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THE DEGRADATION OF REAL SAMPLES OF PLASTIC BOTTLES FROM ADRIATIC MARINE LITTER: VIBRATIONAL SPECTROSCOPY EVALUATION

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In the framework of the compelling problem of anthropogenic debris negatively affecting the marine ecosystems, with a strong impact on marine water quality and life, many studies were carried out in the last decades concerning plastic degradation with the aim of understanding the processes occurring to plastic litter in the marine and coastal environment. The investigation on degradation can be directed toward the comparison of compostable plastics with respect to conventional ones, to the evaluation of plastics recyclability, or to an estimation of the potential generation of secondary microplastics [1, 2].

Notwithstanding, up to now, most of literature studies concerned degradation of standard polymers references as induced by artificial weathering conditions, mainly through exposition to UV radiation, heat or/and microorganisms (photo-, thermo-, bio-degradation). In some cases, natural outdoor ageing and/or immersion in saline water were also experimented [3], mostly using standard polymers or, more rarely, non-degraded objects. Very few works were carried out on real marine litter (ML), one of which performing ATR-FTIR measurements on polyethylene terephthalate (PET) bottles, taking advantage of the temporal sequence provided by the expiration dates still present on some sampled bottles [4].

Within the Italy-Croatia Interreg "ML-Repair" (REducing and Preventing, an integrated Approach to Marine Litter Management in the Adriatic Sea) project, a selection of about 150 marine litter bottles was examined. These were a result of Fishing for Litter (FfL, the removal and correct disposal of ML recovered during fishing activities) practiced from Italian Northern Adriatic and Dalmatian (Croatia) channel waters and open waters. A systematic investigation was carried out on PET bottles bodies and necks – parts that undergo different manufacturing and are also differently exposed to the environment - and, where present, on their caps and seals, made of HD-PE (high density polyethylene). This allowed a parallel study of two polymers evolution in the marine environment.

After preliminary phases of cleaning, decalcification and removal of biogenic incrustations, Attenuated Total Reflectance Fourier Transform Infrared (FTIR-ATR) and Raman (excitation wavelength: 785 nm) Spectroscopy were performed acquiring three spots of analysis for both the interior and the exterior sides of each of the four parts of the bottles. The obtained spectra were compared with those of references of virgin PET and HD-PE, and with those acquired on similar new bottles, caps and seals of different colors. This was done in order to

take into account also additives and colorants and their influence on the acquired spectra. Furthermore, the results obtained showed that most of the new bottles display as well on their external surface some signals generally attributed to effects of photo- or thermo-oxidation, as reported in Figure 1 for PE ATR-FTIR spectra, where 1712, 1740 and 3300 cm^{-1} signals are highlighted [5]. This information is important to evaluate the real extent and the type of degradation occurring on plastic bottles in the marine environment. The spectroscopic data collected by FTIR-ATR on ML bottles also show a marked biodegradation [6] (Fig.1c) and indicate that the bottle necks interiors are the least degraded sections.

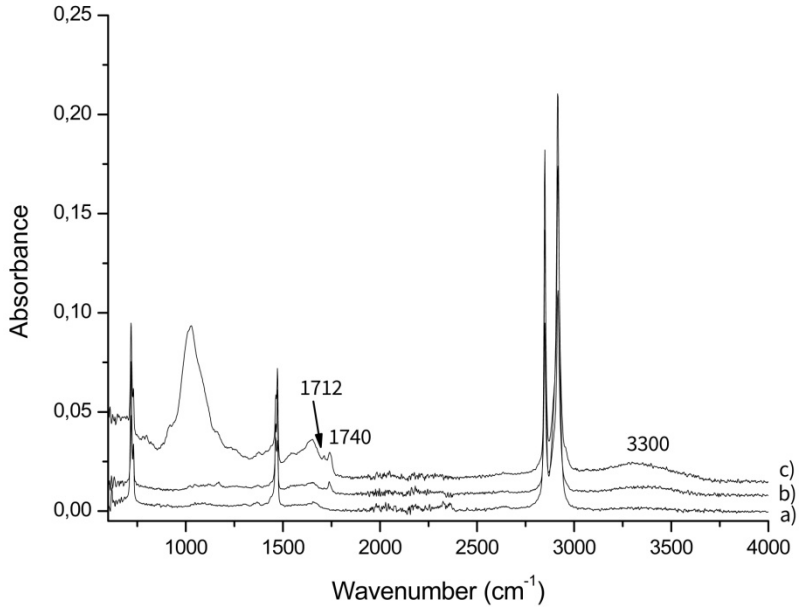

Figure 1. FTIR-ATR comparative spectra of virgin HD-PE (a) and of the external surfaces of a white cap of a new bottle (b) and of a ML one (c), respectively; an offset was applied for an easier visualization.

The Raman spectra of ML samples, though interestingly different according to the colors and the parts analyzed (body or neck), resulted strongly affected by fluorescence, especially where the biodegradation is more intense.

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