Legacy additives in a circular economy of plastics: Current dilemma, policy analysis, and emerging countermeasures

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ABSTRACT

Plastics are widely used because of their diverse mechanical and physicochemical properties, however, many plastic products can only achieve their specific characteristics if mixed with additives, like flame retardants, stabilizers, and plasticizers. Some of the formerly used plastic additives, however, are in the meantime evaluated as substances of very high concern (SVHC) or even persistent organic pollutants (POP) and are referred to as “legacy additives”. Therefore, the improper disposal of legacy plastic waste as well as the recycling and reuse of such can lead to continuous circulation of harmful additives into the environment, threatening plant and animal life, and human health. The environmental threats posed by hazardous additives have been addressed by international regulations like the Registration, Evaluation, and Authorization of Chemicals (REACH) regulation and the Stockholm Convention. They set thresholds for hazardous chemicals including some legacy additives, which regulate trading and waste management, and aim at a fast phase out of hazardous compounds. At the same time, governmental, non-governmental and industrial players support a circular economy of goods including plastics, which resulted and will further result in increasing recycling quotas for waste plastics. When it comes to plastics containing legacy additives a conflict of objectives may arise, namely saving polymeric resources versus phase-out of hazardous compounds. This review paper discusses legacy additives in plastic waste streams, their end-of-life treatment options related to legislation covering these additives and links between regulation and waste management.

1. Introduction

Plastics have become indispensable in everyday life, and recent decades can even be regarded as the ‘age of plastics’. We wake up listening to our plastic alarm clock, brush our teeth with a plastic brush, eat food wrapped in plastic, and wear synthetic clothes, indeed, finding any part of our daily life not influenced by plastics is difficult. Current plastic production exceeds 335 million tonnes worldwide (2017 data), and growth is predicted to continue (Plastics Europe, 2018). After use, all plastic products become waste, however, the lifespan of different products covers a wide range (Geyer et al., 2017; Kalmykova et al., 2015; Barnes et al., 2009). For example, plastics used in construction (e.g. polyvinyl chloride (PVC) window frames) are expected to last decades, whereas plastics used as food packaging may be in use for as little as a few minutes (e.g. takeaway coffee cups). Furthermore, many plastic products are actual mixtures of plastics and other substances such as glass fibres, which makes their recycling and disposal issues even more challenging (Job, 2015; Knappich et al., 2017; Oliveux et al., 2015; Knappich et al., 2019).

In 2014, 59 million tonnes of plastics were produced in the EU and 25.8 million tonnes of plastic waste were generated (EU 28+2, including Norway and Switzerland) (PlasticsEurope, 2016). Short-lived products such as food packaging account for 63% of this waste stream, the remainder originates from building and construction (∼6%), the automotive industry (∼5%), agriculture (∼5%), the disposal of waste electric and electronic equipment (WEEE) (∼5%), houseware and leisure items (∼3%) and others, like furniture or medical waste (∼13%) (European Commission DG ENV, 2011). The handling with plastic waste differ within the EU. While in the northern countries with a landfill ban (e.g. Sweden, Germany, Denmark) the recycling rates amount to up to 50% (while the rest is incinerated), in the southern and eastern countries (e.g. France, Italy, Bulgaria, Hungary) still 30–80% of plastic waste are landfilled (Plastics Europe, 2018). Globally, most plastic waste goes to landsfills (40%), another 32% finds its way into the environment through illicit means such as unauthorised dumping, and ∼28% is recovered by recycling or destroyed by incineration.
Substances of very high concern used as plastic additives and their regulations (ppm = parts per million, phr = parts per hundred rubber).

<table>
<thead>
<tr>
<th>Additive</th>
<th>Purpose</th>
<th>Common content</th>
<th>Regulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexabromocyclododecane (HBCD)</td>
<td>Flame retardant</td>
<td>1%–1.2% in polystyrene (EPS, XPS)</td>
<td>x</td>
</tr>
<tr>
<td>Tetrabromodiphenyl ether</td>
<td>Flame retardant</td>
<td>in polystyrene (HIPS)</td>
<td>x</td>
</tr>
<tr>
<td>Pentabromodiphenyl ether</td>
<td>Flame retardant</td>
<td>in ABS, HIPS, PA</td>
<td>x</td>
</tr>
<tr>
<td>Hexabromodiphenyl ether</td>
<td>Flame retardant</td>
<td>in ABS, HIPS, PA</td>
<td>x</td>
</tr>
<tr>
<td>Decabromodiphenyl ether (DecaBDE)</td>
<td>Flame retardant</td>
<td>in ABS, HIPS, PA</td>
<td>x</td>
</tr>
<tr>
<td>Polybrominated biphenyls (PBBs)</td>
<td>Flame retardant</td>
<td>in ABS, HIPS, PA</td>
<td>x</td>
</tr>
<tr>
<td>Diethylhexyl phthalate (DEHP)</td>
<td>Plasticiser</td>
<td>in PVC</td>
<td>x</td>
</tr>
<tr>
<td>Dibutyl phthalate (DBP)</td>
<td>Plasticiser</td>
<td>in PVC</td>
<td>x</td>
</tr>
<tr>
<td>Diisobutyl phthalate (DIBP)</td>
<td>Plasticiser</td>
<td>in PVC</td>
<td>x</td>
</tr>
<tr>
<td>Cadmium compounds</td>
<td>Stabiliser</td>
<td>in PVC</td>
<td>x</td>
</tr>
</tbody>
</table>

* The production of these substances was stopped decades ago, but they can still be found in old stocks as well as in recycled products.

In this review article, we describe some different types of hazardous substances (Marvin et al., 2011; Linares et al., 2015; Zarean et al., 2016; Fernández et al., 2011).

