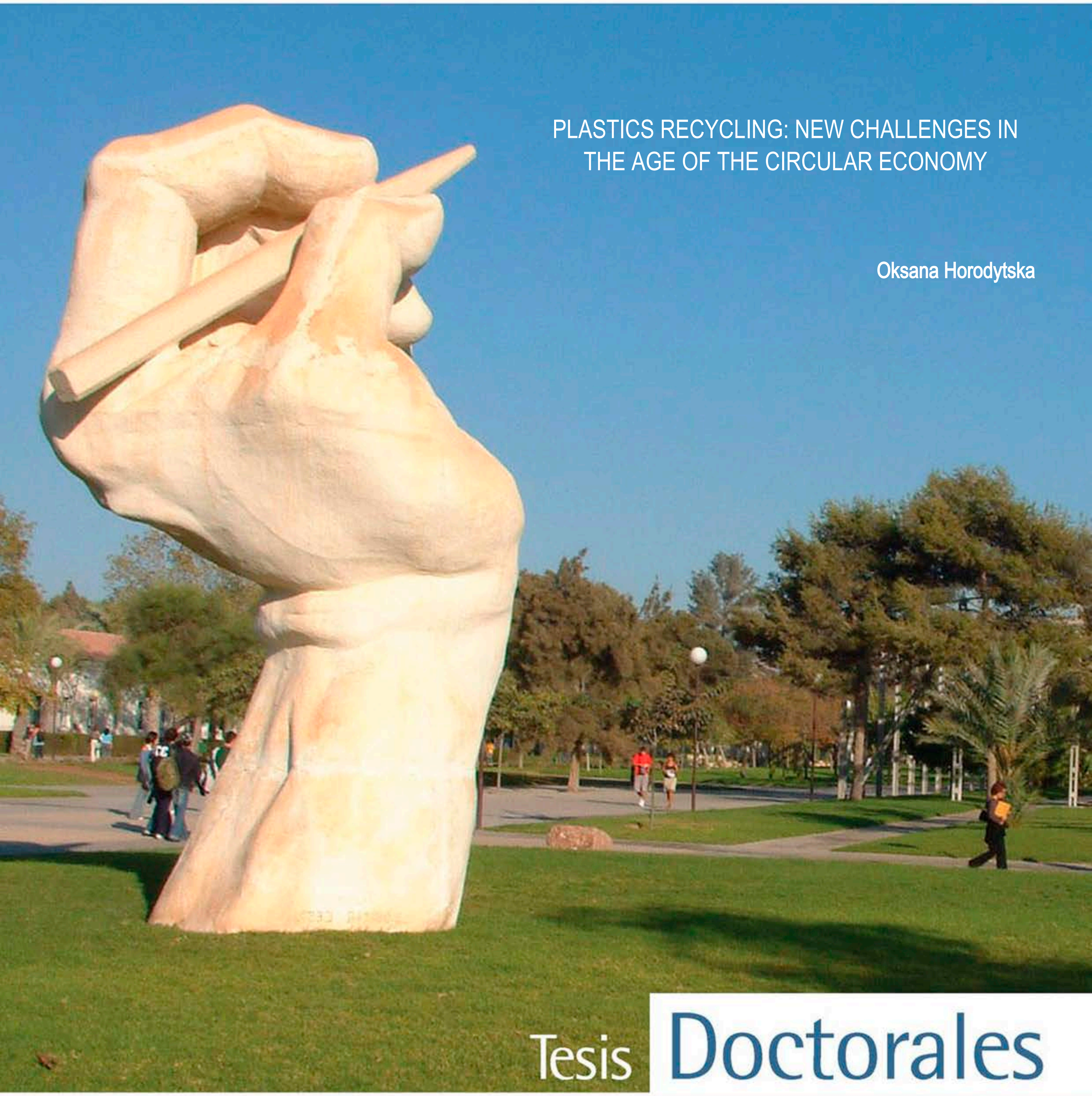

PLASTICS RECYCLING: NEW CHALLENGES IN THE AGE OF THE CIRCULAR ECONOMY

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CERTIFICADO DEL DIRECTOR

Dr. Andrés Fullana Font, Catedrático de Ingeniería Química de la Universidad de Alicante

CERTIFICA:

Que Oksana Horodytska, Ingeniera Química, ha realizado, en el Departamento de Ingeniería Química de la Universidad de Alicante, bajo mi dirección, el trabajo que con el título "PLASTICS RECYCLING: NEW CHALLENGES IN THE AGE OF THE CIRCULAR ECONOMY", constituye su memoria para aspirar al Grado de Doctor de Ingeniería Química, reuniendo, a mi juicio, las condiciones necesarias para ser presentada y defendida ante el tribunal correspondiente.

Y para que conste a los efectos oportunos, en cumplimiento de la legislación vigente, firmo el presente certificado en Alicante, a 19 mayo de 2020.

Andres

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Fdo. Dr. Andrés Fullana Font

TO MY GRANDPARENTS

The wisdom of a human is to remain silent when environment is speaking.

Lina Kostenko

SUMARRY

The plastics sector is experiencing a significant change of direction towards sustainability and innovation. The idea of a new Circular Economy as an alternative to the traditional "take-make-waste" model has made a deep impact on our society. Recovery and recycling of plastics have become an important marketing tool used by companies from small size to the leading businesses in different sectors. Consequently, the demand for recycled feedstock is expected to grow. The question which arises is whether the recycling sector is prepared to fulfil this demand, not only in term of quantity but also in terms of quality. In this Thesis, current recycling methods have been assessed from three different perspectives: environmental, operational efficiency and consumer safety.

Chapter 1 presents the results of a comprehensive review of the state-of-the-art on plastics recycling conducted to identify the main weak points and uncertainties of the sector. Several upcycling technologies of plastic waste have been reviewed since they improve the quality of recycled pellets and ensure the circularity of the material. Special attention has been paid to flexible plastics (or films) due to their lower recyclability and increasing consumption. Chapter 2 contains the main objectives laid down in this Thesis.

In Chapter 3, the environmental impacts caused by an innovative upcycling process of printed plastic scrap have been assessed through Life Cycle Analysis (LCA) methodology. The process consists of removing the inks from the plastic surface before extrusion, so that clear high quality pellets are obtained, suitable to be used in high added value applications (such as packaging). The upcycling technology is compared with two traditional plastic waste treatments: conventional recycling (or downcycling) and

incineration with energy recovery. Finally, the system boundaries have been extended until the end-of-life of the products manufactured with the upcycled plastics, i.e. the second life cycle.

Dewatering of plastic films is a highly energy-consuming recycling operation that largely affects the quality of the recycled product. Despite the importance of good drying, this operation has not been studied at laboratory or pilot plant scale. In Chapter 4, mechanical dewatering of blown film grade plastics has been assessed using a laboratory centrifuge. The influence of operational parameters such as centrifugation force and time has been studied to optimize the design of drying equipment. Furthermore, it has been concluded that the plastics characteristics (such as flake size and the plastic surface area) significantly affect the dewatering efficiency. On the contrary, the polymer type and the surface degradation show little influence.

In Chapter 5, the recycled plastics consumer safety has been assessed by the identification and semi-quantification of semi-volatile organic compounds (SVOCs) present in a number of samples. The lack of knowledge on the composition of the recycled plastics is one of the main bottlenecks for the incorporation of these materials in high added value applications. Solvent extraction followed by gas chromatography and mass spectrometry has been used as analytical technique. Recycled plastics from post-industrial and post-consumer waste have been analysed. In addition, four commercial plastic additives have been selected to identify their main components and possible contaminants. In total, 30 substances have been identified in the pure plastic additives and 81 compounds in the recycled pellets. All the SVOCs were divided in three groups: additives, degradation products and contaminants.

In Chapter 6, the main conclusions drawn from the research results are summarized and suggestions for future work are presented.

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LIST OF SYMBOLS AND ABBREVIATIONS

HDPE	High density polyethylene
LDPE	Low density polyethylene
MDPE	Medium density polyethylene
LLDPE	Linear low density polyethylene
PP	Polypropylene
PET	Polyethylene terephthalate
PUR	Polyurethane
PVC	Polyvinylchloride
MRF	Materials recovery facility
IAS	Intentionally added substances
NIAS	Non-intentionally added substances
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Inventory Analysis
S (in chapter 3)	Virgin plastic substitution ratio
MS	Market share
PDF	Potentially Disappeared Fraction of species
DALY	Disability-Adjusted Life Years
y	year
PC	Post-consumer
PI	Post-industrial
RCF	Relative centrifugal force
DSC	Differential Scanning Calorimetry
SEM	Scanning electron microscopy
AFM	Atomic force microscopy
e_w	Water layer thickness
τ (%)	Moisture content on a dry matter basis
τ_S	Specific moisture content
m	Plastic mass
x	Film thickness
ρ	Density
μ	Viscosity
A	Plastic surface area
s	Standard deviation
t	Centrifugation time

L	Flake side length
G	Centrifugation force
w	Rotational speed
R	Distance from the centre of rotation to the sample
g	Gravitational acceleration
S (in chapter 4)	Saturation
S_T	Transient saturation
S_∞	Equilibrium saturation
S_t	Free liquid saturation
S_z	Pendular liquid saturation
S_c	Superficial liquid saturation
S_p	Bound liquid saturation
t_d	Dimensionless time
H	Cake height
d_h	Hydraulic diameter
ε	Cake porosity
d	Diameter of the particle
K	Cake permeability
σ	Interfacial tension
θ	Contact angle
N_c	Capillary number
B_o	Bond number
FCM	Food contact material
VOC	Volatile organic compound
SVOC	Semi-volatile organic compound
RT	Retention time
Q	Match quality
GC	Gas chromatography
LC	Liquid chromatography
HPLC	High performance liquid chromatography
MS	Mass spectrometry
DCM	Dichloromethane
AS	Antistatic additive
AO	Antioxidant additive
PPA	Polymer processing aid

Chapter 1:
INTRODUCTION

A review article based on this chapter is already published in the international peer journal *Waste Management:*

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1.1.Introduction to plastic materials

The presence of plastics in our society has increased enormously during the last decades reaching almost every aspect of our lives. The emergence of cheap, easy to produce materials with numerous properties revolutionised many industries. Indeed, our modern lifestyle would not be possible without plastics.

Initially, synthetic and semi-synthetic plastics were few and their production were limited. Around 1920, a German scientist Herman Staudinger theorized that these high molecular weight substances were in fact macromolecules formed by covalent bonds. His macromolecular theory was fundamental for the development of new polymers and their applications and, eventually, in 1953 Staudinger was awarded the Nobel Prize for his contribution. Some of the most used polymers such as polyethylene (PE) and polypropylene (PP) were synthetized for the first time between the 30s and the 50s. Others like polyethylene terephthalate (PET) were introduced later (in 1978). Since then, the production of plastics has been constantly increasing. Global production in 2018 almost reached 360 million tonnes, which represents an increase of around 40% over a decade. In Europe (EU28+NO/CH), plastic production has oscillated around 62 million tonnes during the last few years (Plastics Europe, 2019). Although waste management strategies are variable depending on the part of the world, the geographical scope of this Thesis include only Western countries where recycling technologies are more developed.

Plastic materials are usually divided in two main categories: thermoplastics and thermosets. Thermoplastic materials consist of linear or branched chains linked by intermolecular interactions. This is a flexible structure which allows thermoplastics to flow when the temperature is high and to solidify when the temperature decreases. Some of the polymers belonging to this group are polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), and polyethylene terephthalate (PET). Thermosetting polymers present highly cross-linked structures which provide the materials with high mechanical and physical strength and heat stability. Well known thermosets are epoxy and phenolic resins, polyurethanes (PUR) and acrylonitrile butadiene styrene (ABS). These materials are mainly used when heat and chemical resistance is required (e.g., automotive manufacture, construction equipment, electrical components). In this Thesis, the focus has been put on thermoplastics since they can be melted at high temperature and cooled repeatedly. On the contrary, thermosets cannot be reshaped with temperature. So that, they are usually used as fillers after grinding or pulverization, or they are sent to incineration with energy recovery (Pickering, 2006).

Plastic products can be produced in a rigid or a flexible form. Some plastics, such as PE and PP, change from rigid to flexible form when the thickness of the material decreases. The thickness of monolayer plastic flexible films ranges between 20 and 200 µm. The flexibility of other materials like PVC depends on the additives used during processing. Flexible films are becoming increasingly popular, especially in the packaging sector, due to their versatility, lightness, resistance and printability. A current trend, for example, is to substitute rigid beverage packaging by flexible materials with the aim to reduce virgin plastic consumption and some negative effects on the environment. For instant, the production of plastic films requires less energy and the emissions produced during transportation are lower owing to their lightness. Hence, the market share of flexible materials is continually growing (Televisory, 2019). In Western and Central Europe there are already more than 1200 flexible plastic extrusion companies (AMI, 2017). Due to the increasing production of flexible plastics and consequently its presence in the waste stream, in this Thesis the focus has been mainly put on plastic films waste treatment. Moreover, the recycling rates of these materials are lower compared with rigid products. Therefore, most of the plastic films waste is sent to incineration and landfilling.

1.2.Main thermoplastic materials

According to the European demand, PE, PP, PVC, and PET are the most used plastic resins (Plastics Europe, 2019). Altogether, these polymers cover almost 67% of the total demand (Figure 1.1). It is important to know the main characteristics, properties, and applications of plastic materials in order to perform a comprehensive and accurate study on waste management systems and technologies.

1.2.1. Polyethylene

Polyethylene is one of the most versatile polymers owing to a varying degree of chain branching. The polymerization conditions can be altered to produce the desired structure, which largely determines the properties of the material. There are two types of PE: branched and linear. Both of them can be composed of one type of monomer (homopolymer) or by two or more types of monomers (copolymer). Branched PE has lower crystallinity because of irregularities in the structure leading to lower density.is commonly known as low density PE (LDPE). This polyolefin is characterized by its clarity, flexibility, and heat sealability. Also, it presents a good water vapour barrier but poor gas barrier properties. It is widely used as plastic bags, agricultural films and shrink and stretch wrap films, among others (Selke and Culter, 2016a). Another branched PE is the medium density PE (MDPE), which is to some extent stronger, less flexible and less permeable that LDPE. It is used for gas pipes and fittings, sacks, crew closures, and shrink and packaging films when blended with LDPE (Vasile and Pascu, 2005). Two types of copolymers are usually used in LDPE polymerization: olefinic compounds and compounds with polar functional groups.

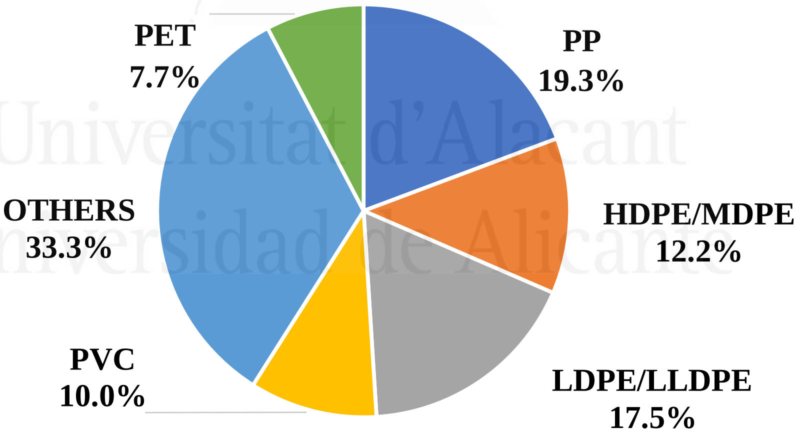

Figure 1.1. *European demand of plastic resins in 2018 (EU28+NO/CH). (Plastics Europe, 2019).*

Unlike branched PE, linear PE (such as high density PE or HDPE) presents nearly totally linear structure and higher crystallinity. The HDPE is less transparent, has good mechanical and moisture barrier properties, but it is a poor barrier to oxygen and organic compound. Rigid HDPE is widely produced for milk and juice bottles, and personal and home care products containers (detergents, bleach, shampoo, etc.). Flexible HDPE films are used in flexible packaging applications (cereals, snack food, etc.) and carrier bags (Selke and Culter, 2016a). The use of alkene monomers during copolymerization introduces very short branches in the linear structure of the polymer resulting in a lower density. The polymer obtained in this way is called linear low density PE (LLDPE) or ultra-low density PE (ULDPE). Compared with the branched LDPE, the density is very similar but some mechanical properties (tensile strength, tear properties, elongation, and puncture resistance) are improved in LLDPE. Nevertheless, it is less flexible and less transparent. Finally, the use of metallocene catalysts for copolymerization of LLDPE has become very popular due to better control on comonomer content and improved molecular weight distribution. As a result, the polymer presents better mechanical and heat seal properties. Common LLDPE applications are packaging films, stretch and cling films, and heavy duty shipping sacks (Vasile and Pascu, 2005). Figure 1.2 shows the family of polymers based on the ethylene monomers.

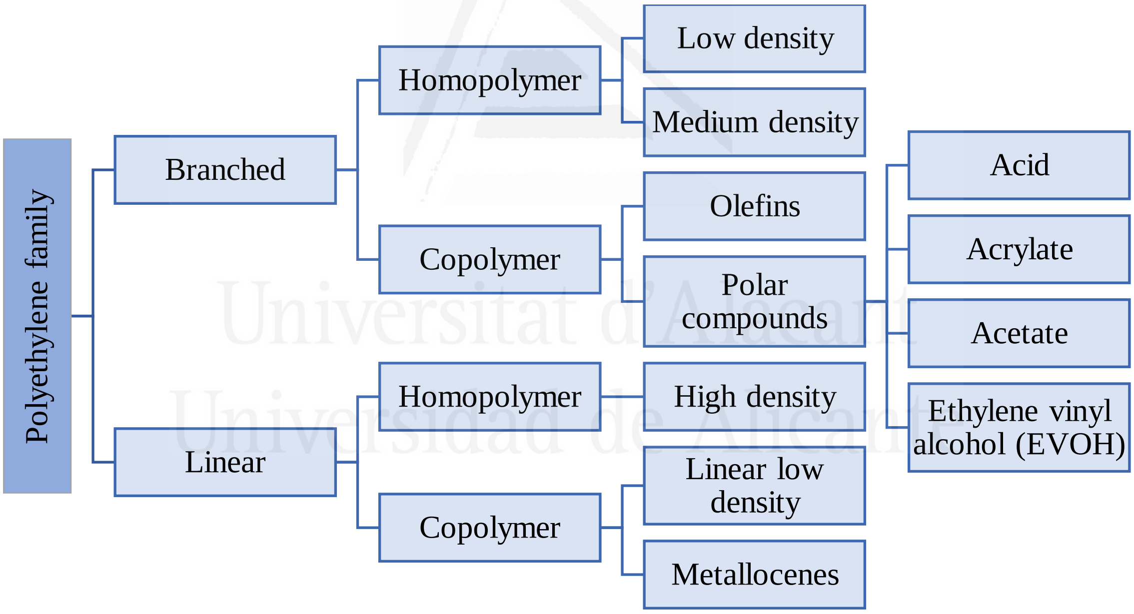

Figure 1.2. Polyethylene family diagram. (Selke and Culter, 2016a).

1.2.2. Polypropylene

Polypropylene is the second most used thermoplastic largely owing to its good resistance to chemicals and mechanical fatigue, as well as stress cracking. The polymer presents high crystallinity when the methyl groups are placed on the same side of the chain (isotactic PP). Compared with PE, the PP has lower density and higher melting point (Table 1.1). Processability of the polymer permits obtain both flexible and rigid plastics. The PP film can be oriented to improve optical characteristics (clarity and gloss) and strength, which is ideal for the packaging application. It is widely used in dry food packaging owing to its high moisture barrier properties. Rigid PP presents high heat resistance, therefore microwave containers, sterilizable materials, pipes, and automotive parts are some examples of products made of this polymer. The copolymerization of PP is achieved by addition of ethylene groups leading to lower crystallinity of the polymer. Consequently, the material obtained is clearer and more flexible suitable to be used in medical and food packaging, shrink wraps, etc. (Selke and Culter, 2016a).

1.2.3. Polyvinylchloride

This is a tough and rigid polymer with small degree of crystallinity formed by vinyl chloride monomers. It has a higher melting temperature and higher density than PE and PP (Table 1.1). It can be found either as a rigid container or as a flexible film depending on the additives used in the processing stage. The main applications of rigid PVC are window frames, pipes, garden hoses, floor and wall covering, etc. (Plastics Europe, 2019). Flexible PVC is commonly used as cling film and food packaging (Leadbitter, 2003). The material can be transparent and opaque, and it has good barrier properties. Nevertheless, its use as food contact material has been challenged due to the migration of residual vinyl chloride monomer, which is a carcinogen (Selke and Culter, 2016a).

Table 1.1. *Density and melting point temperature of common thermoplastics.*

Type	Density (g/cm^3)	Melting temperature (°C)
LDPE	0.910-0.925	105-115
MDPE	0.925-0.940	120-129
LLDPE	0.910-0.925	112-124
HDPE	0.940-0.965	120-138
PP	0.890-0.902	160-175
PVC	1.100-1.500	160-210
PET	1.290-1.400	245-265

1.2.4. Polyethylene terephthalate

PET when processed is a semi-crystalline polymer formed from terephthalic acid or dimethyl terephthalate, and mono ethylene glycol monomers. It has a higher melting temperature and higher density than the polyolefin-based materials (Table 1.1). The degree of crystallinity depends on the processing conditions and defines the application of the material. Mechanical stretching of the polymer permits chain orientation and formation of small crystals when the material is quickly cooled. Oriented PET is transparent, tough, and possess good oxygen and carbon dioxide barrier properties. Accordingly, its largest application is in soft drink bottles and other types of bottles and containers. In a film form, biaxially oriented PET is an excellent odour and gas barrier and it is widely used in multilayer packaging (Selke and Culter, 2016a). A thermal crystalized PET is opaque, more rigid and it is used in applications where the product must withstand moderate temperatures. This is achieved by slow cooling stage where larger crystals are formed (De Cort et al., 2017). The main advantage of PET over other plastics in food packaging applications is its high inertness, i.e., low interaction and mass transfer between the package and the foodstuff (Welle, 2014).

1.3.Plastic products manufacturing

The manufacturing of plastic products is comprised of several processes starting with raw materials in pellet form and finishing with the product´s desired shape according to each application. The transformation of plastic materials is also known as a converting process. The first stage in the majority of applications is extrusion, which consists in melting the plastic pellets and shape the melt using pressure. The equipment used is an extruder formed mainly by a feed hopper, a barrel containing a screw, and a die or nozzle (Figure 1.3). The main functions of the extruder are to fully melt the material, to ensure uniform melt temperature and compositions, and to generate sufficient pressure for downstream processes (Selke and Culter, 2016b). The extrusion temperature varies depending on the resin type (Table 1.2).

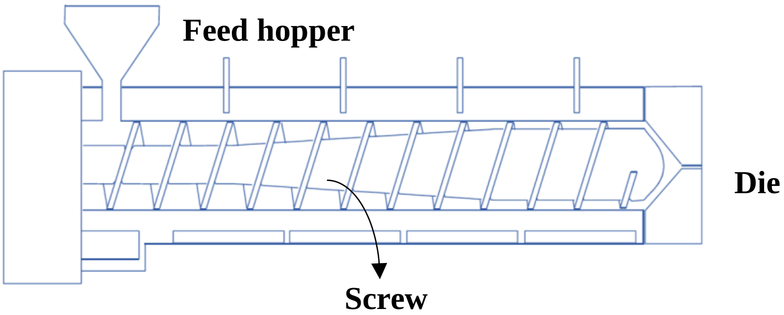

Figure 1.3. *Simplified scheme of a single screw extruder. (Selke and Culter, 2016b).*

The main plastic films converting methods are blown film extrusion and cast film extrusion. During blown film extrusion the melt is forced though a tubular die and it is inflated with air to form a thin film bubble. The blown film is usually quenched with air, however, water quenched systems also exist. The plastic material obtained is in general denser, with higher haze, less transparency, and higher barrier properties compared with other technologies. It is widely used for packaging applications. Regarding cast film extrusion, the melt goes through a flat die adopting its final shape and it is rapidly quenched on a rotating cold roll. As a result, the film has smaller degree of crystallinity, thus it is softer and more transparent. Nevertheless, mechanical properties are lower since the film is oriented only in one direction. The main applications are food and textile packaging, flower wrapping and substrates extrusion for more complex films production (Morris, 2017).

Table 1.2. *Extrusion temperature range for common thermoplastics.*

Polymer	Recommended extrusion temperature (°C)
LDPE	150-315
LLDPE	190-250
HDPE	200-280
PP	205-300
PVC	160-210
PET	260-280

Both technologies are used for coextrusion of multilayer films, which are composed of several layers of different materials. The coextrusion consists of joining different polymer layers, each one melted previously in an individual extruder, before exiting the die. Multilayer films have gained popularity mainly in the packaging sector owing to the combination of different materials, which transfer a specific property or properties to the product. Other technologies, such as coating and lamination, exist to produce multilayer structures. There are two main differences with the coextrusion. Firstly, non-polymeric substrates (paper, aluminum foil, fabric, etc.) can be incorporated and, secondly, the layers are joined together after the extrusion. In the extrusion coating and extrusion lamination, the extruded thermoplastic material is placed on the substrate or between two layers acting as an adhesive. Finally, in the adhesive lamination, as its name suggests, a liquid adhesive is used to join the layers (Selke and Culter, 2016b).

Converting operations also include printing, trimming, hole punching and die cutting, among other. Printing is of great importance, especially in the packaging industry. The main printing technologies used in this sector are rotogravure, flexography, and digital printing. The types of ink available on the market are diverse including solvent based, water based, and radiation (UV/EB) cured. Nevertheless, the composition is common containing resins (polyamide, nitrocellulose, polyurethane, etc.), pigments, colourants, and other additives (Abdel-Bary, 2003). The printing can be placed on the outer layer of the film, which is known as surface printing. Or, in the case of multilayer structures, the printed film can be laminated to another film by the ink side (i.e., the ink remains between layers). This process is called reverse printing.

1.4.Waste generation

Plastic materials have brought numerous benefits to our society, nevertheless, they contribute enormously to waste generation and environmental pollution mainly because of rapidly increasing production, and lack of defined and efficient waste management strategy. Global plastic waste generation in 2015 reached 302 million metric tonnes. Geyer et. al. estimated that around 6300 million metric tonnes of cumulative waste have been generated between 1950 and 2015, only 20% of which has been incinerated or recycled and the rest is accumulating in landfills or in the environment (Geyer et al., 2017).

Plastic waste is usually divided into three groups depending on its origin: post-industrial, post-commercial, and post-consumer. The first one is generated during plastic converting processes such as extrusion, trimming, die cutting, etc. The plastic scrap generated in the converting companies represents between 5-12% of the total production. The advantage is that scrap is usually homogeneous, composed of single type of polymer, and clean. The post-commercial waste is mainly composed of secondary and tertiary packaging from retail industry area (clear bags and stretch wrap films). Its composition is usually known and homogeneous and the level of contamination is low. Finally, post-consumer or domestic waste gathered by municipal collection schemes is a mixture of different polymer types, dirty, highly contaminated and has suffered degradation during the service life (RSE USA, 2017).

In the EU28+No/CH, 29.1 million tonnes of post-consumer plastic waste have been collected in 2018, of which more than 60% corresponds to plastic packaging applications (Plastics Europe, 2019). Around 32.5% of the waste has been recycled, mainly PET and HDPE bottles from domestic sources (Bio Intelligence Service, 2011). In the U.S. and Canada around 34 million tonnes (U.S. short tonnes) of plastic waste (including residential, commercial and institutional sources) have been produced in 2015. Only 9.1% of this waste was recycled, 15.5% was incinerated and 75.4 was landfilled (EPA, 2018). In the U. S, plastic waste represents about 13% of the municipal solid waste stream (EPA, 2014) and in EU-27 the percentage varies among countries from 5% in Germany and Finland to 15% in Switzerland (Hannequart, 2004). In 2017, it has been estimated that in Norway and Sweden more than 50% of plastics in household waste are films, mainly PE films (Mepex Consult AS, 2017). Flexible films are usually considered as a non-recyclable fraction of the domestic waste stream; thus, they are sent to landfill or energy recovery. Agricultural plastics are also considered post-consumer waste. In the EU, around 615,000 tonnes are generated every year (Bos et al., 2008).

Post-industrial waste generation is more difficult to calculate since the scrap does not enter the usual waste management systems, but rather it is re-processed in the same facilities or sold to the private sector. Nevertheless, assuming that the converting companies generate around 10% of plastic scrap and knowing the plastic production in Europe (section 1.2), it can be estimated that around 6.2 million tonnes of scrap is generated every year. This represents around 0.22 million tonnes per country. The recycling rates are generally very high reaching 95% in the UK and almost 100% in

Germany (Bio Intelligence Service, 2011). The situation is very different in U.S. and Canada where the potential for clean and homogeneous waste to be mechanically recovered is completely unexploited.

Regarding post-commercial waste, there is no official record of waste generated or collected mainly because companies usually prefer not to spread this information. To get a rough estimation, data on LDPE films demand and commercial films share on the market can be used. In EU, around 9 million tonnes of LDPE and LLDPE have been consumed in 2018 (Plastics Europe, 2019). If it is assumed that all this plastic was used to produce films and that commercial films cover 38% of LDPE/LLDPE (PRE, 2019) applications (including shrink wraps, stretch films, and other bags and sacks), the resulting amount of waste will be below, but close to 3.5 million tonnes. The average recycling rate of commercial packaging in 2008 was 34.7% (Bio Intelligence Service, 2011). The recycled pellets can be used for stretching films, shopping bags, agricultural films, and also for rigid applications such as plastic lumber, pipes, automotive parts, etc. (RSE USA, 2017).

1.5. Waste management

Waste management includes several activities such as minimization, collection, sorting, treatment, transport and disposal. In this Chapter, only collection, sorting, and treatment will be assessed since it is considered that these processes show the biggest difference between flexible and rigid plastics.

1.5.1. Collection

Post-industrial and post-commercial waste is usually collected directly on site by private companies and transported to the recycling facilities. Converting companies sell their waste when it is clean and homogeneous, thus obtain some benefits. Nevertheless, in the case of multilayer films where non-compatible materials are combined, the waste-producing company must bear the costs of its management.

Post-consumer waste collection is a more complex task. Different collection schemes have been adopted worldwide, including curbside (or door-to-door), bring points, civic amenities, deposit and return, and retail return systems (Figure 1.4). In curbside collection systems, the waste is collected directly from the householder buildings or houses. It is usually applied in the US for recyclables materials recovery. There are two types of residential collection of recyclables: single-stream and dual stream. The first one consists of mixed collection of all potentially recyclable materials (paper, glass, plastics, and metal) placed in the same bin. The second one implies the segregation of recyclables into paper and cardboard in one bin, and the rest of materials (i.e., plastics, glass, metals, etc.) in another bin. Both approaches have been adopted with success in other countries such as Canada, Australia, United Kingdom, Ireland and France (Cimpan et al., 2015). However, plastic films are rarely allowed to be discarded with rigid plastic waste. To increase plastic films recycling rates, in the US, it is quite common to find the so-called retail return systems which encourage consumers to return recyclable materials (e.g. plastic bags and other wraps) to specific stores and supermarkets for recycling. A study from 2017 reported that there are about 18,000 drop-off sites where solely clean and dry polyethylene films are accepted (RSE USA, 2017). For instance, Bag-2-Bag programme aims to the collection of plastic retail bags, dry cleaning bags, cereal box liners, paper towel and toilet paper wrap, among others. Collected bags and wraps are cleaned, processed and re-granulated for new bags production (Novolex, 2017).

Figure 1.4. *Different waste collection options. (a) Curbside collection in Erlangen (Germany). (b) Bring point collection in Alicante (Spain). (c) Multimaterial collection system in Lausanne (Switzerland). Pictures by Andrea Cabanes and Oksana Horodytska.*

In E.U. waste collection for recycling differs across the Member States. Door-to-door and bring point collection systems are the most popular. In bring points collection systems different waste streams are disposed in special containers placed near residential areas in order to be accessible for citizens. In populated areas, bring points are more frequently used than curbside collection, due to lower transportation costs. The systems where different recyclables are placed in an individual bin or container are called single fraction.

On the contrary, in co-mingled fraction two or more recyclables are collected together (Seyring et al., 2015). Also, deposit and return systems are very popular in several counties, for instance, Germany, the Netherlands, and Denmark, among others. This system aims to encourage the citizens to return a specific product after its use, therefore, ensuring high purity and homogeneity of the waste stream. In return, the users receive incentives such as money or discounts. But for now, mainly rigid containers are allowed, whilst flexible films are not contemplated. Germany and Austria are considered to have the most comprehensive gathering of lightweight packaging in contrast to abovementioned France and the UK. Nevertheless, in the UK, drop-off sites (or retail return systems) for post-consumer household films have become quite frequent ensuring separate collection and higher recycling rates. Moreover, around 71 local authorities have plastic films collection programmes (AMEC and Axion Consulting, 2016). Plastic films waste is generally easier to include in co-mingled than multi-streams systems. But then downstream recovery facilities prepared to accept this material are required. Finally, civic amenities are similar to bring point systems where all recyclable fraction are accepted, and the citizens must deliver the waste by their own means. In Table 1.3, a summary of different collecting schemes in EU Members is presented. It is indicated if some film collecting strategy is available. The information in the table represents the general situation in each country, taking into account that it can change in some municipalities.

Table 1.3. *Separate collection schemes and programmes in the EU (Cimpan et al., 2015, Haig et al., 2012, Seyring et al., 2015).*

Collection type		**Materials**	**EU countries**	**Film collection**
Door-to-door	Single fraction	Paper	Austria, Belgium, Germany, Denmark, United Kingdom	
		Glass	Netherlands, Finland, Slovenia, Luxemburg	
		Plastic	Austria	Comingled flexible and rigid plastic collection
			Netherlands	Comingled flexible and rigid plastic collection
			Denmark	Not collected
			Latvia	Not collected
		Metal	Finland, Netherlands, Denmark	
		Bio-waste	Austria, Belgium, Germany, Finland, Netherlands, United Kingdom, Czech Republic	
	Co-mingled	Plastic and metal	Belgium	Not collected
			Germany	Collected with mixed plastics
			France	Some collection with mixed plastics
			Italy	Rigid and film plastics are collected separately
			Slovenia	Collected with mixed plastics
			Bulgaria	Not collected
			Luxemburg	Not collected
			Cyprus	Not collected
			Hungary	Collected with mixed plastics
		Paper, plastic and metal	Romania, Malta	Not collected

Table 1.3. *Waste collection schemes and programmes in the EU (Cimpan et al., 2015, Haig et al., 2012, Seyring et al., 2015). Cont.*

Collection type		**Materials**	**EU countries**	**Film collection**
		Glass, plastic and metal	United Kingdom	Not collected
		All in one bin	Greece	Not collected
			Ireland	Collected with mixed recyclables
Bring points	Single Fraction	Paper	Czech Republic, France, Spain, Portugal, Sweden, Poland	
		Glass	Austria, Czech Republic, Belgium, Denmark, Germany, Spain, France, Italy, Portugal, Poland	
		Plastic	Sweden	Collected with mixed plastics
		Metal	Austria, Estonia, Sweden	
		Bio-waste	Spain	
	Co-mingled	Plastic and metal	Spain	Collected with mixed plastics
			Latvia	Not collected
			Portugal	Collected with mixed plastics
			Croatia	Not collected
			Poland	Not collected
Civic amenities		Metal	Czech Republic, Latvia	
		Metal and bio-waste	Slovakia	
Deposit and return		Plastic	Netherlands	
		Plastic and metal	Norway, Sweden	
		Plastic, metal and glass	Denmark, Germany, Lithuania, Croatia, Estonia, Finland, Iceland	
Retail return system		Plastic	United Kingdom	Plastic (PE) films collected separately

1.5.2. Separation and sorting

Separation is the process of segregation of a waste stream in several smaller streams containing the desired material type, for instance, separation of metals from plastics or paper from containers. The main goal of this stage is to increase the purity and homogeneity of the waste stream. The waste requiring separation is the one coming from the co-mingled collection of recyclables and from mixed collection. The process is carried out in the so called materials recovery facilities (MRF).

Technologies and equipment settled in different MRFs depend on the input waste stream. There are two main types of MRFs. Although every plant is singular due to the diversity of collection strategies in different countries and even in different municipalities. On one hand, the plants that receive mixed-waste from householders are known in Europe as Mechanical-Biological Treatment (MBT) plants because mechanical and biological processes are used. In the U.S. the name is Dirty or Mixed MRFs. The input waste stream consists of organic kitchen waste and recyclable materials. The recoveredmaterials are generally metals, beverage cartons and plastics such as LDPE, HDPE and PET containers. Frequently, the separation of different fractions is carried out manually. However, more automated equipment is being incorporated. For instance, a trommel is used for size separation, and magnets and eddy current systems for ferrous and aluminium metals removal (Montejo et al., 2013). Flexible films are currently considered contaminants and removed from the conveyed stream mainly because they can block or damage the line. Unfortunately, rejected plastic films are frequently sent to landfills with other rejects from the plant.

On the other hand, the segregation of recyclable materials from separate collection programmes is performed in single-stream or clean MRFs. The input waste consists of co-mingled recyclables (paper/cardboard, plastic and glass). In the first stage of the process, plastic bags are removed from the waste stream. The most common method is still manual sorting by well-trained, experienced operators. But different mechanical equipment is on the market intended to facilitate the task. For instance, bag-splitters can be used to open and empty the plastic bags (Haig et al., 2012) and vacuum systems are installed for collecting and conveying handpicked material (Impact Air Systems, 2017). In the next stage, flexible films (2-dimensional materials) must be separated from rigid heavy items (3-dimensional materials). Well-known technology for this purpose is ballistic separation. The 3D heavy components are collected at the bottom of an inclined screen while 2D lightweight parts are pushed to the upper end of the separator. An alternative technology is an air separation where the light materials are conveyed in an air stream and the heavier ones stay in the conveyor. Both ballistic and air separators have the same limitation; they cannot distinguish between different lightweight material (e.g. paper and plastic film) (RSE USA, 2017).

After separation of different recyclable materials in individual streams, sorting processes are needed to separate the plastics according to resin type, polymer grade, colour, etc. The aim of this stage is to prepare the materials to meet the market acceptance criteria. Again, manual sorting is widely used, for instance, to separate coloured and clear films or to remove non-polyethylene plastics. The costs can be prohibitive due to film lightness and low bulk density. Therefore, optical sorting technologies like Near Infrared (NIR) system are developing rapidly. This technique is based on the wavelengths reflected by the material after NIR light illumines its surface. The results of a recent study have shown that PP, PE and mixed polyolefins can be identified by NIR (McKinlay and Morrish, 2016). These materials can be extracted from the waste stream using flotation or hydrocloning but cannot easily be separated from each other (Barlow and Morgan, 2013). Furthermore, different multi-material structures such as PET/PE and PP/PE were detected. NIR is currently the most promising technology for efficient flexible films sorting. However, there are a few limitations: neither thin coating layers (e.g. PVdC) nor black parts can be detected, and the equipment cannot distinguish between surface and reverse printing. In the case of laminated films with an aluminium layer, induction sorters with metal detection or eddy current separators can be used (McKinlay and Morrish, 2016).

1.5.3. Plastic solid waste treatment

According to (Dijkema et al., 2000) ‘‘the waste is only a temporary attribute of a resource”. Plastics waste has a high potential to become a resource again after several suitable processes. The total number of possible material cycles depends on the degradation of the material through all stages of its life cycle. The EU through the Waste Framework Directive (2008/98/EC) (Council

Directive, 2008) has established the following waste management hierarchy: prevention, reuse for the same purpose, recycling, energy recovery and disposal. Nevertheless, the Directive cannot be strictly applied to manage all kind of waste due to the diversity of materials, level of contamination and degradation of waste from different sources. In this Chapter the focus has been put on recycling and energy recovery since these processes implies waste treatment. Prevention and reuse are related to the product before it becomes waste, and disposal should be minimized.

Recycling can be split in two groups: mechanical and chemical. Although, energy recovery is sometimes denominated as recycling (quaternary recycling), in this Thesis it is considered as a separate waste treatment method. Different terminology exists to define waste treatment processes, which are summarized in Table 1.4.

Table 1.4. *Plastic recycling terminology (Hopewell et al., 2009).*

ASTM D7209 – definitions (withdrawn 2015)	Equivalent ISO 15270 standard definitions	Other equivalent terms
Primary recycling	Mechanical recycling	Closed loop recycling
Secondary recycling	Mechanical recycling	Downgrading
Tertiary recycling	Chemical recycling	Feedstock recycling
Quaternary recycling	Energy recovery	Valorisation

Mechanical recycling is carried out by different mechanical processes and the polymer structure of the product remains unchanged. This is a widely applied technique because of its technical and economic feasibility. There are two possible configurations (closed loop and open loop) that are differentiated by the final application of the recycled product. In closed loop processes, the quality and properties of the recycled material are very close to the original material. Therefore, it can be used as feedstock for high added-value products manufacturing. The input waste is usually a single type of polymer and slightly contaminated. The process consists of waste transformation by means of extrusion where the plastic is melted and re-granulated. So, this recycling method is also called re-extrusion. Sometimes decontamination operations prior to the re-granulation can be included. The perfect example of closed loop recycling is the treatment of PET bottles to produce new bottles. The open loop mechanical recycling consists of several mechanical processes such as shredding, washing, drying and re-granulating, among others (Figure 1.5). The input waste is a single type of polymer material or a mixture of compatible plastics. The waste stream usually contains some contaminants (e.g., undesired plastic additives, inks, remnants of incompatible polymers) that worsen recycled plastic properties during reprocessing, making it suitable only for less demanding applications (trash bags, pipelines, products for agricultural applications, etc.). Continuing with the PET examples, the recycled pellets from beverage bottles are frequently used for non-food applications such as clothes.

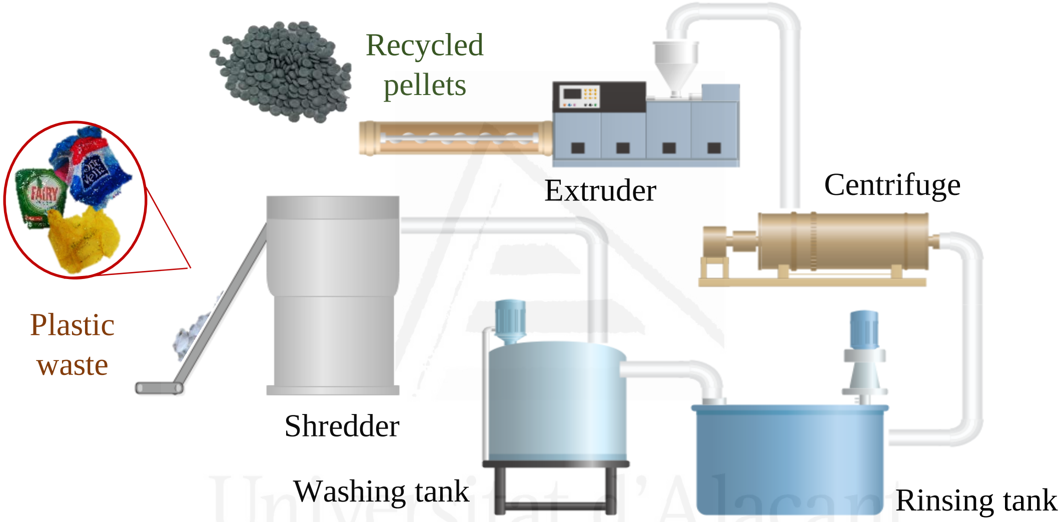

Figure 1.5. *Simplified diagram of a conventional mechanical recycling process. Source: own elaboration (made with Edraw Max).*

Chemical recycling is based on breaking down processes of the polymer structure to obtain the original monomers or other valuable chemicals (Achilias et al., 2007). The recycled products can be used as feedstock for new polymer production (Hamad et al., 2013). Depolymerization (methanolysis, glycolysis and hydrolysis), partial oxidation (gasification) and cracking (pyrolysis) are the principal chemical recycling processes. Pyrolysis (thermal and catalytic) is widely used for polyolefins and other addition polymers recycling (Panda et al., 2010). The products of pyrolysis are liquid and gas that enclose the desired substances. The costs of separation operations are often too high, and the recycled products are used as fuel. Although the quality of chemically recycled products is higher than in mechanical recycling, the technology is still underdeveloped, and the energy costs are too high.

Energy recovery from plastic waste is carried out by incineration (combustion). Waste incineration is carried out for electricity production and district heating with efficiencies of above 90% (Technical University of Denmark, n.d.). Plastic products are a high yielded source of energy materials due to their high calorific value. After incineration, the volume of waste can be reduced by 90–99%, which is a big advantage when there is space scarcity and landfilling is limited. Moreover, chlorofluorocarbons (CFCs) and other harmful compounds are removed (Al-Salem et al., 2009). Incineration of plastic waste is carried out through various methods. Co-incineration of municipal solid waste with a high fraction of plastic waste is performed by direct one-stage, two-stage and fluidized bed combustion process. In the cement industry, plastic solid waste is frequently used as a fuel in cement kilns to reduce the energy costs. Blast furnaces are also a common destination for plastic waste (Al-Salem et al., 2010). Despite the economic and some environmental benefits, energy recovery treatments are contrary to the circular economy principle which dictates that plastic products should be managed in closed loop systems. Hence, reuse and recycling processes are considered the first option for waste management and energy recovery should be applied to the non-recyclable fraction.

1.6. Plastic films waste treatment

The methods applied for the treatment of plastic films waste are mainly mechanical recycling and energy recovery. Although mechanical recycling is technically and economically feasible, different technical problems arise during flexible films processing. For instance, common issue for plastic recyclers is the presence of ink on film surface that can affect the final properties of the recycled materials. At certain temperatures, the inks volatilize, and the gases produce bubbles and imperfections in the pellets (RSE, 2013). Therefore, the recovered plastic is suitable only for non-demanding products manufacturing because of the dark colour of the pellets. Plastic film recycling differs from rigid plastic recycling mainly due to the low bulk density of the films. Thus, all equipment needs to be properly adapted to flexible films behaviour (Snyder, 2016). Multilayer film recycling has some additional problems such as the large variety of materials used for each layer and their differences in the processing properties, lack of systems for identification of multilayer film and lack of economically viable systems of segregation of the various materials (Tartakowski, 2010).

Waste source largely influences the selection of the waste treatment mainly due to different degree of contamination and dirtiness. Monolayer and multilayer films present different structure and compositions. As a result, they must be treated separately to ensure the highest environmental and economic benefits. In this section, the three waste types have been analysed separately.

1.6.1. Post-industrial and post-commercial waste treatment

Mechanical recycling is currently the most suitable recovery method for post-industrial and post-commercial waste because of the homogeneity and cleanliness of the waste (Aznar et al., 2006). Monolayer films scrap presents the highest recycling rates. In the industry, many converters use developing technologies to recycle their own scrap without leaving their facilities. This type of in-house recycling allows the recovery of material with good properties, suitable for high quality products manufacturing. There are several types of extrusion equipment on the market aimed at re-granulating clean plastic scrap. In this way, converters reduce the volume of waste and decrease the consumption of virgin plastics. However, this closed-loop recycling is only feasible with clear, not printed scrap (Niaounakis, 2020a, Sadat-Shojai and Bakhshandeh, 2011). Printed plastic waste is usually treated by external recycling companies which collect the waste from different converting facilities and recycle the material mechanically in an open loop. More complex extrusion technologies are required to obtain recycled materials from printed plastic waste. Most of them include filtration, homogenization and degassing stages with the final extrusion of recycled pellets (Feichtinger et al., 2015). Unfortunately, some loss of properties occurs and the granules usually present a dark colour (Figure 1.6a). As a result, the final product is only suitable for less demanding applications such as trash bags, pipes, plastic lumber, etc.

Intending to solve the problem of the ink during the plastic recycling, researchers from the University of Alicante have developed an innovative process to remove the ink from plastic surfaces (Fullana and Lozano, 2015) based on the research carried out by Gecol et al. (Gecol et al., 2001, Gecol et al., 2002, Gecol et al., 2003, Gecol et al., 2004). Its technical and economic viability has been proven by setting up a semi-industrial deinking plant (Cadel Deinking, n.d.). The deinking process consists of washing the material with no environmentally hazardous chemicals in a water-based solution. This is closed-loop recycling where the printed plastic films go through several mechanical steps (grinding, deinking, washing, drying and pelletizing) to obtain ink-free recycled plastic which quality is similar to the original plastic (Figure 1.6b). Therefore, recycled pellets can be used for high added value product manufacturing. Although Cadel Deinking´s process has been developed for flexible plastics recovery, it is also suitable for rigid plastic waste. The only limitation is that the ink has to be on the surface. Furthermore, a specific water treatment system has been designed to minimize the water consumption and to recover the deinking chemicals.

