Secondary reactions in the analysis of microplastics by analytical pyrolysis

Irene Coralli [a], Valerio Giorgi [b], Ivano Vassura [b,d], Alessandro G. Rombolà [a], Daniele Fabbri [a,c,*]

[a] *Department of Chemistry "Giacomo Ciamician", University of Bologna, Tecnopolo di Rimini, via Dario Campana 71, Rimini, Italy*
[b] *Department of Industrial Chemistry "Toso Montanari", University of Bologna, via Dario Campana 71, Rimini, Italy*
[c] *C.I.R.I. MAM, University of Bologna, Tecnopolo di Rimini, via Dario Campana 71, Rimini, Italy*
[d] *C.I.R.I. FRAME, University of Bologna, Tecnopolo di Rimini, via Dario Campana 71, Rimini, Italy*

ARTICLE INFO

ABSTRACT

Mixtures of plastic particles of different types were analysed by Py-GC-MS in order to investigate the effect of polymer interactions on the composition of pyrolysates. Pyrolysis products associated to secondary reactions were observed when particles of poly(ethylene terephthalate) (PET) were pyrolysed in the presence of poly (vinylchloride) (PVC) and the polyamides PA6 (polycaproamide) and PA66 (poly(hexamethylene adipamide)). Co-pyrolysis of PET in the presence of PVC particles produced mono and dichloroethyl esters of terephthalic acid due to the addition of HCl to the double bond of the vinyl group. Benzyl chloride, benzoyl chloride, 4-chlorobenzoic acid were also tentatively identified. The interaction between PET and PA6 and above all PA66 brought about the formation of aromatic nitriles including methyl and ethyl benzonitrile, 1,4-benzenedicarbonitrile, 4-cyanoethyl benzoate, 4-cyano benzoic acid. In addition, co-pyrolysis of PET and PA66 particles produced N-alkyl amides of benzoic acid. Pyrolysis of benzoic acid generated benzene and diphenyl, while N-hexylbenzamide was observed from the pyrolysis of benzoic acid with hexyl-1-amine or hexan-1,6-diamine. PE (polyethylene), PP (polypropylene), PS (polystyrene) and PVC did not exhibit significant interactions. Calibration curves built up with single plastic types in the 10–120 µg range were used to quantify each polymer in the mixture using typical pyrolytic markers. The highest deviations of recovery and the lowest RSD were observed for PET and PA6, while polyolefins produced satisfactory recovery and RSD. The detection of pyrolysis products from secondary reactions can be used as markers for the co-presence of different polymers supporting their identification.

1. Introduction

MPs are emerging contaminants of great concern because of their pervasive occurrence in the environment, predicted to increase due to worldwide rise of plastic production [1]. MPs constitute a heterogeneous class of contaminants which is difficult to define [2,3]. This factor, in combination with their low concentration in chemically complex matrices, makes their analysis a challenge. Most of our present knowledge on the potential exposure to MPs was obtained by microscopic observation and vibrational spectroscopy, but in the last years thermoanalytical techniques are gaining increasing importance [4–7]. Pyrolysis combined with gas chromatography and mass spectrometry (Py-GC-MS), non-reactive or in the presence of the methylating reagent tetramethylammonium hydroxide TMAH (thermally assisted hydrolysis and methylation, THM), has been applied to the quali-quantitative analysis of MPs in different matrices such as drinking waters [8], sea waters [9], sea salts [10], biosolids [11], sediments [12], seafood [13]

and miscellaneous [14–16]. The main advantages of analytical pyrolysis over optical-spectroscopic techniques reside in its capability to provide concentration values on mass units instead of particle number [17] and in its high selectivity due to the combination of chromatographic and mass spectrometric separation [18]. In addition, Py-GC-MS does not have constraints due to different shape (e.g. fibre or sphere), colour or size of the polymer particles. The pyrolysis products characteristic of a given polymer type (pyrolytic markers) are separated by GC and the ions generated in the mass spectrometer are separated and quantified. Selected pyrolytic markers and their associated ions are used for quantitation based on calibration protocols. Calibration is generally constructed by pyrolysing different quantity of standard polymers, but this procedure is not immune from flaws. Calibration protocols are based on the investigation of linear response for polymers pyrolysed individually [8,11,12,17,18] or in their mixture [9,10,14–16], simulating real conditions. A main drawback is matrix effect due to concomitants in the sample that may alter the pyrolytic behaviour of the polymer, in

---

comparison to the isolated form, or create interfering peaks [14,19]. When concomitants are constituents of the matrix, other than MPs, the problem can be solved by proper sample treatments. The selectivity of Py-GC-MS enables the analysis of mixture of MPs, avoiding the need of isolating single particles. However, different polymer types can interact leading to secondary reactions that may affect analytical results [20].

In the literature several studies have been published on the pyrolysis of polymers and their mixtures, particularly in the field of plastic waste recycling [21–31]. Nevertheless, there are very limited studies on polymer interactions concerned with the analysis of MPs [20]. It has been shown that poly(ethylene terephthalate) (PET) can cause interference in the analysis of polyurethane (PU) when the diisocyanate was used as pyrolytic marker for quantitation [20]. The explanation given by the authors was that benzoic acid produced from the pyrolysis of PET catalysed the hydrolysis of the diisocyanate into the corresponding amine. Procedural strategy can be adopted to tackle the problem of interference as performing calibration with polymers mixtures [32].

Nevertheless, identifying the occurrence of polymer interactions and understanding fundamental aspects on the chemistry of interactions are important to identify and solve possible bias. The investigation on polymer interaction is normally performed by co-pyrolysing different polymers and comparing the results with those obtained from single polymers pyrolysed under the same conditions.

This approach has been followed in this study that aimed at confirming previous studies and providing novel information on the formation of secondary pyrolysis products from the co-pyrolysis of plastic particles of different types. Different polymer types were selected among the most common synthetic polymers found in the environment. The attention was focused to PET as this polymer exhibited the most important interactions. Benzoic acid, a relevant pyrolysis product of PET, was pyrolysed in the presence nitrogenated compounds in order to gain a better understanding of the interactions between polyesters and polyamides.

2. Materials and methods

2.1. Samples

Common polymer material items were selected instead of pure standard polymers in order to mimic situations closer to real environmental samples. Small fragments in the range of 10–120 micrograms were obtained by cutting with a scalpel specimen of HDPE (bottle cap), PP (lid of a food container), PS (disposable glass), PET (disposable plastic clear bottle), PA-6 (standard pellet), PVC (pipe connector) and PA-66 (tie-wraps). In addition to the comparison of pyrograms with literature [33], the identity of the polymers was also confirmed by FTIR spectra, obtained with a Cary 630 FTIR spectrometer with an ATR diamond crystal in the 650–4000 cm^{-1} range [34]. Additives typically present in commercial polymers (such as stabilisers for polyolefines) were not revealed in the pyrograms [35] and FTIR spectra [34], probably due to their low concentrations (< 1 %). A small broad peak in the ATR spectrum of PVC centred at 1765 cm^{-1} was typical of commercial PVC resins and attributed to C=O groups introduced into the polymer chain in processing steps [36] (the signal of the C=O stretching of phthalates falls around 1730 cm^{-1}).

Benzoic acid, caprolactam, hexan-1-amine, hexan-1,6-diamine were purchased from Sigma-Aldrich.

2.2. Py-GC-MS

Pyrolyses were performed on single polymers and their mixtures. PET and PA or PVC particles were also pyrolyzed separated by a piece of quartz filter (Whatman® Q-MA). Benzoic acid was pyrolysed alone and in mixture with hexan-1-amine or hexan-1,6-diamine. Analyses were conducted with a multi-shot pyroliser (EGA/PY-3030D Frontier Lab) interfaced to a gas chromatograph coupled with mass spectrometer

(7890B and 5977B Agilent Technology). Each analyte was inserted inside a cup which free-fell into the pyrolyser furnace. Pyrolysis experiments were conducted at 500 °C and the pyrolysates were instantly introduced into the GC column fused silica capillary column (HP-5MS, stationary phase 5 %-diphenyl, 95 %-dimethylpolysiloxane 30 m x 0.25 mm i.d. x 0.25 μm film thickness). The gas chromatograph was operated in a constant helium flow of 1.0 mL min^{-1}, and a 1:20 split ratio. The injector temperature was 280 °C and the oven programmed temperature started at 50 °C. A first ramped rate of 3.7 °C min^{-1} led the temperature to 160 °C and a second rate of 20 °C min^{-1} to 310 °C, where it was held for 3 min. MS detector of both studies was operated in electron ionisation at 70 eV with scans in the 35–600 *m/z* range. Temperature of the ion source and the interface were 230 °C and 240 °C, respectively.

