Study of Plastics Debris Collected on the North Beaches of the Garda Lake After the Severe Storm Vaia in Autumn 2018

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1 Introduction

Research for Facts and Sharing Knowledge are two of the six commitments outlined by Marine Litter Solution in the declaration to reducing ocean pollution [1]. This presentation represents our recent contribution to the study of the Garda Lake contamination with plastic debris after the severe storm Vaia that hit the north side of Italy in Autumn 2018 [2]. The average rainfall in Trentino reached 275 mm during the three days 27–29 October, with the max peak of 600 mm according to Meteotrentino [3]. Moreover, the gales of up to 120 km/h brought down thousands of trees e.g. in the Fiemme Valley. In the following days all the rivers in the area increased their stream bed, which brought about intense "cleaning" of their side banks. It was also the case of the Sarca River which is draining about one fourth of Trentino, and it is the main tributary of the Garda Lake. Consequently, to avoid the danger of flooding, the water of the Adige river was redirected to this lake through the Torbole tunnel (Trento) from October 29th until November 1st with a flow rate of 350 m^3/s. Thus, various organic/vegetable and inorganic materials were continuously transported and dispersed into the lake, and then accumulated on the shoreline, due to the local south wind "Ora".

2 Experimental

The first monitoring/collection of northern beaches of the Garda took place November 2nd–11th, whereby various macroplastics and microplastics were gathered. Zone 1, Zone 2 and Zone 3 correspond to the local Municipalities of Riva del Garda, Arco and Nago-Torbole, respectively (as shown in Fig. 1).

Afterwards, further surveys were also organized in the following period February–July 2019. In particular, more than thirty volunteers from Liceo Maffei checked and retrieved plastics items in the same selected position of Zone 1A and Zone 1B, as on November 15th and March 14th (see identification position by gps coordinates in Tables 1 and 2).

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Fig. 1. Shoreline of the North-side of the Garda Lake and the Zones of plastics survey. Direction of water stream tributary (Sarca River and Tunnel from Adige River) and Ora Wind are indicated by full and dot arrows, respectively.

2.1 Methods of Survey and Collection

First inspection was performed in the first days after Vaia storm along the easily accessed beaches of Riva del Garda, Arco and Nago-Torbole, that are usually frequented by tourists for bathing and/or surfing in the summer season. In agreement with the suggestion of recent Gesamp Report, several positions were fixed for the collection of samples in the selected areas, initially 1 m^2 in November 2018, and then in 2 m^2 [4].

2.1.1 Collection of Samples

The selected positions of survey on gravel shoreline of the Garda beaches were registered by the gps coordinates, and collected plastics specimens were distinguished by position and date. Two types of collection were carried out: (1) collection of large items mainly from Piles (see Figs. 2) and collection of small items as typical microplastics (Figs. 3).

Various plastics were counted and weighted. Progressive characterization was primarily focused on the identification of polymers, and then specific testing procedures were used for the evaluation of sample weathering, which were in agreement with literature [4] and with the procedures adopted in our laboratories [5].

Fig. 2. Example of waste Pile in Zone 1A Sabbioni Beach (left) and Zone 2A Baia Azzurra (right – in distance). The selected area of 1 m^2 for collection of small size samples is also evidenced (left) (November 4th, 2018).

Fig. 3. Example of large size (left) and small size (right) plastic wastes collected in Zone 1B. (Purfina Beach, November 4th, 2018)

2.2 Materials and Testing Techniques

2.2.1 Materials

Representative compositions and types of various plastic materials retrieved in several survey (Zone 1A and Zone 1B) are well corresponding to marine plastic wastes as reported in literature by Gesamp 2016 [6]. In particular polyethylene, polypropylene, polystyrene, polyurethane, polyethyleneterephthalate, polyvinylchloride, polyamide, rubber, and so on.

