CHAPTER 12

Vitrimer Design for Flame Retardancy[†]

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12.1 Introduction

Nowadays, vitrimers are emerging as a new class of polymeric materials that can be considered intermediate between thermoplastics and thermosets: indeed, beyond a certain temperature that is strictly correlated with its chemical structure and functionality, a vitrimeric material can be re-processed (and mechanically recycled), whereas, below this temperature, it exhibits a three-dimensional unmeltable and insoluble network, and the typical thermo-mechanical and physico-chemical properties of a thermo-setting system.[1–5] These features are possible thanks to the formation of dynamic covalent bonds in the vitrimer structure, which allow for breaking and reforming the polymer network, exploiting either dissociative or (more often) associative exchange mechanisms.[6–10]

Vitrimers can potentially find interesting applications in several advanced sectors (*e.g.* electronics, electrochemistry, composites, and biomedical

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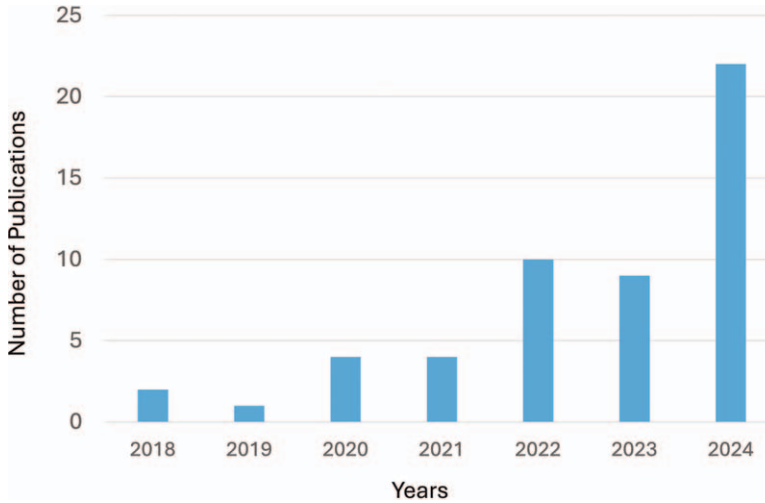


Figure 12.1 Number of publications (from 1999 to 2023) in peer-reviewed journals, dealing with "vitrimers AND flame retardant" (data collected from the Web of Science™ database, accessed on January 5, 2025).

engineering, among others).[11–18] However, one of the main weaknesses of vitrimers is their flammability: indeed, they burn vigorously when exposed to an irradiative heat flux or a direct flame. In recent years, academia has devoted significant efforts to designing flame retardant vitrimers to mitigate or resolve this issue. This activity is reflected in the increasing number of publications that have appeared in the scientific literature (Figure 12.1).

Therefore, this chapter aims to summarise the research activities carried out on flame retardant vitrimers since 2023 and to give the reader some perspectives for the coming years.

12.2 How to Assess the Flame Retardancy of Vitrimers

This section aims to provide readers who are not familiar with the topic with an overview of the main tests that can be exploited for evaluating the flame retardant behavior of vitrimeric systems. Generally speaking, these tests are divided into two categories, *i.e.* flammability and forced-combustion measurements. Flammability tests comprise flame spread tests (UL94) and limiting oxygen index (LOI) analyses, while forced-combustion tests refer to cone calorimetry analyses.

12.2.1 Flame Spread and LOI Tests

Flame spread tests were designed by Underwriters Laboratory Inc. They assess the ignitability and flame spread rate of polymeric specimens, either

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vertically or horizontally oriented. In vertical orientation (*i.e.* the most severe configuration), the specimen ($127 \times 13 \times 2$ mm^3) is vertically clamped; moreover, some cotton indicator is placed 300 ± 5 mm below the sample itself. Then, the specimen undergoes the application of a 20 mm length blue flame (gas: CH_4) 10 mm from the bottom of the sample for 10 s; the flame is subsequently removed, and the time duration of the burning after flame removal (the so-called after-flame time) is measured. Successively, the specimen undergoes a further 10 s application of the flame. In addition to the after-flame time, the after-glow time is measured: the latter corresponds to the time duration of the glowing after flaming stops or after the removal of the external methane flame. Meanwhile, the ignition of the cotton indicator by incandescent drops originating from the sample burning is monitored. The test is usually repeated on at least five samples: after the elaboration of the data, the material can be classified according to V-0, V-1, and V-2 ratings (also including NC, not classifiable). In this classification, V-0 represents the highest rank and is, thus, referred to as a self-extinguishing polymer system showing an after-flame time below 10 s, no dripping phenomena, no ignition of the cotton indicator, no flame or glow up to the sample clamp, and the sum of after-flame time and after-glow time after the application of the second flame below 30 s.

LOI is another typical flammability test that aims to evaluate the minimum concentration (volume %) of oxygen in a flowing oxygen/nitrogen mixture, which is required to keep the combustion process of a specimen.[19] The specimen is put in a glass chimney with a vertical orientation to perform the test (according to the ASTM D2863 standard). Then, the oxygen/nitrogen mixture flows upward through the chimney for a specific time (*i.e.* 30 s) to achieve a uniform burning atmosphere. Subsequently, the top of the specimen is ignited, and its candle-like combustion starts. Successively, the oxygen concentration in the flowing mixture is lowered until a critical value is reached. Since the oxygen content in standard air is around 21 vol%, all the specimens with a limiting oxygen index beyond this value are indicated as self-extinguishing: indeed, they stop burning in atmospheric conditions after the external flame is removed. Below 21%, any polymer sample is classified as self-combustible.

12.2.2 Forced-combustion Tests

These tests require the use of a cone calorimeter that represents the most commonly utilised bench-scale heat release rate apparatus.[20] The measurements are carried out according to the ISO 5660 standard on square samples (usually $100 \times 100 \times 4$ mm^3), which are exposed to a constant irradiative heat flux (generally from 10 kW m^{-2} up to 100 kW m^{-2}) delivered by an electric conical heater. The latter accounts for the occurrence of pyrolysis phenomena that originate gaseous products as the material starts degrading; these gases are then ignited employing an electric spark that is removed immediately after the ignition. Subsequently, the volatile products originating from combustion of the specimen are captured by an exhaust hood and analysed in terms of composition (oxygen, carbon monoxide and carbon

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dioxide), pressure, temperature, flow rates, and smoke density. The heat release rate per unit of surface area (HRR, $kW\,m^{-2}$) and its variations over time are continuously monitored and calculated by evaluating the oxygen diminution in the exhaust pipe. In addition to HRR, the following thermal and smoke parameters are evaluated: time to ignition (TTI, s), total heat release (THR, $MJ\,m^{-2}$), peak of heat release rate (pHRR, $kW\,m^{-2}$), total smoke production (TSP, m^2), smoke extinction area (SEA, $m^2\,g^{-1}$), and smoke production rate (SPR, $m^2\,s^{-1}$).[20,21] Very often, compared to pristine/unmodified counterparts, efficient flame retarded polymer systems exhibit decreased THR and pHRR values, as well as reduced SEA, SPR, and TSP when the systems also show smoke suppressant features.[22]

12.3 Recent Advances in Flame Retardant Vitrimers

This section will provide a summary of the research activities carried out during the last three years on flame retarded vitrimeric systems. The section is divided into two subsections, one discussing vitrimeric polymer systems and the other vitrimeric composites.

12.3.1 Flame Retardant Vitrimeric Polymers

Shao and co-workers synthesised epoxy vitrimers (derived from diglycidyl ether of bisphenol A) bearing exchangeable disulfide bonds and cured with 4,4′-dithiodianiline.[23] To provide them with flame retardant features, ammonium polyphosphate microencapsulated in melamine-formaldehyde resin was incorporated into the epoxy formulation at different loadings (namely, 2.5 wt%, 5 wt%, 7.5 wt%, and 10 wt%). At the highest flame retardant loading, the LOI values increased from 19.5% to 25.3%; besides, as revealed by UL94 vertical flame spread tests, dripping phenomena were prevented, though it was not possible to classify the samples according to the standard. These findings were attributed to the char-forming character of the incorporated flame retardant.

2-Hydroxyethyl methacrylate phosphate was employed as a reactive flame retardant with bio-based epoxidised soybean oil, using tannic acid as a charring additive.[24] The obtained vitrimers exhibited a high crosslinking density with enhanced mechanical features (tensile and flexural strength were around 20 MPa and 36 MPa, respectively), self-healing ability and recyclability, thanks to the transesterification of dynamic β-hydroxyl phosphate esters. In addition, as assessed by vertical flame spread tests, the flame retardant vitrimeric networks achieved a V-0 rating in UL94 tests, with LOI values of 26.7%. These findings were ascribed to synergism between tannic acid and phosphate esters, with the formation of a stable and protective char in the condensed phase and the release of non-flammable gases (namely, CO_2 and water vapor) in the gas phase (*i.e.* through a dilution effect).

Hu and co-workers[25] synthesised vanillin-based polyurethane networks bearing disulfide and imine bonds. To this aim, hexamethylene diisocyanate trimer

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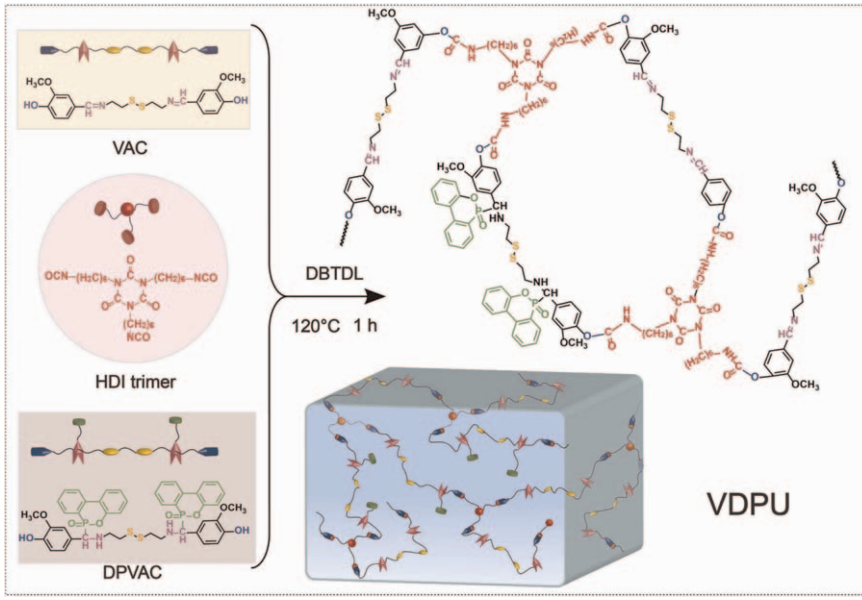


Figure 12.2 Synthetic pathway for the design of vanillin-derived vitrimeric polyurethanes. Legend: VAC = vanillin derivative after reaction with cystamine dihydrochloride; HDI = hexamethylene diisocyanate; DPVAC = vanillin polyol bearing flame retardant groups; DBTDL = dibutyltin dilaurate; VDPU = final vitrimeric polyurethane. Reproduced from ref. 25 with permission from Elsevier, Copyright 2023.

was reacted with a vanillin derivate containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) groups and disulfide linkages (Figure 12.2).

Apart from interesting reprocessability and self-healing features (about 100% healing efficiency after a thermal treatment carried out at 120 °C for 90 min), the so-obtained vitrimers exhibited self-extinction and V-0 rating in vertical flame spread tests, as well as high LOI values (around 30% *vs.* 19.9% for the unmodified vitrimeric polyurethane).

Pursuing this research, the same group focused on the synthesis of multifunctional polyurethane vitrimers derived from bio-based naringenin and vanillin and bearing dynamic phenol-carbamate bonds.[26] A schematic illustration of their synthesis is presented in Figure 12.3.

Treating the vitrimers at 100 °C for up to 40 min was enough to achieve self-healing; besides, the ease of reprocessability was demonstrated at the same temperature by applying 5 MPa pressure for shorter times (*i.e.* 30 min). Interestingly, the vitrimers showed antioxidant ability (witnessed by a radical scavenging ability of 90%) and achieved a V-1 rating in vertical flame spread tests. The flame retardancy was ascribed to the charring effect provided by the modified vanillin (condensed phase action) and the quenching of active radicals in the gas phase.

Tian and co-workers synthesised epoxy thermosets by reacting a bio-based glycerol triglycidyl ether with a vanillin-derived imine compound (hardener)

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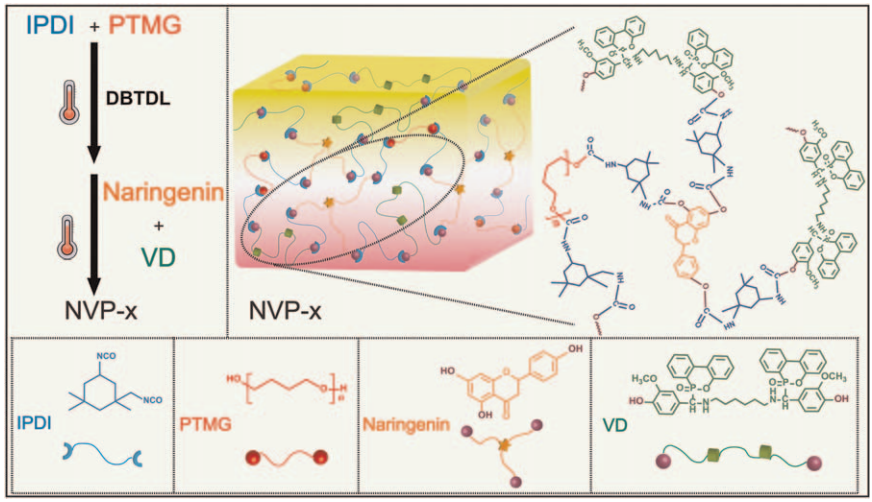


Figure 12.3 Synthetic pathway for the design of vanillin- and naringenin-derived vitrimeric polyurethanes. Legend: DBTDL = dibutyltin dilaurate; IPDI = isophorone diisocyanate; VD = vanillin-based diol containing organic phosphorus moieties; NVP-x = final vitrimeric polyurethane; PTMG = polytetramethylene ether glycol. Reproduced from ref. 26 with permission from Elsevier, Copyright 2024.

in the presence of different amounts (*i.e.* 1 wt%, 3 wt%, and 6 wt%) of DOPO (employed as reactive fire-retardant additive).[27] Apart from reprocessability and recyclability, the vitrimeric epoxy with the highest DOPO loading exhibited self-extinction and V-0 rating in UL94 tests, as well as an increased LOI value (about 26.4% *vs.* 20.4% for the reference without DOPO). Further, as assessed by forced combustion tests (irradiative heat flux: 35 kW m^{-2}), compared with the reference vitrimer, the presence of 6 wt% DOPO accounted for increased TTI (from 48 s to 61 s) and decreased THR and pHRR (by about 31% and 33%, respectively). These findings were ascribed to the radical scavenging action exerted by the DOPO decomposition products (gas-phase mechanism), and to the formation of a coherent and compact char slowing down the heat and mass transfer (condensed-phase mechanism).

