NET4mPLASTIC PROJECT

Activity 4.2

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Identification and classification of plastic debris via Image analysis and Fourier-Transform Infrared Spectroscopy

Rev.0 2022/06/09

CONTRIBUTING PARTNERS	UNITS

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1 Introduction

This document reports on the analysis carried out on samples collected by Croatian partners and sent to the University of Trieste for analysis on May 04, 2022. Collection sites were not specified but can be speculated from the names on the sample holders (Rab, Susak, Klimno)

2 Materials and methods

2.1 Samples identification and classification

Samples in the form of debris of different composition, size and shape were received inside 13 sample holders. Each container was identified by a text string ("Rab", "Susak", "Klimno") followed by a number. Containers were opened; digital picture (with an appropriate scale) of their content was taken, then samples were counted and classified according to their color and shape. A unique id number was assigned to every object inside the package (for instance: R for Rab, S for Susak, K for Klimno, followed by the container number and -a, b, c etc.). The type of samples was defined as "pellet" (PL), "fragment" (FR) or "filament" (FL). Objects labeled as "pellets" are spherical or cylindrical in shape, and typically are small granules used as raw material in plastic production. Objects labeled as "filaments" are thin and have a high aspect ratio (ratio between longer and shorter dimensions). Irregular objects were categorized as "fragments". The color was attributed according to the best match to the following: black (BLK), blue (BLU), brown (BRW), green (GNR), red (RED), sky blue (SKY), transparent (TRS), white (WHT), yellow (YEL).

2.2 Sample size

Samples sizes (dimensions and area) were measured directly on the pictures with the help of an image-editing software (GIMP); aspect ratio was defined as the ratio between the longer and the shorter measured dimension.

2.3 Sample composition

Sample composition was assessed by means of Fourier-Transform Infrared Spectroscopy (FT-IR). FT-IR spectra were acquired via a Thermo-Nicolet Nexus 470 spectrometer, equipped with an Attenuated Total Reflectance (ATR) accessory, in the 4000-500 cm^{-1} spectral range. Different plastic materials were identified by comparison with known reference spectra of the most common polymers; the most important vibrational bands were used as fingerprints as suggested by Jung et al (2018). These bands are shown in Table 1Table 3.

Other compounds (such as sand, calcium carbonate or cellulose) were identified by their characteristic vibrational bands reported in Table 2. Strong peaks in the 1400-1440 cm^{-1} region ($CaCO_3$ vibrational mode 2) or in the 1100 cm^{-1} region (SiO_2), when superimposed to the polymer spectra, were related to the presence of sand (carbonate or siliceous origin) in the plastic debris. The ratio between the peak intensity and the main peak of the polymer spectrum was also calculated. Spectra with only a broad, not well-defined vibrational band in the 1000-1050 cm^{-1} region (compatible with C-O-C stretch in polysaccharides) were assigned (also after visual examination of the sample) to fragments of algae or paper (cellulose). Samples with only $CaCO_3$ vibrational bands (aragonite?) were identified as fragments of shells or exoskeleton (biological origin).

Table 1: vibrational bands used to identify the most common polymers. Most intense peak for each polymer is labeled with (#)

polymer	Vibrational bands (cm^{-1})	assignment
Low-density polyethylene (LDPE); High-density polyethylene (HDPE)	2915 / 2845	CH_2 stretch (#)
	1472 / 1462	CH_2 bend (NB: single peak in HDPE; multi peak in LDPE)
	730 / 717	CH_2 rock
	2915 / 2845	CH_2 stretch
	1472 / 1462	CH_2 bend
	1377	CH_3 bend
	730 / 717	CH_2 rock
Polypropylene (PP)	2950 / 2915 / 2838	CH & CH_2 stretch (#)
	1455	CH_2 bend
	1377	CH_3 bend
	1166	CH bend; CH_3 rock; C-C stretch
	997	CH_3 rock; CH_3 bend; CH bend
	972	CH_3 rock; C-C stretch
	840	CH_2 rock; C-CH_3 stretch
Polystyrene (PS)	3024	arom. CH stretch
	2847	CH_2 stretch
	1601	arom. ring stretch
	1492	arom. ring stretch
	1451	CH_2 bend
	1027	arom. CH bend
	694	arom. ring out of plane bend (#)
Acrylonitrile butadiene styrene (ABS)	2922	CH & CH_2 stretch
	1602	arom. ring stretch
	1494	arom. ring stretch

