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Challenges and opportunities of solvent-based additive extraction methods for plastic recycling



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ABSTRACT

Additives are ubiquitously used in plastics to improve their functionality. However, they are not always desirable in their 'second life' and are a major bottleneck for chemical recycling. Although research on extraction techniques for efficient removal of additives is increasing, it resembles much like uncharted territory due to the broad variety of additives, plastics and removal techniques. Today solvent-based additive extraction techniques, solid-liquid extraction and dissolution-precipitation, are considered to be the most promising techniques to remove additives. This review focuses on the assessment of these techniques by making a link between literature and physicochemical principles such as diffusion and Hansen solubility theory. From a technical point of view, dissolution-precipitation is preferred to remove a broad spectrum of additives because diffusion limitations affect the solid-liquid extraction recoveries. Novel techniques such as accelerated solvent extraction (ASE) are promising for finding the balance between these two processes. Because of limited studies on the economic and environmental feasibility of extraction methods, this review also includes a basic economic and environmental assessment of two extreme cases for the extraction of additives. According to this assessment, the feasibility of additives removal depends strongly on the type of additive and plastic and also on the extraction conditions. In the best-case scenario at least 70% of solvent recovery is required to extract plasticizers from polyvinyl chloride (PVC) via dissolution-precipitation with tetrahydrofuran (THF), while solid-liquid extraction of phenolic antioxidants and a fatty acid amide slip agents from polypropylene (PP) with dichloromethane (DCM) can be economically viable even without intensive solvent recovery.

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Abbreviations: TFE, 2,2,2-Trifluoro ethanol; MEHP, 2-Ethylhexyl phthalate; HMBP, 4-Hydroxymethyl-2,6-di-*tert*-butylphenol; ASE, Accelerated Solvent Extraction; ABS, Acrylonitrile butadiene styrene; BTPS, Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate; BBP, Benzyl butyl phthalate; B_p, Boiling point; BFR, Brominated flame retardant; CS₂, Carbon disulfide; CCl₄, Carbon tetrachloride; CYHA, Cyclohexane; deca-BDE, Decabromodiphenyl ether; DEHP, Di(2-ethylhexyl phthalate); DMEP, Di-2-methoxyethyl phthalate; DBP, Dibutyl phthalate; DiDP, Di(isodecyl phthalate); DiBP, Di(isobutyl phthalate); DIHP, Di(isoheptylphthalate); DiNP, Di(isononyl phthalate); DCB, Dichlorobenzene; DCM, Dichloromethane; DOA, Dioctyl adipate; DOP, Dioctyl phthalate; DPHP, Dipropylheptyl phthalate; Supersoft, Ethylene–propylene heterophasic copolymer; FT-IR, Fourier transform infrared spectrometry; Tg, Glass transition temperature; HSP, Hansen solubility parameter; HBCD, Hexabromocyclododecane; HFP, Hexafluoropropane; HDPE, High density polyethylene; HIPS, High impact polystyrene; HALS, Hindered amine light stabilizer; h, Hour; LLDPE, Linear low density polyethylene; LDPE, Low density polyethylene; MP, Persistent organic pollutants; PMMA, Poly (methyl methacrylate); PBDE, Poly brominated diphenyl ether; PBT, Poly(1,4-butylene terephthalate); PB, Poly-1-butene; PA, Polyamide; PC, Polycarbonate; PE, Polyethylene; PTFE, Polyettrafluoroethylene; PUR, Polyurethane; PVB, Polyvinyl butyral; PVC, Polyvinylchloride; PVDF, Polyvinylidine fluorie; PEB, Potential economic benefit; RT, Room temperature; sc-CO₂, Supercritical fluid; SFE, Superc

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1. Introduction

Plastic materials are indispensable for our daily life. They are used in different applications such as electronics, the automotive industry, packaging, manufacturing of consumer products, among others (Horodytska et al., 2018; Plastics Europe, 2018; Reingruber et al., 2010). New trends open even more specialized features such as adsorbents, electromagnetic interface shielding, sensors and so on (Chen et al., 2019; Jiang et al., 2019b; Jiang et al., 2019a; Li et al., 2019b; Wang et al., 2018a; Yang et al., 2019). Due to their increased functionality associated with low production costs, plastic production is expected to vastly increase over the next decades. However, due to the current relatively low recycling rate (\sim 30%), a huge amount of plastic waste is still landfilled or incinerated, which negatively impacts the environment and presents a significant economic cost (European Parliament, 2018). Therefore, in the last years, more initiatives have risen in order to improve waste management in various fields (Kong et al., 2018b; Kong et al., 2018a; Li et al., 2017; Wang et al., 2018c). For example, The Ellen MacArthur Foundation launched the Plastic Pact network in order to accelerate collaboration within countries to create a shared vision of a circular economy in which plastics do not end up as waste or pollute the environment (Ellen MacArthur Foundation, 2017). In addition, the European Commission adopted a Circular Economy Package which aims for increased recycling rates and re-use of plastics to minimize the negative environmental impacts and also to increase economic growth (European Commission, 2018).

Within the fraction that is currently recycled, best practices focus mainly on open-loop recycling, meaning that the application after recycling is different compared to the original application. Usually the new application is of lower quality, which is the reason why this is also called 'downcycling'. As such, open-loop recycling does not completely eliminate the need for new raw materials as the high-end markets still need virgin feedstock (Huysman et al., 2015). Furthermore, the market demand for 'downcycled' products is not endless. Compared to open-loop recycling, closed-loop recycling is stated to be a more circular option which aims to keep materials at their highest value (Huysman et al., 2015).

The general challenges encountered during closed-loop recycling processes of plastics are associated mainly with several types of contaminations. This can for example be cross contamination of other polymers due to imperfect separations or odour caused by organic contamination, but also the presence of additives can be an issue. During the manufacturing of plastics, additives are often incorporated in order to improve their physicochemical properties in terms of thermal and impact resistance, strength, stiffness and also to overcome processing problems correlated with high temperature/viscosity and environmental instability, among others (Bart, 2005).

Within this paper, we categorize plastic additives in 4 categories, so-called functional additives, colourants, fillers and reinforcements (Hahladakis et al., 2018; Hansen et al., 2013). Functional additives are also subdivided into different groups, such as stabilizers, flame retardants, antioxidants, slip agents, plasticizers, lubricants, among others (Hansen et al., 2013). Based on the application requirements, different kind of additives are incorporated into plastics in different quantities. For example, flame retardants are used to prevent the development of ignition, antistatic agents allow to liberate static electricity, slip agents reduce friction and pigments offer a wide range of colours for marketing purposes (Hahladakis et al., 2018).

These additives are optimized for their processing and use phase of the first cycle, but not for recycling. In addition, these added substances might even cause concerns related to food safety. For instance, azo dyes and bisphenol A additives are classified as toxic and endocrine disruptors for humans (European Chemical Agency). Some brominated flame retardants can cause neurotoxic effects and alter the function of the thyroid hormone (Dingemans et al., 2011). Moreover, some phthalates are also toxic to a variety of aquatic micro-organisms (Heudorf et al., 2007). In order to minimize the negative impact associated with additives, regulation norms for the use of some additives were implemented. For example, food contact plastics are in compliance with legislation norms such as Regulation 1907/2006 concerning Registration, Evaluation, Authorization of Chemicals (REACH) in order to avoid health and environmental risks (Ashby et al., 1997). Also, the use of bisphenol A in toys and carcinogenic dyes are regulated by the Toy Safety Directive 2009/48/EC and EU Directive 67/548/EEC (European Chemical Agency; European Union, 2009). Apart from these potential environment and health risks, additives can also disturb market demands, such as the need for transparent or coloured plastics from a mix of coloured plastics, which typically results in dark coloured or even black recycled products.

The removal of additives in an effective way could broaden the closed-loop recycling options and minimize the detrimental effects of additives. Therefore, there is a growing interest in additive extraction methods such as different types of solid-liquid extraction and dissolution-precipitation processes (Strandberg and Albertsson, 2008). However, until now there are only a few pilotscale additive extraction processes on the market focused on plastics. For example, the CreaSolv® technology patented by Fraunhofer Institute has been adapted from a process to remove brominated flame retardants from electrical electronic equipment waste via dissolution-precipitation (Fraunhofer IVV, 2019; Unilever, 2017). Similarly, the APK's Newcycling[®] technology is a chemical dissolution process which is used to separate different polymer types such as polyethylene (PE) and polyamide (PA) from multilayer plastic waste (APK, 2019). In addition to dissolutionprecipitation technologies, Norec® and Cadel Deinking use a solid-liquid extraction technique to remove unwanted substances, mainly colourants, from different types of plastics (Cadel Deinking; Norec, 2018). Another technology, PureCycle, uses both solidliquid extraction and dissolution-precipitation in succession for purification of polypropylene (PP) (Milliken, 2019). It is clear that these technologies are relatively new and more research is required to optimize these techniques in order to make them more profitable and more environmentally friendly. For example, the VinyLoop plant founded by Solvay for the recycling of polyvinyl chloride (PVC) from films and cables was closed in 2018 because new EU's REACH legislation declared that phthalates used in the production of PVC were hazardous and also the process was not economically feasible (Plastic Information Europe, 2018; Zero Waste Europe, 2019). In addition to solvent-based extraction. chemical degradation of polymers can also be an option to remove additives from certain plastics. For instance, a technology developed by Ioniga removes colourants with a magnetic fluid via chemical degradation of PET (Ioniga Technologies, 2019). Despite of all these technologies, efficient removal of additives is still complicated due to a broad variety of chemical properties of both additives and plastics. Recently, much attention also goes to thermochemical recycling technologies such as pyrolysis and gasification. However, on the one hand it is unclear how fast these processes would become technically sufficiently robust and economically and environmentally beneficial, thus mechanical recycling will still be applied for many years. Furthermore, also these thermochemical recycling methods are sensitive to elemental impurities (Ragaert et al., 2017). Therefore, additives removal might also be beneficial for these processes on the longer term.

Because of all aforementioned arguments, this review focuses on the challenges and opportunities related to using solvents for additives removal including physicochemical principles, technological status and efficiency, economic feasibility and environmental impact. As there are hardly any demonstrations on industrial scale, much literature is taken from batch scale experiments, which also provides learnings that are useful towards scale-up.

The review is, therefore, structured as follows:

1. Classification of additives based on their functionality and properties, including their typical occurrence and concentrations in plastics, as the extraction efficiency of additives depends on their physicochemical properties (Section 2).

- 2. Overview of the technologies that can be used for additive extractions, summarizing experiences from literature and linking this to theoretical aspects such as solubility and diffusivity theories (Section 3).
- 3. Assessment of the extraction methods based on technical, economic and environmental aspects by amongst others basic Life Cycle Assessment and Cost Benefit Analysis (Section 4).

2. Application and classification of additives

Additives are classified as functional additives, fillers, reinforcements and colourants. Among these additive groups, functional additives are most essential because they are used to improve functional properties of plastics. Typically they are divided into different classes: antioxidants, stabilizers, flame retardants etc. For each class, the critical additives that are in the authorization list are included. Since the physical properties of additives affect the choice of extraction method and efficiency, their molecular weight (MW), boiling/melting point (B_p/M_p), typical chemical structure and concentration in the plastics are summarized in Table 2.1 for each additive class. In addition, typical annual consumption values of additives are included in order to evaluate the extraction priority per type of additives.

2.1. Functional additives

2.1.1. Antioxidants

Antioxidants are used in various polymer resins in order to postpone oxidation when exposed to ultraviolet (UV) light, heat or atmospheric oxygen (Hahladakis et al., 2018; Xu et al., 2020). Heat, mechanical shear and radiation generate free radicals which cause degradation of the polymer. Additionally, the presence of tertiary atoms make the polymer susceptible to the formation of free radicals resulting in chain scission. Antioxidants terminate these free radical reactions (Bhunia et al., 2013; Murphy, 2001). They are mostly used in hydrocarbon polymer types such as PE, PP, PS and ABS (Murphy, 2001).

Antioxidants can be categorized as primary and secondary antioxidants. The first ones are radical scavengers and typically react fast. Hindered phenols and secondary aromatic amines constitute a big part of the primary antioxidants (Murphy, 2001). They can act as hydrogen donors in order to deactivate free radicals by stabilizing the polymer against oxidation. In addition, they are highly efficient and low in volatility due to their high molecular weight (Dopico-Garcia et al., 2012). High-molecular-weight Irganox 1076 and Irganox 1010 are the most used phenolic antioxidants since the low molecular weight molecules can leach from polymers causing potential environmental and health issues (Reingruber et al., 2010). The secondary antioxidants are also called hydroperoxide decomposers since they react with hydroperoxide by reducing them into more stable alcohol forms (Gensler et al., 2000). Phosphite and phosphonites are mostly used as secondary antioxidants since they provide good colour stability and gas-fade resistance compared to the primary antioxidants during processing (Murphy, 2001). Irgafos 168 is an example of a phosphite antioxidant (El Mansouri et al., 1998). Primary and secondary antioxidants can be combined in order to create a synergistic effect to achieve a higher efficiency against oxidation (Deanin, 1975). In addition, the efficiency of antioxidants is related to their solubility in the polymer, volatility, diffusion rate and concentration which starts from 0.05% up to 1% (w/w) or more. (Deanin, 1975; Fayolle et al., 2000; Hahladakis et al., 2018). The antioxidants authorized under REACH regulation are bisphenol A, cadmium compounds, lead compounds, nonylphenol compounds, octylphenol, 1,3,5-tris

Table 2.1

Classification and physical properties of some additives.