Klinger and co-workers designed an epoxy vitrimer (based on diglycidyl ether of bisphenol A), incorporating phosphonate units (P content up to 8%) covalently bonded to the network.[28] To this aim, the epoxy monomer was reacted with 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide and subsequently cured with isophorone diamine, in the presence of triazabicyclodecene as transesterification catalyst. The material's recyclability and reprocessability were accomplished by the incorporation of at least 5% phosphorus. Conversely, 2.5% content of this element accounted for V-0 rating in vertical flame spread tests, as well as a significant decrease in both pHRR and TSP values (by about 75% and 72%, respectively, compared with the standard epoxy resin network). These findings were ascribed to a

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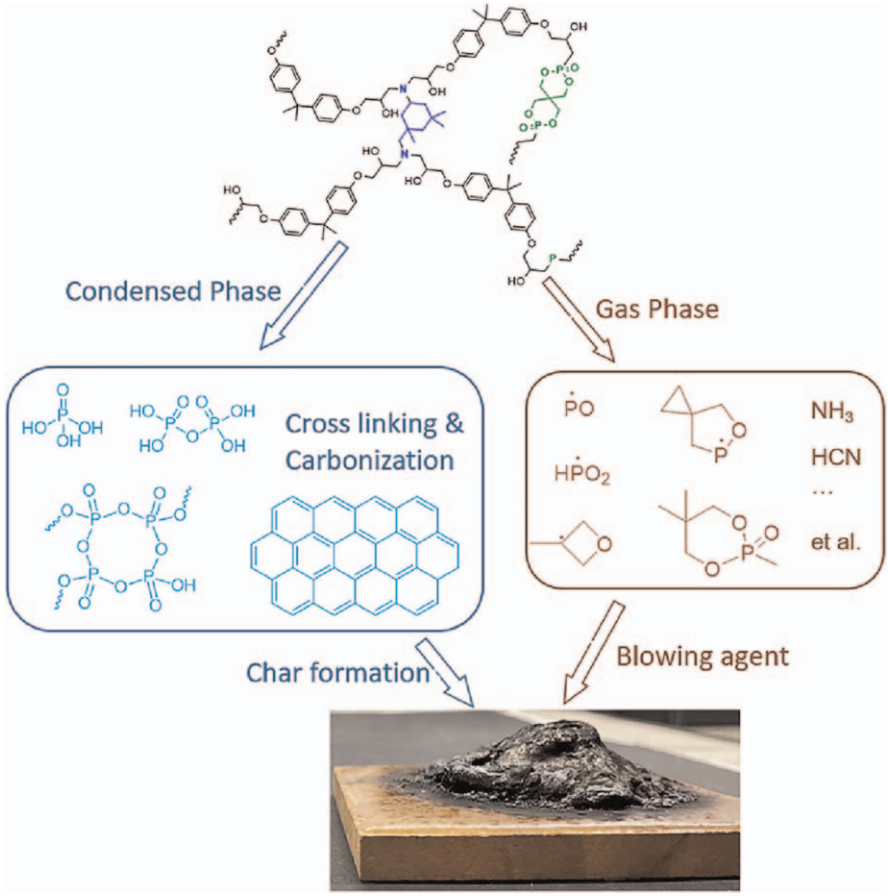


Figure 12.4 Proposed decomposition mechanisms in both condensed and gas phases. Reproduced from ref. 28, https://doi.org/10.1016/j.cej.2023.143051, under the terms of the CC BY 4.0 license, https://creativecommons.org/licenses/by/4.0/.

complex combination of mechanisms occurring in both condensed (through char formation) and gas (radical scavenging and release of non-flammable gases) phases (Figure 12.4).

Chen *et al.* covalently bonded diethyl bis(2-hydroxyethyl)aminomethylphosphonate to diglycidyl ether of bisphenol A cured with methylhexahydrophthalic anhydride.[29] The presence of about 20 wt% of the P-containing ester accounted for an easy reprocessability at 190 °C, V-0 rating in vertical flame spread tests and a LOI value of 28.3% (*vs.* 19% for the system cured with *N*-methyl diethanolamine, used as a reference). In addition, as assessed by forced-combustion tests carried out at 35 kW m^{-2} irradiative heat flux, the flame retardant epoxy vitrimer exhibited decreased values of THR, pHRR, and TSP (by about 74%, 62%, and 79%, respectively) compared to the reference system (not containing phosphorus). Besides, the residues at the end

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of the tests significantly increased (from around 6% to 86%), indicating an important char-forming effect in the condensed phase.

Ding *et al.* exploited the imine chemistry to combine flexibility and rigidity in epoxy flame retardant vitrimers.[30] For this purpose, diglycidyl ether of bisphenol A was first reacted with vanillin; the so-obtained product was then equipped with a flexible siloxane spacer through the reaction with 1,3-bis(3-aminopropyl)tetramethyldisiloxane and finally cured with 4,4′-diaminodiphenylmethane. The epoxy vitrimer exhibited self-healing features at 100 °C under stress-free conditions and reprocessability (through compression molding at 140 °C for 1 h at 10 MPa pressure). Besides, as assessed through forced-combustion tests (35 kW m^{-2} irradiative heat flux), compared with the reference system (*i.e.* diglycidyl ether of bisphenol A cured with 4,4′-diaminodiphenylmethane), the epoxy vitrimer showed an anticipation of TTI (39 s *vs.* 69 s), due to the early degradation of the flexible siloxane spacer, as well as decreased pHRR, THR, and TSP values (by around 51%, 25%, and 40%, respectively). These findings were attributed to an intense charring in the condensed phase action, promoted by the silica deriving from the decomposition of the siloxane segments.

Zhang and co-workers[31] employed a phosphonated epoxy monomer (synthesised for the purpose) in combination with two diacids (1 : 2 mole ratio), namely 1,4-cyclohexanedicarboxylic acid (cyclic product) and dodecanedioic acid (long-chain aliphatic product), as shown in Figure 12.5, to design a self-healing and reprocessable vitrimer network.

As revealed by UL94 vertical flame spread tests, the vitrimer achieved a V-0 rating; further, its LOI was as high as 31%. These findings were ascribed to a flame retardant action both in the condensed and gas phases, through charring and radical scavenging, respectively.

Liu and co-workers synthesised a flame retardant epoxy vitrimer (based on diglycidyl ether of bisphenol A and incorporating phosphonate and carboxylate esters), employing (2-carboxyethyl)phenylphosphinic acid as curing agent.[32] Compared with the resin cured with 4,4′-diaminodiphenylmethane, the vitrimer was easily recyclable without the need for a catalyst and exhibited self-healing features. Besides, as observed in UL94 vertical flame spread tests, the vitrimer was self-extinguishing and V-0 rated. Finally, forced combustion tests carried out at 35 kW m^{-2} irradiative heat flux highlighted a significant decrease in both pHRR and THR values (by about 70 and 34%, respectively). These results were interpreted based on the high char-forming character of the flame retarded system (condensed phase mechanism).

A similar approach was used by Ren *et al.*, who incorporated bis(3-hydroxypropyl) phenylphosphonate (synthesised for the purpose) into diglycidyl ether of bisphenol A cured with methylhexahydrophthalic anhydride.[33] The so-obtained vitrimer was self-extinguishing, exhibited a LOI as high as 37.3% (*vs.* 19.9% for the cured system not containing the phosphonate-containing diol), and achieved a V-0 rating in vertical flame spread tests. Moreover, as assessed by forced-combustion tests (35 kW m^{-2} irradiative

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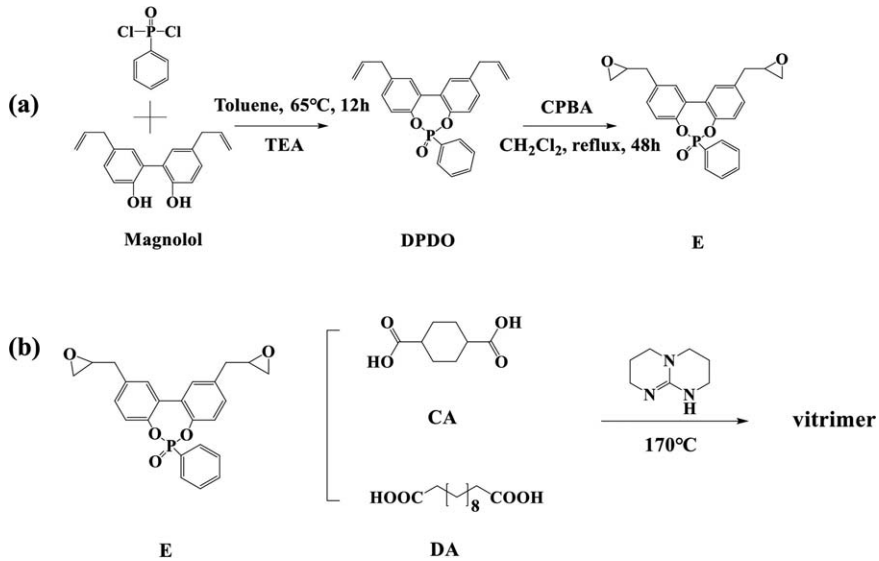


Figure 12.5 Synthesis (a) of the phosphonated epoxy monomer and (b) of the flame retardant vitrimer. Legend: Magnolol = 5,5′-diallyl-biphenyl-2,2′-diol; TEA = triethyl amine; DPDO = magnolol-based cyclic phosphonate with double bonds; CPBA = 3-chloroperbenzoic acid; E = phosphonated epoxy monomer; CA = 1,4-cyclohexanedicarboxylic acid; DA = dodecanedioic acid. Adapted from ref. 31 with permission from Elsevier, Copyright 2023.

heat flux), compared with the cured system not encompassing the phosphonate-containing diol, the flame retarded vitrimer exhibited a significant decrease in pHRR and THR values (by about 41 and 39%, respectively), as well as increased residues at the end of the tests (20.2% *vs.* 2.5%). These findings were attributed to an important flame retardant action in both condensed (thanks to the formation of such dehydrating species as pyrophosphoric acid, polyphosphoric acid, and phosphoric acid, which promote the formation of a stable and protective char) and gas (radical-quenching) phases.

5 wt% of DOPO incorporated into bio-epoxy glycerol triglycidyl ether (cured with a vanillin-based hardener bearing imine bonds, Figure 12.6) accounted for self-extinction and a V-0 rating in vertical flame spread tests performed on the obtained vitrimeric networks.[34] Besides, compared to the epoxy vitrimer without DOPO, forced-combustion tests (35 kW m^{-2} irradiative heat flux) showed a remarkable decrease in both pHRR and THR values (by around 38% and 26%, respectively). The observed fire behavior was explained through the char-forming character of the DOPO in the condensed phase, as well as the quenching of active radicals by the P-containing radicals (*e.g.* PO· and HPO·) originated in the gas phase.

Ye and co-workers designed a multifunctional Schiff base vitrimer obtained from the reaction of bio-based vanillin with phenylphosphonic

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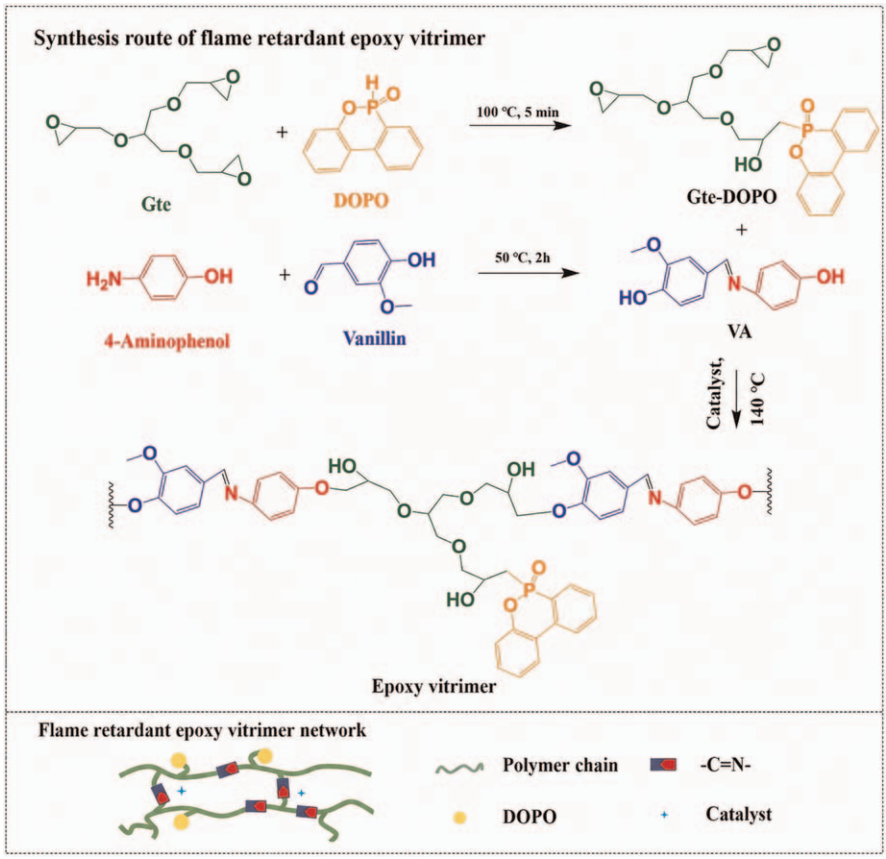


Figure 12.6 Scheme of the synthesis of the vanillin-based hardener and of the vitrimer. Legend: Gte = glycerol triglycidyl ether; DOPO = 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. Reproduced from ref. 34 with permission from Elsevier, Copyright 2024.

dichloride, triazine-containing cyanuric chloride, and isophorone diamine.[35] The material showed easy reprocessability by compression at 140 °C for 10 min, as well as enhanced toughness and antibacterial features (with bactericidal rates against *S. aureus* and *E. coli* of about 72% and 82%, respectively). Its multifunctionality also comprised enhanced flame retardant properties: more specifically, the presence of about 13.2 wt% of phenylphosphonic dichloride accounted for a significant decrease in both THR and TSP values (respectively by around 20.6% and 19.4%, compared to the system without phosphorus), as assessed by forced combustion tests (35 kW m^{-2} irradiative heat flux). These results were ascribed to the high char-forming character provided by C═N bonds and phosphate ester groups present in the vitrimer network.

