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Characterization of post-consumer plastic film waste from mixed MSW in Spain: A key point for the successful implementation of sustainable plastic waste management strategies

Alberto Gala[a,*], Marta Guerrero[a], Jose Manuel Serra[b]

[a]*Department of Innovation, Technological Waste Innovation Centre (CIAM), URBASER S.A., C/ Azufre 120, 50720 La Cartuja Baja (Zaragoza), Spain.*

[b] *Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Av. Los Naranjos s/n, 46022 Valencia, Spain.*

Abstract

The purpose of this paper is to provide a full characterization of post-consumer plastic film recovered from mixed municipal solid waste (MSW) treatment plants in Spain. Currently, this type of plastic waste is not recycled due to technical or economic barriers and is still sent to landfill. Different types of municipal plastic waste (MPW) from manual and automated sorting were studied: i) colour plastic film recovered by ballistic separators and then manual sorting in different seasons; ii) colour plastic film recovered by automated sorting (air suction); and iii) white plastic film from primary manual sorting process. The samples were characterized by different techniques, including the ultimate and proximate analysis, Higher Heating Value (HHV) and Lower Heating Value (LHV), metal content, Thermogravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG), Fourier Transform Infrared (FT-IR) analysis and Differential Scanning Calorimetry (DSC). The results

were compared to those obtained for pretreated colour and white plastic film waste and contrasted with industrial recycled film granules of polyethylene (as a reference material for packaging film). Additionally, pretreated plastic film samples were also characterized by analysing viscosity, Pressure-Volume-Temperature (PVT) diagram, specific heat capacity and halogen and sulphur contents. Characterization data from this study will contribute to identify and develop potential recycling alternatives for a more sustainable municipal plastic waste management, which is recognized as a priority in the European Circular Economy Action Plan to use resources in a more sustainable way.

Keywords: municipal plastic waste, sorting, plastic waste characterization, recycling, circular economy.

Nomenclature:

Cp: Specific heat capacity [$J \cdot g^{-1} \cdot {}^{o}C^{-1}$]

T5: Temperature at which 5 wt. % loss occurs in TGA/DTG analysis [ºC]

T10: Temperature at which 10 wt. % loss occurs in TGA/DTG analysis [ºC]

T50: Temperature at which 50 wt. % loss occurs in TGA/DTG analysis [ºC]

T80: Temperature at which 80 wt. % loss occurs in TGA/DTG analysis [ºC]

Tmax: Temperature at which maximum weight loss rate occurs in TGA/DTG analysis [ºC]

η: Dynamic viscosity of fluid [Pa·s]

$\dot{\boldsymbol{\gamma}}$: Shear rate [s^{-1}]

Abbreviations:

ACF: Colour plastic film recovered by automated sorting from MSW

ACF-W: Colour plastic film recovered by automated sorting from MSW - Season: Winter.

CF: Colour plastic film recovered by manual sorting from MSW

CF-A: Colour plastic film recovered by manual sorting from MSW - Season: Autumn

CF-S: Colour plastic film recovered by manual sorting from MSW - Season: Summer

CF-SP: Colour plastic film recovered by manual sorting from MSW - Season: Spring

CF-W: Colour plastic film recovered by manual sorting from MSW - Season: Winter

CG: Granules obtained from colour plastic film recovered by manual sorting

DSC: Differential Scanning Calorimetry

DTG: Derivative Thermogravimetry

EU: European Union

FT-IR: Fourier Transform Infrared

HDPE: High Density Polyethylene

HHV: Higher Heating Value

ICP-OES: Inductively Coupled Plasma-Optical Emission Spectroscopy

IG: Industrial recycled film granules

LDPE: Low Density Polyethylene

LHV: Lower Heating Value

LLDPE: Linear Low Density Polyethylene

MDSC: Modulated Differential Scanning Calorimetry

MPW: Municipal Plastic Waste

MSW: Municipal Solid Waste

PE: Polyethylene

PP: Polypropylene

PVT: Pressure-Volume-Temperature

TGA: Thermogravimetric analysis

WF: White plastic film recovered by manual sorting from MSW

WF-S: White plastic film recovered by manual sorting from MSW - Season: Summer

WF-W: White plastic film recovered by manual sorting from MSW - Season: Winter

WG: Granules obtained from white plastic film recovered by manual sorting

*Corresponding author:

E-mail: ajgala@urbaser.com

1. Introduction

Nowadays, plastics are used for a large and growing variety of products, applications and sectors, becoming an essential part of the daily life (Faraca and Astrup, 2019; Hestin et al., 2015; Lopez, et al., 2017; Park et al., 2019; Wang et al., 2015). An evidence of this is that the European plastic industry had a trade balance of more than 15 billion euros in 2018 (Plastics Europe, 2019a). At the same time, those characteristics that make plastics so useful, such as durability, lightweight and other intrinsic properties, also lead to challenging sustainable waste management (Wong et al., 2017), and this is becoming more critical due to the continuous increase in the amount of plastic waste. It has been estimated that about 10.6 wt. % of plastic waste contributes towards the total municipal waste (Singh et al., 2019). The magnitude of plastic waste problem can be surmised from plastic market data because many applications are characterized by a short life (Lopez et al., 2017; Panda et al., 2010). According to the latest data provided by Plastics Europe (2019a), total European converter demand reached 51.2 Mt in 2018 and 3.9 Mt (7.6 %) corresponded to Spain. Polypropylene (PP) and low-density polyethylene (LDPE) / linear low-density polyethylene (LLDPE) were the most demanded polymer types in 2018. The major end-user of this type of polymers is the packaging industry, which consumes the largest share of plastics (39.9 % in 2018); and hence this industry is the most contributing to the plastic waste stream, accounting for 61 % of the total post-consumer collected plastic waste in Europe. This is partly because packaging plastics tend to have a shorter lifetime than other plastic products (Achilias et al., 2007). In 2016, about 2.3 Mt of post-consumer plastic waste was collected through official schemes in Spain (Plastics Europe, 2018), of which 46.4 % was still sent to landfill. This value is above the European average (24.9 %) (Plastics Europe, 2019a). Just as in Europe, the largest

volume of plastic waste collected through official schemes in Spain in 2016 was also packaging waste (1.5 Mt) and landfill was the second treatment option for plastic packaging waste in Spain, accounting for 38.2 % (Plastics Europe, 2018). According to the waste hierarchy established by the Waste Framework Directive (EU, 2008), landfill is the least preferred waste treatment option because of the serious environmental impact and evident loss of resources. In this sense, EU policies are directed to transform Europe into a more circular and resource efficient economy by adopting new directives, aimed at achieving a maximum MSW landfilling of 10 % by 2035 (i.e. EU, 2018). To accomplish this ambitious target, sustainable plastic waste management must play a key role (Circular economy strategy, 2019; Yan et al., 2020). Based on URBASER database (multinational environmental service provider), the most common polymers in MPW in Spain are polyolefin compounds: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and linear low-density polyethylene (LLDPE). Such polymers account for 67 % of the total post-consumer collected plastic waste. Other polymers, accounting for 28.9 %, are mainly represented by polystyrene (PS) (13.3 %), vinyl polychloride PVC (10.3 %) and polyethylene terephthalate PET (5.3 %). At present, the main recycling route to recover the intrinsic value of plastics relies on mechanical recycling (Ellen MacArthur Foundation, 2016; European Parliamentary Research Service Blog, 2017; Ragaert et al., 2017). However, only two types of plastic products recovered from mixed MSW are currently suitable for mechanical recycling: HDPE and PET; any other type of municipal plastic waste is not economically viable for mechanical recycling due to the lack of quantity (steady production) and/or purity/quality due to the presence of particle and/or molecular contamination (homogeneity) (Dahlbo et al., 2018; Faraca and Astrup, 2019). It is thus essential to consider new developments or innovations, e.g. chemical recycling, as

complementary recycling methods to mechanical recycling in alignment with the European Commission's strategy (Plastics Europe, 2019b), especially for LDPE/LLDPE (main components of packaging film) that makes up the greatest fraction of municipal plastic waste and is still sent to landfill (Dahlbo et al., 2018; Diaz-Silvarrey and Phan, 2016; Horodytska et al., 2018; Kunwar et al., 2016). According to several authors (e.g. Bisinella et al., 2017; Faraca and Astrup, 2019), detailed knowledge on the composition and impurities in plastic waste streams is a crucial point to identify potential sustainable plastic waste management technologies to transform plastic waste into a valuable new resource, for Life Cycle Assessment (LCA) of waste management solutions and to support their successful commercial application (i.e. pyrolysis), since there is a strong relationship between raw material composition and the product quality/commercial value and yield (Angyal et al., 2007; Kunwar et al., 2016; Pinto et al., 1999). Among these innovative recycling technologies, pyrolysis is receiving renewed attention since it enables to directly transform plastics into very valuable products with high potential to be used as fuel or petrochemical feedstock (Czajczyńska et al., 2017; Khoo, 2019; Sharuddin et al., 2016). In this sense, leading petrochemical sector companies are currently revealing an increasing interest in the use of pyrolysis liquids from municipal plastic waste for the production of new plastics (BASF, 2018; NESTE, 2018; REPSOL, 2020), which is a clear example of closed loop in a circular economy practice.

