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# Molecular scale understanding of the embrittlement in polyethylene ocean debris

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19 KEYWORDS

20 polymer, plastics, polyethylene, weathering, X-ray scattering, Raman spectroscopy, differential  
21 scanning calorimetry, size exclusion chromatography

22

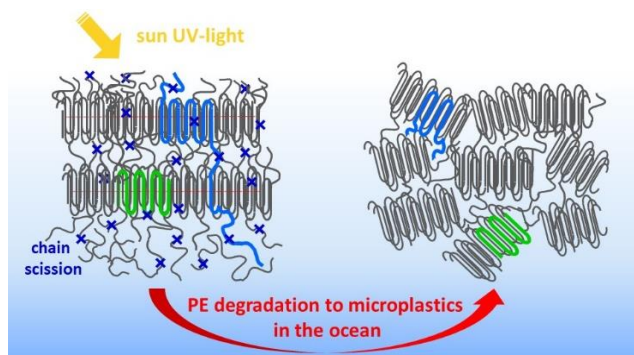
23 ABSTRACT

24 The fate of plastic waste is a pressing issue since it forms a visible and long-lived reminder of  
25 the environmental impact of consumer habits. In this study we examine the structural changes in  
26 the lamellar arrangements of semi-crystalline polyethylene (PE) packaging waste with an aim to  
27 understand the physical mechanisms of embrittlement in PE exposed to the marine environment.  
28 PE microplastics and macroplastics from identifiable PE packaging were collected in the Atlantic  
29 Ocean and compared to new PE boxes. Several experimental techniques interrogate the effects of  
30 environmental exposure on their bulk and surface properties. Size exclusion chromatography  
31 determines the molecular weight distribution of the PE polymer chains and differential scanning  
32 calorimetry gives the crystallinity. Small and wide angles X-ray scattering examines the packing  
33 of PE chains into semi-crystalline lamellae. Longitudinal acoustic mode Raman spectroscopy  
34 provides a complementary measurement on the length of PE polymer chains extending through  
35 the crystalline lamellar domains. The overall picture at the molecular scale is that although PE  
36 becomes more crystalline with environmental exposure, the lamellar order present in new packing  
37 boxes, is disrupted by the weathering process. This process has important implications for  
38 embrittlement and subsequent degradation.

39

40 TOC Abstract Art

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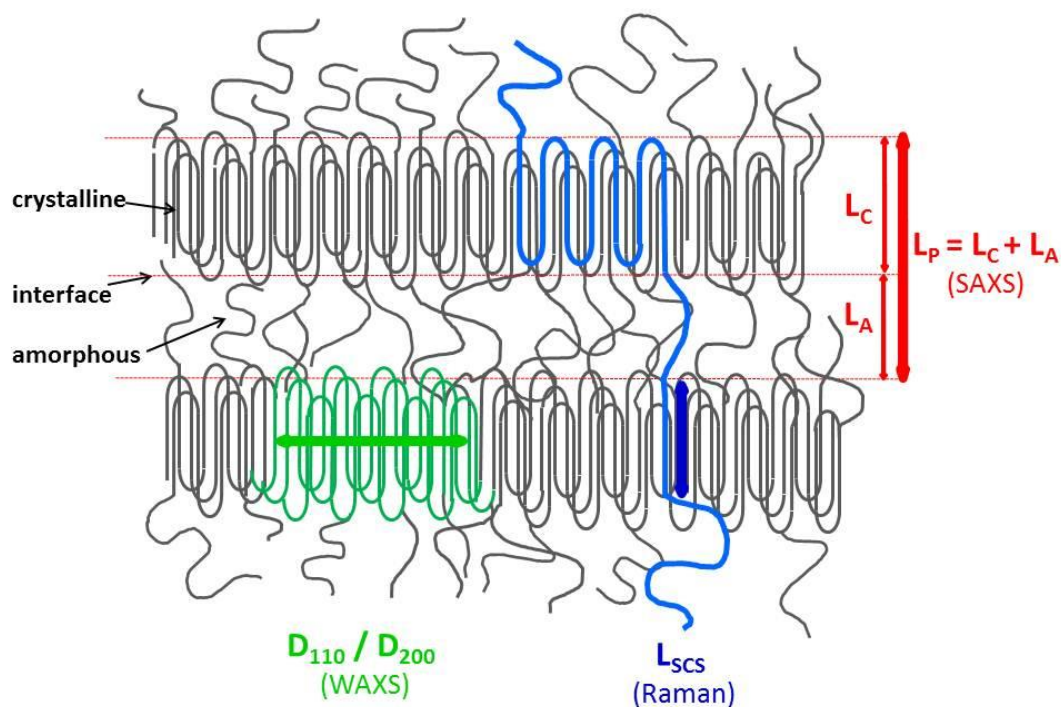
## 45 INTRODUCTION

46 In recently past decades consumer habits have changed the dominant packaging material  
47 deposited into the biosphere.<sup>1, 2</sup> Polyethylene, and more generally polyolefins, are produced  
48 extremely efficiently on an industrial scale and have become the first choice for low cost single  
49 use barrier materials. This usage was once dominated by cellulose, had well-defined pathways for  
50 the degradation and metabolic utilisation by the biosphere of the glucose monomer; such pathways  
51 for polyethylene are limited.<sup>3</sup> As a result the environmental load of polyethylene waste steadily  
52 increases with little incorporation into the biosphere.<sup>1, 2</sup> In this study we consider the physico-  
53 chemical transformations of an important thermoplastic, polyethylene, under the influence of  
54 prolonged environmental exposure, drifting in the ocean.

55 The conceptual framework for organisation of polyethylene in packaging<sup>4</sup>, and understanding  
56 the subsequent nanostructural changes due to environmental exposure are outlined in Fig. 1.  
57 Physically, this structure represents the competition between the energetically favourable  
58 crystallisation process and its kinetic limitation by the entanglement of the long extended polymer  
59 chains which span the amorphous regions and could enter the a given lamellae more than once.<sup>4</sup>  
60 There is a kinetic arrest of the crystallisation process started from the melt<sup>4</sup> and so the degree of  
61 crystallisation for packaging materials is a strong function of the processing conditions (thermal  
62 history and shear) and initial starting material (molecular weight and chain branching). Previously  
63 we have shown that exposure to UV light causes growth of the crystalline lamellae through  
64 progressive release of the kinetic constraints via chain scission.<sup>5, 6</sup> This physical transformation,  
65 increasing crystallinity, has been shown to immediately influence the mechanical stability of the

66 material (embrittlement)<sup>6</sup> but also the permeability of the polyethylene to oxygen and subsequent  
67 chemical reaction/degradation.

