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Plastics additives and green chemistry*

Evan S. Beach‡, Brian R. Weeks, Rebecca Stern, and
Paul T. Anastas

*School of Forestry and Environmental Studies, Yale University, New Haven, CT
06511, USA*

Abstract: The plastics enterprise depends on a small number of commodity polymers to perform in diverse applications, requiring additives to produce desired properties and performance. Toxic effects and environmental persistence of certain additive chemicals impact the sustainability of the industry. Green chemistry has been and will continue to be applied to find solutions to these issues. This review focuses on alternatives to phthalate plasticizers and halogenated flame retardants, two categories that together account for a significant portion of the global additives market and the global dispersion of endocrine-disrupting chemicals. Small-molecule alternatives that exist in various stages of research and commercialization will be discussed, with emphasis on the use of renewable resources. The rise of biorefineries and new bio-based monomers may help overcome existing economic barriers to adoption of alternatives. Increasing the molecular weight of additives or covalently linking them to polymer backbones are two promising strategies for reducing both mobility and toxicity that will also be discussed. Finally, the design of new polymers that show desirable properties without the use of additives will be considered. The substances put forward as "green" alternatives have yet to receive the same level of scrutiny as diethylhexyl phthalate (DEHP, also known as dioctyl phthalate) or polybrominated diphenyl ethers (PBDEs). Cooperation between chemists, engineers, and the environmental health community will be critical to ensure the safety and sustainability of new technologies.

Keywords: bio-based chemicals; flame retardants; plasticizers; polymers.

INTRODUCTION

Global plastic resin consumption occurs on the scale of hundreds of millions of metric tons, and the corresponding demand for additives is about 5 % by weight of all the plastic products manufactured in a year [1]. Plasticizers, mostly used in poly(vinyl chloride) (PVC), account for more than 50 % of additives used (by mass), and flame retardants are reported to be one of the fastest-growing sectors [2]. In Europe, these two categories together account for over 75 % of the additive market (by mass) [3]. Within these categories, phthalate plasticizers and polybrominated diphenyl ether (PBDE) flame retardants have been the subject of intense scrutiny for negative health effects on humans, animals, and other organisms, particularly because of evidence for biological activity at low doses with non-monotonic effects [4].

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‡Corresponding author

Phthalate plasticizers: Occurrence and toxicity

Phthalates are diesters of 1,2-benzenedicarboxylic acids (phthalic acids) with chemical characteristics that depend on the nature of the side-chains [5]. Since phthalate additives in plastic are not covalently linked to the host polymer, they can leach into the environment [6]. Although they are generally nonpersistent, contamination in the environment is still significant due to widespread use; low- and high-molecular-weight phthalates are commonly found in household dust, soil, and indoor and outdoor air, and as detectable residues in foods [5]. Phthalate exposures may occur through ingestion, inhalation, dermal absorption, and parenteral administration [7]. Several studies have shown that some phthalates possess endocrine-disrupting effects in male rat offspring, following in utero or lactational exposure, which manifest as hypospadias, cryptorchidism, testicular cancer, decreased testosterone levels, and reduced semen quality [5]. Phthalate activation of peroxisome proliferator-activated receptors alpha and gamma (PPARα and PPARγ), adjuvant activity, induction of cell proliferation, suppression of apoptosis, oxidative DNA damage, and production of reactive oxygen species (ROS) have been implicated as well [8–11]. It has been proposed that oral exposure in rats and humans allows diethylhexyl phthalate (DEHP) to enter the gastrointestinal tract, where it is rapidly metabolized to mono-(2-methylhexyl) phthalate (MEHP), 2-ethylhexanol, and phthalic acid via pancreatic lipases. At low concentrations, most DEHP is absorbed as metabolites, but at high doses, unaltered DEHP can also be absorbed. Absorption of DEHP and its metabolites leads to distribution throughout the body and further metabolism, mostly in the liver. MEHP and its downstream metabolites can be glucuronidated and eventually excreted [5,8]. In vitro and in vivo studies have shown that phthalate monoesters may be more bioactive than the parent compounds [5]. One proposed mechanism of action for MEHP, demonstrated in vivo in adult female rats and in vitro in rat ovarian granulosa cell cultures, is that DEHP/MEHP mimic the effects of fatty acids on granulosa cells, acting as ligands for fatty acid binding protein and thus interfering with a steroid hormone pathway [12]. Studies on female mice have shown that immunostimulatory effects (adjuvant activity) of phthalates and phthalate-like chemicals can be influenced by lipophilicity, chain length, and regiochemistry [10]. In isolation, the properties are not predictive; for example, the non-phthalate chemical methyl palmitate has lipophilicity comparable to DEHP but was shown to have no adjuvant effect. Significant differences were seen when comparing ortho-diesters to para-diesters.

