

Article

An FTIR and EA-IRMS Application to the Degradation Study of Compostable Plastic Bags in the Natural Marine Environment

Federico Rampazzo ¹, Nicoletta Calace ², Malgorzata Formalewicz ¹, Seta Noventa ¹, Claudia Gion ¹, Lucia Bongiorno ³ , Amelia De Lazzari ³, Valerio Causin ⁴ and Daniela Berto ^{1,*}

¹ Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA), Brondolo 5, 30015 Chioggia, Italy; federico.rampazzo@isprambiente.it (F.R.); malgorzata.formalewicz@isprambiente.it (M.F.); seta.noventa@isprambiente.it (S.N.); claudia.gion@isprambiente.it (C.G.)

² Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA), Via Vitaliano Brancati 48, 00144 Rome, Italy; nicolella.calace@isprambiente.it

³ Consiglio Nazionale delle Ricerche, Istituto di Scienze Marine, Tesa 104–Arsenale, Castello 2737/F, 30122 Venezia, Italy; lucia.bongiorno@ve.ismar.cnr.it (L.B.); amelia.delazzari@ve.ismar.cnr.it (A.D.L.)

⁴ Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italy; valerio.causin@unipd.it

* Correspondence: daniela.berto@isprambiente.it

Abstract: The present study aims to explore the degradation process of compostable, starch-based (i.e., Mater-Bi®) shopping bags in the marine environment using isotope ratio mass spectrometry and Fourier-transform infrared spectroscopy (FTIR). The mixing model applied to the isotopic data suggested that the compostable shopping bags had a mixed composition with a higher percentage of polyesters (61% to 72%). Changes in the isotopic composition over a 73-day period of marine water immersion showed a decrease in the corn starch constituent (of 14% to 13%), with a similar rate in both types of bags in accordance with the evidence derived from the infrared spectra. The time required for complete degradation of the starch fraction was estimated by an isotopic approach from 124 to 180 days, following zero-order kinetics. The coupled application of these two analytical methodologies promises to (i) show complementary evidence regarding the time-course degradability of different polymers via FTIR changes, and (ii) infer potential degradation mechanisms via carbon isotope analyzes. We encourage the use of this information to support advancements in the development of more sustainable-by-design plastic materials.

Keywords: biopolymers; shopping bags; carbon isotopes; IRMS; FTIR; biodegradation



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1. Introduction

Plastics have gained great importance in modern society due to their durability, versatility, lightness, ease of processing and low production costs as well as a broad range of polymer- and formulation-specific properties such as water repellency, resistance to corrosion and electrical, mechanical, acoustic and thermal insulation ([1] and authors therein). However, some of these properties become disadvantageous when plastic products become waste. According to Plastics Europe (2022) [2], global plastics production reached 390.7 million tonnes in 2021 (57.2 million tonnes in Europe). A considerable fraction of plastic waste ends up in various environmental compartments due to littering or mismanagement. The marine environment is considered the final sink for most of the waste dispersed on land. Since 2010, between 4.8 and 12.7 million tonnes of plastics produced by 192 coastal countries (93% of global population) have been discarded in the ocean [3]. Once there, plastics accumulate and can even remain for centuries, depending on the specific plastic's properties and composition as well as the environmental conditions [4], which negatively impacts marine ecosystems, biodiversity and, potentially, human health. According to the DeFishGear Project's report [5], which investigated the different types of

waste present in the Adriatic and Ionian Seas, plastic bags (26.5%) were the most abundant floating wastes.

Many worldwide efforts have been put into place to regulate the growing plastic pollution crisis. In Europe, the 2018 European Strategy for Plastics in a Circular Economy [6] has provided a roadmap for tackling plastic pollution and leading the transition toward a sustainable and circular economy for plastic polymers. In this strategy, as in other international initiatives, the design, production and use of polymeric materials that ensure the performance of classic plastic types while having more degradation properties, is proposed as part of a potential solution to plastic pollution [7]. At present, different types of plastic materials are on the market whose degradation properties are based on different processes, primarily microbial-, oxidative-, hydro- and photodegradation ([8] and authors cited therein). Biodegradable and compostable plastics consumption was estimated at 335,000 tonnes in 2017, an amount that is expected to grow thanks to the commitment of national and international policies for a transition towards a circular, bio-economy [9,10].

Compostable plastics, which are generally marketed through certification or labeling (e.g., TÜV Austria, OK compost), are largely used in several commercial sectors, primarily in foodware, dishes, cutlery and bags. The spectrum of polymers includes aliphatic polyesters and copolyesters such as polylactic acid (PLA), polyhydroxyalkanoates (PHAs), polybutylene succinate adipate (PBSA), polycaprolactone (PCL), polyglycolic acid (PGA), aliphatic-aromatic polyesters such as polybutylene adipate terephthalate (PBAT) and carbohydrates (e.g., cellulose, cellulose acetate, starch and starch blends). As for almost all plastics compositions, these materials can be generated from fossil carbon sources (*compostable petroleum-based plastics*) or biological resources (*compostable bio-based plastics*). The origin of carbon does not influence the compostability of the material which, conversely, depends on the chemical structure of the polymers and, possibly, on the presence of specific additives (e.g., pro-oxidant additives [9,11]).

At present, there are several commercial *bio-based* plastics on the market that are certified as compostable in industrial facilities (e.g., PLA, PHAs, some of the starch blends, cellulose-based plastics and lignin-based polymer composites) [10]. Despite posing some risks, the use of compostable *bio-based* plastics in different sectors is strongly encouraged due to their potential for a double win, both in terms of sustainable end-of-life and a shift to renewable carbon feedstock and low greenhouse gas emissions [6]. However, items made of compostable *bio-based* plastics are often accidentally or intentionally found dispersed in terrestrial and aquatic environments as a result of improper disposal due to the widespread false belief that compostable plastics are completely degradable under environmental (uncontrolled) conditions.