68 Here we combine several experimental approaches that provide complementary perspectives on  
69 selected PE samples, going from original PE packaging, to weathered macroplastics (>20 mm) and  
70 weathered microplastics (1 to 5 mm - Tables SI-1 and SI-2). The objective is to obtain a deeper  
71 understanding of the nano-structural evolution of the PE materials during environmental exposure,  
72 especially the evolution of the lamellar organisation. First, differential scanning calorimetry (DSC)  
73 and size exclusion chromatography (SEC) provide information on the kinetic arrest process; DSC  
74 by providing the crystallinity (with no assumption on the crystallite morphology) and SEC by the  
75 indication of the molecular weight distribution of the constituent polymer chains. Wide angle X-  
76 ray scattering (WAXS) provides, again, an experimental perspective on the crystallinity of the  
77 materials, and results are compared to those obtained from DSC. Furthermore, since WAXS is  
78 sensitive to the packing of the PE chains inside the crystalline lamellae, it gives a measure of the  
79 coherence length along specific crystallographic directions -  $D_{110}/D_{200}$  - of the crystalline  
80 arrangement of the PE chains (Fig. 1).



81

82 **Fig. 1:** The semi-crystalline lamellar model for PE. The individual chain highlighted in blue  
 83 spans both crystalline and amorphous regions and extends over several crystalline lamellae. The  
 84 long period  $L_P$  (measured by SAXS) is the distance between adjacent crystalline lamellae;  $L_P$  is  
 85 the sum of the lamella thickness ( $L_C$ ) and the extension of the amorphous sub-region ( $L_A$ ). The  
 86 crystalline order is characterized by WAXS through the coherence lengths (in green). Inside  
 87 crystalline lamellae, polymer chains are all parallel to each other. They may also be slightly tilted  
 88 but for simplicity, the Figure is drawn without a tilt angle. The straight chain segment length  
 89  $L_{SCS}$  is measured by Raman spectroscopy across the crystalline lamellae. Note that  $L_{SCS}$  and  $L_C$   
 90 may be slightly different (see text).

91

92 The nanoscale organisation of PE is probed by combining small angle X-ray scattering (SAXS)  
 93 and Raman spectroscopy. A peak in the SAXS measurements gives direct evidence of the lamellar  
 94 semicrystalline organisation<sup>4</sup> and the characteristic distances in the lamellar structure (Fig. 1; the  
 95 long period  $L_P$  is the sum of a crystalline lamella thickness  $L_C$  and of the amorphous sub-region  
 96 extension  $L_A$ ; the linear crystallinity,  $linC$ , is defined by the ratio  $linC = L_C/L_P$ ). Longitudinal  
 97 acoustic mode (LAM) Raman measurements are sensitive to  $L_{SCS}$ , the length of the straight

98 polyethylene chain segments inserted through the lamellae (Fig. 1). Values of  $L_C$  and  $L_{SCS}$  are  
99 always very close, but not exactly identical, as will be discussed afterwards. For example, a tilt  
100 angle (typically  $35^\circ$ , following literature data <sup>7-10</sup>) of the polymer chains may be present inside the  
101 crystalline lamellae, depending on the way the PE samples were prepared. However, in Figure 1,  
102 for simplicity, the semi-crystalline organisation is depicted with no tilt angle. Values of  $L_C$  and  
103  $L_{SCS}$  are compared with the caveat that X-ray scattering probes the bulk organisation of the PE  
104 chains in the volume of the transmitted X-ray beam (about  $1 \text{ mm}^3$ ), whereas Raman spectroscopy  
105 is probing smaller volumes (a few  $\mu\text{m}^3$ ) at the surface of the sample.

106

## 107 MATERIALS AND METHODS

### 108 SAMPLE COLLECTION

109 Macroplastics and microplastics were collected from the Guyavoile sailing vessel in the  
110 accumulation area of the North Atlantic subtropical gyre, in May 2014 and June 2015, during the  
111 “7th Continent” French expedition.<sup>11</sup> Macroplastics were visible from the boat and floated on the  
112 sea surface. Microplastics were collected using a manta net (mesh size  $300 \mu\text{m}$ ). Details of how  
113 the debris were collected, sorted out and stored are described elsewhere.<sup>11</sup> All the sample’s  
114 collection details and labelling are given in Tables SI-1 and SI-2. Some samples were not analysed  
115 by the full suite of techniques due to limited amount of sample.

116

### 117 SIZE EXCLUSION CHROMATOGRAPHY AND DIFFERENTIAL SCANNING 118 CALORIMETRY (DSC)



119 High temperature SEC and DSC analyses were used to analyse the molecular weight distribution  
120 and crystallinity of PE samples, respectively. The experimental practice and analysis have been  
121 discussed elsewhere<sup>12</sup> and are detailed in the Supplementary Information (SI).

122

123 X-RAY SCATTERING

124 X-ray scattering involves the measurement of the scattered intensity at a defined angle relative  
125 to the incident X-ray beam,  $\theta$ . The scattered intensity,  $I$ , is expressed as a function of the scattering  
126 vector,  $q$ , defined by:

$$127 \quad q = 4\pi \cdot \sin(\theta/2)/\lambda \quad (1)$$

128 ,where  $\lambda$  is the wavelength of the incident radiation. WAXS and SAXS measurements, which  
129 differ in the range of scattering vectors considered, were both performed on a homebuilt instrument  
130 (Laboratoire de Physique des Solides, Université Paris-Sud, France) operating with  
131 monochromatic copper radiation ( $\lambda_{\text{CuK}\alpha} = 0.1542 \text{ nm}$ ) delivered to the sample by a multilayer W/Si  
132 optics coupled with a rotating anode generator (Rigaku HU3R, 40kV-40mA).

133 WAXS images were recorded on a sensitive image plate detector MAR345 (marXperts,  
134 Hamburg, Germany) with a pixel size of  $0.150 \text{ mm}^2$ , placed at a distance of 100 mm from the  
135 sample. Acquisition time for each measurement was 300 s. WAXS 1-D diagrams were obtained  
136 by radial integration of the intensity of each image. The analysis and processing of the 1-D WAXS  
137 data in terms of coherence length of the  $D_{110}$  and  $D_{200}$  crystallographic planes and fractional  
138 crystallinity are detailed in the SI.

139 2D SAXS images were acquired on a two-dimensional Pilatus 200K detector (Dectris, Baden,  
140 Switzerland) using a sample to detector distance of 1236 mm. The gaps between detector modules  
141 were eliminated by combining 2 images with slight positional offsets. The size of the X-ray beam  
142 on the sample was  $0.8 \times 0.8 \text{ mm}^2$ . The data was reduced to the radially averaged intensity versus  
143  $q$  form,  $I(q)$ , using the measurement geometry, a pixel size of  $0.172 \text{ mm}^2$  and a background  
144 subtraction of the empty beam in air, scaled by the sample transmission using the NIKA macros<sup>13</sup>  
145 written for IgorPro (Wavemetrics, Oswego, USA). The final  $q$ -range was  $0.094 < q < 1.64 \text{ nm}^{-1}$ .