Continued commercial use of phthalates

One strategy to reduce the global dispersion and health impacts of phthalate additives would be to replace PVC with alternative polymers. In Europe in 2007, PVC accounted for 80 % of plasticizer use, and that market continues to be dominated by phthalates (75–85 %) [3,13]. These numbers reflect the high proportions of phthalates that are used in flexible PVC formulations. Whereas pipe products may contain >95 % PVC by weight, in some applications such as fishing lures the proportion can drop as low as 14 %, and the polymer is effectively a gelling agent for liquid plasticizer [14]. However, use of PVC is not expected to abate in the near term. It was estimated that due to growth in Asia and developing markets (Fig. 1) production has more than doubled from 1992 to 2012, from 22 million to 50 million t/yr, and as of 2007 PVC accounted for 35.3 million t or about 17 % of all polymer resin sold [15].

Even if PVC production diminishes, plastics that fill the gap will demand additives as well. Global production of bioplastics was estimated to quintuple from 2007 to 2011, and if biorefineries become a major source of chemical feedstocks in the future, demand may continue to rapidly increase. Poly(lactic acid) (PLA) is currently one of the most widely used bioplastics and has been the focus of intensive additives-for-bioplastics research. PLA demands a variety of additives including plasticizers to perform in a wide range of applications [16]. Cellulose-, starch-, and wheat gluten-based polymers are formulated with plasticizers as well [17].

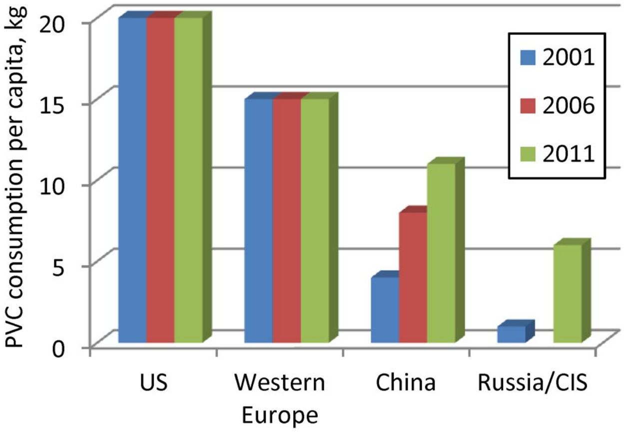


Fig. 1 Estimated PVC consumption per capita, 2001–2011. Data from *Plastics Additives & Compounding* (2008) [15].

PBDE flame retardants: Occurrence and toxicity

The inherent flammability of most commercial polymers means that flame retardant additives are critical for plastics used in electronics, textiles, foam padding, and other applications where accidental fires pose a risk. Global flame retardant demand has increased annually in recent years to around 2.2 million metric tons/yr. Demand for both halogen-free materials and brominated flame retardants is expected to grow [18]. Among halogenated flame retardants, PBDEs are increasingly the subject of environmental monitoring, toxicity assessment, and regulatory activity.

Similar to phthalates, PBDEs are not fixed in polymer products through covalent binding and therefore can leach into the environment. PBDEs occur as 209 congeners formulated into mixtures; to varying degrees these are persistent organic pollutants that bioaccumulate, bioconcentrate, and biomagnify in the environment to varying degrees [19–21]. For example, the atmospheric half-life of PentaBDE is estimated to be 10–20 days, while experiments with rats suggest a biological half-life of 19–119 days [22]. Tetra-, penta-, and hexa-PBDEs are the most common congeners found in the human body [21]. Evidence shows that higher-brominated congeners can be metabolized by organisms or degraded abiotically (e.g., via photolysis) producing the more toxic and more bioaccumulative lower-brominated congeners [20,23–25]. In the United States, diet and house dust are the main sources of human exposure [19,21,26]. PBDEs may also convert into other toxic, persistent pollutants such as dioxins or furans as a result of incineration [22]. DecaPBDE is still used in the United States and is commonly found in ethylene vinyl acetate (EVA) and other polymers for wires and cables, polyester resins, low-density polyethylene, and high-impact polystyrene (PS) (e.g., television cabinets) [27]. U.S. manufacturers have committed to a voluntary phase-out to be completed in 2012–2013. Prior to phase-out in the United States, penta-BDEs were used in flame-retardant flexible polyurethane foam for furniture and upholstery and octa-BDEs were used in flame-retardant acrylonitrile butadiene-styrene (ABS) copolymers (e.g., computer casings and monitors) as well as in formulations of nylon, phenol-formaldehyde resins, and unsaturated polyesters [27,28].