2.2.2 Analytical Techniques

Analytical techniques were selected in accord with the previous literature survey [5]. An analytical balance Gibertini E42 (sensitivity 0.1 mg) was used for evaluation of sample weight and density following ASTM D-682. Density measurement of foamed PS and PU samples was carried out by means of the forced immersion in distilled water [7].

Fourier Transform Infrared (FTIR) spectroscopy was employed in the range 4000–650 cm^{-1} by using PerkinElmer Spectrum One in order to identify the polymer composition and to evaluate the level of oxidation by detecting the carbonyl peak [5].

Differential Scanning Calorimetry (DSC) was performed from 0 to 300 °C at 10 °C/min (flushing air at 100 ml/min) by using a Mettler DSC30 to evaluate the glass transition temperature (Tg), temperatures of the crystallization and melting peaks, the degree of crystallinity, and to monitor the Oxidation Onset Temperature (OOT) [8, 9].

The melt flow index (MFI) was measured according to ASTM D 1238 standard, by means of the Kayeness Co. model 4003DE capillary rheometer, at the temperature of 190 °C with an applied load of 2.16 kg [10].

Vicat softening temperature VST defined by ASTM standard was indicated by ATS-FAAR mod. MP/3 machine (Milan, Italy) at heating rate of 2 °C/min and 10N of loading [11].

SEM analysis (Carl Zeiss AG Supra 40 field emission scanning electron microscope FESEM) was performed on fracture surfaces.

Mechanical tests were carried out in both longitudinal and transversal directions with the dumbell specimens ISO 527-2 (gauge length 25 mm; width 5 mm;) by using an Instron testing machine mod 4502 at crosshead speed of 2 or 20 mm/min.

3 Results and Discussion

During the first survey in Nov-2018 several larger size samples were found (see Figures). In particular Piles of wastes localized in Zone 1A (Sabbioni Beach) and Zone 1B (Purfina Beach) were investigated for retrieval of plastic residues before Municipal Waste Collection Service. Collected samples were counted and weighed. Results from Pile collection and relative position are reported in Table 1.

Table 1. Positions of lake-waste Piles for plastics retrieval on the Riva beaches Zone 1A (Sabbioni) and Zone 1B (Purfina) of the survey on Nov 15th 2018. Number of particles, total and average weights are given.

Position Lat N/Long E	Macro-pieces/Weight/ (g)	Average weight (g/p)	Small-pieces/Weight/ (g)	Average weight (g/p)
Sabbioni Pile1 45.88140/10.84864	9/155.3/	17.3	115/228.8/	2.0
Sabbioni Pile2 45.88133/10.84896	21/651.0/	31.0	109/115.8/	1.1
Sabbioni Pile3 45.88062/10.84963	38/463.7/	12.2	46/68.0/	1.5
Purfina Pile1 45.87918/10.85344	41/1824.0/	44.5	101/401.7/	4.0
Purfina Pile2 45.87907/10.85356	8/78.6/	9.8	37/154.8/	4.2
Purfina Pile3 45.87896/10.85408	44/1291.3/	29.4	35/89.4/	2.6
Purfina Pile4 45.87874/10.85470	45/300.0/	6.7		

Moreover, in selected areas of 1–2 m^2, an initial survey of sample collection was repeated after 4 months and 8 months. The data on number, weight, average weight of collected samples are reported in Table 2.

Table 2. Positions for Plastics retrieval on the Riva beaches of the initial and two subsequent surveys after 4/8 months. Place size of 2 m^2 (N-S oriented). Number of particles, total and average weights are given.