	1452	CH_2 bend
	966	=C-H bend
	759	arom. ring out of plane bend (#)
Ethylene Vinyl acetate (EVA)	2917 / 2848	CH & CH_2 stretch (#)
	1740	C=O stretch
	1469	CH_2 & CH_3 bend
	1241	C-O bend
	1020	CH_2 rock
	720	CH_2 rock
Polyurethane (PU)	2865	CH & CH_2 stretch
	1731	C=O stretch (#)
	1531	C-N stretch
	1451	CH_2 bend
	1223	C(=O)O stretch
Polyamide (PA)	3298	NH stretch
	2932 / 2858	CH & CH_2 stretch
	1634	C=O stretch (Amide-I) (#)
	1538	NH bend, C-N stretch (Amide-II)
	1464	CH_2 bend
	1372	CH_2 bend
	1274	NH bend, C-N stretch
	1199	CH_2 bend
	687	NH bend, CO bend

Table 2: vibrational bands used to identify other compounds

	Vibrational bands (cm^{-1})	**assignment**
$CaCO_3$	1400 - 1450	$CaCO_3$ v3 mode
	855 - 875	$CaCO_3$ v2 mode
SiO_2	1100	Si-O-Si stretch (asymm)
	801	Si-O-Si stretch (symm)
	471	Si-O bend
algae, cellulose	1000 - 1030	C-O-C (polysaccharides?)

3 Results

Sample classification, size and composition is reported in Table 3. A total number of 51 debris were categorized. Type, shape and color codes are those reported in para. 2.1 and 2.2.

The composition was assessed as reported in para 2.3.

Table 3: sample ID, classification and size

Envelope ID		ID1	ID2	Type	color	Dim L1 (mm)	Aspect ratio	Composition	SiO_2	$CaCO_3$
Rab	1-5	R15	a	FR	BLU	1.3	1.6	PET	x	
Rab	1-5	R15	b	FR	BLU	1.4	2.0	PET	x	
Rab	2-9	R29	a	FR	SKY	1.8	2.0	PP	x	
Rab	2-9	R29	b	FR	SKY	0.8	1.0	PP	x	
Rab	2-9	R29	c	FL	WHT	9	7.5	PE		x
Rab	2-9	R29	d	FL	WHT	5	5.0	PE		x
Rab	2-9	R29	e	FL	GRN	10	50.0	PET		
Rab	3-9	R39	a	FR	BLU	3.2	2.1	PET		
Rab	3-9	R39	b	FR	WHT	6	1.5	not id		
Rab	3-9	R39	c	FR	WHT	2.1	1.1	PE	x	x
Rab	3-9	R39	d	FR	BRW	1.6	1.6	SiO		
Rab	4-5	R45	a	FR	RED	3.4	1.8	PET	x	x
Rab	4-5	R45	b	FR	TRS	10.2	4.6	PP	x	x
Rab	4-9	R49	a	FR	TRS	2.4	1.4	CaCO3		
Rab	4-9	R49	b	FL	WHT	14	70.0	PA		
Rab	5-5	R55	a	FR	TRS	7.4	2.4	PE		x
Susak	1-9	S19	a	FR	BLU	15	10.7	PE		x
Susak	1-9	S19	b	FR	BLU	7.2	2.7	PP	x	x
Susak	1-9	S19	c	FR	BRW	2.5	4.2	PVC		x
Susak	1-9	S19	d	FL	GRN	28	140.0	PA		
Susak	1-9	S19	e	FL	GRN	31	155.0	PA		
Susak	1-9	S19	f	FL	GRN	33	165.0	PA		
Susak	2-9	S29	a	PL	BLK	4.9	1.0	PE		x
Susak	2-9	S29	b	FR	BLU	2.9	1.9	PVC		x
Susak	2-9	S29	c	FR	BLU	2.8	1.2	PVC		x
Susak	2-9	S29	d	FR	BLU	2.4	1.6	PVC		x
Susak	2-9	S29	e	FL	TRS	6.2	20.7	not id		
Susak	2-9	S29	f	FL	WHT	12.6	25.2	natural fiber		
Susak	3-9	S39	a	FR	BLU	17	2.7	PE	x	x

