



## Short Communication

## Artificial weathering of plastics used in oyster farming

Marion Hingant <sup>a,\*</sup>, Stéphanie Mallarino <sup>b</sup>, Egle Conforto <sup>b</sup>, Emmanuel Dubillot <sup>a</sup>, Pierrick Barbier <sup>d</sup>, Arno Bringer <sup>a,c,1</sup>, Hélène Thomas <sup>a,1</sup>

<sup>a</sup> Littoral Environnement et Sociétés (LIENSs), UMRI 7266 CNRS - La Rochelle Université, 2 rue Olympe de Gouges, F-17042 La Rochelle Cedex 01, France

<sup>b</sup> Laboratoire des Sciences de l'Ingénieur pour l'Environnement (LaSIE), UMR 7356 CNRS - La Rochelle Université, Avenue Michel Crépeau, 17042 La Rochelle, France

<sup>c</sup> Qualyse, 5 Allée de l'Océan, 17000 La Rochelle, France

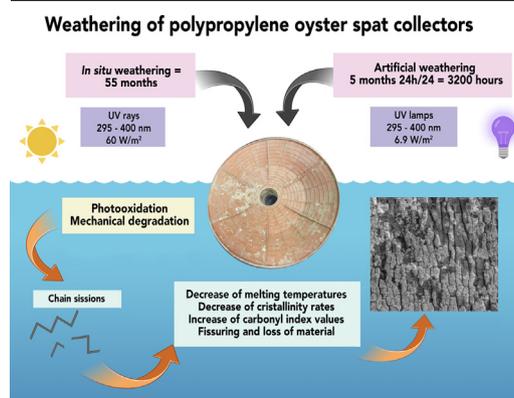
<sup>d</sup> Centre pour l'Aquaculture, la Pêche et l'Environnement de Nouvelle-Aquitaine (CAPENA), Prise de Terdoux, 17480 Le Château d'Oléron, France



## HIGHLIGHTS

- Oyster spat collectors were notably damaged after 55 months of *in situ* weathering.
- Artificial weathering with UV lamp (295–400 nm) was compared to *in situ* weathering.
- Photooxidation was the main weathering mechanism for polypropylene oyster spat collectors.
- This work orients professionals to better storage of these collectors by protection from UV rays.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

Editor: Yolanda Picó

## Keywords:

Oyster farming  
Polypropylene  
Photooxidation  
*In situ* weathering  
Artificial weathering

## ABSTRACT

With the omnipresence of plastic litter from oyster farming in marine coastal areas, the objective of this work was to better understand the weathering of plastics used in this field, focusing on oyster spat collectors. During their use, around fifteen years, collectors made of polypropylene (PP) undergo numerous degradations, alternatively submerged, emerged in seawater, and stored outdoor until the next cycle. They weaken, crack, break, end up fragmenting and disseminated in the environment as microplastics associated to persistent organic pollutants. In this work, a comparison of 55 months of *in situ* weathering with five months of artificial weathering in air or in artificial seawater in a home-made UV chamber was conducted to better understand the mechanisms involved. Chemical, thermal and surface characterizations of virgin and weathered samples were conducted using Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC) and Environmental Scanning Electron Microscopy (ESEM). After 55 months of *in situ* weathering, collectors were notably damaged with large fissures and loss of microplastics (MPs) associated with an increase of carbonyl index values and a decrease of melting temperatures and crystallinity rates. Considering only UV irradiation, five months of artificial weathering at 30 °C under continuous irradiation of 6.9 W/m<sup>2</sup> under UV lamps (295–400 nm) reproduced approximately 4.4 months of natural sunlight. Artificial weathering confirmed that photooxidation by combined effects of UV rays and oxygen was the main weathering mechanism and was reduced in seawater. These results help to understand the mechanisms involved in the weathering of these collectors in the marine environment and provide valuable information for industrials and professionals. Our study suggests a better storage away from UV rays and a reduction of the duration of use compared to current practices.

Abbreviations: PP, polypropylene; MPs, microplastics; POPs, persistent organic pollutants.

\* Corresponding author.

E-mail address: [marion.hingant@univ-lr.fr](mailto:marion.hingant@univ-lr.fr) (M. Hingant).

<sup>1</sup> Equal contribution.

<http://dx.doi.org/10.1016/j.scitotenv.2023.161638>

Received 7 November 2022; Received in revised form 3 January 2023; Accepted 12 January 2023

Available online 14 January 2023

0048-9697/© 2023 Elsevier B.V. All rights reserved.

## 1. Introduction

At now, a total of five ocean gyres with high concentrations of plastics debris have been identified (Avio et al., 2017; Law et al., 2010). 80 % of these marine debris are land-based sources and 20 % are ocean-based sources like fisheries and maritime activities (Avio et al., 2017; Bringer et al., 2021b). Since the arrival of plastic from petrochemicals in the 1950s, professionals in aquaculture activities have progressively turned to this new material, which is more resistant, durable, and economical. Due to their stability, plastics persist in the environment for hundreds of years (Cai et al., 2018; Gewert et al., 2015). Degradation of plastics can proceed by chemical, physical degradations and biological degradations (Gewert et al., 2015; Singh and Sharma, 2008; Song et al., 2017). Degradation rates are dependent on the manufacturing process (Han et al., 2018), the presence of stabilizers, additives and the weathering conditions including sunlight, temperature, and mechanical stress (Avio et al., 2017; Kalogerakis et al., 2017; Masry et al., 2021; Rajakumar et al., 2009). In seawater, degradation rates are lower and more uniform compared to landfill due to lower and less variable conditions as UV irradiation, oxygen content and temperatures (Cai et al., 2018; Gewert et al., 2015). But in any cases, degradations finally lead to the release of microplastics (MPs) in the environment which can be accumulated by a wide range of marine organisms from zooplankton (Cole et al., 2013), to fishes through bivalves (Bringer et al., 2021a) being transferred along food chains until humans (Avio et al., 2017). Some studies have reported the presence of MPs in human organs (Hermabessiere et al., 2017), blood (Leslie et al., 2022) and feces (Zhang et al., 2021). MPs exposure by ingestion, inhalation or dermal contact can cause physical damages, with oxidative stress, or inflammatory lesions (Prata et al., 2020).