Despite comprehensive knowledge on plastic waste characteristics can play a critical role for further innovations and improvements in recycling technologies (including new developments in chemical recycling), there is still very limited information about the characteristics of plastic packaging waste and more studies should be performed on both

quantities and qualities of plastic waste streams (Dahlbo et al. 2018; Faraca and Astrup, 2019) in order to identify the major contaminants, which are significantly affected by the type of sorting (Ruj et al., 2015).

In this context and considering that more than half of all post-consumer plastic waste is collected via different mixed waste collection schemes (Plastics Europe, 2019b), the overall aim of this paper is to provide a full characterization of real post-consumer plastic film waste recovered by manual and automated sorting from mixed MSW in Spain. This waste cannot be recycled due to technical or economic barriers and is still sent to landfill. The influence of seasonality on plastic film waste quality is also analysed. In addition, the results are compared to those obtained for pretreated plastic film waste samples and contrasted with LDPE/LLDPE industrial recycled film granules (as a reference material for packaging film). The comparative characterisation provides a better way to give an overview of contamination and to identify major contaminants in plastic film waste streams. This study will provide a valuable insight into plastic film waste characteristics and thus will contribute to the commercial development of cost and energy-efficient alternatives. Among them, pyrolysis seems to be one of the most promising technologies. This novel use for post-consumer plastics pave the way towards a circular economy in the plastic sector.

2. Materials and methods

2.1. Selection of materials

The focus of this work is on post-consumer plastic film originating from household waste in Spain and collected as part of mixed MSW. According to the guide published by the Waste and Resources Action Programme (2016), packaging film waste produced

184 by households comprise carrier bags and packaging of a large range of domestic
185 products. Although there are different types of polymers used to produce film packaging
186 due to the variability in packaging film characteristics (Balakrishnan et al., 2014; Waste
187 and Resources Action Programme, 2016), polyethylene (PE) is the most common one
188 (derived from British Plastics Federation website). LDPE is widely used for utility bags
189 with moderate strength and stretch properties. LLDPE is employed for food bags,
190 newspapers bags, shopping bags and garbage bags. HDPE is also an excellent material
191 for manufacturing carrier bags and food wrapping material. Plastic film waste from co-
192 mingled streams is generally recovered by ballistic separation or air separation at MSW
193 treatment plants in Spain. The use of suction systems to extract these lighter materials
194 from a co-mingled stream does not separate the individual 2D material types, meaning
195 plastic film may be contaminated by paper and cardboard materials, as well as other
196 light materials such as PET bottles. In this study, two types of municipal plastic waste
197 from manual sorting were studied: 1) colour plastic film obtained from 2D flat and light
198 materials which are conveyed to the upper part of ballistic separators and then recovered
199 through manual sorting (CF); 2) white plastic film recovered from primary sorting
200 process in which bulky materials are manually separated in a closed booth (WF). The
201 waste sampling activities were carried out at the Zaragoza MSW treatment plant
202 according to CEN/TR 15310-3:2006 (CEN, 2006). Regarding colour plastic film, the
203 sampling activities were carried out during week days in the four seasons of a year.
204 White film sampling was conducted during the winter and summer seasons. In order to
205 assess the influence of manual/automated sorting systems on the quality of plastic film
206 recovered from mixed MSW, post-consumer plastic film waste recovered by suction
207 system (ACF) was also studied. These samples were taken in winter season from one of
208 the mechanical-biological sorting plants of Madrid. Despite plastic film is separated as a

positive flow, mixtures of polyolefins are too difficult to separate into mono-materials streams (Mastellone, 2019) and a pretreatment step is necessary for chemical recycling technologies like pyrolysis (Oasmaa et al., 2020). Taking this into account, colour and white film waste samples from manual sorting were pretreated using conventional methods (optical sorting, shredding in flakes having a size of 40 mm, wet cleaning and drying) and then clean flakes were feeding into an extruder to produce a granulated material. Colour and white film waste granules (CG and WG, respectively) were also fully characterized and their properties were compared to those of colour and white film waste samples. LDPE/LLDPE industrial recycled film granules (IG), used as a reference material for packaging film (Abraham et al., 1992), were also characterized and their properties were further contrasted.

2.2. Characterization of plastic film waste samples

The characterization of the different plastic film waste samples was performed by the "Alfonso Maíllo" Technological Waste Innovation Centre (CiAM) at Urbaser (Zaragoza), in collaboration with AIMPLAS (Plastics Technology Centre from Valencia) and ITENE (Technological Centre in packaging, logistics, transport and mobility from Valencia). Samples studied and characterization techniques used are summarised in supporting information. Table 1 shows the standards and commercial equipment used for analysing chemical composition, heating values (Higher Heating Value -HHV, and Lower Heating Value -LHV), metal content, Differential Scanning Calorimetry (DSC) analysis and halogen content. Detailed description of each technique is shown in supporting information. The methodology followed for the rest of characterization parameters is described below.

Thermogravimetric analysis (TGA) and Derivative Thermogravimetry (DTG) analysis were used to study thermal stability. A *TA Instruments Q5000 IR* was used for the measurement of weight change as a function of temperature. Samples were heated under nitrogen flow (100 $mL \cdot min^{-1}$) from 25 to 800 ºC at a heating rate of 10 $ºC \cdot min^{-1}$. Additionally, DTG curve (rate of change of weight) was used to aid interpretation. In this regard, temperatures corresponding to maximum degradation rates (Tmax) were determined from the DTG plots. Fourier Transform Infrared (FT-IR) spectroscopy analysis was carried out in a *TENSOR-27 FT-IR Spectrometer* with ATR crystal from *BRUKER* in order to analyse the compositional functional groups and to identify organic, polymeric and inorganic materials. Characteristic absorption bands were obtained from 64 scans at a resolution of 4 cm^{-1}, in the mid-infrared wavenumber range of 4000 to 600 cm^{-1}. The determination of viscosity was performed using an *AR-G2* magnetic bearing, rotational rheometer (*TA Instruments*) with a 25 mm parallel plate measuring system. Continuous flow tests were performed at 260, 270, 280 and 300 ºC over the shear rate range of 0.001-1000 s^{-1} under nitrogen atmosphere. The rheological model based on the Cross Equation (Cross, 1965) was used for extrapolating viscosity data (η) as a function of shear rate ($\dot{\gamma}$). The effects of pressure and temperature on the specific volume (PVT diagram) were studied using a *HAAKE PVT-100* apparatus, which is based on the piston-die technique. The isobaric cooling mode was used by the piston-die dilatometer in the temperature range from 50 to 200 ºC. The specific volume was recorded along isobars from 200-1000 bar, with a fixed cooling rate of 5 $ºC \cdot min^{-1}$. The specific volume at atmospheric pressure was obtained by Tait correlation (Dymond and Malhotra, 1988). IKV model (Boyard and Delaunay, 2016) was used to describe the dependence of specific volume on temperature and pressure. A *TA Instruments Q2000* DSC was used to measure specific heat capacity using Modulated Differential Scanning

Calorimetry (MDSC). The conditions used were: i) modulation period of 80 s; ii) heating rate of 1 ºC·min^{-1}; and iii) temperatures from 50 to 320 ºC. Sulphur content at trace level was determined by oxidative pyrolysis and UV fluorescence detection, using a *Mitsubishi TS-100/SD-100*.

