Thermal behavior and pyrolytic degradation kinetics of polymeric mixtures from waste packaging plastics

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Abstract. The thermal behavior and pyrolytic kinetic analysis of main waste polymers (polypropylene (PP), polyethylene film (PE), poly(ethylene terephthalate) (PET), polystyrene (PS)) and three synthetic mixtures representing commingled post-consumer plastics wastes (CPCPWs) output from material recovery facilities were studied. Thermogravimetry (TG) pyrolysis experiments revealed that the thermal degradation of single polymers and the synthetic mixture enriched in PP occurred in one single step. The other two mixtures underwent a two-consecutive, partially overlapping degradation steps, whose peaks related to the first-order derivative of TG were deconvoluted into two distinct processes. Further TG experiments carried out on binary mixtures (PS/PP, PET/PP, PET/PEfilm and PP/PEfilm) showed a thermal degradation reliance on composition, structure and temperatures of single polymer components. A kinetic analysis was made for each step using the Kissinger-Akahira-Sunose (KAS) method, thus determining almost constant activation energy (E_a) for pyrolysis of PS, PET, PP and PE film in the range $0.25 < \alpha < 0.85$, unlike for pyrolysis of CPCPWs, with particular reference to CPCPW1 and the second step of CPCPW2 and CPCPW3, both ascribable to degradation of PP and PE film. To account for the reliability of these values the integral isoconversional modified method developed by Vyazovkin was also applied.

Keywords: thermal properties, packaging plastic waste, polymeric mixtures, chemical recycling, pyrolysis kinetics

1. Introduction

Starting from the early 1990s, the worldwide plastics production has increased at a rate of 5 wt% per year, achieving a global amount of 322 Mt in 2015 [1]. In 2014, 25.8 Mt of post-consumer waste plastics was generated in Europe, 62 wt% of which came from the packaging application [2, 3]. In many European countries landfilling is still the main option, and about 8 Mt of plastics have been landfilled in 2014 [2]. The EU Packaging and Packaging Waste Directive [4] set by 2008 an overall recovery target of 60 wt% and recycling targets for each specific packaging category (60, 50, 22.5 and 15% for glass and paper/cardboard,

for metals, plastics and wood, respectively). In some European countries these objectives have been achieved. The targets concerning recycling of packaging waste including plastics was increased to 75% because of the Waste Framework Directive [5], and a target to reduce landfilling to maximum of 10% of municipal waste was established by 2030. Furthermore, it can be noted that plastics recovery target is very low in comparison with those of other recycling materials, because of its modest recycling rate, and it is getting more and more difficult to increase such rate, since the residual streams are provided with a heterogeneous composition (many different polymers

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are used for packaging), intermingled and therefore quite difficult to separate [6].

The municipal packaging waste from recycling bins is delivered to waste selection facilities where it is separated and classified into the various materials in order to be sent to recycling companies. The portion of plastic material that is rejected depends on the market trends (in Italy basically HDPE and PET containers for liquids are sold through telematics auctions) and on the efficiency of the separation plant, but in any case this large portion is made up of a heterogeneous plastic mixture (principally, polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET)), contaminated by foreign materials such as aluminum, paper, adhesives and textile. This kind of waste plastic mixture is generally indicated as a commingled post-consumer plastic waste (CPCPW), while the residue outputting the separation plants is defined (at least in Italy) as *plasmix* [7]. *Plasmix* composition is variable over time in the same plant and over the geographical area. In 2013, the *plasmix* accounted for about 40 to 50 wt% of the input plastics and, nowadays in Italy is used as plastic granules for building industry (7.5 wt%), as reducing agent for the steel plant (20 wt%) and the remainder is incinerated or landfilled. The high organic substance and energy content in waste plastics is totally lost by disposal and, although plastics is not biodegradable, breaks into small particles harmful for humans and the environment. For these reasons and in order to preserve non-renewable fossil resources, it becomes very urgent to find alternative feedstocks or fuels. Pyrolysis is considered a well-proven technology to material and energy recovery from polymeric waste [8–10]. The material is heated at moderate temperatures (300–800 °C) under inert atmosphere. The polymers are then decomposed into a variety of smaller molecular fragments made up of a large number of different molecular species [11]. Pyrolysis products, mainly in liquid and gaseous state can be used either as fuels or feedstock for chemical synthesis. A smaller amount of solid residue is also formed, which consists of short-chained molecules coming from cracking phenomena of hydrocarbon polymers (char) mixed with the unaltered inorganic fraction of early additives present in the original plastics (ash).

The first step for a suitable design of any pyrolysis reactor is the knowledge of the process kinetics of

the input plastic matrices. Many extensive studies on thermal degradation kinetics of single plastics have been carried out [12–18], and most of them have been developed on the assumption that the reaction can be described by a first or an *n*th order reaction model. This assumption can result in the Arrhenius parameters deviating from the real ones [19–21]. In any case, many discrepancies can be found in literature data between the same polymers (usually virgin/commercial polymers) that arise scattered and inconsistent because of the different samples (different manufacturing processes and eventual presence of additives) and different experimental conditions and methodology used [22]. Finally, limited literature is available on the degradation of plastic mixtures (essentially studies on binary or tertiary systems) and their kinetics [12, 13, 23–28], particularly using the model free approach [29, 30]. The majority of these studies are based on accurate knowledge of qualitative and quantitative composition of the synthetic tested mixtures, but this kind of approach is not suitable to investigate real unknown matrices. Indeed, the proportion of main polymers in municipal plastic wastes (MPWs) is scarcely predictable in less than an accurate commodity analysis. Finally, according to our knowledge only few papers concerning the kinetic study of waste plastic mixtures were available in the literature [28, 30–32].

