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Review

From epoxy vitrimers to DOPO–based (bio–)epoxy vitrimers: Current state-of-the-art and perspectives

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ABSTRACT

Epoxy thermosets have become indispensable in various applications from household plastics to automotive and aeronautics due to their outstanding features, such as excellent chemical stability and thermo–mechanical properties. During the past two decades, the use of epoxy systems in fire safety applications has significantly increased. Unfortunately, epoxy resins are highly flammable, and their thermosets are neither reprocessable nor recyclable after their lifetime. These drawbacks result in fire hazard and waste accumulation toward environmental pollution, breaching green principles and worldwide laws for sustainable development. The organophosphorus 9,10–dihydro–9–oxa–10–phosphaphenanthrene–10–oxide (DOPO) and its derivatives are some of the most extensively researched flame retardants (FRs) for epoxy resins. DOPO derivatives, either reactive or non–reactive, not only render epoxy systems fireproof but also enhance other properties (e.g., non–oxidative capacity, adhesion, thermo–mechanical stability, and water repellency). With this in mind, the scientific community has focused its research on developing epoxy thermosets that incorporate both fire safety and recyclability. As a solution to the reprocessability/recyclability major issue, in 2011, vitrimers were first reported. These new materials consist of covalent adaptable networks (CANs) which can modify their topology via heat–triggered bond–exchange reactions. This work aims to review the advances in flame retardant (FR) DOPO–based epoxy vitrimers, emphasizing such key aspects as chemistry, flame retardancy, thermo–mechanical features, and sustainability. CANs are summarized and classified via the dynamic covalent bond types. Representative examples in the last five years from both fossil and bio–based DOPO–containing epoxy systems are reviewed and matched within the up–to–date circular economy context to design novel, green, and sustainable materials.

1. Introduction

Nowadays, plastics represent a household name synonymous with daily life because of their presence in every industry and almost all application domains and commercial sectors, such as packaging, civil engineering, energy storage, transportation, and biomedicine, among others [1]. According to statistics by the PlasticsEurope Organization [2], the world plastic production was 400.3 Mt. (58.7 Mt. in Europe) in 2022, with a trade balance of 9.2 billion € and a turnover of over 400 billion €. Unfortunately, due to their long lifetime, most polymer materials become environmentally persistent and hazardous pollutant waste at their end of life (EoL) if not accurately managed and effectively recycled. This issue, along with global oil price fluctuations, compelled both academia and industry to invest massively in research for efficient strategies in reducing polymer wastes and establishing economic pathways toward upcycling/recycling them, hence fulfilling the current circular economy legislation [3,4]. Looking at European waste management statistics in the last five years (Table 1) [5], while the amount

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Abbreviations: EoL, End–of–Life; FR, flame retardant; FRs, flame retardants; DOPO, 9,10–dihydro–9–oxa–10–phosphaphenanthrene–10–oxide; MPP, melamine polyphosphate; APP, ammonium polyphosphate; T_g, glass transition temperature; CAGR, compound annual growth rate; EU, European Union; CANs, covalent adaptable networks; EC, European Comission; ERC, European Research Council; DGEBA, diglycidyl ether of bisphenol A; BPA, bisphenol A; DDM, 4,4′–diaminodiphenylmethane; DDS, 4,4′–diaminodiphenyl sulfone; UL 94 VB, vertical burning test; LOI, limiting oxygen index; TTI, time to ignition; p–HRR, peak of heat release rate; BDE, bond dissociation enthalpy; DFT, density functional theory; $T_{5\%}$, thermal degradation temperature at 5 % mass loss; T_v, topology freezing point temperature; E_a, activation energy; THR, total heat release.

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Table 1

EoL plastics fate in the last five years (values in Mt. units) [5].

Year	2020	2021	2022	2023	2024
Recycled	34.1	35.9	41.2	47.5	53.6
Incinerated	67.9	69.5	69.9	70.7	72.3
Landfilled	177	181.3	183.9	179.6	177.1
Mismanaged	80.8	81.8	80.6	78	76.4

of recycled plastics followed an increasing trend up to ~53 Mt, it is still the lowest compared to the incinerated (~72 Mt) and mismanaged (~76 Mt) amounts, with particular emphasis on the landfilled-confined quantity (177 Mt). Literature studies report that almost all plastic products containing FRs and other additives follow the same tendency as their pristine counterparts, their landfilled waste contaminating the soil and generating greenhouse gases [6].

Polymer systems can be classified according to two main types of materials, thermoplastics and thermosets. Thermoplastics (e.g., poly(ethylene terephthalate), poly(vinyl chloride), poly(ethylene), and poly(styrene)) consist of linear polymer chains connected via physical forces and may be re–melted and recycled to some extent by mechanical processing at elevated temperatures [7]. These physical forces break down at high temperatures, and the material state shifts from solid to viscoelastic liquid. Unlike thermoplastics, thermosets (e.g., epoxy, silicone, melamine-formaldehyde and urea-formaldehyde resins) are covalently cross–linked three–dimensional networks generated during the curing process and therefore cannot be recycled or re–processed [8]. Despite their features endowing them with superior thermo–mechanical properties compared to thermoplastics, thermosets usually decompose before melting. This is because their chemical cross–links cannot be easily cleaved regardless of the high temperatures. This drawback generally makes thermosets more suitable for reuse as fillers or fuel [9,10].

Thermosets currently account for 20 % of the global market at an average annual production of around 65 million tons [9]; among thermosets, epoxy resins account for 70 % of the global market and more than 60 % of the world coatings industry. They are the most versatile structural adhesives due to their excellent compatibility with various substrates, which they provide with a wide variety of properties through surface modification. To lighten the transportation weight of different vehicles and reduce fuel usage, epoxy–based adhesives and structural composites will dominate the market in the coming years. Therefore, an emerging issue is the recovery of both the epoxy matrix and filler material within the epoxy thermoset. Epoxy thermosets possess two major disadvantages. First, they are highly flammable, hence inappropriate for fire–safe applications. Then, they are chemically cross–linked networks, thus infusible, insoluble, unprocessable, and non–recyclable [9]. Two are the main strategies to make thermosets flame retardant [11]. The first implies the incorporation of organic and/or inorganic additives into the epoxy matrix, usually exploiting e.g., halogen–based fire retardants [12]. The drawbacks of this approach may be additives' leaching, accumulation,

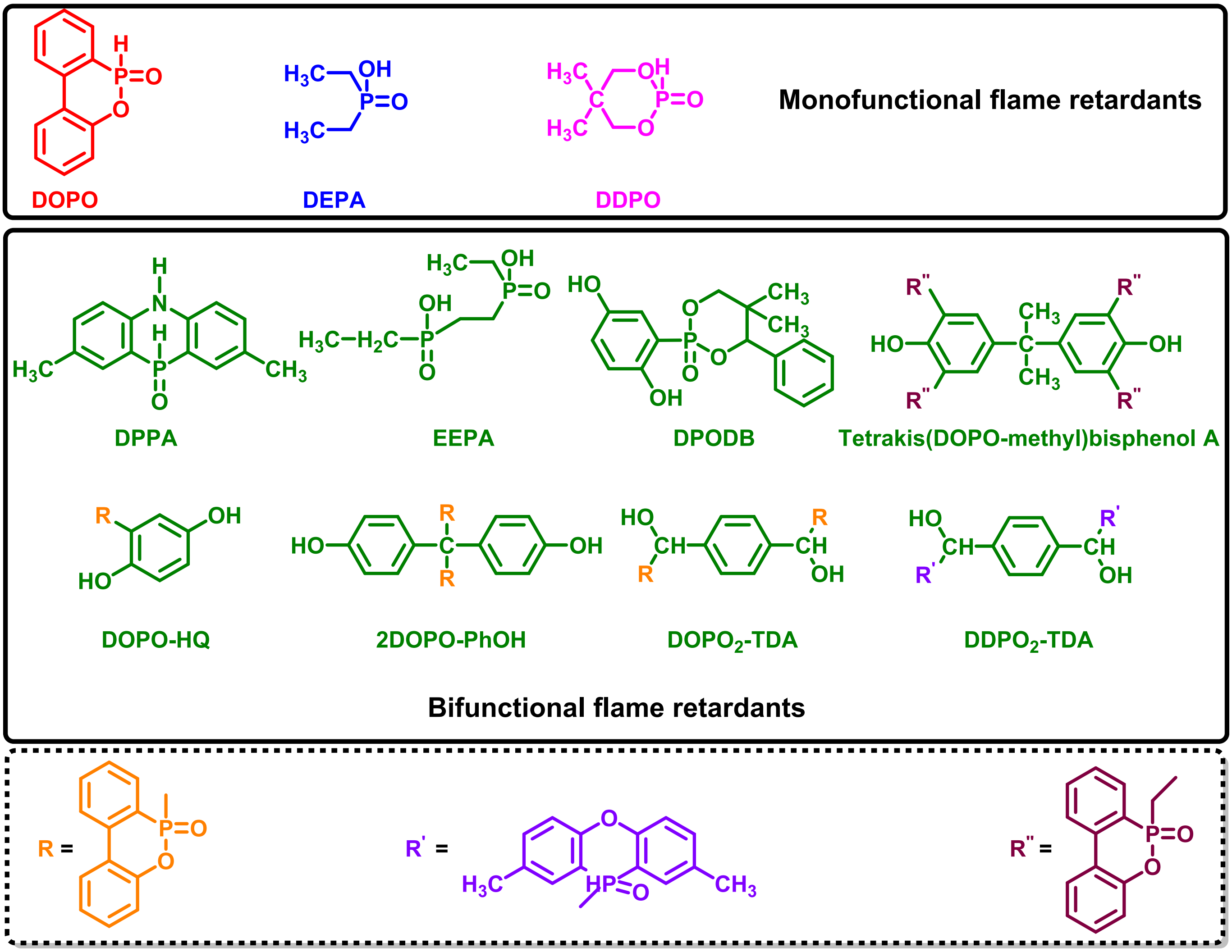


Fig. 1. Some phosphorus-based FRs.

and persistence in the environment. To overcome this issue, the research for greener alternatives led to phosphorous–containing FRs (Fig. 1), such as 9,10–dihydro–9–oxa–10–phosphaphenanthrene–10–oxide (DOPO), phosphazenes, melamine polyphosphate (MPP), diethyl phosphonic metal salts and ammonium polyphosphate (APP) [13]. The second approach is the reactive pathway that is more efficient than the former since DOPO and phosphates and cyclophosphazene derivatives can be covalently bonded to the polymer thermoset, preventing their leaching during chemical or thermal treatments of the epoxy material. Nevertheless, the reactive strategy may have a significant impact on the mechanical properties and glass transition temperature (T_g) [14]. To overcome these issues, also considering the targeted properties and the envisaged application fields, the following strategies have been developed: (i) direct covalent bonding of the FR to the epoxy resin via a pre–reaction; (ii) use of the reactive FR as curing agent; (iii) combination of pathways (i) and (ii); (iv) design and preparation of epoxy composites embedding such fillers as nano–silica in the matrix cured with FR and (v) FR-functionalized silica–containing nanostructures [15,16].

According to a recent study, the European FRs market expanded at a compound annual growth rate (CAGR) of around 5.08 % in the years 2019–2024, with a climax in the building construction and electronics industries [17]. The most common FRs for epoxies are based on halogens, phosphorus, nitrogen, and metals [18,19]. However, halogen–based FRs are toxic to human health and the environment: thus, they were banned by many European Union (EU) regulatory authorities [20–27]. As a result, a lot of research is currently being focused on the development of environmentally friendly FRs for epoxy resins, such as those based on phosphorus, carbon or silicon materials, and nanocomposites [28]. In recent years, significant efforts have been put into the development of organophosphorus FRs. Among them, DOPO (Fig. 1) has gained increasing interest due to its excellent features, i.e., highly reactive character, FR efficiency, and an overall enhancement of other properties of epoxy systems (e.g., thermo–mechanical stability, adhesion to different substrates, water resistance, anti–oxidation behavior, and eco–friendly character) [29,30].

In 2011, Leibler's group [31] introduced a new generation of materials that possess dynamic covalent bonds and named them vitrimers. Vitrimers are polymer networks at room temperature and undergo heat-triggered topological rearrangements by "flowing" at elevated temperatures: these peculiarities disclosure a high potential for the design of new materials with such properties as self–healing or recyclability within a broad temperature range [32]. The group of Bowman [33] coined the wider term "covalent adaptable networks" (CANs) with vitrimers as a distinctive subclass, including Si–O–Si and disulfides exchange, reversible ester bonds, transalkylation, imine, and dioxaborolane metathesis, among others [34,35]. CAN-designed networks can cleave and reconnect reversibly when exposed to an external stimulus, making the material reprocessable [36,37]. Combining functional FRs with CANs allows for obtaining fire retardant recyclable materials (even bio-sourced systems) showing a good balance between thermo–mechanical properties, stiffness, and chemical reprocessability [38]. For example, Wang et al. [39] obtained simultaneously recyclable and FR bio–based thermosets from vanillin. These types of materials with both flame resistance and recyclability will surely expand their application palette and lifetime toward environmental safety and following circular economy principles.

Despite several research efforts spent on the investigation and review of flame retarded vitrimers [40–42], the use of DOPO and its derivatives as effective FRs for (bio)epoxy vitrimers has not been reviewed yet. Indeed, apart from some experimental works dealing with FR DOPO-based (bio)epoxy vitrimers, recent reviews mainly focus on flame retarded epoxy vitrimers, some of which are DOPO-derived [20,38,41] or, with a more general approach, on flame-retardant thermosets, which also include DOPO-based epoxy systems, but not vitrimers [43,44]. Therefore, the purpose of the review is to fill this gap by presenting an up-to-date overview of the current progress in the design and implementation of effective DOPO-based FR (bio)epoxy vitrimers. These combine the unique FR properties of DOPO and its derivatives with the reprocessability, reshapeability, and easy recyclability of epoxy vitrimers. The proposed review focuses on the technological advances of these new systems within the last five years and highlights key aspects like their specific chemistry and structure-fire behavior relationships, underlying their importance within the circular economy context and the sustainability concept.

2. Global context

2.1. Overview of linear and circular economy

The European Commission (EC) issued the definition of bioeconomy as "the production of renewable biological resources and conversion of these resources and waste streams into value added products, such as food, feed, bio–based products and bioenergy" [45]. This aspect is due to the growing demand for sustainable bioresources, the reduction of petroleum–based ones, and to address current climate change issues. To achieve these purposes, the EC has created a Bioeconomy Strategy based on a three-plan outlook relying on the development of: (i) new processes and technologies; (ii) competitiveness and markets, and (iii) cooperation between stakeholders and policymakers. Bioeconomies rely on bioresources (i.e., microorganisms, plants, animals, organic waste) and all industrial and economic sectors exploiting these resources with an emphasis on sustainability and circularity in both efficient use of resources and biodiversity preservation and enhancement.

Linear economies refer to the "end–of–life" model of a product, from the (non–)renewable raw materials in the production line to product usage and its generated waste. Recent efforts managed to establish an additional feedback loop, according to which some constituents of the consumer product, such as different packaging (e.g., plastic, paper), are reintegrated into the production line, managing to reduce waste (Fig. 2a & b), though without reconstructing the initial product [46,47].

The circular economy is dedicated to the long-term preservation of resources and product value, and describes a closed-loop system based on the reuse, repair and recycling of a product to eliminate waste and pollution by minimizing raw materials and carbon emissions (Fig. 2c). [48]. This involves the use of high, cheap, and accessible quantities of raw materials and energy and waste valorization on one hand, and preserving product values, resources, energy, equipment, and infrastructures for a longer time, on the other [49]. For these purposes, waste and energy must be either introduced in a technological process or integrated as bioresources in nature [50]. Hence, the general objective of the circular economy is to obtain products and processes with lowest energy consumption and zero waste generation.

2.2. Epoxy thermosets: present and future

Epoxy resins are one of the most important classes of thermosetting resins due to their chemical versatility and wide range of application domains, from multi–substrate adhesives to the aerospace industry. Their thermosets are endowed with remarkable features, such as excellent chemical and abrasion resistance, as well as interesting thermal, mechanical, and dielectrical properties [51–54]. Epoxy monomers also possess very good dimensional stability after cross–linking with an adequate hardener [55]. The versatility of epoxy monomers is due to the presence of at least two reactive oxirane rings that can generate thermosets with a wide palette of hardeners, such as amines [56], anhydrides [57], amides [58], acids [59], phenols [60] and thiols [61], to obtain materials with pre-designed properties (Fig. 3) for targeted applications [62–66]. The hardeners may also possess multiple reactive sites that can generate further cross–linking. The choice of hardener and reaction conditions are crucial in pre–designing the properties of the final material [67]. A wide palette of epoxy resins with different chemical properties can be designed for specialized applications through

Fig. 2. The linear economy: (a) from raw materials in the production chain to marketed and used product, ending in waste, and (b) encompassing feedback loops where raw material enters production followed by product marketing, usage, recycling, reintroduction in production, but ending in waste. (c) The circular economy is based on raw materials introduced into the production line, with respect to sustainable waste recycling back into production, to eliminate waste and minimize raw materials usage. Adapted with permission from references [46, 47].

the tailoring of their various backbones via different chemical modifications and cross–linking degrees [68].

Two major issues are related to unmodified epoxies, namely, their weak flame retardancy and extremely difficult reprocessability. The features that recommend epoxies as candidates for high–performance applications greatly limit their recycling possibilities. Furthermore, the presence of FRs, either reactive or as non-reactive additives incorporated into the epoxy matrix, strongly affects the recycling pathway and its steps. The complex composition of epoxy–based products excludes the sole focus on a specific recycling technology as a viable solution. Usually, the product bulk is of non–organic nature, and often incompatible with chemical recycling. All the challenges of recycling epoxy-based FR materials have raised awareness and prompted the members of the European Research Council (ERC) to constantly search for novel recycling strategies to extend the EU's circular economy goals.