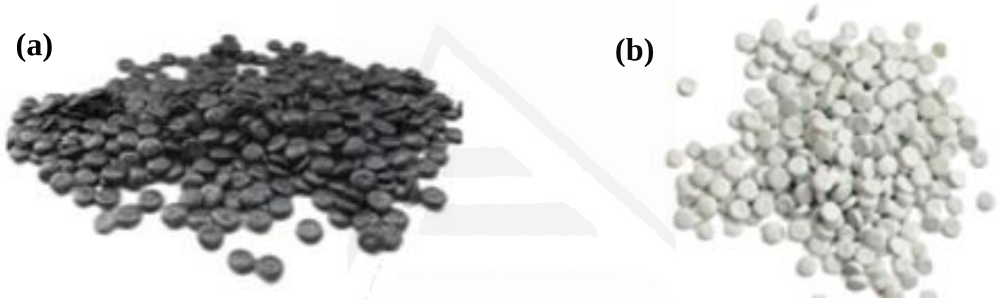

Figure 1.6. *Conventionally recycled dark pellets (a) and deinked clean pellets obtained with the Cadel Deinking´s process (b).*

The use of detergents for plastic films deinking was also described in the Duchenaud Uniflexo patent (Piolat, 2004). In this process, the ink is removed from the unwound film rolls using rotating brushes. Apart from a non-ionic surfactant, the detergent solution contains organic solvents. Despite very high deinking efficiency (99.9%), the quality of recycled plastic decreases notably in comparison with the virgin material (poor mechanical/optical properties and odour). Moreover, scaling-up the process is not feasible due to the use of dangerous products and high cost. An Italian company Gamma Meccanica offers a deinking technology comparable to this patent (Gamma Meccanica, 2016). While most of the printed scrap consists of defective end products (shopping bags, packages, etc.), this process is limited to plastic film rolls. Thus, grinding stage is needed to cover a large number of film waste. In the U.S, Geo-Tech Company provides a technology for plastic coating removal, including inks, paints and labels (Geo-Tech Polymers, n.d.). This process is also water-based and non-hazardous chemicals are used for rigid and flexible plastics recycling. In Brazil, Rhaaplex Company is using a deinking process to recycle plastic films waste (Metalúrgica Rhaaplex, 2011). The patent specifications of this process indicate that the ink and other contaminants are removed through alternating friction system and a solvent-based solution (Haas, 2011). Another technology for deinking and deodorisation of post-industrial polyolefin films has been studied in a European-funded project CLIPP+, where carbon dioxide in supercritical conditions has been used. The results showed that the recycled films could be used in secondary packaging applications (AIMPLAS, 2013).

Plastic retail bags and other wrap films can be recycled into high quality materials suitable for the same application as the original one if the waste is clean and uncontaminated. Conventional recycling processes comprised of shredding, washing, drying, and pelletising are used. The amount of ink on the plastics surface is usually very low, thus deinking process is optional. Nevertheless, other contaminants such as soil, dust and paper labels can reach significant percentage and adversely affect the quality of the recycled pellets. Efficient washing stage and a good melt filter in the extrusion system are paramount to remove the contaminants.

1.6.2. Domestic waste

Flexible film from curbside collection is usually considered as a contaminant, thus it is removed from the waste stream. At best, it is sent to energy recovery but very often it ends up in landfills. The main problem is the mixture of numerous polymer types, film grades, colours, multilayer films, etc. Sorting of the flexible fraction is too costly to make its recycling profitable. When efficient sorting can be achieved, only the single polymer fraction is recycled in an open loop process. Two main end uses for recycled post-consumer films are film and sheet production and composite lumber production (MOORE Recycling Associates Inc., 2017).

The household waste contains a high amount of primary packaging which is usually made of multilayer flexible film. Recycling of multilayer films is considerably more challenging mainly due to the combination of incompatible materials. Consequently, the multilayer films waste is sent to energy recovery or landfilling. A number of recycling technologies are being developed in an attempt to recover the materials. There are three main approaches: compatibilization, delamination and dissolution-precipitation methods. Nevertheless, the viability of plastics recovery from household multilayer films is subject to major advances in the sorting technologies. Indeed, all the technologies developed can be also applied for post-industrial scrap treatment.

Compatibilizers (specific additives, similar to adhesives) are added to the mixture in order to enhance the union between different polymers. (Wyser et al., 2000) studied the recycling of multilayer PP/PET/SiOx films from packaging waste compatibilized with maleic anhydride-grafted polypropylene. The results showed that the mechanical properties of the blend were enhanced at a concentration of 5% wt of the compatibilizer. Mixtures of PE, PA6 and PET can be extruded together with compatibilizers like oxazoline groups, ethylene/acrylic acid copolymer or block copolymer styrene-ethylene/butylene-styrene-grafted-succinic acid (Jeziórska, 2003). (Pawlak et al., 2002) investigated about PET and HDPE blends compatibilized with ethylene-glycidyl methacrylate (EGMA) and styrene-ethylene-butylene-styrene grafted with maleic anhydride and concluded that it is possible to use these blends for film extrusion. More recently, a group of researchers from Brazil completed the study of PET/PE blends by using the design of experiments methodology (Uehara et al., 2015). The factors analysed were the concentration of compatibilizers (EGMA and a copolymer of ethylene-a- olefin grafted with maleic anhydride (PE-g-MA)) and the PET/PE weight ratio. Important petrochemical companies have placed on the market a great variety of compatibilizers. Dow Chemical Company has developed RETAIN^{TM} Polymer Modifiers to make easier the recycling of post-industrial barrier films, containing EVOH or PA (The Dow Chemical Company, 2015). DuPont also offers a range of compatibilizing resins (for instance, Fusabond$^{®}$) for film applications (DuPont, 2017).

Delamination method is based on the segregation of different layers of the film and recycling of the polymers and other materials separately. The adhesive used to join the layers is usually attacked with a solvent to weaken the bonding. Then, the layers are separated by friction. (Fávaro et al., 2013) studied a new process to recycle multilayer food packaging which contains PE, aluminium and PET. Acetone was used to delaminate the multilayer film and PET was depolymerized by ethanol in supercritical conditions. The solvents used were recovered by distillation, so the process can be considered environmentally friendly. (Cinelli et al., 2016) have proposed a new PET/PE multilayer structure with whey protein as a central adhesion layer. Whey protein acts as an excellent barrier against oxygen and moisture, replacing petrochemical non-recyclable materials. The protein layer can be removed by washing with enzymatic detergents containing protease enzymes to separate PET and PE. Another invention proposes the use of alkaline liquor for the recycled PET production from multilayer structures where polyurethane-based adhesives are used (García Fernández, 2013). In general, the main limitation of the delamination methods is the long time needed for the delamination solution to reach the adhesive layer. Researchers from the University of Alicante has solved this problem by introducing a microperforation step before washing (patent application number P201930975). The aim is to create multiple entry points for the solution without changing the properties of the materials. The company Saperatec in Germany started a delamination process at industrial scale focusing on multilayer structures with an aluminium foil. A mixture of water, glacial acetic acid, phosphoric acid, and sodium hydroxide is used as a separation liquid (Lovis and Schulze, 2019).

Selective dissolution-precipitation has gained popularity over the last few years. It is a mechanical recycling method where solvent or non-solvent systems are used to dissolve one material in each step and then recover it usually by precipitation. After the dissolution of the polymer, a separation step such as filtration is necessary (Achilias et al., 2007). Several researchers have investigated the possibilities of this technique over the past 25 years. The dissolution media proposed by different researchers can be xylene (García Fernández, 2011), mixture of an alcohol with water (Michelena et al., 2004), organic solvents (Linder et al., 2004) depending on the target material. A number of patents exists related to this recycling method (Niaounakis, 2020b). In Europe, the German APK AG is running a dissolution-precipitation process at industrial scale to recover plastic materials from mixed waste and multilayer packaging (Wohnig et al., 2018). Also, in Spain, the company Sulayr is successfully recovering PET and PE from multilayer thermoformed trays by using xylene to dissolve the PE (Sulayr Global Service, 2017). The dissolution-based processes are not exclusive to multilayer films. In fact, mixtures of solid plastics can be efficiently separated in case that mechanical separation is not possible.

1.6.3. Agricultural waste

In agriculture, plastic materials are widely used for different applications: greenhouse, low tunnel, mulching and silage films, or pesticide cans and fertilizer bags, among others. LDPE is the most common resin in agricultural film production followed by LLDPE, HDPE and EVA. The thickness of the film differs according to its application. For instance, films with the thickness of 140–200 mm are used for greenhouse covering, 60–100 mm for low tunnels and smaller thickness of 20–50 mm for mulching films (Scarascia-Mugnozza et al., 2012).

Mechanical recycling of agricultural post-consumer films is favoured due to the high amount of homogenous, single polymer waste available. However, still around 50% plastic waste from agriculture is going to landfill, mainly due to its low profitability (Briassoulis, Babou et al., 2013). The film goes through general mechanical operations such as washing, shredding, drying and pelletizing. Mechanical properties of the recycled material depend strongly on the degradation during plastic lifetime and the contamination with soil, sand, organics, or other polymers (Briassoulis et al., 2012). (La Mantia, 2010) studied the possibility to reuse recycled material from greenhouse covering in closed-loop. The best results were obtained with monopolymer blends of virgin and recycled material, and coextruded blends where the recycled material is placed between two virgin layers. Earlier, (Abdel-Bary et al., 1998) achieved to use recycled greenhouse plastic film in a multilayer structure with virgin polymer for the same application. Sometimes, mechanical recycling is too expensive because of high costs of sorting and drying stages or low quality of the input material. In this case, energy recovery is the selected options to avoid landfilling (Briassoulis, Hiskakis et al., 2013).

1.7. Circular economy

Current Linear Economy model based on production, use and disposal of products is not sustainable from environmental point of view, especially in the case of fossil-based non-biodegradable plastics. Several associations and academic institutions have joined forces to develop the idea of new economy model, the Circular Economy (Figure 1.7).

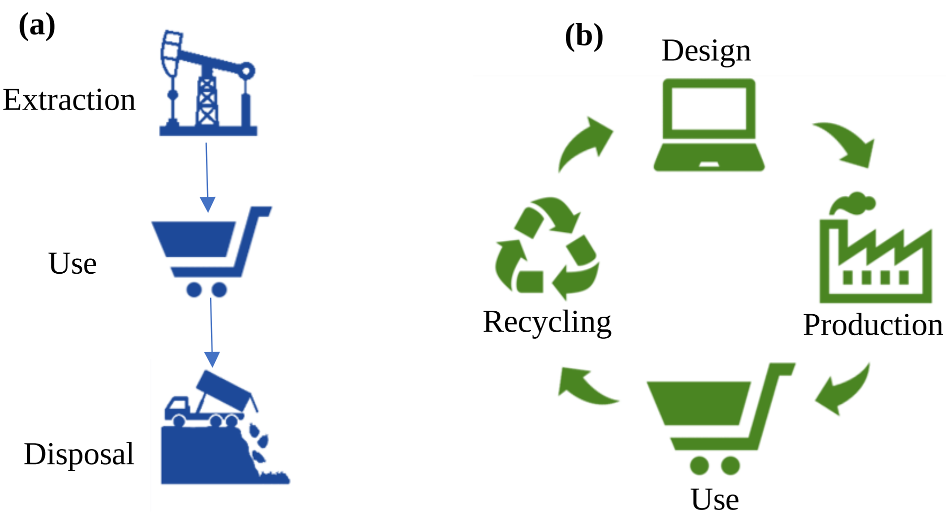

Figure 1.7. *Schematic representation of the Linear Economy Model (a) and the Circular Economy Model (b). (Ellen MacArthur Foundation, 2016).*

The fundaments lie in trying to mimic the natural ecosystems. Zero waste, diversity, use of renewable energy and interaction between systems are the main principles of this economy approach. Furthermore, Webster (2017) states that products, components and material should be kept at their highest utility and value. Regarding plastics and other non-biodegradable materials, the following actions should be taken when the product comes to its end-of-life (in order of preference): maintenance, reuse, refurbishment, and finally recycling. A large volume of plastic products, especially from the packaging sector, have a short service life and cannot be reused or refurbished. These products should be completely recyclable to facilitate its waste treatment. Closed-loop mechanical recycling and upcycling provide the highest economic and environmental benefits. Therefore, the quality of the recycled pellets should be maintained so that they can be used in high demanding applications. By contrast, energy recovery and landfilling must be minimized since these processes do not contribute to the circularity of the products.

The recycling processes can be split in two groups: downcycling and upcycling (Figure 1.8). On one hand, downcycling is a process of plastic waste recovery which results in a reduction in quality of the material (inferior physical properties, dark colours, disturbing odour, etc.). Plastic degradation leads to a reduction in circularity potential, i.e., the ability to recover the material in a closed-loop (Eriksen et al., 2019). Thus, recovered materials are intended for low added value applications (e.g., trash bags, pipelines, agricultural buckets, etc.). On the other hand, during upcycling the quality is improved so that the material is suitable to be used in the same or more demanding application as the original product (Sung, 2015).

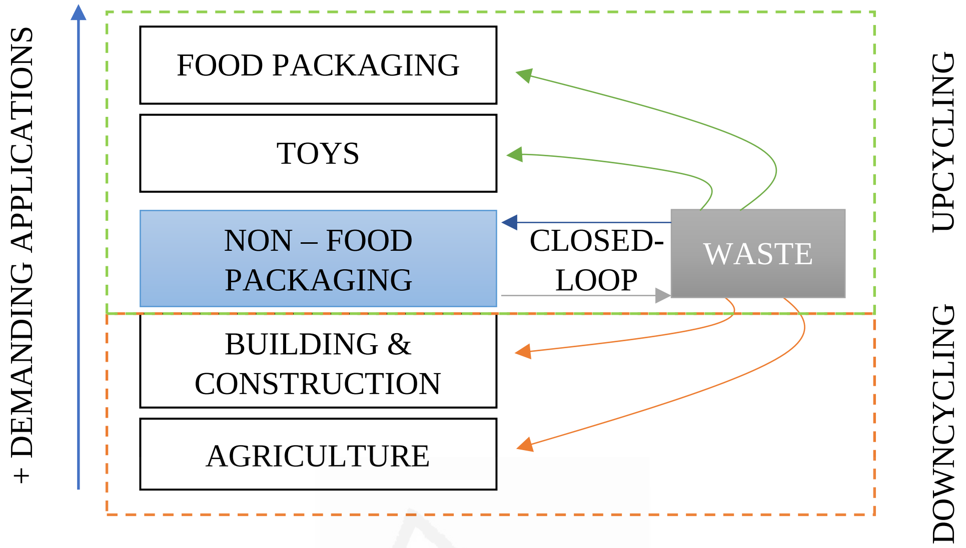

Figure 1.8. *Schematic representation of possible recycling options for plastic waste.*

Therefore, upcycling of plastic waste must prevail over other treatment options in order to preserve the quality of the material and ensure the maximum number of material cycles. This might satisfy the growing interest of the plastic sector in recycled materials. Plastic producers are more and more committed to the green marketing, which is in turn induced by social pressure. For instance, some laundry and home care products manufacturers have committed to use certain percent of a proper quality recycled plastics in their packages (Henkel, 2020).

Currently, upcycling is feasible only with clean, non-contaminated waste. Contamination and inappropriate use of plastic goods significantly diminish material´s quality. Furthermore, degradation also occur during recycling operations. There are different types of plastic contaminants. For example, intentionally added substances (IAS) during manufacturing such as coatings, inks, adhesives, and additives produce defects (bubbles, voids, gels, degradation products, etc.) when the material goes through re-extrusion at high temperature. Other contaminants (labels, missorted non-compatible polymers, etc.) and dirtiness adhere to the plastic products during the use phase and collection. The undesired compounds found in plastics are denominated non-intentionally added substances (NIAS), for instance, additive and polymer degradation products, impurities, external contaminants. The NIAS can migrate from the packaging layer and may constitute a hazard to human health. These substances are hard to detect and, if detected, it is difficult to establish their origin. Therefore, to ensure effective recycling into value-added secondary products, plastic waste requires decontamination. Moreover, upcycling technologies usually require higher energy and resources consumption risking the economic viability of the process.

1.8. Importance of the research conducted in this thesis

Plastic materials and numerous plastic waste treatment methods have been addressed in many studies aiming to mitigate the global problem of plastic trash pollution. Nevertheless, this issue remains highly controversial since there is no defined and common waste management strategy, even within the same country. Recently, plastics recovery initiatives have been given a boost through the implementation of the Circular Economy model, which has been supported by the industry, the administrations and the society. The demand for recycled plastics is expected to increase considerably because many brand owners are starting to use sustainability as a marketing tool.

The data on real recovery of plastic materials (less than 10% of total production) indicate that the recycling sector might not be prepared to meet the demand. The recycling processes require optimization and upgrading. Therefore, there is room for further research. Until now, the focus has mainly been put on rigid products meaning that there is a lack of experimentation on flexible materials recycling. Currently, there is a growing problem of environmental sustainability since the demand for plastic films is increasing rapidly while their recycling rates are still deficient. This results in loss of material resources and environmental pollution.

The implementation of new recycling technologies must be accompanied by a comprehensive study of environmental impacts (positive and negative) associated with this activity. Despite the importance of this topic, the number of studies available in the literature is very low. Furthermore, the Circular Economy model implies the use of recycled products in high demanding application such as packaging. The contaminants and undesired substances present in recycled plastics must be studied to ensure the consumer safety.

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Chapter 2:
OBJECTIVES

The main objective of this thesis is to study the recyclability of plastic products, especially flexible films, in the context of the Circular Economy. The recycling sector must adapt to new quality requirements established by this economy model since conventional recycling methods have proven to be inefficient. There are several challenges which the recycling industry must face, for instance, implementation of innovative environmentally-friendly technologies, process optimization to reduce energy consumption, and consumer safety.

In this thesis, several aspects of plastic recycling in general and flexible films in particular will be assessed. The specific objectives established are:

- To study the environmental benefits of upcycling technologies using life cycle assessment (LCA) methodology and compare the results with conventional waste treatment options. Both post-industrial and post-consumer waste streams will be included.
- To study the appropriateness of traditional LCA for the quantification of environmental impacts in the context of the Circular Economy.
- To detect the weaknesses of the recycling lines and the possibilities for improvement.
- To study the behaviour of flexible plastics and use the results for process optimization, thus operational costs reduction. The degradation of the plastic surface during the service life of a product will be studied to determine if post-industrial and post-consumer waste present different behaviour.
- To assess the possibility of introducing the recycled plastics in high added value products manufacturing in term of consumer safety. The contaminants present in post-industrial and post-consumer waste and their origin will be studied.

The thesis has been divided into several chapters in which the main recycling challenges have been assessed separately.

- **Chapter 3:** *Life cycle assessment of plastic upcycling and comparison with conventional waste treatments*. This chapter is composed of two parts. In the first part, the treatment of printed plastic scrap produced in a plastic film converting company has been assessed from the environmental point of view. In the second part, the environmental impacts of two material cycles (post-industrial and post-consumer waste) have been quantified.
- **Chapter 4:** *Centrifugal dewatering performance in plastic films recycling*. This chapter is also composed of two parts. In the first part, the dewatering of post-industrial plastic film made of high density polyethylene has been studied considering several operational parameters and characteristics of the material. In the second part, other polymeric materials were assessed such as post-industrial polypropylene and polyethylene terephthalate, and post-consumer polyethylene of different types.
- **Chapter 5:** *Non-target analysis of semi-volatile organic compounds (SVOCs) present in recycled plastic*. This chapter has been divided into three parts. In the first part, the main compounds present in four commonly used plastic additives have been analysed. In the second part, the composition of recycled plastics from post-industrial and agricultural sources have been studied. And in the last part, two samples of recycled plastics from domestic waste have been analysed.

Chapter 3:

LIFE CYCLE ASSESSMENT OF PLASTIC UPCYCLING AND COMPARISON WITH CONVENTIONAL WASTE TREATMENTS

Results presented in this chapter have been published in the international peer Journal of Cleaner Production.

O. Horodytska, D. Kiritsis, A. Fullana. Upcycling of printed plastic films: LCA analysis and effects on the circular economy. Journal of Cleaner Production. Online 14 of May 2020, 122138.

Research work presented in this chapter has been partially developed in *the Institute of Mechanical Engineering, École polytechnique fédérale de Lausanne (EPFL), Switzerland*, under the supervision of Prof. Dimitris Kyritsis.

3.1. Introduction

Plastics are versatile materials with numerous properties which make them suitable for a large number of applications. In 2018, the world production of plastics almost reached 360 million tonnes and 62 million tonnes in Europe (Plastics Europe, 2019). The use of plastics has several economic and environmental advantages, especially, compared with other common materials such as glass or metal. The production processes are simple, and the costs are low. As a consequence, a vast number of plastic products are currently designed for a single-use or have a short service life. Plastics have become a cheap and abundant material which is immediately discarded after use. Therefore, the increasing generation and accumulation of non-biodegradable waste is a global issue that requires the attention of politicians, industry and citizens.

In this Chapter, two types of waste are considered: post-industrial and post-consumer. The first one is produced in the converting industry during plastic products manufacturing. It is clean and homogeneous, and its origin and composition are generally known. The second one is domestic waste from municipal collection schemes. It is dirty, highly contaminated and heterogeneous, and its origin and composition are difficult to trace. In Europe, around 6.2 million tonnes of post-industrial scrap are generated every year and about 90% is recovered, mainly, by mechanical recycling (Bio Intelligence Service, 2011). Regarding post-consumer waste, 29.1 million tonnes were produced in 2018 of which 32.5% was recycled (Plastics Europe, 2019). The largest volume of recycled materials corresponds to rigid PET and HDPE. Flexible films from domestic waste are usually rejected from the conveyed stream during the sorting stage and sent to landfills or incineration. On the contrary, flexible films from post-industrial sources present high recycling rates mainly owing to the waste homogeneity and traceability. In the Circular Economy model, two types of recycling are considered: downcycling and upcycling. During downcycling, the materials suffer degradation and loss of quality so that the recycled pellets are used in low demanding applications. In the case of upcycling processes, the quality and properties are maintained similar to the original product so that the recycled plastics can be used in a closed-loop or even in more demanding applications.

Plastic scrap generation in plastic films converting companies reaches around 10% of the total production. Only pure industrial scrap without contaminants such as printing inks, pigments, adhesives, etc. can be recycled in a closed-loop by direct re-extrusion in the same converting plant. The scrap generated during converting operations which take place after the extrusion (e.g. printing, lamination, surface treatment, etc.) are currently recovered in an open-loop. The recycling process consists of reprocessing the materials in the extrusion machine and occasionally a cold wash is used to remove the dust and soil. Nevertheless, the presence of contaminants such as printing inks on the plastic surface decreases the quality of the recycled products (Figure 3.1). During the extrusion, the inks break down due to high temperature and produce volatiles which end up in the pellets and cause imperfections (RSE, 2013). Moreover, the colour of the recycled plastics is usually dark because of the mixture of pigments and colourants. As a result, these pellets are used in low value application (e.g. pipes, trash bags, flowerpots, etc.) producing the downcycling of the plastics. Advanced extrusion machines including filtration, homogenization and degassing stages are required to recycle printed films.

Figure 3.1. *Printed plastic scrap from plastic films converting company.*

High quality pellets similar to virgin plastics can be obtained if the inks are removed from the plastic surface before extrusion. Several technologies exist in the market, but the majority use solvent-based solutions which generate high costs and adversely affect the properties of the material (Haas, 2011, Gamma Meccanica, 2016). Researchers from the University of Alicante have developed an innovative process to remove the ink from plastic surfaces in a water-based solution (Fullana and Lozano, 2015). The technology is currently commercialised by the company Cadel Deinking which has built a semi-industrial demonstration plant in Alicante (Spain) (Figure 3.2). This is closed-loop mechanical recycling where the printed plastic film goes through several steps (shredding, deinking, washing, drying and pelletizing). Deinked pellets can be used for the same application as the original material or in higher added value product manufacturing. Therefore, this process is considered an upcycling.

Figure 3.2. *Cadel Deinking´s demonstration plant in Alicante (Spain). Reproduced with permission of Cadel Deinking.*

Upcycling processes are better aligned with the Circular Economy model, which defends that the plastic waste is a valuable resource with the potential to be recirculated in a new material cycle. To ensure the highest number of cycles, products, components and material should be kept at their highest utility and value (Webster, 2017). Post-industrial waste has a big potential for upcycling because of its characteristics. However, this is not what is happening in the recycling sector because upcycling processes are more complex and energy and resource-intensive. Accordingly, the environmental benefits of plastic upcycling are frequently called into question. As a consequence, downcycling methods are implemented owing to their lower complexity and costs, regardless of the irreversible and meaningful loss of quality (Singh et al., 2017). In addition, the virgin plastic substitution ratio (S) in the downcycling scenario is usually high because the recycled pellets are used in low demanding applications. The virgin plastic substitution ratio is defined as the amount of recycled plastic that can substitute virgin resins over the total amount of plastic necessary for the manufacturing of a product. For example, ordinary garbage bags can contain up to 100% of recycled material. However, when some specific requirement must be met (strength or impermeability) then the substitution rate decreases because virgin plastic must be added to improve the properties of the product. The upcycled pellets are used in more demanding applications (for instance, packaging), which accept only a small content of recycled material in their products since the quality requirements are higher. Finally, post-industrial waste is sometimes sent to incineration for electricity and heat production due to its high calorific value (Zevenhoven et al., 1997, Sahlin et al., 2007).

Life Cycle Assessment (LCA) methodology has been widely used for comparison of environmental impacts of different plastic waste management scenarios (Perugini et al., 2005, Lazarevic et al., 2010, Merrild et al., 2012, Hou et al., 2018). The majority of studies put the focus on mixed waste from domestic sources (Bovea et al., 2010, Song et al., 2013, Fernández-Nava et al., 2014, Erses Yay, 2015). The general conclusion was that sorting processes of mixed waste are required to recover potentially recyclable materials. The remaining fraction should be incinerated with energy recovery. All the authors agree that mixed waste landfilling is the least environmentally friendly option, although global warming impact is very low. Gu et al. have assessed mechanical recycling of several plastic materials made of PE including film scraps, agricultural films and shopping bags from an environmental point of view. The environmental impacts of different process stages, such as washing, sorting, shredding, extrusion and re-granulation were assessed. The results showed that extrusion has the largest impact on the environment (Gu et al., 2017). Nonetheless, mechanical recycling provides considerable environmental benefits compared to virgin plastic production. Lazarevic et al. studied several LCAs to compare reported results of post-consumer plastic waste end-of-life scenarios including mechanical recycling, feedstock recycling, incineration and landfilling. The majority of LCA reviewed indicated that mechanical recycling is the environmentally preferred option. But the results are strongly influenced by the virgin material substitution ratio and the amount of organic contamination (Lazarevic et al., 2010). Rigamonti et al. compared plastic recycling with incineration concluding that LCA results are largely influenced by the assumption of the marginal energy. Thus, electrical substitution from incineration becomes the leading option when marginal electricity is based on coal and marginal heat on a mix of fuels. By contrast, plastic recycling contributes to the largest savings when marginal electricity is based on natural gas (Rigamonti et al., 2014). Laurent et al. have prepared an extensive review of 222 LCA studies focused on solid waste management systems. The authors could conclude that LCA results depend strongly on the specifications, composition, properties, etc. of the waste as well as on the conditions and efficiency of the treatment technologies (Laurent et al., 2014).

In the particular case of plastic waste recycling, the quality of the recovered material and, hence, the intended applications are not usually considered (Huysman et al., 2017).

This Chapter has been divided into two parts. In Part 1, Life Cycle Assessment methodology has been used to study the environmental impacts of the post-industrial plastic waste upcycling process, and to compare them with the impacts associated with the conventional recycling process (or downcycling) and incineration. The influence of assumptions made in LCA has been evaluated, and a few modifications have been suggested to include when plastic waste management options are assessed. In Part 2, the system boundaries have been extended to the end-of-life stage of the secondary plastics produced with the upcycled post-industrial waste. The environmental impacts of two material cycles were computed considering the current post-consumer waste management scenario and then compared with two possible scenarios. The results show the direction in which the waste management strategy should be developed.

3.2. Life cycle assessment of post-industrial waste treatment methods (PART 1)

The LCA analysis has been performed following the ISO 14040:2006 Standard (ISO-Norm, 2006). The main stages of an LCA are goal and scope definition, inventory analysis (LCI), impact assessment (LCIA) and interpretation (Figure 3.3). The goal and scope should define the product system or process to be studied and the importance of the results to the intended audience. The LCI is based on the collection and calculation of data related to the process inputs and outputs. The aim of the LCIA is turning the LCI results into potential environmental impact on selected categories. Different methodologies have been developed to simplify the procedure for the user and to make the results comparable. Some examples are Cumulative Energy Demand (CED) method, ReCiPe and IMPACT 2002+. The selected environmental area and characterization procedure are the main differences among methods (Jungbluth, 2020). Finally, during the interpretation phase, the results and conclusions of the analysis are presented in accordance with the scope and goal definition. During the assessment process, modifications can be made in all stages as more information is acquired.

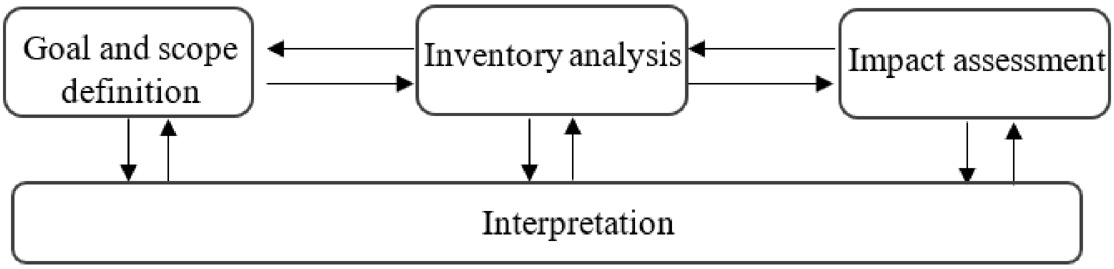

***Figure 3.3**. Life cycle assessment framework. (ISO-Norm, 2006).*

3.2.1. Goal and scope definition

The goal of this study is to determine if the environmental benefits of plastic waste upcycling compensate for the bigger energy and resources consumption required to improve the quality of recycled products. The results are compared with the environmental impacts of conventional recycling (or downcycling) and incineration with energy recovery. The outcomes can be used by converting and recycling companies to select the proper waste management option. The scope is described as follows. The waste is originated in a medium-size plastic film converting company, which transforms the input material (plastic pellets, additives, inks, etc.) into new products. This company produces mainly polyethylene flexible packaging for personal and home care products. The main fabrication stages are blown film extrusion, printing and bag-making. It is precisely during printing and bag-making steps that the printed scrap is generated. Around 8% of their annual production become waste, which the company sends to the waste treatment facilities.

The approach of the study is 'gate to grave' focusing on the end-of-life of printed plastic scrap from converting industry, i.e. waste treatment operations. This study does not consider the whole life cycle of the product as in a ‘cradle to grave’ approach. The system boundaries are drawn around the waste treatment facility where the input is the plastic scrap (Figure 3.4).

The upstream life cycle stages of a plastic product (production phases) are not included since a) plastic scrap is considered as a waste, b) they are similar between the compared scenarios and would not provide any insights for the analysis. Transport of waste has not been considered either because it is similar in all scenarios (i.e., from the company where the waste is generated to the waste treatment plant) nor the impacts associated with the infrastructure (equipment).

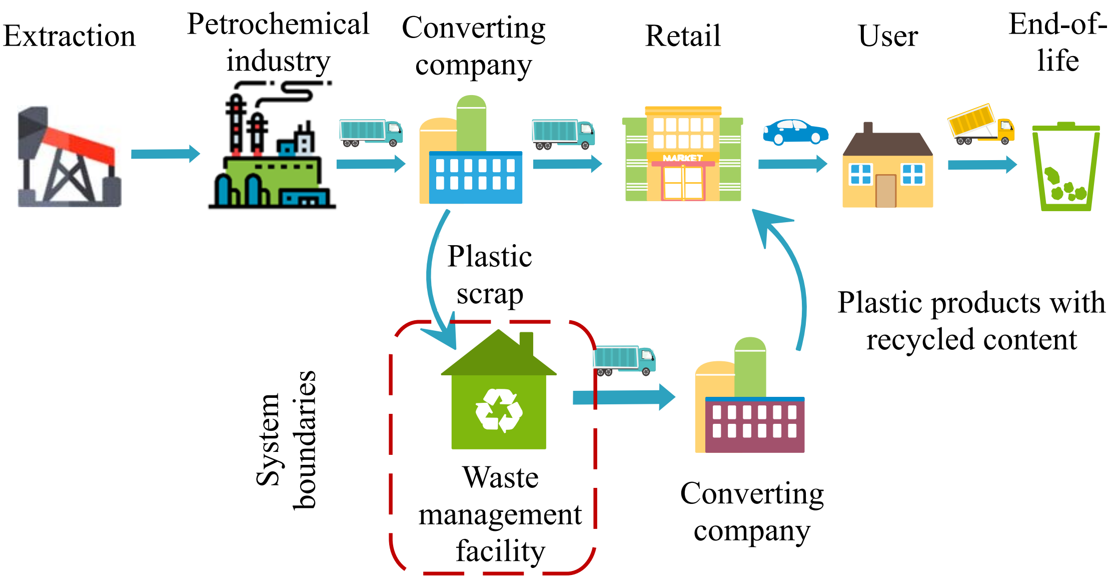

__Figure 3.4.__ Plastic product life cycle and the system boundaries. (Some of the icons used are made by Freepik and Nhor Phai from www.flaticon.com).

In all scenarios, the following aspects have been considered: (a) the manufacture of the auxiliary inputs of the recycling process, e.g. deinking reagents, (b) the operation of the plant, (c) the management of the remaining waste from the recycling process, (d) the use phase of the outputs. To get the most comprehensive perspective, the production chain (when it can be identified) of each direct flow is considered in the computation. The function is defined as the treatment of printed plastic scrap and the functional unit is 1000 kg of plastic waste.

The processes assessed in this study yield to a single product, i.e. recycled plastic pellets in the downcycling and upcycling scenario, and energy in the incineration scenario. All the remain outputs are considered waste. Therefore, an allocation is not necessary to distribute the inputs and outputs of the systems.

3.2.2. Life cycle inventory (LCI)

The main assumptions and data used to quantify the potential impacts of the inputs and outputs of each scenario are described here.

3.2.2.1. Description of scenarios and data inventory

The study focuses on three waste treatment scenarios: upcycling, downcycling and incineration (Figure 3.5). The main products of each process are high quality deinked pellets, low quality recycled pellets with a dark colour and energy. There are no by-products or secondary products, therefore, all the outputs other than the main product are considered residues.

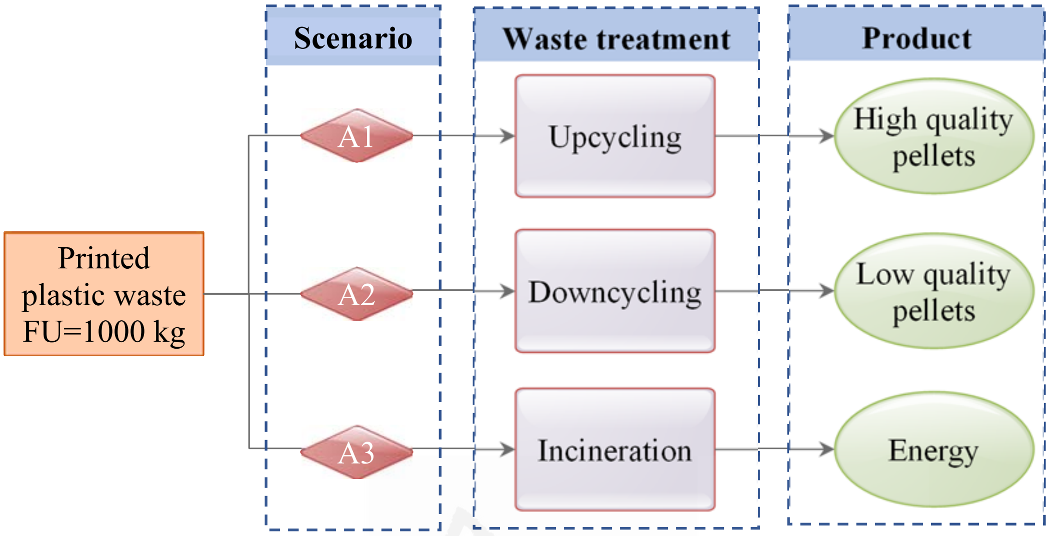

Figure 3.5. *Diagram of the studied scenarios for plastic waste treatment.*

Scenario A1: Upcycling (Recycling with deinking)

Upcycling of plastic scrap is a recycling process with a deinking stage. This is an innovative technology that removes the ink from plastics surface before extrusion. As a result, mechanical and thermal properties of the recycled plastics are similar to the original material owing to minimal degradation during reprocessing. Also, the aesthetical properties are improved since the material has a clear white colour or it is transparent. The ink is removed during the washing stage where some washing agents (detergents) in water-based solution and temperature are used. The mechanical operations included in this scenario are shredding, washing with deinking, drying through centrifugation, extrusion and wastewater treatment (Figure 3.6).

The production capacity of this plant is 500 kg/h. The electricity consumption of the deinking process (including shredding, washing, water heating, drying and wastewater treatment) is around 600 kWh per tonne of input plastic. An average energy need for the extrusion machine is 750 kWh per tonne of input plastic. European electricity mix is also considered in this scenario. As mentioned before, non-hazardous reagents are used for deinking. Also, during the wastewater treatment, specific chemicals are added. In total, the process requires 46 kg of reagents per tonne of input plastic. Despite the recirculation of treated water, it is necessary to add a small quantity of tap water to cover the losses originated during the process (1200 L per tonne of input plastic). The secondary outputs of the plant are wastewater not collected for treatment (44 kg per tonne of input plastic) and an aqueous sludge containing inks (90 kg per tonne of input plastic). The wastewater is purified in a medium-size municipal wastewater treatment plant. And the sludge is managed through municipal incineration as non-hazardous waste. The recycling efficiency is 97% and the remaining part is collected and sent to landfill.

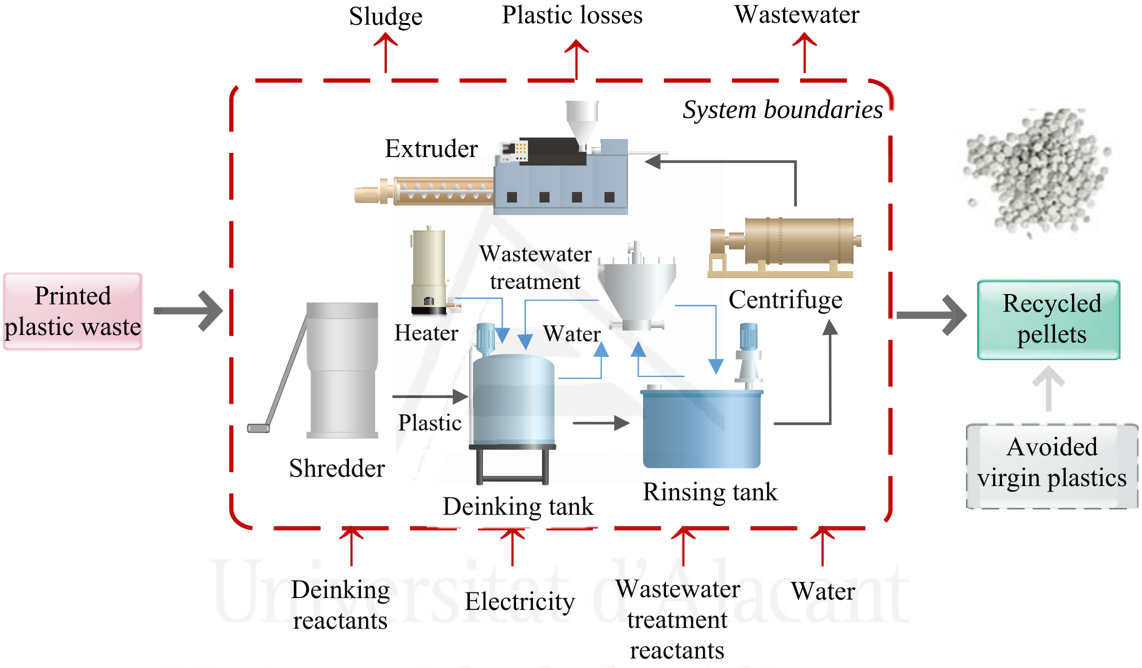

***Figure 3.6**. Overview of system flows. Scenario A1 – Upcycling of plastic waste. Source: own elaboration (made with Edraw Max).*

In this case, the converting company uses the recycled pellets for high added value products manufacturing. The quality requirements are higher and, therefore, the recycled content should be lower than in the downcycling scenario. In this case, the selected virgin plastic substitution rate is 20%.

Scenario A2: Downcycling

Post-industrial plastic waste is usually managed separately from post-consumer streams to avoid contamination. Since the material is homogeneous and its origin is well known, no sorting or separating technologies are required (just some manual sorting). Also, washing is not necessary because the input waste is clean enough for existing technologies. Therefore, the printed waste is directly sent to extrusion. Extrusion machines must be properly conditioned to process heavily printed material. For instance, ultrafine filtration, homogenization and degassing stages are required to ensure the highest quality of the recycled pellets (EREMA, 2016).

In this study, 80% substitution rate has been considered, representing a broad range of possible applications. The energy consumption is limited to the extrusion equipment and it is around 750 kWh. European electricity mix has been considered to determine the burdens associated with energy production. The recycling efficiency varies between 91-99% (Gu et al., 2017). The common efficiency rate of 97% was established for the study (Figure 3.7).

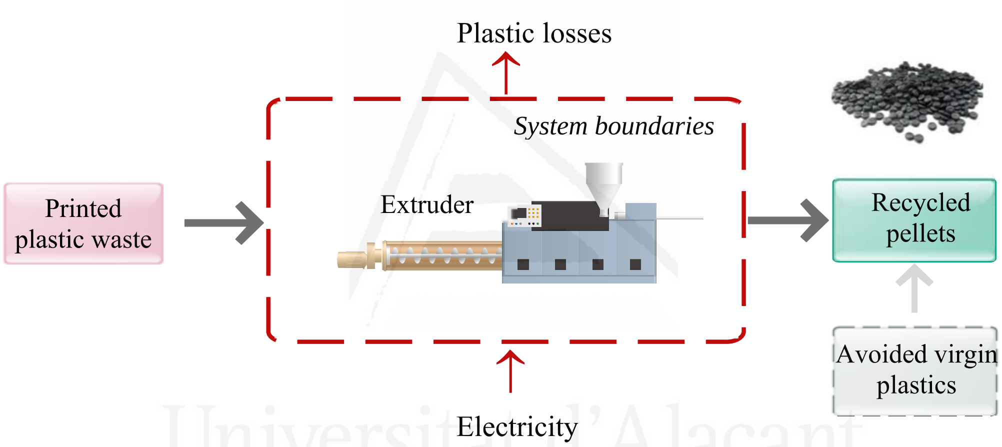

Figure 3.7. *Overview of system flows. Scenario A2 - Downcycling of plastic waste. Source: own elaboration (made with Edraw Max).*

Scenario A3: Incineration

Flexible plastic waste is usually sent to incineration plants along with the municipal solid waste stream. This operation is well described in the Ecoinvent 2.2 database (disposal, polyethylene, 0.4% water, to municipal incineration [kg]), which contains the data required for the LCA analysis. The calorific value of plastic films is reported to be 41.41 MJ/kg (Asamany et al., 2017). And the energy obtained is used to produce electricity (21% of efficiency) and heat (74% of efficiency) (Merrild et al., 2012). Therefore, incineration is more beneficial in cold climate zones.

The most relevant LCI data have been summarized in Table 3.1.

Table 3.1. *LCI data for the three studied scenarios.*

	Downcycling	**Upcycling**	**Incineration**
Energy (kWh/tonne plastic)			
- Deinking	-	600	-
- Extrusion	750	750	-
Reagents (kg/tonne plastic)	-	46	-
Water (L/tonne plastic)	-	1200	-
Residues (kg/tonne plastic)			
- Wastewater	-	44	-
- Sludge	-	90	-
Substitution ratio (%)	80	20	-
Process efficiency (%)	97	97	
- Electricity	-	-	21
- Heat	-	-	74
Calorific value (MJ/kg)	-	-	41.41

3.2.2.2. Data sources and data quality

The data used in scenario 1 and 2 come from an existing recycling plant located in Alicante (Spain). It is assumed that the data can be extended to any part of Europe due to the type of technology. Regarding scenario 3, Ecoinvent 2.2. database, which is widely recognized due to a large number of high quality processes, has been used. Additional data were obtained from research papers published in Q1 peer-reviewed journals. The data have been validated in regard to temporal, geographic and technological representativity.

3.2.2.3. Sensitivity analysis and model simulations

Certain parameters described in data inventory section were assumed for this study but may change from application to application. The most important assumptions made are the virgin plastic substitution rate in the recycling scenarios, the market share of recycled pellets and the substituted material for energy production in the incineration scenario. Several simulations were carried out to determine the influence of these parameters on the LCA results.

3.2.3. Life cycle impact assessment (LCIA)

LCIA methodology IMPACT 2002+ vQ2.2 (version adapted by Quantis) has been used to connect the LCI results to the corresponding environmental impacts (Humbert et al., 2012). This methodology is a combination of the classical impact assessment and the damage oriented methodologies. The evaluation of the potential environmental impacts is performed in two steps. First, the elementary flows identified during the LCI analysis are associated with a number of impact categories at the midpoint level. Some midpoint categories are human toxicity, aquatic ecotoxicity, aquatic eutrophication, global warming, non-renewable energy, etc. The impact on each category is obtained through a characterization factor expressed in kg-equivalents of a studied substance compared to a reference substance. Secondly, all the midpoint categories are grouped into four damage categories (the end-point in the cause-effect chain): human health, ecosystem quality, climate change and resources.

Different units are used to express the impact in selected categories. Disability-Adjusted Life Years (DALY) is used in the human health category and represents the disease severity, considering both mortality and morbidity. In other words, the number of DALYs represents the number of years of life lost over the overall population (not per person). The midpoint categories included in the computation are human toxicity, respiratory effects, ionizing radiation, ozone layer depletion and photochemical oxidation. The ecosystem quality is expressed in Potentially Disappeared Fraction of species over a certain amount of square metre during a certain amount of year ($PDF \cdot m^2 \cdot y$). It is the sum of aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification/nutrification, land occupation, and, aquatic acidification, aquatic eutrophication and water turbined. The unit used in the climate change category is kg equivalent of carbon dioxide, which is used as a reference substance. The midpoint category used is the global warming potential. Finally, in the resources category, MJ is used to express the energy extracted or needed to extract the resource. Two midpoint categories are considered here: non-renewable energy consumption and mineral extraction.

The environmental burdens of the recycling processes have been determined as a difference between the negative impacts from the recycling operations (i.e. because of use of energy or chemicals) and the avoided negative impacts associated with the production of virgin plastic (i.e. non-renewable resources consumption). The results are shown as positive and negative potentials (positive and negative values in the graphs). A positive potential indicates a burden to the environment (negative environmental effect or impact), while a negative potential indicates environmental savings (positive environmental effect or impact). The avoided consumption of virgin plastics at a converting company depends on the efficiency of the recycling process and the substitution rate. The impacts of the incineration treatment have been calculated using the municipal waste incineration data from Ecoinvent 2.2. and subtracting the avoided impacts of using renewable and non-renewable sources (European energy mix) for electricity production and natural gas, burned in cogeneration, for district heating. In the EU, fossil fuels are still the major source of energy representing more than 70% of the gross inland consumption (Directorate-General for Energy, European Commission, 2018).

The LCA software Quantis Suite 2.0 and Ecoinvent 2.2 has been used for computing the impacts of the studied processes.

3.2.4. Results of the LCA of plastic films waste treatment methods

Results indicate that, at a converting company level, the upcycling process appears to be the worst waste management option for all impact categories assessed (Figure 3.8). It has a negative environmental impact on human health, ecosystem quality and climate change. It shows some benefits regarding resource conservation. However, the savings are around 30 times lower than for downcycling. These negative results for the upcycling process can be attributed to the difference in substitution rate and a greater need for resources (e.g. energy, water and chemicals). The recycled material from the downcycling process substitutes a higher amount of virgin plastic due to more forgiving applications of the product. Therefore, it produces a positive effect on resource conservation, climate change and human health.

This approach also shows the benefits of plastic waste incineration over recycling processes (Figure 3.8). The high heating value of polymeric materials makes them attractive for electricity or heating production avoiding the use of such environmental pollutants as fossil fuels.

