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Chemical Innovation and Regulation (ChIR)

Environmental Risk of Plastic Pollution: E02

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**Topic: Assessment of hazards and effects of polymers and their
additives in the plastic on fauna.**

Presented

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Abstracts

The wide range of applications of plastic materials has resulted in the accumulation of diverse waste streams, which create environmental problems. The production of plastics involves the use of monomers and additives that exhibits toxic and health hazards upon release into the environment.

Introduction

The production of plastic materials started to thrive on an industrial scale in the 1940s and 1950s with extensive ranges of applications in packaging and insulators. The Global plastic demand is dominated by thermoplastic types of polypropylene (PP) (21%), low -and linear low-density polyethylene (LDPE and LLDPE) (18%), polyvinyl chloride (PVC) (17%), and high-density polyethylene, (HDPE) (15%). Other plastic types in high demand are polystyrene (PS), expandable PS (8%), polyethylene terephthalate (PET)(7%, excluding PET fiber), and thermosetting plastic polyurethane(Hahladakis et al., 2018).

During the last 15 years, the global annual production of plastics has doubled, reaching approximately 299 million tonnes in 2013 (Plastics Europe, 2009). In Europe, the use of plastics is mostly dominated by packaging (38%), followed by building and construction (21%), automotive (7%), electrical and electronic (6%), and other sectors (28%), such as medical and leisure. Plastics are important in our society providing a range of benefits for human health and the environment., but unfortunately also have drawbacks(Lithner et al., 2011).

However, the extensive application of plastic materials has resulted in the accumulation of diverse waste streams. The large volumes of plastic wastes are produced, are due to the short lifespan of many plastic products (it is estimated that 40% of plastic products have a service life of less than 1 month). Most plastics can be persistent in the environment, and at the same time, plastics for single-use or short-term use dominate the waste stream. For example, the packaging sector alone accounts for 38% of the European (virgin) plastic production (Plastics Europe 2009).

These large volumes of plastic waste create serious environmental and management problems. Despite significant advances in management, treatment, recycling, and recovery of plastics in the last three decades, the largest fraction of plastic waste still possibly ends up in dumpsites or is openly burned, emitting carbon monoxide (CO) and carbon dioxide (CO₂)(Hahladakis et al., 2018). These problems of plastic pollution are widespread with extensive accumulation in oceans, landfills, and other terrestrial compartments, affecting wildlife and human health.

The knowledge of human and environmental hazards and toxicological effects from chemicals associated with the many types of plastic products is very limited. Most chemicals used for producing plastic polymers are derived from non-renewable crude oil, and several are hazardous. These chemicals may be released during the production, use, and disposal of the plastic product (Lithner et al., 2011).

Source of plastic in the environment.

The sources of plastic litter vary from land-based releases, e.g. land littering (especially in coastal areas), plastics that could have been blown from open dumpsites or leached sewage effluents,(Gregory, 2009) as well as spillage during transport and/or accidents with only a minor share from dumping at the sea(Hahladakis et al., 2018). This plastic waste can then be transported far away by currents, e.g. to the great oceanic gyres, and/or accumulated in the center of gyres(Hahladakis et al., 2018).

The exact amount of plastics entering the marine environment is yet unknown, by linking worldwide data on solid waste, and using population density, a rough estimate within the range of 4.8–12.7 Mt per year on the mass of land-based plastic waste entering the ocean has been calculated (Gregory, 2009).