While many manufacturers claim the degradability of *bio-based* materials under marine conditions based on the available degradation standard methods (e.g., ASTM D6691-17, ASTM D7081-05; “OK biodegradation MARINE” label based on the criteria of ASTM D7081), the scientific community is concerned that these approaches are not effectively assessing biodegradation under realistic scenarios, as they do not account for the heterogeneous and variable properties of marine environments potentially impacting degradation processes [9,12,13].

In this paper, we aim to explore the degradation process of compostable starch-based (i.e., *bio-based*) plastic shopping bags in the marine environment by using Fourier-transform infrared spectroscopy (FTIR) and isotope ratio mass spectrometry (IRMS). The methods commonly used for assessing degradability for certification purposes rely on measurements of carbon to CO₂ conversion (or to CH₄ under anaerobic conditions), biological demand for oxygen and secondary parameters (e.g., the evolution of weight loss, the decrease of molecular weight and the deterioration of mechanical properties) under different degradation environments (e.g., industrial compost, home compost, soil, sea, water and aerobic/anaerobic conditions) [9].

FTIR is an established methodology used to identify the polymeric composition of plastic material. The obtained infrared spectrum allows for the determination of the

chemical structure of the mixture focusing on the observation of specific functional groups. IRMS has only recently begun to be explored for applications in plastics research and nowadays is an established methodology used to identify the polymeric composition of plastic materials [1]. It measures the relative abundances of stable isotopes, which depend on natural isotopic fractionation (the partitioning of the heavier and lighter isotopes due to different biotic and abiotic processes). The approach used in this study provides an easy and time/cost-saving technique that does not require laborious preparative steps and thus is more easily applicable in routine laboratory activities (compared to other techniques like GC-MS and LC-MS). The coupled application of these two analytical methodologies is intended to gain complementary evidence regarding: (i) the time-course degradability of different polymers usually present in the blend (i.e., starch and polyester) by measuring changes in the FTIR spectral signatures, and (ii) potential degradation mechanisms by analyzing changes in carbon isotopes rates (i.e., ^{13}C vs. ^{12}C , via IRMS). To our knowledge, there is no literature addressing the biodegradability of plastic polymers in marine environments when a coupling of these two analytical methods is used. The outputs of this study will contribute to a better understanding of degradation processes and the end-of-life of compostable (and, more generally, degradable) plastics in marine environments and thus support advancements in the development of more sustainable-by-design plastic materials.

2. Materials and Methods

2.1. Samples

In this study, two types of shopping bags were compared in terms of degradation processes: ultra-lightweight bags with a wall thickness below 15 microns (ULB) and lightweight bags (LSB) produced in compliance with the EN 13432 standard method with a wall thickness below 50 microns, both licensed by Mater-Bi[®] (Novamont, Novara, Italy). Shopping bags made of polyethylene (PE) were used as control samples. The analyzed bags were collected from large-scale retail distribution supermarkets in Italy.

2.2. Shopping Bags Degradation Experiment

Shopping bags were exposed to in situ marine conditions by placing them at a 1 m depth in the tourist marina of Chioggia (Venice, Italy) (45.223186 N, 12.281897 E), in order to simulate a dispersed bag floating in the water column. The experiment was carried out in the summer from 21 June to 1 September 2019 for a total of 73 days of exposure. Average physicochemical water conditions of the period were: temperature 26.8 ± 1.1 °C; salinity: 33.71 ± 1.03 PSU; pH: 8.17 ± 0.05 ; oxygen: 5.54 ± 0.67 mg/l (data available from the Hydrobiological Station of Chioggia, University of Padua (45.22340 N, 12.28434 E; <https://chioggia.biologia.unipd.it/banche-dati/parametri-laguna/parametri-2019/>, accessed on 30 September 2019). The bags were fixed on the surface of polyethylene supports previously filled with seawater in order to regulate their buoyancy, and the supports were immersed in the water column along ropes tied to the piers of the marina. Six samplings were carried out at regular intervals (T1: 4 July 2019; T2: 16 July 2019; T3: 31 July 2019; T4: 8 August 2019; T5: 21 August 2019; T6: 1 September 2019) during the exposure period of about two months. During each sampling, fragments of the different bags were collected, fouling organisms were gently removed by hand and samples were rinsed with deionized water. Samples were successively dried at room temperature and then subjected to isotopic (IRMS) and spectroscopic (FTIR) analyzes.

2.3. EA-IRMS

Isotopic analysis was performed by Delta V Advantage, an isotope ratio mass spectrometer, coupled with Flash 2000, an elemental analyzer (both Thermo Fisher Scientific, Bremen, Germany), operating in dynamic flash combustion mode.

Small pieces (<4 mm largest dimension) were cut from each sample and introduced into tin capsules. Capsules were gently crimped closed and introduced into the combustion reactor by means of MAS 200 R autosampler (Thermo Fisher Scientific, Bremen, Germany),

and the reaction was supported by an oxygen pulse of 3 s. The furnace temperature was 900 °C. A helium flow of 100 mL/min carried the gases formed during combustion through the chromium oxide catalyst, the reduced copper and the silver cobaltous-cobaltic oxide layer. After water removal on a magnesium perchlorate trap, gases reached the GC separation column through the ConFlo IV interface and then were subjected to the isotopic composition determination on IRMS. The isotopic composition was equal to the ratio between the abundance of the heavy isotopic form compared to the light one ($^{13}\text{C}/^{12}\text{C}$) and was expressed as a deviation in parts per thousand (‰), from an internationally identified standard benchmark material (Vienna Pee Dee Belemnite—VPDB). Carbon isotopic ratios were expressed according to the Equation (1):

$$\delta^{13}\text{C} (\text{‰}) = [(^{13}\text{C}/^{12}\text{C}_{\text{sample}})/(^{13}\text{C}/^{12}\text{C}_{\text{VPDB}}) - 1] \times 1000 \quad (1)$$

where $^{13}\text{C}/^{12}\text{C}$ is the ratio between abundances of the masses of the heavy isotope and of the light one, $^{13}\text{C}/^{12}\text{C}_{\text{sample}}$ is the ratio measured in the sample and $^{13}\text{C}/^{12}\text{C}_{\text{VPDB}}$ is the ratio measured for the international standard. A positive value of $\delta^{13}\text{C}$ showed that the heavy isotope had been enriched in the sample compared to the standard, while a negative value showed that, in the sample, the heavy isotope had been depleted.