The general aim of this paper is to provide a full thermochemical characterization regarding the most representative four polymers in MPWs and, in particular, in the *plasmix*. The thermal behavior of the four single polymers and quaternary mixtures (representative of real *plasmix*), as well as pyrolytic kinetics was studied using data from thermogravimetry (TG) experiments. The thermal behavior of single plastic components regarding degradation is the basis for understanding the pyrolysis of commingled plastics, since the absence (or presence) of interactions among the components in a synthetic or real mixture should be revealed by the fact that at each given temperature the overall degradation rate of the mixture is equal (or not) to the weighed sum of the degradation rates of the components. The degradation peak temperature (corresponding to the peak temperature of the first-order derivative of TG, DTG) and the apparent activation energy (E_a) of degradation were analyzed in order to evaluate if interactions among polymers occur during pyrolysis and to determine the first parameters for the set-up and the scale-up of a pyrolysis

process on these plastic wastes [24, 29]. As stated previously, only few authors used model free methods to study degradation processes in plastic mixtures. Furthermore, to the best of our knowledge, no papers are available in literature on the deconvolution procedure adopted to resolve the overlapping DTG peaks due to the occurrence of multi-step degradation of the investigated mixtures. In this way it is possible to determine the kinetic parameters of a multi-step degradation of real plastic wastes, regardless the knowledge of its qualitative and quantitative composition.

2. Experimental

2.1. Origin and preparation of the samples

Plastics used in this work were provided by Remaplast, a plastics recovery and selection plant located in Pomezia (Italy). After the separation in the saleable fractions (HDPE, LDPE and PET), a rejected portion (*plasmix*) composed of heterogeneous materials but principally of polyolefins and other thermoplastics is generated and accounts for about 50 wt%. An average composition extracted from *plasmix* commodity related sheets drawn by household plastics recovery facility was reported and discussed in a previous work [33]. These sheets related to commodity were worked out together with product analysis data taken by literature [6, 34] and the four most representative polymers were selected for the thermochemical and kinetic analysis. To understand the behavior of plastic waste during the pyrolysis and whether different compositions can lead to different thermal and kinetic behaviors three simulated and predefined quaternary sample mixtures were also tested. The four most representative polymers with the composition of the simulated samples are presented in Figure 1. The three simulated quaternary mixtures (CPCPW1,

Figure 1. Most representative polymers in CPCPW and their composition in the simulated samples with respect to just the four most representative packaging plastic

Table 1. Composition of the binary mixtures studied

Binary mixtures	Composition [%]			
	PEfilm	PP	PS	PET
PS10PP90		90	10	
PS30PP70		70	30	
PS50PP50		50	50	
PS70PP30		30	70	
PS90PP10		10	90	
PP30PE film70	70	30		
PP50PE film50	50	50		
PP70PE film30	30	70		
PET30PP70		70		30
PET50PP50		50		50
PET70PP30		30		70
PET30 PE film70	70			30
PET50 PE film50	50			50
PET70 PE film30	30			70

CPCPW2 and CPCPW3) are the same studied by Cafiero *et al.* [33] and have different composition with respect to the four polymers in order to explore a small part of the huge variability of composition of these plastic wastes. As further simplification, a thermogravimetric analysis was carried out also on binary mixtures (PS/PP, PET/PP, PEfilm/PP and PET/PE film, whose compositions were displayed in Table 1) in order to examine how the polymer degradation temperatures change with composition and different pairs of polymers.

The plastic materials were identified by Fourier transformed infrared measurements using a single reflection attenuated total reflectance (FTIR-ATR) IRAffinity-1 FTIR Shimadzu apparatus (Kyoto, Japan), properly cleaned in order to avoid any contamination. The FTIR spectra of the four single polymers compared with the library spectra of the instrument are shown in Figure 2. The samples were then milled to a particle size lower than 0.35 mm for the successive analyses and with the view to improve the miscibility of the components in the simulated samples. The plastic powder of each component was stowed away and the physical mixtures (binary or quaternary) were prepared just before performing the experiments in order to ensure every time unvarying samples.

2.2. Thermochemical characterization

Prior to the kinetic study, each single polymer was characterized aiming at determining the thermochemical properties. The proximate method used in

Figure 2. FTIR spectra of packaging plastic samples: a) PE film, b) PP, c) PS, d) PET. The dotted lines relate to the library spectra of the instrument.

this study was described in detail in a previous work [33], while the weight percentage of carbon, nitrogen, hydrogen, sulphur and oxygen (experimentally measured) found in the sample were determined using a Macro VARIO Cube Elemental Analyser (Elementar Analysensysteme GmbH, Langenselbold, Germany). In order to examine the thermal behavior (determination of degradation temperature) and analyze the pyrolysis kinetics of the single polymers and mixtures, thermal analysis experiments were carried out on about 10 mg of powder sample, under a nitrogen flow of $60 \text{ mL} \cdot \text{min}^{-1}$, in the temperature range between 298 and 873 K, using a Mettler Toledo TG/DSC 2950 instrument (Columbus, Ohio, USA) equipped with a STARe software and alumina crucibles, using high-purity metals ($>99.998\%$) as standards (indium and zinc, IMPAG AG, Zurich, Switzerland). Temperature uncertainty was estimated not higher than $\pm 1^\circ \text{C}$. The degradation temperatures of single polymers and their mixtures were determined at $10 \text{ K} \cdot \text{min}^{-1}$ while four different constant heating rates ($2, 5, 10$ and $15 \text{ K} \cdot \text{min}^{-1}$) were used for the kinetic experiments. A preliminary ‘blank experiment’ was performed before each run to correct the TG baseline

accounting for the gas buoyancy effect over the whole temperature investigated.

Each measurement was performed with three to five replicates for each sample. Calisto Software, supplied by SETARAM (Caluire-te-Cuire, France), processed the convoluted DTG curves of CPCPWs in the frame of the kinetics analysis through a peak separation procedure (using a Gaussian function) that allows the interpretation and characterization of overlapping thermal processes.