146

## 147 RAMAN SPECTROSCOPY

148 In semi-crystalline polymers, the Straight Chain Segments length  $L_{SCS}$  can be approximated from  
149 the position of Raman first-order Longitudinal Acoustic Mode ( $\sigma_{LAM}$ ) using Mizushima–  
150 Simanouti equation<sup>14, 15</sup>:

$$151 \quad L_{SCS} = \frac{1}{2c\sigma_{LAM}\sqrt{\frac{\rho}{E}}} \quad (2)$$

152 In Eq. (2),  $\rho$  is the density of the crystallites,  $E$  their Young's modulus and  $c$  is the speed of light.

153 In this study we shall use  $\rho = 972 \text{ kg.m}^{-3}$  (the experimental density of PE single crystals<sup>16</sup>) and  $E$   
154  $= 305 \text{ GPa}$  (Young's modulus in the direction of "all-trans" PE chains in interaction).<sup>17-20</sup> Eq. (2)

155 pairs one unique  $\sigma_L$  wavenumber with each  $L_{SCS}$  value and the experimental spectrum  $I_{LAM}(\sigma_L)$  is  
156 classically converted into a Lamellar Thickness Distribution (LTD) using Eq. (3)<sup>21</sup> (see details in

157 the SI) where the  $\left(1 - e^{-\frac{hc}{kT}\sigma_L}\right)$  term is the thermal population factor from Maxwell-Boltzmann  
158 statistics:

$$159 \quad N(L_{SCS}) \propto I_{LAM}(\sigma_L) \times \left(1 - e^{-\frac{hc}{kT}\sigma_L}\right) \times \sigma_L^2 \quad (3)$$

160 Samuel and Hamagushi<sup>22</sup> recently introduced a correction factor in Eq. (3) but discarding it  
161 makes no difference for our samples, as discussed in the SI.

162 All spectra were recorded in backscattering mode using the 514.5 nm line of an Innova 90C-  
163 6UV Ar<sup>+</sup> ion laser (Coherent) and a LabRam HR 800 Raman spectrometer equipped with an Ultra  
164 Low Frequency (ULF) module for Rayleigh scattering filtration (Horiba Jobin Yvon). A minimum  
165 of five spectra were recorded for each sample. Depending on the signal to noise ratio, either the  
166 most intense one or the average one was fitted, after correction of the ULF-induced distortion

167 through a procedure described in the SI. Further details on the experimental setup, the probed  
168 volume, fluorescence quenching and peak fitting procedures may also be found in the SI.

169

## 170 STATISTICAL ANALYSIS

171 Statistical tests were performed on the full set of data. A Fisher test was first performed to compare  
172 the variances of the samples before applying a Student's t-test if appropriate. Owing to the low  
173 number of macro samples, Fisher's test failed in some cases. Mann Whitney tests were then  
174 performed considering non-parametric data. The corresponding indications are reported in the  
175 Figures.

176

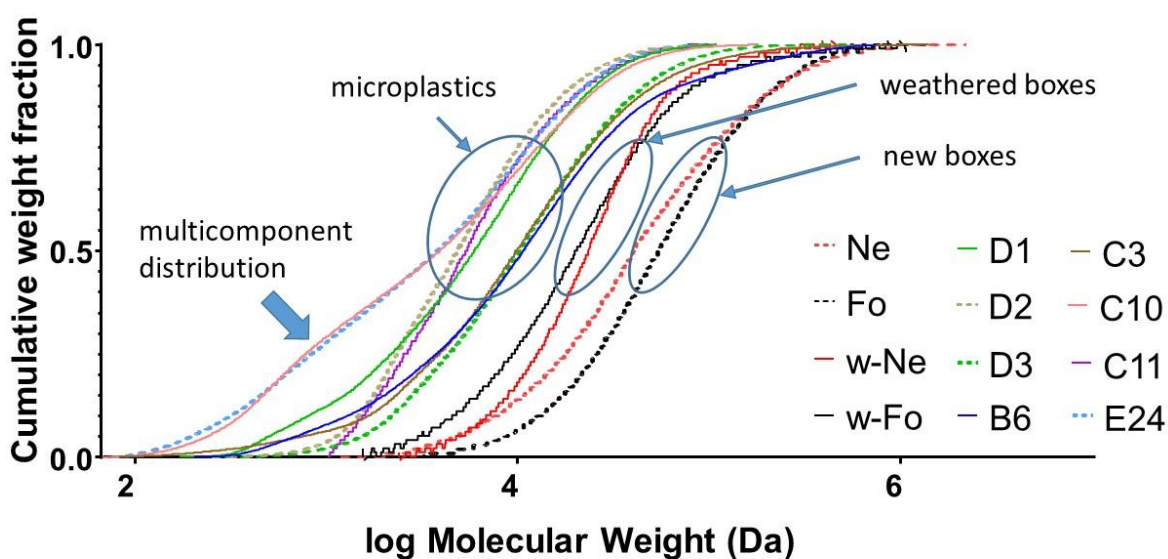
## 177 RESULTS AND DISCUSSION

178 The focus is the nanostructural evolution of PE, crystallization, in several types of original  
179 packaging and weathered samples. Firstly, we assess the differences between commercial  
180 packaging samples (Nesquik and Folgers boxes, code names Ne and Fo) and the corresponding  
181 weathered macroplastics (w-Ne and w-Fo). Secondly, these macroplastics are compared to several  
182 microplastics of unknown origin. Because of the much smaller physical dimensions of the latter  
183 (see Table SI 1), it is assumed that they have been weathered for a longer time, and have therefore  
184 reached a more advanced oxidation state.<sup>12</sup> However, because the history of the samples (before  
185 they were collected) and the starting material are not well defined, the conditions of formation of  
186 the debris are largely unknown. Secondly, owing to the small number of microplastics presented  
187 here (10), statistical tests were systematically performed to compare with original packaging and  
188 the paired macro-plastics.

189

190 SIZE EXCLUSION CHROMATOGRAPHY

191 SEC was performed to determine the molecular weight distribution of the polymer chains.  
192 Typical SEC profiles are shown in Figure SI 1. The cumulative weight fractions obtained from the  
193 analysis are shown in Fig. 2. The analysis is elaborated in Table SI 3. Samples D19 and C8 did not  
194 have sufficient material for the analysis.  
195



196 **Fig. 2:** Cumulative weight fraction showing the mass distribution of the polymer chains in the  
197 different samples.  
198

199  
200 The cumulative mass distributions shown in Fig. 2 indicate a strong decrease in molecular weight  
201 when the weathered boxes (w-Ne, w-Fo) are compared to the original ones (Ne, Fo). The micro-  
202 plastics present even lower molecular weights and their distribution tends to become multi-  
203 component, as can be seen from the tails in Fig. 2.  
204 Table SI 3 summarizes the initial interpretation of the SE molecular weight distributions in terms  
205 of single and, in some cases, bimodal average values. Mn values are particularly low (below 5000

206 g.mol<sup>-1</sup>) for all microplastics and their size distribution is better described by a multimodal  
207 distribution, with average molecular weights  $M_{n1}$ ,  $M_{n2}$  and corresponding average degrees of  
208 polymerisation,  $N_1$ ,  $N_2$ . Microplastics E24, C11 and C10 have a mean  $M_n$  value close to 1000  
209 g.mol<sup>-1</sup>, indicating that they have, on average, smaller polymer chains than D1, D2, B6, C3 and  
210 D3 microplastics. Macro or new materials have a significantly higher  $M_n$  value and longer polymer  
211 chain lengths than the micro debris. The polydispersity index (PDI) is in general much larger for  
212 microplastics. The statistical significance of these observations is shown in Fig. SI 2.