This number was then multiplied by 1000 so that $\delta^{13}\text{C}$ was expressed in units of parts per thousand (‰).

Reference materials sucrose IAEA CH6 ($-10.449 \pm 0.033\text{‰}$, International Atomic Energy Agency, IAEA, Vienna, Austria), caffeine IAEA-600 ($-27.771 \pm 0.043\text{‰}$, International Atomic Energy Agency, IAEA, Vienna, Austria) oxalic acid ($-14.48 \pm 0.21\text{‰}$, International Atomic Energy Agency, IAEA, Vienna, Austria) and L-glutamic acid ($-26.389 \pm 0.042\text{‰}$, National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA) were used to calibrate the instrument.

The $\delta^{13}\text{C}$ values for the standards were linearly plotted against their expected values (certified) with a regression coefficient (R^2) ranging from 0.95 to 0.99 in order to ensure the complete combustion of the samples. The linear regression curve was then applied to correct the $\delta^{13}\text{C}$ results for the samples [14].

The measurement trueness was evaluated through the analysis of certified material CH7 polyethylene IAEA ($-32.04 \pm 0.04\text{‰}$, International Atomic Energy Agency, IAEA, Vienna, Austria). The analytical precision of carbon isotope measurements, calculated as the mean of standard deviations (see Table 1) was 0.2‰.

2.4. FTIR

IR absorption spectra were acquired on a Nexus FTIR spectrometer (Thermo Nicolet, Madison, WI, USA) in attenuated total reflection (ATR) mode with an ATR ITX accessory (Thermo Nicolet, Madison, WI, USA) equipped with a diamond ATR crystal. A MIR Global source was used and the detector was of the DTGS type. The spectral region spanned from 4000 to 650 cm^{-1} , with a resolution of 4 cm^{-1} . In the acquisition of the IR spectrum of each sample, 128 scans were collected. Nicolet Omnic software (version 7.2) was used for the treatment of spectra. No ATR correction was applied to IR data.

Integration of the peaks was performed displaying the spectra in the absorption scale. The same integration limits were chosen for all the samples. These limits were chosen to encompass about 95% of the total area, excluding the band edges [17,18].

In order to quantify and interpret the chemical modifications which generated the spectral evolution, three areas in the infrared spectra were selected: the region from 3100 to 3600 cm^{-1} related to the hydroxyl groups, the interval 1690–1810 cm^{-1} due to the carbonyl group in carboxylic acids and esters and, finally, the range between 1020 and 1070 cm^{-1} where the absorptions were due to C-O-C bonds from alcohols and esters [19,20]. In order to normalize and obtain data independent of the sample size, the integrated intensities listed above were divided by the area of the peak at 730 cm^{-1} , which was assigned to the backbone of the polyester chains (C-H and C=O out of plane bending). The functional

groups were quantified by calculating the ratio between the area of the peak of the relevant functional group and the area of the reference peak at 730 cm^{-1} . Therefore, the hydroxyl group index was obtained by the ratio between the absorptions around 3300 cm^{-1} and 730 cm^{-1} and the carbonyl group index by the ratio of the peaks at about 1711 cm^{-1} and 730 cm^{-1} [21].

Table 1. $\delta^{13}\text{C}$ values for matrices analyzed: mean, standard deviation (SD) and number of replicates (n); * certified value $-32.151 \pm 0.050\text{‰}$; ** only range reported.

Sample Type	Mean $\delta^{13}\text{C}$ (‰)	SD (‰)	n	Reference
Shopping bags				
Ultra-lightweight food bag—ULB T0	−21.14	0.13	5	This study
Lightweight shopping bag—LSB T0	−22.87	0.09	5	This study
Polyethylene bag—PE T0	−30.41	0.51	5	This study
Natural samples				
Corn starch	−12.23	0.10	3	This study
Corn	−11.38	0.55	3	[15]
Corn	−10.7 to −10.8 **		3	[16]
Potato starch	−25.52	0.00	2	This study
Potato	−27.80	0.01	2	[15]
Potato	−27.2 to −25.8 **		3	[16]
Sunflower oil	−29.04	0.10	2	This study
Rapeseed oil	−30.14	0.08	2	This study
Polymer samples				
Polylactic acid (PLA)	−9.48	0.40	2	This study
Polylactic acid (PLA)	−13.87	2.18	6	[15]
Polyhydroxybutyrate (PHB)	−11.83	0.20	3	This study
Polycaprolactone 10000 (PCL)	−27.15	0.40	3	This study
Polycaprolactone 80000 (PCL)	−27.33	0.20	3	This study
Polybutylene succinate (PBS)	−27.47	0.20	3	This study
Polyethylene terephthalate (PET)	−27.84	1.71	7	[15]
IAEA CH-7 polyethylene standard (PE) *	−32.04	0.04	3	This study

2.5. Statistical Analysis

One-way ANOVA was used to determine whether there was a statistically significant difference among the isotopic carbon data of the three polymers (PE, ULB and LSB) of the exposed shopping bags. The method used to discriminate the means was Fisher's Least Significant Difference LSD, performed by Statgraphics Plus software (version 5.0). Statistically significant differences between the isotopic results obtained from the different exposition times of each bag's typology were also tested.