The indiscriminate disposal of plastics carries multiple risks, because many plastic products contain additives that modify their physico-mechanical properties, e.g. fire retardants and stabilisers. Previously used additives include chemicals now declared as "substances of very high concern" (SVHC, a list of critical chemicals according to European Chemicals Agency (ECHA)) or even as "persistent, organic pollutants" (POPs, according to UN Stockholm Convention), including polybrominated diphenyl ethers (PBDEs), phthalates and hexabromocyclododecane (HBCD). When plastics are discarded into the environment, these additives can be emitted through different routes (e.g. abrasion, degradation, leaching) into the environment, where they can be taken up by animals, humans and plants and eventually enter the food chain (Bouwmeester et al., 2015; Hahladakis et al., 2018). Several studies have demonstrated the adverse effects caused by uptake of these substances (Marvin et al., 2011; Linares et al., 2015; Zarean et al., 2016; Fernández et al., 2011).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Purpose</th>
<th>Common content</th>
<th>Regulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPS, XPS in insulation</td>
<td>Flame retardant</td>
<td>in polystyrene (EPS, XPS)</td>
<td>x</td>
</tr>
<tr>
<td>HIPS, PA, PBT, PA</td>
<td>Flame retardant</td>
<td>in polystyrene (HIPS)</td>
<td>x</td>
</tr>
<tr>
<td>ABS, HIPS, PA</td>
<td>Flame retardant</td>
<td>in polystyrene (ABS, HIPS, PA)</td>
<td>x</td>
</tr>
<tr>
<td>PVC, ABS, PA, PO</td>
<td>Flame retardant</td>
<td>in polystyrene (PVC, ABS, PA, PO)</td>
<td>x</td>
</tr>
</tbody>
</table>

In this sense, climate actions, in which recycling of plastics plays an important part, and the regulation of SVHCs/POPs are incompatible, yet both are essential for a circular economy. One solution to this discrepancy is the development of recycling techniques, which enable the separation and safe destruction of such substances.

Numerous reviews describe the types of additives found in plastics, how they enter the environment especially those present in WEEE, and the current disposal methods for these plastics. For example Buekens et al. describe the amount and the compositions of WEEE (i.e. their polymer and additives contents) and the legal requirements for treating this waste in different countries. Furthermore Buekens and Sevenster give an overview of recycling techniques for WEEE, including the CreaSol® Process (Buekens and Sevenster, 2010). Bakhiyi et al. focus on hazardous compounds found in WEEE. Here again compounds with migration potential and their paths worldwide, especially those originating from WEEE, are listed, along with their potential effects on human health (Bakhiyi et al., 2018). Hahladakis et al. give a broad overview of plastic packaging additives with migration potential to food or to the environment. They also point out the release of some potentially toxic compounds via unsound recycling techniques in undeveloped regions and summarise the EU’s legal handling of recycling plastics containing these substances (Hahladakis et al., 2018). Král et al. propose more qualitative than quantitative recycling, where hazardous substances are removed in ‘clean cycles’. They suggest that final sinks for these hazardous substances should be identified or developed to avoid their further circulation of these (Král et al., 2013). All of the aforementioned authors recommended better policy in treating waste containing hazardous substances and improvement of sound disposal strategies.

In this review article, we describe some different types of hazardous...
additives found in plastics, how they are regulated and, how their regulation influences the effectiveness of recycling targets. Finally, we describe potential solutions to harmonise the need for strict regulations and ambitious recycling policies on a European and global scale. After a general view on these issues the example of BFRs is discussed in greater detail.

2. Harmful additives in plastics

2.1. Overview

Additives are substances mixed with a base polymer during manufacturing to improve processability and modify the physical or chemical properties of the final plastic material. Additives include flame retardants, stabilisers, phthalates, antioxidants and emulsifiers (Zweifel et al., 2009). After decades of additive use, attention has now turned to the potential environmental impact of additives in plastic waste, which has in turn led to the introduction of more restrictive legislation up to and including complete bans on the production, manufacture and disposal (Hahladakis et al., 2018; Harrad, 2015).

Additives may be present in a polymer as substances by themselves or may have reacted in the polymer matrix. In the first case, the additives are not designed to react covalently with polymer molecules, but instead they interact via weaker non covalent bonds (Alaee et al., 2003). Accordingly, these weakly-bound additives can leach into the environment during the normal use of plastic materials containing them, but especially during the degradation of plastics after improper disposal (Watanabe, 2003). Whereas leaching only through molecular diffusion appears to be very slow (half-life $10^3–10^9$ years at ambient temperature) major emission originate from wear-and-tear and pulverisation (Sun et al., 2016). Depending on their chemical structure, these substances may be toxic and may become enriched in environmental compartments because of their persistence and bio accumulative properties, thereby posing a threat to living organisms. In addition they may degrade into smaller and likely toxic persistent and bio-accumulative molecules (Sun et al., 2016; Khaled et al., 2018; Pivnenko et al., 2017; Birnbaum and Staskal, 2004). Reactive additives are inert and do not leach into the environment unless they are not fully polymerised during production, as is the case with tetramobisphenol A (TBBPA) in epoxy thermosets (Abdallah et al., 2008). In this review, we discuss three examples of plastic additives that may have adverse effects on environment, when they leak from plastics.

2.2. Brominated flame retardants

Brominated flame retardants (BFRs) are hydrophobic or reactive and halogenated additives used during the manufacture of fire-resistant plastic products (see Table 1). Today more than 75 different BFRs are in place and a few are restricted. New BFR types are brominated polymers replacing HBCD and reactive BFRs (Birnbaum and Staskal, 2004). Although they cannot prevent ignition, they can delay the spreading of flames by mechanisms such as endothermic degradation and thermal shielding (The Handbook of Environmental Chemistry, 2011). BFRs work by releasing bromine radicals at high temperatures, which interrupt flame propagation by absorbing reactive hydrogen atoms and preventing their interaction with oxygen, which would otherwise lead to the formation of high-energy oxygen and hydroxyl radicals (Zweifel et al., 2009).

