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Resin pellets aging and degradation investigation from long term in situ experiment: First results

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Introduction

Recent studies establish that plastic waste accounts for more than 75% of the total marine litter [1]. The micrometric fraction of marine litter is increasing in coastal debris finds and in the marine environment [2] and of these resin pellets represent a percentage ranging from 3% up to 30% [3]. Resin pellets are considered as the first generation microplastics and due to their loss during transport, storage and processing, they can enter the environment. Polyethylene (PE) and Polypropylene (PP) represent a large portion of plastic debris in the environment [4]. Moreover, the use of biopolymers is increasing. European Bioplastic indicates that in 2021 bioplastics constitute the 1% of the 367 million tons of plastic produced globally, with a forecast growth trend of over 5 million tons in 2026 [5]. Among these, biodegradable plastics account for over 64% of the global bioplastics production capacities in 2021, with 19.2% for polybutylene adipate-co-terephthalate (PBAT) and 18.9% for polylactic acid (PLA). However, the objects and fragments stranded or recovered in the sea do not tell us the time they spent in the sea, their trip, their history before arriving there. These factors are important to evaluate the real effects due to the permanence of these materials in the marine environment even if it is not always easy to determine them. Here, an experiment lasting three-years was carried out on a simulated beach (sandbox) and in a real marine environment in Santa Teresa Bay (Gulf of La Spezia, Italy) [6]. The experiment aims at investigating the behaviour of plastic items and HDPE, PP, PLA and PBAT pellets in both environments. The comparison between the properties of the raw pellets and those placed in the two different environments after six months is discussed in this work.

Experimental

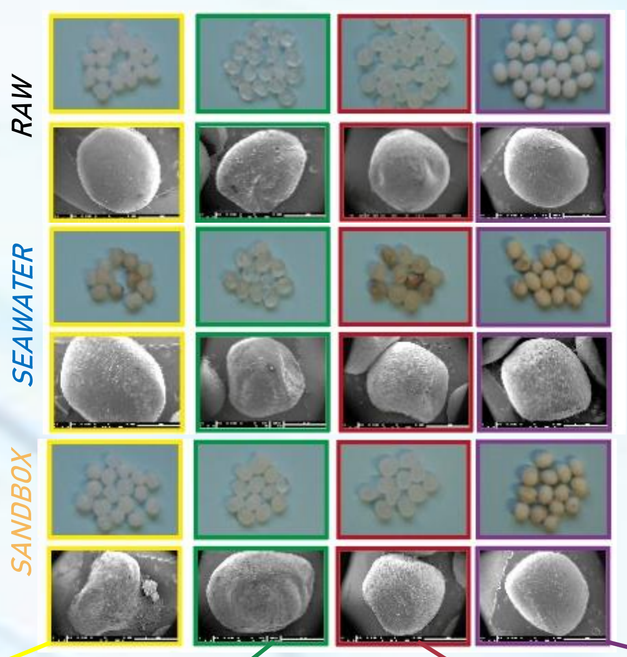
Carrying out a long-term experiment, started on March 2020 and programmed to be ended after 36 months. Four type of polymers pellets (HDPE, PP, PLA and PBAT) put in marine environment and regularly collected to be analysed. Two types of experimental set up:
a) in cylindrical cages installed on the structure of the underwater observatory, LabMARE coastal station at 44°4'55.08"N - 9°52'50.46"E, placed at a depth of ten meters and about 60 m from the shore line. The submarine station is equipped with Conductivity, Temperature, Depth (CTD) sensor, for monitoring environmental parameters, recording data every 10 min.
b) in a sandbox at 44°7'51.04"N - 9°57'28.88"E (located in Sarzana), containing sand taken from the Gulf of La Spezia, in order to carry out a comparative study on a "simulated beach".