3. Results and discussion

3.1. Ultimate and proximate analysis and heating values

Table 2 reports the results of the ultimate and proximate analysis along with the heating values of the different types of post-consumer plastic film waste studied. Results for industrial recycled granules (IG) are also included as a reference for polyethylene. Oxygen content was determined by the difference between the sum of the weight percentages of C, H, N, S and ash (on a dry basis) subtracted from 100. The results of ash content on a dry basis are also included in Table 2. Likewise, the values of H/C ratio on a molar basis were also calculated and shown. For colour film waste samples from manual sorting (CF) samples, carbon was found to be in the range of 69-77 %, hydrogen was about 11-12 %, nitrogen was less than 2 %, oxygen reached values up to 6 % and sulphur content was negligible. According to carbon and hydrogen values, the energy contents were remarkably high (HHV: 36366-42394 kJ/kg; dry basis), as expected since PE is the major component. The ash content varied from 8.7 to 13.1 % (dry basis). This fact is indicative of the presence of 2D materials different from PE (e.g. paper/cardboard). Proximate analysis reported values of moisture content in the range of 11-15 %. The volatile matter was about 73.4-81.2 % and fixed carbon varied from 0.1 to 0.9 %. No clear influence of seasonality on plastic waste quality has been observed, as sorting was carried out by hand-picked after the ballistic separator. Colour film waste recovered by automated sorting (ACF-W) (automated sorting) exhibited higher oxygen

284 (11.8 %) and fixed carbon (3.3 %) values compared to those obtained from manual
285 sorting (CF), as well as lower H/C ratio. These observations may be attributed to the
286 presence of PET in waste coming from automated sorting, which is consistent with the
287 use of air separation system for film fraction recovery. Note that PET as an individual
288 component consists of around 30 % oxygen content and 6 % fixed carbon (Diaz-
289 Silvarrey and Phan, 2016). The presence of PET is also corroborated by DSC results
290 (see section 3.4). White film (WF) presents higher carbon and hydrogen contents (80-81
291 % and 13-14 %, respectively) in comparison with colour film waste samples (CF).
292 Therefore, their heating values (HHV > 43500 kJ/kg; dry basis) and volatile matter (>
293 92 %) are also higher. It is also remarkable that oxygen (< 3 %), ash (< 5 %) and
294 moisture contents (3 %) are much lower in WF. These observations reveal that WF
295 contains less undesired materials than CF and has a higher quality and potential to be
296 used directly as a source of fuels and chemicals. Note that the chemical composition of
297 WF is very close to that found in industrial recycled film granules (IG). For colour and
298 white film waste granules (CG and WG, respectively), the contents in carbon and
299 hydrogen are larger compared to CF and WF. This fact is due to the removal of
300 undesired materials (e.g. paper/cardboard, organic fraction, PET, etc.) attained through
301 the pretreatment process. The increase in carbon and hydrogen percentages is
302 accompanied with an increase in the heating values. Although there are no significant
303 differences between CG, WG and IG, it is interesting to note that the percentages of
304 carbon, hydrogen and volatile matter are slightly lower in CG. The ash content is higher
305 in CG in contrast with WG and IG (5.4, 1.0, and 1.0 %, respectively). Considering that
306 undesired materials (e.g. paper/cardboard, abrasive materials, PET, etc.) were
307 practically removed during the waste pretreatment, the higher ash content observed in
308 CG may be indicative of a higher presence of PP in colour film waste granules. This is

in agreement with Dwivedi et al. (2019) that reported that the ash content in PP is much higher than that found in other municipal plastic waste, including PE, PET or PS. As expected, the ash content in CG and WG was lower than that found in untreated samples (CF and WF, respectively).

It is important to notice that ultimate analysis and heating values are key data in order to set out mass and energy balances and subsequently to design new recycling processes. In addition, the absence of oxygen and the relatively low values of fixed carbon make post-consumer film especially suitable for pyrolysis technologies. In addition, volatile matter confirms this hypothesis, i.e. the higher volatile matter in plastics being pyrolyzed, the higher the yield of liquid products (Al-Salem, 2019).

3.2. Metal content

Table 3 reports the results of the metal content in all post-consumer plastic film waste samples, including metals in industrial recycled film granules (IG) as a point of reference. The typical elements found in a variety of plastic materials are listed in supporting information. Metal-containing compounds are present in additives that are used for improving processability, stability or mechanical properties of polymers. As has been reported elsewhere (Ambrogi et al., 2017), there are different types of additives, including protective additives (antioxidants, photo-stabilizers, heat stabilizers and flame retardants), mechanical properties modifiers (plasticizers and impact modifiers), dyes and pigments, compabilizers and fillers (the most used additives). In addition, the presence of undesired materials in post-consumer plastic film waste may also contribute to increase the content in metals. As can be seen in Table 3, calcium is the most abundant element detected in all of the samples under study. Calcium is widely employed in a variety of plastics as a filler (mainly as calcium carbonate; calcium

334 silicate) and photo-stabilizer (e.g. calcium-zinc and organo-calcium compounds), and,
335 to a lesser extent, as an antacid, lubricant (e.g. calcium stearate) or to increase resistance
336 to impact, stress and compression (e.g. calcium sulphate). The concentration of this
337 element is much higher in colour film samples from manual sorting (CF), exceeding the
338 value of 30000 $mg \cdot kg^{-1}$. This finding could be due to the presence of HDPE in a higher
339 proportion, based on results reported in the literature. Scott and Granchell (2013)
340 reported that the calcium content in HDPE bottles is 93903 mg·kg-1, which is higher
341 than that observed by Sarker and Rashid (2013) for LDPE (963 $mg \cdot kg^{-1}$). The high
342 concentration of calcium may also be attributed to the presence of paper, since calcium
343 carbonate is used in paper mills as a filler material in the alkaline papermaking process
344 (Hubbe and Gill, 2016). It is important to note that relatively high concentrations of Al,
345 Fe, K, Na, Mg, Ti, Si, P and Zn were also detected in all the materials. High
346 concentration of Al may be attributed to the presence of aluminium trihydroxide
347 commonly used as a flame retardant. Aluminium silicate is also used as an additive in
348 polymers for increasing chemical resistance. High levels of Fe come from inorganic
349 pigments in the form of iron oxide or sulphide. K and Na may originate from additives
350 used mainly as thermal stabilizers (e.g. mica). Some K-compounds such as orthoclase
351 are also used for enhancing chemical resistance. Sodium benzoate is employed as a
352 nucleating agent in PP production. The high level of Na may suggest the presence of
353 this type of polymer in colour plastic waste samples from manual (CF) and automated
354 sorting (ACF). This is in agreement with the high sodium content found for PP by
355 Sarker and Rashid (2013) (5966 $mg \cdot kg^{-1}$). The presence of PP in CF and ACF samples
356 is also supported by DSC results (see section 3.4). The common use of hydrated
357 magnesium silicate as a filler is the probable cause for the high concentrations of Mg
358 and Si detected, particularly in colour film plastic waste from manual sorting (CF). High

359 concentrations of Ti were also found due to its use as an inorganic pigment in the form
360 of titanium dioxide (white colour). Likewise, rutile titanium oxide is one of the most
361 effective and commonly used light absorbers. The presence of Ti may also be attributed
362 to catalyst residues from polymerization process. Organophosphorus antioxidants and
363 phosphorus-based flame retardants may be responsible for the high concentration of P
364 detected in plastic waste. Zn detected at concentrations up to about 400 $mg \cdot kg^{-1}$ in
365 colour film obtained from manual sorting (CF) is mainly attributed to the use of both
366 Zn-based pigments (e.g. zinc oxide, zinc chromate) and heat stabilizers (e.g. zinc-based
367 salts, zinc carboxylate). Pb, Sn, Cr, Cu, Ba have also been detected, particularly in CF.
368 These elements are used in a number of pigments (in the form of oxides and sulphides)
369 and heat stabilizers (in the form of metallic salts, carboxylates, mercaptans and
370 sulphides). The data obtained from both colour and white film samples (CF and WF,
371 respectively) recovered by manual sorting (Table 3) reveal that there is no a significant
372 influence due to seasonal variations. However, the type of sorting (manual or
373 automated) plays an important role. As can be observed, higher concentrations of Ca, K,
374 Mg, P and Ti are found in CF (manual sorting) compared with ACF-W (automated
375 sorting). This fact may suggest the presence of a greater fraction of paper/cardboard in
376 samples obtained from manual sorting, since those elements are widely used as
377 additives in alkaline papers (e.g. calcium carbonate, mica, talc, titanium oxide,
378 phosphates esters etc.). This observation is in agreement with ash content results (see
379 Table 2). During the conditioning process, undesired components (e.g. paper/cardboard,
380 metal, glass, etc.) were removed from waste, decreasing the content of some elements.
381 Table 3 reveals that the concentration of some metals such as Al, Ca, Fe, K, Mg, Na and
382 P -present in paper/cardboard additives (Hubbe and Gill, 2016)- is minor in CG
383 compared with CF. It is interesting to note that metals in colour film waste granules

(CG) are similar to those found in industrial recycled film granules (IG). Regarding the metal content, the main differences between colour and white film waste granules (CG and WG, respectively) are found in the contents of Ca and Fe. The concentration of these elements is higher in the case of CG. It is also interesting to point out that the total content of metal in colour film (CF) reaches values ranging from 2.9 to 5.2 %, whereas the metal content in white film samples (WF) is significantly lower, around 1-2 %. This is in agreement with the results of ash content reported in Table 2. Also it is noteworthy to indicate that some metals promote the thermo-oxidative degradation of plastic materials (e.g. Fe, Co, Ni, Mn, Ti, V and Cu) (Gorghiu et al., 2004; Ojeda, 2013). Special attention should also be paid to the concentration of some elements (e.g. Si, Ca, K, Na, Fe, P, V, Ni and As), especially when plastic waste is going to be used as a raw material in catalytic processes, since they act as poisons for catalysts, decreasing their activity and lifetime (Argyle and Bartholomew, 2015). Consequently, if the materials are going to be used in catalytic pyrolysis, a pretreatment step may be essential.

