Toxic additives in plastic

Plastic materials are organic substances that are polymers or a combination of high molecular weight polymers modified or combined with additives. The primary distinction between pure polymers and plastics lies in the additives, such as fillers, plasticizers, stabilizers, and pigments, which give polymers the desired properties and transform them into processable plastic materials. Currently, there are more than 30 types of primary polymers which, when mixed with various additives, can produce thousands of types of plastic materials.[1] Very few basic polymers are utilized and processed in their pure form; typically, plastics consist of a blend of polymers and additives that provide the properties necessary for a specific application..

Typical additives for plastics[2]

(a) Stabilizers: Stabilizers extend the life of the polymer by inhibiting degradation due to ultraviolet light, oxidation and other phenomena. Typical stabilizers absorb ultraviolet light or function as antioxidants; the stabilizer group also includes additives that increase the thermal stability of the polymer.
(b) Fillers: Many plastics contain fillers to enhance performance or reduce manufacturing costs. Common fillers include mica, talc, kaolin, calcium carbonate, barium sulfate, and cellulose fibres. Most fillers are relatively inert and inexpensive, which lowers the product's cost; however, they can significantly increase the specific weight of the products. Some fillers possess a distinct fibrous structure (like cellulose and capron) and are referred to as reinforcing agents.
(c) Plasticizers: By weight, plasticizers are often the most common additives. They impart plasticity (softness and flexibility) to the materials in which they are incorporated. Typical polymers without plasticizers tend to be too stiff and brittle for certain applications.
(d) Colorants: Colorants (pigments, e.g. soluble azo dyes) are another common additive;
(e) Flame retardants as standalone additives include specialized options such as brominated flame retardants and short to medium chain chlorinated paraffins, as well as nitrogen and phosphorus-containing flame retardants. Additionally, many fillers (refer to point b) can also function as flame retardants. In the recent past, antimony trioxide has been utilized as a flame retardant for industrial applications.
(e) Other functional additives: antistatic agents, antioxidants, lubricants, slip agents, hardening agents, foaming agents, water and oil repellents, etc.

1 Silvestre,Cl., Cimmino,S., 2013, Ecosustainable Polymer Nanomaterials for Food Packaging: Innovative Solutions, Characterization Needs, Safety and Environmental Issues.
2 UNEP/CHW/OEWG.12/INF/14

It is important to emphasize that many of these additives are highly toxic and can negatively impact human health and the environment. Hazardous additives remain persistent in the environment and can decompose and leach into soil, air, and groundwater from landfills or industrial emissions. Incinerating plastic waste can release harmful substances, such as unintended POPs like dioxins. Many of these additives have long been banned yet continue to circulate in new products made from recycled materials.

Additives of particular concern due to their toxicity include:

Stabilizers

Stabilizers, among other substances, may contain polymerization products of bisphenol A (BPA) because they strongly absorb UV light and raise the softening point of the material. Lead, cadmium, and tin compounds enhance the heat resistance of plastics by primarily binding to defects in the polymer structure.[3] Half of all stabilizers are used in PVC.[4]

It is important to note that stabilizing additives are not the primary use of bisphenol A. The largest quantity is found in polycarbonate plastic, which is actually produced from this monomer. Bisphenol A is classified as one of the endocrine-disrupting substances. Studies have indicated that perinatal exposure to BPA and early-age exposure are associated with behavioural problems in children.[5] Human exposure to BPA elevates the risk of specific cancers in adults and developmental disabilities in children.[6]

According to a joint report by the International Pollutant Elimination Network and the Endocrine Society[7], BPA is linked to polycystic ovary syndrome (PCOS), a complex hormonal condition associated with irregular menstrual cycles, reduced fertility, and an increased risk of diabetes. In men, BPA impacts fertility and is linked to sexual dysfunction among those exposed to high occupational levels. Despite its toxicity, the Global BPA Market Outlook 2021 and Forecast to 2030 indicates that production will only rise.[8] Meanwhile, the primary consumers of this substance are nations in the Asia Pacific, Europe, and North America.