3. Theoretical kinetic background

One of the most important factors in driving and controlling a pyrolysis reaction is the knowledge of how fast the products are generated. This issue is discussed through the kinetics analysis, which allows determining the reaction time of degradation needed in turn to evaluate the reactor geometry. In this study pyrolysis was studied from a kinetic point of view by processing non-isothermal TG data by applying two model-free isoconversional multiple-heating rate methods for the calculation of E_a : Kissinger–Akahira–Sunose (KAS) [35] and the modified Vyazovkin methods [36–38]. All isoconversional methods are

based on the principle that the reaction rate at constant extent of conversion is only a function of temperature and that the thermal degradation occurs by a single step mechanism. The following general rate Equation (1) referred to solid substances can be used:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the degree of conversion, $k(T)$ is the rate constant and $f(\alpha)$ is a function called reaction model, $k(T)$ is a temperature function, usually expressed as the Arrhenius equation (Equation (2)):

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (2)$$

where E_a is the apparent activation energy [$\text{kJ}\cdot\text{mol}^{-1}$], A is the pre-exponential factor [mol^{-1}], T is the absolute temperature [K] and R is the universal gas constant [$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$]. In few cases plastic or other organic hazard compounds may undergo physical degradation (sublimation and/or vaporization) without appreciable degradation, following a first-order kinetics ($f(\alpha) = 1 - \alpha$), for which vaporization enthalpy and activation energy are in very close agreement [36, 39]. When non-isothermal experiments were carried out under constant heating rate ($\beta = dT/dt$), the time dependency of a reaction rate is replaced by its corresponding temperature dependency (Equation (3)):

$$\frac{d\alpha}{dt} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (3)$$

After separation of variables in Equation (3) and integrating both left- and right-hand side, Equation (3) becomes Equation (4):

$$\int \frac{d\alpha}{f(\alpha)} = g(\alpha) = \left(\frac{A}{\beta}\right) \cdot \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (4)$$

The temperature integral in Equation (4) has no exact analytical but approximate solutions that give rise to some of the most common isoconversional methods, whose equations for each fixed extent of conversion have the following general form (Equation (5)):

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^B}\right) = \text{Const} - C \cdot \left(\frac{E_a}{RT_{\alpha,i}}\right) \quad (5)$$

where i -subscript refers to the i^{th} heating program and B and C are adjustable parameters, whose values depend on the approximation made. In particular, the KAS method adopted [35] the Doyle's approximation [40] with $B = 2$ and $C = 1$. From Equation (5),

by plotting $\ln(\beta_i/T_{\alpha,i}^2)$ versus $1/T_{\alpha}$ for each α , the corresponding E_a values are determined from the slope of the regression lines.

Further increase in the accuracy can be accomplished by using numerical integration. Vyazovkin proposed a numerical integration of Equation (4) [36–38], based on the minimization of the following function (see Equations (6) and (7)) for each α :

$$\Phi(E_a) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_a, T_{\alpha,i}) \beta_j}{I(E_a, T_{\alpha,i}) \beta_i} \quad (6)$$

where:

$$I(E_a, T_{\alpha}) = \int_0^{T_{\alpha}} \exp\left(-\frac{E_a}{RT}\right) dT \quad (7)$$

which is numerically solved obtaining a dependence of E_a on α .

Since all integral isoconversional methods are based on solving the temperature integral under the assumption that the E_a value remains about constant over the whole interval of integration, if E_a varies significantly with α (difference between the maximum and minimum values of E_a more than 20–30% of the average E_a), as instead often it happens, a systematic error in the value of E_a is introduced. This error can be eliminated in integral methods by fractioning the whole range of α into intervals $\Delta\alpha$ of such amplitude to ensure the constancy of E_a as it is shown in Equation (8):

$$I(E_a, T_{\alpha}) = \int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha}} \exp\left(-\frac{E_a}{RT}\right) dT \quad (8)$$

4. Results and discussion

4.1. Thermal behavior

Results of the ultimate analysis are summarized in Table 2, along with that of the proximate one, already published in a previous paper [33]. It is worth noting that they are very similar to those of the homologous virgin polymers. Furthermore, volatile matter was found close to 100% (except for PET), and the ash content extremely low [33]. These findings demonstrated that these materials were not treated with organic or inorganic additives, and that they may be converted by pyrolysis almost completely from solid to liquid or gas.

Taking into account the TG curves of the four single polymers shown in Figure 3, one can observe that the thermal degradation represents a volatilization occurring in one step of mass loss, which is almost complete for all polymers (except for PET), due to

Table 2. Elemental and proximate analysis of packaging plastic samples. The mass percentages are referred to completely anhydrous sample.

Plastic sample	C ^a [%]	H ^a [%]	N ^a [%]	S ^a [%]	O ^a [%]	Volatile matter ^b [%]	Fixed carbon ^b [%]	Ash ^b [%]
PEfilm	86.1±0.3	14.2±0.1	not detected	not detected	not detected	99.5±0.2	0.06±0.01	0.04±0.01
PP	84.2±0.6	14.1±0.1	not detected	not detected	not detected	98.9±0.3	0.04±0.01	1.1±0.20
PS	91.7±0.5	7.7±0.1	not detected	not detected	not detected	99.9±0.4	0.06±0.01	not detected
PET	62.3±0.2	4.0±0.1	not detected	not detected	34.7±0.1	83.5±0.7	16.0±0.50	0.16±0.05
CPCPW1 ^c	82.3±0.3	12.3±0.1	–	–	4.7±0.1	97.1±0.2	2.29±0.07	0.52±0.08
CPCPW2 ^c	85.5±0.2	12.4±0.1	–	–	1.7±0.1	98.6±0.2	0.85±0.03	0.37±0.06
CPCPW3 ^c	85.3±0.2	12.7±0.1	–	–	1.7±0.1	98.6±0.2	0.85±0.03	0.32±0.05