Additive type	Examples	M _p , B _p (°C)	MW (g/mol)	Typical amount in plastics (% w/w)	Mostly used in which plastics	Typical annual consumption (Mt/year)*	Ref.
<i>Primary antioxidants</i> Hindered phenols	Irganox 1010 $H_0 \rightarrow H_1 \rightarrow H_2 \rightarrow H_$	M _ρ : 110-125°C Bp: 1005.8 °C	Low-high	0.05-1	PE, PP, PS and ABS	0.15	(Bolgar et al., 2008; ChemBK; Hahladakis et al., 2018; Pelzl et al., 2019; Pritchard, 1998; Pritchard, 2005; Shahidi et al., 1992; Songwon, 2017; Stepek, 1983)
Secondary aromatic amines	4,4'-Bis(α, α dimethylbenzyl) diphenylamine	M _p : 99-103 °C B _p : 535.2 °C					
<i>Secondary antioxidants</i> Phosphite type thioethers, organosulfur compounds	Irgafos 168	M _p : 181-184°C B _p : 361 °C	Medium-high	-			
Stabilizers Benzophenones, hindered amines, benzotriazole, salicylate esters, cyanoacrylates and benzylidenes.	2,4-Dihydroxybenzophenone	M _p : 144-147 °C B _p : 409±14 °C	Low-high	0.1-10	PVC, PE, PA	>0.75	(BASF, 2004; Bolgar et al., 2008; Brydson, 1999; Chemical Book; Crompton, 2007; Pelzl et al., 2019; Polymer Database, 2015; Pritchard, 2005; Wypych, 2015)

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(continued on next page)

Ref.				
Typical annual consumption (Mt/year)*				
Mostly used in which plastics				
Typical amount in plastics (% w/w)				
MW (g/mol)				
M _P , B _P (°C)	M _p : 82-85 °C B _p : 552.6±50°C	M _p : 60-67 °C B _p : 500.2±60°C	M _b : -8.6 °C B _p : 220-224 °C	Mp: 95-97 °C B _p : 174 °C
Examples	Bis(2,2,6,6-tetramethyl-4-piperidyl-1-oxyl) Sebacate	Methyl 3-(3-tert-butyl-5-(2H-benzotriazol- 2-YL)-4-hydroxyphenyl)propionate	Methyl salicylate	Ethyl-2-cyano-3,3-diphenylacrylate
Additive type		·		

Table 2.1 (continued)

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1

Additive type	Examples	M _P , B _P (°C)	MW (g/mol)	Typical amount in plastics (% w/w)	Mostly used in which plastics	Typical annual consumption (Mt/year)*	Ref.
	Tetraethyl 2,2'-(1,4- phenylenedimethylylidene)dimalonate	M _P : 136-137°C B _p : 484.4±45°C					
<i>Plasticizers</i> Esters of aliphatic or aromatic carboxylic acids (c.a), phosphate esters	Dioctyl phthalate (DOP)	M _p : -50 °C B _p : 384 °C	Medium-high	20-50	PVC	5.7	(Bolgar et al., 2008; Daihachi Chemical Industry; Deanin, 1975; Pritchard, 2005; Wypych, 2004)
	Dioctyl adipate (DOA) $\begin{pmatrix} 1 \\ 4 \end{pmatrix} \begin{pmatrix} 0 \\ 4 \end{pmatrix} \begin{pmatrix} 1 \\ 4 \end{pmatrix} \begin{pmatrix} 0 \\ 4 \end{pmatrix} \begin{pmatrix} 1 \\ 4 \end{pmatrix} \begin{pmatrix} $	M _p : -67.8 °C B _p : 214 °C					
	Tricresyl phosphate $\left[\underbrace{\left\{\begin{array}{c} c_{H_3} \\ c_{H_3} \end{array}\right\}_3}$	M _p : (-25)-(-30) °C B _p : 410 °C					

Additive type	Examples	M _p , B _p (°C)	MW (g/mol)	Typical	Mostly	Typical annual	Ref.
				amount in	used in	consumption	
				plastics (%	which	(Mt/year)*	
				w/w)	plastics		
Flame retardants Halogen containing, Organophosphate flame retardants, nitrogen flame retardants, inorganic flame retardants	Decabromodiphenyl ether Br br	M _p : 294-296°C B _p : 425 °C	Low-high	10-20	PS, PE, PP	1.67	(Beard and Angeler, 2010; Bolgar et al., 2008; ICL - INDUSTRIAL PRODUCTS; Innes and Innes, 2004; Morgan, 2018; Pritchard, 2005)
(antimony trioxide, alumina trihydrate, magnesium hydroxide, zinc borate)	Tris(2-chloroethyl) phosphate	M _P : -51 °C B _p : 330 °C					
<u>.</u>	Melamine NH2 NH2 NH2 NH2	M _P : 345 °C B _P : 557.5±33 °C					
· · · · · · ·	Antimony trioxide	M _p : 656 °C B _p : 1425 °C					
	Alumina trihydrate	M _p : decomposes B _p : N/A					
	Aluminum hydroxide HoOH OH	M _P : 300 °C B _P : N/A					

Additive type	Examples	M _p , B _p (°C)	MW (g/mol)	Typical	Mostly	Typical annual	Ref.
				amount in plastics (% w/w)	usea in which plastics	consumption (Mt/year)*	
	Magnesium hydroxide	M _p : 350 °C					
	Но_бм_он	B _p : decomposes					
	Zinc borate	Mp: 980 °C					
		B _P : N/A					
Lubricants	Stearic acid	M _p : 69-72 °C	Low-high	0.1-3	PVC,	>0.3715	(Bolgar et al., 2008;
Fatty acids, fatty acid	0=	B _p : 383 °C			polyolefi		Hahladakis et al., 2018: Maier and
esters, fatty alcohols, fatty acid amides metallic soans (calcium	HO				ns, PS		Calafut, 1998a; PCC Chemax, 2013; Pritchard, 2005)
zinc, lead stearates)	Butyl stearate	Mp: 27 °C					
	0—	Bp: 343 °C					
	Stearyl alcohol	M _p : 59.5 °C					
	HOLI	B _p : 336 °C					
	Oleamide	M _p : 102-104 °C					
	•	B _p : >200 °C					
	Calcium stearate	M _p : 179 °C					
	0=	B _p :~ 360 °C					
	16 ca						
	۲ 2						

Additive type	Examples	M _b , B _b (°C)	MW (g/mol)	Typical	Mostly	Typical annual	Ref.
:			Ì	amount in	used in	consumption	
				plastics (%	which	(Mt/year)*	
				w/w)	plastics		
Antistatics Glycerol monoacyl	Glycerol monostearate 0	M _p :78-81 °C B _p :~ 410 °C	Low-high	0.1-2	PVC, polyolefi	>0.00573	(Dufton, 1998; Hahladakis et al., 2018; Halperin, 1979-80; Jeen
esters, aliphatic amides, quaternary ammonium salt	но но но				ns		International Cooperation, 2017; Murphy, 2001; Pionteck and Wypych,
derivatives, organic phosphates	Lauric Diethanolamide 0	M _p : 42-47 °C B _p : 238-243 °C					
	HO N N N N N N N N N N N N N N N N N N N						
	О						
	Behentrimonium chloride	Mp: 60-65 °C P - N/A					
		Dp. IV/A					
Slip agents	Erucamide	M _p :75-80 °C	Low-medium	0.1-3	PE films	0.7	(Hansen et al., 2013; Plastics Engineering 2015:
Fatty acid amides, and esters	H2N H2N H	Bp: 5/3 C					Wypych, 2005)
	Glyceryl Monooleate ou	M _p : 35 °C B _p :~ 410 °C					
	HO O () () () () () () () () ()						

ming agents Ammonium lauryl sulfate Mp: N/A imonium sulfate, sstituted ureas and Mp: N/A sstituted ureas and $11^{0} \circ 5^{0} \circ NH_{4}^{+}$ Bp: 418 °C dicarbonamide $M_{11} \circ 5^{0} \circ NH_{4}^{+}$ Bp: 418 °C bis $M_{12} \circ 5^{0} \circ NH_{4}^{+}$ Bp: 418 °C dicarbonamide $M_{11} \circ 5^{0} \circ NH_{4}^{+}$ Bp: 418 °C dicarbonamide $M_{12} \circ 5^{0} \circ C$ Bp: 418 °C Biuret $M_{12} \circ 5^{0} \circ C$ Bp: 141-142 °C triazine $M_{12} \circ 10^{0} \circ C$ Bp: 141-142 °C triazine $M_{12} \circ 10^{0} \circ C$ Bp: 260 °C Arodicarbonamide $M_{12} \circ 25^{0} \circ C$ Bp: 225 °C	M _P , B _P (°C) I	MW (g/mol)	Typical amount in	Mostly used in	Typical annual	Ref.
ing agentsAmmonium lauryl sulfate $M_{p}: N/A$ onium sulfate, $M_{p}: 130 °C$ $B_{p}: 418 °C$ tiuted ureas and $H_{11} O ^{\circ} O ^{\circ} NH_{4}^{+}$ $B_{p}: 118 °C$ carbonamide $H_{11} O ^{\circ} O ^{\circ} NH_{4}^{+}$ $B_{p}: 118 °C$ carbonamide $H_{2} N ^{\circ} N_{14}^{\circ}$ $M_{p}: 190 °C$ Biuret $M_{p}: 130 °C$ (decomposes) $B_{p}: N/A$ $B_{p}: N/A$ $B_{p}: N/A$ $B_{p}: N/A$ $M_{p}: 13, 5-Tris[3 M_{p}: 141-142 °C$ (dimethylamino)propyl]hexahydro-1,3,5- $B_{p}: 141-142 °C$ $N = M ^{\circ} N ^{\circ$			amount m plastics (% w/w)	useu m which plastics	consumption (Mt/year)*	
Biuret $M_{p_{1}}: 130 ^{\circ}C$ θ_{n} θ_{n} H_{2} θ_{n} H_{2} H_{2	M _p : N/A B _p : 418 °C	MO	0.5-2	Polyolefi ns, EVA, PVC	0.03	(Dufton, 1998; Hansen et al., 2013; Landrock, 1995; Simionescu and Benedek, 1982; Stepek, 1983)
1,3,5-Tris[3- (dimethylamino)propyl]hexahydro-1,3,5- triazine // / / / / / B _p : 141-142°C B _p : 141-142°C M _p : 242°C M _p : 24 °C HN—C—NH Cynamide HN—C—NH Azodicarbonamide M _p : 225 °C	M _p : 190 °C (decomposes) B _p : N/A					
Cynamide M _P : 44 °C HN HNCNH B _P : 260 °C (decomposes) Azodicarbonamide M _P : 225 °C	M _p : N/A 3,5- B _p : 141-142°C					
Azodicarbonamide Mp: 225 °C	M _p : 44 °C B _p : 260 °C (decomposes)					
H ₂ N NH ₂ B _p : N/A	M _p : 225 °C (decomposes) B _p : N/A					

Additive type	Examples	M _P , B _P (°C)	MW (g/mol)	Typical	Mostly	Typical annual	Ref.
				amount in plastics (% w/w)	used in which plastics	consumption (Mt/year)*	
Biocides Arsenic and organic tin compounds, metallic soaps of copper, zinc, mercury and tin	Tributyltin oxide	M _p : < -45 °C B _p : 173 °C	Low-medium	0.001-1	PUC, PE, PUR	0.025	(Gumargalieva et al., 1999; Hahladakis et al., 2013; Hansen et al., 2013)
	Methylarsonic acid	Mp: 160.5 °C Bp: 393.3 °C					
	Zinc Oleate $z_n^{++} \left[\begin{array}{c} 0 \\ 0 \\ z_n^{++} \\ \end{array} \right]_2$	M _p : 70 °C B _p : 360 °C					
Fillers Calcium carbonate, kaolin, talc, silica, clays, calcium sulfate, mica, silicates and alumina	Calcium carbonate	M _p : 825-1339 °C B _p : decomposes	Low-medium	< 50	PVC, PA, polyest er, polyolef	1.436	(Deanin, 1975; Dufton, 1998; Ebewele, 2000; Hahladakis et al., 2018; Maier and Calafut, 1998b; Wypych, 2000; Zhang et al., 2019b; Zhao et al.,
trihydrate, natural fillers	Kaolin Aloosioon Aloosioon Aloosioon Aloosioon Aloosioon Aloosioon	M _p : 740-1785 °C B _p : N/A					2019)

Additive type	Examples	М _р , В _р (°С)	MW (g/mol)	Typical amount in plastics (% w/w)	Mostly used in which plastics	Typical annual consumption (Mt/year)*	Ref.
	Talc $O^{-} O^{-} O^{-$	М _р :~ 800 °С В _р : N/А					
Reinforcements Glass fibers, aramid fibers, carbon or graphite fibers, mica, talc, nanocomposite fibers	Aramid fiber (Kevlar)	M _p : > 500 °C B _p : N/A M _p : 700-1000 °C	Medium-high	15-30	PP, PS, nylon	>0.57	(Cui et al., 2018; Dong et al., 2018; Dong et al., 2019; Gong et al., 2019; Gu et al., 2019c; Gu et al., 2019a; Gu et al., 2019b; Hansen et al., 2013; Lee, 1992; Li et al., 2019a; Maier and Calafut, 1998b;
Colourants Oxides of iron, chromium, molybdenum, cadmium, nickel, antimony, and	Sudan I	B _p : N/A M _p : 131 °C B _p :~ 391 °C	Low-medium	0.01-5	PS, PMMA, PE	2.025	2018; Seymour, 1976) (Crompton, 2007; Hansen et al., 2013; Hunger, 2003; Maier and Calafut, 1998a)
titanium, metal oxides, carbon black, cadmium sulfides, azo derivatives	Titanium dioxide o==o Cadmium sulfide s==Cd	M _p : 1843 °C B _p : 2500-3000 °C M _p : 980 °C (sublimes) B _p : N/A	-				

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Low MW: <500 g/mol Medium MW: 500-1000 g/mol High MW: >1000 g/mol B_p: boing point M_P: melting point

*average annual consumption value (Mt/year) of additives used in plastics

(See above-mentioned references for further information.)

(oxiran-2-ylmethyl)-1,3,5-triazinane-2,4,6-trione and 1,3,5-tris [(2S and 2R)-2,3-epoxypropyl]-1,3,5-triazine-2,4,6-(1H,3H,5H)-tri one (Hansen et al., 2013).

2.1.2. Stabilizers

Stabilizers are used to improve the mechanical properties and eliminate issues caused by chemical degradation such as colour change during processing (Vulic et al., 2001). They have been integrated into the polymer matrix in small quantities, typically from 0.1% to 10% w/w (Brydson, 1999) and they can be categorized as heat stabilizers and light stabilizers, which are used against thermal degradation and photo-oxidation, respectively (Subramanian, 2013). While some polymers such as polyvinylchloride (PVC) and PVC blends need heat stabilizers in order to preserve their functionality, other polymers such as PE and PA can keep their stability even at high temperatures (Crompton, 2007). One of the most common UV absorbers are hindered amine light stabilizers (HALS). which can also play a role as heat stabilizers in some plastics (Bolgar et al., 2008). Other UV absorbers consist of benzotriazoles and benzophenones, salicylate esters, cyanoacrylates, malonates and benzylidenes (Bolgar et al., 2008). Typically, cadmium and lead compounds are used as heat stabilizers; however, recent sustainability concerns have led to a decrease in the use of lead compounds (Hahladakis et al., 2018; Murphy, 2001; Wei et al., 2018). Therefore, calcium/zinc carboxylates are introduced as an alternative option in order to delay severe degradation of materials (Bacaloglu and Stewen, 2001). The use of lead stabilizers and cadmium/barium systems are restricted due to their adverse effect on human health and the environment. Also, among heat stabilizers, nonylphenol barium and calcium salts are included in the authorization list (Hansen et al., 2013).

2.1.3. Plasticizers

Plasticizers are used as a lubricant as they decrease the stiffness of the polymer via reduction of the cohesive intermolecular friction along the polymer chain (Subramanian, 2013). They are mostly used for polymers which are in a glassy state at room temperature such as PVC, and their flexibility is improved via strong interaction between the plasticizer and polymer chain units (Stepek, 1983). In addition, they reduce shear during polymer processing and improve the impact resistance of the final material (Bhunia et al., 2013).

Plasticizers are typically organic liquids with high molecular weight and boiling point. The used concentration varies between 20 and 50% of the total plastic weight (Deanin, 1975). The flexibility of the material varies based on type and level of plasticizers. Therefore, the chemical structure of the plasticizer is crucial for controlling the degree of plasticity in the polymer (Subramanian, 2013). Plasticizers with solubility parameters similar to the polymer are preferred in order to increase the effectivity of incorporating them into the polymer (Subramanian, 2013).