In a further effort toward sustainability, Mahaninia and Yan exploited a dual crosslinking approach, consecutively reacting chitosan with citric acid and a vanillin-based phosphorus-containing epoxy crosslinker synthesised

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for the purpose.[36] The resulting vitrimers showed recyclability and self-healing features, thanks to dual dynamic bond-exchange sites derived from an extended formation of ester and amide bonds. Besides, a LOI value of about 42% was attained, together with self-extinction and V-0 rating in vertical flame spread tests. Also, as revealed by cone calorimetry tests carried out at 50 $kW\,m^{-2}$ irradiative heat flux, compared with the vitrimer not containing phosphorus, the flame retarded system exhibited a remarkable decrease in both pHRR, THR, and TSP values (Figure 12.7). These findings were ascribed to the flame retardant action occurring both in the condensed and gas phases, through the formation of a stable and protective char and radical quenching, respectively.

Luo *et al.* designed flame retarded vitrimers based on diglycidyl ether of bisphenol A, containing different amounts (namely, 5 mol%, 7.5 mol%, and 10 mol%) of a P-rich compound (used as a catalyst and obtained through the reaction of dibenzyl chlorophosphonate and triethanolamine) and cured with sebacic acid.[37] Apart from self-healing features and recyclability, the so-obtained vitrimers showed an enhanced fire behavior: in particular, for the vitrimers containing the highest amount of P-rich compound, cone calorimetry tests (35 $kW\,m^{-2}$ irradiative heat flux) demonstrated a significant decrease in pHRR and THR values (by about 66% and 50%, respectively, compared with the epoxy system not containing the P-rich compound and cured in the presence of triethanolamine), as well as a remarkable increase in the final residue (30.2% *vs.* 6.0%). These results were interpreted based on a strong action of the flame retardant in the condensed phase through the formation of a stable and coherent char.

Zhao and co-workers modified polyimine vitrimers with [BMIM]PF_6, an ionic liquid that contains N, P, and F.[38] The extended H-bonding between the ionic liquid and the polyimine network accounted for a remarkable increase in the mechanical strength, even at a very low concentration of the ionic liquid (*i.e.* 1 wt%). Besides, the vitrimers exhibited an easy reprocessability by compression under mild conditions (at 85 °C for 20 min at 1 MPa) and self-extinction (V-0 rating) in vertical flame spread tests. The results from vertical flame spread tests were explained based on the charring effect provided by the ionic liquid in the condensed phase, as well as on the radical quenching in the gas phase.

Meunier *et al.* used reactive extrusion of poly(butylene terephthalate) with diglycidyl ether of bisphenol A, zinc(II) acetylacetonate hydrate (as transesterification catalyst), and aluminium(III) phosphinate (as flame retardant, at 20 wt% loading).[39] The resulting vitrimer reached self-extinction, no dripping, and a V-0 rating in vertical flame spread tests. Besides, it was highlighted that aluminium phosphinate behaves not only as a flame retardant char-forming additive (in the condensed phase) but also as an effective transesterification catalyst, lowering the relaxation times of the vitrimer and envisaging its application to the design of continuous processes.

Huang *et al.*[40] succeeded in obtaining an epoxy vitrimer easily repairable through hot compression at 185 °C, progressively increasing the pressure up

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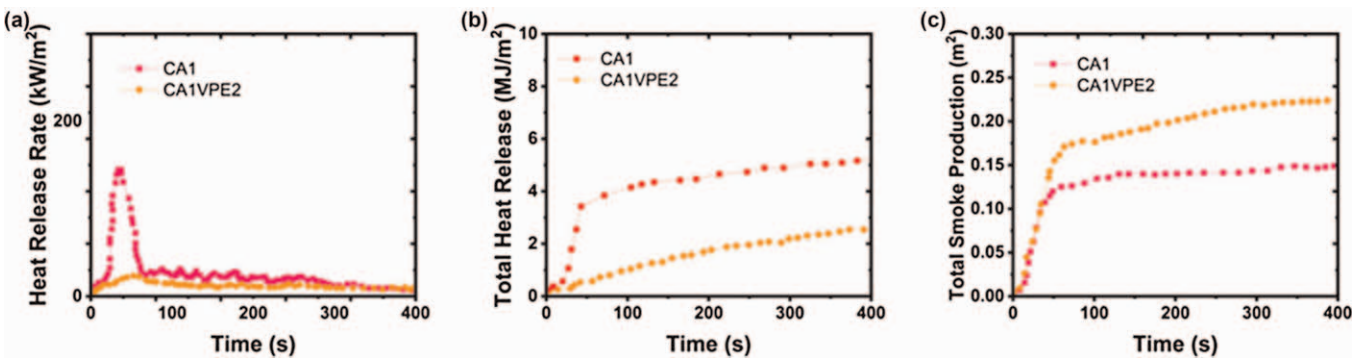


Figure 12.7 (a) Heat release rate curves, (b) total heat release curves, and (c) total smoke production curves obtained from cone calorimetry tests (50 kW m^{-2} irradiative heat flux). Legend: CA1 = system obtained by crosslinking chitosan with citric acid; CA1VPE2 = phosphorus-containing vitrimer (1 : 1 : 1 molar ratio of chitosan/citric acid/vanillin-derived crosslinker). Reproduced from ref. 36 with permission from American Chemical Society, Copyright 2024.

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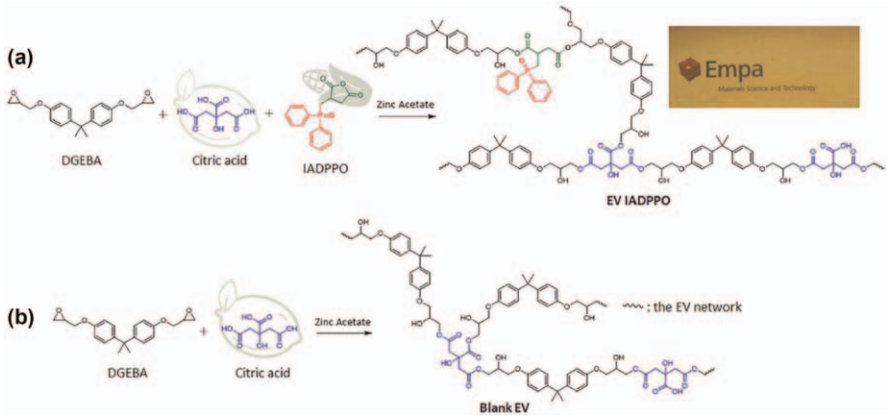


Figure 12.8 (a) Synthesis of the flame retarded epoxy vitrimer; (b) synthesis of the vitrimer not containing the P-based flame retardant. Legend: DGEBA = diglycidyl ether of bisphenol A; IADPPO = diphenylphosphine oxide itaconic anhydride; EV IADPPO = flame retarded epoxy vitrimer; Blank EV = epoxy vitrimer cured with citric acid only. Adapted from ref. 40, https://doi.org/10.1016/j.jmst.2024.01.062, under the terms of the CC BY 4.0 license, https://creativecommons.org/licenses/by/4.0/.

to 15 MPa, for a total time of 11 min. To this aim, as shown in Figure 12.8, diglycidyl ether of bisphenol A was reacted with diphenylphosphine oxide itaconic anhydride (obtained from the reaction between DOPO and itaconic acid) and citric acid using a solvent-free process. As a reference system, the epoxy vitrimer cured with citric acid only was also prepared.

The flame retarded vitrimer achieved self-extinction and V-0 rating in UL94 vertical tests, as well as 27% LOI (*vs.* 18% for the reference). Further, as revealed by cone calorimetry tests (performed at 35 kW m^{-2} irradiative heat flux), the presence of the P-containing moiety in the vitrimeric network accounted for a significant decrease in pHRR and THR values (by around 33% for both), as well as for a 370% increase of the residues at the end of the test. These results were ascribed to the formation of a compact and protective char (in the condensed phase) and the radical scavenging exerted by the P-containing free radicals originated from the decomposition of the flame retardant reactive additive.

Hung and Liu synthesised a Meldrum's acid-functionalised and P-containing (DOPO-modified) bisphenol compound, used as a curing agent (and flame retardant) for diglycidyl ether of bisphenol A.[41] The resulting network showed recyclability and reprocessability features when compressed at 230 °C for 1 h (at 16 MPa), as well as self-extinction and V-0 rating in vertical flame spread tests.

Meng *et al.* demonstrated the possibility of tuning the flame retardant properties of vitrimeric poly(isocyanurate urethane)s by tuning the feed ratios (namely, 3 : 2, 2.75 : 2 and 2.5 : 2) of their constituents, *i.e.* tri(2-hydroxyethyl) isocyanurate and dimethyl carbamate.[42] In particular, using a 2.5 : 2

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feed ratio accounted for self-extinction and a V-0 rating in UL94 vertical tests. Further, this vitrimeric poly(isocyanurate urethane) showed reprocessability features thanks to the occurrence of transurethane and transesterification reactions that activated the network rearrangement.

Zhang and co-workers synthesised a reprocessable and flame retardant vitrimeric system through the reaction of a furan-derived tri-aldehyde monomer (derived from 5-hydroxymethyl-2-furaldehyde and phosphorus oxychloride) with a furan-derived diamine monomer (obtained from furfurylamine and acetone).[43] The vitrimer exhibited a LOI value of 35% and achieved self-extinction and a V-0 rating in vertical flame spread tests; these findings were attributed to a high char-forming action taking place in the condensed phase.

In a further research effort toward sustainability, Ferretti and co-workers exploited thiol–ene click chemistry to synthesise a vitrimeric system obtained from the reaction of a cardanol-derived epoxy with a diboronic ester dithiol (namely, 2,2′-(1,4-phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane]).[44] The so-obtained vitrimers exhibited very low relaxation times and activation energies (about 4 s at 70 °C and 48 kJ mol^{-1}, respectively), as well as easy reshapeability (by heating the material at 150 °C for 15 min under a pressure of 3 MPa). Further, horizontal flame spread tests indicated the absence of dripping phenomena, probably due to the charring activity of the boron-containing compounds present in the vitrimeric network.

Cuminet *et al.* exploited phosphoric acid to crosslink (through ring-opening polymerisation) three commercially available bio-based epoxy resins from cardanol, vanillic alcohol, and linseed oil.[45] As a reference system, the same bio-based epoxy resins were crosslinked using citric acid. In all cases, the epoxy:acid equivalent ratio was set at 1 : 1. The resulting vitrimers showed reprocessability *via* a thermal treatment performed at 120 °C for 45 minutes and interesting flame retardant behavior: as revealed by forced-combustion tests, the crosslinking with phosphoric acid accounted for a significant decrease in pHRR and THR values (by about 56% and 50%, respectively, compared with the system crosslinked by citric acid), as well as for a remarkable increase in the residues at the end of the test (from 0.1% for vitrimer crosslinked with citric acid to 22.6% for vitrimer crosslinked with phosphoric acid). These results were interpreted based on an important charring effect occurring in the condensed phase.

A similar approach was exploited by Liu and co-workers,[46] who incorporated a Schiff base and phenyl-phosphonate bonds into diglycidyl ether of bisphenol A through epoxy ring-opening reactions with an amine curing agent (namely, di(4-(((4-((4-benzaldehyde)disulfanyl)phenyl)imino)methyl) phenyl)phenyl-phosphonate), synthesised for the purpose. The vitrimers exhibited easy reshapeability through hot compression carried out at 160 °C under 5 MPa for 30 min. Moreover, as assessed through vertical flame spread tests, the vitrimers reached self-extinction and a V-0 rating. Finally, compared with the system cured with diaminodiphenylmethane, curing with the amine containing P, S and N allowed for a notable decrease in pHRR, THR, and TSP values (by around 31%, 27%, and 38%, respectively) as revealed by

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cone calorimetry tests (performed at 35 kW m^{-2} irradiative heat flux). These findings were ascribed to the formation of a compact and protective char in the condensed phase.

Wang *et al.* designed a lignocellulosic polyimide vitrimer starting from two lignin-derived aldehyde monomers and a cellulose-derived diamine monomer and exploiting a Schiff base reaction.[47] The vitrimers exhibited easy reprocessability through hot compression at 150 °C for 10 min under a pressure of 10 MPa. Besides, as assessed through vertical flame spread tests, the concurrent presence of P and N within the vitrimeric network accounted for self-extinction and a V-0 rating, thanks to extended charring phenomena taking place in the condensed phase.