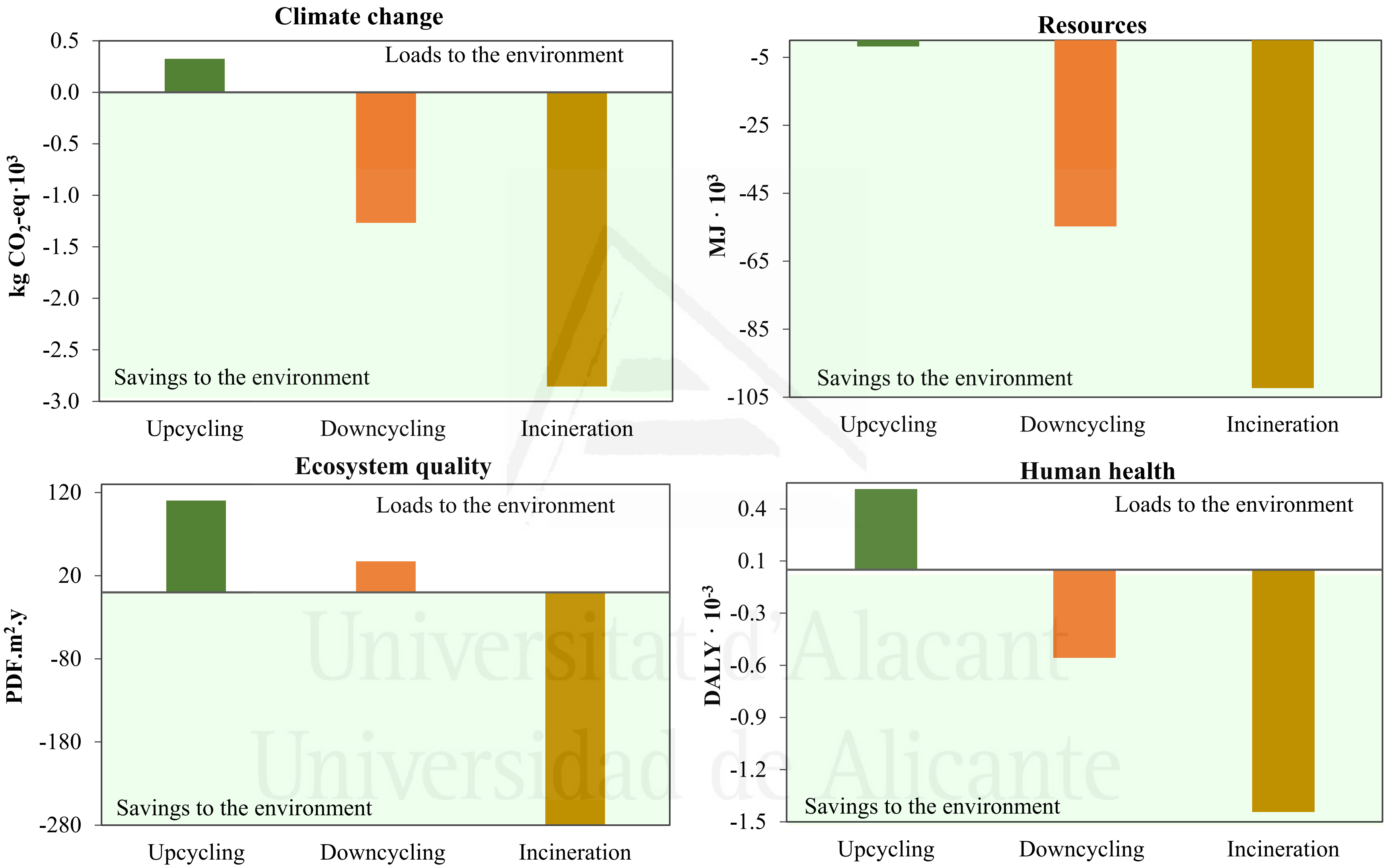

Figure 3.8. *Environmental impacts of the three plastic scrap treatment scenarios on four impact.*

Therefore, it generates a positive effect on resource conservation and climate change. Also, the absence of operations which consume energy and materials combined with efficient treatment of gas to remove air pollutants contributes to increasing the positive effect on human health and ecosystem quality. Despite the described environmental savings, incineration is contrary to the circular economy principles and the quality and potential of plastic waste is not considered. Moreover, saying that plastic waste substitutes fossil fuels is not totally correct because conventional plastics are obtained from oil, natural gas, or coal. Therefore, incinerating plastic waste means burning fossil resources that had been diverted for materials production.

The elements in the upcycling scenarios which contributes positively to the total impact are reactants, energy consumption, and residue generation to a lesser extent. The avoided production of virgin polymers counteracts the burdens to the environment. It is observed that the energy consumption causes the highest impact (Figure 3.9). Therefore, optimization of recycling processes to reduce energy requirements will contribute to decreasing the negative effects on the environment.

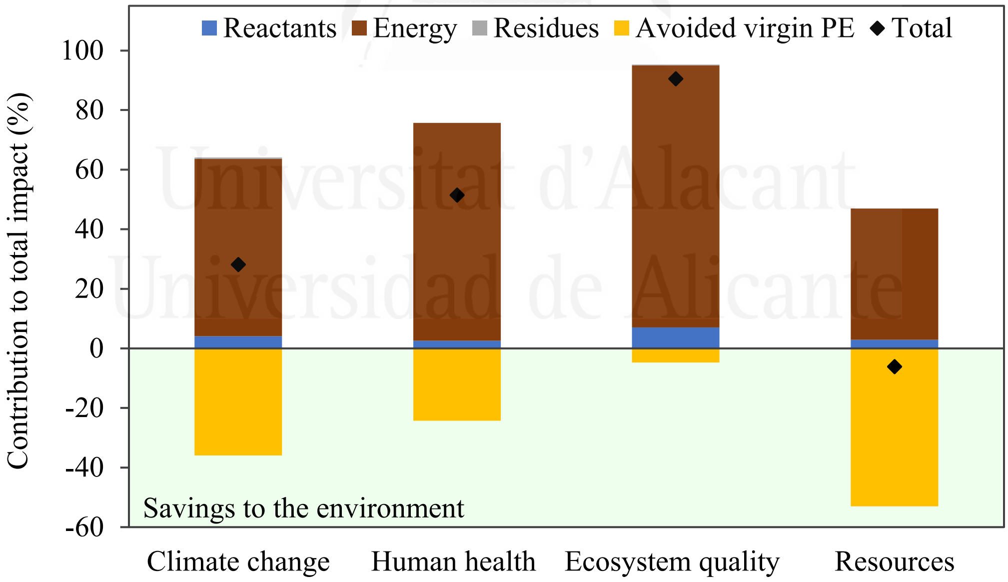

Figure 3.9. Contribution of each element to total impact (%) for the four damage categories in the upcycling scenario with S=0.2.

In conclusion, the results shown in Figure 3.8 lead one to make decisions which go against the circular economy principles and the EU waste hierarchy. The reason for this is that the assumptions made in the LCA do not represent the studied systems fairly. A deeper analysis of the problem reveals that two modifications should be included in the initial approach.

Firstly, if the LCA analysis is based on the virgin plastic substitution rate, important parameters such as the quality of the recycled pellets and the intended applications are not considered. As a result, the recycling option in which poor quality pellets suitable only for low demanding (usually single-use) products are obtained seems to be more environmentally beneficial than the recycling process that produces high quality recycled resins. In this study, it is suggested to include the market share where the plastic products can be introduced.

Secondly, if it is assumed that the recovered energy from incineration substitutes the energy from fossil fuels, then recycling will surely be a less favourable option. This is because fossil-based plastics have a high content of feedstock energy (i.e. heating value) since polyolefins are mainly produced from hydrocarbon feedstocks diverted from energy production. In comparison, the energy requirements for virgin PE production are usually lower. For instance, (Vlachopoulos, 2009) estimated the process energy requirements for LDPE at 28 MJ/kg, which is around 1.5 times lower than the heat value of LDPE (the value used in this study: 41.41 MJ/kg). Therefore, the energy saved by combustion is usually higher than the energy saved by avoiding virgin granulates production. So that the scenario with fossil fuels substitution will surely be more beneficial. However, the energy for electricity or heat production can be obtained from sources different from fossil fuels. The circular economy strategy promotes the use of renewable energy which should predominate in the near future. Hence, fairer energy substitution criteria should be implemented when recycling and incineration scenarios are compared.

3.2.5. Sensitivity analysis

3.2.5.1. Influence of the virgin plastic substitution ratio

The environmental impacts of the recycling methods strongly depend on the virgin plastic substitution ratio. Therefore, a sensitivity analysis has been performed to assess how this parameter affects the benefits and burdens of the upcycling scenario. The chosen ratio values are 20%, 40%, 60% and

80%. The last one is equal to the substitution ratio in the downcycling scenario.

The results show that the environmental benefits increase with the substitution ratio, which was to be expected (Figure 3.10). The upcycling produces a positive environmental effect on climate change when the substitution ratio is higher than 40%. The emissions are reduced by around 130% when the ratio changes from 20% to 40% and continue to decrease with higher ratios (around 250% from 20% to 60% of substitution and near to 400% from 20% to 80% of substitution). The benefits in the resources category also decrease. For instance, the positive effect increases around 10 times when the substitution ratio varies from 20% to 40%, around 18 times from 20% to 60% and 27 times when the ratio reaches 80%. Regarding the ecosystem quality category, the upcycling continues to produce a negative effect even when the substitution ratio reaches 80%. The reduction achieved by increasing the ratio is considerably lower than in other categories. The difference between 20% and 40% of virgin plastic substitution is only 5% and it increases to 10% and 15% when the ratio changes to 60% and 80%, respectively. This could be influenced by the data associated with the virgin plastic production in the Ecoinvent database. Finally, there is a change from negative to positive effect in the human health category when the substitution is higher than 60%. The variation between the studied ratios is around 47%, 94% and 141%. Despite the increasing benefits of the upcycling scenario, downcycling seems to be more environmentally beneficial than upcycling even when the same substitution ratio (80%) is considered.

In sum, the virgin plastic substitution ratio has shown a big influence on the environmental impacts of the recycling scenario. Therefore, high substitutions ratios must be implemented in the plastic sector to achieve bigger environmental benefits. To do so, the quality of the recycled pellets must be considerably improved.

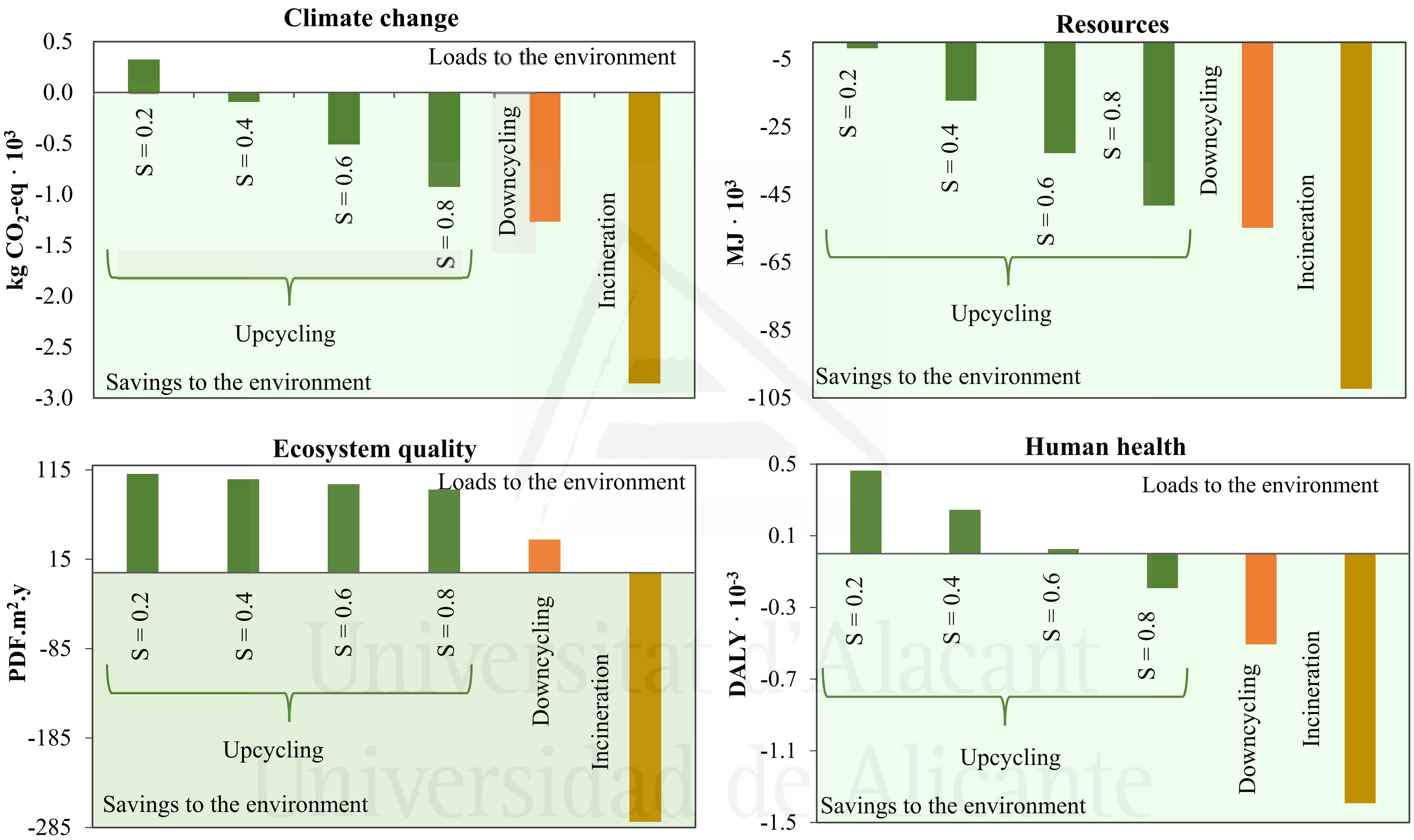

Figure 3.10. *Environmental impacts of upcycling with different substitution rates compared with downcycling and incineration. At converting company level.*

3.2.5.2. Influence of recycled products quality and their target market

The quality of the recycled products influences the environmental impacts of the recycling processes. A sensitivity analysis of this parameter has been carried out by studying the market share of the applications where the recycled pellets can be used.

In section 3.2.4, the avoided burdens have been calculated based on the virgin plastic substitution within the limits of a converting company. To determine the global environmental impacts, the boundaries should be extended to the entire market of plastic products. In this way, the quality of the recycled pellets plays a pivotal role in determining the global virgin plastic substitution potential. This is due to different quality requirements that vary depending on the intended applications. High quality pellets can be used in a larger number of applications; thus, its market share is higher. Therefore, the total avoided production of raw plastics is determined as a product of the amount of waste, the efficiency of the recycling process, the substitution rate (S) and the market share (MS).

European market of LDPE films can be divided into a number of sectors. So far, recycling companies have earmarked the post-industrial plastic recyclates for low demanding applications because this one was the only market which has been accepting a recycled content in its products. However, the current trend in the plastic sector is to introduce recycled content in high quality applications so that the target market for recovered materials expands. To achieve this, innovative recycling technologies are needed to preserve the quality of the plastic material regarding properties, appearance, odour, etc. Conventional dark coloured pellets from downcycling processes are suitable for building and construction, automotive and other less demanding applications, which together represent 24% of the LDPE market (Eriksen et al., 2019). On the other hand, it is assumed that deinked pellets owing to their higher quality can be used for all applications from food packaging to electronics or building materials. So, its market share reaches 100% (Figure 3.11).

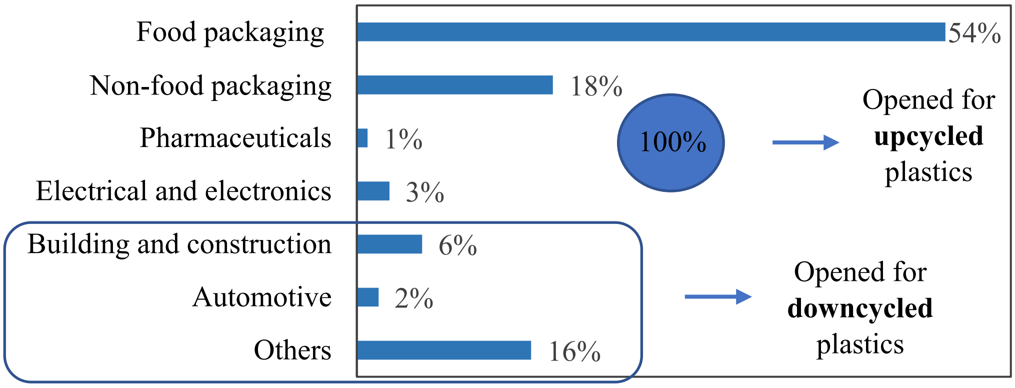

Figure 3.11. *European market share (%) of LDPE film (Eriksen et al., 2019).*

Several virgin plastic substitution rates have been included in the study of the upcycling scenario. Different results than in section 3.2.4 were obtained since the potential of the recycled material to substitute virgin plastic is calculated based on the entire market (Figure 3.12). The environmental savings of the downcycling process decrease for climate change from 1266 $kgCO_2eq$ to 24 $kgCO_2eq$ and for resources from 54,700 MJ to 6615 MJ. The impact on human health changes from positive ($-5\cdot10^{-4}$ DALY) to negative environmental effect ($1.7\cdot10^{-4}$ DALY). Finally, the negative effect on ecosystem quality increases from 37 $PDF.m^2.y$ to 55 $PDF.m^2.y$. Even so, the upcycling process with 20% of substitution appears to be less favourable than the downcycling. This scenario shows higher environmental burdens on climate change, ecosystem quality and human health. Also, the savings accomplished in resource conservation are lower. However, this perspective changes when the substitution rate is higher than 40%. For instance, for climate change and resources categories, the use of 40% of recycled content produces a positive environmental effect (negative impact potential) and both values are above the levels of the downcycling process. Regarding ecosystem quality, the negative environmental effect decreases with the increase in the substitution rate. Nevertheless, these values remain higher than in the downcycling scenario due to the use of chemical agents during the deinking operation. For human health category, 60% of recycled content is necessary to decrease the negative effects below the level of the downcycling. It is possible to produce savings to the environment if the substitution rate increases over 60%.

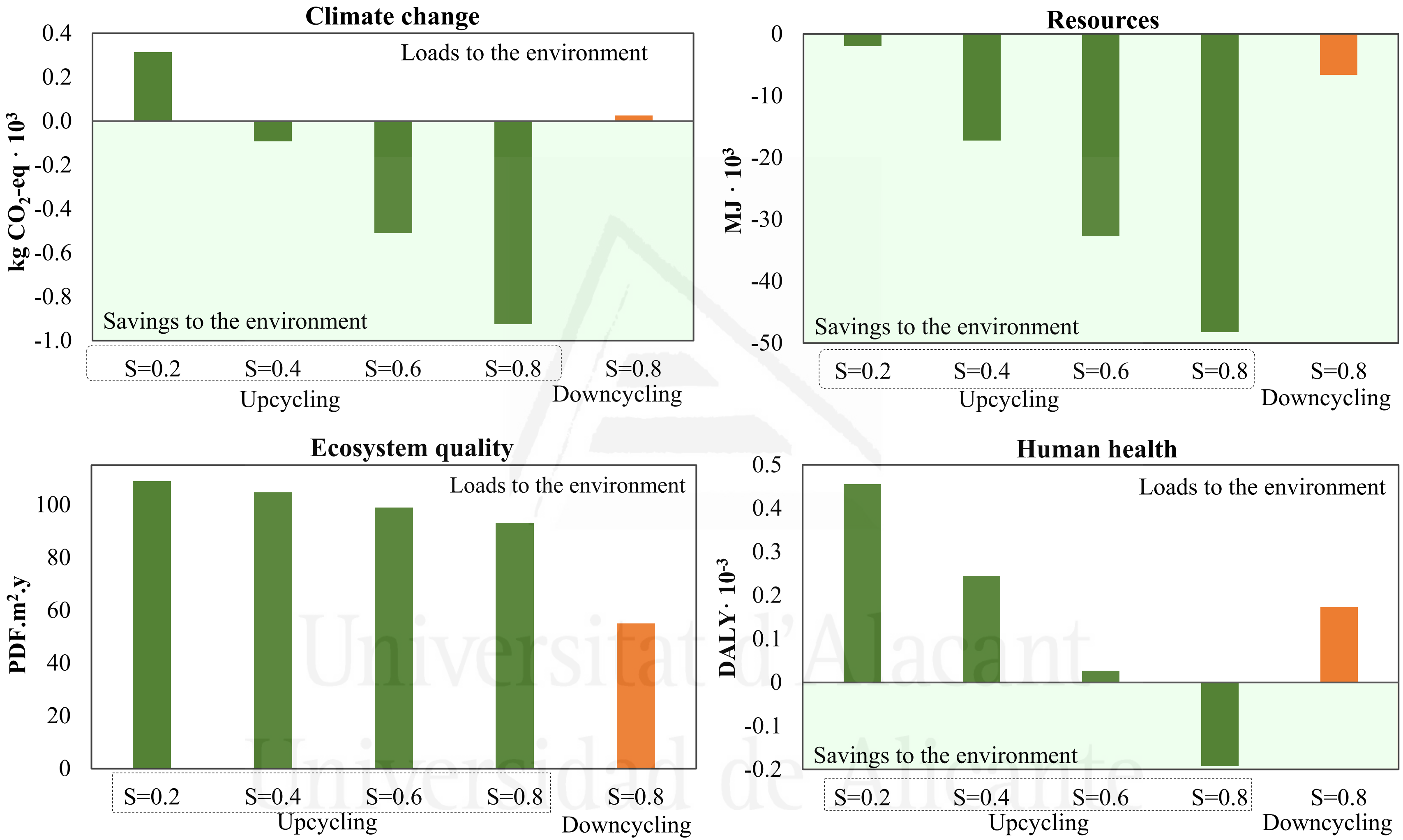

***Figure 3.12**. Environmental impacts of upcycling and downcycling considering the market share (MS upcycling=1; MS downcycling=0.24). Influence of increasing substitution rates in the upcycling process included.*

Therefore, the environmental benefits of the upcycling process are revealed when the avoided virgin plastic production is computed considering the global market. This approach takes account of the quality of the recycled plastic and the value of the products produced using recycling content. The additional effort that recycled materials upgrading requires is offset by the expansion of the target market. For instance, deinked clean pellets can be used for packaging manufacturing meanwhile conventional dark pellets are only suitable for less demanding applications. Moreover, if the more clean and homogeneous waste stream is diverted to new markets, then post-consumer plastic waste with lower quality can be introduced more easily for more forgiving applications.

3.2.5.3. Influence of the source of substituted energy

As mentioned in section 3.2.4, the electricity and heat must be produced from renewable sources according to circular economy principles. Therefore, in LCA analysis the energy obtained during plastic waste incineration should substitute energy from non-fossil sources. In this study, three examples of renewable energy have been assessed: biogas from agricultural plants, hydropower and solar energy. The environmental impacts in the four studied categories are shown in Figure 3.13.

This approach shows that regarding the climate change category, upcycling is the most beneficial scenario. Production of energy from renewable sources does not emit carbon dioxide to the environment. So, its substitution would be senseless. The effects on the other impact categories vary depending on the energy source. For instance, incineration with substitution of biogas and photovoltaic energy is more beneficial for natural resources conservation category. This can be explained with the fact that both sources require the use of extensive areas of land and, in the case of solar cells, exhaustible resources such as silica are consumed. The use of land can also explain the positive effects of these energy sources substitution on ecosystem quality. Regarding substitution of hydropower energy, the environmental savings on this category are much higher probably due to the loss of aquatic habitat, harm to the fish population, deterioration of the landscape, etc. related to this source. Finally, three scenarios produce a negative effect on human health indicator: upcycling, incineration with hydropower energy and solar energy substitution .

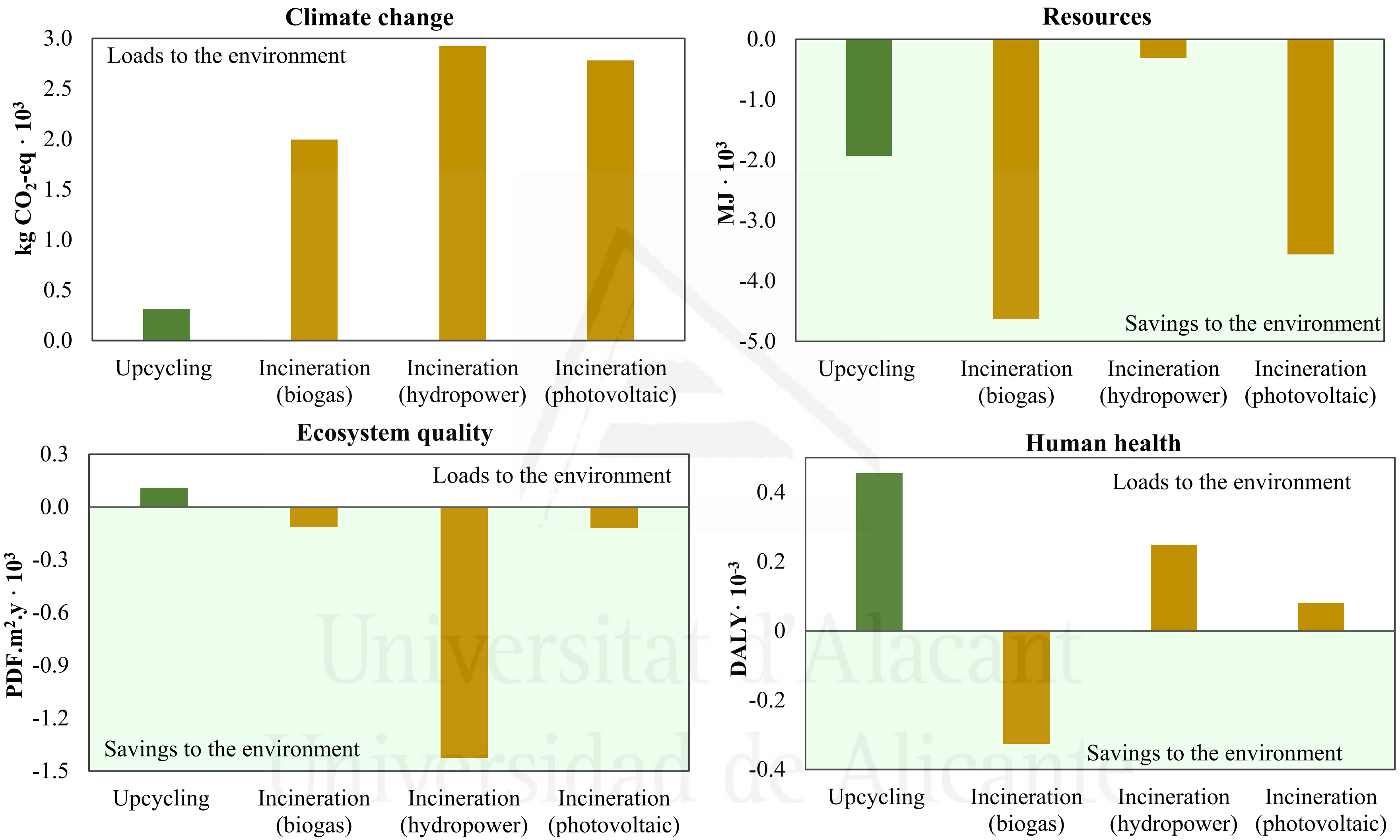

***Figure 3.13**. Environmental impacts of upcycling considering the market share compared with incineration substituting renewable energy sources.*

The burdens of the upcycling process are related to the use of electricity obtained from fossil fuels (European energy mix). And the savings due to hydropower and solar energy production are not enough to counter the emissions originated during plastic waste incineration. On the other hand, the production of energy in agricultural biogas plants affect negatively human health. This is possibly caused by the use of pesticides, fertilizers, etc., and also by the emissions from biogas combustion. As a result, its replacement by incineration produces a positive effect.

In sum, the upcycling process presents a clear advantage in the climate change category over incineration with the substitution of energy from renewable sources. Nonetheless, it impacts negatively on categories such as ecosystem quality and human health. This is largely attributed to high energy consumption; thus the recycling processes must be optimized and an alternative energy source must be implemented.

3.3.Upcycling of plastic waste and circular economy (PART 2)

3.3.1. Definition of the system

It has been shown in section 3.2.5 that the upcycling of post-industrial plastic waste brings savings to the environmental, especially on the impact categories such as climate change and resources conservation. This is largely attributed to the fact that recycled plastics are used to produce new products, which initiate a new life cycle. In view of these results, it has been proposed to study the environmental impacts of the next life cycle stages.

In previous sections, the system boundaries have been drawn around the recycling plant. Nevertheless, the product´s higher quality leaves open the possibility for post-consumer plastic waste to be recycled after the use phase (Hahladakis and Iacovidou, 2018). Additional recycling cycles contribute to decreasing the virgin plastic production. Therefore, in this section, the system boundaries have been extended to the end-of-life stage of the products manufactured with recycled plastic (Figure 3.14). Landfilling has not been included in this study because it is the less preferred option for plastic waste treatment and it has been banned in several European countries (Plastics Europe, 2018). So that the two post-consumer plastic waste treatment options are recycling and incineration.

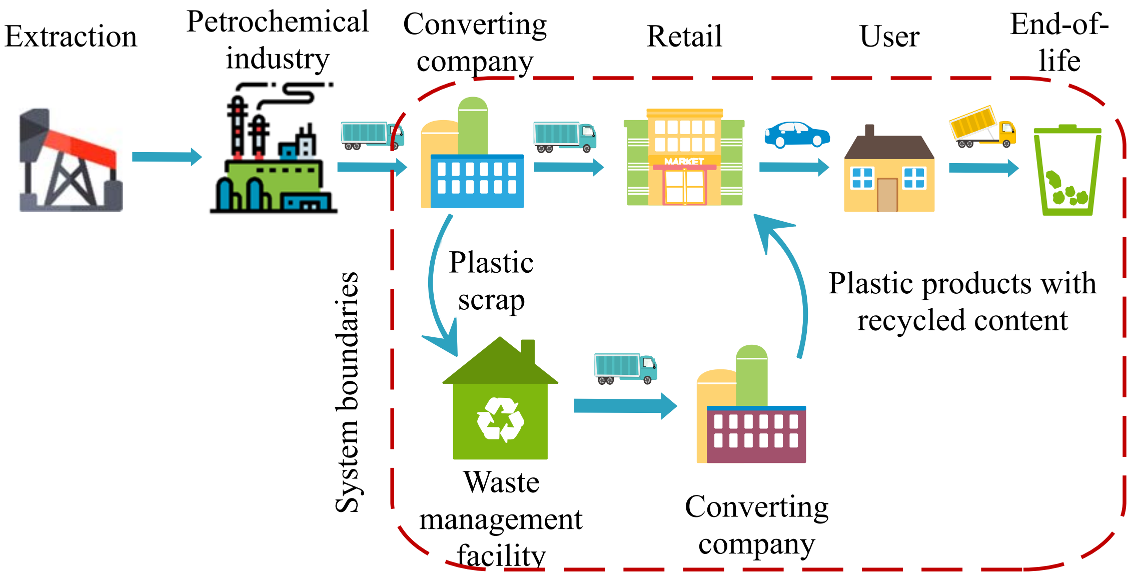

Figure 3.14. *Plastic product life cycle and extended system boundaries. Source: own elaboration (made with Edraw Max, some of the icons used are made by Freepik and Nhor Phai from www.flaticon.com).*

The upcycling stage of post-industrial waste is the same described in section 3.2.2.1. The substitution rate of virgin plastic by post-industrial recycled pellets (in the first material cycle) is 40%, which is the minimum rate necessary to generate savings for the environment. The converting and use phase were not included in the computation since they are similar in all scenarios. Regarding post-consumer waste, three possible scenarios have been proposed. The system flows included in the computation has been represented in Figure 3.15.

- **Scenario B1:** the recycling rate of post-consumer waste is 40% and 60% is incinerated. These data correspond to the European countries where landfill restriction has been implemented (Plastics Europe, 2018). The energy produced during incineration is used to generate electricity and heat. It is assumed that the energy source replaced is biogas from agricultural plants. The post-consumer plastic waste is currently treated through downcycling processes since existing technologies are not prepared to remove all the contaminants and impurities. Hence, the efficiency of the recycling process is 90%, the substitution rate is 80% and the market share is 24%.

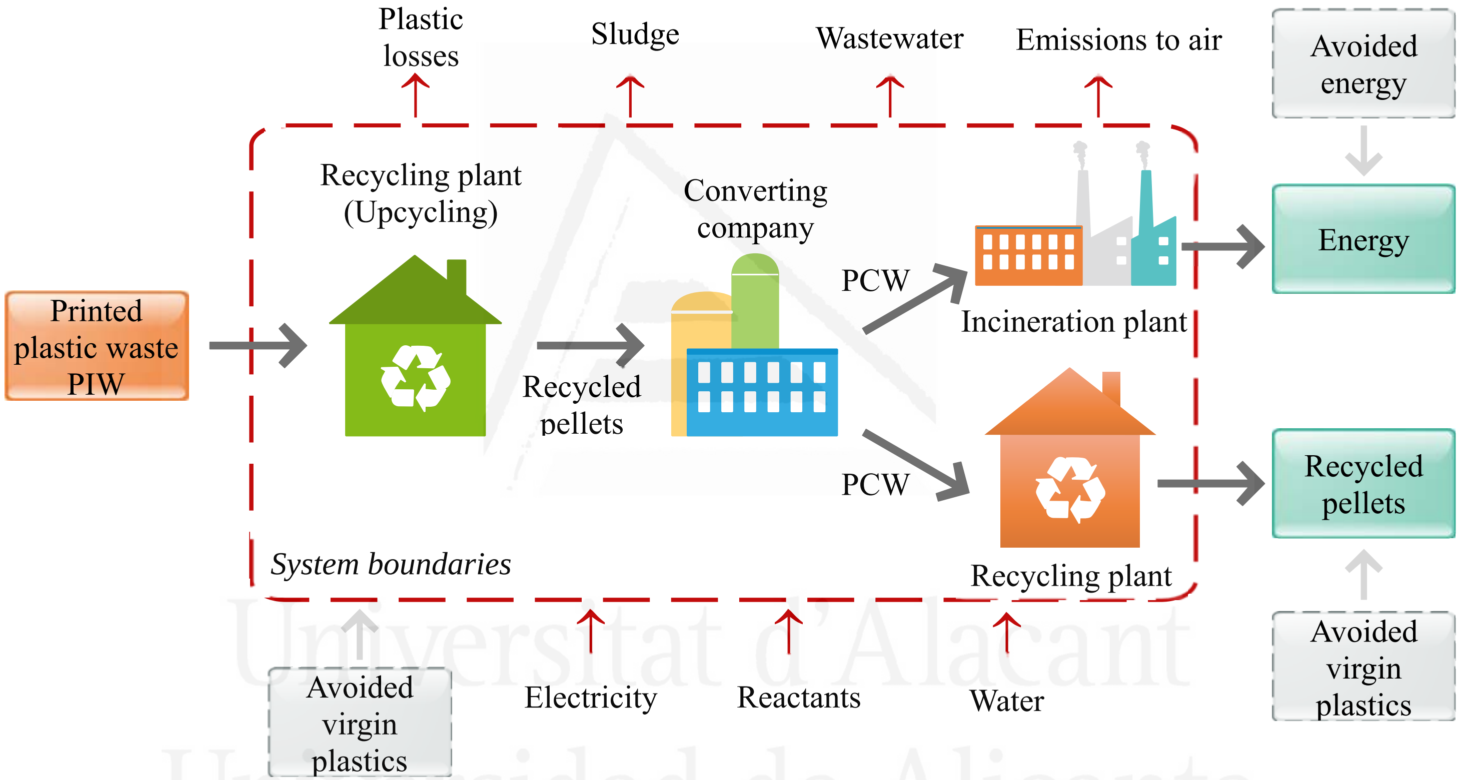

Figure 3.15. *Modelled scenarios with extended boundaries and overview of system flows for both post-industrial waste (PIW) and post-consumer waste (PCW) treatment. Source: own elaboration (made with Edraw Max).*

- **Scenario B2:** the recycling rate of post-consumer plastic waste has been increased to 80%, therefore, 20% is incinerated. The downcycling process is considered for the recycling stage (efficiency of the recycling process is 90%, the substitution rate is 80% and the market share is 24%).
- **Scenario B3:** the recycling rate of post-consumer plastic waste is 80% and it is considered that the upcycling process has been implemented so that the recycled pellets can be used in all applications (efficiency of the recycling process is 90%, the substitution rate is 80% and the market share is 100%). It is assumed that the energy and resources necessary for the upcycling of plastics from post-consumer waste are similar to the deinking process data reported in section 3.2.2.1.

Scenario B1 represent the current waste management system in some European countries. Scenario B2 and B3 concern hypothetical cases which have been raised for discussion about the evolution of plastic waste management.

3.3.2. Environmental impacts

This approach has been used to show the environmental effects of post-consumer plastic waste treatments (Figure 3.16). As has been discussed in section 3.2.5, incineration with renewable energy substitution increases the emissions of carbon dioxide. Therefore, the scenario B1 with 60% of plastic waste incinerated causes the biggest environmental burdens to the environment. The decrease of the incineration rate in scenario B2 results in negative net impact, which means saving to the environment. Higher recycling rate slightly increases the positive effect on the environment (around 2 times). On the contrary, the savings of post-consumer waste recycling are considerably higher (around 20 times) in scenario B3 when the target market expands. The same trend is observed on resources conservation category. The net impact of scenario B2 increases by around 3% compared with scenario B1. Nevertheless, in scenario B3 the net impact increases by almost 63% compared with scenario 1. These results show that it is good to recycle more. But it is more important to maintain the quality and the value of plastic products since upcycling of plastic waste produces the highest environmental savings. Regarding ecosystem quality and human health category, the recycling processes continue to produce burdens to the environment in all scenarios assessed. Although, the recycling (especially upcycling) of post-consumer waste produces savings in the human health category. As mentioned in the previous section, the negative impact potential of the recycling processes depends largely on energy consumption, which should be minimized.

The results obtained in this section show that upcycling processes are also necessary to treat the post-consumer plastic waste. The major savings to the environment are obtained when the target market of recycled products expands. To make possible the conditions established in scenario 3 (substitution rate and market share), post-consumer plastic waste recycling processes must be upgraded considerably. The quality of recycled post-consumer plastics is currently quite poor owing to the high level of contaminants, odours, non-intentionally added substances (NIAS), etc. Innovative decontamination (such as deodorization) technologies are needed to prepare the recycled content for more demanding applications.

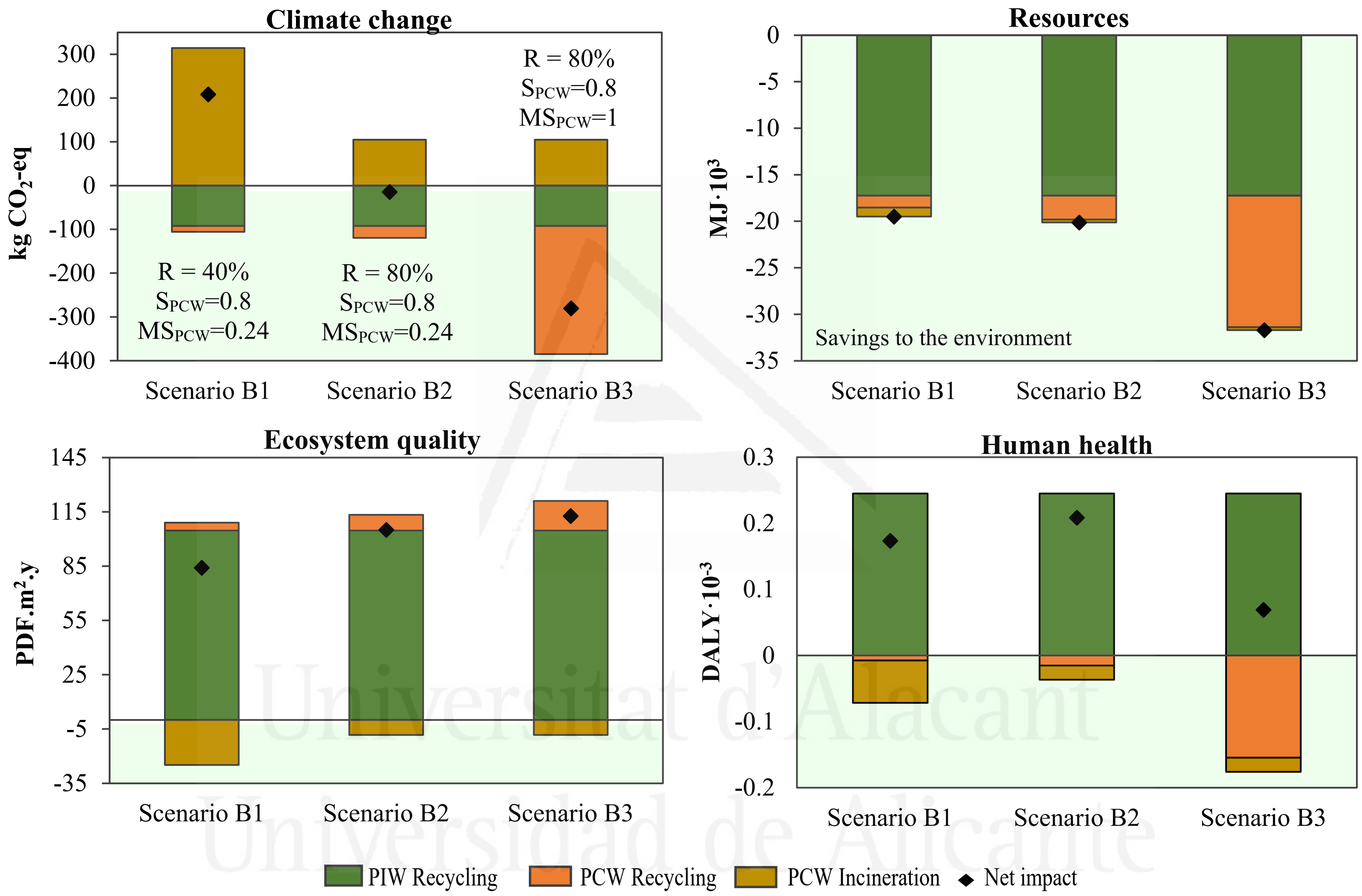

Figure 3.16. *Environmental impacts of the upcycling process considering two material cycles. Three studied scenarios: current post-consumer waste management scenario (scenario B1) and simulated scenarios (scenarios B2 and B3). PCW (post-consumer waste). PIW (post-industrial waste).*

3.4. Discussion

The computation of the environmental impacts associated with the recycling of plastic waste differs among published studies. Gu et al. studied the mechanical recycling of different plastic materials where the recycled pellets were used in high value and low value applications. The avoided virgin plastic production was calculated based only on the substitution ratio. The authors state that the substitution ratio decreases with the increasing value of the final product and attribute this to the inferior quality of the recyclates (Gu et al., 2017). Nevertheless, they do not mention that the quality requirements in high value applications are much stricter, which strongly influences the substitution ratio. Huysman et al. use the percentage of substituted virgin materials and the recycling rate in the computation of impacts produced during the recycling of post-industrial plastic waste. The authors compare two waste streams which undergo different recycling options and calculate a circularity indicator based on the polymer compatibility. Finally, they concluded that the recycling option where recovered plastics are used to produce low value garbage bags is more environmentally beneficial than the scenario where the recycled plastics are used in high added value applications (Huysman et al., 2017). This can be attributed to the difference in the substitution ratio (80% and 20% respectively) determined by the quality requirements of the final user. According to the results of the present study, these conclusions could have changed if the authors had considered the market share of the intended applications. In a study presented by Hou et al., the recycling of plastic films from post-consumer waste (mixed and recyclable) has been assessed. The parameters used for the computations were the recycling rate, utilization rate (equal to the substitution ratio), composition of polymers in the film waste, and the mass fraction of films in the waste stream. The authors studied only one scenario with 66% of substitution ratio, but in the sensitivity analysis concluded that the results are strongly dependent on this parameter (Hou et al., 2018). In general, the lack of uniformity in the procedure adopted by different authors makes it difficult to compare and to determine the accuracy of the LCA results. In fact, Viau et al. recently published an article where 51 LCA studies on municipal waste management were reviewed to assess the discrepancies in the modelling of the raw materials substitution. Based on the study by (Vadenbo et al., 2017), the authors state that the substitution potential must be calculated considering four parameters: the amount of potentially recoverable materials, the recycling efficiency, the substitution ratio, and the market response. The analysis showed that none of the revised articles mentions all four parameters. At the same time, 100% of selected articles take into account the substitution ratio. Nevertheless, 22% are not explicit and 65% were not justified by the authors of the studies. Therefore, there is a lack of rigour in LCA studies on municipal solid waste management (Viau et al., 2020). In the present study, all four parameters were considered and the substitution ratios have been established based on the information provided by a real plastic film converting company regarding quality requirements in different applications. Also, the importance of the market response parameter has been shown, especially when upcycling and downcycling processes are compared.

The incineration of plastic waste with energy recovery has been addressed in numerous studies and the results vary depending on the waste composition, the heating value, the electricity or heat production efficiency, and the source of substituted energy. Merrild et al. concluded that incineration of municipal waste can be more beneficial than recycling when the level of energy recovery at the incineration plant and the plastic fraction within the waste stream is high (Merrild et al., 2012). On the contrary, Perugini et al. showed that plastic waste combustion is the less preferable option, which can be explained by the fact that the heating value used in this study is lower and the recovered energy is used only to produce electricity with an efficiency of 25% (Perugini et al., 2005). Similar results were obtained in a study by (Cossu et al., 2017), in which several scenarios of the treatment of the residues obtained during the selection process of plastic materials have been assessed. Both studies are based on Italian waste management scenarios. Therefore, it can be concluded that in Italy and other southern countries where incineration plants are mainly used for the production of electricity (there is no need for district heating), the energy recovery scenarios produce burdens to the environment. Regarding the substitution of energy, in general, all the authors agree that only the displacement of coal-fired power produces environmental savings (for instance, (Hou et al., 2018). In this study, the most favourable incineration scenario was built considering a high energy recovery incineration plant with the production of both electricity and district heating. The composition of the waste stream is 100% polymeric with a high calorific value. In these conditions, incineration is more beneficial than recycling if the recovered energy substitutes the energy from fossil sources. Nevertheless, the substitution of energy from renewable resources is senseless, especially for the climate change category.

Regarding the upcycling of post-consumer plastic waste (section 3.3), no LCA studies covering both post-industrial and subsequent post-consumer waste treatment were found. Nevertheless, a few similar studies can be mentioned. For instance, Toniolo et al. compared the environmental impacts of using recycled plastics to produce potentially recyclable or non-recyclable products. The authors showed that assuring the recyclability of the final products produces the highest environmental savings, which is in line with the results obtained in this study (Toniolo et al., 2013). Sevigné-Itoiz et al. conducted a comprehensive study of post-consumer plastic waste treatment in Spain. The authors studied the effects of increasing the amount of collected plastics sent to recycling and concluded that the environmental benefits could be significantly increased (Sevigné-Itoiz et al., 2015). In this study, the benefits of increasing the recycling rate were also presented in addition to the benefits obtained from upgrading the quality of the recycled product.

3.5. Conclusions

LCA analysis was used to determine the environmental impacts of printed plastic scrap upcycling process compared with conventional recycling and incineration. It has been concluded that both the virgin plastic substitution rate and the intended market for the recycled plastic must be considered to compute the environmental impacts of recycling processes. The market share depends on the quality of the recycled pellets, which is considerably higher in upcycling processes. Therefore, a higher consumption of energy and materials is counterbalanced with a bigger number of applications where recycled content can be introduced. Furthermore, it has been proposed that in LCA studies comparing recycling processes and incineration as waste treatment options, the energy produced during incineration should replace energy from renewable sources instead of fossil fuels to make a fairer comparison.

It has been calculated that the upcycling processes produce saving in the climate change category when the virgin plastic substitution ratio is higher than 40%. Both upcycling and downcycling present a positive effect in the resources conservation category. In this case, also 40% substitution is required so that the upcycling is more beneficial than downcycling. Regarding the ecosystem quality category, both processes produce burdens to the environment mainly due to the energy consumption. Finally, the upcycling process produces a positive effect on human health when the substitution ratio reaches 80%. The effect of the downcycling process with the same substitution is negative.

The use of energy from renewable sources is highly beneficial in the climate change category. Nevertheless, a negative effect can be produced on other categories such as resources conservation and ecosystem quality. Therefore, the selection of the energy source or a combination of sources is an ongoing task.