213  
214 In conclusion, SEC shows a strong decrease of the polymer chain length between the original  
215 packaging and the macroplastics. Interestingly, the size distributions of the microplastics are  
216 usually multimodal. A spatially homogeneous scission would result in only a broadening of the  
217 initial distribution. Here a spatially heterogeneous scission is most likely taking place. It could be  
218 attributed to a preferred degradation at the surface (compared to the bulk) or related to selective  
219 degradation in the semi-crystalline morphology (coexistence of crystalline and amorphous parts,  
220 see Fig. 1) or a combination of both mechanisms.

221

222

## 223 DIFFERENTIAL SCANNING CALORIMETRY

224 DSC brings insights on: i) the kinetic arrest of PE crystallisation; and ii) the aging processes that  
225 altered the polymer organization (through the enthalpy of first fusion). Samples C8, D19 and E24  
226 were too small to be characterized.

227 Fig. SI 3 shows typical DSC traces and the results of the statistical analysis are given in Table  
228 SI 4. The new boxes and macroplastics do not exhibit measureable differences whereas all  
229 microplastics have significantly higher crystallinity values (~70 %, on average, compared to ~50  
230 % for macroplastics).

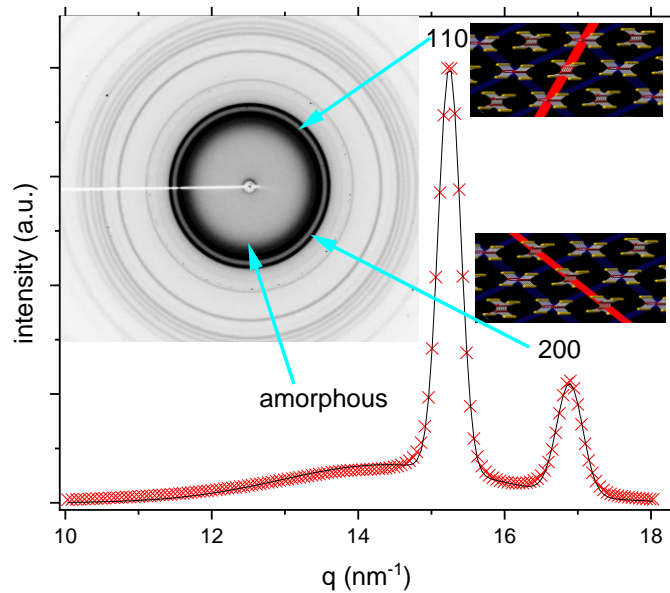
231 The melting can either be characterized by the peak position or at the beginning of the transition,  
232 *i.e.* the onset value (Table SI 4). No significant difference in the melting peak position was  
233 observed (Fig. SI 3). The onset temperatures were significantly lower for macro- compared to  
234 microplastics. The melting of the D1, B6 and C10 microplastics starts around 123-124°C. For the  
235 other microplastics, the fusion starts at higher temperatures: around 128°C for D2, C11 and C3;  
236 around 130°C for D3.

237 By comparing the SEC (Table SI 3) and DSC (Table SI 4) characterizations, it appears that the  
238 samples which are melting at lower temperatures (B6 and C10) exhibited the highest PDI. This is  
239 relevant with shortened chains being able to melt earlier. Moreover, the samples with the lower  
240 crystallinity exhibit a lower onset temperature of melting (macro versus micro samples). Owing to  
241 the very narrow distribution of the melting temperature between the microplastics (Fig SI 3), it is  
242 however impossible to compare SEC and DSC results more precisely. This is not surprising since  
243 physical properties are known to be poorly sensitive to molecular weight in these long chain  
244 polymers, contrary to small molecules and oligomers.<sup>4</sup>

245

246 WAXS

247 The radially averaged WAXS profile of Nesquik commercial packaging is shown In Fig. 3, along  
248 with the original 2D pattern (in the inset). Similar data are available for the other samples in Fig.  
249 SI 4. The WAXS patterns typically consist of many sharp and radially symmetric Debye-Scherrer  
250 rings and a single broad peak which is characteristic of the poorly defined interatomic distances of  
251 an amorphous solid.<sup>23</sup> The radial isotropy shows the lack of orientation expected from PE (powder  
252 pattern), along with a very limited number of spotty diffraction rings from filler or pigment  
253 material.



254  
255 **Fig. 3:** Typical radially averaged WAXS data (red crosses) from Nesquik packaging material.  
256 Inset shows the corresponding 2D pattern. The black solid line shows the fit with three Gaussians  
257 described in the SI. Each lattice plane is shown in red on the cartoon next to the corresponding  
258 Bragg peak.

259  
260 Using the crystal structure from Bruno et al.,<sup>24</sup> our analysis has focussed on the  $10 < q < 18 \text{ nm}^{-1}$   
261 <sup>1</sup> q-range containing the 110 and 200 reflections and the broad amorphous halo. There are  
262 numerous other peaks due to other less intense X-ray reflexions from PE and from the many



263 additives (e.g. colouring and fillers) which are found in commercial PE packaging.<sup>25</sup> The important  
264 fitted parameters are summarised in Table SI-5. From the FWHMs of the Bragg peaks (see Eqn's  
265 SI 3 and SI 4) we obtain the average coherence lengths  $D_{110}$  and  $D_{200}$  (see Fig. 1). The results of  
266 the analysis are given in Table 1. Crystallinities determined by WAXS and DSC are different but  
267 agree qualitatively (Figure SI-5). It is important to note that WAXS crystallinity is very sensitive  
268 to the data fitting procedure, and to the way the contributions of Bragg peaks are separated from  
269 the contribution of the amorphous peak.<sup>26</sup> This may explain that for all microplastics the values of  
270 the crystallinity derived from WAXS are overestimated compared to DSC.

271 The two average coherence lengths inside crystallite lamellae ( $D_{110}$  and  $D_{200}$  - Fig. 1) are  
272 significantly smaller for the microplastics than for the macroplastics (Table 1). For example, the  
273 value of  $D_{110}$  decreases in average value from 34 to 23 nm between macro and microplastics. The  
274 coherence length is defined as the extension of crystalline order normal to the specified  
275 crystallographic direction. We find that the in-plane crystalline order extends over a few tens of  
276 nanometres and decreases with weathering. Note here that the overall lateral size of the crystalline  
277 lamellae is expected to be much larger than the coherence length, typically of a few microns.<sup>4</sup> The  
278 in-plane order of the lamellae can be visualized as a collection of nano-sized crystalline domains.  
279 In conclusion, a higher crystallinity of these samples is associated to a smaller coherence length in  
280 the in-plane direction of the lamellae.