3. Results

3.1. IRMS Analysis

Data concerning the $\delta^{13}\text{C}$ values of the shopping bags analyzed in this study are reported in Table 1. Mater-Bi® bags were found to be made principally with corn starch (the only declared component) and PCL [22,23] or partially *bio-based* copolyester prepared from vegetable oils [24]. Instead, Eich et al. (2015) [25] mentioned that the Mater-Bi® bag analyzed in their study consisted of a starch-based biopolymer/polyethylene terephthalate (PET) blend. The $\delta^{13}\text{C}$ values of $-21.14 \pm 0.13\text{‰}$ and $-22.87 \pm 0.09\text{‰}$ for ULB and LSB, respectively, suggest a mixed composition of the used blends. In particular, the contribution of starch and polyester components to the bag's composition was estimated by applying a two end-member mixing model. Considering the literature, references [22–24,26,27] and $\delta^{13}\text{C}$ values determined for different polyesters and natural raw materials, corn starch and biodegradable polyesters PCL and PBS were chosen as end-members. Potential raw materials, such as polymers, potato and corn starches (C3 and C4 plants, respectively)

and vegetable oils were considered in this study as possible end-members for isotope mixing analysis. A similar approach was adopted for several environmental studies ([28] and authors cited therein). The following equations were used for mixing calculations (Equations (2) and (3)):

$$F_{\text{starch}} + F_{\text{polyester}} = 1 \quad (2)$$

$$\delta^{13}\text{C}_{\text{bag}} = F_{\text{starch}} \times \delta^{13}\text{C}_{\text{starch}} + F_{\text{polyester}} \times \delta^{13}\text{C}_{\text{polyester}} \quad (3)$$

where F is the fraction percentage, $\delta^{13}\text{C}_{\text{starch}}$ and $\delta^{13}\text{C}_{\text{polyester}}$ are the two end-members (-11.45‰ and -27.32‰ , respectively) calculated as the mean of values reported in the literature [15,16] and those determined in this study.

The results of mixing calculations showed a higher percentage of polyesters in LSB with respect to ULB (72% and 61%, respectively).

The changes in isotopic composition over time (immersion in seawater) of the shopping bags (ULB and LSB) showed that over the 73-day exposure period and under variable conditions of temperature and salinity (i.e., $24.24\text{--}28.76\text{ °C}$ and $31.19\text{--}36.28\text{ PSU}$, respectively), the $\delta^{13}\text{C}$ values of both Mater-Bi® bags showed a gradual decrease towards more negative values (Figure 1). The recorded $\delta^{13}\text{C}$ variation ($\Delta\delta^{13}\text{C}$) was 2.16 and 2.84‰ for ULB and LSB, respectively. During the experiment, all ULB and LSB samples showed structural changes with the formation of numerous heterogeneous pinholes, cracks and grooves. The evidence that ULB fragments were not found at T6 is presumably linked to the mechanical action of waves, rather than to chemical degradation [13,29]. The PE control bags did not show a marked decrease of $\delta^{13}\text{C}$ and their observed $\delta^{13}\text{C}$ variation ($\Delta\delta^{13}\text{C} = 0.41\text{‰}$) was close to the uncertainty of the analytical method, which is different from what was observed for compostable bags.

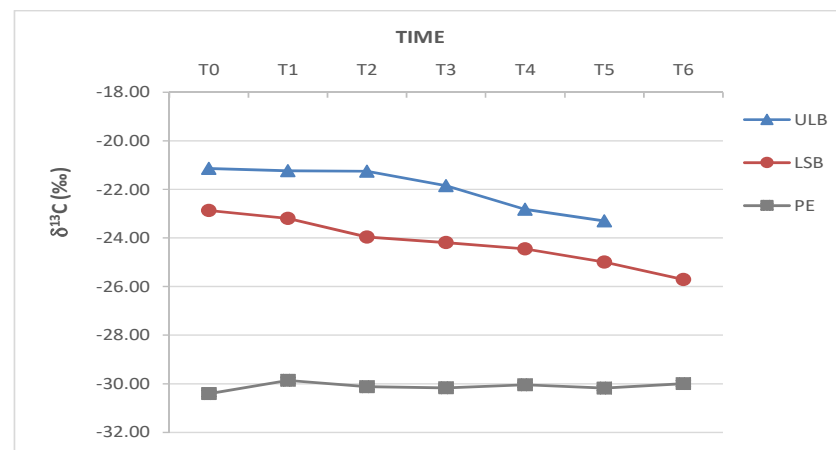


Figure 1. Changes in $\delta^{13}\text{C}$ values in polyethylene bag (PE), lightweight shopping bag (LSB) and ultra lightweight bag (ULB) during exposure time points.

By applying the mixing approach to the isotopic values of the samples (T0–T6), where T0 indicated values relative to the starting composition of the shopping bags, we observed that the percentage of starch fraction decreased at a similar rate in both types of shopping bags, independently of its initial proportion. Indeed, between T0 and T5 (T6 was analyzed only for LSB) 14% and 13% of starch were lost, respectively for ULB and LSB (Figure 2). This implied a progressive enrichment in polyesters in both types of bags, even if ULB showed an initial difficulty in degrading.