Susak	3-9	S39	b	FR	BLU	12.2	1.2	PE	x	x
Susak	3-9	S39	c	FR	GRN	9.1	2.1	PE	x	x
Susak	3-9	S39	d	FL	RED	22	31.4	natural fiber		
Susak	3-9	S39	e	FL	TRS	40	133.3	fibra vetro?		
Susak	4-9	S49	a	FR	TRS	20.5	1.4	PET		
Susak	4-9	S49	b	FR	BRW	1.7	1.1	natural fiber		
Susak	4-9	S49	c	FR	BRW	1.6	1.8	natural fiber		
Susak	4-9	S49	d	FR	BRW	1.3	1.3	natural fiber		
Susak	4-9	S49	e	FR	BLU	1.9	1.6	natural fiber		
Susak	4-9	S49	f	FR	YEL	2.3	1.5	$CaCO_3$		
Susak	5-9	S59	a	FL	BRW	2.3	23.0	PET	x	
Susak	5-9	S59	b	FL	BRW	5.1	51.0	PET	x	
Klimno	4-5	K45	a	FL	WHT	51	56.7	not id		
Klimno	4-5	K45	b	FL	WHT	11.5	12.8	not id		
Klimno	4-5	K45	c	FL	WHT	18.4	20.4	not id		
Klimno	4-5	K45	d	FL	WHT	6.3	7.0	not id		
Klimno	4-5	K45	e	FL	WHT	4.9	5.4	not id		
Klimno	4-5	K45	f	FL	WHT	4	4.4	not id		
Klimno	4-5	K45	g	FL	WHT	8.1	9.0	not id		
Klimno	4-5	K45	h	FL	WHT	6.7	7.4	not id		
Klimno	4-5	K45	i	FL	WHT	4	4.4	not id		
Klimno	4-5	K45	j	FL	WHT	4.7	5.2	not id		

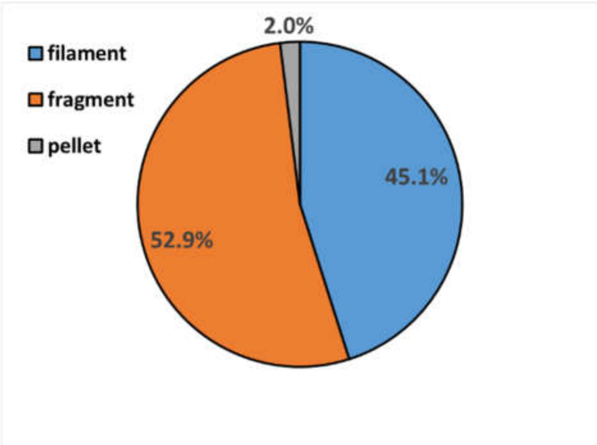
4 Discussion

Among the different polymers produced worldwide, the most common plastics found in marine waste include polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), polyurethane (PUR), polyethylene terephthalate (PET) and nylon (polyamide – PA) (Thushari 2020, Solomon 2016, Andrandy 2014). Table 4 shows the common applications of these plastics and their specific gravity.

