



From macroplastics to microplastics: Role of water in the fragmentation of polyethylene

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HIGHLIGHTS

- Fragmentation of polyethylene films into microplastics were studied in water and at air.
- The cracking of films did not appear correlated with the oxidation level.
- The presence of water appeared as a promoter of cracking propagation.
- The mechanical properties and the fabrication process play a major role in the fragmentation and influence the distribution in size of fragments.
- Many steps of fragmentation appear necessary from PE macroplastics to reach microplastics in the aquatic environment.

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ABSTRACT

In this work, the artificial photodegradation of polyethylene films was studied in laboratory to compare the fragmentation pathways of this polymer at air and in water. Oxidation, surface mechanical properties, crystallinity and crack propagation were monitored to investigate their influence on fragmentation. Without any external stress, fragmentation only occurred in water despite a higher level of oxidation for films weathered at air. The cracking of the films did not appear correlated with the oxidation level and the presence of water appeared as a promoter of cracking propagation. The results also showed that the mechanical properties at the surface play a major role in the fragmentation pathway whereas the fabrication process may influence the propagation direction of the cracks. Consequently, the distribution in size of plastic fragments in the aquatic environment may be linked to the nature of the polymer but also to its manufacturing process. In this study, after 25 weeks of weathering in water, 90% of the fragments were >1 mm with very similar shapes showing that micrometric fragments were not yet abundant. These results suggest that long times of weathering in water and many steps of fragmentation appear necessary from macroplastics to reach sizes <1 mm in the aquatic environment. These results constitute a first attempt to understand the pathways leading from macroplastics to microplastics in water. They have to be confirmed for other polymers and the long-term behavior of the fragments needs to be studied to predict their decrease in size among time.

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1. Introduction

After 60 years of industrial life, plastics have become omnipresent in our lives but their end of use raises concern. It was approximated that in the last 50 years, 12,000 Mt of plastics escaped from the waste management cycle and entered in landfills or directly in the environment (Geyer et al., 2017). Once in the aquatic environment, macro debris of plastic undergo mechanical

(erosion, abrasion), chemical (photo-oxidation, hydrolysis) and biological (degradation by microorganisms) modifications (Andrady 2017). All these actions lead to the weathering and the fragmentation of plastic macro debris in smaller and more abundant pieces called microplastics when their size is under 5 mm (Arthur et al., 2009). Theoretically, the final degradation of a polymer would be reached when it is mineralized. The amount of time for a complete degradation of inert plastic polymers such as PE or PP in the marine environment is roughly estimated to several hundreds of years and this degradation is probably the results of several complex processes with various kinetics (Barnes et al., 2009; Gewert et al., 2015). It is particularly difficult to monitor all

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these processes in the real environment and laboratory studies are still necessary to obtain more accurate data and to identify the pathways leading to an eventual bio-assimilation of plastic debris in the aquatic environment. Among all processes, the abiotic degradation of polymers in the environment leading to their fragmentation is of particular interest. Indeed, a lot of studies aimed to study the loss of mechanical properties in polymer during their ageing but experimental studies on their fragmentation at air or in water are scarce (Jahnke et al., 2017; Kalogerakis et al., 2017) and the ultimate size distribution of polymer fragments that can be generated during environmental fragmentation is not really known raising the question of the possible presence of great quantities of nanoplastics in the future (Koelmans et al., 2017).

The parameters that can modify the fragmentation pathways (polymer nature or structure, environmental conditions) are not totally identified and it is important to verify if some of these parameters can impact the ultimate size of generated fragments. However, monitoring fragmentation in real environment is quite impossible due to the potential loss of generated fragments. In this study, the long-term artificial weathering of polyethylene films was studied in laboratory in order to monitor the first stages of the fragmentation under two different environments: in air or in Milli-Q water. Since this work is a first study to provide understanding of the fragmentation pathways and kinetics, models as simple as possible were selected in order to identify to what extent each parameter (water vs air) impact separately the processes at stake. Polyethylene was chosen as it is the polymer the most commonly found in the environment (Phuong et al., 2016). Fragments are supposed to be generated when cracking lines converge. The key to predict the fragment number and size is then to study the appearance and behavior of cracks in the material. Crack propagation inside a material follows two principal modes differing by their speed of propagation, either named rapid crack propagation (RCP) or slow crack growth (SCG) (Alkhadra et al., 2017; Šindelář et al., 2005). SCG mechanism has been widely studied in polymers, these fractures are characterized by the stable growth of a crack with little deformation in the plastic material. RCP has been mainly studied in mineral material but it has been also observed for HDPE pipes in contact with pressurized gas or chlorine solution (Choi et al., 2009; Frank et al., 2009). The fragmentation mechanism is not completely elucidated for semi-crystalline polymers, especially in water, but observation seems to indicate that cracks are initiated on an impact event and can travel long distances rather quick. The aim of this work is to provide information on the link between oxidation, cracks formation and size of fragments in polyethylene films under weathering and to investigate the role of water in these processes.

