



## From macroplastics to microplastics: role of water and polymer microstructure in the fragmentation mechanism

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### **Introduction**

Once in the aquatic environment, macro debris of plastic undergo mechanical (erosion, abrasion), chemical (photo-oxidation, hydrolysis) and biological (degradation by microorganisms) modifications [1]. 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. 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 polyethylene (PE) or polypropylene (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 [2], [3]. It is particularly difficult to monitor all 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 at studying the loss of mechanical properties in polymers during their ageing but experimental studies on their fragmentation at air or in water are scarce [4], [5] 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 [6]. 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.

### **Material and Methods**

In this study, the long-term artificial weathering of polyethylene and polypropylene films were studied in laboratory in order to monitor the first stages of the fragmentation under two different environments: in air or in Milli-Q water. Films were extruded to control their composition and placed in a weathering chamber during several weeks. The aim of this work was 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.

### **Results**

Oxidation, surface mechanical properties, crystallinity and crack propagation were monitored through contact angle, spectroscopic and Atomic Force Microscopy measurements to investigate their influence on fragmentation.

The role of water was demonstrated with the study of LDPE films. As shown by Figure 1, 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 [7].

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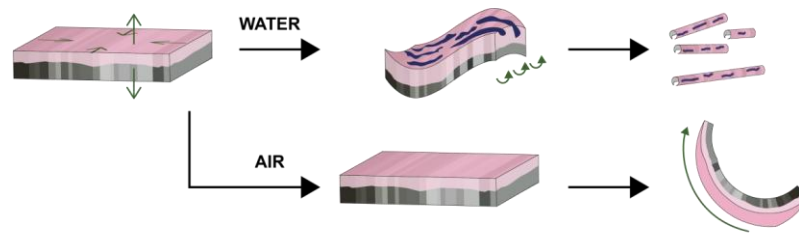


Figure 1. Sketch resuming the behavior of LDPE film in different weathering environments.

The role of polymer microstructure was demonstrated with the study of polypropylene films. For these films, it was shown that the presence of spherulites (crystalline structure) strongly influence the crack propagation and the resulting fragments' distribution (Figure 2).

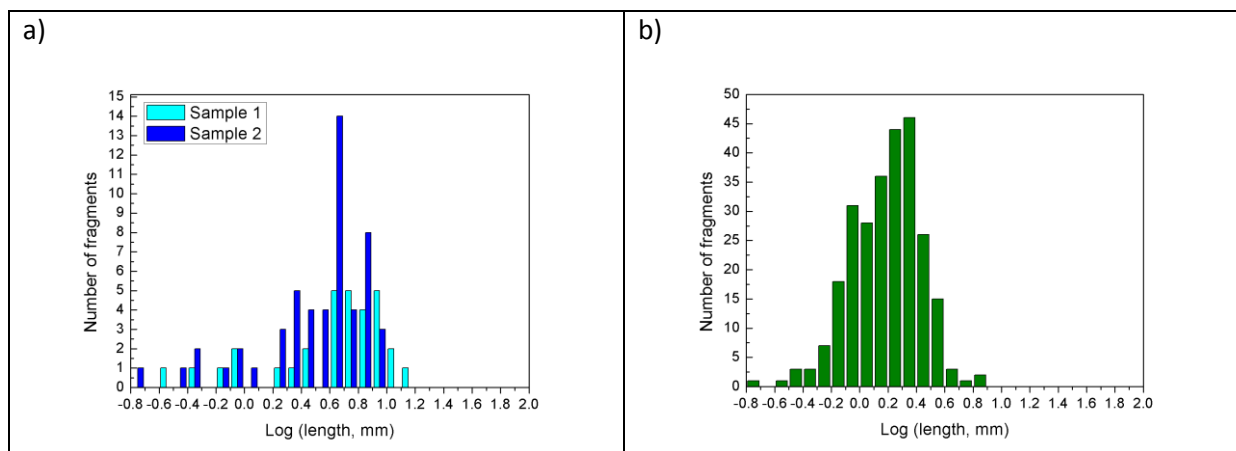


Figure 2 : Fragments size distribution (in numbers) after 27 weeks of accelerated ageing for LDPE (a) and PP (b) films.

## Conclusion

In both weathering conditions, the cracking of polymers did not appear correlated with the oxidation level. In water, the distribution in size of plastic fragments generated during polymer degradation appears strongly dependant on the nature of the polymer but also on its manufacturing process.

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