



Commercial plastics claiming biodegradable status: Is this also accurate for marine environments?

Monick Nazareth^a, Mônica R.C. Marques^a, Marcia C.A. Leite^a, Ítalo Braga Castro^{b,*}

^a Programa de Pós-Graduação em Química do Instituto de Química, Universidade do Estado do Rio de Janeiro (UERJ), Rua São Francisco Xavier, 524 Pavilhão Haroldo Lisboa da Cunha, 20559-900, RJ, Brazil

^b Instituto do Mar, Universidade Federal de São Paulo (IMAR-UNIFESP), Rua Maria Máximo, 11030-100, Santos, SP, Brazil

ARTICLE INFO

Keywords:

Greenwashing
Biodegradable polymers
Biodegradation
Plastic pollution
Marine pollution

ABSTRACT

Concerns about plastic pollution and global public policies have encouraged consumers to acquire environmentally friendly products. Thus, products made of biodegradable plastics have been preferred by the public, despite their costs. However, greenwashing practices, promising more environmental benefits than the products actually offer, has become frequent. Nevertheless, no studies assessing the occurrence of greenwashing in commercial plastic products sold in large world economies have been performed. The present study aimed to experimentally evaluate alterations in structure and chemical composition of selected plastic products marketed in Canada, USA and Brazil. The aging experiments carried out by seawater immersion for 180 days showed no evidence of degradation in 4 out of the 6 studied samples, despite product claims of biodegradability or 100% degradability status. This finding denotes unequivocal greenwashing practices, even including bags made of polyethylene, an ordinary non-biodegradable polymer. Thus, the inadequate adoption of green marketing is deceiving to consumers and may lead to improper disposal of these materials. These practices are highly counterproductive in view of the global public policies recently adopted to control plastic pollution. Therefore, considering the technologies currently available for identification of polymers, a strict control should be exercised over products that claim biodegradable status.

1. Introduction

Plastics are persistent residues of a global environmental concern [1,2]. Such products began to be commercially used in the mid-twentieth century due to the seemingly boundless technological advances provided by their simple fabrication process, resistance and versatility [3,4]. However, decades of excessive use, inadequate disposal and environmental persistence (mainly in aquatic systems) has turned these residues into the focus of researches related to marine contamination [3,5,6]. A recent estimate pointed out that the amount of plastic in the oceans has reached 20 million tons, making up to 80% of marine anthropogenic debris [7]. Sources of these materials to marine environments include the direct disposal in coastal zones or landfills, load transportation, accidents, fishing and tourism, among others human activities [8]. In this context, plastic debris have been found in coastal areas, including sediments [5] and seawater [7] or even in remote zones of the Antarctic Ocean [9] and submarine trenches in the deep-sea floor [10].

The occurrence of plastic residues in marine environments causes

esthetic and economical harm, affecting both, marine life and ecosystem balance [1,11]. However challenging it may be to monetize such parameters, modelling techniques have allowed to infer that the impact of plastic disposal would reach US\$ 13 billion/year [12]. Additionally, disposable packages and plastic bags made of polypropylene (PP) and polyethylene (PE) have been considered the most harmful residues to marine environments [8,12]. Nevertheless, between 500 billion and 1 trillion tons of these packages have been produced each year [13], while 79% of all plastics ever produced have been accumulated in landfills or in natural environment after an average use of only 12 min [14,15].

Seeking to reduce production, use and disposal of plastic bags, several public policies has entered into force in the world's largest economies [5,14]. These strategies encourage recycling, restrictive use, charging for plastic bags and even a complete banish has been implemented. In this regard, the distribution of plastic bags in California (USA) was banned in 2016 [12]. Denmark and Austria were successful in achieving 80–100% recovery of plastic wastes [17]. In Ireland, a tax was introduced on the use plastic bags in 2002 [16]. On the other hand,

* Corresponding author.

E-mail address: ibcastro@unifesp.br (Í.B. Castro).

<https://doi.org/10.1016/j.jhazmat.2018.12.052>

Received 8 September 2018; Received in revised form 13 December 2018; Accepted 15 December 2018

Available online 17 December 2018

0304-3894/ © 2018 Elsevier B.V. All rights reserved.

in South American countries there are few public interventions seeking to address such problem [14]. Furthermore, the substitution of conventional polymers by biodegradable materials have been used as an alternative for reducing environmental accumulation of these debris [5,14].

Several biodegradable products may be formulated from renewable feedstocks as starch, cellulose, or biosynthesized supplies. Such materials are degraded by microbial activity under certain conditions, decreasing their environmental persistence [18,19]. During the biodegradation process, water, CO₂, methane and biomass are expected to be produced in a short time [5]. However, recent studies showed that some biodegradable materials have not been properly tested to certify their degradation rates in marine environment, yet still claim biodegradable and/or sustainable status [5].

Oxo-biodegradable polymers are formulated using conventional resins like PE and polystyrene (PS) added with degrading agents, photoinitiators or other compounds susceptible to degradation [20]. In this sense, oxo-biodegradation is a serial process including oxygen action combined with light and heat, followed by breaking of some chemical bonds in the polymeric chain. The final step of this process is the bioassimilation and mineralization by microorganisms [20,21]. Nevertheless, as oxo-biodegradable PE products age slowly and cannot be labeled as biodegradable by companies [22], manufacturers have tried to attract customers using friendly ecological marketing strategies known as green marketing [23]. Withal, the use of greenwashing practices (advertising more environmental benefits than products actually offer) has influenced buyers to purchase products under the belief of sustainable or environmentally friendly prerogatives [24,25]. Thus, new methodologies and experimental designs have been developed to assess the level of greenwashing in products, aiming to inform and protect consumers [26].

Considering the scarcity of available information on degradation of plastic waste in aquatic systems and the typical use of greenwashing practices against consumers, assessing the aging of commercial products that claim biodegradable and/or sustainable status has now become critically important. Therefore, the present study aimed to experimentally evaluate the chemical composition and aging mechanisms of selected plastic products marketed in the three largest economies of the American continent (Canada, USA and Brazil). Plastic samples were analyzed before and after natural seawater exposure, and occurrence of greenwashing practices related to these materials was evaluated based on the information provided by manufacturers in the product publicity.

2. Materials and methods

2.1. Obtaining plastic samples

Plastic products were acquired in supermarkets, restaurants, stores and webstores in Brazil, Canada and USA. The items were randomly selected among products displaying advertisements associated to green marketing, as summarized in Table 1. In addition, the information about product composition provided in the product labels or by manufacturer websites were collected. In laboratory, experimental samples were prepared cutting and weighing (in a precision analytical scale) the

products to obtain 2.5 g of materials for each sample. Weight was the parameter adopted herein as the samples assessed had different thicknesses and densities. These samples were kept submerged using nylon wires attached to the aquaria bottom. The experiments were performed in triplicate using a different aquarium for each sample, which were analyzed at the beginning ($T_0 = 0$ days) and end ($T_{180} = 180$ days) of the experiment.

2.2. Plastic aging experimental design

The simulated marine environment was prepared in glass aquariums filled with 15 l of natural seawater. An additional aquarium without samples was used as the blank, to assess the water quality control. All aquariums were kept under constant aeration, 12 h light-dark cycle (using led lamps, photon irradiance = $5 \mu\text{mol m}^{-2} \text{s}^{-1}$) and the temperature was stabilized at $30 \pm 2^\circ\text{C}$ using a submerged thermostat connected to a thermometer to follow up with daily temperatures. The natural seawater used in the aquariums was collected in Pernambuco beach ($23^\circ 57' 54.8''\text{S}$ and $46^\circ 11' 05.9''\text{W}$), located in the city of Guarujá, São Paulo (Brazil), in a site distant from any effluent disposal. During the experiments, the aquarium's water volume was checked every 3 days and, when needed, adjusted using ultrapure water. These interventions were made to avoid abrupt salinity fluctuations due to seawater evaporation.