The most commonly used class of plasticizers are phthalates, which have polar groups attached to the polarizable aromatic ring (Bolgar et al., 2008). Among them, dioctyl phthalate (DOP), diisodecyl phthalate (DiDP), diisononyl phthalate (DiNP) and other phthalate esters are the most commonly used (Bolgar et al., 2008). Particularly, in PVC, phthalates behave like dipolar compounds, establishing a link between the chlorine atoms and increasing the flexibility of the polymer (Ambrogi et al., 2017). However, since phthalate plasticizers are not chemically attached to PVC, they can leach or evaporate, which causes environmental contamination and health risks (Heudorf et al., 2007). Among these phthalate plasticizers, di(2-ethylhexyl phthalate) (DEHP), diisoheptylphthalate (DIHP), benzyl butyl phthalate (DBP) and diisobutyl phthalate (DiBP) are included in the authorization list, which means these cannot be placed on the market until their authorization is granted (Hansen et al., 2013).

2.1.4. Flame retardants

Flame retardants are chemical compounds which are used to slow down or inhibit ignition or oxidation reactions of polymers in order to protect them against high temperatures by forming an insulating layer (Stepek, 1983). They can act physically and/or chemically in different phases (Innes and Innes, 2004). Their concentrations in plastics are frequently between 10 and 20% w/w (Deanin, 1975). They mostly consist of phosphorus, antimony, aluminum, and boron-containing compounds, chlorides and bromides (Hahladakis et al., 2018). Less common flame retardants are compounds containing lead, zinc, silicon, zirconium, tin, bismuth, sulfur, and selenium (Subramanian, 2013). When the effectiveness of different flame retardants is compared, phosphorus compounds are stated to be more efficient than the ones containing antimony. chlorine, and bromine. The most efficient ones are reported to be the synergetic blends of phosphorus and bromine containing compounds (Stepek, 1983). Brominated flame retardants are mostly used in thermoplastic resins such as polystyrene (PS), polyesters, polyolefins. Within this class, decabromodiphenyl oxide is the most common one (Bolgar et al., 2008). Other compounds based on bromine such as poly brominated diphenyl ether (PBDE) are highly effective especially for PS, PE and PP (Innes and Innes, 2004). However, their usage is regulated since they are categorized under persistent organic pollutants (POP) (Bolgar et al., 2008; Innes and Innes, 2004). Beside halogenated flame retardants, short and medium chain chlorinated paraffins, boric acid, and tris-2chloroethyl phosphate are currently included on the authorization list (Hansen et al., 2013).

2.1.5. Lubricants

Lubricants are used to decrease shear rate during processing by improving the melt flow. Moreover, they protect plastics against thermal damage and polymer chain scission which occurs during high shear levels (Bolgar et al., 2008; Deanin, 1975). They are classified as external and internal lubricants. While the former delay fusion by decreasing friction in order to prevent the polymer melt to stick to the screw, the latter promote fusion by reducing the viscosity of molten polymer in the extruder (Crompton, 2007; Subramanian, 2013). The lubricant should be chosen properly to avoid decomposition of the polymer or detriment other properties. The most common types of lubricants include calcium, zinc, and lead stearates, fatty acid esters, amides and alcohols (Bolgar et al., 2008; Deanin, 1975; Subramanian, 2013). The typical concentration in plastics varies between 0.1 and 3% (w/w) (Hahladakis et al., 2018). Since some of these lubricants contain heavy metals, they can cause problems during recycling or raise environmental concerns. On the other hand, mineral based lubricants such as oleochemical esters are stated as more 'green' alternative lubricants (Subramanian, 2013).

2.1.6. Antistatic agents

Most plastics are good insulators. However, electrostatic charges can be created by friction between the plastic and moving equipment and between the plastic itself or by electroinisation from dust or radiation (Crompton, 2007; Subramanian, 2013). These charges cause problems such as sticking of the polymer powder, malfunctioning of machinery and even explosions (Bajaj et al., 2000; Crompton, 2007). Therefore, antistatic agents are used in order to eliminate electrostatic charges by decreasing the surface resistance by behaving as a lubricant (Jonas and Lerch, 1997; Subramanian, 2013). Their concentration in plastics varies between 0.1 and 2% (w/w) (Hahladakis et al., 2018). They can be grouped as internal and external antistatic agents (Lehmann,

1992). Internal agents are integrated within the polymer mix before processing; therefore, they can migrate to the polymer surface slowly and continuously to block static charges by adsorbing water (Ebewele, 2000). On the other hand, the external ones are applied after the polymer processing via spraying or wiping and they can easily move on the plastic surface (Subramanian, 2013). External antistatic agents are used in lower amounts compared to the internal ones; however, they can lead to printing problems on the plastic surface because of the non-uniform coating (Fink, 1985). Therefore, the internal ones are preferred. The major types of antistatic agents are hydrophilic compounds such as quaternary ammonium salt derivatives, amines and their derivatives, polyoxyethylene glycol esters, and organic phosphates (Ebewele, 2000; Halperin, 1979-80). Lauric diethanolamide is mainly used in polyolefins (Crompton, 2007). Antistatic agents are under FDA control in case their concentration exceeds 2% (w/w) (Richardson and Lokensgard, 2004).

2.1.7. Slip agents

Most polymers adhere to themselves or to the machinery during processing due to the high friction coefficient (Subramanian, 2013). Slip agents help to modify the surface features of polymers in order to decrease these frictional forces between surfaces, which makes it easier to manipulate the polymer (Titow, 1990). Slip agents are typically long chain aliphatic and fatty acid amides, such as erucamide and oleamide (Nielson, 1991). They are mainly used in polyolefins and are generally added between 0.1 and 3% (w/w) depending on the chemical structure of the slip agent and the polymer (Hansen et al., 2013). The drawback of this type of additives is that they can cause discolouration when interacting with phenolic compounds which are adsorbed from the atmosphere. Besides, they can degrade during film extrusion due to high temperatures, typically observed in PE films (Subramanian, 2013). Therefore, the use of erucamide for the manufacture of packaging for food contact is regulated by the European Regulation No. 10/2011 (EUR-Lex, 2011).

2.1.8. Foaming agents

Foaming agents are mostly used in order to reduce the cost of plastic since foaming allows to decrease the cost per volume compared to unfoamed plastics. Also, they improve sound and thermal insulation, and the softening ability of plastics. Foaming of polyolefins is induced by incorporation of blowing agents, which evaporate or decompose at high temperatures in order to make place for gases (Subramanian, 2013). After foaming, temperature is decreased to stabilize the plastic structure. They include substituted isocyanates, ammonium-carbonylsulfonate, substituted ureas, 2,4-dioxo-1,2-dihydro-4-benzoxazine and its derivatives, substituted triazines, cyanamide, and azodicarbonamide derivatives (Hansen et al., 2013; Stepek, 1983). In plastics, mainly azodicarbonamide is used in a concentration between 0.5 and 2% (w/w) (Simionescu and Benedek, 1982). However, in 2012 azodicarbonamide was added as a candidate substance of very high concern to the REACH regulation (European Chemical Agency, 2012).

2.1.9. Biocides

Biocides are used to protect plastic materials against microbiological degradation especially when plasticizers are incorporated into the material, which are susceptible to microbiological activity (Bart, 2005; Subramanian, 2013). The presence of plasticizers such as phthalates increases adhesion of fungi and their biodegradation (Webb et al., 1999). Biocides are mainly used in PVC and PUR materials because they generally contain a plasticizer (Gumargalieva et al., 1999). Biocides can be both organic and inorganic. Most used biocides include oxybisphenoxarsine (OBPA), trichlorophenoxyphenol (TCPP) which is also known as Triclosan (Bart, 2005; Murphy, 2001). In addition, metallic soaps of copper, zinc, mercury and tin are also effective biocides for different applications with typical concentration of 0.001–1% w/w (Hahladakis et al., 2018; Hansen et al., 2013). However, the use of bis(tributyltin)oxide and tributyltin and also mercury compounds at concentrations exceeding 0.01% (w/w) are restricted under REACH and EU Regulation 2017/852 (European Parliament, 2017; Hansen et al., 2013).

2.2. Fillers

Fillers are used to increase the bulk of the plastic at low cost, decrease mould shrinkage and modify basic properties of plastics such as hardness, chemical resistance, impact and tensile strength and so on (Crompton, 2007; Stepek, 1983). In recent years specific fillers are also prepared with flame retardant properties (Wang et al., 2018b; Xu et al., 2019b). However, it is important to have good matrix adhesion of fillers with the plastics in order to improve the properties since high surface energies cause dispersion problems (Nardin, 2006). Different types of fillers are used in resin formulations and the most common ones are graphene, calcium carbonate, kaolin, talc, silica, clay, calcium sulfate, mica, glass structures, and alumina trihydrate (Ebewele, 2000; Guo et al., 2019; Hahladakis et al., 2018). Furthermore, also biopolymers are also used as a filler more recently (Huang et al., 2019; Shi et al., 2019b; Shi et al., 2019a; Xu et al., 2019a). Fillers are mostly incorporated into polyvinyls, and in smaller amounts into polyesters (Deanin, 1975; Elias and Mulhaupt, 2016). They can be found in plastics up to 50% (w/w) (Hahladakis et al., 2018). Regarding health hazards, there is concern over the presence of crystalline silica but to the best of our knowledge there is no legislation on their restriction (Rothon, 2002).

2.3. Reinforcements

The main purpose of using reinforcements is to increase the mechanical strength and stiffness even at high processing temperatures. Reinforcers are generally fibers or filaments both used in thermoplastic and thermosetting materials. Especially the fibrous structures are known to provide good reinforcement to the plastic (Ma et al., 2019a; Murphy, 2001). Glass fibers improve the modulus and the strength under tensile stress, increase heat resistance and decrease creep formation (He et al., 2019; Ma et al., 2019c; Seymour, 1976). Especially at high temperatures, the mechanical properties of plastics are less affected when reinforcements are incorporated into them. In addition to glass fibers, aramid fibers such as Kevlar help to improve the mechanical properties of plastics as well (Raia, 1973). The use of carbon fibers is an alternative solution for applications in which low densities are needed such as aviation and automotive applications (Gill et al., 1972). In recent years also the use of nanofibers is substantially increasing (Gu et al., 2019d; Ma et al., 2019b; Yuan et al., 2019; Zhang et al., 2019a; Zhu et al., 2019). The concentration in plastics depends on the density of reinforcement, but they are generally used in a concentration between 15 and 30% (w/w) (Hansen et al., 2013). Carbon and glass fibers are generally associated with an increased risk of skin cancer but there is no regulation on their use due to lack of evidence (Oregon OSHA, 2014).

2.4. Colourants

The main purpose of colourants is to make plastics more aesthetically pleasing. Besides, they can be applied for resistance to heat and light intensity. Colourants used in plastics are classified as pigments and dyes based on their physical behaviour (Tolinski, 2015). While pigments are insoluble in water or organic solvents, dyes are soluble in those media (Bart, 2005). Therefore, while colouration with pigments requires a dispersion, colouration with dyes needs a dissolving method (Subramanian, 2013). As a result of the solubility, dyes do not migrate sufficiently fast, limiting their use as a polymer colourant. Contrarily, pigments show good migration and heat stability (Ebewele, 2000).

Most pigments are inorganic such as titanium dioxide which is used for whitening in a concentration range of 0.01 to 1% (w/w), cadmium sulfides or sulfoselenides (yellow, red, brown) are typically added at 0.1% (w/w) and carbon black from 0.2 to 2% (w/w) (Crompton, 2007). On the other hand, dyes are generally organic substances and azo derivatives are extensively used due to their low price. They are mainly incorporated into PS, PMMA and cellulose plastics to obtain a bright and transparent colour in concentrations between 0.25 and 5% (w/w) (Hansen et al., 2013). However, these chromophoric azo group shows toxicity risks (Ahlstrom et al., 2005). All lead based pigments and dyes and also chromium compounds are included in the authorization list due to their adverse health effects (Hansen et al., 2013).

3. Additive extraction processes

The knowledge on both occurrence and physicochemical properties of additives is the starting point to develop additive extraction processes. In this section, first some theoretical considerations related to solvent extraction are introduced such as solubility and diffusivity phenomena that are the basis for our later evaluation of literature. Next, the different types of solid-liquid extraction methods that have been developed are explained, namely ultrasonic extraction, shake-flask extraction, Soxhlet extraction, microwave assisted extraction (MAE), supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE). In addition to solid-liquid extraction methods, dissolution-precipitation is also included.

3.1. Theoretical considerations for removal of additives

The removal of molecules from a solid matrix is a complex process which is very difficult to model in a proper way as there are many factors that are relevant, ranging from pore size to chemical interactions between solute, solvent and solid matrix (Crompton, 2007). Furthermore, different models are valid in the case of solid-liquid extraction and dissolution-precipitation, the latter being a special case in which the polymer is also dissolved, next to the solute. Furthermore, there are intermediate methods which consider partial dissolution or swelling of the polymer. Without aiming at describing all possible models for all possible phenomena in detail, here we focus in the part below on one of the driving forces of mass transfer, which is the partition coefficient, basically depending on product solubility. Next, especially relevant towards profitability of the process, is a fast mass transfer rate, usually controlled by diffusion. In principal, removal of substances from a porous solid matrix is an integrated process of chemical interactions between the pore solution and the solid phase together with mass transfer due to gradients in chemical potential, pressures or concentration (Ahlstrom et al., 2005; Van der Sloot et al., 2009). Permeability of the solid matrix is the main physical factor which controls the rate mechanism of mass transport. When a solvent is in contact with the solid matrix, it is likely to percolate through the permeable matrix and remove the substances based on their solubility with a specific rate which is controlled by the diffusivity. Therefore, permeability depends on both solubility and diffusivity and it is defined by the following equation:

$$\mathbf{P} = \mathbf{D}.\mathbf{S} \tag{3.1}$$

where *P* is the permeability coefficient (mol/ms Pa), *D* is the diffusion coefficient (m^2/s) and *S* is the solubility coefficient (mol/m^3 Pa).

3.1.1. Solubility

The efficiency of solvent-based extraction techniques are amongst others determined by the physical properties of additives (shown in Table 2.1) since these properties determine the solubility of a certain additive in a selected solvent during an extraction process. The solubility of an additive in a solvent can be predicted via solubility theories such as the theories of Hildebrand and Scott, Burrell, and Hansen, among others (Hansen, 2012; Huggins, 1951; Miller-Chou and Koenig, 2003). Hildebrand and Scott utilize cohesive energy density of a solvent to determine the solubility of a given solute (Huggins, 1951). According to this theory, the difference in solubility parameters of solvent and polymer should be small to be able to dissolve the polymer (Burrell, 1968). However, the Hildebrand solubility parameters do not consider specific interactions such as hydrogen bonding. Therefore, Burrell (Salman and Salih, 2016) proposed a method that takes into account hydrogen bonding to overcome inconsistencies in the Hildebrand theory. The Burrell method was further developed by Hansen (Hansen, 2012) by considering different type of interactions beside hydrogen bonding. Therefore, in this paper the solubility parameters proposed by Hansen (Salman and Salih, 2016) are used since it allows three-dimensional analysis of the affinity between a polymer/an additive and a solvent. The principle of Hansen solubility parameters (HSP) is based on the total energy of vaporization of a liquid which consists of three interactions: nonpolar/dispersion (δ_d), polar (δ_p) and hydrogen bonding (δ_h) (Hansen, 2012). The suitability of a solvent to dissolve or swell a certain polymer or additive can be assessed by calculating the distance between the solubility parameters of an additive/polymer and a solvent according to Eq. (3.2) (Hansen, 2012).

$$D_{S-P} = \sqrt{4 \times \left(\delta_{d,P} - \delta_{d,S}\right)^2 + \left(\delta_{p,P} - \delta_{p,S}\right)^2 + \left(\delta_{h,P} - \delta_{h,S}\right)^2}$$
(3.2)

where $\delta_{i,P}$ and $\delta_{i,S}$ (MPa^{1/2}) are the *i*th component of polymer/additive and solvent, respectively.