Li and co-workers synthesised polyimine vitrimers exploiting the condensation of a hexasubstituted cyclotriphosphazene derived from vanillin with two bio-based amines (a castor oil polyamine and a furan-derived diamine), tuning the ratio between them.[48] The resulting vitrimers were reprocessable at 120 °C under a pressure of 15 MPa for 15 min. In addition, the presence of nitrogen and phosphorus in the vitrimer network accounted for self-extinction in horizontal flame spread tests and a LOI value as high as 28.8% (*vs.* 21.5% for the system not containing the furan-derived diamine). These findings were ascribed to the charring effect promoted in the condensed phase by the cyclotriphosphazene, as well as to a combined dilution effect and active radical scavenging taking place in the gas phase.

Luo and co-workers exploited the synergistic effect provided by the combination of a bio-based casein phosphopeptide chelating zinc together with a DOPO derivative (obtained by reacting DOPO with itaconic acid), to prepare diglycidyl ether of bisphenol A vitrimers, using sebacic acid as the curing agent.[49] The flame retarded vitrimers exhibited self-extinction and a V-0 rating in vertical flame spread tests. Further, as revealed by forced-combustion tests (irradiative heat flux: 35 kW m^{-2}), the presence of the two additives accounted for a significant decrease in pHRR and TSP values (respectively by about 74% and 27%, compared with the unfilled control vitrimer). These results were interpreted based on the char-forming character of the bio-based casein phosphopeptide chelating zinc in the condensed phase and the free-radical scavenging of the decomposition products of the DOPO derivative occurring in the gas phase.

Wang and co-workers designed and synthesised a multifunctional epoxy vitrimer through the room temperature reaction of bis(2,3-epoxypropyl)-cyclohex-4-ene-1,2-dicarboxylate with a phosphaphenanthrene-containing polyethylenimine (bio-based and synthesised for the purpose).[50] When the content of the latter was 45 wt%, the resulting vitrimer achieved self-extinction and a V-0 rating in vertical flame spread tests. Besides, its LOI was as high as 34%. Further, it is worth noticing that the designed vitrimers possessed excellent adhesion toward different substrates (and especially on wood, where the measured adhesion strength was about 7.9 MPa).

Jin *et al.* succeeded in producing bio-vitrimeric pads by reacting tannic acid with phosphoric acid, and, subsequently, with poly(vinyl alcohol).[51] A

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thermal treatment performed for 3 h at 100 °C under 5 MPa was enough to provide the vitrimers with reprocessability. Further, all the synthesised materials, irrespective of the phosphoric acid content, were self-extinguishing and V-0 rated in vertical flame spread tests, achieving LOI values as high as 75.7%.

Berner and co-workers thoroughly investigated the flame retardant features of epoxy vitrimers obtained from the reaction of diglycidyl ether of bisphenol A and butanediol diglycidyl ether with 4-aminophenyldisulfide, in the presence of different flame retardants.[52] In particular, the system containing 23.1 wt% Exolit® EP 360 (which supplies 1.5 wt% phosphorus) exhibited self-extinction and a V-0 rating in vertical flame spread tests (Figure 12.9). It is worth noting that these characteristics were maintained even after having performed a mechanical recycling process on the flame retarded vitrimer. Besides, cone calorimetry tests (carried out at 50 kW m^{-2} irradiative heat flux) highlighted a significant decrease in both pHRR and THR values (by around 38% and 34%, respectively) for the vitrimer incorporating 23.1 wt% of Exolit® EP 360, compared with the blank counterpart. These findings were ascribed to a strong radical quenching action in the gas phase.



Figure 12.9 Snapshots from vertical flame spread tests for the epoxy-derived vitrimers cured with 4-aminophenyldisulfide. Legend: EV-0 = epoxy vitrimer without Exolit® EP 360; EV-8 = epoxy vitrimer incorporating 23.1 wt% of Exolit® EP 360. Reproduced from ref. 52 with permission from Elsevier, Copyright 2025.

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Ye *et al.* designed a catalyst-free, closed-loop recyclable transesterification vitrimer by introducing a tertiary amine/phosphorus-containing reactive oligomer into diglycidyl ether of bisphenol A epoxy resin.[53] The vitrimer containing 1.5 wt% phosphorus exhibited V-0 ranking in vertical flame spread tests, and LOI values as high as 35.2% (*vs.* 19.2% for the neat epoxy). Besides, as revealed by forced-combustion tests carried out at 35 $kW\,m^{-2}$ irradiative heat flux, compared to the neat epoxy reference, the flame retarded epoxy vitrimer showed a remarkable decrease in both pHRR and THR values (by about 45% and 31%, respectively). These findings were ascribed to: (i) the charring effect of the tertiary amine/phosphorus-containing reactive oligomer in the condensed phase, and (ii) flame inhibition in the gas phase.

Liu and co-workers[54] recently demonstrated the effectiveness of using phenylphosphonic acid and *n*-octylphosphonic acid to partly substitute (2-carboxyethyl)phenylphosphonic acid in the synthesis of phosphonic/carboxylic mixed-ester epoxy (diglycidyl ether of bisphenol-A) vitrimers (Figure 12.10).

Compared to epoxy vitrimers that were solely cured with (2-carboxyethyl) phenylphosphonic acid, introducing phenylphosphonic acid or *n*-octylphosphonic acid (both at 5 mol%, 10 mol%, or 15 mol%) accounted for a simultaneous enhancement of both flame retardancy and recycling efficiency (which achieved a maximum of about 79% at 60.7 MPa), without significantly increasing the complexity of the synthesis process or necessitating the utilisation of a specific catalyst. As assessed through vertical flame spread tests, the vitrimers achieved self-extinction and were ranked V-0 (Figure 12.12). Further, forced-combustion tests carried out at 35 $kW\,m^{-2}$ irradiative heat flux highlighted a beneficial effect of the presence of phenylphosphonic acid or *n*-octylphosphonic acid in the vitrimer formulation, with a decrease in THR and TSP by up to 21.6% and 10%, respectively (Figure 12.11). These findings were ascribed to a mixed flame retardant effect in the condensed (char formation) and gas (reactive radical scavenging) phases.

Ye *et al.* incorporated a hydroxy-terminated hyperbranched polyester (obtained through the esterification of triethanolamine with 9,10-dihydro-10-(2,3-dicarboxypropyl)-9-oxa-10-phosphaphenanthrene 10-oxide) into bisphenol A diglycidyl ether at different loadings, ranging from about 21 wt% to 25 wt%; methyl tetrahydrophthalic anhydride was employed as the curing agent.[55] The good compatibility between the hyperbranched polyester and the epoxy resin accounted for a tough and highly transparent vitrimer (with transmittance beyond 80% in the whole visible wavelength range). Besides, as assessed through vertical flame spread tests, 25 wt% hyperbranched polyester (which corresponds to 1.8 wt% P) achieved self-extinction and V-0 rating; further, this vitrimer showed high LOI values (32.6% *vs.* 19.2% for the reference epoxy system). In addition, for the vitrimer embedding 1.8 wt% of P, cone calorimetry tests carried out at 35 $kW\,m^{-2}$ irradiative heat flux highlighted a remarkable decrease in both peak of heat release rate and total

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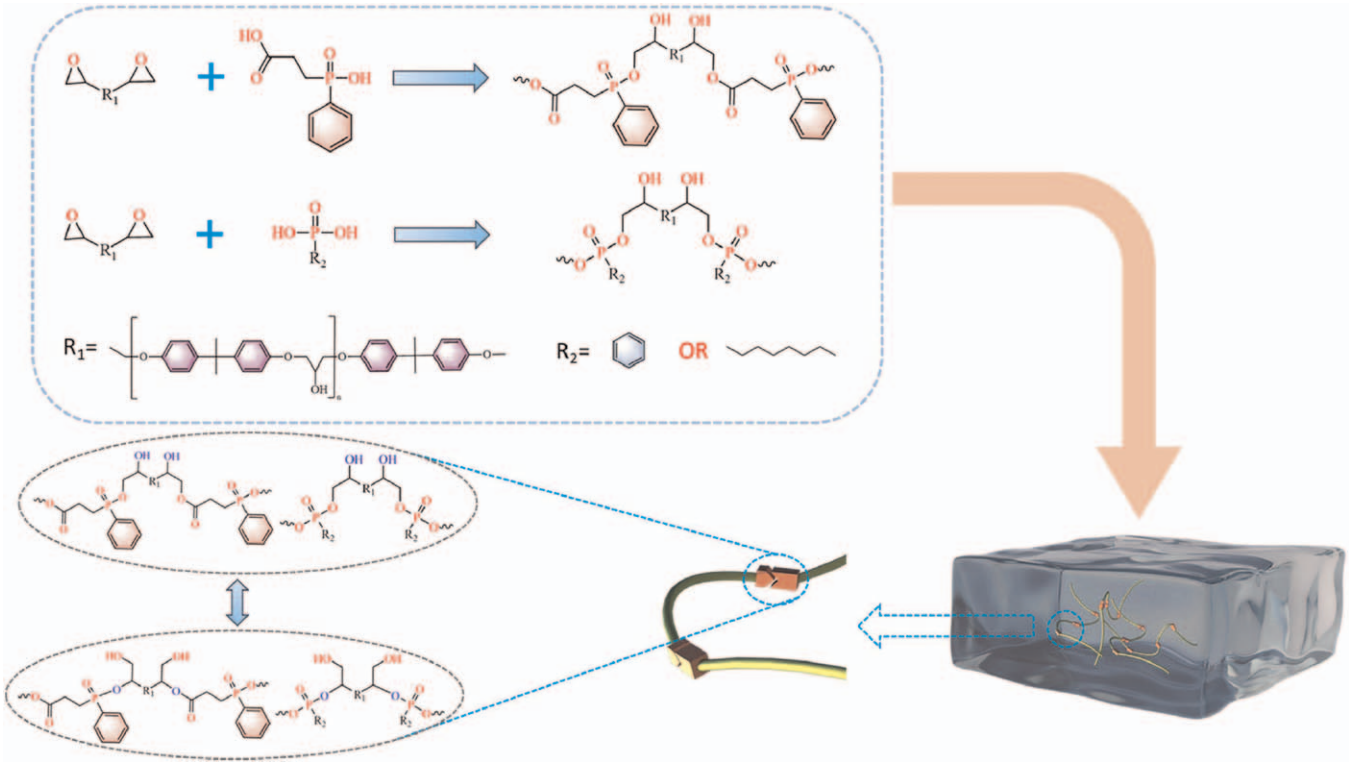


Figure 12.10 Scheme of the synthesis of the phosphonic/carboxylic mixed-ester epoxy vitrimer. Reproduced from ref. 54 with permission from Elsevier, Copyright 2025.

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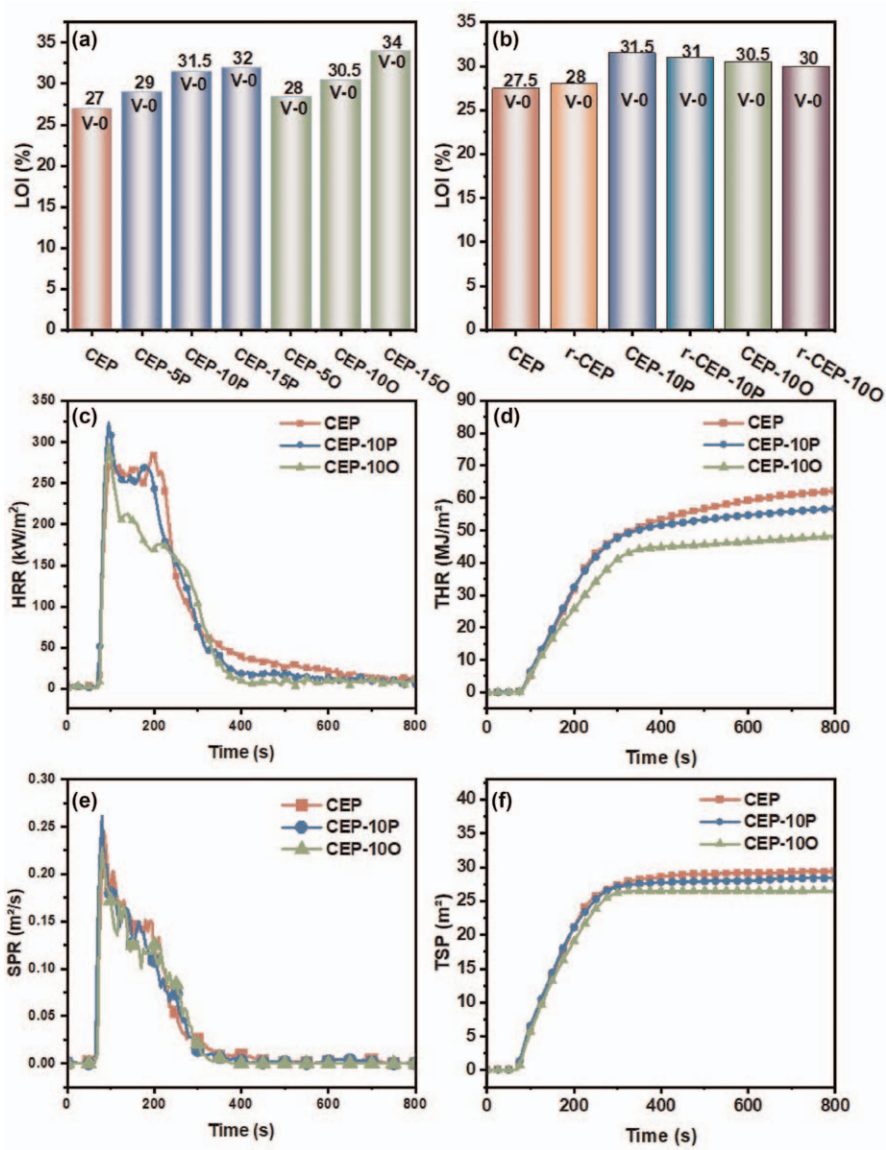