Position Lat N/Long E	1st Survey (1 m^2)	2018 Nov 15th	2nd Survey (2 m^2)	2019 Mar 14th,	3rd Survey (2 m^2)	2019 Jul 20th,
	Pieces/Weight/ (g)	Average weight (g/p)	Pieces/Weight/ (g)	Average weight (g/p)	Pieces/Weight/ (g)	Average weight (g/p)
Sabbioni Beach1 45.88144/10.84870	22/5.8/	0.26	176/37.2/	0.21	7/0.3/	0.04
Sabbioni Beach2 45.88114/10.84876	7/3.9/	0.56	57/19.2/	0.34	12/0.8/	0.07
Sabbioni Beach 3 45.88135/10.84890	20/5.3/	0.27	62/15.5/	0.25	21/2.7/	0.13
Sabbioni Beach 4 45.88127/10.88906	3/0.7/	0.23	47/3.6/	0.08	14/0.7/	0.05
Sabbioni Beach 6 45.88113/10.84925	18/4.6/	0.26	42/5.5/	0.13	9/0.1/	0.01
Sabbioni Beach 7 45.88104/10.84933	5/1.9/	0.38	11/5.9/	0.53	6/1.0/	0.17
Purfina Beach 1 45.87909/10.85332	19/3.4/	0.18	25/13.8/	0.55	10/3.8/	0.38
Purfina Beach 2 45.87910/10.85344	27/8.0/	0.30	26/5.5/	0.21	5/1.3/	0.26
Purfina Beach 3 45.87909/10.85332	22/33.3/	1.51	9/6.0/	0.67	7/1.5/	0.21

It is worth noting that the number of pieces collected in the 2nd survey was higher than that in the first one, probably due to the cumulative enrichment and deposition of plastic wastes during the winter season [12]. On the other hand, during the 3rd survey after 8 months the number of pieces and their average weights were considerably reduced.

3.1 Results for Specific Plastic Wastes

3.1.1 Foamed Products

Various types of foamed plastics have been collected, typically polystyrene (EPS) and polyurethane (PU) with fragment dimensions in the range of the macroplastic and microplastics.

In the case of EPS the effect of fragmentation and compression it is well evident. Due to the specific production process, foamed EPS products easily break and form single or multi-aggregate sferoids (Fig. 4). The density of various samples depends on the initial production for instance 0.039 + 0.003 g/cm^3, and on the level of aging and compression. Damaged EPS specimens with density 0.062 + 0.007 g/cm^3 and even higher were found.

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Fig. 4. EPS particles at different level of fragmentation

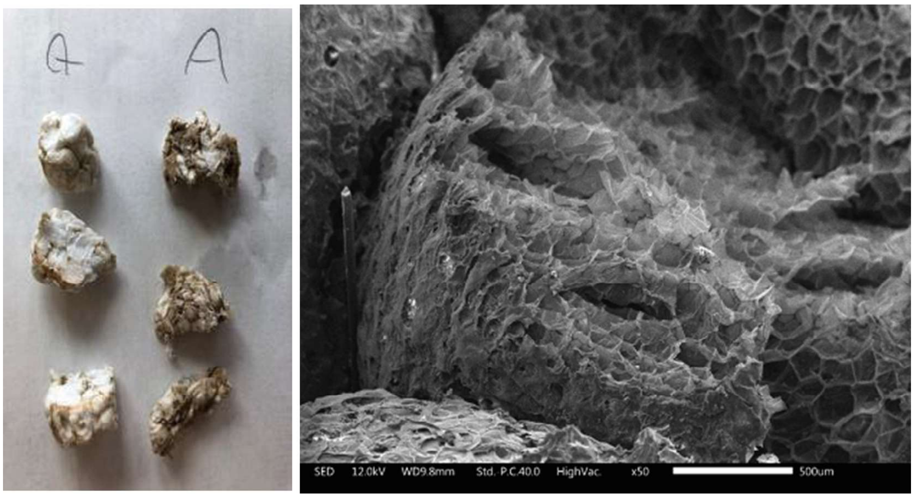

Fig. 5. Selected EPS specimens used for density measurements (left) and ESEM image (right) of PS fragmented particles. Evident precursor of EPS-microplastics can be seen.

ESEM micrography evidences the damage extent of foamed particles, with a clear indication of microplastic formation (Fig. 5b). Single sferoidal particles tend to detach after ageing due to the low level of adhesion energy.

