

1 **THERMAL AND SPECTROSCOPIC (TG/DSC-FTIR) CHARACTERISATION OF MIXED**
2 **PLASTICS FOR MATERIALS AND ENERGY RECOVERY**
3 **UNDER PYROLYTIC CONDITIONS.**

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13

14 **Abstract**

15 Seven waste thermoplastic polymers (polypropylene, polyethylene film, polyethylene terephthalate,
16 polystyrene acrylonitrile-butadiene-styrene, high impact polystyrene and polybutadiene
17 terephthalate, denoted as PP, PE (film), PET, PS, ABS, HIPS and PBT, respectively) and four
18 synthetic mixtures thereof with different compositions representing commingled post-consumer
19 plastic waste (CPCPW) and waste of electrical and electronic equipment (WEEE) were studied by
20 means of simultaneous Thermogravimetry/Differential Scanning Calorimetry coupled with Fourier
21 Transform Infrared Spectroscopy (TG/DSC-FTIR) under pyrolytic conditions (inert atmosphere). By
22 summing all the heat change contributions due to physical and/or chemical processes occurring (i.e.
23 melting, decomposition, etc.) an overall energy, defined as the degradation heat, was determined for
24 both single-component and their mixtures. It was found to be about 4–5 % of the exploitable energy
25 of the input material. Vapors evolved during the pyrolysis of single-component polymers and their
26 mixtures, analyzed using the FTIR apparatus, allowed identifying the main reaction products as
27 monomers or fragments of the polymeric chain. Results from TG/DSC runs and FTIR analysis show
28 that there is no interaction among the plastics components of the mixtures during the occurrence of
29 pyrolysis.
30

31 **Keywords:** Waste, Commingled post-consumer plastic waste, WEEE plastics, Degradation heat,
32 **Pyrolysis.**

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33 **Introduction**

34 Waste packaging plastics are associated to a low mechanical recycling rate since the residual streams
35 have a heterogeneous and variable composition [1]. Even plastics contained in Waste Electric and
36 Electronic Equipment (WEEE), accounting for about 30% w/w cannot be exclusively treated by
37 mechanical recycling because of their inherent structural complexity and heterogeneity [2,3].

38 Pyrolysis is a promising technology for the treatment of complex mixtures of polymers contaminated
39 with other materials, without the need of any pre-cleaning operation [4].

40 The current recycling target for packaging plastics, valid for all EU Member States, was set at 22.5%
41 w/w according to the EU Packaging Waste Directive [5]. This target counts exclusively material
42 recycled back into plastics and appears relatively low with respect to other packaging waste categories
43 such as glass or paper.

44 Separation effectiveness poses serious challenges to mechanical recycling; in fact each stream must
45 be separated according to homogeneous polymer type, grade, structure (i.e. high density polyethylene,
46 HDPE and low density polyethylene, LDPE), as plastics categories are tailored to specific
47 applications. A suitable separation system should be capable to distinguish among about thirty
48 different plastics and blends. Instead, the use of mixed fractions is limited to known thick walled
49 applications.

50 Current figures [6] show that a residue higher than 50% w/w, which results from the poor selectivity
51 of the sorting process, is usually generated in most countries of Europe. This heterogeneous material
52 is mainly composed by a mixture of polyolefins contaminated with food residues, mineral fragments,
53 and a proportion of other waste fractions, such as paper, aluminum and glass. These streams are
54 commonly known as commingled post-consumer plastic wastes (CPCPWs). CPCPWs can be used in
55 replacement of impregnated wood, concrete and metals products at the cost of complex combined
56 washing and sorting treatments. By contrast, they are not generally cheap and pose the challenge of
57 their recycling at the end of their service life [4].

58 Beside to packaging, waste plastics come also from the world of dismissed electric and electronic
59 equipment. Whereas most non-durable packaging is ready for disposal less than two years after its
60 introduction on the market, the electrical appliance has an average service life ranging from 5 to 15
61 years, even though the most recent trend in the consumer electronics has displayed shorter lifetimes
62 for the last ten years. Styrene-based polymers (acrylonitrile-butadiene-styrene, high impact
63 polystyrene and polystyrene denoted as ABS, HIPS, and PS) account for more than 50% w/w of the
64 plastics employed in the manufacture of the housing of domestic devices (TV-sets, personal
65 computer, vacuum cleaner, radio, etc.), while polyterephthalates and polyamides are the major
66 components of thermoplastics (1-3% w/w of the total amount) contained in the printed circuit boards
67 (PCBs) [7,8].