Pre- and postnatal in vivo exposures of mice and rats to PBDEs have been shown to affect thyroid hormone and hepatic enzyme activity [29,30]. Additionally, mono- and di-hydroxylated PBDE metabolites have been identified as potential endocrine disrupters due to their structural similarity to T4 thyroid hormone and their ability to bind to plasma thyroid hormone transport protein transthyretin (TTR) [29,31–35]. PBDEs share chemical properties with polychlorinated biphenyls (PCBs), suggesting aryl hydrocarbon receptor (AhR) induction as a relevant mechanism of action for further study [32,36]. Other activities including steroidogenesis, neurotoxic, genotoxic, acetylcholine receptor, constitutive androstane receptor (CAR), androgen and estrogen receptor, and oxidative stress have been implicated and are the subject of ongoing investigation [20,31,32,34,35,37–39]. Research on the metabolism of PBDEs has suggested that epoxidation of the phenyl ring is a key initial reaction in mammals [37,38]. Subsequent reactions lead to hydroxylation, formation of unstable carbocations, or conjugation to glutathione. The carbocation intermediate can potentially bind to proteins in the liver whereas other pathways lead to conjugation and elimination from the body [38]. In vitro studies have shown formation of quinone intermediates that can form adducts with DNA [34], however, this has not yet been validated with animal models. Many studies of toxicity and environmental fate have been performed with technical mixtures, and thus the specific metabolic pathways for most PBDE congeners remain unknown [40].

Continued commercial use of PBDEs and halogenated alternatives

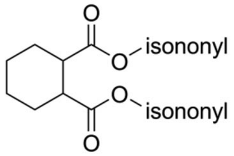
Halogenated flame retardants are designed to intercept radicals in the gas phase during a combustion event. In general, fluorine- or iodine-based chemicals do not give acceptable performance, and organobromines have been favored over organochlorines due to greater efficiency [22]. Out of the more than 70 known varieties of brominated flame retardants, PBDEs have been considered the most stable, cost-effective, and efficient [41]. As voluntary and regulatory phase-out of PBDEs continues in state, national, and international jurisdictions, a range of halogenated aliphatic or aromatic substances are employed as alternatives to PBDEs [22]. Some of these additives are persistent in human environments; for example, tris(1,3-dichloroisopropyl) phosphate (TDCPP) was found to be widespread in polyurethane foam collected from baby products [42]. The same study detected chlorinated and brominated additives not previously observed in environmental samples. In addition to persistence, many of the halogenated flame retardants present toxicity hazards [43]. For these reasons, recent research has focused on developing non-halogenated flame retardants. These will be further discussed below.

SOLUTIONS

The following sections provide an overview of non-phthalate plasticizers and non-halogenated flame retardants. Examples are taken from the literature as well as from commercial products. This review is intended to be illustrative rather than comprehensive, to demonstrate that numerous choices exist in various stages of commercial development. We have highlighted bio-based alternatives in particular as one of the principles of green chemistry recommends that chemists should use renewable resources and feedstocks whenever possible [44]. However, it cannot be assumed that natural origin means reduced hazard, nor does the absence of a phthalate or organobromine moiety. We wish to stress that green chemistry can be understood as a continuum—greening of products and processes depends on continuous improvement and efforts to eliminate tradeoffs between environmental impacts—and the examples cited below must be subject to the same level of scrutiny as existing technologies.

Small-molecule plasticizers

Numerous alternatives to DEHP have been proposed, as well as alternatives to the entire phthalate class of molecules. Di-isononyl cyclohexane-1,2-dicarboxylate (DINCH, **1**) may be the most rigorously tested drop-in replacement for DEHP to date. Prior to commercialization, DINCH passed a battery of eco- and genotoxicity tests covering a variety of species from bacteria and daphnids to zebrafish, earthworms, rats, rabbits, and guinea pigs [45]. Production capacity recently increased to 100 000 t/yr [13].