2.3. Identification and quantitation

Compound identification was based on matching mass spectra of NIST 14 database or published literature, pyrolysis of model compounds, or mass spectrum interpretation. Additionally, comparison was made with temperature programmed Kovats' Retention Indices (RI) when available. RI were calculated using the retention times of the *n*-alkanes determined in the pyrogram of PE from the equation:

$$RI_x = 100(n + \frac{tR_x - tR_n}{tR_{n+1} - tR_n})$$

in which tR_x, tR_n, and tR_{n+1} are the retention times of compound x, the *n*-alkane with n the carbon atoms eluting immediately before compound x, and the n-alkane with n + 1 carbon atoms eluting immediately after the compound x, respectively.

Calibration protocols were made by pyrolysing individual polymers weighed by the microbalance of a Mettler Toledo STDA851 TGA with a sensitivity of 0.001 mg. Characteristics pyrolytic markers for each polymer are indicated in Table 1.

Recovery (R) was calculated as the percentage ratio of weight calculated from the single-polymer calibration curve to the weight of the pyrolysed particle:

$$R = \frac{WEIGHT\ calculated}{WEIGHT\ pyrolysed} 100$$

Analytical standard deviations (s_{x0}) were calculated for each calibration protocol, indicating the random error of the analytical process for each polymer. s_{x0} resulted by the following equation:

$$s_{x0} = \frac{s_{xy}}{b} = \frac{\sqrt{\frac{1}{n-2}(SS_{yy} - \frac{SS_{yx}^2}{SS_{xx}})}}{b}$$

where s_{xy} is the residual standard deviation which indicates the calibration error, b is the slope of the calibration curve, n is the number of calibration points, SS_{xx}, SS_{yy} and SS_{yx} are the Sum of Squares [37].

3. Results and discussion

3.1. Py-GC-MS of polymer mixtures

Fig. 1 shows the pyrogram obtained from Py-GC-MS of a mixture of plastic particles of different polymers (PE, PP, PS, PVC, PET, PA6, PA66). From the comparison between the pyrograms of polymer mixtures and the pyrograms of each single polymer, the production of additional peaks was highlighted. In addition to the typical pyrolysis products of the investigated polymers [33], new peaks were revealed produced by nitrogen-bearing aromatic compounds and chlorinated benzoic acid derivatives (Table 2 and Table 3). These new pyrolysis products were observed when particles of PET were co-pyrolysed with particles of PA or PVC and were attributed to secondary reactions in the polymer melt or vapour phase. Pyrolysis products indicative of

Table 1

Calibration data obtained from Py-GC-MS of single polymeric materials. Retention indices RI experimental and RI$_{lit}$ from literature [33].

Polymer	Marker	*m/z*	RI	RI$_{lit}$	Equation	R^2	s$_{x0}$
PE	*n*-tetradec-1-ene	55	1392	1392	y = 5.4 10^2 x + 1.1 10^3	0.996	2.7
PP	2,4-dimethyl-1-heptene	43	837	845	y = 8.5 10^3 x + 6.1 10^4	0.993	3.4
PS	2,4-diphenyl-1-butene	208	1729	1749	y = 3.4 10^3 x + 1.3 10^4	0.993	5.4
PVC	2-methylnaphtalene	142	1293	1320	y = 2.9 10^2 x + 7.5 10	0.944	11
PET	vinyl benzoate	105	1137	1143	y = 2.7 10^3 x – 2.3 10^4	0.878	25
	divinyl terephthalate	175	1570	1577	y = 3.5 10^3 x – 1.0 10^4	0.958	14
PA-6	caprolactam	113	1277	1265	y = 2.9 10^3 x + 1.7 10^4	0.992	6

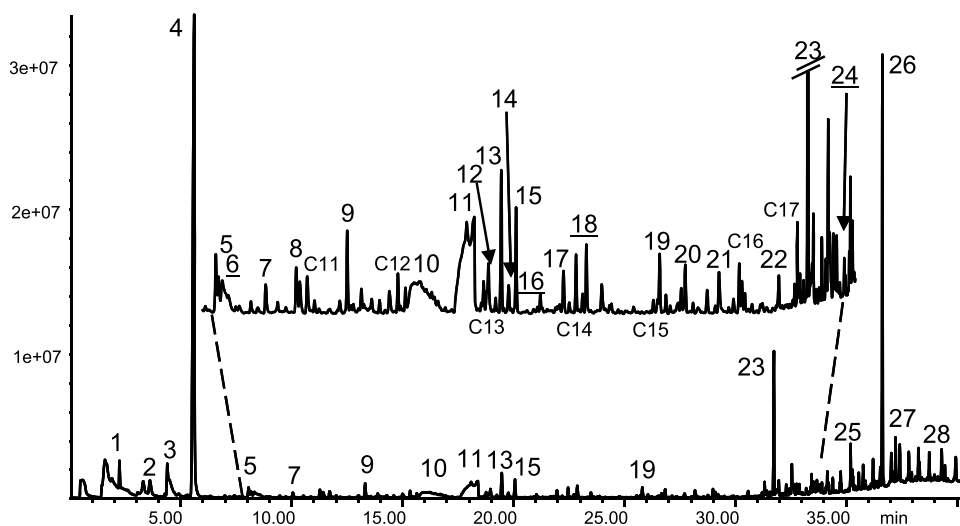**Fig. 1.** Pyrogram from a mixture of plastic particles (PE, 14 μg; PP, 13 μg; PS, 12 μg; PET, 12 μg; PA6, 13 μg; PA66, 10 μg; PVC,10 μg) Peak numbers refer to compounds listed in Table 2. **Cx:** alkadiene, alkene, alkane triplets with x carbon atoms (PE). Peak numbers underlined: products not found in the pyrograms of single polymers.

secondary reactions were not identified in the case of PE, PP and PS in accordance to literature [20]. The presence of chlorinated pyrolysis products of PP (2-chloro-2-phenyl propane, 2-chloro-2-methyl propane, 2-chloro-2-methyl pentane) were suggested from the pyrolysis of municipal waste plastic mixtures [25], but these products could not be identified in the pyrograms of our study. In accordance with our results, it was reported that PVC did not affect the thermal behaviour of poly-olefins [24].

Besides qualitative features, the mutual interactions between poly-mers can affect quantitative analysis as highlighted by Matsueda et al. [20].

In order to investigate this latter aspect, calibration curves were produced by pyrolysing single polymers. Particle weights were selected within the calibration ranges typically reported in the literature (0.1–1070 μg) [8,11,12,14]. The results are summarised in Table 1. These calibration curves were utilised for calculating the quantity of each polymer particle in mixtures, and the differences between expected and measured values were expressed as recovery R (Fig. 2). Recoveries were acceptable for polyolefins (mean ± RSD (n = 3): PE 96 % ± 4 %, PP 97 % ± 1 %, PS 104 % ± 11 %, PVC 108 % ± 14 %). This finding would indicate that interactions between polyolefins were minimal. This observation apparently contrasts with studies performed on mixtures of polyolefins with PS [29] and mixtures of PE, PP, PS, PVC and PET [30] were important changes of the pyrolytic behaviour of polymers were observed in comparison to isolated species. Williams and Williams re-ported a much higher concentration of aromatic compounds in the py-rolysis oil of PE/PS and PP/PS mixtures in comparison to single polymers, while a strong decrease of benzene concentration was observed in PVC/PS mixtures in comparison to PVC [29]. Similarly, an increase of styrene and other aromatic compounds in pyrolysis oils from mixtures of PE/PP/PS/PVC/PET in comparison to those of individual

polymers was observed by Muhammad et al. [30]. However, these studies employed a fixed-bed gas-purged pyrolytic reactor [29] and two-stage fixed bed pyrolysis-catalytic reactor [30] where interactions are supposed to be more significant with respect to flash pyrolysis, due to a higher residence time. In agreement with this interpretation, not important changes were found by Predel and Kaminsky [31] in the py-rolytic behaviour of PE, PP and PS mixtures. When these polymers were individually pyrolysed and co-pyrolysed in binary and ternary mixtures under flash pyrolysis conditions, no significant variations were identi-fied, except for PP/PS pyrolysis where an enhanced production of un-saturated waxes was revealed for compounds with a number of C > 30, mostly dienes [31].

