion mechanism. In the buffer at the initial stage of degradation (up to day 7), for the 100/0 sample, a reduction in the rate of degradation is observed. Hydrolytic degradation of PLA strongly depends on the pH of the medium. The rate of this process increases at a very low and very high pH, which follows the mechanisms for the acid- and base-catalyzed PLA hydrolyses [45, 46]. However, the faster disintegration of the samples increases the surface area available for the degradation

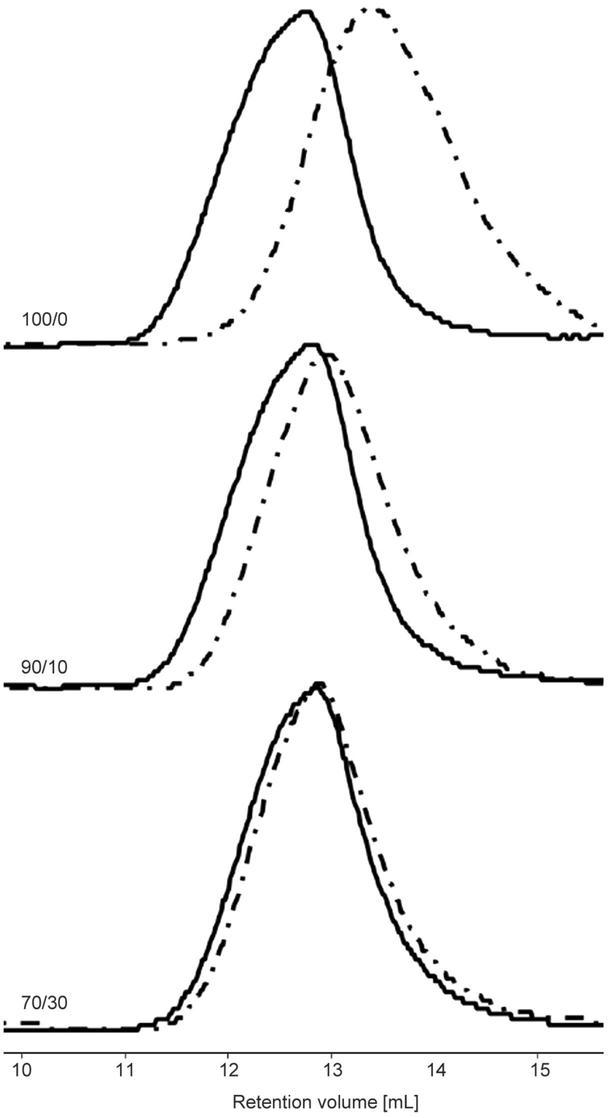

Figure 4. Overlay of selected GPC elugrams of the neat PLA (100/0) and PLA/cork composite samples with the mass ratio of 90/10 and 70/30 before (solid line) and after 21 days of incubation in compost (dotted line).

Table 2. Molar mass (M_w) and dispersity (M_w/M_n) before and after degradation in different environments of neat PLA and PLA/cork composites.

PLA/cork (mass ratio)	**Time [days]**	**M_w [g/mol]**	**M_w/M_n**
Water/buffer			
100/0	0	138 000	1.6
	7	18 000/23 000	1.8/1.8
	14	6 000/6 000	1.4/1.6
	21	6 000/6 000	1.4/1.4
	42	4 000/4 000	1.4/1.3
	84	2 000/4 000	1.4/1.3
90/10	0	127 000	1.7
	7	45 000/24 000	2.0/1.8
	14	25 000/8 000	3.8/1.6
	21	5 000/6 000	1.3/1.4
	42	4 000/4 000	1.2/1.3
	84	2 000/3 000	1.5/1.3
70/30	0	112 000	1.9
	7	51 000/46 000	1.9/2.0
	14	13 000/12 000	2.5/1.8
	21	8 000/7 000	1.7/1.4
	42	4 000/4 000	1.4/1.4
	84	2 000/3 000	1.4/1.3

medium and thus causes the increase of PLA molar mass reduction during the experiment.

The 90/10 composite shows a similar degradation rate in the buffer to the neat PLA. The increase in the filler content has an influence on the migration of the buffer into the sample, and its greater amount (70/30) slows down the degradation in the initial stage, which is because PLA shows very slow degradation in neutral conditions [45].