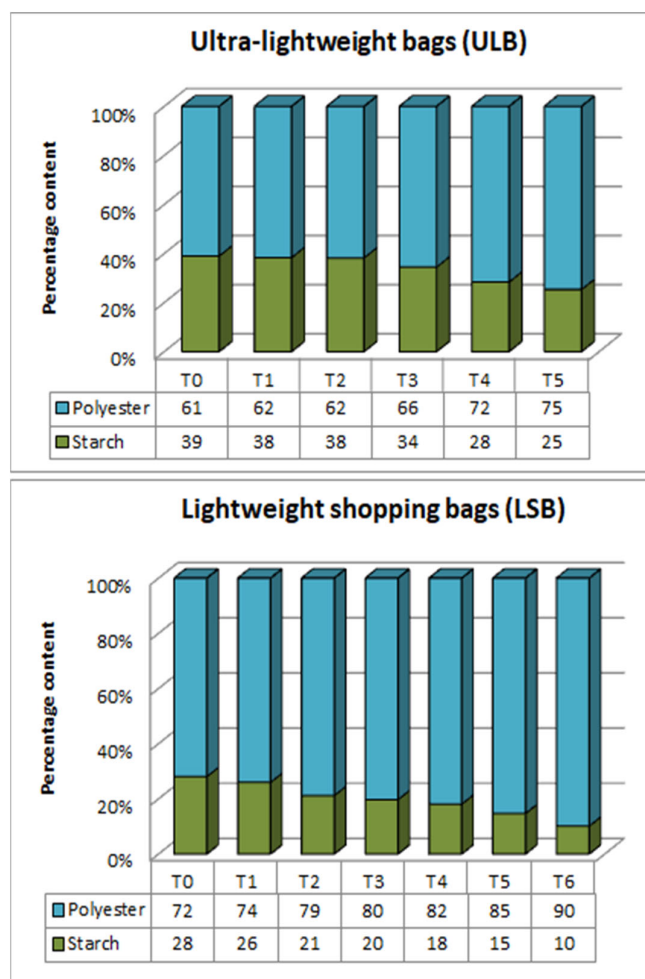


Figure 2. Changes in composition of ultra-lightweight (ULB) and lightweight (LSB) shopping bag samples during exposure to coastal marine environments.

The degradation process of starch follows zero-order kinetics (Figure 3). The uncertainty associated with different immersion times was found to range between 2% and 5% and the degradation process curve can be considered statically robust.

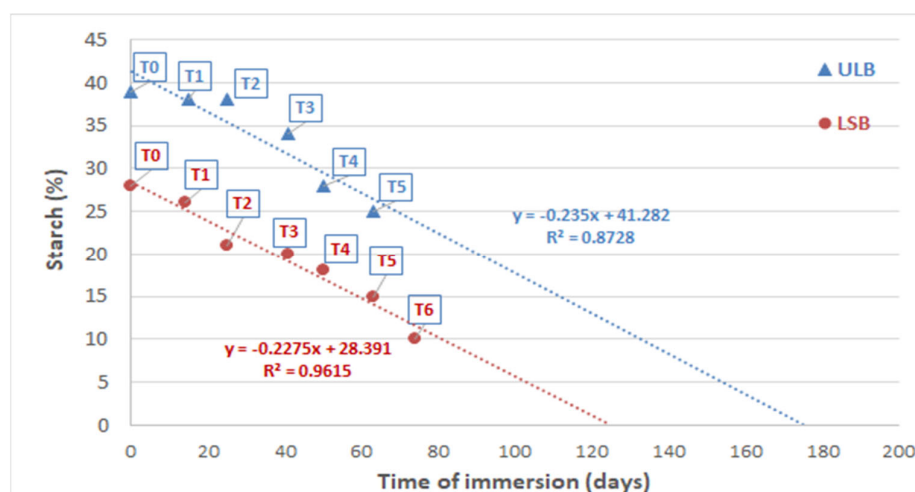


Figure 3. Estimation of starch component degradation time in ultra lightweight bag (ULB) and lightweight shopping bag (LSB).

Considering the intercept in the X-axis, we could predict the time necessary for the biodegradation of starch components considering the environmental conditions present during the experiment, estimating it in about 180 and 124 days for ULB and LSB, respectively.

3.2. FTIR Results

Integration of the peaks was performed displaying the spectra in the absorption scale. The same integration limits for all the samples were chosen. These limits were chosen to encompass about 95% of the total area, excluding the band edges [17,18]. Even though the formulation of the bioplastic used for the tested bag is proprietary and unknown, the spectra were consistent with those expected by a mixture of starch and a polyester (PEs) (Figure 4).

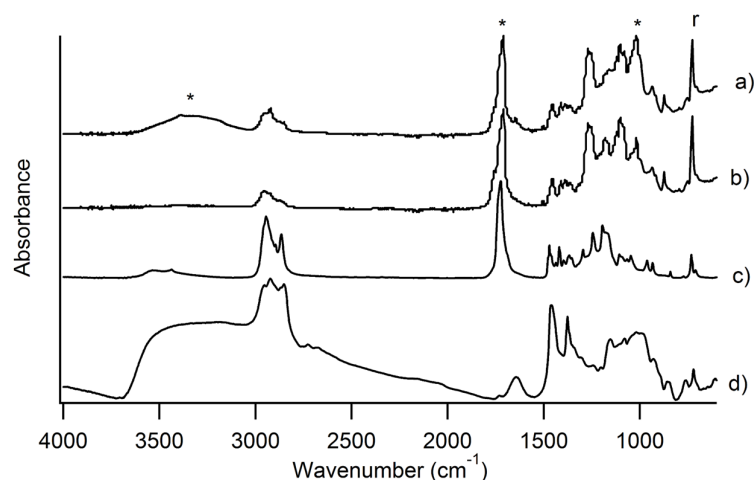


Figure 4. FTIR spectra of (a) ULB, (b) LSB, (c) PEs, (d) starch. The peaks which were integrated are denoted by * in the ULB spectrum; the peak taken as reference is indicated by r in the ULB spectrum.

Table 2 reports the absorption bands which characterize the functional groups for PEs, starch, ULB and LSB bags, respectively. The spectral results for ULB show an absorption band centered in 3391 cm^{-1} due to the O-H stretching and another one centered in 2921 cm^{-1} related to the C-H stretching; weak chemical bonds are also present in the spectral region between 1455 and 1388 cm^{-1} assigned to C-H bending. A very strong absorption band is centered at 1712 cm^{-1} due to C=O stretching of the ester group in association with a strong band at 1268 cm^{-1} due to C-O stretching of the O=C-O group. Some bands are present at 1119 , 1102 cm^{-1} , assigned to aliphatic ethers, and at 1080 and 1018 cm^{-1} , due to the presence of primary and secondary alcohols, in association with a weak band at 1646 cm^{-1} due to C-O bending associated with the OH group. The spectral results for LSB are very similar to those of ULB, except for the intensity of the signals assigned to the primary and secondary alcohols that in the ULB spectrum are negligible and the CH_2 chains region between 1455 and 1388 cm^{-1} stronger than in ULB.

Table 2. Absorption bands of functional groups stretching for PEs, starch, ULB and LSB bags.