More than 75 % of the epoxy polymers are based on the petrochemical monomer diglycidyl ether of bisphenol A (DGEBA) which is obtained from the reaction between the toxic fossil–based epychlorohydrin and bisphenol A (BPA) (Fig. 3), an environmental pollutant and endocrine–disrupting compound, affecting the central and immune system. Chen [69] recently reviewed the progress in sustainable bio-based epoxy technologies. Bio-based epoxy resins are obtained by using the bio-based epychlorohydrin to replace the fossil-based epychlorohydrin in the reaction with BPA. Typical bio-based conventional epoxy resins are bio-based BPA, bisphenol F, phenol novalac and glycidyl amine-based epoxy resins. Since the building blocks and synthesis are the same in bio-based and conventional epoxy resins, the former can be easily used in applications with no performance issues. Bio-based novel epoxy resins may be obtained via epoxidation of epychlorohydrin from raw renewable resources (i.e., tannins, unsaturated vegetable oils, cardanols, saccharides, lignin, rosins and terpenes) with BPA [70–75]. Obtaining totally bio-based epoxy resins, however, remains a big challenge, as BPA is fully fossil-based. BPA infiltrates into water resources mainly via its industrial manufacturing and products, wastewater treatment plants, decomposition of polymer products, leachates, and household garbage ignition. Through contaminated water, food, and ecosystems, BPA enters the human body. The main sources of BPA spreading pathways in water are shown in Fig. 4 [76]. Therefore, the disposal and recycling of waste from epoxy resins and their composites has become an increasing challenge due to its hazardous effects on both health and the environment. A grim scenario estimates the doubling of global overall plastic production within the next 20 years, and with only 18 % recycling rate, generating around 12,000 Mt. of plastic waste in the environment by 2050 (Fig. 5) [68,77].

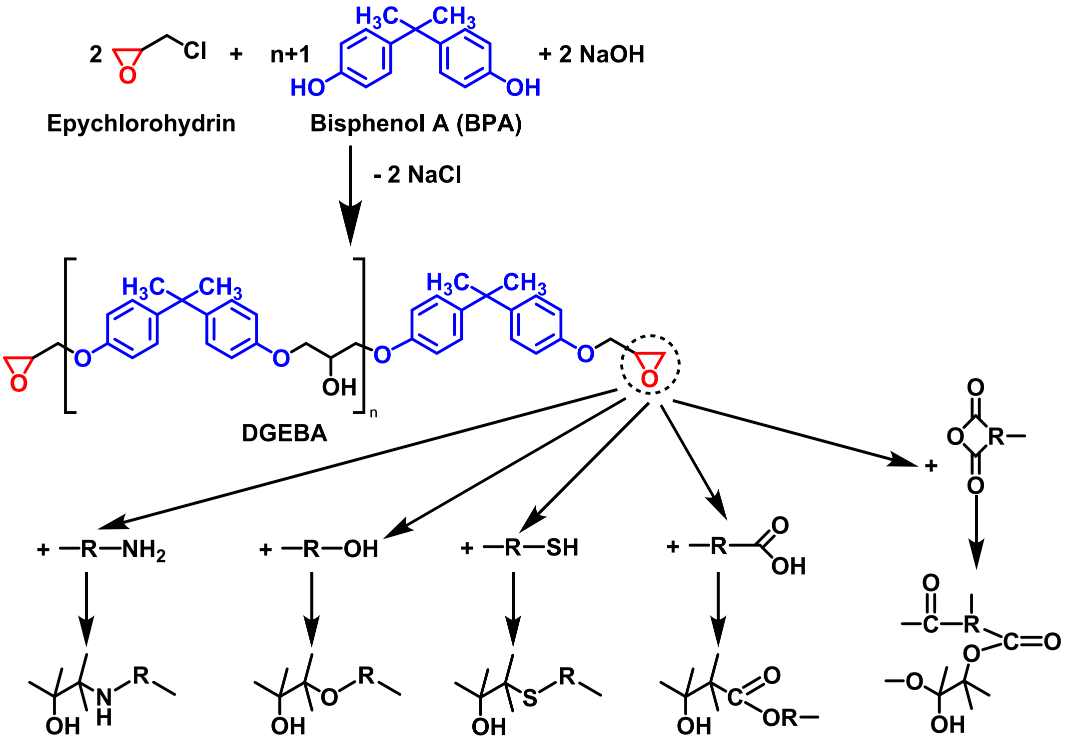


Fig. 3. The synthesis of an epoxy resin and the oxirane ring reactions with different hardeners.

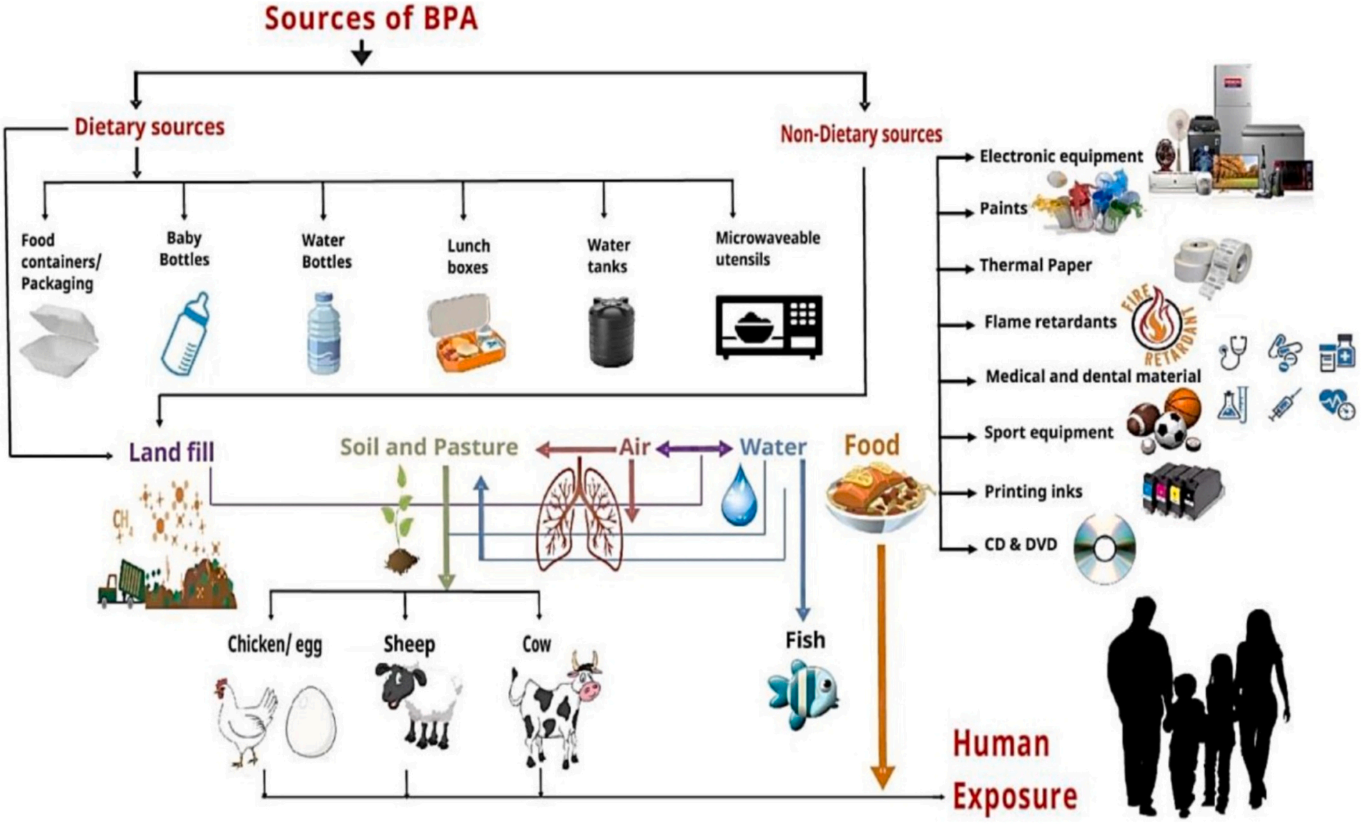


Fig. 4. Potential sources of BPA contamination and spreading pathways. Dietary sources (different food and water packaging, microwave utensils) and non-dietary sources. Reprinted from reference [76] under Creative Common Attribution CC.BY.4.0.

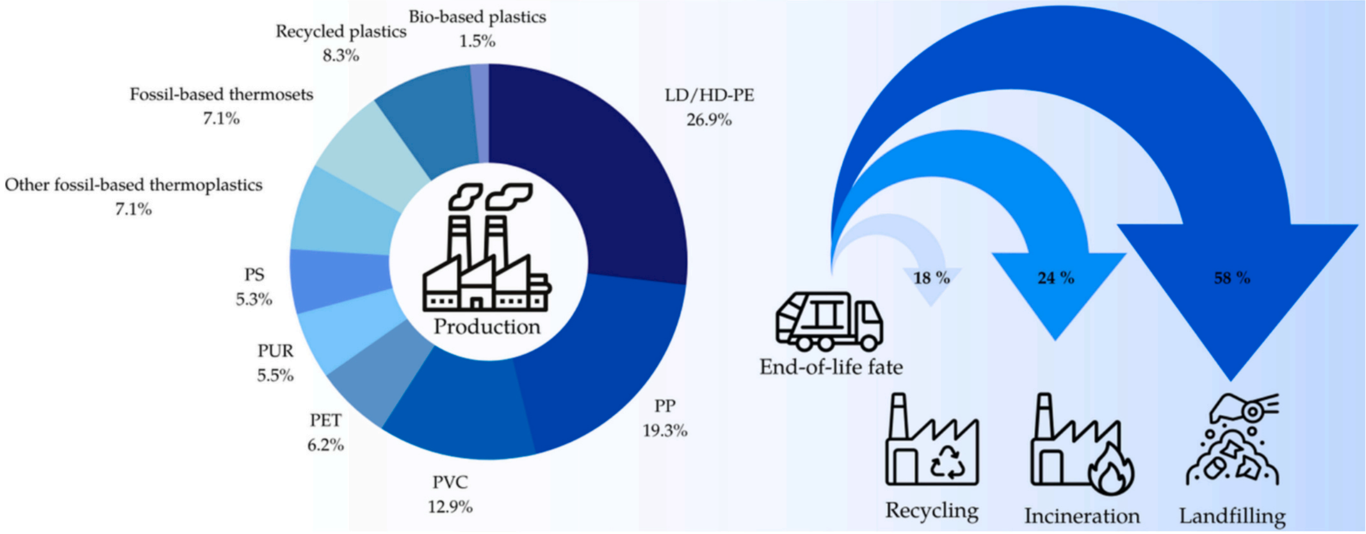


Fig. 5. Production status (in 2021) and End-of-Life fate (in 2017) of plastics. Reprinted from reference [68] under Creative Common Attribution CC.BY.4.0.

Epoxy thermosets accounted for 7.1 % of the global plastic production in 2021 and, as previously mentioned, they generally dominate around 70 % of the global market. Also, the demand for flame retarded (bio)epoxy thermosets is increasing [78]. This is especially due to the evolving development of sustainable technologies for lightweight materials (e.g., for electric vehicles or on- and off-shore wind power plants). It is therefore that sustainable recycling strategies are continuously sought to meet resource demand and to minimize waste in the epoxy composite industry. The typical recycling pathways for epoxies, i.e., pyrolysis, solvolysis, and nitric acid treatment, require rough process conditions (e.g., high pressure and temperature, corrosive chemicals), polluting and generating large quantities of CO_2 emissions [79].

Integrating both fire resistance and recyclability in covalent thermosets will surely extend their application palette and prolong their lifetime toward an eco–friendly, safe, and sustainable circular economy. Moreover, to prevent FR thermoset waste treatment, avoid the use of solvents or the often complicated synthesis pathways, and assure material recycling, the best alternative relies on the design of inherently FR and reprocessable thermosets from the beginning [80].

Since 2011, academia and relevant industrial stakeholders have set their attention on a new class of materials named “vitrimers” which, unlike conventional thermosets, contain associative CANs within their structures [81]. CAN–based vitrimers behave as cured networks at ambient temperature but undergo heat-triggered topological rearrangements at specific temperatures causing them to “flow”. Zhang et al. [82] provided a general overview of the recycling strategies for vitrimers. Rashid et al. [38] reviewed CAN–based intrinsically recyclable FR thermosets. Klingler et al. [83] recently summarized various types of CANs with covalently functionalized pendant or embedded flame–retardant entities. Bifulco et al. [84] highlighted the main advantages and drawbacks of the current recycling methodologies, classifying them on the different chemistry of the FR polymer classes (thermoplastics, thermosets, composites, and CANs), including their recent progress, challenges, recyclability opportunities, and reprocessing approaches.

3. DOPO–containing flame retardants

3.1. Classification and current status of flame retardants

FRs are one of the largest types of additives for plastic processing (Fig. 6). In 2020, the FR market was estimated at 7.46 billion USD, with an increase of more than 350 million USD compared to 2019 (7.09 billion USD). In 2020, the transport, electrical, and construction sectors used the highest number of FRs [85], their number estimated at around

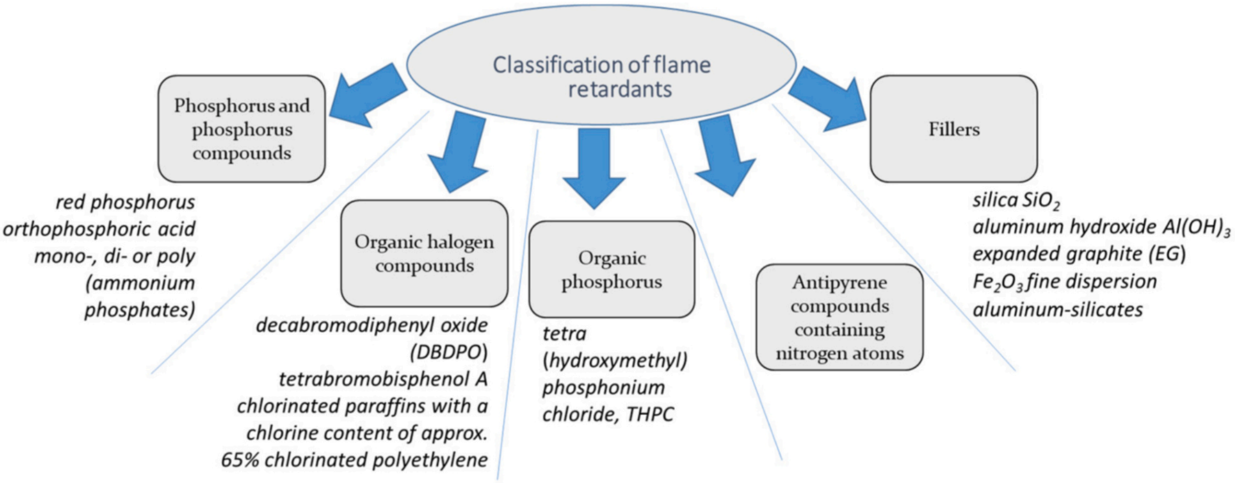


Fig. 6. Classification of FRs. Reprinted from reference [86] under Creative Common Attribution CC.BY.4.0.

180. FRs are classified into reactive and additives [86].

The non–reactive (additive) FRs are chemical entities blended with the polymer matrix during processing without chemically reacting with the polymer. Examples of non–reactive FR are based on the following elements: phosphorus, aluminum, bromine, antimony, boron, or chlorine. The global FR market value was 8.63 billion USD in 2022 [85], and it is predicted to increase at a CAGR of 7.1 % by 2030. According to the same study, the consumption of different FR classes has significantly grown in the last four years. Many industries (e.g., electronics, transportation, aeronautics, construction, etc.) are using and/or producing increasing FR–based products for fire safety and prevention regulations. The increasing demand for FR products is also generated by growing consumer awareness of the need to improve fire safety of combustible materials and products. There are many non–reactive additive FRs such as hydrated metal salts (e.g., aluminum hydroxide, boron, ammonium oxides), which undergo endothermal degradation when exposed to fire, slowing down the pyrolysis of the burning product. During their degradation, they release water vapor that dilutes volatile, flammable species in the gas phase [85].

Reactive FRs are compounds chemically bonded to the polymer matrix. Most of them are halogen- (chlorine, bromine) or phosphorus–based. Because of the increased toxicity, the use of halogenated FRs is discouraged. Conversely, phosphorus FRs have become increasingly attractive, with a global usage of 15 % in 2022, occupying the third place after aluminum oxide FRs (40 %) and brominated FRs (20 %), and followed by chlorinated FRs (11 %), antimony oxides (8 %), and others (6 %) [85]. Therefore, the non–halogenated FRs accounted for 60.9 % of the total revenue in 2022 and are expected to have the fastest CAGR increase of 8.0 % by 2030 [85]. This trend is due to the increasing demand for eco–friendly, low-toxic FRs. For example, antimony trioxide combined with brominated organic moieties is usually applied as a FR mixture in molding compounds, though with deleterious environmental consequences. Further, the mixture of antimony trioxide and hydromagnesite fillers confers good flame retardancy, but also has hazardous environmental effects. As a consequence, the demand for environmentally safer alternatives, e.g. non–halogenated FRs, is more and more growing.

Everyday life has become synonymous with thermoplastic polymers that are found in almost every application domain, from household to automotive industry; therefore, a great deal of financial resources and research is currently invested into their fire protection. These aspects also apply to highly flammable feedstock in materials (e.g., plastics, composites, textiles, and clothing). An ideal FR material for a polymer should comprise the following peculiarities [87,88]: low cost, ease of use, homogeneity, physico–chemical stability, high FR effect with no more than 10 wt% loading in the polymer, non–toxic and/or corrosive emissions during use, environmental friendliness, and UV and humidity resistance, preservation or improvement of the physico–mechanical properties and aesthetics of the polymer. Up to now, no compound/composite exhibiting all the above mentioned features has been invented yet and intensive worldwide research is being invested in obtaining the optimal flame retarded system. The difficulty in attaining a universal FR for polymers arises from the variety of their structures and the multiple effects taking place among the components in the polymer systems. The combustion inhibition capacity of a FR must not be referred to the individual components but the polymer system as an entire entity. Therefore, various types of synergistic FR combinations (phosphorus, nitrogen, nano–fillers) are increasingly reported to replace toxic flame retardants (e.g., halogenated compounds) [86].