Additionally, the upcycling process scenario considering two material cycles has been studied. This is because new products manufactured with upcycled pellets are of higher quality, which means that they have a big potential to be recycled again. Accordingly, a bigger number of material cycles is possible. The results show that the reduction of the incineration rate (i.e. higher recycling rate) produces a positive effect on the environment. Nevertheless, the major savings are obtained when the target market for recycled plastics expands. This is to say that upcycling processes are also necessary for post-consumer waste since it is more beneficial to recycle with high quality than in a big quantity. The quality of the recycled pellets must be considerably improved in order to increase the virgin plastic substitution rate in high added value applications. The current 20% of substitution is not enough to produce benefits to the environment.

In conclusion, it has been argued that upcycling of plastic waste produces large savings to the environment and accelerates the transition towards the circular economy model. Nevertheless, the current technologies are not prepared to get the most benefit from plastic recycling. One barrier is the high energy consumption which can be partially attributed to the lack of optimization of recycling operations, especially, in the case of flexible films. Another barrier is the quality requirements of plastic pellets for high added value application. The presence of contaminants poses a risk to consumer safety since the origin and composition of the plastic waste is usually unknown. Therefore, the detection and identification of contaminants are paramount to ensure the safe use of recycled products. Also, decontamination technologies must be developed for both post-industrial and post-consumer waste to maintain the quality of the materials. In Chapter 3 and 4 both optimization of recycling operations and composition of recycled products will be studied in depth.

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Chapter 4:

CENTRIFUGAL DEWATERING PERFORMANCE IN PLASTIC FILMS RECYCLING

A research article based on this chapter is already published in the international peer journal *Waste Management:*

O. Horodytska, F.J. Valdés, A. Fullana. Centrifugal dewatering performance in plastic films recycling. Waste Management Journal. Volume 80. October 2018. Pages 211-217.

https://doi.org/10.1016/j.wasman.2018.09.015

4.1.Introduction

The use of plastic flexible films is on the increase in different sectors, especially in packaging and agriculture. Despite the economic and environmental benefits of thin and light films, there is a grave disadvantage which is their low recycling rates. This is in part because current recycling processes have been developed for the treatment of rigid plastics and then extended to plastic films without optimization. The problem is that flexible films behave differently so that technical issues appear during recycling operations and efficiency decreases.

Mechanical recycling consists of several operations such as shredding, washing, drying, and re-granulation. The washing stage is important because the waste contains dirtiness and contamination that affects the quality of the recycled material. An effective drying process is needed afterwards because the excess of water during extrusion increases the chance for defects to occur, causes deterioration of product’s properties and pushes up energy costs (Grigore, 2017, Tietz Roda, n.d.). But in practice, the drying technologies used for films treatment frequently do not reach the required level of efficiency. In addition, drying is considered one of the most expensive operations (de Lima et al., 2016) and, along with extrusion, is one of the stages that contribute most to the global warming potential and fossil depletion potential (Chen et al., 2019). For these reasons, the study of plastic films and the optimization of drying systems are of great interest to recycling companies.

The most common drying systems are centrifuges (or spin dryers), screw presses, hot air systems, and rotating screens with hot air crossing. The centrifuges and screw presses are used to remove most of the water and the thermal drying is added to remove the remaining moisture (Briassoulis et al., 2013). Centrifugation is usually the preferred option since screw presses present several disadvantages such as high investment, operational problems and the fact that dirt remains in the plastic material. Sometimes, recycling companies use several centrifuges in series to increase efficiency. In all cases, recyclers must cope with high operational costs. The design of the centrifugal dryers or spin dryers has been focused on rigid plastic flakes or granules. A number of patents can be found related to optimization or upgrading of dewatering equipment for hard plastics (Holmes and Rybka, 2011, Yore, 1997, Rudolph, 1993, Hundley III, 1986). The conventional system consists of a strainer basket or a cylindrical mesh disposed within a housing and a coaxial bladed rotor used to convey the wet plastics and sling them against the screen. The water is removed by the centrifugation force while the plastics are retained by the mesh. A blower is usually placed at the end of the dryer to help the material to leave the chamber and to remove the humid air formed inside. A similar configuration has been used previously for other material drying, for instance, wet grain or ceramics (Ginther, 1954). The adaptation to plastic pellets was done around 1960 (Vernon E., 1969). Nevertheless, patents related to plastic films drying equipment were not found, meaning that the centrifugal dryers used were not optimized to treat this material which presents different characteristics and behaviour compared with rigid plastics.

The maximum moisture content that the system can handle depends on the extrusion profile of the material and the extruder characteristics, such as venting and degassing efficiency. For instance, some machines with a pre-drying system and innovative technologies can process materials with up to 12% moisture content (EREMA, n.d.). However, in conventional extruders, the limit is usually lower. Some machinery manufacturers assure that a correctly designed centrifuge should be able to remove all the water from the plastic materials (Tietz Roda, n.d.) and the thermal step would not be necessary then (Recytechnologies, n.d.). This requires a better understanding of dewatering processes in plastic films systems. However, the information existent in the literature is very scarce. So far, the research has been focused on studying the moisture sorption mechanism in plastics exposed to humid air (Fan, 2008, Fan et al., 2009). But dewatering of plastics, especially films, has not been addressed.

The chapter has been divided into two parts. In part 1 the dewatering of post-industrial HDPE film is assessed. Several experiments have been carried out to study the influence of operational parameters (centrifugation time, centrifugal force, and plastic mass) and material´s characteristics (flake size and film thickness). In Part 2, other plastic materials have been studied including films from post-industrial waste (PP, PET and embossed LDPE) and post-consumer waste from different sources (mixed collection, separate collection and agricultural). The surface of the plastic films has been analysed by microscopic techniques.

4.2. Dewatering of plastic films made of HDPE (PART 1)

4.2.1. Materials

Plastic films made of HDPE coming from typical shopping bags were used in the experiments. The average thickness of the film was 17 µm, measured with a micrometer. The plastic films have been cut by hand into small flakes for all experiments, except for the smallest flake size where a laboratory mill has been used to shred the plastic. In no case was cryogenic milling (or cold grinding) employed. The melting point of the material was determined by Differential Scanning Calorimetry (DSC). The sample was submitted to two heating cycles to erase the thermal history of the polymer. The melting peak obtained from the second heating was around 127ºC. This data was used to estimate the density of the material (0.94 g/cm^3 approximately) (Hitachi, 1986). A relatively low density indicates also a low degree of crystallinity of the polymer (Selke and Culter, 2016a).

The materials were provided by a recycling company that treats mainly plastic waste from post-industrial sources, i.e. rejects and offcuts from the converting sector. Therefore, these materials have suffered minimal thermal and mechanical degradation.

4.2.2. Methods

The experiments have been carried out using a laboratory centrifuge with a swinging bucket rotor and centrifuge tubes of 250 ml. The distance (R) from the centre of rotation to the midpoint of the tube (where the sample is placed) was 16.2 cm. The maximum rotation speed of the centrifuge was 1900 rpm.

The shredded material has been placed in water and agitated for 30 minutes to simulate the washing stage of the recycling process. The initial moisture content on a dry matter basis (τ_0 (%)), calculated as an initial weight of water per dry matter content, was around 730%. Thus, the mass of water is initially between 6-8 times higher than the mass of dry plastic films. The wet flakes have been placed in a sachet made of a permeable material. The sachet has been fastened on the upper half of the centrifuge tube and removed water has been collected on the bottom of the tube (

Figure **4.1**). During the experiment, the moisture content has been determined by weighing the sample between defined time intervals. The total duration of each experiment was 64 minutes.

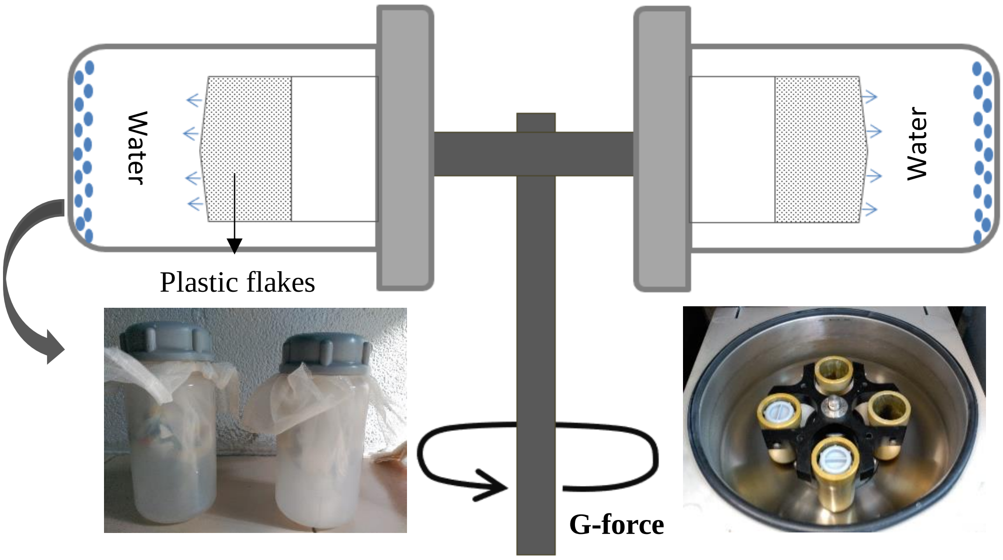


Figure 4.1. *Schematic representation of the centrifugation of plastic films using 250 ml tubes and a sachet.*

4.2.3. Experimental setup

All the experiments can be grouped according to the variables studied.

- **Influence of time and centrifugal force:** four experiments have been carried out at different rotation speeds (500, 1000, 1500, and 1900 rpm). The average flake size has been 2.5 cm and they had an irregular geometry (Figure 4.2a). The plastic mass used was 2 g.
- **Influence of flake size:** a square shape has been cut by hand in all experiments. The flake size is defined by the side length of the square (L). Six experiments have been conducted at 1500 rpm with the following side lengths: 0.1 cm, 0.5 cm, 1 cm, 2 cm, 4 cm and 6 cm (Figure 4.2b). The plastic mass used was 2 g.
- **Influence of plastic mass:** four experiments have been carried out to study the influence of material mass on the dewatering efficiency. The plastic mass in each experiment was 0.8, 1.5, 3.0 and 5.0 g. An experiment with more plastic mass was not possible due to the limitations of the experimental material, i.e., the capacity of the centrifuge tubes. The hand-cut square shape flakes with the side length of 2 cm have been used. The rotation speed during the experiments was 1500 rpm.
- **Influence of film thickness:** two experiments with different film thickness have been carried out to study the effects of the plastic surface. Both materials have been HDPE from shopping bags. The thickness of the

films was 17 µm and 35 µm. The same square shape flakes with 2 cm in length have been cut by hand (Figure 4.2c). The rotation speed was 1500 rpm and the plastic mass used was 2 g.

Four samples were tested in each experiment to calculate the standard deviation and validate the method.

Figure 4.2. *Plastic flakes used in (a) Experiment 1, (b) Experiment 2 and (c) Experiment 4.*

4.2.4. Results

4.2.4.1. Influence of time and centrifugal force

The first two parameters that have been assessed are the centrifugation time and the G-force. The relative centrifugal force (RCF) o G can be easily calculated according to the following equation (1), where w is the angular velocity in radians per unit time, n is the rotation speed in revolutions per unit time, and g is earth´s gravitational acceleration. The distance (R) from the centre of rotation to the sample is 16.2 cm (section 4.2.2).

$$RCF = \frac{F_c}{F_g} = \frac{a}{g} = \frac{Rw^2}{g} = \frac{R\,(2\pi \cdot n)^2}{g} \qquad (1)$$

In this work, rotation speed (n_{rpm}) has been used to express the centrifugal force in order to facilitate the reading and comprehension of this chapter. The RCF can be used to compare with the results obtained with different centrifugation equipment. The RCF related to the rotation speeds used in this work are presented in Table 4.1.

***Table 4.1**. Relative centrifugal force (RCF) calculated with the rotation speed (rpm).*

n (rpm)	RCF
500	45
1000	181
1500	408
1900	654

Centrifugation curves (moisture content over time) for HDPE flexible plastic have been drawn for different rotations speeds (Figure 4.3). The results show that the moisture content decrease with increasing centrifugation time and rotation speed. The downward slope of the drying curve increases with the G-force, although its influence tends to decline. The difference between the moisture content at the same time interval decrease with rotation speed increase. Hence, the data of the 500 rpm experiment are significantly higher than the 1000 rpm data. However, the deviation between 1500 rpm and 1900 rpm is almost negligible. The first conclusion is thus that the moisture content of the sample remains almost unchanged at speeds above 1500 rpm. Regarding the centrifugation time, it can be noticed that the largest loss of water takes place during the first 10 minutes. Then the curve decreases slowly.

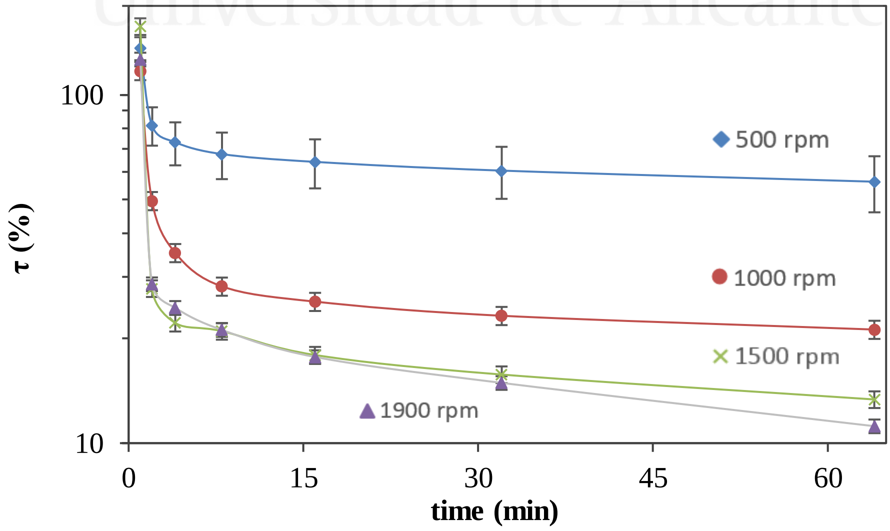


***Figure 4.3.** Drying curves of HDPE film at different rotational speeds.*

4.2.4.2. Influence of flake size

The influence of time and centrifugal force has been studied with heterogeneous size and shape plastic films. However, it has been observed that the flexible films tend to curl and to fold. Therefore, some water drops become trapped within the flake folds. This is because the water drop needs to slide on the material surface without barriers in order to leave the structure. The flake size can affect the tortuosity of the material and, consequently the water content. Therefore, the influence of the flake size has been studied with 6 experiments where the flake size has been changed from 0.1 cm to 6 cm.

The average moisture content on a dry matter basis influenced by the flake size and its standard deviation are shown in Figure 4.4. It can be noticed that there is a minimum of moisture for the side length of the flakes around 1 cm and 2 cm. Bigger o smaller size of the flakes causes an increase in material moisture. The water content increases faster when the flake size is bigger than 2 cm showing near to exponential growth. Nevertheless, it was not possible to conduct additional experiments with bigger flake sizes because of the limitations of the experimental setup (i.e. the centrifugation tube and the sachet). Regarding the smaller flakes, the increase in water content is also observed in the industry. Indeed, the formation of fines is considered a problem in the recycling sector because of the loss of material and poor drying efficiency.

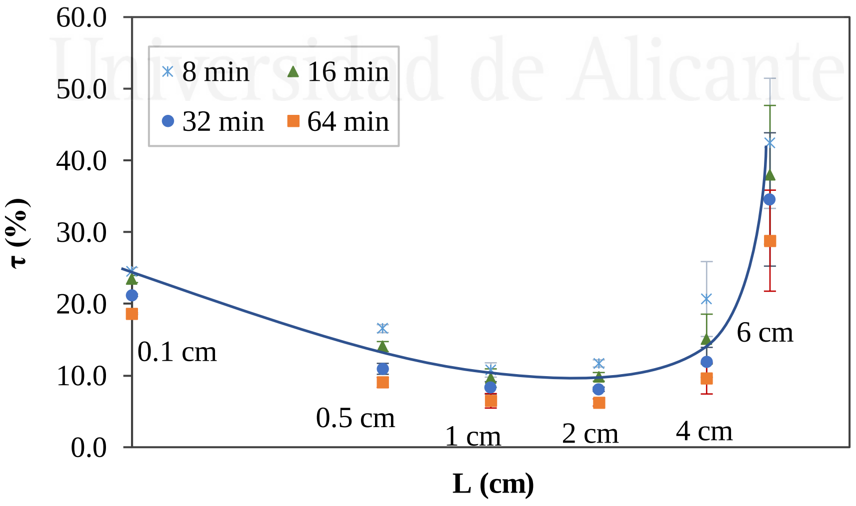


Figure 4.4. *Influence of the flake size on the plastic films moisture content (L = flake side length).*

Figure 4.5 shows that a quadratic function fits almost perfectly the experimental data. This mainly means that the moisture content apart from the flake size also depends on the square of the flake size, which represents the surface area of the plastic sample.

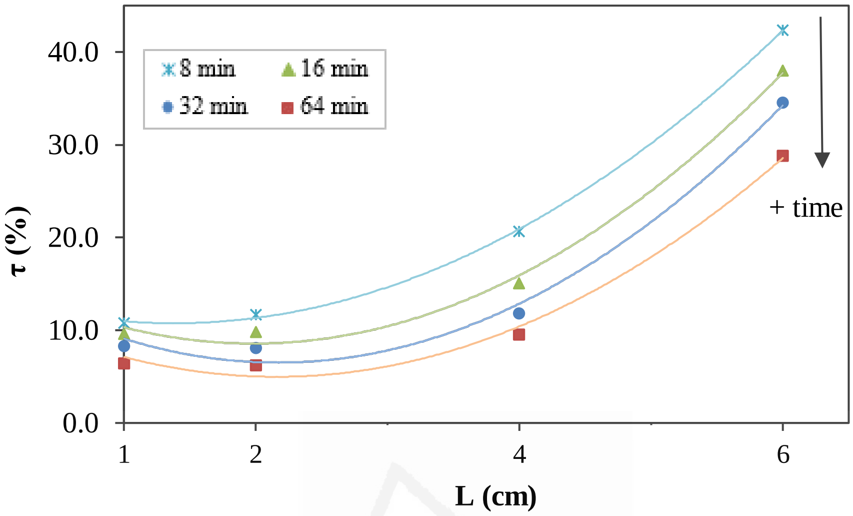


Figure 4.5. *Regression model used to describe the experimental data.*

4.2.4.3. Influence of plastic mass

Figure 4.6 is the plot of the moisture content on dry matter basis versus centrifugation time. The experimental results of all samples are shown. It appears that the moisture content of all samples after the same centrifugation time is similar. The standard deviation (s) has been calculated to quantify the difference between the experimental data. Furthermore, no clear tendency of water loss with increasing plastic mass has been found.

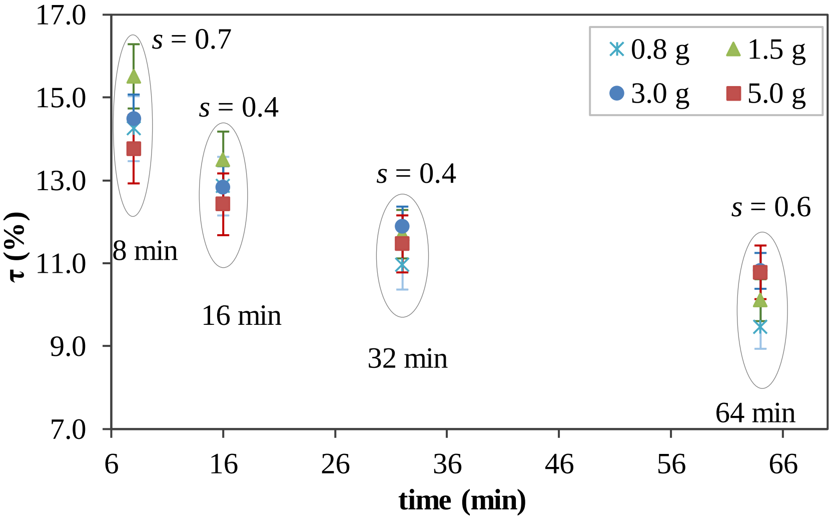


Figure 4.6. *Influence of the plastic mass on the moisture content (1500 rpm).*

4.2.4.4. Influence of film thickness

Two plastic films made of HDPE with different thicknesses (17 µm and 35 µm) were used in this case. The moisture content on a dry matter basis was obtained and represented versus the centrifugation time (Figure 4.7). The results indicate that the moisture content on the dry matter basis of the 35 µm sample is lower than the moisture of the 17 µm sample. It could be concluded that thicker films retain a smaller amount of water.

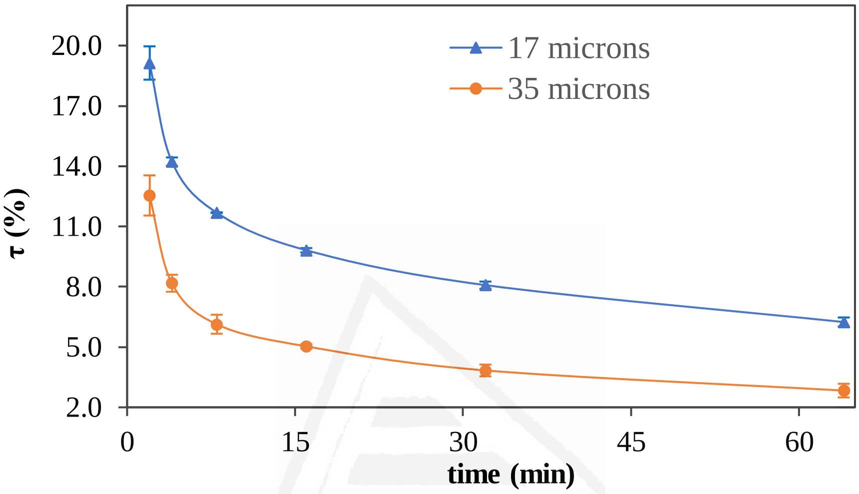


Figure 4.7. *Moisture content on a dry matter basis of HDPE films with different thicknesses (1500 rpm).*

So far, moisture content on a dry matter basis has been calculated. Nevertheless, this study proposes that the parameter that determines the degree of wettability of the material is the plastic surface in contact with the liquid, rather than the dry mass (section 4.2.4.3). Therefore, the moisture content should be expressed as mg of water per cm^2 of the plastic surface area (A), which has been denominated specific moisture (τ_S). Plastic surface area (equations 2 and 3) depends on the plastic mass (m), material´s density (ρ) and thickness (x). The expression is multiplied by 2 because both film sides are considered. The side area is negligible compared to the upper and lower sides due to the small thickness of plastic films (< 200 µm).

$$A = m \cdot k \qquad (2)$$

$$k = \frac{2}{\rho \cdot x} \qquad (3)$$

A different result from Figure 4.7 is obtained when the specific moisture versus centrifugation time is represented (Figure 4.8). The results indicate that the specific moisture content of both samples is similar whereas the moisture content on a dry matter basis is different. This supports the hypothesis that the water content depends on the plastic surface area and not on the amount of the material. Knowing the surface area, it is possible to calculate the thickness of the water layer (e_W) formed on the plastic surface. The water layer is similar in both samples, as happens with the specific moisture content. The average thickness at the end of the experiment is 0.5 µm, which corresponds to the equilibrium saturation. The thickness of the water layer decreases with the G force and the centrifugation time.

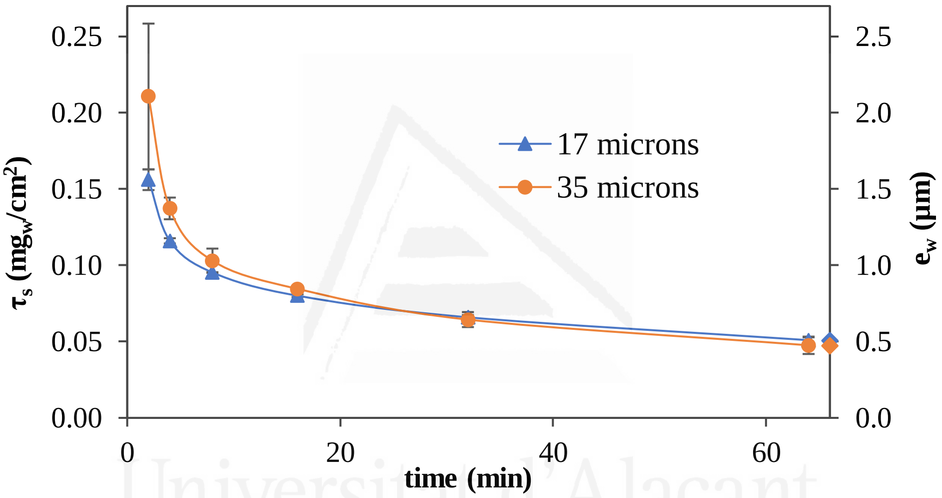


Figure 4.8. *Specific moisture content (τ_S) and water layer thickness (e_W) of HDPE films with different thicknesses (1500 rpm).*

4.2.5. Discussion

4.2.5.1. Formation of wet plastic cake

The plastic material is compressed by the centrifugal force and a plastic cake similar to the sludge cake is formed. In view of the results, the hypothesis of the existence of different types of retained liquid within the cake is proposed to explain the dewatering of the flexible plastic flakes. Therefore, the possibility arises that the saturation of shredded plastic films is a function of three types of water.

- Free water: the amount of water in the pores and voids of the plastic cake (Figure 4.9a).

- Water retained by capillarity: there are two types: (1) superficial water is a thin layer of water between the flake superficies (Figure 4.9b). The capillary force keeps the flakes together; (2) pendular water is the amount of water that is in the contact points of the flakes (Figure 4.9c).
- Water trapped due to the tortuosity of the material: the amount of water that becomes trapped in the folds and curvatures of the film (Figure 4.9d).

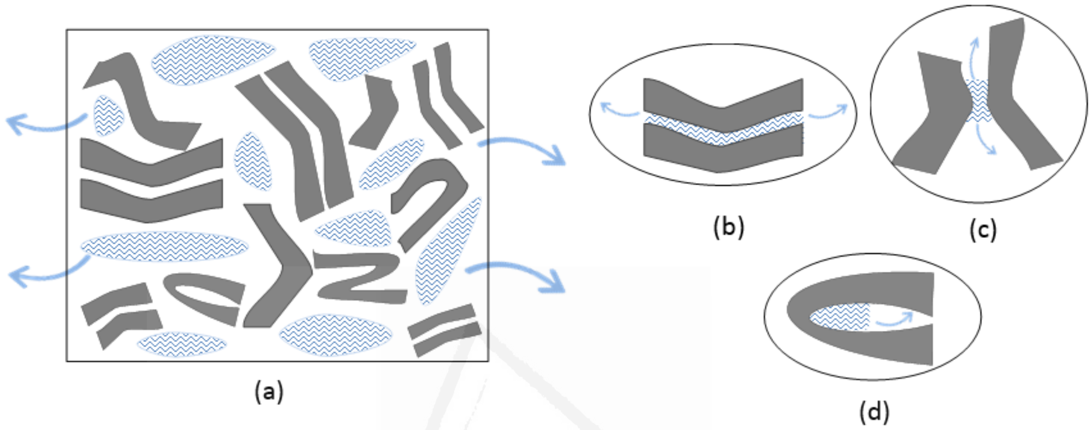


Figure 4.9. *Different types of trapped water within the plastic cake. (a) Free water. (b) Superficial water retained by capillarity. (c) Pendular water retained by capillarity. (d) Water trapped due to the tortuosity of the plastic mass.*

The dewatering of wastewater treatment sludge has been extensively studied. The equations used to describe the drainage or dewatering of wet cake formed during filtration were used in this work to explain the plastic drying. The moisture content is usually expressed by the saturation value (S). The saturation is the volume fraction of the wetting liquid within the pores and voids of the cake. The material is considered fully saturated (S=1) when all the pores and voids are filled with the liquid. During the centrifugation, the saturation decreases up to an equilibrium point (S_∞) that is reached after a large amount of time. The total saturation is a sum (equation 4) of the equilibrium saturation and the transient saturation ($S_T(t)$), which is a function of time (equation 5). Different types of trapped liquid exist within the cake: free liquid in the cake pores ($S_t(t)$), pendular liquid in the particle contact points (S_z), liquid retained by capillary forces (S_c), and bound liquid in the particle pores (S_p). The moisture content at the equilibrium cannot be totally removed with increasing centrifugation time but it depends on the centrifugation force (G) (equation 6).

$$S_{total} = S_{\infty} + S_T(t) \tag{4}$$

$$S_T(t) = (1 - S_c)(1 - S_p - S_z)S_t(t) \tag{5}$$

$$S_{\infty} = S_c + (1 - S_c)(S_p + S_z) \tag{6}$$

The drainage of the free liquid is a function of the centrifugation time raised to n (equation 7). The parameter t_d is the dimensionless time (equation 8), which is a function of the liquid density and viscosity (ρ and μ), the cake height (H), the G force and the centrifugation time (t). The exponent n is equal to 0.5 when the particle surface is smooth and to 0.25 for rough surfaces. It also depends on the hydraulic diameter (d_h) of the particle that is given by equation 9.

$$S_t(t) = \left(\frac{4}{3}\right)\left(\frac{1}{t_d^n}\right) \tag{7}$$

$$t_d = \frac{\rho\, G\, d_h^2\, t}{\mu\, H} \tag{8}$$

$$d_h = 0.667\frac{\varepsilon\, d}{(1 - \varepsilon)} \; or \; d_h = 7.2\frac{(1 - \varepsilon)K^{1/2}}{\varepsilon^{3/2}} \tag{9}$$

Where ε is the cake porosity, d is the diameter of the particle and K is the cake permeability.

The saturation due to capillary rise is affected by the G-force, some properties of the wetting liquid (density, interfacial tension (σ) and contact angle (θ)) and several characteristics of the cake (height, porosity, and permeability) (equations 10 and 11).

$$S_c = \frac{4}{B_0} \tag{10}$$

$$B_0 = \frac{\rho\, G\, H\, d_h}{\sigma \cos\theta} \tag{11}$$

The pendular saturation is reliant on the value of the capillary number N_c (equations 12-14). The G-force, the hydraulic diameter and some properties of the liquid are needed to calculate this number (equation 15).

$$
\begin{cases}
S_z = 0.075 & N_c \leq 5 \quad (12) \\
S_z = \dfrac{5}{(40 + 6N_c)} & 5 \leq N_c \leq 10 \quad (13) \\
S_z = \dfrac{0.5}{N_c} & N_c \geq 10 \quad (14)
\end{cases}
$$

$$N_c = \frac{\rho\ G\ d_h^2}{\sigma\ \cos\theta} \quad (15)$$

Finally, the bound liquid depends on the particle characteristics.

This approach and the equations presented will be used to explain the results obtained in section 4.2.4.

4.2.5.2. Influence of time and centrifugal force

The drying curves presented in section 4.2.4.1 show that the largest loss of water takes place during the first 10 minutes. The initial drop probably corresponds to the loss of most of the free liquid. With increasing centrifugation time, the moisture content approaches slowly to the equilibrium point. According to equations 6, this moisture depends on the amount of the water retained by capillarity (superficial and pendular) and the water trapped due to the tortuosity of the plastic films. The equilibrium moisture content is constant in each experiment and decreases with increasing G-force.

Equations 7 and 8 show that only the loss of free liquid is reliant on the centrifugation time. Since the plastic surface is considered smooth (n=0.5), it is a function of the inverse of the square root of the time. Figure 4.10 shows that a linear relationship between the moisture content and the t $^{-0.5}$ at different rotation speeds exists. This representation corresponds to equation 4 where the moisture content is equivalent to the total saturation. The free term of the linear equation is the moisture content at the equilibrium point (or S_∞). The equilibrium component is given by equation 6. Its value depends on the water retained by capillarity (superficial and pendular) and the bound liquid, which is a function of the particle characteristics. The capillary rise is reliant on the inverse of the G-force that is directly proportional to the square of the rotational speed (equations 1, 10 and 11).

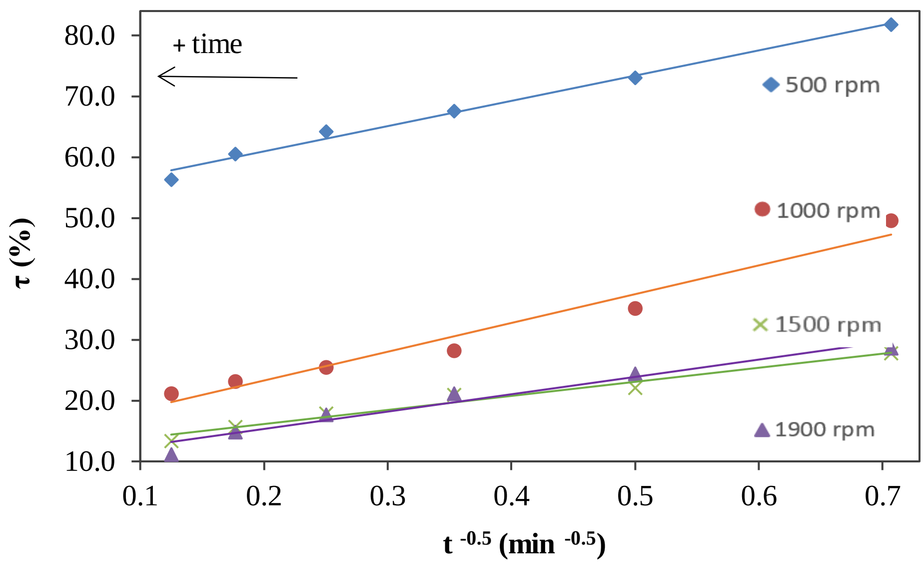


Figure 4.10. *Moisture content versus the inverse of the square root of the centrifugation time.*

In order to assess the variation of the equilibrium moisture, the experimental results of the moisture content (τ (%)) were plotted against n_{rpm}^{-2} (Figure 4.11). With increasing centrifugation time, the data sets seem to respond better to the linear adjustment. This might be due to the excess of free water at the beginning of the experiments. After 64 minutes the moisture content is probably very close to the equilibrium point. The pendular saturation might be constant since the experimental data fit a linear model. Therefore, only the superficial moisture varies with the G-force.

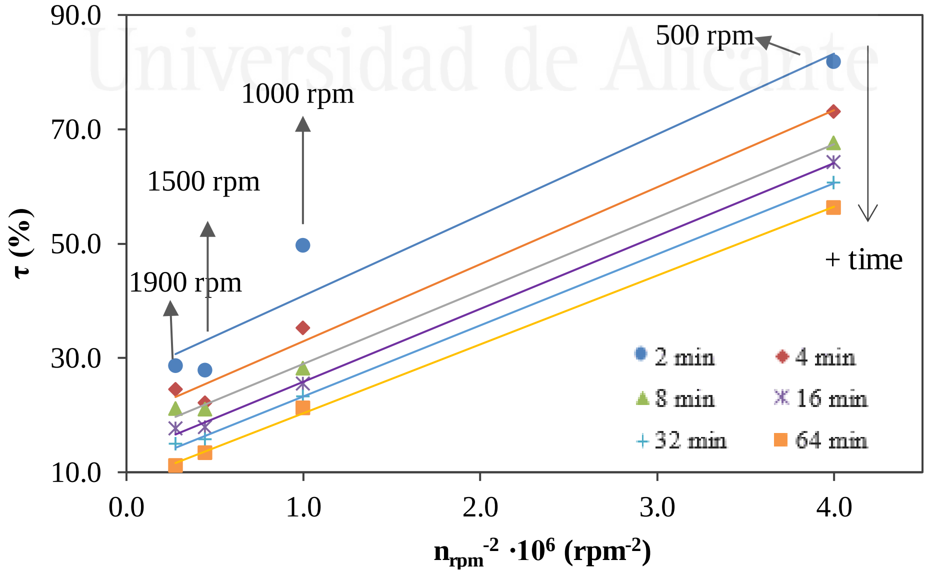


Figure 4.11. *Moisture content versus the inverse of the square of the rotational speed.*

The experimental data fit the proposed equation quite well. Therefore, the hypothesis of different typed of water within the plastic cake can be justified.

The results suggest that the optimal design of the centrifugation equipment might be based on two-stage process. During the first stage the G force can be relatively low, sufficient to remove the free water and avoid an excessive compaction of the plastic cake. During the second stage, the G force is much higher to remove the water retained by capillarity and the trapped water. Between the two stages, an intermediate step can be included to break up the plastic cake, for instance, using compressed air. The aim is to minimize the amount of trapped water from the previous stage. The increasing G force can be achieved by increasing the diameter of the rotor. Therefore, the new equipment can be a variable-diameter rotating drum. In this way, the use of energy is more efficient because the highest centrifugation force is used to remove the water retained within the plastic mass due to capillarity and not the free water. The reason for using one centrifugation unit instead of two separate centrifuges working at different rotation speeds is that the energy consumption of the blowers used to move the plastic flakes is usually high. Thus, in order to reduce the energy needs of the recycling process, conveying the plastic mass should be avoided whenever possible.

4.2.5.3. Influence of flake size

It has been found that bigger o smaller size of the flakes than 1-2 cm causes an increase in material moisture. Two different explanations of this phenomenon are proposed in this work: the effect of tortuosity and pendular saturation Figure 4.12. On one hand, the tortuosity of plastic films increases with the flake size since the material tend to curl and to fold more. Thus, a bigger number of water drops might become trapped due to the tortuosity of the plastic films resulting in higher moisture content. On the other hand, when the flake size is too small, the total roughness of the sample increases because of many small flakes lying side by side. Therefore, the number of contact points between flakes increases and the pendular moisture content predominates. Higher moisture content in the samples with the biggest size suggests that the tortuosity within the cake have a greater influence on the equilibrium moisture than the pendular effect.

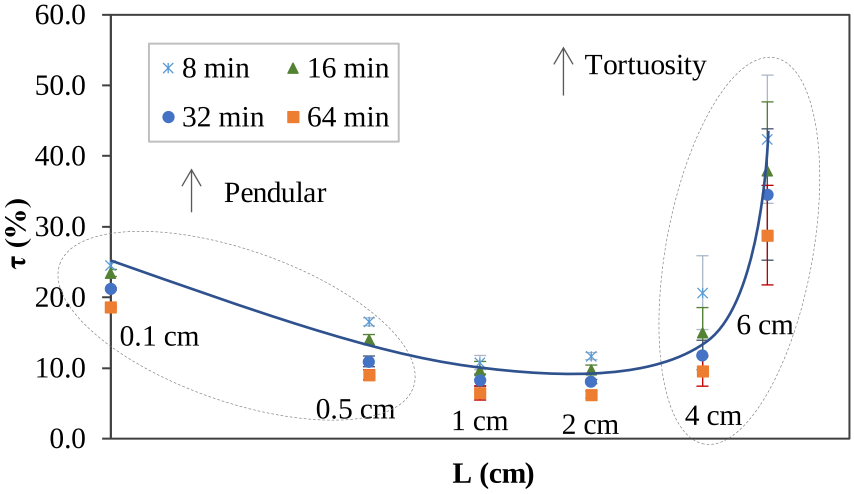


***Figure 4.12**. Influence of the flake size on the plastic films moisture content based on the retained water type.*

4.2.5.4. Influence of film thickness

It has been found that the moisture content depends on the plastic surface area rather than on the dry mass. Materials with smaller thickness are generally considered to retain more moisture. This is because smaller thickness results in a bigger surface area, thus more water can be deposited on the plastic film. To compare the moisture content on the dry matter basis between samples with different thicknesses, a correction factor (a ratio between the two thicknesses) should be applied (equation 16). Equation 16 is also useful to predict the moisture content of a plastic film if the moisture content of another film with different thickness is known.

$$\tau_1(\%) = \tau_2\,(\%) \cdot \frac{x_2}{x_1};\ x_1 < x_2 \tag{16}$$

4.3. Other materials dewatering (PART 2)

The dewatering performance of plastic materials different from HDPE was studied to assess the reproducibility of the results. The drying curves of a post-industrial PP and PET plastic films were obtained, and the influence of time and centrifugation force was evaluated. The dewatering of a so-called embossed plastic film made of LDPE has been studied due to its different processing methods. Nano o micropatterns are used to modify the surface of the plastic films. Since the water content is reliant of the plastic surface, the dewatering of embossed films could show differences compared with conventional films.

In addition, three samples from the post-consumer waste stream have been analysed to determine if the material degradation influences the dewatering efficiency. Post-consumer products suffer degradation during their life cycle, and the degree of degradation depends on the use phase and the waste collection system. The plastic surface can be modified and, in the following sections, it will be discussed if this affects the dewatering processes.

4.3.1. Materials

The PP, PET and embossed LDPE films were from post-industrial sources. The average thickness of the PP sample was 40 µm and the melting temperature obtained by DCS was 158°C. The PET sample was thinner (around 14 µm) and its melting point was around 253°C. Regarding the embossed LDPE film, the measured thickness was 37 µm and the melting point was determined around 124°C. This value suggests that the polymer is, in fact, a linear low density polyethylene (LLDPE). PP has a lower density than PE and PET. The average value is 0.90 g/cm^3. The density of PET varies between 1.29 and 1.40 g/cm^3. In this work, a mean density of 1.35 g/cm^3 is considered since the measured melting point corresponds to the midpoint of the typical melting temperature range for PET (Selke and Culter, 2016b). The density of LLDPE used is 0.93 g/cm^3. The typical density range for this material is 0.915-0.935 g/cm^3 and the melting temperature varies between 122°C and 124°C (Abdel-Bary, 2003). The samples have been provided by local plastic films converting company.

Regarding post-consumer waste samples, one of them comes from mixed domestic waste (grey bin in Spain), another one comes from a separate collection (yellow bin in Spain) and the last one is an agricultural film (Figure 4.13). The thickness of these films has been measured and the melting temperature determined by DSC. The mixed waste sample is 45 µm thick and its melting temperature is around 124°C, which can correspond to HDPE or LLDPE. Knowing the original application of the film, a grocery bag, it can be assured that the material is HDPE. The sample from the separate collection is 65 µm thick and it presents two melting peaks at 110°C and 123°C, suggesting that the material is an LDPE/LLDPE blend. Finally, the thickness of the agricultural film is 25 µm and it is also an LDPE/LLDPE blend since there are two melting peaks, the first one at 106°C and the second one at 120°C. The samples were provided by a local material recovery facility (MRF) and they showed clear signs of deterioration.

Figure 4.13. *Post-consumer waste samples: (a) mixed waste, (b) separate collection, (c) agricultural film.*

4.3.2. Methods

The centrifugation method is the same as explained in section 4.2.2. Additionally, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) have been used to observe and compare plastic surfaces. The SEM equipment used was JEOL JSM 840 and AFM model was NT-MDT NTEGRA PRIMA. The preparation of the samples for SEM analysis consisted of coating the plastic surface with gold (Au) using a sputtering method. The AFM technique does not require sample preparation. The scanning area size in AFM was 100 x 100 µm and the scanning speed was 20 m/s.

4.3.3. Experimental setup

In the case of PP and PET samples, four experiments have been carried out at different rotation speeds (500, 1000, 1500, and 1900 rpm) to obtain the drying curves. One experiment at 1500 rpm was conducted with the embossed plastic film and with each of the post-consumer samples to compare the results to the HDPE film. In all experiments, the flakes were cut by hand with an average side length of 2 cm, and the plastic mass was 2 g. The standard deviation was determined from four measurements.

4.3.4. Results

4.3.4.1. Plastic film waste from post-industrial sources

The drying curves of PP and PET samples (Figure 4.14) are equivalent to the drying curves of HDPE sample presented in section 4.2.4.1. Thus, the explanation of the influence of centrifugation force and time has been supported by assessing two different materials from the original HDPE. Although PP is also a polyolefin, its molecular structure, and mechanical and thermal properties differ from those of PE. PET belongs to the family of polyesters and its properties are also different. The fact that materials with different chemical structure show the same behaviour during centrifugation suggests that the drying performance depends on the film characteristics (thickness, flake size, etc.) rather than on the type of polymer.

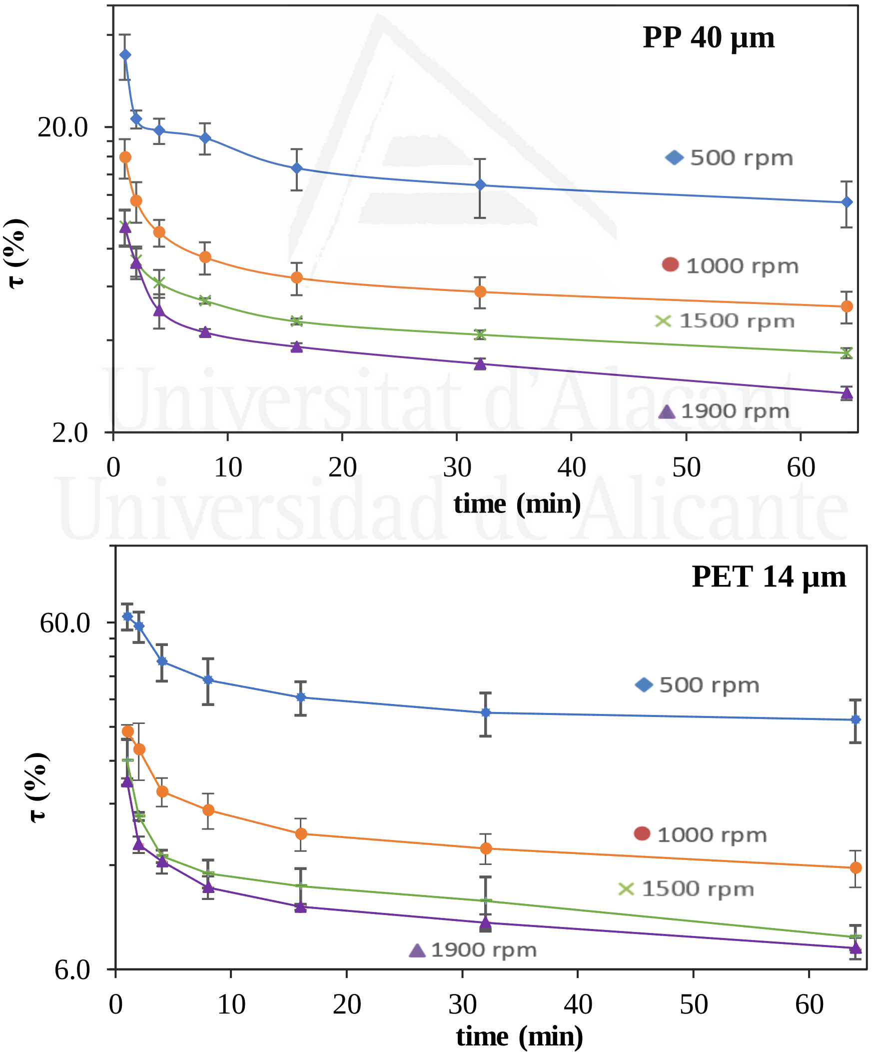


Figure 4.14. *Drying curves of PP 40 µm and PET 14 µm films.*

Regarding the specific moisture content (τ_S), the results of this experiment show that the HDPE, PP and PET are similar, which is in line with the results presented in section 4.2.4.4. Nevertheless, the specific moisture is significantly higher in the embossed film (Figure 4.15), meaning that the amount of water per the same surface area is bigger. This material apparently contradicts the assumption that the specific moisture content is very similar in all plastic films. The thickness of the water layer on the plastic surface has been calculated and represented along with the specific moisture content. The average thickness of the conventional PP, PET, and HDPE films is 0.6 µm whereas the thickness of the embossed film reaches 3.5 µm.