Figure 12.11 Phosphonic/carboxylic mixed-ester epoxy vitrimers: (a) LOI and (b) UL-94 rating; (c) HRR, (d) THR, (e) SPR, and (f) TSP curves obtained from cone calorimetry tests (35 kW m^{-2} irradiative heat flux). Reproduced from ref. 54 with permission from Elsevier, Copyright 2025.

heat release (by about 38% and 34%, respectively) with respect to the neat epoxy. These findings were attributed to dual condensed-phase (charring effect) and gas-phase (reactive radical scavenging) mechanisms. Finally, the vitrimer (1.8 wt% P content) recycled through hot pressing at 200 °C for 1 h

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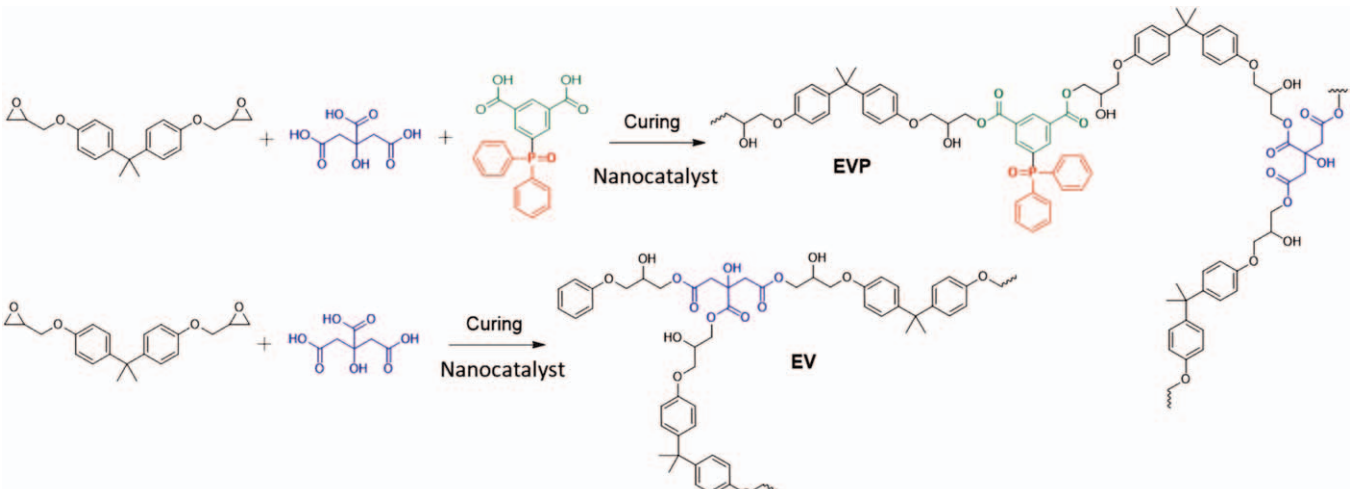


Figure 12.12 Synthetic routes for the epoxy vitrimers with (EVP) or without (EV) diphenyl phosphine oxide containing dicarboxylic acid. Reproduced from ref. 56, https://doi.org/10.1016/j.susmat.2025.e01477, under the terms of the CC BY 4.0 license, https://creativecommons.org/licenses/by/4.0/.

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showed self-extinction, V-0 rating, and a LOI of 32.2%, hence confirming the flame retardant performance of the pristine material.

Palumbo and co-workers[56] synthesised a diphenyl phosphine oxide containing dicarboxylic acid (namely, 5-(diphenylphosphoryl)isophthalic acid), which was used as hardener together with citric acid for epoxy vitrimers (Figure 12.12); as solid acid catalysts, mixed binary (SiNb, SiP) and ternary (SiNbP) oxides were derived by sol–gel methods starting from such precursors as tetraethyl orthosilicate, ammonium niobium oxalate hydrate, and orthophosphoric acid.

The efficiency of esterification during the initial curing process was enhanced by these mixed oxides, which promoted the decrease in activation energy for the crosslinking reactions (from 212 kJ mol^{-1} for the reference epoxy vitrimer to 100 kJ mol^{-1} for the vitrimer containing 2.4 wt% of P). Besides, the vitrimers were easily reprocessable through hot pressing at 250 °C, and the reprocessed materials (especially those embedding 5-(diphenylphosphoryl)isophthalic acid) showed almost unchanged glass transition temperatures with respect to the pristine counterparts. Finally, vertical flame spread tests revealed self-extinguishing character and V-0 rating for all the flame retarded epoxy vitrimers (even at very low P loadings, *e.g.* 2 wt%). In addition, forced-combustion tests carried out at 35 kW m^{-2} highlighted a significant decrease in pHRR (by about 63% compared to the reference epoxy vitrimer) and an increase in the TTI (by around 70%): these findings were ascribed to an intense flame retardant action in the condensed phase. Further, the incorporation of the mixed oxides into the vitrimeric formulations accounted for an important decrease, up to 62%, in the TSR, regardless of the presence of 5-(diphenylphosphoryl)isophthalic acid); also, the release of P radicals upon the decomposition of the latter promoted a significant inhibition effect in the gas phase.

Wang *et al.* exploited nucleophilic substitution and the oxidation of hexachlorocyclotriphosphazene with eugenol to obtain a star-shaped hexafunctional cyclotriphosphazene. This was then mixed with diglycidyl ether of bisphenol A at various loadings (6%, 10.2%, and 13.3% by weight), and used, together with glutaric anhydride, as the curing agent.[57] At the highest loading, the hexafunctional cyclotriphosphazene accounted for a significant increase in the glass transition temperature of the vitrimer (achieving 113 °C, *vs.* 79 °C for the reference epoxy system), thanks to the increase in the crosslinking density of the network. The latter was also responsible for the enhancement of the mechanical behavior, particularly referring to the Young's moduli (3080 MPa *vs.* 2730 MPa, for the vitrimer containing 13.3 wt% of hexafunctional cyclotriphosphazene and for the reference epoxy system, respectively). The vitrimers showed good reprocessability and recyclability through hot pressing at 200 °C, 5 MPa pressure for 2 h, exhibiting a recovery efficiency of 69%. Further, as revealed by flammability tests, the same vitrimer was rated V-1 in vertical flame spread tests and reached a LOI of 26.2% (*vs.* 21.6% for the reference epoxy). Finally, cone calorimetry tests (Figure 12.13) carried out at 25 kW m^{-2} irradiative heat flux highlighted a

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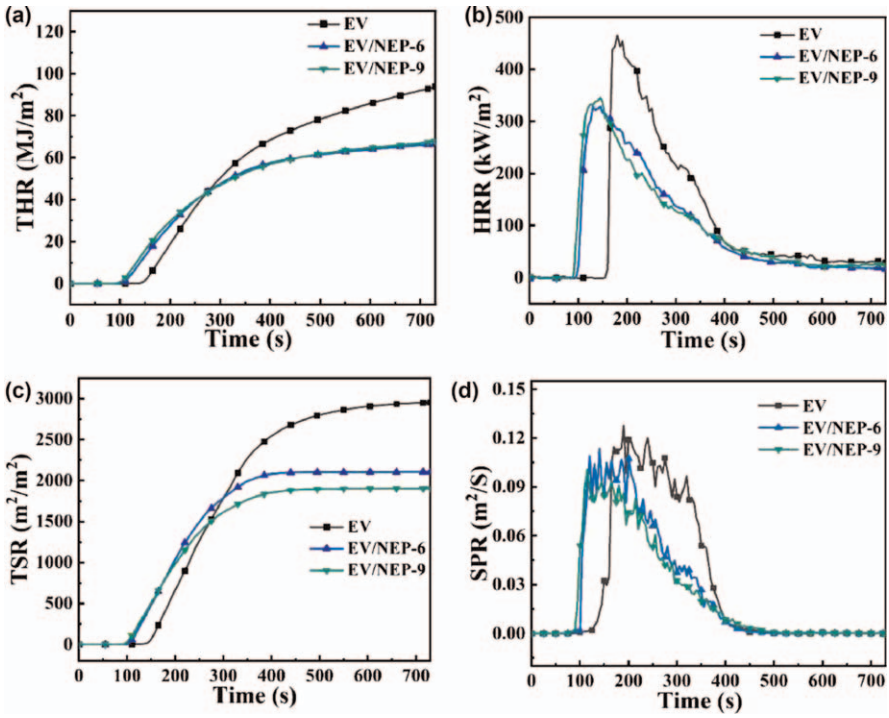


Figure 12.13 Results from cone calorimetry tests (carried out at 25 kW m^{-2} irradiative heat flux) for the reference epoxy vitrimer (EV), and the vitrimers containing 10.2 (EV/NEP-6) and 13.3% (EV/NEP-9) of star-shaped, hexafunctional cyclotriphosphazene. Reproduced from ref. 57 with permission from Elsevier, Copyright 2025.

significant decrease in both the peak of heat release rate, total heat release, and total smoke release (by about 29%, 30%, and 29%, respectively, compared to the reference epoxy). These findings were attributed to dual activity of the hexafunctional cyclotriphosphazene, namely its char-forming character in the condensed phase and its dilution effect in the gas phase.

Zhang *et al.* synthesised a phosphorus-containing vitrimer (Figure 12.14) and incorporated it into poly(methyl methacrylate) at 2 wt% loading, together with a hybrid of piperazine pyrophosphates and aluminium diethylhypophosphate (at 20 wt% loading).[58]

The resulting vitrimer achieved a V-0 rating and self-extinction in vertical flame spread tests. Additionally, the vitrimer showed an increased LOI value (*i.e.*, 24.3%) compared to the neat poly(methyl methacrylate) (17.6%). Finally, as assessed by forced-combustion tests performed at 35 kW m^{-2} irradiative heat flux, compared to the neat polymer, the concurrent presence of the vitrimer and the hybrid accounted for a significant decrease in both pHRR and THR (by about 64% and 38%, respectively). These outcomes were ascribed to the flame retardant activity in the condensed phase

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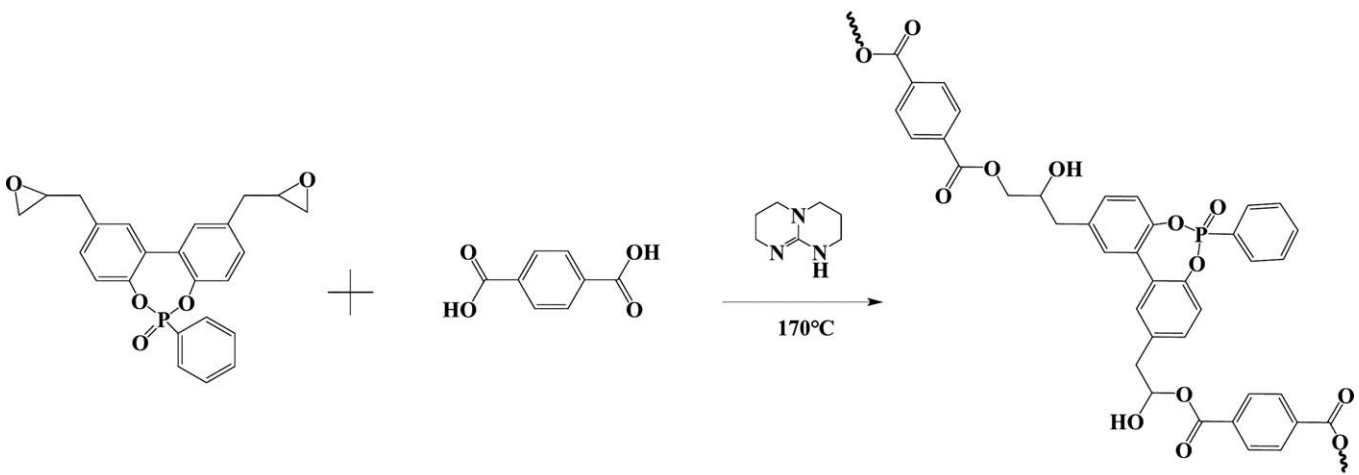


Figure 12.14 Synthetic route for obtaining the phosphorus-containing vitrimer (V). Legend: E = phosphorus-containing epoxy; CA = terephtalic acid. Reproduced from ref. 58 with permission from Elsevier, Copyright 2025.

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(through the formation of a stable and swollen intumescent char), as well as to a dilution of the gaseous flammable products in the gas phase.

Liu and co-workers[59] synthesised P-doped (*i.e.* grafted with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide – DOPO) carboxylic acid-type carbon dots that were employed as dynamically exchangeable bonds, nano-reinforcements, flame retardants, and curing agents for diglycidyl ether of bisphenol A (Figure 12.15).

Thanks to the presence of carbon dots, the vitrimers exhibited blue fluorescence under UV exposure (at 365 nm wavelength); their transparency was maintained even after three cycles of hot pressing at 200 °C under 10 MPa pressure for 3 hours. Then, the incorporation of 11 wt% of P-doped carbon dots into the epoxy vitrimers achieved a LOI of 31.3% (*vs.* 25.1% for the reference vitrimer containing undoped carbon dots), as well as self-extinction and V-0 rating in vertical flame spread tests. Further, forced-combustion tests carried out at 35 $kW\,m^{-2}$ irradiative heat flux revealed a decrease in pHRR, THR, and TSP (respectively by around 46%, 64%, and 12%) compared to the reference epoxy vitrimer containing undoped carbon dots. These findings were attributed to the formation of a stable, coherent, and protective char in the condensed phase, and a radical scavenging effect occurring in the gas phase.