68 Similarly to what it is usually done for packaging, homogenous streams (*i.e.*, PS and ABS) are
69 recommended to be used for mechanical recycling of WEEE plastics. This process encounters several
70 further difficulties (need for manual disassembly, presence of different blends, relevant use of
71 additives like flame retardants, plasticizers and stabilizers). In particular, the presence of flame
72 retardants containing polybrominated diphenyl ethers (PBDEs), such as decabromodiphenyl ether,
73 in styrene-based polymers amounts from 2 to 20% w/w, frequently in combination with antimony
74 trioxide for synergistic effect (from 3 to 6% w/w). UE directives [9] do not permit the use of PBDEs
75 even though they may still be found in WEEE because of the long service life of these devices.
76 Recycling of these WEEE plastics could lead to the release into the environment of hazardous
77 substances like PBDEs.

78 In conclusion, the more complex and contaminated the waste, the more difficult, if not impossible, is
79 recycling it mechanically. Furthermore, it is very important to stress that the repeatedly processing
80 and the natural aging expose all polymeric materials to mechanical, thermal and chemical (oxidative)
81 stresses, which may induce irreversible changes in their properties. Therefore, since perpetual cycles
82 of plastic materials do not exist there is the need to provide other recovery technologies.

83 These alternatives may be represented by feedstock recycling, i.e. the use of plastics waste as the raw
84 material for petrochemical processes such as cracking and hydrogenation coking. Pyrolysis is
85 recognized to be the thermal assisted feedstock recycling since it promotes the breakdown of the
86 polymeric chains into valuable products for the chemical industry. The pyrolytic process allows
87 obtaining high rates of conversion into oil to be exploited as feedstock or fuel. In addition, a gas with
88 a high caloric value may be used as fuel in the process and a solid residual stream, the char, useable
89 as activated carbon or fillers. On the other hand, a remarkable amount of literature data can be
90 collected from pyrolysis kinetics and thermal stability studies focused on single commercial or virgin
91 polymers [10-15].

92 The aim of this study is to define the amount of heat required for degradation and volatilization of a
93 unit mass of plastic material belonging to CPCPW or WEEE from ambient to decomposition
94 temperature by means of differential scanning calorimetry (DSC). This quantity is one of the key
95 properties defining a pyrolysis process, able to estimate the required energy for supporting
96 endothermic reactions. Furthermore, the vapors evolved during the TG/DSC experiments were
97 analyzed by FTIR in order to study both the thermal degradation and the main pyrolysis products.

98

99

100 **Experimental**

101 **Materials**

102 Samples of waste packaging plastics were provided by a treatment plant located in Central Italy. After
103 sorting into the saleable fractions (basically HDPE, LDPE and polybutadiene terephthalate, denoted
104 as PET), the CPCPW fraction is generally about 40-50 % w/w. Table 1 displays the results of a recent
105 product analysis from which the great heterogeneity of CPCPW is inferable. It can be observed that
106 the largest component is film that usually consists in polypropylene (PP) and PE. Shrink wrap
107 represents a little portion and is made up of PET and PP. Other plastic objects represent plastics not

108 used for packaging purpose but inappropriately placed into the municipal bin where only plastic
109 packaging should be collected.

110 Finally, not plastic materials count for 17.5% w/w and the most important fraction is paper. By
111 combining the analysis of products like that given in Table 1 with literature data [1,16], the four most
112 representative polymers were identified by FTIR and selected for the further analysis: PP, PE (film),
113 PET and PS. To better understand the behavior of the waste mixed plastics during the pyrolysis and
114 whether different compositions can lead to different thermal behaviors, three simulated homogenous
115 and predefined samples were also tested and reported in Table 2.

116 Samples of WEEE plastics, also supplied by WEEE selection and treatment plants came from
117 dismantling of small appliances, including external housing and PCBs. Details of sample selection
118 and preparation are reported in a previous work [17]. The representative WEEE mixed plastics was
119 denoted as “Real WEEE” and made up of the following ternary polymeric mixture: ABS, 64% w/w,
120 HIPS, 33% w/w and PBT, 3% w/w.

