INFLUENCE OF NATURAL BIOFOULING IN THE DEGRADATION AND IDENTIFICATION OF POLYPROPYLENE

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Introduction

Polypropylene is one of the most produced plastics in the world which is eventually discarded into the environment. Once released, plastics may degrade through several agents, as formation of biofouling in the polymer surface that can alter the weathering process affecting their floatability, or slowing photochemical degradation through light screening.

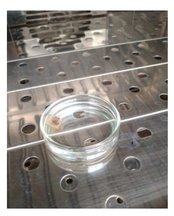
Experimental

In the frame of the MicroplastiX project (JPI Oceans) 9 different polymers, were exposed to marine environment throughout the summer season in Ría de Ares, A Coruña. Samples were subsampled at T0, T7, T15, T30, T60 and T90 days of exposition.

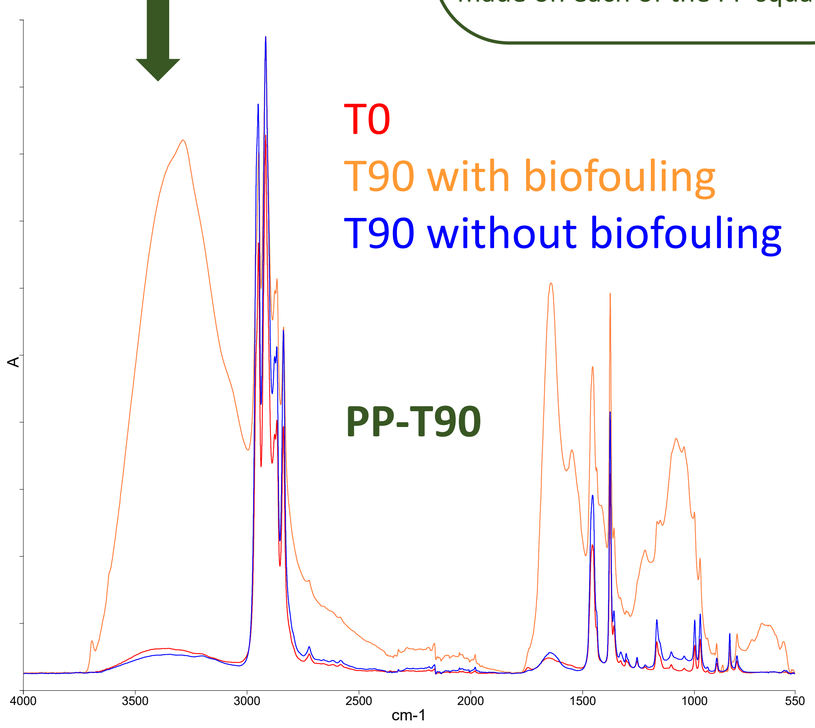
Puerto Náutico de Ares (España)
43º25'20''N-8º14'22''W

Nalgene™ container interior after 90 days of exposure

Measurements of non-biofouled PP are made after soft digestion (10% H_2O_2, 40ºC) to identify the origin of the new bands in their IR spectra.

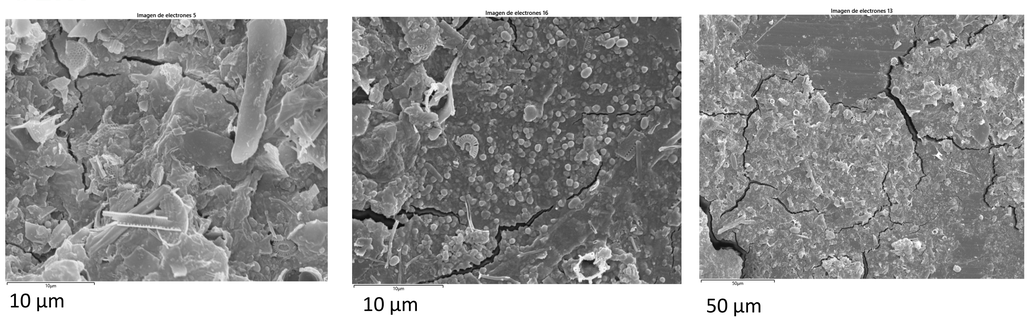


FTIR measurements were done using a 400 FT-IR/FT-NIR PerkinElmer Spectrometer (4000-650 cm^{-1}, 4 cm^{-1} nominal resolution, Beer-Norton strong apodization, 50 scans per spectrum, background-, depth-penetration- and baseline-corrected) equipped with a horizontal one-bounce diamond crystal (Miracle ATR, Pike). 10 different measurements were made on each of the PP squares.