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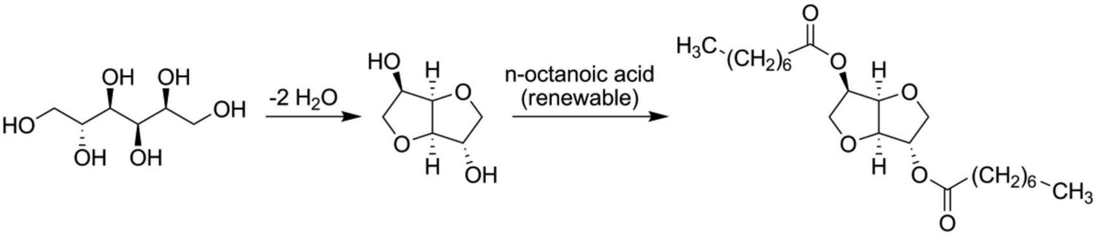
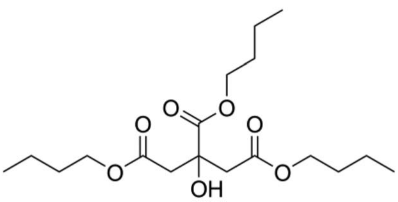
One class of plasticizers entirely based on renewable resources is based on isosorbide, a dehydration product of glucose-derived sorbitol (**2**). The performance can be tuned by selecting various alkanoic acids. Isosorbide di-(*n*-octanoic acid) ester (**3**) has capabilities similar to DEHP. Isosorbide esters are fully biodegradable and have passed tests for acute toxicity, sensitization, mutagenicity, and estrogenicity [46,47].



2 **3**

Citrate esters are well-known plasticizers for PVC and PLA. Tributyl citrate (TBC, **4**), acetyl tributylcitrate (ATBC), acetyl trihexylcitrate, and butyryl trihexylcitrate are all available commercially and the toxicological literature shows that this family of compounds is generally nontoxic by most assays. However, some studies have found that ATBC has cytotoxic effects [48–50], suggesting citrates will require further study. Epoxidized soybean oil is another well-known commercial plasticizer. It has tested negative for harmful effects in a range of tests (estrogenicity, mutagenicity, carcinogenicity, and embryotoxicity), except it is noted that some grades affected organs in rats [47,51,52]. A product based on the castor oil derivative **5** has lower volatility than DEHP and high resistance to extraction [53]. The patent literature suggests that the product is finding applications in PLA resins as well [54]. Several dibenzoate esters of bio-based diols show excellent performance in comparison to conventional plasticizers, but biodegradation and estrogenicity are concerns. Di(ethylene glycol)dibenzoate and di(propylene glycol)dibenzoate were shown to form toxic, stable metabolites when treated with yeast [55]. The related chemical 1,5-pentanediol dibenzoate shows improved biodegradability [56]. The outlook is promising, but it was reported that a technical-grade plasticizer containing predominantly di(propylene glycol) dibenzoate showed estrogenic properties [47], so more thorough testing is needed.



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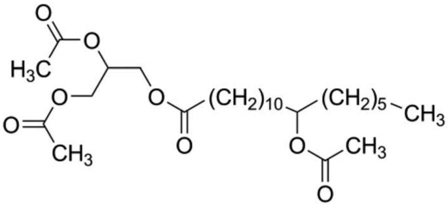
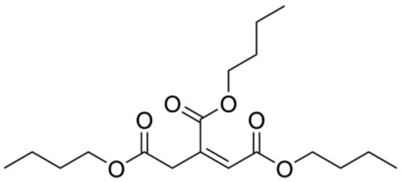


5

The use of waste products, particularly those from agricultural processes, will promote low-cost, environmentally friendly plasticizers. Tributyl aconitate (TBA, **6**) made from aconitic acid, a waste product of sugar cane processing, shows some advantages over citrates. TBA imparted better flexibility to PVC than di(isononyl)phthalate or TBC and had better migration properties than TBC [57]. According to TOXNET, TBA has an LD_{50} >500 mg/kg (mouse), indicating relatively low toxicity, but further study is needed to confirm the safety of this plasticizer. Another low-value agricultural product is unrefined "biodiesel coproduct stream" (BCS, consisting of glycerol, free fatty acids, and fatty acid methyl esters). BCS has been shown to be an effective plasticizer for gelatin. The thermoplastic gelatin produced may be used in extrusion, injection molding, or foam applications [58]. The use of BCS in plastic may raise the value of the biorefinery product and expand the range of applications for gelatin and other biopolymers.