121

122 *Instruments*

123 Determination of humidity, volatile matter, fixed carbon and ash content were carried out using a TA
124 Instruments TGA 2950 macro thermobalance. Experiments were performed with about 1 g of sample
125 according to the US technical specification ASTM D7582 – 12 [18] adopted for coal and coke. The
126 temperature program adopted in this study was described in a previous paper [17]. The organic matter
127 is the sum of the volatile fraction plus the fixed carbon (determined by difference), while the ash
128 content represents the inorganic matter. Simultaneous TG/DSC measurements were carried out with
129 a STARe software at a heating rate of $10^{\circ}\text{C min}^{-1}$ under a stream of nitrogen at 60 ml min^{-1} using a
130 Mettler Toledo TG/DSC 2950 instrument equipped with alumina crucibles using high purity metals
131 as standards (indium and zinc in this study). Temperature and enthalpy change uncertainties were
132 estimated as $\pm 0.3^{\circ}\text{C}$ and $\pm 0.6\text{ J g}^{-1}$. A preliminary “blank experiment” was performed before the
133 sample runs. The use of small material samples (from 5 to 10 mg), milled to a particle size lower than

134 0.35 mm, coupled to relatively slow heating rate ($10^{\circ}\text{C min}^{-1}$) minimize the effect of heat and mass
135 transport inside the sample on heat flow.

136 The vapors evolved during the TG/DSC experiments were conveyed to a Thermofisher Scientific
137 Nicolet iS10 Spectrophotometer linked through a 200°C heated transfer line. The instrument allows
138 monitoring the actual reaction trend, by collecting a spectrum each 11s (eight scans performed at 0.5
139 cm^{-1} intervals, resolution of 4 cm^{-1}).

140 The low heating value (LHV), which represents an estimation of the maximum energetic potentially
141 extractable from the examined materials, was obtained by measuring directly the high heating value
142 (HHV) using a C5000 Berthelot-Mahler Calorimeter IKA. About 0.5 g of powder was weighed into
143 a crucible and placed inside a stainless steel container. The decomposition vessel was filled with 3
144 MPa of technical oxygen and ignited. The heat created during the burning process of organic matter
145 was determined using the adiabatic measurement procedure. The calibration consisted in assessing
146 the heat capacity of the decomposition vessel by burning tablets of certified benzoic acid. Once the
147 HHV were measured, the LHV can be derived by the following expression:

$$148 \quad \text{LHV} = \text{HHV} - 9(\text{HyC}) - 2.5(\text{HuC}) \quad (1)$$

149 where HyC and HuC are the hydrogen (determined using a Macro VARIO Cube Elemental Analyser)
150 and the humidity content, respectively, expressed as % w/w in the sample.

151

152

153 **Results and discussion**

154 Table 4 reports the proximate analysis characterization. Humidity of all samples (as weight loss at
155 105°C) ranged between negligible and 0.3% w/w, sign of waterproof material quality ascribable to
156 these plastics. Fixed carbon is very low for all but polyterephthalates (PET and PBT), which achieve
157 16%. This finding can be attributed to the production of conjugated aromatic rings, which present a
158 remarkable thermal stability [19]. The ash content is less than 3% for all examined samples and this
159 result coupled with elemental analysis (data not shown) reveals that these plastics are very similar to

160 the homologous virgin polymers. The only exception is PBT (used in PCBs), which shows a
161 remarkable high ash content ($\geq 20\%$) because of the presence of additives as flame-retardants [17].
162 Figure 1 shows the results of TG/DSC particularly meaningful experiments, performed on single as
163 well as on mixed polymers samples. Two distinct peaks can be observed in almost all DSC curves of
164 single samples. The lowest at about 200 °C is not accompanied by weight loss (see TG curves) and
165 is assumed to correspond to the melting process; the exception is represented by PS-based polymers
166 (PS, ABS, HIPS) which have a completely amorphous structure and don't show the melting process.
167 The positions of the other peak match the sample mass loss and therefore are associated with a single-
168 step decomposition reaction (TG curves). Taking into account the TG curves, one can observe that
169 volatilization occurs in one step and is almost complete for all but PBT and PET polymers. These last
170 ones show a remarkable residue amount, which can be attributed, as Table 4 already confirmed, to
171 the high concentration of various inorganic additives and complex aromatic compounds. As far as the
172 mix samples are concerned, it is worth noting that Real WEEE DSC curve displays a single
173 decomposition peak analogous to the main styrene-based polymer components, as the PBT amounts
174 for only 3% in the mixture. Conversely, the CPCPW samples are made up with polymeric chains of
175 different nature (olefins, aromatics, esters), which implies the decomposition occurring in one
176 (CPCPW1) or two steps (CPCPW2 and CPCPW3). Instead, the melting process occurs separately for
177 each component, reproducing the temperatures of the single polymers.