2.3. Sample characterization by Fourier Transform Infrared spectroscopy (FTIR)

Polymer identification and chemical modifications from the samples exposed to seawater were assessed using Fourier Transform Infrared Spectroscopy (Perkin Elmer, model FT-IR / FIR Spectrometer - Frontier) coupled to a module of attenuated total reflectance (ATR). The spectra were collected in transmission mode, $4000 - 600 \text{ cm}^{-1}$ in a 4 cm^{-1} resolution. This analysis was used to identify the most significant degradation markers. Spectrum alteration during aging experiments have been already identified, mainly for PE [27]. For biodegradable polymers such as poly(butylene adipate co-terephthalate), (PBAT) and poly(lactic acid) (PLA), alterations in carbonyl groups are the main indicators of degradation in aged samples [21,28,29]. Therefore, carbonyl indexes (CI) were calculated as the ratio of the absorbance area for the bond peak relative to the value of a reference peak [27]. The reference peaks obtained in literature were used to calculate the CI as detailed in Table 3. Triplicate measurements were performed for the samples and areas were determined using Perkin Elmer® Spectrum software (Version: 10.03.02.0077). The normality and homogeneity of carbonyl indexes were verified using Shapiro–Wilk and Levene tests, respectively. Next, differences between temporal measurements obtained in T_0 and T_{180} were assessed by t-tests. These statistical analyses were performed using Statistica® (version 12.0 (Statsoft)), with a significance level of 0.05.

2.4. Morphological and elemental characterization of the samples

For evaluation of the plastic surfaces and morphological

Table 1
Selected plastic products and provided manufacturer information.

| Product | Sample | Environmental claims | Country | Compositions information ^a | Brand / seller or distributor |
|---------|--------|------------------------------------|---------|---|--------------------------------------|
| Cup | S1 | Renewable and compostable | USA | PLA | Nature Works/ Karat Earth |
| Cup | S2 | Biodegradable formed by bioplastic | Brazil | Starch, PP, PLA, Ethylene vinil acetate and additives | EECOO sustainability / EECO web site |
| Bag | S3 | Compostable | Canada | not available | Glad / supermarket |
| Bag | S4 | 100% Biodegradable | Brazil | PE | Res D2W™ / Nespresso store |
| Bag | S5 | Biodegradable | USA | not available | EPI / Ardene store |
| Bag | S6 | 100% degradable | Canada | PE | EPI / The market stores |

^a Information provided by manufactures, sellers or distributors. (PLA = poly (lactic acid), PP = polypropylene, PE = polyethylene).

Table 2

The seven sins of greenwashing according to described by TerraChoice Environmental Marketing Agency [30].

| Sins of greenwashing | Claims |
|--------------------------|--|
| Hidden Trade-off | Suggestion that a product is 'green' based on a narrow set of attributes without attention to other important environmental issues. |
| No Proof | An environmental claim that cannot be substantiated by easily accessible supporting information or by a reliable third-party certification. |
| Vagueness | A claim that is so poorly defined or broad that its real meaning is likely to be misunderstood by the consumer. |
| Worshipping false labels | A product that, through either words or images, gives the impression of third-party endorsement where no such endorsement exists; fake labels, in other words. |
| Irrelevance | An environmental claim that may be truthful but is unimportant or unhelpful for consumers seeking environmentally preferable products. |
| Lesser of two evils | A claim that may be true within the product category, but that risks distracting the consumer from the greater environmental impacts of the category as a whole. |
| Fibbing | Environmental claims that are simply false. |

characterization, the samples were prepared in carbon tapes, metalized with gold and observed using a scanning electron microscopy (SEM - Model JEOL JSM-6510LV). The SEM operational conditions were set to 20 kV electron beam acceleration and high vacuum at 70 Pa. To evaluate the diversity of elements, the surface of each sample was swept using energy dispersive spectroscopy (EDS).

2.5. Greenwashing evaluation

Identification and evaluation of greenwashing practices was based in a protocol issued by TerraChoice Environmental Marketing Agency [30]. This report pointed out hidden trade-offs, no proof, vagueness, irrelevance, lesser of two evils, fibbing and worshipping false label as the seven common patterns (or sins) of greenwashing (Table 2) [26,30]. Thus, to categorize and estimate the level of greenwashing in the studied samples, chemical and morphological characterizations were performed before and after the aging experiments. Subsequently, the claims displayed in labels and websites from each product were evaluated and classified based on the experimental outcomes.

3. Results and discussion

3.1. Sample characterization by FTIR

In the FTIR characterization for S1, the bands 1747 cm^{-1} (vibration of the C=O group), 1454 cm^{-1} (asymmetric vibration of the CH_3 group), 870 cm^{-1} (vibration of the CH_2-CH_3), 1265 cm^{-1} (stretching vibration of O=C-O-C) and C-C-O stretch (1180 cm^{-1}) were very intense (Fig. 1). All these peaks are the typical pattern detected in PLA samples [31]. In aged PLA samples, two of these bands are often used to indicate degradation: C=O stretching (1750 cm^{-1}) and 1180 cm^{-1} [29,32]. In this study, the CI presented no significant (*t-test*, $p = 0.35$) variation after aging (Fig. 2). Although the degradation of PLA occurs mainly through the ester bonding hydrolysis, some studies also evaluated C-C-O index, which may also be a more susceptible region to chemical modification [29]. As showed by Oliveira et al., [29], in the studied bands, only the C-C-O stretch at 1180 cm^{-1} underwent a small increase after immersion. According to Martin et al. (2014), PLA can degrade over a shorter timescale than traditional polymers. However, the conditions under which it can degrade require industrial

Table 3

Absorption bands used to estimate the degradation and calculate the carbonyl indices derived from FTIR spectroscopy.

| Sample | Carbonyl Index (cm^{-1}) | Reference peak (cm^{-1}) | References |
|--------|-------------------------------------|-------------------------------------|------------|
| S1 | 1700–1810 | 1455 | [29] |
| S2 | 1700–1810 | 2885–2940 | [21,28] |
| S3 | 1700–1810 | 1455 | [30] |
| S4 | 1700–1810 | 1400–1520 | [27,28] |
| S5 | | | |
| S6 | | | |

composting, enzymatic biodegradation and high temperatures. Seeing the absence of such conditions in marine environments, whether PLA will degrade considerably faster than ordinary plastics in the ocean is rather questionable [33]. Other studies pointed out, that PLA requires longer immersion times under non-natural conditions (pH, temperature, moisture and the oxygen content) to be completely degraded [34,35].