In comparison to polyolefins, the recoveries of PET and PA6 were less satisfactory in terms of both mean values and variability (RSD). In the case of PET, the recovery was 123 % ± 30 % when using vinyl benzoate as pyrolytic marker, and 76 % ± 48 % with divinyl terephthalate. PA-6 presented low recovery and high variability (63 % ± 32 %). The dif-ference from polyolefins could be due to the poor calibration data for PET (Table 1) that exhibited the lowest determination coefficients R^2 and highest s$_{x0}$. The poor calibration behaviour of PET was also reported in the literature, mostly in the absence of an internal standard [9,10,13, 19]. However, deviations could also be caused by possible interactions between polymers as demonstrated in the case of PU with PET and PA6 [20]. Co-pyrolysis experiments with PVC and PA6 showed that HCl evolved from PVC increased the pyrolytic yield of aliphatic nitriles and favoured the depolymerisation of PA6 into caprolactam [23,28]. The formation of 6-chlorohexanenitrile was also reported as pyrolysis product from PVC-PA6 co-pyrolysis [28]. Instead, the pyrolytic behav-iour of PA66 did not appear to be influenced by PVC [23]. Apparently, these interactions did not affect quantitative results of PVC and PA microplastics in mixtures [20]. While interactions between PVC and PA

Table 2

GC-MS data and structural attribution of peaks labelled in the pyrogram of Fig. 1 obtained from Py-GC-MS of polymer mixture.

#	Compound	RI	*m/z*	Polymers
1	benzene	–	51, 52, **78**	PVC (PET)
2	cyclopentanone	–	41, **55**, 84	PA66
3	2,4-dimethyl-1-heptene	837	**43**, 70, 126	PP
4	styrene	898	51, 78, **104**	PS
5	α-methylstyrene	982	103, 117, **118**	PS
6	benzonitrile	993	50, 76, **103**	PET+PA
7	indene	1043	63, 115, **116**	PVC
8	2,4,6-trimethyl-1-nonene	1079	41, 69, 168	PP
9	vinylbenzoate	1137	77, **105**, 148	PET
10	benzoic acid	1214	77, **105**, 122	PET
11	caprolactam	1277	**55**, 84, 113	PA6
12	2-methylnaphthalene	1296	115, **141**, 142	PVC
13	2,4,6,8-tetramethyl-1-undecene	1307	**43**, 69, 154	PP
14	1-methylnaphthalene	1313	115, **141**, 142	PVC
15	2,4,6,8-tetramethyl-1-undecene	1324	**55**, 69, 154	PP
16	benzamide	1357	77, **105**, 121	PET+PA66
17	diphenyl	1379	76, 153, **154**	PET
18	2-chloroethylbenzoate	1415	**105**, 122, 184	PVC+PET
19	*n*-pentadec-1-ene	1497	**43**, 55, 210	PE
20	2,4,6,8,10-pentamethyl-1-tridecene	1527	**43**, 69, 196	PP
21	divinyl terephthalate	1567	76, 104, **175**	PET
22	1,3-diphenylpropane	1659	**92**, 105, 196	PS
23	styrene dimer	1726	**91**, 104, 208	PS
24	unknown	1863	175, **211**, 213	PVC?+ PET?
25	ethandiol dibenzoate	2190	77, **105**, 227	PET
25	1,4-benzenedicarboxylic acid, di-2-chloroethyl ester	2190	**166**, 211, 213	PVC+PET
26	styrene trimer	2510	**91**, 117, 312	PS
27	2-(benzoyloxy) ethylvinylterephthalate	2662	105, 149, **297**	PET
28	unknown	2980	**105**, 211, 213	PVC+PET

have been described in the literature, there are few articles on the interactions between PVC and PET [24], and no published studies dealing with the interactions between PET and PA to the best of our knowledge. Therefore, our attention was focused to the co-pyrolysis of PET particles with polyamides (PA6 and PA66) and PVC.

3.2. Py-GC-MS of PET with PA

Py-GC-MS of PET produced a pyrogram characterised by several peaks (Fig. 3a) identified by their known GC-MS characteristics [33]. Although benzoic acid was the predominant pyrolysis product, its poor chromatographic behaviour in GLC with non-polar stationary phase

precluded us from choosing it as a suitable pyrolytic marker. Moreover, when it was used as a pyrolytic marker by other authors, it produced non-linear calibration curves in polymer mixtures attributed to secondary reactions [20]. Vinyl terephthalate and divinyl terephthalate produced calibration plots with a better linearity in comparison to benzoic acid [20]. Vinyl benzoate was also used as a pyrolytic marker for PET [11].

The pyrolysate of PA6 (Fig. 3b) was dominated by caprolactam in accordance with literature [38,39]. When particles of PET and PA6 were co-pyrolysed, variations in the retention behaviour of benzoic acid and caprolactam were observed in the resulting pyrograms (Fig. 3c). The retention time of benzoic acid shifted with a concurrent reverse of the shape of peak tail. This change was noticed when benzoic acid was pyrolysed in the presence of caprolactam under the same conditions (data not shown). This behaviour was attributed to interactions between these two compounds inside the Py-GC system that along with reactions leading to benzonitrile could be responsible for the observed low recoveries (Fig. 2).

Benzonitrile and 4-cyanobenzoic acid were identified as new pyrolysis products from the co-pyrolysis of PET and PA6 (Fig. 3c and Table 3). In order to gather some information about their formation, benzoic acid was pyrolysed individually and in the presence of aliphatic amines, typical pyrolysis products of polyamides. Py-GC-MS of pure benzoic acid produced benzene, diphenyl and occasionally benzophenone (data not shown). Benzene and diphenyl can be formed from phenyl radical produced by the cleavage of the carbon-carbon single bond of benzoic acid [40]. An anionic mechanism of decarboxylation involving the phenyl anion was proposed for the formation of benzene in the case of sodium, potassium and calcium benzoates [41]. These reactions are favoured by experimental conditions (presence of water or catalysts) and hence could be of relevance in the analysis of MP mixtures. In fact, benzene is a common pyrolytic marker of PVC and its production from PET pyrolysis may interfere with the quantitation of PVC. Interestingly, thermal degradation products of benzoic acid such as diphenyl [13] and benzophenone [32] have been used as pyrolytic markers for the analysis of PET MPs.

Pyrolysis of a mixture of benzoic acid and 1-hexanamine brought about the formation of the *N*-hexylbenzamide, in addition to the obvious volatilisation of benzoic acid and 1-hexanamine (Fig. 4a). Benzonitrile could not be revealed. The production of benzonitrile was revealed when benzoic acid was co-pyrolysed with hexan-1,6-diamine (Fig. 4b). The *N*-hexylbenzamide was also tentatively identified (Fig. 4b). A possible mechanism that explains the formation of the above mentioned products is the following: the nitrogen of alkylamine reacts with the carbon of carbonyl group of the benzoic acid forming the corresponding alkylamide which is thermally decomposed into the corresponding nitrile derivative (Fig. 5). It is long known that nitriles are thermal decomposition products of amides [42]. Benzonitrile was revealed from the reaction of benzoic acid with hexan-1,6-diamine, but not with 1-hexanamine even though both generated N-hexylamide. A possible explanation is that *N*-hexylbenzamide was volatilised faster than its decomposition occurred, while the less volatile products from hexan-1, 6-diamine (e.g. hexyl-bis-benzamide) remained long enough in the hot zone to undergo thermal degradation. Hexanamine and hexan-1, 6-diamine are pyrolysis products of PA66 (Fig. 6a). Concordantly with the results from the analyses of low molecular weight compounds described above, the co-pyrolysis of PET and PA66 yielded benzonitriles and amides as relevant pyrolysis products, not present in the pyrograms of the isolated polymer particles (Fig. 6b). Because aromatic compounds are not formed from the pyrolysis of PA, and this latter is the source of nitrogen atoms, it is evident that aromatic compounds with nitrogen-containing functional groups are derived from the interaction between PET and PA. In the case of PA66, pyrolysis products from secondary reactions that were tentatively identified included: benzonitrile, methylbenzonitrile, ethylbenzonitrile, dicyanobenzene, benzamide, cyanobenzoic acid, benzamide, N-hexylbenzamide (Table 3).