^adata obtained by original experimental measurements.^bdata taken from a previous work [33].^cvalues calculated as weighted average from experimental content of single polymers. **Figure 3.** Comparison of TG curves of the four principal components of CPCPW at the heating rates of 10 K·min⁻¹ in N₂ atmosphere

the formation of complex aromatic compounds [41]. Degradation of these thermoplastic polymers occurs in the temperature range 673–773 K, usually described by the random scission mechanism [19]. The stability of the free radicals so obtained follow the decreasing order: benzylic, allylic > tertiary > secondary > primary. As a consequence, it is expected that the C–C bond dissociation may be in the following sequence: PS, PET, PP, PE film. The inflection points of TG curves correspond to two different temperature ranges: the first range (at about 700 K) includes the C–C bond dissociations of PS and PET with phenyl groups as branches, while the second range (at about 740 K) comprises the breaking down of C–C bonds of PP and PE film, giving methyl group moieties [23]. The degradation temperatures of the four single polymers are shown in Table 3 along with those of the three mixtures. Regardless the heating rate used, the TG curve of CPCPW1 stands out on one degradation step corresponding to a wide DTG peak, while those of CPCPW2 and CPCPW3 show two mass losses, associated to two more narrow DTG peaks (Figure 4). The first peak of CPCPW2

Table 3. Degradation temperatures of the single-component polymers and mixtures determined from the maxima of DTG peaks at 10 K·min⁻¹

Sample	Experimental temperature [K]		Estimated temperature ^a [K]	
	Step 1	Step 2	Step 1	Step 2
PEfilm		750±2		
PP		729±1		
PS	684±1			
PET	707±1			
CPCPW1	726±1		730±1	
CPCPW2	691±1	734±1	689±1	741±1
CPCPW3	691±1	738±1	690±1	743±1

^aValues calculated as weighted average from the experimental degradation temperatures of single polymers involved (after normalization): for the single peak of CPCPW1, PEfilm, PP, PS and PET; for the first peak of CPCPW2 and CPCPW3, PS and PET; for the second peak of CPCPW2 and CPCPW3, PEfilm and PP.

and CPCPW3 seems to lie in the degradation temperature range of both PS and PET, according to the findings of a previous FTIR analysis carried out on the gases evolved during the pyrolysis of CPCPWs [33], while the second one is close to the range of PP and PE film. The DTG peak temperature of pyrolysis for CPCPW1 (726±1 K) is close to that of the most abundant polymer in this mixture, PP, (729±1 K). Actually, the first and the second peak temperatures of CPCPW2 and CPCPW3 are very similar to those of PS and PP, respectively (Table 3). Probably, the presence of a single peak related to degradation of CPCPW1 is due to a different composition with respect to CPCPW2 and CPCPW3, as the largest and the lowest amounts of PP and PS were respectively found. The higher value of the second peak temperature of CPCPW3 with respect to that of CPCPW2 could be reasonably explained with a higher amount of PE film, since it undergoes pyrolysis at the highest

Figure 4. TG and DTG curves at different heating rates (from 2 to 15 K·min⁻¹, from left to right) for the simulated plastic mixture: (a) CPCPW1, (b) CPCPW2, (c) CPCPW3

temperature (750 ± 1 K) among those of the other polymer components. The estimated values, calculated as weight averages of the degradation temperatures of the involved polymers, and compared in Table 3 with those experimentally determined, might provide an estimate of the pyrolysis temperature of a plastic mixture that could serve for prediction purpose. The agreement between the two sets of values is better for data regarding the first step, where the differences are within the error of the measurement, while for CPCPW1 and the second step the differences are not negligible. The disagreement between experimental and estimated degradation temperatures in the case of CPCPW1 could depend on the presence of a single peak describing the occurrence of simultaneous degradation of all the polymers. For the second step, the estimated values calculated as weight average of PP and PE film only for CPCPW2 and CPCPW3 are higher than the experimental ones, thus demonstrating that for both mixtures the influence of PS and PET in lowering the degradation temperature of this step cannot be excluded.

To understand the behavior of these quaternary mixtures during degradation and how the composition of the polymers and their degradation temperature can affect the pyrolysis rate of CPCPWs, some binary mixtures with different relative amount of polymers were analyzed and the DTG curves compared (Figure 5). The choice fell on those couples of polymers exhibiting degradation temperatures either wide or narrow from each other. In addition, another pair of polymers, different from the previous selection was used to confirm the thermal behavior observed. In Figure 4a the DTG curves of different mixtures

of the two components most likely responsible for peaks in CPCPW2 and CPCPW3 are presented. Starting from pure PS and increasing the PP content, it is evident that the peak related to pyrolysis of PP begins to appear in the PP30PS70 mixture. On the other hand, the DTG profiles of PP70PS30 and PP90PS10 (Figure 5a) are similar to those of CPCPW2 and CPCPW3 (Figure 4b and 4c, respectively), probably due to the fact that their total content of polyolefins (75 and 80%, respectively) is close to PP content in the PP70PS30 and PP90PS10 binary mixtures. Furthermore, the total content of polyaromatics in CPCPW2 and CPCPW3 is 25 and 20%, in agreement with the PS content in the PP70PS30 and PP90PS10 binary mixtures. Increasing the PP concentration in the PP/PS mixtures, the degradation temperature of PS shifted towards higher values: from 684 ± 1 K for pure PS to 696 ± 1 K for PP90PS10. The trend of degradation temperature for PP is opposite: from 729 ± 1 K (pure PP) to 723 ± 1 K (PP30PS70). The presence of two DTG peaks in the PP/PS mixtures, whose temperatures depend on the composition suggest us a possible interaction between the two polymers during the occurrence of pyrolysis. In order to demonstrate that some interactions between plastic materials occur or not during their thermal degradation many authors considered some parameters related to this process (degradation temperature corresponding to the DTG peak, activation energy E_a or $d\alpha/dT$ representing the energy barrier and the reaction rate associated to pyrolysis) [23, 24, 28, 42]. The eventual discrepancy between the experimental and reconstructed parameters was used to establish if interaction among the polymer components is found