For S2, the bands 2950 cm^{-1} and 2915 cm^{-1} (C-H stretch), 1455 cm^{-1} (vibrations of the angular deformation of CH_2), 1377 cm^{-1} (symmetrical deformation of the CH_3), 997 cm^{-1} (CH bend) PP characteristic were detected [36] (Fig. 1). In addition, a large band in the 3350 cm^{-1} region associated with the thermoplastic starch (TPS) structure was found [37]. TPS is a low-cost biodegradable polymer derived from a natural source. It may be added to other polymers, but the results of this blending are usually undesired mechanical properties and high water-sensitive [37]. Several studies investigating the production of starch-based polymer blends showed degradation rates greater than the pure conventional polymer [37–39]. A small band around 1738 cm^{-1} (C=O) was detected in T_0 and may be associated with oxidation of TPS caused during the molding process of the object or by the presence of ethylene vinyl acetate and additives as glycerol monoesters [40,41]. Moreover, after the immersion period, a small band (1651 cm^{-1}) may emerge due to starch consumption, according to report by Bergel et al. [41]. Our results showed spectrum variations after aging (T_{180}) followed by decrease of the characteristic starch band, suggesting consumption of the starch fraction. A non-significant (*t-test*, $p = 0.61$) increase in CI was observed at T_{180} (Fig. 2). However, this may be associated to hydrolysis of existing carbonyls, rather than material biodegradation.

In S3, the following bands were found: 1712 cm^{-1} (stretching vibration of the C=O in the ester group), 1270 cm^{-1} (stretching vibration of the O=C-O-C), 1100 cm^{-1} (stretching vibration of the carbon bonded to the hydroxyl and C-O) and 3400 cm^{-1} (stretching vibration of the O-H) associated with the TPS [38] (Fig. 1). The manufacturer of this package did not provide information about the material composition. The bands observed in the spectrum and comparisons with literature data, suggests that such material may be PBAT added with thermoplastic starch mixture [32,38]. PBAT is an aliphatic aromatic polyester classified as biodegradable, according to Oliveira et al., [40]. The use of blends including PBAT and starch is an effective way to reduce costs while producing a new material with good performance and easily degradable in the environment [39,42]. Among the studied samples, S3 presented the most intense alterations after aging, followed by a significant variation (*t-test*, $p = 0.001$) in the CI (Fig. 2). These findings are consistent with previous reports on the PBAT degradation [40].

The bands 2916 cm^{-1} and 2849 cm^{-1} (C-H stretching asymmetric and symmetric vibrations), 1472 cm^{-1} (CH_2 scissoring vibrations) and 731 and 719 cm^{-1} (CH_2 rocking vibrations) were identified in spectra obtained from S4, S5 and S6 (Fig. 1). According to Musioł et al. [37,38,21], these bands are consistent with a polyethylene (PE) spectrum, although manufacturers had indicated a composition based on

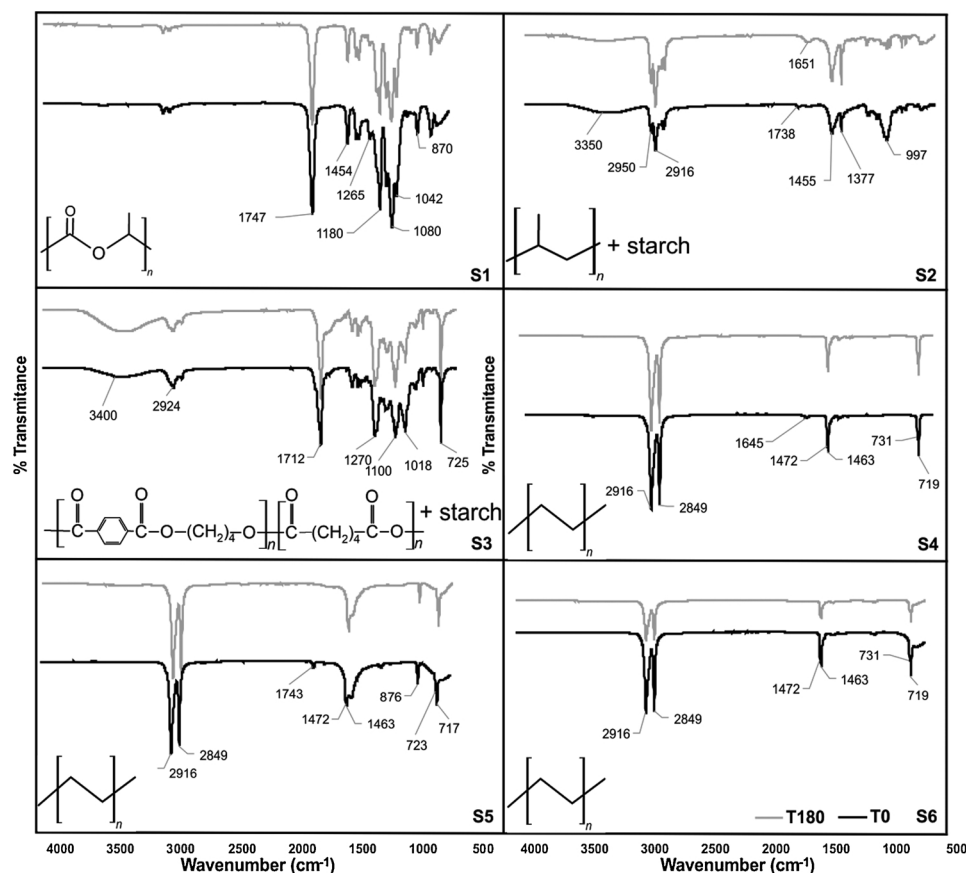


Fig. 1. Spectra obtained by Fourier Transform Infrared spectroscopy (FTIR) from the studied samples before (T_0) and after (T_{180}) aging experiment.

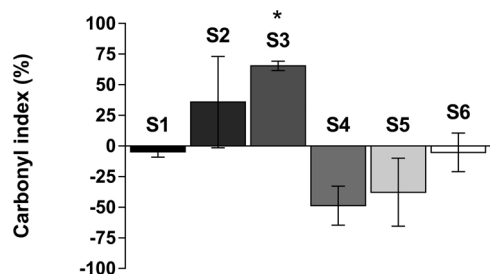


Fig. 2. Variation of carbonyl index in studied samples after 180 days (T_{180}) of immersion in seawater. * denote statistical differences between T_0 and T_{180} .

biodegradable polymers. Accordingly, there were no significant alterations in the spectra obtained for these samples after T_{180} , suggesting no changes in the chemical structure of these bags. Similarly, variations in the calculated CI did not present relevant statistical differences for S4 (t -test, $p = 0.42$), S5 ($p = 0.84$) and S6 ($p = 0.21$) after 180 days of sea water immersion (Fig. 3). In fact, studies investigating PE degradation showed a very high persistence of this polymer in natural environments [27].

3.2. Morphological evaluation of plastic surfaces by SEM

Images generated in SEM have been used in several studies about biodegradation and aging of polymers. Through micrographs obtained from the material surface, it is possible to visualize texture alterations produced by mechanical and oxidative weathering during environmental exposure [43]. The micrographs from S1 showed a very smooth surface, presenting a uniform and continuous matrix before (T_0) and after the experiment (T_{180}) (Fig. 3). Based on the micrographs, there were no perceptible alterations in S1 surface during the experiment.

Considering the composition of S1 (see section 2.1), some studies suggested PLA hydrolysis at temperatures higher than those normally detected in aquatic ecosystems [44] and in a compost environment, especially during the thermophilic phase of the composting process [45]. However, there are few studies investigating the degradation behavior of PLA in aquatic environments [35]. Therefore, the biodegradability of PLA in marine systems is still subject to debate.

From SEM images obtained for S2, a spheroid shaped phase distributed in the polymer matrix was observed. Such spheroids are typically found in thermoplastic starch, which is probably related to the starch phase of the material. After immersion (T_{180}), the size of spheres decreased and cavities of 5 μm , in average, were observed (Fig. 3). Similarly, an aging evaluation using PP/starch-based additive was performed in soils showing that the starch phase is the first to degrade, without affecting the PP matrix [37]. Moreover, SEM images examined by Gómez et al. [46], confirmed no degradation of polypropylene in environmental conditions, even after adjustments with additives meant to confer biodegradability. Indeed, PP based products are not considered biodegradable [37,38].