Density of aged samples of light blue extruded polystyrene (XPS) was measured 39 ± 6 kg/m^3. Mechanism of fragmentation and compression of aged XPS was different from that of EPS.

The densities of PU foams were found in the typical range 0.039 ± 0.003 g/cm^3 (Fig. 6-left). As they are based on polyether and/or polyester precursors, PU foams are differently susceptible to hydrolytic and/or oxygen/light induced degradation. Their physical aspect, which is very similar to that of the river stones, is derived from the progressive erosion and smoothing of the surface, due to the relatively easy micro-fragmentation during abrasion and friction in water waving.

Some sample evidenced an increased density in the range 0.150–0.715 g/cm^3 due to the adsorption of various amounts of present contaminants (Fig. 6-right)

Fig. 6. Example of aged PU foam samples.

3.1.2 Case Study 1 - Macroplastic HDPE Pallet-Box

In the first fortnight after Vaia, various fragmented part of a large fruit pallet-box were retrieved in different shorelines. The main part #1 was found in Zone 2A (Fig. 7), and other large pieces easily recognized by light green colour were retrieved in various beaches Zone 1A (fragment #2 of 3.7 kg) and 1B (fragment #3 of 544 g); Zone 2B (fragment #4 of 788 g; see Fig. 8). The thickness of various sections is ranging between 3.3 and 7.5 mm. The impact multi-fracture evidences high energy produced by Vaia storm.

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Fig. 7. Main part #1 of HDPE pallet-box after extraction from water in Zone 2A. (Baia Azzurra November 4th, 2018).

Fig. 8. HDPE-fragment #4 (weight 788 g; length 53 cm) retrieved in Zone 2B. (November 3rd, 2018). Three specimens for Vicat test and grinded parts for MFI analysis are showed.

Analysis of HDPE pallet-box showed the OOT value of 217 °C (much lower than 260 °C, the reference value of new HDPE). Moreover a crystallinity of 62% found for aged HDPE (66% on the external surface layer) was slightly higher than 56-59% of virgin HDPE. Similarly, Vicat temperature 129 ± 1°C was even higher than that of common polyolefin plastic; the reason could be attributed to the surface stiffening, as documented by the higher crystallinity. The found melt flow (MFI) of 7.6 ± 0.1 g/10 min is typical of injection molded product. This type of thick HDPE plastic waste exhibit good properties and it could be considered for direct recycling.

3.1.3 Case Study 2 – PE Pluriball (Zone 1B)

Pluriball is a packaging foil made of low density polyethylene with various sizes of air balls for light impact protection. An aged Pluriball sample was found in Zone 1B on spring 2019 (Fig. 9) with evidence of the cut specimens for mechanical testing (longitudinal and transversal direction).