The European Union bans the use of bisphenol A in containers for:
-food products for children under 3 years of age, (in France for any food products),
-specialty medical and dietary nutrition,
-milk products,
-processed grain products.

BPA levels in children are generally higher than in adults. This is due to a greater food intake relative to body weight at a young age, the ingestion of dust from hand-to-mouth contact, and the more frequent use of plastic products. Infants are exposed to BPA when it leaches from bottles and other containers into the beverages and food they consume. Analysis of average BPA exposure among different age groups in EU countries[9] shows values ranging from 100 to 400 ng/kg body weight per day. To obtain a dose of 400 ng/kg, a child weighing 5 kg would need to drink approximately 0.5 to 1 litre of water per day from the containers of the two samples analysed (05; 13), where BPA was detected at 2376 ng/L and 1239 ng/L, respectively.

In the European Union, BPA was prohibited in baby bottles as of 2011 due to evidence that infants› metabolic systems are more susceptible than those of adults.

Water and oil repellents

Plastic products also contain per- and polyfluoroalkyl substances (PFAS), which are known for their thermal and chemical stability, as well as their high resistance to water and oil repellency.[10] The usage of these substances as grease and stain removers in consumer products started in 1950. These properties render PFAS especially suitable for various food contact materials. However, PFASs are highly resistant to degradation in biota and the environment[11], leading to their ubiquitous presence. PFAS are a group of synthetic chemical compounds that include perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and many others. PFAS encompasses more than 5,000 per- and polyfluoroalkyl substances, of which PFOA and PFOS are regulated under the Stockholm Convention on Persistent Organic Pollutants. This regulation covers substances whose decomposition produces PFOA and PFOS, as well as related compounds.

PFOA, its salts, and related compounds have been widely used in the manufacture of fluoroelastomers and fluoropolymers, nonstick cookware, and food processing equipment. PFOA-related compounds have also been used as surfactants and surface treatments in textiles, paper, paints, and firefighting foams. PFOA has been found in industrial waste, stain-resistant carpets, carpet cleaning fluids, household dust, water-resistant paper food bags, water, food, and Teflon, which has long used PFOA as an emulsifier.

The unintentional formation of PFOA occurs due to the incineration of fluoropolymers found in municipal solid waste. Under the Stockholm Convention on Persistent Organic Pollutants (POPs), PFOA, its salts, and related compounds are listed in Annex A for the cessation of their production and use. The list of specific exemptions that permit the continued use of PFOA does not encompass its application in consumer products.[12]

It is important to note that in 2013, the Conference of the Parties to the Stockholm Convention, during its 6th meeting, encouraged parties to consider phasing out the use of PFOS, its salts, and related chemicals in applications where PFOS-free and non-chemical alternatives have been identified and are commercially available. These applications include, among others, carpets, leather, clothing, textiles, and upholstery. In September 2016, a Consolidated Guidance on Alternatives to PFOA, PFOS, and Related Chemicals was presented at the twelfth meeting of the Stockholm Convention›s Persistent Organic Pollutants Review Committee (POPRC 12). The Guidance explains, among other things, that «there are currently no parties registered for special exemptions for carpets, leather, clothing, textiles, and upholstery,» indicating that PFOS should no longer be used for these materials.

The Conference of the Parties to the Stockholm Convention, held in July 2022, endorsed the recommendations of the Committee for the Review of New POPs and included PFHxS

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7 Plastics Pose a Threat to Human Health | IPEN
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12 POPs Chemicals Mandeeps hidden module

(perfluorohexane sulfonic acid, its salts and related compounds) in Annex A of the Convention without any exceptions.

It is emphasized that PFAS are endocrine-disrupting substances identified as particularly dangerous, posing a threat to human health and safety even at extremely low doses. They may contribute to the development of cancer, as well as reproductive, developmental, and cognitive disorders.