Thermogravimetric analysis of the samples during incubation in water shows slight changes in thermal stability associated with the gradual formation and elution of the degradation products. After 84 days of incubation, the temperature of the maximum rate of mass loss (T_{max}) of all samples reaches a value visibly lower than before the degradation (Table 3). For the 100/0 and 90/10 samples, there is a slow, gradual decrease in T_{max} with some non-significant fluctuations until the 42nd day of incubation. In the case of the 70/30 sample, an increase in thermal stability is observed until day 14, and then it decreases. Variations in thermal stability observed during degradation in water may result from different rates of formation of degradation products and their leaching from the matrix. The increased amount of cork makes this effect more pronounced, which may be influenced by the greater stability of the filler in relation to the matrix. This can be caused by the impediment of volatile decomposition products diffusion from the materials, like in the case of the presence of dispersed silicate layers, which leads to the slowed-down release of degradation products during thermal decomposition [47]. The presence of various organic compounds in cork can additionally crosslink PLA, which also increases thermal stability [48]. Not without significance is the shrinking effect, which may also hinder the release of thermal degradation products.

In the case of degradation in the buffer, a more pronounced decrease in T_{max} is observed for all the samples (Table 4). Also, there is no increase in thermal stability during degradation in the initial stage for the samples, especially with the highest filler content, unlike degradation in water. Only after 84 days of incubation an increase in thermal stability is observed for all samples due to the changes probably caused by the presence of the salts from the buffer.

In the case of residual mass at 600 °C for the composites, an initial decrease followed by an increase

Table 3. Calorimetric parameters of PLA and PLA/cork composites before and after degradation in water at 70 °C.

PLA/cork (mass ratio)	Time [days]	T_{max} [°C]	R_{d600} [%]	T_{cc} [°C]	ΔH_{cc} [J/g]	T_g [°C]	T_m [°C]	ΔH_m [J/g]
100/0	0	366.7	1.2	123.4	33.4	62.9	171.8	33.1
	7	363.4	0.6	–	–	56.9	165.6/170.7	52.1
	14	364.1	0.5	–	–	48.8	156.4	64.1
	21	363.4	0.5	–	–	48.6	155.2	64.3
	42	363.8	0.6	–	–	43.5	145.9	57.9
	84	359.9	0.6	–	–	30.5	121.3	37.3
90/10	0	362.8	3.3	120.8	23.2	63.4	174.3	34.2
	7	363.6	3.0	–	–	58.3	170.3	46.5
	14	363.6	2.5	–	–	50.1	160.0	59.1
	21	361.5	2.5	–	–	49.1	156.5	60.4
	42	361.3	2.9	–	–	44.3	148.3	55.9
	84	349.6	8.2	–	–	28.5	115.5	26.0
70/30	0	353.9/413.9	8.3	110.1	10.9	64.4	171.1/176.2	26.1
	7	360.9/414.9	6.2	–	–	60.3	169.5	45.4
	14	364.1/419.5	6.0	–	–	51.4	161.7	53.6
	21	363.7/422.4	6.9	–	–	53.7	162.7	46.3
	42	358.7/421.6	7.3	–	–	48.4	147.9	47.6
	84	349.2/423.1	11.1	–	–	39.4	130.0	39.3

T_{max}: maximum decomposition temperature,
R_{d600}: residual mass at 600 °C,
T_{cc}: the maximum of the exothermic peak of the cold crystallization temperature,
ΔH_{cc}: cold crystallization enthalpy,
T_m: melting temperature,
ΔH_m: melting enthalpy (first heating scan, 20 °C/min),
T_g: glass transition temperature (second heating scan after rapid cooling, 20 °C/min).

Table 4. Calorimetric parameters of PLA and PLA/cork composites before and after degradation in buffer at 70 °C.