Figure 5. DTG curves of the binary mixtures (a) PS/PP, (b) PP/PEfilm, (c) PET/PP, and (d) PET/PEfilm with different compositions

or not when degradation takes place. Some authors agree that PS appears to be responsible for the shift

of TG curves of polyolefins towards lower degradation temperature when mixed together, while PS itself

seems to be stabilized or unaltered [24, 43, 44]. The mixing effect on the rate of degradation was interpreted in terms of an intermolecular radical transfer between different polymer radicals; Miranda *et al.* [24] suggest that intermolecular hydrogen transfer could be the predominant reaction path. Whichever type of radical involved in PS degradation, these species attack the chains of the other polymers. Moreover, the presence of a more stable polymer impedes or at least slows down the diffusion of radicals of PS towards other polystyrenic chains. Indeed, McNeil and coworkers [45–48] found that the nature of the interaction between different polymers during the occurrence of thermal degradation strongly depends on the physical state of the mixture (nature of the polymer, miscibility among the polymer components and the degree of phase dispersion). In a heterogeneous blend, interactions occur in the bulk of one or both domains and in the phase boundaries through the diffusion of small mobile molecules or radicals from one to the other through the interfacial layer. On the other hand, the degradation products of one polymer in homogeneous samples are directly in contact with the other polymers. As a result, their combined effect on thermal degradation is amplified. Regardless the miscibility of the components in the blend, the degradation products of one polymer may stabilize or destabilize the other polymers in the blend. For Faravelli and co-workers [27] the interactions depend on the mixing scale of the components (in their case virgin PS and PE): if the mixing scale of the polymers is poor, the degradation of each polymer behaves independently on the other. Conversely, when mixing reaches the molecular scale, a co-pyrolysis takes place with partial interactions. Only for PP10PS90 there is no interaction since the experimental degradation temperature is exactly the same of that estimated (688 ± 1 K), due to the remarkable difference in concentration between PS and PP. When the degradation temperatures of the polymers involved in the mixtures are close each other, a single peak is observed in the DTG curves whatever is the components concentration (Figure 5b and 5c). The DTG peaks of PP/PE film mixtures are narrower than the PP/PET peaks probably because of the partial miscibility of PP and PE due to high similarity among their structures [49]. In any case, as the concentration of the more thermally stable polymer increases, the degradation temperature of the mixture is shifted towards higher temperatures and the estimated values

disagree (often for only few degrees) with the experimental ones. Also, Csomorová *et al.* [26] studied binary mechanical mixture of different composition of PP and PE (but also PE/PMMA and PP/PMMA). They found that depending on the mixture composition PP destabilizes PE, while PE shows a stabilizing effect on PP. Furthermore, they concluded that the thermal behavior of polymer blends is related to the miscibility of the respective components in the blend, and to their interactions, where immiscible blends show better stability than miscible ones. Finally, two DTG peaks are shown in the PET/PE film mixture (Figure 5d), because of the large difference between their degradation temperatures and, similarly to what has been observed for PP/PS, the presence of a component has a stabilizing or destabilizing effect on the other depending on its composition. Hujuri *et al.* [28] used another approach to study the possible interactions between these polymers in a series of binary or ternary mixed powders (PE/PET, PE/PP, PET/PP, PE/PP/PET). They aimed at correlating and predicting the thermal degradation kinetics of these mixtures from the kinetics of single polymer components. A better correlation between experimental and calculated data was found using the so-called interacting model, in which a quadratic mixing rule type expression is used to express the degradation kinetics, rather than the non-interacting model, based on the assumption that the degradation rate of the mixture is expressed as a weighted sum of those of the single polymer components. Furthermore, the characteristic broader DTG peaks in comparison with those of the single polymer components and the complex nature of the product distribution pattern were indicative of possible interactions between different PP and LDPE mixtures at given stages of degradation and at given temperatures [29].

To conclude, it must be stressed that there is a plethora of studies in which interaction between the polymers in the blends during thermal degradation is denied. As an example, Wu *et al.* [23] studied two complex mixtures of commercial grade polymers (containing different amount of HDPE, LDPE, PP, PS, ABS, PVC) and concluded that there are no significant interactions, since the calculated curve of residual weight fraction (assuming a weighting sum of the individual components) superimposes very well the experimental one. Knümann and Bockhorn [25] investigated mixtures of PVC/PE, PVC/PP, PVC/PS in the form of powder or melted samples and found no observable

interaction or just small discrepancies in the case of PVC/PS. The degradation rate was expressed as the sum of those of the components in the mixture. Westerout *et al.* [13] agreed and claimed that pyrolysis of polymer mixtures behaves quite similarly to pure polymers and the additivity rule is the correct approach to study the degradation kinetics of a plastic mixture. Analogously, Bockhorn *et al.* [50] come to similar conclusions about the low influence of PE on PS degradation. On the contrary, they observe a quite significant reduction of the apparent activation energy when PE is pyrolyzed in presence of PS. In the case of HDPE/LDPE, Miranda *et al.* [24] found that the experimental TG and DTG curves are very similar to the calculated one (on the assumption of no-interaction between them), while the E_a of degradation for individual polymers and mixtures are very close, thus confirming that their mixing unaffected their degradation kinetics. Taking into account the results of a recent our investigation on degradation kinetics of plastics from WEEE [30] according to this point of view, the experimental degradation temperatures, E_a and $\ln A$ values for degradation of the ‘Real WEEE’ mixed sample, made up of ABS (64%), HIPS (33%) and PBT (3%), were very similar to the calculated ones, 690 ± 1 K, 214 ± 6 kJ·mol⁻¹ and 35 ± 1 min⁻¹ versus 690 ± 1 K, 218 ± 5 kJ·mol⁻¹ and 36 ± 1 min⁻¹, respectively (assuming an averaged

weighting sum of E_a or $\ln A$ of the individual components). The reason of this agreement could be ascribable to the very low amount of PBT in the mixture that couldn’t affect the degradation kinetics of the two styrene-based polymers (ABS and HIPS). By analyzing all these findings it would seem that mixtures having a similar polymer chain structure, such as HDPE/LDPE or styrene-based polymer mixtures as PS, ABS, SAN, HIPS, SBR, have weaker interactions, since they are structurally similar and the fragments produced during the degradation are substantially almost equal to those derived by the degradation of the individual components.