Table 3

GC-MS data and tentative structural attribution of pyrolysis products derived from polymer interactions between PET and PA or PVC. Rt: retention time (minutes); RI: retention index, RI$_{lit}$: retention index from PubChem, n.f. not found. *m/z*: mass to charge ratio of relevant ions, bold base peak, italics molecular ion. ID, identification by MS comparison with library (XX % match), [XX] literature, INT. mass spectrum interpretation.

Compound	Rt	RI	RI$_{lit}$	*m/z*	polymers	ID
benzonitrile	8.28	993	937–940	50, 76, **103**	PET+PA	97%
benzylchloride	9.16	1020	978–1479	65, **91**, *126*, 128	PET+PVC	93%
Benzoyl chloride	11.30	1083	1037–1095	51, 77, **105**, *140*, 142	PET+PVC	96%
methylbenzonitrile	12.31	1111	1071	90, ***117***	PET+PA66	95%
Ethylbenzonitrile	15.82	1208	n.f.	89, 103, **116**, *131*	PET+PA66	87%
1,4-benzenedicarbonitrile	18.21	1274	n.f.	50, 64, 101, ***128***	PET+PA66	95%
4-chlorobenzoic acid	20.68	1344	1336	111, **139**, 141, *156*, 158	PET+PVC	91%
benzamide	21.1	1357	1339–1344	51, 77, **105**, *121*	PET+PA66	94%
N-methyl benzamide	22.4	1394	1390–1404	77, **105**, 134, *135*	PET+PA66	88%
2-Chloroethyl benzoate	23.09	1415	1366–2159	51, 77, **105**, 122, *184*, 186	PET+PVC	[27]
N-ethylbenzamide	23.85	1438	n.f.	77, **105**, 148, *149*	PET+PA66	INT.
Ethyl 4-cyano benzoate	24.03	1443	n.f.	102, **130**, 147, *175*	PET+PA66	90%
4-methylbenzamide	24.76	1465	n.f.	65, 91, **119**, *135*	PET+PA66	92%
4-cyanobenzoic acid	25.60	1491	n.f.	102, **130**, 147	PET+PA66; PET+ PA6	87%
N-propylbenzamide	26.89	1529	1526	51, 77, **105**, 134, 162, *163*	PET+PA66	INT.
4-methyl benzoic acid,2-chloroethyl ester	26.99	1532	n.f.	65, 91, **119**, *198*, 200	PET+PVC	[27]
3,4-dichlorobenzoic acid	27.21	1538	n.f.	145, 147, **173**, 175, *190*, 192	PET+PVC	83%
N-butylbenzamide	30.08	1637	1642	51, 77, **105**, 134, 135, *177*	PET+PA66	INT.
N-pentylbenzamide	31.92	1743	n.f.	51, 77, **105**, 134, 148, 162, *191*	PET+PA66	INT.
4-acetyl benzoic acid, 2-chloroethyl ester (#)	32.72	1817	n.f.	147, 164, **211**, 213, *226*, 228	PET+PVC	[26] INT.
Benzamide derivative	32.96	1844	n.f.	51, 77, **105**, 130, 162	PET+PA66	INT.
N-hexylbenzamide	33.04	1853	n.f.	77, **105**, 135, 148, 162, 176, *205*	PET+PA66	92%
1,4-benzenedicarboxylic acid, 2-chloroethyl ester, ethyl ester (§)	33.59	1922	n.f.	149, **166**, 194, 211, 213, *256*, 258	PET+PVC	[27]
1,4-benzenedicarboxylic acid, mono-2-chloroethyl ester (§)	33.64	1929	n.f.	65, 121, **149**, 166, *228*, 230	PET+PVC	[27]
unknown	34.52	2066	n.f.	102, **130**	PET+ PA66	
unknown	35.01	2156	n.f.	102, **130**	PET+ PA66	
1,4-benzenedicarboxylic acid, di-2-chloroethyl ester (*)	35.25	2202	n.f.	149, **166**, 211, 213, *290*, 292, 294	PET+PVC	[27]

(#) overlapping with unknown *m/z* 194. (§) Overlapping with 1,4-benzenedicarboxylic acid (*m/z* 121, **149**, **166**) and biphenyl-4-carboxylic acid (*m/z* 152,181,***198***); (*) overlapping with 1,2-ethandiol dibenzoate with *m/z* 77, **105**, 227, *270*.
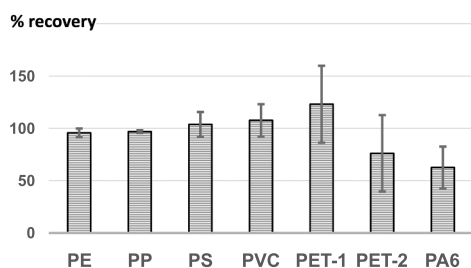

Fig. 2. Recovery values from Py-GC-MS of polymer particle mixtures using the calibration protocols reported in Table 1; PET-1 marker: vinyl benzoate, PET-2 marker: divinyl terephthalate.

Benzoic acid derivatives substituted with a nitrile group exhibited mass spectra with an intense peak at *m/z* 130 (4-formylbenzonitrile ion) and *m/z* 102 (benzonitrile ion), thus these ions can be used to verify PET-PA co-presence in the MP mixture (Fig. 5). Some of these products were identified by library matching, others could not be assigned, but their GC-MS data are reported in Table 3. Interestingly, benzamide and its *N*-alkyl series from methyl to hexyl were revealed (mass spectra characterised by base peak at *m/z* 105, molecular ion and loss of alkyl radical) supporting a chain scission mechanism from the longer alkyl chain of the amide precursor.

All together these results suggest that a possible route towards the formation of nitriles involves the formation of amides (Fig. 5). The nucleophilic attack of amines to the carbonyl group of benzoic/terephthalic acid leading to amides could occur in the vapour phase between low molecular weight pyrolysis products or in the melt between oligomers or polymer chains (e.g. terminal NH$_2$ group of PA66 and esters of benzoic acids). Py-GC-MS of PET particle physically separated by the particle of PA6 with a quartz filter produced benzonitrile; benzonitrile and amides were revealed by a similar experiment with PET and PA66. These results demonstrated that secondary products can be observed even when the particles are physically separated.

The presence of ε-caprolactame, a typical pyrolysis product of PA6, in the pyrolysate of standard PA66 has been reported [33,38], but in our case it could be due to the co-presence of the two polymers in the commercial specimen.

3.3. Py-GC-MS of PET with PVC

Co-pyrolysis of PET and PVC particles resulted in the formation of chlorinated derivatives of benzoic and terephthalic acids as secondary pyrolysis products (Fig. 7). The identification of some compounds was based on comparison with the mass spectra reported by Kulesza and German [27] who investigated the co-pyrolysis of PVC and PET. Specifically, the 2-chloroethyl esters of benzoic acid, 4-methylbenzoic acid and 1,4-benzenedicarboxylic acid (Table 3). The 2-chloroethyl ester of 4-acetylbenzoic acid was tentatively identified from the interpretation of the mass spectrum: molecular ion at *m/z* 226 (*m/z* 228 ^{37}Cl isotopic ion) and fragment ions from the loss of methyl radical at *m/z* 211 (*m/z* 213 ^{37}Cl isotopic ion), loss of C$_2$H$_2$ClO radical at *m/z* 147, loss of vinyl chloride from the rearrangement with H transfer at *m/z* 164. This compound was reported as a pyrolysis product from Py-GC-MS of 1/1 PVC/PET mixture even though the mass spectrum was not reported [26]. The cluster of chlorine isotopes differing of two relative mass units with the characteristic 100:33 relative abundances in the mass spectrum was fundamental for the assignment of mono-chlorinated species. The chlorinated compounds reported in Fig. 7 and Table 3 exhibited mass spectra with at least one identifiable isotopic cluster of chlorine. The ions at *m/z* 211 and 213 with about 100 and 33 relative abundances represented a typical situation attributed to the ions C$_{10}$H$_8$^{35}ClO$^+$ and C$_{10}$H$_8$^{37}ClO$^+$, respectively. The structural unit is the 2-chloroethyl ester of 4'-formyl benzoic acid ion (see Scheme 5). The chloroethyl unit can be thought as virtually formed by the addition of HCl evolved by the thermal dehydrochlorination of PVC to the vinyl group of the pyrolysis products of PET (vinyl ester of benzoic acid and terephthalic acid).