Furthermore, plastics are associated with additives and stabilizers (Zhang et al., 2021). Plasticizers as di-n-butyl phthalate, antioxidant agents as bisphenol A, flame retardants as tris-2-chloro-ethyl phosphate, are chemicals added during the manufacturing process to obtain certain desired properties (Avio et al., 2017; Masry et al., 2021). Because they are usually not covalently bonded to the polymers (Gewert et al., 2015; Paluselli et al., 2019), these chemicals can migrate from the polymeric matrix towards the surrounding environment. In seawater, leaching of these chemicals by diffusion is dependent on their solubility, their polarity, and their affinity to the matrix (Paluselli et al., 2019). Some of these chemicals are known to be harmful to the marine ecosystems and humans causing dysfunctions of the immune and reproductive systems, cancers and neurodegenerative disorders (Avio et al., 2017; Hermabessiere et al., 2017).

Plastics are also able to absorb various pollutants called persistent organic pollutants (POPs) present in the marine environment such as pesticides as dichlorodiphenyltrichloroethane, polycyclic hydrocarbons as naphthalene, and heavy metals as cadmium and lead for examples (Boucher et al., 2016; Gewert et al., 2015; Hermabessiere et al., 2017; Holmes et al., 2012; León et al., 2018; Paluselli et al., 2019). These pollutants can be ingested and bioaccumulated by marine organisms and humans, often vectorized by MPs (Avio et al., 2017; Gewert et al., 2015; Guo and Wang, 2019; Prata et al., 2020). The risks that MPs and these persistent organic pollutants (POPs) pose to marine life and humans are widely recognized and have been included in national and international marine protection strategies, policies, and legislation (EU Marine Strategy Framework Directive).

With nearly 30,000 tons of Pacific oysters *Crassostrea gigas* produced each year, the department of Charente-Maritime in France represents the first French production area with one third of the national production (AGRESTE 2019). Different types of plastics such as polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC) are now used at each stage of production. Oyster spat collection is the first phase of production in traditional oyster farming. Collectors have a specific design of a disc of 160 mm diameter, slightly concave, flexible and ribbed, with a thickness of 0.6 mm, designed in order to collect a maximum of oyster spats in seawater during the reproductive period between July and March. After collecting, collectors are taken out of seawater, oysters are detached and

then transferred to oyster bags. The environmental image of the profession is criticized today given the omnipresence of plastic waste from oyster farming in coastal areas. Around 200 tons of plastic waste from oyster farming, including 60 tons of oyster spat collectors, are found each year in the Atlantic south coast (National Establishment of Agricultural and Sea Products Report 2020). During their use around fifteen years, collectors made of PP or PE undergo numerous degradations. They weaken, crack, break, end up fragmenting, disseminating MPs and chemicals in the marine environment. The toxicity of weathered MPs and associated chemicals from oyster farming was recently evaluated on early stages of bivalve development (Bringer et al., 2021a). Dimethylphthalate used as plasticizer and naphthalene as polycyclic hydrocarbons absorbed in the marine environment have been identified on weathered oyster crops, collectors, and pipes (Bringer et al., 2021b). Faced with the growing risk associated to plastics used in oyster farming for marine life and humans, it is necessary understand and reduce their anthropogenic impacts.

*In situ* and artificial weathering of PP have been described in many studies (Badji et al., 2018; Lv et al., 2015; Rajakumar et al., 2009; Tang et al., 2019) but were never established for PP oyster spat collectors. These collectors are interesting because they have a chemical composition and mechanical properties, with additives and stabilizers designed for aquaculture activities specifications and because, *in fine*, oysters are destined for human consumption. In this work, a comparison of 55 months *in situ* weathering with five months of artificial weathering in a homemade UV chamber was conducted to better understand the mechanisms involved in PP collectors degradations. With the aim of understanding the mechanisms of degradation of these collectors in the marine environment, chemical, thermal, and structural characterizations of virgin and weathered collectors were performed using Environmental Scanning Electron Microscopy (ESEM), Differential Scanning Calorimetry (DSC), and Fourier Transform Infrared Spectroscopy (FTIR).

## 2. Materials and methods

### 2.1. Oyster collectors

#### 2.1.1. *In situ* weathering

In 2017, a project conducted by the Center for Aquaculture, Fisheries, and the Environment of Nouvelle-Aquitaine (CAPENA) had the objective to compare petrosourced and biosourced collectors in terms of oyster spat collection efficiencies. Collectors have a specific design of a disc of 160 mm diameter, slightly concave, flexible and ribbed, with a thickness of 0.6 mm. These collectors were immersed in the area of the Pertuis Charentais, in the French department Charente-Maritime (45°51'41.7"N 1°12'19.0"W) during three cycles of eight months collecting oyster spats in seawater between 2017 and 2020. These collectors were alternatively submerged and emerged in seawater during collection and were stored outdoors until the next collection cycle. Each cycle started in July and stopped in March. In total, these collectors spent 24 months in seawater, and 31 months stored outdoors until the start of this work in January 2022. A continuous environmental monitoring during *in situ* weathering measured seawater temperature from 6 to 21 °C, salinity from 26 to 34 g/L, outdoor temperature from 5 °C to 23 °C and a mean solar irradiance of 1200 kW/h/m<sup>2</sup>/year. Virgin collectors, as references, were stored indoors and protected from humidity and UV rays. Virgin and *in situ* weathered collectors were characterized by FTIR, DSC, and ESEM as described below.