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Ionic liquids have also emerged as a new class of plasticizers. Low volatility, low migration compared to DEHP, and reduced flammability hazard are all expected benefits [59], though toxicity will be a concern for many structural classes [60]. To date, the ionic liquids reported to have plasticizer effects have all been derived from petroleum, but the development of bio-based ionic liquids may offer new opportunities for environmentally benign innovations in the plastics field [61].

Small-molecule flame retardants

Non-halogenated flame retardants are the focus of a thriving research field. Scientists, government, and industry have produced numerous reviews of PBDE alternatives. The U.S. Environmental Protection Agency (EPA) has published a study on expected environmental effects of various phosphorus-based flame retardants [62]. Industry groups like the High Density Packaging User Group (HDPUG) have made similar efforts [63]. Flame retardant manufacturers have created a website, http://www.halogen-free-flameretardants.com, compiling performance and environmental data for a variety of applications [64]. The EPA considers environmentally positive attributes of flame retardants to include ready biodegradation or safe incineration, very large diameters (>10 Å) or high molecular weights (>1000 Da), ability to chemically bind to the substrate, and low toxicity [62]. A few examples of commercial technologies based on small molecules are highlighted here.

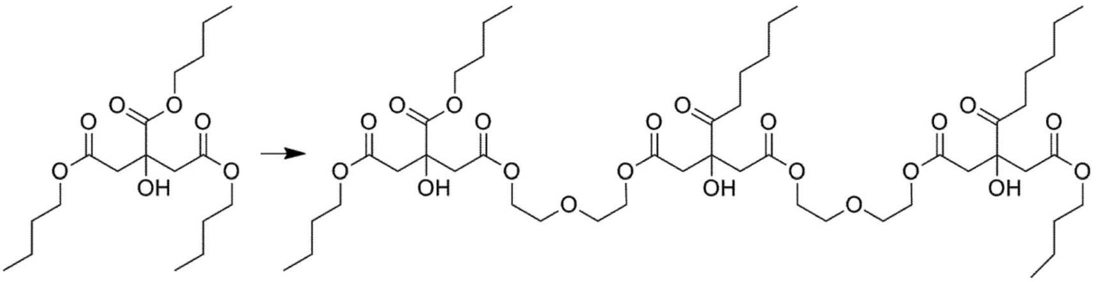
For polycarbonate plastics, certain metal sulfonates impart flame resistance at low levels, in the range of 0.05–0.1 % loading. An example of a non-halogenated, commercial sulfonate is potassium diphenyl sulfone sulfonate. The sulfonate technology exemplifies the potential benefits of taking advantage of unique flame-retardant mechanisms [65]. In the polyester industry, it is estimated that 40 % of resins are flame-retarded, usually with halogen-based agents. Melamine polyphosphate (e.g., DSM Melapur® 200) is one of the commercial non-halogenated alternatives [66]. Melamine polyphosphate thermal decomposition reactions are endothermic, and combustion generates N_2, contributes to char, enhances char properties, and shows synergy with other flame-retardant additives [67]. Better understanding of chemical mechanisms, in particular, synergies between materials (e.g., systems containing aluminum, phosphate, and nitrogen that achieve very high flammability standards) will help inform the design of new materials [68].

A product called Molecular Heat Eater® (MHE) is available in various formulations based on carbonate and phosphate salts and relatively benign organic acids (such as citric, glutaric, succinic, oxalic, formic, acetic, and stearic acids). Many of these components are available as agricultural waste products. MHE is typically dispersed in a polymer matrix as micron-sized particles, which require a strong endothermic reaction to decompose, resulting in the flame retardant effect. Performance of MHE in thermogravimetric analysis testing is reportedly similar to that of PBDEs, and in cone calorimeter tests MHE exceeded ISO standards [69]. MHE is one of the rare halogen-free technologies that make extensive use of bio-based materials. Further development of flame-resistant materials from biologically familiar chemicals would be highly desirable from a green chemistry standpoint.