3.3. Thermogravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG) results

TGA/DTG curves of CF-W, ACF-W, CG, WG and IG materials are displayed in Fig 1. Detailed data are listed in Table 4. T5, T10, T50, T80 and Tmax represent the temperatures at which 5 wt. %, 10 wt. %, 50 wt. %, 80 wt. % and the maximum weight loss rate occurred, respectively. According to E2550-17 (ASTM International, 2017), the onset temperature was determined by selecting the point on the TGA curve where deflection is first observed from the established baseline prior to the thermal event. It can be observed that the thermal decomposition of the industrial recycled film granules (IG), used as a reference material for packaging film, starts at approximately 350 ºC and

409 the main devolatilization takes place in the range of 450 and 500 ºC. This fact is in
410 agreement with results reported in the literature related to polyethylene devolatilization
411 under nitrogen atmosphere, occurring in a single step (Diaz-Silvarrey and Phan, 2016;
412 Heikkinen et al., 2004; Kumar and Singh, 2011). In addition, it can be noted that the
413 char content is about 3.5 % (remaining solid at 800 ºC). DTG data show that the
414 temperature corresponding to maximum degradation rate (Tmax) of IG is 485 ºC. The
415 degradation onset temperatures of colour film waste from manual and automated sorting
416 (CF-W and ACF-W, respectively) were displaced to the range of 185 ºC. The DTG
417 curve of CF-W shows that there are three separate steps of devolatilization (Fig. 1b). It
418 can be stated that the first step, occurring at temperatures ranging from 250 to 380 ºC
419 with a Tmax of 336 ºC, may be correlated with paper/cardboard devolatilization
420 (Alvarenga et al., 2016). The second step was observed in the range of 395-505 ºC,
421 presenting the maximum rate of weight loss at 476 ºC. Comparing TGA/DTG curves of
422 CF-W with IG, it can be concluded that this step is mainly associated with polyethylene
423 devolatilization, but minor presence of other types of polymers (e.g. PP, PS, PET) or
424 lignocellulosic materials may be probably present due to the broad band observed
425 (Heikkinen et al., 2004). It should be noted that PP has been detected in DSC results
426 (see section 3.4). The third devolatilization step is detected at temperatures of 625-650
427 ºC, which may be attributed to silica dehydroxylation or thermal decomposition of
428 carbonates or aluminates (Pereira et al., 2017). It may also be due to the presence of
429 pigments/dyes or other types of additives (Alvarenga et al., 2016). The char content in
430 CF-W is much higher than IG (13.5 % vs. 3.5 %), confirming the presence of undesired
431 materials (mainly paper/cardboard) in plastic waste recovered by manual sorting. ACF-
432 W (automated sorting) presents a devolatilization step at a Tmax of 345 ºC, which may
433 be attributed to the presence of organic or lignocellulosic fractions. It can also be

observed two decomposition stages, partially overlapped in the range of 395-505 ºC. The DTG peak at 480 ºC is due to polyethylene degradation, whereas the lower DTG band may be probably accounted for the presence of PET in accordance with DSC analysis. Results in literature show that Tmax of PET occurs at about 434-441 ºC (Hujuri et al., 2008; Pereira et al., 2017). Hujuri et al. (2008) already suggested that substituted/branched polymers like PET or PP degrade at lower temperatures than linear polymers (LLDPE/LDPE/HDPE). However, it is important to point out that the weight loss may also be due to lignocellulosic materials since lignin degradation occurs in the temperature range of 250-500 ºC (Lafia-Araga et al., 2012). The char content in ACF-W is lower than that detected in CF-W (8 % vs. 13.5 %, respectively). This observation is consistent with the values of ash content reported in Table 2, revealing that samples from automated sorting contain less paper/cardboard than those recovered by manual sorting. TGA-DTG curves for granules obtained from colour and white film waste (CG and WG, respectively) are similar to those obtained for IG, suggesting that the major component of both materials is polyethylene. The char content in CG is equal to that detected in IG (3.5 %). For WG, no appreciable char content was observed at 800 ºC. Note that the DTG peak height at any temperature gives the rate of weight loss. In this sense, it can be observed in Fig. 1b that CF-W (manual sorting) presents the lowest rate of degradation, followed by the ACF-W (automated sorting). CG, WG and IG materials have high rates of degradation, especially at temperatures above 450 ºC. Thermal stability increases after the pretreatment of plastic waste due to the removal of undesired materials, mainly organic and lignocellulosic fractions. As can be seen in Table 4, thermal stability increases after the pretreatment of plastic waste due to the removal of undesired materials, mainly organic and lignocellulosic fractions. For example, it is worth to note that T5 increases from 226-289 ºC for untreated plastic wastes (CF-W and

ACF-W, respectively) to temperatures above 400 ºC for CG (404 ºC) and WG (424 ºC). The fact that CG shows a lower thermal stability than WG reveals that PP content is higher in CG, since PET and undesired materials were largely removed during the pretreatment. All this information related to thermal stability and degradation rates is essential to design thermochemical technologies because it is directly related to the operational temperatures or reactors, especially in energy optimized processes in which energy efficiency is a key point to maximise the process sustainability.

3.4. Fourier Transform Infrared (FT-IR) spectroscopy and Differential Scanning Calorimetry (DSC) analysis

In order to obtain detailed information about compositional functional groups, post-consumer plastic waste from manual and automated sorting (CF-W and ACF-W, respectively) and pretreated samples (CG and WG) were examined using FT-IR spectroscopy in the mid-infrared range (4000-600 cm^{-1}). Industrial recycled film granules (IG) were also analysed by FT-IR as a reference for polyethylene. Results from FT-IR also allow identifying the presence of organic, polymeric and inorganic materials. As has been previously indicated (see section 2.1), plastic film waste mainly consists of polyethylene because is the main polymer used to produce packaging film. Therefore, characteristic bands of polyethylene are expected in the reflection infrared spectra of all the samples analysed (CF-W, ACF-W, CG and WG). IR spectra obtained are shown in Fig. 2. Note that the characteristic bands of polyethylene are given by IG spectrum used for reference. In this sense, two polyethylene peaks can be observed at approximately 2915 and 2850 cm^{-1} (fig. 2a), assigned to asymmetric and symmetric stretching vibrations of C-H bonds in methylene groups (Heydariaraghi et al., 2016). In addition, a strong absorption band at 1470 cm^{-1} and a less strong peak at 720 cm^{-1} (Fig. 2b) due to the bending vibrations of C-H bonds in polyethylene are also an indication of