Bands	Absorption Bands (cm^{-1})	PEs	Starch	ULB	LSB
O-H groups (hydroxyl) stretching	3600–3300	✓	✓	✓	
C-H stretching	2930–2900	✓	✓	✓	✓
C=O stretching (carboxylic and ester groups)	1730–1705	✓		✓	✓
C-O bending associated with OH group	1650–1637		✓		✓
C-H bending	1460–1375	✓	✓	✓	✓
C-O stretching	1270–1050	✓	✓	✓	✓
C-O-C stretching (aliphatic ethers)	1180–1150	✓	✓	✓	✓
C-H and C=O bending (out of plane)	970–750	✓		✓	✓

PEs FTIR spectrum is characterized by C=O stretching centered in 1710 cm^{-1} of the carbonyl band of the ester group and C–O stretching in 1240 cm^{-1} and 1090 cm^{-1} . The bands at $2950, 2910\text{ cm}^{-1}$ are assigned to C–H symmetrical stretching in CH_2 chains and $1460\text{--}1375\text{ cm}^{-1}$ are assigned to C–H bending. C–H and C=O bending (out of plane) around 700 cm^{-1} [30–35] is typically present in polyesters. The broad band at around 3300 cm^{-1} for starch is due to the stretching mode of the O–H groups. The adsorption band at 1650 cm^{-1} is attributed to C–O bending associated with the OH group together with the band at 1150 cm^{-1} assigned to C–O stretching. The bands at $2955\text{--}2920\text{ cm}^{-1}$ and $1460\text{--}1375\text{ cm}^{-1}$ are assigned to C–H stretching and C–H bending, respectively. In addition, the characteristic C–O–C ring vibration on starch leads to an absorbance peak at around $1180\text{--}1150\text{ cm}^{-1}$.

In summary, both ULB and LSB seem to be composed of polyester and starch, as already found by the isotopic analysis approach. The diverse relative proportion of the two components in ULB and LSB explain the spectral differences found among them, confirming the higher percentage of starch in ULB than that in LSB.

Figure 5 shows that the ratio I_{3300}/I_{730} , related to the quantity of hydroxyl groups, increases as a function of immersion time. This can be ascribed to the hydrolytic degradation of the constituting polymer. It is well known that the decrease in molecular weight brings about an increase in the number of terminal groups and, therefore, a strengthening of the OH signal.

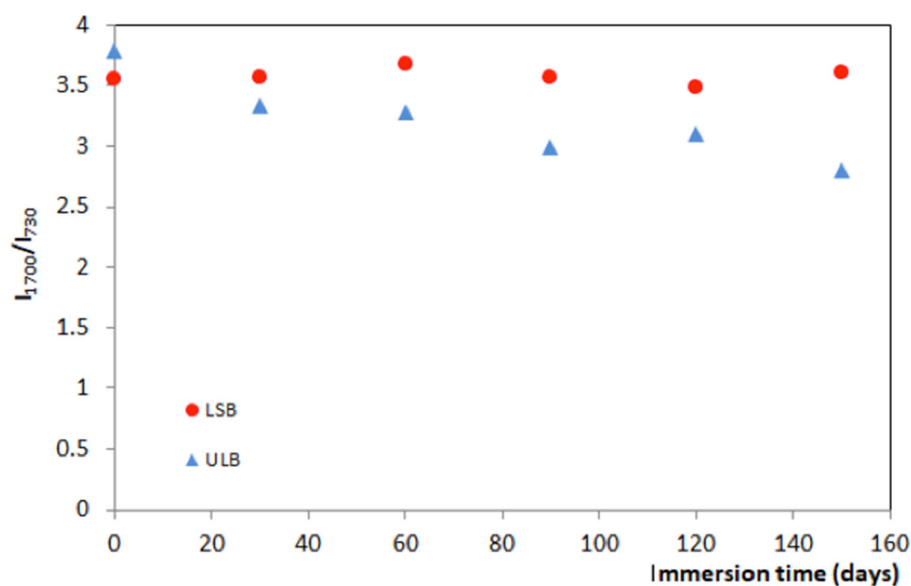


Figure 5. Ratio I_{3300}/I_{730} , related to the quantity of hydroxyl groups as a function of immersion time for ULB (blue triangle) and LSB (red circle).

Interesting to note is that no trend was observed for LSB when the C=O functional groups (I_{1700}/I_{730}) were monitored (Figure 6), while a mildly decreasing trend was observed for ULB. This indicates that the degradation process does not influence such functional groups or that it influences them very slowly. If hydrolysis happens at the expense of starch (Figure 4), the reduction in chain size brings about the formation of smaller polysaccharides, with no formation of significant further carbonyl groups, but with an increase in hydroxyl terminal groups. Therefore, in this scenario, the IR signal at 1700 cm^{-1} remains unaltered. However, when a polyester group is hydrolyzed, the C=O group is retained, but a shift should be observed from the characteristic frequencies of the esters and those of the carboxylic acid. However, the shape of the peak at about 1700 cm^{-1} does not significantly change, reflecting the fact that the polyester moiety is not involved in the degradation process. Therefore, IR data point towards a preferred degradation of the starch component of the formulation, with the polyester part remaining unaltered.