2. Experimental part

2.1. LDPE films

Low density Polyethylene (LDPE) films (2×2 cm) with the same thickness (i.e. $24(3) \mu\text{m}$ as measured by micrometer) and the same roughness (i.e. $25(5) \text{ nm}$ as measured by AFM on $30 \times 30 \mu\text{m}^2$ image) were selected from a film obtained by a blown-extrusion process. To avoid external mechanical stress which can promote fragmentation sample manipulation was as limited as possible. The films were cut to make a distinction between the top face (toward the lamp) and the bottom face (toward the beaker). The manufactured pellets (Alcudia PE-003) were provided with the mention: «does not contain any additives» and no additives could be detected by Infrared and Raman spectroscopies. As determined by Differential Scanning Calorimetry, LDPE films have a melting point of

112°C and a degree of crystallinity of 32%. This partial level of crystallization corresponds to a semi-crystalline polymer.

2.2. Accelerated weathering conditions

Two environments conditions were modeled. Films were placed either in empty quartz beakers for air condition (directly in contact with the bottom of the beaker.) or beakers filled with MilliQ water without stirring (water condition). It has to be noted that since LDPE is less dense than water, films are floating on the surface of the water. For each condition, two replicates that were never manipulated until the fragmentation were characterized.

To reproduce the sunlight exposure, each sample was placed in a XLS + chamber equipped with a xenon lamp. The ageing conditions were fixed to correspond to the ISO 4892–3:2013 standard. The irradiation intensity was around 60 W/m^2 which correspond to a total amount of solar radiation $9 \times 10^9 \text{ J/m}^2$, and a temperature between 32 and 44°C .

2.3. Characterization of fragments

FTIR spectra were acquired using a Fourier transform infrared microscopy system ($\mu\text{FT-IR}$; Spotlight 200i FT-IR microscopy system, PerkinElmer) in transmission mode as the thickness of the samples was small enough to avoid saturation, therefore spectra and indices take into account both sides of the film and its volume. For each film, three measurements were done randomly on the film using the microscope with an aperture of $100 \times 100 \mu\text{m}$. Measurements were realized with 32 accumulations ranging from 4000 to 600 cm^{-1} . The spectra were then baseline corrected with the software “Spectrum”.

To evaluate the oxidation of PE, three oxidative indexes were calculated as the ratios of integrated intensities for different wavelength as follows $\text{CI} = \frac{I_{1970-1560}}{I_{1450-1540}}$, $\text{HI} = \frac{I_{2900-3200}}{I_{1450-1540}}$ and $\text{VI} = \frac{I_{940-885}}{I_{1450-1540}}$.

Raman spectroscopic measurements were conducted using a confocal laser Raman spectrometer (Xplora, Horiba). The Raman signals were recorded in a spectral range $600\text{--}3500 \text{ cm}^{-1}$ with an integration time of 30 s using a 638 nm laser excitation wavelength in combination with a $\times 50$ objective of an Olympus B \times 41 microscope. Raman analysis, were only performed once the films were fragmented into small pieces and it was not possible to guarantee which face was under investigation. Accordingly, the measurements were performed on several fragments and then averaged. All the raw data were then treated with Lab Spec 5 software for linear baseline correction, and Peakfit software for the smoothing and the peaks deconvolution. The crystallinity was calculated as $1 - \frac{I_{1303}}{I_{1292}}$.

Atomic Force Microscopy (Agilent 5500AFM) was used. Surface topography was measured in ambient condition using tapping mode with tip (calculated tip stiffness = 5 N/m). Force-volume measurements (100 curves/sample) were performed in contact mode (calculated tip stiffness = 43 N/m). Measurements of the elastic properties of the weathered films were conducted following the procedure developed by Oliver and Pharr (Schiffmann, 2011).

2.4. Fragment size distribution

After 25 week of aging the PE film appeared fragmented in water. The vial containing the PE fragments was placed between a polarizer and a circular analyzer to take a photograph in polarized light. The device can image objects down to a size of $50 \mu\text{m}$, below which the contours become blurred, so no conclusion could therefore be drawn on the part of the distribution below this size. The images were processed using the Gwyddion software, giving access to the numbers, sizes and positions of the objects. The

longest size of each fragment was measured, ranked and the distribution could be traced.