485 the presence of methylene as a functional group (Heydariaraghi et al., 2016). By
486 comparing IG spectrum with the rest of samples, it can be confirmed the presence of
487 polyethylene in all plastic waste samples. However, the presence of polypropylene is
488 also observed in all samples, because there is an additional peak at 1375 cm^{-1} assigned
489 to symmetrical bending vibrations of C-H bonds in methyl groups (Fig. 2b)
490 (Heydariaraghi et al., 2016; Marshall et al., 2005). It is important to note that the
491 intensity of polyethylene bands related to methylene groups is much stronger than that
492 of the peaks corresponding to methyl groups. This finding confirms that plastic waste
493 samples are mainly made up of polyethylene with minority presence of polypropylene.
494 The observed changes in peak intensity imply some changes in relation to the phase or
495 crystallinity of the polymers (polyethylene and/or polypropylene). This observation has
496 also been corroborated by DSC results (Fig. 3). Regarding the pretreatment influence,
497 Fig. 2 reveals the presence of undesired materials (e.g. paper/cardboard, PET, etc.) in
498 untreated samples (CF-W and ACF-W), because characteristic absorption bands,
499 assigned to lignocellulosic materials and PET, have been detected in the FT-IR spectra
500 of CF-W and ACF-W, whereas these additional bands are negligible in the spectra of
501 pretreated materials (CG and WG) and polyethylene (IG). In this regard, it can be
502 observed that CF-W and ACF-W presents two broad bands in the wavenumber ranges
503 of 3600-3000 cm^{-1} and 1200-900 cm^{-1}, which are characteristics for stretching
504 vibrations of O-H and C-O bonds in lignocellulosic materials (Hospodarova et al.,
505 2018). The presence of PET may also contribute to those observed peaks in line with
506 characteristic bands of PET polymer reported by Pereira et al. (2017). In addition, the
507 presence of this type of polymer has also been detected by DSC (Fig. 3) for ACF-W
508 (automated sorting). The intensity of characteristics bands of undesired materials is
509 higher in plastic waste recovered from automated sorting (ACF-W) than manual sorting

510 (CF-W). Considering this fact, along with results from ultimate analysis and TGA/DTG
511 analysis, it can be concluded that ACF-W presents a higher PET contamination than
512 CF-W. This fact should be taken into account by chemical recycling technology users
513 when they select the feedstock origin based on the requirements of each technology.
514 As indicated in section 3.2, a great variety of chemical compounds are used in
515 polymers, such as antioxidants (e.g. phenols, amines, thioester, etc.), photo-stabilizers
516 (hydroxyaromatic compounds), heat stabilizers (metallic salts, organometallic
517 compounds, etc.), flame retardants (aluminium trihydroxide and magnesium hydroxide,
518 halogenated compounds, phosphorous-based compounds, etc.) and pigments. According
519 to this fact, the presence of characteristic bands due to the stretching vibrations of C-O,
520 O-H, N-H, C=O, C=C, C=N, organometallic and halogenated bonds (Larkin, 2011) is
521 also detected (Fig. 2b) in all samples. For example, the presence of absorption peaks at
522 1170 and 1260 cm^{-1}, assigned to C-O stretching vibrations, are consistent with the
523 presence of phenolic compounds used as polymer additives, mainly primary
524 antioxidants. Characteristic band assigned to C=O stretching vibrations of carboxylic
525 acid group at 1730 cm^{-1} was also detected in all samples, which may be attributed to the
526 presence of polymer additives or the photo-thermal oxidative phenomena typical of
527 polymeric materials occurring at one or all of the manufacturing, processing and end-
528 use stages (Gardette et al., 2013). In addition, the broad absorbance band in the range of
529 1430 cm^{-1} due to the antisymmetric stretching vibration of C-O as well as the peak
530 appeared at 875 cm^{-1} due to the plane of bending vibration of C-O may confirm the
531 presence of calcite (Harris et al., 2015; Sağm et al., 2012), the most used polymer
532 additive for improving mechanical properties of polyethylene. According to literature
533 (Marshall et al., 2005; Öztas and Yürüm, 2000), the overlapped peaks observed in the
534 region of 1200-900 cm^{-1} may also be assigned to the presence of silica (Si-O stretching

vibrations at 1100-1000 cm^{-1}). These observations are also supported by the results of metal determination (Table 3).

FT-IR results related to polymer composition are confirmed by DSC analysis, in which the values of endothermic peak maximum indicate the melting point and type of polymer. The ratio of peak areas is an indication of the polymeric composition. Fig. 3 shows the DSC scans obtained from the second heating scanning of the post-consumer plastic film waste CF-W (manual sorting), ACF-W (automated sorting), pretreated samples (CG and WG, respectively) and industrial recycled film granules (IG; reference material for polyethylene), showing a double peak with maxima at around 110 and 122 ºC for all the samples. This is due to the molecular weight distribution in polyethylene. According to literature (Liu et al., 2002), the former temperature peak corresponds to LDPE (melting peak ranging from 105-115 ºC) while the latter one to LLDPE (melting peak ranging from 115-128 ºC). These values are shifted to lower temperatures as the crystallinity degree is decreased. It is important to note that the higher the density is, the higher the peak temperature and the larger the melting point are. The values of total melting heat associated with these peaks are 97.3 J/g (CF-W), 58.7 J/g (ACF-W), 108.7 J/g (CG), 115.4 J/g (WG) and 105.1 J/g (IG), which correspond to 33.2, 20.0, 37.1, 39.4 and 35.9 % crystallinity, respectively, based on the reported theoretical value of 293 J/g for 100 % crystalline polyethylene (Wunderlich, 1990). By comparing the ratio of peak areas between LDPE and LLDPE, it can be concluded that samples obtained from colour film mainly comprise LLDPE, whereas the amount of LDPE is higher in white film samples. An additional peak is observed at around 160-165 ºC. This peak is ascribed to the presence of polypropylene, which appears to be higher in colour film waste (see comparative DSC scans for CG and WG in supporting information). ACF-W (automated sorting) also presents a peak at 240 ºC, which is assigned to PET (see

specific DSC scan for ACF-W in supporting information). It is important to indicate that the presence of PET can only be corroborated from DSC results for ACF-W.

3.5. Rheological study

Fig. 4 plots the viscosity curves obtained at different temperatures of the pretreated materials (CG and WG), revealing that temperature and shear rate are critical variables. It is also found that viscosity is shear rate dependent. Both materials exhibit a decreased viscosity with increasing shear rate when the stress is large enough (especially at values greater than 0.1 s^{-1}), showing an abrupt transformation in flow regimes over a relatively narrow range of stress (~ 0.1-1 s^{-1}). This fact is indicative of a shear-thinning non-Newtonian fluid (Xie and Jin, 2016). Viscosity also decreases significantly as the temperature of the molten polymer increases (see supporting information). The Cross rheology equation has been widely used to investigate non-Newtonian behaviours (Xie and Jin, 2016). Considering this, Fig. 4 shows the comparison between numerical (Cross model) and experimental results at different temperatures. Note that the fitting using Cross model faithfully reproduces the experimental data. Cross model parameters are listed in supporting information. In flow curves, in which high-shear rates could not be experimentally reached, viscosity values were modelled considering a shear-thinning behaviour similar to that of the same material at the minimum temperature tested (260 ºC). On the basis of the analysis of Fig. 4, it can be concluded that viscosity values at a given shear rate and temperature are higher for CG (colour film granules) than for WG (white film granules). This may be an indication of a higher LLDPE content in CG. As previously reported (Abraham et al., 1992; Brydson, 1999; Liu et al., 2002), the greater the branching of polyethylene is, the lower the viscosity is.

586 It is well known that viscosity curves are an important tool for the design of processes
587 in which non-Newtonian fluids take place. In this case, the results of the rheological
588 study could be particularly important keeping in mind that the materials consist of
589 blends of recycled plastics (Ponz, 2009).
590
591 *3.6. PVT diagram*
592 Fig. 5 shows the PVT diagrams of the pretreated materials (CG and WG), describing the
593 specific volume as a function of pressure and temperature. Specific volume data enables
594 to gain better understanding about unitary steps in industrial processing of polymers or
595 as an input for constitutive models used in process simulation software. This justifies
596 the need of accurately determining the specific volume at conditions comparable to
597 industrial processing conditions. As can be observed in Figure 5, specific volume
598 increases when increasing temperature and decreasing pressure. For example, the
599 specific volume for WG (white film granules) at 7 bar is observed to increase from 1.37
600 $cm^3 \cdot g^{-1}$ at 200 ºC to 1.60 $cm^3 \cdot g^{-1}$ when temperature is increased up to 400 ºC. An
601 increase in pressure for WG from 7 to 200 bar at 200 ºC results in a decrease in specific
602 volume from 1.37 to 1.35 $cm^3 \cdot g^{-1}$. It is worth to note that the influence of pressure on
603 specific volume is less important than temperature. From the results shown in Figure 5,
604 it can also be concluded that specific volume at a given temperature and pressure is
605 significantly higher for WG (white film granules) than CG (colour film granules). The
606 higher density of CG compared to WG confirms the greater presence of LLDPE in CG,
607 since this type of polymer contains lower amounts of long-chain branching than LDPE,

as well as a minor average molecular weight (Liu et al., 2002). This finding is also in agreement with rheological and DSC results, showing a higher LLDPE content in CG than in WG. There is also a thermal transition in both types of materials, corresponding to the change of state between solid and melted. The type of thermal transition observed in both samples reveals that they are semi-crystalline polymers because the structural continuity is maintained above the glass transition temperature (Wang, 2012). IKV model parameters for CG and WG are summarized in supporting information.