178 Table 5 reports the temperature and heat of the melting and decomposition processes. It can be
179 observed that heat of fusion is about 10% of heats of decomposition; Concerning the decomposition
180 temperatures of mixtures, it can be noted that the decomposition temperatures of Real WEEE and
181 CPCPW1 (which showed an unique peak) are the arithmetic average of the decomposition
182 temperatures of their components while in the CPCPW2 and CPCPW3 the DSC curves had two
183 distinct peaks whose temperatures are very similar to those of PS and PP (the first and the third
184 component to decompose).

185 Polyolefins had the highest heats of decomposition among styrene-based polymers and
186 polyterephthalates, and PE has its highest value. Therefore, the heat required for decomposition of
187 CPCPW mixtures increases with increasing the PE content. Taking into account all the usual
188 difficulties found when plastics materials of different origin are compared, a further complexity arises
189 from the fact that the polymers tested in this study belong to waste treatment plants. Nevertheless, a
190 reasonable agreement between the experimental and literature heats of decomposition [20,21] has
191 been found in particular for PE and PS, while large deviations refer to values for PP and PET. On the
192 other hand, remarkable deviations are found by comparing the literature values for the same virgin
193 material belonging from the two studies [20,21].

194 A good correlation between the experimental heats of decomposition of the mixture samples and the
195 theoretical ones, computed as weighted averages, is worth noting. The best agreements is found for
196 Real WEEE, probably due its the substantial homogeneous composition (styrene-based polymer
197 components). This result indicates that it is possible to predict with acceptable deviations the heats of
198 decomposition of this kind of plastic mixtures simply by knowing the values related to single
199 polymers.

200 For each of the examined samples, both the melting and the heats of decomposition coupled with the
201 sensible heat from ambient to decomposition temperature (the proper specific heats related to the
202 solid phase (before T_m) and liquid (between T_m and T_d) were taken from literature [20,22]) allow to
203 compute the overall energy needed for a fully degradation or pyrolysis, according to Eq. (2):

$$204 \quad Q_T = \int_{T_a}^{T_m} C_p(s) dT + Q_m + \int_{T_m}^{T_d} C_p(l) dT + Q_d \quad (2)$$

205 where Q_T is the total degradation heat ($J g^{-1}$), T_a the ambient temperature ($25\text{ }^\circ C$), T_m the melting
206 temperature ($^\circ C$), $C_p(s)$ the specific heat of the solid components ($J g^{-1} ^\circ C^{-1}$), $C_p(l)$ the specific heat
207 of the melted components ($J g^{-1} ^\circ C^{-1}$), T_d the decomposition temperature ($^\circ C$) and Q_d the heat of
208 decomposition ($J g^{-1}$).

210 This overall energy is defined as «degradation heat» and permits to establish the consumption energy
211 costs subtracted from energy content of the products (Table 5). The computation of degradation heat

212 for the mixtures tested was carried out by assuming that each component was heated apart, as melting
213 and decomposition processes take place separately. This permits to calculate the overall degradation
214 heat, averaging the contribution of the single heating, taking each component with its percentage
215 amount. It was ascertained that the required energy to volatilize the examined materials ranges
216 between 779 to 2162 J g⁻¹. In particular, it can be observed that PE (film) requires the highest
217 degradation heat as it gives the highest contributions to the overall heat computation. Conversely, the
218 polyterephthalates require the lowest energy amount. HIPS and PS present similar heats of
219 decomposition, but the other terms of heat make HIPS enhance the overall degradation heat at a higher
220 value than PS. In the end, among the examined mixtures, the Real WEEE requires the lowest energy
221 consumption due to the predominant presence of ABS; on the other hand CPCPW1 needs the lowest
222 energy consumption because of the low content of PE (film) and the high content of PET, whereas
223 the energy need for CPCPW2 and CPCPW3 are quite similar.

224 In Table 6 the experimental HHV, the relative LHV calculated by Eq. (1) and the degradation heat
225 are reported in MJ kg⁻¹. Taking into account their LHV, between 40 to 43 MJ kg⁻¹ for the polyolefins,
226 between 37 and 39 MJ kg⁻¹ for styrene-derivatives and around 20 MJ kg⁻¹ for polyterephthalates, one
227 can observe that the minimum energy consumption for pyrolysis amounts to 4 – 5 % of the exploitable
228 energy of the input material (last column on the right of Table 7) and it is proportional to their heat
229 of combustion. On the other hand, from the more useful point of view of the feedstock recycling
230 application, it can be stated that comparison of LHV and degradation heat enable estimating the
231 plastics mass fraction required to sustain energetically the pyrolytic process.