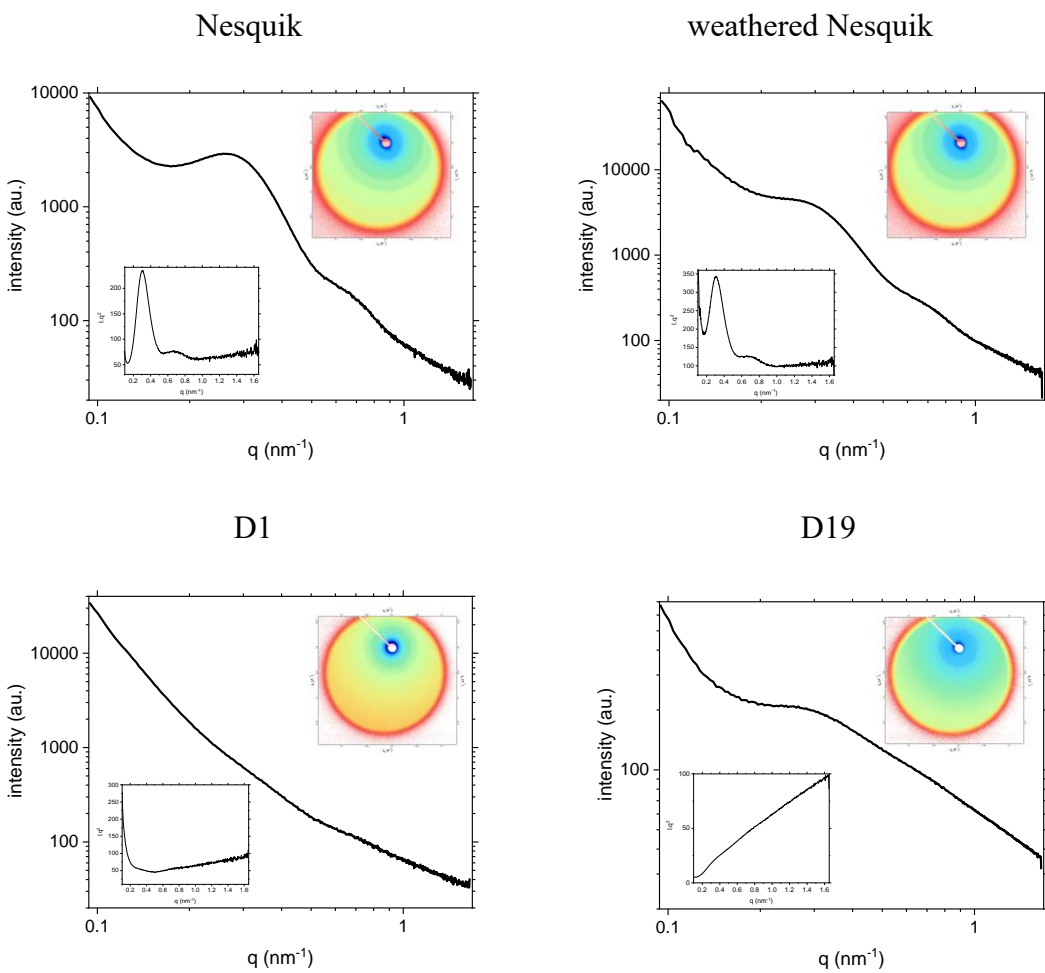
281

## 282 SAXS

283 In the semi-crystalline polymer model (Fig. 1) PE is organised in alternating lamellae of  
284 crystalline and amorphous polyethylene (PE) with electron densities,  $\rho_c$  and  $\rho_a$ , and thicknesses  
285  $L_c$  and  $L_a$ , respectively. Because of this contrast in electron density, it is possible with SAXS to

286 measure the inter-lamellar spacing, called the long period  $L_P$ , with  $L_P = L_c + L_a$ . Fig. 4 shows the  
 287 variation in 2D scattering patterns and the corresponding 1D SAXS profiles for different samples:  
 288 Commercial Nesquik packaging (Ne), the corresponding weathered sample (w-Ne) and two  
 289 microplastics (D19 and D1). All other SAXS patterns are given in Figure SI 6. As with WAXS,  
 290 all the SAXS patterns are isotropic, and there is no preferential orientation of the lamellar structure.  
 291 We will thus restrict the following discussion to the radially averaged 1D data.

292  
 293



294  
 295  
 296

297 **Fig. 4:** Typical SAXS 1D profiles, with the corresponding 2D images (top right hand side insets)  
 298 and Lorentz transformed data (bottom left hand side insets).  
 299

300  
 301 The intensity of the broad lamellar peak exhibits strong variations depending on the sample (Fig.  
 302 4 and Fig. SI 6). Generally, the raw packaging materials (Ne and Fo) have the most obvious peak.

303 The weathered macro debris (w-Ne and w-Fo) have a slightly less obvious feature. The  
 304 microplastics exhibit either a very weak lamellar peak (D13 and C11), or no peak at all (C3, C10  
 305 and E24). Importantly, despite not exhibiting ordered lamellae, these samples do not exhibit any  
 306 strongly different DSC crystallinities compared to the other samples in the same group: packaging;  
 307 macroplastics; and microplastics. An exception is E24, the only sample that has no lamellar peak  
 308 and a low crystallinity, comparable to that of the macroplastics.

309 The position of the peak in reciprocal space,  $q_{max}$ , may be converted to the real space lamellar  
 310 spacing:

$$311 \quad L_P = \frac{2\pi}{q_{max}} \quad (4)$$

312 The very broad SAXS peak is superimposed upon a sloping background. A convenient way of  
 313 visualising the position of  $q_{max}$  is the Lorentz plot<sup>27</sup> -  $q^2 \cdot I(q)$  (shown for the four spectra of Figure  
 314 4).

315 In order to estimate the linear crystallinity ( $linC=L_c/(L_a+L_c)$ ) from those samples exhibiting a  
 316 clear lamellar diffraction feature, we applied a cosine transform to the Lorentz transformed data.  
 317 We thus obtained the linear correlation function ( $\gamma_1(x)$ ), which maximum corresponds to  $L_c$ .<sup>6</sup>:

$$318 \quad \gamma_1(x) = \frac{\int_0^\infty I(q)q^2 \cos(qx) dq}{\int_0^\infty I(q)q^2 dq} \quad (5)$$

319 The values obtained from the Lorentz plot and the subsequently cosine transformed data were  
 320 consistent but the transform method was not suitable for those samples which exhibited very weak  
 321 features. The SAXS plot for sample C8 was truncated by the limited solid angle of the 2D SAXS  
 322 detector and it was difficult to extrapolate the high- $q$  behaviour. The distributions of the  $L_P$  for  
 323 samples that exhibit diffraction feature and/or were amenable to transformation to  $\gamma_1(x)$  are shown  
 324 in Fig. SI 7 and reported in Table 1. The value of  $L_P$  is rather constant for all samples, with  $L_P$

325 close to 20 nm. According to Mann-Whitney test, no significant difference between the macro-  
326 and microplastics is observed.