3.2. *DOPO-based flame retardants*

3.2.1. *Overview and flame retardant mechanism of DOPO based flame–retardants*

During the last decades, phosphorus–based FRs (organic and inorganic) have been extensively applied to epoxy resins, polypropylene and polyurethane foams, because of their low toxicity, good thermal stability, high flame retardancy, acceptable eco–friendly character, and low smoke and toxic emissions, as the phosphorous is mostly trapped in the char [89]. Among phosphorus–containing FRs, DOPO and its derivatives have attracted increased interest in the scientific community because of the previously mentioned features and excellent molecular versatility [90].

Various chemical approaches have been developed to synthesize numerous non–reactive and reactive mono– and multi–DOPO derivatives [91]. Organophosphorus heteroatomic compounds result from the conversion of the reactive P − H bond in DOPO into P—N, P—O, P—S, or P—C bonds via molecular rearrangement, nucleophilic addition, or substitution to enhance the thermal stability and flame–retardancy [92]. The conversion of the P—H bond in DOPO also accounts for the formation of physical cross–linking within the epoxy matrix, endowing the thermoset material with synergistic FR effects and improved mechanical properties. The incorporation of DOPO derivatives into an epoxy resin (e.g., DGEBA) cross–linked with aromatic curing agents, such as 4,4′–diaminodiphenylmethane (DDM) and 4,4′–diaminodiphenyl sulfone (DDS), enhances its fire and mechanical features. As further reported, the DOPO moiety may be active in both gas and condensed phases through the release of phosphorus species as radical scavengers and which catalyze matrix dehydration, favoring the char formation, yielding a V-0 rating in vertical flame spread tests (UL 94 VB) and increasing the limiting oxygen index (LOI) values even at low phosphorous loadings (e.g. 1–2 wt%) [93]. Low contents of DOPO derivatives with triazine may also endow epoxy systems with self-extinction, prolonging the time to ignition (TTI) and delaying the peak of heat release rate (p–HRR), as assessed by forced-combustion tests [94]. DOPO can also be used in small amounts (e.g., 1.5 wt%) as a compatibilizer for epoxy with other FRs employed as fillers or charring agents, conveying the matrix with excellent overall flame resistance and mechanical properties [95]. Both DOPO–based non–reactive and reactive additives require similar phosphorus loading to yield a V-0 classification in UL 94 VB tests. Despite the reactive approach not yet being adopted by the industry, it is extensively researched by academia due to the P—H bond from hydrogen phosphinates or phosphonates, which allows for the direct covalent bonding of the FR to the oxirane ring. The DOPO moieties covalently attached to the polymer backbone lead to good adhesion, enhanced thermo–oxidative stability, improved flame retardancy, good solubility, and low birefringence of the resulting thermoset material [96]. In addition to epoxy resins, DOPO derivatives possess the versatility to also react with wide range of other electron-deficient monomer classes, such as alkenes [97], terephthaldicarboxaldehyde [98], bismaleimide [99], diaminobenzophenone [100], maleic acid [101], pararosaniline chloride [102], isocyanate [103], and imine [104].

Bifulco et al. [105] and Varganici et al. [106] recently reviewed advances in non–reactive and reactive classic DOPO–based epoxy systems, classifying them into mono– and multi-DOPO derivatives and subgroups based on the conversion of the P—H bond into P—C, P—O, P—N, and P—S bonds. The authors also discussed the effects provided by nanomaterials, reactive monomers, curing agents, and hybrid structures containing DOPO, with an emphasis on their fire retardant mechanisms and thermal and mechanical performances. As shown in Fig. 7a, after the incorporation of a DOPO–based FR into an epoxy matrix, the P—C bond becomes integrated in the polymer system. During the pyrolysis of the epoxy system, the P—C bond undergoes scission, generating phosphorus–containing entities like phosphoric acid and its derivatives, which catalyze charring during pyrolysis and generate a protective char layer at the polymer–flame interface. This is the condensed phase mechanism, as the generated char layer protects the material surface against reactive oxygen radicals and restricts heat transmission to the underlying material [107].

In the gas phase, flame retardancy is achieved through the evolved phosphorus–containing gases not only diluting oxygen and other

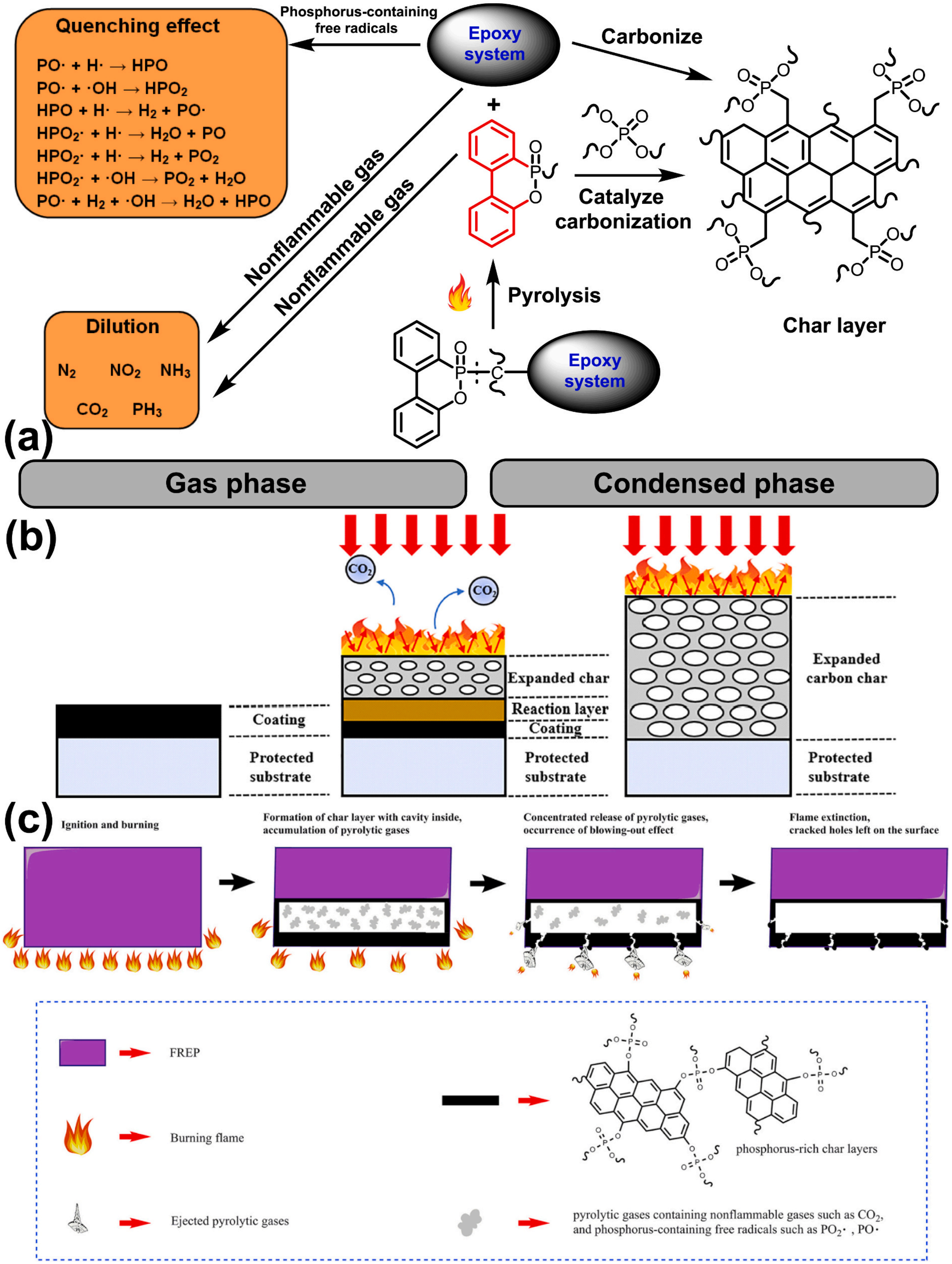


Fig. 7. Schematic of the: (a) general FR mechanism of DOPO and epoxy systems containing DOPO–based FRs; (b) FR mechanism of an intumescent FR coating; and (c) blowing-out effect of a flame-retarded epoxy thermoset (FREP) during combustion. Adapted with permission from references [109, 113].

flammable gases but also through a quenching effect by the scavaging of free radicals, e.g., PO• and PO_2• radicals covering active hydroxyl and hydrogen radicals (Fig. 7a) [108].

The condensed phase may occur via a charring phenomenon. This is typically named the intumescent effect (Fig. 7b) [109]. DOPO and its derivatives possess good char generating capacity during burning. Initially developed for coating applications, intumescent formulations generate low smoke and toxicity during combustion by foaming or swelling and generating an expanded carbonized layer onto the polymer surface (Fig. 7b). In epoxies, intumescence is achieved by adding to the resin an acid source (e.g., APP) [110], often accompanied by a carbonizing agent (e.g., pentaerythrithritol) [111] and/or a blowing agent (e.g., melamine cyanurate) [112]. DOPO and its derivatives are highly effective in intumescent FR formulations. DOPO derivatives exhibit both condensed-phase and gas-phase mechanisms. Through chemical modification or in combination with other elements (such as nitrogen, phosphorus and silicon), they significantly enhance the thermal stability and flame retardancy of epoxy systems, while lowering their toxicity.

The synergistic effect between phosphorus and nitrogen atoms during combustion may induce a direct blowing–out effect of the flame (Fig. 7c) [113]. This effect is generated by the continuously evolving phosphorus-based radicals and non-flammable pyrolysis gas within the carbonaceous char layers that delay their emission during combustion. When the carbonaceous char layers storage capacity is exceeded by the quantity of pyrolysis gas within them, the pyrolysis gas release blows out the flame, therefore exhibiting a blowing-out effect (Fig. 7c).

According to the literature, both conventional DOPO-based epoxy non–vitrimeric systems and DOPO–based (bio)epoxy vitrimers exhibit similar FR mechanisms, with no influence from the embedded CANs. Moreover, DOPO-based vitrimers, especially those containing bio-based (functionalized) DOPO derivatives, demonstrated enhanced flame retardancy and thermo-mechanical properties: in this context, recent studies report enhanced thermal stability, higher charring effects, and superior mechanical features in these modified vitrimers [20,30,114].

The current research is oriented toward achieving maximum fire performance with the lowest phosphorus content. For example, in such industries as automotive and aviation, relatively low loadings of non–reactive DOPO–containing FRs are required to achieve enhanced flame retardancy, while maintaining the mechanical performance of epoxy systems [115–117].

3.2.2. *Influence of the P—C bond on the flame retardancy of DOPO derivatives*

The scission of the P—C bonds during fire exposure is extremely important as it influences the combustion inhibiting potential and the FR mechanism(s) in the epoxy system. The main thermodynamic feature of the P—C bond is its strength, quantified by determining the homolytic bond dissociation enthalpies (BDEs). Jiao et al. [92] recently studied the P—C bond strength via a high–level ab initio algorithm and used the density functional theory (DFT) [118] to calculate its BDEs, taking into account specific test parameters, namely: LOI, thermal degradation temperature at 5 % mass loss ($T_{5\%}$) and rating in UL 94 VB tests. Through the applied protocols, authors validated the FR efficiency of

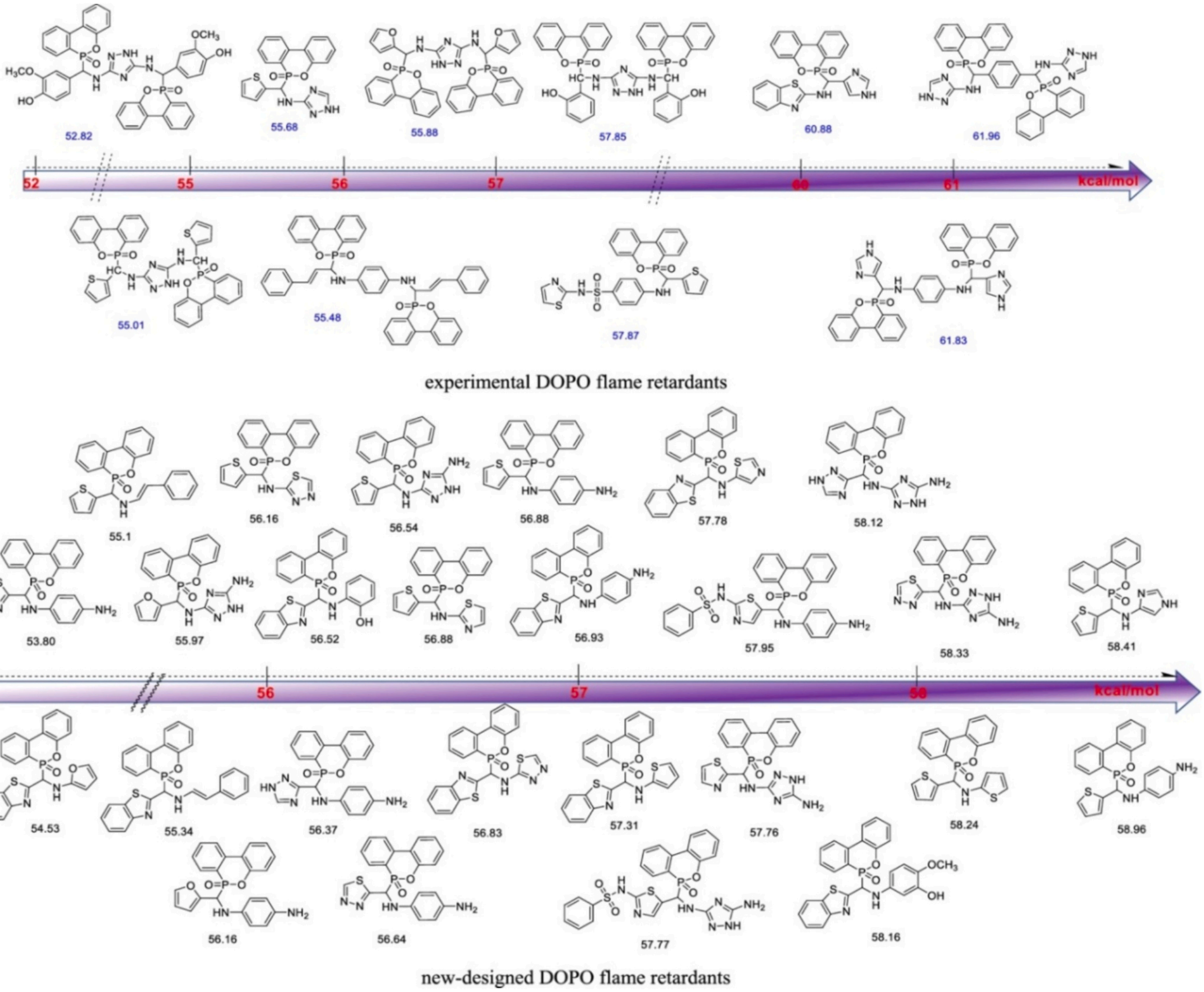


Fig. 8. P−C BDEs (in kcal/mol) of DOPO FRs. Reprinted with permission from reference [92].

several DOPO derivatives, such as benzo[*d*]thiazol–amine, thiophen–amine, triazol amine, and aniline. The authors managed to regulate the FR performance of the DOPO derivatives through the adjustment of substituent groups on the P—C bond, making possible the modification of their reactivity.

Therefore, through molecular modeling, the authors established a theoretical foundation for obtaining and implementing DOPO–based FRs as valuable guidance for future experimental work. The authors calculated and compared P − C BDE values between experimentally reported and newly designed DOPO derivatives, as depicted on the two scales in Fig. 8, highlighting that the P − C BDEs are in the range 52.82–61.96 kcal/mol for the experimental molecules. The lowest BDEs were registered for the molecules with dual DOPO fragments indicating a good flame–retardant effect, achieved by triazol–amine, thiophenamine, benzo[*d*]thiazol–amine, and aniline DOPO derivatives with the gradual increase of the P − C BDEs. The P − C BDEs of the newly designed DOPO derivatives were in the range 53.80–58.96 kcal/mol, the lowest values being registered for DOPO derivatives with furan fragments, and were lower compared to other fragments of the same category. Also, the P − C BDEs of DOPO derivatives with triazole fragments were lower compared to those with imidazole moieties, with the former group showing superior flame retardancy compared to the latter. In general, the P − C BDEs of DOPO derivatives with thiazole fragments were consistently lower with respect to those with thiophene moieties. Therefore, the presence of the furan moiety is the most suitable for reducing BDEs and increasing the flame–retardant efficiency of the DOPO derivatives.

4. Covalent adaptable networks (CANs)

4.1. Context and definition of CANs

The excellent features of thermosets make them indispensable and extensively used in a wide range of applications that generate huge quantities of waste. Chemically cross–linked thermosets cannot be reprocessed, especially those used as matrices for the design of composites reinforced with carbon fibres, glass, metal, or FRs [119,120].

Therefore, there exists an increasing interest in designing new high-performing thermosets with EoL reprocessability toward the fulfillment of the circular economy approach, where, at their lifetime end, the products may be reused in different ways or introduced as a feedstock for other new materials. A breakthrough in the development of such materials is the design of CANs [121,122]. CANs are polymer–based structures having covalent bonds that become reversible when exposed to such external stimuli as light, temperature, catalyst, or pH. In the absence of the stimuli, the CANs in the thermoset endow it with features (e.g., good thermo–mechanical behavior and durability), which are peculiar to cross–linked networks. Besides recyclability (Fig. 9), thanks to their dynamic character, CANs can also impart properties like shape memory, malleability, and self–healing (Fig. 10), as opposed to traditional thermosets. During the last two decades, the domain of CANs has undergone increasing progress, with a high number of publications reported on their structure–property relationships and applications [123–128].