232 The vapors evolved from the TG/DSC experiments were conveyed to the FTIR spectrophotometer.
233 Firstly, the analysis on single polymers degradation was examined. Table 7 reports the compounds
234 showing the best match percentages between the FTIR spectra of the unknown vapor species evolved
235 during the TG experiments and those selected from the database available from the software. In the
236 case of single polymers, the related monomers (i.e. from PS to styrene) or fragments of the polymeric
237 chain (i.e. from PE to heptene or hexene) are the most likely products of pyrolysis with matches close

238 to 90%. No further compound was practically identified on examining the FTIR spectra collected at
239 different sample temperatures, but only some changes in the intensity of absorbance. More complex
240 is the spectrum of PBT, where it is possible to reveal the presence of at least three different molecules.
241 These findings are confirmed by literature [23], where degradation of PBT is found to occur in the
242 following steps: the primary formation of cyclic oligomers, their further decomposition to generate
243 unsaturated oligomers (butadiene) plus terephthalic anhydride containing oligomers; besides,
244 tetrahydrofuran results to be a secondary product of the polycondensation of PBT from 1,4
245 polybutanediol and terephthalic acid [24].

246 The TG/DTG curves of the Real WEEE in Fig. 2a show its thermal degradation occurring in a single
247 step in the range 330-490°C, while the three FTIR spectra in Fig. 2b are related to the vapors extracted
248 during the TG experiments at three different temperatures (390, 415 and 440°C). As expected,
249 according to the results of FTIR measurements related to the single polymers, the vapor substances
250 extracted at all three different temperatures (practically all over the range between 330 and 490°C)
251 are composed mainly by styrene, since Real WEEEs are substantially made up of styrene-based
252 components (ABS and HIPS). In particular, characteristic peaks of styrene (around 3000-3082 cm^{-1}
253 and at 698-759 cm^{-1}), whose intensities increase with increasing the temperature of the vapors
254 extracted from 390°C (curve a) to 440°C (curve c) were identified. Besides these peaks, the following
255 ones were found: the characteristic bands associated to the presence of aromatic rings or substituted
256 phenyl rings, the stretching vibrations of the aromatic ring around 1450-1492 cm^{-1} , while the peak at
257 1600 cm^{-1} is caused by the stretching vibration of the aromatic carbon-carbon double bond, the peak
258 at 2850-2920 cm^{-1} is related to the $\nu\text{-CH}_2$ of alkyl groups, probably due to the butadiene fragment
259 and finally the peak at 2200-2300 cm^{-1} characteristic of CO_2 , coming from the rupture of the ester
260 group of PBT.

261 Interpretation of results appears more complex for CPCPW samples than for Real WEEE because
262 they are made up both of styrene-based and polyolefin-based polymers, and in comparable amounts.
263 In fact, the TG/DTG curves of CPCPW2 given in Fig. 3a show two partially overlapped steps of

264 pyrolysis, the first of which occurs between 350 and 430°C (similarly to what observed for the Real
265 WEEE). It is reasonable to ascribe this step of mass loss to evolution of styrene derived by pyrolysis
266 of PS, confirmed mainly by the FTIR spectrum of vapors extracted at 405 (Fig. 3, lower plot, curve
267 a). The second step of pyrolysis of CPCPW2, which takes place in the range 430-495°C, can be
268 attributed to the thermal degradation of polyolefin-based polymers (particularly, PE (film) and PP).
269 Higher concentrations of these polymers can be justifiable by observing in Table 4 the high
270 decomposition temperatures of PE (film) and PP, while that of PS is quite lower (markedly outside
271 the experimental temperature range of the second step).

272 In addition, the FTIR spectrum of vapors extracted at the highest temperature (475°C, Fig. 3b)
273 confirmed the presence of a high concentration of heptene: the stretching and bending of CH₂ and
274 CH₃ at 2960-2850 cm⁻¹ and 1460-1370 cm⁻¹, respectively. On the other hand, characteristic bands of
275 styrene related to aromatic rings or substituted benzenes (stretching and bending of C-H around 3000-
276 3082 and 698-759 cm⁻¹, respectively) confirm the presence of a lesser amount of styrene, still present
277 at higher temperature. Furthermore, different peaks appear at 3600 and 1750 cm⁻¹ in the FTIR
278 spectrum of CPCPW1 (not shown), where PET is more abundant, thus revealing also the presence of
279 benzoic acid.