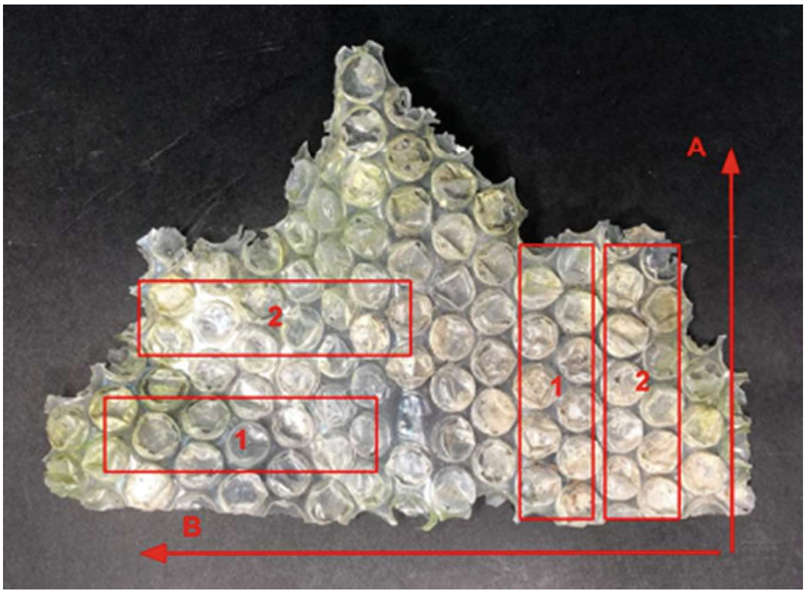

Fig. 9. Aged Pluriball with the evidence of many points of fragmentation of the balls (internal diameter of 8 mm). See magnification in Fig. 10.

FTIR spectra and the decrease of OOT (198 °C with respect of 215 °C of new Pluriball) confirmed the high level of oxidation and degradation. Both optical and electronic micrographs evidenced fragile fracture (Fig. 10). Correspondingly a significant decrease in mechanical properties was also observed. Mechanical tests of aged samples were compared with those of a New Pluriball of similar geometry (Fig. 11).

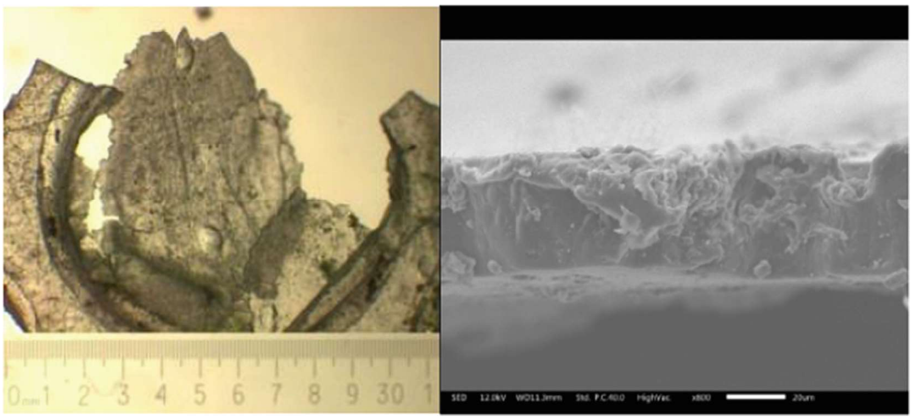

Fig. 10. Magnification of fragmented ball in aged Pluriball. View of broken ball (left) and micrograph of cross-section along the thickness after fragile fracture (right).

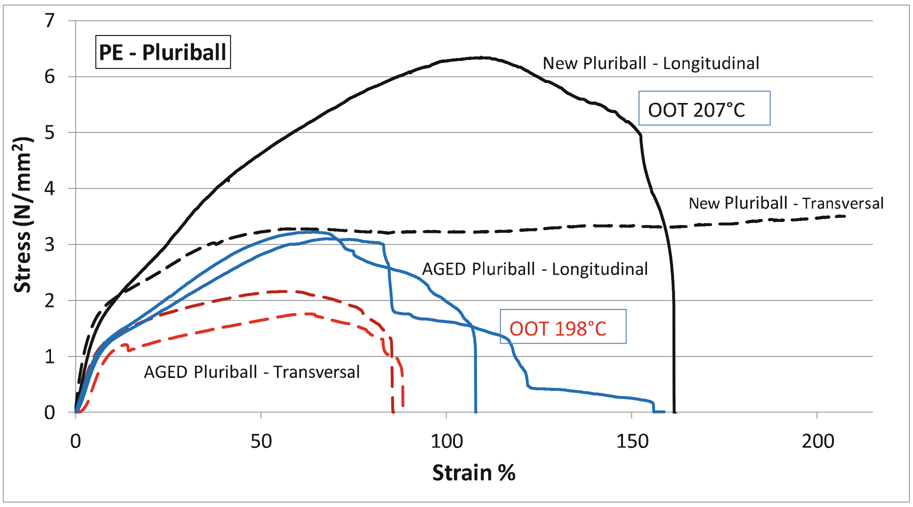

Fig. 11. Stress-strain curves of Aged and New Pluriball (Longitudinal and Transversal direction).