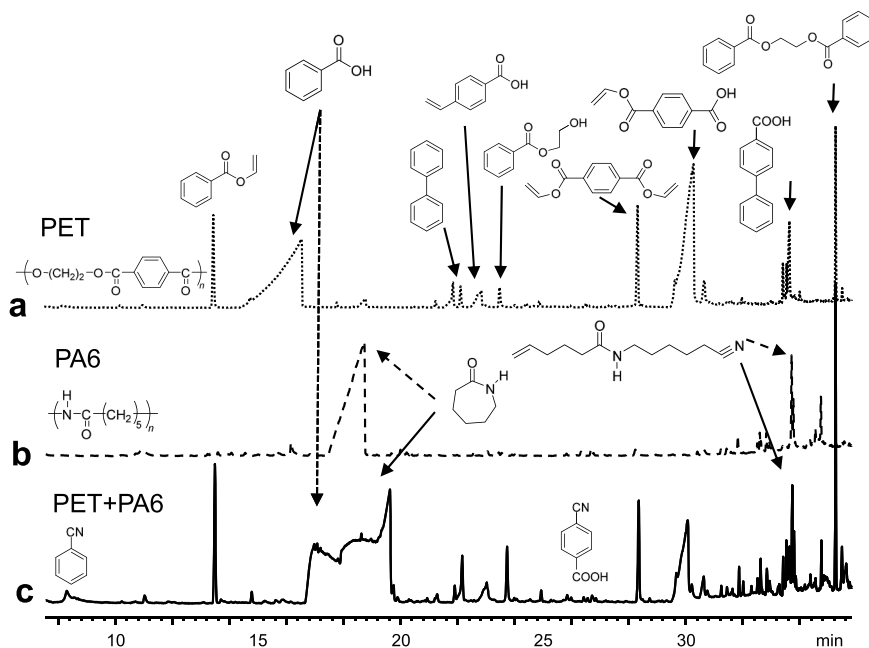Benzoyl chloride and chlorobenzoic acid were also revealed, the

Fig. 3. Pyrograms obtained from Py-GC-MS of particles of (a) PET, (b) PA6, (c) PET (50 μg) and PA6 (48 μg).
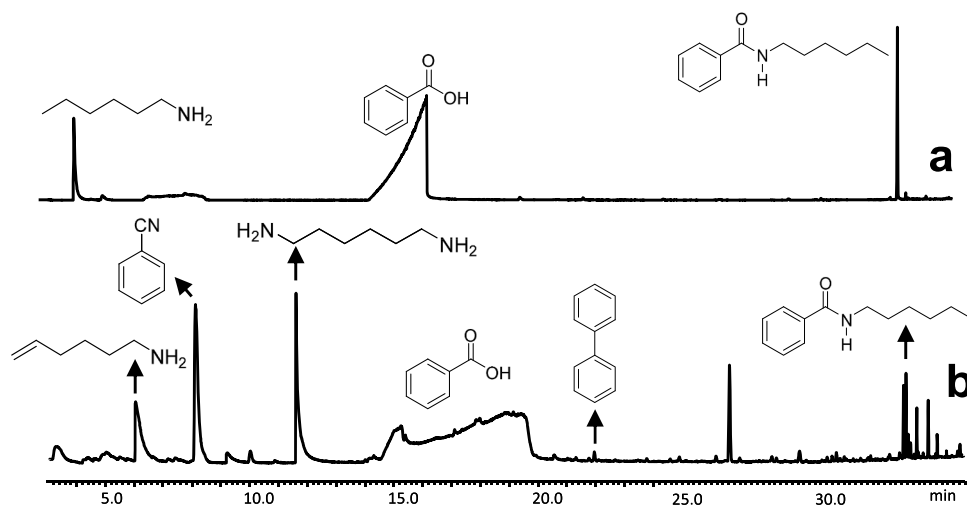

Fig. 4. Pyrograms obtained from Py-GC-MS of benzoic acid with (a) hexan-1-amine and (b) hexane-1,6-diamine.

latter compound in agreement with Czégény et al. [26]. All these compounds, reported in Table 3, were not detected in the pyrogram of PVC or PET single particles. However, two unknown compounds displaying the ions *m/z* 211 and 213 (100:32 abundance ratio) were observed at RI 1863 and 2980, respectively, in the pyrograms of mixtures (Table 2), PVC/PET (peaks 15 and 20 of Fig. 7) and occasionally in the pyrograms of PVC and PET. The origin and structure of these compounds could not be assigned. The possible chlorination of additives like diesters of *o*-phthalic acid cannot be excluded, but difficult to explain as phthalates are generally esters of saturated alcohol without aliphatic double bonds capable to add HCl. Besides, phthalates were not detected in the IR spectra. At this stage of the investigation, the origin of these two compounds remained uncertain and only tentatively attributed to secondary reactions. These two compounds as well as those listed in Table 3 were observed when Py-GC-MS was conducted on the particles of PET and PVC physically separated by a quartz filter indicating that physical contact is not necessary for polymer interaction and secondary reactions may occur in the gas phase.

The presence of chlorinated derivatives of benzoic or benzenedi-carboxylic acids was not reported in the literature dealing with the analysis of polymer mixtures by THM-TMAH. The use of TMAH, which is quite common in the analysis of MPs, has probably the effect of reducing PET-PVC interactions due to the neutralisation of HCl and the formation of methyl ester in place of vinyl esters.