280 Moreover, it is worth noting that all peaks of the FTIR spectra recorded in this study do not univocally
281 match the peaks of a unique substance. In spite of this fact, it may occur that some peaks belong to
282 many substances at the same time can mask the presence of weaker peaks: some of them may be IR
283 active because of a high sensitivity to IR radiation, while some other because of their at high
284 concentration. As a result, preliminary pyrolysis tests carried out at 500°C on a Real WEEE sample
285 (different from the one examined in this study), revealed that the pyrolysis oil obtained by the
286 pyrolytic test (analyzed by gas chromatography coupled with mass spectrometry) was composed by
287 more than 100 species, the most concentrated of which appeared to be styrene, with a relative
288 concentration of about 40%.

289 Finally, the TG/DSC analysis especially when coupled with FTIR seems to confirm that each
290 component of the mixtures autonomously decomposes and that the pyrolysis products do not have
291 enough time to react as they were carried away by the gas carrier (nitrogen) towards the IR detector.

292

293

294 **Conclusion**

295 The thermal characterization of mixed plastics from packaging and electric equipment residues was
296 carried out showing the advantages of applying a pyrolysis feedstock recycling from the energetic
297 point of view. Application of the simultaneous TG/DSC techniques enabled to establish that the
298 energy required to pyrolyze the examined materials ranges between about 0.8 and 2.2 MJ kg⁻¹ and is
299 proportional to their heats of combustion, by observing that about 4–5 % w/w of the input material
300 has to be used as energetic self-supply of the degradation reaction. The FTIR analysis of evolved
301 vapors was used to identify the major products of pyrolysis. The obtainment of oligomers or
302 monomers appears to be encouraging for applying pyrolysis as a promising technique of feedstock
303 recycling to recover waste mixed plastics. It is worth noting to stress that TG/DSC coupled with FTIR
304 and the estimated heats of decomposition seem to demonstrate the absence of interactions among the
305 polymers within the various waste mixtures investigated (WEEE as well as CPCPW) during the
306 occurrence of pyrolysis reactions.

307

308 **References**

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365 **Table 1** Average composition of CPCPW from a waste sorting plant in Central Italy

366

Component	Amount/%	Component	Amount/%
PET (containers for liquids)	7.83	Aluminum	0.89
PET (bowls)	0.63	Iron and steel	2.44
Plastic shrink wrap	0.21	Cardboard	1.10
HDPE (containers for liquids)	1.35	Tetrapack	2.03
PP (containers for liquids)	0.90	Wood	0.93
PP (bowls)	8.73	Glass	0.74
Film	43.30	Paper	4.11
Other plastic objects	15.72	Textile	0.74
PS (rigid and expanded)	2.65	Inert	2.19
Polyvinyl chloride	1.25	other	2.30

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380 **Table 2** Composition of the most representative polymers in
 381 the three mixtures simulating real CPCPWs.

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Polymer	Composition of the mixture/%		
	CPCPW1	CPCPW2	CPCPW3
PE (film)	37	45	55
PP	42	30	25
PS	7	20	15
PET	14	5	5

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384 **Table 3** Results of the Proximate Analysis of the plastics tested
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Plastic sample	Volatile matter/%	Fixed carbon/%	Ash/%
PE (film) ^a	99.5 ± 0.2	0.06 ± 0.01	0.04 ± 0.01
PP ^a	98.9 ± 0.3	0.04 ± 0.01	1.1 ± 0.2
PS ^a	99.9 ± 0.4	0.06 ± 0.01	n.d.
PET ^a	83.5 ± 0.7	16.0 ± 0.5	0.16 ± 0.05
ABS ^b	97.3 ± 0.2	1.0 ± 0.3	1.4 ± 0.3
HIPS ^b	98.7 ± 0.4	0.14 ± 0.05	1.2 ± 0.2
PBT ^b	69.3 ± 0.7	7.9 ± 0.6	22.6 ± 0.8
CPCPW1 ^c	97.0	2.3	0.5
CPCPW2 ^c	98.6	0.9	0.4
CPCPW3 ^c	98.6	0.9	0.3
Real WEEE ^b	96.5 ± 0.2	0.93 ± 0.09	2.4 ± 0.3

386 n.d. = non detected.