BFRs, whether non-reactive or non-polymeric, must fulfil two main requirements. First, they must be compatible with the polymer to which they are added (i.e. they must not interact to the extent that they influence its foreseeable mechanical properties). Second, they must remain stable for the anticipated lifespan of the plastic product (The Handbook of Environmental Chemistry, 2011). However, these exact properties are also responsible for their negative impact on the environment: their lack of covalent bonding promotes leaching, and their stability causes them to be persistent, and some may bio-accumulate (The Handbook of Environmental Chemistry, 2011). Because the BFRs bind to polymers i.a. via hydrophobic interactions, they can also be released into the environment during production, (re-)processing, transportation, usage, storage and disposal (Hahladakis et al., 2018; UNEP, 2011). Emissions during manufacturing are now a minor issue because the BFRs, which are now declared as POPs, are no longer approved (c-PentaBDE 1997 EU/2004 USA, China; c-OctaBDE 2004; HBB 1976). But, however, the unregulated recycling of existing products, and decomposition into lower-molecular weight brominated molecules (PBDEs) in landfills, provides a possible route for BFRs to enter the environment (UNEP, 2017a). As much as 1818 kg of PBDEs are released into the environment every year globally, especially at dismantling sites in Asia (Sun et al., 2016). The effects on human health by up taking, for example through food and air, of such are diverse. For PBDE adverse effects i.a. on the fertility and impair on neurodevelopment has been shown, based on experimental studies on animals and epidemiological observations on humans (Linares et al., 2015). However, the degree of dissemination of BFRs into the environment depends on their physical and chemical properties. In the case of PBDEs the ratio of bromination decides over the degree of volatility. Lower brominated PBDEs (e.g. BDE 47), known to have higher vapour pressures than higher-molecular-weight brominated congeners, are found in ambient air in much higher concentration then higher brominated PBDEs (e.g. BDE 209), which have extremely low volatility (Birnbaum and Staskal, 2004). The environmental occurrence of HBCDs as a non-aromatic cyclic alkane depends on the water solubility of the 16 different stereoisomers with α-, β- and γ-HBCD forming the major part of the commercial mixture (α: 10–13%, β: 1–12%, γ: 75–89%) (Covaci et al., 2006; Birnbaum and Staskal, 2004). When materials containing this mixture are produced and processed at temperatures greater than 160 °C, rearrangement of the stereoisomers can occur (Covaci et al., 2006). Although γ-HBCD is present in higher concentrations in commercial mixtures, α-HBCD is found in higher concentrations in biota because of its greater solubility in water (α-HBCD 48.8 µg/L and γ-HBCD 2.1 µg/L) or because of rearrangement (Covaci et al., 2006).

2.3. Plasticisers

Plasticisers improve the flexibility of plastics by increasing the distance between the polymer chains, thereby loosening the dipolar forces and allowing the chains to slide against each other more easily (Erythropel et al., 2016; Wypych, 2012). The most common plasticisers are phthalates, which are used in 90% of PVC-P products (2008) (Erythropel et al., 2016). In the past, di-2-ethylhexyl phthalate was the most widely used plasticiser in the EU, with 595,000 tonnes produced in 1997 (Western Europe) and a decreasing trend in subsequent years (2007: approx. 20,000 tonnes in Western Europe) (ECHA, 2010). As previously mentioned, the weak interactions with the polymer enable these additives to leach into the environment, and several studies have shown that humans can take up phthalates via the air, or dust and by direct contact with products (Net et al., 2015), but mostly via the consumption of foods and beverages containing these additives (Larsson et al., 2017; Wittassek et al., 2011; Fromme et al., 2013). The Federal Environment Agency of Germany (Umweltbundesamt) found especially high concentrations of DEHP in tinned food (fish: 1370 µg/g; vegetables: 500 µg/g) (Umweltbundesamt, 2012). Some phthalates are thought to act as i.a. endocrine disruptors, with effects on testicular and ovarian development based on experimental studies on rodents (Zarean et al., 2016). Because of their negative impacts on the environment and humans, several regulatory authorities have banned certain phthalates, particularly in toys (EU:2005; USA: 2008; Canada: 2010) (Erythropel et al., 2014). Currently, four phthalates (DEHP, BBP, DBP, DIBP) are on the candidate list of SVHCs in Annex XIV of the REACH Regulation (European Commission, 12/17/2008).
2.4. Stabilisers (exemplary on heavy metals)

Stabilisers protect plastic materials from thermal degradation during processing or use. Heat, illumination, and mechanical stress can trigger the scission of polymer chains and hence the formation of hydroperoxides. The hydroperoxides subsequently degrade into radicals and destroy other polymer chains (Murphy, 1996; Bilitewski et al., 2012). This process of autoxidation results in embrittlement, melt-flow instability, loss of tensile properties and, discoloration of the plastic material. Stabilisers are antioxidants, which interrupt the degradation process by directly protecting the polymer chains or by eliminating the hydroperoxides. PVC is particularly sensitive to heat. In the past, PVC was often stabilised by adding lead-based (pipes, cables in EEE) or cadmium-based (building profile) compounds (Murphy, 1996). However, exposure to such heavy metals can cause severe health issues including bone softening and kidney failure following exposure to cadmium, and learning difficulties in children exposed to lead (Rodríguez and Mandalunis, 2018; Wani et al., 2015). Metal-based additives can migrate into the environment during the manufacture, use and disposal of PVC products, and the concentrations of heavy metals in soils are rising. Humans are exposed to cadmium primarily through food, whereas most lead is absorbed following contact with contaminated soil and dust (Alloway, 2013). European regulations were introduced for cadmium in 1991 (Regulation 91/338/EEC) and for lead in 2015 (Regulation 2015/628), and a voluntary phase-out of lead and cadmium based additives in industry (Viny/2010) has reduced the amount that enters the environment (Bilitewski et al., 2012; Buekens and Sevenster, 2010; European Commission, 4/22/2015; Bächter and K., 1995).

3. Current end-of-life options for plastics containing legacy additives

After plastics reached the end of their service life, waste managers and traders decide whether collected plastics undergo incineration or recycling processes for reutilisation of the resources, or if less preferred end-of-life options are chosen, including landfill or environmentally unsound processing. Depending on the plastic type and their additives today several techniques (Fig. 1) are applied with different impacts on the environment, which are explained in the following.