3.7. Determination of specific heat capacity

Specific heat capacity was measured by using MDSC (Modulated Differential Scanning Calorimetry) for CG (colour film granules) and WG (white film granules) samples. Fig. 6 shows how specific heat capacity (Cp) changes as a function of temperature. The endothermic peaks observed at temperatures near 120 (WG) – 125 ºC (CG) indicate the glass transition due to polymer melting. As can be observed, the values of the specific heat capacity for WG are significantly higher than CG prior to melting point. The specific heat capacity reaches up to approximately 4.2 $J \cdot g^{-1} \cdot ºC^{-1}$ for WG, while this value is 3.3 $J \cdot g^{-1} \cdot ºC^{-1}$ for CG. These observations are indicative of a higher LDPE/LLDPE ratio in WG compared to CG. These results are consistent with DSC, rheological and PVT diagram data. Once the temperature is increased above the melting region, the value of the specific heat capacity is remarkably lower and no substantial differences are observed between both materials. The data obtained by DSC technique together with determination of specific heat capacity are particularly important in processes involving phase changes where heat transfer and temperatures play an essential role. This is the case in the most of chemical recycling processes.

3.8. Determination of halogen and sulphur contents

Halogen and sulphur containing compounds are often added as plasticizers, flame retardant and heat stabilizers. Due to their serious impact, it is important to know the content of halogens and sulphur when polymers are recycled or used as a raw material in thermochemical technologies. The pretreated materials (CG and WG) were found to contain very little halogens and sulphur. Sulphur was found to be in a low concentration (~ 85 ppm) in colour and white film granules (CG and WG, respectively). The halogen content expressed as chlorine is slightly higher in WG (1095 ppm) compared to CG (928 ppm).

4. Conclusions

Detailed characterization of different post-consumer plastic film waste samples coming from mixed MSW in Spain and recovered by manual (CF: colour film waste; WF: white film waste) and automated sorting (ACF: Colour film waste) samples, provided critical information for Life Cycle Assessment (LCA) and implementing innovations in chemical recycling technologies (i.e. pyrolysis) to enable the transformation of plastic waste into valuable resources. The results were contrasted with those obtained for pretreated plastic film waste (CG – colour film granules and WG – white film granules) and industrial recycled film granules (IG; as a reference material for packaging film). It was found that the type of sorting plays an important role on the plastic waste quality and composition, strongly affecting the presence of additives and contaminants (quantity and type). It can also be concluded that the pretreatment may be needed for the successful commercial application of novel cost and energy-efficient alternatives of current chemical recycling, especially in the case of colour plastic film waste management. However, white plastic film waste stream exhibited a greater potential to

be used directly in chemical recycling process, since its characteristics were observed to be very close to those observed for industrial recycled film granules (IG). Despite this, it is important to note that even white plastic film may require a pretreatment step depending on the final application. For each recycling technology, a specific pretreatment should be designed based on the process requirements. Finally, no clear influence of seasonality on plastic waste quality recovered by manual sorting was observed, so characteristics of this plastic waste stream are always kept constant. This is a positive issue to improve and optimize the design of pretreatment processes, guaranteeing its use in fastly-evolving recycling technologies.

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Tables and Figures

Table 1.

Standards and commercial equipment used for analysing chemical composition, heating values, metal and halogen contents.

Parameter	Standard	Reference	Equipment
Ultimate analysis			
CHN/S	EN 15407:2011	CEN, 2011a	LECO CHNS628 / (628S module)
Proximate analysis			
Moisture	EN 15414-3:2011	CEN, 2011b	Memmert UFE550
Volatile matter	EN 15402:2011	CEN, 2011c	Carbolite AAF 11/18
Ash	EN 15403:2011	CEN, 2011d	Carbolite AAF 11/18
Fixed carbon*			
Heating values			
HHV	EN 15400:2011	CEN, 2011e	Parr 6100
LHV**	EN 15407:2011	CEN, 2011f	
Metal content	EN 15410:2011	CEN, 2011g	Milestone-ETHOS One (microwave digestion) SPECTRO-GENESIS/SOP (ICP-OES)
DSC analysis	EN ISO 11357-3:2018	CEN, 2018	TA Instruments Q200 DSC
Halogen content	EN 53087-2:2005	AENOR, 2005	Mitsubishi TOX-100 analyser

**By difference*

*** By calculation from HHV and hydrogen content*

Table 2.

Results of ultimate analysis (wt. %; dry basis), H/C ratio (molar basis), ash (wt. %, dry basis), proximate analysis (wt. %; as received) and heating values (kJ/kg; dry basis).

	Manual Sorting						Autom. sorting	Pretreatment		Industrial
	Colour film	Colour film	Colour film	Colour film	White film	White film	Colour film	Colour film	White film	Recycled film
	winter	spring	summer	autumn	winter	summer	winter	granules	granules	granules
	CF-W	CF-SP	CF-S	CF-A	WF-W	WF-S	ACF-W	CG	WG	IG
Ultimate analysis										
C	72.7	77.4	69.3	71.8	80.9	81.8	70.7	80.4	84.3	82.8
H	12.3	12.6	11.1	11.4	13.8	13.2	11.1	13.5	14.3	13.9
N	2.4	0.4	0.3	0.4	0.1	0.1	0.6	0.1	0.0	0.0
S	0.3	0.1	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.1
O*	0.6	0.8	6.0	6.1	2.6	0.1	11.8	0.5	0.3	0.2
H/C ratio	2.03	1.95	1.92	1.91	2.05	1.94	1.88	2.01	2.03	2.01
Ash	11.7	8.7	13.1	10.1	2.4	4.7	5.5	5.4	1.0	3.0
Proximate analysis										
Ash	9.8	7.7	11.2	8.8	2.3	4.6	5.0	5.4	1.0	1.0
Moisture content	15.9	11.0	14.8	13.1	3.0	3.0	9.3	0.1	0.1	0.2
Volatile matter	74.2	81.2	73.4	77.2	94.1	92.3	82.4	94.4	98.8	97.5
Fixed carbon	0.1	0.1	0.6	0.9	0.6	0.1	3.3	0.1	0.1	1.3
)Heating Values										
HHV	41127	42394	36366	37775	43727	44684	37541	43581	45947	44860
LHV	38519	39718	34080	35430	40885	41863	35262	40801	43167	41996

** By difference*

Table 3.

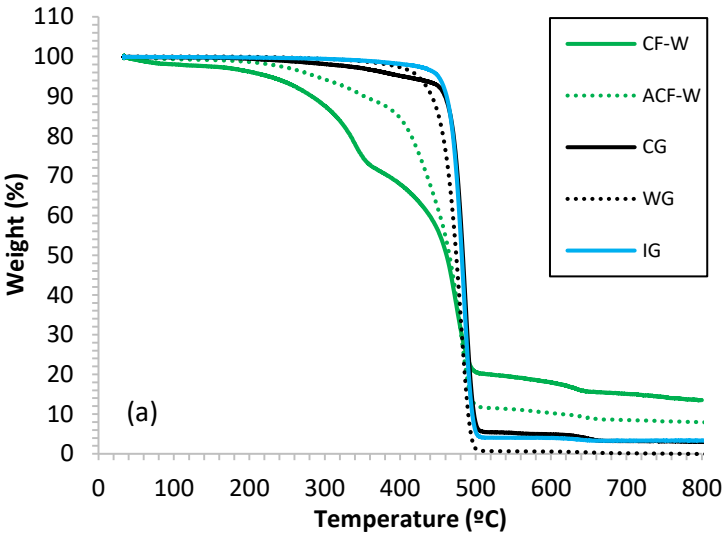
Results of metal content (mg·kg^{-1}).