Before the test (T_0), the surface of S3 presented uniformity. However, the morphology, revealed by SEM after 180 days of immersion, showed an irregular surface containing grooves, cavities ranging from 10 to 15 μm and lighter areas (Fig. 3). According to Oliveira et al. [40], these findings suggests biodegradation. Tosin and colleagues [47] reported complete visual degradation of PBAT/starch bags after 9 months exposed to marine sedimentary conditions. In addition, this blend was evaluated in composting using SEM images, which confirmed a substantial biodegradation [46]. Thus, morphological alterations observed in S3 are in agreement with changes in chemical structure detected by the CI. These results are in further accordance with recent studies, suggesting that PBAT/starch blends presents great potential to replace ordinary polymers [39,46,48].

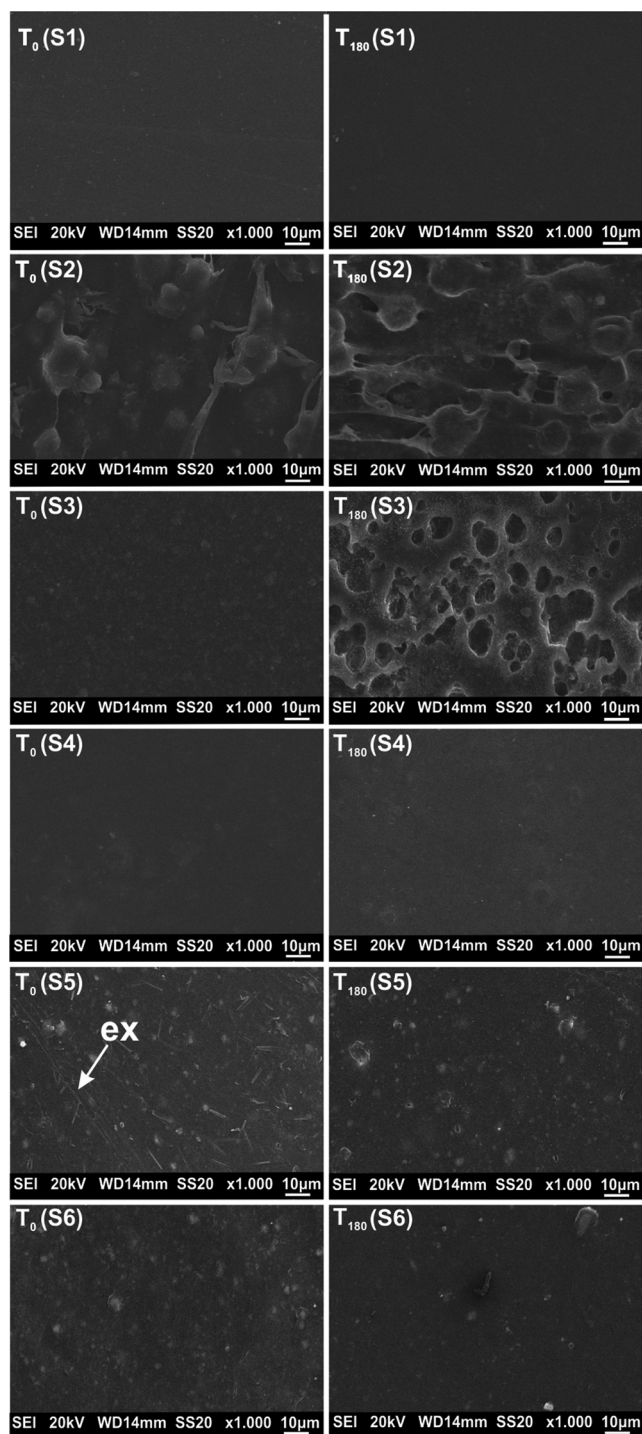


Fig. 3. Micrographs of the surface of studied samples obtained before (T_0) and after (T_{180}) immersion in seawater. Arrow indicate extrusion mark.

SEM images analyzed for S4, S5 and S6 presented relatively smooth and uniform surfaces before (T_0) and after (T_{180}) the experiment (Fig. 3). Characteristic cracks that suggest aging of the polymer and, moreover, mechanical and oxidative weathering were not apparent on the plastic surface [43]. On the other hand, some imperfections on the sample surfaces were observed in S5 before the aging test (see arrow in Fig. 3). These alterations may be associated with marks of the extrusion process, additives or distribution of surface charges, as observed by Parandoush and Lin [49]. These observations reinforce the results from FTIR, which showed stability in the chemical structure of S4, S5 and S6,

even after 180 days exposure.

3.3. Evaluation of the plastic surfaces by EDS

As suggested by Palazzo et al. [50] energy dispersive spectroscopy provides analyses related to composition of inorganic surfaces. Therefore, EDS enables identification and quantification of additives used in the material formulation. These pro-oxidant additives are usually added to the polymers to start a cleavage chain and degradation process [21]. Hence, degradation of the material is quickly initiated [22], resulting in fragments (microplastic and metals) which remain in the environment [51]. Some studies have criticized the use of these materials due to the formation of microplastic [21]. The present study observed that biodegradable polymeric samples (S1 and S3) presented only C and O in their compositions (Fig. 4). The other samples (S2, S4, S5 and S6) showed inorganic ions (Mg, Al, Ca, Ti and Si) distributed on the polymer's surface, which are frequently observed in oxo-biodegradable polymers, such as PE and PS [20,21]. In the sample S4, the peaks corresponding to Al, observed in T_0 and T_{180} , are probably due to the presence of an aluminized coating in this bag. Moreover, the Al decrease detected after the experiment is a result of the element leaching to seawater. The SEM images obtained for S5 before the experiment (T_0) presented granular structures, probably due to calcium ions particles mapped by EDS images (Fig. 5). These calcium peaks were also detected in S2, S5 and S6, having been originated from calcite crystals which are the most common inorganic fillers used in plastic resins to reduce the costs of production [43,52]. After 180 days, particles composed of inorganic ions such as Na, K, Si, Al, Mg and Cl, were found in S2, S3, S4 and S5. According to Kedzierski et al. [52], during aging experiments using seawater the emergence of cavities on the polymer's surface allows the entrapment of small particles to come from exposure media. Moreover, in the EDS map obtained in T_0 , some particles exhibiting high amounts of titanium in S2, S5 and S6 (Fig. 5) were detected. Titanium oxides have been used in plastic formulations as UV stabilizers or whitening agents [53] and as effective photocatalytic bactericide in food packaging [3]. In this regard, Marisa et al. [54] suggests that TiO_2 may source a potential risk for filter-feeding animals in the marine environment. Nevertheless, Andrady et al. [55] pointed out that environmental release of additives from plastics in aquatic systems may produce adverse impacts on marine biota related to their concentration and toxicity.

3.4. Greenwashing evaluation

Surface changes and alterations in chemical composition have been used as indicatives of biodegradation, as described by several studies [42,52,56]. Thus, based in our results, S2, S4, S5 and S6 cannot be considered biodegradable, although claiming such status. Considering the seven sins of greenwashing listed in the protocol issued by Terra-Choice Environmental Marketing Agency [25,30,57], the manufacturers of these products are engaging in greenwashing practices (Table 3). Therefore, these items marketed in the major economies of the American continent may induce consumers to a misleading act of consumption.