4.2. Kinetic analysis

The mass conversion into volatiles shows similar behavior for all the single polymers considered at all the applied heating rates (Figure 6). Similar shapes of the α vs. temperature curves confirm the existence of the same single or sequence of mechanisms regardless the heating rate, thus allowing the adoption of model-free methods for kinetic computations.

As stated above, by observing the shapes of the TG/DTG curves of CPCPWs in Figure 4, two overlapping steps of mass loss were identified for CPCPW2 and CPCPW3 (Figures 4b and 4c, respectively). According to the ICTAC recommendations [36] it is preferable to proceed to the kinetic computations

Figure 6. Conversion plots for the single step of pyrolysis occurring in the packaging plastic samples at different heating rates (from 2 to $15 \text{ K} \cdot \text{min}^{-1}$, from left to right) for: (a) PEfilm, (b) PP, (c) PS and (d) PET

through the deconvolution of the corresponding DTG curves. Conversely, it is not necessary to proceed with the deconvolution since the shapes of TG/DTG curves of CPCPW1 do not reveal superimposition of two or more steps of mass loss. Figure 7 shows the experimental, single deconvoluted and reconstructed DTG curves of CPCPW2 and CPCPW3 curves at $10 \text{ K} \cdot \text{min}^{-1}$. The theoretical reconstructed curve (Peak 1+2) derived by the two deconvoluted peaks overlaps remarkably the experimental one, thus enabling to obtain the integral α vs. temperature individual curves (Figure 7). In particular, the conversion plots corresponding to the first peak, is ascribable to degradation of PS and PET in both CPCPW2 and CPCPW3, while those of the second peak are referred to the degradation of PP and PE film in CPCPW2 and CPCPW3. In spite of the fact

that degradation of CPCPW1 occurs in a single step in a temperature range close to those of PP and PE film, the corresponding single DTG peak should be attributed to degradation of all the four polymer components. Summarizing, on the basis of the assumptions made (first step to degradation of PS and PET, while second step to degradation of PP and PE film) the kinetic findings were analyzed separately but, taking in account the evidences on binary mixtures, where i.e. PS affects PP and vice versa, we can't exclude that the two pairs (PS-PET and PP-PE film) may influence each other.

The dependence of E_a on α (from 0.05 to 0.95) calculated by the KAS method for the non-isothermal degradation of the single polymers and the synthetic mixture are presented in Figure 8. For degradation of the single polymers E_a is found to change with α

Figure 7. Deconvolution of the DTG curve of the samples recorded at $10 \text{ K} \cdot \text{min}^{-1}$ into its two constituent peaks, the reconstructed curves and the relative conversion trends: (a) CPCPW2 and (b) CPCPW3

Figure 8. Conversion dependences of activation energy according to the KAS method for pyrolysis of the packaging plastic samples: (a) the single plastics (PS and PET) and the related first peak of the simulated mixtures (CPCPW2 and CPCPW3), (b) the single plastics (PP and PE film), the single peak of CPCPW1 and the related second peak of CPCPW2 and CPCPW3

only in short ranges, corresponding to α values close to 0 and 1, due to possible minor errors in determining the baseline [36]. Since E_a is substantially constant over the conversion range between 0.25 and 0.85 it is likely that the processes are dominated by a single reaction step and average E_a values were calculated and listed in Table 4. Similarly, the E_a values regarding the degradation of the mixtures are roughly constant in the range from about 0.25 to 0.85, and deviations from the average values are lower than 13% (Table 5). As far as the first degradation peak of the mixtures are concerned, it is found that E_a shows a slowly decreasing trend for low values of α , while increasing the extent of conversion it becomes constant. For the second peak as well as the single degradation peak of CPCPW1 E_a values start to increase moderately with α for degradation of CPCPW1 and CPCPW3, while a significant variation is observed in the case of CPCPW2. This conversion dependence of activation energy decreases with increasing the values of α for degradation of all the mixtures. The experimental E_a values related to each step are in good agreement with those for degradation of the single polymers involved in that step.

It is difficult to make comparisons between these results on single polymers and those found in similar studies carried out on the same commercial or packaging waste plastic, due to different operating conditions adopted (type of carrier gas, flow rate, heating rate), the method used for kinetic computations, different characteristics of polymers, such as additives, structure and molecular weight composition (Table 4). All these remarkable differences may be responsible of the wide range of E_a values reported in literature. As an example, Westerhout and co-workers

[13] found even significantly different E_a values for the degradation of two different samples of PP (244 and $188 \text{ kJ}\cdot\text{mol}^{-1}$), due to their different average molecular weights. In any case, the average E_a values calculated for degradation of PE film, PP, PS and PET by the KAS method in this study falls within the wide range reported in literature, and the agreement is better with those derived by isoconversional methods (Table 4). Despite the E_a values taken from literature are scattered, the authors usually agree in affirming that PS and PET are certainly weaker and less stable than the polyolefins PE and PP (see also the degradation temperature in Table 2), with PE generally more stable than PP. For this reason, a waste mixture rich in PS and PET is more easily (quickly) degradable in a pyrolysis process, even if a PET-rich waste will lead to an unfavorable increased production of char (Table 2).

The averages of the experimental E_a values for the degradation of the three mixtures and the estimated ones (calculated as weighted average from the experimental E_a values of degradation for the single polymers in the range $0.25 < \alpha < 0.85$) were compared in Table 5. Indeed, the estimated E_a can be used to predict the E_a of degradation of the mixture within the limits of the standard deviation. In fact, the errors associated to the experimental values are, especially for the second step, almost one magnitude order larger than those of the singles polymers. Moreover, taking into account the results regarding the degradation temperatures and both the average experimental and estimated E_a values, it seems that the two peaks related to the two degradation steps of the mixtures can be approximately considered independent and can be treated separately for the following kinetic computations.