3. Results

3.1. Fragmentation

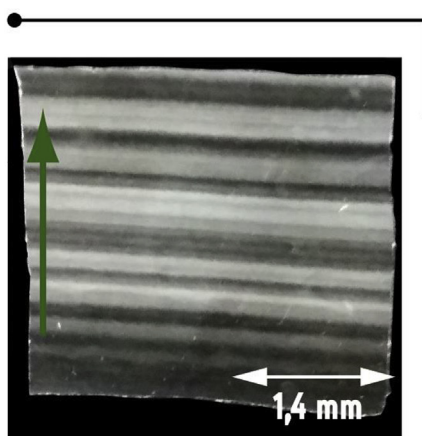
As shown by Fig. 1, between crossed polarizer, lines parallel to the film extrusion direction can be observed on the as prepared (pristine) LDPE film. These lines originate from the induced stress brought by the process of film formation (passage through the extrusion die and fast coldening) (Zhang et al., 2004). After 25 weeks of accelerated weathering with no manipulation, the replicates in water have fragmented in anisotropic bended fragments with the longer length in a normal direction toward the extrusion direction. The size of the fragments appeared as a large distribution from 0.4 to 7 mm in length with 62% on average of the fragments which correspond to the definition of microplastics (<5 mm). After the same weathering time in air, the films were not fragmented but appeared coiled upon themselves along the extrusion direction. These first observations indicate clearly that the environment influences the fragmentation pathways of LDPE films.

3.2. Surface analysis

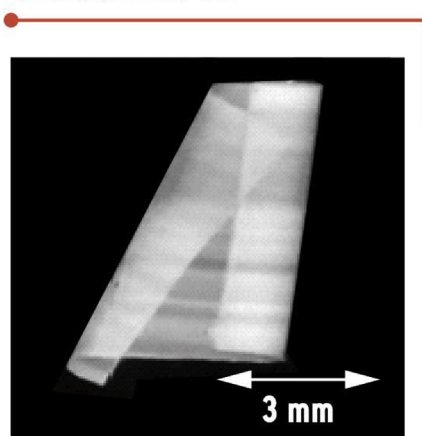
In order to detect the presence of cracks on the film surfaces, their surface microstructures were studied by optical microscopy and Atomic Force Microscopy (Fig. 2). Optical microscopy images indicate that macrocracks (defined here as cracks with length > 100 μm) are only visible on the films weathered in water and that these cracks are oriented perpendicularly to the extrusion direction. For air condition, the macroscopic structure of the film surfaces appear unchanged compared to pristine films.

At a lower range, AFM topography images show that for all the films, micrometric lines in parallel to the extrusion direction lines are visible. They represent the crystalline lamellae alignment due to stress caused by the film formation process and are similar for all films (Zhang et al., 2004). On the water-weathered films, microcracks (length < 10 μm) are visible between the macrocracks, normally to the extrusion direction (Deblieck et al., 2011) whereas no such defaults appear for the air condition. As already described in literature, the main mechanism for the fracture development in a semi-crystalline polymer is initiated through the formation of nano-cavities (voids) in the amorphous phase. It appears here that such voids in the amorphous region led to microcracks only in the

Pristine film



Weathered in air



Weathered in water

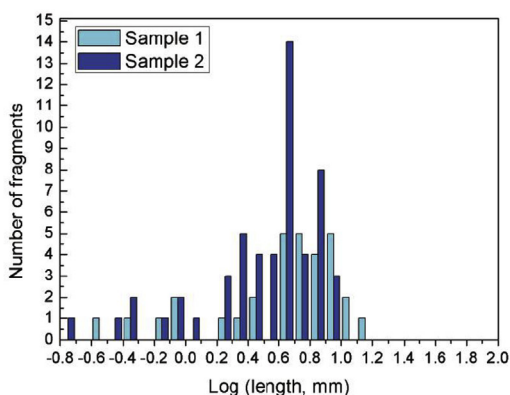
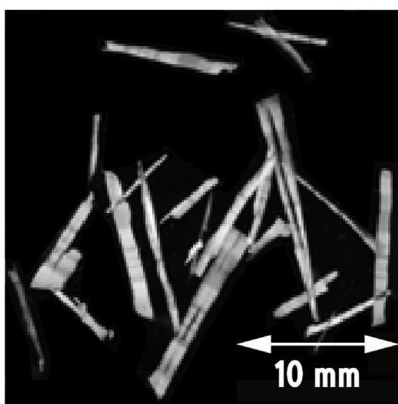


Fig. 1. Photography between crossed polarizers of the pristine, air weathered and water weathered films after 25 weeks. Size distribution in abundance of fragments from samples weathered in water.