327 The values of  $linC$  are higher than the values obtained from DSC and WAXS measurements  
328 (Fig. SI 5), with  $linC$  values close to 80% instead of 50% for the macroplastics. This difference is  
329 generally rationalised by considering that the value obtained for  $linC$  is not sensitive to the  
330 amorphous material outside the semicrystalline lamellae.<sup>4</sup>WAXS analysis does not rely on the  
331 assumption of a lamellar structure whereas SAXS analysis does and some samples could consist  
332 of bulk amorphous regions outside lamellae. In Table 1, last column, by proportional subtraction  
333 of values of  $linC$  from the overall crystallinity (determined by DSC), we estimate the amount of  
334 lamellar regions inside the material, in coexistence with extra amorphous regions.

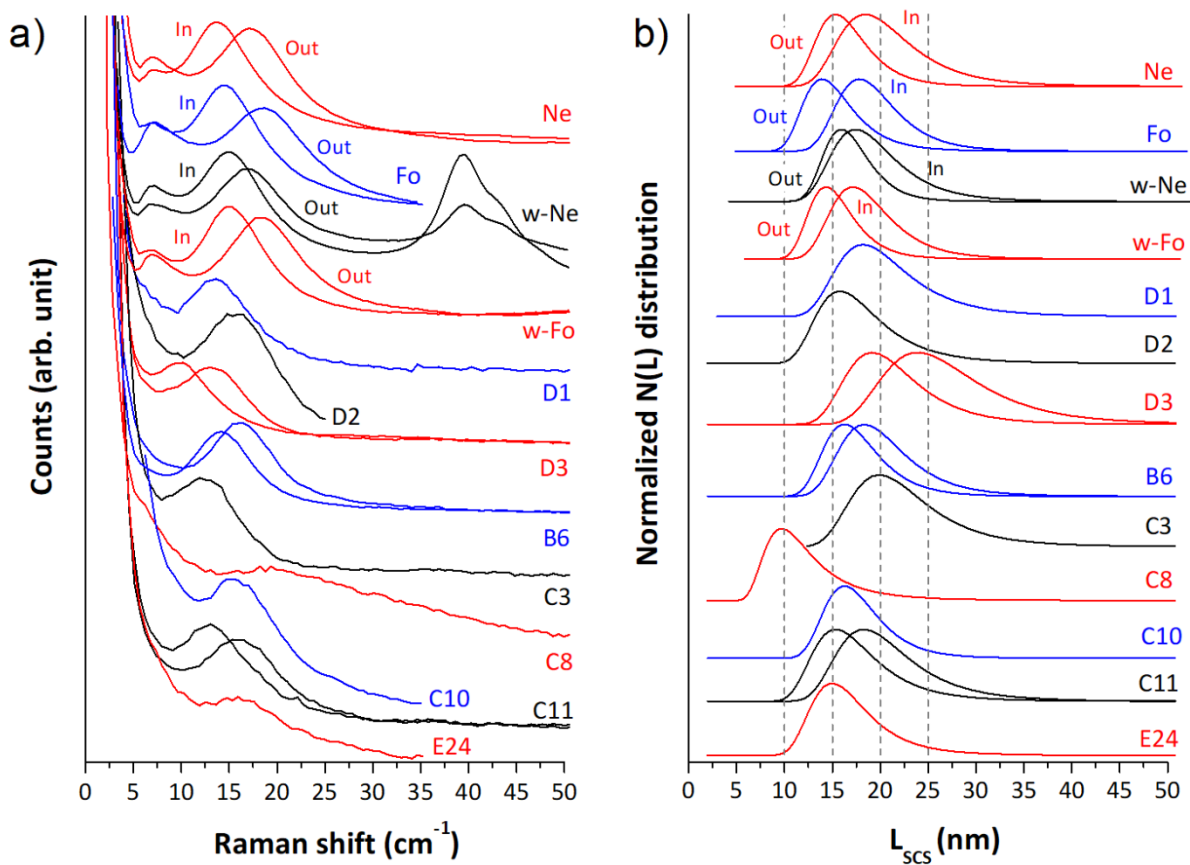
335 In conclusion, unlike previous studies on PE samples with a well-defined environmental history,<sup>6</sup>  
336 we do not observe change or growth of  $L_P$ . Moreover, for microplastics, the long period peak in  
337 SAXS is not present or has a very weak intensity. A clear trend to the disruption of the lamellar  
338 order in the microplastics is observed.

339

#### 340 RAMAN SPECTROSCOPY

341 Fig. 5a presents the low frequency Raman spectra collected from the samples and Fig. 5b gives  
342 the normalised linear thickness distributions (LTD) calculated from the mathematically adjusted  
343 LAM mode (Eqn.'s 2 and 3). Note that the fitted LAM position did not systematically match the  
344 apparent one in the raw spectrum. This points the importance of a spectral treatment to correct for  
345 the filtering-induced distortion, for superimposing contributions (mostly Rayleigh diffusion wing)  
346 and for the difficulty to set Raman shift origin precisely on the laser wavenumber with a pixel  
347 width  $\sim 0.5 \text{ cm}^{-1}$  (see discussion in SI).

348 All the fitted LAM positions and corresponding L values ( $L_{SCS-avg}$ ) are given in Table SI 6, as  
 349 well as the most probable L value ( $L_{SCS-mp}$ ) and the FWHM retrieved from each LTD (see SI). As  
 350 a consequence of the distribution asymmetry, the most probable  $L_{SCS}$  is systematically about 2 nm  
 351 below the average value.



352  
 353 **Fig. 5:** (a) Low frequency Raman spectra corrected for the Rayleigh filtering stage (see SI); two  
 354 spectra are given when distinct populations were observed depending on the point of analysis;  
 355 In/Out labels specify which packaging wall was analysed; spectra from samples Fo, D2, C10 and  
 356 E24 were truncated for clarity (b)  $L_{SCS}$  number distribution obtained from the fitted LAM profile  
 357 (see Eqns 2 and 3 and SI).

358  
 359 The SCSs may be at an angle with the normal to PE lamellae but the average tilt is  
 360 usually low enough ( $\sim 35^\circ$ )<sup>23-26</sup> to still consider LSCS a good estimate for the lamellar  
 361 thickness. As a matter of fact, the excellent agreement observed between the LSCS-mp

362 values obtained from low frequency Raman spectroscopy and  $L_C$  values derived from  
363 SAXS (Table 1), while not specifically investigated here, is suggestive of a relatively  
364 low tilt angle in our samples.