Flame retardants

Some plastics contain flame retardants as additives. In 2023, delegates to the Stockholm Convention Conference of the Parties included the flame retardant Dechlorane Plus in Annex A of the Convention, requiring a global ban, as a substance that meets all the characteristics of POPs.

Additives in plastics include short-, medium-, and long-chain chlorinated paraffins; boric acid; brominated flame retardants such as polybrominated diphenyl ethers (PBDEs), deca-BDE, and tetrabromobisphenol A (TBBPA); phosphorus flame retardants; hexabromocyclododecane (HBCD); and various compounds known as dechloranes. PBDEs are the most commonly used flame retardants for plastics. They are particularly used in electrical and electronic appliances, coatings, automotive parts, coated textiles, furniture, building materials, and some packaging that consists of or contains plastics.

Polybrominated diphenyl ethers include hexabromodiphenyl, heptabromodiphenyl (hexa- and hepta-BDE), tetrabromodiphenyl, and pentabromodiphenyl ether (tetra- and penta-BDE), as well as deca-BDE groups, which are listed in Annex A of the Stockholm Convention. All PBDEs have been used as flame retardants in plastics. These additives were marketed commercially as c-PentaBDE, c-OctaBDE, and c-decaBDE.

Hexabromocyclododecane (HBCD) - flame retardant, production is banned, but the substance is found in recycled plastic products

Tetrabromodiphenyl ether - flame retardant, production is banned, but the substance is found in recycled plastic products.

Pentabromodiphenyl ether - flame retardant, production is banned, but the substance is found in recycled plastic goods

Hexabromodiphenyl ether - flame retardant, production is banned, but the substance is found in recycled plastic products

Heptabromodiphenyl ether - flame retardant, production is banned, but the substance is found in recycled plastic products

Decabromodiphenyl ether (DecaBDE) - flame retardant, production is banned, but the substance is found in recycled plastic products

One primary application of polybrominated diphenyl ethers and other brominated compounds is to render plastics resistant to flammability. This is particularly important for plastics used in electronics, electrical engineering, and certain finishing materials. Recycled plastic from discarded electronic equipment that contains toxic polybrominated compounds (polybrominated flame retardants) contaminates new plastic products meant for household use, including children›s toys.

The most common types are brominated diphenyl ethers. This group includes various isomers of tetra-, penta-, hexa-, hepta-, octa-, nona-bromodiphenyl ethers, and deca-bromodiphenyl ether.

OctaBDE, DecaBDE are widely used in the manufacture of electronic equipment and are major toxic components of waste electronic products. PentaBDE has been used almost exclusively in the manufacture of flexible polyurethane foam (FPU) for furniture and upholstery in homes and vehicles, packaging material, and non-foaming polyurethane for cladding electronic device housings. HBCD is mainly used in the manufacture of polystyrene insulation for buildings, but is also found in electronic equipment.

The levels of these substances found in household products indicate that they were not added directly during manufacture. Instead, the flame retardants likely came from the use of recycled plastic, such as e-waste, as a material for these products. Plastic items created from plastic recycling contain the same toxic flame retardants that were added to virgin plastic used in electronics.

In many countries, PBDE values in commodities can be assessed against EU regulations[13] of 10,000 µg/kg (10 mg/kg) for primary material commodities, and with a PBDE level in waste of 50,000 µg/kg (50 mg/kg) as negotiated under the Stockholm Convention on Persistent Organic Pollutants (POPs) and advocated by the International Pollutants Elimination Network[14]. This level of PBDEs in waste is consistent with the level justified in the scientific

13 REGULATION (EU) 2019/ 1021 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL - of June 20, 2019 - on persistent organic pollutants (europa.eu)

14 ipen-low-pops-factsheet-v1_5-en_web.pdf

review «Are emission reductions of industrial organic pollutants in rich countries achieved in part by exporting toxic waste?»[15] .