3.1. Landfill

Several types of landfills exist: the best landfills are engineered and controlled, others are poorly engineered, the worst landfills are dumps with no control and are often illegal. Although landfilling is the least-preferred method for the disposal of plastic waste, worldwide most of it ends up in dumps (40%) (World Economic Forum et al., 2016). However, poorly or uncontrolled landfills constitute a large threat to the environment. Hazardous substances (e.g. PBDEs), which are found in landfilled electronic scrap or demolition waste, can leach into the environment and contaminate soil and groundwater. Landfill leachate, which undergoes waste water treatment and is then directed into rivers, has been shown to contaminate fish and sediments with PBDEs concentrations as high as 3400 ng/g lipid weight and 1950 ng/g TOC (Weber et al., 2011; Oliaei et al., 2002). Consequently PBDEs can be found in humans such as in mothers milk (Harrad, 2015; Linares et al., 2017), in 2015 (Regulation 2015/628), and a voluntary phase-out of lead and cadmium (Weber et al., 2011; Oliaei et al., 2002). Consequently PBDEs can be introduced for cadmium in 1991 (Regulation 91/338/EEC) and for lead in the environment through i.a. dust. During the use phase of plastics, additives can be emitted through i.a. leaching, abrasion. After the use phase the plastics are collected and sorted. Several options for the waste management are practised today: export, landfill, incineration and recycling. At each step, additives can be released into the environment. While at environmentally unsound processing and landfill these additives can be enriched in soil, water and organisms through i.a. leaching, during incineration hazardous pollutant can be formatted. Through recycling critical additives stays in the economic cycle, if not separated.

Fig. 1. Fate of plastics and their containing critical additives: already at the stage of compounding, additives can be released into the environment through i.a. dust. During the usage phase of plastics, additives can be emitted through i.a. leaching, abrasion. After the use phase the plastics are collected and sorted. Several options for the waste management are practised today: export, landfill, incineration and recycling. At each step, additives can be released into the environment. While at environmentally unsound processing and landfill these additives can be enriched in soil, water and organisms through i.a. leaching, during incineration hazardous pollutants can be formatted. Through recycling critical additives stays in the economic cycle, if not separated.
combined heat and power mode (CHP), however, significant differences in their performance where revealed, mainly related to the average size and to the availability of a heat market (Grosso et al., 2010; Hulgaard and Vehlow, 2010).

Finally, incineration constitutes an environmentally friendlier alternative to landfilling, because waste is not spread in the environment, nonetheless, resources are depleted by this alternative.

### 3.3. Recycling

Recycling, according to the EU, means “any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic materials but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations” (European Commission, 11/19/2008). In general two options exist for recycling plastics: material recycling and feedstock recycling. Material recycling implies pre-treatment steps e.g. pre-sorting or pre-washing, in where foreign materials (e.g. other polymers) and impurities (e.g. food residues) are mostly removed. The sorted fraction is then shredded and re-melted with the addition of auxiliary materials (stabilisers, antioxidants, etc.) in an extruder. With this recycling technique the material or the macromolecule remains intact, consequently, polymerisation energy will be conserved. In addition to the lower recycle quality, which is achieved through remelting, semivolatile hazardous additives like flame retardants plasticizers and stabilizers can only be removed via imprecise pre-sorting using density separation, X-ray fluorescence (XRF) or near-infrared (NIR) spectroscopic sorting technologies, causing a high rejection rate for plastics with increased levels of legacy additives (Arends et al., 2017). Legal thresholds might be reached through dilution practices i.e. mixing with virgin or BFR free material, however, this practice violates certain POPs regulations that prohibit mixing of hazardous and uncontaminated materials (UNEP, 2017b). By contrast, feedstock recycling consumes large amounts of energy (up to 1100 °C) through decomposing the polymers into smaller units such as monomers and oligomers. Depending on the process (pyrolysis, gasification, etc.) different products can be generated from polymers. Coke, oils and gases can be either used as fuel or as raw materials for the synthesis of new polymers or solvents (Ragaert et al., 2017). With this recycling route hazardous substances such as those previously mentioned are destroyed, through specific measures the formation of dioxins and furans is avoided (Martens and Goldmann, 2016). Feedstock recycling, however, is only considered profitable if very substantial amounts of plastic waste are available (Hopewell et al., 2009). A promising approach constitutes the debromination of flame retarded plastics by hydrothermal treatment technology (Uddin et al., 2003). Unsorted plastic mix can be treated under subcritical or supercritical conditions, in where the carbon-carbon bond is destroyed. Through hydrothermal cracking, hydrolysis, free radical reaction, nucleophilic substitution, and cyclization reactions the polymers are decomposed into monomers (Zhao et al., 2019). In comparison to feedstock recycling this technology has a shorter reaction time and does not use a catalyst, which makes the procedure more economic viable (Uddin et al., 2003). So far, this technology is only proven at academic environment.

The decision, of which recovery method for plastic waste is applied, depends on economic, ecological and technical viability aspects. Although the EU’s 7th Environmental Action Programme (EAP) calls for reutilisation of plastics, incineration can be more reasonable if the energy consumption for recycling exceeds the caloric value of the polymer or if the environment is threatened by recycling through legacy additives. Nevertheless, recycling generally leads to reduced energy consumption and reduced CO₂ emissions (Tyskeng and Finnveden, 2010).

### 3.4. Export

The transboundary movement of plastic waste is not a real end-of-life treatment option, since this is an intermediate step for final treatment, but is practised especially by high income countries (Brooks et al., 2018). The export of plastic waste is carried out, when the country does not have the infrastructure or facilities needed for the treatment or when the treatment in the country of origin is not attractive for economic reasons (European Parliament, 6/14/2006). Then such waste is transported to regions e.g. with lower labour costs, legally or illegally. Although the transboundary movement of plastics containing legacy additives to developing regions is forbidden, through changes in declaration e.g. WEEE into used EEE or through insufficient controls, such waste still lands in regions with less developed waste management systems (Baldé et al., 2017). In 2012, it is estimated that 1.3 million tonnes of WEEE left the EU undocumented (Colley-Jones et al., 2020). Consequently, valuable materials are extracted through simple techniques like melting and open burning, in where legacy additives might leak into the environment (Breivik et al., 2011).