#### 2.1.2. Artificial weathering

Inspired by ISO 4892:2016 part 3 and ATSM G154:06, a homemade UV chamber was equipped with five UV lamps with wavelength between 295 and 400 nm (KFMS reference PH710932 15 W). These UV lamps were selected because they can give a good reproduction of natural sunlight in the UV range (Andrade et al., 2019; Cai et al., 2018) and because this medium energy is particularly efficient in facilitating photodegradation of PP (Andrady, 2015). Virgin PP collectors were weathered under UV rays in two different conditions: in air (UV+) or immersed in artificial seawater

at 30 g/L (UV + /SW). Negative controls, not exposed to UV rays, were installed in a box in the chamber (UV – and UV – /SW). Artificial seawater was made by mixing milliQ water and commercial salt. Virgin PP collectors were installed directly under UV lamps at 15 cm (UV +) or in borosilicate crystallizers filled with 500 mL of 30 g/L of artificial seawater (SW) and closed with a borosilicate lid to limit evaporation but letting pass UV rays through. This experiment was conducted for five months, at 30 °C, under 24 h/24 continuous UV irradiation. Temperature was monitored weekly with a mercury thermometer. Intensity was monitored weekly with a radiometer (RS Pro reference IM-213) placed at 15 cm from the lamps and was approximately equal to 6.9 W/m<sup>2</sup> in an empty crystallizer and 3 W/m<sup>2</sup> in artificial seawater. Salinity was monitored weekly with a multiparameter (WMW reference Multi3430 with Tetracon 925 probe) and was adjusted to 30 g/L by adding milliQ water if necessary. Each month, one triplicate for each condition was removed and stored in glass petri dishes at 4 °C, in the dark, to stop weathering.

## 2.2. Characterization

### 2.2.1. Environmental Scanning Electron Microscopy (ESEM)

The scanning electron microscope used in this work is an Environmental FEI Quanta 200 — ESEM/FEG (LaSIE, La Rochelle University) working at 9 kV of electron beam accelerating voltage and 0.1 nA of beam current under 200 Pa of water vapor pressure in the specimen chamber (Conforto et al., 2015). Secondary electron-type images, providing topographical information from the surfaces, were obtained in environmental mode using a “Gaseous Large-Field” detector. The low-energy beam and environmental conditions used are necessary to observe plastic materials, which are thermally sensitive and poor electrical and thermal conductors, without any preparation. In fact, if a surface metallization (which is part of the sample preparation procedure) was performed, it could partially or totally mask cracks. The latter are an important parameter used to evaluate the weathering of plastic. Surface topography of different parts of virgin and weathered collectors was observed. We made sure that the results were coherent, homogeneous, and reproducible. Ten fissures lengths were measured on random fissures and averaged with FIJI software.

### 2.2.2. Fourier Transform Infrared Spectroscopy (FTIR)

In order to identify the different types of chemical bonds, FTIR was used. Infrared frequency identical to the vibrational frequency of a bond results in absorption, creating a spectrum acting as a molecular “fingerprint” of the sample. The position, shape, and intensity of peaks in the spectrum reveal details about the molecular structure of the sample. Different parts of virgin and weathered collectors were analyzed using a thermoscientific Nicolet iS50 FTIR spectrophotometer equipped with an attenuated total reflectance mode (ATR). We made sure that the results were coherent, homogeneous, reproducible. Each spectrum was recorded as the average of 32 scans in the spectral range of 500 to 4000 cm<sup>-1</sup>, with a spectral resolution at 4.0 cm<sup>-1</sup>. Ten spectra were done randomly at the surface of each sample averaged with a corrected baseline, and analyzed with Spectragryph 1.2 software.

### 2.2.3. Differential scanning calorimetry (DSC)

Specific temperatures of the samples such as melting temperature and crystallization, as well as the enthalpy values associated with these phenomena were examined on a differential scanning calorimeter TA Instrument Q100. Samples were cut, weighed, and heated from –60 °C to 210 °C in an aluminum pan, then cooled to 40 °C. All experiments were performed at a rate of 20 °C/min under nitrogen flow (50 mL/min) to avoid thermal degradation. For the sake of repeatability, at least two samples for each type of collector were used for the DSC measurements. The analysis of DSC thermograms was carried out with TA Universal Analysis software.

## 3. Results

### 3.1. Surface analysis

Surface images were obtained by using environmental scanning electron microscopy (ESEM). Virgin PP collectors exhibited relatively homogeneous, smooth and compact textures without any fissures (Fig. 1a). *In situ* weathered PP collectors (Fig. 1c and d) exhibited heterogeneous surfaces, with large and deep averaged fissures up to 24 μm. Loss of material was observed at lower magnification (Fig. 1d) caused by mechanical stress as tides, currents during submersion, wind and rain during emersion but also handling. This loss of material suggests a release of MPs in the environment. Crystals of sodium chloride salts and algae and diatom residues were also observed and confirmed that the collectors stayed in seawater. Artificially weathered collectors under UV rays (UV +) start fissuring after five months with the observation of 2 μm length fissures (Fig. 1b). No fissures were observed for the other conditions as negative control (UV –) and immersion in artificial seawater for five months (UV – /SW and UV + /SW) (Results not presented). Artificial weathering confirmed that fissuring started after five months exposed to UV rays.

### 3.2. Chemical analysis

The averaged infrared spectra of a virgin PP collector, used as reference, is presented in the Fig. 2 (blue). The spectra showed absorption peaks located at wavenumbers of 971, 995, 1167, 1375, 1454, 2838, 2865, 2918, and 2953 cm<sup>-1</sup> corresponding to specific vibrations of rocking, bending and stretching and identified as the native hydrocarbon bonds of virgin PP (C<sub>3</sub>H<sub>6</sub>)<sub>n</sub> (Badji et al., 2018; Tang et al., 2019). Photooxidation, by combined effects of UV rays and oxygen, is known to be the main weathering process for thermoplastics such as PP (Andrady, 2015; Gewert et al., 2015; Kalogerakis et al., 2017; Masry et al., 2021). UV radiation has sufficient energy to break the C—C and C—H bonds (Singh and Sharma, 2008). Diminution of C—C and C—H bonds on the *in situ* weathered collector (Fig. 2 — orange) were observed at wavenumbers between 2800 and 3000 cm<sup>-1</sup> confirming their break. The free radicals produced during photooxidation reacted freely with atmospheric oxygen to form hydroxyl groups (O—H) peaking at wavenumbers between 3000 and 3700 cm<sup>-1</sup> and carbonyl groups (C=O) including carboxylic acids and ketones peaking at wavenumber 1711 cm<sup>-1</sup>, esters and aldehydes peaking at wavenumber 1740 cm<sup>-1</sup> and lactones peaking at wavenumber 1780 cm<sup>-1</sup> (Badji et al., 2018; Lv et al., 2015; Masry et al., 2021). These new significant peaks at around wavenumbers 3000–3700 cm<sup>-1</sup> and 1500–1800 cm<sup>-1</sup> were identifiable on *in situ* and artificially weathered collector infrared spectra (Fig. 2) and their areas were a function of weathering conditions (Cai et al., 2018; Rajakumar et al., 2009; Tang et al., 2019).