Higher-molecular-weight plasticizers

One origin of the DEHP exposure problem is its tendency to leach from plastics. The mobility of additives within a polymer matrix can be limited by increasing molecular weight, and the effect can be dramatic. For example, a study of a poly(butylene adipate) plasticizer found that lower-weight oligomers (<1100 Da) making up 24 % of the mixture accounted for 90 % of migration from PVC into olive oil, and their migration rate was 90 times faster than that of the higher-weight species [70]. High molecular weight can also result in reduced toxicity: transportation across biological membranes is limited, avoiding toxic effects that would occur after absorption by an organism. In this case, degradability (planned or otherwise) can be a potential concern, because the lower-weight degradation products would need to be considered [71]. As before, this section will focus primarily on plasticizers derived from renewable resources.

Low-molecular-weight citrate and malonate ester plasticizers and are compatible with PLA but will separate from the polymer with aging. Using oligomeric analogues limits, the migration and results in morphological stability. A trimer (**7**) of tributylcitrate (**4**) with diethyleneglycol spacers showed signs of phase separation from the PLA matrix but due to its molecular weight, it was unable to migrate to the polymer surface. Oligomers of bis(hydroxymethyl) malonic acid adipate were more compatible with PLA than the malonate ester monomer and showed no signs of phase separation after aging [72].



4 **7**

Similar results have been seen with commercial polymeric adipates. Adipic acid can be produced from genetically engineered microbes (a Presidential Green Chemistry Challenge Award-winning technology) [73]. The product Glyplast® based on 1,3-propanediol (produced by DuPont and Tate & Lyle's Bio-PDO™ process) has molecular weights in the 1500–2500 Da range, and was found to be a better plasticizer for PLA than monomeric di-(2-ethylhexyl) adipate [74]. Another polymeric adipate for PLA is BASF's Ecoflex® (a biodegradable polyester from 1,4-butanediol, adipic acid, terephthalic acid) [16].

Products based on 1,4-butanediol may be of concern since it is metabolized in humans to γ-hydroxybutyric acid, which acts on the central nervous system in humans. In 2007, the presence of 1,4-butanediol as a plasticizer in children's toys led to several hospitalizations [75]. Other, less potentially hazardous diols could be used to prepare poly(adipate) esters. For applications where plasticized PVC comes in contact with food, the European commission has approved higher migration limits (relative to phthalates) for certain polymeric adipates [76]:

- polyesters of adipic acid with glycerol or pentaerythritol, esters with even-numbered, unbranched C12–C22 fatty acids
- polyesters of 1,2-propanediol and/or 1,3- and/or 1,4-butanediol and/or polypropyleneglycol with adipic acid, also end-capped with acetic acid or fatty acids C12–C18 or *n*-octanol and/or *n*-decanol

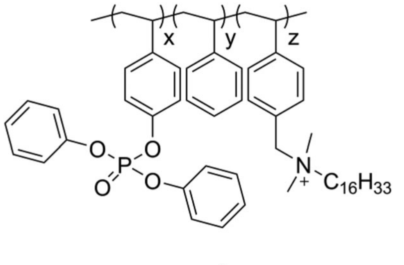
When linear polymer plasticizers are used, a tradeoff often arises: at low molecular weight, compatibility with the polymer improves but increased migration becomes a problem; at high molecular weight, migration is limited but processing becomes difficult. Polymer branching has been shown in several cases to mitigate this problem; branching helps improve melt viscosity and therefore processability [77]. For example, hyperbranched poly(ε-caprolactone) performed better than its linear counterpart, and as effectively as DEHP, in a PVC formulation. Migration under harsh conditions was not detectable, whereas the corresponding mass loss of DEHP was greater than 77 % in one test [78]. Work on branched poly(butlyene adipates) in PVC found that molecular weight, degree of branching, and selection of end groups could be tuned to give desirable material properties while limiting migration [77].

Lignin, an abundant biopolymer and waste product of the pulp and paper industry, is showing promise as a secondary plasticizer. In PVC/PVA blends for flooring applications, formulations with lignin improved the mechanical properties of the product, reduced the amount of polymer and plasticizer used, and allowed for the substitution of DEHP with alternative plasticizers [79]. A similar approach could be taken with other polymer systems to take advantage of lignin's status as a renewable and relatively harmless feedstock

Higher-molecular-weight flame retardants

Research on flame retardants has often focused on introducing flame-resistant chemical functionality directly into the backbone of the polymer host, either through copolymerization with special monomers or by grafting reactive flame retardants to the polymer product. In addition to the advantages of limited migration and reduced bioavailability, this strategy has a benefit in many cases: the amount of flame retardant can be greatly reduced [80]. For example, an epoxy resin made with partially organophosphate-modified monomers showed better flammability properties than the conventional resin blended with low-weight organophosphates after curing [81].