387 ^adata obtained by original experimental measurements.

388 ^bdata taken from a previous work [17].

389 ^cvalues calculated as weighted average from experimental content of single polymers

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392 **Table 4** Melting and decomposition temperatures and related heats of single-component
 393 polymers and mixtures determined from DSC measurements
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Sample	Melting		Decomposition		
	<i>T</i> /°C	Q _m /J g ⁻¹	<i>T</i> /°C	Q _d /J g ⁻¹	
				Experimental ^a	Estimated ^b
PE (film)	122.2±0.1	97±2	475±1	975±8	
PP	163.8±0.2	66±1	453.6±0.6	944±60	
PS			413±1	855±28	
PET	244.9±0.2	35±1	434±1	217±16	
ABS			419.8±0.5	647±14	
HIPS			428.9±0.3	822±28	
PBT	218.30±0.	22±3	389±1	106±4	
	04				
CPCPW1			444±1	892±25	848±26
CPCPW2			418.8±0.5	990±66	904±19
			457±4		
CPCPW3			417.7±0.6	1005±34	911±16
			464±2		
Real WEEE			423±1	662±47	689±13

395 ^aValues comprehensive of the ash content

396 ^bValues calculated as weighted average from the experimental decomposition enthalpies of the single
 397 polymers.

Table 5 Parameters for computation of the heat contribution over each temperature range

Parameter	PE (film)	PP	PS	PET	ABS	HIPS	PBT	CPCPW1	CPCPW2	CPCPW3	Real WEEE
$C_p(s) / J g^{-1} °C^{-1}$ ^a	1.56	1.62	1.83	1.70	2.08	1.90	1.61				
$C_p(l) / J g^{-1} °C^{-1}$ ^a	2.66	2.64		1.97	2.34	2.59	1.99				
$Q_{T_a}^{T_m} / J g^{-1}$	151	225		374			312	203	154	158	9
$Q_{T_m}^{T_d} / J g^{-1}$	939	765	711 ^b	371	878 ^b	926 ^b	339	770	812	833	878
$Q_T / J g^{-1}$	2162	2000	1566	997	1525	1748	779	1934	2022	2047	1550

^aValues taken from literature [20,22]. For ABS and HIPS, which do not present melting, two different values were adopted one for a low temperature range (25-200 °C) and for a high temperature range (from 200 °C onwards). For PS a unique value was used, average of three specific heats at 27, 127 and 327 °C.

^bValues calculated from T_a to T_d .

Table 6 Results of the calorimetric analysis of the plastic samples and the minimum energy consumption requested for the pyrolysis process from the exploitable energy of the input material

Sample	HHV/MJ kg ⁻¹	LHV/MJ kg ⁻¹	Q _T /MJ kg ⁻¹	(Q _T /LHV)/%
PE (film) ^a	46.5 ± 0.1	43.3	2.2	5.0
PP ^a	46.2 ± 0.2	43.0	2.0	4.7
PS ^a	41.9 ± 0.1	40.2	1.6	3.9
PET ^a	23.0 ± 0.1	22.1	1.0	4.5
ABS ^b	38.91 ± 0.03	37.14	1.5	4.1
HIPS ^b	41.06 ± 0.01	39.15	1.7	4.5
PBT ^b	18.98 ± 0.02	18.10	0.8	4.3
CPCPW1 ^c	-	40.0	1.9	4.8
CPCPW2 ^c	-	41.5	2.0	4.9
CPCPW3 ^c	-	41.7	2.0	4.9
Real WEEE ^c	-	37.2	1.6	4.9

^adata obtained by original experimental measurements.

^bdata taken from a previous study [17].

^cvalues calculated as weighted average from the experimental content of the single polymers.

Table 7 Identification of vapor species evolved at the DTG peak temperature on the basis of the best match percentages between the FTIR spectra of the unknown vapor species and those selected from the database available from the software.

Samples	Compound	Match/%
PE (film)	1-heptene/1-hexene	89
PP	2,3-dimethyl-1-hexene	88
PS	Styrene (monomer)	94
PET	Benzoic acid	88
ABS	Styrene (monomer)	94
HIPS	Styrene (monomer)	94
PBT	Carbon dioxide + 1,3 butadiene + tetrahydrofuran	78 ^a

^amatch percentage is related only to comparison with the spectrum of carbon dioxide.