The carbonyl index (CI) has been used to quantify the degree of weathering of various samples (Almond et al., 2020a, b; Badji et al., 2018; Julienne et al., 2019; Rajakumar et al., 2009; Song et al., 2017; Tang et al., 2019). This index is defined as the ratio of the integrated area of the carbonyl group peak at around wavenumbers 1700 cm<sup>-1</sup> to an internal constant peak. In this work, boundaries between wavenumbers 1390 and 1340 cm<sup>-1</sup> were chosen for the constant peak because it remained unchanged during weathering. Consequently, boundaries between wavenumbers 1820 and 1570 cm<sup>-1</sup> were chosen for the carbonyl peak. Carbonyl index of *in situ* and artificially weathered samples calculated on the average of ten spectra for each sample and after baseline correction are resumed in Table 1. Carbonyl index values for the virgin collector and negative control (UV –), as references, were similar and equal to 0.7 and 0.5 respectively. These values were not equal to zero probably due to thermal degradation of the material during injection. Negative control (UV –) also confirmed that no additional degradation occurred during the five months of artificial weathering. Consequently, only UV ray exposure and immersion in seawater can be considered in this experiment. After five months of artificial weathering in seawater (UV – /SW), the carbonyl

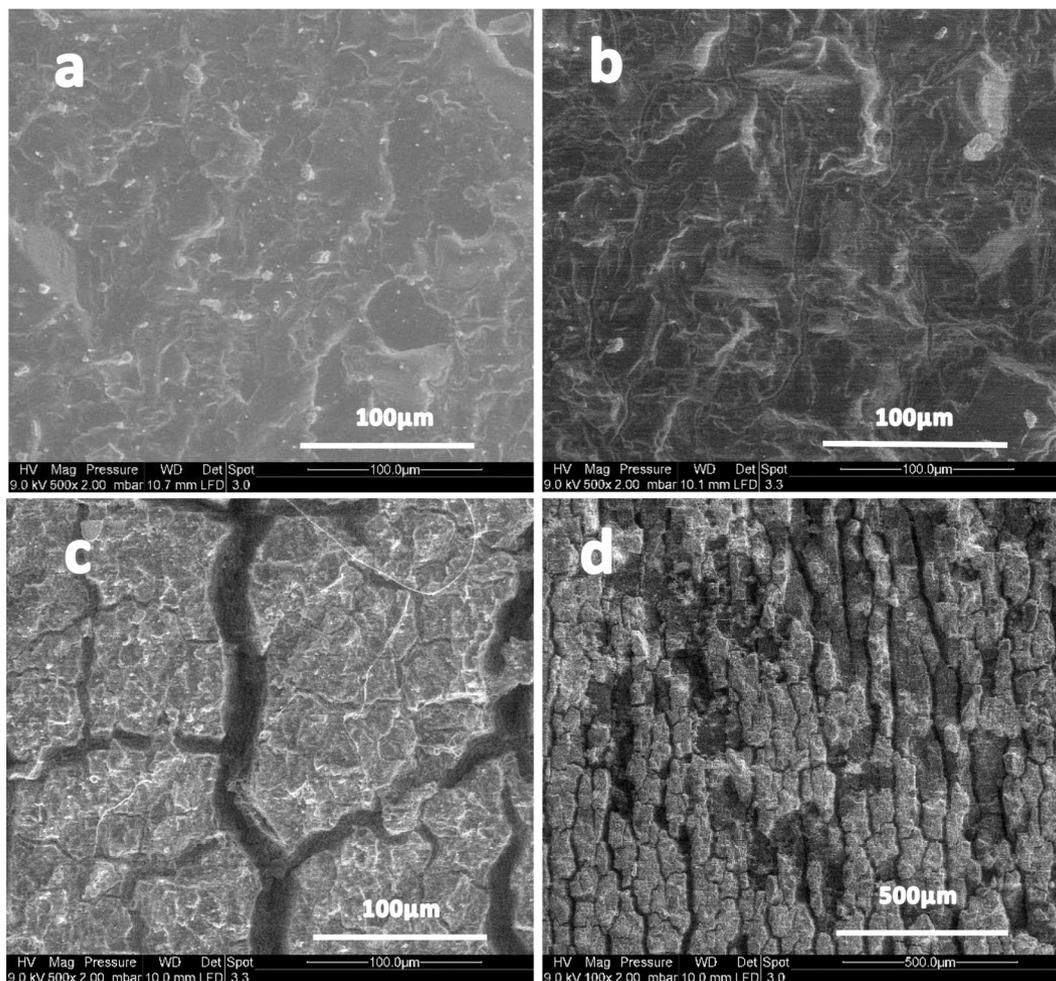


Fig. 1. ESEM pictures of (a) virgin PP collector  $\times 500$ ; (b) five months artificially weathered PP collector under UV rays  $\times 500$ ; (c) and (d) 55 months *in situ* weathered PP collector ( $\times 500$  and  $\times 100$  respectively).

index value reached 1.9. Additionally immersed and exposed to UV rays (UV + /SW), this value increased to 2.1. Finally, upon exposure to UV rays only during five months (UV +), the carbonyl index reached the value of 3. In this experiment, the highest value for carbonyl index was therefore found after five months artificially exposed to UV rays only (UV +). After 55 months of *in situ* weathering, the carbonyl index value reached 4.2.