Table 4: common plastics found in marine waste, their common application and specific gravity

Plastic type		**Common application**	**Specific gravity**
Low density polyethylene	LDPE	Plastic bags, film, packaging	0.91 – 0.93
High density polyethylene	HDPE	Bottle caps, storage containers	0.92 – 0.95
Polypropylene (PP)	PP	Ropes, storage containers, bottle caps	0.90 – 0.92
Polystyrene - expanded	EPS	Boxes, packaging	0.01 – 1.00
Polystyrene	PS	Utensils, cups	1.05 – 1.10
Polyvinyl chloride	PVC	Pipes, containers, insulators, films	1.20 – 1.30
Polyamide (Nylon)	PA	Ropes, fishing nets	1.15 – 1.20
Polyethylene terephthalate	PET	Bottles	1.35 – 1.40
Polyurethane	PU	Adhesives, foams	variable

A total number of 51 fragments have been categorized by means of visual analysis and then identified by FTIR. Of these, 53% were labeled as “fragments” (irregular shape), 2% as “pellets” (cylindrical or spherical) and 45% as “filaments” (very elongated, thin sheets). Fragments and filaments are most likely secondary microplastics (originated from the breakdown of large plastic items), while pellets (which represents almost the 20% of the total) can be categorized as primary microplastics (originally and intentionally manufactured in that size). These pellets are pre-production plastic pellets, made of raw resin, which are usually melted and used in the manufacturing of everyday plastic items. They somehow entered the environment before plastic objects production stage (most likely lost during transportation) and were subsequently found in areas of marine waste concentration. A summary of debris categories, sizes and aspect ratio is reported in Figure 1 and Figure 2. It is possible to notice that the majority of debris are between 2 and 5 mm (considering their greater measured size), and roughly half have an aspect ratio between 1 and 5. About 30% of the collected object are clearly elongated (aspect ratio > 10).



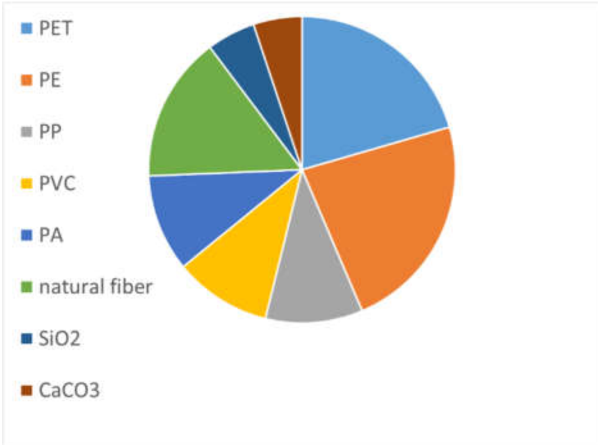
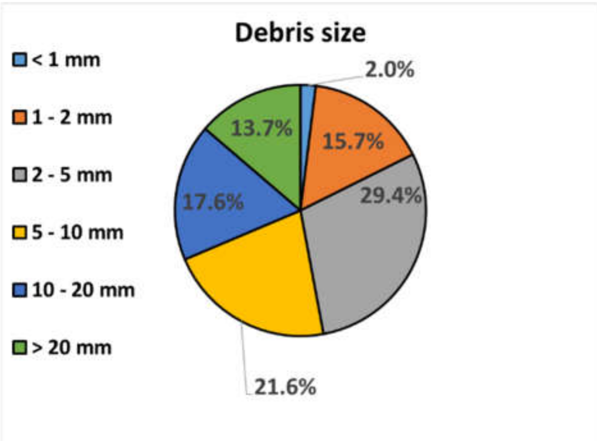


Figure 1 – debris classification, according to shape (left) and composition (right)



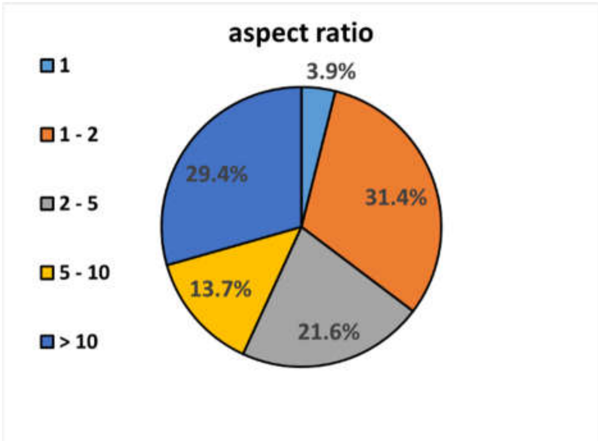


Figure 2 – debris size and aspect ratio

About 75% of the collected objects were plastic debris, while 25% were non-plastic (calcium carbonate, silica or glass and natural fibers/paper). Chart showing composition and color of analyzed fragments are shown in Figure 3 and Figure 4.