Although poly(lactic acid) (PLA) is known as biodegradable polymer, the time spent for its total degradation in real environmental conditions is still uncertain [34,58]. Our results based in CI and SEM analyses performed before and after the experiment showed no degradation evidences for S1. This observation is consistent with several studies which investigated PLA in environmental conditions [29,33,34]. No greenwashing practices were detected in S1, since the product label complies with chemical and structural characterizations. In addition, PLA was developed to be a biodegradable polymer, although this property remains questionable for marine environments [33,56]. A study involving the biodegradation of PLA revealed that, in soils and wastewater sludges, some bacteria (biofilm) adhere to the

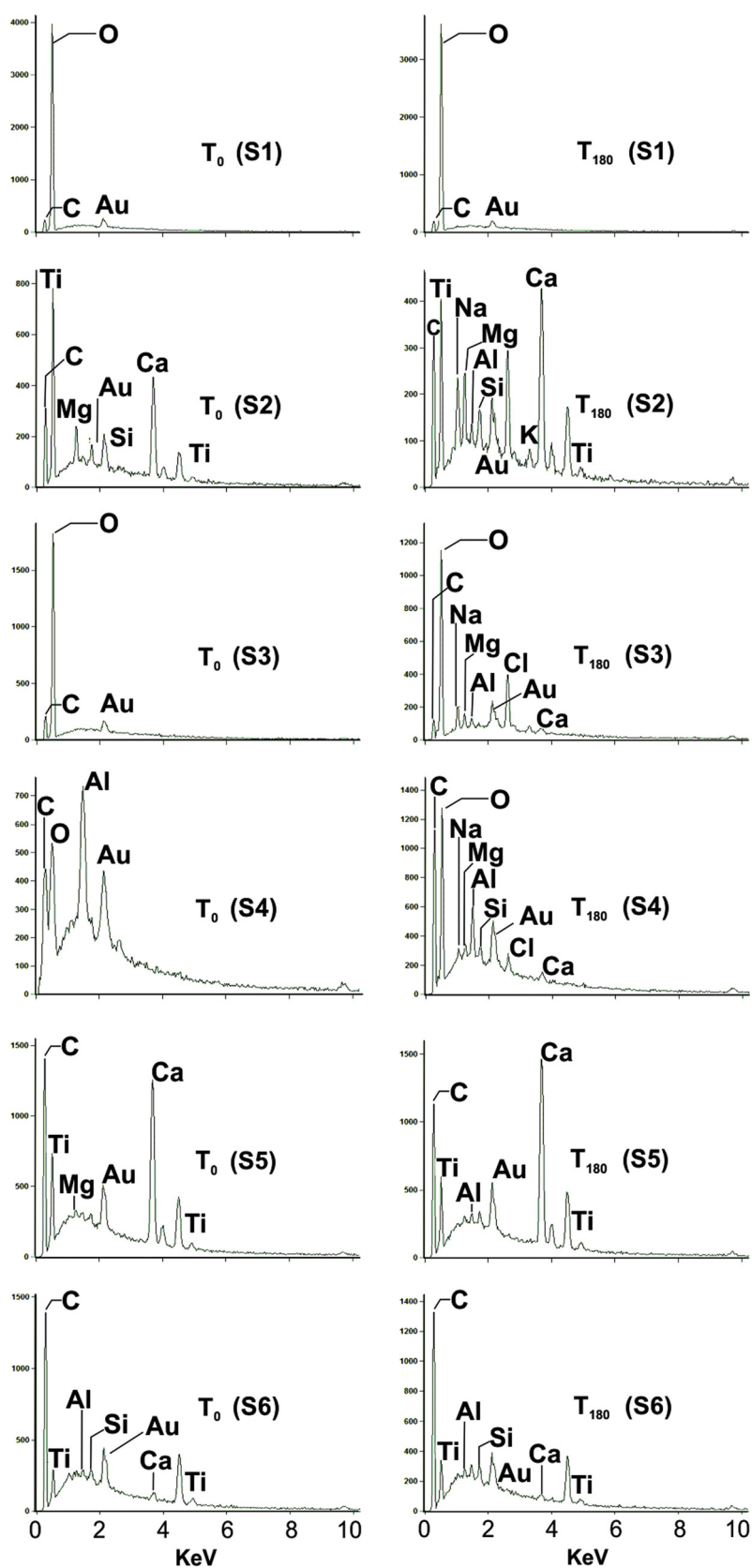


Fig. 4. Composition of inorganic surfaces provided by energy dispersive spectroscopy (EDS) for the studied samples before (T₀) and after (T₁₈₀) immersion in seawater.

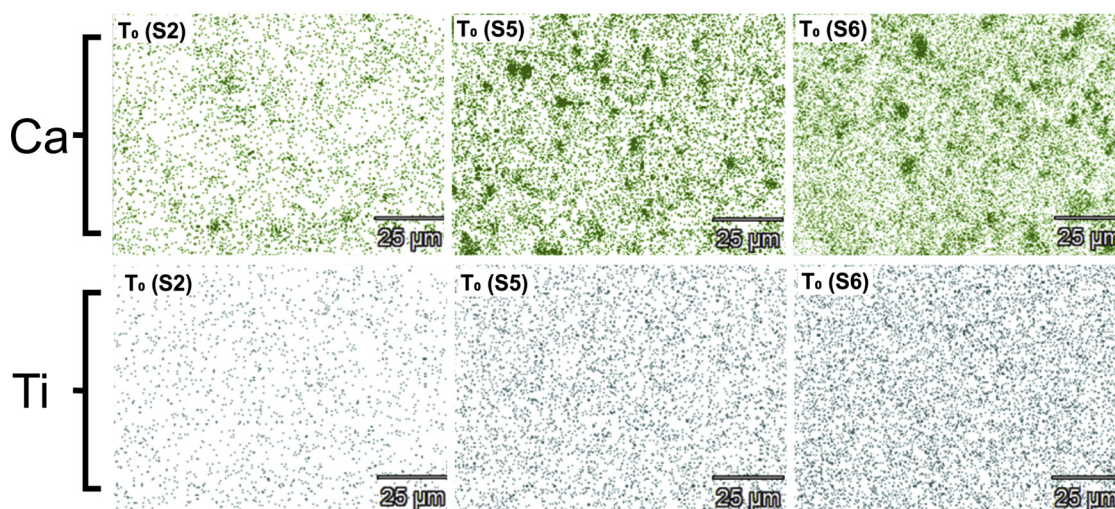


Fig. 5. Mapping of the occurrence of calcium (Ca) and titanium (Ti) particles, obtained by EDS, on the surface of samples S2, S5 and S6.

surface of PLA samples, suggesting a biodegradation process [59]. However, studies investigating aging of PLA by immersion in sea water indicated that short periods (5–10 weeks) at natural environmental temperatures are not sufficient to produce an effective degradation [58,60]. To improve degradation rates of PLA in natural environments, composites using natural fibers and materials of vegetal origin, such as cellulose, have been proposed as alternatives [33,61]. Moreover, the use of blends of PLA/starch have also showed a higher rate of biodegradation when compared with pure PLA under outdoor soil conditions [58]. Thus, despite the low performance of pure PLA biodegradation in marine environments, information on appropriate disposal sites should be added to the marketed products.