Luo and co-workers designed a tannic acid-derived polycarbonate vitrimer by reacting tannic acid with bis(6-membered cyclic carbonate) at different hydroxyl:carbonate molar ratios (varying from 0.4 to 1.2).[60] The vitrimeric character of the obtained networks facilitated three reprocessing cycles performed at 8 MPa and 120 °C for 1 hour, with retention of mechanical properties beyond 83%, hence indicating a good recyclability. Further, it was possible to exploit near-infrared irradiation to induce a quick photothermal healing (healing efficiency about 97%), through a network rearrangement induced by transcarbonation reactions.

Self-extinction and V-0 rating were achieved for the vitrimers with hydroxyl:carbonate molar ratios exceeding 1; also, these materials exhibited LOI values of about 30%. These findings were attributed to the high tannic acid content of these vitrimers, which was responsible for the formation of a stable char that acted as a protective barrier, delaying heat release and suppressing the escape of volatile flammable products during combustion.

Chu *et al.*[61] synthesised epoxy vitrimers by reacting diglycidyl ether of bisphenol A with either glutamic acid, itaconic acid, or 6-oxido-6*H*-dibenz[*c*,*e*]-[1,2]oxaphosphorin-6-ylmethylbutanedioic acid, or with a combination of all three (Figure 12.16).

Keeping a P : N ratio of 1 : 0.5 in the resulting vitrimers accounted for self-extinction and a V-0 rating in vertical flame spread tests. Also, it is worth noting that the concurrent presence of the three acids in the vitrimeric network accounted for an important thermal stability, witnessed by the high degradation onsets (about 311 °C). These findings were attributed to the char-forming ability of the acids in the condensed phase, as well as a dilution/radical scavenging effect in the gas phase.

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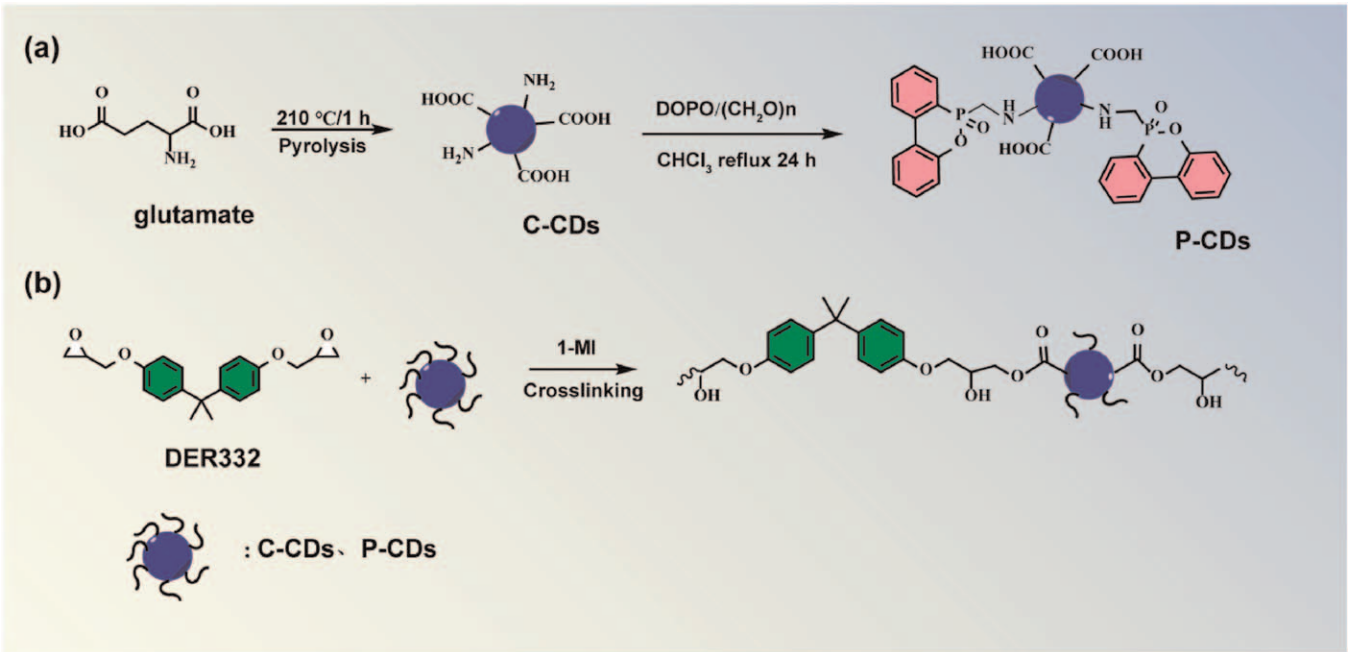


Figure 12.15 Synthetic routes to (a) carbon dots (C-CDs) and P-doped carbon dots (P-CDs), and (b) epoxy vitrimers. DER332 is the bisphenol A diglycidyl ether resin. Reproduced from ref. 59 with permission from Elsevier, Copyright 2025.

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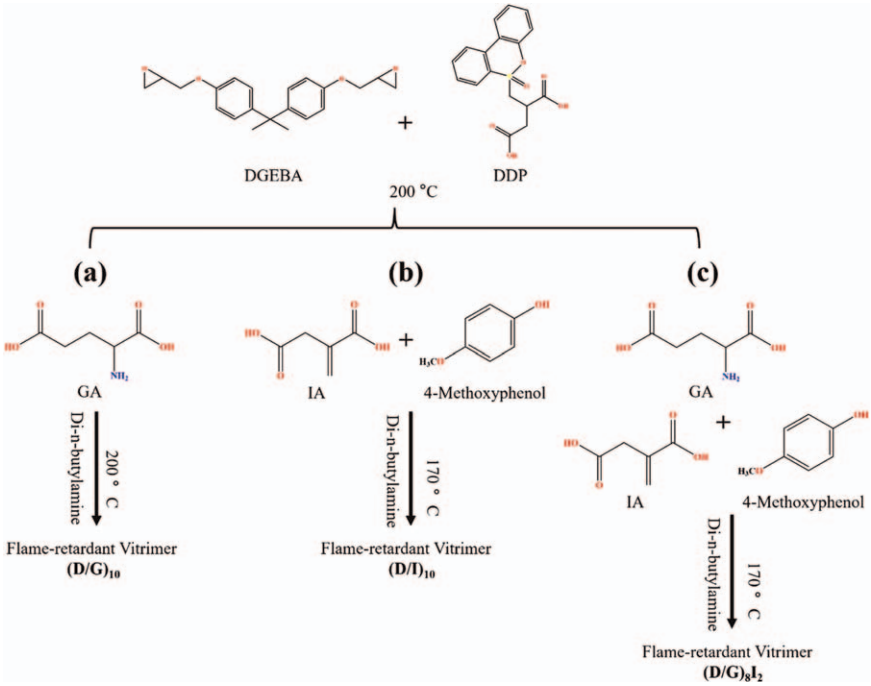


Figure 12.16 Synthetic route to epoxy vitrimers containing different acids. Legend: DDP = [(6-oxido-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-yl)methyl]butanedioic acid; GA = glutamic acid; IA = itaconic acid. Reproduced from ref. 61 with permission from Elsevier, Copyright 2025.

Razzaq and co-workers functionalised a commercial polyether diamine with imine and methacrylic groups, and synthesised an acrylic organophosphorus monomer through the reaction of 2-methyl-1,2-oxaphospholan-5-on-2-oxide with 2-hydroxyethyl methacrylate.[62] Different weight ratios of the two products were used in the UV-LED curing process to obtain the final vitrimers. The vitrimer containing 30 wt% acrylic organo-phosphorus monomer exhibited good reshapeability at 150 °C, as well as interesting shape recovery features utilising 80 °C as the programming temperature. The flame retardant behavior, evaluated through vertical flame spread tests and LOI measurements, highlighted a V-1 rating for the vitrimer containing 30 wt% acrylic organo-phosphorus monomer and a limiting oxygen index value of 26%.

Table 12.1 recaps the various vitrimers discussed above, highlighting their key findings in flame retardancy.

12.3.2 Flame Retardant Vitrimeric Composites

Flame retardancy of vitrimeric composites has also been investigated, though the research efforts carried out so far are quite limited compared to

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Table 12.1 Main outcomes of the vitrimeric systems discussed above.

Vitrimeric system	Main flame retardant outcomes	Ref.
Epoxy containing microencapsulated ammonium polyphosphate	• At 10 wt% flame retardant loading, LOI of 25.3% • No dripping phenomena in UL94 tests	23
Epoxidized soybean oil containing 2-hydroxyethyl methacrylate and tannic acid	• Self-extinction and V-0 rating in UL94 tests • LOI of 26.7%	24
Vanillin-based polyurethane networks containing DOPO	• Self-extinction and V-0 rating in UL94 tests • LOI of 30%	25
Polyurethane networks	• V-1 rating in UL94 tests	26
Epoxy containing DOPO	• At 6 wt% flame retardant loading, self-extinction and V-0 rating in UL94 tests • At 6 wt% flame retardant loading, increased TTI and decreased THR and pHRR in cone calorimetry tests	27
Epoxy incorporating phosphonate units	• At 2.5% phosphorus, V-0 rating in UL94 tests • At 2.5% phosphorus, decreased pHRR and TSP in cone calorimetry tests	28
Epoxy incorporating diethyl bis(2-hydroxyethyl) aminomethylphosphonate	• At 20 wt% P-containing ester loading, self-extinction and V-0 rating in UL94 tests; LOI of 28.3% • At 20 wt% P-containing ester loading, decreased THR, pHRR, and TSP in cone calorimetry tests	29
Vanillin-derived epoxy network containing a siloxane spacer	• Decreased pHRR, THR, and TSP in cone calorimetry tests	30
Phosphonated epoxy network	• Self-extinction and V-0 rating in UL94 tests • LOI of 31%	31
Epoxy network incorporating phosphonate and carboxylate esters	• Self-extinction and V-0 rating in UL94 tests • Decreased pHRR and THR in cone calorimetry tests	32
Epoxy network incorporating bis(3-hydroxypropyl)phenylphosphonate	• Self-extinction and V-0 rating in UL94 tests • LOI of 37.3% • Decreased pHRR and THR in cone calorimetry tests	33
Bio-epoxy network cured with a vanillin-based hardener and incorporating DOPO	• At 5 wt% flame retardant loading, self-extinction and V-0 rating in UL94 tests • At 5 wt% flame retardant loading, decreased pHRR and THR in cone calorimetry tests	34
Schiff-based network embedding phenylphosphonic derivative	• At 13.2 wt% phenylphosphonic derivative loading, decreased THR and TSP in cone calorimetry tests	35

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Table 12.1 (*Continued*)

Vitrimeric system	Main flame retardant outcomes	Ref.
Vanillin-based phosphorus-containing epoxy	• Self-extinction and V-0 rating in UL94 tests • LOI of 42% • Decreased pHRR, THR, and TSP in cone calorimetry tests	36
Epoxy network containing a phosphorus-rich compound	• At 10 mol% of the phosphorus-rich compound, decreased pHRR and THR in cone calorimetry tests	37
Polyimine network modified with an ionic liquid	• Self-extinction and V-0 rating in UL94 tests	38
Epoxy–polyester network embedding aluminium(III) phosphinate	• At 20 wt% flame retardant loading, self-extinction and V-0 rating in UL94 tests	39
Epoxy network cured with diphenylphosphine oxide itaconic anhydride and citric acid	• Self-extinction and V-0 rating in UL94 tests • LOI of 27% • Decreased pHRR and THR in cone calorimetry tests	40
Epoxy cured with a Meldrum's acid-functionalized and DOPO-modified compound	• Self-extinction and V-0 rating in UL94 tests	41
Poly(isocyanurate urethane) network	• Self-extinction and V-0 rating in UL94 tests	42
Furan-derived network	• Self-extinction and V-0 rating in UL94 tests • LOI of 35%	43
Cardanol-derived epoxy	• No dripping phenomena in horizontal flame spread tests	44
Epoxy networks from cardanol, vanillic alcohol, and linseed oil cured with phosphoric acid	• Decreased pHRR and THR in cone calorimetry tests	45
Epoxy network incorporating a Schiff base and phenyl-phosphonate bonds	• Self-extinction and V-0 rating in UL94 tests • Decreased pHRR, THR, and TSP in cone calorimetry tests	46
Lignocellulosic polyimide network	• Self-extinction and V-0 rating in UL94 tests	47
Polyimine networks	• Self-extinction in horizontal flame spread tests • LOI of 28.8%	48
Epoxy network embedded with a DOPO derivative and a bio-based casein phosphopeptide chelating zinc	• Self-extinction and V-0 rating in UL94 tests • Decreased pHRR and TSP in cone calorimetry tests	49
Epoxy network incorporating a phosphaphenantrene-containing polyethyleneimine	• At 45 wt% polyethyleneimine loading, self-extinction and V-0 rating in UL94 tests; LOI of 34%	50
Bio-vitrimer pads derived from tannic and phosphoric acids	• Self-extinction and V-0 rating in UL94 tests • LOI of 75.7%	51

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Table 12.1 (*Continued*)