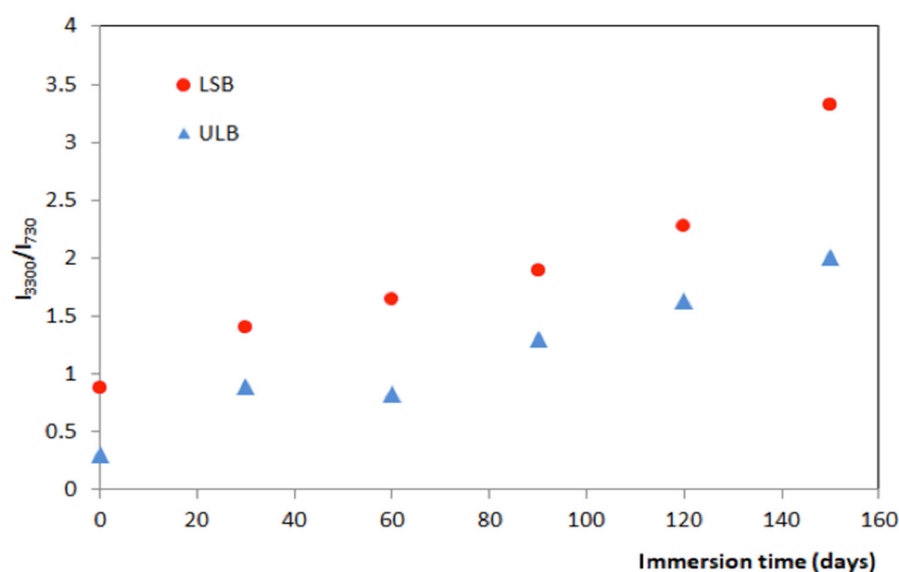


Figure 6. C=O functional groups (I_{1700}/I_{730}) as function of immersed time respectively for ULB (blue triangle) and LSB (red circle).

4. Discussion

The production of bioplastics has increased in recent years and these polymers continue to enter the environment. Understanding the qualitative and quantitative impact of plastic polymers is fundamental for addressing their potential environmental pollution and their toxicological impact [36]. In this regard, the identification and quantification of bioplastic degradation products (solid microparticles and soluble compounds) and residual components, by using different analytical techniques, is a very complex challenge.

Qualitative analysis of bioplastics has been performed using spectroscopic methods (i.e., fluorescence, nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FTIR) and UV-VIS spectrophotometric techniques [37,38]), while the quantitative analysis of solid microdebris of bioplastics uses FTIR micro imaging, gas chromatography with mass spectrometry and thermal analysis [39–41].

The potential utility of IRMS as a complementary analytical method with respect to “traditional” analytical techniques for plastic analyses has been reported in our previous work [1]. In this preliminary study, carbon stable isotope analysis ($\delta^{13}\text{C}$) was applied. This method was used to discriminate different plastic polymers (petroleum- and plant-derived) in plastic and bioplastic materials (among which the shopping bags of Mater-Bi®, Novamont), as well as for the quali-quantitative evaluation of polymers degradability in marine environments. In the present study, the same approach, i.e., the assessment of isotopic values of several polymers and some possible natural raw constituents (corn starch, potato starch and vegetable oils), was applied to identify the carbon source used to manufacture shopping bags. Among the natural sources for biopolymers production, there are C3 plants and C4 plants, which differ in photosynthetic pathways and, consequently, their carbon fingerprint. It has been demonstrated that C4 plants such as sugar cane, millet, corn and tropical grasses, using the Hatch–Slack photosynthetic cycle, have $\delta^{13}\text{C}$ values ranging from -8 to -20‰ , less negative respect to C3 plants (mostly dicotyledons such as wheat, rice, rye and cotton), that employ the Calvin–Benson cycle and have $\delta^{13}\text{C}$ values ranging from -22 to -35‰ [42]. Plant-derived plastic polymers used for food packaging, bags and bottles for drinking water showed a significant difference in isotopic values with respect to petroleum-derived plastic products ([15] and literature therein). Petroleum-derived packaging materials for food, such as shopping bags for fruits and vegetables (HDPE), were characterized by $\delta^{13}\text{C}$ mean values of $-33.97 \pm 1.15\text{‰}$, whereas plant-derived supermarket shoppers (“BIO” bags) recorded $\delta^{13}\text{C}$ mean values of $-25.30 \pm 0.70\text{‰}$, near values characteristic for C3 plants as a starch source. The different polymers analyzed, such as

PCL or PBS (Table 1), showed depleted values (from -27.47 to -27.15‰) with respect to C4-derived polymers (corn starch). PCL as well as PBS are often used in biodegradable polymer blends. PCL, which is a semicrystalline linear polyester [43] produced by polymerization of ϵ -caprolactone commonly derived from fossil sources, received great attention in the 1980s when Novamont created a PCL/starch composite under the trademark Mater-Bi[®] [44]. PBS, poly(butylene succinate-co-butylene adipate) was produced in 1990 through a polycondensation reaction of glycols with aliphatic dicarboxylic acids and their derivatives [45] and its processability and mechanical properties made it a candidate to replace other polymers such as polyethylene and polypropylene [46]. On the other hand, the less negative $\delta^{13}\text{C}$ values were evaluated for PLA and PHB, suggesting that the food bags (ULB and LSB) analyzed in this study ($-21.14 \pm 0.13\text{‰}$ and $-22.87 \pm 0.09\text{‰}$, for ULB and LSB, respectively), are not constituted of these polymers, but rather of polyesters such as PCL (repeatedly mentioned in the literature as a Mater-Bi[®] component) or PBS and corn starch (the only component declared by the producer). Our $\delta^{13}\text{C}$ results suggested a mixed composition of blends used in the shopping bags, as indicated by the results of the mixing model. This showed a higher percentage of polyesters in LSB with respect to ULB (72% and 61%, respectively), suggesting different purposes of the shopping bags' use. In fact, the LSB sample represents a bag type which requires higher tensile strength and flexibility [47]. However, the more negative $\delta^{13}\text{C}$ values reported for PE bags could suggest that bio-bags employed in the experiment do not contain PE, or at least not in large detectable quantities. It must, however, be taken into account that, according to the data obtained, vegetable oils of such common crops like sunflower and rapeseed would give co-polyesters an isotopic footprint between that of PCL (as well as PBS) and PE.

In summary, both ULB and LSB seem to be composed of polyester and starch, as also confirmed by FTIR analysis. In fact, the diverse relative proportion of the two components in ULB and LSB explains the spectral differences found among them, confirming the higher percentage of starch in ULB than that in LSB.