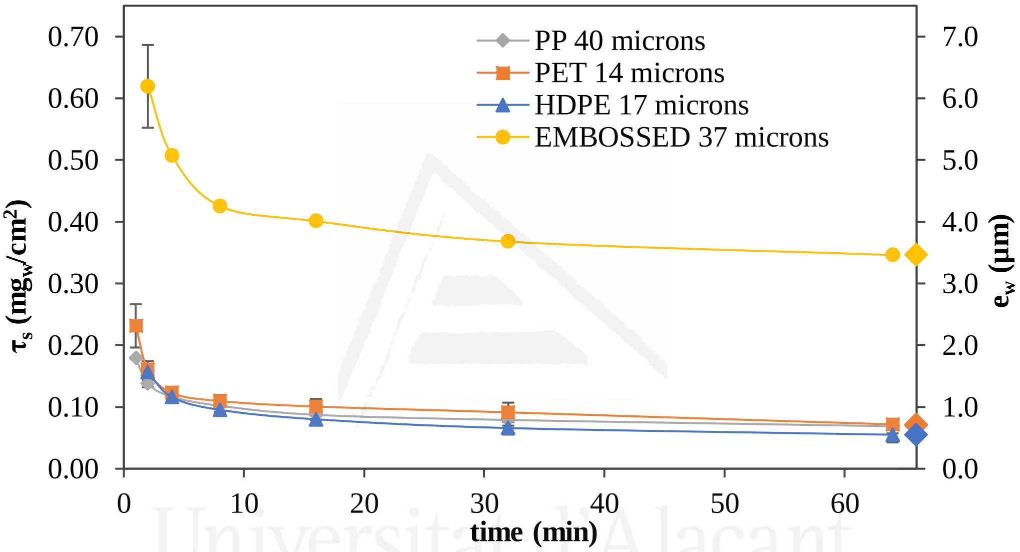


Figure 4.15. *Specific moisture content (τ_S) and water layer thickness (e_w) of post-industrial HDPE, PP, PET and embossed LLDPE samples.*

4.3.4.2. Plastic film waste from post-consumer sources

Plastic films from post-consumer sources were studied and compared with the film from the post-industrial source. The post-consumer materials were obtained from three different sources: plastic waste from the mixed collection, plastic waste from separate collection system in Spain where plastic and metal containers are gathered together, and agricultural waste. The waste source can influence the level of degradation because of the differences in the use phase and the end-of-life stage. The dewatering tests with post-consumer samples showed that the specific moisture is very similar to the post-industrial HDPE film (Figure 4.16). Therefore, the degradation of the surface that the material may suffer during the product's life cycle does not affect the content of water retained on the surface. The degree of degradation of these samples will be discussed in section 4.3.5.3. The thickness of the water layer has been calculated and represented along with the specific moisture content. The average water layer thickness of the post-consumer films is 0.6 µm, which coincides with the value obtained for post-industrial films (section 4.3.4.1). The deviation of the results can be attributed to experimental errors.

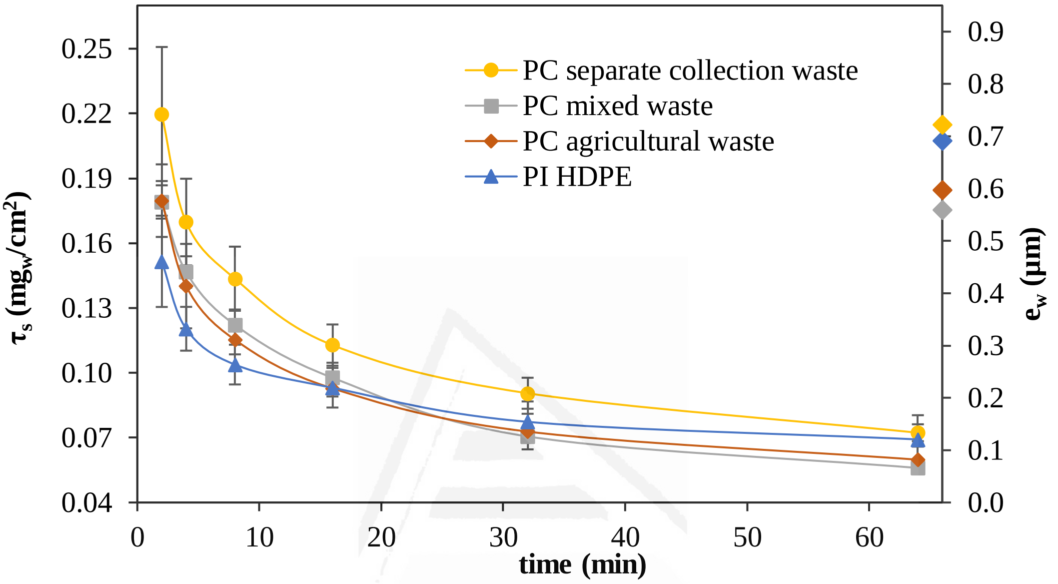


Figure 4.16. *Specific moisture content (τ_S) and water layer thickness (e_w) of post-consumer (PC) films compared with post-industrial (PI) HDPE.*

4.3.5. Discussion

4.3.5.1. Study of the embossed film surface

To explain the contradictory results of the embossed film dewatering, the focus has been put on the plastic surface. The embossing process consists of transferring a nano or microstructure (a pattern) from mould to the surface of the plastic film by pressure. A system with two rollers is usually used: an embossing roller and a roller with the plastic film (Liu et al., 2012). The goal of this process is to change several characteristics of the plastic surface, one of which is the surface area.

The embossed film and the HDPE film were examined by SEM and AFM to compare the plastic surfaces (Figure 4.17 and Figure 4.18). Figure 4.17a shows that the embossed plastic film presents a square pattern on its surface, and the difference with the HDPE surface (Figure 4.17b) is noticeable. Both sides of the embossed film have been analysed by AFM (Figure 4.18a and Figure 4.18b) and the same pattern is observed. The AFM analysis of HDPE film confirms that its surface is completely different from the embossed material (Figure 4.18c). Therefore, the real surface area in contact with the water drops may be significantly higher owing to the relief provided by the micropattern. To determine the real surface area, the equivalent film thickness should be calculated. This thickness is defined as the thickness that the plastic film should have had to obtain the moisture content measured experimentally. According to equation 16 formulated in section 4.2.5.4, the moisture content of the two materials is directly related to the ratio of their thicknesses. So that, if the HDPE sample is considered as a reference and the experimental moisture content of the embossed film is known, the equivalent thickness can be easily calculated and the result is 6.4 µm, approximately. In other words, the total surface area of the embossed film corresponds to the area of a conventional 6.4 µm thick film.

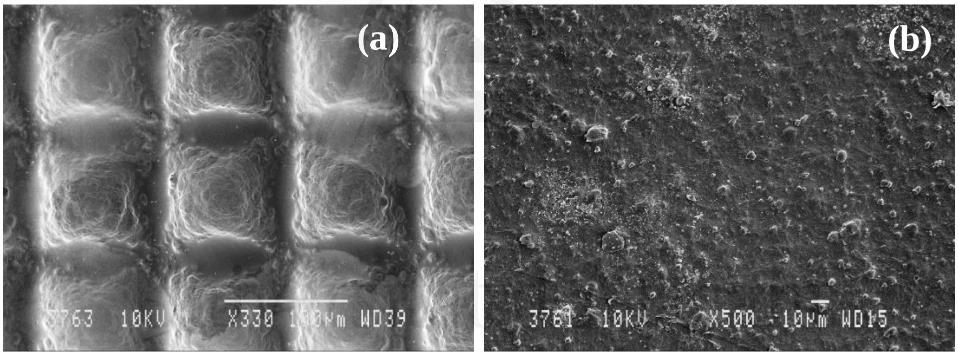
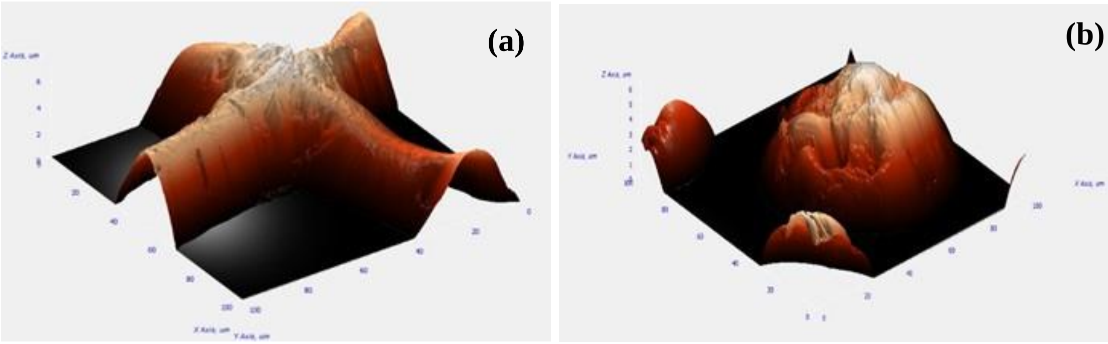


Figure 4.17. *SEM images of plastic film surfaces. (a) Embossed LLDPE film. (b) Conventional HDPE film.*



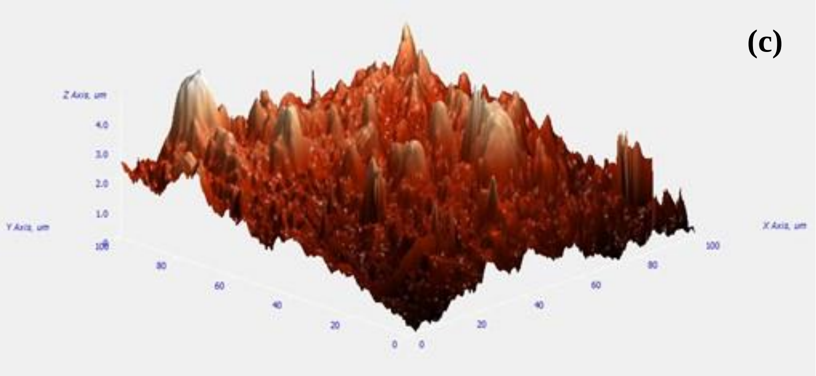


Figure 4.18. *AFM 3D images. (a) Embossed LLDPE film - side A. (b) Embossed LLDPE film – side B. (c) Conventional HDPE film.*

The height of the micropatterns of the embossed film measured by AFM is at least 6 µm. The water layer thickness calculated in section 4.3.4.1 was 3.5 µm, which is half the micropatterns height. The AFM software (Image Analysis P9-Nt-MDT) allows the calculation of an average roughness according to the ASME B46.1 Standard. The average roughness of the post-industrial HDPE film is 0.370 µm and the water layer thickness was 0.55 µm. In this case, the water layer is thicker than the average roughness of the plastic surface.

The specific moisture content of the embossed sample determined with the equivalent thickness is similar to that of the HDPE sample (Figure 4.19). In conclusion, the experiment with the embossed plastic film shows once again that the amount of water retained depends largely on the plastic surface area.

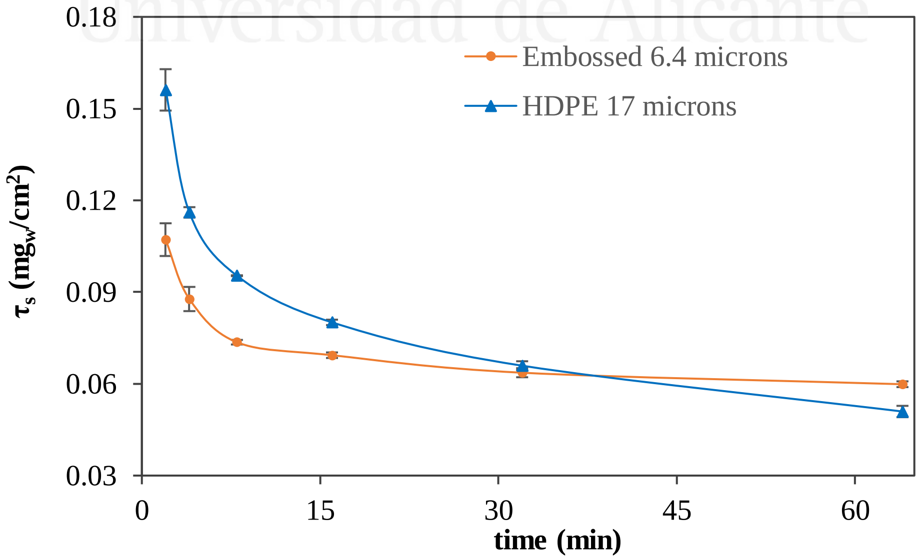


Figure 4.19. *Specific moisture content of the embossed material calculated with an equivalent thickness and compared with the HDPE sample.*

4.3.5.2. Study of the surface of the post-industrial films

SEM images of post-industrial PP and PET films show that the surface of both materials is smooth with some particles on it, which can be fillers used during processing or pigments from printing inks (Figure 4.20). The number of imperfections, such as particles, scratches and grooves, on the PP surface is higher. Consequently, the roughness is also higher. This is confirmed with AFM images where it can be observed that the surface of the PP film is more irregular Figure 4.21. The average roughness of the PP film and PET film calculated according to the ASME B46.1 Standard is 0.159 µm and 0.053 µm, respectively. The average thickness of the water layer at equilibrium point estimated in section 4.3.4.1 is 0.6 µm, which is higher than the average roughness of the plastic surface, as happens with the conventional HDPE film.

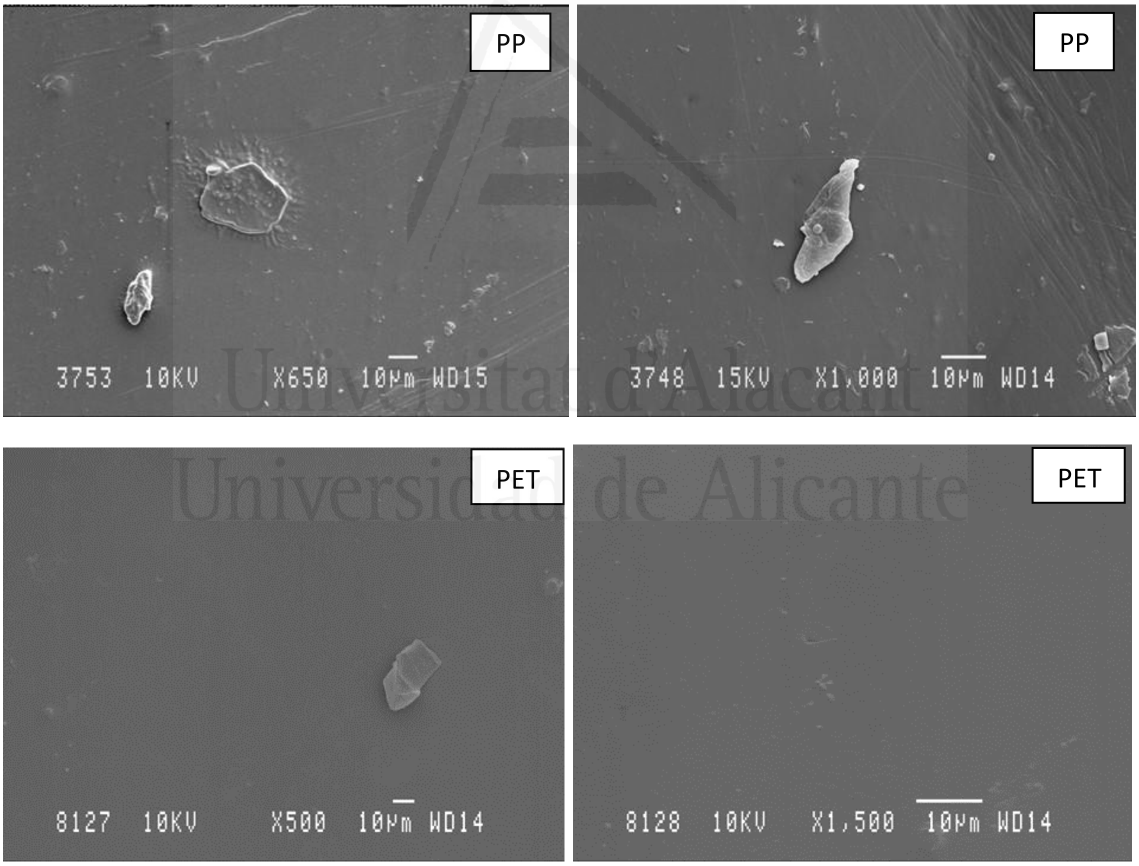


Figure 4.20. *SEM images of post-industrial PP and PET.*

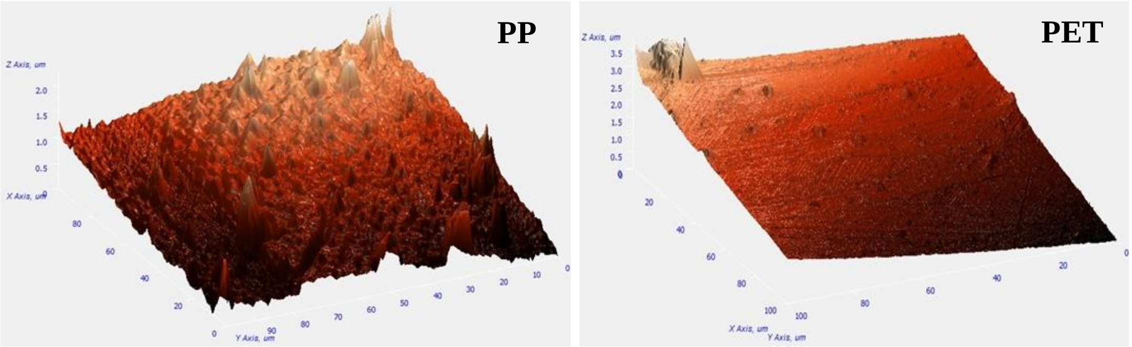


Figure 4.21. *AFM 3D images. Post-industrial PP film and PET film.*

4.3.5.3. Study of the surface of the post-consumer films

SEM images of plastic film from the mixed collection (Figure 4.22) show that the surface is more damaged than the post-industrial films. The surface appears to be fragmented or eroded, with numerous pores and grooves. Moreover, a set of unusual circular shapes, which origin is difficult to determine, has been detected. Nevertheless, it could be assumed that the source is the organic waste mixed with the plastics.

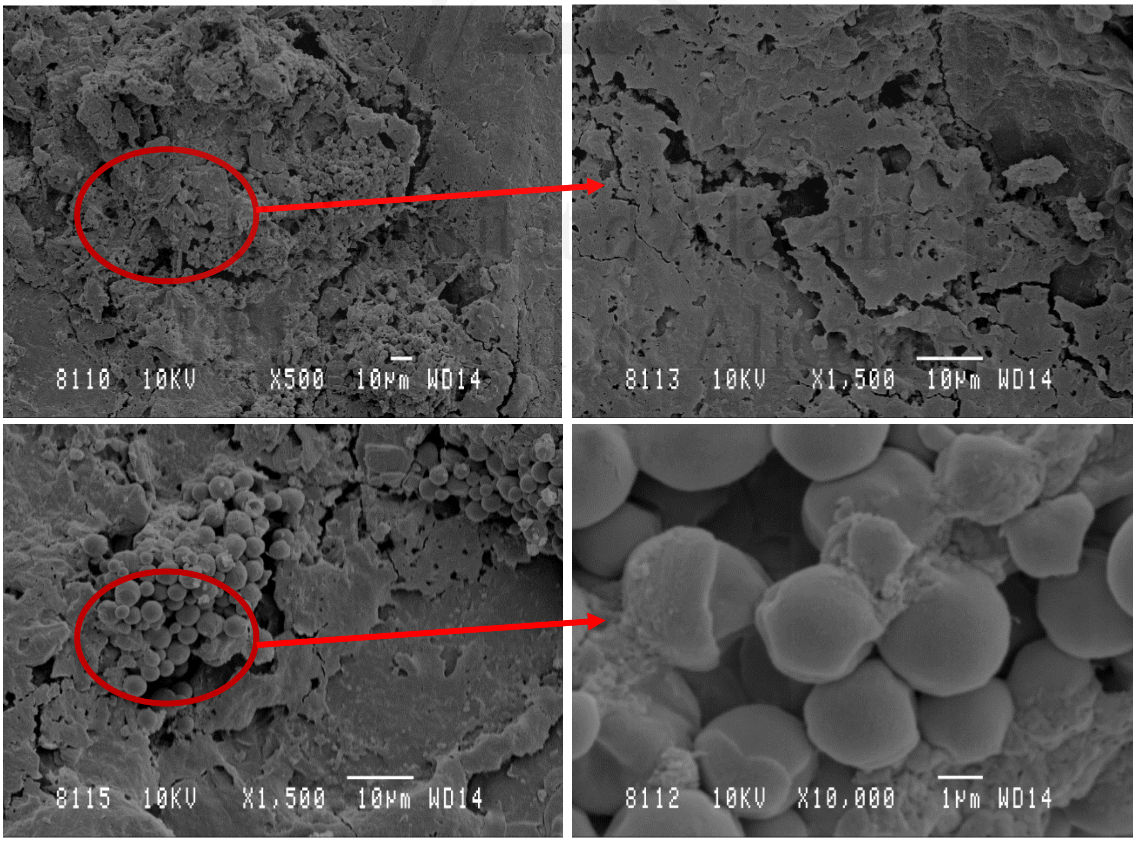


Figure 4.22. *SEM images of post-consumer film from mixed waste collection.*

Regarding the film from a separate collection, it is observed that some areas of the surface have been damaged, while other areas are similar to the post-industrial film surface (Figure 4.23). These results suggest that mixed collection schemes are more detrimental to the quality of the plastic surface than separate collection schemes. However, a detailed study focused on this topic is necessary to confirm this assumption. Unfortunately, this is beyond the scope of this Thesis. Finally, the aspect of the agricultural film surface suggests that the material has suffered some degradation since there are scratches and voids (Figure 4.24). Still, the rate of deterioration is lower than in the mixed waste film. Again, more samples are needed to complete the study and information about the use phase of the material, such as exposure time, weather conditions, etc.

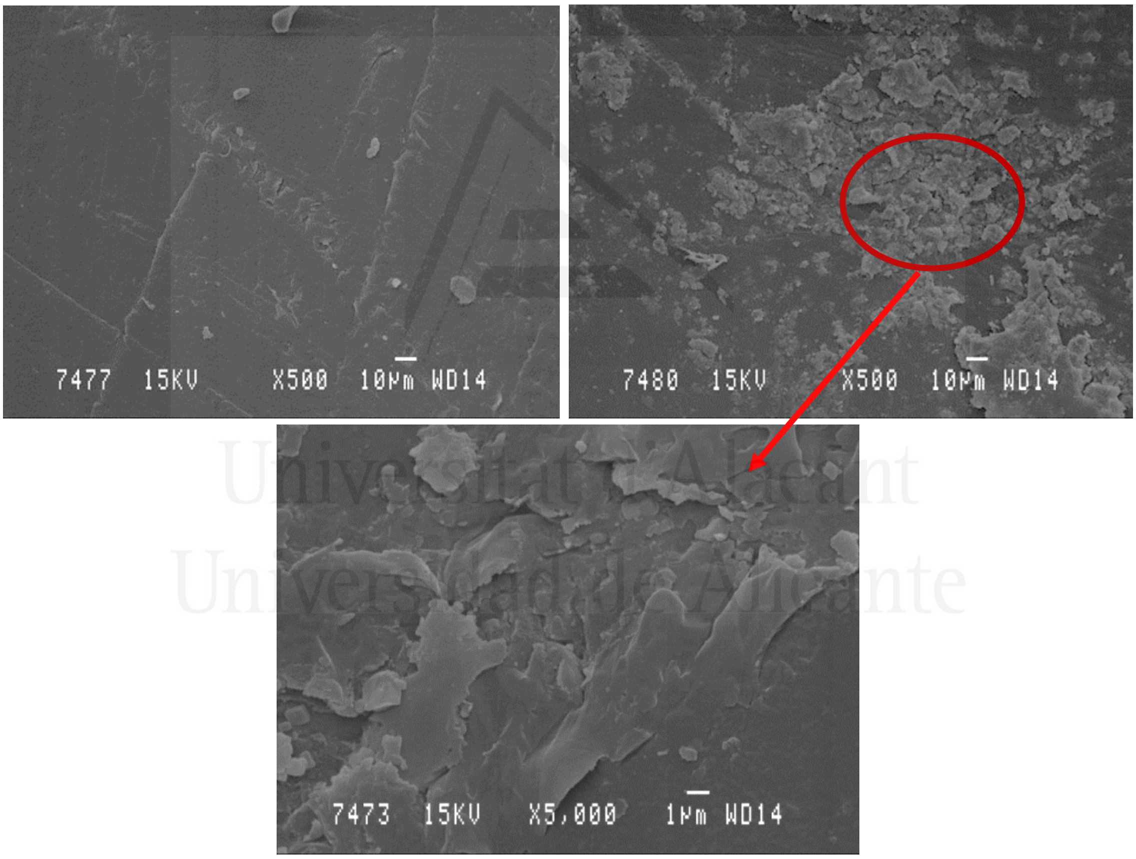


Figure 4.23. *SEM images of post-consumer film from separate waste collection.*

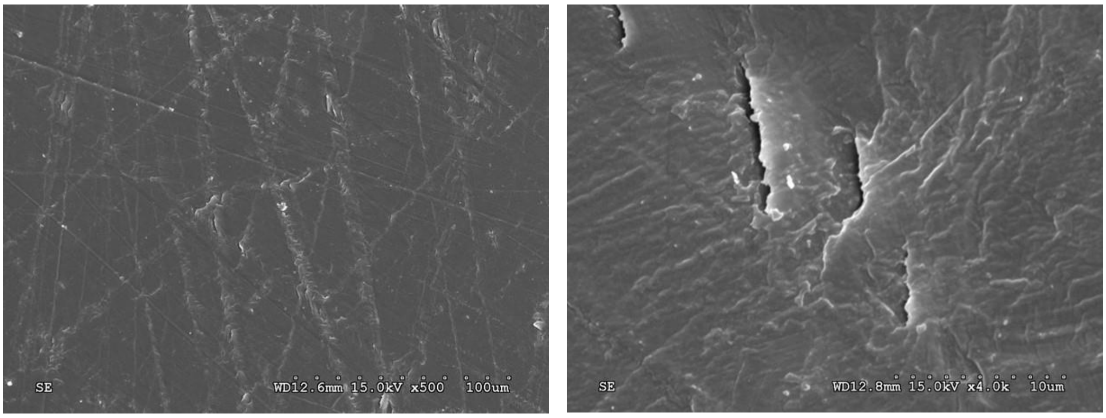
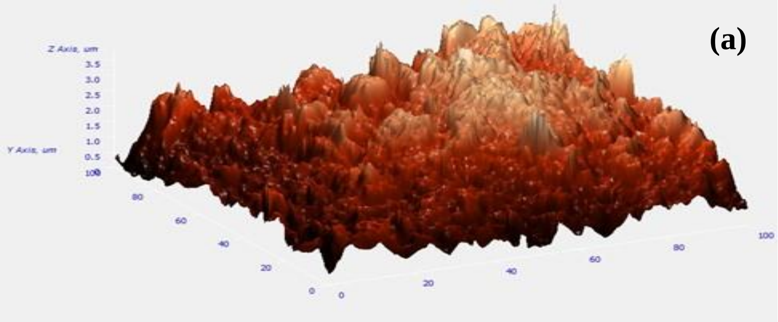


Figure 4.24. *SEM images of post-consumer film from agriculture.*

AFM images show that the mixed waste film presents the highest roughness, followed by the film from the separate collection. The agricultural film has the smoothest and homogeneous surface (Figure 4.25). This can be attributed to the fact that agricultural films are transparent and do not contain fillers or pigments. Nevertheless, it is observed that the surface has been scratched. The average roughness of the samples calculated according to the ASME B46.1 Standard is 0.365 µm for the film from the mixed collection, 0.111 µm for the film from the separate collection and 0.097 µm for the agricultural film. The average roughness of the conventional HDPE film is 0.370 µm (section 4.3.5.1), which is similar to the mixed waste film. This suggests that the deterioration of the material during its life cycle does not affect significantly the roughness, which depends on the additives and fillers added during manufacturing. As in the case of post-industrial films, the average roughness of post-consumer films is higher than the thickness of the water layer formed on the plastic surface. It can be assumed that the material roughness does not affect the amount of water retained on the surface if the thickness of the water layer is higher than the average roughness, which does not happen with the embossed films.



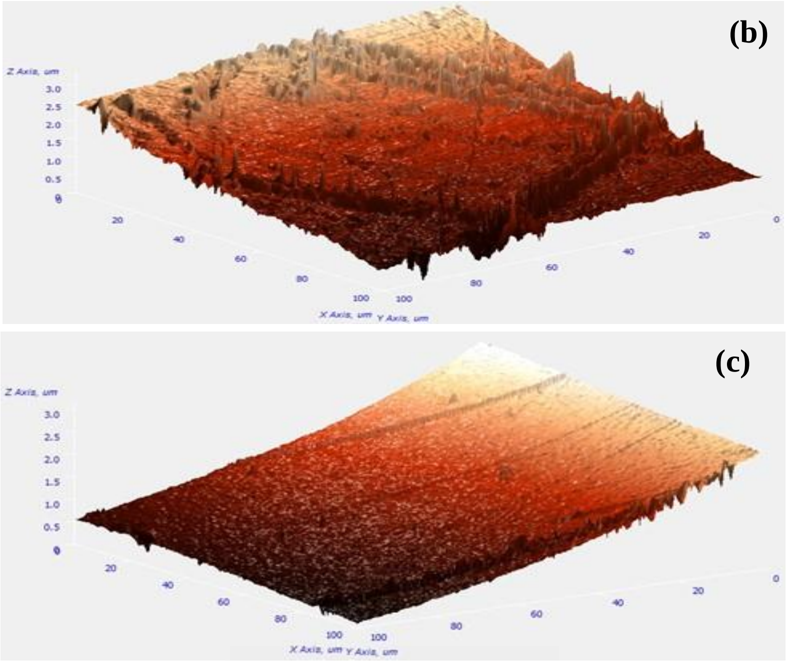


Figure 4.25. *AFM 3D images. (a) Mixed waste film, (b) Separate collection film, (c) Agricultural film.*

4.4. Conclusions

In this chapter, the dewatering of plastic flexible films by centrifugation has been assessed for the first time at a laboratory scale. Different polymer types have been included such as PE, PP and PET from post-industrial and post-consumer waste.

During centrifugation, a plastic film cake, similar to a wastewater sludge cake, is formed under the action of the G force. Therefore, the equation used to describe the drainage or dewatering of wet cake can be extended to plastic films drying. Three types of liquid coexist within the plastic cake: free water, water retained due to capillar force (superficial and pendular), and trapped water due to tortuosity of plastic flakes. The free water depends on the G force and the centrifugation time, and it has been almost completely removed during the first 10 minutes of centrifugation. On the contrary, the water content retained due to capillarity and tortuosity cannot be completely removed with long centrifugation times since it is reliant on the G force and the plastic characteristics (flake size, cake height, porosity, etc.). This explains why using several centrifuges in series with the same operating conditions, which is common practise in the recycling sector, do not ensure high drying efficiency. In view of the results, a new design of the centrifugation unit has been proposed consisting of a variable-diameter rotating drum with an injection of compressed air to avoid the compaction of the plastic cake.

It has been found that the water content is linearly dependent on the inverse of the square root of the centrifugation time and the inverse of the square of the rotational speed. The experimental results show that an optimum side length exists. The moisture content is minimized when the flake side length lies between 1 and 2 cm. Bigger size causes higher water retention due to films tortuosity and smaller size increases the pendular water content.

The water content is reliant on the plastic surface area and it is independent from the plastic mass. Therefore, the specific moisture content (mass of water per plastic surface area) is similar in all samples. While the moisture content on dry matter basis changes with the film thickness. Thus, the specific moisture content should be used to study the dewatering efficiency of different plastic films, as well as for equipment design and process control. In other words, a centrifuge dryer must be designed to remove a certain amount of water per plastic surface area and during processing, the flow rate must be adjusted so that it equals that value. The embossed plastic film presents higher water content than other films with similar thickness. This is because the total surface area has been increased during processing by transferring nano or micropatterns to the plastic surface. Therefore, special attention should be paid to these materials during the drying stage and real surface area in contact with water must be calculated.

Finally, it has been observed that plastic materials present different roughness depending mainly on the composition of the plastic. The surface roughness does not affect the dewatering process if the thickness of the water layer formed on the plastic surface is higher than the average roughness of the material. In the opposite case, for instance, the embossed films, the high roughness causes total surface area growth, thus increasing the amount of water retained. The degree of degradation is considerably higher in post-consumer films from mixed waste collection schemes compared with post-consumer films from separate collection system and agricultural films. Nevertheless, the condition of the surface does not affect the dewatering efficiency. Thus, the specific moisture content of post-consumer films is similar to post-industrial films.

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Chapter 5:

NON-TARGET ANALYSIS OF SVOCs PRESENT IN RECYCLED PLASTICS

A research article based on this chapter is already published in the international peer journal *Chemosphere:*

O. Horodytska, A. Cabanes, A. Fullana. Non-intentionally added substances (NIAS) in recycled plastics. Chemosphere Journal. Volume 251. July 2020. 126373.

https://doi.org/10.1016/j.chemosphere.2020.126373

5.1. Introduction

Recycled plastics demand is on the increase in EU due to factors like social pressure and special European incentives and support measures. In 2015, the EU launched a pledging campaign to ensure that 10 million tonnes of recycled plastics are used for new products manufacturing by 2025, which means to triple the demand (European Commission, 2018). In total, 70 companies and business associations have shown their interest in participating. Among them, important brand owners of food and non-food applications can be found (e.g., Danone, LIDL, P&G, Unilever). Despite the efforts made, it has been estimated that the real demand for recycled plastics that can be reached is only 6.4 million tonnes (European Commission, 2019). The main barriers are the low quality of recycled plastics and the lack of traceability, which brings uncertainty about the chemical composition.

The life cycle of plastics consists of several stages from raw materials production until plastic products end-of-life. Plastic polymers are produced by polymerization and polycondensation with the use of specific catalysts, solvents, fluid carriers and other secondary chemicals. The monomers come from different sources such as crude oil, coal, starch, etc. The processing of plastic resins implies the addition of certain additives during extrusion or moulding stages. The process of mixing additives into plastic resins is known as compounding. The selection of proper additives depends on the polymer type and the final application of the product (Selke and Culter, 2016). The fabrication of flexible plastics combines several operations such as extrusion, lamination, coating and printing. Different adhesives, coatings and inks are incorporated into the product. All the components used for the manufacturing of plastic products are considered intentionally added substances (IAS) and must be reported by the manufacturer.

Nevertheless, a number of undesired compounds can appear during the lifetime of a product. These compounds are denominated non-intentionally added substances (NIAS). They can originate as polymer or additives degradation products, impurities, neoformed compounds and contaminants (Nerin et al., 2013). Degradation processes occur mainly due to exposure to high temperature or high irradiation energy. Therefore, NIAS can be generated during converting operations where high temperatures are used to process the materials, and/or during product preparation processes at both industrial (sterilization) and domestic level (microwave heating). Recycling of thermoplastics implies re-extrusion at high temperatures, thus the amount NIAS is likely to increase in each heating cycle. The impurities are undesired substances present or formed during the manufacturing or extraction of the substances used in plastic production, i.e., additives, monomers, solvents, etc. (European Commission, 2011). Neoformed compounds are mainly reaction products of coatings or adhesives with compounds from external sources. Finally, there are two types of contaminants: process contaminants and unknown contaminants from external sources (Koster et al., 2015). In Figure 5.1 the life cycle of a flexible plastic product is depicted including the sources of IAS and NIAS.

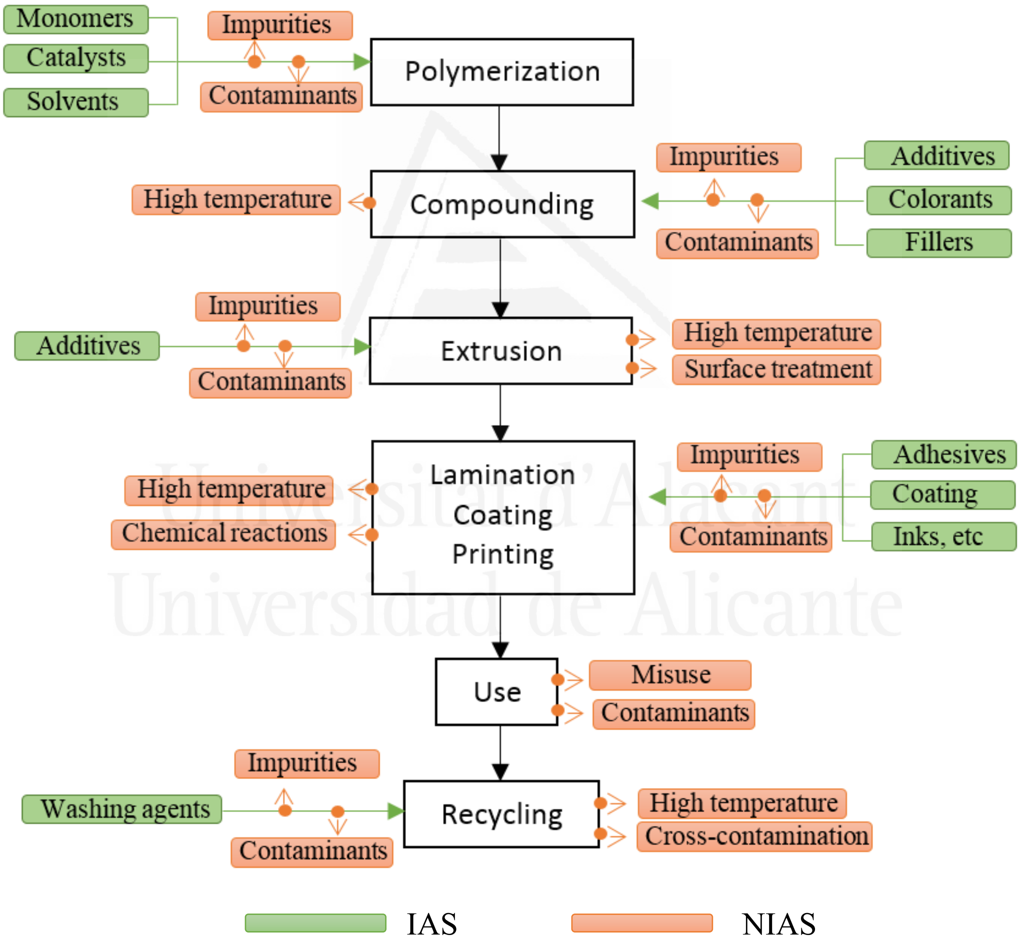

Figure 5.1. *The life cycle of flexible plastics including IAS addition and NIAS generation points. (Source: own elaboration).*

The plastic packaging market is the biggest market for plastic products and also very restrictive. The European Food Safety Authority (EFSA) is the organization in charge of assessing and communicating risks related to the food chain. In particular, plastic materials and articles must comply with the Commission Regulation (EU) No 10/2011, which establishes the Union List of substances approved to be used for FCM plastics manufacturing. Some substances from the list cannot be transferred into food over a specific quantity, Specific Migration Limit (SML), due to their toxicity. The overall migration of all substances may not exceed 60 mg/kg of food or 10 mg/dm^2 of the contact material (Overall Migration Limit (OML)). Recycling processes must obtain authorization from EFSA to prove that the recycled plastics can be used for FCM safely (European Commission, 2008). Until now, around 90% of approved technologies are made for PET recycling. Regarding polyolefins, 4 processes have been approved by EFSA for recycling of PP and HDPE crates for fruits and vegetables (EFSA CEF Panel, 2010, EFSA CEF Panel, 2012, EFSA CEF Panel, 2013a, EFSA CEF Panel, 2013b). Additionally, a process for recycling milk and juice bottles, as well as trays for fruit and vegetables or animal products made of HDPE was approved (EFSA CEF Panel, 2015). Recycling of polyolefins for food contact applications is progressing, albeit slowly due to their higher permeability (Geueke et al., 2018). Therefore, most recycled plastics must be allocated for non-food applications. However, more forgiving applications and lack of specific legislation on using recycled plastics do not mean that there is no concern about chemical contaminants present in the recycled pellets, especially, when they come from post-consumer waste. For instance, Burberry, a British luxury fashion house, has elaborated a list of product restricted substances applicable to any finished product or raw material used (Burberry, 2018). The list includes bisphenol A, chlorobenzenes, chlorophenols and phthalates among others. Consumer safety is also important in the hygienic sector. For example, P&G (an American multinational specialised in personal care and hygienic products) claims that they do not use ingredients like alkylphenols, benzenes, bisphenol A and PAHs (polycyclic aromatic hydrocarbons) (Procter & Gamble, 2020). As all these substances could migrate from the plastic package produced with recycled pellets, studying the composition of post-consumer recycled plastics is imperative when it comes to high added value application, both food and non-food.

The detection and identification of IAS and NIAS in recycled products are paramount, especially, when the source of plastic waste is unknown or changeable. The formation of NIAS can be predicted if the composition of the plastic product is known. However, it becomes an arduous task when the materials come from a waste stream. The analytical methods can be split into two groups: targeted analysis of predicted substances and non-targeted analysis or screening of unpredicted substances. The selection of the analytical method depends on the volatility of the compounds of interest. The volatile substances are usually analysed through thermal desorption or headspace solid-phase microextraction (SPME) followed by gas chromatography flame ionisation detection (GC-FID) or gas chromatography mass spectrometry (GC/MS). The semi-volatile and non-volatile substances are first extracted into one or more solvents, then the semi-volatiles are analysed with GC-FID or GC-MS and the non-volatiles with liquid chromatography ultraviolet detection (LC-UV), LC-evaporative light scattering detection (ELSD) or LC high resolution MS. Other techniques like inductively coupled plasma (ICP)-MS and nuclear magnetic resonance (NMR) can be used. An estimated quantification of unknown substances can be carried out using an internal standard with a similar response to that of the analysed substances (Koster et al., 2015).

The information about the composition of recycled polyolefins is still scarce. Huber and Franz studied migratable contaminants in recycled post-consumer HDPE by GC-FID and GC/MS concluding that the majority of contaminants were originated from personal care products and cleaning agents (Huber and Franz, 1997). Nerín et al. carried out a non-target analysis of multicomponent recycled plastics by extracting contaminants with solvents and analysing them with HPLC and GC/MS (Nerín et al., 1998). Several additives and degradation products were identified, nevertheless, the recycling technology used (homomicronization) is unusual in conventional recycling lines. Other authors analysed the VOCs present in recycled plastics using different extraction techniques such as microwave-assisted extraction (MAE), thermal desorption and SPME followed by GC/MS (Camacho and Karlsson, 2000, Stangenberg et al., 2004, Yamashita et al., 2009, Dutra et al., 2011). Pivnenko et al. performed a comprehensive analysis of phthalates present in waste plastics, recycled and virgin granules using solvent extraction and GC/MS. The results showed that the origin of these substances is rather the use of adhesives, glues, and waxes than the plastic material itself. The most abundant compound detected is diethylhexyl phthalate (DEHP), which can be used as an indicator of phthalate contamination (Pivnenko et al., 2016). Several research studies focus on odorous contaminants present in waste plastics and recycled plastics (Strangl et al., 2018, Strangl et al., 2019, Strangl et al., 2020). The main technique used was high resolution GC/MS and olfactometry. The study of the origin of the odorous compounds suggests that the main sources are the filling products in packaging materials, chemical degradation and microbial spoilage processes (Strangl et al., 2017). Furthermore, the waste collection systems affect the composition of the odorous compound. Cabanes et al. reported that cheesy and faecal smelling odorants are predominant in plastics waste from non-separate or mixed collection system, while earthy and moody smells predominate in separated at source plastics (Cabanes et al., 2020). In sum, so far research has been focused on VOCs identification, especially odorous compounds, in waste plastics and recycled resins. Therefore, a comprehensive analysis of less volatile substances is lacking.

In this Chapter, non-target analysis of semi-volatile organic substances (SVOCs) present in recycled plastic pellets from different sources has been conducted. These substances are likely to migrate from the plastic products and they are hardly removed during the reprocessing steps due to their lower volatility. The analytical method used is solvent extraction followed by GC/MS. Also, the composition of one virgin plastic and four masterbatch additives have been studied for comparison between raw and recycled materials. The results of this study will expand the current knowledge on the composition of recycled plastics which is fundamental to introduce a recycled content in high added value application and ensure its safety for the consumer. Furthermore, the results can be used as a basis for target analysis of substances that might pose a risk for consumer safety.

5.2. Methods

5.2.1. Extraction of semi-volatile organic compounds into a solvent

Semi-volatile organic compounds were obtained from the plastic samples by extraction into a solvent. Plastic pellets were grounded to powder using a cryogenic grinder to increase the contact area. An amount of 1.0 ± 0.02 g of grounded plastic was introduced into a 20 ml vial with 10 ± 0.05 mL of dichloromethane (DCM). The vials were sealed, and the samples were stirred for 24 hours. After the extraction period, the solvent was decanted from the sample and stored for 12 hours at 4°C to separate remaining solids. The extracts were then pre-filtered through glass wool and concentrated under a stream of nitrogen up to 1.5 mL (Pasvial sample vial concentration JSD). The extraction method has been adapted from (Huber and Franz, 1997). DCM was used as an extraction solvent due to potentially high diffusion of polyolefin constituents into this solvent (Feigenbaum et al., 2002). The DCM (HPLC quality) was purchased from VWR Chemicals (Barcelona, Spain). The analysis was carried out once for each sample since this is a qualitative study.

Two standards were added to make possible the comparison between the samples since the extraction method can create differences regarding the abundance of the substances, especially, during the concentration stage. Therefore, the area of each substance has been corrected with the area of the nearest compound from the standard. In total, 10 µL of internal standard Mix26 from Dr. Ehrenstorfer in DCM and 5 µL of anthracene-d10 from AccuStandard Inc in DCM were added. The Mix26 is composed of 6 deuterated compounds: 1,4-dichlorobenzene-D4, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12 in DCM. The concentration of each compound is 4000 µg/ml, which has been used to perform a semi-quantification of the substances identified in the samples. Standards were purchased from Sigma Aldrich Química (Barcelona, Spain).

5.2.2. Analysis of semi-volatile organic compounds by gas chromatography and mass spectrometry

Gas chromatography (Agilent 7890A) coupled with a quadrupole mass spectrometer (Agilent 5975C) has been used to identify the SVOCs extracted from the plastic materials. The non-polar HP5 capillary column (30 m length, 0.25 mm diameter, supplied by Agilent Technologies) was used. The method set in the GC/MS for the SVOCs analysis is described in Table 5.1.

***Table 5.1**. Operating conditions in the gas chromatography-mass spectrometry device for SVOCs identification.*

GC Conditions	PART 1	PART 2	PART 3
Split mode	Split 1:20	Splitless	Splitless
Injector temperature	250 °C		
Flow rate	1 mL/min		
Temperature program	T(°C)	Rate (°C/min)	Hold (min)
	40		5
	290	12	6
	320	20	10
MS Conditions			
Solvent delay	5 min	5 min	8 min
Scan mode	35 m/z – 550 m/z		
Method of ionization	Electron impact		

5.2.3. Methodology for semi-volatile organic compounds identification.

The SVOCs were identified via GC/MS assisted by NIST library with the previous deconvolution of the chromatogram using AMDIS software. To facilitate the data treatment, a programming code in MATLAB developed by the research group was used to manipulate the document provided by AMDIS and organize the organic compounds identified in all the samples simultaneously.

Of the total detected compounds, only the ones with a match quality higher than 80% were determined as tentatively identified compounds, and the ones with a match quality between 65 and 80% were considered as low quality tentatively identified compounds. The parameter of quality refers to the probability of an identified mass spectrum to match the mass spectrum of the reference compound from the NIST library, for which we used NIST MS search 2.0 software.

5.3. SVOCs in plastic additives (PART 1)

5.3.1. Materials

Four widely used additives in the plastic industry were analysed to identify the main SVOCs present in each one: an antioxidant, a slip agent, an antistatic agent and a polymer processing aid. All the samples were provided by a local plastic converting company dedicated to producing flexible packaging.

The function of the slip agent is to reduce the coefficient of friction between the plastic surface and the equipment. It is mainly used in polyolefin-based plastic packaging to ensure high speed in packaging lines (Chen et al., 2007). The antioxidants are intended to minimize the negative effects of oxidative degradation on the polymers caused by high temperature during processing, ultraviolet light, and chemical attack among others. The antioxidant effect is achieved by either removing free radicals or preventing their generation. The antistatic agents are added to remove static electricity generated on the polymer surface by increasing the conductivity or reducing resistivity (Selke and Culter, 2016). Finally, processing aids are mainly lubricants and fluoropolymer-based additives used to improve plastics processability and handling (Drobny, 2014).

5.3.2. Results

The chromatograms obtained are similar among the studied additives (Figure 5.2. Chromatograms of four widely used plastic additives and distribution of compounds.There are 3-4 major peaks in each chromatogram, which are considered heavy SVOCs since they were detected at higher retention time (over 20 minutes). The most abundant substances are considered IAS. Additionally, several smaller peaks were detected. Some of them can be contaminants from the additive production phase, thus they are considered NIAS. The peak area percentage (the area of the peak over the total area of the sample) was calculated and the substances with peak area over 1% have been included in this study.