The Hansen's model uses spheres for polymers to show their solubility range in a 3D graph (Hansen, 1967). This specific polymer sphere is determined via the Hansen solubility parameters and the interaction radius (R_0) of the polymer which is calculated experimentally based on the highest difference allowed to obtain a good interaction between a polymer and a solvent (Hansen, 2012). If the solubility parameters of a solvent are inside the boundary of a Hansen polymer sphere, then the solvent is a good match for that polymer, and as such the solvent will most probably be able to dissolve the polymer (Hansen, 2012).

The HSP for a selected compound can be determined via theoretical or experimental methods. Since there are only a few additives for which the HSP values already have been determined, the theoretical group contribution method, proposed by Van Krevelen (Van Krevelen and Te Nijenhuis, 2009), is used in order to estimate HSPs of the intended compounds. In this method, the structure of the compound is broken down into different functional groups which have specific molar attraction constant (F) and cohesive energy (E) values. By using the equations below from Hoftyzer and Van-Krevelen, HSP values can be calculated (Van Krevelen and Te Nijenhuis, 2009).

$$\delta_{\rm d} = \frac{F_{\rm di}}{V} \tag{3.3}$$

$$\delta_{\rm p} = \frac{\sqrt{\sum F^2_{\rm pi}}}{\rm V} \tag{3.4}$$

$$\delta_{\rm h} = \frac{\sqrt{\sum E_{\rm hi}}}{\rm V} \tag{3.5}$$

where F_{di} is the group contribution value of a certain group to the dispersion parameter of the molar attraction constant $(J^{1/2} \text{ cm}^{3/2}/\text{mole})$, F_{pi} is the group contribution to the polar component of molar attraction constant $(J^{1/2} \text{ cm}^{3/2}/\text{mole})$, E_{hi} is the group contribution to the hydrogen bonding energy component (J/mole), and V is the molar volume of the material (cm³/mole) (Van Krevelen and Te Nijenhuis, 2009). Based on these equations, HSP of some mentioned additives are calculated (see Appendix A) and depicted in Fig. 3.1 together with the Hansen spheres of some common polymers (PE, PP, PS, PC etc.) and the HSP of some hydrophilic and hydrophobic solvents. In this way, the selection of a solvent to extract an additive or dissolve/swell a polymer selectively can be made based on rational considerations. For example, it can be deduced from Fig. 3.1 that toluene (S2) is a better solvent compared to n-propanol (S11) to dissolve PE (P1 and P2) since the distance between the solubility parameters of toluene and PE is smaller compared to the distance between propanol and PE. In addition, phthalate plasticizers are more soluble in polar solvents such as DCM, chloroform etc. compared to apolar ones. Therefore, it is expected to obtain higher extraction yields of phthalate plasticizers with polar solvents.

3.1.2. Diffusivity

Apart from the fact that molecules should dissolve in a solvent, the process should also allow that the molecule effectively moves from one medium (the polymer) to another (the solvent).



Fig. 3.1. Hansen solubility parameters (δ_d , δ_p and δ_h) of selected solvents (shown as blue dots with S numbers), additives (shown as red dots with A numbers) and polymers (shown as green sphere with P numbers) * HSP of CO₂ at 1 atm and 25 °C (Hansen, 2004; Hansen, 2012). (see appendix A for the values of Hansen solubility parameters). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Regarding extraction of additives, it is useful to explain the effect of parameters on the migration of additives from a polymer matrix to the solvent media via diffusivity. Diffusion is a process in which a certain penetrant is transferred from one part of the system to another through random molecular movements (Masaro and Zhu, 1999). Diffusion in liquids depends on various factors such as the temperature, viscosity, solute size, among others (Vesely, 2008). However, diffusion of molecules in polymer systems is more complex than those in liquids since there are more factors affecting diffusivity such as morphology, pore size and swelling of the polymer, volatility and concentration of solutes, crystallinity, surface energy differences and so on (George and Thomas, 2001).

Diffusivity is explained by variations of Fick's law (Fick, 1855) which basically shows steady-state (Fickian diffusion) and unsteady-state diffusion (non-Fickian diffusion) of small molecules through the polymer systems. A Fickian and non-Fickian diffusion is observed when the temperature is well above (rubberv state) and below (glassy state) the glass transition temperature (T_{σ}) of the polymer, respectively (Grinsted and Koenig, 1992). However, it is not possible to calculate diffusion in polymers only through Fick's law due to their complexity. Therefore, different models (Mercea, 2007; Mercea and Piringer, 2000) exist to estimate theoretically the diffusion in polymers. At first glance, the diffusion coefficient (D_p) is estimated via a correlation with relative molecular mass of the migrant M_r, a polymer specific parameter A_P and the absolute temperature T (Hamdani et al., 1997; Limm and Hollifield, 1996; Piringer, 1994). The estimation of D_p for polymers is further developed by Brandsch et al. (Brandsch et al., 2002) and a specific upper-bound diffusion coefficient D_P* is used instead of actual D_p values in order to obtain a simpler formula. D_P^* (cm²/s) can be estimated by the following empirical equation (Brandsch et al., 2002; Piringer, 2007):

$$D_{p}^{*} = 10^{4} exp \left[A_{p}^{*} - 0.135 M_{r}^{\frac{2}{3}} + 0.003 M_{r} - \frac{R.10454}{R.T} \right]$$
(3.6)

where: $A_p^* = A_p^{'*} - \frac{\tau}{T}$

where M_r is the relative molecular mass of a migrant (Dalton), T is the temperature (K), $A_p^{'*}$ is the upper bound polymer specific diffusion parameter, τ is the polymer specific activation energy parameter (K) and R.10454 represents the reference activation energy (K).

The polymer specific diffusion parameter (A_p^*) pronounces diffusion behaviour of a polymer in relation to the migrants. For example, soft/flexible polymers such as LDPE have higher A_p^* values, thus higher diffusion coefficient values, whereas stiff-chain polymers such as polyesters show lower diffusion coefficients for the same migrant due to lower A_p^* values (Brandsch et al., 2002). In addition, A_p^* and A_p^* show upper-bound values, thus migration will be overestimated which leads to the calculations for a worst-case scenario. The parameter τ with constant 10,454 number contributes to the diffusion activation energy $E_a = (10454 + \tau)^* R$ where R = 8.3145 (J mol.⁻¹ K⁻¹) is the gas constant. Calculated E_a values based on this formula are in good agreement with the data from literature (Brandsch et al., 2002).

According to Eq. (3.6), the diffusion of solutes decreases by increasing the molecular mass of the migrant (M_r) and increases exponentially with temperature. In case of extraction of highmolecular-weight additives (as shown in Table 2.1) from a polymer matrix, the diffusion rate can be increased by increasing the temperature and pore size and by decreasing the particle size. Regarding the morphology of the polymer, diffusion tends to be lower in glassy polymers, which have higher T_g values compared to rubbery polymers, due to the low free volume and less polymer chain segmental mobility (George and Thomas, 2001). For instance, polymers such as PA, PET, PS have T_g values above 50 °C show low diffusivity, while polymers like HDPE and LDPE with Tg values lower than -40 °C exhibit high diffusivity as shown in Fig. 3.2 (European Chemical Agency, 2019).

3.2. Solvent-based extraction methods

The mechanisms of the widely used solvent-based extraction techniques and the parameters affecting the extraction efficiency such as temperature, pressure, size and molecular weight of additives, type of solvent, among others are explained through introduced solubility and diffusivity phenomena. In addition, extraction conditions and recovery percentages (% w/w) to remove different types of additives from various plastics based on literature data are summarized in Table 3.1 for each extraction technique based on analytical and industrial experiences.

3.2.1. Solid-liquid extraction

Solid-liquid extraction is an extraction method in which the compounds of interest are extracted from the solid matrix by using solvents (Bart, 2005). The principle of this type of extraction is a mass transfer of a solute from the solid phase to the solution, which depends amongst others on the solubility of the solutes. (Holden, 1999). Other factors that influence the rate of extraction are the molecular weight of the additive, the particle size and porosity and also the extraction conditions such as temperature, pH, time, pressure among others (Bart, 2005). In the next section,



Fig. 3.2. Schematic presentation of the glass transition temperature (Te) and its relation with diffusivity (Dimarzio and Gibbs, 1963; Polymer Properties Database, 2019).

Table 3.1 Summary of extraction methods and conditions based on the additive and polymer type.

Polymer type	Additive type	Solvent	Temp. (°C) Pressure (MPa)	Time	Recovery (% w/w)	Ref.
Shake-flask ex	traction					
PE pellets	Hindered phenol antioxidants (lonol, Santonox)	Carbondisulfide and isooctane	RT	1–3 h with carbondisulfide and 50–72 h with isococtane	-9 8%	(Spell and Eddy, 1960)
PE pellets	Fatty acid amide slip agent (oleamide)	Carbon tetrachloride	RT	21 h	93-100%	(Spell and Eddy, 1960)
PP	Phenolic antioxidants (Irganox 1010)	Chloroform or THF	RT	24 h with chloroform and 72 h with THF	99%	(Wims and Swarin, 1975)
PP	Phenolic antioxidants (Irganox 1010)	DCM	RT	24 h	50%	(Wims and Swarin, 1975)
LDPE	Phenolic antioxidants (α -tocopherol)	THF	RT in darkness	24 h	82-86%	(Graciano- Verdugo et al., 2006)
Soxhlet extract	tion					
PP	Fatty acid amide slip agents (oleamide and erucamide), lubricants (stearates), UV absorbers (Topanol CA) and phenolic antioxidant (Irganox 1076)	DCM	~40 °C	48 h	~100%	(Haney and Dark, 1980)
Polyolefin	Hindered amine light stabilizers (Tinuvin 770 and Hostavin TMN 20)	Chloroform	-60 °C	16 h	96%	(Sevini and Marcato, 1983)
PP	Phosphite and hindered phenolic type antioxidants	DCM	50 °C	6 h	Phosphite type > phenolic type	(El Mansouri et al., 1998)
PE	Primary and secondary antioxidants, HALS	Chloroform	~60 °C	6 h	-	(Munteanu et al., 1987)
PE	Phenolic antioxidants (Anox PP18 and Anox 20)	Heptane		10 h	60-90%	(Malaika et al., 1999)
PET	Cyclic trimer and other low molecular weight oligomers	Xylene, DCM, acetone, water and hexane	~140 °C	24 h	-60%	(Costley et al., 1997)
PE, PS	Flame retardant (DecaBDE)	Toluene	~110 °C	6 h	~70%	(Costley et al., 1997; Ranz et al. 2008)
PUR foam	Plasticizer (Organophosphates)	DCM	40 °C	15 h	37%	(Carlsson et al., 1997)
PVC	Azo dyes (Sudan I, Sudan IV, Disperse RED I)	Methanol	~65 °C	7 h	22.6-95.3%	(Garrigos et al., 2002)
PP	Primary antioxidants (aromatic compounds)	DCM	~40 °C	9 h	-	(Marque et al., 1998)
LDPE	Phenolic antioxidant (Irganox 1076)	Chloroform	40 °C	3 h	>95%	(Molander et al., 1999)
PE	Phenolic antioxidant (Santonox R)	Chloroform	~60 °C	5 h	-	(Lundback et al., 2006)
PE	Phenolic UV stabilizer (Cyasorb 531)	Hexane or chloroform	~60-70 °C	12 h	-	(Lehotay et al., 1980)
РР	Phenolic and phosphite type antioxidants (Irganox 1010 and 3114, Irgafos 168), HALS (Tinuvin 770, 440 and P), fatty acid amide slip agent (erucamide)	Diethyl ether	~35 °C	15 h	_	(Raynor et al., 1988)
Ultrasonic extr HDPE	raction HALS (Tinuvin 770 and Chimassorb 944)	CYHA:DCM (1:1 v/v) and CYHA:2- propaged (1:1)	RT	1-5 h	< 20%	(Caceres et al.,
LDPE	HALS (Chimassorb 944), phenolic antioxidant (Irganox 1010) and phosphite	Chloroform	30–60 °C	5-60 min	-100%	(Haider and Karlsson, 1999)
PP, HDPE and LDPE	Primary and secondary antioxidants (BHT, Irganox 1010, Irganox 1076) and fatty acid amide slip agent (erucamide)	CYHA:2-propanol (90:10 v/v), CYHA: 2-propanol (50:50 v/v), DCM: 2-propanol (75:25 v/v) and DCM: 2-propanol (98:2 v/v)	RT	30–60 min	> 90%	(Nielson, 1991)
PUR foam	Plasticizer (Organophosphates)	DCM	RT	20 min	> 95%	(Carlsson et al., 1997)
HIPS	BFRs (TBBPA, HBCD and, deca-BDE)	2-propanol /methanol $(1:1 v/v)$ or 2-propanol /hexane $(1:1 v/v)$	65 °C	60 min	10-50%	(Vilaplana et al., 2008)
Polyolefin	Sorbitol type additives	Hexane/chloroform solvent mixture	40–70 °C	60–120 min	> 85%	(Vilaplana et al., 2008; Yoshika Yamada and
PVC	Plasticizers (phtalate)	Hexane	RT	30 min	20-87%	(Dong et al., 2013)

(continued on next page)

Table 3.1 (continued)