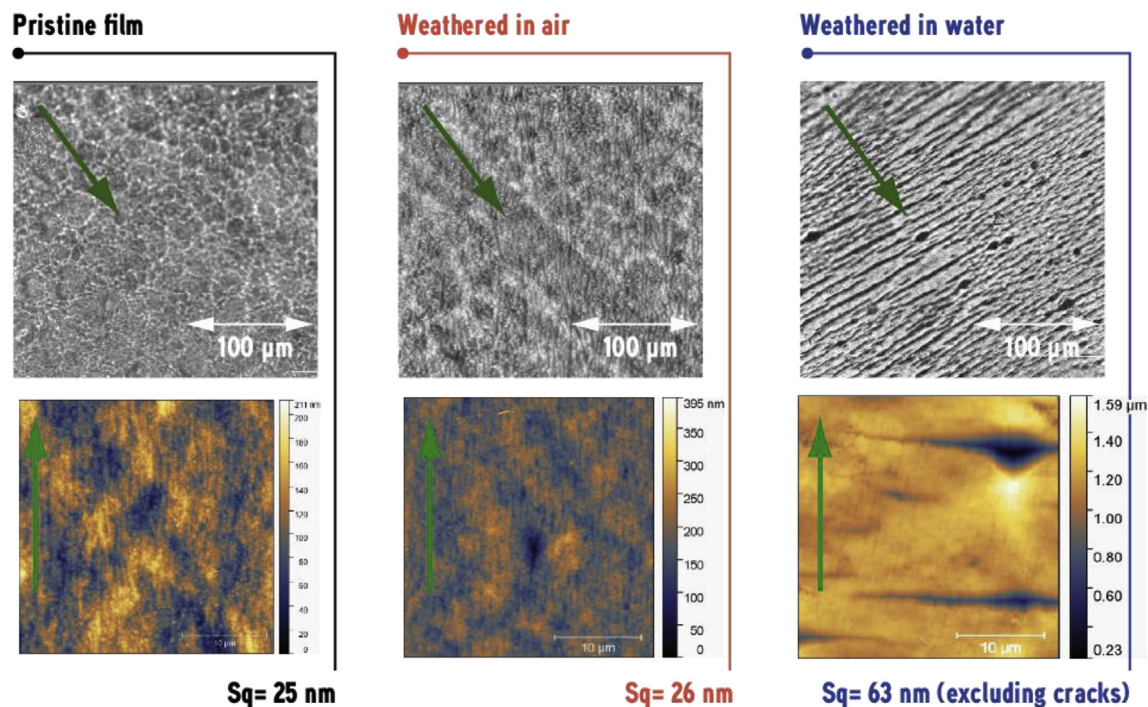


Fig. 2. Optical microscopy ($800 \times 600 \mu\text{m}$, top) and AFM topography ($30 \times 30 \mu\text{m}$, bottom) images of the different films after 25 weeks. The green arrow represents the extrusion direction. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

water condition together with an increase of the surface roughness between the microcracks as indicated by the topography analysis (63 nm vs 26 nm). During weathering these voids can coalesce, leading eventually to the formation of micro and macrocracks preferentially in the direction of the tie chains (Zhang and Jar 2016). The propagation of the macrocracks along the direction normal to the extrusion direction lead to the fragmentation of the film in fragments with longitudinal shapes (Fig. 1). These observations are schematized on Fig. 3 which represents the structure of a blown-extruded film with the aligned crystalline phases (bold and black vertical lines) parallel to the extrusion direction. Polymer chains in the crystalline region extend into the amorphous regions as tie chains (green longitudinal lines). In the amorphous phase, voids are created and when weathering in water, they coalesce until the formation of macrocracks which will drive the shape of generated fragments.

3.3. Oxidation monitoring

Photodegradation leads to modification of the polymer

chemistry through the introduction of various oxygenated moieties. These molecular changes conduct to competitive reactions of chain scission and crosslinking (Xiong et al., 2016). Chemical modification of the weathered films were characterized by FTIR spectroscopy through the study of the variation of different indexes namely carbonyl index (CI) for the apparition of C=O bonds; hydroxyl index (HI) for O–H bonds and vinyl index (VI) for C=C bonds. Although, the definition of the frequency range and the choice of the reference band can vary from one study to another, the evolution of these indexes are good indicators of the evolution of the oxidative reactions (Andrady 2017; ter Halle et al., 2017).

Fig. 4 shows the normalized FTIR spectra of the different films and the evolution of the different indexes after 25 week of weathering in air and water. It can be seen that independently of the condition all indexes increased after weathering indicating a strong chemical modification of the LDPE films. Whereas no clear difference is observed between air and water for the evolution of VI, weathering in air leads to higher CI and HI than weathering in water. Despite the presence of cracks in water-weathering films which is supposed to increase the exposed surface to light

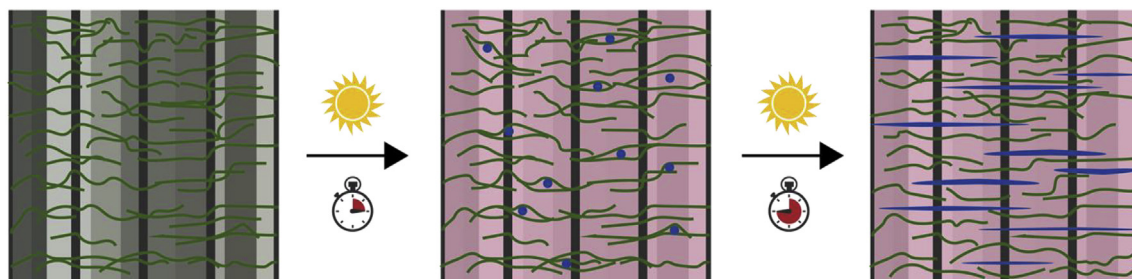


Fig. 3. (a) Schematic structure of the blown-extruded LDPE films. The crystalline lamellae (bold straight lines) are aligned in parallel to the extrusion direction and perpendicularly to the amorphous phase (i.e. tie chains, light longitudinal lines). (b) Due to the weathering, crack initiation begin with the formation of void (blue circles), (c) in water, the coalescence of voids leads to the formation of micro- and macro-cracks (blue horizontal lines).