4. Conclusions

This study evidenced that secondary pyrolysis products can be produced from Py-GC-MS of mixtures of plastic particles. PET resulted the most critical polymer as benzoic acid and its derivatives, such as vinyl esters, can be involved in various reactions leading to new products. Nitrogen-containing aromatic compounds, such as nitriles and amides, are indicative of interactions between PET and polyamides, in particular PA66. Nitriles are probably generated by the dehydration of amides in turn generated by reactions with alkyl(di)amines and benzoic acid derivatives. The occurrence of PET-PA66 interactions can be monitored in
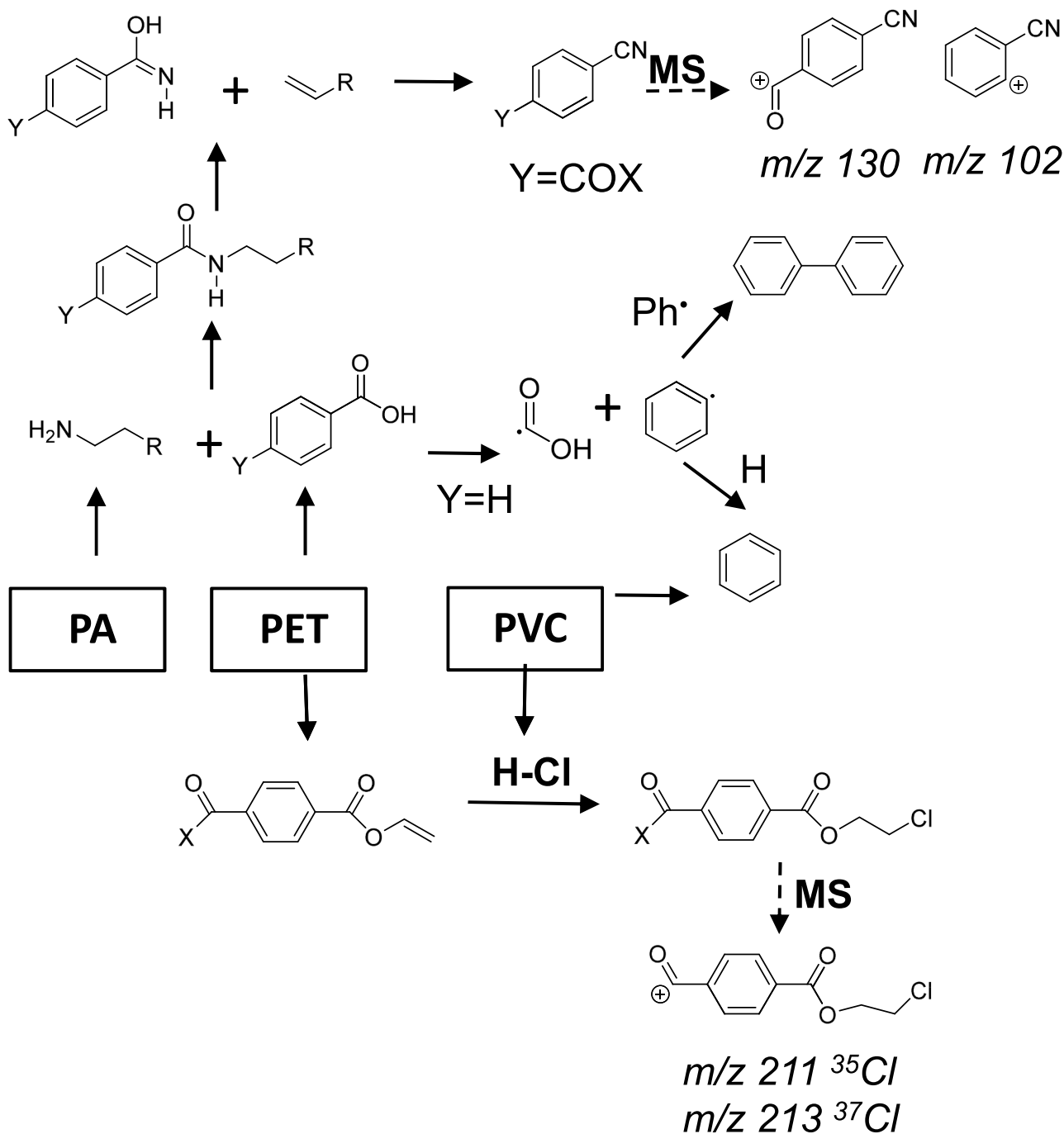
Fig. 5. Scheme summarising the formation of secondary products from the pyrolysis of PET with PA and PVC. The structure and *m/z* values of relevant ions in the mass spectrum are reported.

the MS-pyrograms by selecting the ions at *m/z* 102 and 130. Chlorinated pyrolysis products of PET are formed from the addition of HCl to the double bond of the vinyl ester of benzoic and terephthalic acids. The occurrence of PET-PVC interactions can be monitored in the MS-pyrograms by selecting the ions at *m/z* 211 and 213.

The results of this study did not provide firm evidence that these secondary reactions were responsible of the deviations observed in quantitative analysis, however, they highlighted the role they may play in method optimisation. It is expected that two main procedures adopted in the determination of microplastic by analytical pyrolysis may reduce the extent of secondary reactions: the use of TMAH (e.g. neutralisation of HCl, methylation of benzoic acid) and dilution with a solid material. While this latter method has been proved to be effective in reducing

secondary reactions in recent publications, polymer interactions in the presence of TMAH is a topic worth of consideration in future studies.

CRediT authorship contribution statement

D. Fabbri, I. Vassura: Conception and design of study. **I. Coralli, A. G. Rombolà, V. Giorgi**: Acquisition of data. **D. Fabbri, A.G. Rombolà, I. Coralli**: Analysis and/or interpretation of data. **D. Fabbri**: Drafting the manuscript. **D. Fabbri, I. Coralli**: Revising the manuscript critically for important intellectual content. **I. Coralli, V. Giorgi, A.G. Rombolà, I. Vassura, D. Fabbri**: Approval of the version of the manuscript to be published (the names of all authors must be listed).
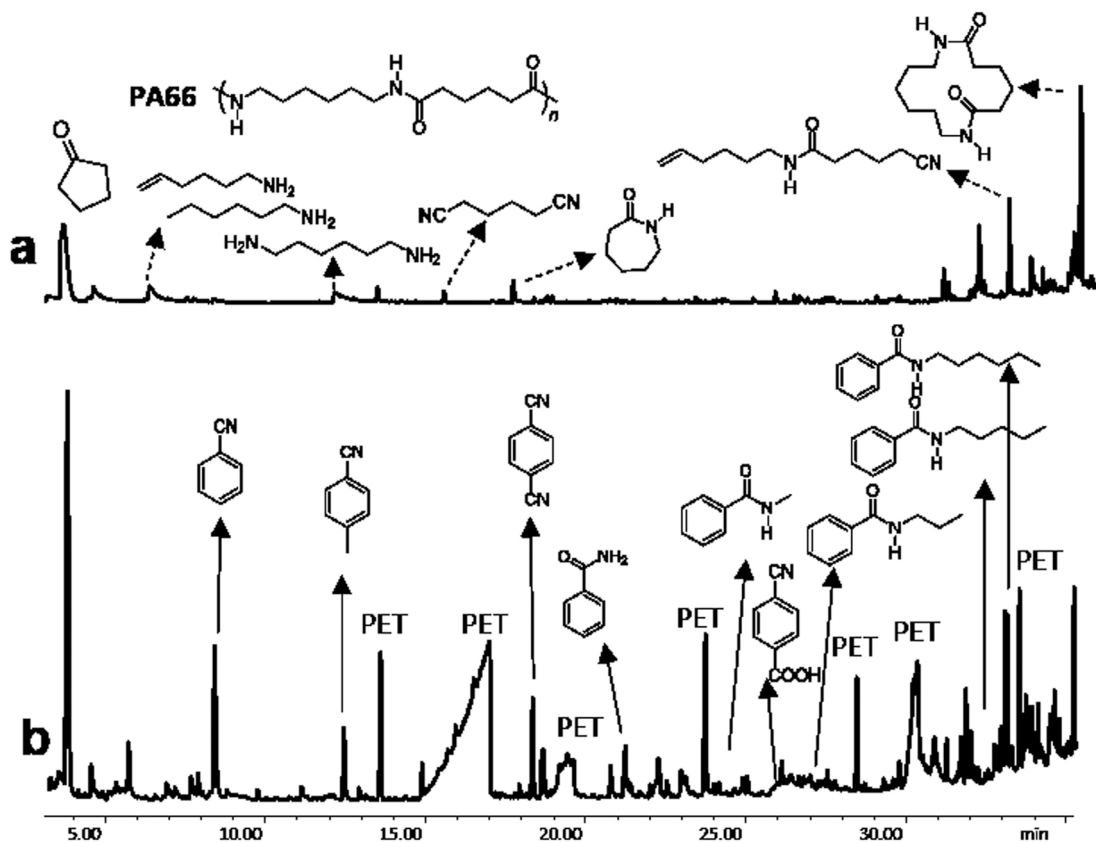
Fig. 6. Pyrograms obtained from Py-GC-MS of (a) PA66 particle, and (b) PET (71 μg) with PA66 (63 μg) particles.
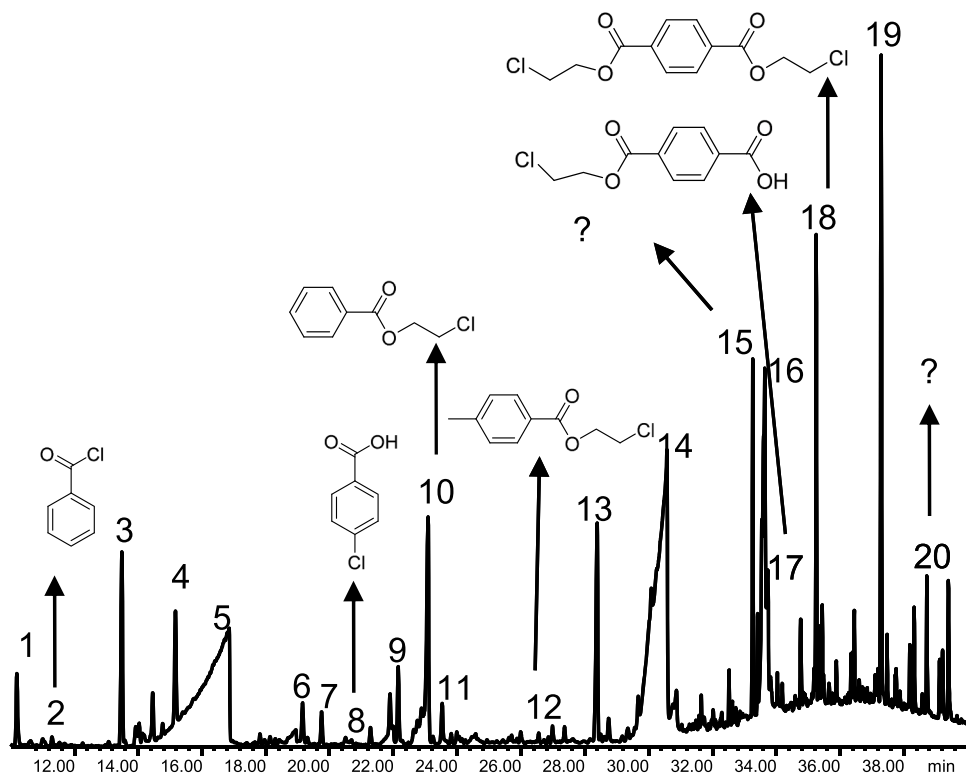