Table 4. Comparison between the activation energy for pyrolysis of PEfilm, PP, PS and PET and those reported in literature after 1990

Reference	Kinetic method	TG experiment information	E_a [kJ·mol ⁻¹]			
			PE	PP	PS	PET
[23]	Friedman	N ₂ , dynamic, pure polymers	233 (HDPE) 206 (LDPE)	183	172	–
[13]	Model fitting first order	N ₂ , isothermal, pure polymers	220 (HDPE)	244 (PP1) 188 (PP2)	204	–
[54]	Based on CDRC ^a	N ₂ /He, CRTA ^b , pure polymers	–	–	–	201
[12]	Model fitting	N ₂ , dynamic, pure polymers	445 (HDPE) 341 (LDPE)	337 (PP)	312	–
[15]	Model fitting DTG curve fitting	N ₂ , dynamic, polymers	240 (HDPE) 222 (LDPE)	126	176	242
[24]	Model fitting	N ₂ , dynamic, pure polymers	100 and 220 (LDPE, 2 steps) 250 (HDPE)	125	80 and 270 (2 steps)	–
[19]	Vyazovkin	N ₂ , dynamic, pure polymers	~240 0.2< α <0.9	150-250	~200 0.2< α <0.9	–
[20]	Friedman	N ₂ , dynamic, pure polymers	247 (HDPE) 221 (LDPE)	188	–	–
	OFW		243 (HDPE) 218 (LDPE)	183	–	–
	KAS		238 (HDPE) 215 (LDPE)	179	–	–
[53]	Vyazovkin	N ₂ , dynamic, plastic waste	–	–	–	180-210
[55]	Vyazovkin	N ₂ , dynamic, plastic waste	180–220	–	–	–
[56]	Vyazovkin	N ₂ , dynamic, pure polymers	–	135-150	–	–
[57]	Model fitting RTP	N ₂ , isothermal, pure polymers	–	130 (step I) 99 (step II)	–	–
[52]	OFW	N ₂ , dynamic, pure polymers	175 (HDPE)	–	–	–
	KAS		171 (HDPE)	–	–	–
[21]	KAS	N ₂ , dynamic, lastic waste	202 (HDPE) 268 (LDPE)	261	193	198
	Friedman		375 (HDPE)	–	–	–
This study ^c	KAS	N ₂ , dynamic, plastic waste	254±8 (PE film)	227±2	205±3	208±3

^aCDRC is the controlled decomposition rate control^bCRTA is the controlled rate thermal analysis^cCalculated as average value in the conversion range 0.25< α <0.85 according to Equation (5).**Table 5.** Average activation energies for pyrolysis of the CPCPW mixtures calculated by KAS method in the conversion range 0.25< α <0.85

Sample	E_a , experimental [kJ·mol ⁻¹]		E_a , estimated ^a [kJ·mol ⁻¹]	
	Step1	Step2	Step1	Step2
CPCPW1	242±21		233±4	
CPCPW2	208±7	237±30	206±2	243±5
CPCPW3	212±5	259±14	206±2	246±6

^aValues calculated as weighted average from the experimental activation energy of single polymers involved (after normalization): for the single peak of CPCPW1, PEfilm, PP, PS and PET; for the first peak of CPCPW2 and CPCPW3, PS and PET; for the second peak of CPCPW2 and CPCPW3, PEfilm and PP.

Based on both the degradation temperature and E_a -data, it can be stressed that the best agreement between average experimental and estimated values is found for the first degradation step.

Looking carefully at the literature findings, the thermal degradation kinetics of plastic waste or virgin mixtures has not sufficiently been developed. Only few studies [24, 26, 43, 44, 51] reported the E_a values for degradation of polymer mixtures, by assuming that the reaction rate is affected by the interactions among the polymer components. In particular, Miranda *et al.* [24] found that the difference between

the E_a of degradation of each polymer in the HDPE/LDPE/PS/PP quaternary mixture and those related to degradation of the single polymers did not exceed about $13 \text{ kJ}\cdot\text{mol}^{-1}$, thus concluding that both PP and PS caused destabilization of LDPE and HDPE via intermolecular H-abstraction. Two early studies [26, 51] reported a decrease of E_a for degradation of PE in some PE/PP mixtures, similarly to what has been observed in previous studies [43, 44].

By observing the non-negligible variation of activation energy with the extent of conversion for the second degradation step of CPCPW2 and CPCPW3 as well as for degradation step of CPCPW1 (Figure 8b), it has been decided to apply even the most accurate method developed by Vyazovkin: the modified isoconversational method [38]. In particular, the application of the modified method is necessary in the case of the second step of CPCPW2, where the difference between the maximum and minimum values of E_a with respect to the average value calculated in the range $0.25 < \alpha < 0.85$ is 39%, which is more than that claimed by Vyazovkin (20–30%) to apply traditional integral isoconversational methods [36]. Figure 9 shows the E_a vs. α curves calculated according to the Vyazovkin method for pyrolysis of both single polymers and mixtures. The values of E_a related to the first peak of CPCPW2 and CPCPW3 (Figure 9a) are almost overlapped because they are attributed to pyrolysis of the individual PS and PET (whose E_a values are almost identical). On the contrary, the conversion dependences of E_a values for degradation of PP and PE film shown in Figure 9b are significantly different, being the values for degradation of PE film higher than those of PP, as it was also found by using the KAS method. For low values of α , the trend of E_a vs.