The cup labeled as sample S2 is sold as a biodegradable product and, according to manufacturers, is composed of a mixture of 60–75% starch, 5% PP, 10–15% PLA, ethylene vinyl acetate, glycerol monoesters and several additives. FTIR spectra presented clear PP fractions, but no PLA bands were found. From these results, a divergence between the manufacturer's information and the actual composition was evidenced, characterizing the following greenwashing practices: hidden trade-off and no proof and vagueness (Table 4). On the other hand, the bag S3 was the only sample that presented visual, chemical and morphological modifications during the experiment, being completely degraded after almost 180 days of aging. Accordingly, no greenwashing practices were detected in S3.

The most evident greenwashing cases were observed in the plastic bags analyzed as S4, S5 and S6. For these bags, the manufacturers used a green marketing strategy, reporting those to be biodegradable or

100% degradable products (Table 4). However, FTIR spectra indicated that all of them are composed by PE, an ordinary non-biodegradable polymer [46] which did not present significant chemical modifications after aging. In the case of S4, the bag sold by a Brazilian manufacturer uses a persuasive green marketing slogan, with a sentence freely translated as “our bag is as biodegradable as a leaf from a tree” in their website [62]. The inadequate use of green marketing is misleading to consumers and may lead people to discard these materials improperly [21]. In addition, these strategies can also positively influence purchase decisions [23]. Indeed, an evaluation performed in 2009 pointed out, over 98% of the 2219 products surveyed in North America committed at least one greenwashing sin [26,30]. These practices are highly counterproductive in view of the global public policies recently adopted to control plastic pollution.

4. Conclusions

The present study showed, through a 180 days exposure protocol in natural seawater, that 4 of the 6 samples of plastic products claiming biodegradable or compostable status did not display evidences of chemical and morphological degradation. These cups and bags composed by PE and PP are marketed in the three largest economies of the American continent (Canada, USA and Brazil). Pondering upon the greenwashing sins, these items may induce consumers to oblige to two different mistakes: misleading purchase decision and improper discharge of products. In both cases, the practice of greenwashing is highly counterproductive in views of current policies, which aim to reduce

Table 4

Greenwashing Sins detected in the analyzed samples based in the protocol issued by TerraChoice Environmental Marketing Agency.

| Sample | Claim (country of origin) | Greenwashing practice | Justification |
|--------|---|---|---|
| S1 | Renewable and compostable (USA) | | – |
| S2 | Biodegradable formed by bioplastic (Brazil's website) | hidden trade-off no proof vagueness | Contains titanium in the formulation. There is no evidence or certification that blends from TPS/PP are 100% biodegradable. The material is not produced from only natural sources. |
| S3 | Compostable for garbage disposal (Canada) | | – |
| S4 | Biodegradable (Brazil) | no proof vagueness | PE is not a biodegradable polymer. Product labeled as biodegradable and compostable. |
| S5 | Biodegradable (USA) | hidden trade-off no proof vagueness | Contains titanium in formulation. PE is not a biodegradable polymer. Product labeled as biodegradable and compostable. |
| S6 | 100% degradable (USA) | hidden trade-off no proof vagueness | Contains titanium in formulation. PE is not a biodegradable polymer. Product labeled as biodegradable and compostable. |

global plastic pollution. Thus, considering the technologies currently available to identify polymers, a strict control should be exercised over products that claim a biodegradable status, and such strategies should be adopted before consumers' confidence is lost due to this environmental rip off.

Acknowledgments

M. Nazareth was sponsored by Coordination of Improvement of Higher Education Personnel (CAPES). I.B. Castro was sponsored by CNPq (PQ 306486/2015-6). We thank the staff of the bioassay laboratory of the Universidade Federal de São Paulo for the technical support during the experiments. We also thank Paula C. Jimenez for English revision and Brazilian research agencies CAPES, CNPq and FAPERJ for financial support.