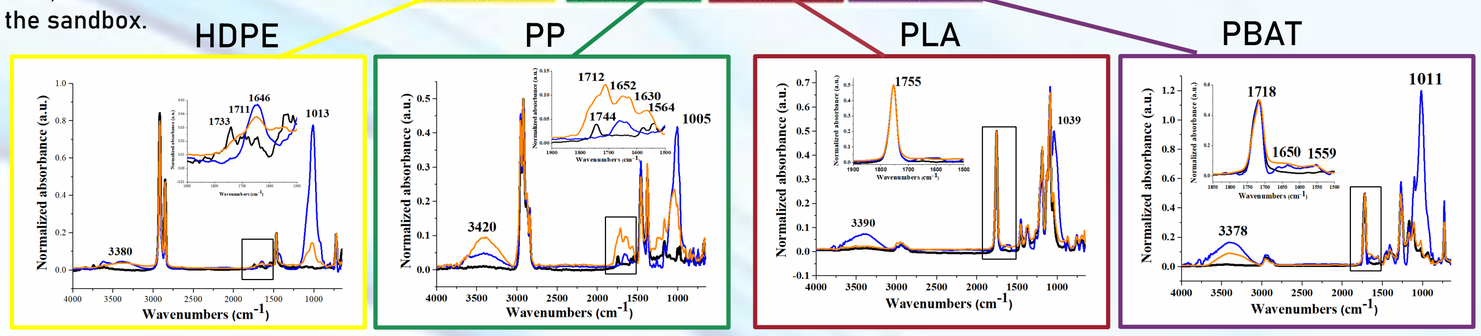
Results and discussion

Parameters measured in LabMARE				
	Aver. Temp. (°C)	δ (°C)	T_{min} (°C)	T_{max} (°C)
March 2020	13.70	0.32	12.93	14.32
April 2020	15.07	0.78	13.69	17.33
May 2020	18.20	0.72	16.93	20.16
June 2020	20.88	0.85	18.97	23.19
July 2020	21.25	0.59	19.75	23.35
August 2020	23.68	2.20	22.12	25.24
Parameters measured in sandbox				
	Aver. Temp.(°C)	δ (°C)	T_{min} (°C)	T_{max} (°C)
March 2021	12.88	7.15	1.95	36.16
April 2021	14.98	6.45	0.123	36.21
May 2021	18.64	6.05	8.28	42.08
June 2021	25.64	7.48	11.79	45.60
July 2021	27.69	6.82	17.84	48.69
August 2021	29.06	7.19	18.81	51.63

ENVIRONMENTAL ANALYSES:
- Similar average temperature between sandbox and sea;
- Greater temperature range between day and night in the sandbox with a larger standard deviation;
- Increased stress on the materials in the sandbox.

ATR-FTIR:
- in sandbox samples more intense double bond bands, C=C and C=O, (photooxidation);
- peaks due of -OH stretching, (hydrolysis of the chains);
- bands of contamination at about 1010 cm^{-1} (residual sand).



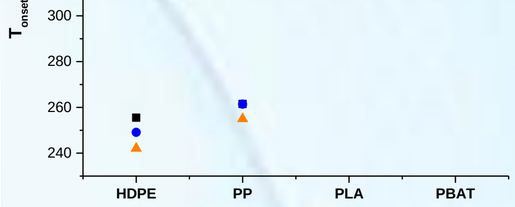


- Yellowing up to an amber colour for the samples in seawater and for PBAT also in the sandbox.
- SEM images show an increase in surface roughness.

DSC ANALYSES
- No particular change in thermal transitions.

Sample	$\overline{Mn}$ (KDa)	$\overline{Mw}$ (KDa)	PDI
PLA raw	84.6	146.3	1.7
PLA seawater	82.2	145.2	1.8
PLA sandbox	88.9	149.7	1.7
PBAT raw	21.5	47.3	2.2
PBAT seawater	19.8	45.2	2.3
PBAT sandbox	12.6	35.8	2.8

SEC ANALYSES (for biodegradable pellets):
- High reduction of $\overline{Mn}$ and $\overline{Mw}$ for PBAT from the sandbox.



TGA ANALYSES:
- Decrease in Tonset for HDPE and PBAT;
- The greatest decrease occurs in the sandbox.

Conclusions

The first results here reported are obtained over a period of six months from a long-term (3 years) *in situ* experiment on exposing microplastics (pre-production resin pellets) to sunlight and open sea and simulated sand conditions. The project aims to study the change of some of the chemical and physical characteristics of the structure of polymeric compounds during the aging in marine environments. Traditional plastics (HDPE and PP) and bioplastics (PLA and PBAT) are compared in a real, free and uncontrolled marine environment. After 6 months of experiment (from March to September 2020) the materials immersed in the sea result to be subjected to less thermal stress than the corresponding ones in sandbox, because of the lower solar radiation and reduced thermal excursion. Changes in the chemical-physical properties of the materials suggest a material aging and the beginning of a degradation process but with an evolution time that is still long and to be established. The experiment is still running and a deeper evaluation of the aging and degradation process will be discussed in future works.

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