Fig. 7. Pyrogram obtained from Py-GC-MS of PET (121 μg) and PVC (114 μg) 1: indene (PVC); 2: benzoylchloride (PET+PVC); 3: vinylbenzoate (PET); 4: naphthalene (PVC); 5: benzoic acid (PET); 6: 2-methylnaphthalene (PVC); 7: 1-methylnaphthalene (PVC); 8: 4-chlorobenzoic acid (PET+PVC); 9: diphenyl (PET and PVC); 10: 2-chloroethylbenzoate (PET+PVC); 11: 2-hydroxyethylbenzoate (PET); 12: 4-methylbenzoic acid, 2-chloroethylester (PET+PVC); 13: divinylterephthalate (PET); 14: terephthalic acid, monovinylester (PET); 15: unknown (m/z 104, 149?, 175, **211**, 213, Table 2); 16: terephthalic acid (PET); 17: diphenylcarboxyilic acid (PET) 1,4-benzenedi-carboxylic acid (PET)+terephthalic acid, mono-2-chloroethyl ester (PET+PVC); 18: terephthalic acid, di-2-chloroethyl ester (PET+PVC), overlaps with 1,2-ethandiolbenzoate; 19:2-(benzoyloxy)ethylvinylterephtalate (PET); 20: unknown (m/z 77, **105**, 211, 213, Table 2).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

References

[1] A.A. Horton, A. Walton, D.J. Spurgeon, E. Lahive, C. Svendsen, Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities, Sci. Total Environ. 586 (2017) 127–141, https://doi.org/10.1016/j.scitotenv.2017.01.190.

[2] N.B. Hartmann, T. Hüffer, R.C. Thompson, M. Hassellöv, A. Verschoor, A.E. Daugaard, S. Rist, T. Karlsson, N. Brennholt, M. Cole, M.P. Herrling, M.C. Hess, N.P. Ivleva, A.L. Lusher, M. Wagner, Are we speaking the same language? Recommendations for a definition and categorization framework for plastic debris, Environ. Sci. Technol. 53 (2019) 1039–1047, https://doi.org/10.1021/acs.est.8b05297.

[3] Y.K. Müller, T. Wernicke, M. Pittroff, C.S. Witzig, F.R. Storck, J. Klinger, N. Zumbülte, Microplastic analysis—are we measuring the same? Results on the first global comparative study for microplastic analysis in a water sample, Anal. Bioanal. Chem. 412 (2020) 555–560, https://doi.org/10.1007/s00216-019-02311-1.

[4] R. Peñalver, N. Arroyo-Manzanares, I. López-García, M. Hernández-Córdoba, An overview of microplastics characterization by thermal analysis, Chemosphere 242 (2020), 125170, https://doi.org/10.1016/j.chemosphere.2019.125170.

[5] J. La Nasa, G. Biale, D. Fabbri, F. Modugno, A review on challenges and developments of analytical pyrolysis and other thermoanalytical techniques for the quali-quantitative determination of microplastics, J. Anal. Appl. Pyrolysis 149 (2020), 104841, https://doi.org/10.1016/j.jaap.2020.104841.

[6] N. Yakovenko, A. Carvalho, A. ter Halle, Emerging use thermo-analytical method coupled with mass spectrometry for the quantification of micro(nano)plastics in environmental samples, TrAC Trends Anal. Chem. 131 (2020), 115979, https://doi.org/10.1016/j.trac.2020.115979.

[7] Y. Picó, D. Barceló, Pyrolysis gas chromatography-mass spectrometry in environmental analysis: focus on organic matter and microplastics, TrAC Trends Anal. Chem. 130 (2020), 115964, https://doi.org/10.1016/j.trac.2020.115964.

[8] A. Gomiero, K.B. Øysæd, L. Palmas, G. Skogerbø, Application of GCMS-pyrolysis to estimate the levels of microplastics in a drinking water supply system, J. Hazard. Mater. 416 (2021), 125708, https://doi.org/10.1016/j.jhazmat.2021.125708.

[9] C. Dibke, M. Fischer, B.M. Scholz-Böttcher, Microplastic concentrations and distribution in German bight waters by pyrolysis–gas chromatography–mass spectrometry/thermochemolysis reveal potential impact of marine coatings: do ships leave skid marks? Environ. Sci. Technol. 55 (2021) 2285–2295, https://doi.org/10.1021/acs.est.0c04522.

[10] M. Fischer, I. Goßmann, B.M. Scholz-Böttcher, Fleur de Sel—an interregional monitor for microplastics mass load and composition in European coastal waters? J. Anal. Appl. Pyrolysis 144 (2019), 104711 https://doi.org/10.1016/j.jaap.2019.104711 (accessed September 9, 2021).

[11] E.D. Okoffo, F. Ribeiro, J.W. O'Brien, S. O'Brien, B.J. Tscharke, M. Gallen, S. Samanipour, J.F. Mueller, K.V. Thomas, Identification and quantification of selected plastics in biosolids by pressurized liquid extraction combined with double-shot pyrolysis gas chromatography–mass spectrometry, Sci. Total Environ. 715 (2020), 136924, https://doi.org/10.1016/j.scitotenv.2020.136924.

[12] A. Gomiero, K.B. Øysæd, T. Agustsson, N. van Hoytema, T. van Thiel, F. Grati, First record of characterization, concentration and distribution of microplastics in coastal sediments of an urban fjord in south west Norway using a thermal degradation method, Chemosphere 227 (2019) 705–714, https://doi.org/10.1016/j.chemosphere.2019.04.096.

[13] F. Ribeiro, E.D. Okoffo, J.W. O'Brien, S. Fraissinet-Tachet, S. O'Brien, M. Gallen, S. Samanipour, S. Kaserzon, J.F. Mueller, T. Galloway, K.V. Thomas, Quantitative analysis of selected plastics in high-commercial-value Australian seafood by pyrolysis gas chromatography mass spectrometry, Environ. Sci. Technol. 54 (2020) 9408–9417, https://doi.org/10.1021/acs.est.0c02337.

[14] M. Fischer, B.M. Scholz-Böttcher, Simultaneous trace identification and quantification of common types of microplastics in environmental samples by pyrolysis-gas chromatography–mass spectrometry, Environ. Sci. Technol. 51 (2017) 5052–5060, https://doi.org/10.1021/acs.est.6b06362.

[15] G. Dierkes, T. Lauschke, S. Becher, H. Schumacher, C. Földi, T. Ternes, Quantification of microplastics in environmental samples via pressurized liquid extraction and pyrolysis-gas chromatography, Anal. Bioanal. Chem. 411 (2019) 6959–6968, https://doi.org/10.1007/s00216-019-02066-9.