Health effects of brominated flame retardants

Brominated diphenyl ethers accumulate in humans[16] and animals[17], in soil and sediments[18] [19], food[20] and mother›s milk[21] [22] [23]. Interestingly, the gradual replacement of chlorine- by bromine-containing flame retardants over time has led to similar shifts in impurities in milk [24]. The widespread use of plastic leads to high levels of PDBE in house dust[25] [26]. According to[27,28] excretion of the substance from the body takes months and varies greatly depending on the specific substance.

Epidemiologic data obtained from a sample of workers at plastic recycling facilities[29] , show a correlation between thyroid hormone system abnormalities and flame retardant levels in the body. Similar data were also obtained in an entirely different population, unrelated to plastic recycling.[30] Laboratory animals fed brominated diphenyl ethers have thyroid abnormalities and altered expression levels of genes associated with thyroxine metabolism.[31,32] PBDEs exhibit immunomodulatory effects[33] [34,35]and result in, for example, an inadequate immune response to viral infection[36], as well as multiple effects on the developing fetal nervous system[37] . A dose of 0.2mg/kg body weight of an animal leads to altered offspring behavior, such as hyperactivity and impaired formation of behavioral skills[38].

15 Are Reductions in Industrial Organic Contaminants Emissions in Rich Countries Achieved Partly by Export of Toxic Wastes? | Environmental Science & Technology (acs.org)
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When heated in air to temperatures above 300-400 °C, PBDE brominated flame retardants start to oxidize, forming significantly more toxic compounds such as dioxins.[39] This poses significant risks for specialty plastics and recycled plastics when they are sent to incinerators. Additionally, the emission of dioxins raises concerns about the viability of using brominated flame retardants for fire safety. The effort to mitigate fire risks by neutralizing free radicals with halogen atoms is counterbalanced by the potential formation of toxic combustion byproducts.

Remember that polybrominated diphenyl ethers are additives that are not chemically bonded to the plastic but are instead dissolved and dispersed in the plastic melt, making them easily released into the environment.

Plasticizers

Diethylhexyl phthalate (DEHP) - plasticizer [40]
Benzylbutyl phthalate (BBP) - plasticizer [41]

Dibutyl phthalate (DBP) - plasticizer, banned for use in toys in the EU[42] and EAEU countries[43]

Diisobutyl phthalate (DIBP) - plasticizer[44]

The largest number of additives, primarily stabilizers and plasticizers, are used in PVC, one of the most commonly used plastic materials.[45] Thus, about 80% of plasticizers are used in PVC, while the remaining 20% are used in cellulosic plastic.[46] Global use of plasticizers was 8.4 million tons in 2015 and is projected to reach 9.75 million tons in 2024.[47]

Transparency and traceability of chemicals in plastics

The transparency of chemical information in materials and commodities, along with its traceability to individual products, forms the foundation for informed decision-making by all stakeholders involved in the production and usage of plastics. Both transparency and traceability are essential strategies for a resource-efficient circular economy that must be devoid of harmful chemicals.

This vision was outlined in a recent report prepared by researchers from Norway titled «The State of the Science of Plastic Chemicals» [48]. According to this new study, over 16,000 chemicals are used in plastic, with more than 4,000 identified as hazardous. However, there is insufficient information on nearly 12,000 of these chemicals to determine whether they are harmless to humans and the environment. The report concludes that no plastic products are chemically safe for humans and emphasizes the need for transparency in the chemical

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41 Ibid
42 Ibid
43 Banned in toys in EAEU countries (Belarus, Russia, Kazakhstan, Kyrgyzstan) according to the Technical Regulation „On Safety of Toys", https://docs.cntd.ru/document/902303210
44 The EU imposes restrictions on the use of phthalates in toys that are listed as carcinogenic, mutagenic or toxic to reproduction (CMR) under the Classification, Labeling and Packaging (CLP) Regulation at a concentration equal to or greater than 0.1% by weight of the plasticized product material https://echa.europa.eu/documents/10162/aaa92146-a005-1dc2-debe-93c80b57c5ee
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48 https://www.plasticpollutioncoalition.org/resource-library/plastchem-state-of-the-science-onplastic-chemicals

identification of materials and products throughout the life cycle of plastics. In 2023, UNEP conducted a similar study of chemicals in plastic.[49] It produced a technical report noting that plastic contains 13,000 chemicals, a quarter known as toxic chemicals.