4.2. General aspects and classification of CAN–based vitrimers

In 2011, Leibler et al. [31] introduced the term ‘vitrimer’ representing a new class of CANs. The name was given due to their viscosity vs. temperature behavior, similar to that of vitreous silica, showing Arrhenius–type dependence. This behavior is explained by the nature of the dynamic covalent bonds that follow a dissociative–associative mechanism, i.e., being cleaved and reformed within the network afterwards (Fig. 11) [129]. In general, vitrimers contain associative cross–links, the bonds being cleaved only when new ones are formed. As result, the cross–linking density is almost constant for associative CANs, regardless of the nature of the external stimuli [130–132]. This aspect draws two consequences for associative CANs: (i) an extended rubbery

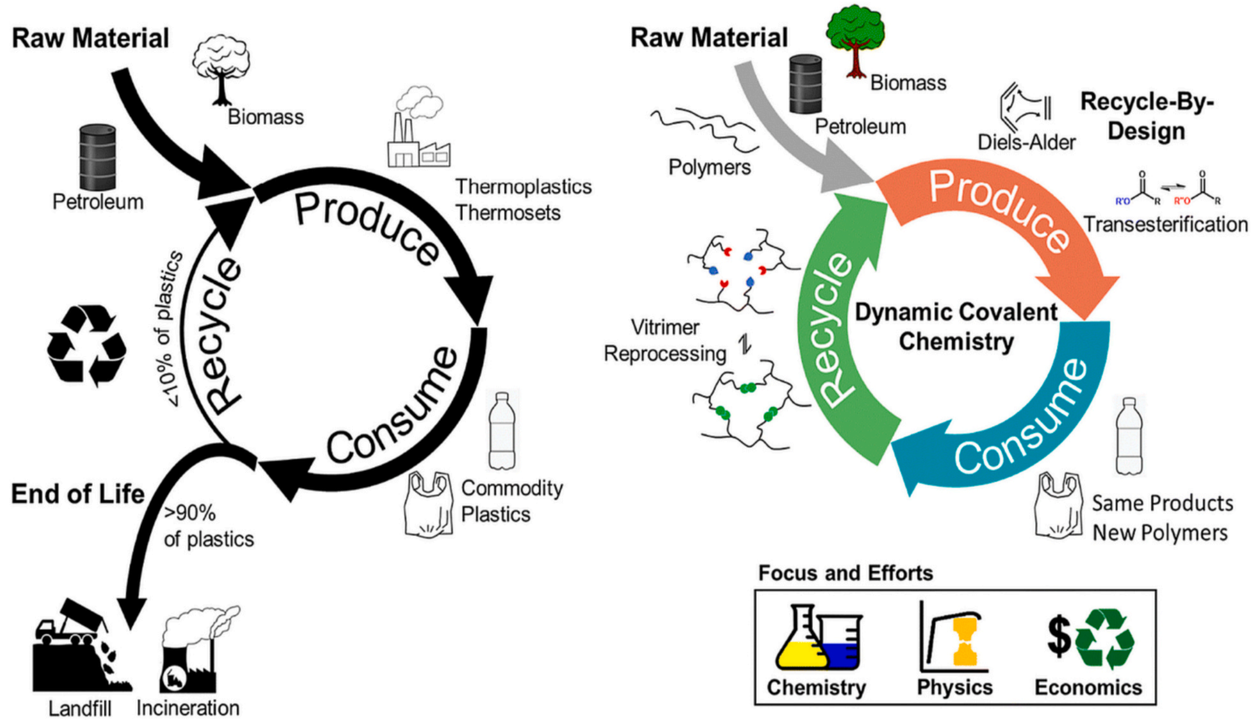


Fig. 9. (Left) Current circularity challenge and conventional recycling efforts with less than 10 wt% of recycled plastics and over 90 wt% of landfilled or incinerated plastics. (Right) Closed–loop circularity through dynamic covalent chemistries generates increased retention of plastics in the production and consumption cycle. Reprinted from reference [128] under Creative Common Attribution CC.BY.4.0.

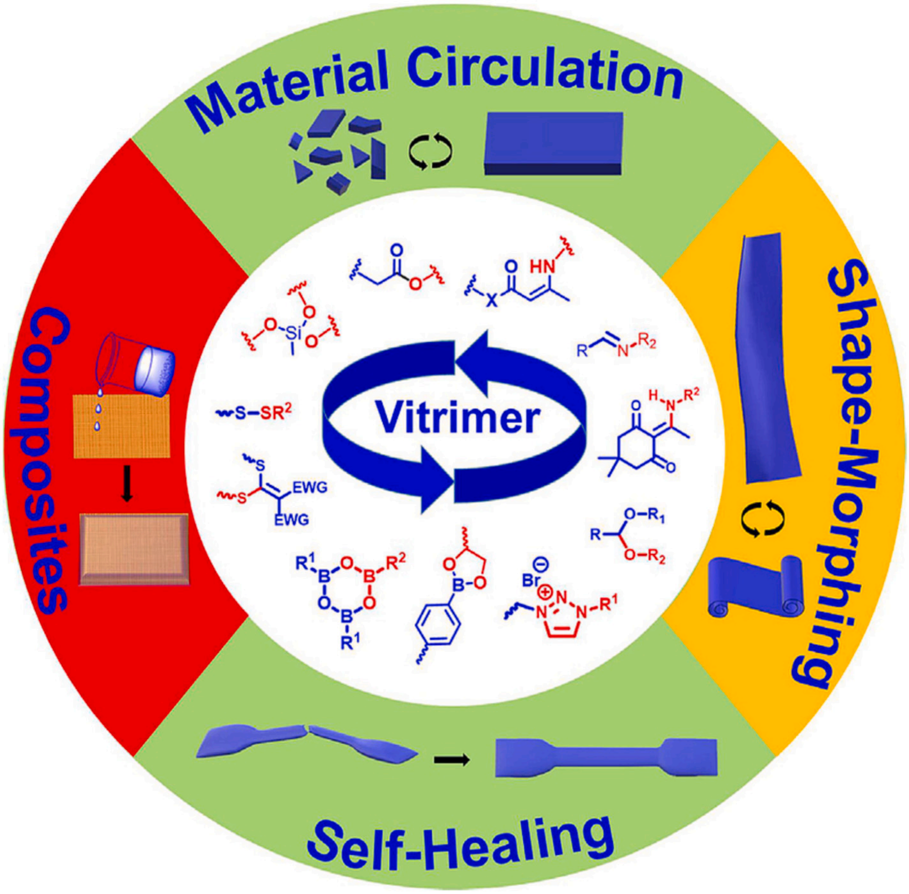


Fig. 10. CANs applied in vitrimeric materials according to their applications. Reprinted with permission from reference [10].

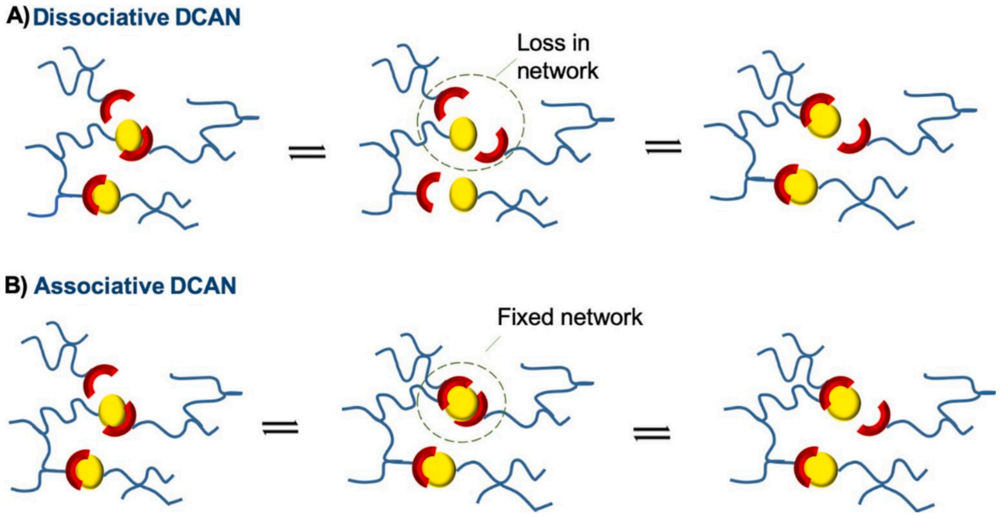


Fig. 11. Dissociative (a) and associative (b) exchange in CANs. Reprinted with permission from reference [144].

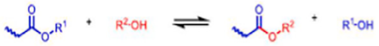
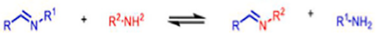
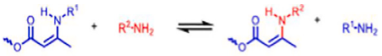
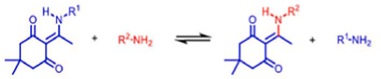
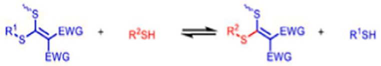
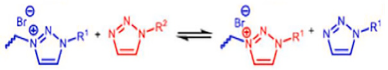
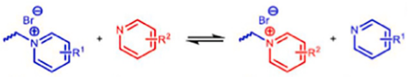
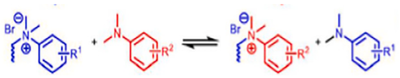
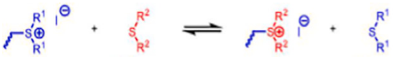
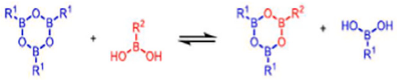
phase during heating, unlike dissociative CANs, which swiftly change from solid to liquid state (Section 4.3) and (ii) some groups exhibiting superior creep and chemical resistance [133].

One must note that the type of mechanism may be difficult to elucidate solely through the observation of the physical properties of a vitrimer. For example, there may be situations, in which materials following the dissociative mechanism can possess rheological properties inconsistent with vitrimers [134]. This is a consequence of the difference between the rate constants of bond formation and bond dissociation, with the former being significantly higher compared to the latter, generating a small proportion of dissociated bonds. These materials can be considered vitrimer–like, as their viscosity vs. temperature behavior still follows the Arrhenius law (Section 4.3) [133]. Moreover, covalently cross–linked polymer systems also include physical interactions (i.e., hydrogen bonds, van der Walls forces, and metal–ligand coordination), which also sustain the network and its mechanical features. Therefore, the classification of vitrimers solely based on the type of chemical bond may be questionable, since certain covalent bonds may undergo both mechanisms under specific conditions. As an example, the urethane bond undergoes a predominant dissociative mechanism in the absence of hydroxyl groups [135], whereas the carbamate bond follows an associative transcarbamoylation mechanism with an excess of hydroxyl groups [136].

Since Leibler's report, the scientific literature on vitrimers has significantly widened, introducing a wide variety of chemical bonds (e.g., (conjugate) addition–elimination reactions, transalkylation, heteroatom exchanges (siloxanes, boronates)). With the increase in chemical bonds and polymers, different catalysts and catalytic systems to ease material reprocessability have also been reported (e.g., chemically bonded catalysts [137], neighboring group catalysis [138,139], catalyst–free reactions [140]) for multiple applications (e.g., recyclable adhesives, shape-memory materials, self–healing materials, nanomaterials and materials for 3D printing); they are summarized in Table 2 [10].

Table 2

Overview of dynamic covalent bonds found in vitrimer(−like) materials. Adapted with permission from reference [10].

Dynamic bond	Scheme	Mecha-nism‡	Ea /kJ/mol	Catalyst#	*Tg* / °C	Mechanical Properties
Ester		A	60–150	Uncat.;Zn(II); base	80	1.8 GPa [a]
Carbamate		A/D	90–140	Sn(II)	54	72 ± 11 MPa[a] 2.2 ± 0.4 GPa [b]
Carbonate		A	80–120	Ti(IV)	15–35	0.1–1.2 GPa [b]
Carbamide		A/D/M	70–80	Uncat.	– 70	> 20 MPa [a]
Acetal		A/D/M	555–140	Uncat.; acid	66–71	27.2–33.3 MPa [a] 0.8–1.1 GPa[b]
Imine		A/M	10–130	Uncat.	55–135	10–64 MPa [a] 0.13–1.0 GPa [b]
Vinylogous Urethane		A	30–80	Uncat.; acid; Sn(II)	87	90 MPa [a] 2.4 GPa [b]
Diketo-enamine		A	30–50	Uncat.	125	38 MPa [a] 1.8 GPa [b]
Thioether		A	55–70	Uncat.	– 110	0.4–1.5 MPa
Triazolium		D	140–150	Uncat.	– 8 to 23	15 MPa [c]
Pyridinium		D	45	Uncat.	– 22	1.3–3.4 MPa [b]
Anilinium		D	50–60	Uncat.	11–15	225–380 kPa [b]
Sulfonium		A	113	Uncat.	30–60 †	40–60 MPa [b]
Dioxaborolane		A/M	40–80	Uncat.	98	28 MPa [a] 1.8 GPa [b]
Boroxine		A	80	Uncat.	68	32.9 MPa [a] 0.7 GPa [b]
Silyl Ether		A/M	80–180	Uncat.;acid	125	1.8 GPa [b]
Disulfide		D	50–60	Uncat.	127	2.5 GPa [b]

An in-depth description of CANs chemistries, highlighting their pros and cons, has recently been reviewed by other research groups [37,83,84,133], and it will not be the objective of the present review.

4.3. The chemistry behind vitrimers – transition temperatures in vitrimers

Vitrimers are identified by their temperature-dependent viscoelastic behaviors, since the rate of covalent exchange is associated with the thermal transition temperatures. Hence, vitrimers exhibit distinct physical properties at different temperatures. Vitrimers are characterized by two transition temperatures. The first one is the T_g, at which the material shifts from a glassy to a rubbery state (Fig. 12a). The possibility to control the system viscosity allows for processing vitrimers over a wide temperature domain without affecting the cross–linking density compared to thermoplastics and dissociative CANs, where viscosity and cross–linking density significantly drop as temperature increases [141]. The second transition temperature, unique to vitrimers, is the topology freezing point temperature (T_v) positioned between the viscoelastic solid and viscoelastic liquid domains with a viscosity threshold value of 10^{12} Pa·s [142]. T_v can be located above or below T_g. Regardless of the case, the dynamic covalent bond exchange occurs beyond T_g. In the former case ($T_v > T_g$) the dynamic covalent bond exchange has a viscoelastic solid or rubbery–like behavior until reaching T_v; subsequently, the system is capable to flow like a viscoelastic liquid, following the Arrhenius law (Fig. 12b). In the latter case ($T_v < T_g$) segmental motion is frozen up to T_g because of zero chain mobility [143]. Beyond T_g, the dynamic covalent bond exchange occurs in an uncontrolled manner for a certain period of time respecting *the* William–Landel–Ferry (WLF) behavior, possibly following the Arrhenius law (Fig. 12c) [144].

Both T_g and T_v may be tuned by varying such parameters as monomer structure, cross–linking density, bond E_a, and type of catalytic system. By using rigid monomer structures with high cross–linking density one may obtain materials with enhanced strength [145].

5. Bio–sourced vs. fossil–derived vitrimers

As previously mentioned, the design, formulation, and preparation of vitrimers started from fossil–based monomeric precursors, developing and implementing standard chemical synthetic pathways (Fig. 13). It is worth highlighting that, although fossil-derived vitrimers offer established performance and potentially lower costs in some cases, they contribute to environmental concerns associated with the extraction and processing of fossil fuels [146,147]. Conversely, in general, vitrimers derived from fossil fuels exhibit well-established performance characteristics, such as high mechanical strength and thermal stability [124,144,148]. However, they may not be as recyclable or self-healing as those derived from bio-sources [4,129,149–151]. These issues well justify the significant efforts that, during the last years, have been made toward formulating bio-based/bio-sourced vitrimeric systems (Fig. 14) [152–155].

Indeed, these latter possess intriguing peculiarities that justify the increasing academic research carried out during the last five years. In particular, as they derive from such renewable resources as lignin, carbohydrates, agricultural wastes, cellulose, vegetable oils, and starch, among others, bio–sourced vitrimers show a limited dependence on fossil resources, together with a lower carbon footprint compared to the fossil–based counterparts [156]. Besides, they show a promising potential for being composted or biodegraded [157,158], hence fulfilling the current circular economy concept [129,159].

Conversely, fossil–based vitrimeric systems are usually non–biodegradable: this drawback undoubtedly contributes to the accumulation of plastic wastes in the environment, as well as to microplastic pollution; their EoL disposal generally requires energy–intensive methods (like incineration). Furthermore, fossil–based vitrimers could be potentially toxic, as they rely on hazardous chemical products during their synthesis and, possibly, give rise to the formation of harmful/unsafe degradation species [158].

One of the advantages of fossil–based vitrimers refers to their quite well–established synthesis processes; conversely, the synthesis of bio–sourced vitrimers is more complex, as it may require specific equipment and tailored/optimized processing parameters [160]. Besides, for these latter systems, the overall costs can fluctuate within a wide range, as they refer to the particular biomass employed, the specific preparation process, the need for pre–treatments on the biomasses, and separation/purification steps as well [157]. Finally, the scalability of fossil–based vitrimers is quite easy, though involving a high carbon footprint, while that of bio–sourced counterparts is still a challenge and needs further technological and economic efforts [161–163].

To summarize, Table 3 compares the two types of vitrimers, highlighting the difference in performance, the environmental pros and cons, the availability of raw materials, and the current challenges in synthesis and scalability.

6. Flame retardant DOPO–based (bio–)epoxy vitrimers

This section will review the progress and advances in designing, synthesizing, and characterizing DOPO–based (bio–epoxy) FR systems. Despite the research in this “niche” topic being still in its infancy, the research efforts so far spent in the scientific literature clearly witness the interest in combining DOPO and its derivatives with epoxy–based CANs, even using bio–sourced vitrimeric resins.

Li and co–workers [164] exploited the high reactivity of DOPO P—H bonds with a DGEBA resin to obtain epoxy–based CANs containing disulfide bonds (provided by using 4–aminophenyl disulfide as curing agent, Fig. 15). The DOPO loading was varied between 1 and 4 wt%. First, the mechanical behavior of the obtained vitrimers was assessed

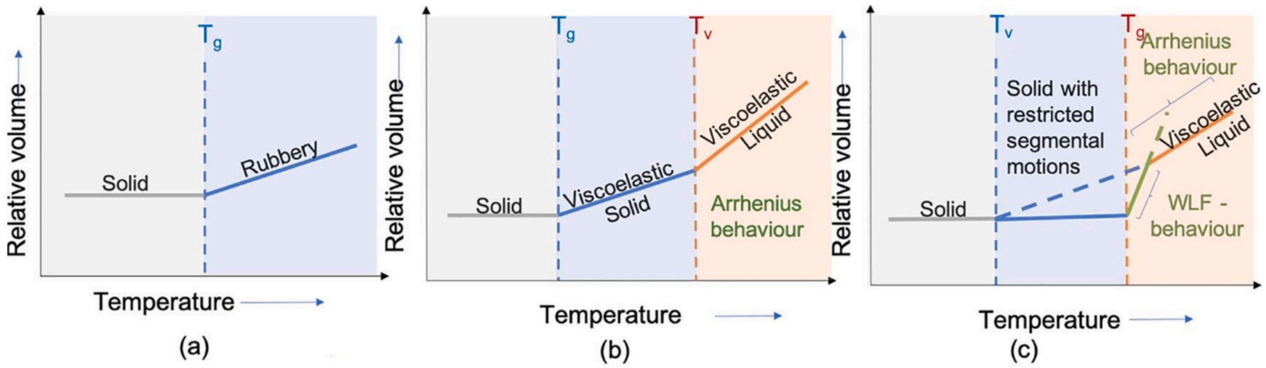


Fig. 12. The ideal viscosity vs. temperature relationship in vitrimers with (a) thermoplastic and dissociative CANs phase transitions; thermosetting vitrimer following: (b) $T_g < T_v$ and (c) $T_v < T_g$. Adapted with permission from reference [144].