References

- N.A. Welden, P.R. Cowie, Degradation of common polymer ropes in a sublittoral marine environment, *Mar. Pollut. Bull.* 118 (2017) 248–253, <https://doi.org/10.1016/j.marpolbul.2017.02.072>.
- P.P. Gandara e Silva, C.R. Nobre, P. Resaffe, C.D.S. Pereira, F. Gusmão, Leachate from microplastics impairs larval development in brown mussels, *Water Res.* 106 (2016) 364–370, <https://doi.org/10.1016/j.watres.2016.10.016>.
- J.P. da Costa, P.S.M. Santos, A.C. Duarte, T. Rocha-Santos, (Nano)plastics in the environment – sources, fates and effects, *Sci. Total Environ.* 566–567 (2016) 15–26, <https://doi.org/10.1016/j.scitotenv.2016.05.041>.
- J. Zalasiewicz, C.N. Waters, J.A. Ivar do Sul, P.L. Corcoran, A.D. Barnosky, A. Cearreta, M. Edgeworth, A. Galuszka, C. Jeandel, R. Leinfelder, J.R. McNeill, W. Steffen, C. Summerhayes, M. Waprich, M. Williams, A.P. Wolfe, Y. Yonon, The geological cycle of plastics and their use as a stratigraphic indicator of the anthropocene, *Anthropocene* 13 (2016) 4–17, <https://doi.org/10.1016/j.ancene.2016.01.002>.
- E. Balestri, V. Menicagli, F. Vallerini, C. Lardicci, Biodegradable plastic bags on the seafloor: a future threat for seagrass meadows? *Sci. Total Environ.* 605–606 (2017) 755–763, <https://doi.org/10.1016/j.scitotenv.2017.06.249>.
- Q. Chen, D. Yin, Y. Jia, S. Schiwy, J. Legradi, S. Yang, H. Hollert, Enhanced uptake of BPA in the presence of nanoplastics can lead to neurotoxic effects in adult zebrafish, *Sci. Total Environ.* 609 (2017) 1312–1321, <https://doi.org/10.1016/j.scitotenv.2017.07.144>.
- M. Landon-Lane, Corporate social responsibility in marine plastic debris governance, *Mar. Pollut. Bull.* 127 (2018) 310–319, <https://doi.org/10.1016/j.marpolbul.2017.11.054>.
- D.K.A. Barnes, F. Galgani, R.C. Thompson, M. Barlaz, Accumulation and fragmentation of plastic debris in global environments, *Philos. Trans. R. Soc. Lond. B: Biol. Sci.* 364 (2009) 1985–1998, <https://doi.org/10.1098/rstb.2008.0205>.
- C. Munari, V. Infantini, M. Scoponi, E. Rastelli, C. Corinaldesi, M. Mistri, Microplastics in the sediments of Terra Nova Bay (Ross Sea, Antarctica), *Mar. Pollut. Bull.* 122 (2017) 161–165, <https://doi.org/10.1016/j.marpolbul.2017.06.039>.
- V. Fischer, N.O. Elsner, N. Brenke, E. Schwabe, A. Brandt, Plastic pollution of the Kuril–Kamchatka Trench area (NW pacific), *Deep Sea Res. Part II Top. Stud. Oceanogr.* 111 (2015) 399–405, <https://doi.org/10.1016/j.dsr2.2014.08.012>.
- C.G. Avio, S. Gorbí, F. Regoli, Plastics and microplastics in the oceans: from emerging pollutants to emerged threat, *Mar. Environ. Res.* 128 (2017) 2–11, <https://doi.org/10.1016/j.marenvres.2016.05.012>.
- D. Xanthos, T.R. Walker, International policies to reduce plastic marine pollution from single-use plastics (plastic bags and microbeads): a review, *Mar. Pollut. Bull.* 118 (2017) 17–26, <https://doi.org/10.1016/j.marpolbul.2017.02.048>.
- O. Alam, M. Billah, D. Yajie, Characteristics of plastic bags and their potential environmental hazards, *Resour. Conserv. Recycl.* 132 (2018) 121–129, <https://doi.org/10.1016/j.resconrec.2018.01.037>.
- T.P. Wagner, Reducing single-use plastic shopping bags in the USA, *Waste Manag.* 70 (2017) 3–12, <https://doi.org/10.1016/j.wasman.2017.09.003>.
- R. Geyer, J.R. Jambeck, K.L. Law, Production, use, and fate of all plastics ever made, *Sci. Adv.* 3 (2017), <https://doi.org/10.1126/sciadv.1700782>.
- R. Spranz, A. Schlüter, B. Vollan, Morals, money or the master: the adoption of eco-friendly reusable bags, *Mar. Policy* 96 (2018) 270–277, <https://doi.org/10.1016/j.marpol.2018.01.029>.
- S.M. Emadian, T.T. Onay, B. Demirel, Biodegradation of bioplastics in natural environments, *Waste Manag.* 59 (2017) 526–536, <https://doi.org/10.1016/j.wasman.2016.10.006>.
- T. O'Brine, R.C. Thompson, Degradation of plastic carrier bags in the marine environment, *Mar. Pollut. Bull.* 60 (2010) 2279–2283, <https://doi.org/10.1016/j.marpolbul.2010.08.005>.
- B. Laycock, M. Nikolic, J.M. Colwell, E. Gauthier, P. Halley, S. Bottle, G. George, Lifetime prediction of biodegradable polymers, *Polym. Sci.* 71 (2017) 144–189, <https://doi.org/10.1016/j.progpolymsci.2017.02.004>.
- T. Ojeda, A. Freitas, E. Dalmolin, M.D. Pizzol, L. Vignol, J. Melnik, R. Jacques, F. Bento, F. Camargo, Abiotic and biotic degradation of oxo-biodegradable foamed polystyrene, *Polym. Degrad. Stab.* 94 (2009) 2128–2133, <https://doi.org/10.1016/j.polyimdegradstab.2009.09.012>.
- M. Musiol, J. Ryzd, H. Janeczek, I. Radecka, G. Jiang, M. Kowalczyk, Forensic engineering of advanced polymeric materials part IV: case study of oxo-biodegradable polyethylene commercial bag – aging in biotic and abiotic environment, *Waste Manag.* 64 (2017) 20–27, <https://doi.org/10.1016/j.wasman.2017.03.043>.
- B. Eyheraguibel, M. Leremboure, M. Traikia, M. Sancelme, S. Bonhomme, D. Fromageot, J. Lemaire, J. Lacoste, A.M. Delort, Environmental scenario for the degradation of oxo-polymers, *Chemosphere* 198 (2018) 182–190, <https://doi.org/10.1016/j.chemosphere.2018.01.153>.
- N. Koenig-Lewis, A. Palmer, J. Dermody, A. Urbye, Consumers' evaluations of ecological packaging – rational and emotional approaches, *J. Environ. Psychol.* 37 (2014) 94–105, <https://doi.org/10.1016/j.jenvp.2013.11.009>.
- C. Fuentes, How green marketing works: practices, materialities, and images, *Scand. J. Manag. Stud.* 31 (2015) 192–205, <https://doi.org/10.1016/j.scaman.2014.11.004>.
- C. Blome, K. Foerstl, M.C. Schleper, Antecedents of green supplier championing and greenwashing: an empirical study on leadership and ethical incentives, *J. Clean. Prod.* 152 (2017) 339–350, <https://doi.org/10.1016/j.jclepro.2017.03.052>.
- Dahl Richard, Green washing, *Environ. Health Perspect.* 118 (2010) A246–A252, <https://doi.org/10.1289/ehp.118-a246>.
- M. Lu, P. Liu, S. Zhang, W. Yuan, S. Ding, F. Wang, Y. Ding, M. Yang, Anti-aging behavior of amino-containing co-condensed nanosilica in polyethylene, *Polym. Degrad. Stab.* 154 (2018) 137–148, <https://doi.org/10.1016/j.polyimdegradstab.2018.05.028>.
- J. Brandon, M. Goldstein, M.D. Ohman, Long-term aging and degradation of microplastic particles: comparing in situ oceanic and experimental weathering patterns, *Mar. Pollut. Bull.* 110 (2016) 299–308, <https://doi.org/10.1016/j.marpolbul.2016.06.048>.
- M. Oliveira, E. Santos, A. Araújo, G.J.M. Fachine, A.V. Machado, G. Botelho, The role of shear and stabilizer on PLA degradation, *Polym. Test.* 51 (2016) 109–116, <https://doi.org/10.1016/j.polymertesting.2016.03.005>.
- Greenwashing Report, The Sins of Greenwashing: Home and Family Edition, accessed 17 december 2019 (2009) <http://sinsogreenwashing.com/findings/the-seven-sins/index.html>.
- R.Y. Tabasi, A. Aiji, Selective degradation of biodegradable blends in simulated laboratory composting, *Polym. Degrad. Stab.* 120 (2015) 435–442, <https://doi.org/10.1016/j.polyimdegradstab.2015.07.020>.
- K. Janczak, K. Hryniewicz, Z. Znajewska, G. Dąbrowska, Use of rhizosphere microorganisms in the biodegradation of PLA and PET polymers in compost soil, *Int. Biodeterior. Biodegrad.* 130 (2018) 65–75, <https://doi.org/10.1016/j.ibiod.2018.03.017>.
- R.T. Martin, L.P. Camargo, S.A. Miller, Marine-degradable polylactic acid, *Green Chem.* 16 (2014) 1768–1773, <https://doi.org/10.1039/C3GC42604A>.
- X. Qi, Y. Ren, X. Wang, New advances in the biodegradation of Poly(lactic) acid, *Int. Biodeterior. Biodegrad.* 117 (2017) 215–223, <https://doi.org/10.1016/j.ibiod.2017.01.010>.
- M. Deroine, A. Le Duigou, Y.-M. Corre, P.-Y. Le Gac, P. Davies, G. César, S. Bruzard, Accelerated ageing of polylactide in aqueous environments: comparative study between distilled water and seawater, *Polym. Degrad. Stab.* 108 (2014) 319–329, <https://doi.org/10.1016/j.polyimdegradstab.2014.01.020>.
- M.R. Jung, F.D. Horgen, S.V. Orski, V. Rodriguez C, K.L. Beers, G.H. Balazs, T.T. Jones, T.M. Work, K.C. Brignac, S.-J. Royer, K.D. Hyrenbach, B.A. Jensen, J.M. Lynch, Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms, *Mar. Pollut. Bull.* 127 (2018) 704–716, <https://doi.org/10.1016/j.marpolbul.2017.12.061>.
- T.A. Oliveira, R.R. Oliveira, R. Barbosa, J.B. Azevedo, T.S. Alves, Effect of re-processing cycles on the degradation of PP/PBAT-thermoplastic starch blends, *Carbohydr. Polym.* 168 (2017) 52–60, <https://doi.org/10.1016/j.carbpol.2017.03.054>.
- W.H. Ferreira, R.R. Khalili, M.J.M. Figueira, C.T. Andrade, Effect of organoclay on blends of individually plasticized thermoplastic starch and polypropylene, *Ind. Crops Prod.* 52 (2014) 38–45, <https://doi.org/10.1016/j.indcrop.2013.10.016>.
- M.F.L. Oliveira, A.L. China, M.G. Oliveira, M.C.A.M. Leite, Biocomposites based on Ecobras matrix and vermiculite, *Mater. Lett.* 158 (2015) 25–28, <https://doi.org/10.1016/j.matlet.2015.05.030>.
- A. Cadenato, X. Ramis, J. Salla, J.M. Moranco, L. Contat-Rodrigo, A. Vallés-Lluch, R. Amparo, Calorimetric studies of PP/Mater-Bi blends aged in soil, *J. Appl. Polym. Sci.* 100 (2006) 3446–3453, <https://doi.org/10.1002/app.22084>.
- B.F. Bergel, S. Dias Osorio, L.M. da Luz, R.M.C. Santana, Effects of hydrophobized starches on thermoplastic starch foams made from potato starch, *Carbohydr. Polym.* 200 (2018) 106–114, <https://doi.org/10.1016/j.carbpol.2018.07.047>.
- A. Nauendorf, S. Krause, N.K. Bigalke, E.V. Gorb, S.N. Gorb, M. Haackel, M. Wahl, T. Treude, Microbial colonization and degradation of polyethylene and biodegradable plastic bags in temperate fine-grained organic-rich marine sediments, *Mar. Pollut. Bull.* 103 (2016) 168–178, <https://doi.org/10.1016/j.marpolbul.2015.12.024>.
- Z.-M. Wang, J. Wagner, S. Ghosal, G. Bedi, S. Wall, SEM/EDS and optical microscopy analyses of microplastics in ocean trawl and fish guts, *Sci. Total Environ.* 603–604 (2017) 616–626, <https://doi.org/10.1016/j.scitotenv.2017.06.047>.
- N. Lesaffre, S. Bellayer, H. Vezin, G. Fontaine, M. Jimenez, S. Bourbigot, Recent advances on the ageing of flame retarded PLA: effect of UV-light and/or relative humidity, *Polym. Degrad. Stab.* 139 (2017) 143–164, <https://doi.org/10.1016/j.polyimdegradstab.2017.04.007>.
- P. Stloukal, A. Kalendova, H. Mattausch, S. Laske, C. Holzer, M. Koutny, The influence of a hydrolysis-inhibiting additive on the degradation and biodegradation of