Polymer-clay nanocomposites are a potentially sustainable solution to flame retardant issues. Compared to metal hydroxide flame retardants, the higher compatibility of clay results in excellent flame-retardant properties at much lower loadings (aluminum hydroxides may be added at >60 %; clays are <5 % in many cases). When polymer chains are sandwiched between clay nanosheets, or when the polymer and silicates are uniformly dispersed, volatile thermal decomposition products cannot migrate easily. Formation of structurally regular chars protects the bulk of the polymer from combustion occurring at the interface [82]. Heat release rate is also significantly reduced. For example, a PS resin with 3 % intercalated nanoclay had comparable performance to a PS resin with decabromodiphenyl oxide/antimony trioxide flame retardant at 30 % loading [83]. There are currently few commercial plastic formulations containing nanoclay additives [84]. This is in part because some flammability characteristics are not improved, and therefore they must either be used in combination with other additives, or they should be modified to introduce new fire safety mechanisms [85]. There is a growing research effort to improve nanoclay performance. One particularly interesting approach is the preparation of phosphorus-modified oligomeric counterions (**8**) for the clay. By making the flame-retardant functional groups an integral part of the clay, dispersion throughout the polymer is made possible [86]. This approach is attractive from a green chemistry standpoint in that the flame retardant is less able to leach from the polymer.



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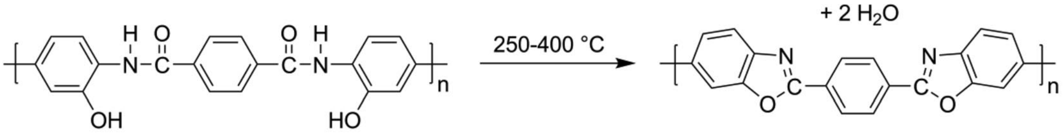
Another promising application of nanotechnology is the use of multiwall carbon nanotubes (MWCNTs) in flame-retardant resins. Their hydrophobic nature makes them easy to disperse in nonpolar plastics. At low loadings, their use reduces fire hazards in a variety of plastics including polycarbonate, polyamide, polyethylene, polypropylene, and PS. In the polycarbonate study, for example, it was noted the presence of MWCNTs slightly alters the mechanical properties of the polymer, but 40–50 % reduction in heat release rate could be seen at just 2 % loading of additive [87]. It was concluded that MWCNTs cannot act as a stand-alone additive for PC, but since there are few examples of flame retardants that are halogen-, metal-, and even phosphorus-free, the results are promising. As noted by NIST, the lack of high-quality life cycle assessment and health and safety data on nanoparticles should be addressed as this field of research continues to progress [88].

Engineered polymers

Advances in thermoplastic elastomer (TPE) polymers have given rise to a variety of commercial plastics that provide plasticity without the use of phthalates or other additives. TPEs can be made from both commodity and higher-value monomers. Polyolefins produced by metallocene catalysis have been used as plasticizer-free alternatives to PVC for more than a decade in medical, automotive, construction, and packaging applications, with improved mechanical performance, higher material efficiency, and reduced maintenance. In 1998, it was estimated that metallocene polymers could potentially capture 50 % of the flexible PVC market [89]. A wide variety of TPEs have been commercialized. A recent example is Dow's Infuse™ block copolymers, which use a zinc "shuttle" catalyst to pass growing polymer chains between a zirconium catalyst selective for ethylene polymerization and a hafnium catalyst selective for 1-octene polymerization. The result is a copolymer with alternating crystalline and amorphous blocks [90]. A recent push in TPE technology is the use of bio-based monomers. These include Pebax® Rnew (ether and castor oil-based polyamide blocks, with up to 95 % renewable carbon content), Grilflex® PEBA (containing castor oil- or canola oil-based polyamide blocks), and Pearlthane® Eco (a vegetable oil-derived thermoplastic polyurethane) [91].