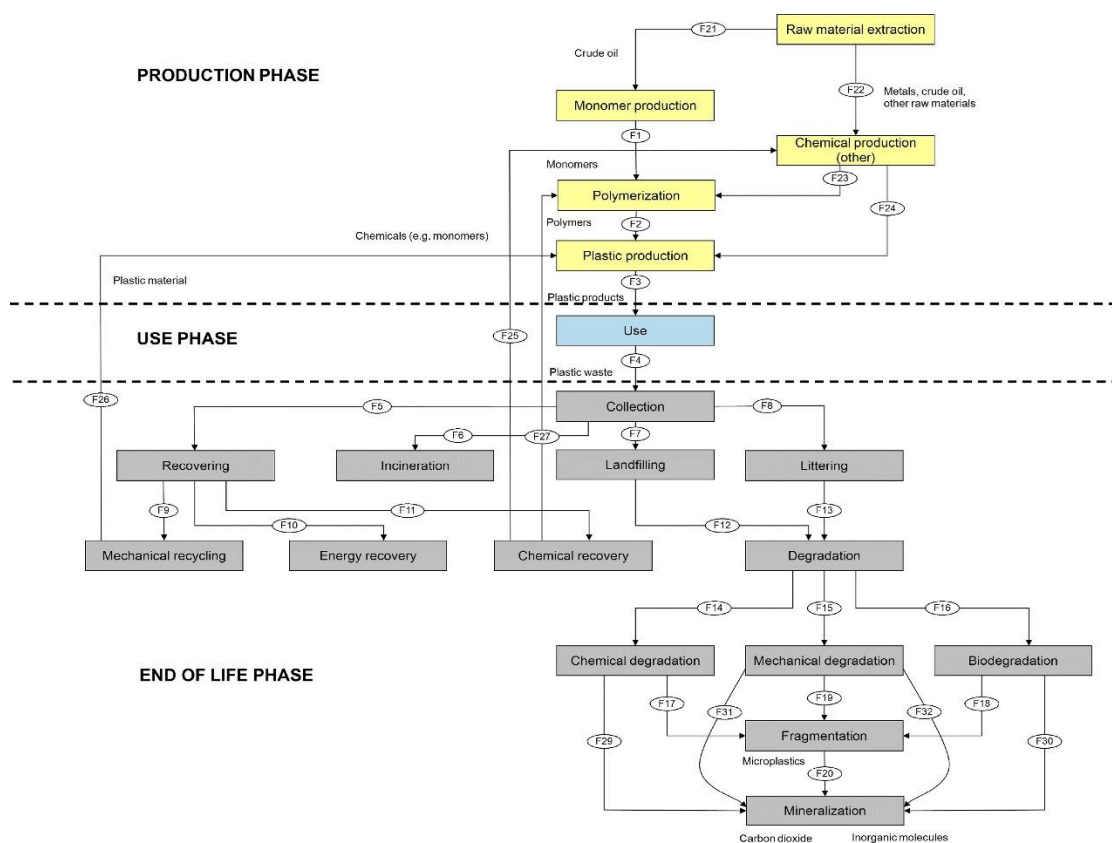


Figure 1 The life cycle of plastic products

Created in STAN (Substance flow Analysis) Software

(source: Hahladakis et al., 2018)

Plastic materials persistence and degradation

Most engineered polymers are manufactured with the long-term stability of their properties in mind: they are not meant to break down easily, which in many cases is part of the core functionality delivered by the material in the intended use (UNEP, 2016). For example in a PET polymer, only a mere 0.1% of the carbon will be transformed into CO₂, per year, via biodegradation and that will only occur under ideal laboratory conditions (Hahladakis et al., 2018).

Non-biodegradable polymers can be degraded and fragmented by various mechanisms: physical, such as heat and light, and chemicals, such as oxidation, ionic radiation, and hydrolysis. Certain air pollutants such as CO, sulfur dioxide (SO₂), nitrous oxide (NO), and ozone (O₃) can also play a major role in the degradation of polymers (Ravve, 2013). Biodegradable plastics today have a minor and continuously growing, share in the plastics market. However, not all of them are entirely biodegradable in the natural environment (O'Brine & Thompson, 2010)

At the molecular level, various degradation mechanisms exist and the domination of one mechanism over the others often depends on the polymer type. Chain scission, for example, involves breaking the chemical bonds of the polymer molecule (Lithner et al., 2011). Another degradation mechanism is chain stripping according to which the side atoms/groups attached to the polymer chain are released; usually, these are volatile molecules. Under marine conditions, any degradation that might occur would be quite slow, given the main involving mechanisms e.g. solar radiation and slow thermal oxidation (Gregory, 2009). Therefore, the time frame for a complete degradation could be extensively prolonged, reaching, in some cases, even hundreds of years (Hahladakis et al., 2018).

The degradation products of plastics are polymer type dependent and the quantity of degradation products may be influenced by degradation mechanisms and the presence of polymerization impurities and/or surrounding factors, e.g. temperature and oxygen (La Mantia, 2002). During thermal degradation, nitrogen-containing plastics (e.g. nylons, polyacrylonitrile, and polyurethanes) release hydrogen cyanide; chlorine-containing materials (e.g. PVC) release hydrogen chloride and dioxins; and fluorine-containing polymers (e.g. polytetrafluoroethylene (PTFE) and polyvinylidene fluoride) release hydrogen fluoride and perfluoro isobutene by a chain stripping mechanism and other degradation pathways (Lokensgard, 2016).

After the Stockholm Convention (UNEP, 2020) on persistent organic pollutants, micro and nano plastics were proposed to be persistent organic pollutants (POPs) due to increasing evidence concerning their environmental persistence, bioaccumulation, long-range transfer, and impacts from exposure (Lohmann, 2017).