Regarding the changes in composition of the shopping bags (ULB and LSB) over the 73-day period of immersion in marine water, data showed a depletion of $\delta^{13}\text{C}$ values for ULB and LSB ($\Delta\delta^{13}\text{C}$ of -2.16 and -2.84‰ , respectively), which was not observed for the PE control bags. The isotopic shift observed could be reasonably related to the degradative actions that occur in the marine environment (e.g., chemical and/or biological processes) such as photodegradation, thermo-oxidation, hydrolysis and biodegradation. These processes indeed could be responsible for the depolymerization and the subsequent assimilation and metabolism of the monomers by microorganisms ([15] and literature therein).

The lack of carbon depletion in the PE control bags suggested a very low PE degradation (if any) with respect to Mater-Bi[®] bags, as already observed by some authors [48,49]. In the work by Rutkowska et al. [48], PE bags exposed for 20 months at a depth of 2 m in the Baltic Sea showed no biodegradation and low changes in tensile elongation at break. Moreover, in the present study, the isotopic data of Mater-Bi[®] bags showed a faster loss of corn starch which has been suggested to be a more bioavailable and hydrophilic component compared to polyesters. Similar results were reported elsewhere [50].

Results obtained by FTIR spectroscopy showed that both ULB and LSB seem to be composed of polyester and starch confirming the outputs of the isotopic analysis approach. In particular, the absence of aromatic overtone signals in the region between 2000 and 1650 cm^{-1} could suggest the absence of co-polyesters containing aromatic monomers like terephthalic acid, in favor of the presence of PCL.

In fact, during the shopping bags degradation experiment, FTIR spectra showed an increase in hydroxyl groups (ratio I_{3300}/I_{730}), ascribed to the hydrolytic degradation of the constituting polymers. The decrease in molecular weight with an increase in the number of terminal groups, which contributes to the strengthening of the OH signals, is a well-known phenomenon. Hydrolysable ester bonds in a polymer backbone make polymers more susceptible to microbial degradation [16,45,51]. In particular, inorganic salts and bacteria have been reported to play a fundamental role in the degradation of PCL either

through slow non-enzymatic bulk hydrolysis in aseptic water bodies or by rapid enzymatic degradation in bacteria-containing water bodies [52]. These authors hypothesized that the enzymatic degradation occurred, in particular at increasing degradation time, at the sample surface, while the inner part remained unaffected. On the other hand, if hydrolysis happens at the expense of starch, the reduction in chain size brings about the formation of smaller polysaccharides, with no formation of significant further carbonyl groups (Figure 6), but with an increase in hydroxyl terminal groups (Figure 5). Therefore, in this scenario, the IR signal at 1700 cm^{-1} remains unaltered. However, when a polyester group is hydrolyzed, the C=O group is retained, but a shift should be observed from the characteristic frequencies of the esters and those of the carboxylic acid. In this study, the shape of the peak at about 1700 cm^{-1} does not significantly change, reflecting the fact that the polyester moiety is not involved in the degradation process. Therefore, IR data point towards a preferred degradation of the starch component of the blends analyzed, with the polyester part remaining unaltered.

The preferential microbial degradation of starch in blends exposed to the marine environment reported in the literature [25,52,53], clearly depended on microbial abundance and composition. According to the trend we have observed, the preferential removal through degradation of isotopically heavier corn starch (medium value of -11.45‰) from the analyzed compostable blends lead to polyester enrichment in the remaining matrix. This results in the decrease of the $\delta^{13}\text{C}$ values over time, reaching lighter values characteristic of polyesters such as PCL. The degradation time of starch estimated in this study (180 and 124 days for ULB and LSB, respectively) during the present degradation experiment, is in accordance with observations of Niaounakis et al. (2019) [54], who reported that the hydrolysis of the starch component and loss of plasticizer after 8 months of seawater exposure. These authors also reported a severe loss of tensile properties of Mater-Bi® film.

However, it is not possible to accurately estimate how long it would take the polyester fraction to decompose. In this regard, Eich et al. (2015) [25] reported, using Scanning Electron Microscopy analysis, that the holes that appeared after 15 and 33 days of exposure to the marine environment in the plastic's surface might have developed due to dissolving or mineralization of the starch fraction. In this regard, the experiment conducted on PCL degradation under different environmental and laboratory conditions [52] showed that, after a one-year immersion in seawater, a weight loss of about 30% was observed, principally due to the superficial microbial enzymatic degradation, but no significant molecular weight changes were recorded, indicating that, under these conditions, the internal non-enzymatic hydrolysis is negligible.

Avella et al. (2000) [55] reported that in composting conditions with controlled temperature and moisture, pure PCL degrades in a few tens of days, while its blend with starch at 50% disappears in about 3 weeks. However, under marine conditions, PCL items exposed to seawater were still recoverable after 12 months, even if numerous cracks in the surface and the complete loss of tensile strength were observed [56].

All of these findings led us to hypothesize that biodegradable polymers can contribute to increasing the pool of microplastics in the marine environment. In fact, even though PCL-degrading microorganisms were found in a wide range of marine habitats, like bacteria belonging to the genus *Pseudomonas* [57], some PCL fragments were identified as micro- and meso-plastics polluting the Mediterranean Sea ([58] and literature therein).

5. Conclusions

Studies addressing the degradability of polymers in marine environments are very recent and focus mainly on a short-term scale, whereas long-term biodegradation dynamics and the effects on the marine biota are still missing. Furthermore, standard analytical methods to trace and quantify the biodegradation pathways are scarce and need improvements, considering that most studies are at the laboratory scale and not representative of different environmental conditions and habitats. Hence, the lack of knowledge about long-term degradation and the occurrence of residual biopolymers in the marine envi-

ronment can generate speculations about their sustainability and contribution to marine plastic pollution.

This study revealed that two types of Mater-Bi® materials seem to be composed of polyester and starch, and that, once in the marine environment, the starch fraction is subjected to fast degradation (hydrolysis) estimated at about 124–180 days.

The combination of the IRMS technique with FTIR has been revealed as a promising and time/money-saving tool to more efficiently address the biodegradation of polymers in the marine environment and infer their degradation times and kinetics.

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