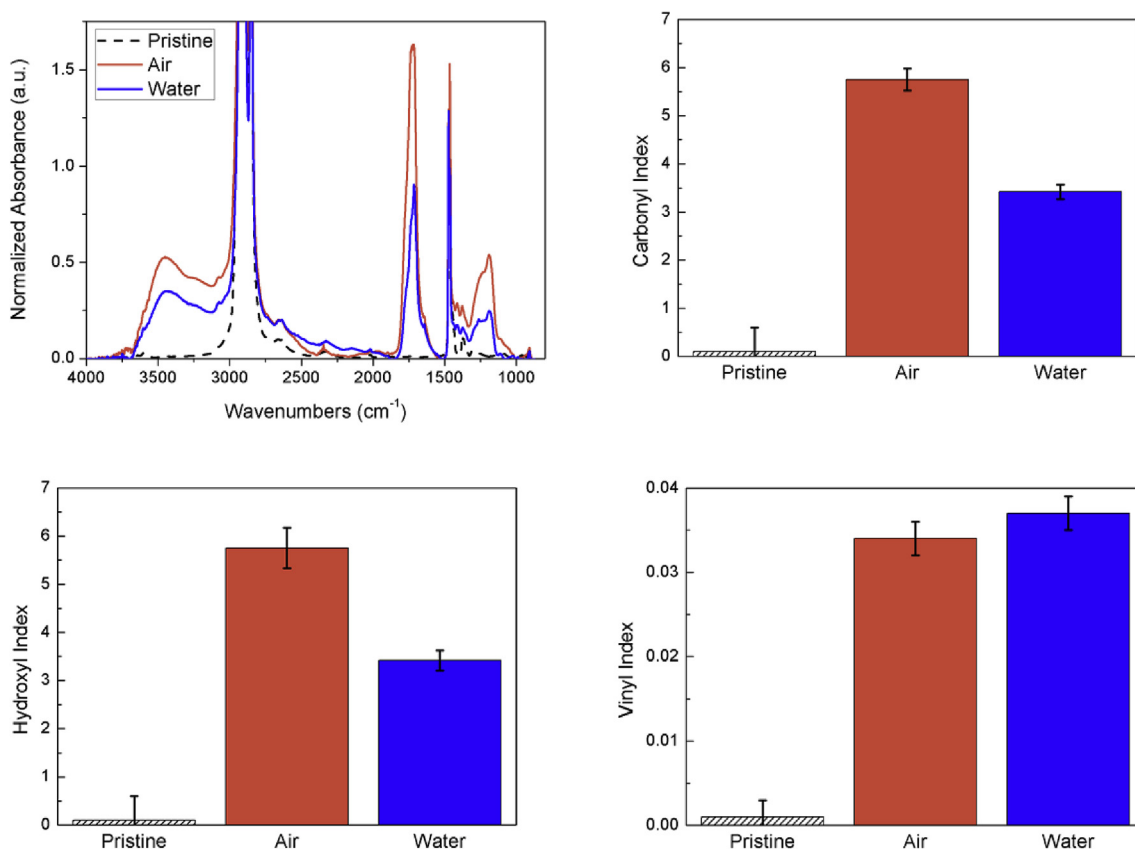


Fig. 4. FTIR normalized spectra and corresponding evolution of CI, HI and VI for the different weathering conditions after 25 week of weathering.

modification, these results indicate that a higher quantity of C=O and O–H bonds were produced on the LDPE surfaces during the weathering in air.