Polymer type	lymer type Additive type Solvent		Temp. (°C) Pressure (MPa)	Time	Recovery (% w/w)	Ref.	
РР	Primary antioxidants (aromatic	DCM	~40 °C	9 h	-	(Marque et al.,	
PE	Phenolic antioxidants, HALS, BFR	Acetonitrile	RT	20 min	65–94%	(Lin et al., 2011)	
Styrene- butadiene rubber	Phosphite type stabilizer (tris(nonylated phenyl) phosphite)	Isooctane	RT	$2 \times 20 \text{ min}$	_	(Brandt, 1961)	
Microwave ass	sisted extraction (MAE)						
PP	Antistatic agent (Glycerol monostearate) phenolic antioxidants and azo type dyes	DCM	60 °C	15 min	~100%	(Noguerol-Cal et al., 2011)	
PE, PS	Flame retardant (DecaBDE)	Toluene: methanol (75:25 v/v)	100– 140 °C	10–40 min	85–95%	(Costley et al., 1997; Ranz et al. 2008)	
HDPE, LDPE, PP	Primary and secondary antioxidants (BHT, Irganox 1010, Irganox 1076) and fatty acid amide slip agent (erucamide)	CYHA: 2-propanol (90:10 v/v) CYHA: 2-propanol (50:50 v/v), DCM:CYHA (75:25 v/v) and DCM: 2-propanol (98:2 v/v)	48 °C	20 min	>90%	(Nielson, 1991)	
HDPE, LDPE, PP	Phenolic antioxidant (Irganox 1010), phosphite type antioxidant (Irgafos 168) and HALS (Chimassorb 81)	Acetone:heptane (50:50 v/v) or 1,1,1 trichloroethane	High	2–6 min	>90%	(Freitag and John, 1990)	
HDPE, PP	Aromatic antioxidants (Irganox 1010 and Irgafos 168)	CYHA: 2-propanol (50:50 v/v), hexane:acetone (50:50 v/v) and xvlene:DCM (50:50 v/v)	70–120 °C	30–60 min	8–100%	(Camacho and Karlsson, 2001)	
HIPS	BFRs (TBBPA, HBCD and deca-BDE)	Methanol: 2-propanol (1:1 v/v) and hexane/2-propanol (1:1 v/v)	130 °C	60 min	TBBPA and HBCD: >90 deca- BDE: ~30%	(Vilaplana et al., 2008)	
PET	Cyclic trimer and other low molecular weight oligomers	Xylene, DCM, water, acetone and hexane	70-140 °C	30-120 min	-60%	(Costley et al., 1997)	
PVC	Plasticizer (di-2-ethylhexyl adipate and phthalates)	Methanol ethanol, 2-propanol and acetone/CYHA (50:50 v/v)	120 °C	10 min	71–96%	(Cano et al., 2002)	
PVC	Azo dyes (Sudan I, Sudan IV, Disperse RED I)	Methanol	120 °C	20 min	59.5-99.8%	(Garrigos et al., 2002)	
LDPE	Hindered phenol and phosphite type antioxidants (Irganox 1076 and Irgafos	DCM and the mixture of DCM and acetonitrile	25-50 °C	10–77 min	-	(Garcia et al., 2004)	
PP, HDPE, LLDPE, HECO, Supersoft	Hindered phenol and phosphite type antioxidants, dispersing agent and lubricant	Mixtures of acetone, hexane, heptane, 2-propanol and ethyl acetate	125– 140 °C	30, 40 min	>95%	(Marcato and Vianello, 2000)	
and PB LDPE	Phenolic antioxidant (Irganox 1076)	Acetonitrile	120 °C	40 min	>95%	(Molander	
PP	Phenolic antioxidants (Irganox 1010 and 1076)	2-propanol	80–110 °C	~40 min	-	(Burman and Albertsson,	
LDPE	Phenolic antioxidants (Irganox 1076 and α -tocopherol)	Acetonitrile or chloroform:2- propanol (10:1 v/v) mixture	80-100 °C	40-45 min	-	(Strandberg and Albertsson, 2005)	
Supercritical fl PP	uid extraction (SFE) Phenolic antioxidants	CO ₂ with hexane or methanol as a modifier	30–60 °C	90–180 min	>80%	(Garde et al., 1998)	
PP, Nylon, PET	HALS, Phenolic antioxidants, cyclic trimer and fatty acid amide lubricant (ethyl bis- stearamide)	Sc-CO ₂	70 °C, 5– 40 MPa	2–30 min	>90%	(Cotton et al., 1991)	
PUR foams	Flame retardants (chlorinated organophosphate)	Sc-CO ₂	60 °C, 20.27 MPa and 30 4 MPa	5–10 min	<50%	(Mackay and Smith, 1993)	
PE, PP	Phenolic antioxidants (Irganox 1010, 1076), phosphite type antioxidants (Irgafos 168), slip agents (erucamide), HALS (Thumin 270, Tinunia 226)	Sc-CO ₂	50.4 MPa 50 °C, 13.8 MPa or 41.4 MPa	15	>92%	(Ryan et al., 1990)	
PVC	Plasticizer (di-2-ethylhexyl adipate and	Methanol	41.4 MPa 95 °C, 48.3 MPa	30 min	60-85%	(Cano et al.,	
PE, PP	Phenolic UV stabilizer (Cyasorb UV-531), Phenolic antioxidants (Irganox 1010, 1076 1230)	Sc-CO ₂	5 °C, 25.3 MPa	2 h	80-90%	(Hirata and Okamoto,	
PET	Cyclic ethylene terephthalate trimer	Sc-CO ₂	70 °C, 40.5 MPa	0-390 min	10–70%	(Bartle et al., 1991)	
PVC	Phthalate plasticizers (DIOP) and phenolic antioxidant (Topanol CA)	Sc-CO ₂ with methanol as a modifier	45–115 °C, 7–45 MPa	10-435 min	10-90%	(Hunt and Dowle, 1991)	
PVC	Phthalate plasticizers (DOP and DBP)	Sc-CO ₂	80–100 °C, 25–65 MPa	2-30 min	30–98%	(Marin et al., 1996)	

Table 3.1 (continued)

Polymer type	Additive type	Solvent	Temp. (°C) Time Pressure (MPa)		Recovery (% w/w)	Ref.		
HDPE	Phenolic antioxidant (Ethanox 330)	Sc-CO ₂ with methanol	110 °C, 35 MPa	70 min	>90%	(Pinto and Taylor 1998)		
PP	Hindered phenol and phosphite type antioxidants (Irganox 1010 and Irgafos 168)	$Sc-CO_2$ with methanol as a modifier	120 °C, 38.4 MPa	60 min	60-75%	(Thilen and Shishoo, 2000)		
РР	Hindered phenol and phosphite type antioxidants (Irganox 1076, Irgafos 168 and Irganox 1010)	Sc-CO ₂ with methanol as a modifier	100 °C, 68 MPa	30 and 40 min	\geq 95% for Irganox 1076 and Irgafos 168, 62% for Irganox 1010	(De Paepe et al., 2006)		
PMMA	Hindered phenol and phosphite type antioxidants (Irganox 1010 and Irgafos 168)	$Sc-CO_2$ and methanol as a modifier	0–90 °C, 45 MPa	30 min	>75%	(Ashraf- Khorassani et al., 2003)		
PE	Hindered phenol and phosphite type antioxidants (Irganox 1010 and Irgafos 168)	Sc-CO ₂ with methanol as a modifier	75 °C, 45 MPa	30–120 min	\geq 93% for recycled LDPE, 83% for HDPE (120 min)	(Salafranca et al., 1999)		
HDPE, LDPE	Hindered phenol and phosphite type antioxidants (Irganox 1010 and 1076 and Irgafos 168)	$Sc-CO_2$ with methanol as a modifier	60–80 °C, 30–45 MPa	10–50 min	20–90%	(Arias et al., 2009)		
PVC	HALS (Tinuvin 326 and P)	Sc-CO ₂	50 °C, 30 MPa	10 min	-	(Mackay and Smith, 1995)		
PVC	Metal based stabilizer (organotin stabilizer)	Sc-CO ₂ with formic acid as a modifier	90 °C, 18 MPa	60 min	~ 100%	(Oudsema and Poole, 1993)		
PE	Fatty acid amide slip agent (erucamide)	Sc-CO ₂	45 °C, 15 MPa	15 min	-	(Engelhardt et al., 1991)		
PE	Phenolic antioxidant (Irganox B 6878 and 1330)	Sc-CO ₂	45 °C, 20 MPa	30 min	-	(Engelhardt et al., 1991)		
PE	Phenolic antioxidants, HALS (Chimassorb)	Sc-CO ₂	40 °C, 60 MPa	30 min for LDPE and 5 h for HDPF	-	(Juo et al., 1995)		
PP	Phenolic antioxidants (BHT and Irganox 1010) HALS (Tinuvin 326)	Sc-CO ₂	30–90 °C, 8–30 MP∍	30 min	~ 100%	(Daimon and Hirata 1991)		
PP	Phenolic antioxidants (Irganox 1010 and 1076)	Sc-CO ₂	40 °C, 35 MPa	10 min	-	(Baner et al., 1992)		
PUR	Phenolic antioxidant (BHT), plasticizers (adipate acid and phthalate ester)	Sc-CO ₂	60 °C, 30 MPa	10 min	-	(Mackay and Smith, 1994)		
Accelerated sol	lvent extraction (ASE)							
PE	HALS and phenolic antioxidants	2-propanol with THF and/or CYHA swelling solvents	80–110 °C, 10.3 MPa	2–22 min	>97%	(Garrido-Lopez and Tena, 2005)		
PP	Phenolic antioxidant (Irganox 1010)	2-propanol	150 °C and 13.8 MPa	5 min	~ 90%	(Vandenburg et al., 1998)		
PP, PVC	Phenolic antioxidant (Irganox 1010) and phthalate plasticizer (DOP)	CYHA/2-propanol	170 °C	13 min-1 h	~ 100%	(Vandenburg et al., 1999)		
HIPS	BFRs (TBBPA, HBCD, and deca-BDE)	Methanol/2-propanol (50:50 v/v) and hexane/2-propanol (50:50 v/ v)	90, 110, 130 and 150 °C, 10.3 MPa	3 min of cycles	TBBPA, HBCD: 95–100% deca- BDE: 50%	(Vilaplana et al., 2008)		
HDPE	Primary and secondary antioxidants (Irganox 1076 and PS802 Irgafos 168), HALS (Chimassorb 81, Tinuvin 326), fatty acid amide slip agent (erucamide)	2-propanol/DCM (75:25 v/v)	105 °C, 10.3 MPa	15 min of cycles	-	(Gillet et al., 2010)		
Dissolution-pro	Dissolution-precipitation							
РР	Phosphite and hindered phenolic type antioxidants and phosphite derivatives	Toluene as a solvent and methanol as a nonsolvent	110 °C	Until dissolves PP	50–80% for phosphite derivatives	(El Mansouri et al., 1998)		
PE, PP	HALS stabilizer (Chimassorb 944)	Decalin as a solvent and precipitation by cooling	120 °C	30 min	>97%	(Gharfeh, 1987)		
HIPS	Brominated flame retardant (deca-BDE)	Limonene as a solvent, sc- CO_2 fluid as a nonsolvent	170 °C	-	97%	(Peng et al., 2012)		
PP	HALS (Cyasorb 3529)	Toluene as a solvent and acetone as a nonsolvent	130 °C	30 min	90%	(Hintersteiner et al., 2014)		
PET	Cyclic trimer and other oligomers up to the heptamer	DCM:HFP (7:3 v/v) as a solvent	RT	Until dissolves	-	(Barnes et al., 1995)		
Polyolefins	HALS (Chimassorb 944)	Toluene as a solvent and methanol-triethylamine mixture as a nonsolvent	130 °C	40 min	>90%	(Freitag, 1988; Matuska et al., 1992)		
Polyolefin	Hindered phenol antioxidants (BHT, Irganox 1010/1076)	Decalin as a solvent and precipitation by cooling	90–120 °C	30 min	>95%	(Schabron, 1986)		

(continued on next page)

Table 3.1 (con	ntinued)
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Polymer type	Additive type	Solvent	Temp. (°C) Pressure (MPa)	Time	Recovery (% w/w)	Ref.
PE	Fatty acid type lubricant (stearic acid)	Toluene/chloroform mixture as a solvent and methanol as a nonsolvent	105 °C	Until dissolves	>90%	(Wang and Buzanowski, 2000)
HDPE	HALS (Tinuvin 770 and Chimassorb 944)	o-DCB as a solvent and methanol as a nonsolvent	160 °C	1 h	Tinuvin 770 : 70% Chimassorb 944: 65%	(Caceres et al., 1996)
PE, PP	Hindered phenol and phosphite type antioxidants (Irganox 1010, Irganox 1076 and Irgafos 168)	0.04% triethyl phosphite in o- xylene as a solvent and precipitation by cooling	130 °C	2 h	74–126%	(Green et al., 2010)
Blend of PC, ABS and PMMA	Primary and secondary antioxidants	Chloroform as a solvent and methanol as a nonsolvent	RT	Until dissolves	-	(Wang, 2000)
РА	Primary and secondary antioxidants (Irgafos 168, Irganox 1010 and 1098, Ultranox 626, Hostanox O3)	TFE as a solvent and the mixture of 50% chloroform + 49% 2- propanol + 1% CYHA as a nonsolvent	~80 °C	Until dissolves	-	(Angeli and Marino, 2007)
PP and HDPE	HALS	Toluene as a solvent and methanol as a nonsolvent	~110 °C	Until dissolves	-	(Coulier et al., 2005)
PE	Hindered phenol and phosphite type antioxidants (Irganox 1010, Irgafos 168, α -tocopherol)	N-heptane or n-heptane/2- propanol mixture as a solvent and precipitation by cooling	160 or 170 °C	1.5 h	>97%	(Macko et al., 1995)
LDPE	Phenolic antioxidant (Irganox 1076) Toluene as a solvent and precipitation by cooling		70 °C	Until dissolves	-	(Galotto et al., 2011)
LDPE	Phenolic antioxidants (α -tocopherol)	Toluene as a solvent and methanol as a nonsolvent	65 °C	15 min	95.8-106%	(Siro et al., 2006)
РР	HALS (Chimassorb 944, Cyasorb UV 3346)	Xylene as a solvent and 2- propanol as a nonsolvent	~140 °C	30 min	90-100%	(Marcato et al., 1991)
HDPE, LDPE	Hindered phenol and phosphite type antioxidants (Irganox 1010 and 1076 and Irgafos 168)	Toluene or xylene as a solvent and methanol as a nonsolvent	60–160 °C	15–120 min	75–97%	(Arias et al., 2009)
PE	Phenolic antioxidants, HALS (Chimassorb)	Toluene as a solvent and ethanol as a nonsolvent	~110 °C	3 h	-	(Juo et al., 1995)
PVC	Phthalate plasticizers	THF as a solvent and ethanol as a nonsolvent	~65 °C	20-30 min	>90%	(Gimeno et al., 2014)

the different variations in solid–liquid extraction are discussed, shake-flask (batch single-stage), Soxhlet (batch multi-stage), ultrasonic, microwave assisted extraction (MAE), supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE), respectively. Furthermore, extraction efficiencies within these techniques, obtained from literature, are explained based on the aforementioned theoretical considerations.

3.2.1.1. Shake-flask extraction/ batch single-stage extraction. As much of the current literature on solid-liquid extraction is taken from lab-scale research or analytical papers, terminology is accordingly. Usually, these papers refer to the shake-flask extraction method, which is one of the most commonly applied solid-liquid extraction methods. Translated to an industrial application, this would be equivalent to batch single-stage extraction in which a batch of material is fed into a reactor and mixed with the extraction solvent for a determined time period, typically until equilibrium (Fig. 3.3) (Jackson et al., 1984; Raynie, 2000; Yadav et al., 2015). For industrial applications, this would usually be designed as a multi-stage operation, typically in counter-current, to maxi-



mize the mass transfer and minimize the solvent use. Yet, lessons can be learned from these lab-scale experiments. This type of extraction is based on the penetration of the solvent through the pores of the solid matrix and the dissolution of the compound of interest. This method is performed by placing a solid sample into a container and adding an appropriate solvent and then shaking or mixing it for a time period until all desired compounds are dissolved in that solvent. After the extraction, the insoluble solid matrix can be separated via decantation, filtration or centrifugation (Bart, 2005). This process can be repeated several times by using fresh solvent and the extracted compounds can be combined in order to obtain higher yields, as such making it equivalent to industrial multi-stage extractions.