α for degradation of all the CPCPW mixtures follow that of PP, and this result is particular evident for CPCPW1 in which PP is the main component (Figure 1). Furthermore, the E_a values for degradation of CPCPW1 in this range are substantially equal to those of degradation of PS and PET, since this process is described as a single step, where at its beginning the degradation of both PS and PET takes place almost simultaneously. An increasing trend of E_a values is observed for degradation of all three CPCPW mixtures with increasing the values of α , and a better agreement is found with that of PE film. It is worth noting that the higher is the PE film content in the mixture the lower is the value of α for which the increase toward higher values of E_a is achieved: $\text{CPCPW1} < \text{CPCPW2} < \text{CPCPW3}$.

Finally, similarly to the findings of the present study, Chowlu *et al.* [29] found that the E_a values for the degradation of PP/LDPE mixtures with different compositions shifted from E_a values close to those for degradation of PP to the values found for degradation of LDPE with increasing the values of α . By comparing the trends of E_a vs. α obtained with the KAS method with those derived by the Vyazovkin method (according to Equation (8)) it is evident that the latter are more scattered, since the integration procedure involves a fewer number of points than in all the integral isoconversational methods (like KAS) [38, 58].

4.3. Present and future perspectives

General perspectives can be drawn taking into account the most relevant results achieved in this study. When the composition of a plastic mixture is unknown, the separation of overlapping peaks through

Figure 9. Conversion dependences of activation energy according to the Vyazovkin modified method for pyrolysis of the packaging plastic samples: (a) the single plastics (PS and PET) and the related first peak of the simulated mixtures (CPCPW2 and CPCPW3), (b) the single plastics (PP and PE film), the unique peak of CPCPW1 and the related second peak of CPCPW2 and CPCPW3

deconvolution and the application of the isoconversional methods based on processing data obtained from the reconstructed curves have proved to be the key method for kinetic analysis. Conversely, when the composition of polymeric mixtures is known, their degradation temperatures as well as the E_a values for their degradation process can be estimated as weighted averages of the corresponding properties of the single components, since possible interactions produce negligible or small deviations with respect to experimental results. Furthermore, small discrepancies between the experimental and estimated kinetic parameters need to be tested if they won't lead to large differences on the computation of the corresponding reaction times. Certainly, a further study that could examine a huge number of samples/mixtures should be carried out in the near future to confirm this result.

5. Conclusions

This study deals with the thermal behavior of the four main plastics contained in the typical stream from packaging waste selection facilities during the thermal degradation of single polymeric components or representative synthetic mixtures. Some interactions take place among the plastics during pyrolysis of the mixtures: the comparison between the temperatures measured and calculated in the hypothesis of non-interaction, clearly shows that the DTG peaks are slightly but significantly altered in terms of both peak shape and position. The magnitude of these interactions depends on the characteristics of the polymers involved as well as on their content in the mixture. In particular, interactions seem to be more significant when:

- structurally different polymers are mixed together and when the polymer components form homogeneous blends. The intensity of the interaction mainly depends on the reactivity of the degradation intermediate products. On the contrary, when the mixture is composed by very similar polymers (e.g. styrene based polymers or HDPE/LDPE), the behavior of the mixture in term of degradation temperature, TG profiles and kinetic parameters are easily predictable.
- concentration of the mixture components plays an important role. In fact, when one of the components is present in large amount, then a single peak results whose degradation temperature is similar or

equal to the degradation temperature of the main component.

- the interactions are more evident when degradation processes of the single polymers occur in close temperature ranges, so that the DTG peaks relatively close or at least they superimpose. On the contrary, if one polymer begins to decompose while the other has not even started to 'melt', it is more difficult to have interaction and several separate peaks would be obtained at the temperatures of the pure components.

By contrast, when the E_a parameter is taken into consideration, the different behaviors between the single polymers and the mixtures are flattened because of the larger uncertainty with which this parameter is determined. Comparison between the experimental E_a values obtained by the KAS method related to each step in the mixture with the theoretical ones shows small and not significant differences. As far as the degradation temperatures are concerned, the first step is easily predictable since it can be really considered as the degradation of a binary mixtures composed by PS and PET, where PE film and PP can be considered as inert. Conversely, the prediction is not easily feasible in the case of the second degradation step of the CPCPW2 and CPCPW3, because the assumption of considering both them as binary mixture composed only by PE film and PP is not completely correct, being the degradation of PE film and PP still affected by the presence of PS and PET (whose process occur at lower temperature).

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Nomenclature

α	degree of conversion
β	heating rate, dT/dt
A	pre-exponential factor [min^{-1}]
ABS	acrylonitrile butadiene styrene
ATR	attenuated total reflectance
CPCPWs	commingled post-consumer plastics wastes
CPCPW1	commingled post-consumer plastics wastes having the following composition [wt%]: 37% of PEfilm, 42% of PP, 7% of PS and 14% of PET
CPCPW2	commingled post-consumer plastics wastes having the following composition (wt%): 45% of PEfilm, 30% of PP, 20% of PS and 5% of PET

CPCW3	commingled post-consumer plastics wastes having the following composition (wt%): 55% of PEfilm, 25% of PP, 15% of PS and 5% of PET
DSC	differential scanning calorimetry
DTG	First-order derivative of thermogravimetry
E_a	apparent activation energy [$\text{kJ}\cdot\text{mol}^{-1}$]
$f(\alpha)$	reaction model function
FTIR	Fourier Transform Infrared Spectroscopy
HDPE	high density polyethylene
HIPS	high impact polystyrene
ICTAC	International Confederation for Thermal Analysis and Calorimetry
KAS	Kissinger–Akahira–Sunose method
$k(T)$	specific rate constant in the kinetic equation of thermal degradation
LDPE	low density polyethylene
PP	polypropylene
PBT	poly(butadiene terephthalate)
PE	polyethylene
PET	poly(ethylene terephthalate)
PMMA	poly(methyl methacrylate)
PS	polystyrene
PVC	poly(vinyl chloride)
R	universal gas constant [$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$]
SAN	styrene acrylonitrile
SBR	styrene butadiene rubber
T	temperature [K]
TG	thermogravimetry
WEEE	waste electric and electronic equipment

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