### 3.3. Thermal analysis

Semi-crystalline PP has a heterogeneous structure, consisting of crystalline and amorphous phases (Masry et al., 2021). The crystallinity rate and the melting temperature are impacted by weathering (Badji et al., 2018). Monitoring the evolution of these parameters using Differential Scanning

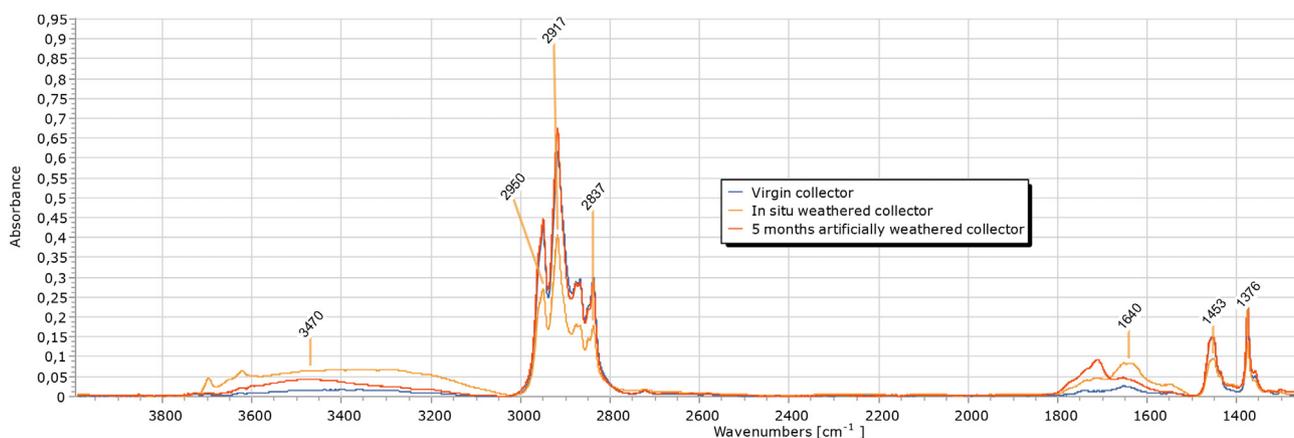


Fig. 2. FTIR spectra of a virgin PP collector (blue), *in situ* weathered PP collector (orange) and a 5 months artificially weathered collector (UV +) (yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

Carbonyl index values, melting temperatures, crystallinity rates, and fissure lengths for virgin PP collectors, 55 months *in situ* weathered PP collectors, and five months artificially weathered PP collectors.

	Virgin PP collector	55 months <i>in situ</i> weathered PP collector	5 month artificially weathered PP collectors			
			UV –	UV +	UV – /SW	UV + /SW
Carbonyl index values	0.7	4.2	0.5	3.0	1.9	2.1
Melting temperatures (°C)	169	164	169	164	169	169
Crystallinity rates (%)	29	25	31	26	30	30
Fissures lengths (µm)	0	24	0	2	0	0

Calorimetry (DSC) gave a global indication of weathering degree of the samples. On the DSC thermograms (Fig. 3), the heat flow exhibited endothermic peaks related to the melting of PP allowing the measure of melting temperatures and melting enthalpies ( $\Delta H_m$ ) corresponding to the energy needed to melt the sample. Crystallinity rates can be calculated as this relation:

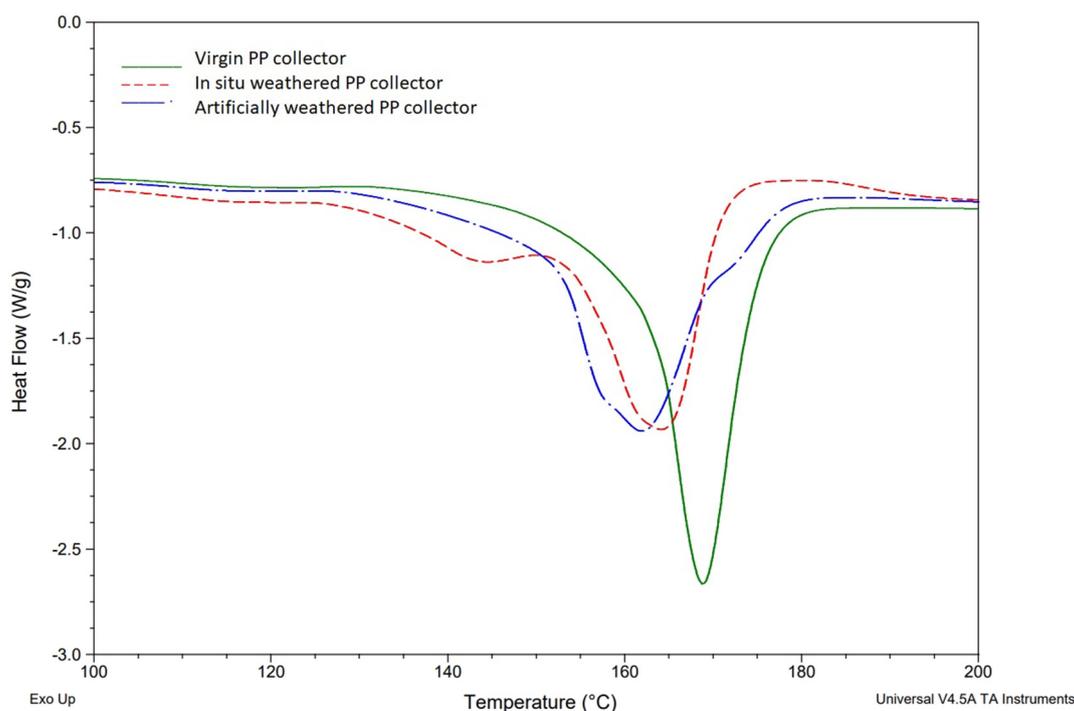
$$\text{Crystallinity rate (\%)} = \frac{\Delta H_m}{(\Delta H_{inf})} \times 100 \quad (1)$$

with  $\Delta H_{inf}$  equal to 209 J/g for PP corresponding to the theoretical melting enthalpy of a fully crystalline PP (Badji et al., 2018; Han et al., 2018)  $\Delta H_m$  can be calculated with TA analysis software. Melting temperatures and crystallinity rates of virgin, *in situ* and artificially weathered PP collectors are summarized in Table 1. For the virgin collector, as reference, melting temperature was equal to 169 °C, melting enthalpy was equal to 59 J/g and crystallinity rate was equal to 29 % (Eq. 1). These values were equivalent for the negative control after five months of artificial weathering without UV rays (UV –). After *in situ* weathering, significant decreases of the melting temperature from 169 to 164 °C, and crystallinity rates from 29 to 25 % were observed. Changes in melting temperature and crystallinity rate were observed on samples exposed to UV rays (UV +). No differences were observed for the other conditions in seawater (UV + /SW, UV – /SW).