Inherently, flame retardant plastics are also well known. A partial list includes aramids, melamine, poly(benzimidazoles), polyphenylene sulfides, polyetheretherketones, and preoxidized polyacrylonitriles. Many of these materials require such a high concentration of oxygen for combustion that they are self-extinguishing under normal conditions and can achieve required flammability ratings without additives [92]. Cost, mechanical properties, and processing difficulties are all factors that would preclude most of these materials from being used in commodity applications, but they provide a starting point for design of new polymers. A U.S. Federal Aviation Administration (FAA) study suggested that the essential design elements for an inherently flame-retardant carbon-based plastic are heteroatoms (e.g., halogens, O, N, S, and P), aromatic rings, heteroatomic rings, or chemical units that can lead to cross-linking or fused aromatic rings. An example of these guidelines in practice is the high fire resistance of poly(hydroxyamide) (**9**) and its derivatives. At temperatures of 250–400 °C, these polymers cyclize to more stable poly(benzoxazole) (**10**) rings. The cyclization is endothermic and releases water, both of those properties interfering with combustion [93]. The FAA study recommends further research into flame retardant mechanisms; for example, it is not currently understood how the minor structural difference between Nomex® and Kevlar® aramid polymers (para- vs. meta-substituted aromatic rings) leads to dramatic changes in heat release capacity.



9 **10**

Wool is an inherently flame-retardant material found in nature that may provide a starting point for biomimetic technologies. It has high nitrogen and moisture content, does not melt during combustion, and forms a protective char with excellent insulating properties. Because of these characteristics, wool is often used in aircraft furnishings and other applications where fire resistance and smoke suppression are critical [94]. Further study of wool, from its macrostructure to its chemical mechanism of flame retardancy, may aid the future development of bio-based flame-resistant plastics.

DESIGNING LESS HAZARDOUS CHEMICALS

Very few (if any) of the alternative additives discussed in this review have received the same level of scrutiny as DEHP and PBDEs. Examples have been highlighted here to demonstrate that functional alternatives are abundant, and that progress has been made in adoption of green chemistry principles. The use of renewable resources (particularly those widely recognized as safe) should be encouraged, but ideally all green chemistry principles must be met. Comprehensive assessments of hazards at all stages of the chemical lifecycles need to be completed for many promising technologies. The criteria considered by the EPA Design for the Environment team in its assessments of flame-retardant materials [62] provide a set of endpoints for any chemical designated for mass markets:

- acute toxicity
- carcinogenicity
- bioconcentration
- subchronic and chronic toxicity
- neurotoxicity
- degradation and transport
- reproductive toxicity
- immunotoxicity
- aquatic toxicity
- developmental toxicity
- genotoxicity
- terrestrial organism toxicity

The hazard screening process for new additive technologies will ideally be aided by computational methods, and eventually simple molecular design rules, to aid chemists and engineers in selecting which polymer additives are worthy of more comprehensive study. A hierarchy of design information for designing safer chemicals has been proposed (in order of increasing utility) [95]:

- molecular modifications that decrease bioavailability
- molecular modifications affecting absorption, distribution, modification, and excretion parameters
- quantitative structure–activity relationships that predict safe or problematic structural classes
- knowledge of the precise mechanism of action

Some progress has been made in articulating guidelines that can be easily adopted by chemists and other molecular designers, for example, in predicting biodegradability [96]. Designing for minimal harm to humans (particularly in regards to emerging issues like endocrine disruption and epigenetic effects) remains a significant challenge. Shape Signatures, a computational approach that relies on molecular geometry and polarity information, has been used to identify novel estrogen antagonists [97] and may prove useful in screening new polymer additives. Statistical partitioning analysis has also shown that computed physical/chemical properties can be related to human toxicity in a way that can distinguish between a sample of chemicals from the EPA Toxics Release Inventory and a random sample of commercial chemicals [98], and the work has been further developed as an in silico prescreening tool for acute and chronic ecotoxicity endpoints [99,100]. As research efforts continue to reveal new links between molecular structure and harmful effects, one productive application of the results will be the screening of libraries of chemicals that can be readily produced from biorefinery products (by esterification, hydrogenation, or other green processes) [101]. As bio-based chemical platforms begin to supplement and possibly supplant the petroleum platforms, new molecular structures will appear in the commodity chemical markets. This development will facilitate transformative advances in green chemistry of polymer additives.

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