In the 18% of these plastic debris it was possible to identify a clear signal related to the presence of SiO_2; in the 12% $CaCO_3$ signal was noticeable; 14% of the samples have both signals. Given their sampling location (most likely Adriatic beaches – there was no information about the sampling location on the envelopes) it is possible to speculate a contamination of the samples with sand and/or shells.

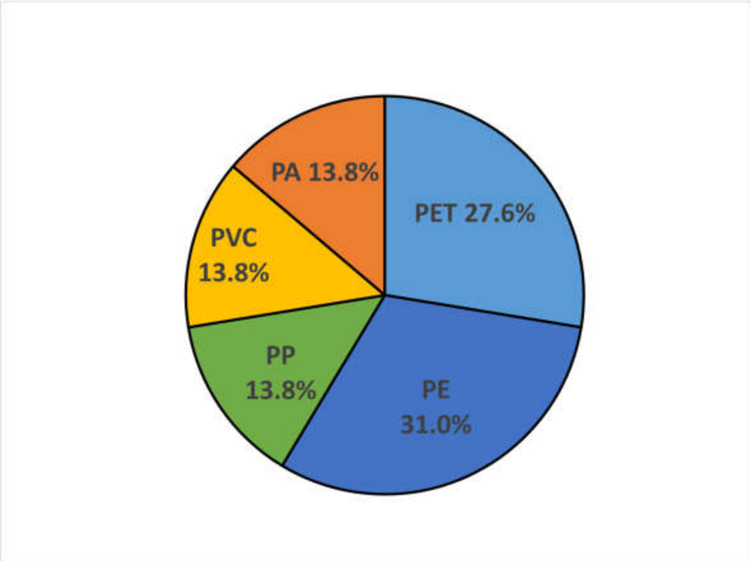


Figure 3 – relative abundance of polymers among the analyzed plastic objects

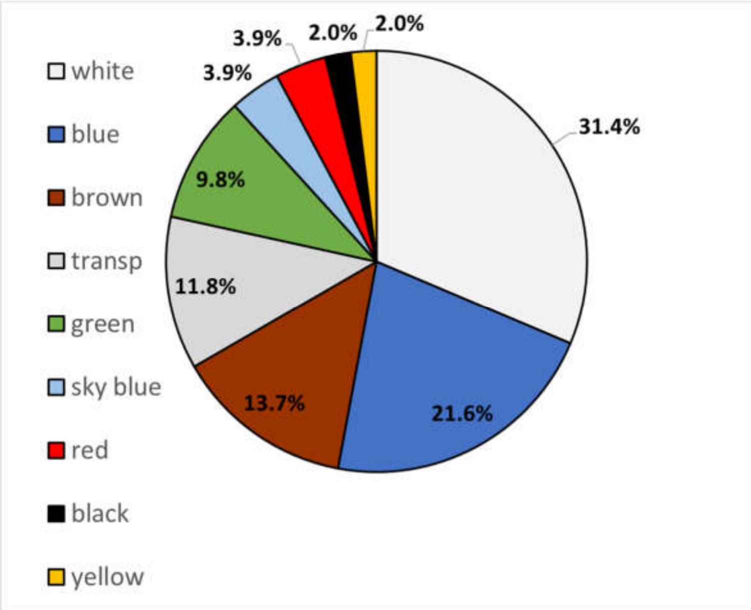


Figure 4 –colors of the analyzed plastic objects

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