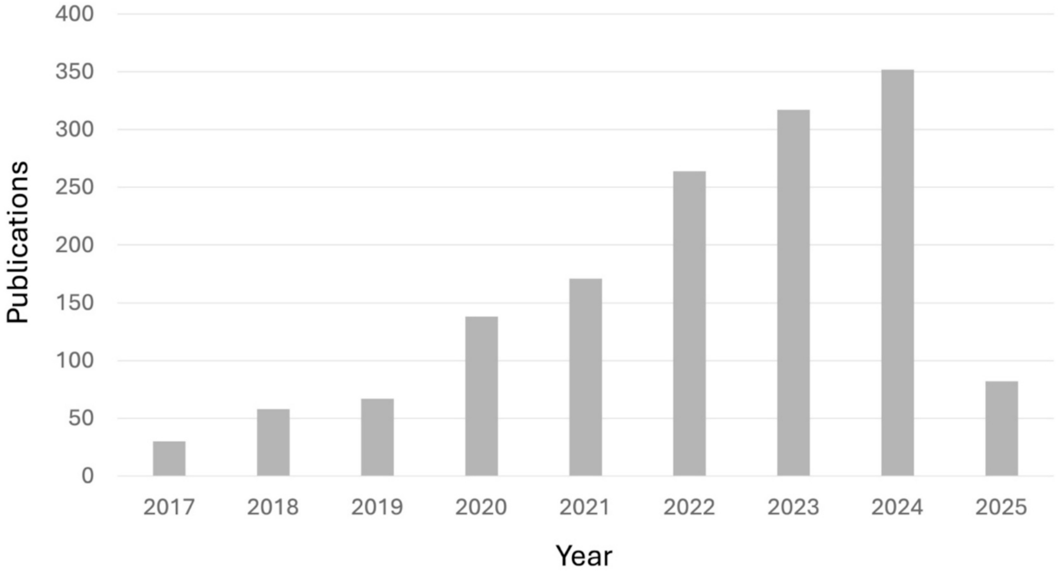


Fig. 13. Number of publications (from 2017 to 2025) in peer–reviewed journals dealing with "vitrimers" (data collected from the Web of Science™ database, accessed on March 20, 2025).

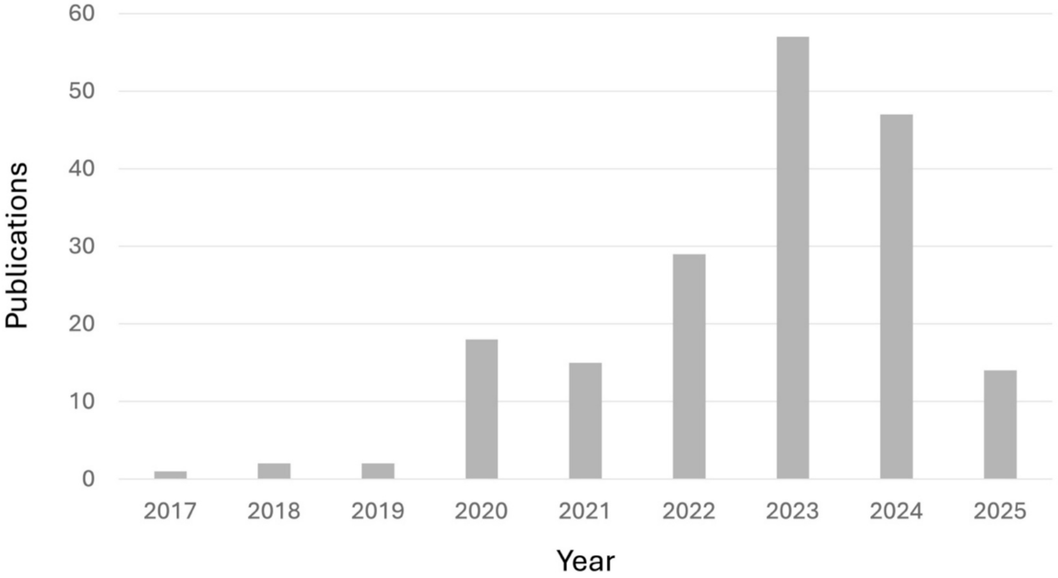


Fig. 14. Number of publications (from 2017 to 2025) in peer–reviewed journals dealing with "bio–based vitrimers" (data collected from the Web of Science™ database, accessed on March 20, 2025).

through stress relaxation tests and dynamic-mechanical analyses. In particular, due to the reaction of some epoxy groups with DOPO, the crosslinking density of the vitrimeric network decreased with increasing the DOPO loading, as confirmed by the decrease in T_g values (from 130 °C for the neat epoxy system, to 105 °C for the vitrimer containing 4 wt% of DOPO). This resulted in a decrease in the storage modulus (at 200 °C) from 20 to 10 MPa, respectively for the neat epoxy network and the vitrimer with the highest DOPO content. Besides, the E_a of the relaxation processes decreased with increasing the DOPO loading, reaching 123 kJ/mol for the network embedding 4 wt% of DOPO (E_a of the neat epoxy network: 167 kJ/mol). Further, the recyclability of the FR vitrimers was demonstrated through hot-pressing, operating at 200 °C and 100 bars for 5 min. 3 wt% of DOPO accounted for self–extinction and V–0 rating in vertical flame spread tests; besides, the LOI value of this formulation was as high as 27.8 % (vs. 21.7 % for the neat epoxy system). Finally, as assessed by forced–combustion tests (carried out at 50 kW/m^2 irradiative heat flux), the vitrimers showed a significant decrease in the p–HRR (by about 44 %) in comparison with the reference vitrimer without DOPO. All these findings were ascribed to a dual FR mechanism in both condensed (charring effect) and gas (active radical scavenging) phases.

Yang et al. [165] synthesized two vanillin–based epoxy monomers, exploiting an in situ condensation reaction with diamino diphenylmethane and addition reaction with DOPO, and subsequent epoxidation with epichlorohydrin (Fig. 16). Then, the resulting resins were cured with a diamine hardener (namely, poly(propylene glycol) bis (2–aminopropyl ether), D230). The obtained vitrimer (mass ratio of the two monomers set at 7:3) showed elastic modulus and tensile strength of about 2.5 GPa and 76 MPa, respectively, i.e., around 19 % and 49 % higher than the network not embedding DOPO. This finding was attributed to the rigid aromatic ring structure of the vanillin-derived epoxy monomers and the strong N—H interactions formed by

Table 3
Fossil- vs. Bio-based vitrimers: a comparison of performance and characteristics.

Parameter	Fossil-based vitrimers	Bio-based vitrimers
Performance indices	- established chemistries - well-defined properties - easy tailoring of performance for specific applications	- new (and often challenging) chemistries - significant changes in performance depending on the specific bio-based building blocks and dynamic covalent chemistry used
Environmental impact	- high carbon footprint - contribution of extraction and processing to environmental concerns	- low carbon footprint - possible biodegradability
Raw material availability	- readily but finite long-term availability	- relatively high abundance of some resources only (e.g., vegetable oils and lignin)
Synthetic routes	- quite well-established chemical reactions	- complex chemical reactions often involved
Scalability	- quite easy	- challenging, especially for new bio-based building blocks or emerging dynamic chemistries - some biobased resources may need to be developed or optimized further for large-scale production

intermolecular hydrogen bonds. Additionally, the vitrimer exhibited a high stress relaxation rate due to the presence of dynamic imine bonds within its topological crosslinking network. The recyclability of the material was demonstrated through hot-pressing at 140 °C under 10 MPa pressure, for 10 min. Finally, when the mass ratio of the two monomers was set at 8:2 (which corresponds to a phosphorus content as low as 0.66 %), the vitrimer achieved self–extinction and V–0 rating in vertical flame spread tests, and 27 % of LOI. Again, these results were attributed to a FR action in the condensed and gas phases, through charring and active radical scavenging, respectively.

Chen and co–workers [166] synthesized a recyclable, shape––memory, and FR epoxy vitrimer, exploiting the incorporation of ester linkages having catalytic transesterification activity in the polymer network. For this purpose, DGEBA was cured with a DOPO derivative, namely [(6–Oxido–6*H*–dibenz[c,e][1,2]oxaphosphorin–6–yl)methyl] butanedioic acid and adipic acid, in the presence of triazabicylo[4.4.0]dec–5–ene (as transesterification catalyst, Fig. 17). 10 wt% of the DOPO derivative was responsible for a significant increase in both Young's modulus and tensile strength (by about 14 and 33 %, respectively, compared with the network not containing the FR). This finding was ascribed to the presence of rigid DOPO that restricted the chain mobility of the epoxy network: the latter was also consistent with the significant increase in T_g, which raised from about 70 °C (reference epoxy network) to 111 °C (vitrimer containing 30 wt% of DOPO derivative). Further, reshapeability and recyclability of the vitrimers was demonstrated through compression molding tests carried out at 200 °C, applying a pressure of 5 MPa for 15 min: no significant loss in the mechanical features was observed after three consecutive compression molding

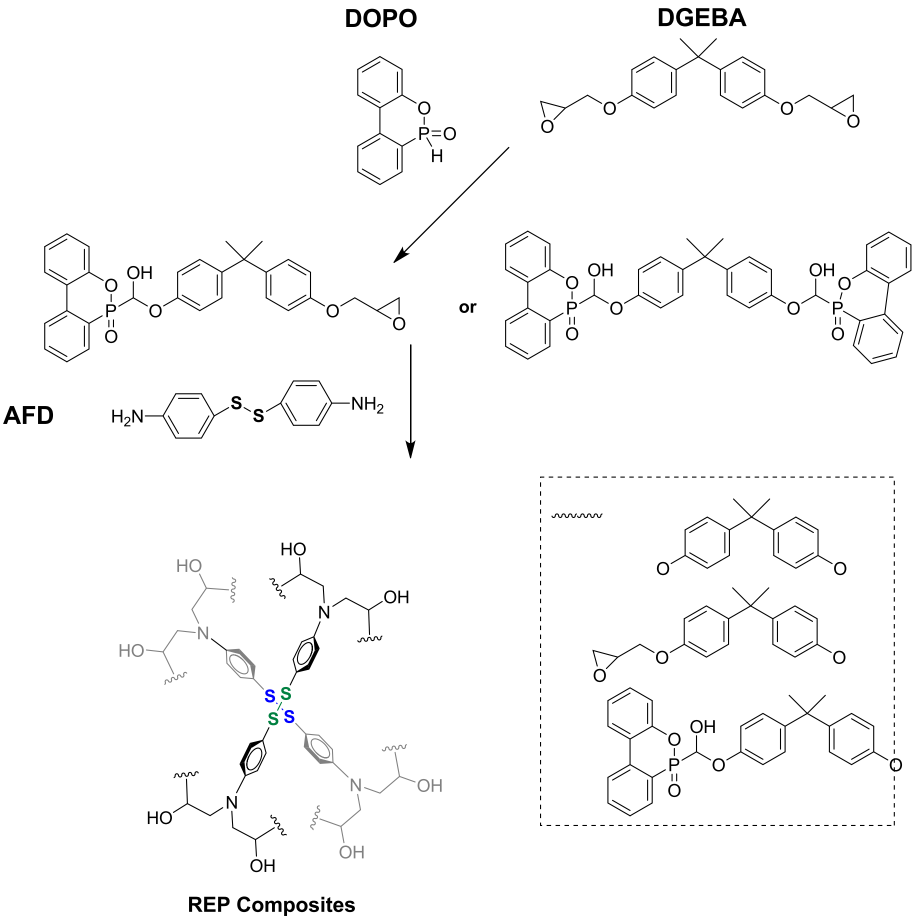


Fig. 15. Synthetic path of the DOPO–based epoxy vitrimers. Legend: AFD = 4–aminophenyl disulfide; REP = recyclable epoxy resin. Reprinted with permission from reference [164].

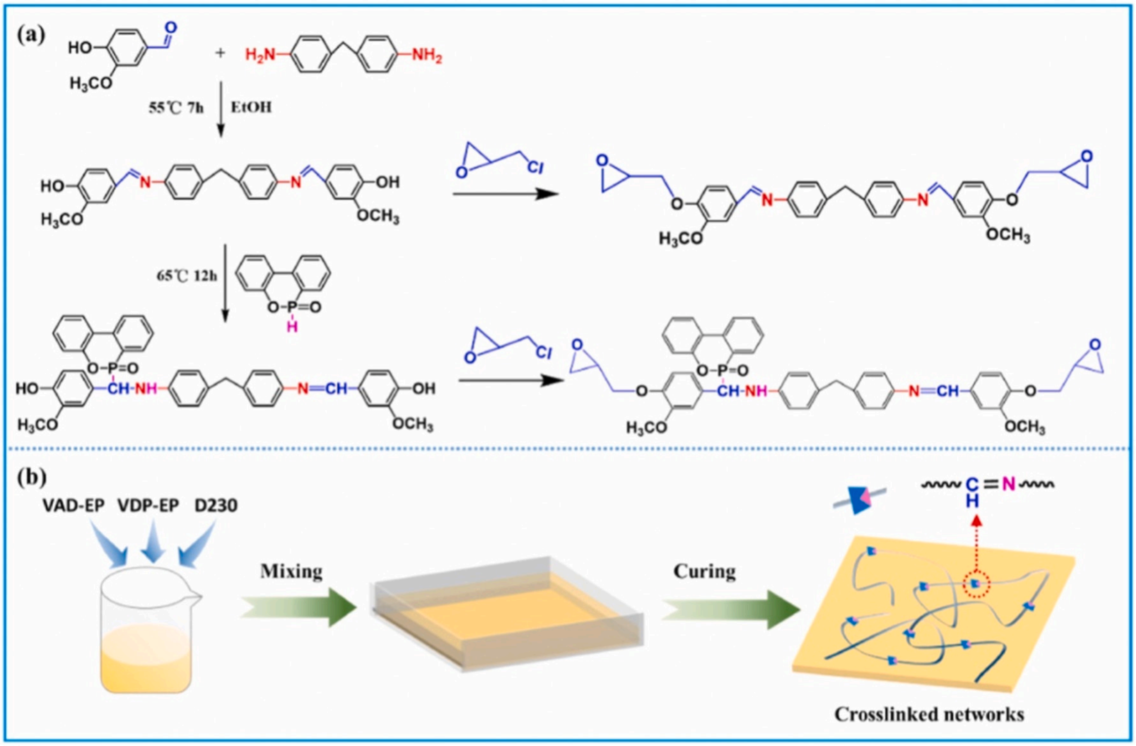


Fig. 16. (a) Synthesis paths of the vanillin–derived epoxy monomers (VAD–EP and VDP–EP, the latter embedding DOPO); (b) Scheme of the preparation of the vitrimer (D230 is the diamine hardener – poly(propylene glycol) bis(2-aminopropyl ether)). Reprinted with permission from reference [165].

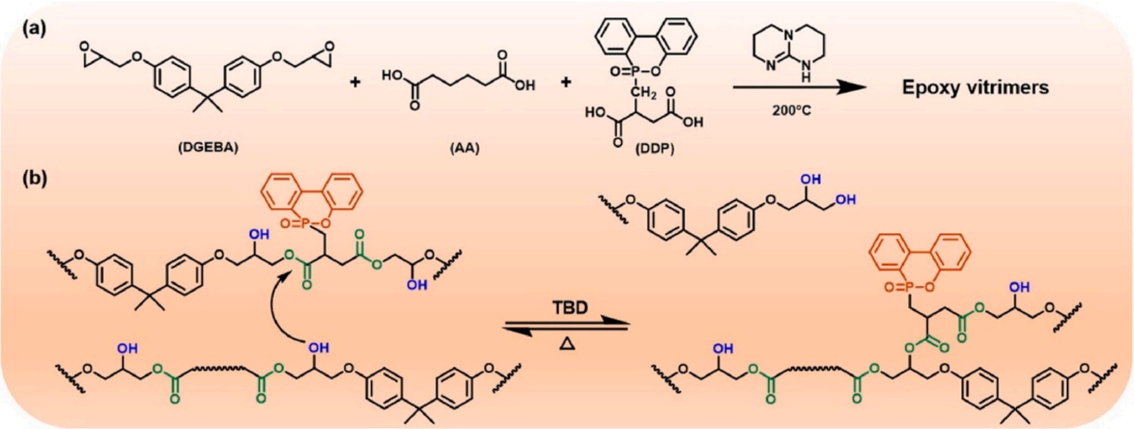


Fig. 17. (a) Synthesis paths of the vanillin–derived epoxy monomers (VAD–EP and VDP–EP, the latter embedding DOPO)); (b) Scheme of the preparation of the vitrimer (D230 is poly(propylene glycol) bis(2–aminopropyl ether), used as a diamine hardener). Reprinted with permission from reference [166].

tests. Moreover, 30 wt% of the DOPO derivative accounted for self–extinction in vertical flame spread test, as well as high LOI values (34.5 %, vs. 28 % of the control epoxy vitrimer obtained from DGEBA and adipic acid). Furthermore, for the same vitrimeric formulation, cone calorimetry tests carried out at 35 kW/m^2 heat flux highlighted a remarkable decrease in the p–HRR and total heat release (THR) (by about 63 and 32 %, respectively, compared to the control epoxy vitrimer), as well as a significant increase in the residue at the end of the test (2.4 vs. 24.9 %). These findings were ascribed to the extensive charring activity promoted by the DOPO derivative in the condensed phase.