PLA/cork (mass ratio)	Time [days]	T_{max} [°C]	R_{d600} [%]	T_{cc} [°C]	ΔH_{cc} [J/g]	T_g [°C]	T_m [°C]	ΔH_m [J/g]
100/0	0	366.7	1.2	123.4	33.4	62.9	171.8	33.1
	7	362.5	0.3	–	–	50.0	161.8	56.3
	14	339.1	0.9	–	–	47.9	156.9	66.6
	21	332.2	1.2	–	–	50.4	156.9	64.7
	42	299.7	4.2	–	–	52.8	156.0	66.3
	84	308.1/320.1	2.5	–	–	45.0	145.3	58.0
90/10	0	362.8	3.3	120.8	23.2	63.4	174.3	34.2
	7	357.8	2.5	–	–	58.7	168.0/172.5	50.1
	14	336.7	2.5	–	–	50.5	158.6/161.1	63.1
	21	319.3	3.8	–	–	50.8	163.6	55.4
	42	302.2	7.5	–	–	51.3	158.6	59.0
	84	309.8	5.0	–	–	45.5	148.2	54.9
70/30	0	353.9/413.9	8.3	110.1	10.9	64.4	171.1/176.2	26.1
	7	348.5/412.0	6.4	–	–	62.3	174.8	38.5
	14	338.8/411.3	6.2	–	–	52.7	160.9	53.7
	21	333.4/413.3	7.9	–	–	52.6	160.2	50.4
	42	293.5/393.6/441.8	11.1	–	–	53.3	150.8/157.6	47.3
	84	304.2/411.8	9.3	–	–	46.2	132.5/139.6/141.6/146.3	57.8

T_{max}: maximum decomposition temperature,
R_{d600}: residual mass at 600 °C,
T_{cc}: the maximum of the exothermic peak of the cold crystallization temperature,
ΔH_{cc}: cold crystallization enthalpy,
T_m: melting temperature,
ΔH_m: melting enthalpy (first heating scan, 20 °C/min),
T_g: glass transition temperature (second heating scan after rapid cooling, 20 °C/min).

was observed, both in water and in the buffer. This effect was also seen for the 100/0 sample during degradation in the buffer, which may indicate the entry of the buffer components into the sample or that some degradation products insoluble in the buffer environment remain in the polymer matrix. For all samples degraded in this environment, a decrease in the residue after 84 days of incubation was observed, which resulted from the disintegration of the material (see Figure 1) and the release of some components into the solution.

The presence of cork in the material resulted in a higher glass transition temperature, which suggests the occurrence of physical entanglement [2, 12, 49, 50].

The presence of buffer residues inside the samples also affected the T_g value; it increased where a clear increase of residual mass at 600 °C was observed. A similar effect was observed for the PLA/PCL blend to which hydroxyapatite was added; the T_g value corresponding to PLA increased with the addition of the additive [51].

The presence of cork affects the T_g of the tested materials; not only a higher value of this parameter is observed after adding the filler T_g is 62.9, 63.4, and 64.4 °C for initial 100/0, 90/10, and 70/30 samples, respectively), but also a sample with its 30% content shows a slowdown in its reduction and even a slight increase during degradation in water (see Table 3).

The observed cold crystallization peak (T_{cc}) for the initial samples before incubation could be ascribed to the crystallization from the nuclei formed during cooling [52]. For initial 100/0, 90/10, and 70/30, the T_{cc} equals 123.4, 120.8, and 110.1 °C respectively. The addition of cork caused not only a decrease of T_{cc} but also cold crystallization enthalpy (ΔH_{cc}) from 33.4 for 100/0 to 23.2 and 10.9 J/g for 90/10 and 70/30, respectively. After degradation of the samples in water and buffer, T_{cc} was not presented.

Changes in the melting temperature (T_m) value have the same downward trend for all the materials in both environments; however, for degradation in the buffer, this decrease is slower. During the degradation, additional values of the T_m appear, indicating the creation of different populations of crystals caused by the presence of oligomers of different masses [53–55]. A clear increase in the melting enthalpy in the initial stage of degradation indicates an increase in the mobility of PLA chains resulting from a significant decrease in the molar mass (Table 2). Shorter chains are easier to reorganize themselves, which increases the degree of crystallinity of the samples [56, 57]. After some time, the melting enthalpy (ΔH_m) begins to decrease or fluctuate, which may be due to the increasingly difficult movement of the chains and the gradual disintegration of the samples.