3.1.4 Case Study 3 - PE Sack Bag (Zone 3B)

The case of an aged polyethylene Sack-bag is similar to that of PE Pluriball. Both FTIR and OOT analyses showed the effect of oxidative action in aged sack-bag. Stress strain curves in longitudinal direction are reported in Fig. 12 and relative results of longitudinal/ transversal properties are summarized in Table 3. An aging factor has been proposed for comparing the weathering effects.

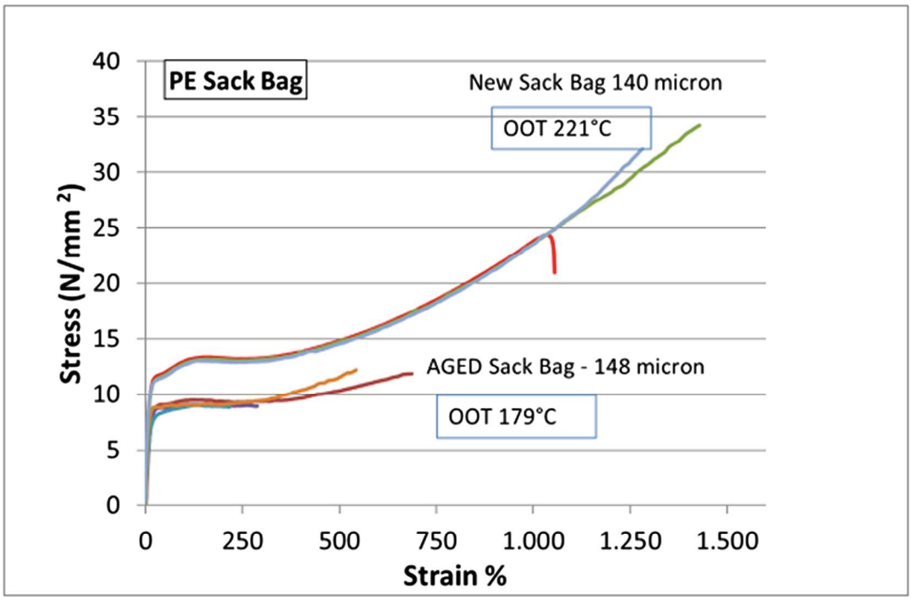

Fig. 12. Stress-strain curves of Aged and reference New Sack-bag (longitudinal direction). T

Table 3. Strength and strain at break of the PE Sack bag. New sample and aged sample (Zone 3B).

PE sack-bag sample	Strength [MPa]	Strain at break [%]	Aging factor*
NEW Longitudinal	30 ± 5	1250 ± 197	1.00/1.00
AGED Longitudinal	10 ± 2	482 ± 270	0.33/0.39
NEW Transversal	28 ± 2	1576 ± 42	1.00/1.00
AGED Transversal	12 ± 2	399 ± 313	0.43/0.25

*calculated as the ratio of the correspondent values of aged and new samples.

3.1.5 Case Study 4 - Polypropylene Jar (Remained Fragmented Bottom) PP95

An interesting case of micro-fragmented plastic was found for the residual bottom part of polypropylene cup, a disk of diameter 190 mm.

The sample had been produced by injection molding as documented by the printed information (see Fig. 13a). It is very interesting to note the date of production (March 1995), the name of producer (ISI Plast, Correggio RE-Italy), the type of polymer (PP), and the application (food contact – EURO V.6).

FTIR and OOT documented the high level of oxidation and degradation.

The sample appears to be a fragile multilayer system due to the long time of aging (Fig. 13b). This large debris (45.157 g) represents a potential source for the fragmentation in more than 1000 micro-plastic pieces of 40 mg. Its original and unmodified thickness was about 1.15 mm, whereas the thickness of pre-fragmented portions was found in the range of 0.15–0.55 mm, thus confirming a high level of weathering and degradation.