Tian et al. [167] designed bio–based epoxy vitrimers made of glycerol triglycidyl ether and cured with a vanillin–derived imine compound (obtained through the reaction of vanillin with p–phenylenediamine), in the presence of DOPO as reactive FR at 1, 3, and 6 wt% loading (Fig. 18). The incorporation of DOPO (up to 6 wt%) did not affect the T_g of the vitrimeric network; furthermore, the vitrimers containing 1 and 3 wt% of DOPO showed a mechanical behavior similar to the reference epoxy network not embedding the FR. Conversely, further increasing the DOPO loading accounted for a decrease in tensile strength and deformation at break by about 11 and 38 %, respectively, as well as an increase in Young's modulus (by about 35 %). These findings were attributed, on one hand, to the decrease in crosslinking density and, on the other hand, to the increase in the network rigidity with increasing DOPO loading. In addition, E_a decreased with increasing the DOPO content from about 106 kJ/mol (reference epoxy network) to 78 kJ/mol (network containing 6 wt% of DOPO) because of the lowering of the crosslinking density of the network and the increased chain mobility. Further, the quick stress relaxation of the vitrimeric networks induced by the exchange reactions of imine bonds provided the vitrimers with easy reshapeability and reprocessability through compression molding

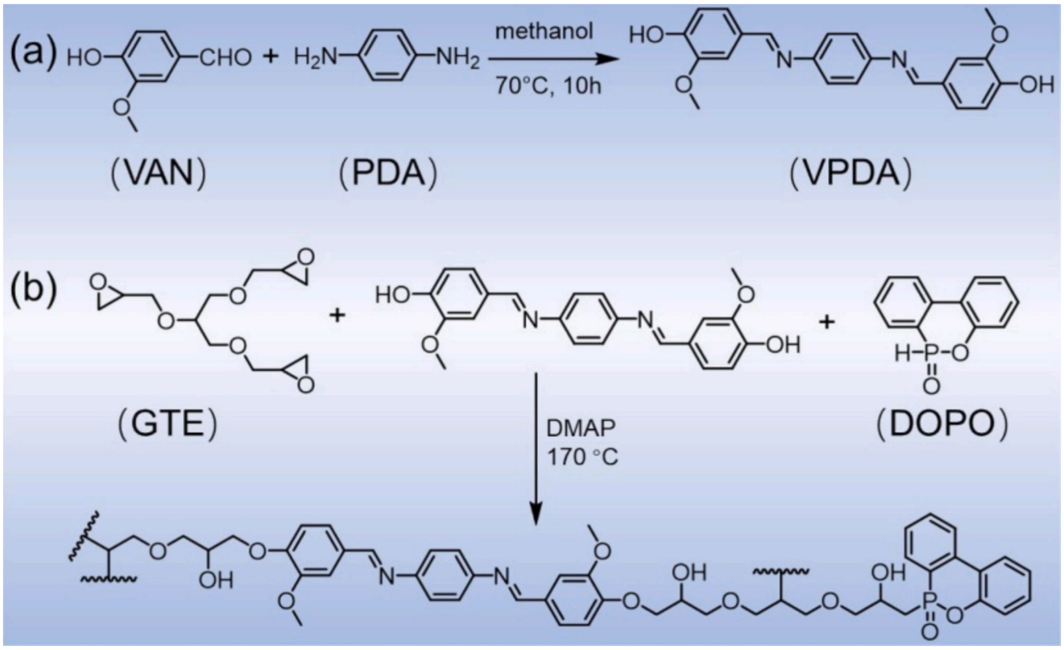


Fig. 18. (a) Scheme of the synthesis of the vanillin-derived imine hardener; (b) Scheme of the preparation of the flame retarded vitrimer. Legend: VAN = vanillin; PDA = p–phenylenediamine; VPDA = vanillin–derived imine hardener; GTE = glycerol triglycidyl ether; DMAP = 4–dimethylaminopyridine. Reprinted with permission from reference [167].

performed at 170 °C for 20 min, under 15 MPa. Also, the vitrimers showed good chemical recyclability (with more than 85 % recovery of tensile strength). As shown in Fig. 19, the incorporation of 6 wt% of DOPO in the vitrimeric network accounted for self–extinction and V–0 rating in vertical flame spread tests; besides, the same vitrimer achieved a LOI value of 26.4 % (vs. 20.4 % of the vitrimeric control sample, not embedding DOPO). Besides, as revealed by forced–combustion tests carried out at 35 kW/m^2 irradiative heat flux, the presence of DOPO in the bio–based vitrimer accounted for increased TTI (by 21 % compared to the control vitrimer) and decreased THR and p–HRR values (respectively, by about 30 and 33 %). These findings were attributed to the active radical scavenging of DOPO in the gas phase.

A similar approach was further proposed by Zhou and co–workers [168], who designed a biobased epoxy vitrimer by reacting glycerol triglycidyl ether and cured with a vanillin–derived imine compound (obtained through the reaction of vanillin with 4–aminophenol), in the presence of DOPO as reactive FR (up to 7 wt% loading). The scheme of the synthesis pathway for the bio–based epoxy vitrimer is shown in Fig. 20. The incorporation of increasing amounts of DOPO in the vitrimer accounted for a progressively decreased tensile strength (from about 51 MPa – reference epoxy without DOPO, to 40 MPa – vitrimer containing 7 wt% of DOPO); meanwhile, the Young's modulus increased by about 10 % thanks to the enhanced rigidity of the network due to the presence of aromatic rings. Besides, the obtained vitrimers showed a very good reprocessability through compression molding at 140 °C for 10 min under 10 MPa pressure: the reprocessed material retained about 88 % of the original tensile strength.

5 wt% DOPO accounted for the achievement of self–extinction and V–0 rating in vertical flame spread tests; in addition, this bio–based epoxy vitrimer reached a LOI value of 31 %, regardless of the already high value of the control epoxy vitrimer (i.e., 28.7 %). More interestingly, as revealed by forced–combustion tests carried out at 50 kW/m^2 irradiative heat flux, the incorporation of increasing amounts of DOPO in the vitrimer accounted for progressively decreased THR and p–HRR values, achieving, for the highest DOPO loading, a significant reduction by about 47 %, respectively, compared to the control epoxy vitrimer. Again, all these findings were ascribed to the dual activity of DOPO in the condensed (as char–former) and the gas phases (as active radical scavenger).

Wei et al. [169] synthesized an epoxy vitrimer from the reaction of DGEBA, an itaconic acid–derived hyperbranched epoxy monomer (designed on purpose, Fig. 21), and (1,3,5–hexahydro–*s*–triazine–1,3,5–triyl) benzyl mercaptan; different loadings of the itaconic acid–derived hyperbranched epoxy monomer (namely, 5, 10, 15, and 20 phr) were employed.

10 phr of itaconic acid–derived hyperbranched epoxy monomer accounted for a remarkable increase in both impact and tensile strength (by about 285 % and 35 %, respectively, compared with the reference system not containing the hyperbranched epoxy monomer). Further, the presence of the hexahydro-*s*-triazine and ester structure in the vitrimers allowed for an excellent recyclability through chemical recycling (using tetrahydrofuran both as a reactant and solvent to degrade the network). The vitrimer containing 15 phr of the itaconic acid–derived hyperbranched epoxy monomer accounted for self–extinction in vertical flame spread tests (Fig. 22), and LOI values as high as 34.8 % (vs. 21.4 % for the vitrimer not containing the DOPO derivative). Further, as observed in forced–combustion tests (35 kW/m^2 irradiative heat flux), the same vitrimeric system showed a significant decrease in both THR and p–HRR values (respectively by around 18 and 28 % compared to the control sample). These results were attributed to the high carbonization effect of the DOPO derivative in the condensed phase and its prevention of the release of flammable volatiles in the gas phase.

Lian and co–workers [170] designed a Diels–Alder delivery–release adduct through the Diels–Alder cycloaddition reaction between a DOPO-furanodiene derivative and a maleimide dienophile. The so–obtained adduct was incorporated into DGEBA at different loadings (namely, 10, 20, and 30 wt%) and cured with 2–ethyl–4–methylimidazole (Fig. 23).

The resulting vitrimers, after a thermal treatment at 150 °C for 1 h, followed by treatment at 95 °C for 12 h, showed a good reprocessability and self-healing capability: in particular, 20 wt% of the adduct was enough to provide stress retention rates beyond 75 %, after three thermal cycles, compared to the reference vitrimer. Further, the presence of 30 wt% of the adduct accounted for a significant decrease in THR and p–HRR (by about 22 % and 43 %, respectively) with respect to the control vitrimer. These findings were attributed to synergism occurring between P and N atoms, which facilitated an intense charring activity in

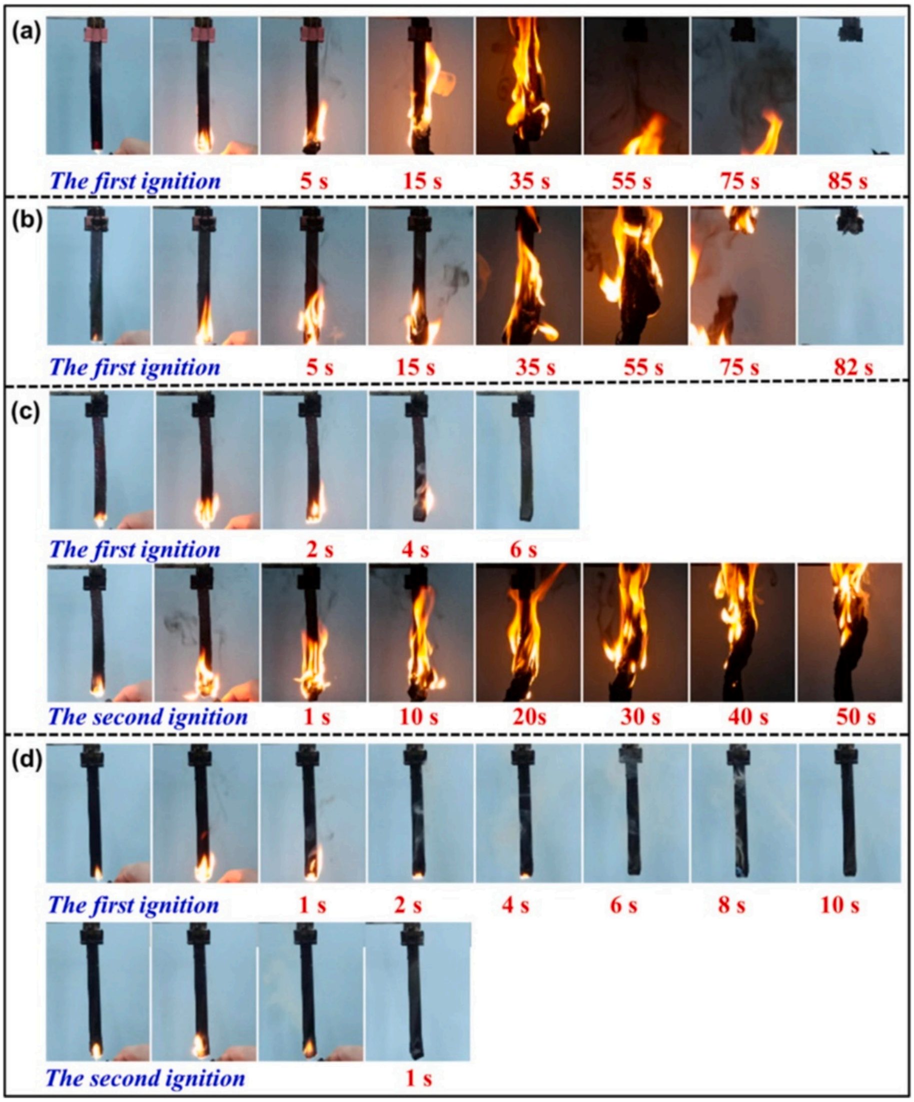


Fig. 19. Snapshots from vertical flame spread tests for the control vitrimer (a) and the formulations containing DOPO at 1 wt% (b), 3 wt% (c), and 6 wt% (d). Reprinted with permission from reference [167].

the condensed phase, as well as active radical quenching in the gas phase.

Interestingly, the use of DOPO for the design of high–performing epoxy vitrimers has also been investigated for conferring flame resistance to vitrimeric composites. In this context, Tian et al. [171] designed and synthesized bio–epoxy vitrimers by reacting DGEBA with a vanillin–derived imine hardener, and incorporating 10–(2,5–dihydroxyphenyl)–10–hydro–9–oxa–10–phosphaphenanthrene–10–oxide (i.e., a reactive DOPO derivative, Fig. 24) at different loadings (up to 22.5 wt%). Then, the so–obtained epoxy vitrimers were employed for producing carbon fiber–reinforced vitrimeric composites (the fiber volume fraction was around 65 %).

First, the incorporation of the reactive DOPO derivative in the vitrimer was responsible for an increase in the T_g of the networks, from 135 °C (reference vitrimeric network without DOPO derivative) to 146 °C (vitrimer containing 22.5 wt% of DOPO derivative). As already observed, the decreased crosslinking degree as a consequence of incorporating increasing amounts of DOPO derivative into the vitrimeric network accounted for progressively decreased values of E_a (from 66.3 kJ/mol – reference material, to 43.8 kJ/mol - vitrimer containing 22.5 wt% of DOPO derivative). The vitrimers showed good reprocessability and recyclability after compression molding cycles at 180 °C under 10 MPa for 20 min: more specifically, the material retained over 90 % of its original tensile strength after three consecutive compression molding cycles. Then, 22.5 wt% of the DOPO derivative in the vitrimeric matrix accounted for self–extinction and a V–0 rating in vertical flame spread tests. Besides, as assessed by forced–combustion tests (35 kW/m^2 irradiative heat flux), compared with the epoxy vitrimer not embedding the DOPO derivative, the carbon fiber–reinforced composite containing 22.5 wt% of the DOPO derivative in the vitrimeric matrix showed increased TTI (by about 23 %), as well as decreased THR and p–HRR (by around 44 and 54 %, respectively). Again, this impressive fire performance was attributed to the high char–forming character of the DOPO derivative in the condensed phase, as well as its active radical quenching in the gas phase.

In a further research effort, the same group [172] synthesized another DOPO derivative by reacting DOPO with 5–amino–1H–tetrazole, and p–hydroxybenzaldehyde (Fig. 25). Both DOPO and DOPO derivative were then reacted with DGEBA and a vanillin–derived imine hardener, hence obtaining the bio–epoxy vitrimeric matrix that, in turn, was employed for preparing carbon fiber–reinforced composites (the fiber mass fraction was around 50 %). The resulting vitrimer (incorporating 10.5 wt% of DOPO and 2.9 wt% of

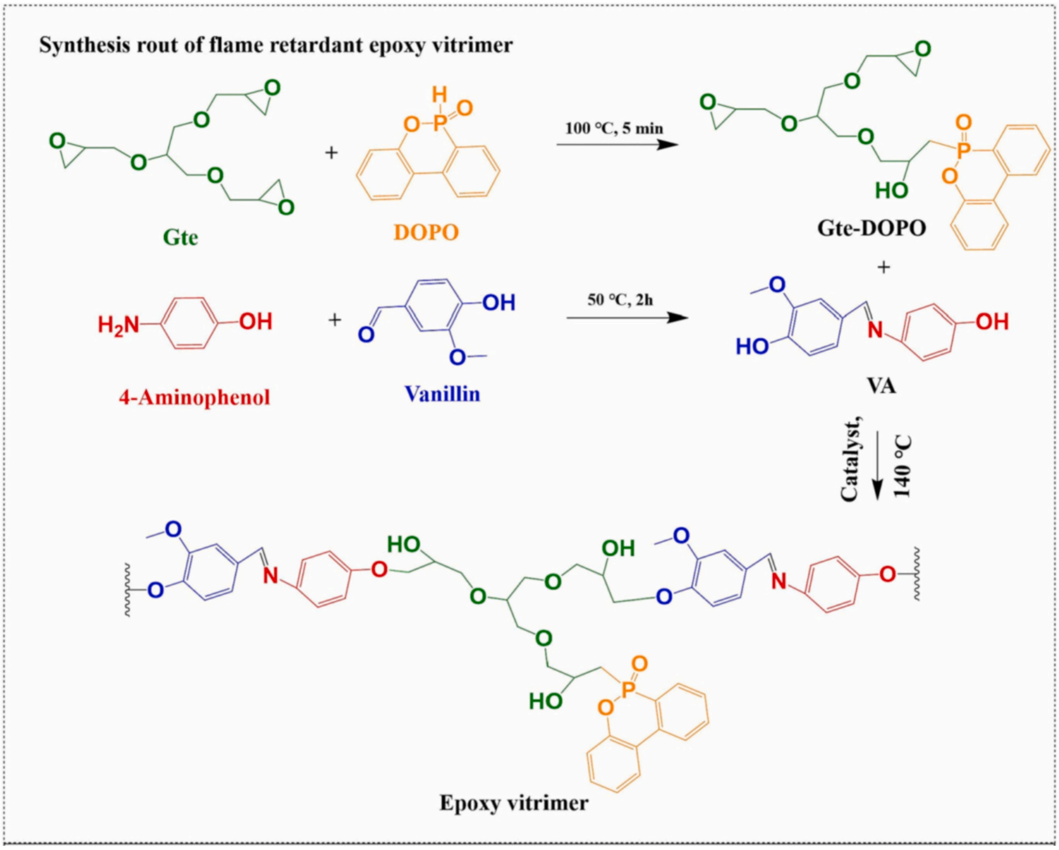


Fig. 20. Scheme of the synthesis of the DOPO–containing epoxy monomer and vanillin–based hardener. Legend: Gte = glycerol triglycidyl ether; Gte–DOPO = DOPO–containing epoxy monomer; VA = vanillin–based hardener. Adapted with permission from reference [168].

DOPO derivative) showed an excellent mechanical behavior, with high Young's modulus and tensile strength (5.8 GPa and 679 MPa, respectively), as well as high thermal stability (decomposition temperatures beyond 330 °C). Further, the composite demonstrated excellent recyclability, with the carbon fiber able to be non-destructively recycled. These recycled fibres were used to make a recycled composite with similar mechanical properties to the original. As far as the flame retardancy is considered, the concurrent presence of DOPO (at 10.5 wt %) and DOPO derivative (at 2.9 wt%) in the composite matrix accounted for self–extinction in vertical flame spread tests (Fig. 26) and the achievement of a LOI as high as 35 %.