In semi-crystalline polymers such as LDPE, oxidation mainly occurs in amorphous regions in which oxygen can readily diffuse. This oxidation process induces chain splits and accordingly low molecular weight free segments are formed. Due to their smaller size, they can rearrange into a crystalline phase leading to the process of chemi-crystallization which can be illustrated by an increase of the crystallization degree after weathering (Ojeda et al., 2011). In this study since some samples were fragmented, determination of the crystallinity using Differential Scanning Calorimetry (DSC) was not possible. Moreover since chemi-crystallization is a surface phenomenon (Yakimets et al., 2004), confocal Raman spectroscopy which is sensitive to the first micrometers of the film surfaces can be used (Delorme et al., 2003). To our knowledge no simple method based on Raman spectrometry is able to give quantitative crystallinity degree values. However, since crystalline and amorphous domains exhibit unique conformational characteristics, the frequency and bandwidth of the corresponding vibrational modes in Raman spectrum are different. The study of the relative evolution of these vibrational bands can give some qualitative information on the evolution of the crystallinity of the material. Fig. 5 shows the evolution of the ratio of area integral Raman intensity between the 1416 cm⁻¹ band (CH₂ crystalline phase) and the reference 2720 cm⁻¹ band (CH stretching) for the different weathering conditions (Lin et al., 2007). Fig. 5 indicates no clear increase of the surface crystallinity for the weathered samples compared to the pristine film.

3.4. Mechanical properties

The mechanical properties of the film surfaces were studied by AFM. Indeed, AFM has the ability compared to classical mechanical tests (tensile tests, DMA ...) to allow measurements of the elastic properties even on small fragments. The elastic modulus of the films can be calculated using the following equation (Schiffmann, 2011):

$$E = \frac{S\sqrt{\pi}}{2\sqrt{A} \times (1 - \nu^2)}$$

where S is the experimentally measured stiffness (Fig. 6) of the very beginning region of the unloading curve, A is the projected area of contact between the indenter and the sample at the corresponding deformation, and ν is the Poisson ration ($\nu = 0.4$ for LDPE) (Jee and Lee, 2010). The projected contact area A between the indenter and the sample was estimated from the surface area of the AFM tip which was determined by deconvolution (Ferencz et al., 2012).

All results are summarized in Table 1. The film elastic modulus of pristine LDPE was found to be 0.17 GPa which is in agreement with previous studies validating the measurement procedure (Jee and Lee, 2010). After 25 weeks of weathering, whatever the environment, a hardening of the film surface (i.e. increase of the elastic modulus) can be observed but with different magnitudes. The averaged elastic modulus increases by a factor of 30 for the films weathered in air and only by a factor of 4 for the film weathered in water.

The increase of the surface rigidity impacts the crack propagation process. Indeed assuming Irwin model (Yarema, 1996), the critical stress for crack propagation can be expressed as:

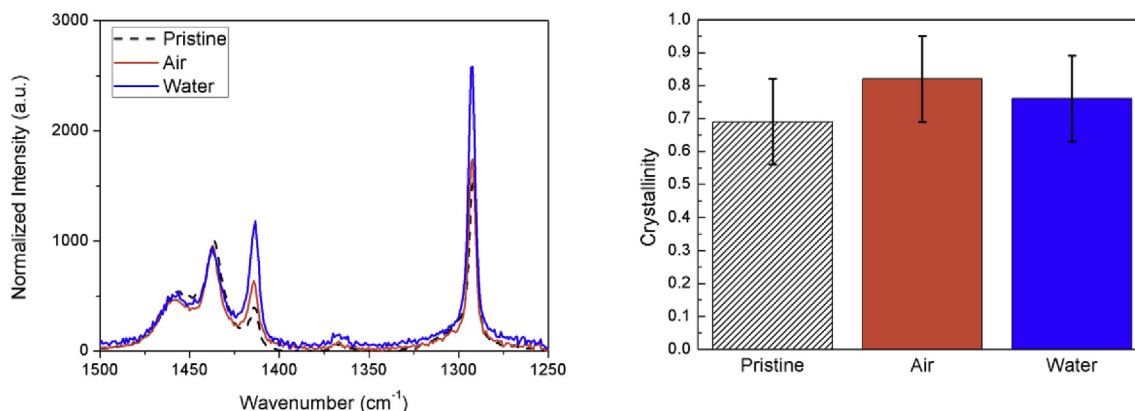


Fig. 5. Normalized (with 2720 cm⁻¹ band) confocal Raman spectra and corresponding evolution of crystallinity after 25 week of weathering.