365 The SCSs may be at an angle with the normal to PE lamellae but the average tilt is low enough  
366 ( $\sim 35^\circ$ )<sup>7-10</sup> to consider  $L_{SCS}$  a good estimate for the lamellar thickness. There is a small but  
367 systematic difference between the  $L_{SCS-mp}$  values obtained from low frequency Raman  
368 spectroscopy and  $L_C$  values derived from SAXS (Table 1), while not specifically investigated here,  
369 is suggestive of a relatively low tilt angle. Yet, SAXS results are averaged over the entire thickness  
370 of the samples whereas the penetration depth of Raman spectroscopy (a few micrometers below  
371 the surface, see SI) makes it possible to evidence structural differences between the inner and outer  
372 walls of the Folgers and Nesquik samples, without the need for sample sectioning. Besides, the  
373 Raman method is able to give a clear indication of the crystalline lamellar thickness when this is  
374 not possible for SAXS measurements, i.e. there is no SAXS diffraction feature.

375 The LTD is systematically increased by about 4 nm in the inner wall compared with the outer  
376 one (Tables 1 and SI 6). This is the first time, to our knowledge, that an inside vs. outside difference  
377 has been characterized in the literature on commercial PE packaging. This difference most  
378 probably results from a temperature gradient during the blow-moulding process. For those  
379 microplastics that reveal a two-mode distribution (D3, B6 and C11 samples) we might infer they  
380 corresponded to the inner and outer walls of the original packaging.

381 The direct comparison between a pristine and weathered sample of either Nesquik or Folgers  
382 packaging would obviously be questionable since they may not come from the same manufacturer  
383 or batch (see Fig 5(a) the  $\sim 40\text{ cm}^{-1}$  contribution that is detected in w-Ne but not observed in Ne  
384 sample). Yet, the general impression given by Fig. 5b and the Raman derived parameters from

385 Table SI 6 is that most  $L_{SCS-mp}$  values stand in the ~15-20 nm range and that no systematic  
386 evolution of the LTD can be evidenced going from the pristine PE samples to weathered  
387 macroplastics and, ultimately, microplastics. The two outlier distributions are also the less reliable  
388 ones: C8 sample had very diffuse Raman scattering and the lowest peaks from D3 sample were at  
389 the  $\sim 10 \text{ cm}^{-1}$  detection limit (Fig. SI 8a).

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395 **Table 1.** Summary of the experimental results: **(i)** SEC-derived average number of monomer units  
396 per chain for monomodal (N) or bimodal ( $N_1$  and  $N_2$ ) size distributions (see Table SI 3 for details);  
397 **(ii)** DSC- and WAXS-derived crystallinity; **(iii)** WAXS-derived  $D_{110}$  and  $D_{200}$  coherence lengths;  
398 **(iv)** SAXS-derived values of the long period ( $L_p$ ), the linear crystallinity (linC) and  $L_C = L_p \cdot \text{linC}$ ;  
399 **(v)** Raman-derived most probable  $L_{SCS}$  value; **(vi)** Estimation of the amount of lamellar phase (lam  
400 phase, %) in coexistence with extra amorphous regions; #: sample not analysed; \*: irrelevant data.

Sample	N (N <sub>1</sub> , N <sub>2</sub> ) SEC	Cryst. (%) DSC	Cryst. (%) WAXS	D <sub>110</sub> (nm) WAXS	D <sub>200</sub> (nm) WAXS	L <sub>P</sub> (nm) SAXS	LinC (%) SAXS	L <sub>C</sub> (nm) SAXS	L <sub>SCS-mp</sub> (nm) Raman	Lam phase (%)
Probed vol.	1 mg	mm <sup>3</sup>	mm <sup>3</sup>	mm <sup>3</sup>	mm <sup>3</sup>	mm <sup>3</sup>	mm <sup>3</sup>	mm <sup>3</sup>	μm <sup>3</sup>	
<b>Ne</b>	721	53	53	33.8	28.4	20.2	78	15.8	15.4 – 18.5 (outer - inner)	68
<b>Fo</b>	1046	45	49	34.7	29.7	20.5	76	15.6	13.9 – 17.8 (outer - inner)	62
<b>w-Ne</b>	546	51	49	34.7	26.5	20.0	82	16.4	15.8 – 17.5 (outer – inner)	61
<b>w-Fo</b>	386	50	58	24.0	19.5	19.5	79	15.4	14.4 – 17.2 (outer – inner)	68
<b>D1</b>	82	64	74	23.1	20.8	no peak	*	*	18.2	*
<b>D2</b>	111 (418/68)	72	76	23.6	20.8	19.8	*	*	16.0	*
<b>D3</b>	186 (386/61)	69	77	23.1	21.1	23	*	*	19.1 – 24.2 (2 populations)	*
<b>D19</b>	#	*	72	22.7	20.8	18.2	89	16.2	#	81
<b>B6</b>	125 (179/9)	64	75	22.7	20.5	19.5	84	16.4	16.0 – 18.4 (2 populations)	83
<b>C3</b>	139 (357/27)	71	77	34.7	32.0	no peak	*	*	19.9	*
<b>C8</b>	#	*	74	23.1	20.8	8.3	76	6.3	9.7	97
<b>C10</b>	39 (189/14)	60	73	22.3	20.5	no peak	*	*	16.5	*
<b>C11</b>	36	72	77	23.6	21.1	18.5	*	*	15.5 – 18.4 (2 populations)	*
<b>E24</b>	34 (193/12)	#	52	23.6	19.2	no peak	*	*	15.0	*