Luo and co–workers [173] synthesized a bio–based casein phosphopeptide chelating zinc, acting as a FR and smoke suppressant in combination with an itaconic acid–grafted DOPO derivative for DGEBA; sebacic acid was employed as a co–curing agent for the epoxy system. The T_g of the epoxy vitrimers increased with increasing the DOPO derivative loading, because of the rigid structure of this latter, reaching 56 °C when 35 wt% of DOPO derivative was incorporated into the vitrimeric network (T_g of the reference epoxy: 25 °C). Then, the self-healing ability of the vitrimers was assessed by making a cut in the material's surface with a razor blade on a hot bench set to 180 °C: the vitrimers were capable to heal in just 10 min. Furthermore, their reshapeability was demonstrated through compression molding at 200 °C for 1 h: the reprocessed material retained over 72 % of its original mechanical strength. The incorporation of 35 wt% of the bio–based casein phosphopeptide chelating zinc accounted for self–extinction and V–0 rating in vertical flame spread tests. Moreover, this vitrimeric formulation achieved a LOI of 32.3 %. Finally, cone calorimetry tests performed at 35 kW/m^2 irradiative heat flux highlighted a decrease in both THR and p–HRR by about 41 % and 73 %, respectively, compared to the vitrimer without the DOPO derivative. The excellent FR features observed in the design of the epoxy vitrimers were attributed to the char formation catalyzed by the metal complexes and the phosphoric acid groups or their derivatives originating from the decomposition of the FRs (condensed phase mechanism). Meanwhile, the DOPO derivative showed gas–phase activity, as P–containing radicals generated during the thermal decomposition of DOPO groups could exert a quenching effect on the active radicals supplied by the epoxy matrix, thus slowing down the combustion process in the gas phase.

Chu et al. [174] synthesized P—N flame–retardant epoxy (BGEDA) vitrimers, combining a DOPO derivative (namely, [(6–Oxido–6H–dibenz[*c*,*e*][1,2]oxaphosphorin–6–yl)methyl]butanedioic acid), glutamic acid, and itaconic acid at different molar ratios. The presence of the DOPO derivative in the vitrimers accounted for an increase in stiffness of the networks, whereas increasing amounts of itaconic acid promoted a decrease in the crosslinking density, from 0.88×10^{-3} to 0.73×10^{-3} mol/cm^3, repectively for the reference network (not containing itaconic acid) and the vitrimer embedding 21 mol% of itaconic acid). Conversely, the incorporation of itaconic acid improved processability by accelerating ester exchange reactions, as evidenced by reduced stress relaxation times. Then, the introduction of secondary amines made it possible to form self-catalytic structures, resulting in a material with exceptional thermal stability (temperature degradation onset of 349 °C in an inert atmosphere). Interestingly, it was demonstrated that keeping a P:N ratio of 1:1 or 1:05 allowed for achieving self–extinction and V–0 rating in vertical flame spread tests. Besides, using a P:N ratio of 1:0.5 accounted for a LOI value of 32 %.

The use of DOPO for conferring FR features to epoxy vitrimers has recently highlighted a niche application in the field of high–performing and recyclable adhesives. In this context, Zhang and co–workers [175] developed a FR carbon fiber–reinforced epoxy vitrimeric composite (61 wt% fiber mass fraction), using tetraglycidyl methylene diphenylamine

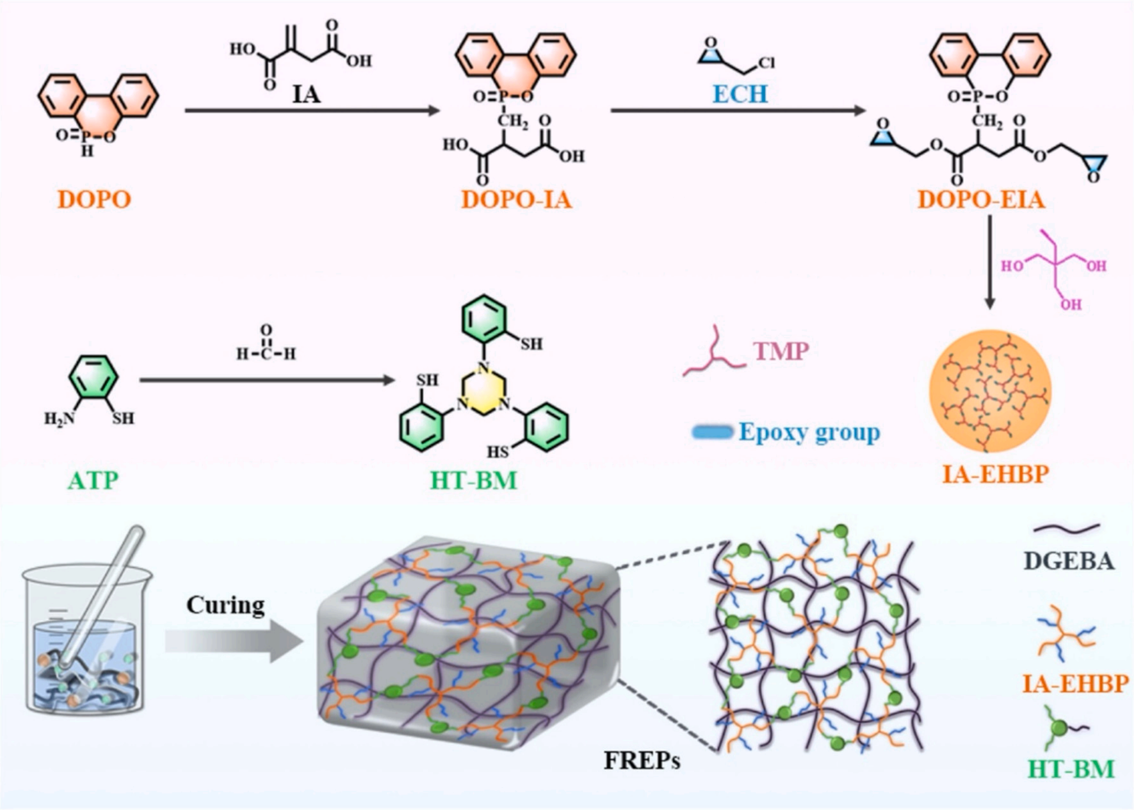


Fig. 21. Synthetic scheme of itaconic acid–derived hyperbranched epoxy resin (IA–EHBP), (1,3,5–hexahydro–*s*–triazine–1,3,5–triyl) benzyl mercaptan (HT–BM), and the flame retarded epoxy vitrimer (FREPs). Legend: IA = itaconic acid; DOPO–IA = DOPO–itaconic acid derivative; ATP = 2–aminothiolphenol; ECH = epichlorohydrin; DOPO–EIA = DOPO–itaconic acid derivative epoxy monomer; TMP = trimethylolpropane. Reprinted with permission from reference [169].

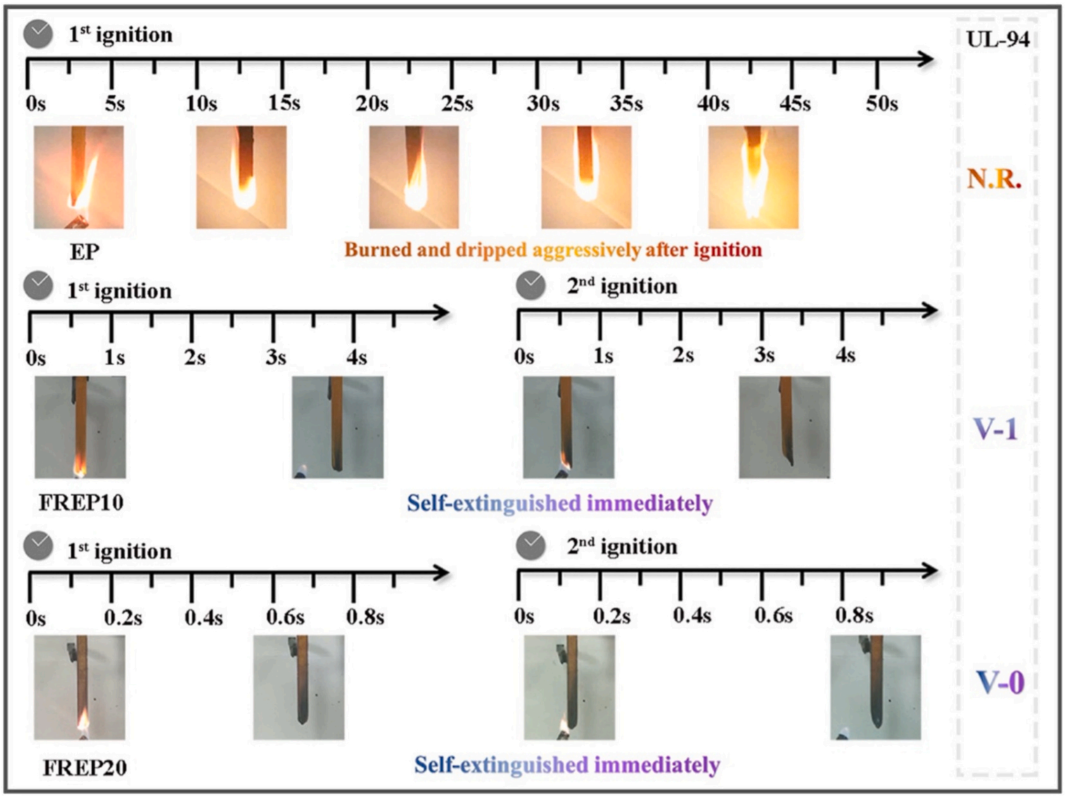


Fig. 22. Snapshots of the vitrimers taken during vertical flame spread tests. Legend: EP = epoxy vitrimer control; FREP10 and FREP20 = flame retarded epoxy vitrimers embedding 10 and 20 phr of the itaconic acid–derived hyperbranched epoxy monomer. Adapted with permission from reference [169].

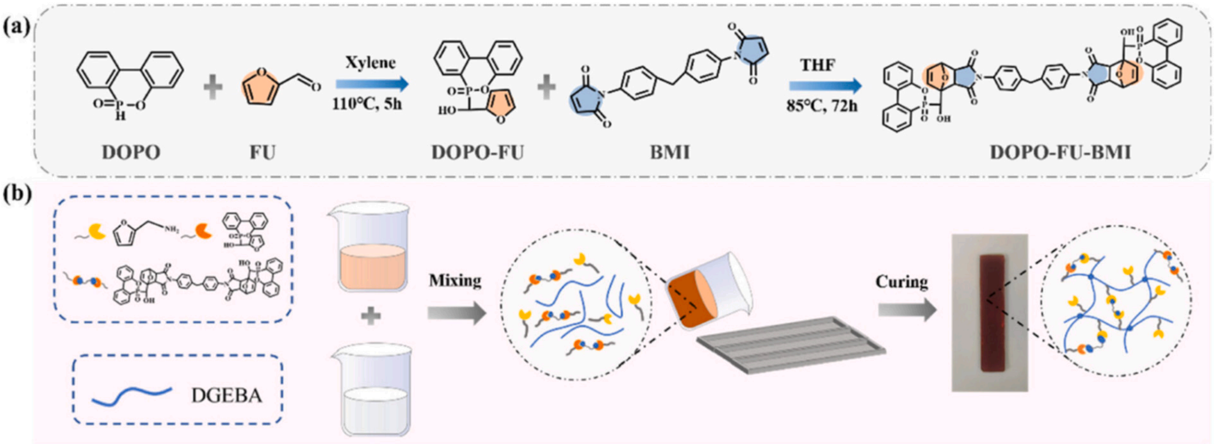


Fig. 23. (a) Preparation of the Diels–Alder adduct; (b) preparation of the modified epoxy vitrimer. Legend: FU = furfural; DOPO–FU = DOPO–furanodiene derivative; THF = tetrahydrofuran; BMI = 1,1′– (methylenedi–4,1–phenylene)bismaleimide. Adapted with permission from reference [170].

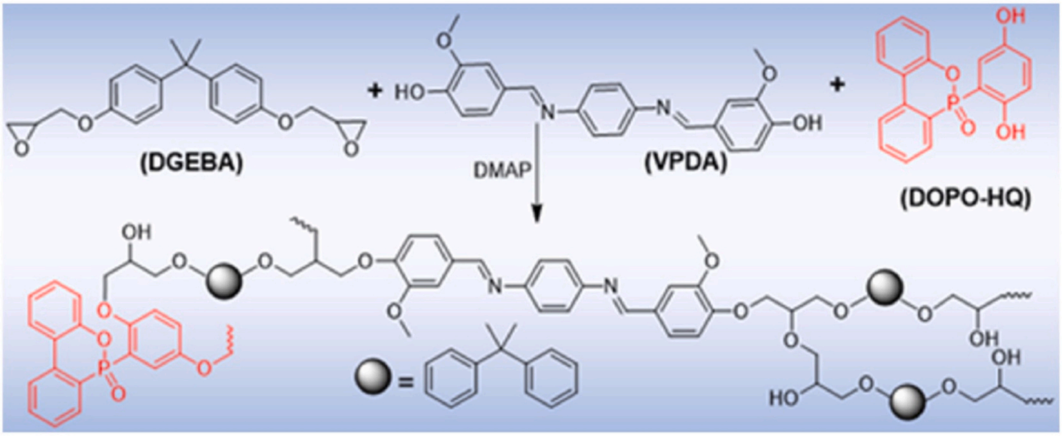


Fig. 24. Synthesis of the flame retarded bio–epoxy vitrimer. Legend: DMAP = 4–dimethylaminopyridine; DOPO–HQ = 10–(2,5–dihydroxyphenyl)–10–hydro–9-oxa–10–phosphaphenanthrene–10–oxide; VPDA = vanillin–derived imine hardener. Reprinted with permission from reference [171].

as the epoxy resin, dihydro–3–[(6–oxide–6 h–dibenz[c,e] [1,2]oxaphosphorin–6–yl)methyl]–2,5–furandi–one as the curing agent and triethanolamine as the transesterification modifier and catalyst. The rigid structures of tetraglycidyl methylene diphenylamine and curing agent resulted in a T_g exceeding 180 °C. The presence of tertiary amines in tetraglycidyl methylene diphenylamine and hydroxyl groups in triethanolamine led to thermally induced dynamic transesterification at temperatures beyond 200 °C. This facilitated the hydrolysis of the ester bonds present in the vitrimeric network, enabling the thermosetting matrix and the carbon fibres in the composite to be separated. The recycled carbon fibres exhibited a tensile strength of 3.1 GPa, consistent with the original reinforcement. Besides, as revealed by vertical flame spread tests, all the composites containing the DOPO derivative achieved self–extinction and V–0 rating; besides, the LOI reached about 33 % (vs. 22.6 % for the control material). The interesting FR features were further demonstrated by cone calorimetry tests that highlighted a 33 % decrease in the THR. Interestingly, the vitrimeric matrix was capable of degrading in pure water; moreover, the degradation products were able to re–form the vitrimeric matrix showing very good adhesive features.

Very Recently, Wang and co–workers [176] designed and developed a FR epoxy vitrimer coating by curing, at room temperature, bis(2,3–epoxypropyl)cyclohex–4–ene–1,2–dicarboxylate with a phosphaphenanthrene–containing polyethylenimine, synthesized on purpose (Fig. 27).

Apart from a high adhesive strength on wood (7.9 MPa, which was very close to the original value even after five chemical recycling cycles), and the possibility of reshaping the material through hot-pressing at 100 °C for 4 h, the vitrimeric coating containing 45 wt% of phosphaphenanthrene–containing polyethylenimine provided wood with interesting FR features, namely: self–extinction and V–0 rating in vertical flame spread tests, and a LOI value of 34 % as well. Besides, as assessed by forced–combustion tests (35 kW/m^2 irradiative heat flux), the same coating deposited on wood highlighted a decrease in both p–HRR and THR by around 37 % and 41 %, respectively, compared with uncoated wood. Again, these results were ascribed to a dual FR mechanism provided by the DOPO groups, which promoted the formation of a stable and protective char (in the condensed phase), and the quenching of active radicals (in the gas phase).

To summarize, Table 4 collects the different types of DOPO-derived vitrimers, together with their main characteristics.

7. Summary and perspectives

7.1. Summary

Their high flammability and chemically cross–linked nature make epoxy thermosets hazardous and non–recyclable at the end of their lifetime. This results in fire peril and waste accumulation, thus infringing global circular economy principles and environmental legislation for sustainable development. Therefore, endowing epoxy

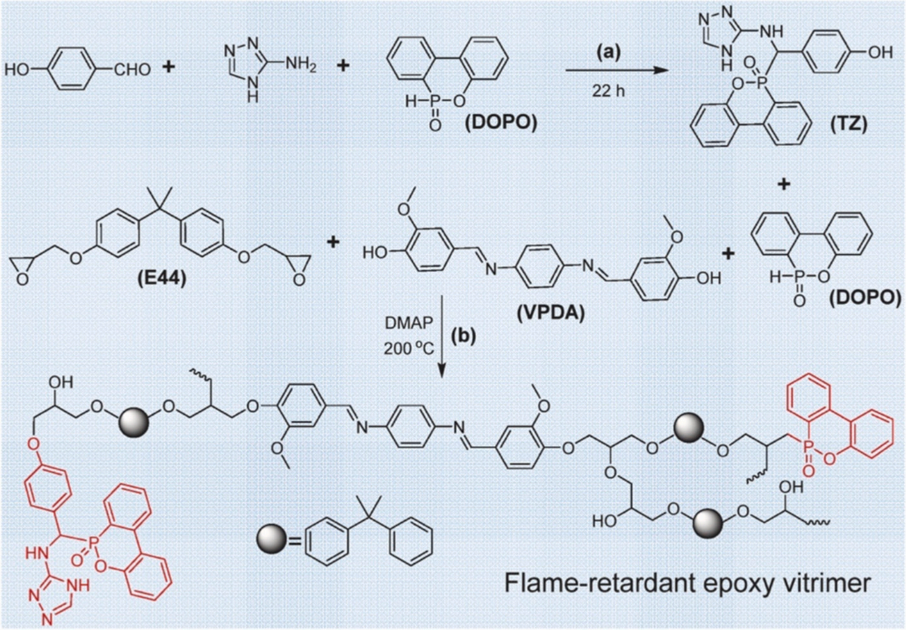


Fig. 25. Synthesis of the flame retarded bio–epoxy vitrimer. Legend: DMAP = 4–dimethylaminopyridine; TZ = DOPO derivative; VPDA = vanillin–derived imine hardener; E44 = DGEBA. Reprinted with permission from reference [172].