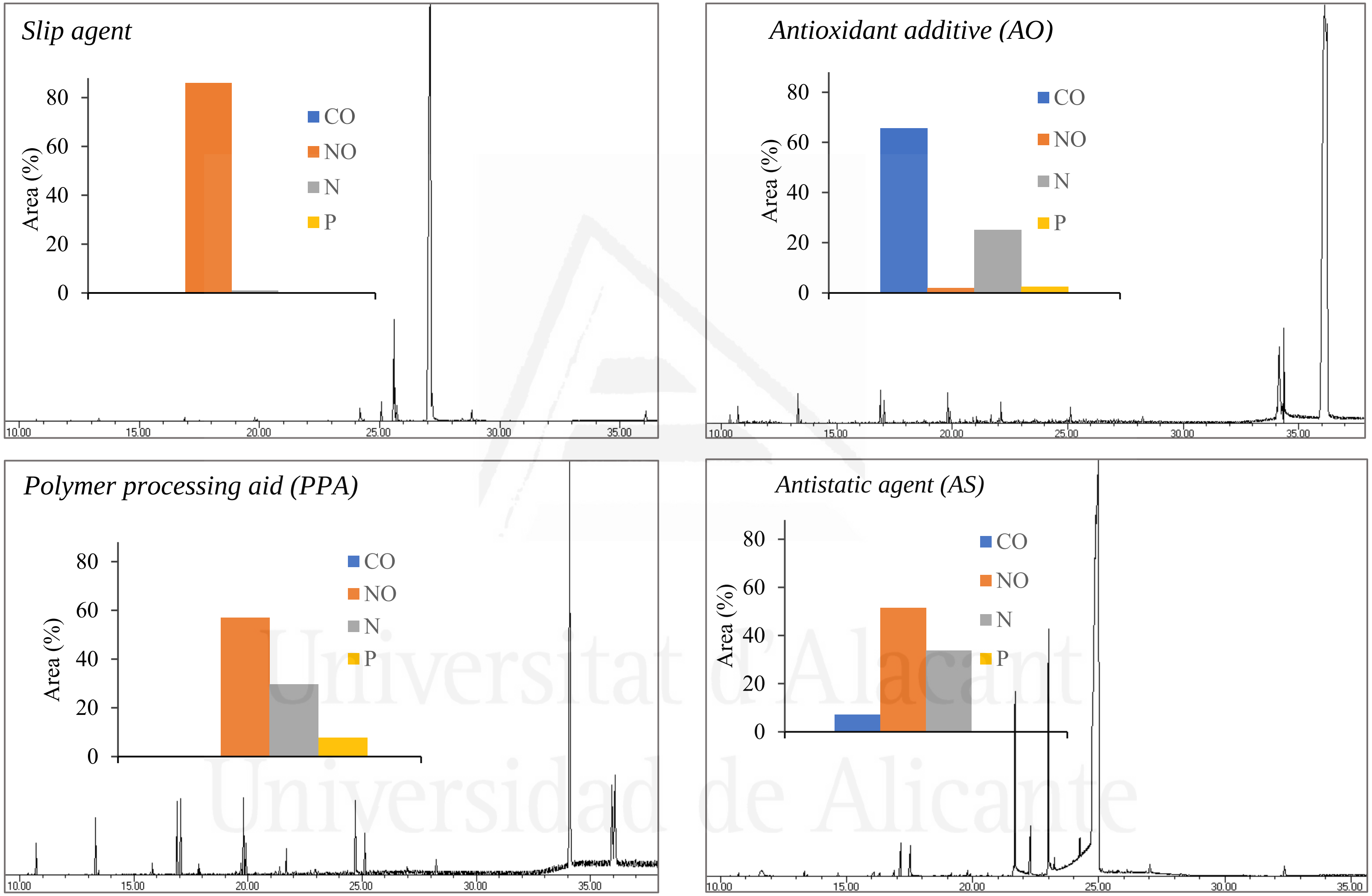

Figure 5.2. *Chromatograms of four widely used plastic additives and distribution of compounds.*

The compounds containing carbons and oxygen (CO), nitrogen and oxygen (NO), nitrogen (N) and phosphorus (P) are presented together with the sample chromatogram. The highest number of SVOCs was found in the antioxidant additive (14) followed by the antistatic agent (9), the polymer processing aid (8) and, finally, the slip agent (5). In the last three additives, the substances containing NO elements are predominant. Only in the antioxidant additive the compounds containing CO elements predominate. Substances with nitrogen attached to non-oxygen elements are present in all additives in different concentration. While the only compound with P was found in PPA and AO.

All the substances detected by GC/MS with peak area over 1% are reported in Table 5.2, classified according to their molecular structure as esters, amides, amines, cyclic compounds and others. The CAS number, formula, retention time (RT), match quality and peak area percentage are included. The parameter of quality refers to the probability of an identified mass spectrum to match the mass spectrum of the reference compound from the NIST 05 library. Substances with match quality over 80% are considered tentatively identified and between 65% and 80% are identified with low quality. Under 65% the substances cannot be identified with certainty; however, they can be used for comparison among samples since the analytical method is the same. Regarding the additives analysed, 20% of detected substances were tentatively identified, 13% were identified with low quality and 67% have a match quality under 65%.

The classification according to the molecular structure shows that amides is the predominant group in three of four additives: slip, antistatic and polymer processing aid. In the antioxidant additive, esters constitute the most abundant group (Figure 5.3). The most abundant substance in the slip additive is (Z)-13-docosenamide (or erucamide) (no. 8), which was also reported in different studies (Cooper and Tice, 1995, Farajzadeh et al., 2006, Garrido-López et al., 2006). N,N-bis(2-hydroxyethyl)-dodecanamide (no. 12) is the most abundant substance in antistatic and polymer processing additive. Finally, the biggest peak area in the antioxidant additive corresponds to octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (no. 2), which is widely known as Irganox 1076 (ECHA, 2020b).

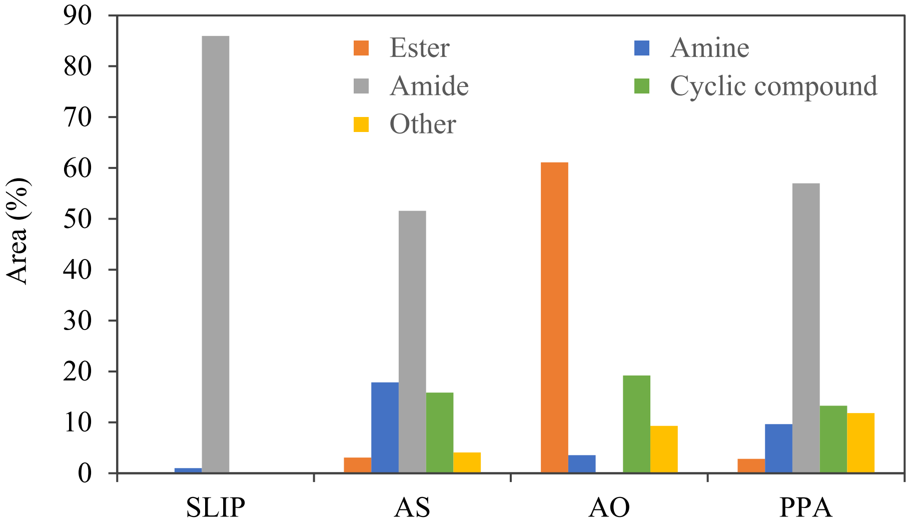

Figure 5.3. *Distribution of compounds identified in pure plastic additives.*

5.3.3. Discussion

A large list of additives exists in the market, such as plasticisers, antioxidants, lubricants, flame retardants, etc. The selection of the proper additives and their quality (or grade) depends greatly on the final application of the plastic product. For instance, substances intended to be used in food contact materials must meet the highest quality requirements subject to Regulation EN 10/2011.

The most abundant substances detected in the additives analysed are included in the Union List of Regulation EN 10/2011. Nevertheless, other compounds which are not accepted for food contact are present. Usually, the general composition of the masterbatch additives is reported in the technical datasheet. In addition, a declaration of compliance (DoC) is a document provided by a manufacturer to ensure that all the substances are authorised for use (ChemSafetyPro, 2019). Nevertheless, the NIAS such as impurities and contaminants are obviated. The number of contaminants increases when the quality of the additives decreases. Therefore, using low quality additives could jeopardize consumer safety after the material´s recycling.

5.4. SVOCs in post-industrial recycled pellets (PART 2)

5.4.1. Materials

In total, nine samples have been analysed to study the composition of different plastic pellets after mechanical recycling. One of the samples is virgin LDPE pellets obtained from a raw material producer. This sample has been included for comparison between virgin and recycled plastics. The recycled plastics are also made of LDPE, although they have a different origin. There are pellets from in-house recycling produced by re-extrusion of clean unprinted scrap in a converting company, six types of post-industrial pellets from two recycling companies and differentiated by colour, and recycled pellets from agricultural plastic waste. All the samples and their nomenclature are described hereafter.

- Virgin – raw LDPE from a petrochemical company.
- Regrind – white post-industrial plastic pellets from in-house recycling.
- Black R1 – black post-industrial plastic pellets from recycling company Nº1.
- Coloured R1 – coloured post-industrial plastic pellets from recycling company Nº1.
- Transparent R1 – transparent post-industrial plastic pellets from recycling company Nº1.
- White R1 – white post-industrial plastic pellets from recycling company Nº1.
- Black R2 – black post-industrial plastic pellets from recycling company Nº2.
- Brown R2 – brown post-industrial plastic pellets from recycling company Nº2.
- Agricultural R3 – recycled pellets from agricultural plastic waste from recycling company Nº 3.

5.4.2. Results

5.4.2.1. Overall emissions

In total 334 substances have been detected in this study. The number of compounds in each sample and their total concentration vary depending on the source of the materials (Figure 5.4). Virgin plastic and recycled granules from in-house recycling (Regrind) show the highest concentration compared to other samples. Nevertheless, the number of compounds detected is less than the average in the other samples. Accordingly, the concentration of substances in the pellets from the recycling companies (R1-R3) is lower, whilst their number is higher.

One might expect the concentration in the virgin plastic to be the lowest since it should only contain the polymer and some components used during polymerization. But virgin pellets existing in the market generally contain some of the common plastic additives such as slip agent, plasticisers or stabilisers. More additives are added during plastic processing depending on the final application of the product. Therefore, re-extruded plastic scrap contains a higher concentration of substances. Generally, plastic additives are consumed during the lifetime of the product. For instance, the function of the antioxidant additive is to prevent the degradation of the polymer by reacting with free radicals, thus destroying the original structure of the molecule (Bradley and Coulier, 2007). In consequence, the concentration in recycled plastics is lower. The degradation and reaction of the additives also explain the increase in the number of detected substances.

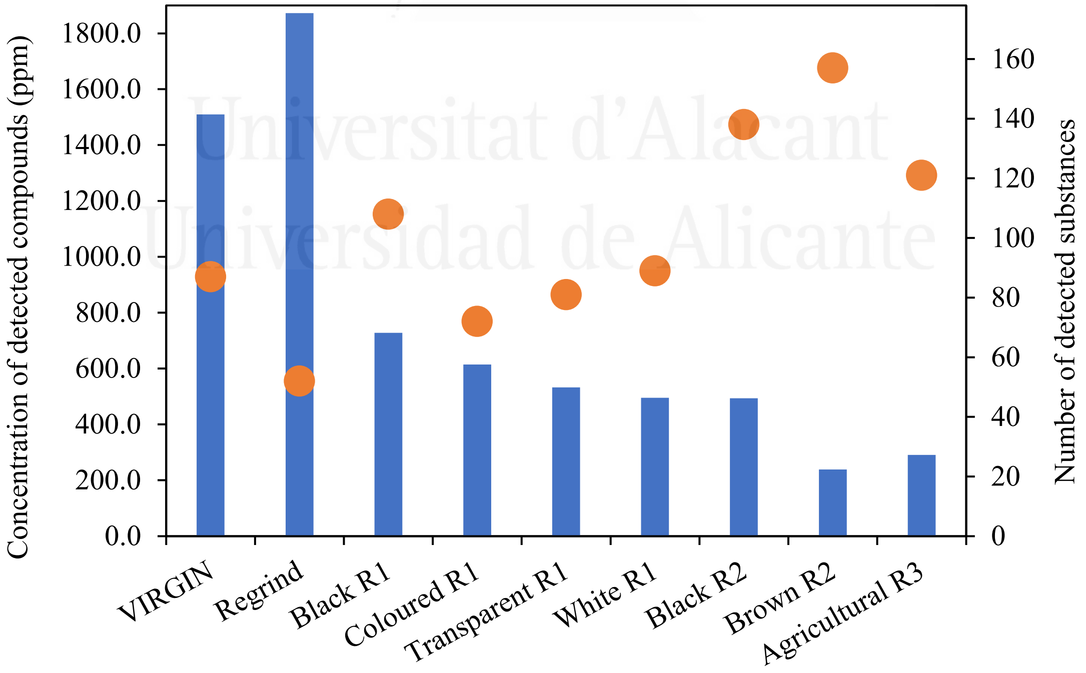

Figure 5.4. *Total concentration of detected compounds (blue bars) and their number in the sample (orange dots).*

The volatility of the main compounds varies among the samples, except for the fact that the percentage of substances detected between 0 and 15 minutes is minimal (around 1.5%) (Figure 5.5). Compounds with RT between 15 and 30 minutes predominate in the virgin plastic, the regrind, and the black and brown recycled pellets from the recycler Nº2. Conversely, the most abundant substances in the black and transparent samples from the recycler Nº1 are less volatile, i.e. detected between 30 and 45 minutes. Finally, in the coloured and white samples from the recycler Nº1, and the agricultural pellets, the concentration of medium and low volatile substances is similar.

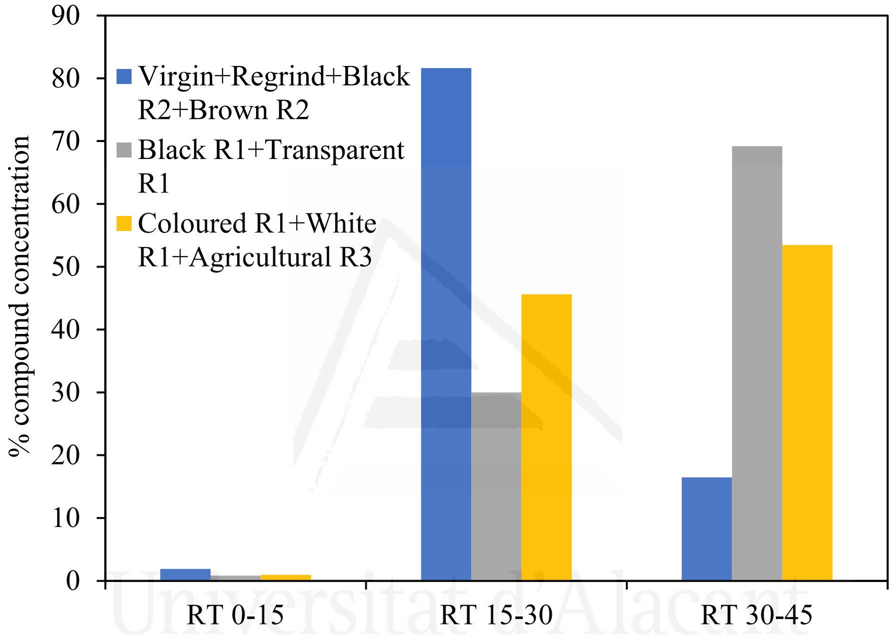

Figure 5.5. *Profile of SVOCs in virgin and post-industrial recycled plastics according to the retention time (RT) that the molecules remain in the HP5 capillary column.*

The classification of detected substances according to the chemical groups shows that amides are the most abundant group in the virgin plastic (around 93%). Other substances with lower concentration belong to the groups of esters, hydrocarbons, amines, alcohols, azoles and ketones. The major groups presented in the in-house recycled pellets (Regrind) are amides and esters (71% and 28% respectively). Regarding post-industrial plastic pellets, the distribution of substances changes compared with previous samples. In this case, the major group is esters (64%) followed by amides (14%). Some substances with low concentration were put together in the group of others containing aldehydes, acids, cyclic compounds, etc. This group represents 9% of all detected substances. The concentration of hydrocarbons, alcohols, azoles and ketones is higher than in virgin and in-house recycled pellets. Conversely, the concentration of amines is almost negligible (Figure 5.6).

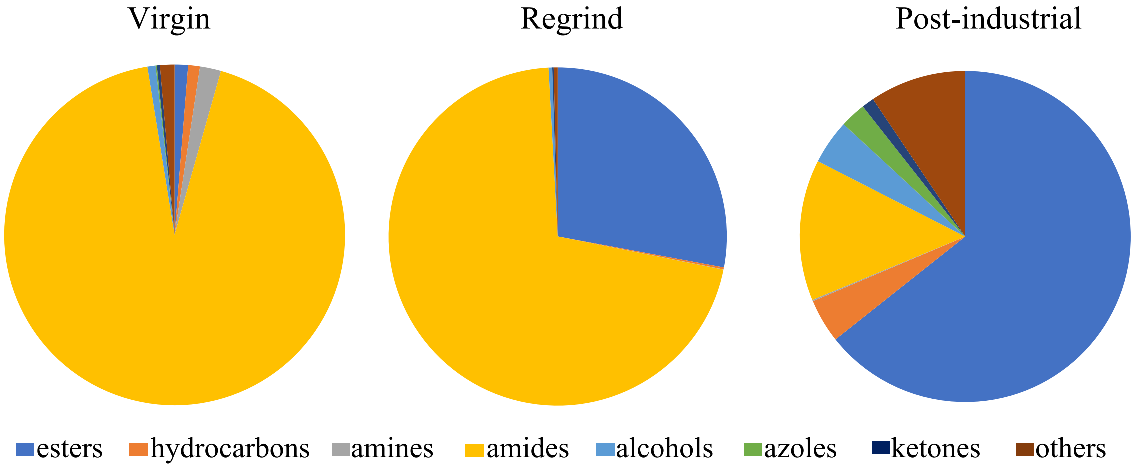

Figure 5.6*. Distribution of detected substances according to the chemical group.*

5.4.2.2. Identified substances

The identified substances are detailed in Table 5.3 in the Appendix including the CAS number, formula, retention time, match quality and approximate concentration. In total, 12 substances have been identified with match quality over 80%, of which two are alcohols: diethylene glycol (no. 1) and 2,4-di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol (no. 2); two are esters: bis(2-ethylhexyl) isophthalate (no. 5) and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (no. 7); two are amides: N-butylbenzenesulfonamide (no. 8) and (Z)-13-docosenamide (no. 9). Also, one ketone and one azole have been identified: (1-hydroxycyclohexyl) phenyl-methanone (no. 10) and bumetrizole (no. 16), respectively. The other substances are benzestrol (no. 18), 7,9-di-tert-butyl-1-oxaspiro (4,5) deca-6,9-diene-2,8-dione (no. 20), octadecanoic acid (no. 21) and 1-(phenylmethoxy)-naphthalene (no. 22).

Four substances are present in all the samples: octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, (Z)-13-docosenamide, (1-hydroxycyclohexyl) phenyl-methanone and 7,9-Di-tert-butyl-1-oxaspiro (4,5) deca-6,9-diene-2,8-dione. Benzestrol and octadecanoic acid were found in all the recycled plastics but not in the virgin plastic. Several substances appear only in post-industrial recycled pellets: 1,3-benzenedicarboxylic acid, bis(2-ethylhexyl) ester, N-butylbenzenesulfonamide, bumetrizole and 1-(phenylmethoxy)-naphthalene. The alcohols diethylene glycol and 2,4-di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol were detected each one in one recycled plastic (black R2 and white R1 respectively). The substance with the highest concentration is (Z)-13-docosenamide followed by octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate and 1,3-benzenedicarboxylic acid, bis(2-ethylhexyl) ester.

A total of 11 substances were identified with a quality between 65 and 80%. The major group (5 substances) is formed by alkylbenzenes, i.e., a benzene attached to a carbon chain, namely decyl benzene, dodecyl benzene, tetradecyl benzene, hexadecyl benzene, and octadecyl benzene (no. 11 to no. 15). Three esters have been found: methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (no. 3), tributyl acetylcitrate (no. 4) and glycerol tricaprylate (no. 6). Other substances detected are pentamethyl cyclopentane (no. 17), 2(5H)-furanone (no. 19), and 2,2'-methylenebis(6-tert-butyl-p-cresol) (no. 23).

Pentamethyl cyclopentane is the only substance present in all samples. Tributyl acetylcitrate has been found in post-industrial recycled pellets but not in virgin plastic nor in in-house recycled. Finally, all alkylbenzenes appear in virgin plastic and some of them in recycled pellets (regrind, black R1, black R2 and agricultural R3). The most abundant compound is tributyl acetylcitrate followed by glycerol tricaprylate and pentamethyl cyclopentane.

In addition to the tentatively identified substances, there are several substances which chemical structure cannot be established with certainty because of their poor match quality (under 65%). Nevertheless, some of these substances are present in high concentration and should be included in the study. In total, 21 additional substances were analyzed: 5 alcohols, 5 esters, 4 amides and 7 other compounds such as acids, cyclic compounds, amines and phosphines. The substances with the highest concentration are benzoic acid, 3,5-dicyclohexyl-4-hydroxy-, methyl ester (no. 33), methylenebis (2,4,6-triisopropylphenylphosphine) (no. 43), n-hexadecanoic acid (no. 39) and mono(2-ethylhexyl) phthalate (no. 32).

5.4.3. Discussion

The identified substances were categorized by their origin in three groups: additives, degradation products, and contaminants. The additives are considered IAS because they are part of the original formulation of the plastic product and were added during the manufacturing process. On the contrary, NIAS, such as degradation products and contaminants, may appear during the manufacturing processes or the lifetime of the product.

5.4.3.1. Additives

In total, 14 substances have been classified as additives. Seven substances were identified with match quality over 80%. Namely, 2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol used as a light stabiliser (Groh et al., 2018)), bis(2-ethylhexyl) isophthalate found as PVC plasticiser (Rani et al., 2015)), octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (antioxidant), N-butylbenzenesulfonamide used as PUR and PA plasticiser, the slip agent (Z)-13-docosenamide, bumetrizole known as a light stabiliser (Groh et al., 2018)), and octadecanoic acid which is polyolefins plasticiser and lubricant (ECHA, 2018). The antioxidant additive and the slip agent coincide with the substances identified during the analysis of the additives´ masterbatch in Part 1. Three possible additives have been identified with match quality between 65% and 80%: tributyl acetylcitrate used as PUR and PVC plasticiser, glycerol tricaprylate found as a lubricant (Galmán Graíño et al., 2018)), and 2,2'-Methylenebis(6-tert-butyl-p-cresol) a polyolefin antioxidant (ECHA, 2018). Although the substances detected with match quality under 65% cannot be identified with certainty, there is a possibility that some of them belong to the group of additives. These substances are 2,4-bis(1,1-dimethylethyl) phenol used as an antioxidant (Frontier Laboratories, n.d.), bisphenol A (a multifunctional additive used in PC, PVC, epoxy resins (Groh et al., 2018)), diisooctyl adipate used as plasticiser (Frontier Laboratories, n.d.), and mono(2-ethylhexyl) phthalate (plasticiser).

The approximate concentration of the identified additives in the virgin and recycled plastics is represented in Figure 5.7. The concentration of the slip agent is significantly higher (around 20 times) in the virgin and in-house recycled pellets than in the post-industrial pellets. This can be attributed to the fact that the (Z)-13-docosenamide migrates to the surface of the plastic to reduce the coefficient of friction, and once there, it could undergo chemical change or decomposition (Shuler et al., 2004). The similar concentration of erucamide between the virgin plastic and the in-house recycled pellets suggests that the additive suffers little decomposition during extrusion since it has good thermal stability (Murphy, 2001). Other additives present in the virgin plastics are the antioxidant Irganox 1076 and a plasticiser (possibly mono(2-ethylhexyl) phthalate).

The post-industrial recycled pellets and the plastic from agriculture contain diverse concentrations of antioxidants, slip agent, plasticisers, and other additives such as lubricants and/or light stabilisers. A greater variety of additives in these samples coincide with the diversity of detected compounds reported in Figure 5.6. The loss of additives during the service life and recycling processes must be compensated during the manufacturing of new products. Some of the plasticisers named are mainly used in polymers different from the LDPE (for instance, PUR and PVC), which means that the waste stream used for the production of the recycled pellets had been contaminated with incompatible polymers.

Moreover, several additives are not included in the Union list of Regulation EN 10/2011. Therefore, these recycled pellets cannot be used in food contact applications. The use of other additives like bisphenol A is restricted due to its toxic for reproduction and endocrine disrupting properties (ECHA, n.d.). Although the European legislation permits the use of this additive in food contact material with a specific migration limit of 0.05 mg/kg, its use is completely banned in baby's food packages and containers. In general, the presence of phthalates in plastic materials is of increasing concern because some of them are listed as Endocrine Disruptive Chemicals (EDC), carcinogenic, mutagenic, and teratogen (can cause birth defect) (Ferguson et al., 2014, Garí et al., 2019). Furthermore, phthalates can enter the human bodies in several ways: ingestion, inhalation and dermal absorption (Koch and Calafat, 2009). So, consumer safety issues are not exclusive to food contact materials. Other sectors such as hygienic packaging could be affected negatively.

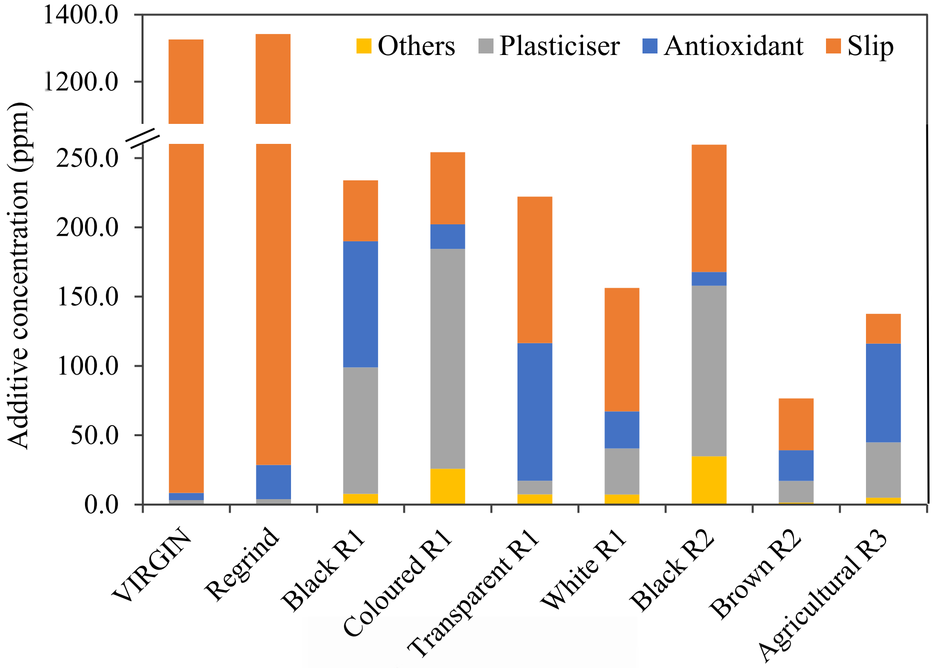

Figure 5.7. *Concentration of plastic additives.*

5.4.3.2. Degradation products

One substance with match quality over 80% has been tentatively identified as additive degradation product, specifically 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione described as a degradation product of hindered phenol-type antioxidants (Bradley and Coulier, 2007). The alkylbenzenes tentatively identified between 65% and 80% might be degradation products of antioxidants based on hindered phenols and exposed to high temperature (Wang, 2000). The virgin plastic and some recycled pellets (regrind, black R1, black R2, and agricultural R3) contain these types of substances. The virgin plastic is usually exposed to high temperatures during compounding processes and the recycled plastics during several extrusion cycles. Nevertheless, in the literature, alkylbenzenes have been also described as breakdown products produced by the degradation of alkylbenzene sulfonates, widely used as anionic surfactants in detergents and cleaning agents. Therefore, these substances could also be contaminants from the washing stage. Another compound identified with less quality (between 65% and 80%) which could be an impurity or degradation product of an antioxidant additive is methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (Bradley and Coulier, 2007). Also, 2 substances have been described as polymer degradation products, namely pentamethyl cyclopentane and 2(5H)-furanone (Salvalaggio et al., 2006, Bradley and Coulier, 2007).

Regarding the substances detected with match quality under 65%, the group of esters and phthalates has been considered degradation products of antioxidant additives and plasticisers, respectively. The group of amides might be impurities or degradation products of erucamide or another amide additive. Alcohols can be degradation products of certain plasticisers and stabilisers or external contaminants such as fragrances and flavour constituents (Bradley and Coulier, 2007). Acids like dodecanoic acid and hexadecanoic acid are also common degradation products. The compound methylenebis(2,4,6-triisopropylphenylphosphine) is considered a degradation product of a PPA additive since it has been detected at a similar retention time during the analysis of the additive masterbatch (Table 5.2).

5.4.3.3. Contaminants

In this study, contaminants are all the substances that adhere to the plastic products during their lifetime, including manufacturing, service life and recycling, and all of them have been tentatively identified with match quality over 80%. There are 2 substances, diethylene glycol and (1-hydroxycyclohexyl)phenyl-methanone, which are used in adhesives, inks, dyes, and coatings (ECHA, 2019b, ECHA, 2020a). In this case, it is difficult to establish if these substances were added intentionally or not since it is almost impossible to trace back the formulation of all the products collected for recycling. Besides, tributyl acetylcitrate is used in both additives and inks manufacturing (ECHA, 2019c), so that it could be classified also as a contaminant. The compound 1-(phenylmethoxy)-naphthalene is used for the manufacture of pulp and paper (ECHA, 2019a). Its presence in several recycled pellets (transparent R1, black R2, brown R2, and agricultural R3) suggest that the plastic waste stream has been contaminated with paper products. Another contaminant identified with high certainty is benzestrol. This substance is a synthetic estrogen used in medical treatments with no apparent relationship with plastic materials (Blanchard and Stebbins, 1945, CDC, n.d.). Since it has been detected in all the recycled pellets including the regrind (Table 5.3), first, a standard should be used to verify the identity of the substance and, second, the exact source of contamination should be studied. Unfortunately, this verification cannot be done in this study because of the large volume of work already accomplished. Nevertheless, this leaves open the possibility to continue with the research.

5.4.3.4. Distribution of SVOCs according to their origin

The classification of the identified substances according to their origin shows that the highest concentration of additives corresponds to the virgin plastic and the in-house recycled scrap (regrind). In the recycled pellets, the concentration of additives decreases in different proportions, likely, depending on the conditions to which the material has been exposed to. In several recycled samples (black R1, coloured R1, transparent R1, and white R1) the degradation products exceed the additives and the concentration of contaminants is negligible. It should be noticed that all these samples come from the same recycling company, whereas the samples from the second and third recycling company show a different distribution. These results suggest that the origin of the waste and the recycling processes have a great influence on the generation of NIAS. Finally, a higher concentration of contaminants in samples black R2, brown R2, and agricultural R3 indicates that the waste stream requires better collection, sorting and manufacturing practices (Figure 5.8).

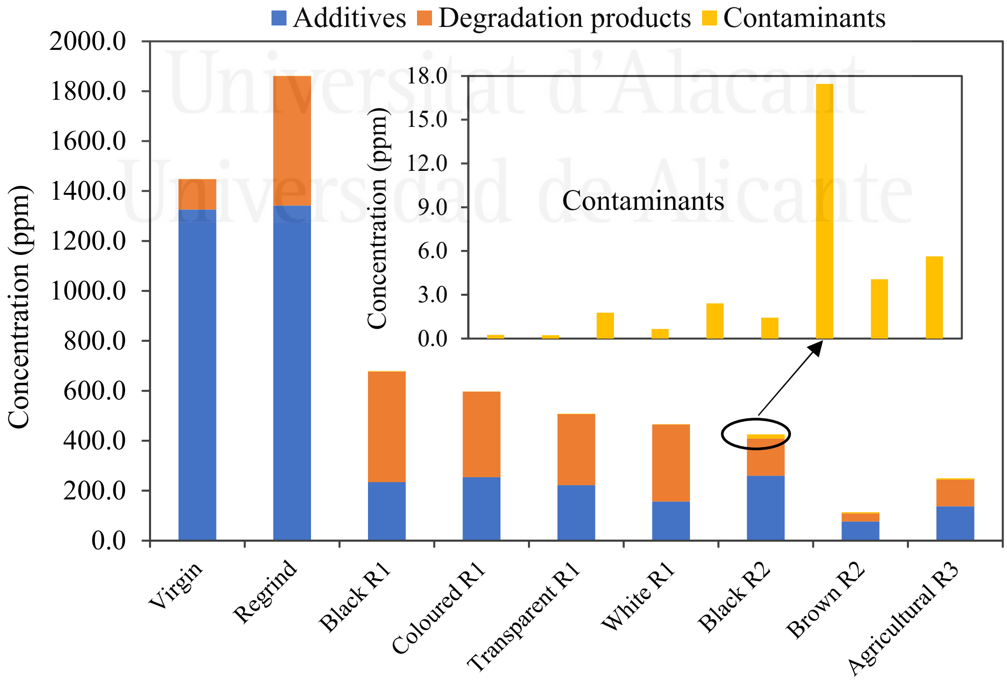

Figure 5.8. Concentration of the group of additives, degradation products and contaminants.

5.5. SVOCs in post-consumer recycled pellets (PART 3)

5.5.1. Materials

Two samples were analysed in this study consisting of recycled pellets from post-consumer low-density polyethylene (PC-LDPE) and high-density polyethylene (PC-HPDE) from yellow sack collected in Germany. PC-LDPE waste consists of single layer LDPE bags and films, and PC-HDPE consists of rigid bottles from detergents, shampoo and other cleaning products. The pellets were produced by a recycling company. During the recycling process the plastic waste was washed with cold water solely, dried by centrifugation, and finally, extruded with a degassing system and pelletized, obtaining pellets with 5 mm diameter. The percentage of post-consumer LDPE and HDPE in the recycled pellets is 100%. The LDPE and HDPE samples used are a mixture of the granules from three different lots produced by the recycling company.

5.5.2. Results

5.5.2.1. Overall emissions

The chromatograms of PC-HDPE and PC-LDPE show that the amount of SVOCs is higher in the LDPE sample than in the HDPE sample (Figure 5.9). The total area under the LDPE chromatogram is around 5 times higher than the total area of HDPE. More than 800 compounds were detected as a sum of both samples, but not all of them provided a reliable match with the NIST library. The identified compounds are divided into three main groups: hydrocarbons, oxygenated and nitrogenous. The 66% of the total PC-LDPE area corresponds to substances containing oxygen while the remaining area is almost equally represented by hydrocarbons and nitrogen-compounds (around 16% each). Regarding PC-HDPE, the largest group is also formed by oxygenated compounds amounting to 45% of the total area. The percentage of hydrocarbons and nitrogen-compounds is also similar in this sample, 26% and 25% respectively.

Regarding the volatility of SVOCs, PC-LDPE presents a higher concentration (almost 80%) of compounds with RT between 15 and 30 minutes. Less volatile compounds (30<RT<45 minutes) represent around 20% of the total mass. These two groups cover nearly the totality of detected SVOCs since the percentage of substances between 0 and 15 minutes is barely 0.2%. The PC-HDPE sample shows a similar proportion of compounds in the medium (15<RT<30 minutes) and low volatility (30<RT<45 minutes) region, around 48% and 46% respectively. The remaining fraction corresponds to compounds detected between 0 and 15 minutes (Figure 5.10).

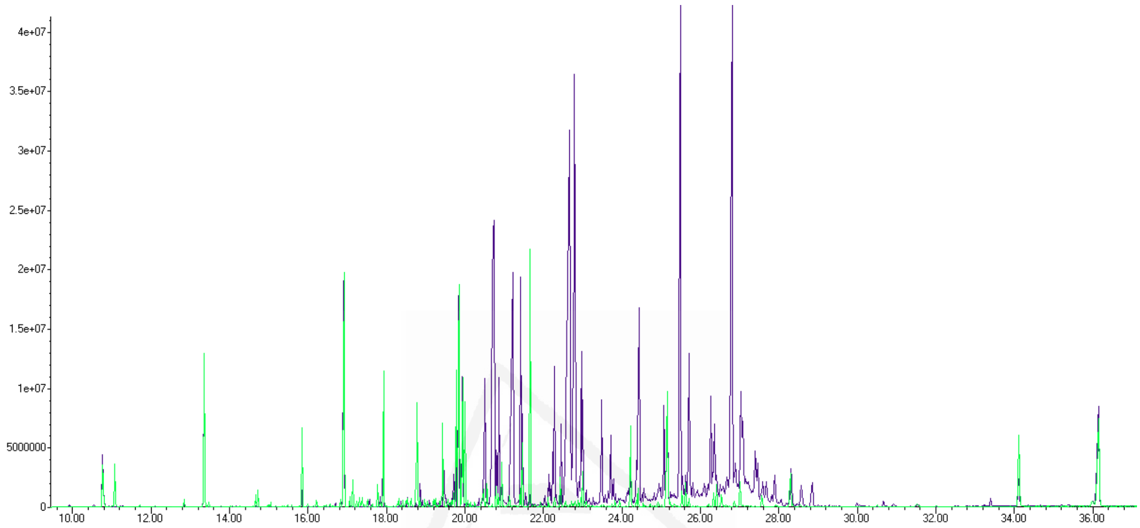

Figure 5.9. *Chromatogram of post-consumer LDPE (purple) and post-consumer HDPE (green) recycled pellets obtained by solid-liquid extraction and GC/MS.*

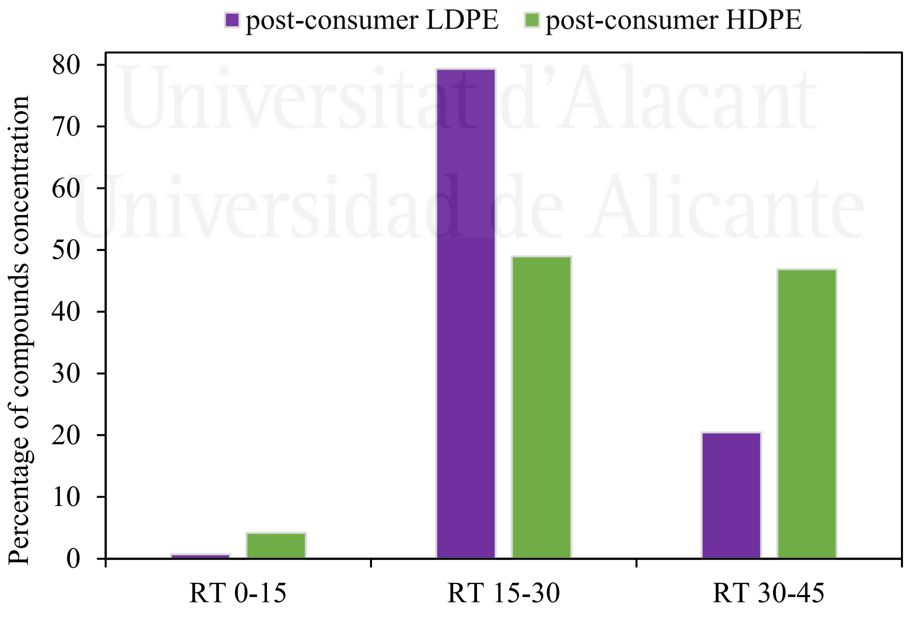

Figure 5.10*. Profile of SVOCs in post-consumer HPPE and LDPE according to the retention time (RT) that the molecules remain in the HP5 capillary column.*

5.5.2.2. Identified substances

All the substances identified in the post-consumer recycled plastics are listed in Table 5.4 moved to the Appendix including the CAS number, formula, retention time, match quality and approximate concentration. In the sum of the two samples, 7 of all organic compounds detected by GC/MS have been tentatively identified since their match quality is higher than 80%. The largest group is represented by esters (4 substances): 2-ethylhexyl salicylate (no. 14), tributyl acetylcitrate (no. 20), methyl abieta-8,11,13-trien-18-oate (no. 22) and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (no. 26). All these substances have been detected in the PC-LDPE sample, and only the last one is present in the PC-HDPE sample. The remaining three substances belong to a different functional group. These substances are (1-butylheptyl) benzene (no. 4) (found in both samples), bumetrizole (no. 27) (found in PC-HDPE) and diethylene glycol (no. 1) (found in PC-LDPE). Therefore, in total, 6 substances have been tentatively identified in PC-LDPE and 3 substances in PC-HDPE. The use of internal standards allows performing a semi-quantification of the concentration (substance weight per sample weight). The most abundant compound of the PC-LDPE sample is tributyl acetylcitrate (around 22.0 ppm) followed by octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (around 20.0 ppm). The esters 2-ethylhexyl salicylate and methyl abieta-8,11,13-trien-18-oate have been detected with a concentration of around 4.0 ppm. The least abundant substances were diethylene glycol and (1-butylheptyl) benzene with 0.3 ppm and 0.1 ppm, respectively. Regarding PC-HDPE sample, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate presents the highest concentration (around 15.0 ppm), followed by bumetrizole (7.0 ppm) and (1-butylheptyl) benzene (1.6 ppm).

Regarding the substances with lower match quality identification, in total, 25 compounds have been identified with a match quality between 65 and 80%. Specifically, 20 substances were found in PC-LDPE and 13 substances in PC-HDPE. In this case, 8 compounds were detected in both samples. The groups with the largest number of substances are esters (10 compounds) and carboxylic acids (3 compounds). Other smaller groups are ketones and alkylbenzenes (with 2 compounds each one) and aldehydes, amides and phthalates (with 1 compound each one). The rest contain different substances such as 2,2,4,4,6,8,8-heptamethylnonane (no. 30), 7,9-Di-tert-butyl-1-

oxaspiro(4,5)deca-6,9-diene-2,8-dione (no. 31), diphenyl sulfone (no. 32), tert-butyl-(4-tert-butylphenyl) phosphinic acid (no. 10) and dipropylene glycol (no. 2). The most abundant compound in PC-LDPE sample is bis(2-ethylhexyl) isophthalate (no. 29) which concentration is around 272.0 ppm. This is more than 3 times higher than the concentration of hexadecanoic acid (no. 9) and (Z)-13-docosenamide (no. 28), which amounts to around 80 ppm each. The concentration of the group of carboxylic acid esters varies between 1.8 ppm and 38.0 ppm. The least abundant compounds in the PC-LDPE samples are (1-ethyldecyl) benzene (no. 5) and diphenyl sulfone (no. 32) (0.2 ppm and 0.1 ppm, respectively). The concentration of substances detected in PC-HDPE is significantly lower than in PC-LDPE. The most abundant compound identified with low quality in PC-HDPE is (Z)- 13-docosenamide (no. 28), with 14.0 ppm approximately, which is more than 5 times lower than the concentration of the same substance in PC-LDPE and around 20 times lower than the most concentrated substance in PC-LDPE.

Finally, 6 substances have been detected in high concentration, but with a poor match quality (under 65%). These substances cannot be identified with certainty; however, they are worth to mention due to their high abundance. Methyl 3,5-dicyclohexyl-4-hydroxybenzoate (no. 38) is present in the highest concentration in both samples (around 343.0 ppm in PC-LDPE and 239.0 ppm in PC-HDPE). Other substances detected in PC-LDPE with high concentrations were di-n-octyl phthalate (no. 35) (170.0 ppm), ethyl oleate (no. 34) (160.0 ppm), (Z)-6-octadecenoic acid (no. 33), (146.0 ppm), methylenebis(2,4,6-triisopropylphenylphosphine) (no. 37) (35.0 ppm) and (Z)-9-octadecenamide (no. 36) (32.0 ppm). The latter two were also found in PC-HDPE with concentrations of around 60.0 ppm and 23.0 ppm, respectively.

5.5.3. Discussion

The same classification used in section 5.4.3 in Part 2 has been adopted to categorize the substances identified in the post-consumer HDPE and LDPE samples. The three groups are additives, degradation products, and contaminants. Polymer and additives degradation products are usually generated due to excessive heat and irradiation energies (Nerin et al., 2013). The contaminants identified in the PC-HDPE and PC-LDPE samples are mainly associated with cosmetics, food aromas, organic waste or inks, as detailed hereafter. The origin assigned to each substance and the bibliographic references can be found in Table 5.4 (Appendix).

5.5.3.1. Additives

A total of 11 substances were related to plastic additives, three of which with a match quality higher than 80%, namely tributyl acetyl citrate (no. 30), bumetrizole (no. 27) and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (no. 26). The substances with a match quality between 65 and 80% reported as additives are benzophenone (no. 11), dodecanoic acid (no. 7), tetradecanoic acid (no. 8), hexadecanoic acid (no. 9), (Z)-13-docosenamide (no. 28), bis(2-ethylhexyl) isophthalate (no. 29), of which the latter one is not included in the list from Regulation EN 10/2011, but the rest are accepted as food contact additives. Additionally, possible additives found as major compounds but identified with an approximate molecular structure in the chromatogram (match quality < 65%) are ethyl oleate (no. 34) and di-n-octyl phthalate (no. 35). These two are neither included in the list from Regulation EN 10/2011. The most abundant additives in the PC-HDPE sample are the antioxidant octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate and the slip agent (Z)-13-docosenamide (14.8 ppm and 13.6 ppm, respectively). Regarding PC-LDPE sample, the most abundant additive is bis(2-ethylhexyl) isophthalate used as plasticiser (272.8 ppm).

The additives which do not comply with the food contact regulation usually come from less demanding applications and, therefore, might pose safety issues to consumers of recycled products. Besides, the presence of composite materials containing inks, coating, functional barriers, etc. increases the number of substances in recycled plastics. Accordingly, the lack of traceability in post-consumer plastic waste represents currently an obstacle for the implementation of the circular economy through closed-loop recycling, which is in line with previous studies on this topic (McKinnon et al., 2018). Overall, the additives identified in this study are mainly antioxidants, plasticisers and processing aids, as well as a UV absorber and slip agent to a less extent.

5.5.3.2. Degradation products

In the semi-volatile fraction, 2 substances were identified with match quality over 80%, namely methyl abieta-8,11,13-trien-18-oate (no. 22) and diethylene glycol (no. 1), 11 substances between 65% and 80% including ethyl tetradecanoate (no. 13), methyl hexadecanoate (no. 15), ethyl palmitate (no. 16), propyl hexadecanoate (no. 18), methyl octadecanoate (no. 19), propyl octadecanoate (no. 21), dodecyl hexadecanoate (no. 23), hexadecyl hexadecanoate (no. 25), 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (no. 31), tert-butyl-(4-tert-butylphenyl) phosphinic acid (no. 10) and dipropylene glycol (no. 2) and, finally, four substances under 65%, 6-octadecenoic acid (no. 33), (Z)-, 9-octadecenamide, (Z)- (no. 36), methylenebis(2,4,6-triisopropylphenylphosphine) (no. 37) and methyl 3,5-dicyclohexyl-4-hydroxybenzoate (no. 38). The chemical structure of the substances with low quality match are approximate. Nevertheless, based on their chemical structure, it has been suggested that they are possible degradation products of lubricants, slip agents and antioxidant additives. Two compounds have been also identified in the additives masterbatch in section 5.3.2 (no. 36 and 37). They could have been formed as degradation products or secondary products during additives manufacturing processes.

Only 2,2,4,4,6,8,8-heptamethylnonanone (no. 30) was detected with the analysis of SVOCs compounds. It is believed that a higher number of polymer degradation products exists, but its quality match was too low for the identification.

5.5.3.3. Contaminants from external sources

A total of 14 substances were tentatively identified as plastic contaminants, 3 with match quality over 80% and 11 with match quality between 65% and 80%. These compounds are 2-ethylhexyl salicylate (no. 14), (1-butylheptyl) benzene (no. 4), bumetrizole (no. 27), benzophenone (no. 11), 2-acetyl-5-methylfuran (no. 12), 2-(phenylmethylene)heptanal (no. 3), isopropyl palmitate (no. 17), glycerol tricaprylate (no. 24), dodecanoic acid (no. 7), tetradecanoic acid (no. 8), n-hexadecanoic acid (no. 9), (1-ethyldecyl) benzene (no. 5), (1-methylundecyl) benzene (no. 6) and diphenyl sulfone (no. 32). It can be noticed that several substances (no. 7, 8, 9, 11 and 27) have been classified as additives and contaminants simultaneously. This is because these substances appear in several data sources, for instance, in the list of substances permitted as additives for food packaging (EN 10/2011) and in the CosIng database (cosmetic ingredients). Most contaminants belong to the group of cosmetics, including surfactants, cleaning agents and emollients, as well as to their degradation products. Other contaminants can be incompatible thermosetting plastics as a result of cross-contamination, for instance, diphenyl sulfone.