Since the T0 spectrum corresponds perfectly with that obtained at T90 without biofouling, it could be said that the biofouling formed apparently "protects" the PP from weathering, mainly from photooxidation.

SEM

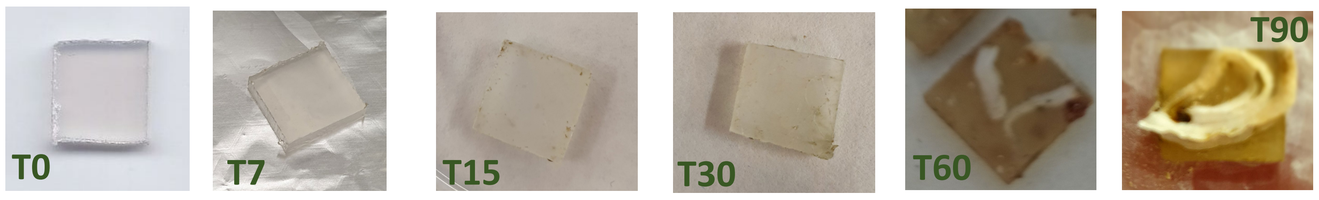


10 µm 10 µm 50 µm

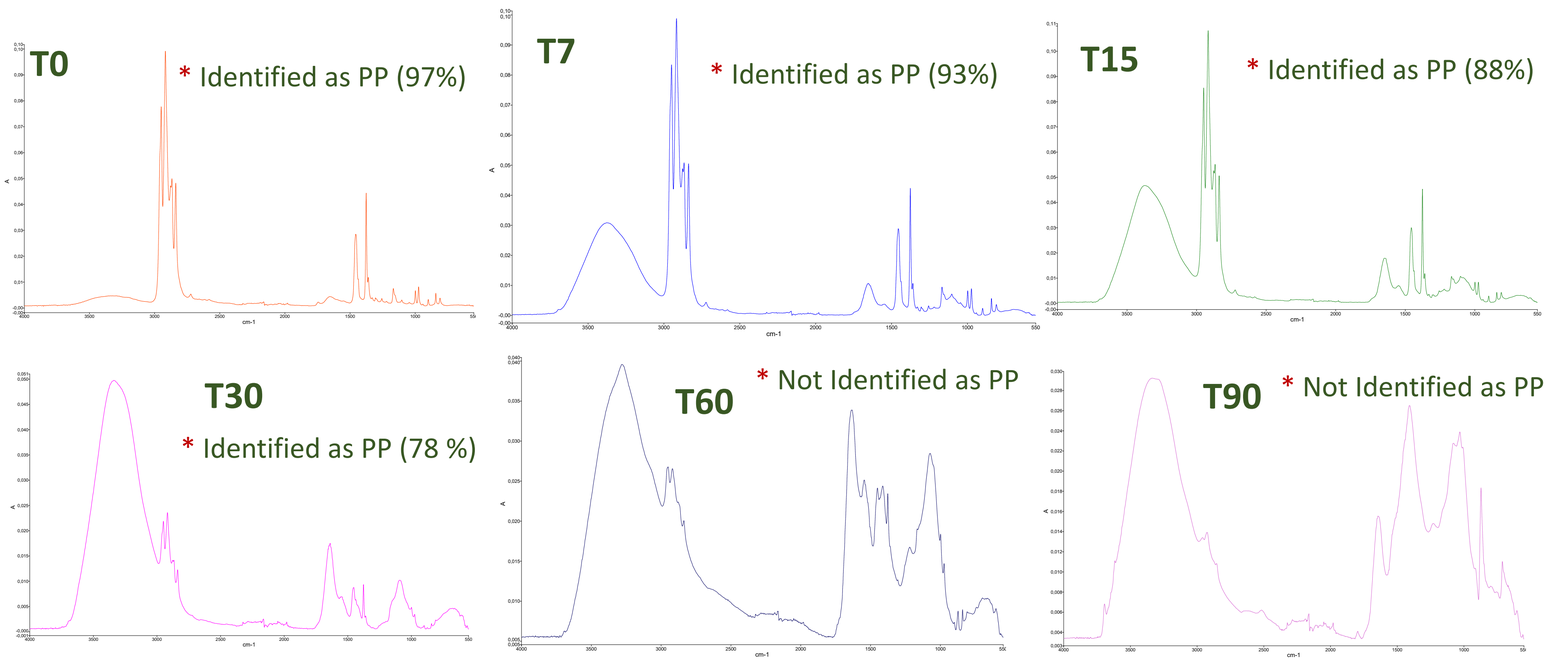
SEM microscopy was also done in order to study the changes caused by biofouling growth or natural weathering, and even to identify some of the organisms growing on the surface of the plastic. Different species of polychaetes, bacteria and diatoms have been identified.