19 **Figure captions**

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21 **Figure 1.** TG (solid line) and DSC (dotted line) curves at $10\text{ }^{\circ}\text{C min}^{-1}$ for: a) PE film, b) CPCPW3,
22 c) ABS, d) PBT and e) Real WEEE.

23 **Figure 2.** TG (solid line) and DTG (dotted line) curves for the thermal degradation (pyrolysis) of
24 the Real WEEE at $10\text{ }^{\circ}\text{C min}^{-1}$ (a) and FTIR spectra (b) of the vapor products evolved at 390, 415
25 and 440°C .

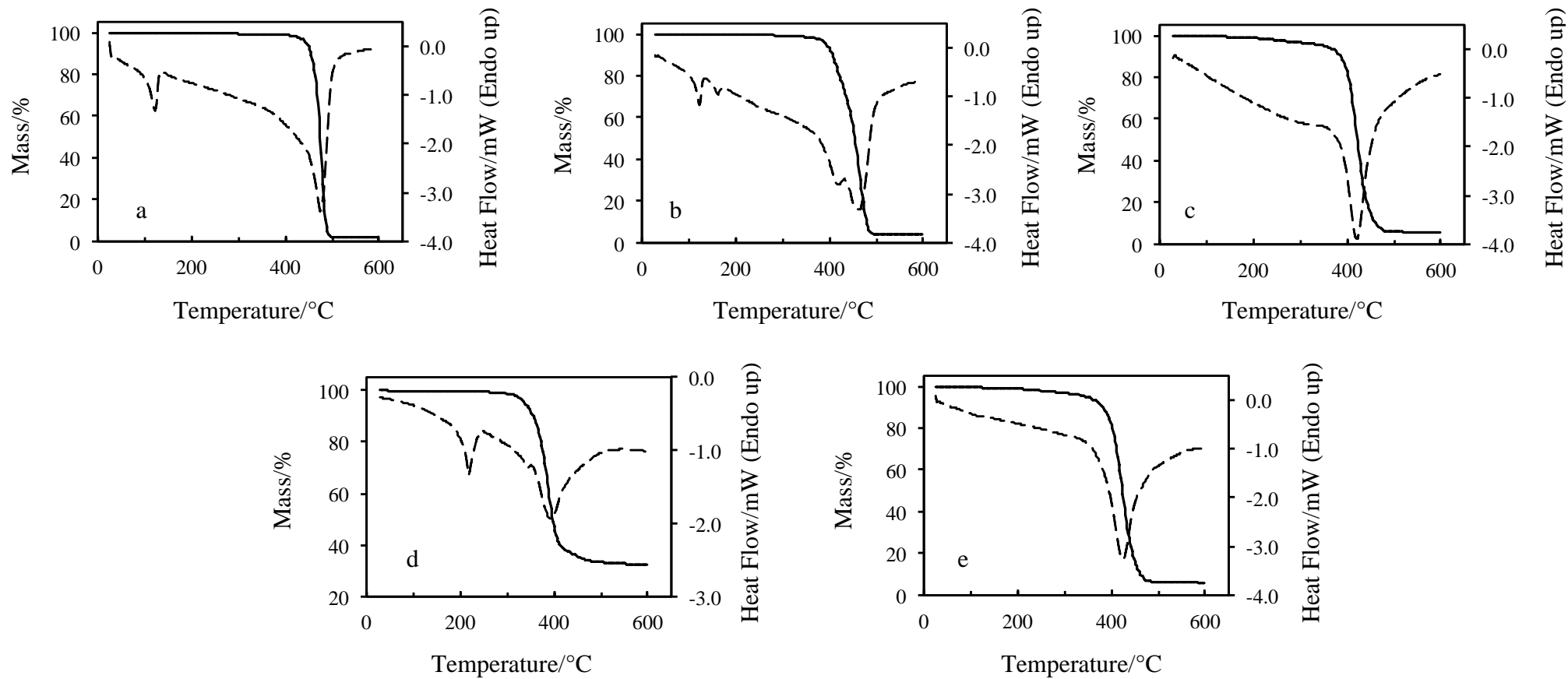
26 **Figure 3.** TG (solid line) and DTG (dotted line) curves for the thermal degradation (pyrolysis) of
27 CPCPW2 at $10\text{ }^{\circ}\text{C min}^{-1}$ (a) and FTIR spectra (b) of the vapor products evolved at 405, 440 and
28 475°C .

29 Figure 1.

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35 Figure 2
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