The parameters already highlighted to affect extraction efficiency are the type of solvent, the particle and pore size of the solid compound and the extraction time. Regarding the effect of particle size, it was observed that the smaller the particle size, the higher the specific surface area, thus the lower the extraction time (Hunt and James, 1993; Spell and Eddy, 1960). For example, when a PE matrix was powdered to a 50 mesh size (0.297 mm) from pellets, the shaking time for the additive extraction was reduced by more than 60% (Spell and Eddy, 1960). Furthermore, the effect of solvent choice on the extraction time and efficiency has already been investigated (Spell and Eddy, 1960; Wims and Swarin, 1975). As indicated in Table 3.1 in the study of Spell and Eddy (1960) carbon disulphide (CS₂) and isooctane were used to extract hindered phenol antioxidants like Ionol and Santonox from a PE matrix (Spell and Eddy, 1960). It has been noticed that CS₂ extracts Ionol and Santonox in 30-40 min while isooctane recovers Ionol in 125 min and Santonox in 2000 min. This follows the Hansen solubility parameters as seen in Fig. 3.1. Based on Eq. (3.2), the distance

of Ionol (A12) and Santanox (A22) to CS_2 (S17) is 5.8 MPa^{1/2} and 10.6 MPa^{1/2}, respectively, whereas the distance of those to isooctane (S16) is 6.8 MPa^{1/2} and 14 MPa^{1/2}, respectively. Similarly, in the study of Wims and Swarin (1975) different extraction yields were obtained based on the type of solvent as shown in Table 3.1.

Shake-flask or batch single-stage extraction is a simple method, but it needs high residence times to increase extraction efficiency, making it especially difficult if the goal is to extract a range of additives with different properties.

3.2.1.2. Soxhlet extraction/batch multi-stage extraction. Soxhlet extraction is a solid-liquid extraction method which requires heat. which is not necessarily the case in shake flask or batch singlestage extraction. The Soxhlet principle is based on a continuous extraction of the target compounds by a suitable solvent which repeats boiling-condensation cycles by enabling refreshed hot fluid for the matrix regularly compared to shake-flask extraction (Bart, 2005; Raynie, 2000). Basically, this technique can be seen as a multi-stage cross flow extraction, in which each time fresh solvent is added to the same solid material. This method starts by placing a solid sample in a Soxhlet thimble, which is a porous container made of thickened filter paper. Then this thimble is placed into a Soxhlet apparatus and a suitable solvent is added into the flask which is connected to the Soxhlet apparatus. During the extraction process, the solvent boils and condenses into the Soxhlet thimble and the soluble molecules leach out to the boiling flask (Fig. 3.4) (Hunt and James, 1993). This process is repeated until the target molecules are separated from the solid sample. Since the boiling point of the extracted compounds is normally higher than the solvent, compounds stay in the flask while the solvent recirculates (Bart, 2005; Dean, 1998).

Soxhlet extraction is one of the extraction methods that increases the diffusion rate due to use of heat and increasing the concentration difference by using fresh solvent each time. In this type of extraction, solid-liquid ratios vary from 1:10 to 1:50, allowing to dissolve even less soluble additives (Hawthorne et al., 1995). However, it is not always feasible to desorb the compounds of interest if they are strongly bound. Therefore, the choice of solvent, the molecular weight of the additive and the temperature are crucial parameters for efficient removal of compounds (Crompton, 2007). The solvent should ideally swell the polymer, which increases the permeability and then additives should be selectively removed based on the differences in solubility between the matrix and additive (Lou et al., 1997). The importance of choosing the



Fig. 3.4. Mechanism of Soxhlet extraction.

right solvent (or mixtures) in order to obtain high recoveries in a shorter time period was already studied (Dettmer et al., 1999; Haney and Dark, 1980; Kozlowski and Gallagher, 1997; Sevini and Marcato, 1983). For example, as shown in Table 3.1 Haney and Dark (1980) reported the extraction of fatty acid amide slip agents such as oleamide and erucamide, stearates as lubricant and phenolic antioxidant, Irganox 1076 and Topanol CA, from a PP matrix by using DCM as a solvent (Haney and Dark, 1980). In this paper, it was concluded that sodium stearate and Topanol CA recovery was very low, although their HSPs are close to those of DCM (Fig. 3.1) (Haney and Dark, 1980). This might be due to their high molecular weight (see Table 2.1). This indicates that the molecular weight of the additive is an important criterion as well, generating diffusion limitations. This was also proven in the study of Malaika et al. (1999) (see Table 3.1) in which Soxhlet extraction on HDPE plaques was performed by using heptane as a solvent and then the recovery of different molecular weight antioxidants, Anox PP18 (531 g/mol) and Anox 20 (1178 g/mol) was compared (Malaika et al., 1999). It was observed that the extraction efficiency of the additives (% w/w) increases with decrease in molecular weight of the additive (Malaika et al., 1999). Similarly, in the study of Garrigos et al. (2002) broad recovery was obtained for the extraction of azo dyes because of their different polarity and molecular weight (Garrigos et al., 2002). Furthermore, temperature can be adjusted as well during a Soxhlet extraction in order to avoid any degradation or dissolution of the polymer matrix or any loss of highly volatile additives.

Based on literature, it can be stated that Soxhlet extraction or multi-stage solid-liquid extraction processes can be applied with reasonably high efficiencies on soluble molecules with lower molecular weights. Currently, there are not really industrially proven solid-liquid extraction processes for plastic waste available on the market. Examples that come closest are currently not based on solvents. The most basic industrial example is friction washing in cold or hot water, or caustic solutions for instance to remove odorous components and organic residue. These are typically already organized as counter-current processes. However, these industrial washing processes also often need to conclude that odour is not completely removed with such washing techniques, which is easily explained due to choice of solvent (in this case thus often water) and the difficulty of removing high-molecular-weight odorous substances. Similarly, not based on solvents but on detergents is the Cadel deinking process, which is a continuous process to remove inks from a range of plastics and includes recovery of the medium via hydrocyclone (Cadel Deinking). Such processes are potentially efficient for molecules adsorbed only to the surface (such as inks), but have more difficulties when molecules are deeper embedded in the polymer (such as masterbatch colors). Soxhlet extraction is mainly applied in the agriculture industry such as extraction of solutes from plants and there is still no pilot-scale application in plastic industry (Poirot et al., 2007).

3.2.1.3. Ultrasonic extraction. The principle of ultrasonic extraction is based on the use of ultrasonic frequencies ranging from 20 kHz to 2000 kHz in order to detach the targeted additives by agitating and creating cavitation in the solid matrix (Bart, 2005). This acoustic cavitation force is the main driving force in ultrasonic extraction, which induces a series of compressions and rarefactions in the solvent causing formation of bubbles (Shirsath et al., 2012). The accessibility of a solvent to the compound is improved via implosion of bubbles which experience pressure from the surrounding fluid and become unstable on the surface of the solid compound. Collapse of these unstable bubbles creates a strong fluid jet, which increases solvent diffusion in the material (Fig. 3.5) (Bart, 2005; Crum, 1995). Ultrasonic extraction can be performed via direct sonication by using an ultrasonic bath or via



Fig. 3.5. Creation of a microjet in Ultrasonic extraction technique (Nagalingam and Yeo, 2018).

indirect sonication, in which the material is kept in a container inside a water containing ultrasonic bath and ultrasonic frequencies are transmitted to the material through water. Mostly direct sonication with an ultrasonic probe is preferred since it can develop a higher power compared to an ultrasonic bath (Pico, 2013).

As shown in the other extraction methods, the parameters which are expected to affect the efficiency and yield of ultrasonic extraction are temperature, particle size, type of solvent and concentration, among others (Tiwari, 2015). Temperature is a factor which increases the solubility of a compound and enhances the diffusion rate and thereby the extraction yield as well as introduced in Section 3.1.2. However, typically relatively low temperatures are used in ultrasonic extraction, which is one of the disadvantages of the method. It was proven that if temperature is below the glass transition temperature (T_g) of a polymer, the chain mobility and diffusion of the solvent is restricted causing a low recovery of additives (Caceres et al., 1996; Vilaplana et al., 2008). In addition, the effect of solvent on the solubility of additives was studied extensively (Haider and Karlsson, 1999; Nielson, 1991). For example, as indicated in Table 3.1 in the study of Haider and Karlsson (1999) hindered amine light stabilizer (Chimassorb 944) and phenolic (Irganox 1010) and phosphite antioxidants (Irgafos 168) are extracted from a low density polyethylene (LDPE) matrix via ultrasonic extraction by using chloroform at 60 °C (Haider and Karlsson, 1999). The total recovery was obtained after 15 min. 45 min and 60 min for Irgafos 168. Irganox 1010 and Chimassorb 944. respectively (Haider and Karlsson, 1999). This result can be explained via Fig. 3.1 in which the distance between HSPs of Irgafos 168 (A23) and chloroform (S6), which is 3.2 MPa^{1/2}, is lower compared to the distance between Irganox 1010 (A20) and chloroform, which is 8 MPa^{1/2}. Similarly, as shown in Table 3.1 in the study of Marque et al. (1998) DCM was not a good solvent to extract aromatic antioxidants from a PP matrix since desirable recoveries could not be obtained, even after 9 h (Marque et al., 1998). The positive effect of a smaller particle size on the extraction yield was highlighted for example in the study of Vilaplana et al. (2008) in which ultrasonic extraction yields of brominated flame retardants (BFRs) from granulated and powdered HIPS were compared by using 1:1 v/v mixtures of 2-propanol/methanol or 2propanol/n-hexane at 65 °C during 60 min (Vilaplana et al., 2008) (see Table 3.1). Higher extraction recoveries of tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD) (50-60% w/w) with the 2-propanol/n-hexane mixture were obtained by using polymer powder (Vilaplana et al., 2008).

In spite of the long extraction time and low recoveries especially for high-molecular-weight and highly soluble compounds in a fluid, ultrasonic extraction method might be preferred for thermolabile compounds due to the low temperatures that are required. Currently, mainly the pharmaceutical/nutraceutical and the food industries have shown interest in the adoption of ultrasonic extraction due to its low cost, reproducibility and broad solvent range. However, it is still challenging to scale up to industrialscale because huge plastic volumes might create engineering problems (Vinatoru et al., 2017). 3.2.1.4. Microwave assisted extraction (MAE). The principle of MAE is based on the extraction of additives from a matrix by using solvents which are heated by using microwave energy with frequencies ranging from 30 GHz to 300 MHz (Dean, 1998; Subramanian, 2013). Microwave heat is transferred to the solid sample via a dual mechanism of ionic conduction and dipole rotation, which takes place simultaneously in the solvent and in the sample and converts microwave energy to thermal energy (Llompart et al., 2018; Lynch, 1995). During ionic conduction, heat is generated due to the resistance of the medium to the ion flow (Llompart et al., 2018). In dipole rotation, the vibration and multiple collisions which are triggered by realignment of dipoles of molecule due to changing electric field produce heat (Fig. 3.6) (Llompart et al., 2018). MAE can be performed in an open system at atmospheric pressure or in a closed system under pressure (Destandau et al., 2013).

Unlike the aforementioned extraction methods, the selected solvent should have microwave absorbing properties in order to be heated by a microwave, which is determined by the magnitude of the solvent dipole moment (Bart, 2005). A larger dipole moment allows solvent molecules to oscillate faster under the microwave field (Hasty and Revesz, 1995). Polar solvents such as water and acetone are more suitable for MAE since nonpolar solvents have low permittivity and are thus not affected by microwave energy (Bart, 2005; Garrigues and De La Guardia, 2011). These nonpolar solvents are, however, typically used to extract additives from polymers such as HDPE. To perform MAE, it is, therefore, probable that a polar/nonpolar solvent mixture is needed, as the nonpolar solvent enables a polymer to swell and the polar solvent allows microwave heating (Bart, 2005; Camacho and Karlsson, 2001; Costley et al., 1997; Freitag and John, 1990). For example, as shown in Table 3.1 Cano et al. (2002) studied the effect of experimental conditions for the extraction of adipate and phthalate plasticizers from PVC matrices, in which methanol is preferred as an extraction solvent over ethanol, 2-propanol and a 1:1 mixture of acetone/cyclohexane due to its higher swelling ability of the PVC matrix without causing dissolution (Cano et al., 2002). This can be explained via Fig. 3.1 which shows that the distance between the HSPs of PVC (P7) and methanol (S8) is 21 MPa^{1/2}, whereas the distance between PVC and ethanol (S9), and PVC and n-propanol (S11) is 17 MPa^{1/2} and 15 MPa^{1/2}, respectively. Similarly, Camacho and Karlsson (2001) obtained different extraction yields of aromatic antioxidants, ranging from 8% to 100% based on the solvent mixture (Camacho and Karlsson, 2001) (see Table 3.1). In addition, the type of additives plays an important role in the extraction efficiency. In the study of Garrigos et al. (2002) different recoveries were obtained for the extraction of azo dyes from a PVC matrix (Garrigos et al., 2002). Compared to the other extraction methods,



Fig. 3.6. Heat generation mechanisms in MAE by the change in electric field: dipole rotation and ionic conduction.



Fig. 3.7. Representative mechanism of the removal of additives from a polymer matrix via SCF, adapted and redrawn from (Di Maio and Kiran, 2018).

particle size has a dual effect in MAE. While a decrease in the particle size allows to increase the migration rate of additives due to higher penetration, huge amount of microwave energy is not absorbed but is reflected by reducing particle size (Llompart et al., 2018). Therefore, the matrix size should be optimized in order to obtain higher extraction efficiencies. The volume of solvent is another criterion that affects recovery of additives, thus this needs optimization based on the type and size of the matrix. It is stated that approximately 10-fold lower amount of solvent is used when applying MAE compared to classical extraction methods (Llompart et al., 2018). However, probably a proper engineering of full-scale processes might also save solvent quantities for the different S/L extraction methods, so it is still difficult to compare techniques at this stage of maturity.

MAE is a relatively new technique that allows a high level of automation, speed and convenience, however, extraction conditions are quite specific for each type of additive and plastic, thus profound investigation is required to optimize the extraction conditions (Zlotorzynski, 1995).