Results

This study focuses on the characterization of the changes that biofouling growth produces in polypropylene using ATR-FTIR, identifying new bands in its spectrum and studying how this process interferes with natural weathering and with the identification in monitoring studies of plastics and microplastics.

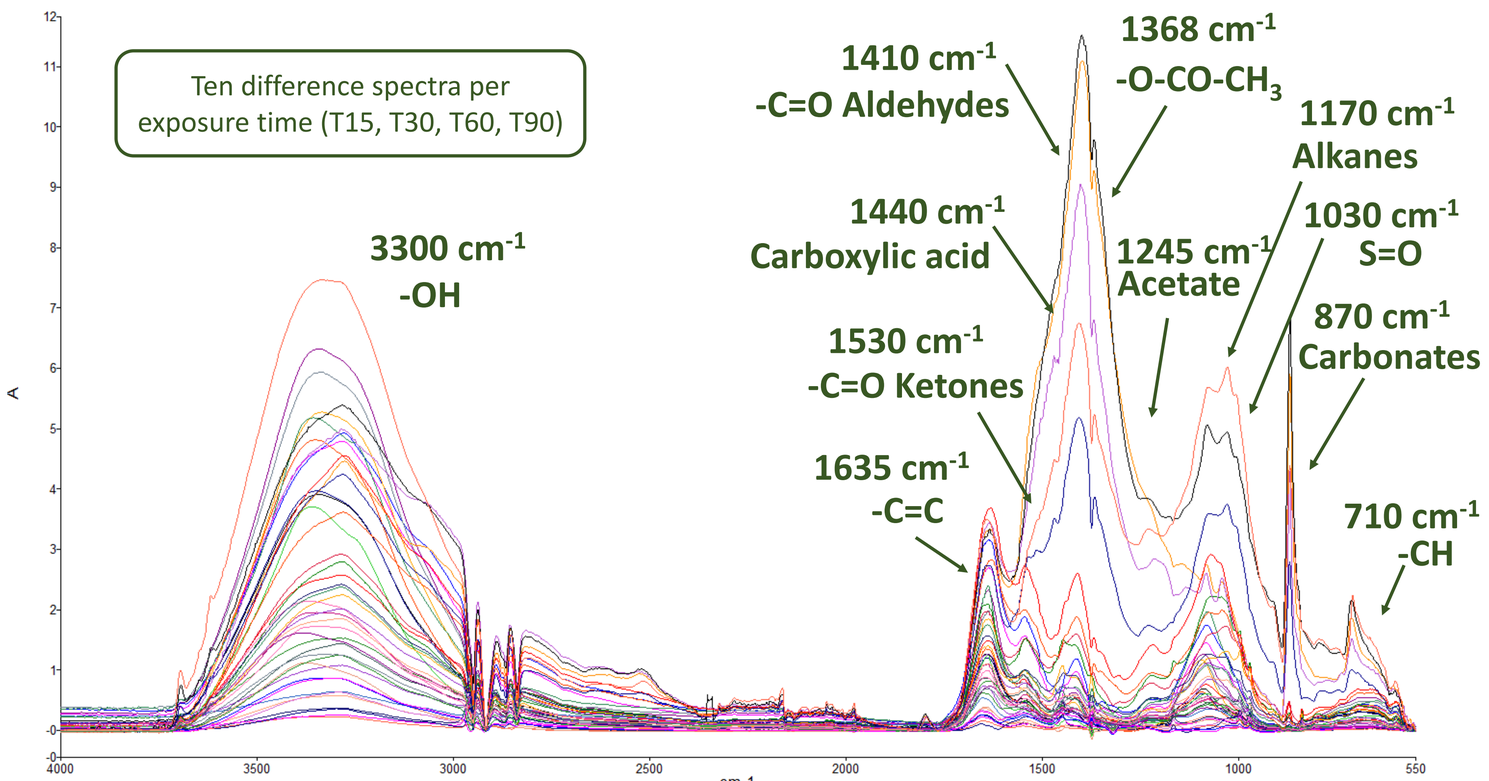


*correlation percentage compared to the Perkin Elmer polymer library



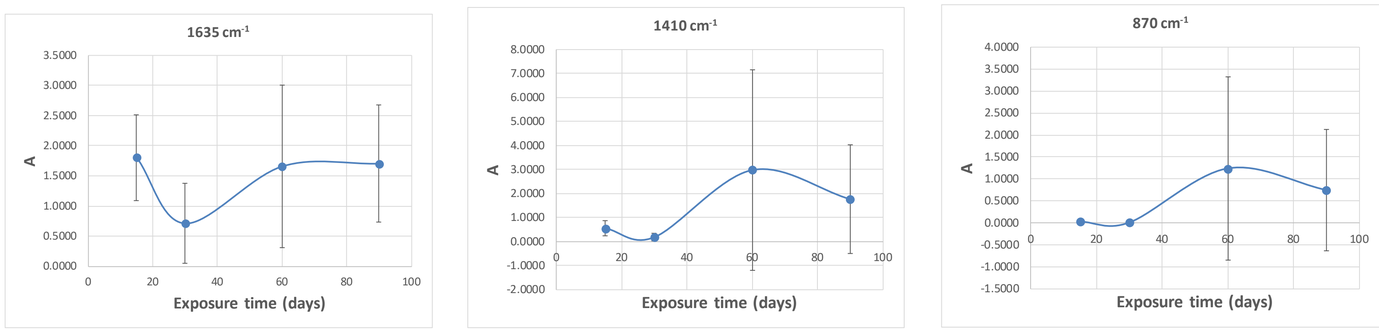
Difference spectra (PP with biofouling – PP without biofouling)

To identify new spectrum bands as a result of exposure to natural environment, mainly due to the formation of biofouling, difference spectra have been obtained (after normalization), resulting from the subtraction of spectra of PP with biofouling - PP without biofouling.



Examples of evolution of new PP spectrum bands associated to biofouling

The evolution of these bands with exposure time was studied by taking the average and standard deviation of the 10 measurements made for each time (T15, T30, T60 and T90). Although there is a lot of variation depending on the measurement area in the PP square, an upward trend is observed with increasing time for each of these bands, which are attributed to the growth of biofouling on the surface of the polymer.



Conclusions

Preliminary results indicate that biofouling growth is visible in the spectrum within a few weeks of exposure to the marine environment, producing, at T90, a significant change in the ATR-FTIR spectrum. As the exposure time increases the identification of the polymer by ATR-FTIR is more affected. In the samples corresponding to T60 and T90 it is not possible to identify it as PP when compared to commercial libraries. It also appears that, the growth of biofouling on the surface of the polymer exerts a protection against ageing (mainly photo-oxidation). The bands in the spectra due to biofouling are identified and an increasing trend with exposure time is observed.

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