Vitrimeric system	Main flame retardant outcomes	Ref.
Epoxy networks containing different flame retardants	• At 23.1 wt% Exolit® EP 360 loading, self-extinction and V-0 rating in UL94 tests • At 23.1 wt% Exolit® EP 360 loading, decreased pHRR and THR in cone calorimetry tests	52
Epoxy network derived from a tertiary amine/phosphorus-containing oligomer	• At 1.5% phosphorus loading, V-0 rating in UL94 tests and LOI of 35.2% • At 1.5% phosphorus loading, decreased pHRR and TSP in cone calorimetry tests	53
Phosphonic/carboxylic acid mixed ester epoxy network	• The presence of 5–15 mol% of phenylphosphonic acid or *n*-octylphosphonic acid accounted for self-extinction and V-0 rating in UL94 tests • The presence of 5–15 mol% of phenylphosphonic acid or *n*-octylphosphonic acid promoted decreased THR and TSP in cone calorimetry tests	54
Epoxy network embedding a DOPO-derived hyperbranched polyester	• At 25 wt% of DOPO-derived hyperbranched polyester, self-extinction, V-0 rating in UL94 tests and LOI of 32.6% • At 25 wt% of DOPO-derived hyperbranched polyester, decreased pHRR and THR in cone calorimetry tests	55
Epoxy network cured with 5-(diphenylphosphoryl)isophthalic acid and citric acid and containing sol–gel-derived mixed binary and ternary oxides	• Self-extinction and V-0 rating in UL94 tests • Increased TTI and decreased pHRR in cone calorimetry tests • The sol–gel-derived mixed binary and ternary oxides acted as smoke suppressants	56
Epoxy network containing a star-shaped cyclotriphosphazene	• At 13.3 wt% star-shaped cyclotriphosphazene loading, V-1 rating in UL94 tests and LOI of 26.2% • At 13.3 wt% star-shaped cyclotriphosphazene loading, decreased pHRR, THR, and TSR in cone calorimetry tests	57
Poly(methyl methacrylate) incorporating a phosphorus-containing vitrimer, piperazine pyrophosphates, and aluminium diethylhypophosphate	• Self-extinction and V-0 rating in UL94 tests; LOI of 24.3% • Decreased pHRR and THR in cone calorimetry tests	58

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Table 12.1 (*Continued*)

Vitrimeric system	Main flame retardant outcomes	Ref.
Epoxy network incorporating phosphorus-doped carbon dots	• At 11 wt% of phosphorus-doped carbon dots, self-extinction, V-0 rating in UL94 tests and LOI of 31.3% • At 11 wt% of phosphorus-doped carbon dots, decreased pHRR, THR, and TSP in cone calorimetry tests	59
Tannic acid-derived polycarbonate	• With hydroxyl:carbonate molar ratios beyond 1, self-extinction and V-0 rating in UL94 tests; LOI of 30%	60
Epoxy network derived from glutamic acid, itaconic acid, and/or 6-oxido-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-ylmethylbutanedioic acid	• At P : N ratio of 1 : 0.5, self-extinction and V-0 rating in UL94 tests	61
Acrylic organo-phosphorus network	• At 30 wt% organo-phosphorus monomer loading, V-1 rating in UL94 tests; LOI of 26%	62

those spent on the vitrimeric polymers.[63] The main outcomes are summarised here.

Nabipour and co-workers[64] exploited a two-pot strategy for preparing a bio-based epoxy vitrimer composite reinforced with carbon fibres. To this aim, 5-hydroxymethylfurfural was first reacted with 1,3-diaminoguanidine monohydrochloride to obtain a Schiff base that was subsequently reacted with epichlorohydrin. The final product, once mixed with a furan-based curing agent synthesised for the purpose, was employed for impregnating carbon fibre layers, hence obtaining the composites after thermal curing in an oven. The fire behavior of the vitrimer was compared with that of diglycidyl ether of bisphenol A cured with 4,4′-diaminodiphenylmethane. The vitrimeric composites were self-extinguishing and V-0 rated in vertical flame spread tests: these findings were ascribed to a significant charring effect provided by –C═N– structures in the condensed phase.

A similar approach was proposed by Ren and co-workers,[65] who synthesised 2-(bis(2-hydroxyethyl)amino)ethyldiphenylphosphinate that was employed as a transesterification modifier in a diglycidyl ether of bisphenol A–methylhexahydrophthalic anhydride curing system. The so-obtained vitrimers were used as a matrix for manufacturing carbon fibre-reinforced composites through hand lay-up followed by compression molding. 0.25 mol% 2-(bis(2-hydroxyethyl)amino)ethyldiphenylphosphinate embedded in the vitrimeric system achieved self-extinction and V-0 rating in vertical flame spread tests, as well as 32.8% LOI (*vs.* 19.9% for the system not embedding the phosphinate additive). Further, cone calorimetry tests (irradiative heat flux: 35 $kW\,m^{-2}$) performed on the composites highlighted the intrinsic flame retardant effect provided by the additive, with a decrease in pHRR and

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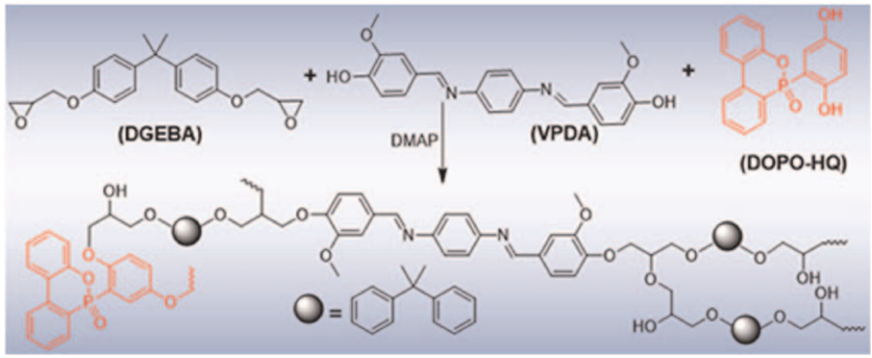


Figure 12.17 Scheme of the synthesis of the epoxy vitrimer. Legend: DGEBA = diglycidyl ether of bisphenol A; VPDA = Schiff-base vanillin-derived hardener; DOPO-HQ = 10-(2,5-dihydroxyphenyl)-10-hydro-9-oxa-10-phosphaphenanthrene-10-oxide; DMAP = 4-dimethylaminopyridine. Reproduced from ref. 66 with permission from Elsevier, Copyright 2024.

THR values (by about 9% and 29%, respectively), compared with the blank counterpart. These findings were attributed to the formation of a compact and protective char (condensed phase action), as well as to the active radical quenching phenomena in the gas phase.

Tian and co-workers[66] cured diglycidyl ether of bisphenol A with a vanillin-derived imine hardener, in the presence of 10-(2,5-dihydroxyphenyl)-10-hydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-HQ) as a reactive flame retardant (Figure 12.17). 22 wt% of the latter accounted for 35.5% LOI, as well as self-extinction and V-0 rating in vertical flame spread tests for the vitrimeric composites (reinforced by carbon fibres, about 65% volume fraction), even after one recycling process (Figure 12.18). These findings were attributed to the char-forming character of the incorporated flame retardant in the condensed phase.

Zhang *et al.*[67] designed flame retardant, reprocessable, and recyclable carbon fibre-reinforced epoxy composites (carbon fibre loading: 61 wt%). For this purpose, tetraglycidyl methylene diphenylamine was cured with a P-containing anhydride (namely, dihydro-3-[(6-oxide-6*H*-dibenz[*c*,*e*] [1,2] oxaphosphorin-6-yl)methyl]-2,5-furandione) in the presence of triethanolamine, employed as both transesterification modifier and catalyst. The so-obtained composites showed excellent flame retardant properties, witnessed by V-0 rating in vertical flame spread tests and by a significant decrease in pHRR and THR values (respectively by about 18 and 49%, compared to the reference composite cured with methylhexahydrophthalic anhydride). These outcomes were ascribed to the carbonisation effect exerted by the P-containing flame retardant in the condensed phase.

This approach was further exploited by the same group to prepare catalyst-free, flame retardant (V-0 rated), and diglycidyl ether of bisphenol A-derived vitrimer composites (carbon fibre loading: 62 wt%). To this aim, the epoxy

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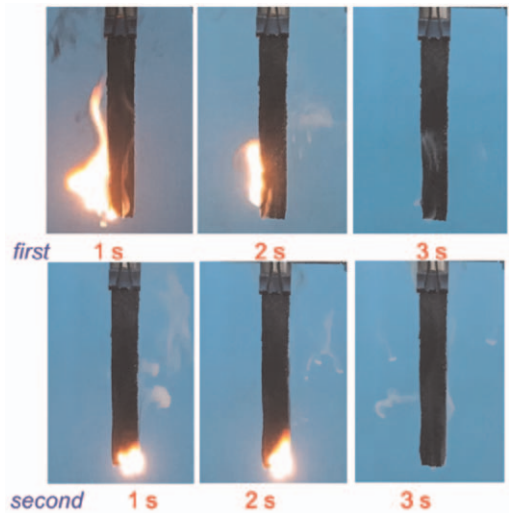


Figure 12.18 Snapshots of vertical flame spread tests (first and second flame application) performed on the epoxy/vanillin-derived vitrimer composite containing 22 wt% 10-(2,5-dihydroxyphenyl)-10-hydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-HQ) after one recycling process. Reproduced from ref. 66 with permission from Elsevier, Copyright 2024.

resin was reacted with a phosphaphenanthrene-derived anhydride (synthesised for the purpose), in the presence of triethanolamine as a multifunctional transesterification modifier.[68]

Niu *et al.* succeeded in preparing a carbon fibre-reinforced vitrimeric composite by reacting vanillin, tyramine, and furfurylamine and exploiting successive hand lay-up and vacuum infusion methods.[69] The resulting vitrimeric composite exhibited self-extinction and a V-0 rating in vertical flame spread test. Moreover, compared with the reference system cured with 4,4′-diaminodiphenylmethane, the vitrimeric flame retarded composite showed decreased pHRR, THR, and TSP values (by about 74%, 53%, and 57%, respectively). These findings were attributed to a condensed phase mechanism, with the formation of a stable and protective char during the application of the flame or the exposure to the irradiative heat flux.

Zamani and co-workers synthesised a vanillin-derived secondary amine curing agent through the reaction of six-vanillin-functionalised cyclophosphazene with 2-(piperazin-1-yl) ethanamine.[70] This product was employed as a curing agent for diglycidyl ether of bisphenol A (Figure 12.19), once the mixture was applied to pre-impregnate carbon fibres. The high N and P content in the vitrimeric composite justified the formation of a stable and protective char that was responsible for the achievement of high flame retardant features (*i.e.* self-extinction and V-0 rating in vertical flame spread tests, Figure 12.20).

Toldy *et al.* thoroughly evaluated the flame retardant mechanisms of carbon fibre-reinforced polyimine composites containing two additive flame

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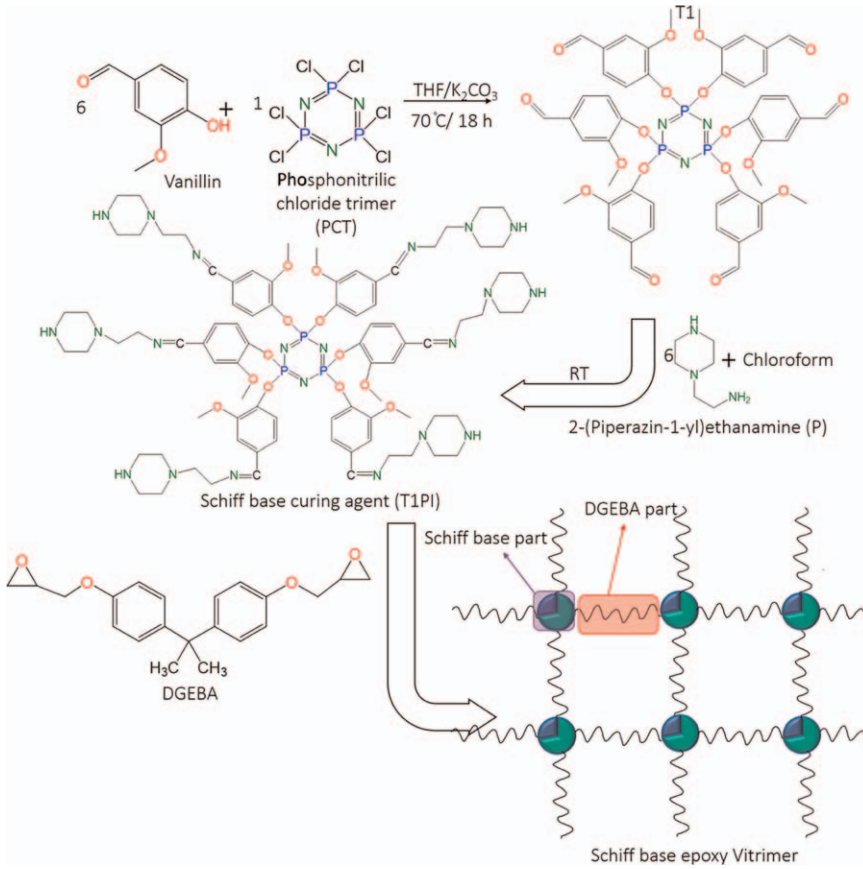


Figure 12.19 Synthesis of the vanillin-derived secondary amine curing agent and obtainment of the final epoxy vitrimer. Legend: DGEBA = diglycidyl ether of bisphenol A; THF = tetrahydrofuran. Reproduced from ref. 70 with permission from American Chemical Society, Copyright 2024.

retardants (*i.e.* ammonium polyphosphate and resorcinol bis(diphenyl phosphate)) and a reactive (*i.e.* *N*,*N*′,*N*″-tris(2-aminoethyl)-phosphoric acid triamide) phosphorus-based flame retardant.[71] The flame retardant performance of these vitrimeric composites (fibre content about 43 wt%) was compared with that of a benchmark pentaerythritol-based aliphatic epoxy resin composite. In particular, the incorporation of the additive flame retardants accounted for a decrease in the crosslinking enthalpy of both epoxy resin and vitrimer systems. Conversely, the presence of the reactive flame retardant promoted an increase in both reaction enthalpy and glass transition temperature (up to 113 °C). 3 wt% phosphorus in the vitrimeric composites, regardless of the type of employed flame retardant, achieved self-extinction and V-0 rating in vertical flame spread tests. Besides, as revealed by cone calorimetry tests carried out at 50 kW m^{-2}, the incorporation of 3 wt%

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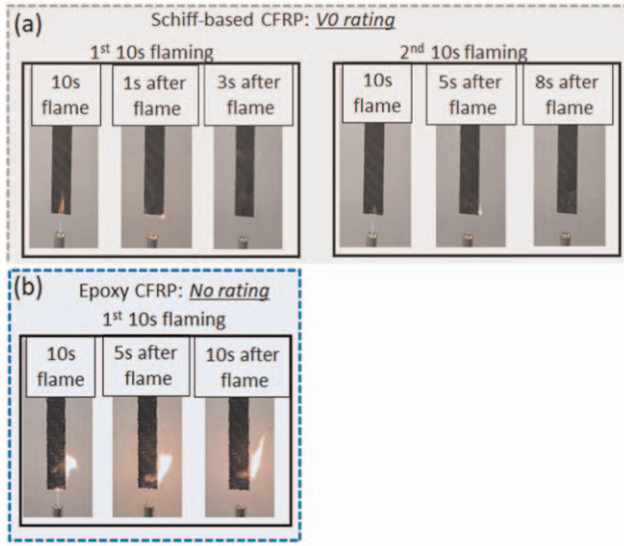


Figure 12.20 Results from vertical flame spread tests (a) for the Schiff base carbon fibre-reinforced composite and (b) for the reference epoxy composite. Adapted from ref. 70 with permission from American Chemical Society, Copyright 2024.

ammonium polyphosphate or resorcinol bis(diphenyl phosphate) promoted a significant decrease in pHRR (Figure 12.21). Finally, different modes of flame retardant action were observed, either in the solid phase (for ammonium polyphosphate), primarily in the gas phase (for resorcinol bis(diphenyl phosphate), or in both condensed and gas phases (for *N*,*N*′,*N*″-tris(2-aminoethyl)-phosphoric acid triamide).