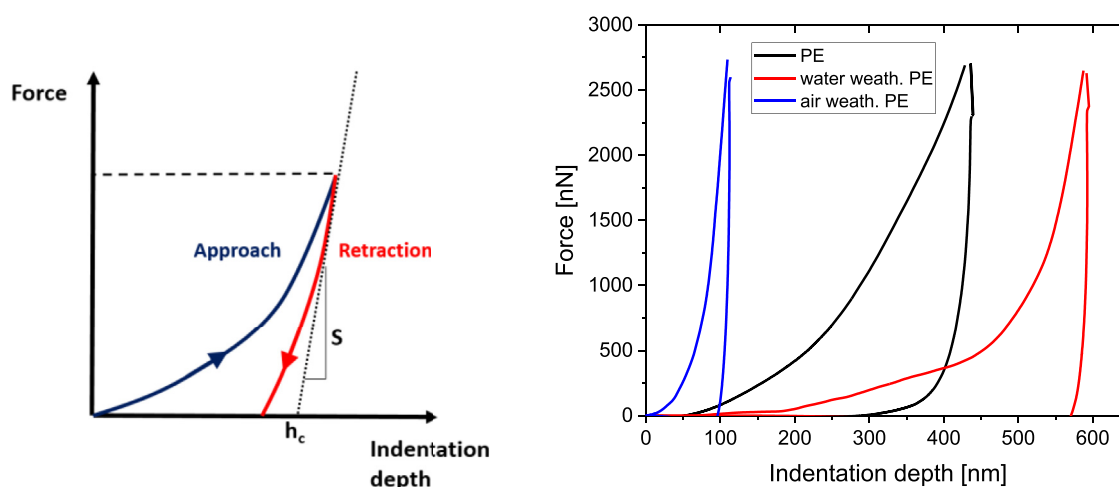


Fig. 6. a) Schematic force-indentation curve on polymer and corresponding characteristic parameters b) Averaged force-indentation curves measured as function of the weathering conditions.

Table 1

Surface elastic moduli and corresponding experimental parameters extracted from the averaged force indentation curves presented on Fig. 6.

	S (N/m)	h _c (nm)	A (m ²)	E (GPa)
Pristine PE	339	430	4,54E-12	0,17
Air weathered	2549	112	3,06E-13	4,86
Water weathered	1975	592	8,60E-12	0,71

$$\sigma \tau^2 = GE/(\pi a)$$

where G is the total strain energy (plastic + elastic), $2a$ is the length of the crack and E is the elastic modulus. Crack propagation only occurs when the released strain energy is greater than the energy required to create a fracture surface. The higher the Young modulus is, the higher will be the resistance to crack propagation (Deblieck et al., 2011).

3.5. Discussion: from oxidation to fragmentation

All the results show that the presence of water influences clearly the fragmentation pathways of LDPE films. After a long weathering duration, a difference of surface oxidation was monitored between

water and air conditions. The lowest oxidation observed on the films in water may be explained by a light exposure less important due to the light absorption by the water molecules. This was already described for polymers weathered in the natural environment (Andradý 1990; Brandon et al., 2016). In this study, it is not the case because LDPE films (e.g. density = 0.92) float on the water surface and the exposition intensity is the same than for sample weathered in air. The lower temperature of the film in water compared to the film in air may also explain the difference of oxidation since the temperature is known to accelerate the oxidation process (i.e. thermooxidation). However, in this experiment the temperature difference is rather low (59 °C for air and 53 °C for water). Consequently, it is probable that the lower oxidation of the LDPE films in water observed here may be explained by the lower oxygen availability in water compared to air (Truesdale et al., 2007). Because of the non-polar nature of LDPE and the absence of heteroatoms, aging by hydrolysis was not considered (Gewert et al., 2015).

Oxidation promotes chain scissions in the amorphous phases, chains rearrangement (with increase of the crystallinity) and crosslinking between chains in the amorphous phase. It can be assumed that these changes result in an increase of the surface rigidity (Craig et al., 2005). Indeed, after a long weathering duration in the air, the films present a higher oxidation level and a higher crystallinity at their surface compared to water condition resulting

in a high surface rigidity as demonstrated by AFM. For water condition, the oxidation and crystallinity degrees increased less than at air, leading to a lower surface rigidity. Besides, the huge difference in rigidity observed here can also be explained by the role of water as a plasticizer (Levine and Slade, 1988). Actually, this effect consists in the penetration of small molecules between the polymer chain which prevents the rearrangements of polymer chains involved in crosslinking (Robeson, 2013). All these chemical modifications - thickness of the crystalline lamellae, side chain concentration, fraction of ordered molecules in the crystalline regions, surface rigidity - appear first at the surface of the polymer. Yakimets et al. (2004) demonstrated that polymer films having undergone photodegradation are first altered in surface and no molecular chain scission appear in the core until the molar mass of the sample at the surface decreases considerably. This results in an incompatibility between tensile stress within the upper degraded layer (surface) and the compressive stress in the unchanged material layer. In addition together with manufacturing stress, these stresses cause the bending of the film along the extrusion direction (Choi et al., 2005) as shown in air condition (Fig. 1).

Moreover, the modification of surface rigidity clearly influences the resistance of the polymer to crack initiation (Barry and Delatycki, 1992). According to Irwin model, the increase of the surface rigidity prevents the cracks propagation. The results presented here suggest that in air condition, the surface rigidity of the film is too high to allow crack initiation and propagation. An external stress is necessary to achieve fragmentation (Kalogerakis et al., 2017). On the contrary, the plasticizer effect of water may limit the increase of the rigidity of the film weathered in water, decreasing its resistance to crack initiation. Moreover, as a liquid, water governed by driving forces can transport through the craze fibril structure facilitating stress cracking as was already shown for liquids with high degree of absorption into a polymer (Robeson, 2013). However to our knowledge and probably because of the lack of affinity of water toward polyethylene material, the ability of water to be a crack promoter for polyolefins has never been studied. Nevertheless, the oxidation of LDPE due to the weathering is going to increase the hydrophilicity of LDPE and increase the ability of water to act as a crack promoter. The enlargement of cracks lead to the fragmentation of the polymer in water without the necessity of any other external stress. In this case, the cracking propagation and the manufacturing process appear to be the major factor governing the initial shape of the fragments.