[16] M. Fischer, B.M. Scholz-Böttcher, Microplastics analysis in environmental samples – recent pyrolysis-gas chromatography-mass spectrometry method improvements to increase the reliability of mass-related data, Anal. Methods 11 (2019) 2489–2497, https://doi.org/10.1039/C9AY00600A.

[17] S. Primpke, M. Fischer, C. Lorenz, G. Gerdts, B.M. Scholz-Böttcher, Comparison of pyrolysis gas chromatography/mass spectrometry and hyperspectral FTIR imaging

[18] spectroscopy for the analysis of microplastics, Anal. Bioanal. Chem. 412 (2020) 8283–8298, https://doi.org/10.1007/s00216-020-02979-w.

[18] R. Becker, K. Altmann, T. Sommerfeld, U. Braun, Quantification of microplastics in a freshwater suspended organic matter using different thermoanalytical methods – outcome of an interlaboratory comparison, J. Anal. Appl. Pyrolysis 148 (2020), 104829, https://doi.org/10.1016/j.jaap.2020.104829.

[19] Z. Steinmetz, A. Kintzi, K. Muñoz, G.E. Schaumann, A simple method for the selective quantification of polyethylene, polypropylene, and polystyrene plastic debris in soil by pyrolysis-gas chromatography/mass spectrometry, J. Anal. Appl. Pyrolysis 147 (2020), 104803, https://doi.org/10.1016/j.jaap.2020.104803.

[20] M. Matsueda, M. Mattonai, I. Iwai, A. Watanabe, N. Teramae, W. Robberson, H. Ohtani, Y.-M. Kim, C. Watanabe, Preparation and test of a reference mixture of eleven polymers with deactivated inorganic diluent for microplastics analysis by pyrolysis-GC–MS, J. Anal. Appl. Pyrolysis 154 (2021), 104993, https://doi.org/10.1016/j.jaap.2020.104993.

[21] S. Kumagai, T. Yoshioka, Latest trends in pyrolysis gas chromatography for analytical and applied pyrolysis of plastics, Anal. Sci. (2020), https://doi.org/10.2116/analsci.20SAR04.

[22] M. Blazsó, B. Zelei, E. Jakab, Thermal decomposition of low-density polyethylene in the presence of chlorine-containing polymers, J. Anal. Appl. Pyrolysis 35 (1995) 221–235, https://doi.org/10.1016/0165-2370(95)00910-7.

[23] Z. Czégény, M. Blazsó, Thermal decomposition of polyamides in the presence of poly(vinyl chloride), J. Anal. Appl. Pyrolysis 58–59 (2001) 95–104, https://doi.org/10.1016/S0165-2370(00)00152-2.

[24] Z. Czégény, E. Jakab, M. Blazsó, Thermal decomposition of polymer mixtures containing poly(vinyl chloride), Macromol. Mater. Eng. 287 (2002) 277–284, https://doi.org/10.1002/1439-2054(20020401)287:4<277::AID-MAME277>3.0.CO;2-#.

[25] T. Bhaskar, Md.A. Uddin, K. Murai, J. Kaneko, K. Hamano, T. Kusaba, A. Muto, Y. Sakata, Comparison of thermal degradation products from real municipal waste plastic and model mixed plastics, J. Anal. Appl. Pyrolysis 70 (2003) 579–587, https://doi.org/10.1016/S0165-2370(03)00027-5.

[26] Zs Czégény, E. Jakab, M. Blazsó, T. Bhaskar, Y. Sakata, Thermal decomposition of polymer mixtures of PVC, PET and ABS containing brominated flame retardant: formation of chlorinated and brominated organic compounds, J. Anal. Appl. Pyrolysis 96 (2012) 69–77, https://doi.org/10.1016/j.jaap.2012.03.006.

[27] K. Kulesza, K. German, Chlorinated pyrolysis products of co-pyrolysis of poly(vinyl chloride) and poly(ethylene terephthalate), J. Anal. Appl. Pyrolysis 67 (2003) 123–134, https://doi.org/10.1016/S0165-2370(02)00057-8.

[28] F. Kubatovics, M. Blazsó, Thermal decomposition of polyamide-6 in the presence of PVC, Macromol. Chem. Phys. 201 (2000) 349–354, https://doi.org/10.1002/(SICI)1521-3935(20000201)201:3<349::AID-MACP349>3.0.CO;2-Y.

[29] P.T. Williams, E.A. Williams, Interaction of plastics in mixed-plastics pyrolysis, Energy Fuels 13 (1999) 188–196, https://doi.org/10.1021/ef980163x.

[30] C. Muhammad, J.A. Onwudili, P.T. Williams, Thermal degradation of real-world waste plastics and simulated mixed plastics in a two-stage pyrolysis–catalysis reactor for fuel production, Energy Fuels 29 (2015) 2601–2609, https://doi.org/10.1021/ef502749h.

[31] M. Predel, W. Kaminsky, Pyrolysis of mixed polyolefins in a fluidised-bed reactor and on a pyro-GC/MS to yield aliphatic waxes, Polym. Degrad. Stab. 70 (2000) 373–385, https://doi.org/10.1016/S0141-3910(00)00131-2.

[32] T. Ishimura, I. Iwai, K. Matsui, M. Mattonai, A. Watanabe, W. Robberson, A.-M. Cook, H.L. Allen, W. Pipkin, N. Teramae, H. Ohtani, C. Watanabe, Qualitative and quantitative analysis of mixtures of microplastics in the presence of calcium carbonate by pyrolysis-GC/MS, J. Anal. Appl. Pyrolysis 157 (2021), 105188, https://doi.org/10.1016/j.jaap.2021.105188.

[33] S. Tsuge, H. Ohtani, C. Watanabe, Pyrolysis–GC/MS Data Book of Synthetic Polymers - Pyrograms, Thermograms and MS of Pyrolyzates, Elsevier, 2012.

[34] M.R. Jung, F.D. Horgen, S.V. Orski, V. Rodriguez C, K.L. Beers, G.H. Balazs, T.T. Jones, T.M. Work, K.C. Brignac, S.-J. Royer, K.D. Hyrenbach, B.A. Jensen, J.M. Lynch, Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms, Mar. Pollut. Bull. 127 (2018) 704–716, https://doi.org/10.1016/j.marpolbul.2017.12.061.

[35] F. Akoueson, C. Chbib, S. Monchy, I. Paul-Pont, P. Doyen, A. Dehaut, G. Duflos, Identification and quantification of plastic additives using pyrolysis-GC/MS: a review, Sci. Total Environ. 773 (2021), 145073, https://doi.org/10.1016/j.scitotenv.2021.145073.

[36] M. Beltran, A. Marcilla, Fourier transform infrared spectroscopy applied to the study of PVC decomposition, 33 (1997) 1135–1142. https://doi.org/10.1016/S0014-3057(97)00001-3.

[37] M. Reichenbächer, J.W. Einax, Challenges in Analytical Quality Assurance, Springer Science & Business Media, 2011.

[38] H. Ohtani, T. Nagaya, Y. Sugimura, S. Tsuge, Studies on thermal degradation of aliphatic polyamides by pyrolysis-glass capillary chromatography, J. Anal. Appl. Pyrolysis 4 (1982) 117–131, https://doi.org/10.1016/0165-2370(82)80003-X.

[39] S.V. Levchik, E.D. Weil, M. Lewin, Thermal decomposition of aliphatic nylons, Polym. Int. 48 (1999) 532–557, https://doi.org/10.1002/(SICI)1097-0126(199907)48:7<532::AID-PI214>3.0.CO;2-R.

[40] K. Winter, D. Barton, The thermal decomposition of benzoic acid, Can. J. Chem. 48 (1970) 3797–3801, https://doi.org/10.1139/v70-641.

[41] R. Dabestani, P.F. Britt, A.C. Buchanan, Pyrolysis of aromatic carboxylic acid salts: does decarboxylation play a role in cross-linking reactions? Energy Fuels 19 (2005) 365–373, https://doi.org/10.1021/ef0400722.

[42] D. Davidson, M. Karten, The pyrolysis of amides, J. Am. Chem. Soc. 78 (1956) 1066–1068, https://doi.org/10.1021/ja01586a051.