5.5.3.4. Distribution of SVOCs identified in PC-LDPE and PC-HDPE

The total number of compounds detected in the PC-HDPE sample is lower than the number of compounds in the PC-LDPE sample (19 versus 32). It has been found that the total mass of the identified substances per mass of the plastic sample is around 4 times higher in PC-LDPE than in PC-HDPE. The group of additives shows the highest concentration in the LDPE sample, followed by additive degradation products. The concentration of contaminants is significantly lower, and the concentration of polymer degradation products is almost negligible. This is likely because many of these substances are volatile and could be obtained in the light fraction using analytic techniques such as headspace solid phase microextraction (HS-SPME). In the HDPE sample, the additive degradation products predominate (Figure 5.11).

The most abundant additive in the PC-LDPE sample is bis(2-ethylhexyl) isophthalate (no. 29), commonly used as a plasticizer, with 272.8 ppm, approximately. As mentioned in section 4.1, this additive is not included in the positive list of additives accepted for food contact materials manufacturing (EU 10/2011). Therefore, its migration from the final recycled product should be studied together with an appropriate risk assessment. Two additional substances with high concentration were identified as possible additives although with a match quality lower than 65%: ethyl oleate (no. 34) with 160.0 ppm and di-n-octyl phthalate (no. 35) with 170.0 ppm. Regarding additive degradation products, the most abundant substances were identified with low match quality: 6-octadecenoic acid, (Z)- (no. 33) with 146.3 ppm and methyl 3,5-dicyclohexyl-4-hydroxybenzoate (no. 38) with 343.7 ppm.

Among the additives tentatively identified in the PC-HDPE sample, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (no. 26), used as an antioxidant, presents the highest concentration (around 15.0 ppm), followed by (Z)-13-docosenamide (no. 28), with nearly 14.0 ppm. Both substances appear on the Union list of Regulation EU 10/2011, however, only the former presents a specific migration limit (SML), which determines the maximum amount permitted of the additive accumulated in the packed food. The slip agent (Z)-13-docosenamide, must comply with an overall migration limit of 10 mg of total constituents per dm^2 of the food contact surface. Additives degradation products with the highest concentration were identified with low match quality: 9-octadecenamide, (Z)- (no. 36) with 23.0 ppm, methylenebis(2,4,6-triisopropylphenylphosphine) (no. 37) with 60.3 ppm and methyl 3,5-dicyclohexyl-4-hydroxybenzoate (no. 38) with 239.0 ppm.

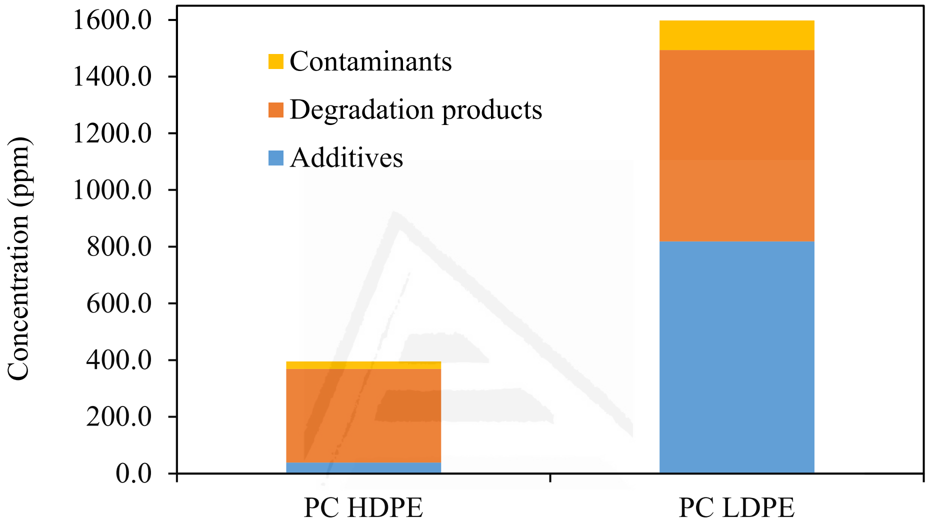

Figure 5.11. *Concentration of SVOCs identified in post-consumer LDPE and HDPE samples according to their origin.*

These results suggest that LDPE waste can cause safety problems during its second life cycle mainly due to the present additives and their degradation products, whereas HDPE waste from rigid packaging contains a high number of contaminants from the use phase which could be harmful to human health.

Finally, both post-consumer samples have been compared with de post-industrial recycled resins described in section 5.4. (Figure 5.12). An average concentration of additives, degradation products and contaminants identified in the post-industrial samples from the recyclers R1 and R2 (6 materials in total) has been calculated for the comparison. It has been found that the total concentration of substances in the post-industrial samples, in average, is similar to the total concentration in post-consumer HDPE sample. Although, the amount of additives is higher in the post-industrial LDPE, which is in line with the results presented in this section. Regarding the LDPE samples from different sources, it is shown that the post-consumer material presents significantly (nearly 3.5 times) higher concentration of identified substances than the post-industrial material. The increase occurs in all categories (i.e. additives, degradation products and contaminants). Several additives were found in both samples at different concentration. In general, the concentration of phthalates (plasticisers) such as bis(2-ethylhexyl) isophthalate is higher in the post-consumer LDPE (272.8 ppm versus 31.5 ppm). The same occurs with the fatty acids (e.g. n-hexadecanoic acid, octadecanoic acid) which concentration is around 100 ppm in the post-consumer sample and 30 ppm in the post-industrial one. On the contrary, the amount of (Z)-13-docosenamide (slip agent) is similar in both samples (around 70.0 ppm). Only the antioxidant octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate increases in the post-industrial LDPE (40.4 ppm versus 19.5 ppm). The higher concentration of additives in the post-consumer sample increases the amount of additive degradation products. Finally, the mass of contaminants per sample mass is also higher in the post-consumer LDPE. Nevertheless, it has been pointed out that the contaminant substances might have higher volatility. Thus, it is necessary to apply other analytical methods for their detection and identification, and consequently to be able to discuss the differences among materials.

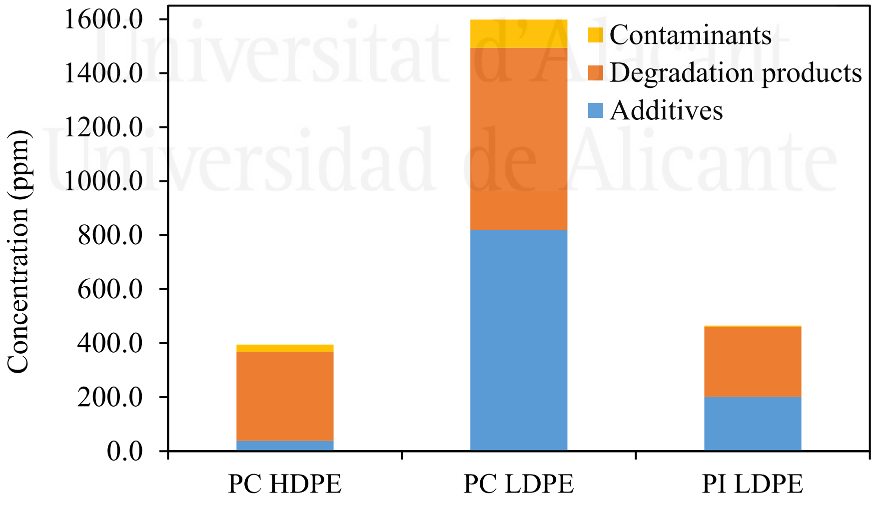

***Figure 5.12**. Concentration of SVOCs identified in post-consumer LDPE and HDPE, and post-industrial LDPE samples according to their origin.*

5.6. Conclusions

Solid extraction into a solvent followed by GC/MS has shown to be an efficient analytical technique for detection and identification of additives and their degradation products present in recycled plastic pellets. Nevertheless, other extraction techniques such as HD-SPME should be used to identify more volatile substances which can belong to the group of contaminants or polymer degradation products, and LC/MS for the detection and identification of non-volatile substances. The results presented in this Chapter and the conclusion drawn are tied to the materials analysed and represent a good starting point. In principle, they can be extended to the overall recycling sector. Nevertheless, analysis of a bigger number of samples is required.

Plastic additives are an important source of NIAS, especially when they are of low quality. In this study, four commonly used additives (slip agent, antioxidant, antistatic and polymer processing aid) have been analysed. The major compound in each additive has been identified, namely (Z)-13-docosenamide in the slip agent, N,N-bis(2-hydroxyethyl)-dodecanamide in the antistatic and polymer processing aid, and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate in the antioxidant. Apart from the main substance, many others have been detected which could be impurities or contaminants from the production stage.

Post-industrial plastics contain mainly additives and their degradation products. The major groups correspond to antioxidants, plasticisers and the slip agent. Moreover, some restricted substances can appear due to the unknown source and heterogeneity of the waste. In this case, bisphenol A and some phthalates have been identified with low match quality. These substances are considered harmful to health and/or the environment, thus hinder the use of recycled plastics. The amount of contaminants is considerably lower, however, their origin can be very diverse. The presence of ink and adhesive constituents indicates that the decontamination efficiency of conventional recycling processes is insufficient.

Regarding post-consumer plastics, the additives and their degradation products are also present in high concentrations, especially in the PC-LDPE sample used mainly in flexible packaging. The mixture of plastics from different applications found in a municipal waste stream increases the variety of additives in the recycled material even more than in post-industrial pellets. The contaminants belong to the group of cosmetics and cleaning agents, which probably come from the use phase of the product.

Conventional recycling technologies are suitable to eliminate neither surface coating (e.g., inks, adhesives, lacquers) nor substances from inside the plastic (additives, degradation products and some contaminants). Therefore, innovative technologies are required to increase the quality of the recycled plastics, including de-inking, de-coating and de-contamination processes. Moreover, the upcycling of plastic waste could require source separation, for instance, to not mix flexible LDPE and rigid HDPE which composition is different. Also, all the additives should be of the highest quality regardless of application to ensure that the recycled pellets can be used in high added value products.

Appendix

Table 5.2. *List and percentage area of SVOCs identified in pure plastic additives (masterbatch).*

Nº	NAME	CAS	FORMULA	RT (min)	Q (%)	SLIP (%)	AS (%)	AO (%)	PPA (%)
	Esters								
1	Dodecanoic acid, methyl ester	111-82-0	$C_{13}H_{26}O_2$	17.14	82		3.1		
2	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	2082-79-3	$C_{35}H_{62}O_3$	36.24	61			52.6	
3	5-(Acridin-9-ylamino)-pentanoic acid methyl ester	194363-00-3	$C_{19}H_{20}N_2O_2$	34.36	46			3.0	
4	3,4-Dimethyl-2-(3-methyl-butyryl)-benzoic acid, methyl ester	71940-29-9	$C_{15}H_{20}O_3$	17.05	40			2.7	
5	Isocyanic acid, ethyl ester	109-90-0	C_3H_5NO	10.37	41			1.9	
6	Phthalic acid, cyclobutyl pentyl ester	EPA-314900	$C_{17}H_{22}O_4$	36.23	19			1.0	
7	Benzoic acid, 3,4-dimethoxy-, 4-[ethyl[2-(4-methoxyphenyl)-1-methylethyl]amino]butyl ester	3625-06-7	$C_{25}H_{35}NO_5$	34.09	70				2.8
	Amides								
8	(Z)-13-Docosenamide	112-84-5	$C_{22}H_{43}NO$	27.11	91	71.3			
9	(Z)-9-Octadecenamide	301-02-0	$C_{18}H_{35}NO$	25.59	38	7.5			
10	Dodecanamide	1120-16-7	$C_{12}H_{25}NO$	25.66	50	4.6			
11	8-Methyl-6-nonenamide	EPA-293209	$C_{10}H_{19}NO$	25.62	24	2.5			
12	N,N-bis(2-hydroxyethyl)-Dodecanamide	120-40-1	$C_{16}H_{33}NO_3$	24.74	98		46.9		56.0
13	N-(2-hydroxyethyl)-Dodecanamide	142-78-9	$C_{14}H_{29}NO_2$	22.29	57		4.7		
14	N-{1-[(13Z)-10-(butan-2-yl)-16-methoxy-8,11-dioxo-2-oxa-6,9,12-triazatricyclo[13.3.1.$0^{3,7}$]nonadeca-1(18),13,15(19),16-tetraen-6-yl]-4-methyl-1-oxopentan-2-yl}-2-(dimethylamino)-3-phenylpropanamide	38496-00-3	$C_{37}H_{51}N_5O_6$	34.08	42				1.0
	Amines								
15	N-methyl-1H-Imidazole-4-ethanamine	673-50-7	$C_6H_{11}N_3$	27.12	18	1.0			
16	Bis-(2-ethyl-butyl)-amine	54774-85-5	$C_{12}H_{27}N$	21.68	20		7.9		
17	N-acetyl-1-carboethoxy-1-[5-tetrazolyl]-Pentylamine	EPA-227362	$C_{10}H_{17}N_5O_3$	21.68	8		5.9		
18	7-Tridecylamine	22513-16-2	$C_{13}H_{29}N$	21.67	51		4.0	2.6	9.7
19	Cyclopentylamine	1003-03-8	$C_5H_{11}N$	10.37	69			0.9	

Table 5.2. *List and percentage area of SVOCs identified in pure plastic additives (masterbatch).*

Nº	**NAME**	**CAS**	**FORMULA**	**RT (min)**	**Q (%)**	**SLIP (%)**	**AS (%)**	**AO (%)**	**PPA (%)**
	Cyclic compounds								
20	1-Ethyl-3-(hexahydroazepin-2-ylidene)-2-indolinone	EPA-260864	$C_{16}H_{20}N_2O$	23.02	39		15.9		
21	21α,22α-Epoxy-21,22-dihydro-4,14-dihydroxy-3-methoxy-19-methyl-16,19-secostrychnidine-10,16-dione	62421-66-3	$C_{23}H_{26}N_2O_7$	34.13	97			13.4	2.3
22	1,2-Bis(1,4,7-trioxa-10-azacyclododec-10-yl)-ethane	79645-07-1	$C_{18}H_{36}N_2O_6$	19.88	74			2.3	11. 0
23	1,3,5-tritert-butyl-3-[(1,3,5-tritert-butyl-4-oxocyclohexa-2,5-dien-1-yl)methyl]bicyclo[4.1.0]hept-4-en-2-one	19719-70-1	$C_{38}H_{62}O_2$	36.24	31			1.4	
24	4a,5,7,8,8a,9-Hexahydro-9-methylene-6H-[1,2,4]triazolo[1,5-a]indole	49629-06-3	$C_{10}H_{13}N_3$	34.22	8			1.1	
25	1,3,5-Tri-tert-butyl-3-(3,5-di-tert-butyl-4-hydroxybenzyl)norcaran-4-en-2-one	19719-71-2	$C_{34}H_{54}O_2$	36.12	67			1.1	
	Others								
26	Dodecanoic acid	143-07-7	$C_{12}H_{24}O_2$	17.53	86		3.0		
27	8-Hexadecanol	19781-83-0	$C_{16}H_{34}O$	17.14	7		1.1		
28	2-Heptadecenal	EPA-143486	$C_{17}H_{32}O$	22.11	20			6.9	
29	Methylenebis(2,4,6-triisopropylphenylphosphine)	EPA-159591	$C_{31}H_{50}P_2$	34.15	90			2.4	7.8
30	3-Hydroxy-1-methylquinolin-4(1H)-one	55759-83-6	$C_{10}H_9NO_2$	34.09	30				4.0

Table 5.3. *List and approximate concentration (ppm) of SVOCs identified by GC/MS in virgin plastic and post-industrial recycled pellets from different sources. RT=retention time; Q = match quality.*

Nº	NAME	CAS	FORMULA	RT (min)	Q (%)	VIRG -IN	Re-grind	Black R1	Coloured R1	Transp. R1	White R1	Black R2	Brown R2	Agricul. R3
	Alcohol													
1	Diethylene glycol	111-46-6	$C_4H_{10}O_3$	9.78	81							0.3		
2	2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol	3864-99-1	$C_{20}H_{24}ClN_3O$	26.17	81						0.1			
	Esters													
3	Methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	638-63-85	$C_{18}H_{28}O_3$	20.92	69	0.1		0.2	0.1	0.3	0.1	0.2		0.1
4	Tributyl acetylcitrate	77-90-7	$C_{20}H_{34}O_8$	23.32	76			5.4	4.4	1.1	0.6	0.5	0.1	1.1
5	Bis(2-ethylhexyl) isophthalate	137-89-3	$C_{24}H_{38}O_4$	26.59	86			68.8	10.0	6.5	17.5	82.1	4.0	16.2
6	Glycerol tricaprylate	538-23-8	$C_{27}H_{50}O_6$	29.15	74				1.0		0.2			3.9
7	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	2082-79-3	$C_{35}H_{62}O_3$	35.71	98	0.5	23.1	86.9	13.4	94.0	20.1	6.7	21.4	69.8
	Amides													
8	N-Butylbenzenesulfonamide	3622-84-2	$C_{10}H_{15}NO_2S$	19.60	86							2.0	0.1	0.5
9	(Z)-13-Docosenamide	112-84-5	$C_{22}H_{43}NO$	26.83	81	1317.7	1313.3	43.9	52.0	105.7	89.1	91.9	37.3	21.5
	Ketones													
10	(1-hydroxycyclohexyl) phenyl-methanone	947-19-3	$C_{13}H_{16}O_2$	18.80	96	0.2	0.1	0.3	0.2	0.1	0.4	0.1	0.6	0.2
	Alkylbenzenes													
11	Decyl benzene	104-72-3	$C_{16}H_{26}$	18.55	66	0.1						2.0		
12	Dodecyl benzene	123-01-3	$C_{18}H_{30}$	20.41	79	0.2								
13	Tetradecyl benzene	1459-10-5	$C_{20}H_{34}$	22.09	73	0.5	0.6	0.1				0.2		0.1
14	Hexadecyl benzene	1459-09-2	$C_{22}H_{38}$	23.63	77	0.7						0.1		

Table 5.3. *List and approximate concentration (ppm) of SVOCs identified by GC/MS in virgin plastic and post-industrial recycled pellets from different sources. RT=retention time; Q = match quality.*

Nº	**NAME**	**CAS**	**FORMULA**	**RT (min)**	**Q (%)**	**VIRG-IN**	**Re-grind**	**Black R1**	**Coloured R1**	**Transp. R1**	**White R1**	**Black R2**	**Brown R2**	**Agricul. R3**
15	Octadecyl benzene	4445-07-2	$C_{24}H_{42}$	25.04	66	0.8								
	Azoles													
16	Bumetrizole	3896-11-5	$C_{17}H_{18}ClN_3O$	25.46	86			6.4	24.3	7.4	6.9	32.9	1.4	0.6
	Others													
17	Pentamethyl cyclopentane	'EPA-152797	$C_{10}H_{20}$	8.88	67	0.7	0.6	0.6	0.7	0.7	0.6	0.6	0.1	0.4
18	Benzestrol	85-95-0	$C_{20}H_{26}O_2$	19.12	90		0.1	1.5	0.4	1.8	1.1	16.1	3.1	3.0
19	2(5H)-Furanone	497-23-4	$C_4H_4O_2$	19.55	66					0.1				
20	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	$C_{17}H_{24}O_3$	20.76	92	1.1	2.2	4.5	1.5	2.7	2.0	1.2	0.3	3.3
21	Octadecanoic acid	57-11-4	$C_{18}H_{36}O_2$	22.58	96		0.8	2.3	137.4	0.1	14.2		0.1	1.3
22	1-(phenylmethoxy)-naphthalene	607-58-9	$C_{17}H_{14}O$	22.73	90					0.6		1.0	0.4	2.4
23	2,2'-Methylenebis(6-tert-butyl-p-cresol)	119-47-1	$C_{23}H_{32}O_2$	24.51	71			0.6		0.6			0.1	
	Predominant SVOCS with match quality < 65 %													
	Alcohol													
24	Isopropyl Alcohol	67-63-0	C_3H_8O	6.30	12	2.6	2.8	2.5	2.7	2.7	2.4	2.5	1.9	2.1
25	2,4-bis(1,1-dimethylethyl) phenol	96-76-4	$C_{14}H_{22}O$	16.91	58	4.6	1.6	3.6	4.4	4.7	6.7	3.2	0.6	1.5
26	4-Nonylphenol	104-40-5	$C_{15}H_{24}O$	18.99	37	0.4	1.4	4.5	2.3	1.6	3.9	3.7	3.3	1.5
27	Bisphenol A	80-05-7	$C_{15}H_{16}O_2$	22.79	54			1.3	0.5			1.9		0.5
28	1-Hexadecanol	36653-82-4	$C_{16}H_{34}O$	24.57	5			2.4				3.3	12.6	5.7
	Esters													
29	Diethyl Phthalate	84-66-2	$C_{12}H_{14}O_4$	17.787	41	0.2	0.4	0.2	0.3	0.4	0.3	1.1	0.4	0.4

Table 5.3. *List and approximate concentration (ppm) of SVOCs identified by GC/MS in virgin plastic and post-industrial recycled pellets from different sources. RT=retention time; Q = match quality.*

Nº	NAME	CAS	FORMULA	RT (min)	Q (%)	VIRG-IN	Re-grind	Black R1	Coloured R1	Transp. R1	White R1	Black R2	Brown R2	Agricul. R3
30	Phthalic acid, 6-ethyl-3-octyl butyl ester	EPA-315174	$C_{22}H_{34}O_4$	21.07	14	0.4	0.6	0.2	7.7	0.4		22.0	3.4	1.0
31	Diisooctyl adipate	1330-86-5	$C_{22}H_{42}O_4$	24.27	64			1.7	0.8	0.3	0.1	4.5	0.6	18.4
32	Mono(2-ethylhexyl) phthalate	4376-20-9	$C_{16}H_{22}O_4$	25.30	53	3.2	3.1	12.9	5.9	1.8	0.7	33.8	10.9	2.3
33	Benzoic acid, 3,5-dicyclohexyl-4-hydroxy-, methyl ester	55125-23-0	$C_{20}H_{28}O_3$	35.84	13		491.2	288.3	254.4	257.2	274.8	102.3	4.4	87.2
	Amides													
34	(Z)-9-Octadecenamide	301-02-0	$C_{18}H_{35}NO$	24.05	43	2.3	4.7	0.9	0.8	1.2	1.8	2.6	3.3	2.5
35	'Octadecanamide	124-26-5	$C_{18}H_{37}NO$	24.75	37	5.4	3.4		0.3		0.2			
36	'cis-11-Eicosenamide	10436-08-5	$C_{20}H_{39}NO$	25.45	33	34.0	7.1							
37	'Tetradecanamide	638-58-4	$C_{14}H_{29}NO$	26.30	20	41.4								0.1
	Others													
38	Dodecanoic acid	143-07-7	$C_{12}H_{24}O_2$	17.33	32				0.3	0.2	0.2			0.1
39	n-Hexadecanoic acid	57-10-3	$C_{16}H_{32}O_2$	20.97	6	0.1	1.9	1.2	58.7	1.7	22.5	1.0	1.3	1.8
40	1,1''-dodecylidenebis[4-methyl-cyclohexane	55334-09-3	$C_{26}H_{50}$	24.41	10	0.6						4.8		0.2
41	1-cyclopentyl-4-(3-cyclopentylpropyl)-dodecane	7225-68-5	$C_{25}H_{48}$	26.86	7					6.3				
42	'N-(4-Methylbenzylidene)-3,5-diphenyl-2-furanamine	95855-33-7	$C_{24}H_{19}NO$	26.91	12	30.0								
42	2-heptyl-4-octadecyloxymethyl-1,3-Dioxolane	EPA-155583	$C_{29}H_{58}O_3$	28.41	8					3.2			1.9	

Table 5.3. *List and approximate concentration (ppm) of SVOCs identified by GC/MS in virgin plastic and post-industrial recycled pellets from different sources. RT=retention time; Q = match quality.*

Nº	**NAME**	**CAS**	**FORMULA**	**RT (min)**	**Q (%)**	**VIRG -IN**	**Re-grind**	**Black R1**	**Coloured R1**	**Transp. R1**	**White R1**	**Black R2**	**Brown R2**	**Agricul. R3**
43	Methylenebis(2,4,6-triisopropylphenylphosphine)	EPA-159591	$C_{31}H_{50}P_2$	33.84	55		2.0	137.5	12.4	5.1	0.3	0.8		

Table 5.4*. List and approximate concentration (ppm) of SVOCs tentatively identified by GC/MS originating from post-consumer HDPE (PC HDPE) and post-consumer LDPE (PC LDPE). Q= match quality percentage; RT=retention time; A= additive; D=Degradation product; C=contaminant; deg=degradation.*

Nº	**Compound name**	**CAS No**	**RT (min)**	**Q (%)**	**PC HDPE**	**PC LDPE**	**Classification**		**Source**
							Type	**Origin**	
	Glycols								
1	diethylene glycol	111-46-6	9.92	89		0.3	D	Antioxidant	(Bradley and Coulier, 2007)
2	dipropylene glycol	110-98-5	10.93	77		0.6	D	Antioxidant	(Bradley and Coulier, 2007)
	Aldehydes								
3	2-(phenylmethylene)-heptanal	122-40-7	18.49	66	0.8		C	Cosmetics	(CosIng EC, n.d.)
	Alkylbenzenes								
4	(1-butylheptyl)benzene	4537-15-9	18.31	82	1.6	0.1	C	Surfactant deg	(Kosswig, 2000)
5	(1-ethyldecyl)benzene	2400-00-2	19.56	67	1.3	0.2	C	Surfactant deg	(Kosswig, 2000)
6	(1-methylundecyl)benzene	2719-61-1	19.91	75	0.8		C	Surfactant deg	(Kosswig, 2000)
	Acids								
7	dodecanoic acid	143-07-7	17.54	71	1.4	3.0	A or C	Processing aid/Surfactant	EU 10/2011 /(CosIng EC, n.d.)
8	tetradecanoic acid	544-63-8	19.46	77		8.8	A or C	Processing aid/Cleansing	EU 10/2011 /(CosIng EC, n.d.)
9	n-hexadecanoic acid	57-10-3	21.18	69	1.9	84.8	A or C	Processing aid/Emollient	EU 10/2011 /(CosIng EC, n.d.)
10	tert-butyl-(4-tert-butylphenyl)phosphinic acid	25097-42-1	23.69	71	0.2		D	Antioxidant	(Frontier Laboratories, n.d.)

***Table 5.4**. List and approximate concentration (ppm) of SVOCs tentatively identified by GC/MS originating from post-consumer HDPE (PC HDPE) and post-consumer LDPE (PC LDPE). Q= match quality percentage; RT=retention time; A= additive; D=Degradation product; C=contaminant; deg=degradation.*

Nº	Compound name	CAS No	RT (min)	Q (%)	PC HDPE	PC LDPE	Classification Type	Classification Origin	Source
	Ketones								
11	benzophenone	119-61-9	18.37	74		1.0	A or C	UV absorber/ Cosmetics	EU 10/2011 /(CosIng EC, n.d.)
12	2-acetyl-5-methylfuran	1193-79-9	20.70	75	0.04		C	Odour compound	(Paravisini et al., 2015)
	Esters								
13	ethyl tetradecanoate	124-06-1	19.72	72	0.2	1.8	C or D	Cosmetics/ Lubricant impurity	(CosIng EC, n.d., Bradley and Coulier, 2007)
14	2-ethylhexyl salicylate	118-60-5	19.94	85		4.3	C	Cosmetics	(CosIng EC, n.d.)
15	methyl hexadecanoate	112-39-0	20.86	72		18.8	D	Lubricant	(Bradley and Coulier, 2007)
16	ethyl palmitate	628-97-7	21.42	76		37.7	C or D	Cosmetics/ Lubricant	(CosIng EC, n.d., Bradley and Coulier, 2007)
17	isopropyl palmitate	142-91-6	21.65	69	9.9	1.9	C	Cosmetics	(CosIng EC, n.d.)
18	propyl hexadecanoate	2239-78-3	22.17	70		4.9	D	Lubricant	(Bradley and Coulier, 2007)
19	methyl octadecanoate	112-61-8	22.45	72	0.8	13.0	D	Lubricant	(Bradley and Coulier, 2007)
20	tributyl acetylcitrate	77-90-7	23.48	86		22.3	A	Plasticizer	EU 10/11, (Bradley and Coulier, 2007)
21	propyl octadecanoate	3634-92-2	23.66	71		4.0	D	Lubricant	(Bradley and Coulier, 2007)
22	methyl abieta-8,11,13-trien-18-oate	1235-74-1	24.24	82		4.0	D	Adhesives	(Nerin et al., 2013)
23	dodecyl hexadecanoate	42232-29-1	28.56	70		13.8	D	Lubricant	(Bradley and Coulier, 2007)
24	glycerol tricaprylate	538-23-8	29.43	67	1.7		C	Cosmetics	(CosIng EC, n.d.)
25	hexadecyl hexadecanoate	540-10-3	33.39	76		16.4	D	Lubricant	(Bradley and Coulier, 2007)
26	octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	2082-79-3	35.99	82	14.8	19.5	A	Antioxidant	EU 10/11
	Azoles								

Table 5.4*. List and approximate concentration (ppm) of SVOCs tentatively identified by GC/MS originating from post-consumer HDPE (PC HDPE) and post-consumer LDPE (PC LDPE). Q= match quality percentage; RT=retention time; A= additive; D=Degradation product; C=contaminant; deg=degradation.*

Nº	Compound name	CAS No	RT (min)	Q (%)	PC HDPE	PC LDPE	Classification		Source
							Type	Origin	
27	bumetrizole	3896-11-5	25.62	85	6.7		A or C	UV absorber/Cosmetics	EU 10/11 /(CosIng EC, n.d.)
	Amides								
28	13-docosenamide, (z)-	112-84-5	27.02	65	13.6	76.0	A	Slip agent	EU 10/11
	Phthalates								
29	bis(2-ethylhexyl) isophthalate	137-89-3	26.80	72		272.8	A	Plasticizer	(Frontier Laboratories, n.d.)
	Others								
30	2,2,4,4,6,8,8-heptamethylnonane	4390-04-9	15.05	80		0.7	C D	Cosmetics Polyethylene	(CosIng EC, n.d., Bradley and Coulier, 2007)
31	7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	20.93	79	7.1	2.9	D	Antioxidant	(Bradley and Coulier, 2007, Biedermann et al., 2014)
32	diphenyl sulfone	127-63-9	21.07	73		0.1	C	Thermosetting plastics	(Tiwari and Mhaisekar, n.d.)
	Predominant SVOCS with match quality < 65 %								
33	6-octadecenoic acid, (z)-	593-39-5	22.67	23		146.3	D	Possible lubricant	(Bradley and Coulier, 2007)
34	ethyl oleate	111-62-6	22.81	23		160.0	A	Possible plasticizer	(Waskitoaji et al., 2012)
35	di-n-octyl phthalate	117-84-0	25.49	22		170.1	A	Possible plasticizer	(PubChem, 2019)
36	9-octadecenamide, (z)-	301-02-0	25.62	33	23.0	32.2	D	Possible slip agent	(Bradley and Coulier, 2007)
37	methylenebis(2,4,6-triisopropylphenylphosphine)	EPA-159591	34.11	62	60.3	34.7	D	Possible antioxidant	(Bradley and Coulier, 2007)
38	methyl 3,5-dicyclohexyl-4-hydroxybenzoate	55125-23-0	36.14	23	239.0	343.7	D	Possible antioxidant	(Bradley and Coulier, 2007)

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Chapter 6:

CONCLUSIONS

6.1.Conclusions

In this Thesis, the recycling of plastic waste in general and flexible films in particular has been assessed to evaluate the current status and weaknesses that could hinder the transition to a circular economy. The demand for plastic films is rapidly growing, especially in the packaging sector, which covers around 40% of the total plastic demand in the EU. Nevertheless, their recycling is usually inefficient and economically unprofitable, mainly due to high energy costs and low quality of recycled pellets. Consequently, the flexible plastics are sent to incineration or landfilling, causing an irreversible loss of non-renewable resources and environmental pollution. Moreover, even if plastic films are collected for recycling, the processes applied usually produce low quality pellets suitable only for non-demanding applications. In other words, plastic films are downcycled, which is more akin to the linear economy model since after using, the products are likely to be incinerated or landfilled.

Recycling of plastic waste has been assessed from different perspectives which have been divided into three Chapters. The key conclusions of each Chapter are presented hereafter.

Chapter 3: Life cycle assessment of plastic upcycling and comparison with conventional waste treatments

- Upcycling processes, which are aligned with the circular economy model, sometimes are shown as the worst waste treatment option from the environmental point of view due to the assumptions made during the description of LCA scenarios. Therefore, it has been suggested that certain assumptions must be used provided upcycling processes are compared with other treatment options. Firstly, both virgin plastic substitution rate and the recycled product´s market share should be considered. Secondly, the energy produced during waste incinerations should replace the energy from renewable sources.
- The additional efforts in terms of energy and reactant consumption that the upcycling of plastic waste requires are offset by the expansion of the target market. Clean decontaminated pellets can be used in a larger number of applications than conventionally recycled dark pellets, therefore, the virgin plastic substitution is higher.

- In the upcycling scenario, the virgin plastic substitution rate should be more than 40% to produce benefits to the environment in the climate change category. For this to be possible, the quality of the recycled pellets must be considerably improved.
- The energy required for upcycling produces the largest burdens to the environment. Therefore, the optimization of mechanical operations to reduce energy consumption is paramount.
- Upcycling processes are also necessary for post-consumer waste treatment since the major environmental savings are produced when recycled pellets can be used in high demanding applications. To make this possible, innovative decontamination technologies must be implemented.

Chapter 4: Centrifugal dewatering performance in plastic films recycling

- Dewatering performance of plastic films must be studied to optimize the design of the equipment and reduce operational costs by decreasing the energy consumption.
- During centrifugation a plastic cake is formed, similar to a wastewater sludge cake, where three types of bounded water exist: free water in the pores and voids, capillary water (superficial and pendular), and trapped water due to material´s tortuosity.
- The free water is reliant on the centrifugal force (G-force) and it is rapidly removed. Nevertheless, the water retained due to capillarity and tortuosity depend on the plastic cake characteristics (porosity, permeability and the flake size) and cannot be completely removed by centrifugation. This is known as saturation at equilibrium. Therefore, long centrifugation time and high G-force do not ensure that the moisture content will be completely removed.
- The moisture content depends on the plastic surface area. So that the specific moisture content (τ_s, water mass per plastic surface area) is practically the same in all the materials, while the moisture content on a dry matter basis ($\tau_{\%}$) varies with the film thickness. The polymer type has little influence on the dewatering performance.
- An optimum flake size exists in which the moisture content is minimized. The optimum side length of a flake oscillates around 1-2 cm.
- Post-consumer plastic films surface suffers degradation during their life cycle, nevertheless, the average roughness remains unaffected. The

dewatering performance of post-industrial and post-consumer waste is very similar.

Chapter 5: Identification of SVOCs in recycled plastic

- Plastic additives are an important source of non-intentionally added substances (NIAS) in both post-industrial and post-consumer waste. The presence of NIAS in recycled products poses safety problems for the consumers, mainly due to the lack of traceability and unknown material composition. As a result, recycled products cannot be used in high demanding applications, which hinders the transition to a circular economy.
- Gas chromatography and mass spectrometry has shown to be an efficient analytical technique for detection and partial identification of plastic additives and their degradation products.
- The additives masterbatch contains the main compounds, which gives the desired properties to the plastic product, and a number of secondary compounds, which can be impurities from the production phase. The number of impurities increases when the quality of the additives decreases.
- The compounds extracted from the virgin pellets correspond mainly to plastic additives and degradation products to a lesser extent. The concentration of the degradation products increases in the recycled pellets due to re-extrusion processes and it varies among samples from different recyclers. The concentration of extracted contaminants from post-industrial recycled plastic is low, which is coherent with the origin of the waste. These results show that post-industrial waste, which has a high potential to be upcycled because it is clean and homogeneous, contains a high number of NIAS. To study all the undesired compound in plastic waste and perform an appropriate risk assessment is a very challenging task. Therefore, decontamination technologies capable of removing plastic additives and other NIAS during recycling might be needed.
- The analysis of post-consumer waste shows that recycled LDPE contains a higher amount and variety of additives and their degradation products than recycled HDPE. This is likely due to the applications where these materials are used. The concentration of contaminants from the use phase

extracted from both samples is low. This could be because the contaminants are less volatile, and another analytical technique is needed to detect them. In sum, post-consumer recycled pellets, especially LDPE pellets, present a high concentration of NIAS. Thus, decontamination processes intended to remove additives and their degradation products are also needed to expand the market for the recycled plastics.

6.2. Future research

The results of this Thesis show some of the main weak points of the recycling industry and the directions in which the sector should move to become truly sustainable and circular. In this section, a number of recommendations will be given to continue with the research work.

The LCA analysis indicates that the energy consumption during upcycling processes should be reduced and the quality of the recycled pellets should be maintained similar to the original material. This is paramount to ensure the highest environmental benefits. Upcycling of post-consumer waste should be analysed in depth considering all the steps required to obtain the desired quality of the recyclates. Other methodologies such as circularity indicators could be used to evaluate the environmental performance.

Drying is one of the most energy-consuming operations. The results of the centrifugal dewatering performance of flexible plastics could be used to redesign the existent equipment and reduce the energy costs of the drying stage. In addition, other dewatering methods such as pressing and thermal drying should be assessed to compare the dewatering efficiencies. These methods are not optimized either for the treatment of plastic films. Therefore, there is considerable room for improvement in the drying field.

Further research on the NIAS present in recycled plastics is highly important to ensure the circularity of plastic products. It is recommended to continue with the non-target screening of different polymer type samples and different waste sources. In addition, target analysis of potentially hazardous substances should be performed through migration test, regardless of whether the final product is intended for food contact or not. Finally, decontamination technologies for NIAS removal should be developed.

SPANISH SUMMARY

RESUMEN

1. Introducción

Los materiales plásticos se pueden encontrar en todos los aspectos de nuestra vida. Los plásticos convencionales proceden de fuentes fósiles como el petróleo, el carbón y el gas natural, aunque, solo entre 4-6% de los recursos fósiles extraídos se utilizan para fabricar plásticos (BPF, 2019). Los materiales plásticos son versátiles y poseen múltiples propiedades mecánicas, térmicas y ópticas entre otras. Además, los procesos de fabricación son sencillos y los costes son bajos. En consecuencia, la producción de materiales plásticos ha aumentado notablemente desde su síntesis a principios del siglo XX, alcanzando 360 millones de toneladas producidas a nivel global en el año 2018. En la Unión Europea, la cifra oscila sobre los 62 millones de toneladas (Plastics Europe, 2019). Se espera que la demanda de plástico siga aumentando durante los próximos años, a pesar de que en la actualidad se está llevando a cabo una dura campaña en contra de este material. El alcance geográfico de esta Tesis incluye solamente países occidentales, ya que es donde los procesos de reciclaje están más desarrollados.

Los termoplásticos es uno de los grupos más abundantes que se caracteriza por el hecho de que los productos plásticos se pueden fundir y re-moldear para fabricar productos nuevos. Los polímeros más conocidos de este grupo son el polietileno (PE), el polipropileno (PP), el policloruro de vinilo (PVC) y el polietileno tereftalato (PET) (

Figura 1). En conjunto abarcan aproximadamente el 67% de la demanda de plásticos en Europa (Plastics Europe, 2019). El PE a su vez está formado por un grupo de materiales que se diferencian principalmente por el distinto grado de ramificación de la cadena de monómeros. Los más comunes son el polietileno de baja densidad (PEBD), el de media densidad (PEMD), el de alta densidad (PEAD) y el lineal de baja densidad (PELBD). Los plásticos flexibles, también llamados film o película, están ganando popularidad y se utilizan cada vez más, sobre todo, en el sector del envasado debido a su ligereza, funcionalidad y aptitud para la impresión. En general, el espesor de los films varía entre 20 y 200 µm y pueden estar formados por una capa de un mismo material (monocapa) o varias capas de materiales poliméricos y/o no poliméricos (multicapa).

Uno de los mayores problemas de los materiales plásticos es la acumulación de residuos no biodegradables (o que se degradan lentamente) en el medioambiente, debido principalmente a la falta de métodos de gestión eficientes. Se estima que alrededor de 6300 millones de toneladas de residuos plásticos se han generado entre 1950 y 2015, de los cuales solo el 20% se ha incinerado o reciclado (Geyer et al., 2017). El resto permanece en los vertederos o en el medioambiente. Generalmente, se distinguen tres tipos de residuos: industrial, comercial y doméstico. El residuo industrial es la merma que se genera durante la fabricación de los productos plásticos. Suele ser una material limpio y homogéneo con alto potencial para ser reciclado. El residuo comercial es el que se genera por la actividad de los comercios y suele estar formado por el embalaje secundario y terciario. También es un material bastante homogéneo, pero puede contener impurezas, impropios y suciedad. Por último, el residuo doméstico proviene de la recogida de residuos municipales y contiene una mezcla de materiales y un alto nivel de contaminación (RSE USA, 2017).

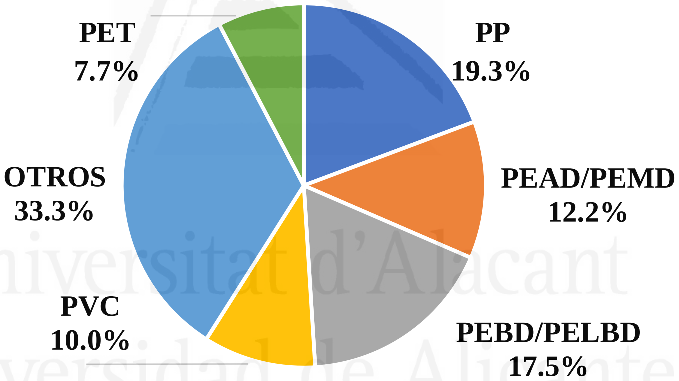

Figura 1. *Demanda de materiales plásticos en Europa en 2018 (EU28+NO/CH).(Plastics Europe, 2019).*

Los métodos de tratamiento de los residuos plásticos se pueden dividir en tres grandes grupos: reciclaje mecánico, reciclaje químico y valorización energética. El reciclaje mecánico consiste en recuperar los materiales mediante operaciones mecánicas sin modificar la estructura de los polímeros. Existen dos tipos de procesos que se diferencian principalmente por las aplicaciones a las que se destinan los plásticos reciclados. Por un lado, en el reciclaje en ciclo cerrado se consigue mantener la calidad de los materiales y el producto reciclado se puede utilizar para la misma aplicación que el producto original. Por otro lado, en los procesos de ciclo abierto la calidad puede verse afectada y los productos reciclados se utilizan en aplicaciones diferentes a la original. El reciclaje químico consiste en la rotura de la cadena del polímero para obtener los monómeros originales u otras sustancias químicas con el objetivo de fabricar nuevos polímeros (Achilias et al., 2007). Actualmente, las tecnologías están en fase de desarrollo y los costes son demasiado altos. Por último, la valorización energética se basa en la combustión de los residuos plásticos debido a su alto poder calorífico y aprovechamiento de la energía para la producción de electricidad y calefacción. Además, se consigue reducir el volumen de residuos en más del 90% (Technical University of Denmark, n.d.).

El tratamiento de los residuos de plástico flexible depende de su origen (Horodytska et al., 2018). Las mermas industriales normalmente se peletizan directamente sin necesidad de lavado. Cuando el residuo es limpio y no ha sido impreso o recubierto, la granza obtenida se puede utilizar en el mismo proceso mezclada con la granza virgen. Sin embargo, si el plástico ha ido impreso, en la extrusión se obtiene una granza de color oscuro que solo se puede utilizar en aplicaciones de menor valor añadido como bolsas de basura, tuberías de riego, etc. Para evitar la pérdida de valor, las tintas se deben eliminar antes de la extrusión. Existen varios procesos desarrollados para el destintado en base disolvente y en base agua. Los residuos comerciales se suelen reciclar mecánicamente incluyendo una etapa de lavado donde se eliminan los impropios. Dependiendo de las características del residuo, el plástico reciclado se puede utilizar para la misma aplicación de embalaje secundario o terciario. En cuanto al residuo doméstico, la recuperación de los films es una tarea difícil debido a la gran variedad de materiales que se utilizan, especialmente en los envases flexibles. Además, la etapa de selección es muy costosa, lo que hace que el proceso no sea rentable. Los films multicapa presentes en la corriente de residuos plásticos no son reciclables, ya que la mayoría están formados por materiales incompatibles. Se están desarrollando varias tecnologías para el reciclaje de estos materiales como la deslaminación, la disolución-precipitación selectiva y la compatibilización. Pero todas están en una fase de desarrollo temprana y están limitadas a un grupo de films específico. Por último, los films se utilizan ampliamente en la agricultura y se reciclan mecánicamente después de su uso. La ventaja de estos residuos es que se puede disponer de una gran cantidad de material homogéneo de un solo tipo de polímero. El problema es que suele estar muy contaminado con tierra, polvo, etc. De modo que las etapas de lavado y secado resultan muy costosas. En los casos en los que el reciclaje no se beneficioso, los residuos plásticos se incineran o se depositan en vertederos.

La selección del tratamiento de residuos plásticos más apropiado no es una tarea sencilla ni evidente. Depende generalmente de la rentabilidad económica y de los beneficios medioambientales. El Análisis de Ciclo de Vida (ACV) es un método que se utiliza frecuentemente para comparar los impactos positivos y negativos de diferentes procesos. Según el modelo de Economía Circular, el reciclaje debe ser la primera opción y la incineración o el depósito de vertederos deben ser minimizados. Además, se debe conservar la calidad y el valor de los productos plásticos en el mayor nivel (Webster, 2017). De modo que se favorecen los procesos de reciclaje en ciclo cerrado y *upcycling* en los que los productos reciclados se pueden utilizar para la misma aplicación que el producto original o incluso en aplicaciones de mayor valor (Sung, 2015). Los procesos en los que se pierde la calidad de los plásticos, por lo que solo se pueden utilizar en aplicaciones de bajo valor añadido, se conocen como *downcycling* y deben ser evitados (Figura 2). Actualmente, la presión social y de la Comisión Europea está haciendo que los fabricantes de productos plásticos apuesten por el uso de plásticos reciclados en nuevas aplicaciones como por ejemplo envases de detergentes y productos de limpieza (Henkel, 2020).

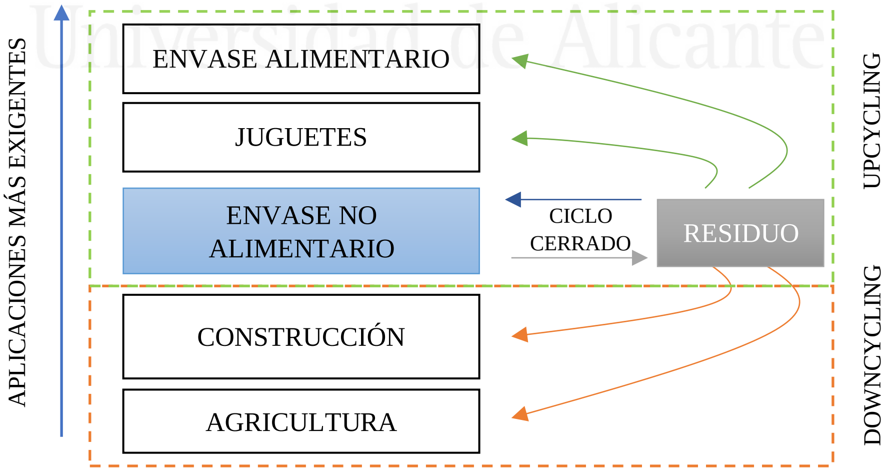

Figura 2. *Representación esquemática de los posibles procesos de reciclaje de los residuos. plásticos.*

En esta Tesis se abordan dos problemas actuales relacionados con la sostenibilidad de los materiales plásticos. En primer lugar, la creciente producción y la falta de sistemas de gestión eficientes hacen que los plásticos flexibles se conviertan en un grave problema de contaminación del medioambiente. Las tasas de reciclaje de estos productos son bajas debido a que surgen problemas técnicos durante las operaciones mecánicas (por ejemplo, el secado). Los procesos de reciclaje actuales no están preparados para tratar este tipo de materiales, ya que fueron diseñados para plásticos rígidos. Además, la baja densidad aparente del material influye negativamente a la rentabilidad del proceso. Por ello, la mayoría de los films se incineran o se depositan en vertederos. En segundo lugar, la transición hacia la Economía Circular requiere que se adopten procesos de *upcycling* para los residuos plásticos. Sin embargo, estos procesos implican mayor consumo de energía y de recursos para la descontaminación y, en estos momentos, la seguridad para el consumidor no está asegurada.

2. Objetivos

El objetivo principal de esta Tesis es estudiar la circularidad de los plásticos en general y de los plásticos flexibles en particular. Entre los objetivos específicos se encuentran los siguientes.