#### 4. Discussion

During their use, PP oyster spat collectors undergo various degradations as the result of photooxidation, thermal degradation, mechanical

degradation, and biodegradation, all based on free-radicals mechanisms (Avio et al., 2017; Singh and Sharma, 2008). After *in situ* weathering, increase of carbonyl index values, and decrease of crystallinity rates, melting temperatures and apparition of fissures were observed (Table 1). Artificial weathering was conducted to better understand the mechanisms involved. Because the temperature in the UV chamber was fixed, homogenous and relatively low, and because no additional mechanical stress was applied, only UV irradiation was considered in this experiment. The highest degradation rate obtained after UV irradiation in air (UV +) and negative control confirmed that no additional degradation than photooxidation occurred. Abiotic degradations precede biotic degradations. Photooxidation by combined effect of oxygen and UV rays is known to be the main weathering mechanisms for PP. Initiated by UV rays absorbed by structural abnormalities or impurities, photooxidation cause chain scissions and produce shorter and more mobile chains with free radicals reacting freely with atmospheric oxygen (Gewert et al., 2015). This mechanism usually starts in the amorphous phase (Andrady, 2015; Julienne et al., 2019; Masry et al., 2021, Han et al., 2018) but results of this work obtained after artificial weathering showed a decrease of crystallinity rate indicating that photooxidation already caused damage in the amorphous phase and then occurred in the crystalline phase. This mechanism, already described by (Badji et al., 2018; Lv et al., 2015; Tang et al., 2019), finally lead to a decrease of the hydrophobicity and the molecular weigh of the polymer. However, the molecular weight remaining high, biodegradation of the long chains stays limited (Gewert et al., 2015; Singh and Sharma, 2008). In fact, PP is often used as a negative control in biodegradation experiments (Kalogerakis et al., 2017; Lott et al., 2020).



**Fig. 3.** DSC thermograms of a virgin PP collector (green line), *in situ* weathered PP collector (red line) and artificially weathered PP collector (blue line) with endothermic peak indicating the melting of the material. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

At the location of the *in situ* weathering, a mean solar irradiance of 1200 kWh/m<sup>2</sup>/year was monitored ([https://re.jrc.ec.europa.eu/pvg\\_tools/fr/#DR](https://re.jrc.ec.europa.eu/pvg_tools/fr/#DR)) which corresponds to an irradiance of 60 kWh/m<sup>2</sup>/year in the total UV range (295 and 400 nm). During artificial weathering, the intensity of the UV lamps in this same range was averaged at 6.9 W/m<sup>2</sup> and was maintained for 3200 h which correspond to a total cumulated irradiance of 22 kWh/m<sup>2</sup> (= 6.9 × 3200). Consequently, artificial weathering reproduced approximately 134 days (22 / 60 × 365) corresponding to 4.4 months (Gewert et al., 2018). This calculation of solar simulation equivalent is theoretical because it is dependent of numerous environmental factors, which varies throughout the seasons.

After five months of artificial weathering in seawater, an increase of carbonyl index values was observed whereas the crystallinity rates and melting temperatures were little impacted (Table 1). Absorption of seawater in PP can allow the entrance of dissolved oxygen into the matrix favoring chain oxidation and hydrolysis (Kalogerakis et al., 2017) but the kinetics of these degradation mechanisms are slower than those for photooxidation. Moreover, intensity of UV irradiance in artificial seawater (3 W/m<sup>2</sup>) was lower than for direct exposure to a UV lamp (6.9 W/m<sup>2</sup>), reducing the photooxidation mechanism in seawater, which it is expected to occur in the marine environment. No fissures were observed for these conditions (UV + /SW and UV - /SW).

Collectors artificially weathered during five months gave approximately the same results than after 55 months weathered *in situ* except for the fissure lengths due to additional degradations involved *in situ*. It is important to consider that *in situ*, degradation of PP collectors was influenced by alternations of tides, day and night cycles, weather and seasonal conditions, presence of spats, biofouling and crystal salts. In conclusion, *in situ* weathering of these PP collectors was mainly caused by photooxidation during emersion and outdoor storage and was enhanced with additional effects of mechanical stresses such as tides, currents, wind and rain but also professional handling. Comparing *in situ* and artificial weathering must be done with caution since there is still not an adequate simulation of the combined effects and synergies of various environmental factors (Andrade et al., 2019; Rajakumar et al., 2009; Yang and Ding, 2006).

## 5. Conclusions

This is the first study comparing *in situ* and artificial weathering of PP oyster spat collectors. This work shows that after only 55 months *in situ*, alternatively submerged and emerged, the collectors were notably damaged, with large fissures and loss of material such as MPs. These damages were mainly due to photooxidation during exposure to UV rays, enhanced by mechanical stress as tides, current, wind, rain and handling all along their use and storage. Considering only irradiation in the UV range, five months of artificial weathering reproduced approximately 4.4 months of natural sunlight *in situ* and confirmed that photooxidation by combined effect of UV rays and oxygen was the main weathering mechanism and was higher in air than in seawater. Degradations as the apparition of the first fissures were observed relatively soon under UV irradiation. This first comparative study gave preliminary results on this topic and help to better understand the mechanisms involved in the degradation of these collectors. This work allows to make recommendations to industrials and professionals including a better storage protected from UV rays and a reduction of the duration of use. It is important to note that there is still a lack of information on the toxicity and the potential environmental hazard of these altered plastics in the marine environment, as vectors of MPs, POPs and microorganisms (Avio et al., 2017; Gewert et al., 2015; Zettler et al., 2013). Consequently, a future work will be focused on the relationship between weathering, fragmentation and toxicity including promising alternatives such as biosourced materials.