Hazard ranking of Chemicals used in Plastics Polymers

The plastic polymer is biochemically inert due to its large molecular size, however, the polymerization reactions involved in the production of plastics are rarely complete and, therefore, also unreacted residual monomers can be found in the polymeric material, several of which are hazardous for human health and the environment and/or affects polymer properties(Araújo et al., 2002)

In a study by Lithner et al., (2011) ranked polymers based on monomer hazard classifications. The hazard classifications were exclusively adopted from Annex VI in the EU classification, labeling and packaging (CLP) regulation which is based on the UN Globally Harmonized System (GHS) (European Parliament and Council, 2008). In this study, the environmental and health hazards of chemicals used in fifty-five thermoplastic and thermosetting polymers are reported. The procedure adopted for calculating the hazard score (sum) for the polymer was based on the classifications of the monomers that the polymer is made of. Lithner et al., (2011) reported that a considerable number of polymers (31 out of 55) are made of monomers that belong to the two worst of the ranking model's five hazard levels, i.e., levels IV–V. The polymers that are ranked as most hazardous are made of monomers classified as mutagenic and/or carcinogenic (category 1A or 1B).

Sixty-one monomers were used for the 55 polymers	Monomer hazard level and score		Used in a number of polymers	Used in the type of polymer(s)
	Level	Score		
Acrylamide	V	22,240	1	PAN comonomer example
Ethylene oxide	V	20,131	2	PUR example, POM copolymer example
Propylene oxide	V	20,061	2	PUR examples
1,3-butadiene	V	20,001	2	ABS, HIPS
4,4'-methylenedianiline (MDA)	V	13,200	1	Epoxy example
Acrylonitrile	V	11,521	6	PAN and its comonomers, SAN, ABS
Epichlorohydrin	V	11,400	3	Epoxy examples
Benzyl butyl phthalate (BBP) — plasticiser!	V	11,100	1	PVC plasticised example
Vinyl chloride	V	10,001	3	PVC
m-phenylenediamine	IV	3410	1	MPD-I
Toluene-diisocyanate (TDI)	IV	3140	1	PUR example
p-phenylenediamine	IV	2410	1	PPD-T
4,4'-methylenediphenyl diisocyanate (MDI)	IV	2240	3	PUR example, TPU examples
Phthalic anhydride	IV	2130	2	UP examples

Sixty-one monomers were used for the 55 polymers	Monomer hazard level and score		Used in a number of polymers	Used in the type of polymer(s)
Maleic anhydride	IV	2110	1	UP examples
Formaldehyde	IV	1500	5	POM, PF, MF, UF
Phenol	IV	1500	2	PF
Bisphenol A	IV	1210	5	Epoxy examples, PC
1,4-dichlorobenzene	IV	1210	1	PPS
Phosgene	IV	1100	1	PC example
Methyl methacrylate	IV	1021	2	PMMA, UP example
Hexamethylenetetramine	IV	1000	1	PF one type
2,6-xylenol	III	400	1	PPO
Sodium sulphide	III	310	1	PPS
Acrylic acid	III	230	1	PAA
Pentane	III	211	1	EPS
Hexamethylenediamine	III	130	2	Nylon 6.6
Vinylidene chloride	III	111	1	Modacrylic
Trioxymethylene	III	110	2	POM copolymers
ϵ -caprolactam	II	50	1	Nylon six
Styrene	II	30	6	PS, EPS, HIPS, SAN, ABS, UP example
Cyclopentane	II	11	1	PUR example
Ethylene	II	11	5	HDPE, LDPE, LLDPE, EVA
Adipic acid	II	10	3	Nylon 6.6, TPU examples
4,4'-diamino diphenyl sulfones (DDS)	II	10	1	Epoxy example
Ethylene glycol	II	10	4	TPU examples, PET
1-butene	I	1	1	LLDPE example
1,3-dioxolane	I	1	1	POM copolymer example
Propylene	I	1	1	PP
Vinyl acetate	I	1	3	PAN comonomer example, EVA, PVAc
In total 21 monomers were not classified. However, for 16 of them, there are OECD SIDS Initial Assessment Reports/Profiles (OECD, 1998– 2009).				
Non-classified monomers	SIDS initial assessment			
11-aminoundecanoic acid	Low (HE) ^a		1	Nylon 11
Melamine	Low (HE) ^a		1	MF