### 4. Circular economy of plastics

In 1972 the Club of Rome published a study on the availability of resources under a scenario of increasing world population and consumption. Defining the limited growth, this study predicted the collapse of the nature-society system, if the world continues to increase the production of goods (Meadows, 1972). 47 years after publication of this report the world’s economy is still dominated by the linear ‘take, make and dispose’ model. However, recent annual consumption of resources exceeds the regeneration capacity of the Earth by a factor of 1.5 and jeopardise the supply of vital resources for future generations (Wijkman and Skanberg, 2015). Therefore, current societal visions propose the transition of the world’s (linear) economy into a circular economy, which implies the reutilisation of these materials after their end of life and extend their use as long as possible to gain the maximum benefit of the manufactured good (Korhonen et al., 2018). A more recent study released by the Club of Rome in 2015 show that in a circular economy carbon emissions can be saved (~70%), new jobs can be created (cutting unemployment rate by 1/3) and the gross domestic product can be increased (+1.5%) (Wijkman and Skanberg, 2015). A circular economy can be realised with different approaches in multiple fields of economics (Yuliyu Kalmykova et al., 2018). In here, approaches for a circular economy for plastics containing legacy additives are discussed.

In response to the growing public awareness of the large amount of pollution through plastics in the environment and the associated waste of resources, governments, NGOs and industry have launched different environmental programmes for a responsible utilisation of the earth’s raw material (European Commission, 2015; Ellen MacArthur Foundation, 2019). For example, the industry committed in VinylPlus to increase the recycling rate and substitute critical additives or in Plastics 2030 to re-designing products and production processes to minimise the plastic waste. The Governments have set binding
recycling targets, such as recycling rates, through regulations (European Commission, 5/30/2018).

A circular economy of plastics, however, implies a high level recycling as the circularity approach addresses target markets in the field where the plastics are initially used. That includes the production of recycled polymers with intact chain lengths and a high purity with respect to foreign materials (non-polymeric) and foreign plastic types. In these cases physical and mechanical properties close to those of virgin materials can be achieved. Down-cycling strategies, by contrast, reduce the quality of materials, which make them suitable for use only in low-quality applications. This would add only one or two additional life cycles to a product. However, in the case of recycling plastic containing SVHCs or POPs, chemical purity (i.e. the compliance of recycled plastic with given threshold limits of SVHC and POPs) becomes an additional requested property.

In the following paragraphs, current regulations for the handling of plastic waste, hazardous substances and how they effect a circular economy for plastics, are explained

5. Legislation covering plastics recycling

5.1. EU directives and regulations on waste

When the European Community was founded in 1957, there were no intentions to regulate environmental matters, however, in 1973 the first environmental action program was agreed upon (EAP1), resulting in the introduction of legislation covering environmental issues (Goodship, 2012). One key instrument was Directive 2008/98/EC (Waste Framework Directive), which has been supplemented and revised numerous times since its introduction. This directive established a waste hierarchy, focusing on the prevention of waste to limit subsequent issues with disposal (Fig. 1). Human health and environmental protection are considered paramount, in particular the protection of water, air, soil, plants and, animals, without negatively affecting the landscape (Goodship, 2012; European Commission 11/19/2008). The current version of the directive sets recycling targets of 55% by 2025 for household waste (including compostable waste), 70% by 2020 for construction and demolition waste and 60% by 2025 for plastic packaging, for all member states (European Commission 11/19/2008; Goodship, 2012; European Commission 5/30/2018).

With the simultaneous introduction of the Directive 2002/96/EC (WEEE Directive) and Directive 2002/95/EC (RoHS Directive) in 2003, the handling of electric scrap was regulated. Since their introduction both directives have been constantly revised to keep pace with the rapid development of the information and communication technology sector. At the time of this writing Directive 2012/19/EU (WEEE2) and Directive 2011/65/EU (RoHS2) are in force.

The WEEE Directive set out laws to minimise the amount of WEEE produced in Europe, and is currently divided into six categories, inter alia, large/small EEE equipment, small information technology and telecommunication equipment, and screens/monitors. WEEE2 also governs collection (45–65%) and recovery rates (55–85%, depending on category) for such equipment (European Commission, 7/4/2012).

The RoHS Directive (restriction of the use of certain hazardous substances in electrical and electronic equipment) implies (with exceptions) the ban of EEEs containing lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBBS) and PBDEs. This group of chemicals should not exceed 0.1% by weight in EEEs, or 0.01% by weight in the case of cadmium compounds (European Commission, 9/25/2010).

Whereas EU directives allow some freedom amongst member states in terms of implementation, EU regulations are binding legislative acts that are immediately applicable and enforceable by law in all member states. EU Regulation 1907/2006/EC concerning REACH was enacted in 2006, which focuses on the protection of human health and the environment. REACH demands physicochemical, toxicological and ecotoxicological data for each chemical with an annual production or trading quantity exceeding 1 tonne (Williams et al., 2009). The ECHA ensures that all manufacturers and importers comply with REACH and that consistent rules are applied in all member states. REACH requires dossiers (chemical safety report, safety data sheet, etc.) that provide information related to the health and safety, environment risks and, measures for the management of risks of chemicals. The ECHA evaluates the dossiers in two steps: the dossiers are first reviewed for completeness (EU requirements) and then in relation to human and environmental safety (Goodship, 2012). Chemicals defined as SVHC, which includes CMR (carcinogenic, mutagenic, reproductive toxic) and PBT (persistent, bio-accumulative, toxic) substances, are added to Annex XIV (authorisation list). Accordingly information must be provided for products (> 1 t/a), in which these substances exceed the limit of 0.1% (w/w). The applicant is granted authorisation for a limited period only when (a) there is proof that no safer alternative is available and (b) all possible controls have been performed. The process of authorisation is complex and each registration is evaluated individually (Williams et al., 2009). This regulation is applied strictly. In the event of non-compliance, e.g. failure to register, the manufacturer or importer is not allowed to place certain chemicals on the market in the EU. Competent authorities from each member state can request the restriction of a chemical, if its use within the EU represents an unacceptable risk for human health and/or the environment. Therefore the applicant must review any alternatives in terms of availability, feasibility and technical viability (Williams et al., 2009).