## CRedit authorship contribution statement

Marion Hingant: Conceptualization, Investigation, Methodology, Formal analysis, Visualization, Writing - original draft.

Stéphanie Mallarino: Investigation, Methodology, Formal analysis, Visualization, Validation, Writing - review & editing.

Egle Conforto: Investigation, Visualization, Formal analysis, Writing - review & editing.

Pierrick Barbier: Resources, Review & Editing.

Emmanuel Dubillot: Resources.

Arno Bringer: Funding acquisition, Conceptualization, Investigation, Methodology, Review & editing.

Hélène Thomas: Funding acquisition, Conceptualization, Methodology, Validation, Supervision, Review & editing, Project administration.

## Funding and acknowledgements

The PLASTIC LAB project (Dégradabilité, effets et comportement des PLASTIques Conchylicoles en Laboratoire), was funded by the FEAMP (Fonds Européen des Affaires Maritimes et de la Pêche) and the SCIC TEO (Taho'E Eco Organisation). The authors thank the CAPENA, and Pierrick Barbier, for providing the oyster collectors used in this work, Latta Socalgame and Fanon Julienne for their help. The authors are grateful to all contributors including Linda Sperling for their proofreading services.

## Data availability

Data will be made available on request.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## References

- Almond, J., Sugumaar, P., Wenzel, M.N., Hill, G., Wallis, C., 2020. Determination of the carbonyl index of polyethylene and polypropylene using specified area under band methodology with ATR-FTIR spectroscopy. *E-Polymers* 20 (1), 369–381. <https://doi.org/10.1515/epoly-2020-0041>.
- Almond, J., Sugumaar, P., Wenzel, M.N., Hill, G., Wallis, C., 2020. Determination of the carbonyl index of polyethylene and polypropylene using specified area under band methodology with ATR-FTIR spectroscopy. *e-Polymers* 20, 369–381. <https://doi.org/10.1515/epoly-2020-0041>.
- Andrade, J., Fernández-González, V., López-Mahía, P., Muniategui, S., 2019. A low-cost system to simulate environmental microplastic weathering. *Mar. Pollut. Bull.* 149, 110663. <https://doi.org/10.1016/j.marpolbul.2019.110663>.
- Andrady, A.L., 2015. Persistence of plastic litter in the oceans. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), *Marine Anthropogenic Litter*. Springer International Publishing, Cham, pp. 57–72. [https://doi.org/10.1007/978-3-319-16510-3\\_3](https://doi.org/10.1007/978-3-319-16510-3_3).
- Avio, C.G., Gorb, S., Regoli, F., 2017. Plastics and microplastics in the oceans: from emerging pollutants to emergent threat. *Mar. Environ. Res.* 128, 2–11. <https://doi.org/10.1016/j.marenvres.2016.05.012>.
- Badji, C., Beigbeder, J., Garay, H., Bergeret, A., Bénétet, J.-C., Desauziers, V., 2018. Correlation between artificial and natural weathering of hemp fibers reinforced polypropylene biocomposites. *Polym. Degrad. Stab.* 148, 117–131. <https://doi.org/10.1016/j.polydegradstab.2018.01.002>.
- Boucher, C., Morin, M., Bendell, L.L., 2016. The influence of cosmetic microbeads on the sorptive behavior of cadmium and lead within intertidal sediments: a laboratory study. *Reg. Stud. Mar. Sci.* 3, 1–7. <https://doi.org/10.1016/j.rsm.2015.11.009>.
- Bringer, A., Cachot, J., Dubillot, E., Lalot, B., Thomas, H., 2021a. Evidence of deleterious effects of microplastics from aquaculture materials on pediveliger larva settlement and oyster spat growth of Pacific oyster, *Crassostrea gigas*. *Sci. Total Environ.* 794, 148708. <https://doi.org/10.1016/j.scitotenv.2021.148708>.
- Bringer, A., Le Floch, S., Kerstan, A., Thomas, H., 2021b. Coastal ecosystem inventory with characterization and identification of plastic contamination and additives from aquaculture materials. *Mar. Pollut. Bull.* 167, 112286. <https://doi.org/10.1016/j.marpolbul.2021.112286>.
- Cai, L., Wang, J., Peng, J., Wu, Z., Tan, X., 2018. Observation of the degradation of three types of plastic pellets exposed to UV irradiation in three different environments. *Sci. Total Environ.* 628–629, 740–747. <https://doi.org/10.1016/j.scitotenv.2018.02.079>.
- Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., Galloway, T.S., 2013. Microplastic ingestion by zooplankton. *Environ. Sci. Technol.* 47, 6646–6655. <https://doi.org/10.1021/es400663f>.
- Conforto, E., Joget, N., Buisson, P., Vendeville, J.-E., Chaigneau, C., Maugard, T., 2015. An optimized methodology to analyze biopolymer capsules by environmental scanning electron microscopy. *Mater. Sci. Eng. C* 47, 357–366. <https://doi.org/10.1016/j.msec.2014.11.054>.