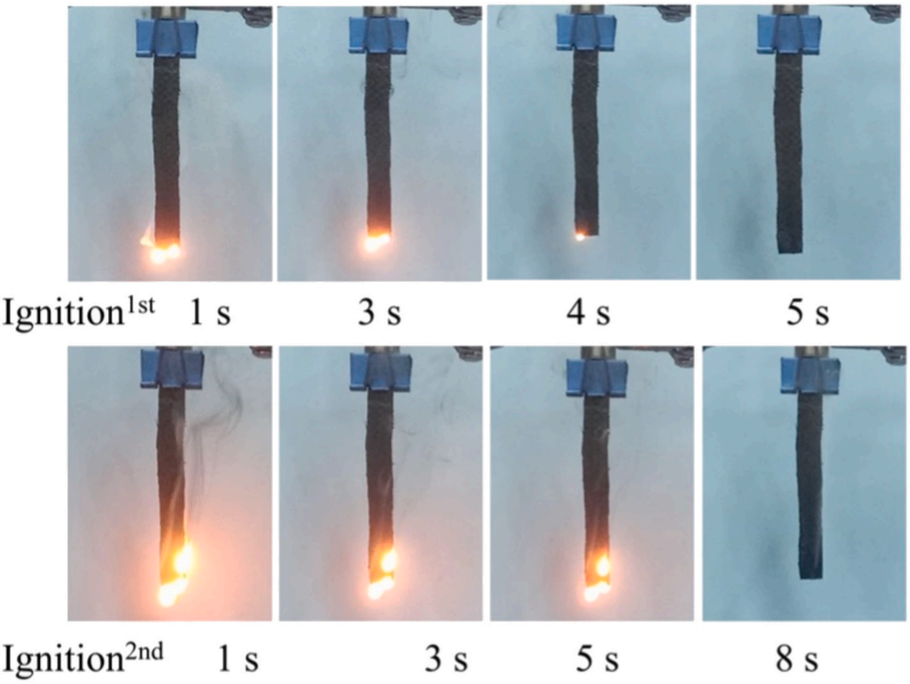


Fig. 26. Snapshots of the carbon–reinforced vitrimeric composite from vertical flame spread tests. Reprinted with permission from reference [172].

thermosets with both flame retardancy and recyclability features, and conferring them with vitrimeric properties, would greatly extend their range of applications and lifetime, while paving the way for the development of the current circular economy concept.

In this regard, the combination of epoxy vitrimeric systems (even bio-based) with DOPO or its derivatives undoubtedly represents a novel and reliable strategy for fulfilling the two aforementioned targets (i.e., excellent flame retardancy and reprocessability/recyclability), giving rise to new materials with very low environmental impact and high potential. Indeed, DOPO and its derivatives, among the P-based FRs, have gained significant ground, being some of the most extensively researched P-based compounds in the last ten years. Their use as non-reactive or reactive compounds in epoxy formulations has frequently been reported in the scientific literature, emphasizing the FR and eco–friendly character of the resulting thermosets that, upon being exposed to a direct flame or an irradiative heat source, show limited toxicity of evolved gases and smoke suppressant features, while simultaneously improving many other properties. It is worth noting that DOPO compounds typically increase the rigidity of vitrimeric epoxy networks into which they are incorporated due to the presence of

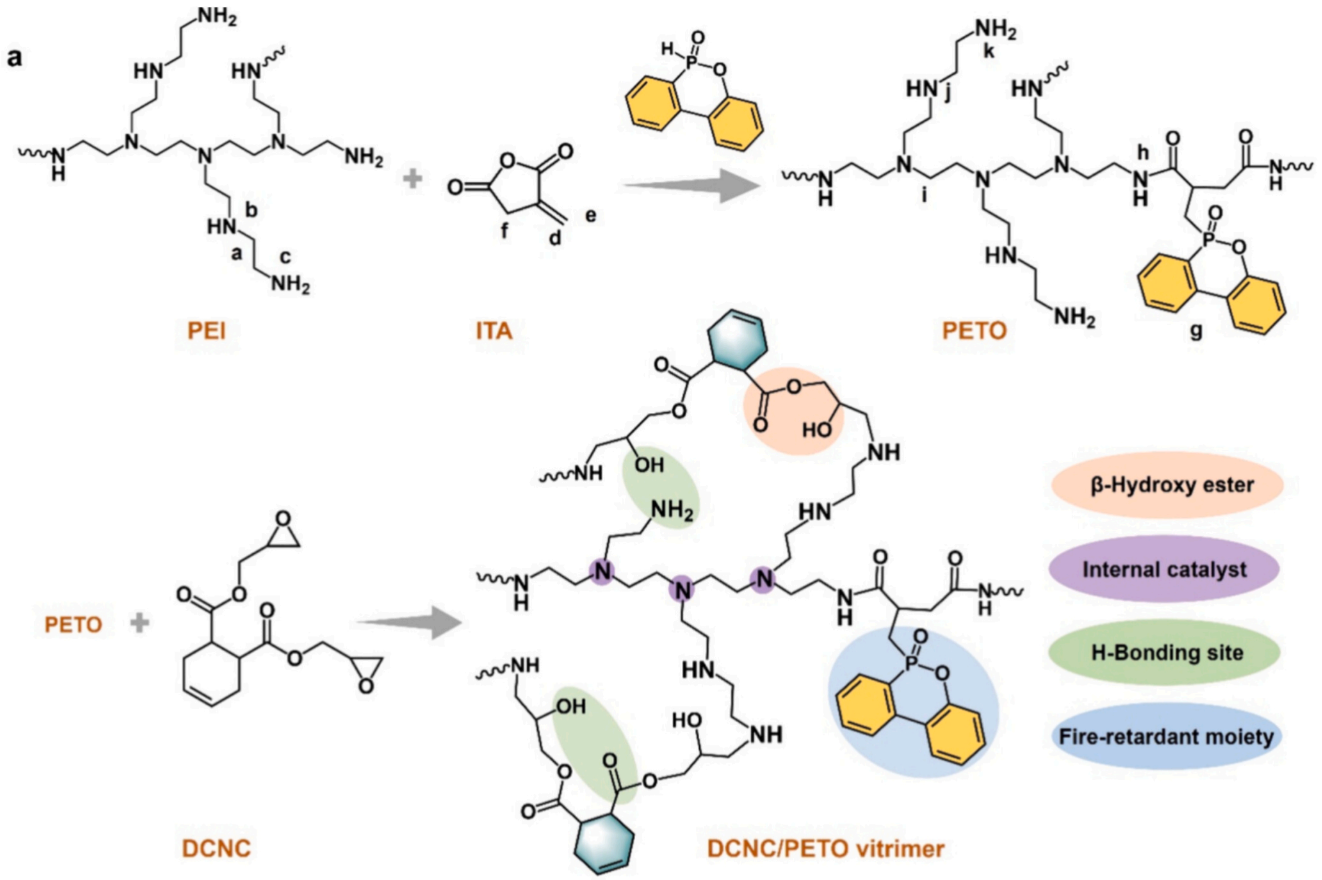


Fig. 27. Schematic illustration for the preparation of bis(2,3–epoxypropyl)cyclohex–4-ene–1,2–dicarboxylate/phosphaphenanthrene–containing polyethylenimine. Legend: PEI = polyethylenimine; ITA = itaconic acid; PETO = phosphaphenanthrene–containing polyethylenimine; DCNC = bis(2,3–epoxypropyl)cyclohex–4–ene–1,2–dicarboxylate. Adapted with permission from reference [176].

aromatic rings. This increases the T_g values and improves the overall mechanical behavior, while shifting reprocessability, recyclability and reshapeability toward higher temperatures. Therefore, it is important to strike a balance between the need for thermally stable, mechanically robust and effectively flame-retardant vitrimeric networks and their ease of recycling. Further, using reactive DOPO derivatives may adversely affect the crosslinking density of the final vitrimeric network: the usually limited loadings of reactive DOPO derivatives in the formulation of high-performance epoxy vitrimeric networks are justified by this.

Finally, specifically referring to flame retardancy, DOPO-based (bio) epoxy vitrimers perform very well. They generally achieve self-extinction, a V–0 rating and a high LOI in flammability tests with very low amounts of FR. They also perform well in forced combustion tests, lowering the thermal parameters and limiting the smoke generation.

7.2. Challenges

Despite the extensive use of DOPO for the design of effective FR systems, its application in epoxy vitrimers is still somewhat limited: this is mainly due to the need for a better understanding of the chemistry behind DOPO and the epoxy vitrimers. In this context, in the last years, several research groups have started to thoroughly investigate the effects of introducing DOPO and its derivatives in (bio)epoxy vitrimers: the aim of these research activities is to clarify the effects of introducing these FRs on the overall behavior of vitrimeric networks. Currently, there is probably still no ideal combination of epoxy vitrimer and DOPO-based FR that optimizes the thermo-mechanical behavior and the reprocessability/recyclability of the resulting flame-retardant polymer network.

Moreover, the reviewed systems are still in their infancy stage, and further development/implementation is required for the coming years. In particular, the research would greatly benefit from the design of more sustainable vitrimerizable epoxy systems. In fact, research into DOPO-based epoxy vitrimers still suffers from its limitation to fossil-derived systems, so further research is needed into the design and exploitation of bio-based epoxy vitrimers. A further limitation of the use of DOPO-(bio)based vitrimers refers to the possibility of setting novel and advanced synthetic pathways that would allow easy scalability at least up to a pilot/pre-industrial plant. Indeed, the current synthetic strategies are still limited to lab-scale experiments and, therefore, they are very far from any potential industrial exploitation. Conversely, being able to produce high quantities of effective and reliable DOPO-(bio) epoxy vitrimers would stimulate the interest of companies toward this intriguing approach, hence reducing the possible time-to-market. In this context, it is worth noting that there is a lack of economic analyses, though using catalyst-free and bio-based feedstocks could reduce the overall cost of DOPO-(bio)epoxy vitrimers [177,178].

Finally, despite their high intrinsic recyclability and potential for reuse, the reviewed systems currently suffer from a lack of their very EoL management: in this view, the further possibility of identifying flame retarded DOPO-(bio)epoxy vitrimers that are biodegradable on demand (the biodegradation products being neither toxic, nor hazardous for man and the environment) would undoubtedly represent a significant added value.

Table 4
Types of DOPO-derived epoxy vitrimers and their main charateristics.

Vitrimeric epoxy system	Main characteristics	Ref.
DOPO-DGEBA containing disulfide bonds	o With increasing DOPO loading: - decreased crosslinking density - decreased glass transition temperatures - decreased storage moduli - decreased E_a o Recyclability via hot pressing at 200 °C, 100 bar for 5 min o Self-extinction in vertical flame spread tests and V-0 rating o LOI of 27.8 % o Decreased p-HRR in cone tests (50 kW/m^2)	[164]
Vanillin-based epoxy monomers	o Elastic moduli of 2.5 GPa o Tensile strength of 76 MPa o High stress relaxation rate o Recyclability via hot pressing at 140 °C, 10 MPa for 10 min o Self-extinction in vertical flame spread tests and V-0 rating o LOI of 27 %	[165]
DOPO derivative-DGEBA	o Increase in Young's modulus and tensile strength in the presence of 10 wt% of DOPO derivative o Increased glass transition temperatures (up to 111 °C) o Reshapeability and recyclability via compression molding at 200 °C, 5 Mpa for 15 min (with no significant changes after three consecutive compression molding tests) o Self-extinction in vertical flame spread tests (for the system incorporating 30 wt% of DOPO derivative) o LOI of 34 % o Decrease in p-HRR and THR in cone calorimetry tests (35 kW/m^2)	[166]
Vanillin-derived imine compound-DOPO-glycerol triglycidyl ether	o Unchanged glass transition temperatures by incorporating DOPO (up to 6 wt%) o Beyond 6 wt% of DOPO, decrease in tensile strength and deformation at break o Decreased E_a values with increasing DOPO loading o Quick stress relaxation o Reshapeability and recyclability via compression molding at 170 °C, 15 MPa for 20 min o Good chemical recyclability o Self-extinction in vertical flame spread tests and V-0 rating o LOI of 26.4 % o Increased TTI and decreased THR and p-HRR values in cone tests (35 kW/m^2)	[167]
Vanillin-derived imine compound-DOPO-glycerol triglycidyl ether	o Decrease tensile strength with increased DOPO loadings o Increase in Young modulus o Reprocessability via compression molding at 140 °C, 10 MPa for 15 min (with 88 % of the original tensile strength retained) o Self-extinction in vertical flame spread tests and V-0 rating o LOI of 31 % o Decreased THR and p-HRR values in cone tests (50 kW/m^2)	[168]
DGEBA-itaconic acid-derived hyperbranched monomer-1,3,5-hexahydro-*s*-triazine-1,3,5-triyl)benzyl mercaptan	o Remarkable increase of impact strength and tensile strength by using 10 phr of the hyperbranched monomer o Self-extinction in vertical flame spread tests and V-0 rating (by using 15 phr of the hyperbranched monomer) o LOI of 34.8 % o Decreased THR and p-HRR values in cone tests (35 kW/m^2)	[169]
DOPO-furanodiene derivative- maleimide dienophile-DGEBA	o Good reprocessability and self-healing capability after a thermal treatment at 150 °C for 1 h (with stress retention rates beyond 75 % after three thermal cycles) o Decrease in THR and p-HRR values in cone tests (using 30 wt% of the DOPO derivative)	[170]
Vanillin-derived imine compound-DOPO-DGEBA	o Increased glass transition temperatures (up to 146 °C) o Decreased crosslinking degree o Decreased E_a values o Good reprocessability and recyclability via compression molding at 180 °C, 10 MPa for 20 min (with over 90 % retention of the original tensile strength after three compression molding cycles) o Self-extinction in vertical flame spread tests and V-0 rating (by using 22.5 wt% of the DOPO derivative) o Increased TTI and decreased THR and p-HRR values in cone tests (35 kW/m^2)	[171]
DOPO-DOPO derivative-BGEDA	o High Young's moduli and tensile strength values o Excellent recyclability o Self-extinction in vertical flame spread tests o LOI of 35 %	[172]
Itaconic acid-grafted DOPO-casein phosphopeptide chelating zinc-DGEBA	o Increased glass transition temperatures (up to 56 °C) o Self-healing capability in a short time (10 min) o Good reshapeability via compression molding at 200 °C for 1 h (retention over 72 % of the original mechanical strength) o Self-extinction in vertical flame spread tests and V-0 rating o LOI of 32 % o Decreased THR and p-HRR values in cone tests (35 kW/m^2)	[173]
DOPO derivative-glutamic acid-itaconic acid-BGEDA	o Decreased crosslinking density and enhanced processability with increased amounts of itaconic acid o Increased network stiffness with increased amounts of DOPO derivative o Exceptional thermal stability o Self-extinction in vertical flame spread tests and V-0 rating o LOI of 32 %	[174]

(*continued on next page*)

Table 4 (*continued*)

Vitrimeric epoxy system	Main characteristics	Ref.
DOPO derivative-tetraglycidyl methylene diphenil amine	o High glass transition temperatures (beyond 180 °C) o Occurrence of dynamic transesterification beyond 200 °C o Easy hydrolysis of ester bonds of the vitrimer and recovery of the reinforcement o Easy degradation of the vitrimer in pure water o Self-extinction in vertical flame spread tests and V-0 rating o LOI of 33 % o Decrease in THR as assessed by cone tests	[175]
Bis(2,3-epoxypropyl)cyclohex-4-ene-1,2-dicarboxylate-phosphaphenanthrene-containing polyethylenimine coatings	o High adhesive strength on wood, which is maintained after five chemical recycling cycles o Reshapeability via compression molding at 100 °C for 4 h o Self-extinction in vertical flame spread tests and V-0 rating of the vitrimer coated on wood o Decreased THR and p-HRR of the vitrimer coated on wood, as assessed by cone tests (35 kW/m^2)	[176]

7.3. Opportunities

For sure, the use of DOPO in epoxy vitrimers, at least considering the valuable research outcomes produced so far, represents an added value, with a very promising potential for further development and implementation.

Switching from DOPO-based epoxy to DOPO-based bioepoxy vitrimers could open up new possibilities for these fascinating materials, providing an opportunity to expand the range of flame-retardant epoxy systems to include bio-sourced, environmentally friendly products. This could potentially mitigate our reliance on fossil fuels by making use of renewable resources.

The examples discussed in the present review highlight the high potential of the investigated DOPO-based (bio)epoxy vitrimers in terms of their overall (i.e., thermal, mechanical and fire) performance and recyclability/reprocessability. The fact that these networks retain their original mechanical behavior even after several reprocessing cycles makes them very appealing for use in such advanced sectors as automotive, aerospace, and electronics. Moreover, the possibility of tailoring the properties of these vitrimers by adjusting the type and ratio of (bio)-based epoxy monomers, curing agents, and exchangeable bond chemistries may offer a wide versatility in demanding applications. Further research efforts should also be spent on widening the portfolio of reactive DOPO derivatives, specifically suitable for epoxy vitrimers. These new FRs should be well-optimized so that they can be used at the lowest possible concentration (being, at the same time, extremely high performing), do not suffer from leaching phenomena (for this purpose, reactive DOPO derivatives, which are covalently linked to the vitrimeric network, should be preferred), and do not affect the reversible characteristics of CANs.

Further research is expected to be undertaken in addressing these key challenges in the coming years, hence opening new pathways toward the development of efficient and sustainable FR epoxy vitrimers.

CRediT authorship contribution statement

Cristian-Dragos Varganici: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Data curation, Conceptualization. **Liliana Rosu:** Writing – original draft, Data curation. **Dan Rosu:** Writing – original draft, Data curation. **Giulio Malucelli:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Data curation, Conceptualization.

Declaration of competing interest

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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Data availability

No data was used for the research described in the article.

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