5.2. International treaties for the management of hazardous substances

At the international level, the production and trading of chemicals requires systems in which the properties of each substance, their potential risks, and safe handling procedures are summarised on a special form. To avoid conflicts between the legacy administrative and legal procedures developed by individual countries, the United Nations decided at the Rio Earth Conference in 1992 to develop a Globally Harmonized System for the Classification and Labelling of Chemicals (GHS) listing 16 danger classes. The GHS combines physicochemical data, health data and environmental risks, and communicates the potential risks to different target groups (workers, consumers, transportation and first-aid staff). Chemicals are now labelled with universal pictograms depicting their associated risks. The UN adopted the GHS in 2002 and requested that participating nations apply it by 2008. The EU implemented the GHS in its own CLP regulations (Classification, Labelling and Packaging of Chemicals). The difference between CLP and REACH is that chemicals are classified and labelled in CLP, whereas they are evaluated and regulated in REACH (Umweltbundesamt, 2013).

One of the first international treaties aimed to prevent the widespread dispersal of hazardous substances in the environment was the Basel Convention on the Control of Transboundary Movements of Hazardous Waste and their Disposal (22 March 1989 resolution; 5 May 1992 implementation). At the current state in May 2018, 186 countries have signed up (excluding the USA) ratified the convention, and therefore agreed neither dump nuclear or industrial waste into oceans, nor dispose of that waste in third world or less-developed countries. The working groups of this treaty developed several technical guidelines for the environmentally-sound management of various waste streams, including marine littering, WEEE and POPs (UNEP, 2014). In June 2006 this Convention was adapted into Europeans law under Regulation (EC) No 1013/2006 (European Parliament 6/14/2006).

Following the 1992 UN Earth Summit held in Rio de Janeiro, where member nations agreed to develop an action plan to remove toxic chemicals from the environment or to minimise their effects, a binding global treaty was not ratified until 12 years later. This treaty was the Stockholm Convention on Persistent Organic Pollutants, which was developed according to proposals introduced at the Basel Convention. The Stockholm Convention was ratified on 17 May 2004.
(Vanden Bilcke, 2002). The main objective of the Stockholm Convention is to protect human health and the environment against POPs, which are ubiquitous (transported over long distances from source to remote areas), persistent (do not degrade for a long time), bio-accumulative (enrich in fatty tissue) and toxic (cause adverse effects to organisms). At the time of implementation, 12 substances were identified as POPs (the ‘dirty dozen’), PCBs, dioxins, furans, aldrin, dieldrin, endrin, dichlorodiphenylchloroethene, chlordane, hexachlorobenzene, mirex, toxaphene and heptachlor (Vanden Bilcke, 2002). Thus far (May 2018), 29 substances have been defined as POPs, and they are subject to three categories of regulations (Convention, 2019):

- Annex A: Substances that must be eliminated from the markets of the parties completely. Actions: ban of production and use, ban of import as a pure substance or as a mixture or as part of products.
- Annex B: Substances that must be restricted, but not banned, except for certain applications are possible.
- Annex C: Substances, including intermediates, produced unintentionally during chemical processes. Their formation is not manageable. In this case the occurrence of these substances should be minimised to the extent possible or prevented if technically feasible.

The Stockholm Convention also describes rules for the handling of old stock, and the transportation and waste disposal of listed substances (including mixtures, part of products) as well as reporting obligations (Convention, 2019). The EU adopted the Stockholm Convention into its own law on April 2004, with Regulation (EC) No 850/2004, also known as the POPs Regulation. Annexes I-V list the hazardous substances and their thresholds (European Parliament, 4/29/2004):

- Annex II: List of substances subject to restrictions.
- Annex III: List of substances subject to release reduction provisions.
- Annex IV: List of substances subject to waste management provisions.

In accordance with the Basel and Stockholm Conventions, an international definition of “low POP content” was agreed upon. Depending on the specific risk posed by individual POPs, a maximum safe concentration was determined for each chemical, and different levels were stipulated for waste. The convention states that substances that contain POPs concentration greater than the “low POP content” level must be destroyed or irreversibly transformed. If destruction is neither possible nor environmentally preferable, then an environmentally sound disposal method should be implemented. Substances containing POPs below the “low POP content” level are excluded from this regulation (UNEP, 2017b).

6. Effects of regulations and action programmes on plastic recycling

6.1. Effects of reach

Because recycling, i.e. the recovery of used materials is carried out for manufacturing new articles, in principle, recycled plastics fall under the purview of the aforementioned REACH registration process. Although some specific exemptions from the registration requirements exist for recycled plastics, these are repealed by the presence of SVHCs (Jepsen et al., 2012). In principle, this regulatory framework appears to counteract efforts to meet the recycling targets for plastics, given that SVHCs must not exceed the 0.1% (w/w) limit set by REACH guidelines. However, at non-compliance with REACH within a recycling process in cases where regulations have changed, recyclers can request a REACH authorisation, which involves a compliance process. The intended and positive effect of REACH, however, is a revision of recycling strategy to achieve a separation that is more effective and a removal of the banned additives. If separation and removal are not technically or economically feasible, recycling must cease and incineration or landfill must be chosen instead. A good example of the aforementioned scenario is the Vinyloop PVC recycling plant, which started production in 2002 in Ferrara, Italy. This plant had previously reported a plant capacity of more than 10,000 tonnes of PVC waste per year, including PVC containing banned phthalate plasticisers such DEHP (Patrick, 2005). Following the decision of the European Commission to include DEHP on the REACH authorisation list (Annex XIV) in February 2015, products containing this phthalate must not exceed the 0.1% DEHP threshold (European Commission, 2/17/2011). The company followed correct procedures and was granted REACH authorisation for the production of recycled PVC containing DEHP. However, criticism of this decision from governmental and non-governmental organisations led to the EU refusing to extend the authorisation beyond 2019. As a result, in June 2018, Vinyloop announced in a press release its shutdown (PlastEurope, 7/4/2018). Another example concerns lead compounds, which have been used as stabiliser in PVC. Lead compounds are now under review for the designation as a SVHC and might be restricted in applications with a limit concentration of 0.1%. If no exemption for recycling will be granted, PVC recycling, e.g. of window frames, could terminate. Accordingly, supporters of PVC recycling demand a permission of 1% lead content in recycled PVC products (Dutch National Institute for Public Health and the Environment, 2016).