It is evident that information regarding chemicals in plastics is continually evolving. The only constant is the extremely low level of disclosure about this information.
Ideally, full disclosure of chemicals in plastics should be accessible to all stakeholders, including not only producers of plastic products, but also regulators, consumers, retailers, and plastic recyclers. Regulators require this information to enhance the effectiveness of existing chemicals legislation and to undertake proactive regulatory action. Waste recyclers also need this information to ensure that hazardous chemicals are not reused in new goods made from recycled materials, and that other chemicals, even those deemed safe for human consumption, do not impact the recycling process. Furthermore, chemicals currently considered safe may later be reclassified based on new scientific evidence.

However, at the very least, all stakeholders must be informed about the chemicals in products according to their hazardous properties. These properties are outlined in the UNEP Chemicals in Products Program.[50] [51]Specifically, these are substances that are persistent, bioaccumulative, and toxic; they may be carcinogens or mutagens, or they may adversely affect the reproductive, endocrine, immune, or nervous systems. Substances that exhibit one or more of these hazardous properties should be prioritized for disclosure regarding their presence in products.

During the negotiations for a new global treaty on plastics[52] , some countries have attempted to establish criteria for chemicals to be included in the so-called negative list of those that should be strictly regulated or banned in plastics. However, such a list alone cannot guarantee a circular economy free from harmful chemicals.

There is a need for traceability of information in individual materials and products. First, we do not know which substances will be included in the initial list for regulating their use in plastics. For instance, it may only comprise substances that are already banned internationally, which represents only about 4% of known hazardous chemicals. For example, the Stockholm Convention on POPs regulates just 17 persistent organic pollutants used in plastics.
It is not known whether the initial list of negative chemicals in plastics will include all 4,200 chemicals identified in the Norwegian report or the 3,200 chemicals identified by UNEP in 2023. In either case, the list should be live, i.e., open to the inclusion of additional chemicals for control and banning in plastics.

However, not all chemicals that would be on the initial list of hazardous chemicals to control their use in plastics can be immediately banned or restricted because the industry claims that no substitutes exist. Thus, if these chemicals are present in a plastic material›s life cycle, they must be monitored in individual plastic materials and products. Furthermore, it is crucial to monitor chemicals that are already banned or severely restricted in products, as the recycling of materials and products containing them results in the reuse of toxic substances in new products made from recycled materials. Why does this occur? Because there is still no globally harmonized approach to tracking these chemicals in products at the level of existing chemical conventions.

49 https://wedocs.unep.org/handle/20.500.11822/42427
50 https://www.saicm.org/Portals/12/documents/meetings/ICCM4/doc/K1502319%20SAICM-ICCM4-10-e.pdf
51 https://www.unep.org/topics/chemicals-and-pollution-action/chemicals-management/chemicals-products
52 https://www.unep.org/inc-plastic-pollution

Further discussion showed that the problem of disclosing and tracking information on chemicals in plastics is quite acute for the countries of the EECCA region. National practice shows that the waste recycling sector, on which great expectations are placed, needs a new reporting system. The main problem now is the lack of systems to monitor incoming raw materials at recycling facilities. Without such control, it is impossible to assert the safety of recycled products.

The transboundary movement of such wastes requires attention in addition to domestic regulatory measures. Here, regional measures are important, as are internationally harmonized measures. For this purpose, it is proposed to establish a system of classification of plastic waste, e.g., into hazardous and non-hazardous, or to follow a systematic phase-out of plastic and reduce the generation of those wastes that cause the greatest concern.

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