- Gewert, B., Plassmann, M., Sandblom, O., MacLeod, M., 2018. Identification of chain scission products released to water by plastic exposed to ultraviolet light. *Environ. Sci. Technol. Lett.* 5, 272–276. <https://doi.org/10.1021/acs.estlett.8b00119>.
- Gewert, B., Plassmann, M.M., MacLeod, M., 2015. Pathways for degradation of plastic polymers floating in the marine environment. *Environ. Sci.: Processes Impacts* 17, 1513–1521. <https://doi.org/10.1039/C5EM00207A>.
- Guo, X., Wang, J., 2019. The chemical behaviors of microplastics in marine environment: a review. *Mar. Pollut. Bull.* 142, 1–14. <https://doi.org/10.1016/j.marpolbul.2019.03.019>.
- Han, C., Sahle-Demessie, E., Zhao, A.Q., Richardson, T., Wang, J., 2018. Environmental aging and degradation of multiwalled carbon nanotube reinforced polypropylene. *Carbon* 129, 137–151. <https://doi.org/10.1016/j.carbon.2017.10.038>.
- Hermabessiere, L., Dehaut, A., Paul-Pont, I., Lacroix, C., Jezequel, R., Soudant, P., Duflos, G., 2017. Occurrence and effects of plastic additives on marine environments and organisms: a review. *Chemosphere* 182, 781–793. <https://doi.org/10.1016/j.chemosphere.2017.05.096>.
- Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. *Environ. Pollut.* 160, 42–48. <https://doi.org/10.1016/j.envpol.2011.08.052>.
- Julienne, F., Lagarde, F., Delorme, N., 2019. Influence of the crystalline structure on the fragmentation of weathered polyolefines. *Polym. Degrad. Stab.* 170, 109012. <https://doi.org/10.1016/j.polymdegradstab.2019.109012>.
- Kalogerakis, N., Karkanorachaki, K., Kalogerakis, G.C., Triantafyllidi, E.I., Gotsis, A.D., Partinevelos, P., Fava, F., 2017. Microplastics generation: onset of fragmentation of polyethylene films in marine environment mesocosms. *Front. Mar. Sci.* 4. <https://doi.org/10.3389/fmars.2017.00084>.
- Law, K.L., Morét-Ferguson, S., Maximenko, N.A., Proskurowski, G., Peacock, E.E., Hafner, J., Reddy, C.M., 2010. Plastic accumulation in the North Atlantic subtropical gyre. *Science* 329, 1185–1188. <https://doi.org/10.1126/science.1192321>.
- León, V.M., García, I., González, E., Samper, R., Fernández-González, V., Muniategui-Lorenzo, S., 2018. Potential transfer of organic pollutants from littoral plastics debris to the marine environment. *Environ. Pollut.* 236, 442–453. <https://doi.org/10.1016/j.envpol.2018.01.114>.
- Leslie, H.A., van Velzen, M.J.M., Brandsma, S.H., Vethaak, A.D., Garcia-Vallejo, J.J., Lamoree, M.H., 2022. Discovery and quantification of plastic particle pollution in human blood. *Environ. Int.* 163, 107199. <https://doi.org/10.1016/j.envint.2022.107199>.
- Lott, C., Eich, A., Unger, B., Makarow, D., Battagliarin, G., Schlegel, K., Lasut, M.T., Weber, M., 2020. Field and mesocosm methods to test biodegradable plastic film under marine conditions. *PLoS ONE* 15, e0236579. <https://doi.org/10.1371/journal.pone.0236579>.
- Lv, Y., Huang, Y., Yang, J., Kong, M., Yang, H., Zhao, J., Li, G., 2015. Outdoor and accelerated laboratory weathering of polypropylene: a comparison and correlation study. *Polym. Degrad. Stab.* 112, 145–159. <https://doi.org/10.1016/j.polymdegradstab.2014.12.023>.
- Masry, M., Rossignol, S., Gardette, J.-L., Therias, S., Bussière, P.-O., Wong-Wah-Chung, P., 2021. Characteristics, fate, and impact of marine plastic debris exposed to sunlight: a review. *Mar. Pollut. Bull.* 171, 112701. <https://doi.org/10.1016/j.marpolbul.2021.112701>.
- Paluselli, A., Fauvelle, V., Galgani, F., Sempéré, R., 2019. Phthalate release from plastic fragments and degradation in seawater. *Environ. Sci. Technol.* 53, 166–175. <https://doi.org/10.1021/acs.est.8b05083>.
- Prata, J.C., da Costa, J.P., Lopes, I., Duarte, A.C., Rocha-Santos, T., 2020. Environmental exposure to microplastics: an overview on possible human health effects. *Sci. Total Environ.* 702, 134455. <https://doi.org/10.1016/j.scitotenv.2019.134455>.
- Rajakumar, K., Sarasvathy, V., Thamarai Chelvan, A., Chitra, R., Vijayakumar, C.T., 2009. Natural weathering studies of polypropylene. *J. Polym. Environ.* 17, 191–202. <https://doi.org/10.1007/s10924-009-0138-7>.
- Singh, B., Sharma, N., 2008. Mechanistic implications of plastic degradation. *Polym. Degrad. Stab.* 93, 561–584. <https://doi.org/10.1016/j.polymdegradstab.2007.11.008>.
- Song, Y.K., Hong, S.H., Jang, M., Han, G.M., Jung, S.W., Shim, W.J., 2017. Combined effects of UV exposure duration and mechanical abrasion on microplastic fragmentation by polymer type. *Environ. Sci. Technol.* 51, 4368–4376. <https://doi.org/10.1021/acs.est.6b06155>.
- Tang, C.-C., Chen, H.-I., Brimblecombe, P., Lee, C.-L., 2019. Morphology and chemical properties of polypropylene pellets degraded in simulated terrestrial and marine environments. *Mar. Pollut. Bull.* 149, 110626. <https://doi.org/10.1016/j.marpolbul.2019.110626>.
- Yang, X., Ding, X., 2006. Prediction of outdoor weathering performance of polypropylene filaments by accelerated weathering tests. *Geotext. Geomembr.* 24, 103–109. <https://doi.org/10.1016/j.geotextmem.2005.11.002>.
- Zettler, E.R., Mincer, T.J., Amaral-Zettler, L.A., 2013. Life in the “plastisphere”: microbial communities on plastic marine debris. *Environ. Sci. Technol.* 47, 7137–7146. <https://doi.org/10.1021/es401288x>.
- Zhang, N., Li, Y.B., He, H.R., Zhang, J.F., Ma, G.S., 2021. You are what you eat: microplastics in the feces of young men living in Beijing. *Sci. Total Environ.* 767, 144345. <https://doi.org/10.1016/j.scitotenv.2020.144345>.