6.2. Effects of POPs regulation

The POP directive sets “low POP content” thresholds, which, as previously stated, are defined separately for every substance, with different levels stipulated for waste and articles. This approach helps to prevent the re-entry of SVHCs into production cycles and consequently into new products. At the same time, the POP directive puts pressure on recycling companies to ensure the production of recycled plastics, which comply with POP regulations. As the list of POPs is expanding, technical and quality assurance issues arise in such companies and may lower benefits. This effect is further discussed using the example of the new POP DecaBDE. In the latest decision by the European Parliament, the Council and the Commission in February 2019, new thresholds for the BFR DecaBDE and other PBDEs were established. Accordingly, unintentional contamination of DecaBDE for substances must not exceed 10 ppm. Also preparations and articles are subjected to a 500 ppm threshold for the sum of all PBDEs, which presents the halving of the previous threshold of 1000 ppm (Council of the EU, 2/19/2019). In particular current recycling of WEEE plastics, which are partly contaminated with POP–BFR, including DecaBDE, is affected by this decision. State of the art WEEE plastic recycling performs the separation of non-BFR and BFR containing fractions via density separation or x-ray transmission (XRT) sorting technologies with subsequent separation into different plastics (ABS, HIPS, PP) via NIR technology or electrostatic technology (Wagner et al., 2018; Schlummer, 2014). Both bulk technologies work with plastic shred and sort out plastic particles containing higher bromine levels (5000–20,000 ppm). Due to limitation in sensitivity, plastic particles containing lower bromine levels (<5000 ppm) are not separated and remain in the low bromine fraction. However, only a very minor fraction of plastics contain bromine levels in that range, as there is no flame retarding effect in that concentrations. Sindiku et al. report that 3–12% of EoL casing plastics from WEEE contain bromine in the range of 1000–10 000 ppm (Sindiku et al., 2014). As a result, the bromine content of the bulk low bromine fraction is below 2000 ppm. Thus, there is only a minor effect of lacking sensitivity with density or XRT based separations at low bromine levels. As a technical rule a 2000 ppm threshold of bromine
has been established for “bromine-free” fractions by the WEEE LABEX certification system, which has to be confirmed in a depollution document before use as secondary raw material is accepted (Goodship, 2012). A clear link between bromine levels and POP–BFR levels is missing, however, detailed analytical campaigns showed that with 2000 ppm of bromine materials surely comply with POP–BFR levels of 1000 ppm and are considered to comply with the new 500 ppm threshold for the sum of POP–PBDEs (Slijkhuis, 2019). To ensure this compliance the current technologies work in the over-sorting modus, i.e. for separation of 1 bromine containing particle the up to 10-fold amount of particles free of bromine is also rejected. This leads to reduced yields and revenues from recycled polymers at the same process cost.

Technology-wise, a further reduction of bromine or POP–BDE levels with current density of XRT based techniques is questionable, however, the authors expect that the out-phasing of POP–BDE will lead to reduced levels in post-consumer-plastics in a few years’ time. For cathod-ray tube (CRT) TV-set housing (mostly made of ABS and HIPS), which have been reported to contain large amounts of POP–PBDEs (Schlummer and Mäurer, 2006), a decline has been forecasted recently (Kalmykova et al., 2015).

Following the POP regulations plastics containing FRs (heavy fraction of density separation and sorted XRF fraction with BFR > 1000 ppm) are normally not recycled and end up in incineration (Slijkhuis, 2018; Hennebert and Filella, 2018; Andersson et al., 2019).

6.3. Effects of GHS regulation

The classification of a substance hazardousness may have an effect on the treatment on a product containing such after its end-of-life. In June 2017, the EU adopted an amendment to the Waste Framework Directive, which regulate the classification of waste (Council of the EU, 6/8/2017). Amongst others, this amendment sets thresholds for the classification for waste as hazard, containing substances, which are declared according to GHS as HP14 “Ecotoxic”. According to this amendment, WEEE containing the flame retardant Tetrabromomethylsphenol A (TBBPA), a substance classified to GHS as H410 “very toxic to aquatic life” (ECHA, 2019), in a concentration ≥ 2500 ppm, is labelled as hazard and cannot be recycled via current recycling techniques. With this regulation another plastic waste stream goes to incineration.

6.4. Effects of waste legislation and the circular economy activities

As previously stated, in the EU Waste Directives hierarchy, waste recycling comes before recovery and disposal. Because of the increase in pollution from plastic waste in the environment, and its resulting negative effects on human health, the EU has established stepwise recycling targets for all member states. The average EU-wide recycling rate (for municipal waste) is currently 44%, however, the national rate varies considerably, from as high as 64% in Germany to as low as 10% in Slovakia (European Environment Agency, 2016). Of the remaining waste, 27% is incinerated and 24% is consigned to landfills. The EU has set ambitious future targets, aiming to achieve 50% recycling in all member states by 2020, 55% by 2025, 60% by 2030 and 65% by 2035 (Council of the EU, 2/23/2018). Although these targets pose no major difficulties for materials such as aluminium and paper with a homogenous composition, plastics are much more challenging because of the diverse nature of plastic materials, the presence of composites, large variety of used polymers and, as discussed herein, SVHCs.

The vision of the circular economy for plastics implies the collection of the majority of them. Sorting of plastics containing legacy additives, especially when considering the effect of over-sorting (compare 5.2), leads to an increasing amount of plastics rejected from recycling and sent to incineration. These quantities will be missing in the balance of the circular economy. The presence of legacy additives is mostly reported for technical goods (cable, electr(on)ic devices, flooring, etc.) and not for high volume waste plastic streams as packaging. Sorting of plastic with these additives does not significantly reduce the overall plastic recovery, but it limits the plastic recycling from specific branches (WEEE, ELV, construction and demolition) considerably.