	Manual Sorting						Autom. sorting	Pretreatment		Industrial
	Colour film	Colour film	Colour film	Colour film	White film	White film	Colour film	Colour film	White film	Recycled film
	winter	spring	summer	autumn	winter	summer	winter	granules	granules	granules
	CF-W	CF-SP	CF-S	CF-A	WF-W	WF-S	ACF-W	CG	WG	IG
Ag	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8
Al	2093	1093	1539	1858	669	543	2340	190	205	571
As	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
B	17	< 4	< 4	9	< 4	< 4	< 4	< 4	< 4	< 4
Ba	115	145	102	96	33	17	53	30	8	36
Bi	6	< 0.6	237	< 0.6	< 0.6	115	< 0.6	-	-	< 0.6
Ca	38856	20597	31568	31081	6088	4740	13583	13236	1300	9464
Cd	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Cr	14	< 0.8	15	68	22	8	12	8	7	6
Cu	52	38	24	108	40	< 0.3	22	19	4	170
Fe	1352	2378	-	1760	97	-	1848	187	< 10	162
Ga	< 9	15	41	28	< 9	72	< 9	-	-	11
Hg	-	< 0.2	153	< 0.2	< 0.2	93	< 0.2	< 0.2	< 0.2	< 0.1
K	2326	1089	917	1773	520	491	688	< 208	< 208	< 208
Li	< 4	< 4	< 4	5	7	< 4	< 4	< 4	< 4	< 4
Mg	1428	618	824	926	466	< 422	439	< 422	< 422	< 422
Mn	73	32	9	25	11	< 4	11	< 4	10	-
Mo	< 4	< 4	< 4	8	< 4	< 4	< 4	< 4	< 4	-
Na	1697	1223	1317	2481	691	426	1839	< 185	< 185	< 185
Ni	< 4	20	< 4	26	6	< 4	< 4	< 4	< 4	33
P	914	658	1661	550	202	1986	221	13	29	106
Pb	31	236	< 4	429	5	< 4	< 4	19	< 4	16
Sb	< 10	< 10	< 10	29	< 10	< 10	< 10	< 10	< 10	< 10
Se	< 9	< 9	-	29	< 9	-	< 9	-	-	< 9
Si	< 214	356	1622	484	< 214	1024	< 214	< 214	< 214	380
Sn	23	< 0.8	295	14	2	35	6	9	5	< 0.8
Sr	106	24	19	34	12	7	14	9	< 4	< 4
Ti	1796	495	1605	793	45	812	222	< 4	< 4	427
V	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	-
Zn	399	265	87	201	86	60	139	93	37	< 0.1
Total (%)	5.2	2.9	4.2	4.3	1.9	1.1	2.2	1.5	0.3	1.2

Table 4.

Summary of the TGA/DTG results (Fig. 1) of post-consumer plastic film waste (manual sorting CF-W; automated sorting ACF-W; granules: CG, WG, IG).

	T5 (ºC)	T10 (ºC)	T50 (ºC)	T80 (ºC)	Tmax (ºC)	Char content at 800 ºC (wt. %)
CF-W	226	283	461	518	476	13.5
ACF-W	289	352	465	488	480	8
CG	404	459	483	493	486	3.5
WG	424	442	474	486	477	-
IG	451	462	482	491	485	3.5



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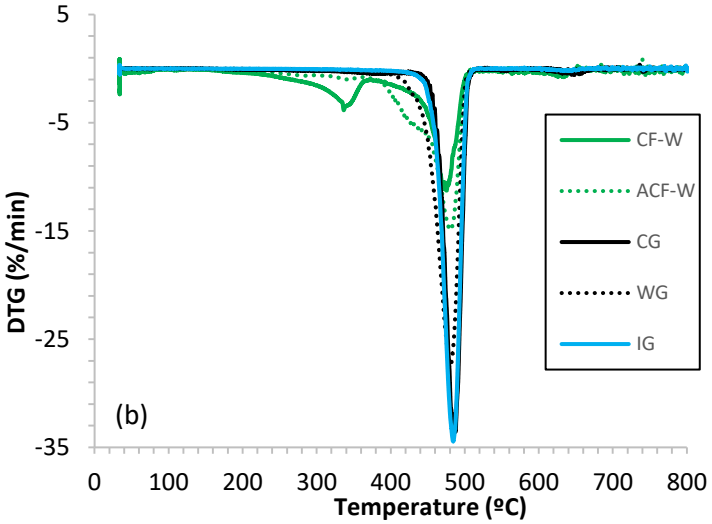

968

969 **Fig. 1.** TGA-DTG curves obtained in nitrogen flow at 10 ºC·min^{-1} for post-consumer plastic film waste

970 samples (manual sorting CF-W; automated sorting ACF-W; granules: CG, WG, IG). a) TGA curves; b)

971 DTG curves.

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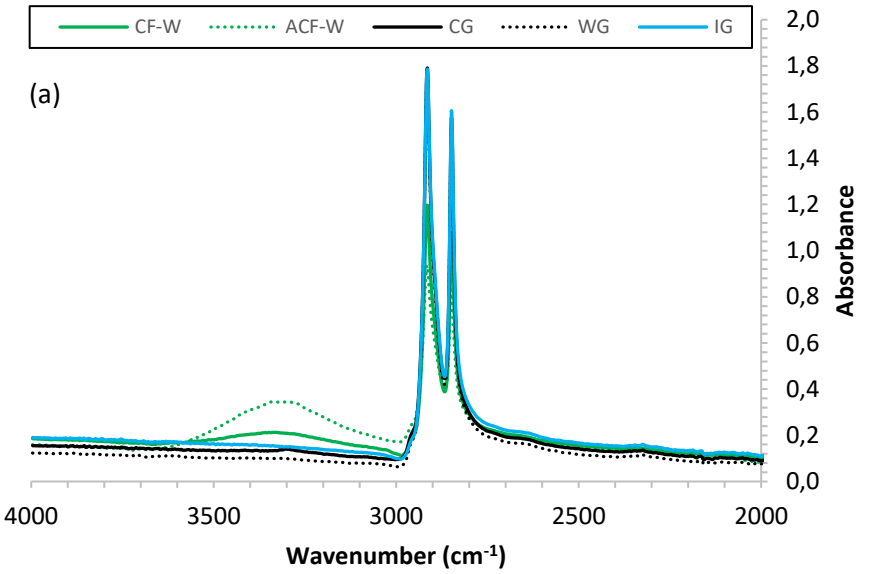

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976 **Fig. 2.** FT-IR spectra of post-consumer plastic film waste samples (manual sorting CF-W; automated

977 sorting ACF-W; granules: CG, WG, IG) in the wavenumber range of a) 4000-2000 cm^{-1} and b) 2000-400

978 cm^{-1}.

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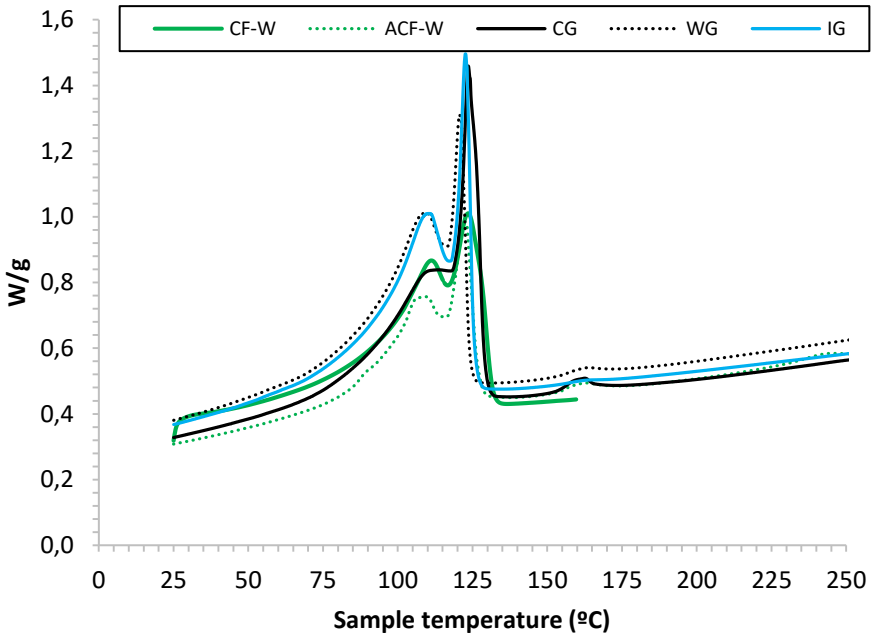

Fig. 3. DSC scans of post-consumer plastic film waste samples (manual sorting CF-W; automated sorting ACF-W; granules: CG, WG, IG).