Sixty-one monomers were used for the 55 polymers	Monomer hazard level and score	Used in a number of polymers	Used in the type of polymer(s)
Dicyandiamide	Low (HE) a	1	Epoxy example
Dimethyl terephthalate	Low (HE) a	2	PET example, PBT
Propylene glycol	Low (HE) a	2	UP examples
Sorbitol	Low (HE) a	1	PUR example
Terephthalic acid	Low (HE) a	1	PET example
Urea	Low (HE) a	1	UF
Vinylidene fluoride	Low (HE) a	1	PVDF
Lactic acid	Low (HE) a	1	PLAY
Diisodecyl phthalate (DIDP) — plasticiser!	No classification d	1	PVC plasticised example
Diphenyl carbonate	Low (H), (E) b	1	PC example
1-Hexene	Low (H), (E) b	1	LLDPE example
1-Octene	Low (H), (E) b	1	LLDPE example
Lauryl lactam	Low (H), (E) b	1	Nylon 12
1,4-Butanediol	Low (E), (H) b	5	TPU examples, PBT
HCF-134a	? c	1	PUR example
Isophthaloyl chloride	? c	1	MPD-I
Sebacic acid	? c	1	Nylon 6.10
Terephthaloyl chloride	? c	1	PPD-T
Tetrafluoroethylene	? c	1	PTFE

Table 1 Hazard ranking of monomers and their presence in polymers.

(source: (Lithner et al., 2011))

All monomers that are used in the 55 polymers and with a hazard score and the polymers in which they are used.

- a Low (HE) = low level of concern for human health and the Environment indicated by the SIDS initial assessment reports/profiles.
- b
? (H), (E) = indication of elevated concern for either Health or Environment (requiring more studies).
- C
? = No SIDS Initial Assessment Reports, lack data.
- d
[European Commission Joint Research Centre \(2003\)](#) did not suggest any classification.

The most environmentally hazardous of the monomers are m-phenylenediamine (for MPD-I), p-phenylenediamine (for PPD-T), 1,4- dichlorobenzene (for polyphenylene sulphide), and the phthalate plasticiser BBP (for some PVC). These monomers are all very toxic to aquatic life with long-lasting effects (Aq. Chronic 1), and very toxic to aquatic life (Aq. Acute 1) (Lithner et al., 2011)

It should be noted that a polymer ranked as hazardous in this study does not mean the same as the polymer being hazardous. The ranking is specific to the fact that polymer is made from hazardous substances. However the release of these hazardous substances or degradation products may occur during the production, use, and end of life phase, and thereby there is a hazard associated with the ranked polymer type(Lithner et al., 2011)

Additives and their impacts on fauna

Additives are chemical compounds added to the polymer to improve and enhance the performance, characteristics, functionality, and ageing properties. The most commonly used additives in different types of polymeric packaging materials are: plasticizers, flame retardants, antioxidants, acid scavengers, light and heat stabilizers, lubricants, pigments, antistatic agents, slip compounds, and thermal stabilizers(Hahladakis et al., 2018)

These additives present in all plastic materials can also contribute to marine pollution. Some plastics contain POPs as additives (e.g. hexabromocyclododecane (HBCDD or HBCD) and/or polybrominated diphenyl ether (PBDE)) at a concentration of 0.7–25% wt. (Hahladakis et al., 2018). Most organic additives used in plastic production are hydrophobic (Kwon et al., 2017), which can enhance the hydrophobicity of the surface of the associated micro and nano plastics particulates, and thus can potentially increase the sorption of toxic organic compounds to the Micro and nano plastics(Sridharan et al., 2022). Additives exhibit more toxicity and health hazards to biota and humans upon contact or ingestion, which are attributed to their chemical nature (Liu et al., 2020)

Many factors affect the adsorption or release of additives by micro and nano plastics in the environment. Generally, pH and organic matter are proposed to be the major driving forces(Sridharan et al., 2022). Additives are usually not chemically bound to the plastic compounds and, can easily get released, migrate to the polymeric surface and leach out to the environment (Gunaalan et al., 2020). The type and quantity of the additives in plastics largely depends on the nature of their applications. For instance, PVC products can contain around 60% of additives, added in the proper proportion to impart UV stabilization, enhanced elasticity, and other performance parameters (Lee et al., 2020a). However, the migration of the additives in the environment highly depends on the irradiation (UV and solar intensity) and the stability of the additive (chemical structure) (Wang et al., 2021c).