3.2.1.5. Supercritical fluid extraction (SFE). Supercritical fluid extraction (SFE) follows the principles of a regular solid-liquid extraction, but here a supercritical fluid (SCF) is used as a solvent. A SCF state is reached when a compound is brought above its specific critical temperature and pressure (Van Ness and Abbott, 1982). SCF contains intermediate properties between liquids and gases with improved solubilizing properties and diffusivity. For example, the viscosity is similar to the one of gases, while its density is close to the one of liquids. SCF has advantages over organic solvents; for example, they can easily penetrate into a porous matrix, dissolve components and then easily exit the matrix due to the low viscosity and low surface tension. The principle of SFE relies on the extraction of additives according to their chemical nature (Gere et al., 1997). By varying the extraction conditions such as temperature and pressure, the solubility of the SCF is modified, which allows a more selective or even sequential removal of additives if needed (Bart, 2005; Sánchez-Camargo et al., 2014). A wide range of compounds can be used as a SCF. However, the critical point is particular to the extraction solvent, and can significantly differ from each other. Reaching the critical points of organic solvents is expensive and impractical especially at the current maturity of this process (Sánchez-Camargo et al., 2014). Also, the use of some solvents as a SCF is stated to be not particularly eco-friendly (Sánchez-Camargo et al., 2014). Supercritical CO₂ (scCO₂) on the other hand is a SCF that is known to be relatively cheap and nontoxic (Senichev and Tereshatov, 2014). In addition, CO₂ has advantages compared to organic solvents since it is a gas at normal ambient conditions, which allows to obtain a solvent free extract after the extraction process. On the other hand, CO_2 has a very low polarity, thus its ability to extract high polar compounds such as phenolic antioxidants is limited. This problem can be overcome by using more polar solvents such as water as a modifier at low concentrations (<10%) together with CO_2 in order to increase the polarity of the SCF (Sánchez-Camargo et al., 2014). A typical SFE is performed by placing samples in a cartridge which is resistant to high-pressure and temperature followed by a flow of SCF through the sample, and afterwards depressurizing it. After the expansion of the SCF, the extracted compounds, which are not soluble in gaseous CO_2 anymore, are collected in a container (Fig. 3.7) (Mellor et al., 1994).

SFE of additives from polymers is a diffusion driven process which is based on the ability of a SCF to swell the polymer so that the diffusivity of the solute increases (Doolev et al., 1995). Also, SCF should be able to solubilize the solute of interest for a successful extraction. Different parameters play a role on the extraction efficiency (Bart, 2005; Sánchez-Camargo et al., 2014; Vandenburg et al., 1997). For example, it was shown that larger molecules have a slower diffusion rate in a polymer and they are less soluble in CO_2 (Mackay and Smith, 1993; Vandenburg et al., 1997). In this study, 90% of a phthalate plasticizer, diisooctyl phthalate (DIOP) which is in the low-molecular-weight category based on Table 2.1, was extracted from a PVC matrix at 45 MPa and 90 °C during 20 min, whereas only 50% of Topanol CA (high-molecular-weight phenolic antioxidant) could be extracted under the same conditions (Hunt and Dowle, 1991) (Table 3.1). In addition, the amount of CO_2 adsorbed depends on the type of polymer (Bart, 2005). For example, Shieh et al. (1996) observed that amorphous polymers exhibited a higher amount of CO₂ adsorption compared to crystalline ones, as such increasing extraction yields from amorphous polymers, such as PMMA, ABS, HIPS and PUR compared to more crystalline polymers, e.g. Teflon and LDPE (Shieh et al., 1996). Similarly, as shown in Table 3.1 Juo et al (1995) obtained different extraction yields for the extraction of the specific additives from HDPE and LDPE polymers due to differences in the crystallinity of those matrices (Juo et al., 1995). Beside the morphology, the solubility of CO₂ is affected by the polarity of the polymers as well. It was found out that ABS has a low CO₂ uptake due to foam formation, which is caused due to desorption of CO₂. Furthermore, a higher density of SCF enhances the solubility of compounds, which can be achieved by an increase in temperature (Sánchez-Camargo et al., 2014). Therefore, it can be assumed that the extraction rate will rise by increasing the temperature until the solubility in the SCF becomes a limiting factor (Vandenburg et al., 1997). For example, Cotton et al. (1993) investigated the effect of pressure and temperature on the extraction of additives (phenolic and phosphite antioxidants, stabilizers) from a PE and a PP matrix. They observed an increase in the extraction rate at 50 °C by raising the pressure until 30.4 MPa (Cotton et al., 1993) (see Table 3.1). At this point, an increase in temperature leads to a sharp rise in the extraction rate up to the melting point of the polymer. When all these parameters are considered, it can be concluded that SFE of additives can be enhanced by increasing the temperature, adding a modifier to swell the matrix and decreasing the particle size in the case where the extraction rate is diffusion limited (Lou et al., 1996). If the extraction is solubility limited, then a decrease in temperature and an increase in pressure and flow rate will result in the enhancement of the extraction rate (Bart, 2005).

SFE thus seems a 'greener' process that is also promising from a technical perspective, but on the other hand, it requires optimization and a more fundamental understanding of all phenomena. Furthermore, experience with SFE can usually become quite expensive, but it has been widely used in the food industry, for example towards the extraction of caffeine from coffee beans

solvent flow solvent тр polymer matrix diffusion of analyte polymer matrix swells by with additives the solvent and analyte through swollen matrix (red balls) desorbs (blue arrows) to outside of the matrix from matrix and diffuses (green arrow) and to swollen matrix part transport by the flowing bulk of solvent (orange arrow)

Fig. 3.8. Schematic presentation of ASE mechanism, adapted and redrawn from (Bjorklund et al., 2000).

(Zosel, 1976). Currently, there are also some endeavors to use SFE during polymer extrusion (Nalawade et al., 2006).

3.2.1.6. Accelerated solvent extraction (ASE). ASE is a pressurized fluid extraction which is performed at elevated temperatures and pressures with low amounts of solvents for shorter times (Richter et al., 1996). The principle of ASE is based on four subsequent steps:

- Swelling of the polymer matrix by the solvent.
- Desorption of compounds from a solid matrix.
- Diffusion through the solvent placed inside a particle core.
- Transfer to the bulk of flowing fluid (Fig. 3.8) (Giergielewicz-Mozajska et al., 2001).

The procedure consists of a passing flow of hot pressurized solvent through a heated reactor containing the plastics (Bart, 2005). In order to avoid sample agglomeration at a high temperature and pressure, the sample is usually mixed with inert gas such as nitrogen (Richter et al., 1996).

As discussed in previous extraction methods, the use of elevated temperatures and pressures enhances the extraction in terms of solubility and mass transfer (Bart, 2005; Lou et al., 1997). As expected, solubility of the compound is also crucial in ASE (Bart, 2005; Vandenburg et al., 1998). For example, as indicated in Table 3.1 Vandenburg et al. (1999) used a cyclohexane (CYHA)/2propanol solvent mixture in different volume ratios in order to extract the hindered phenolic antioxidant Irganox 1010 from a PP matrix by using ASE. They observed that the mixture with 2.5% v/v CYHA gave a higher extraction yield compared to the mixtures with 5% v/v CYHA and only 2-propanol (Vandenburg et al., 1999). According to Eq. (3.2), CYHA is a better solvent for PP (the distance is 3 MPa^{1/2} with CYHA and 17 MPa^{1/2} with 2-propanol) whereas 2-propanol is a better solvent for Irganox 1010 (the distance is 14 MPa^{1/2} with CYHA and 11 MPa^{1/2} with 2-propanol). Therefore, increasing the % v/v of CYHA to 5% v/v might cause dissolution of the PP matrix instead of swelling, which causes a decrease in the extraction yield as shown in the study of Vandenburg et al. (1999) (Vandenburg et al., 1999). Also in the study of Garrido-Lopez and Tena (2005) the volume ratio of extraction solvents was optimized based on the type of additives (Garrido-Lopez and Tena, 2005). In addition, Waldeback et al. (1998) show that particle size is also an important factor in ASE, but they noticed to be careful in causing degradation of the target compound when performing ASE on LLDPE granules instead of ground samples for the extraction of a phenolic antioxidant (Irganox 1076) (Waldeback et al., 1998).

Although ASE is still in an early stage of development, it is already applied to extract the bioactive compounds in food industry (Turner, 2006). It is an advantageous technique in terms of solvent consumption, extraction time and it allows to be used with a wide range of solvents. However, research on optimizing this method is still limited in the context of plastic recycling.

3.2.2. Dissolution-precipitation

Solid-liquid extraction methods do not always yield sufficient recovery of additives especially in case of high-molecular-weight or less soluble additives. To overcome this drawback, dissolutionprecipitation is an option in order to remove additives from a polymer matrix. The principle of dissolution-precipitation is based on the dissolution of a polymer in a solvent, followed by the precipitation of polymeric constituents by cooling, by evaporating the solvent or by the addition of nonsolvent with a different polarity and solubility (Komolprasert et al., 1995). The basic idea is that the target compounds remain in the solvent-nonsolvent mixture due to the solubility differences between the polymer and the additives (Fig. 3.9) (Komolprasert et al., 1995).

To achieve dissolution-precipitation, solvents should be chosen based on their ability to dissolve and precipitate the polymer matrix. Therefore, the selection of a solvent/nonsolvent combination is the most crucial factor (Bart, 2005). In principle, solvents can be classified as polar and apolar based on their functional groups. Generally polar solvents such as trifluoro- ethanol and hexafloropropane dissolve the polymers containing polar groups such as PA or PET and apolar solvents such as xylene, toluene and decaline are preferred to dissolve more apolar polymers such as polyolefins or PS (Braun, 2013). Although the selected solvent is able to dissolve different type of polymer matrices having similar solubility, different additive-polymer combinations could lead to the selection of different solvents. For example, tetrachloroethane was used to dissolve a PP matrix to remove HALS (Tinuvin 770), whereas xylene was used to dissolve a PE matrix in order to remove a phenolic antioxidant (Irganox B220) (Bart, 2005). Mixtures of solvents also prove to be effective in some cases; for example, Wang and Buzanowski (2000) used a toluene/chloroform mixture at 105 °C in order to dissolve a PE matrix and used metha-



Fig. 3.9. Dissolution-precipitation for separation of additives from a polymer matrix by addition of solvent and nonsolvent respectively.

nol as a nonsolvent for the extraction of a fatty acid lubricant (Wang and Buzanowski, 2000). Similarly, Barnes et al. (1995) used a DCM:HFP (7:3 v/v) mixture in order to dissolve PET for the extraction of cylic trimers and other oligomers (Barnes et al., 1995) (see Table 3.1). Such choices might however make the downstream processing more complex to clean the solvent mixtures. In some studies (Galotto et al., 2011; Gharfeh, 1987; Green et al., 2010; Macko et al., 1995; Schabron, 1986) precipitation of polymers is performed by cooling the solution instead of adding a nonsolvent, which makes the cleaning process of the solvent easier and might reduce the cost significantly.

When choosing a nonsolvent, it should have a different polarity compared to the solvent to cause neither dissolution of the polymer nor precipitation of the additive. Generally, the nonsolvent is used in a 3 to 1 vol ratio with the solvent to allow a proper precipitation of the polymer, which makes this method less desirable in terms of environmental and economic aspects. However, this problem can be solved by optimizing the extraction conditions, using a more suitable nonsolvent or achieving precipitation via cooling or evaporation, which can potentially decrease the cost.

Dissolution-precipitation is advantageous due to its wide applicability, low cost, and high potential to remove a whole range of additives (Bart, 2005). However, it has also some drawbacks. Sometimes it is hard to find a suitable solvent/nonsolvent combination; for example in case the polymer does not dissolve easily (Crompton, 2007). In some cases, high temperatures are needed, causing issues related to viscosity, corrosion, solvent volumes, safety risks and so on. There are already quite some efforts by a whole range of companies to develop this process. The most known technologies are the CreaSolv[®] and Newcycling[®] technologies that are applied for example on electronic sachets and multilayer plastics respectively (APK, 2019; Pappa et al., 2001; Unilever, 2017). Also, few patents exist to extract phenolic antioxidants from polyolefins and brominated flame retardants from PVC, PC, ABS, PET and PVB (Maurer, 2004; Schabron, 1986).

4. Assessment of the extraction methods

The final aim of this review is to assess the different extraction methods in order to provide guidance towards future industrialization of this type of processes. Therefore, the previously discussed methods are assessed towards their technological feasibility by comparing their advantages and disadvantages. In addition, since there is very little information to perform an in-depth environmental and economic assessment on these processes, this review provides a basic cost and environmental benefit analysis of Soxhlet extraction and dissolution-precipitation through simplified examples in order to visualize if these techniques are promising towards sustainable closed-loop recycling of plastics.

4.1. Technical aspects

The selection of a suitable method to remove additives from plastics depends on various factors such as additive type, extraction conditions, amount and type of solvent, among others. In this section a comparison between removal efficiencies of the different methods is made based on these factors. According to our literature review, dissolution-precipitation is extensively preferred in various applications. It seems that dissolution-precipitation is especially promising because it is more convenient for high-molecular-weight compounds, it is applicable for a wider range of polymers, it is relatively fast and it does not necessarily require grinding of the sample (Bart, 2005). Furthermore, it has already been explored at pilot-scale, for example, in the CreaSolv[®] and Newcycling[®] processes. For solid-liquid extractions the diffusion

limitation is a big issue towards industrial applications. As can be seen in Table 3.1, more than 90% w/w of additives are recovered in less than 1 h by using the dissolution-precipitation method, whereas this takes more than 1 h with conventional solid-liquid extraction methods. In contrast, dissolution-precipitation may need high amounts of nonsolvent in order to obtain full precipitation of the polymers. At this point, other precipitation methods, such as cooling or evaporation might be desirable from an economic and environmental perspective.

Much improvement can still be made in solid-liquid extraction methods, by improving knowledge on influence of amongst others temperature, particle size, solvent choice and extraction time. In addition, it is expected that much gains can still be made by overcoming diffusion limitations through developing efficient largescale multi-stage processes, which can already be concluded from the efficiency improvements by lab-scale Soxhlet systems. Although ultrasonic extraction needs a shorter extraction time than Soxhlet, it is more dependent on the solvent polarity, thus the choice of solvents is broader in Soxhlet extraction (Bart, 2005). A promising intermediate solution is attempting to swell the polymer by increasing extraction temperatures under pressure or by using higher boiling solvents for example, as such increasing the diffusion rate. However, this might also cause degradation of thermolabile additives.

Other techniques such as MAE, SFE and ASE allow an increase in the extraction rate but they require more sophisticated equipment. SFE is faster and does not require typical organic solvents unlike Soxhlet extraction. For example, Hirata and Okamoto (1989) compared SFE with Soxhlet extraction (Hirata and Okamoto, 1989). They stated that more than 90% of additives (UV stabilizer and phenolic antioxidant) were extracted from PE and PP by using scCO₂ at 250 atm and at 35 °C within 2 h, whereas this took 24 h with the Soxhlet extraction and resulted in low recoveries due to the evaporation of some solutes (Hirata and Okamoto, 1989). This also shows that the boiling point of additives (indicated in Table 2.1) has an effect on the selection of an extraction method. Furthermore. SFE generally needs a modifier in order to enhance the extraction rate especially in the presence of high-molecularweight and polar compounds since their solubility in scCO₂ becomes a limiting factor. Therefore, ASE is a promising option since it is applicable to a broader range of solvents unlike SFE. However, the choice of solvent is not always straightforward because the selected solvent should preferably swell well the polymer instead of dissolving it. While applying MAE, the heat source is microwave energy and thus the solvents need to be able to absorb microwaves for extraction. Therefore, the solvent choice in MAE is even more limited compared to ASE.