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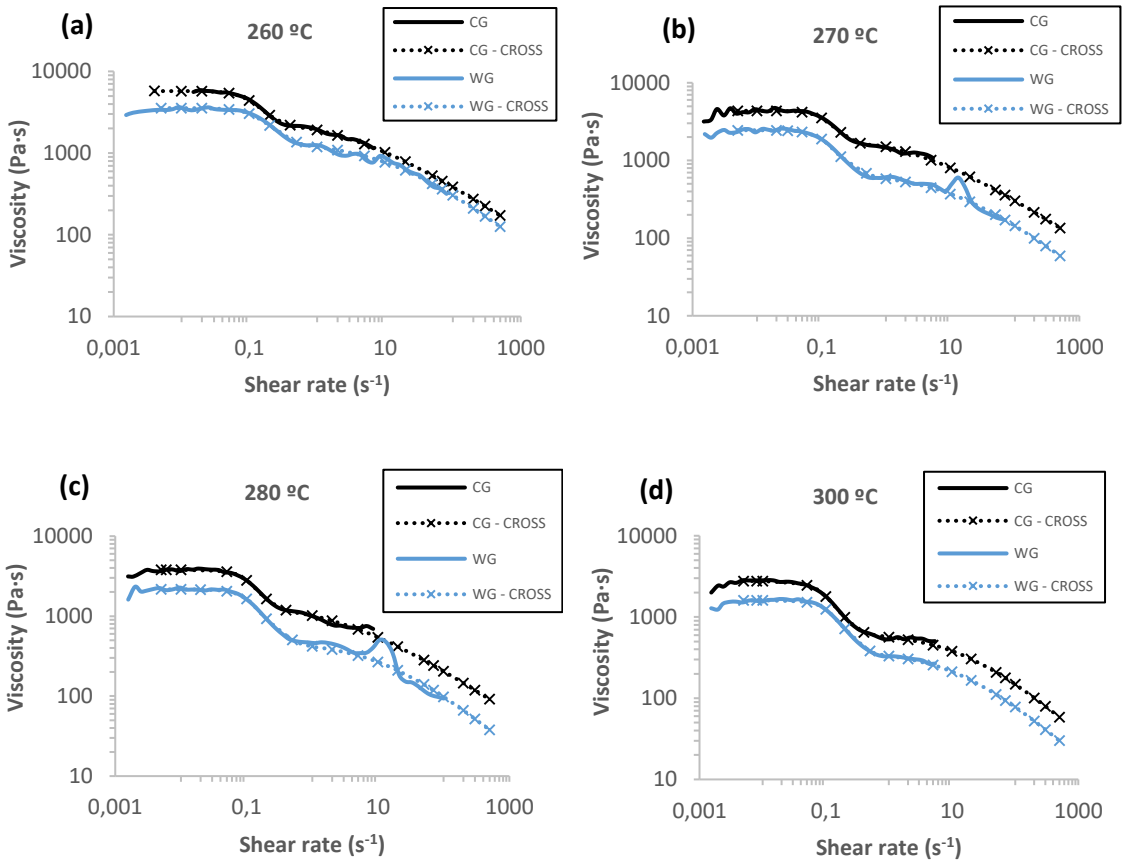

991

992 **Fig. 4.** Comparison of viscosity curves (solid lines) with Cross model fitting results (dotted lines with
993 markers) of CG (colour film granules) and WG (white film granules) samples at different temperatures:
994 (a) 260 ºC; (b) 270 ºC; (c) 280 ºC; (d) 300 ºC.

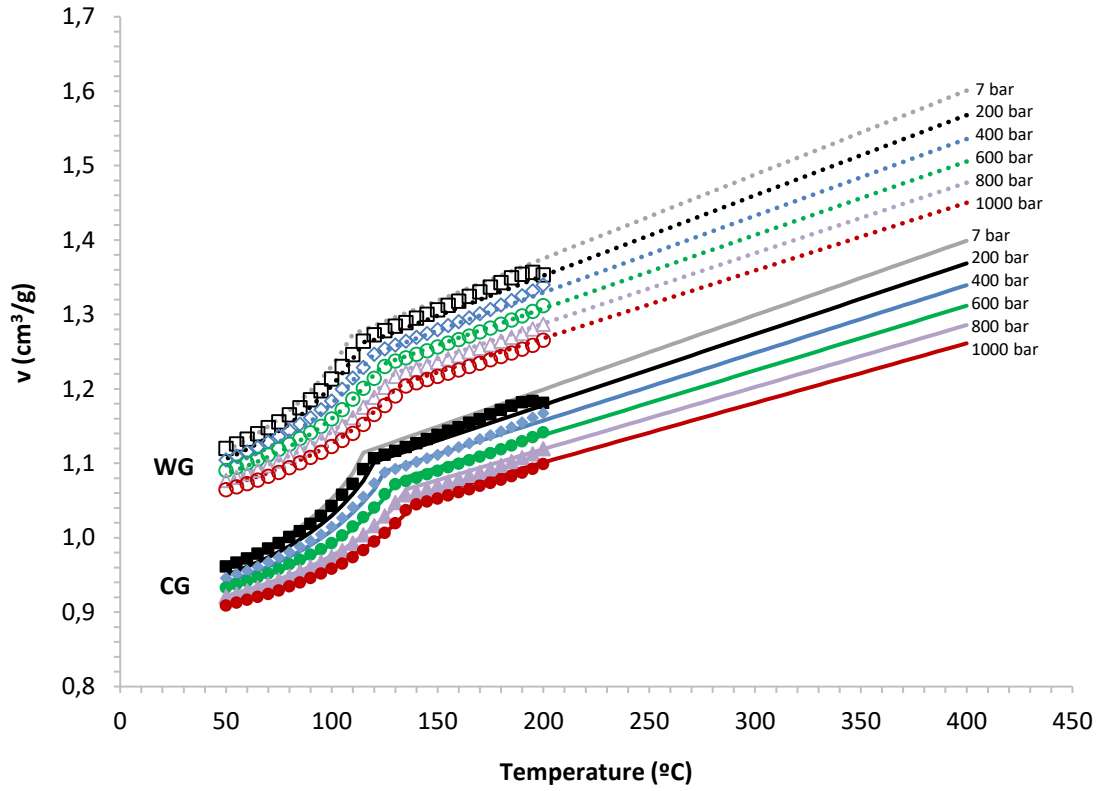

Fig. 5. PVT diagrams (markers) with IKV model fitting results (solid and dotted lines) for CG (colour film granules) and WG (white film granules).

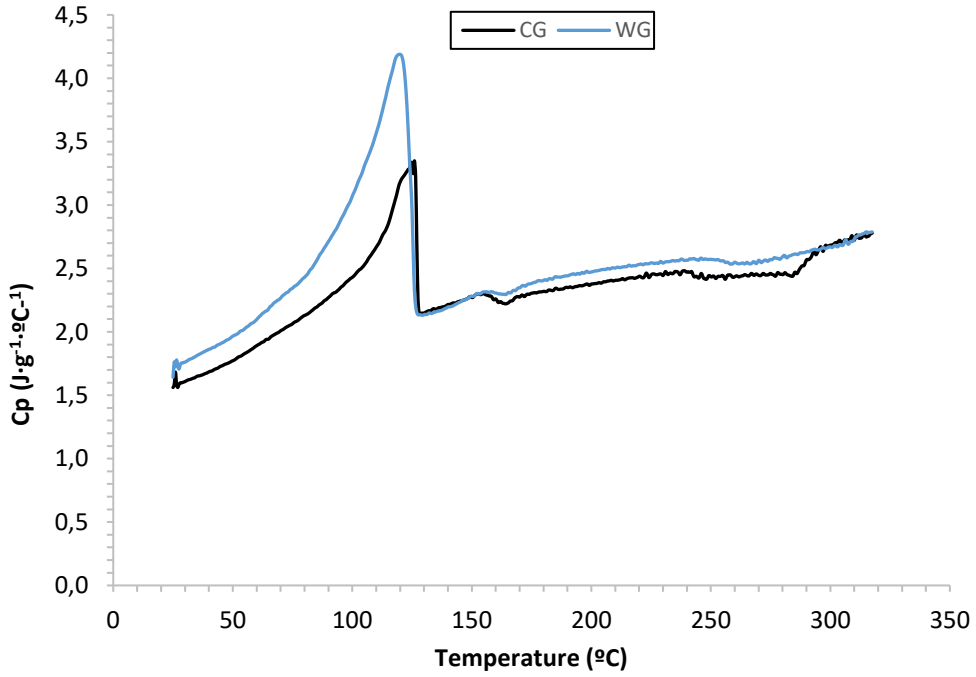

Fig. 6. Evolution of the specific heat capacity (Cp) as a function of temperature in the range of 25-320 ºC for CG (colour film granules) and WG (white film granules).