Even if some of these additives containing polymers are not ingested, they still constitute exposure sources, e.g., increased HBCDD content has been found in oysters on a farm where PS buoys containing HBCDD were used [65]. For example, Jang et al. (2016) identified marine Styrofoam debris as a potential source of hexabromocyclododecane (HBCD) and flame retardants that the regional fauna could be exposed to. Therefore, plastic waste in the environment can transport hazardous additives or other co-pollutants in the food chain.

Tracing the additives associated with the micro and nano plastics polymers can indirectly track the micro and nano plastics levels in the environment (Sridharan et al., 2022). In the marine environment, the commonly reported contaminants resulting from micro and nano plastics are hydrophobic, organic compounds like phthalates, bisphenol A (BPA), nonylphenols, and polybrominated diphenyl ethers (PBDE), and other antioxidants (Hermabessiere et al., 2017). Plastic associated chemicals are widely known to interfere with hormonal modulation (endocrine mimics) and detoxification processes (enzyme inhibition, oxidative stress) and cause apoptosis (cell death) (Liu et al., 2020b).

Additive like fluorescent pigments associated with micro and nano plastics, which are usually toxic to aquatic algae, can easily get released into the environment (Luo et al., 2019). Additives like surfactants, if released into the environment, can also aid in the transport of the associated micro and nano plastics particles. For instance, PE and PP micro and nano plastics in water can easily get suspended by their surfactant-additives like sodium dodecylbenzene sulfonate (SDBS) (anionic) and cetyltrimethylammonium bromide (CTAB) (cationic) (Jiang et al., 2021).

The leaching of additives may be more relevant for species with longer gut retention times (Koelmans et al., 2014). Usually, fish communities that are swallowing-feeders tend to ingest more micro and nano plastics than sucking feeders or filtering-feeders (Li et al., 2021), and this specifies a serious risk of micro and nano plastics and their additives on bioaccumulation in the food chain. A study by Ding et al. (2021), observed a clear avoidance behaviour by *E. fetida* toward micro and nano plastics [PLA, PE, polypropylene carbonate (PPC)] at concentrations greater than 40 $\mu\text{g kg}$. The study reported that biodegradable polymers, which also carried the same toxic additives, were as toxic as the conventional PE micro and nano plastics, throwing light on the potential ecological impacts of bioplastics. Therefore, Bioplastics also possess a risk of human and environmental hazards since all products contain additives.

Additives	Chemical origin	Environmental significance: Why are they hazardous?	References
Plasticizers	The reaction of organic acids and alcohol	Esters: low molecular weight, decreases viscosity (friction): Odourless and colourless, readily ingested by organisms	Vieira et al. (2011)
Flame retardants	Inorganic minerals + nitrogen, chlorine, bromine, or phosphorus	These compounds form a fire-preventive layer at the surface of a material: Easily leachable in the environment	Jang et al. (2021)
Stabilizers	Pb salts, acetylation, or atmospheric oxidation of benzyl compounds	Prevents oxidation: Delays or prevents the degradation of plastic and bioplastic particulates in the environment	Allen and Edge (2021b)
Surfactants	Alkylation of fats or petrochemicals	Ionizes the plastic surface: Enhances binding of Micro and nano plastics to metals or oppositely charged compounds and surfaces	Jiang et al. (2021b)
Synthetic dyes and pigments	Oxidation of petrochemicals (coal tars): Traces of toxic inorganic and organic compounds: Hg, Cr, toluene, etc.	Synthetic pigments are usually hydrophobic: Increase the hydrophobicity of the plastic surface	Allen and Edge (2021b)
Anti-shrinking agents (expansive additives)	Usually, mixtures of alkyl ethers and urea: promote surface expansion and micelles to reduce cracks and shrinkage	Hygroscopic, water soluble: Easily assimilated by organisms that ingest Micro and nano plastics, makes the plastic particulates more stable in the environment	Allen and

Table 2 Overview of the sources of major polymeric additives and their environmental impacts.

Table 2. Overview of the sources of major polymeric additives and their environmental impacts.

(source: Sridharan et al., 2022)

The biophysical or ecological impacts of micro and nano plastics are more likely to result from their physical characteristics (Lozano et al., 2021; Qin et al., 2021) than their chemical structure, this because most conventional plastics are branded to be chemically stable and inert. However, their additives exhibit more toxicity and health hazards to biota and humans upon contact or ingestion, which are mainly attributed to their chemical nature (Liu et al., 2020) and polymerisation reactions are rarely complete and, therefore, also unreacted residual monomers can be found in the polymeric material, several of which are hazardous for human health and the environment and/or affects polymer properties (Araújo et al., 2002)

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