- Estudiar los impactos medioambientales de los procesos de *upcycling* utilizando la metodología de ACV para determinar si los beneficios obtenidos son suficientes para contrarrestar el mayor consumo de energía y de recursos.
- Comparar los impactos medioambientales del proceso de *upcycling* con los métodos de tratamiento de residuos convencionales como el reciclaje convencional (o *downcycling*) y la valorización energética.
- Identificar los puntos débiles de los procesos de reciclaje de los films de plástico y métodos de mejora.
- Estudiar el comportamiento de los films de plástico durante la etapa de secado para reducir el consumo de energía mediante la optimización de las condiciones de operación.
- Estudiar la posibilidad de utilizar los plásticos reciclados en aplicaciones de alto valor añadido desde el punto de vista de la seguridad del consumidor. Para ello, se debe proceder a la detección e identificación

de compuestos no deseados y/o sustancias añadidas no intencionadamente (NIAS).

3. Resultados

3.1. Análisis de ciclo de vida del *upcycling* de residuos plásticos comparado con otros tratamientos convencionales

En el Capítulo 3 se ha estudiado la circularidad de los plásticos dependiendo del tratamiento de residuos aplicado cuando llegan al final de su vida útil. Se ha utilizado el método de Análisis de Ciclo de Vida (ACV) para calcular el impacto producido sobre cuatro categorías: cambio climático, uso de recursos, salud del ecosistema y salud humana. Para ello se ha utilizado la metodología IMPACT 2002+vQ2.2 (Humbert et al., 2012). El alcance del estudio incluye solamente la planta de tratamiento de residuos plásticos. El residuo está impreso en la superficie y es de origen industrial. Se genera en una empresa de fabricación de productos de plástico flexible como envases y bolsas de la compra.

En la primera parte del Capítulo se han planteado tres escenarios de tratamiento de residuos. El primer escenario es el reciclaje convencional de este tipo de residuos que consiste en extruir la merma directamente con la tinta. Debido a que es un residuo industrial, se considera que no es necesario una etapa de lavado. La granza que se obtiene es de color oscuro debido a las tintas y se puede usar en aplicaciones de bajo valor añadido. En el segundo escenario, el residuo pasa por un proceso innovador de *upcycling* donde se elimina la tinta de la superficie del plástico antes del proceso de extrusión. De modo que la granza que se obtiene es de color claro y con propiedades muy similares al plástico original, por lo que puede usarse en aplicaciones de alto valor añadido como el envasado de productos. Por último, el escenario de incineración está descrito y todos los datos están incluidos en la base de datos Ecoinvent, que es la que se ha utilizado para llevar a cabo el análisis. La energía recuperada se utiliza para sustituir la combustión de recursos fósiles que aún constituye el 70% del mix eléctrico europeo (Directorate-General for Energy, European Commission, 2018).

Los resultados del primer análisis indican que el proceso de *upcycling* es el menos beneficioso desde el punto de vida medioambiental. Produce un efecto negativo sobre la categoría de cambio climático, la salud del ecosistema y la salud humana. Solo se genera un efecto positivo sobre la categoría de recursos, aunque es muy inferior a los escenarios de reciclaje convencional e incineración. Se ha comprobado que aumentando el porcentaje de sustitución de la granza destintada se puede obtener algunos beneficios. Por ejemplo, se produce un efecto positivo sobre la categoría de cambio climático con un porcentaje de sustitución del 40% y sobre la salud humana con 60%. Sin embargo, los beneficios obtenidos siguen siendo inferiores comparados con los otros dos escenarios. De modo que, con el planteamiento presentado y las suposiciones adoptadas, se llega a la conclusión de que producir granza reciclada de mayor calidad que se puede utilizar en aplicaciones de alto valor añadido es poco beneficioso, favoreciendo así los procesos donde se pierde la calidad del plástico o donde directamente se destruye.

Estos resultados van totalmente en contra del modelo de Economía Circular, sobre todo, teniendo en cuanta el potencial del residuo post industrial para ser reciclado. Por lo que se plantea la posibilidad de que las suposiciones que se utilizan frecuentemente en el método de ACV no son las correctas. Por ejemplo, en los escenarios de reciclaje solo se ha tenido en cuenta el porcentaje de sustitución del plástico virgen sin tomar en consideración la calidad del plástico reciclado. El reciclaje convencional aparentemente produce mayores beneficios porque la cantidad de plástico virgen que se puede sustituir es mayor debido a que las aplicaciones donde se utiliza son menos exigentes. Aunque precisamente por el tipo de aplicaciones y por la pérdida de calidad del material, es muy probable que el producto secundario fabricado con esa granza no sea reciclable y al final de su vida útil se incinere o se deposite en un vertedero. En consecuencia, los procesos de *downcycling* están más alineados con el modelo de Economía Lineal donde el número de ciclos en los que se puede reutilizar el mismo material es muy limitado. Algunos autores también han llegado a la conclusión de que la omisión de la calidad de material es una limitación del método ACV aplicado a tratamientos de residuos plásticos (Huysman et al., 2017). Por otro lado, si en el escenario de incineración se supone que la energía obtenida sustituye la energía procedente de fuentes fósiles, entonces lo más probable es que el reciclaje sea la opción menos favorable. Esto se debe a que el poder calorífico del plástico es mayor que la energía necesaria para la fabricación de granza virgen. Otros autores también han observado que la fuente de energía seleccionada tiene una importante influencia sobre los resultados del ACV (Rigamonti et al., 2014). Sin embargo, en este trabajo se defiende que esta comparación no es justa debido a que la energía se puede obtener de otras fuentes más sostenibles, mientras que el plástico con las mismas características, prestaciones y coste de fabricación solo proviene de recursos fósiles. Además, según el modelo de Economía Circular la energía se debe obtener de recursos renovables. De modo que, si el sector del plástico se está moviendo hacia este modelo, la sustitución de recursos fósiles no debe utilizarse en la computación de los impactos ambientales.

En la segunda parte del Capítulo se han realizado las modificaciones necesarias para incluir la calidad del plástico reciclado en el análisis y realizar una comparación de la fuente de energía más justa. En el primer caso, la calidad de material establece las aplicaciones donde se puede utilizar el plástico reciclado. Estas aplicaciones cubren una cuota de mercado dependiendo de la demanda. De modo que la calidad del material está directamente relacionada con la cuota de mercado de las aplicaciones donde se puede utilizar. En el análisis de los impactos de los procesos de reciclaje se debe tener en cuenta tanto el porcentaje de sustitución como la cuota de mercado. En el segundo caso, la energía obtenida durante la incineración sustituye la energía procedente de recursos naturales como solar, hidroeléctrica y biomasa. Con estas modificaciones, los resultados del análisis son distintos a los anteriores. El proceso de *upcycling* muestra mayores beneficios, sobre todo, en las categorías de cambio climático y recursos. Los beneficios del reciclaje convencional o *downcycling* se reducen debido a que el número de aplicaciones donde se puede usar es limitado y la cuta de mercado es baja (24%). En cambio, el plástico de mayor calidad se puede usar en cualquier aplicación, por lo que la cuota de mercado es 100%. En cuanto a la incineración, tiene un gran impacto negativo sobre la categoría de cambio climático, ya que no tiene sentido sustituir una fuente de energía que no emite gases de efecto invernadero. Sin embargo, presenta un impacto positivo sobre las categorías de uso de recursos, especialmente, la sustitución del biogás y de la energía solar. Esto se debe a que las dos fuentes requieren el uso de grandes áreas de terreno y, en el caso de la energía fotovoltaica, la explotación de recursos agotables como el silicio. Dependiendo del porcentaje de sustitución, el proceso de *upcycling* puede producir un efecto negativo sobre las categorías de cambio climático, salud del ecosistema y salud humana. La carga ambiental se debe principalmente al uso de energía de fuentes no renovables que constituyen el mix eléctrico. De modo que es necesario optimizar las operaciones de reciclaje para reducir el consumo energético, independientemente de la fuente de energía, ya que se ha observado que los recursos renovables pueden tener un impacto negativo sobre algunas categorías.

Por último, se plantea un tercer caso de estudio donde se extienden los límites del sistema hasta el final de vida útil del producto secundario fabricado con la granza reciclada de alta calidad. Se plantean tres nuevos escenarios teniendo en cuenta el tratamiento del residuo post industrial mediante el proceso de *upcycling* y el tratamiento del residuo post consumo mediante el reciclaje convencional. El primer escenario representa la situación actual de gestión de residuos domésticos en Europa en general. La tasa de reciclaje de los plásticos post consumo es del 40% y el resto se incineran con aprovechamiento de energía. Los procesos de reciclaje que se aplican son de *downcycling* debido a la alta contaminación de la corriente de residuos, especialmente, en el caso de los plásticos flexibles. De modo que el porcentaje de sustitución en el segundo ciclo del material es de 80% y la cuota de mercado es de 24%. Los dos escenarios siguientes son simulaciones realizadas con el objetivo de determinar qué parámetros tienen mayor influencia. En el segundo escenario, se estudia la posibilidad de que aumente la tasa de reciclaje hasta el 80% pero se apliquen los mismos métodos de reciclaje. Y en el tercer escenario, se supone que la granza reciclada del residuo doméstico es de alta calidad y se puede utilizar en cualquier aplicación. Por lo que la cuota de mercado es 100%. Los resultados muestran que la situación actual produce un efecto neto negativo sobre la categoría de cambio climático debido principalmente a la incineración de más de la mitad de los residuos. Además, los beneficios proporcionados por el reciclaje del residuo doméstico son bajos debido a que la granza que se obtiene es de baja calidad. Al aumentar la tasa de reciclaje, se consigue un impacto neto positivo, pero no es significativo. Por último, se consigue una gran mejora en cuanto el plástico que se obtiene es de alta calidad y se aumenta la cuota de mercado. De modo que se puede concluir que reciclar en mayor cantidad está bien, pero lo que aporta mayores beneficios al medioambiente es reciclar bien. Es decir, se deben desarrollar nuevas tecnologías que permitan aumentar la calidad del plástico reciclado tanto de origen industrial como doméstico.

3.2. Secado de films de plástico mediante centrifugación

El secado es un proceso que consume gran cantidad de energía (de Lima et al., 2016). La centrifugación es el método de secado de films más utilizado en el sector del reciclaje. Sin embargo, los fenómenos de eliminación del agua nunca se han estudiado a escala de laboratorio. Para ello, se ha diseñado un procedimiento experimental en el que se calcula la pérdida de humedad en una muestra de film triturado sometido a la fuerza centrífuga. Los parámetros que se han estudiado son la fuerza centrífuga, el tiempo, el tamaño de los trozos de film triturado o copos, la masa y la superficie del plástico en contacto con el agua. La humedad que se calcula es el porcentaje de la masa de agua contenida en una masa de plástico seco.

En la primera parte se ha utilizado una muestra de film de PEAD de 17 µm de espesor. Se han dibujado las curvas de secado representando el porcentaje de humedad frente al tiempo de centrifugación (Figura 3). Los resultados experimentales muestran que el contenido en humedad disminuye al aumentar la fuerza centrífuga y el tiempo. La mayor cantidad de agua se elimina en los primeros 10 minutos y después se va acercando a un valor de equilibrio que es la humedad remanente. La humedad de equilibrio disminuye al aumentar la fuerza de centrifugación, aunque cuanto más altos los valores el efecto es menos significativo.

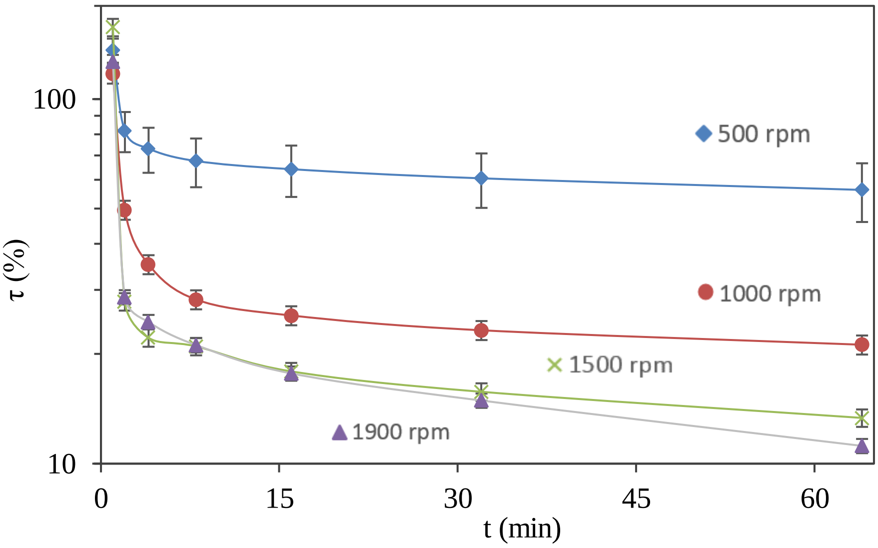

***Figura 3**. Curvas de secado de un film de PEAD de 17 µm.*

Se ha determinado que existe un tamaño de copos óptimo (1-2 cm de largo) con el que se consigue el mínimo porcentaje de humedad (Figura 4). Esto puede deberse a que cuando el tamaño es menor se crean muchos puntos de contacto entre los copos de film en los que el agua queda retenida por una fuerza capilar. Por otro lado, cuando el tamaño de los copos es mayor, el material tiende a arrugarse y plegarse más, por lo que el agua queda retenida por esa tortuosidad de los films. En cuanto a la masa del plástico, se ha comprobado que no tiene prácticamente influencia sobre el contenido en humedad. Finalmente, se ha estudiado el espesor de los films y se ha observado que el porcentaje de humedad en base seca de los films más finos es mayor. Esto coincide con las observaciones realizadas en la industria donde los recicladores deben invertir más tiempo y costes en secar los materiales de menor espesor. Sin embargo, la superficie de estos materiales en contacto con la capa de agua varía. Los films de menor espesor tienen una superficie total mayor. Por lo que se plantea la hipótesis de que la cantidad de agua depende de la superficie del plástico. Al calcular la humedad superficial, se comprueba que es igual en las muestras estudiadas. Es decir, la superficie de los films más finos es mayor y por ello retienen mayor cantidad de agua.

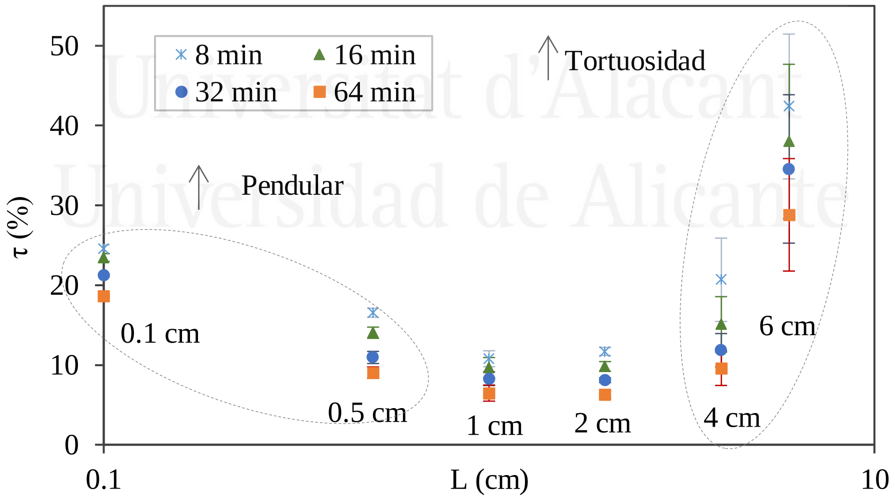

Figura 4. *Porcentaje de humedad en función del tamaño de copo de film triturado (L= longitud).*

Durante la centrifugación se observa que los plásticos forman una torta similar a la torta que se obtiene en los tratamientos de aguas residuales. Se supone que dentro de la torta existes tres tipos diferentes de agua (Figura 5).

El primer tipo es el agua libre que se encuentra en los poros y huecos que se forman entre los copos de plástico. El segundo tipo es el agua que se forma por capilaridad que a su vez puede ser de dos tipos: la que se forma en la superficie del plástico (superficial) y la que se aparece en los puntos de contacto entre los copos (pendular). Por último, el tercer tipo de agua es el agua que queda atrapada por la tortuosidad de los films que se curvan y se arrugan por el hecho de ser flexibles.

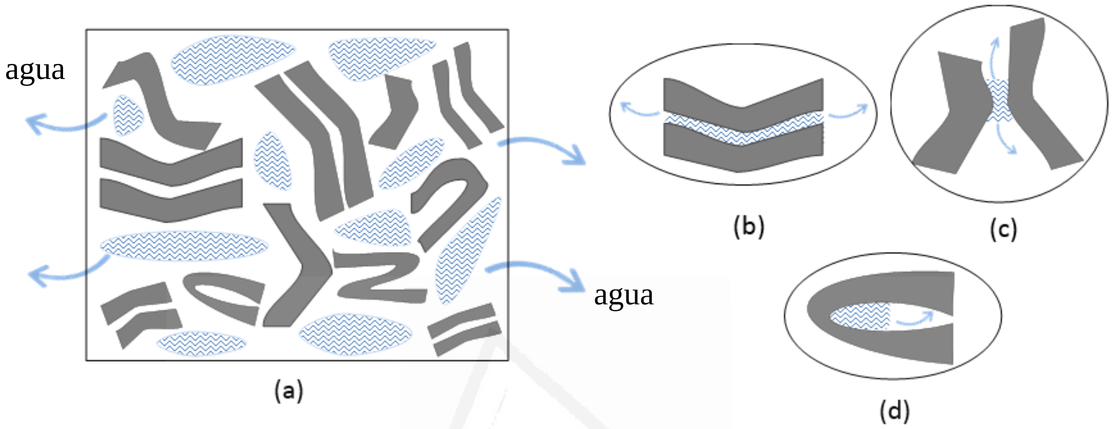

Figura 5. *Tres tipos de agua que se forman en la torta de films de plástico. (a) Agua libre. (b) Agua retenida por capilaridad superficial. (c) Agua retenida por la capilaridad pendular. (d) Agua retenida por la tortuosidad del film.*

El contenido en agua libre depende de la fuerza centrífuga y del tiempo de centrifugación, y es el que se elimina durante los primeros minutos del proceso. La humedad retenida por capilaridad depende de la fuerza centrífuga y la retenida por tortuosidad varía con las características de los copos. La humedad de equilibrio depende de la fuerza centrífuga y las características de la torta y no se puede eliminar con las mismas condiciones de operación. La humedad está directamente relacionada con la inversa de la raíz cuadrada del tiempo de centrifugación y la inversa del cuadrado de la velocidad angular.

En la segunda parte del Capítulo se han estudiado otros materiales con el objetivo de determinar si la eficiencia de secado se ve afectada por el tipo de polímero y por la degradación que sufre durante su vida útil. Por un lado, se ha analizado una muestra de PP de 40 µm, de PET de 14 µm y de PEBD gofrado de 37 µm. Los films gofrados se obtienen mediante el uso de moldes con nano o micropatrones y presión. El objetivo es aumentar la superficie de los materiales plásticos a nivel microscópico. De modo que es un material muy interesante para este estudio. Los tres materiales analizados procedentes de recortes industriales, por lo que no han sufrido prácticamente degradación. Por otro lado, se ha analizado tres muestras de film post consumo de diferentes orígenes. La primera muestra es un PEAD de 45 µm de espesor procedente de la recogida no selectiva o mixta de residuos domésticos. En este tipo de recogida no se produce ninguna segregación de materiales por parte del consumidor, por lo que plástico suele estar sucio y altamente contaminado. La segunda muestra es un film de PEBD de 65 µm obtenido de la recogida selectiva de residuos, es decir, del contenedor de envases. En este caso, el material se puede haber degradado durante la fase de uso, pero el nivel de contaminación suele ser más bajo. La tercera muestra es un film de agricultura de PEBD de 25 µm. La contaminación que contienen estos films es principalmente tierra y polvo, y la superficie suele sufrir degradación por haber estado a la intemperie. Además, se han utilizado dos técnicas de microscopía (el microscopio electrónico de barrido o MEB y el microscopio de fuerza atómica o MFA) para estudiar la superficie de las muestras.

Las curvas de secado obtenidas con las muestras de PP y PET muestran la misma tendencia que las curvas de PEBD presentadas en la primera parte. Además, la humedad específica de estos materiales es muy similar, lo que indica que el contenido de agua no depende de la naturaleza del plástico. Sin embargo, la humedad específica del film gofrado es considerablemente más alta que la de los otros materiales. Como se ha dicho anteriormente, los micropatrones hacen que la superficie externa aumente. Las imágenes obtenidas con el MEB y el MFA muestran claramente la diferencia entre la superficie de un film convencional y uno gofrado (Figura 6 y Figura 7). De modo la superficie calculada con el espesor medido del film puede ser inferior a la superficie real en contacto con la capa de agua. Para calcular la superficie real, se toma como referencia el film de PEAD estudiado en la primera parte. Si la cantidad de agua depende de la superficie, entonces debe existir una relación directa entre el porcentaje de humedad de un film y el porcentaje humedad de otro film de distinto espesor. Por lo que, conociendo la humedad experimental de cada muestra y el espesor del film de PEAD, se puede calcular el espesor que debería tener el film gofrado para que la cantidad de agua por unidad de superficie sea la misma. Con el espesor calculado (6.4 µm) se obtiene la superficie real en contacto con la capa de agua. Con este material se ha podido comprobar que la superficie del plástico tiene una gran influencia sobre el contenido en humedad.

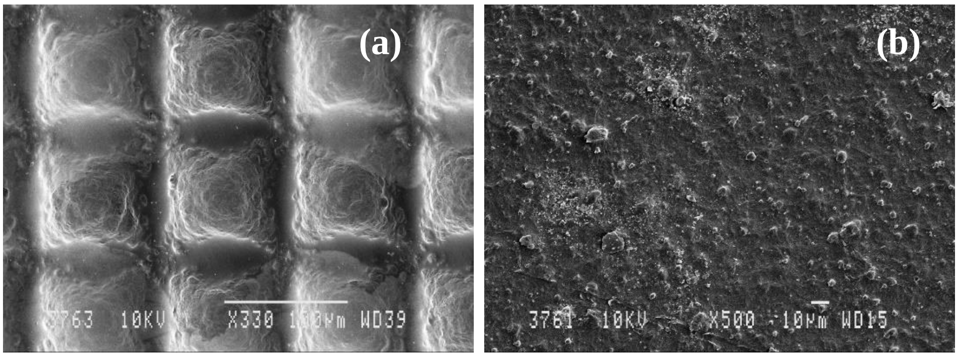

Figura 6. *Imágenes del MEB de la muestra de film gofrado (a) y del film convencional de PEAD (b).*

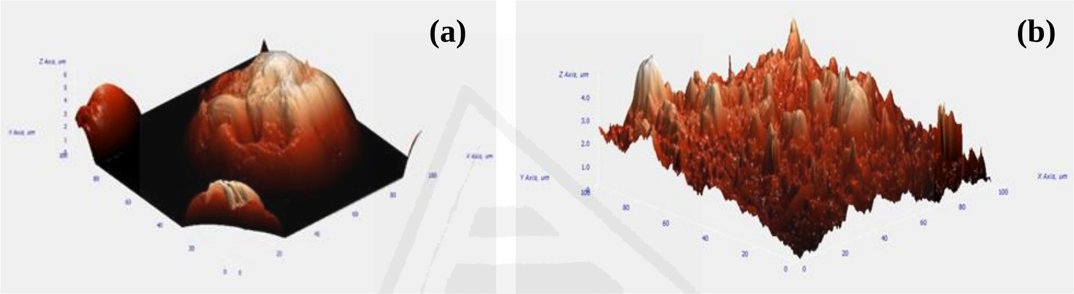

Figura 7. *Imágenes del MEB de la muestra de film gofrado (a) y del film convencional de PEAD (b).*

Finalmente, los resultados de secado de los films post consumo muestran que la humedad específica es muy similar entre las muestras. La degradación de la superficie se ha analizado mediante MEB y MFA. Las imágenes muestran que la muestra de la recogida no selectiva es la que presenta mayor grado de degradación. El film procedente de la recogida selectiva presenta menos signos de degradación, al igual que el film de agricultura (Figura 8). El film de recogida no selectiva también tiene la mayor rugosidad, mientras que el film de agricultura es el más liso. De modo que se puede deducir que la degradación de la superficie no tiene influencia sobre el contenido de agua.

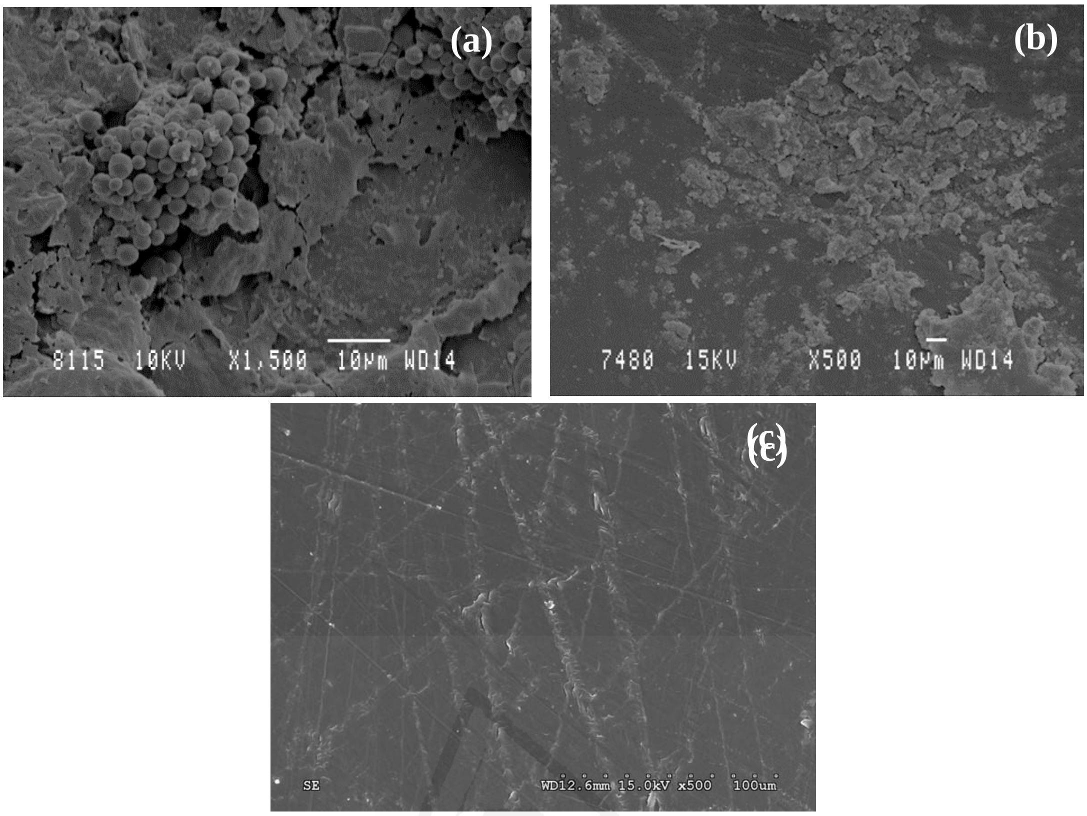

Figura 8. *Imágenes del MEB de la muestra de film de recogida no selectiva (a), de film de recogida selectica (b) y del film de agricultura (c).*

3.3. Identificación de sustancias orgánicas semivolátiles en residuos plásticos

En el Capítulo 5 se han estudiado las sustancias orgánicas semivolátiles (COSV) presentes en diferentes muestras de plástico mediante la técnica de extracción sólido-líquido utilizando diclorometano como disolvente y análisis mediante cromatografía de gases acoplada a espectrometría de masas. En primer lugar, se ha analizado la composición de la granza de *masterbatch* (o mezcla concentrada) de diferentes aditivos ampliamente utilizados en el sector. Estos aditivos son el agente deslizante, el antiestático, el antioxidante y el aditivo de procesamiento. En segundo, lugar se han determinado los COSV de una serie de plásticos reciclados procedentes de la industria y una muestra de la agricultura. Por último, se ha estudiado dos muestras de plástico reciclado post consumo de dos polímeros diferentes (PEAD y PEBD).

El análisis de los aditivos indica que el agente deslizante está compuesto principalmente por amidas, al igual que el antiestático y el aditivo de procesamiento. En el aditivo antioxidante el grupo predominante son los ésteres. El compuesto clave en el aditivo deslizante es la erucamida (13-cis-docosenamida), en el antiestático y el aditivo de procesamiento de polímeros es la N,N-bis (2-hidroxietilo)-dodecanamida y, por último, en el antioxidante el compuesto mayoritario es el octadecil 3-(3, 5-di-tert-butil-4-hidroxifenil) propionato. Además de los compuestos clave, los aditivos contiene otras sustancias en menor concentración que pueden ser productos secundarios, impurezas, etc. De modo que los aditivos pueden ser fuente de sustancias añadidas no intencionadamente, sobre todo, cuando el origen de los residuos es desconocido.

En la segunda parte se han analizado siete muestras de plástico reciclado de diferentes orígenes y una muestra de plástico virgen. Todas las granzas son de PEBD. Cuatro muestras recicladas proceden de la misma empresa recicladora (reciclador 1) y se diferencian por el color (negro, coloreado, transparente y blanco). Dos muestras fueron obtenidas de otro reciclador (reciclador 2) y son de color negro y marrón. Una de las muestras es de reciclaje interno de una empresa de extrusión de films, es decir, mermas del proceso que directamente se peletizan para volver a extruir film. Por último, una muestra procede del sector de la agricultura recuperado por un tercer reciclador (reciclador 3). En total se han detectado 334 sustancias y gracias al uso de patrones internos se ha realizado una semi-cuantificación de la concentración de las sustancias más abundantes.

La concentración total de sustancias en las muestras de plástico virgen y el reciclado interno es la mayor. Esto se debe a que los dos materiales tienen un alto contenido en aditivos. La concentración disminuye en las muestras recicladas porque los aditivos se suelen consumir durante la etapa de uso y los procesos de reciclaje. En este caso aumenta el número de sustancias detectadas que son productos de degradación del polímero y de los aditivos. La muestra de virgen ha sido aditivada con el agente deslizante, siendo éste el compuesto más abundante identificado. El mismo aditivo también es el mayoritario en la muestra de reciclado interno. De hecho, su concentración es muy similar al material virgen a pesar de haber pasado por dos procesos de extrusión. Esto indica a que el agente deslizante no se degrada durante el procesado del material porque es un compuesto estable a altas temperaturas. En las muestras de los tres recicladores, la concentración y el tipo de aditivos es variable. En general, la concentración del aditivo deslizante disminuye porque el compuesto migra hacia la superficie del producto y se consume durante su vida útil. Las muestras del primer reciclador de color negro y coloreado y la muestra de color negro del segundo reciclador presentan una mayor concentración del aditivo plastificante. El contenido del aditivo antioxidante también aumenta en las muestras de color negro y transparente del reciclador 1 y en la muestra de agricultura. La muestra de menor concentración de aditivos es la de color marrón del reciclador 2. Se han identificado algunos aditivos como el bisfenol A y ciertos ftalatos cuyo uso está limitado por tener efectos perjudiciales para la salud humana (Garí et al., 2019). En cuanto a los productos de degradación, su concentración aumenta en las muestras de plástico reciclado, sobre todo, las procedentes del reciclador 1. En las muestras de los recicladores 2 y 3 se ha identificado mayor número de contaminantes como sustancias presentes en tintas y adhesivos, en productos de papel y en tratamientos médicos (Figura 9). En resumen, los residuos post industriales tiene un alto potencial para ser reutilizados en aplicaciones de alto valor añadido debido a su mayor calidad. Sin embargo, en este estudio se muestra que la gran variedad de aditivos utilizados en el procesamiento de los plásticos y las sustancias añadidas no intencionalmente pueden suponer un peligro para la seguridad de los consumidores. De modo que se requieren nuevas tecnologías de descontaminación enfocadas a la eliminación de aditivos, sus productos de degradación y otros contaminantes.

En la tercera parte se han analizado dos muestras de plástico reciclado post consumo procedentes de la recogida selectiva de residuos domésticos. Los plásticos fueron lavados y peletizados en una empresa de reciclaje. Uno de los materiales es PEAD rígido utilizado en el envasado de productos de higiene y limpieza. Y el segundo material es PEBD utilizado en la fabricación de films para envases flexibles, bolsas de la compra, etc. En general, el área total de los compuestos identificados en la muestra de PEAD es 5 veces menor que en la muestra de PEBD. Esto se debe a que la cantidad de aditivos que se utilizan en el procesamiento de los materiales flexibles es mayor, ya que las aplicaciones donde se utilizan son más exigentes.

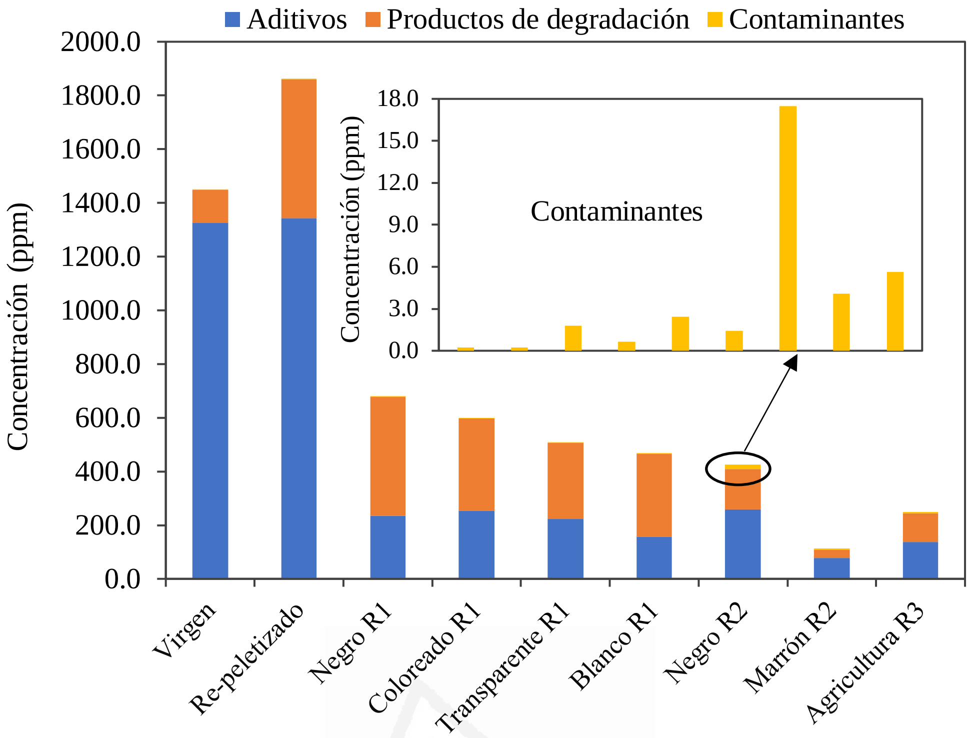

Figura 9. *Concentración relativa de los aditivos, los productos de degradación y los contaminantes.*

Así, el número de aditivos identificados en la muestra de PEBD es el doble que en la muestra de PEAD. La mayor diferencia es que la granza de PEBD contiene una serie de plastificantes y aditivos de procesamiento que no se encuentran en el PEAD. De los aditivos presentes en la muestra de PEBD, el isoftalato de dioctilo utilizado como plastificante es el compuesto mayoritario y no está incluido en la lista positiva de sustancias permitidas para el contacto con alimentos del reglamento EU 10/2011. Los aditivos de mayor concentración en la muestra de PEAD son el octadecil 3-(3,5-di-tert-butil-4-hidroxifenil) propionato y la erucamida. Las dos sustancias están incluidas en la lista positiva. Además, en las dos muestras se ha identificado sustancias añadidas no intencionadamente en alta concentración, siendo el grupo de los productos de degradación de aditivos el más abundante. El número de contaminantes y productos de degradación de polímeros detectados es reducido debido a que éstos son mayoritariamente sustancias más volátiles. De modo que se deben utilizar otras técnicas de extracción, como la microextracción en fase sólida, para estudiarlos. Los contaminantes identificados en las dos muestras son principalmente cosméticos y fragancias que son más propios de PEAD que se utiliza para el envasado de productos de limpieza. Sin embargo, estos compuestos han podido migrar a otros materiales por contaminación cruzada, ya que los plásticos se recogen en el mismo contenedor.

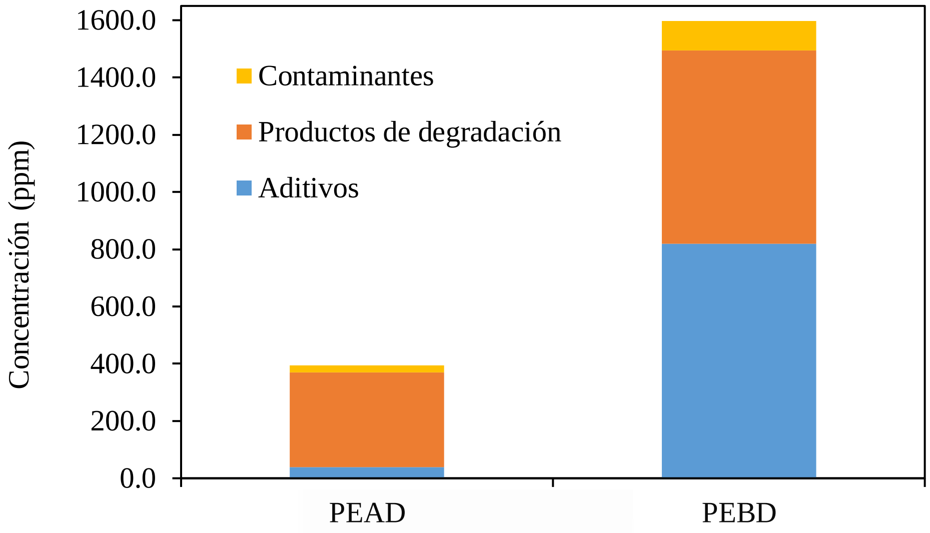

Figura 10. *Concentración (ppm) de COSV detectados en las muestras de plástico reciclado post consumo.*

En resumen, los resultados de este estudio indican que los plásticos de PEBD presentan mayor número y concentración de COSV y, por lo tanto, se necesitan tecnologías de descontaminación más eficientes. Además, la concentración de sustancias identificadas en la muestra de PEBD post consumo es alrededor de 5 veces mayor que en las muestras de plástico de origen industrial. Esto se debe a la gran variedad de productos que se recogen de las fuentes municipales, no solo en cuanto al tipo de polímero, sino también a los aditivos utilizados, a la calidad o pureza de los materiales vírgenes, al uso de tintas, adhesivos, etc. La falta de trazabilidad y tecnologías eficientes de descontaminación, hace que estos materiales solo se puedan utilizar en aplicaciones en las que no supongan un riesgo para el consumidor. El PEAD presente mayor potencial para ser reciclado debido a que el número de aditivos y sustancias añadidas no intencionadamente detectados es menor.

4. Conclusiones

Los resultados obtenidos durante la realización de esta Tesis conducen a las siguientes conclusiones.

- En el análisis de ciclo de vida (ACV) comparativo de procesos de tratamiento de residuos plásticos incluyendo el reciclaje se debe considerar dos parámetros relacionados con la calidad del material reciclado: el porcentaje de sustitución del plástico virgen y la cuota de mercado de las aplicaciones donde se puede utilizar el plástico reciclado.

- En el ACV cuyo objetivo sea estudiar la circularidad de los procesos tratamiento de residuos y que incluya la incineración, la energía obtenida no puede sustituir el consumo de recursos fósiles, ya que es una fuente que no está contemplada en el modelo de Economía Circular. Se debe hacer la suposición de que la energía proviene de recursos renovables para hacer una comparación más justa con los procesos de reciclaje.
- Incluyendo las dos suposiciones en el ACV, resulta que el *upcycling* produce beneficios en la categoría de cambio climático cunado el porcentaje de sustitución es mayor del 40%. El proceso de *downcycling* con un 80% de sustitución produce un impacto negativo sobre la misma categoría. En la categoría de uso de recursos, los dos procesos de reciclaje producen beneficios. El proceso de *downcycling* supera al de *upcycling* solo si el porcentaje de sustitución es inferior al 40%. En cuanto a la categoría de salud del ecosistema, todos los procesos de reciclaje generan un impacto negativo, siendo mayor en el *upcycling* debido al mayor consumo de energía y agentes químicos. Por último, el *upcycling* empieza a producir beneficios en la categoría de salud humana por encima del 80% de sustitución. En cambio, el downcycling sigue siendo perjudicial con el mismo porcentaje de sustitución.
- La sustitución de energía procedente de fuentes renovables tiene un gran impacto negativo sobre la categoría del cambio climático. Sin embargo, en cuanto al uso de recursos y a la salud del ecosistema puede ser beneficioso debido a la degradación de suelos, pérdida de hábitats, explotación de recursos agotables, entre otros relacionados con las fuentes renovables como biomasa, solar e hidráulica. Por último, tanto el *upcycling* como la incineración con sustitución de recursos renovables (a excepción de la utilización de biogás) tiene un efecto negativo sobre la salud humana.
- Los efectos negativos del proceso de *upcycling* se deben principalmente al mayor uso de energía que se requiere para aumentar la calidad del plástico reciclado. De modo que se debe optimizar las operaciones que consumen energía durante el reciclaje, independientemente de la fuente de energía que se utilice, ya que se ha visto que los recursos renovables

también pueden ser perjudiciales, sobre todo, para la salud del ecosistema.

- La gestión del plástico post consumo con una tasa de reciclaje del 40% y un 60% de incineración con sustitución de energía renovable genera un impacto negativo sobre la categoría de cambio climático. Los procesos de reciclaje del residuo doméstico no están preparados para mantener la calidad del material, por lo que la granza reciclada se utiliza en aplicaciones de bajo valor añadido. Suponiendo que la tasa de reciclaje aumente hasta el 80%, se podría obtener beneficios para el medioambiente. Pero la mayor mejora se produce cuando se aumenta la cuota de mercado de las aplicaciones donde se puede utilizar el plástico reciclado, es decir, cuando se aplican métodos de *upcycling*. De modo que reciclar más está bien, pero lo que se debe hacer es reciclar mejor.
- Para que el plástico se pueda utilizar en aplicaciones de alto valor añadido debe ser seguro para el consumidor. La falta de trazabilidad y la composición desconocida de los residuos de plástico suponen un problema para la transición hacia la Economía Circular. Por ello, se necesitan amplios estudios de identificación de sustancias presentes en los plásticos reciclados.
- Se debe optimizar la operación de secado de plásticos flexibles y para ello se deben estudiar los mecanismos de eliminación del agua. En esta Tesis por primera vez se ha realizado un estudio de centrifugación de plástico flexible y se han dibujado las curvas de secado de diferentes materiales.
- Durante la centrifugación de los films triturados se forma una especie de torta de plástico similar a la torta que se obtiene en los tratamientos de aguas residuales. Dentro de la torta existen tres tipos de agua. El primer tipo es el agua libre que se encuentra en los huecos y poros entre los copos de film. El segundo tipo es el agua que se retiene por capilaridad que puede ser superficial y pendular. Por último, está el agua que se retiene por la tortuosidad de los films.
- El agua libre depende de la fuerza de centrifugación y del tiempo. El agua capilar depende de la fuerza centrífuga y el agua retenida por la tortuosidad es función de las características del material. Cuando el tiempo de centrifugación es alto se alcanza una humedad de equilibrio

que está formada por estos dos tipos de agua y no se puede eliminar en las mismas condiciones de operación.

- El porcentaje de humedad depende linealmente de la inversa de la raíz cuadrada del tiempo de centrifugación y de la inversa del cuadrado de la velocidad angular.
- Existe un tamaño de copo óptimo entre 1 y 2 cm con el que el porcentaje de humedad se minimiza. Se debe a que cuando el tamaño es más pequeño aumenta el agua pendular y cuando el tamaño es mayor aumenta el agua retenida por la tortuosidad del material.
- El contenido de agua depende de la superficie del plástico en contacto con la capa de agua. De modo que la humedad superficial es similar en todos los materiales, mientras que el porcentaje de humedad es función del espesor del film. Los plásticos de menor espesor tienen mayor superficie y, por lo tanto, el porcentaje de humedad es mayor. Los materiales gofrados se comportan de manera diferente porque su superficie fue modificada para aumentar el área total, que es mayor que el área de un film tradicional del mismo espesor. De modo que la cantidad de agua que retienen es mayor.
- La eficiencia de eliminación de agua es independiente del tipo de material, de la degradación de la superficie y de la rugosidad. Por ello, los plásticos post consumo se comportan igual que los plásticos de origen industrial.
- La muestra de film post consumo de la recogida no selectiva de residuos tiene la superficie más degradada comparada con las muestras post industriales, la muestra post consumo de recogida selectiva y la muestra de agricultura.
- La rugosidad media de los films no se ve significativamente afectada por la degradación de la superficie, si no que depende de la composición del material. Por ejemplo, los films con alto contenido en cargas como dióxido de titanio o carbonato cálcico presentan una mayor rugosidad.
- Los aditivos utilizados en el procesamiento de plásticos pueden ser una fuente de sustancias añadidas no intencionadamente debido a que los *masterbatches* (o mezclas concentradas de aditivos), además de los compuestos clave, contienen numerosos compuestos secundarios, impurezas, etc. La calidad de los aditivos está directamente relacionada con el contenido de sustancias no deseadas.

- El aditivo deslizante, el antiestático y el de procesamiento de polímeros están formados mayoritariamente por amidas. Y el aditivo antioxidante por ésteres. Otros grupos presentes son aminas y compuestos cíclicos, y en menor concentración aldehídos, alcoholes, etc.
- Se ha realizado por primera vez un análisis global de los COSV presentes en muestras de plástico reciclado post industrial y de la agricultura. La variedad de aditivos identificados es mayor en las muestras de plástico reciclado post industrial y de agricultura que en el plástico virgen y el reciclado interno. Sin embargo, su concentración es menor debido a que los aditivos se consumen o degradan durante el ciclo de vida del producto. Precisamente, la degradación del material hace que, en algunas muestras recicladas como la procedente de la agricultura, el número total de compuestos detectados sea mayor.
- Se han detectado algunos contaminantes en los plásticos reciclados post industriales que pueden deberse a la contaminación cruzada durante las etapas de recogida y almacenamiento de los residuos. De modo que es necesario establecer si no hay o mejorar el cumplimiento de las buenas prácticas de gestión de residuos. Otros contaminantes pueden tener su origen en las tintas, adhesivos, recubrimientos que se utilizan en el sector. Estos compuestos no deseados podrían eliminarse durante el reciclaje si se adoptan nuevas tecnologías como el destintado.
- Se ha realizado por primera vez un análisis global de los COSV presentes en una muestra de PEAD rígido utilizado en el envasado de productos de higiene y de limpieza y una muestra de PEBD film utilizado en aplicaciones como envases flexibles y bolsas de la compra.
- La muestra de PEBD contiene mayor cantidad de aditivos y sus productos de degradación que el PEAD. Se debe principalmente a que estos materiales se utilizan en diferentes aplicaciones, por lo que sus características y propiedades son diferentes. El menor contenido en aditivos y sustancias añadidas no intencionadamente hace que el PEAD rígido tenga más potencial para ser reciclado en ciclo cerrado. Sin embargo, hace falta un estudio más enfocado a los contaminantes.
- Los contaminantes y los productos de degradación de polímeros pueden ser sustancias más volátiles, por lo que no se detectan con el método de extracción utilizado.

- La concentración de COSV en la muestra de PEBD post consumo es alrededor de 5 veces mayor que en las muestras de plástico reciclado de PEBD post industrial. De modo que las sustancias no deseadas suponen un problema para la circularidad de los plásticos, sobre todo, los de origen doméstico.
- La falta de trazabilidad de los residuos, tanto post industriales como post consumo, supone un riesgo para la salud del consumidor por la posible migración de sustancias peligrosas. El análisis de la composición de cada lote de material que se recicla es una tarea muy costosa y no es totalmente eficiente. De modo que se deben desarrollar tecnologías de descontaminación como la eliminación de las sustancias no deseadas mediante el uso de disolventes no volátiles y ecológicos. Las fracciones como el PEBD flexible podrían necesitar técnicas más extremas como el reciclaje químico o la disolución-precipitación del polímero debido al alto contenido en aditivos y sustancias añadidas no intencionadamente.

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CONGRESS PARTICIPATIONS

- **IV Forum Sustainable Chemistry, Innovative and Competitive Companies** (SusChem-Spain). Deinking of printed plastic scrap to produce high added value recycled products. Zaragoza (Spain). 2017. Oral communication.

- **8th World Congress and Expo on Recycling.** Mechanical drying of plastic films. Berlin (Germany). 2018. Oral communication.

- **3rd ANQUE-ICCE International Congress of Chemical Engineering**. How to get the most out of printed plastic scrap: An LCA approach. Santander (Spain). 2019. Oral communication.

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