The observed disappearance of T_{cc} for all of the samples after incubation in compost (Figure 5) could be ascribed to the hydrolysis of PLA and, hence, the increase in ordering of the polymer matrix. The incubation process environment and degradation products induce crystallization of the polymer matrix during incubation. The same effect is visible even after 7 days of incubation in both water and buffer [58, 59].

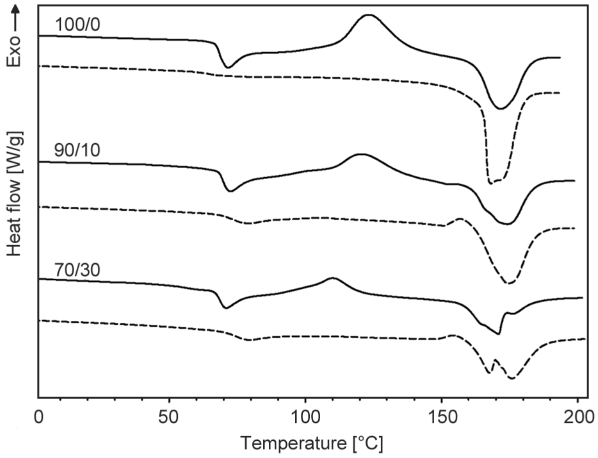

Figure 5. The first DSC heating trace for neat PLA (100/0) and PLA/cork composite samples with a mass ratio of 90/10 and 70/30 before (solid line) and after 21 days of incubation in compost (dotted line).

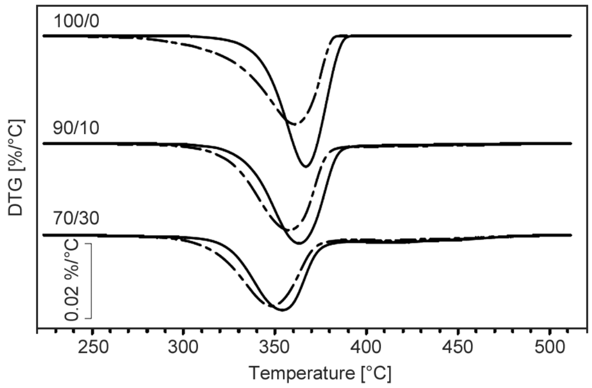

Figure 6. First-order derivative (DTG) of thermal decomposition (TGA) curves of the neat PLA (100/0) and PLA/cork composite samples with the mass ratio of 90/10 and 70/30 before (solid line) and after 21 days of incubation in compost (dotted line).

However, during degradation under industrial composting conditions, the thermal properties of the samples did not change significantly (Figure 5 and Figure 6); they correlate with the decrease in the molar mass by 69, 39 and 19%, which was observed for the 100/0, 90/10 and 70/30 samples, respectively (see Table 2). The first stage of PLA (bio)degradation is abiotic hydrolysis of ester bonds, initiated by water absorption [60]. As a hydrophobic material, cork makes it more difficult for water to get inside the composite and penetrate the polymer matrix, especially when there is less water in the degradation environment, so slower degradation is observed for the composites.

4. Conclusions

In this work, the degradation study of PLA/cork composites in different environments was conducted. During degradation in abiotic laboratory conditions, the shrinkage effect was observed. This phenomenon was more visible after incubation in water than in buffer, which suggests that an acidic environment caused by the release of degradation products enhances this effect. Inserting cork into the PLA matrix did not increase its thermal stability as in the case of the P(3HB-*co*-4HB) matrix [12]. However, during degradation in water, fluctuations in the value of this parameter were observed. This indicates the influence of the formation of degradation products on the properties of the materials, which is enhanced by the presence of the filler. In addition, the shrinkage effect more clearly visible for samples degraded in water may contribute to this phenomenon. Shrinkage of packaging can affect not only its degradation profile but also indicate improper product storage. Therefore, it is necessary to be mindful of storage conditions to maintain the integrity of packaging and ensure its optimal performance. Understanding the impact of the presence of a filler on the degradation profile of the composite matrix is of great importance during processing, use, and disposal. The presence of cork causes differences in degradation in different environments depending on its amount. However, the richness of organic compounds present in cork requires further research on new materials in which single compounds will be introduced into the PLA matrix, enabling precise determination of specific relationships.

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