ESEM micrograph evidences the fragile fracture (Fig. 14).

Fig. 13. Bottom part of fragmented plastic jar “PP95” (left). Residual lateral border with various fragments (right). Precursor of PP microplastics.

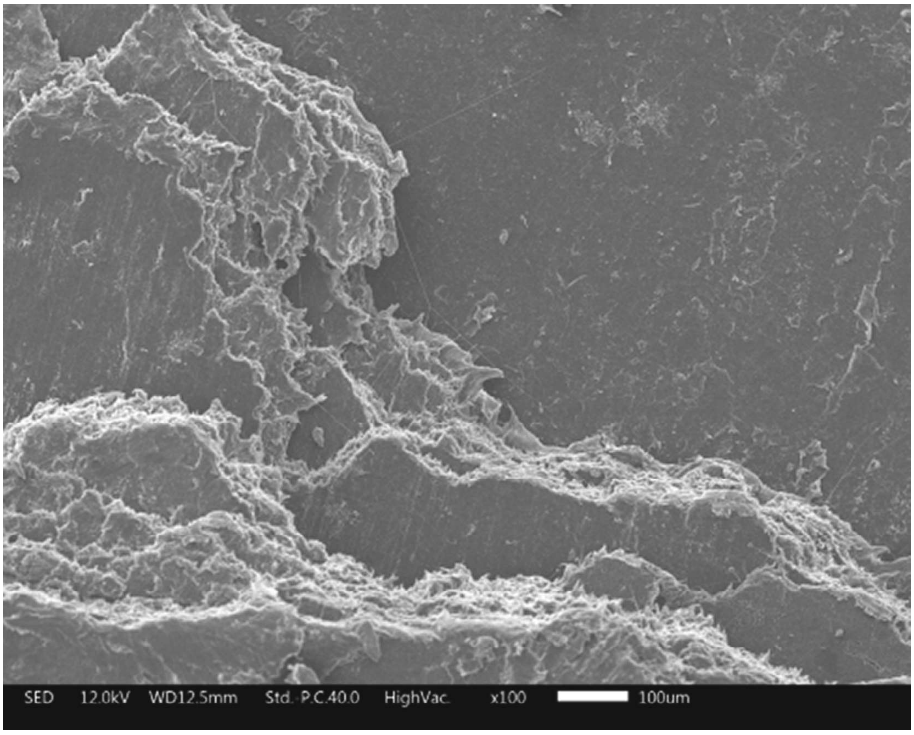

Fig. 14. ESEM image of fragmented surface of the aged sample “PP95” after fragile fracture.

4 Conclusions

The exceptional meteorological event (Vaia 2018) provided unique opportunity to evaluate the level of plastic wastes diffusion in the local sub-alpine region. In particular, the high extension and intensity of the weather perturbation determined the way of cleaning/collection of heterogeneous debris on various water-ways banks Their consequent accumulation in the main rivers, and finally their partial deposition on the lake shores was distinguished by an enormous amount of wooden-detritus. The immediate/rapid survey in the first November fortnight and the repeated inspections along the year 2019 allowed the collection of macroplastics, mesoplastics and microplastics. The various collected items directly derived from the local rivers Sarca and Adige

Specific classification and laboratory characterization of the various aged plastic objects provided interesting information related to the effects of aging. Geometrical size (thickness) has been evaluated as the key-factor for potential formation of polyolefin microplastic as a function of the time of aging.

Mechanical properties were compared with those of corresponding new products, and their relative variation was used as the ageing factor for evaluation of the weathering. Complementary information was obtained by means of morphological observation, FTIR, OOT, and other analyses.

A promising result of this research is related to the activity of dissemination and of the active recruitment of young volunteers for evaluation of the phenomenon. Subsequently, regular surveys in cooperation with local high schools and local/regionale administration have been planned and carried out.

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