As a consequence, the fragments formed in water condition exhibited similar shapes and sizes at the millimetric scale. It appears that fragments with micrometric size (<1 mm) are not abundant as they represent only 10% of the fragments. Surprisingly, the distribution presented here is close to the one reported for an extensive set of environmental samples (Cózar et al., 2014). In our case, it is a model study on PE under photodegradation in water in

abiotic conditions. The degradation is strongly accelerated compared to environmental conditions where lower UV and temperature conjugated with the presence of biofilm at the polymer surfaces are supposed to prevent the degradation (Rummel et al., 2017). It might then be supposed that in the real aquatic environment, the production of small microplastics through fragmentation processes would be a slow and difficult process compared to conditions of weathering at air and with the presence of a mechanical stress.

4. Conclusion

This study confirms that the LDPE films weathering, either in water or at air, leads to the introduction of oxygenated groups, chain scission and rearrangement on the uppermost surface of the films. As observed for the air weathered films, above a threshold value the increase of surface hardening prevents the initiation of cracks because voids formation is limited. Since no cracks can be created and propagate, the induced stress can only be released through the wrapping of the film along the direction of the maximum stress which is in our case the extrusion direction as summarized in Fig. 7. When a weak external stress is then imposed to the aged film, a catastrophic crack propagation is observed, which appears to be independent of the extrusion direction.

For the water-weathered films, the increase of surface rigidity due to crosslinking is not sufficient to prevent the initiation and propagation of cracks. As a consequence, the induced stress can be release partly through crack propagation and partly through film wrapping as observed by the formation of wrapped fragments covered by macro and micro-cracks. Moreover, water probably accelerates the propagation of cracks: once the liquid penetrates to the craze tip, it then begins to plasticize the polymer and allows the craze to grow.

In both weathering conditions, the cracking of polymers did not appear correlated with the oxidation level. Indeed, despite a lower oxidation of plastics weathered in water as shown here and already described in literature for environmental weathering, the fragmentation may be faster in water than at air in the absence of mechanical stress. Moreover, this study shows that the mechanical properties at the film surface play a major role in the fragmentation pathway. The fabrication process is also important since for blown extruded LDPE the orientation of the polymer chains is going to influence the propagation direction of the cracks (i.e. normal to the extrusion direction). This preferential fracture direction may influence the size and shape distribution of the resulting fragments compared to air-weathered films. Consequently, the distribution of plastic fragments in the aquatic environment may be linked to the nature of the polymer but also to its manufacturing process. In this study, after 25 weeks of weathering in water and high oxidation levels, 90% of the fragments were >1 mm in size with very similar shapes showing that micrometric fragments were not yet

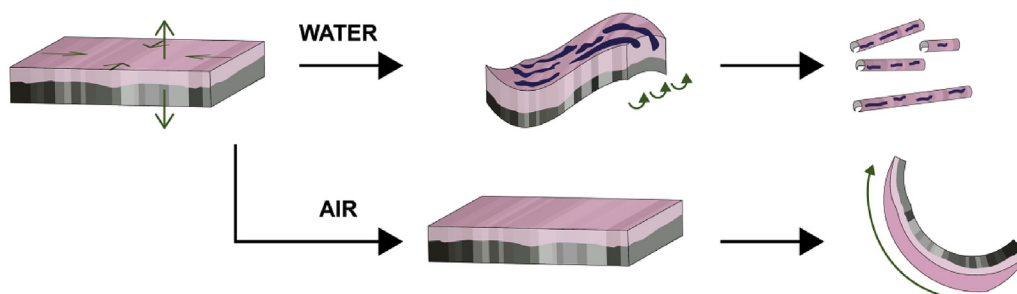


Fig. 7. Sketch resuming the behavior of LDPE film in different weathering environments.

abundant. These results raise questions on the loss of fragments <1 mm that was described in the environment. This loss may be due to the lack of methodology for sampling and analyzing small microplastics but also to the fact that long times of weathering and many steps of fragmentation appear necessary from macroplastics to reach sizes <1 mm in water. These preliminary results have to be confirmed for other polymers and the long-term behavior of the so-generated fragments in water needs to be studied to predict their decrease in size among time. While a lot of studies show that the size of microplastics has a huge role on their impacts on marine life, only a little is known about the formation of microplastics and the parameters that have effects on their size distribution. This work is among the first attempts to understand the pathways leading from macroplastics to microplastics.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.124409>.

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