- PLA and its nanocomposites, *Polym. Test.* 41 (2015) 124–132, <https://doi.org/10.1016/j.polymertesting.2014.10.015>.
- [46] E.F. Gómez, F.C. Michel, Biodegradability of conventional and bio-based plastics and natural fiber composites during composting, anaerobic digestion and long-term soil incubation, *Polym. Degrad. Stab.* 98 (2013) 2583–2591, <https://doi.org/10.1016/j.polymdegradstab.2013.09.018>.
- [47] M. Tosin, M. Weber, M. Siotto, C. Lott, F. Degli Innocenti, Laboratory test methods to determine the degradation of plastics in marine environmental conditions, *Front. Microbiol.* 3 (2012), <https://doi.org/10.3389/fmicb.2012.00225>.
- [48] L. Chen, R.E.O. Pelton, T.M. Smith, Comparative life cycle assessment of fossil and bio-based polyethylene terephthalate (PET) bottles, *J. Clean. Prod.* 137 (2016) 667–676, <https://doi.org/10.1016/j.jclepro.2016.07.094>.
- [49] P. Parandoush, D. Lin, A review on additive manufacturing of polymer-fiber composites, *Compos. Struct.* 182 (2017) 36–53, <https://doi.org/10.1016/j.compstruct.2017.08.088>.
- [50] E. Palazzo, A. Amadasi, M. Boracchi, G. Gentile, F. Maciocco, M. Marchesi, R. Zoja, The detection of metallic residues in skin stab wounds by means of SEM-EDS: a pilot study, *Sci. Justice* 58 (2018) 232–236, <https://doi.org/10.1016/j.scijus.2017.12.007>.
- [51] J.C. Philp, A. Bartsev, R.J. Ritchie, M.-A. Baucher, K. Guy, Bioplastics science from a policy vantage point, *New Biotechnol.* 30 (2013) 635–646, <https://doi.org/10.1016/j.nbt.2012.11.021>.
- [52] M. Kedzierski, M. D'Almeida, A. Magueresse, A. Le Grand, H. Duval, G. César, O. Sire, S. Bruzard, V. Le Tilly, Threat of plastic ageing in marine environment. Adsorption/desorption of micropollutants, *Mar. Pollut. Bull.* 127 (2018) 684–694, <https://doi.org/10.1016/j.marpolbul.2017.12.059>.
- [53] I. Shepa, E. Mudra, M. Vojtko, P. Tatarko, V. Girman, O. Milkovic, T. Sopcak, V. Medvecká, J. Dusza, Preparation of highly crystalline titanium-based ceramic microfibers from polymer precursor blend by needle-less electrospinning, *Ceram. Int.* 44 (2018) 17925–17934, <https://doi.org/10.1016/j.ceramint.2018.06.268>.
- [54] I. Marisa, V. Matozzo, A. Martucci, E. Franceschinis, N. Brianese, M.G. Marin, Bioaccumulation and effects of titanium dioxide nanoparticles and bulk in the clam *Ruditapes philippinarum*, *Mar. Environ. Res.* 136 (2018) 179–189, <https://doi.org/10.1016/j.marenvres.2018.02.012>.
- [55] A.L. Andrad, The plastic in microplastics: a review, *Mar. Pollut. Bull.* 119 (2017) 12–22, <https://doi.org/10.1016/j.marpolbul.2017.01.082>.
- [56] E. Castro-Aguirre, R. Auras, S. Selke, M. Rubino, T. Marsh, Insights on the aerobic biodegradation of polymers by analysis of evolved carbon dioxide in simulated composting conditions, *Polym. Degrad. Stab.* 137 (2017) 251–271, <https://doi.org/10.1016/j.polymdegradstab.2017.01.017>.
- [57] R. Guo, W. Zhang, T. Wang, C.B. Li, L. Tao, Timely or considered? Brand trust repair strategies and mechanism after greenwashing in China—from a legitimacy perspective, *Ind. Mark. Manag.* 72 (2018) 127–137, <https://doi.org/10.1016/j.indmarman.2018.04.001>.
- [58] S. Lv, Y. Zhang, J. Gu, H. Tan, Biodegradation behavior and modelling of soil burial effect on degradation rate of PLA blended with starch and wood flour, *Colloids Surf. B: Biointerfaces* 159 (2017) 800–808, <https://doi.org/10.1016/j.colsurfb.2017.08.056>.
- [59] T. Bupachat, N. Sombatsompob, B. Prapagdee, Isolation and role of polylactic acid-degrading bacteria on degrading enzymes productions and PLA biodegradability at mesophilic conditions, *Polym. Degrad. Stab.* 152 (2018) 75–85, <https://doi.org/10.1016/j.polymdegradstab.2018.03.023>.
- [60] H. Tsuji, K. Suzuyoshi, Environmental degradation of biodegradable polyesters 2. Poly(ϵ -caprolactone), poly[(R)-3-hydroxybutyrate], and poly(L-lactide) films in natural dynamic seawater, *Polym. Degrad. Stab.* 75 (2002) 357–365, [https://doi.org/10.1016/S0141-3910\(01\)00239-7](https://doi.org/10.1016/S0141-3910(01)00239-7).
- [61] M. Murariu, P. Dubois, PLA composites: from production to properties, *Adv. Drug Deliv. Rev.* 107 (2016) 17–46, <https://doi.org/10.1016/j.addr.2016.04.003>.
- [62] D2W, RES d2w™ Biodegradável, (2018) (Accessed 9 March 2018), <http://www.resbrasil.com.br/embalagens-plasticas-inteligentes/res-d2w-biodegradavel/>.