In a further research effort, the same group[72] prepared carbon fibre-reinforced vitrimer composites (based on diglycidyl ether of bisphenol A and an amine-functionalised polyimine hardener) through prepregging and subsequent hot pressing (1 h at 150 °C plus 1 h at 180 °C); the reinforcement loading was around 43 wt%. Again, ammonium polyphosphate or resorcinol bis(diphenyl phosphate) were employed in the design of the flame retardant vitrimeric composites, maintaining 3 wt% phosphorus content. In particular, resorcinol bis(diphenyl phosphate) or ammonium polyphosphate were incorporated into the vitrimeric matrix; in addition, ammonium polyphosphate was also applied as an intumescent coating (with polyimine and epoxy components) at 10 wt% loading directly onto the vitrimeric composite. The intumescent coating accounted for reaching self-extinction and V-0 rating in vertical flame spread tests, removing the candlewick effect (*i.e.* the channelling, exerted by carbon fibres, of the flammable pyrolysis products of the matrix to the flame zone through capillary action), previously seen in the uncoated counterparts. Further, the application of the intumescent coating to the resorcinol bis(diphenyl phosphate)-containing vitrimeric composites

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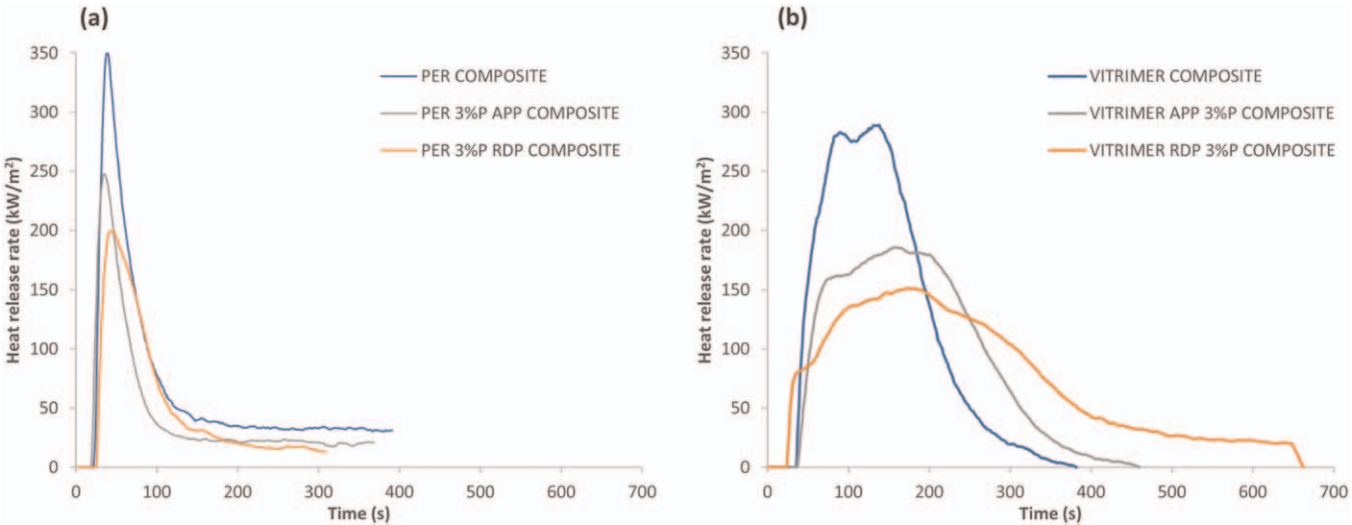


Figure 12.21 Results from cone calorimetry tests (carried out at 50 kW m^{-2} irradiative heat flux) (a) for pentaerythritol-based aliphatic epoxy resin composites and (b) for polyimine composites. All the composites contain 3 wt% phosphorus. Legend: APP = ammonium polyphosphate; PER = pentaerythritol; RDR = resorcinol bis(diphenyl phosphate). Reproduced from ref. 71 with permission from Elsevier, Copyright 2024.

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increased the LOI values (up to 28% *vs.* 21% for the neat vitrimer). Finally, as assessed by cone calorimetry tests (50 kW m^{-2} irradiative heat flux), the coated composites (Figure 12.22) showed significantly reduced pHRR values (up to about 56%, with respect to the reference vitrimeric (non-flame retarded) counterparts. These findings were ascribed to a significant charring effect occurring the condensed phase.

Chang and co-workers designed DOPO–tung-oil-based epoxy (diglycidyl ether of bisphenol A) vitrimers reinforced with carbon fibres.[73] The obtained composites showed high thermal stability, with degradation onset temperatures of about 335 °C. As revealed by flammability tests, the vitrimeric

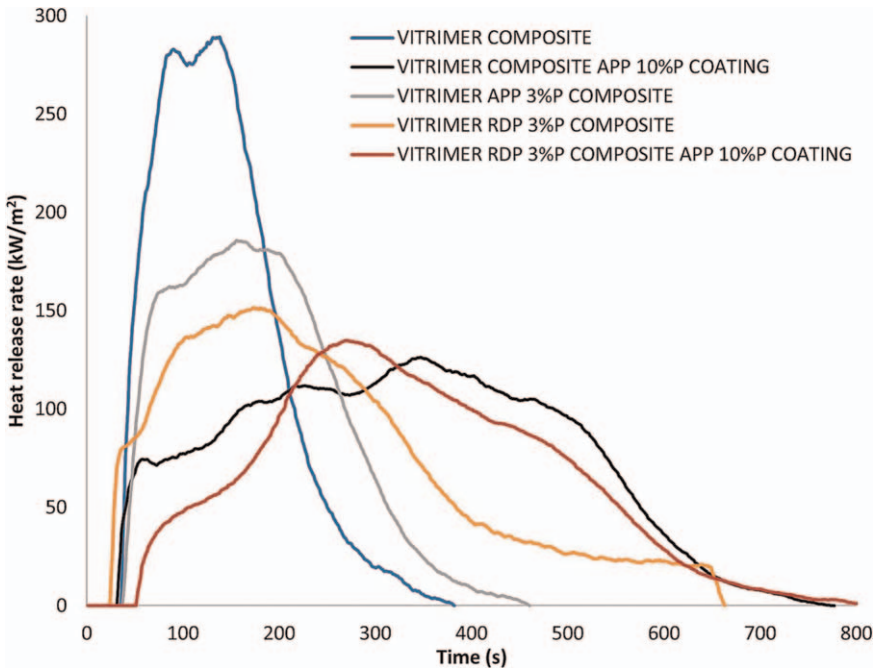


Figure 12.22 Results from cone calorimetry tests (carried out at 50 kW m^{-2} irradiative heat flux) for reference and flame retarded vitrimer composites without and with the intumescent coating. Legend: VITRIMER COMPOSITE = composite without any flame retardant; VITRIMER COMPOSITE APP 10%P COATING = composite coated with the ammonium polyphosphate coating containing 10 wt% phosphorus; VITRIMER APP 3%P COMPOSITE = composite embedding ammonium polyphosphate at 3 wt% phosphorus content; VITRIMER RDP 3%P COMPOSITE = composite embedding resorcinol bis(diphenyl phosphate) at 3 wt% phosphorus content; VITRIMER RDP 3%P COMPOSITE APP 10%P COATING = composite embedding resorcinol bis(diphenyl phosphate) at 3 wt% phosphorus content and coated with the ammonium polyphosphate coating containing 10 wt% phosphorus. Reproduced from ref. 72 with permission from Elsevier, Copyright 2025.

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composites achieved self-extinction and V-0 rating, as well as LOI values as high as 36.4%.

Interestingly, the vitrimeric matrix could be completely removed from the carbon fibres by treating the composites at room temperature in ethanol–water–sodium hydroxide solution. The recycled reinforcement showed surface morphology and mechanical features similar to the pristine counterpart.

Table 12.2 recaps the various vitrimeric composites discussed above, highlighting their key findings in flame retardancy.

12.4 Conclusions and Perspectives

Combining multifunctional properties (such as reshapeability, recyclability, self-healing, thermal and mechanical properties, among others) with flame retardancy is one of the most challenging issues in the science and technology of vitrimers and their composites. This approach can increase the durability and safety of these materials, broaden their use and envisage their suitability even in such advanced industrial sectors as aerospace, automotive, and electronics, where the need to use reliable and high-performance systems is becoming more and more mandatory.

This chapter has summarised the current achievements in the field of flame retarded vitrimers, highlighting the possibility of utilising different types of additive or reactive flame retardants, which usually do not affect the end-of-life strategies foreseen for these materials and may act in the condensed and/or gas phases, depending on their chemical structure (which determines their mode of action).

Despite the interesting research efforts made so far, the world of flame retardant vitrimers and vitrimeric composites needs to be further explored in the coming years, mainly to (i) broaden the portfolio of suitable/effective flame retardants and thus the potential applications of the resulting vitrimers, (ii) better elucidate the flame retardant mode of action of these dynamic covalent networks, as the presence of chemically reversible bonds may significantly affect the degradation/pyrolysis pathways, and (iii) explore the possibility of using not only bio-based chemicals for the synthesis of vitrimers, but also tailor-made bio-based flame retardant additives, thus introducing more sustainability and better fulfilling the current circular economy concept.[74,75]

These goals are not easy to achieve because the chemistry behind the vitrimers and related flame retardants is quite complicated and requires significant research from academia to make the synthesis approaches less difficult and time-consuming, to extend the working temperature ranges of the designed vitrimeric systems, and to improve their overall behavior. Moreover, it is noteworthy that the current research on the design of reliable flame retardant vitrimeric composites is almost in its infancy and requires more efforts. In addition, the scale-up of the production of flame retardant vitrimeric systems from the laboratory scale to at least a pilot/semi-industrial scale is still lacking; the solution of this problem would undoubtedly pave

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Table 12.2 Main outcomes of the vitrimeric composites discussed above.

Vitrimeric composite system	Main flame retardant outcomes	Ref.
Bio-based epoxy composite reinforced with carbon fibres	• Self-extinction and V-0 rating in UL94 tests	64
Epoxy composite embedded with 2-(bis(2-hydroxyethyl)amino) ethyldiphenylphosphinate and reinforced with carbon fibres	• At 0.25 mol% 2-(bis(2-hydroxyethyl) amino)ethyldiphenylphosphinate, self-extinction and V-0 rating in UL94 tests • At 0.25 mol% 2-(bis(2-hydroxyethyl) amino)ethyldiphenylphosphinate, decreased pHRR and THR in cone calorimetry tests	65
Vanillin-derived epoxy composite embedded with DOPO-HQ and reinforced with carbon fibres	• At 22 wt% DOPO-HQ, self-extinction and V-0 rating in vertical flame spread tests even after one recycling process; LOI of 35.5%	66
Epoxy composites cured with a phosphorus-containing anhydride and reinforced with carbon fibres	• Self-extinction and V-0 rating in UL94 tests • Decreased pHRR and THR in cone calorimetry tests	67
Epoxy composites cured with a phosphaphenanthrene-derived anhydride and reinforced with carbon fibres	• Self-extinction and V-0 rating in UL94 tests	68
Carbon fibre-reinforced composite obtained by reacting vanillin, tyramine, and furfurylamine	• Self-extinction and V-0 rating in UL94 tests • Decreased pHRR, THR, and TSP in cone calorimetry tests	69
Epoxy composite cured with a vanillin-derived secondary amine and reinforced with carbon fibres	Self-extinction and V-0 rating in UL94 tests	70
Polyimine composites reinforced with carbon fibres and containing three phosphorus-based flame retardants	• Self-extinction and V-0 rating in UL94 tests • At 3 wt% ammonium polyphosphate or resorcinol bis (diphenyl phosphate), decreased pHRR	71
Carbon fibre-reinforced epoxy composites embedded with ammonium polyphosphate/ resorcinol bis(diphenyl phosphate) and further coated with an intumescent coating	• Self-extinction and V-0 rating in UL94 tests for the coated composites; LOI of 28% • Decreased pHRR in cone calorimetry tests for the coated composites	72
Carbon fibre-reinforced DOPO–tung oil-based epoxy composites	• Self-extinction and V-0 rating in UL94 tests; LOI of 36.4%	73

the way toward an industrial exploitation, which, however, requires an overall cost-effectiveness that can only be achieved by accomplishing a good balance between performance and price.

Efforts produced in the coming years can be expected to bridge this gap and at least partially solve the problems that were highlighted earlier,

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guiding both academia and industry toward new goals in this intriguing research sector.

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