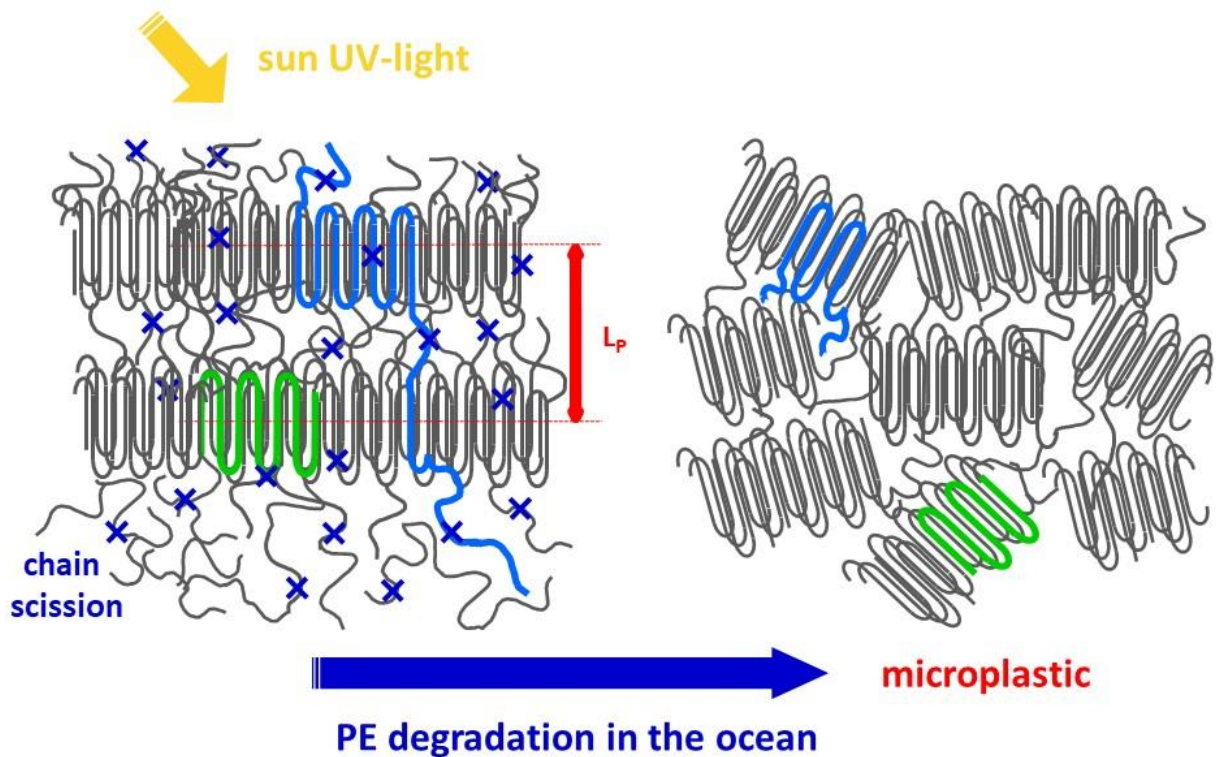
To date most studies on the degradation of polyethylene have focussed on the chemical changes as a result of various interactions with light, the atmosphere and mechanical processes.<sup>28</sup> The dominant chemical reactions during degradation are polymer chain scission and/or oxidation. While ultimately degradation must be considered as a chemical process, physical changes in the solid state packing of polymer molecules have long been acknowledged as important determinant in the ability of many polymers to resist chemical and environmental degradation.<sup>29</sup> Furthermore, the scission of polymer chains by photodegradation has the effect of allowing polymer chains in kinetic arrest to adopt the lowest energy configuration and to crystallise further<sup>6</sup>, which implies a clear link between chemical and physical changes.

A first objective of this work was to compare macroplastics (w-Ne and w-Fo samples) with their corresponding new packaging (Ne and Fo samples). What we observe is that although both samples undergo a reduction in molecular weight of PE, the sample with the greatest reduction in molecular weight (Fo to w-Fo) is the one that shows the greatest changes in nanostructure. Increase in crystallinity and decrease in the coherence length inside the crystalline lamellae are the two changes observed in this macroplastic. This trend is amplified for most microplastics. Importantly, all microplastics have much smaller molecular weight. As already known, scission of the polymer chains is the main chemical evolution that is taking place. We assert that this process underpins all the physical changes in the material. While macroplastics have crystallinities around 50 %, crystallinity in the microplastics is around 70 %, on average. This can be understood by the release of kinetic arrest to crystallization when polymer chains become shorter.

At the same time, Raman and SAXS do not evidence any systematic increase of the thickness of the crystalline lamellae,  $L_c$  and  $L_{SCS}$  always being close to 16 nm. This is quite surprising, as one would expect that increase in crystallinity should induce thickening of the crystalline lamellae,

with crystallisation occurring specifically at the crystalline/amorphous interface between lamellae, as was observed for PE systems exposed to specific doses of UV light.<sup>6</sup> In addition, the lamellar order is disappearing in most of the microplastics, as the peak related to the long period  $L_P$  is very weak or absent. Figure 6 is a cartoon summarising the evolution in the nanoscale structure: increase of the crystallinity and disruption of the lamellar order are taking place simultaneously.

Lastly, it will be important for future studies to take into account the structural heterogeneities of the original samples. It is well evidenced in Raman spectroscopy, with differences in the crystalline lamellar thickness  $L_{SCS}$  between the inside and outside surfaces of the packaging boxes. To date the effect of lamellar thickness on the crack resistance of PE has been investigated indirectly but would seem to be important.<sup>30</sup> There is also an open question regarding the heterogeneous scission of the PE chains evidenced by SEC measurements, most clearly in the microplastics. The resulting bimodal molecular weight distributions could be attributed to a preferred degradation at the surface (compared to the bulk) or related to selective scission inside crystalline versus amorphous PE.



**Figure 6.** Summary of the observed evolution of semi-crystalline PE submitted to environmental conditions. Chain scission (indicated by blue crosses) induces a strong decrease of the average chain length (blue chains) and two main structural changes: increase in crystallinity and disruption of the lamellar order. In addition, no significant change in the thickness of the lamellae is observed and coherence lengths are slightly smaller (green crystalline domains). On the bottom part of the macroplastics scheme, possible coexistence of lamellar regions with extra amorphous regions is not depicted.

While the structural conclusions of this work are clear for each of the samples we have examined here, to directly relate these changes to the long-term effects of physical aging in the marine environment, is more difficult. In the case where the lineage of aged samples can be clearly established, macro samples and commercial packaging, we observe clear changes in the polymerisation degree of PE. Chain scission can be induced by exposure to high-energy radiation or photochemical degradation, and similar changes in crystallinity and subsequent embrittlement were observed.<sup>31-33</sup> In the case of exposure to high energy radiation there is

substantial time lag (years) between the initial exposure/chain scission event and the full realisation of the structural changes.<sup>33</sup> Studies on degradation in model aquatic and marine systems have concluded that the effects of chemical degradation (oxidation) are causing both chain depolymerisation<sup>34</sup> and mass loss<sup>35</sup>, which are associated with embrittlement of the bulk material on a shorter time scale. Though in the latter study<sup>35</sup> there was no explicit examination of the changes in molecular weight. Thus, radiation-induced chain scission and chemical degradation are both likely to occur in the marine environment, but on rather different timescales and with quite different impacts on the bulk and surface degradation of PE particles.

The important structural conclusion of this study is the loss of ordered semi-crystalline lamellar structure in aged microplastics. The arrangements of the lamellae provide a barrier to the diffusion of gases into the bulk polymer.<sup>36</sup> Assuming the crystalline regions present a barrier to diffusion of oxidants (most importantly oxygen) into PE the loss of the lamellar structure shown in Fig. 6 would allow freer chemical degradation with time. We therefore suggest that this important physical change in the arrangement of PE may enhance further chemical degradation of PE.

## ASSOCIATED CONTENT

### **Supporting Information.**

**SI-file-PE-paper - January XX<sup>th</sup>**

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## ABBREVIATIONS

DSC, differential scanning calorimetry; FWHM, Full Width at Half Maximum; LAM, Longitudinal acoustic mode (Raman spectroscopy); linC, linear crystallinity; LTD, Lamellar Thickness Distribution; PDI, polydispersity index; PE, polyethylene; SAXS, small angle X-ray scattering; SEC, Size exclusion chromatography; WAXS, wide angle X-ray scattering.

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