Table 4.1 summarizes different aspects related to the extraction efficiency of the discussed techniques, for example, their suitability towards high-molecular-weight additives, thermolabile and highly polar additives. In addition, it shows the technological maturity of each extraction process via the Technology Readiness Level (TRL) scale based on existence of any pilot-scale applications in the plastic industry.

Concluding, dissolution-precipitation is more preferable for the removal of a broad range of additives, especially also when removal of high-molecular-weight additives is desirable, whereas shake-flask, Soxhlet and ultrasonic extraction are less desirable due to long extraction time and low recoveries. On the other hand, dissolution-precipitation might cause degradation of additives when high temperatures are used to dissolve some polymers. Therefore, still a lot of optimization efforts related to the engineering can be sought. Applying pressure to partially swell the polymer might in this sense also be a promising intermediate solution since higher pressure accelerates the extraction process, thus thermolabile additives are exposed to high temperature for a shorter time.

Table 4.1

Suitability of the extraction methods in specific conditions.

Extraction methods	Shake-flask or batch single-stage	Soxhlet or batch multi- stage	Ultrasonic	MAE	SFE	ASE	Dissolution-precipitation
High-molecular - weight additives	Long extraction time	Long extraction time	Low recovery	+	- Needs modifier	+	++ High extraction recovery due to total dissolution
Thermolabile additives	+	- Degradation due to high temperature	++ Low temperature	++ Short extraction time, thus short- exposure time to high temperature due to pressure	++ Short extraction time, thus short- exposure time to high temperature due to pressure	++ Short extraction time, thus short- exposure time to high temperature due to pressure	Degradation due to high T to dissolve some polymers
Highly polar additives	+	+	+	++ Use of highly polar solvents	Low recovery due to low polarity of sc-CO ₂	+	+
Low amount of solvent	+	+	+	++ Due to pressure	++ Due to pressure	++ Due to pressure	- High amount of nonsolvent to precipitate the polymer
Broad range of solvents	+	+	+	Needs always dielectric solvents	- Modified CO ₂	+	+
TRL scale based on existence of pilot-scale application for plastics	3–5 not proven for plastics, but commonly applied in other sectors (Vang et al., 2016)	5–8 not proven for plastics, but applied in other sectors e.g. agriculture (Dreisinger et al., 2019; Poirot et al., 2007)	3-5 not proven for plastics, but explored in other sectors e.g. extraction of caffeine (Hielscher- Ultrasound Technology, 2019; Poirot et al., 2007; Preece et al., 2017)	5–8 not proven for plastics, but explored in other sectors e.g. agriculture (Turner, 2006)	5–8 not proven for plastics, but applied in other sectors e.g. food and agriculture industries (Turner, 2006)	3–5 not proven for plastics, but explored in other sectors e.g. e.g. food and agriculture industries (Turner, 2006)	8–9 CreaSolv [®] Newcycling [®] for plastics Also explored in other sectors e.g. pharmaceutical industry (APK, 2019; Jakubiak et al., 2016; Turner, 2006; Unilever, 2017)

+ suitable ++ very suitable - not suitable -- might be discarde.



Scheme 4.1. Additive extraction process scheme with solvent recovery for (a) Solid-liquid extraction (based on Soxhlet extraction) (b) Dissolution-precipitation.

4.2. Economic assessment

To gain some insights in the economic viability of additive removal processes, an economic screening assessment is performed on two exemplary case studies which give the highest extraction yields based on literature. Since the principle of solid-liquid extraction and dissolution-precipitation is different from each other as shown in Scheme 4.1., one case-study from each process is used.

One of the scenarios is the removal of phenolic antioxidants (Irganox 1076 and Topanol CA) and a fatty acid amide slip agent (erucamide) from a PP matrix via solid-liquid extraction by using DCM as a solvent (Haney and Dark, 1980). The second one is the extraction of phthalate plasticizers (DOP, DiNP, DiDP and DPHP) from a PVC matrix via dissolution-precipitation by using THF as solvent and ethanol as nonsolvent (Gimeno et al., 2014). For both cases, the potential cost of plastic waste treatment (\mathcal{E} /ton) is calculated through Eq. (4.1).

(Deanin, 1975). The prices of additives, solvents, plastics taken into account during calculations are shown in appendix B (ICIS; Insider; Narayanan and Joshi, 2018a; Narayanan and Joshi, 2018b; Plasticker, 2019; Specialchem; Stanton; Updates).

It is important to note that this is a screening economic assessment, excluding capital costs, labor costs and different operational costs such as cleaning and disposal of the non-recovered solvent, drying of the polymers, pumping operations, censoring, etc. This must thus be seen as a best-case exercise; if it is not profitable in

$$Cost of the process = \begin{bmatrix} \left[\left(C_{S(NS)} \times M_{S(NS)} \right) \times (1 - R_S) \right] + \left[\left(M_{S(NS)} \times c_p \times \Delta T \times C_E \right) + \left(M_{S(NS)} \times L_{S(NS)} \times C_E \times R_S \times R_r \right) \right] + \\ (C_{waste} \times M_{waste}) \end{bmatrix} / E_e$$

$$(4.1)$$

where,

 $C_{S(NS)}$: cost of solvent (nonsolvent) (ϵ /ton),

M_{S(NS)}: net mass of fresh solvent (nonsolvent) (ton),

 c_p : specific heat capacity of solvent (nonsolvent) (MJ/ton K), Δ T: temperature difference between the boiling point of sol-

vent and RT (293.15 K) (K),

 R_s : solvent recovery (%),

R_r: reflux ratio,

 $L_{S(NS)}$: latent heat of solvent (nonsolvent) (MJ/ton), C_E : cost of energy (ϵ /MJ), C_{waste} : cost of plastic waste (ϵ /ton), M_{waste} : mass of plastic waste (ton),

E_e: extraction efficiency (%).

The cost of the extraction processes are calculated based on solvent recovery rates (R_c) varying from 0% until 100%. Since the recovered solvent is used again in the process after distillation. its purity plays a crucial role in the extraction efficiency. Therefore, the reflux ratio (R_r) is taken as 2:1 liquid:distillate for both processes and energy consumption is calculated based on this assumption. In addition, solvent repeats boiling-condensation cycles in the Soxhlet extraction process, which is assumed as 10 cycles. In dissolution-precipitation, generally higher amounts of nonsolvent are used compared to solvent for a proper precipitation, thus the mass ratio of nonsolvent to solvent is considered as 3:1. Regarding the mass of solvent per mass of plastic waste, a 1:1 ratio is taken for both processes. Moreover, since the cost of plastic waste (Cwaste) affects the cost of the extraction process substantially, 3 different plastic waste prices are chosen: -100, 200 and 400 €/ton are considered based on current market prices for the different stages in recycling, respectively plastics with gate fee, sorted plastics and sorted and cleaned plastics. These numbers are based on the situation in Belgium in 2019 based on expert judgment. These different stages are relevant as it will be a crucial choice for additive extraction processes to identify the best stage in the waste value chain to source the plastics.

The potential cost for both extraction processes is calculated at 50% and 100% extraction efficiency and these values are compared with the price of virgin plastic and virgin additive per ton (it is assumed that the additive is recovered as well) to be able to assess the potential economic benefit of each process (Fig. 4.1). The mass of additives is taken based on their typical concentration in plastics as indicated in Table 2.1. For example, the mass of phthalate plasticizers, antioxidants (Irganox 1076 and Topanol CA) and slip agents (erucamide) is assumed as 20, 1 and 3% w/w, respectively

these calculations, then it is unlikely for this process to become competitive at all, even on the long term.

According to Fig. 4.1, the assessment of the solid-liquid extraction and the dissolution-precipitation processes have different conclusions in terms of potential economic profit. In the bestcase scenario which is at 100% extraction efficiency with -100 ϵ /ton plastic waste, the solid-liquid extraction process has economic benefits even without solvent recovery, whereas the dissolution-precipitation process needs to recover at least 70% of the solvent. In the worst-case scenario which is at 50% extraction efficiency with 400 €/ton plastic waste, the Soxhlet extraction process requires almost 100% solvent recovery, while dissolutionprecipitation cannot become economically feasible. In fact, it is important to note that the plastics should be equally clean after both treatments in order to make a proper comparison. This basic assessment shows that the dissolution-precipitation can only become competitive if it is highly efficient in recovery of polymer (and eventually also the additives) and also if proper medium recovery processes are developed. This is not unlikely, however, it seems that there is a long way to go for this process. On the other hand, this analysis, within all its limitations and assumptions, shows that the solid-liquid extraction process has a promising economic potential despite of the limitations from a technical perspective. These limitations were especially related to highmolecular-weight components, but optimizing process parameters such as particle size and swelling conditions for the polymer might solve such diffusion limitations.

4.3. Life cycle assessment

The removal of additives from plastic waste is an important step towards closed-loop recycling in a sustainable circular economy. Therefore, a suitable extraction method should preferably not only be profitable from an economic perspective but also be beneficial from environmental perspective. For this reason, a screening life cycle assessment (LCA) using the OpenLCA software is performed (with the Recipe Endpoint (H) methodology) for both the solidliquid extraction and the dissolution-precipitation case studies. The Environmental Benefit is calculated similarly to the cost of the process as seen in Eq. (4.2), but in this case the impact is expressed in ecopoints per ton plastic treatment (points/ton). Data for the calculations were obtained from the Ecoinvent Database v3. Also in this case, we not only applied the "zero burden assumption", meaning that we did not allocate environmental impact to the waste stream, but we also excluded factors such as logistics, other pretreatments, etc. Again, this is thus a very best-case scenario.

Environmental benefit of the process =
$$\begin{bmatrix} \left[\left(EP_{S(NS)} \times M_{S(NS)} \right) \times (1 - R_S) \right] + \left[\left(M_{S(NS)} \times c_p \times \Delta T \times EP_E \right) + \left(M_{S(NS)} \times L_{S(NS)} \times EP_E \times R_S \times R_r \right) \right] - \\ (EP_A \times M_A) - (EP_{waste} \times M_{waste}) \end{bmatrix} / E_e$$

$$(4.2)$$

where,

 $\text{EP}_{S(NS)}\text{:}$ ecopoints of solvent (nonsolvent) (points/ton),

M_{S(NS)}: mass of solvent (nonsolvent) (ton),

 c_p : specific heat capacity of solvent (nonsolvent) (MJ/ton K),

 Δ T: temperature difference between the boiling point of solvent and RT (293.15 K) (K),

 R_s : solvent recovery (%),

R_r: reflux ratio,

L_{S(NS)}: latent heat of solvent (nonsolvent) (MJ/ton),

EP_E: ecopoints of energy (points/MJ),

EP_A: ecopoints of energy (points/MJ),

M_A: mass of additives incorporated into plastics (ton),

EP_{waste}: ecopoints of plastic waste treatment (points/ton),

Mwaste: mass of plastic waste (ton),

E_e: extraction efficiency (%).

Based on Eq. (4.2), the ecopoints per ton of plastic treatment are calculated for both the solid-liquid extraction and dissolution-precipitation case-study at 50% and 100% extraction efficiencies by varying the solvent recovery from 0% until 100%. The results are shown in Fig. 4.2 together with the environmental impact of the production of virgin plastic as a reference value.

As seen in Fig. 4.2, solid-liquid extraction might be more environmentally friendly compared to dissolution-precipitation. For example, even at 100% extraction efficiency, at least 50% of the solvent should be recovered in the dissolution-precipitation case to have a similar environmental impact compared to virgin plastic production. Under the same circumstances, no solvent recovery is needed in the case of Soxhlet extraction to equalize the environmental impact to virgin plastic production. This is explained by the



Fig. 4.1. Cost per ton plastic treatment (€/ton) versus solvent recovery (%) graphs at 100% and 50% extraction efficiencies with different plastic waste prices for (a) Solid-liquid extraction (based on Soxhlet extraction) (b) dissolution-precipitation.



Fig. 4.2. Ecopoints per ton plastic treatment (points/ton) versus solvent recovery (%) graphs at 100% and 50% extraction efficiencies for (a) Solid-liquid extraction (based on Soxhlet extraction) (b) dissolution-precipitation.

use of high amounts of solvents with high environmental impact during the dissolution-precipitation process. For example, the ecopoints of THF which is used as a solvent in dissolutionprecipitation are more than double of the ecopoints of DCM which is used in the solid-liquid extraction process. Obviously, there is still a lot of room for optimization in both processes. These calculations show that there is a chance for these solvent-based techniques to become competitive, if further research and development is performed within this topic.

5. Concluding remarks & perspectives

Solvent-based extraction techniques show a great potential towards upgrading the plastics waste and making them suitable towards closed-loop recycling. In order to design a proper solvent-based polishing technique, solubility and diffusivity are key to predict the extraction performance. Also, it is essential to make a clear classification of additives based on their physical properties. Furthermore, the extraction conditions such as the type of solvent, temperature and pressure, among others play an important role to design these processes. Therefore, in addition to conventional solid-liquid extraction methods, specific variations of these technologies working with supercritical solvents, microwaves, assisted by pressure, etc. are also being considered. Each of these processes have their specific strengths and weaknesses. For example, the popular SFE technique does not result in high extraction yields for highly polar additives such as for phenolic antioxidants due to the low polarity of scCO₂, yet this might be solved by adding a more polar solvent as a modifier. In MAE, a polar/apolar solvent mixture is needed to be effective to allow microwave heating in the polar phase and polymer swelling in the apolar phase.

Beside the selection of a potential process in terms of extraction efficiency, economic feasibility and environmental impact are crucial to move to higher TRL's. Therefore, two case studies were explored towards their economic and environmental sustainability. According to our screening, solid-liquid extraction case study has economic advantages compared to dissolution-precipitation, even without solvent recovery and for the most expensive plastic waste streams (400 ϵ /ton). Similarly, in terms of environmental impact, solid-liquid extraction has a lower environmental impact compared to dissolution-precipitation in which high amount of solvents with higher environmental impact are used. Solvent choice should thus be based on applicability, e.g. in order to swell the plastics efficiently, as well as on their recoverability, e.g. by distillation, and their net environmental impact during virgin production.

Extraction methods should be specifically tuned based on type of additives and plastics. Although obtaining high extraction yields is theoretically possible and much of the current research has focused on the solvent-polymer-additive interactions, there is a significant lack of process optimization to make these techniques potentially environmentally and economically feasible in the circular economy. For example, regarding plastic industry solid-liquid extraction processes are less frequently used in pilot-scale applications compared to dissolution-precipitation, but based on our assessment they have a higher chance to become competitive if diffusion limitations are overcome. On the other hand, dissolution-precipitation is a widely used technique, but it is not feasible in terms of environmental and economic aspects. It is thus important to note that unless the process allows a highly efficient extraction of additives by using low amounts and relatively cheap solvents at moderate conditions, the process might not be applicable, even in the long term. Concluding, we suggest to perform more research on process optimization and upscaling of solvent-based techniques, including medium recovery, reactor design, search for new and greener solvents, etc. to increase their potential to further unlock the circular economy for plastics.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2020.01.003.

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