7. Perspective recycling technologies for harmonisation of recycling and regulation

The authors do not think that European or global societies will accept a decrease in consumer safety by increasing concentration limits for POPs and for substances listed in REACH Annex XIV nor to keep the current limits as a permanent target. This would extend the agreed phase-out period for harmful substances, prolonging the exposure of humans and allowing larger quantities of the substances to enter the environment. Therefore, efforts are required to establish and improve recycling processes to ensure compliance with current thresholds, and even lower ones that are likely to be enforced in the future.

There are several existing techniques, which might be used in pre-sorting stages at a component or product level. For WEEE, this has been exemplified with un-shredded TV set and monitor housings that have been sorted by laser-induced breakdown spectroscopy (LIBS) or by use of hand-held XRF (Arends et al., 2015; Wagner et al., 2019; Aldrian et al., 2015). Both analytical techniques have higher sensitivities than the XRT approach and may help to reject bromine loaded materials from downstream bulk treatment processes according to the state of the art (Schlummer, 2014; Shameem et al., 2017).

With respect to PC and TV-set housings, Aldrian et al. report a recyclable share of 85% in TV sets and of 53% in PC-housings sortable through a XRF handheld instrument (Aldrian et al., 2015). Arends et al. report slightly lower shares for TV-sets based on density separation (~65%) (Arends et al., 2015). However, this difference in recyclable shares is probably more due to the specific input fractions used in both studies rather than to application of XRF based pre-sorting.

The benefit of these new spectrometric technologies is that they can add to the state-of-the-art separation of plastics with brominated flame retardants, which currently achieve bromine levels below 1000 ppm and PBDE levels below 500 ppm in the recyclable fraction (Arends et al., 2015; Andersson et al., 2019). If applied in manual pre-sorting they will reduce bromine levels in the infed of downstream bulk sorting processes by density separation or XRT. If integrated in-line optical sorting concepts, higher sensitivity will increase the sorting efficiency. Both technological perspectives have the potential to lower remaining PBDE levels to address possible future changes in legislation. However, they might have a negative effect on the share of recyclable material. In addition, LIBS and XRF approaches base on the detection of metals and halogens, they cannot be applied to detect and sort phthalate plasticizers.

Solvent-based recycling technologies follow another approach. They recycle the pure matrix polymer by a dissolution step whereas legacy additives, which are not chemically bound to the polymer, are eliminated from the polymer solution and subjected to destruction (Schlummer et al., 2017). Thus, this approach combines high yield of material recycling with safe destruction of hazardous compounds.

An example of such a solvent-based recycling technology is the CreaSol® Process (Fig. 2), which is suitable for all thermoplastics. In a first step, after pre-sorting, the input waste (e.g. WEEE or insulation containing BFRs) is selectively dissolved using a specific solvent formulation targeting the recoverable of the polymer base material. Second, the residual solids are removed, leaving the polymer in solution, along with any associated additives such as PBDEs or HBCD. Next, the target polymer is selectively precipitated and can be recovered, whereas the additives remain behind in the solvent. Finally, the wet polymer gel is vacuum-dried, extruded and granulated.

The solvents, used in this process, are not considered as hazardous according to GHS and are constantly recovered. The output is a recyclate that complies with regulations concerning the levels of...
contaminants and can be comparable to virgin material in terms of physicochemical properties. Since the list of hazardous chemicals is constantly rising, the CreaSolv® Process has the potential to clean polymers with future POPs. Precondition is that these additives are not bounded covalently to the polymer.

The technical readiness level (TRL) of the CreaSolv® Process is constantly ongoing and has now reached 5–8. In 2015, a consortium of producers, converters and recyclers of expanded polystyrene (EPS/XPS) formed the PolyStyreneLoop cooperative, which aims to recycle the polystyrene from HBCD containing EPS and XPS from construction and demolition waste, which is a prominent source of legacy HBCD. PolyStyreneLoop has developed plans for a pilot-scale recycling plant based on CreaSolv® Technology in Terneuzen, Netherlands, this plant is planned to be operational by 2020, with a projected throughput of 3000 tonnes per year (Wagner et al., 8/30/2018). The pilot plant will be assembled adjacent to an existing bromine-recovery unit, enabling the HBCD-rich fraction remaining from the CreaSolv® Process to be used directly for the destruction and conversion of HBCD into bromine compounds, which can in turn be used for to produce of new flame retardants. This provides an ideal model of a circular economy for EPS and XPS derived from the building and construction industry.

Solvent-based recycling approaches add to state of the art plastic recycling and disposal technologies and do not compete. They have the potential to recycle polymers from fractions rejected by mechanical or optical sorting processes, by separating the legacy additives. These require a safe thermal disposal, most probably by incineration (including waste to energy concepts) or pyrolysis. This is outlined in Figs. 3 and 4.

8. Conclusions

Political decisions regarding the management of hazardous materials and waste at the international level are needed to preserve our environment and reverse damage already caused by pollution. Accordingly, setting quotas for the recycling of plastics and restricting
the use of harmful substances will help to achieve these goals. With respect to plastic waste streams that may contain legacy additives, recycling technologies need to be implemented that enable safe separation of legacy additives. As no technical process can assure a complete removal, definition of technical feasible and environmental sound removal, determination of legacy additives. As no technical process can assure a complete respect to plastic waste streams that may contain legacy additives, recycling technologies provide a method to manage such waste streams in an environmentally friendly and economically feasible manner. Therefore, it is important that either recyclers commit and adopt the concept of decontamination, by sorting or solvent based technologies. Furthermore, a high degree of transparency is required for recycling technologies in order to track the fate of POPs and SVHCs in such processes. In addition, recyclers need a safe regulatory framework allowing a valorisation of recycled plastics. Therefore, it is recommended to include recyclers or their associations in the decisions on changes in threshold limits for POPs or SVHC in recycled plastics. This is important to avoid a situation that recycling activities have to stop, which currently handle SVHC containing plastic streams, separate, and destroy SVHC streams in a controlled and effective way. In such a case, a less controlled end-of-life management may return – as it has been observed in the past 20 years. Due to related thermal treatment cost, there is a high probability that the current situation of illegal exports of such waste streams prevails and undeveloped regions may have to take over the responsibility for an appropriate treatment of SVHCs and POPs without access to suitable technologies.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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